Mechanistic insights into collision induced and catalytic activation of methane from first principles

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

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CATALYTIC ACTIVATION OF METHANE FROM FIRST PRINCIPLES**

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AND CATALYTIC ACTIVATION OF METHANE FROM
FIRST PRINCIPLES**

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Abstract

Methane is the primary component of natural gas, coal bed gases, shale gas and natural gas hydrates, and its commercially recoverable amounts exceed those of petroleum and coal by a few orders of magnitude. The strong C-H bonds of methane make its selective and controlled activation/dissociation difficult and this impedes the widespread utilization of this small alkane as a chemical feedstock to make value added chemicals, fuels and materials. Thus, developing alternate techniques, synthesising new catalytic materials and gaining fundamental mechanistic insights into C-H bond activation on known catalytic surfaces are pivotal to making ‘methane to chemicals and fuels’ a reality.

Using state of the art quantum chemical simulations, it is shown for the first time that mechanical impact of methane molecules induces the dissociation of their strong C-H bonds. This novel bimolecular ‘coupling induced dissociation mechanism’ is demonstrated to convert methane molecules undergoing mechanical impact, directly to C₂ hydrocarbons like ethane and ethylene. The impact induced vibrational excitation of the molecules allow successive transitions to lower potential energy states, leading to the concerted dissociation of C-H bonds of the molecules and coupling of the carbon atoms.

Using *ab initio* molecular dynamics and Metadynamics simulations, it is shown that the mechanical impact of methane on an inactive transition metal like copper, in the form of nanoclusters, can dissociate it with activation free energy barriers between 60 and 90 kJ mol⁻¹. The impact induced vibrational excitation of the molecule and the formation of a collision complex, which serves as a precursor for the dissociation of methane are key reasons for the low free energy barriers. Additionally, the small 3-dimensional copper nanoclusters have electronic structure and morphological features which favour the impact induced dissociation of methane while subsequent dehydrogenation steps have high barriers.

The stabilization of the transition state and the products of dissociation (CH₃ and H) by the under-coordinated Cu-O pair on the CuO surfaces, enable the dissociation of methane with an activation energy barrier as low as 76 kJ mol⁻¹ on the most stable

CuO(111) surface, compared to the barrier of 170 kJ mol^{-1} on Cu(111) surface. Thus, oxygen enhances the activity of copper in methane dissociation. The stronger the H chemisorption on the surface lattice oxygen on the different CuO surfaces, the more active is the surface in dissociating methane, making H chemisorption energy a descriptor for the reactivity of the surface. The weaker the copper- lattice oxygen interaction on the surface, the stronger is the H chemisorption on the lattice oxygen. The difference in the intrinsic metal- oxygen interaction on the different CuO surfaces is the root cause for the differences in their reactivity.

In contrast to CuO, the 5-coordinated surface lattice oxygen on the most stable NiO surface, NiO(100), makes the surface inactive for methane dissociation with activation barrier of 136 kJ mol^{-1} compared to 70 kJ mol^{-1} on Ni(100) surface. NiO surfaces are as active as metallic Ni for methane dissociation when 1) the surface lattice oxygen is 4 coordinated as in the less stable NiO(110) surface; 2) NiO has surface Ni vacancies; and 3) NiO is doped with low valent dopants like Li. On comparing un-doped and doped surfaces, the H chemisorption energy, the descriptor for the reactivity of the lattice oxygen on different NiO surfaces, was found to have a weaker correlation with the intrinsic binding strength of the lattice oxygen on the surfaces. Low valent dopants like Li increase the activity of surface lattice oxygen for methane dissociation by lowering the binding strength of the surface lattice oxygen.

In summary, this thesis reveals unusually high reactivity of methane resulting from collisional impact. The findings have implications for understanding of certain planetary phenomena, offer an explanation for the genesis of ‘abiogenic petroleum’ on the earth and also indicate opportunities for the commercial exploitation of methane. Insights into the role of lattice oxygen, vacancies and dopants on metal oxides in methane dissociation, and H chemisorption energy as a descriptor for reactivity can serve as guidelines in screening and designing efficient multifunctional catalysts for methane dissociation and oxidation reactions.

1 Introduction

1.1 Background

1.1.1 Methane: Properties and Occurrence

Methane is the smallest hydrocarbon and is a colourless and odourless gas and has also been referred to as ‘marsh gas’ and ‘biogas’. It is very stable and relatively inert to most typical chemical reaction types, as can be seen from its inability to react with typical nucleophiles and electrophiles and resistance to acid-base chemistry.¹ The negative free energy of the formation of methane for temperatures up to 800 K suggests that it is highly stable at ambient temperature and that thermal decomposition requires very high temperatures.² Its central carbon atom is tetrahedrally bonded to four hydrogen atoms with a C-H bond length of 1.0869 Å.³ The C-H bonds of methane are very strong with the standard bond dissociation enthalpy reported as 438.9 kJ mol⁻¹ for the first C-H cleavage and 463.1 kJ mol⁻¹, 422.6 kJ mol⁻¹ and 338.8 kJ mol⁻¹ for the subsequent dehydrogenation steps.⁴ Methane forms a weakly interacting homo-dimer as shown in Fig. 1.1. It is a dispersion bound complex, with the interaction energy calculated by state of the art quantum chemical simulations as -2.1 kJ mol⁻¹.⁵

Fig. 1.1 Representation of the structures of methane and methane dimer with the significant bond lengths and bond angles

Methane exists in abundance in the universe as it is a component of many planetary systems and is a significant component of the atmosphere of many planets of the solar system.⁶ This makes methane a molecule of interest for cosmologists and scientists investigating planetary phenomena. It is a constituent and the most abundant organic gas in the earth's atmosphere with sources both natural and anthropogenic.^{7,8} Being a green-house gas, its increasing concentrations in the atmosphere along with CO₂ is

suggested to have strong correlations with changes in Antarctic air temperature and thus, have significant implications in global climate change.⁹ Thus, its release into the atmosphere is an immediate concern requiring urgent attention. Its origins on the earth are primarily via biogenic means, wherein biological organisms convert simple substrates in biochemical pathways. However, there is community of scientists who propose its origins to be in abiogenic pathways without the involvement of biological species.¹⁰ Experimental investigations point to the possibility of formation of methane in the upper mantle of the earth via reduction of carbonates by water, in the presence of iron based catalysts, at high temperatures and pressures.¹¹ Many of the natural sources of methane on the earth release it to the atmosphere and it is cycled through the biogeochemical cycles,⁸ making them inaccessible as commercially exploitable resources.

It is the main component of natural gas and constitutes 80-95% of the volume, depending on its origin.¹² Current proved reserve of natural gas on the earth is estimated to be 186.9 trillion cubic metres.¹³ Natural gas associated with shale formation is referred to as shale gas and world estimates of shale gas stood at around 206.8 trillion cubic metres at the end of 2012.¹⁴ Natural gas components or methane alone, encapsulated in cages of water and existing as solid compounds are referred to as gas hydrates and methane hydrates respectively. These are found in the subsurface permafrost regions and ocean beds across the earth.¹⁵ Estimates of the amount of gas in gas hydrates across the world range from 10^{14} to 10^{16} cubic metres¹⁶ and stand at a few orders of magnitude higher than that in natural gas. Natural gas, shale gas and methane hydrates are commercially exploitable resources and the gas in these resources combined exceeds equivalents of current proved oil reserves by orders of magnitude. Hence, methane is an abundant hydrocarbon feedstock for making a variety of chemicals which are currently derived from conventional and exhaustible petroleum and coal derivatives.

1.1.2 Methane conversion to larger hydrocarbons and chemicals

Methane is the smallest member of the alkane hydrocarbon series. It can undergo reactions to form larger hydrocarbons in mechanisms involving breaking of the C-H bonds and formation of C-C bonds. It can also be converted to a variety of other chemicals by sequential dehydrogenation and functionalization. Some of these

conversions occur as natural phenomena. Using methane as a chemical feedstock to produce value added chemicals has commercial success in certain pathways, although immense potential has been demonstrated for a series of more desirable pathways, without significant commercial success. Some of these natural and industrial conversion processes of methane to other hydrocarbons and chemicals and the immense potential of the chemical value chain around methane are outlined in this section.

1.1.2.1 Methane conversion to larger hydrocarbons under planetary conditions

Experiments with methane at temperatures in the range of 1500-3000 K and pressures between 10 and 50 GPa, as those of the interiors of planets, show evidence of formation of diamond and polymers of methane of varying chain lengths.¹⁷ This is in agreement with results from ab initio molecular dynamics simulations.¹⁸ Experiments also reveal that at temperatures of 1000-1500 K and pressures greater than 2 GPa as expected in the mantle of the earth, methane undergoes polymerization to form alkanes with 2 to 4 carbon atoms.¹⁹ Ab initio molecular dynamics simulations performed for similar ranges of temperature and pressure suggest that larger hydrocarbons along with hydrogen are thermodynamically more stable compared to methane at such conditions.²⁰ This explains the driving force for its dissociation and polymerization. These experimental and simulation results and analyses demonstrating the formation of larger hydrocarbons from methane, point to the possible ‘abiogenic origin of petroleum’ on the earth.^{19,21}

1.1.2.2 Commercial and potential processes for methane conversion to larger hydrocarbons, chemicals and materials

Due to its plentiful availability and clean burning properties, producing lower amount of CO₂ per unit mass, methane is typically used as a vehicular fuel for land transportation systems, as domestic cooking and heating fuel and as an industrial fuel.²² Transport of natural gas from the point of production to the point of consumption has evolved in the recent decades by using the liquefaction technology, producing liquefied natural gas (LNG) as a safer and economically viable alternative to natural gas pipelines.²³ The energy density in methane is much lower compared to liquid fuels to justify its transportation as LNG or through long pipelines from remote locations across the world to the points of consumption.²⁴ This particularly necessitates its transformation to value

added chemicals to justify the costs of production, transport and continued capacity expansion.

Methane's potential as a chemical feedstock to produce value added chemicals and liquid fuels is typically under-utilized. Chemical conversion of methane currently revolves around its indirect utilization by steam or carbon dioxide reforming and partial oxidation to synthesis gas.^{22,25-27} Synthesis gas or syngas is a mixture of CO and H₂. Depending on the compositions of H₂ and CO in the gas mixture, it forms the feedstock for subsequent conversion to bulk commodity chemicals like methanol and ammonia and liquid fuels by the Fischer-Tropsch synthesis method.^{22,27} Reforming of methane is one of the primary sources of industrial hydrogen and is projected to remain so for some time to come.²⁶ The steam reforming of methane, being an endothermic reaction, is typically carried out at temperatures in the range of 900-1200 K and thus is an energy and capital intensive process.²⁶ Catalytic partial oxidation of methane to produce syngas is exothermic and is a more desirable route to produce synthesis gas.²⁷ However, the capital and operational costs involved in supplying pure oxygen for the process makes it slightly uneconomical.²⁷ Thus, the synthesis gas routes for methane utilization are commercial processes producing bulk chemicals and their derivatives and synthetic hydrocarbon fuels, but are energy and capital intensive. More desirable would be pathways for direct and one step transformation of methane to useful chemicals.

Direct utilization of methane to convert it to oxygenates like methanol, formaldehyde and larger hydrocarbons like ethylene and aromatics have been demonstrated.²² Many of the proposed routes for direct utilization of methane involve oxidative upgradation of methane. These include catalytic oxidative coupling to produce ethylene, catalytic oxidative carbonylation to produce acetic acid, catalytic partial oxidation to produce methanol, formaldehyde and formic acid.²⁸ Catalytic oxidation of methane to oxygenates like methanol, formaldehyde and formic acid may be achieved in liquid phase homogeneous reaction systems or in gas phase heterogeneous reaction systems.²⁹ Catalytic oxidative coupling of methane using oxygen on metal oxide catalysts to make ethylene and other larger hydrocarbons has been under investigation from the eighties as ethylene is the organic chemical with the largest volume of consumption and sales in the world.³⁰ In addition to the production of bulk chemicals as described above, methane

is also a hydrocarbon source to make high performance carbon materials like graphene³¹ and carbon nanotubes³² in the chemical vapour deposition process. The current consumption patterns and projected demands for some of these chemicals and derivatives along with halo-alkanes and liquid fuels constitute the chemical value chain around methane and suggest market values of a few hundred billion dollars.²⁴ Fig. 1.2 outlines the resources from which methane can be commercially recovered and a typical chemical value chain involving methane in direct and indirect utilization pathways. Many of the pathways are yet to be commercialised due to a variety of challenges making the processes economically infeasible. Some of the challenges pertaining to the reaction chemistry are presented in the next section.

Fig. 1.2 Schematic representation of the resources of methane on the earth and the methane chemical value chain

1.2 Challenges in methane conversion chemistry

The reactions for conversion of methane to useful chemicals can be classified based on the degree of dehydrogenation of methane and the nature and extent of functionalization of the carbon centre with hetero-atoms. A recent review article described four categories of single step reactions of methane based on these criteria as **a)** complete dehydrogenation of methane to form carbonaceous materials and hydrogen; **b)** partial dehydrogenation of methane and carbon-carbon coupling to form C₂ and larger

hydrocarbons; **c**) complete dehydrogenation of methane and partial oxidation of the carbon centre; and **d**) partial dehydrogenation of methane and introduction of heteroatoms and hetero-groups like halogens, OH and NH₂.³³ Challenges in the reaction chemistry pertaining to these reactions involve controllability and selectivity of the degree of dehydrogenation of methane and functionalization of the carbon atom.³³ For all the processes involving oxidative reaction conditions, one of the key challenges is preventing complete oxidation of methane to carbon dioxide.³⁴ This is in addition to the general challenge of the large activation barrier associated with the breaking of each C-H bond of methane as evident from the standard bond dissociation enthalpies for each dehydrogenation step as depicted in Fig. 1.3. Thus, typical industrial processes for methane conversion, like steam cracking and reforming, are operated at temperatures in the range of 700-1000 °C, necessitating expensive equipment and substantial operational expenses.

Fig. 1.3 Standard bond dissociation enthalpy (BDE) for the sequential dissociation of methane to form carbon. Data is from ref. 4. kJ to be read as kJ mol⁻¹

Development of new technologies and alternate techniques which are more energy and capital efficient can make currently known reaction pathways for methane utilisation commercially viable. Most reactions of methane are carried out in the presence of transition metal,^{26,27} metal oxide^{30,35} and transition metal based^{1,36} catalysts. For realizing the ‘methane to chemicals and fuels’ in the direct pathways, identification of newer and more active catalysts with better selectivity and controllability towards the desired products is inevitable. Additionally, 1) establishing a detailed molecular understanding of the mechanisms of dissociation of the C-H bonds of methane on the known catalytic surfaces, 2) the nature and activity of the active sites on these surfaces and 3) descriptors for reactivity of the different catalysts are necessary for rational catalyst design. Unravelling the effects of dynamics and contributions of entropy to the process and so on are also imperative in tuning current processes. Thus, understanding and mastering methane activation and C-H bond dissociation continue to be some of the biggest challenges for chemists and reaction engineering practitioners to date.

My thesis work aims to develop a mechanistic and molecular level understanding of methane activation and dissociation of the C-H bonds in specific non-catalytic and catalytic processes. The next section presents a summary of the most relevant methods for activation of the C-H bonds of methane, and the key information from existing literature on pertinent dissociation mechanisms, kinetics and reaction dynamics, catalytic materials, and reaction processes.

1.3 Relevant literature on methane activation and C-H bond dissociation

For any reaction of methane to proceed, at least one of the C-H bonds must be broken. The C-H bond in methane can be activated or broken by thermal energy in high temperature pyrolysis processes, involving high energy collisions with other atomic/molecular species and on surfaces, in catalytic processes under finite temperature and pressure, under photo irradiation with low wavelength electromagnetic radiation, in electrochemical processes and so on. Section 1.3.1 discusses dissociation of methane in thermolytic processes. Section 1.3.2 discusses methane dissociation by molecular collision and collisional impact in a concept referred to as ‘Chemistry with a Hammer’. Section 1.3.3 discusses the effects of high energy collision of methane directly on metallic surfaces and the contributions of various molecular degrees of freedom in promoting the dissociation. Section 1.3.4 discusses dissociation of methane in catalytic processes on some typical transition metal and metal oxide catalysts.

1.3.1 Thermal dissociation of methane and methane pyrolysis

Pyrolysis, where substrates or chemicals are heated at very high temperatures to decompose them and initiate subsequent reactions is one of the techniques of converting methane to larger hydrocarbons. Pyrolysis of methane produces a mixture of gases like hydrogen, C₂ hydrocarbons (ethane, ethylene and acetylene) and even larger hydrocarbons including benzene.² However, for practical conversion of methane to C₂ hydrocarbons, thermodynamic considerations impose constraints on the temperature to be more than 1400 K for these processes.^{2,37} Thermal dissociation of pure methane is shown to initiate at temperatures around 1000 K³⁷ and is believed to generate CH₃ radicals ($\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$) which would be coupled to form ethane ($\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$)². This would in turn initiate subsequent reactions to form other hydrocarbons. The

high temperatures required to initiate thermal decomposition of methane is a result of the large bond dissociation energies for every C-H cleavage in methane as indicated in Fig. 1.3.⁴ The thermal decomposition of methane at temperatures over 1000 °C is the key to the chemical vapour deposition (CVD) growth of pyro-carbons from methane, where, an activation barrier of 446 kJ mol⁻¹ was determined for the deposition.³⁸ Such high temperatures make realistic processes involving pyrolysis highly energy intensive and a challenge for reaction engineering as well.

1.3.2 Molecular collision induced dissociation of methane: concept of ‘Chemistry with a Hammer’

Fig. 1.4 Schematic representation of the ‘Chemistry with a Hammer’ concept where weakly physisorbed molecular methane on Ni(111) surface undergoes dissociative chemisorption due to collisional impact of an argon atom. The blue balls represent nickel atoms, the red ball represents carbon, the white ball represents hydrogen and the ochre ball represents argon.

Experiments with weakly physisorbed molecular methane on Ni surfaces showed that methane can be activated and dissociatively chemisorbed on the surface due to the collisional impact from inert argon atoms. This process was referred to as ‘Chemistry with a Hammer’ and is shown in Fig. 1.4.³⁹ The explanation for the phenomenon was that, molecularly adsorbed methane didn’t have sufficient energy to distort its C-H bonds away from the Ni surface to facilitate interaction between the carbon atom and the Ni atoms. This interaction was made possible by the deformation of methane upon collision.⁴⁰ Here the kinetic energy of the incident inert gas atom was transferred to the

physisorbed methane during the impulsive bimolecular collision, facilitating its dissociation. The probability of the dissociation was found to depend linearly on the normal kinetic energy of the incident inert gas atom.⁴⁰ Using quasi-classical trajectory simulations, it was shown that only a fraction of the translational kinetic energy in hyperthermal (energy greater than 4 eV) argon atom is transferred to the methane molecule upon collision in the gas phase.⁴¹ The amount of energy transferred during collision depends on the nature and topology of the potential energy surface between the colliding partners. A significant amount of the translational kinetic energy is transferred to the lower frequency vibrations of the molecule.⁴¹

The above literature shows dramatic effects of energy transfer during molecular collisions and consequences, which are not limited to collision induced vibrational activations but also to processes like dissociative chemisorption.

1.3.3 Collision induced dissociation of methane on transition metals and contribution of different molecular degrees of freedom on dissociation

Understanding reaction dynamics is a key aspect of reaction engineering. Molecular beam experiments, where directed beams of molecules at desired translational kinetic energies can be generated to impinge on surfaces of choice, are ideal to understand gas-surface reactivity and the relevant degrees of freedom contributing to the dissociation.⁴² Molecular beam experiments with methane on a variety of transition metal surfaces have given a wealth of information on the dynamics of such processes. The identified mechanisms of dissociation, origins of the activation barrier, and relevant molecular degrees of freedom contributing to the dissociation are discussed in this section.

1.3.3.1 Effect of translational kinetic energy on dissociation: direct dissociation mechanism

Direct collision induced dissociation of methane on metal surfaces like Ni(111)⁴³ and W(110)⁴² exhibited a significant dependence of the dissociation probability on the normal component of translational kinetic energy of the impinging molecule. The possible origin for the barrier for dissociative chemisorption was believed to be the quantum tunnelling of H⁴² and the deformation of methane⁴³ to facilitate carbon-nickel interaction. This was based on the dependence of the dissociation probability on the normal component of translational kinetic energy of the molecule. These experiments

further suggested that the dissociation of methane on metal surfaces may be a direct phenomenon with dependence primarily on the translational energy of the molecule. Molecular beam experiments on Pt(111) surface however suggested that the normal component of translation kinetic energy upon impact, vibrational energy of the molecules undergoing collision and the surface temperature will all have contributions to enhanced dissociation probability.⁴⁴

1.3.3.2 Trapping or precursor mediated dissociation mechanism

Experiments of methane dissociation on the Ir(111) surface point to the possibility of a trapping mediated⁴⁵ or precursor mediated mechanism⁴⁶ for the dissociation of methane in the lower temperature regimes. This is in addition to the direct dissociation mechanism which is prevalent on Ir(111) surface at higher temperatures and higher translational kinetic energies during collisional impact.^{45,46} In such a mechanism, methane forms a collision complex on the metal surface, and with its remaining translational and vibrational energies, diffuses and explores various vibrational configurations around the metal atom, before dissociating.⁴⁶ A schematic representation of the direct channel for dissociation of methane as well as the ‘precursor mediated’ dissociation channel on a metal surface is depicted in Fig. 1.5.

Fig. 1.5 Schematic representation of the direct dissociation channel and ‘precursor mediated dissociation channel’ for dissociation of methane on metal surfaces. In the direct channel, methane at high collision energy can overcome the activation barrier for

dissociation and directly forms CH₃ and H on the surface in a 0 to 2 transformation. In the precursor mediated channel, methane with low translational energy, molecularly adsorbs on the surface, forming a collision complex, explores various vibrational and molecular configurations and subsequently dissociates in a 0 to 1 and 1 to 2 process. Concept for the figure adapted from ref. 46.

1.3.3.3 Effect of vibrational activation on dissociation: vibrational mode and bond selectivity

With quantum state resolved molecular beam experiments of methane dissociation on metal surfaces, it was shown that the vibrational state of the molecule and degree of excitement of the vibrational state may be more relevant in promoting dissociation than the translational kinetic energy itself.⁴⁷ Other such experiments showed that the nature of vibrational mode also contributes to the reactivity of methane on the metal surface, bringing in the concept of vibrational mode selective reaction.⁴⁸ There is debate to establish the specific vibrational modes of methane affecting the dissociation probability on the specific metal surface on which dissociation was investigated. Reactivity of methane on Pt(110) surface is hypothesized to have contributions from the stretching and bending modes of methane, together playing a concerted role.⁴⁹ Subsequent investigations also show that selective cleavage of specific bonds of methane, possessing specific amounts of vibrational energy, can be achieved as long as vibrational energy in these bonds and modes are not redistributed within the time frame of collisional impact.⁵⁰

1.3.4 Catalytic dissociation of methane on transition metals, chemisorbed oxygen containing transition metals and transition metal oxide surfaces

1.3.4.1 Dissociation of methane on transition metals

Catalytic reforming is the industrial process consuming the largest volume of methane as a chemical feedstock, and the most commonly used industrial catalyst for steam reforming of methane is nickel.²⁷ Through rigorous computational and experimental calculations it has been shown that the activity order of some of the transition metals in the steam reforming of methane follows the trend $Ru \geq Rh > Ni \geq Ir \geq Pt \sim Pd$.⁵¹ The noble metals on either side of nickel in the reactivity trend described, are too expensive for practical commercial use and thus are not of interest for this investigation. The activation energy barrier of $\sim 90 \text{ kJ mol}^{-1}$ for dissociation of methane on Ni(111) surface,

calculated using Density functional theory (DFT) is in agreement with fitted experimental data which suggested a barrier of 87 kJ mol^{-1} .⁵² In comparison to nickel which is quite active in dissociating methane, copper is very inactive with experimentally determined activation barrier for the dissociation on methane on Cu(100) surface of $\sim 200 \text{ kJ}^{-1}$.⁵³ The activation barrier for the dissociation of the first C-H bond of methane on Cu(111) surface has been calculated by DFT simulations to be $170.8 \text{ kJ mol}^{-1}$ and is higher than that on Cu(100) surface which was calculated to be $153.4 \text{ kJ mol}^{-1}$.⁵⁴ A schematic representation of the dissociation of methane on transition metal surfaces is shown in Fig. 1.6a. Ni and Cu are relatively inexpensive and have contrasting behaviours in methane activation. Methane dissociation on Ni and Cu is discussed here to contrast the roles and contributions of oxygen present on these surfaces in the form of chemisorbed oxygen or in the form of lattice oxygen, for methane dissociation. These are discussed in section 1.3.4.2 and 1.3.4.3.

Fig. 1.6 Schematic representation of the mechanisms of dissociation of methane on a) a transition metal surface where it is the oxidative addition mechanism involving a single metal atom as active site; b) a transition metal surface containing dissociatively chemisorbed oxygen on the surface which abstracts hydrogen from methane to form a surface hydroxyl; c) a transition metal oxide surface in a mechanism involving both the metal and lattice oxygen pair, similar to the sigma-bond metathesis pathway, and consists of concerted oxidative addition and hydrogen abstraction by the lattice oxygen; and d) a metal oxide surface where the surface lattice oxygen abstracts hydrogen from methane.

1.3.4.2 Dissociation of methane on chemisorbed oxygen containing transition metals

Since many of the processes involved in methane upgradation are oxidative in nature, consuming pure oxygen or air, the role of dissociatively chemisorbed oxygen in methane dissociation has been a subject of detailed investigations. In typical oxidative reaction conditions, some metals may undergo transformation between the metallic and oxide phases, with intermediate stages of various oxygen coverages, depending on the chemical potential of oxygen.^{55,56} Thus an understanding of the role and contribution of oxygen and the mechanism of dissociation of methane in the presence of oxygen, either chemisorbed or in the form of lattice, are essential to understand the kinetics of the process. Behaviour of chemisorbed oxygen containing metal surfaces and metal oxide surfaces in the C-H bond dissociation process is discussed in this section.

Dissociatively chemisorbed oxygen on the surface was not believed to participate in the dissociation of methane by the hydrogen abstraction mechanism ($\text{CH}_x + \text{O}^* \rightarrow \text{CH}_{x-1} + \text{OH}^*$ where $x = 1$ to 4 and $*$ represents chemisorbed species) on Pt and Rh catalysts during catalytic partial oxidation of methane to syngas.⁵⁷ Schematic representation of the hydrogen abstraction mechanism by dissociatively chemisorbed oxygen on metal surface is depicted in Fig. 1.6b. However, recent experimental and computational investigations reveal an oxygen coverage dependent evolution of the mechanisms of C-H bond dissociation and the kinetics of the oxidation reaction on Pt surfaces and clusters.⁵⁸ It was shown that the C-H bond dissociation is the sole kinetically relevant step and evolves oxidative addition on Pt sites. This evolves to a concerted oxidative addition and hydrogen abstraction mechanism on the Pt and chemisorbed oxygen pairs, with increase in oxygen coverage. At full surface coverage of chemisorbed oxygen, the mechanism changes to only hydrogen abstraction by the chemisorbed oxygen.

On Ni(100) surfaces, the presence of pre-adsorbed oxygen was shown to decrease the chemisorption probability of methane as the pre-adsorbed oxygen atoms were blocking the sites for CH_3 chemisorption.⁵⁹ A computational investigation estimated the activation energy barriers for methane dissociation on chemisorbed oxygen containing Ni(100) to be $130.2 \text{ kJ mol}^{-1}$ while the same on clean Ni(100) was calculated to be 57.9 kJ mol^{-1} .⁶⁰ In contrast, it was shown that pre-adsorbed oxygen on Cu(100) surface,

lowers the apparent activation energy for dissociation of methane from $\sim 200 \text{ kJ mol}^{-1}$ to $\sim 125 \text{ kJ mol}^{-1}$, suggesting a favourable contribution of oxygen in the dissociation process.⁵³ The presence of chemisorbed oxygen on the Cu(111) surface was found to aid in the process of cleaving X-H (X= C, N, O) bonds in a hydrogen abstraction mechanism, producing surface hydroxyl species⁶¹. The same was believed to be applicable to methane dissociation on Cu(100)⁵³ as well. Subsequent computational investigations have shown that the promotional effect of chemisorbed oxygen in C-H bond activation primarily exists only for the coinage metals like Cu, Ag, Au.⁶² For the active metal, oxygen on the surface has an inhibitory role in dissociation of methane.⁶²⁻⁶⁵

1.3.4.3 Dissociation of methane on transition metal oxide surfaces

Unlike Pt described in the last section, Pd can form a stable oxide with change in oxygen chemical potential. With clean Pd surfaces and clusters, the mechanism for methane dissociation is oxidative addition, and evolves to hydrogen abstraction with increase in surface coverage of dissociatively chemisorbed oxygen to full monolayer.⁶⁶ This finally changes to a ‘sigma bond metathesis’ kind of reaction when the oxygen is incorporated into the lattice forming a surface oxide. The mechanisms of C-H activation of methane on metal oxide surfaces is schematically represented in Fig. 1.6c and Fig. 1.6d. The nature of the surface atoms on the oxide surfaces varies significantly with the surface termination in the particular crystal morphology. PdO(101), RuO₂(110) and IrO₂(110) surfaces have coordinately unsaturated (cus) metal and lattice oxygen atoms on the surface. These cus metal sites can interact with the C-H bonds of methane and other alkanes by formation of dative bonded complexes which serve as precursors for dissociation.⁶⁷ Such interactions however may not be relevant for the third row transition metal oxides like those of nickel and copper, although cus atoms may be present on the surfaces.

The third row transition metal oxides like NiO and CuO are considered excellent prospective materials for the chemical looping combustion (CLC)⁶⁸ and chemical looping reforming (CLR) processes.^{69,70} Here combustion of fuels like methane is carried out using oxygen from solid metal oxides, which get reduced in the process and are subsequently regenerated in a separate oxidation cycle. A computational

investigation estimated the activation energy barriers for methane dissociation on NiO(100) to be 158.2 kJ mol⁻¹ as against clean Ni(100), where the activation barrier was only 57.9 kJ mol⁻¹.⁶⁰ Experimental investigations also point to the lower activity of the NiO(100) surface compared to the clean metallic Ni(100) surface for methane dissociation.⁷¹ CuO in specific morphologies like nanowires have also been shown to be excellent oxidation catalysts for methane, where the CH₄ dissociation steps leading to oxidation are likely to be the rate limiting ones.⁷²

Low valent dopants are known to activate irreducible metal oxides for oxidation catalysis by making the lattice oxygen more active and easily removable, increasing reducibility of the surface.^{73,74} Li doped MgO is known to be an effective catalyst to generate CH₃ species in the oxidative coupling process to convert methane to ethylene.^{30,75} Here the Li⁺O⁻ sites generated in the vicinity of the dopant in the oxidative coupling process are believed to be the active sites for the abstraction of H from methane. Dopants like Li can be incorporated into the NiO lattice in proportions up to stoichiometric LiNiO₂.⁷⁶ Li doping may have similar or complementary effects on this reducible oxide, making them more active in methane dissociation and oxidation.

1.4 Motivation for the thesis

Mechanical compression of O₂ clusters or collision of molecular oxygen was shown to transform the molecules from the ground triplet electronic state to highly reactive singlet electronic states in a manner similar to that in the ‘chemistry with a hammer’ concept.^{77,78} Here, it was evident that a small percentage of O₂ molecules in a large cluster, undergoing collisional impact on a surface, gained sufficient energy due to internal collisions to undergo non-adiabatic electronic transitions. The multiple internal collisions allow for successive non-adiabatic transitions, transforming the unreactive triplet ground state oxygen molecules to reactive singlet oxygen for enhanced surface oxidation reactions.

The above observations and the outcomes of molecular collision and the ‘chemistry with a hammer’ concept described in section 1.3.2, suggest the opening of novel channels for energy transformations in molecular collisions, bringing about unusual reactivity in the molecules. Intermolecular collisions of this kind and consequences thereof, have not

been investigated and reported in literature for methane molecules. Such mechanical impact may bring about adiabatic and non-adiabatic excitation of the methane and may lead to subsequent reactions. Moreover, the mechanisms of transformation of methane to larger hydrocarbons under planetary conditions as described in section 1.1.2.1, involving the dissociation of the C-H bonds and coupling of the carbon centres are not elucidated. Due to the high pressures and temperatures, a bimolecular mechanism ($\text{CH}_4 + \text{CH}_4 \rightarrow \text{C}_2$ hydrocarbons) involving the mechanical impact of the methane molecules is anticipated as against the dissociation in the unimolecular thermal dissociation to radicals ($\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$ and $2 \text{CH}_3 \rightarrow \text{C}_2$ hydrocarbons). This is the background for the present investigation of methane intermolecular collisional impact.

Collision dynamics and effects of finite temperature bringing about vibrational activation of the methane molecules and vibrational pre-excitation of the methane molecules undergoing collisional impact have significant contributions to their dissociation on transition metals as described in section 1.3.3. These effects may significantly alter minimum energy paths of reactions initiated due to mechanical impact. Understanding the effects of finite temperature dynamics and mechanical impact of methane molecules on a catalytic system also becomes pertinent. Typical computational investigations using the density functional theory (DFT) and other state of the art quantum chemistry methods provide a wealth of information on the nature of molecular interactions, adsorbate-surface interactions, active sites on catalysts, and activation energy barriers among others. But these methods fail to capture the features of finite temperature reaction dynamics and explicit contributions of entropy to the reaction process. Finite temperature *ab initio* molecular dynamics techniques are far superior in the investigation of reaction dynamics. However, these methods are severely limited in the timescales accessible through simulations. The *ab initio* molecular dynamics in the Car-Parrinello scheme⁷⁹ explicitly accounts for molecular motion, lattice reorganization and molecular vibrations corresponding to finite temperatures, and helps to capture the effects in question. The Metadynamics algorithm⁸⁰ on the other hand helps in accelerating the system to simulate the collision induced dissociation reaction within realistic computational time frames. Hence, impact induced dissociation of methane on copper nanoclusters is investigated using Car-Parrinello molecular dynamics and Metadynamics simulations.

Copper is relatively inactive for dissociation of methane, but, chemisorbed oxygen on the surface lends a promotional effect to copper surfaces for the dissociation of methane. Dissociatively chemisorbed oxygen is metastable on the Cu surface and at higher oxygen saturation, tends to form a surface oxide which is more stable.⁵⁵ CuO has been shown to be effective in dissociating the formyl C–H bonds in sugars with activation barrier of 87 kJ mol⁻¹, during their oxidation to acids.⁸¹ A copper oxo species in a trinuclear Cu-O complex generated on mordenite zeolite structures has been shown to be effective in converting methane to methanol and is initiated by a hydrogen abstraction mechanism with activation barrier of 74 kJ mol⁻¹.⁸² Thus the Cu-O pair/ complex is effective in C-H bond activation, suggesting CuO surfaces will be effective in methane dissociation. In both these cases, the lattice oxygen of CuO has a more active role in the C-H bond dissociation as compared to the Cu atom. A proper understanding of the role and contribution of the lattice oxygen on the CuO surfaces towards C-H bond dissociation will help in controlling the oxidation process on these catalysts.

NiO is one of the more active third row transition metal oxides for the chemical looping combustion and reforming of methane.^{70,83} However, NiO(100) surfaces and chemisorbed oxygen containing Ni(100) surfaces are found to be comparatively inactive for the dissociation of methane with respect to the clean nickel surfaces. The oxygen species is believed to have an inhibitory role on methane dissociation. NiO catalysts and materials synthesised by different techniques predominantly expose the most stable⁸⁴ NiO(100) surface.⁸⁵⁻⁸⁷ However, the high activity of the mesoporous NiO with predominantly exposed NiO(110) for reversible storage of lithium via a conversion reaction ($\text{NiO} + 2\text{Li} + 2\text{e}^- \leftrightarrow \text{Li}_2\text{O} + \text{Ni}$) in lithium ion batteries was attributed to its high surface energy and the existence of larger numbers of under-coordinated sites.⁸⁴ Thus the activity of NiO(110) surface could be quite different from that of the stable NiO(100) for methane dissociation. The role and contributions of the intrinsic nickel and lattice oxygen vacancies on the NiO surfaces^{88,89} towards methane dissociation in a non-oxidative environment are yet to be detailed. NiO and MgO have the same rock salt crystal structure. Li doping in MgO is known to improve the activity of lattice oxygen to facilitate the abstraction of H from methane to generate CH₃ species in the oxidative coupling of methane. Due to the reducible nature of NiO, Li doping may not make it suitable for the oxidative coupling of methane. However, a significant effect in the

dissociation and oxidation of methane is anticipated. The nature and extent of the effect of Li dopant in different NiO surfaces for the dissociation of methane are not reported in literature. All these motivate the investigation of methane activation on NiO surfaces with focus on the role and contribution of lattice oxygen, vacancies and dopants.

1.5 Objectives of the thesis

The overall objective of this thesis is to present 1) a comprehensive mechanistic understanding of methane activation and dissociation resulting from non-catalytic and catalytic mechanical impact; and 2) to elucidate the contributions of lattice oxygen, vacancy defects and dopants in metal oxide surfaces in determining methane activation mechanisms, activation barriers and energetics, and to establish suitable determinants of surface reactivity. The first of these is addressed in chapters 2 and 3. Chapter 2 deals with the non-catalytic mechanical impact and chapter 3 deals with the impact on catalytic systems. Chapter 4 deals with the specific roles and contributions of the lattice oxygen on different CuO surfaces for methane activation while chapter 5 deals with the lattice oxygen, surface vacancies and dopants on NiO surfaces. The specific objectives being addressed in each chapter is detailed in this section.

1.5.1 Key objectives of chapter 2

- To characterise the intermolecular potential energy of the methane-methane system for distances lower than the equilibrium separation in the dimer (~ 3.7 Å).
- To understand the impact induced vibrational excitation of methane molecules and the role of vibrational pre-excitation on the potential energy of the molecules undergoing mechanical impact.
- To identify pathways for the impact induced dissociation of methane and outcomes of the dissociation.
- To compare the kinetics and energetics for the impact induced dissociation and direct transformation of methane to C₂ hydrocarbons along the different pathways.

1.5.2 Key objectives of chapter 3

- To investigate collision induced dissociation of methane on different Cu nanoclusters using finite temperature molecular dynamics simulations and to characterize the features of the corresponding free energy profile.
- To determine the influence of temperature, collisional impact, entropy, and collision dynamics on lowering the activation free energy barriers for the dissociation of methane.
- To contrast collision induced dissociation of methane with catalytic dissociation without collisional impact
- To understand the effects of morphological features, electronic structure of the Cu nanoclusters and cluster reorganization on the free energy barriers for dissociation of methane.

1.5.3 Key objectives of chapter 4

- To understand the mechanisms for dissociation of methane on CuO surfaces and to compare them with those on clean and chemisorbed oxygen containing surfaces.
- To elucidate the role of the lattice oxygen on different CuO surfaces in dissociation of methane along different pathways and its contribution in lowering the activation barriers for dissociation of methane
- To identify factors influencing the intrinsic reactivity of the different surfaces of CuO and the potential descriptors for reactivity of the surfaces.

1.5.4 Key objectives of chapter 5

- To elucidate the inhibiting role of the lattice oxygen on the most stable NiO surface, NiO(100), for dissociation of methane and to compare its activity with that of lattice oxygen on a higher energy surface like NiO(110).
- To understand the role of intrinsic vacancy defects on NiO surfaces in determining the mechanisms of dissociation of methane and their influence on the activation barriers and energetics.
- To understand the contribution of low valent dopants like Li on NiO surfaces in improving the kinetics and energetics of the dissociation of methane.

- To understand the fundamental material properties that determine the reactivity of NiO surfaces, how they can be altered for methane dissociation and to identify potential descriptors for the reactivity of the surfaces.

1.6 Organisation of the thesis

The main contents of this thesis are organised into 4 chapters. Each chapter has a brief introduction about the specific issue addressed in the chapter with relevant literature on the state of the art. This is followed by a brief discussion of the computational methodology as well the computational systems investigated. The key results from the investigation are presented and discussed in the context of current literature. Each chapter concludes with a summary of the key findings.

Following the introduction presented in chapter 1, chapter 2 focuses on the mechanical impact of methane molecules, leading to coupling induced dissociation and direct transformation to C₂ hydrocarbons. Chapter 3 focuses on the mechanical impact induced dissociation of methane on catalytic systems in the form of nanoclusters of inactive transition metal- copper. Chapter 4 deals with the contribution of the lattice oxygen on different CuO surfaces in determining mechanisms, activation barriers and the energetics of methane dissociation. Chapter 5 focuses on the contribution of the lattice oxygen, surface vacancies and dopants in NiO surfaces in determining mechanisms, activation barriers and energetics of methane dissociation. Chapter 6 summarises the conclusions drawn from the work in the thesis and offers some perspectives on them. Chapter 7 lists out additional supporting data and results as appendices to the different chapters. The specific issues addressed in the different chapters of the thesis and the broad outline of the contents of each of the chapters, along with key outcomes are presented in this section.

1.6.1 Chapter 2: First principles investigation of the coupling induced dissociation of methane and its transformation to C₂ hydrocarbons

To get a molecular understanding of phenomena involved in mechanical impact of the methane molecules, state of the art quantum chemical calculations using the Coupled Cluster theory through perturbative triples (CCSD(T)) and second order Møller–Plesset perturbation theory (MP2) were performed. Methane molecules in the equilibrium

dimer as shown in Fig. 1.1 and further along a coordinate corresponding to mechanical impact of the molecules were investigated to understand energy and structure transformations during mechanical impact. In contrast to the conventional understanding about the unimolecular dissociation of the C-H bond of methane to generate radicals and subsequent C-C coupling, a novel concept of bimolecular ‘coupling induced dissociation’ of the methane molecules is presented. Two distinct coupling induced dissociation pathways of methane molecules undergoing mechanical impact, with the corresponding energy barriers and energetics for the conversion C₂ hydrocarbons are presented. Additional pathways for interconversion of C₂ hydrocarbons are also presented.

1.6.2 Chapter 3: First-principles investigation of the collision induced dissociation of methane on copper nano-clusters: interplay of collision dynamics, geometric and electronic effects

Since mechanical impact was shown to bring about chemical reaction in intermolecular collision in chapter 2, the investigation of mechanical impact of methane on an inactive transition metal like copper is pertinent. To understand the reaction dynamics of collision induced dissociation of methane on catalytic systems, dissociation of methane on copper nanoclusters and copper atoms was investigated using Car-Parrinello molecular dynamics and Metadynamics simulations. The significantly lower activation free energy barriers for the collision induced dissociation of methane on the copper nanoclusters, compared to the subsequent cluster catalytic dissociation, is explained based on the collision induced vibrational activation of the molecule and formation of the collision complex. Correlations of the activation free energy barrier for dissociation of methane with the cluster size, cluster morphology, cluster electronic structure and stereo dynamics of the collision were found and an interplay of all these factors was found to determine the activation free energy barriers.

1.6.3 Chapter 4: Insights into the synergistic role of metal-lattice oxygen site pairs in four-centered C-H bond activation of methane: the case of CuO

Mechanical impact of methane on copper with nano-cluster morphologies showed dissociation is facile. Here, the role of oxygen to increase the activity of inactive metallic

copper is investigated. CuO can be synthesised in different morphologies with different surface terminations⁹⁰ and some of these experimentally determined stable facets were investigated for methane dissociation. Density functional theory (DFT) simulations were performed on different crystal facets of CuO to understand the mechanisms of activation and the role of lattice oxygen on these mechanisms. The corresponding activation barriers, energetics and key descriptors for reactivity on these surfaces were also investigated. The most stable surface CuO(111), oxide of an inactive metal, Cu, was found to be highly active for methane dissociation. Lattice oxygen plays an active role in C-H bond dissociation on all the CuO surfaces and the activity of the lattice depends on how strongly they are bound to the surface. Hydrogen chemisorption energy is found to be a suitable descriptor for reactivity of the surfaces for methane dissociation, while, the strength on the surface lattice oxygen binding on the surface determines its activity.

1.6.4 Chapter 5: Insights into C-H activation on NiO surfaces: the role of nickel and lattice oxygen vacancies and of low valent dopants on the reactivity and energetics

Lattice oxygen has a promotional effect for the dissociation of methane on CuO surfaces. DFT calculations were performed on the stoichiometric NiO surfaces to understand the origin of the inactivity of the stoichiometric NiO(100) surface for methane dissociation. To understand the possible contributions of vacancy defects and dopants in increasing the activity of NiO surfaces, NiO surfaces with different vacancy defects and Li dopant were investigated. The high energy NiO(110) surface was found to be comparable in activity to clean Ni(100) surface and is twice as active as the stoichiometric and stable NiO(100) surface. Generating Ni vacancies and doping with Li have kinetically similar consequences, as the presence of either of them increases the activity of the neighbouring lattice oxygen atoms towards methane dissociation. In contrast, a single oxygen vacancy makes the surface inherently inactive for methane dissociation in a non-oxidative environment. H chemisorption energy was found to be a suitable descriptor for comparing the activity of the different surfaces for methane dissociation. This is inherently influenced by the lattice oxygen binding strength on the surface.

1.6.5 Chapter 6: Conclusions and perspectives

The conclusions drawn from the key results of the four chapters are highlighted and perspectives on these are presented.

Fig. 1.7 Summary of the thesis and organization.

2 First principles investigation of the coupling induced dissociation of methane and its transformation to C₂ hydrocarbons

2.1 Introduction

Weak dispersion or van der Waals forces and homo-nuclear dihydrogen contacts have been shown to characterize the interaction of small non-polar alkanes including methane.^{91,92} Interaction of methane molecules with each other and the formation of dimers which are weak van der Waal's complexes have been the subject of numerous investigations.^{5,91,93-97} It is typically accepted that these non-bonded interactions are best understood using high level electronic structure methods involving electron correlation like the Coupled Cluster theory through perturbative triples (CCSD(T)) with sufficiently large basis sets and by applying suitable corrections.⁹⁶ The potential energy curve of the methane dimer obtained using the second order Møller–Plesset perturbation theory (MP2)⁹⁸ or CCSD(T) methods show a shallow well, with a long range attractive tail on one side and a steeply rising head on the other.⁵ The interaction energy of methane molecules in the dimer is estimated to be 0.4-0.6 kcal mol⁻¹^{5,94} at an equilibrium separation of 3.6 Å to 3.7 Å^{5,94}. Many computational investigations attempt to present an accurate description of the inter-molecular potential energy surface (PES) of the homo-dimer of methane, dimers with other small molecules (SiH₄, CCl₄ and so on) and of small alkanes. The PES is essential for investigating their dynamical, fluid and condensed phase properties.^{99,100}

Inspite of the existence of the vast literature on the homo-dimer of methane, characterization of the PES of the methane dimer at inter-nuclear distances which are much lower than the equilibrium separation is not available. Moreover, methane is known to be dissociated and transformed to larger hydrocarbons at extremely high pressures and temperatures, such as those that exist in the interiors of planets.^{17,19,20} The mechanism of such dissociation and formation of larger hydrocarbons involving mechanical impact and collision of methane molecules is yet to be elucidated. Mechanical impact of O₂ molecules has been shown to bring about electronic transitions in them from their ground state to highly reactive excited states.^{77,78} The activation of

methane due to similar mechanical or collisional impact has not been reported in literature.

In this context, first principles calculations using MP2 and CCSD(T) methods on the methane dimer were performed, with focus on the inter-nuclear separation much lower than the equilibrium distance of ~ 3.7 Å. In section 2.3.1, it is shown that approach of the molecules to inter-nuclear distances less than 2 Å can lead to an intrinsic vibrational activation of the C-H bonds of both the molecules. In section 2.3.2 it is shown that vibrational pre-activation of the C-H bonds of the molecules can facilitate their approach towards each other to distances lower than 2 Å, with a net lowering of energy, by successive potential energy curve crossings. In section 2.3.3. the possible reason for the net lowering of energy of the vibrationally excited molecules at very short inter-nuclear separation is explained. A novel bimolecular ‘coupling induced dissociation reaction’ pathway, with transition states (TSs) and energetics for the dissociation of strong C-H bonds of methane and its direct transformation to C₂ hydrocarbons like ethane and ethylene are presented in section 2.3.4. An alternate mechanism for the transformation of methane molecules to ethane and subsequent dehydrogenation of ethane to ethylene, with the corresponding TS and energetics is also presented and compared in section 2.3.5. Section 2.3.6 presents comparisons of the activation barriers and energetics for the transformation of methane to C₂ hydrocarbons along the different reaction pathways and the temperature effect.

2.2 Computational methods

First principles optimizations of the methane dimer in the D_{3d} configuration⁵ were performed using second-order Møller–Plesset perturbation theory (MP2)⁹⁸ with the augmented correlation-consistent (aug-cc-pVTZ) basis set,¹⁰¹ with the GAUSSIAN 09 package.¹⁰² The counterpoise correction method of Boys and Bernardi¹⁰³ was adopted to obtain the basis set superposition error (BSSE). For all optimized geometries, a vibrational frequency analysis was performed to characterize the nature of the stationary points. Single point calculations using the coupled-cluster theory through perturbative triples (CCSD(T)) method using aug-cc-pVTZ basis set were performed on optimized structures to obtain accurate energy values. A tight convergence criterion for the geometry and wavefunction was employed in all calculations. All calculations were

performed using the ground state multiplicity of 1, unless specified explicitly. All the structures and vibrations were visualised and analysed using Gauss View-05.¹⁰⁴

Potential of the 3:3 face staggered configuration of the methane dimer, between C-C distances of 1.6 Å and 3.7 Å was calculated. The optimization was performed with all the C-H bonds and the angles of both the molecules unconstrained, using MP2 theory and aug-cc-pVTZ basis set. Single point calculations were subsequently performed on these optimized structures using the CCSD(T) method and aug-cc-pVTZ basis set to obtain the potential energy surface (PES) shown in Fig. 2.1. Potential energy of the structures with the terminal C-H bonds of both the molecules fixed at 1.1 Å, 1.3 Å and 1.5 Å between C-C distances of 1.55 Å and 3.7 Å were also determined. All the other C-H bonds and angles were unconstrained during this optimization. Additionally, potential energy of the two methane molecules in the configuration of the equilibrium dimer, with all atoms frozen, along the C-C distance was also computed. All these potential energy curves are shown in Fig. 2.2.

Transition state (TS) searches were performed using the MP2/aug-cc-pVTZ combination and TSs were identified by the existence of a single imaginary frequency in vibrational frequency analysis. Obtained TSs were further reconfirmed by connecting them to reactants and products by the Intrinsic Reaction Coordinate (IRC) calculations. Structures from IRC calculations (reactants and products) were further optimized to obtain the actual reactants and products. Single point calculations on the optimized structures were performed to obtain the energy barriers at the CCSD(T)/aug-cc-pVTZ level. Temperature corrections were applied to estimate the free energy of the different molecular configurations at 300 K and 1250 K.

2.3 Results and discussion

2.3.1 Relaxed methane dimer along the C-C distance coordinate

The D_{3d} configuration of the methane dimer, where each methane molecule exposes three of its hydrogen atoms in a staggered arrangement has been reported to be the lowest energy configuration^{5,105} and is shown in Fig. 2.1a. Employing the Counterpoise correction scheme, the equilibrium separation (C-C distance) of the methane molecules in this dimer configuration was calculated to be 3.689 Å using the MP2/aug-cc-pVTZ

combination. The value of the equilibrium separation between the molecules is in agreement with the value of 3.69 Å reported⁹⁷ using the MP2/aug-cc-pVTZ combination and is close to the value of 3.67 Å reported⁵ using the CCSD(T)/aug-cc-pVTZ combination. The equilibrium C-H bond length of methane in the dimer is calculated as 1.086 Å which is in agreement with the value of 1.0859 ± 0.0003 Å reported³ for methane earlier. The equilibrium H-C-H angles have values 109.542° (terminal angle) and 109.400° (face angle).

Fig. 2.1 a) Counterpoise corrected CCSD(T)/aug-cc-pVTZ and MP2/aug-cc-pVTZ potential energy curves of the methane dimer with all C-H bonds relaxed and unconstrained along the C-C distance coordinate. The structures corresponding to the dimer at a C-C distance of 3.7 Å and 1.6 Å are also shown explaining the terminology used in the article for different bonds and angles. b) Variation of the different C-H bonds (on the left axis) and H-C-H angles (on the right axis) of one of the methane molecules of the dimer along the C-C distance coordinate obtained from the MP2/aug-cc-p-VTZ optimized structures. The values of the other methane molecule are the same.

The potential energy of the dimer in the same configuration described earlier, as a function of the C-C distance of the two molecules, was calculated between 1.6 Å and 3.7 Å by optimizing the structures using MP2/aug-cc-pVTZ combination. Subsequently, single point calculations were performed on these optimized structures using the CCSD(T)/aug-cc-pVTZ combination. It is suggested that Basis-set superposition errors (BSSE) may significantly influence the interaction potential of the methane dimer.⁹⁴ Thus, the BSSE has been corrected using the Counterpose correction method and the energy values presented in Fig. 2.1a are the corrected energies. The BSSE is calculated to be 0.00021 hartree (~ 0.55 kJ mol⁻¹) for the configuration at a C-C distance of 3.7 Å but rapidly increases to 0.00191 hartree (~ 5 kJ mol⁻¹) for the configuration at C-C distance of 1.6 Å as shown in Table 2.1.

Table 2.1 Basis Set Superposition Errors (BSSE) in total energy calculations of the relaxed methane dimer along the C-C coordinate estimated using the Counterpose Correction method.

C-C distance (Å)	MP2 counterpoise correction to total energy (kJ mol ⁻¹)	CCSD(T) counterpoise correction to total energy (kJ mol ⁻¹)
1.6	5.83	5.02
1.7	5.38	4.72
1.8	4.95	4.38
1.9	4.52	4.03
2.1	3.64	3.25
2.3	2.89	2.58
2.5	2.28	2.06
2.8	1.60	1.46
3.1	1.12	1.03
3.4	0.80	0.74
3.7	0.58	0.55

The absence of a visible potential well in Fig. 2.1 is due to the scale on the energy axis which is 0.35 hartree (~ 919 kJ mol⁻¹) (depth of well is less than 2 kJ mol⁻¹) and the scale on the C-C distance coordinate being limited to 3.7 Å. The potential energy curve shown in Fig. 2.1a rises steeply when the C-C distance between the methane molecules is less than 2.5 Å. The steep rise in the potential energy along the decreasing C-C distance coordinate can be attributed to the strong repulsive force from the other molecule. A

detailed discussion on molecular deformation and repulsion between the molecules as they approach each other, and their effect on the energy of the system is presented in sections 2.3.2 and 2.3.3.

Analysis of the optimized structures along the C-C coordinate shows significant deformation in both the molecules from their original tetrahedral geometry. Structures corresponding to the distorted dimer at a C-C distance of 1.6 Å and the dimer at 3.7 Å are presented in Fig. 2.1a along with the definitions of the terminal and the face angles and bonds. The variation of the H-C-H angles (both face angles and terminal angles) and the C-H bonds (both terminal and face) of the two molecules along the C-C distance coordinate are presented in Fig. 2.1b. The terminal C-H bonds can be seen to be stretched significantly when the C-C distance between the molecules is less than 2 Å while the remaining C-H bonds shrink slightly. Significant deviations are also observed in the H-C-H angles along the decreasing C-C distance coordinate. The terminal angles undergo negative deviation from the equilibrium value (109.5°), as the face C-H bonds bend outwards (away from the other molecule) to minimise the repulsion. The face angles on the other hand exhibit positive deviation as the CH₃ fragments open up towards an sp² planar configuration. Methane molecules at small inter-nuclear separations, as depicted in Fig. 2.1, may result from severe collisional or mechanical impact. Thus, mechanical impact of the molecules induce vibrational activation of the molecules: stretching of the terminal C-H bonds and outward umbrella bending of the remaining C-H bonds.

2.3.2 Pre-stretched methane dimer along the C-C distance coordinate and potential energy curve crossings

Since mechanical impact-induced vibrational activation involves stretching of terminal C-H bonds of the methane molecules, we investigated this effect in detail. Potential energies of the configurations with stretched and prefixed terminal C-H bonds, along the C-C distance coordinate, were calculated. All C-H bonds of both the molecules except the terminal C-H bonds were unconstrained and relaxed. The potential energy curves with the terminal C-H bonds prefixed at 1.1 Å (equilibrium C-H bond length of methane), 1.3 Å and 1.5 Å, obtained using the CCSD(T)/aug-cc-pVTZ combination are depicted in Fig. 2.2a. Also shown in the figure is the potential energy curve of a rigid

dimer, in its equilibrium configuration, whose bonds were not allowed to relax along the scan. Fig. 2.2a shows that at large inter-molecular separations (C-C distance of 2.2 Å to 3.7 Å), potential energies of the configurations with the terminal C-H bonds prefixed at 1.5 Å and 1.3 Å are much higher than those whose terminal C-H bonds are prefixed at 1.1 Å. However, at smaller inter-molecular separations (C-C distance < 2.2 Å), the gradient of the CH= 1.5 curve is the smallest among the three.

Fig. 2.2 a) Potential energy curves along the C-C distance coordinate of two methane molecules with both the terminal C-H bonds fixed at 1.1 Å, 1.3 Å and 1.5 Å (all other bonds relaxed). Also shown is the potential energy curve for two rigid molecules in the configuration of the equilibrium dimer. The inset shows the potential energy curve crossings within the C-C distance of 1.5 to 1.9 Å. **b)** Variation of the face and terminal angles of one of the methane molecules as a function of the C-C distance, obtained from the above potential energy scan. The red, green and blue curves represent the angles of the methane molecule with terminal C-H bond fixed at 1.1 Å, 1.3 Å and 1.5 Å respectively. Angular variation of the other molecule is similar.

It can be seen from Fig. 2.2a that the potential energy curves corresponding to both CH= 1.5 and CH= 1.3 cross the curve corresponding to CH= 1.1 and also each other at C-C distances lower than 2 Å. The multiple potential energy curve crossings at small inter-nuclear separations enable multiple energy level transitions. The inset of Fig. 2.2a depicts a zoomed in section of the potential energy curves showing successive crossing of the CH= 1.5 and CH= 1.3 curves. A minimum energy pathway along the decreasing C-C distance coordinate can be traced for the CH= 1.1 curve by successively crossing to CH= 1.3 and CH= 1.5 curves, as indicated by the red, green and blue arrows. These successive crossings may be viewed as ascending a terraced slope, whose vertical rise decreases at every step along the ascent. This leads to a summit of lower elevation as depicted in the second inset in Fig. 2.2a. The difference in energy of the CH= 1.5 and CH= 1.1 curves at C-C distance of 1.55 Å in Fig. 2.2a is as large as 142 kJ mol⁻¹. Thus, stretching of terminal C-H bonds of the methane molecules enable them to collide or approach each other to shorter inter-nuclear separations along lower energy pathways. In other words, vibrational pre-activation of the methane molecules in the minimum energy configuration, allows mechanical impact via lower energy paths involving successive potential energy curve crossings. In an actual collision scenario at finite temperatures, a multitude of stretching and bending vibrations of the molecules may be activated. Such vibrational activation may facilitate approach of the molecules towards each other, with lowering of net energy of the system by amounts greater than the 142 kJ mol⁻¹ demonstrated here. A discussion on the reason for lower energy of the vibrationally excited configurations at very short inter-nuclear separation is presented in section 2.3.3.

Additionally, analysis of the structures of the two methane molecules with stretched terminal C-H bonds at C-C distance of 3.7 Å suggests that this stretching facilitates an intrinsic outward bending of the remaining C-H bonds. The outward bending has significant consequences in lowering the energy of the system and is discussed in section 2.3.3. The variation of the face and terminal angles of the methane molecules as a function of the C-C distance coordinate, for the cases with fixed terminal C-H bond of 1.1 Å, 1.3 Å and 1.5 Å are shown in Fig. 2.2b. The terminal angles of the dimer with terminal C-H bonds at 1.5 Å can be seen to be bent outwards even at C-C distance of 3.7 Å. This is not the case with the dimer with the terminal C-H bond fixed at 1.1 Å.

2.3.3 Reason for net lowering of energy of vibrationally excited dimer at short inter-nuclear separation

The total energy of the dimer along the C-C distance coordinate has contributions from the energy of the individual molecules (deformed in some of these cases) and the interaction between the molecules (can be attractive or repulsive). At any point on the C-C distance coordinate, the total energy of the system is the sum of the energy of the two molecules (each may be distorted from the equilibrium structure), and the interaction energy between them. This is analogous to the activation strain model for chemical reactivity proposed by Bickelhaupt and co-workers.^{106,107} In order to understand the energy penalty in molecular deformation and the nature of interaction between the molecules along the C-C distance coordinate, a simple energy decomposition, into these broad components, was performed on the molecules. The energy penalty for the deformation of each methane molecule into configurations along the C-C distance coordinate is calculated with reference to the undistorted equilibrium methane molecule. The deformation energy of each molecule is calculated as

$$\text{Deformation energy of one molecule} = E_{(CH_4 D)} - E_{(CH_4 E)} \quad (\text{Eqn. 2.1})$$

Where $E_{(CH_4 D)}$ is the single point energy of one of the deformed molecules in the dimer (not re-optimized) and $E_{(CH_4 E)}$ is the energy of the optimized equilibrium methane molecule. The deformation energy values for one of the methane molecules in the different cases along the C-C distance coordinate are reported in Table 2.2. Since the dimer is symmetric, deformation energy of the other molecule is expected to be the same.

The nature of interaction between the two molecules at any point on the C-C distance coordinate can be ascertained by the interaction energy between the two molecules in these configurations. A negative sign for the interaction energy suggests attractive interaction and a positive sign suggests repulsive interaction. The interaction energy between the molecules is calculated as

$$\text{Interaction energy} = E_{(CH_4 \text{ dimer})} - 2 \times E_{(CH_4 D)} \quad (\text{Eqn. 2.2})$$

where $E_{(CH_4 \text{ dimer})}$ is the total energy of the optimized dimer at any C-C distance and $E_{(CH_4 D)}$ is the single point energy of one of the fragments of the dimer in the same configuration as in the dimer (without re-optimization). These values for different systems of methane molecules along the C-C distance coordinate are also reported in Table 2.2.

Table 2.2 Deformation energy of one of the methane molecules along the C-C distance coordinate, calculated using (Eqn. 2.1) for the relaxed methane dimer and the dimer with its terminal C-H bonds fixed at 1.1 Å and 1.5 Å. The deformation energy of the other molecule is the same. Also reported is the interaction energy between the two methane molecules along the C-C distance coordinate, calculated using (Eqn. 2.2) in the relaxed methane dimer and the dimer with its terminal C-H bonds fixed at 1.1 Å and 1.5 Å.

C-C distance (Å)	Deformation energy- one methane in relaxed dimer (kJ mol ⁻¹)	Interaction energy- relaxed dimer (kJ mol ⁻¹)	Deformation energy- one methane in dimer with terminal CH= 1.1 (kJ mol ⁻¹)	Interaction energy- dimer with terminal CH= 1.1 (kJ mol ⁻¹)	Deformation energy- one methane in dimer with terminal CH= 1.5 (kJ mol ⁻¹)	Interaction energy- dimer with terminal CH= 1.5 (kJ mol ⁻¹)
1.55			115.84	610.69	257.25	185.43
1.60	181.46	333.40	100.22	564.50	242.80	192.41
1.70	90.99	415.43	73.04	475.55	211.77	208.08
1.80	58.70	367.17	51.64	392.18	184.47	207.80
1.90	38.62	305.42	35.51	316.65	164.99	188.36
2.10	15.96	192.25	15.34	194.37	143.97	127.94
2.30	5.80	109.97	5.80	109.97	135.53	74.16
2.50	1.83	56.91	1.95	56.63	132.50	37.61
2.80	0.24	16.42	0.39	16.24	131.43	9.50
3.10	0.02	1.79	0.17	1.73	131.32	-0.32
3.40	0.00	-2.20	0.14	-2.22	131.32	-2.70
3.70	0.00	-2.63	0.13	-2.63	131.32	-2.67

From Table 2.2 it can be seen that the deformation energy of methane in the configuration at C-C distance of 3.7 Å, with the terminal C-H bond fixed at 1.5 Å is much higher than that of methane with the terminal C-H bond fixed at 1.1 Å. The deformation energy of the molecule increases along the decreasing inter-nuclear separation for both these cases, reaching values of 242.8 kJ mol⁻¹ for the CH= 1.5 case at C-C distance of 1.6 Å, while it is only 100.2 kJ mol⁻¹ for the CH= 1.1 case. At C-C distance of 1.6 Å, the interaction energy between the two methane molecules with their

terminal C-H bonds fixed at 1.5 Å is 192.4 kJ mol⁻¹ while that of the configuration with terminal C-H bonds of 1.1 Å is much higher at 564.5 kJ mol⁻¹. The large positive value of interaction energy for the configuration with terminal C-H bonds fixed at 1.1 Å implies that the repulsion between the molecules in this configuration is significantly higher than the configuration with the terminal C-H bonds fixed at 1.5 Å. The difference of deformation energy of methane molecule at C-C distance of 1.6 Å for the two cases $E_{(deformation\ CH=1.5)} - E_{(deformation\ CH=1.1)}$ is 142.6 kJ mol⁻¹ while that of the interaction energy between the molecules in these two cases $E_{(interaction\ CH=1.5)} - E_{(interaction\ CH=1.1)}$ is -372.09 kJ mol⁻¹. Since the total energy of the configuration has contributions from both the deformation energy (two times that of each methane molecule) and the interaction energy, the total energy at C-C distance of 1.6 Å, for the configuration with CH= 1.5 is lower than that of the configuration with CH= 1.1. In other words, at very close inter-nuclear separation, the more favourable interaction between the molecules (lower repulsion), in the configuration with stretched terminal C-H bonds (CH= 1.5 in this case), compensates for the larger deformation of the molecules. This leads to net lower energies for the stretched configurations, compared to the configurations without pre-stretched bonds.

Table 2.2 shows that the deformation energy and the interaction energy of the configuration with relaxed C-H bonds fall in between that of the cases of CH= 1.1 and CH= 1.5 at C-C distance of 1.6 Å. In the relaxed configuration, the intrinsic stretching of the terminal C-H bonds is lower than 1.5 Å at C-C distance of 1.6 Å. The outward bending of the C-H bonds of the molecules when the terminal C-H bonds are fixed at 1.1 Å is lower compared to that when it is 1.5 Å, as can be seen from the lower negative deviation of the terminal angles in Fig. 2.2b. The terminal C-H bonds, prefixed at 1.1 Å, limit the outward bending of the other C-H bonds in the former case. This is responsible for the larger repulsive interaction between the two molecules at short inter-nuclear separation, as evident from the large positive interaction energy. Thus, the outward bending of the face C-H bonds and stretching of the terminal C-H bonds not only minimizes repulsion between the two molecules but also facilitates interaction between their carbon centres at short inter-nuclear separation. This explains the

significant lowering of energy of the vibrationally pre-excited system (with stretched C-H bonds) upon approach to within 2 Å of each other.

2.3.4 Coupling induced dissociation of methane molecules and formation of C₂ hydrocarbons: transition states, reaction paths, energetics and origin of barrier

Transition state search was performed on the deformed dimer configurations at short inter-nuclear separation to investigate potential coupling induced dissociation reactions. The obtained TS and the intrinsic reaction coordinate (IRC) tracing the descent on either side of the TS are depicted in Fig. 2.3a. The existence of a single imaginary frequency and the IRC pathway connecting the TS with minima on either side of the TS confirms the TS. The terminal C-H bonds of both the methane molecules in TS1 are stretched to 1.75 Å at a C-C distance of 1.66 Å. The vibration corresponding to the imaginary frequency at the TS further suggests that the dissociation of the terminal C-H bonds of both the methane molecules is induced by the coupling of the two molecules.

Optimization of the structure corresponding to reactant in the IRC shown in Fig. 2.3a yields the methane dimer at its equilibrium separation as the reactant. The structure of TS1 suggests that ethane + 2 H radicals may be the products. Optimization of the structure from the IRC gives ethane and two hydrogen radicals as the product with a ground state multiplicity of 3. Optimization of the same as a singlet gives ethylene and two hydrogen molecules. However, there exists an additional transition state, TS2, as shown in Fig. 2.3b which corresponds to the formation of ethylene and two hydrogen molecules. This sequential transition state exists further along the reaction coordinate while descending from TS1 and is found to have its eliminated terminal hydrogens in a trans configuration. Existence of sequential transition states and bifurcation of reaction path is known to involve a valley ridge inflection point on the potential energy surface and these concepts and a few examples are discussed in the review by Houk and co-workers.¹⁰⁸ The IRC for TS2 (Fig. 2.3b) shows abstraction of one hydrogen each from each CH₃ fragment by the eliminated terminal hydrogens and coupling of the two carbon centres to form ethylene and two hydrogen molecules. Thus, ethane and two hydrogen radicals may not lie on the adiabatic PES connecting the methane dimer and ethylene + 2 H₂. However, the former may be obtained in experiments or dynamics trajectories.

Fig. 2.3 The transition state (TS) and the Intrinsic Reaction Coordinate (IRC) path tracing the descent on either side of the TS for a) the coupling induced dissociation of the terminal C-H bonds of the two methane molecules; and b) for the concerted dissociation and coupling of two methane molecules to form ethylene. The two transition states occur in sequence. The values of important bond and angle parameters are shown. The structures corresponding to the minima on either side of the TS along the IRC path are also shown.

The energy barriers for the transformation of two methane molecules to C₂ hydrocarbons are calculated with respect to the optimized reactant and in this case it corresponds to the equilibrium dimer. The energy barrier for this bimolecular coupling induced transformation of methane molecules to form ethane or ethylene via TS1 shown in Fig. 2.3a, at the CCSD(T)/aug-cc-pVTZ level is calculated to be 614.8 kJ mol⁻¹. The corresponding activation enthalpy barrier at 300 K ($\Delta H_{a(300\text{ K})}$) is 579.2 kJ mol⁻¹. Here, the enthalpy is calculated as the sum of CCSD(T) total energy and MP2 thermal correction to enthalpy. The formation of ethane and two hydrogen radicals is energetically uphill by 528.5 kJ mol⁻¹ ($\Delta H_{r(300\text{ K})} = 490.3\text{ kJ mol}^{-1}$) while the formation of ethylene and two hydrogen molecules is energetically uphill by only 242.6 kJ mol⁻¹.

($\Delta H_{r(300\text{ K})} = 63.9\text{ kJ mol}^{-1}$). In pyrolysis of methane, the formation of ethane in the gas phase is typically expected to be the result of gas phase unimolecular dissociation of methane to form methyl radicals, which subsequently couple to give ethane. The standard bond dissociation enthalpy (BDE) is defined as the change in standard enthalpy that occurs upon cleavage of a chemical bond. For methane to form $\text{CH}_3 + \text{H}$ at 298.15 K, the BDE is reported to be 438.9 kJ mol^{-1} and for CH_3 to form $\text{CH}_2 + \text{H}$ it is reported to be 463.1 kJ mol^{-1} .⁴ The activation barriers for both the dissociation steps would thus be higher than the BDE values.

The extremely high energy barrier for this bimolecular coupling induced dissociation pathway via TS1 is due to the large repulsion between the molecules and the distortion required from their equilibrium structures along the C-C distance coordinate, as discussed earlier. As per Bickelhaupt and co-workers,^{106,107} the barrier for a reaction has contributions from the activation strain or the deformation of the reacting molecules and the interaction energy between the molecules along the reaction coordinate. This forms the basis of their ‘Activation Strain model’ for chemical reactivity which gives fundamental insights into the nature and origins of the activation barriers in different reactions.¹⁰⁷ The energy to deform methane from its equilibrium geometry along the IRC path (Fig. 2.3a) is calculated using (Eqn. 2.1) and is reported in Table 2.3.

Points 1 to 5 in Table 2.3 correspond to alternate structures on the IRC path shown in Fig. 2.3a, starting with the reactant, up to the TS. The deformation energy of each molecule and interaction energy of the configuration are calculated by the same method as presented in section 2.3.3. The values of deformation energy of one of the molecules along the IRC path and the interaction energy between the molecules for the same points are reported in Table 2.3. The deformation energy of each methane molecule is observed to increase rapidly from 81.3 kJ mol^{-1} at the first point on the IRC path, reaching a value of 331.9 kJ mol^{-1} at the TS. The interaction energy between the two fragments on the other hand has a value of 174.3 kJ mol^{-1} at the first point on the IRC and decreases along the IRC path, suggesting the transformation from repulsive to attractive interaction. The interaction energy can be seen to become -51.7 kJ mol^{-1} at the TS. Thus, large deformation of the molecules and severe repulsion characterise the reaction coordinate

in this mechanism of bimolecular direct transformation of methane molecules to ethane/ethylene.

Table 2.3 The deformation energy of one of the methane molecules at alternate points along the IRC curve of the TS1 shown in Fig. 2.3a, calculated with respect to an equilibrium methane molecule. The interaction energy between the two molecular fragments at the same points along the IRC curve is also reported. The positive value of interaction energy suggests that the interaction is repulsive and negative value suggests that it is attractive. The deformation energy and interaction energies are calculated in a manner similar to that described in section 2.3.3. using (Eqn. 2.1) and (Eqn. 2.2) respectively.

Points along IRC	Deformation energy of each CH ₄ fragment (kJ mol ⁻¹)	Interaction energy (kJ mol ⁻¹)	Normalised deformation energy of each CH ₄ fragment (kJ mol ⁻¹)	Normalised interaction energy (kJ mol ⁻¹)
1	81.31	174.30	0.00	0.00
2	127.19	178.14	45.88	3.84
3	180.11	166.87	98.80	-7.44
4	233.98	131.47	152.67	-42.84
5	285.00	59.71	203.69	-114.60
TS1	331.90	-51.73	250.59	-226.04

2.3.5 An alternate pathway for coupling induced dissociation of methane molecules to form ethane and pathways for its subsequent dehydrogenation to ethylene

The coupling induced dissociation of two methane molecules to form ethane and ethylene, as depicted in Fig. 2.3, have symmetrical TSs resulting from perfect head-on mechanical impact of the two molecules, in their minimum energy configuration. When the impact is not head-on and symmetrical, the formation of ethane may proceed via a non-symmetrical TS, in a methylene radical-like pathway, eliminating a hydrogen molecule as shown in Fig. 2.4. The elimination of a hydrogen molecule from one of the methane molecules proceeds with simultaneous transfer of hydrogen from the methane molecule to the methylene radical. The energy barrier for this coupling induced transformation of two methane molecules to form ethane and a hydrogen molecule via TS3 shown in Fig. 2.4 is calculated to be 523.9 kJ mol⁻¹ ($\Delta H_{a(300\text{ K})} = 492.9 \text{ kJ mol}^{-1}$). Ethane and the hydrogen molecule formed in the above pathway can undergo further dehydrogenation to form ethylene and two hydrogen molecules in two different

pathways. The search for reaction pathways was limited to those involving hydrogen molecules as the formation of hydrogen radicals was found to be highly uphill in energetics.

Fig. 2.4 The TS and the IRC path tracing the descent on either side of the TS in the formation of ethane. The pathway involves elimination of a hydrogen molecule from one of the methane molecules, transfer of a hydrogen atom from the other methane to the one undergoing H₂ elimination and concerted coupling of two methane molecules. Important bond parameters at the TS and the structures corresponding to the minima on either side of the TS along the IRC path are also shown.

When dehydrogenation of ethane proceeds with no assistance from the eliminated hydrogen molecule, an additional hydrogen molecule is generated via TS4 shown in Fig. 2.5a. Here, each hydrogen in the newly eliminated H₂ molecule has origins from each CH₃ moiety in ethane. This is because the successive elimination of two hydrogens from the same CH₃ moiety of ethane is energetically unfavourable compared to elimination of one hydrogen each from each CH₃ moiety of ethane.⁴ The bond dissociation enthalpy for the formation of CH₃CH₂ from ethane at 298.15 K is reported to be 421.7 kJ mol⁻¹. For the sequential dehydrogenation and formation of CH₃CH from CH₃CH₂ it is reported to be 452.61 kJ mol⁻¹ while that of the formation of CH₂CH₂ from CH₃CH₂ is much lower at 150.59 kJ mol⁻¹.⁴ Ethane may also undergo dehydrogenation, assisted by the eliminated hydrogen molecule via TS5 as shown in Fig. 2.5b. Each hydrogen atom in the previously eliminated hydrogen molecule abstracts one hydrogen each from the two CH₃ moieties of ethane to form two hydrogen molecules. The energy barrier for the dehydrogenation of ethane by hydrogen abstraction by the eliminated hydrogen

molecule is significantly lower with value of $345.1 \text{ kJ mol}^{-1}$ ($\Delta H_{\text{a}}(300 \text{ K}) = 322.6 \text{ kJ mol}^{-1}$). In contrast, the energy barrier for the unassisted dehydrogenation has a value of $511.3 \text{ kJ mol}^{-1}$ ($\Delta H_{\text{a}}(300 \text{ K}) = 484.8 \text{ kJ mol}^{-1}$). The presence of hydrogen is known to have a favourable impact during pyrolysis of methane as the decomposition of methane in the presence of hydrogen initiates at temperatures from 700-800 °C while pure methane decomposes at temperatures over 1000 °C.³⁷

Fig. 2.5 IRC curves tracing the decent on either side of the TS corresponding to a) dehydrogenation of ethane to form ethylene, with no assistance from the pre-eliminated hydrogen molecule, via TS4; and b) dehydrogenation of ethane to form ethylene in a hydrogen abstraction mechanism initiated by the pre-eliminated hydrogen molecule, via TS5. The structures corresponding to minima on either side of the IRC curve are also indicated in each case. The values of relevant bonds of both the TSs are also shown in the figure.

2.3.6 Comparison of activation barriers and energetics of transformation of methane to C₂ hydrocarbons along different pathways.

All the pathways for the formation of ethane and ethylene from two methane molecules and corresponding TSs and energy barriers are shown in Fig. 2.6. The three different sets of reaction paths as discussed earlier, 1) bimolecular coupling induced direct dissociation of the two molecules via TS1 and TS2 to form ethane and ethylene, 2) bimolecular coupling induced dissociation via TS3 to form ethane, and 3) dehydrogenation of ethane to form ethylene, are colour coded with blue, red and green arrows respectively in the figure.

Fig. 2.6 Energy level diagram representing the different pathways for the transformation of two methane molecules to C₂ hydrocarbons showing the transition states (TSs) for each pathway and the energy barriers obtained using the CCSD(T)/aug-cc-pVTZ combination.

The figure suggests that the formation of ethane and H₂ is energetically more favourable compared to ethylene and two H₂. The energetics of the different reaction paths shown in Fig. 2.6 are summarised in Table 2.4. To comment on the thermodynamics and kinetics of the processes, the activation free energy barriers and change in free energy for each of these reaction pathways were calculated for temperatures of 300 K and 1250 K. These values are also summarised in Table 2.4. The free energy in these cases is calculated as sum of the CCSD(T) potential energy and MP2 thermal corrections to Gibb's free energy as reported in the Gaussian 09 based calculations. The activation free energy barrier for the direct bimolecular coupling induced dissociation of methane and

formation of C₂ hydrocarbons is observed to increase by over 100 kJ mol⁻¹ when the temperature increases from 300 K to 1250 K. However, the formation of ethylene via TS1 and TS2 becomes thermodynamically more favourable at 1250 K compared to 300 K although the change in free energy is still positive. The activation free energy barrier for the formation of ethane and H₂ via TS3 is much lower than that of the formation of ethylene and 2 H₂ via TS1 and TS2, irrespective of the temperature. Additionally, the reaction is thermodynamically more favourable compared to the formation of ethylene. The thermodynamic trends of transformation of methane to ethane and ethylene are in agreement with those reported in literature.^{12,37} Similarly, the transformation of ethane to ethylene, although not spontaneous, is more favourable at higher temperatures. From the pathways in Table 2.4, it can be deduced that a two-step transformation of methane, via ethane, is the kinetically and thermodynamically favourable pathway for the formation of ethylene.

Table 2.4 Activation free energy barriers and energetics of transformation of two methane molecules to C₂ hydrocarbons along the different reaction pathways shown in Fig. 2.6 and the temperature effect in the kinetics and thermodynamics of these reactions. The free energies are calculated as sum of CCSD(T) total energy and MP2 corrections to Gibb's free energy as obtained from Gaussian calculations.

Reaction pathway, as shown in Fig. 2.6	CCSD(T) activation energy barrier (kJ mol ⁻¹)	CCSD(T) ΔE for reaction (kJ mol ⁻¹)	Activation free energy barrier- 300 K (kJ mol ⁻¹)	ΔG for reaction - 300 K (kJ mol ⁻¹)	Activation free energy barrier- 1250 K (kJ mol ⁻¹)	ΔG for reaction- 1250 K (kJ mol ⁻¹)
Via TS1 (2 CH ₄ → C ₂ H ₆ + 2 H)	614.8	528.5	612.6	480.1	717.1	433.5
Via TS1 and TS2 (2 CH ₄ → C ₂ H ₄ + 2 H ₂)	614.8	242.6	612.6	189.1	717.1	113.9
Via TS3 (2 CH ₄ → C ₂ H ₆ + H ₂)	523.9	77.9	511.3	73.8	560.4	96.9
Via TS4 (C ₂ H ₆ + H ₂ → C ₂ H ₄ + 2 H ₂)	511.3	164.7	492.2	115.2	513.4	16.8
Via TS5 (C ₂ H ₆ + H ₂ → C ₂ H ₄ + 2H ₂)	345.1	165.1	345.8	113.5	431.7	9.3

2.4 Summary

Mechanical impact of two methane molecules in the equilibrium dimer configuration leads to the activation of the stretching and bending vibrational modes of the molecules. On the other hand, vibrationally pre-activating the molecules in the configuration of their equilibrium dimer, facilitates mechanical impact of the molecules via lower energy pathways involving successive potential energy curve crossings. The vibrations responsible for access to such lower energy pathways include the stretching of the terminal C-H bonds and outward umbrella like bending of the remaining C-H bonds of both the molecules. Stretching of the terminal C-H bonds and outward bending of the remaining C-H bonds minimize repulsion between the molecules and facilitates favourable interaction between the two, giving access to lower energy pathways.

Mechanical impact in the minimum energy configuration can result in the bimolecular coupling induced dissociation of two methane molecules and their transformation into C₂ hydrocarbons like ethane or ethylene. The symmetric transition state in this mechanism shows coupling induced dissociation of the terminal C-H bonds of both the molecules. The adiabatic transformation of the methane dimer in this mechanism results in the formation of ethylene and two hydrogen molecules whereas a non-adiabatic transformation may result in ethane and two hydrogen radicals. The adiabatic transformation involves sequential transition states, the second of which shows a hydrogen abstraction mechanism involving the dissociated/eliminated terminal hydrogens, along with the coupling reaction. The energy barrier for the transformation in this coupling induced mechanism is very high due to the great repulsion between the molecules along the approach towards each other.

The coupling induced transformation of two methane molecules to form ethane may also proceed by a hydrogen molecule elimination mechanism accompanied by intermolecular transfer of a hydrogen atom. The energy barrier along this pathway is lower than that in the pathway involving elimination of terminal hydrogen atoms of both the molecules. Ethane may be further dehydrogenated to form ethylene in two pathways 1) without assistance from the eliminated hydrogen molecule: additional hydrogen molecule eliminated with one coming from each CH₃ fragment of ethane, and 2) with assistance from the eliminated hydrogen molecule: the eliminated hydrogen molecule

splits and abstracts one hydrogen each from each CH₃ fragment. The energy barrier for the hydrogen assisted dehydrogenation is much lower than the non-assisted pathway. The formation of ethylene and two hydrogen molecules is not spontaneous but becomes more favourable at high temperatures over 1250 K.

Ab initio molecular dynamics simulations¹⁸ and experiments in laser heated diamond anvil cells^{17,19} have demonstrated the conversion of methane to larger hydrocarbons and even diamond under extremes of temperature and pressure. The evolution of molecular hydrogen is also reported. At high temperatures and pressures as in the planetary systems, mechanical impact of the methane molecules as well as activation of their vibrational modes may cause their transformation to C₂ hydrocarbons. The pathways and mechanisms discussed in this chapter maybe the pathways for the conversion of methane to C₂ hydrocarbons and molecular hydrogen. These C₂ hydrocarbons may subsequently undergo similar transformation to form C₃ and C₄ hydrocarbons under sequential mechanical impact. Based on the lower bond dissociation enthalpy⁴ values for dehydrogenation of C₂ hydrocarbons, it is speculated that the activation barriers for such sequential dissociation and coupling of C₂ hydrocarbons to form larger hydrocarbons will be lower than that of conversion of methane to C₂ hydrocarbons. Similar hydrocarbon formation from methane in the upper mantle of the earth and subsequent transport to shallower regions of the earth through faults may be an abiogenic source of hydrocarbons in the earth.¹⁹ This process and such hydrocarbon reserve forms the basis of the ‘abiogenic origin of petroleum’ on the earth.

Ab initio molecular dynamics simulations and molecular beam experiments may throw more light on the product distribution and controlling factors in the event of high speed collision of methane molecules. Molecular cluster beam impact on a surface causes multiple internal collisions among the molecules within the interior of the cluster while the molecules on the outside scatter. Such internal collisions during methane cluster impact on surfaces can be utilized to convert it to larger hydrocarbons in the mechanisms described in the chapter.

3 First-principles investigation of the collision induced dissociation of methane on copper nano-clusters: interplay of collision dynamics, geometric and electronic effects

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3.1 Introduction

Collisions of methane with inert gas atoms like argon (Ar) can induce vibrational excitation of the C-H bonds by means of transfer of the translational kinetic energy of the Ar atom to the internal modes of methane.⁴¹ Dissociative chemisorption of methane on a Ni surface, facilitated by colliding argon atoms (“Chemistry with a Hammer”)^{39,40} or via direct collision on the surface^{42,43} is enhanced dramatically by the translational kinetic energy of the colliding atom/ molecule. Vibrational pre-excitation of the colliding molecule was shown to have a significant contribution in increasing dissociation probability, with vibrational energy bringing about peculiar effects like vibrational mode and bond selective dissociation of methane.^{47,48,50} Thus, Collision Induced Dissociation (CID) of methane opens an alternate pathway for the reactions involving methane. In this context, formation of a monolayer of graphite on Pt (111) surface using a supersonic molecular beam of methane¹⁰⁹ was reported in 2004. This collision induced growth of graphene (referred to as monolayer graphite at the time of publication) was observed to be insensitive to the metal surface features and thus offers a pathway for carrying out reactions on non-homogeneous surfaces. Thus, collision dynamics, finite temperature and vibrational excitation have significant contributions to C-H bond dissociation of methane.

Copper is considered a relatively inactive catalyst for dissociation of methane. Theoretical investigations of the dissociation of methane on monocrystalline copper surfaces have revealed the elementary steps of dehydrogenation to be energetically

uphill and thus, thermodynamically unfavourable, with activation energy barriers of 95-190 kJ mol⁻¹ for each step.^{54,110} Thus, understanding the effects of collision dynamics on copper catalysts is pertinent in efforts for better evaluating the prospect of methane dissociation on such surfaces. Small metal clusters of copper with closed d-shells have captured the attention of experimentalists as well as theoreticians due to their peculiar electronic structure and structure/ size sensitive catalytic properties.¹¹¹⁻¹¹⁵ Moreover, small clusters are representative structures of the nano-environment surrounding active sites on bulk surfaces, as only a few surface atoms are involved in the energy exchange in collisional processes.¹¹⁶ Thus, an investigation of collision induced dissociative chemisorption and reactions of methane on Cu clusters is imperative for identifying the role of collisions and size/structure properties of the cluster on the free energy barriers associated with the processes.

Some groups recently developed a remote catalytic/ copper vapour assisted Chemical Vapour Deposition (CVD) process for the direct growth of graphene on inert substrates like SiO₂.¹¹⁷⁻¹¹⁹ In this process, Cu vapour is believed to catalyse the decomposition of methane which subsequently deposits and grow on the inert substrate. However, there is no concrete evidence to prove this claim and the decomposition mechanism which may result from the direct collision of methane on the copper vapour is yet to be elucidated. Additionally, copper deposits observed on the walls of the CVD furnace during the CVD growth of graphene may involve Cu nanoclusters, which would participate in the dissociation of methane like the catalytic Cu foil.

Hence, in view of the great potential of collisions to induce dissociation and the catalytic potential of copper nanoclusters, collision induced dissociation of methane on Cu atom and Cu nanoclusters was investigated using *ab initio* molecular dynamics simulations in conjunction with the Metadynamics⁸⁰ algorithm. The free energy barriers for the collision induced dissociation of methane on Cu atom and various Cu clusters at 1273 K were calculated and factors determining the barrier were identified. The subsequent dehydrogenation steps were observed to have barriers which are higher than those of the former. The dehydrogenation of chemisorbed methane and possible coupling reactions of the chemisorbed species were also investigated. Carbon formation has a very high

barrier on all the Cu nano-clusters and CH_x ($x=1-3$) intermediates on these clusters can couple to form C_2 hydrocarbons with negligible free energy barriers.

The computational techniques employed in this investigation are detailed in section 3.2. Collision induced dissociation of methane on the Cu atom and Cu nanoclusters and subsequent dehydrogenation of chemisorbed methane are presented and discussed in section 3.3. The results of the investigation are summarised and additional conclusions drawn are presented in section 3.4. Results pertaining to coupling of the CH_x ($x= 1$ to 3) species on Cu_8 cluster are reported and discussed in section 7.1.2 (appendix to chapter 3).

3.2 Computational methods

Fig. 3.1 Representation of the simulation systems for collision induced dissociation of methane on a) Cu dimer; b) planar Cu_6 cluster; c) capped pentagonal bi-pyramidal Cu_8 cluster; and d) incomplete icosahedron compact Cu_{12} cluster. In each case, the methane molecule is at a distance greater than $3.5 \text{ \AA}$ from the nearest Cu atom. The two collective variables (CV1 and CV2) employed in the simulations investigating collision induced dissociation of methane are also shown.

First principles molecular dynamics simulations implementing the Car-Parrinello scheme⁷⁹ in conjunction with the Metadynamics⁸⁰ algorithm were performed using the CPMD package¹²⁰ version 3.15.3. In CPMD, the finite and constant temperature dynamics of nuclei are coupled to the electronic system, which is treated quantum chemically using the Kohn-Sham formulation of Density Functional Theory (DFT)^{121,122} via adiabatic fictitious dynamics.⁷⁹ The Metadynamics algorithm implemented with CPMD enables the efficient exploration of the free energy landscape of the system as a function of suitable collective coordinates.^{80,123} It is made possible by the deposition of history dependent potentials at periodic intervals, allowing the acceleration of the

crossover of the system to adjacent free energy minima via the minimum energy pathway. This makes the combination of CPMD-Metadynamics an ideal simulation strategy to investigate the collision induced reactions of methane.

Thus, CPMD-Metadynamics simulations were performed to investigate the collision induced dissociation of methane on Cu atom and various Cu clusters (Cu_2 , Cu_6 , Cu_8 and Cu_{12}) and its subsequent dehydrogenation on the clusters. Even numbered Cu clusters (Cu_2 - linear dimer, Cu_6 - planar, Cu_8 - 3 dimensional and Cu_{12} - incomplete icosahedron), as shown in Fig. 3.1 were considered for the simulations as these clusters have been reported to have paired electrons or closed shell electronic structure.^{124,125} These clusters enable an investigation on size/structure relation to their catalytic efficiency. The chosen structures were based on the available literature^{113,124,126} and no separate calculations were performed to further confirm the ground state structures of these clusters.

The plane-wave implementation of density-functional theory (DFT)^{121,122} with the Perdew– Burke– Ernzerhof¹²⁷ (PBE) exchange-correlation functional and the Vanderbilt ultra-soft pseudopotential¹²⁸ was used for the CPMD section. Nonlinear Core Corrections (NLCC)¹²⁹ were incorporated into the pseudopotential of copper. Prior to investigating the reactive trajectories with CPMD-Metadynamics simulations, each of these systems (Cu_n clusters with a methane molecule) was optimized in a cubic simulation box (10 Å to 15 Å a side) as an isolated system (no periodic boundary conditions). Finite temperature dynamics and thermal equilibration of the systems were performed with the Nosé-Hoover chain thermostat^{130,131} maintaining the temperature of the system at 1273 K. A few simulations were also performed at 300 K for the collision induced dissociation of methane on Cu_8 cluster. The frequency of the ionic thermostat was set at 2900 cm^{-1} and that of the electronic thermostat at 12000 cm^{-1} . The time step for the integration of the equations of motion was set at 3 atomic units (0.073 fs) and the fictitious mass for the electron dynamics was set at 400 atomic units. The molecular dynamics trajectories were visualized using the Visual Molecular Dynamics (VMD) package¹³². CPMD simulations were performed with spin restricted closed shell implementation of DFT for all even numbered Cu clusters and with spin polarisation on

(Local Spin Density approximation) with a ground state spin multiplicity of two for the system containing just one Cu atom.

The collision induced dissociation of methane was investigated using Metadynamics employing two collective variables. The distance of the carbon atom of methane to one of the Cu atoms of the cluster was the first collective variable (CV1) while the coordination number of carbon atom to all the hydrogen atoms was the second collective variable (CV2). Both the collective variables are indicated in Fig. 3.1. Constraints were imposed on dynamics with the distance between the carbon atom and selected Cu atom (one of the collective variables) to ensure that the methane molecule moves closer to the cluster by restricting the exploration of phase space within 5 Å of the two moieties. These two collective variables together accounted for the two significant events which form a part of the reaction coordinate: 1) collision of methane with the cluster, and 2) dissociation of methane followed by adsorption of the fragments on the cluster. The investigation of further dehydrogenation of chemisorbed methane employed the collective variables CV1- the average coordination number of the Cu atoms of the cluster with the hydrogen atoms of methane and CV2- the coordination number of the carbon atom with all the hydrogen atoms. The average coordination number of the copper atoms of the cluster with the hydrogen atoms is used, as each dissociated hydrogen atom can form multiple bonds with the copper atoms of the cluster depending on its 'bridge site' or 'three-fold site' position. Moreover, the dissociated hydrogen on the cluster is very mobile, exploring various sites on the cluster, changing the copper atoms to which it is coordinated. The average coordination number of the copper atoms of the cluster with the hydrogen atoms therefore gives a reasonable estimate of the hydrogen copper interaction and diffusion. A significant change in the value would be noticeable with every C-H dissociation step, adding another hydrogen on the cluster. These two collective variables account for the reactive events of further dehydrogenation of CH₃ and possible surface hopping of the dissociated H atoms. The coupling of CH_x fragments (x= 1 to 3 and of the same kind in one system) on the clusters were investigated using the collective variables CV1- the distance between the carbon atoms of the CH_x fragments and CV2- the average coordination of the carbon atoms to all the hydrogen atoms. Constraints were imposed on the distance between the carbon atoms to ensure the two fragments moved closer to each other by restricting the

exploration of phase space within 4 Å of each other. In all the simulations, Metadynamics was propagated by the sequential deposition of Gaussian tube hills of height 5.25 kJ mol⁻¹ and width 0.12 atom units at intervals of time sufficiently large for the collective variables to explore the space around. The collective variables were further used to reconstruct the free energy landscape from which the free energy barriers for the dissociation of methane on the clusters and the coupling of CH_x fragments to form C₂ hydrocarbons were estimated. Additional details pertaining to the CPMD simulations are provided in section 7.1.1 (appendix to chapter 3).

The electronic structure and bonding in the pure Cu clusters (without methane), were analysed using the electron localization function (ELF)¹³³. Similar analysis was performed for structures from CPMD-Metadynamics simulations corresponding to collision and dissociation of methane, as well as those from coupling of CH_x (x= 1 to 3) fragments on these clusters. The ELF topology analysis was performed in the CPMD package and this gave insights into the electron delocalization within the clusters and the bonding of the CH_x fragments and H on the cluster. Prior to the ELF calculations, the wavefunction of the structures obtained from the CPMD-Metadynamics simulations were optimized with strict convergence criteria (10⁻⁸) using the PBE exchange-correlation functional and the norm conserving Troullier-Martins¹³⁴ pseudopotential with a plane wave energy cut off of 120 Ryd. Norm conserving pseudopotentials are employed here as ELF calculations are not supported with ultra-soft pseudopotentials and a higher cut off was used to obtain smooth ELF isosurfaces. The ELF data files were converted to cube files for visualisation in VMD.

CPMD-Metadynamics simulations cannot ascertain the exact transition states (TS) corresponding to dissociation of methane on the clusters. However, since a minimum energy reaction pathway is followed, these simulations provide very good guess structures to identify the TS. Thus, quantum chemical calculations implementing DFT with the PBE exchange correlation functional were performed in the Gaussian 09 suite¹⁰² using these structures to identify the TS for the dissociation of methane on a Cu atom, Cu₂ and Cu₆ clusters. LANL2DZ effective core potential basis set¹³⁵ for copper and 6-311++g(d) for carbon and hydrogen were employed in these calculations. Vibrational frequency analysis showed the presence of a single imaginary frequency,

confirming the TS. Each TS was reconfirmed by following the intrinsic reaction coordinate (IRC) on either direction of the TS to reach minima corresponding to reactant and product. The obtained structures from the IRC were further optimized to calculate the activation energy barrier for the dissociation. The structures and vibrations were visualised using Gauss View 05¹⁰⁴.

3.3 Results and discussion

This section is organised as follows. The collision induced dissociation of methane on the Cu atom and Cu clusters is discussed in section 3.3.1. Collision induced vibrational activation of the stretching and bending modes of methane facilitating significantly lower free energy barriers for dissociation is discussed in section 3.3.1.1. The dependence of the free energy barriers for dissociation of methane on the cluster size, stereodynamics of collision, collision site morphology, temperature and lattice reorganization of the clusters and pre-adsorbed adsorbates are detailed in sections 3.3.1.2 to 3.3.1.6 respectively. Further dissociation of chemisorbed CH₃ on the clusters and free energy barriers associated with each elementary dissociation step are reported in section 3.3.2.1. The dependence of the free energy barriers for dehydrogenation of chemisorbed CH₃ on the cluster size, cluster morphology and cluster reorganization is presented in section 3.3.2.2 and the effects of the presence of chemisorbed hydrogen and adsorbates on the dissociation of methane are discussed in section 3.3.2.3. The coupling of CH_x groups (x=1 to 3) on Cu₈ cluster and formation/ evolution of C₂ hydrocarbons/ intermediates and their implications on formation of larger hydrocarbons species are discussed in section 7.1.2 (appendix to chapter 3).

3.3.1 Collision induced C-H dissociation in methane on Cu clusters and key factors influencing activation free energy barriers

3.3.1.1 Reactive trajectories, free energy barriers for dissociation of methane, and explanation of low free energy barriers

All CPMD-Metadynamics simulations investigating the collision of methane on the Cu clusters at 1273 K typically show dissociation of methane with both the CH₃ group and H atom adsorbed at different bridge and 3-fold sites on the clusters. The hydrogen is observed to be quite mobile and keeps hopping between different sites. The activation energy barrier for diffusion of hydrogen on Cu(111) surface has been reported¹¹⁰ to be

12.5 kJ mol⁻¹ and thus is expected to be small for Cu clusters as well. However, a preference for the bridge site of two copper atoms was observed from our CPMD trajectories, in agreement with an investigation of hydrogen chemisorption on Cu clusters¹¹¹ and quite unlike copper surfaces where the hollow sites¹¹⁰ are preferred. This trend will be elucidated further in subsequent sections.

The free energy surface (FES) for the collision induced dissociation of the C-H bond in methane on Cu₈ cluster as a function of the two collective variables has a typical L-shape and is shown in Fig. 3.2. Structures corresponding to minima in the FES are also shown. This L-shape is characteristic of collision induced dissociation of methane on all Cu clusters irrespective of the size of the cluster and the temperature of the simulation. The basic features of the free energy landscapes reconstructed from simulations of dissociation of methane on different Cu clusters are similar and hence are not shown.

Fig. 3.2 The free energy landscape reconstructed from CPMD-Metadynamics simulation of collision of methane with Cu₈ cluster with the C-Cu distance and C-H coordination number as collective variables at 1273 K. Representative structures from the trajectory corresponding to significant minima are also shown. Colour scheme for atoms is similar to that in Fig. 3.1

It can be seen that C-H coordination number is nearly invariant at around 3.6 until the C-Cu distance is 1.9 Å or less. A complex of the distorted methane molecule and the cluster, upon collision, serves as a precursor for the dissociation reaction and is represented by the free energy minimum before dissociation, as seen in Fig. 3.2. The free energy barrier for dissociation of methane is calculated with respect to this precursor

state along the dissociation path as shown in Fig. 3.2. This reference reactant state is a contrasting feature of the calculation of the activation free energy barriers from CPMD-Metadynamics simulations compared to an equilibrium calculation where the reference reactant would be physisorbed methane or a methane molecule in the gas phase. The free energy landscape also suggests that there are significant barriers for the movement of methane to the cluster. This implies that a significant number of collisions of methane on Cu clusters and surfaces would result in scattering without dissociative chemisorption. This would be one of the factors contributing to the very low dissociative chemisorption probability (8.6×10^{-9} at 1000 K⁵³) and sticking coefficient (4.7×10^{-15} at 500 K¹³⁶) of methane on copper surfaces.

Table 3.1 Free energy barriers for dissociation of methane on Cu clusters of different sizes obtained from the CPMD-Metadynamics simulations. Most simulations were performed at 1273 K although two simulations were performed at 300 K and are reported. $\theta = 140$, $\theta = 165$ and $\theta = 170$ refer to the values of the C-Cu-Cu angle at the time of collision (just before C-H dissociation) in the three simulations performed on Cu₂ at same temperature. $n = 1$, $n = 2$, $n = 3$, $n = 4$, $n = 6$ refer to the number of nearest neighbouring Cu atoms within a distance of 3 Å from the Cu atom on which methane collides, at the time of collision.

Cu cluster size	Sl. No.	Free energy barriers for dissociative chemisorption (kJ mol ⁻¹)	Temperature (K)
Cu ₂	1	75 $\theta=140$	1273
	2	120 $\theta=165$	
	3	125 $\theta=170$	
Cu ₆	1	60 $n=2$	1273
	2	90 $n=1$	
Cu ₈	1	35 $n=4$	1273
	2	60 $n=3$	
	3	80 $n=3$	
Cu ₈	1	110 $n=6$	300
	2	170 $n=3$	
Cu ₁₂	1	50 $n=4$	1273
	2	65 $n=4$	

The free energy barriers for collision induced dissociation of methane on Cu clusters of different sizes, obtained from simulations with differences in the collision angle and numbers of nearest neighbour atoms, are reported in Table 3.1. The trends in activation free energy barriers and key factors influencing the barriers are discussed further in subsequent sections. Some of the free energy barriers reported in Table 3.1 are significantly lower than what would be expected based on the values of activation

energy barriers reported for dissociation of methane on Cu(111) and Cu(100) surfaces.^{54,110} This can be attributed to the concerted effects of collision and entropic contributions resulting from the high temperature dynamics which induce vibrational activation of methane.

Fig. 3.3 Variation of a) the 4 C-H bonds of methane; and b) the 6 H-C-H angles of methane as a function of the C-Cu distance from CPMD-Metadynamics simulations on Cu₈ cluster at 300 K. Thermal vibrations of the C-H bonds and H-C-H angles as well as collision induced enhanced vibrations, particularly at smaller Cu-C distances, can be seen in each of the cases.

Fig. 3.3a shows the deviations of the 4 C-H bonds and Fig. 3.3b shows the distortion of the 6 H-C-H angles of methane as a function of the Cu-C distance from the simulation on Cu₈ at 300 K. The enhanced stretching of the C-H bonds and enhanced distortion of the H-C-H angles upon collision, seen in Fig. 3.3a and Fig. 3.3b respectively, can be attributed to collision induced vibrational activation. Thus, a combination of stretching and bending vibrations play a significant role in reducing the free energy barrier for C-

H dissociation, as suggested by Bisson *et al.*⁴⁹ The translational kinetic energy of the colliding molecules^{42,43} and vibrational excitation^{47,48,50} have both been shown to dramatically enhance the dissociation of methane on metals surfaces. Collision induced vibrational excitation is observed in all our simulations on all the Cu clusters at temperatures of 1273 K as well. However, since the average thermal vibrations (C-H stretching and H-C-H distortions) at 1273 K are much more prominent than what is shown in Fig. 3.3, the effect of collision is not as distinctively visible as shown here.

3.3.1.2 Geometric and electronic effects of Cu cluster size on CID of methane

It can be seen from Table 3.1 that the barriers for dissociation of methane decrease with an increase in the size of the cluster and the average value remains around the same for clusters larger than 8 atoms. A similar trend in the dissociative chemisorption energy values of H₂ on Cu clusters was reported.¹¹¹ The relative stability of small Cu clusters has been reported to be in the order Cu₂ < Cu₆ < Cu₁₂ < Cu₈¹²⁵ and the barriers we calculated for dissociation of methane on these clusters are also seen to follow the same order. The activation energy for the dissociation of methane on copper is reported to be strongly dependent on the adsorption energy of CH₃ and H, after the dissociation.¹³⁶ Thus, the barriers for dissociation may depend on the number and nature of available bridge and 3-fold copper sites for chemisorption of these species, in the immediate vicinity of the Cu atom on which the collision happens. This explains the trend of the barrier becoming lower with increasing cluster size from Cu₂ to C₁₂, as the number of available sites increases with the increase in the cluster size. The number of available sites is important because the dissociation of C-H bonds of methane on copper is facilitated by charge transfer from copper to methane, polarising the C-H bonds, and subsequently to the chemisorbed fragments.¹¹⁰

In addition to these geometric effects, the possible contribution of electronic effects in lowering the free energy barrier for the dissociation of methane on these clusters were evaluated using the electron localization function (ELF) topology analysis.¹³⁷ The ELF topology analysis provides insights into the bonding within the clusters and into methane-Cu cluster interactions. The fundamental principles and concepts of ELF isosurfaces and applications of ELF topology analysis to investigate chemical bonding

have been detailed in the literature.^{133,137-139} The ELF isosurfaces of isolated Cu clusters Cu_2 , Cu_6 , Cu_8 and Cu_{12} at three different isovalues are shown in Fig. 3.4.

Fig. 3.4 Electronic structure of Cu clusters analysed using the Electron Localization Function (ELF) isosurfaces at three different isovalues. The blue balls represent Cu atoms and the grey transparent surfaces represent the ELF. The core basin is identified as a sphere around the atoms while the valence basins are evident in the first two images of each set.

The local maxima of the localization function, referred to as attractors, are obtained for isovalues of less than 0.4 for these clusters and suggest a fair degree of delocalization of electrons. The topology of the ELF isosurface for Cu₂ shows a disynaptic (as it connects two core basins which are depicted in Fig. 3.4) torus shaped attractor around the bond axis. In the case of planar Cu₆, each pair of copper atoms, of which one atom is the vertex of the cluster triangle, has a torus shaped attractor, like that of the dimer. However, each set of three non-vertex copper atoms is seen to have their disynaptic attractors merged to form a trisynaptic attractor. A similar ELF topology of trisynaptic attractors was also reported for planar Li₆ cluster.¹⁴⁰ ELF topologies of Cu₈ and Cu₁₂ are more complicated as there are multiple disynaptic attractors which are interconnected to form a network of polysynaptic (4 core basins considering tetrahedrons) attractor basins. The ELF attractors seem to be concentrated around the outer tetrahedrons of the clusters, with low electron density in the centre of the cluster. Such 4 centre bonding was also reported for Li₈ clusters of similar morphology although the actual topology was slightly different from that shown here.¹⁴⁰

The ELF topology, with attractors between every pair of Cu atoms, explains the preferential adsorption of H and CH₃ on bridge sites compared to the 3-fold sites, as observed in our CPMD-Metadynamics simulations. However, in Cu₈ and Cu₁₂, we can also see two distinct trisynaptic attractors at comparatively higher isovalues (0.36), unlike Cu₆. Thus, from electron localization in the middle of the Cu-Cu axis in the dimer to intermittent network in planar Cu₆ to contiguous network in 3-dimensional Cu₈ and Cu₁₂ clusters, the electronic structure can be observed to be more delocalized in the larger clusters as the transformation from planar to 3-dimensional morphology occurs. This further explains the trend of larger clusters (Cu₈ and Cu₁₂ in this case) being more efficient in dehydrogenating methane upon collision, as observed in our CPMD-Metadynamics simulations and the analysis of corresponding free energy barriers.

Collision of methane with a single Cu atom was also investigated and the CPMD-Metadynamics simulations show that it can dissociate methane upon collision, with a free energy barrier for the dissociation as low as 50 kJ mol⁻¹. This validates the recent reports on copper vapour assisted dissociation of methane and remote growth of graphene on non-catalytic substrates.¹¹⁷⁻¹¹⁹ Both the CH₃ group and hydrogen atom are

found to be chemically bound to the Cu atom upon dissociation. The reactivity of a Cu atom being greater than that of the dimer doesn't fit the size-reactivity/activity trend explained earlier. To reconfirm and validate our CPMD-Metadynamics results, we also computed the activation energy barrier for the dissociation of methane on Cu atom and Cu dimer, using DFT method in Gaussian 09. We found that Cu atom is more active (activation energy barrier for dissociation-157.5 kJ mol⁻¹) than the Cu dimer (activation energy barrier for dissociation- 170.2 kJ mol⁻¹). The transition states for the dissociation of methane on Cu atom and Cu dimer are shown in Fig. 3.5. The activation energy barrier was calculated as the difference in energy of the TS with respect to the optimised reactant, obtained by following the intrinsic reaction coordinate (IRC).

Fig. 3.5 Transition state (TS) for the dissociation of methane on a) Cu atom; and b) Cu dimer. Both TSs were identified using DFT with PBE exchange correlation functional and LANL2DZ basis set for copper and 6-311++g(d) basis sets for carbon and hydrogen. a1) and a2) are ELF isosurfaces for two isovalues of methane colliding on a Cu atom, as obtained from a CPMD-Metadynamics simulation just before dissociation. b1) and b2) are ELF isosurfaces for two isovalues of methane colliding on a Cu dimer, as obtained from a CPMD-Metadynamics simulation just before dissociation. The blue, red and grey balls represent the copper, carbon and hydrogen atoms respectively, and the grey transparent surfaces represent the electron density.

A possible explanation for the difference in activities of Cu and Cu dimer lies in the difference between their electronic structures. ELF isosurfaces (at two isovalues) of

methane colliding with a Cu atom and Cu dimer are shown in Fig. 3.5a1, Fig. 3.5a2 and Fig. 3.5b1, Fig. 3.5b2, respectively. The structures in Fig. 3.5a1, Fig. 3.5a2 and Fig. 3.5b1, Fig. 3.5b2 are taken from the CPMD-Metadynamics simulations and are snapshots of the trajectory just before the dissociation. A distinct monosynaptic attractor, characteristic of lone pairs, is observed in Cu-CH₄ system (Fig. 3.5a1), suggesting that the electron cloud is localized away from the colliding methane molecule. The unperturbed electron cloud (without the colliding methane) is found as a sphere around the Cu atom and is a contribution from the unpaired electron, with beta spin in our simulations. However, in the case of Cu₂, we observe a disynaptic bonding attractor (Fig. 3.5b1) between two Cu atoms like that in Fig. 3.4a and Fig. 3.4b. Thus, the unpaired electron cloud is distributed over a larger space compared to paired electron region confined to the centre of the dimer axis. We believe that this makes a Cu atom more reactive compared to a dimer. The alignment of the C-H vibrations towards the specific direction of the electron cloud in the case of Cu dimer is not required for the Cu atom and will be explained in detail in the next section.

3.3.1.3 Stereodynamics of collision and effect on CID of methane

Analysis of the trajectories of simulations on different Cu clusters suggests that the collision site on the cluster and features of collision affect the barriers for dissociative chemisorption of methane on the cluster. The values of free energy barriers obtained from three simulations of dissociation of methane on the Cu dimer with three different collision angles are reported in Table 3.1. Collisions of methane with a smaller value of the C-Cu-Cu angle (angle between the carbon atom of methane and the Cu dimer) were observed to have lower barriers for dissociation compared to the head-on coaxial collision (along the axis of the Cu dimer). This can be attributed to the structure of the transition state which has a C-Cu-Cu angle of ~120° as shown in Fig. 3.5b. This configuration of the methane molecule upon collision allows for the C-H stretch vibration to be aligned along the axis of the Cu dimer. The preference for this alignment can be explained based on the ELF topology of the Cu dimer (Fig. 3.4a, Fig. 3.4b and Fig. 3.5b1), where the electron localization is in a torus at the centre of the dimer axis. In the case of the Cu dimer, the alignment of one of the C-H bonds towards this high localization space is not just a favourable factor but a necessary condition for dissociation. Similar alignment of the C-H bond of methane towards the centre of the

edge pair of Cu atoms of Cu₆ cluster has been observed based on the transition state for dissociation of methane on that cluster. This implies that larger Cu clusters with higher number of available sites (electron localization regions) enable greater probability of favourable alignment of the C-H bonds of methane during the collision. Alignment of the C-H stretch vibrations along the surface of the metal has been reported to increase the reactivity considerably in experiments on collision of vibrationally excited methane on Ni surfaces.^{141,142} Thus, pre-alignment of the methane molecule along the collision path allows easier access to the transition state and thus lowers the barrier for dissociation. This suggests that stereodynamic steering along the collision path can significantly alter the barrier for the reaction.

3.3.1.4 Morphology of collision site on the Cu cluster and effect on CID of methane

The activation free energy values computed for the dissociation of methane on Cu₈ and Cu₁₂ clusters have been observed to vary by 40-50 kJ mol⁻¹ depending on the number of nearest neighbour Cu atoms in the immediate vicinity of the atom on which methane collides (Table 3.1). Here we define the nearest neighbours as Cu atoms within 3 Å from the atom on which methane collides. To reconfirm the effect of number of nearest numbers in influencing activation free energy barriers for dissociation of methane, simulations were performed at 300 K on Cu₈, and the results are reported in Table 3.1. Room temperature was chosen for these simulations so that the cluster geometry does not change significantly along the dynamics. A huge difference is observed in the free energy barriers for dissociation of methane colliding on the centre atom (6 nearest neighbours, free energy barrier- 110 kJ mol⁻¹) and capping atom (3 nearest neighbours, free energy barrier- 170 kJ mol⁻¹) at the same temperature. The greater the number of nearest neighbours, the greater is the number of available sites for the adsorption of CH₃ and H, and higher is the probability of favourable alignment of the C-H bond for dissociation. This explains the trend of the barrier for dissociation reducing significantly with increasing number of nearest neighbours during simulations on the same Cu cluster at the same temperature.

3.3.1.5 Effect of temperature and effect of lattice reorganization of the clusters on CID of methane

It is to be noted that the values of free energy barriers reported for these simulations are much higher than those reported earlier and is a consequence of the 4-fold decrease in the temperature of the simulation. It is anticipated that for a reaction of methane on a surface/ cluster, the free energy barrier should increase with increase in temperature, as the reactant, which is a methane molecule in the gas phase, has higher entropy compared to that of the transition state. However, this trend is seen to be violated in the CPMD-Metadynamics calculated free energy barriers from the simulations at 300K and 1273 K on Cu₈ cluster. This difference can be attributed to the specific reactant reference state we consider. The distorted precursor state in the CPMD-Metadynamics simulation (Fig. 3.2), which we refer to as the reference reactant is a “bound” or constrained single entity. The transition state for the dissociation of methane shown in the Fig. 3.5 on the other hand has a highly-stretched C-H bond. Thus, at higher temperatures, the significantly higher contribution from the entropic component of the transition state counterbalances its enthalpic component much more compared to those in the precursor state and thereby lowers the free energy barrier. Thus, we see a reverse trend, of the free energy barriers significantly going down with increase in temperature in our CPMD-Metadynamics simulations.

Analysis of the ELF topology of structures representing snapshots of the trajectories from these simulations shows that changes in the cluster geometry resulting from high temperature dynamics alter the electron localization/ delocalization patterns within the cluster. This is more pronounced in the Cu₆ planar cluster and manifests as high electronic localization, only in the space between the three Cu atoms, as shown in Fig. 3.6a. The localization is evident from the high isovalue (0.59) at which this valence ELF basin can be seen to disappear and is much higher than the isovalues seen for the Cu₆ cluster (Fig. 3.4). The free energy barrier for the dissociation of methane in this case was found to be much higher (90 kJ mol⁻¹) than in the case with lesser distortion (60 kJ mol⁻¹), as shown in Fig. 3.6b. Thus, geometric distortions leading to localization of electrons in a specific region within the cluster significantly increases the free energy barrier for the dissociation of methane on small and planar clusters. The ELF topology

changes with geometric distortions in the 3-dimensional clusters as well. However, the implications of such changes are not as prominent as in planar small clusters.

Fig. 3.6 ELF isosurfaces of the structures representing collision of methane on the vertex atom of Cu₆ cluster showing a) high degree of electron localization in a specific region resulting from the distortion of the cluster and higher free energy barrier for the dissociation of methane (90 kJ mol⁻¹); b) little region specific electron localization and lower free energy barrier (60 kJ mol⁻¹) for dissociation. The structures are obtained from CPMD-metadynamics simulations at 1273 K.

3.3.1.6 Effect of adsorbates on CID of methane

The role of chemisorbed hydrogen during collision induced dissociation of methane on Cu₈ cluster was investigated. Collision of methane on Cu₈ cluster with pre-adsorbed CH₃ and H was simulated. All the trajectories showed the formation of CH₃ + H on the cluster in addition to the pre-adsorbed CH₃ + H. The free energy barriers for dissociation of methane from simulations with three different nearest neighbour configurations are reported in Table 3.2. The free energy barrier for the case of collision of methane on copper atom with 4 neighbouring atoms is similar to that on clean copper cluster of similar configuration. This can be attributed to the fact that the electron delocalization pattern is not significantly affected merely by the presence of chemisorbed hydrogen and CH₃. However, the free energy barrier is observed to increase with decrease in the number of available sites as was observed in the case of the pure cluster. Thus, collision induced dissociation of methane seems to be unaffected by the presence of chemisorbed CH₃ or H on the cluster. This trend is in agreement with observations of Li *et al.*¹⁴³ where no significant effect was noticed in the barrier for dissociation of CH_x on a copper

surface due to the presence of chemisorbed H. Further, the chemisorbed H in the vicinity of collision was observed to have no apparent catalytic role as the hydrogen abstraction reaction (hydrogen from methane being abstracted by the chemisorbed hydrogen followed by evolution of molecular hydrogen) was not observed in any of the simulations, contrary to the hypothesis by Vlassiounk *et al.*¹⁴⁴ Thus it can be concluded that the presence of an adsorbed species (CH₃ or H) in the immediate vicinity of the collision site neither promotes nor inhibits the dissociation as long as there are available sites for hydrogen adsorption at temperatures around 1000°C.

Table 3.2 Free energy barriers for the dissociation of methane on Cu₈ cluster with chemisorbed CH₃ and H at 1273 K. The three simulations presented three different collision site morphologies and thus gave different values of free energy barriers.

Sl. No.	Free energy barrier for dissociative chemisorption (kJ mol ⁻¹)	Remarks
1	40	Nearest neighbours 4. CH ₃ and H are away from the collision site
2	80	Nearest neighbours 3. CH ₃ and H are away from the collision site
3	95	Nearest neighbours 4 but two of them are around 3 Å away. H in 3-fold site containing collision atom

3.3.2 Subsequent dissociation of chemisorbed CH₃ on the Cu clusters and key factors influencing activation free energy barriers

3.3.2.1 Reactive trajectories and free energy barriers

CPMD-Metadynamics simulations were also performed to investigate the dehydrogenation of the chemisorbed CH₃ and the formation of carbon on these clusters. The simulations were stopped after the CH₂ + 2 H was formed on Cu₂ cluster and complete dehydrogenation was simulated only for the larger clusters (Cu₆, Cu₈ and Cu₁₂). The free energy landscape reconstructed from the Metadynamics simulation of the dehydrogenation of chemisorbed CH₃ on a Cu₈ cluster, as a function of the two collective variables as defined in Computational Methods, is shown in Fig. 3.7. The general features of the free energy landscape for dehydrogenation of chemisorbed CH₃ on other Cu clusters are similar and hence are not shown here.

Fig. 3.7 The free energy landscape corresponding to dehydrogenation of chemisorbed CH_3 on Cu_8 cluster, reconstructed from CPMD-Metadynamics simulation, with the H-Cu coordination number and C-H coordination number as collective variables at 1273 K. The structures from the trajectory corresponding to significant minima and barrier corresponding to each dehydrogenation step are also shown.

The formation of carbon on the clusters was observed to proceed through the elementary steps as shown in Fig. 3.7 and Fig. 3.8. Representative structures from the trajectory, corresponding to the minima ($\text{CH}_3 + \text{H}$, $\text{CH}_2 + 2 \text{H}$, $\text{CH} + 3 \text{H}$ and $\text{C} + 4 \text{H}$), and the free energy barriers associated with each transformation are shown in Fig. 3.7. Each dehydrogenation step is observed to bring about a decrease in the C-H coordination number (ultimately going to zero) and a corresponding increase in the average Cu-H coordination number (Fig. 3.7). In the simulation trajectories, CH_3 and CH_2 groups have been observed at the bridge sites and at the 3-fold sites (refer Fig. 3.1), frequently hopping between the two kinds; while the CH groups are typically observed to be found at 3-fold sites. The carbon monomer is found to migrate to the subsurface in the case of Cu_8 and Cu_{12} as reported by Zhang et al.¹⁴⁵ and is coordinated to four Cu atoms. However, in the case of Cu_6 , the originally planar Cu_6 cluster evolved into a 3-dimensional cluster and the carbon monomer was observed to be coordinated to at least 4 and occasionally 5 Cu atoms.

Free energy barriers for the dehydrogenation of chemisorbed CH_3 on the different Cu clusters at 1273 K are shown in Fig. 3.8. It can be seen that the free energy barrier for the dissociation of chemisorbed $\text{CH}_3 + \text{H}$ to give $\text{CH}_2 + 2 \text{H}$ on all clusters are

significantly higher (double or more) than the corresponding free energy barriers for collision induced dissociation of methane. This is in contradiction to the trend reported for successive dissociations of CH₄ on copper surfaces where the second dissociation (formation of CH₂) was shown to have a lower activation energy barrier than the first.^{54,110} However, it is to be noted that the reported values and trends in the literature are from 0 K DFT calculations, which do not account for the collision dynamics and its effects thereof. Collision induced vibrational activation of methane is responsible for lowering the free energy barrier for the dissociation of the first C-H bond and is absent in subsequent dehydrogenation steps. Computational investigation of methane activation on Fe₄ cluster¹⁴⁶ showed that the cleavage of the second C-H bond is more difficult than that of the first and is in agreement with our observation.

Fig. 3.8 Free energy barriers for the elementary steps in the dehydrogenation of the chemisorbed CH₃ on Cu clusters of different sizes, as obtained from the CPMD-Metadynamics simulations at 1273 K.

3.3.2.2 Effects of cluster size, cluster morphology and cluster reorganization on free energy barriers for successive dehydrogenation of CH₃

It can also be seen from Fig. 3.8 that the free energy barrier for the first dehydrogenation of the chemisorbed CH₃ decreases with increase in the cluster size from Cu₂ to Cu₈/Cu₁₂. This trend agrees with that observed during collision induced dissociation on the clusters and can be explained based on the number of nearest neighbours and available chemisorption sites as described earlier. Simulations on Cu₈ and Cu₁₂ clusters suggest that successive dehydrogenation steps have increasingly higher barriers with the last

step of dehydrogenation to carbon having the highest barrier among all elementary steps. This is in agreement with previous reports which show formation of carbon to have the highest barrier among the elementary dehydrogenation steps on Cu(111) surface.^{54,110} This trend can be explained based on the reorganization of the cluster geometry resulting from and necessitated by the successive dehydrogenation steps.

Fig. 3.9 Variation of a) C-H bond distances; and b) C-Cu distance of the CH_x (x = 0 to 3) on Cu₈ cluster during dissociation of CH₃ in CPMD Metadynamics simulation at 1273 K. An increase in coordination number of C with the neighbouring Cu atoms can be seen along the trajectory and shows the reorganization of the cluster as dehydrogenation proceeds. Similar trends are observed in simulations on Cu₆ and Cu₁₂ clusters as well.

Fig. 3.9 shows the variation of the coordination number of carbon atom of methane with the atoms of the Cu₈ cluster during a CPMD-Metadynamics simulation at 1273 K, alongside the dehydrogenation profile. The increase in the C-Cu coordination number, evident from the decrease in C-Cu distances (Fig. 3.9b), coincides with the dehydrogenation of chemisorbed CH₃ (Fig. 3.9a). A significant increase in coordination

number (> 3) also implies reorganization of the cluster and is observed in simulations on Cu_6 and Cu_{12} clusters as well. Fig. 3.10 shows snapshots from the trajectory of simulation of complete dehydrogenation of CH_3 on Cu_6 and Cu_8 clusters showing significant reorganization of the clusters with every dehydrogenation step. The planar triangular Cu_6 cluster can be seen to evolve into distorted 3-dimensional structures as dehydrogenation proceeds (Fig. 3.10a) and the carbon atom can be seen to move to the subsurface of the 3-dimensional clusters (Fig. 3.10b).

Fig. 3.10 Snapshots from CPMD Metadynamics simulations at 1273 K showing the sequence of dehydrogenation of chemisorbed CH_3 on Cu clusters and the corresponding reorganization of the cluster geometry. a) From a simulation on Cu_6 cluster showing the transformation of the planar triangular cluster to a 3-dimensional cluster b) From a simulation on Cu_8 cluster showing the migration of carbon to the sub-surface of the cluster. The dissociating C-H bond is indicated with a red arrow in each structure. Trends on Cu_{12} cluster are similar to those on Cu_8 cluster and hence not shown here.

The increase in C-Cu coordination number with dehydrogenation and the reorganization of the cluster geometry enables the carbon atom to retain its sp^3 character, with the Cu atoms, replacing hydrogen, at each stage of the dehydrogenation. This is in agreement with previous report based on ELF analysis for methane dissociation on a copper slab.¹¹⁰ Even without high temperature dynamics, small Cu clusters have been shown to undergo significant geometric changes upon chemisorption of hydrogen molecule with the magnitude of change being larger for the small clusters up to Cu_6 .^{111,112} The reorganization of the Cu_8 and Cu_{12} clusters is more difficult than in Cu_6 . This is because the binding energy per Cu atom in Cu nano-clusters increases with increase in cluster

size.¹¹¹ This explains the trend of the free energy barrier for formation of carbon via successive dissociation of CH₃ increasing with cluster size from 185 kJ mol⁻¹ on Cu₆ to 220 kJ mol⁻¹ on Cu₁₂ as shown in Fig. 3.8.

3.3.2.3 Effect of chemisorbed hydrogen on subsequent dehydrogenation of chemisorbed CH₃

During simulations of complete dehydrogenation of CH₃ on the clusters, hydrogen of the CH_x (x= 1 to 3) was never observed to be abstracted ($\text{CH}_x + \text{H} \rightarrow \text{CH}_{x-1} + \text{H}_2$)¹⁴³ by another chemisorbed hydrogen on the cluster. This suggests that the chemisorbed hydrogen doesn't aid in further dehydrogenation of CH_x. This is in contradiction to the proposition of Vlasiouk *et al.*¹⁴⁴ where a catalytic role of surface hydrogen was suggested. There was no observation of the evolution of a hydrogen molecule by recombination of surface hydrogen atoms within the time span of these simulations. Formation and evolution of hydrogen molecule have been reported to be a high barrier process by Li *et al.*¹⁴³.

The recombination of hydrogen atom on the cluster with the carbon monomer was observed on the Cu₆ cluster. However, this process was not observed on Cu₈ and Cu₁₂ clusters. The recombination reaction on Cu₆ could possibly be attributed to the saturation of Cu sites on the cluster. The free energy barrier for the recombination of hydrogen with carbon on the Cu₆ cluster was calculated to be around 105 kJ mol⁻¹ and is much lower than that of the elementary dehydrogenation steps on the same cluster. A microkinetic model based analysis by Li *et al.* also showed that the recombination reactions of CH_x (x= 0 to 3) with chemisorbed hydrogen have rate constants higher than those of the corresponding dehydrogenation reactions on Cu(111) surface.¹⁴³ These results suggest that competition of the dehydrogenation reaction and recombination reaction would favour the latter in cases of surface saturation not only in small clusters but also on copper surfaces.

Structures like that in right extreme of Fig. 3.10a which are nearly saturated with hydrogen have virtually no free electron cloud. This would affect further dissociative chemisorption of methane on the cluster. Thus, saturation driven inhibition of dissociative chemisorption/dehydrogenation of CH_x (x= 1-4) serves to slow down the free supply of CH_{x-1} which is necessary for the formation of larger hydrocarbon

precursors on the clusters. This phenomenon in the context of graphene growth on copper thin films is one of the reasons for the ‘self-limiting’ mechanism and combined with the low solubility of carbon in copper bulk, leads to uniform layer control in graphene synthesis by CVD.^{147,148} Since dissociative chemisorption of hydrogen on copper is highly favourable, competitive adsorption of hydrogen from the carrier gas which is a mixture of methane and hydrogen (sometimes argon also) in the CVD synthesis of graphene on copper has been reported to be an inhibitor to graphene growth.¹⁴⁹ This proposition was based on the dissociation probability of methane being a function of the available copper sites. Thus, high hydrogen partial pressures employed in the CVD growth of graphene would result in a controlled supply of CH_x species on the surface via competitive recombination, an extreme case of which has been reported as etching of graphene^{144,150}. The high surface coverage by hydrogen by dissociative chemisorption on copper surfaces will also inhibit further dissociative chemisorption of methane on the surface. Both these factors can suppress the nano carbon growth on the surface.

3.4 Summary

The collision induced dissociation of methane on Cu clusters of different sizes and further dissociation of chemisorbed CH_3 to form carbon were investigated using first principles molecular dynamics and Metadynamics simulations. The claims of copper vapour assisting direct CVD growth of graphene on inert substrates has been validated as Cu atoms can also dissociate methane to CH_3 which would be a precursor for further reactions. Collision induced vibrational activation of the stretching and bending modes dramatically reduces the free energy barrier for the dissociation of methane on the clusters. An increase in cluster size and the order of dimension (1D, 2D and 3D) of the cluster makes available larger number of sites for the chemisorption of the dissociated fragments (CH_3 and H) and thereby reduces the free energy barrier for the dissociation of methane. Additionally, it also increases the probability of favourable alignment of the C-H stretching vibration to the regions of high electron localization, bringing down the barrier for dissociation. The available sites are typically the regions along the axis of every Cu-Cu pair, and therefore, hydrogen adsorbs at these sites unlike metal surfaces, where the hollow sites are preferred. Changes in the geometry and the morphology of

the cluster result in significant changes to the electron localization within the cluster; an effect more prominent in small planar clusters like Cu₆, and increases the free energy barrier for the dissociation of methane.

Dehydrogenation of chemisorbed CH₃ has significantly higher free energy barrier compared to the collision induced dissociation of methane on the same cluster and this decreases with increase in the cluster size. Formation of carbon is a very high barrier process ($> 190 \text{ kJ mol}^{-1}$), with each elementary step of dissociation resulting in progressively increasing barriers. The corresponding barriers increase with cluster size. The cluster size dependence is attributed to the increasingly difficult reorganization of the clusters required to accommodate the CH and C species, which retain the sp³ hybridization of carbon through Cu atoms of the cluster. Chemisorbed hydrogen resulting from the successive dehydrogenation steps does not inhibit or instigate further C-H dissociation. Surface saturation with hydrogen may however severely affect further dissociation, both by increasing the free energy barrier for dissociation and by competitive recombination.

4 Insights into the synergistic role of metal-lattice oxygen site pairs in four-centered C-H bond activation of methane: the case of CuO

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4.1 Introduction

The relatively high activation energy barrier (150–170 kJ mol⁻¹ obtained from calculations)^{54,110,151} for the dissociation of the C–H bond of methane on copper catalysts limits its use to applications like the synthesis of graphene by chemical vapor deposition.^{31,152} However, experiments on the decomposition of methane on Cu(100) surface showed that the chemisorbed oxygen on the surface can abstract hydrogen and lower the activation energy barrier for the dissociation of methane to ~125 kJ mol⁻¹.⁵³ Computational investigations suggest that the presence of oxygen promotes the dissociation of methane on inactive coinage metals like Cu, Ag, Au.^{62,63} The suggested role of chemisorbed oxygen is to favourably alter the thermodynamic driving force for the dissociation reaction.⁶⁵ Though the promotional effect of dissociatively chemisorbed surface oxygen on inactive metal surfaces has been revealed, detailed mechanistic insights into this are either lacking or still a subject of debate. Moreover, chemisorbed oxygen on copper surfaces is metastable and thus does not constitute a stable catalytic surface as compared to its oxide counterparts.⁵⁵

Structured oxides of certain transition metals like PdO, RuO₂ and IrO₂ are considered an important class of catalysts for methane activation and selective oxidation.^{67,153} The activation energy barrier for the dissociation of methane involving both palladium atom and the lattice oxygen on PdO(101) cluster/ surface is lower than that on clean and chemisorbed oxygen covered cluster/ surface.^{66,154} This suggests that oxides could be

better catalysts for methane C-H activation.^{66,154} IrO₂(110) surface has been shown to be active not only in dissociating methane¹⁵⁵ but also for the coupling of the dissociated CH₂ species on the surface, to form ethylene with negligible activation barriers.¹⁵⁶ Thus, we see that investigations of C-H bond activation on transition metal oxide surfaces focus on oxides of late 4d and 5d transition metals.

Cupric oxide (CuO) has attracted significant attention in the recent past due to its versatility. CuO has been synthesized in different morphologies with a wide range of applications, including catalysis.⁹⁰ It has been shown to be effective in dissociating the formyl C-H bonds in sugars with activation barrier of 87 kJ mol⁻¹, during their oxidation to acids.⁸¹ CuO in the form of nanowires was shown to be useful in the oxidation of methane.⁷² It is considered an excellent prospective material for the chemical looping combustion (CLC)⁶⁸ process. Here fuels undergo combustion using oxygen from solid metal oxide, which gets reduced in the process, and is subsequently regenerated in a separate oxidation cycle.⁶⁹ A copper oxo species in a tri-nuclear Cu- O complex generated on mordenite zeolite structures has been shown to be effective in converting methane to methanol and proceeds by a hydrogen abstraction mechanism with activation barrier of 74 kJ mol⁻¹.⁸²

With clear evidence of the participation of the Cu- O system in activating and dissociating C-H bonds in the oxidative processes, the investigation of the role and contribution of lattice oxygen on different surfaces of CuO towards C-H bond activation of methane becomes pertinent. Experimentally observed CuO surfaces like CuO(111), CuO($\bar{1}11$), CuO(01 $\bar{1}$), CuO(010) and CuO(110) were selected to investigate methane activation. The different pathways for the dissociation of methane on these surfaces and the corresponding activation energy barriers are reported in section 4.3.1. The contrast between two different mechanisms of methane activation involving the lattice oxygen atoms and the explanation for trends in activation barriers in those mechanisms are presented in section 4.3.2. The geometrical and electronic characteristics of the different CuO surfaces and the key interactions which govern their activity towards the C-H bond dissociation are presented in section 4.3.3. In addition to the activation of the first C-H bond of methane, subsequent surface reactions of the chemisorbed CH₃ species are also investigated and presented in section 4.3.4.

4.2 Computational methodology and simulation systems

The simulations were performed with the periodic plane-wave implementation of Density Functional Theory (DFT)^{121,122} using the ab-initio total-energy and molecular-dynamics program VASP (Vienna ab-initio simulation program) developed at the Fakultät für Physik of the Universität Wien.^{157,158} The GGA-PBE exchange correlation functional¹²⁷ within DFT and the Projector Augmented Wave (PAW)^{159,160} method for the treatment of the inner core, with a plane wave cut-off energy of 450 eV were used in the electronic structure calculations. The nudged elastic band (NEB) method implemented in VASP was used to locate the transition states (TS) for the dissociation of methane on the different surfaces. The TSs were further reconfirmed with vibrational frequency calculations, where one imaginary frequency confirmed the TS. Spin polarization was turned on for all simulations involving CuO. Since DFT cannot reproduce the electronic and magnetic properties of CuO due to the strongly correlated and localized 3d electrons in copper,¹⁶¹⁻¹⁶³ the implementation of Hubbard U correction in the form of GGA+U (LDAU in VASP) described by Dudarev *et al.*¹⁶⁴ was applied to compute bulk properties and chemisorption energies on CuO surfaces. The values of $U = 7.0$ eV and $J = 0$ eV, as reported by Nolan and Elliott¹⁶² have been used in the calculations of bulk properties, unless otherwise specified. Since charge transfer between the surface and substrate is an important factor influencing the catalytic activity, Bader charges^{165,166} for the stable initial state configuration (IS), TS and the stable final state configuration (FS) were computed. The charge transfer mechanisms and the interactions of the reaction centers were established based on these charges.

The optimized fcc bulk lattice constant of copper was found to be 3.63 Å and was used for all subsequent calculations. Cu(111) and chemisorbed oxygen containing Cu(111) surfaces were modelled as periodic slabs with three atomic layers in 3x3 supercells with a vacuum of 10 Å above the layers. The first two layers were allowed to relax in order to account for lattice relaxation of the catalyst in the course of the reaction, while the bottom layer was fixed. A Monkhorst-Pack¹⁶⁷ type 4x4x1 special k-point grid was used for sampling the Brillouin zone.

CuO has a monoclinic crystal structure and the bulk lattice constant was optimized to $a = 4.68$ Å, $b = 3.43$ Å, $c = 5.14$ Å, $\beta = 99.3^\circ$, which is in agreement with experimentally

determined values.¹⁶⁸ To evaluate the roles of lattice oxygen and copper in the C-H bond activation process, comprehensive investigations were performed on three facets of copper oxide: CuO(111), CuO($\bar{1}11$), and CuO(110). Activation energy barriers and energetics for the dissociation of methane in the different dissociation pathways on CuO(01 $\bar{1}$), CuO(010) surfaces were also calculated. These facets of CuO chosen for investigation have been observed in experiments and can be synthesized.^{81,169-171} CuO(111) has been reported to be the most stable facet among the different possible ones based on the lowest calculated surface energy, and is followed by CuO($\bar{1}11$).¹⁷² CuO(111) and CuO($\bar{1}11$) surfaces have similar surface arrangements and geometric configurations and thus would serve to reconfirm and validate the role and contribution of the metal-oxygen pair in activation.

Fig. 4.1 Surface atomic arrangement and surface sites on CuO facets a) CuO(111) surface with repeating arrangement of O₃-Cu₃-O₄-Cu₄; b) CuO($\bar{1}11$) surface with repeating arrangement of O₃-Cu₃-O₄-Cu₄; c) CuO(110)₀ surface with repeating arrangement of O₃-Cu₄-O₃; d) CuO(01 $\bar{1}$) with repeating arrangement of O₃-Cu₃-O₃; and e) CuO(010) with repeating arrangement of Cu₃-O₂-Cu₃-O₄. The peach color represents copper and the red color represents oxygen atoms.

The surface sites on CuO(111) and CuO($\bar{1}11$) can be classified as 3-coordinated and 4-coordinated copper and oxygen atoms, with repeating arrangement of O₃-Cu₃-O₄-Cu₄, as shown in Fig. 4.1a and Fig. 4.1b. Both CuO(111) and CuO($\bar{1}11$) present adjacent pairs of under-coordinated surface lattice Cu-O site pairs which are potential active sites

for methane activation and dissociation. CuO(01 $\bar{1}$) surface exposes only 3-coordinated copper and oxygen atoms as shown in Fig. 4.1d, while CuO(010) surface shows a repeating arrangement of Cu₃-O₂-Cu₃-O₄ as shown in Fig. 4.1e. CuO(110) is a higher energy surface¹⁷² and can have two types of surface atomic arrangements: 1) Copper terminated- with repeating arrangement of Cu₂-O₄-Cu₄-O₄, where the 2-coordinated Cu atoms project out of the surface or 2) Oxygen terminated- with repeating arrangement of O₃-Cu₄-O₃, as shown in Fig. 4.1c and will be referred to as CuO(110)_o. The Cu(110)_o surface is expected to be more stable than the other surfaces in an oxygen rich environment.¹⁷² On CuO(110)_o surface, all oxygen atoms on the surface are 3-coordinated whereas all copper atoms on the surface are 4-coordinated. Thus, to ascertain the roles of the under-coordinated Cu-O pairs on the CuO surfaces, we investigated methane dissociation on the CuO(110)_o facet. For methane activation and dissociation, all the CuO surfaces were modelled as periodic slabs with three/ four atomic layers in 3x2 supercells with 12 Å of vacuum above them. The first two/ three layers were allowed to relax while the bottom layer was fixed. The Brillouin zone was sampled with a 3x3x1 Monkhorst-Pack k-point grid in each of these cases.

4.3 Results and discussion

4.3.1 Dissociation of methane on clean and chemisorbed oxygen containing Cu and CuO surfaces

Molecular oxygen (O₂) is reported to dissociatively chemisorb on Cu(111) surface with an activation energy barrier of 28 kJ mol⁻¹.⁸¹ However, under typical catalytic conditions of high temperature and under varying oxygen pressures, copper tends to form thin oxide layers which are more stable than layers of chemisorbed oxygen.^{55,173} Thus, the stable oxide surfaces of CuO with both surface copper and oxygen atoms may be more promising catalytic systems.

The activation energy barriers for the dissociation of methane in the present study are calculated with respect to the physisorbed methane on the surface. The interaction of methane with Cu(111), chemisorbed oxygen containing Cu(111) and CuO surfaces is very weak and is evident from the adsorption energy ranging from -1 to 5 kJ mol⁻¹ as shown in Table 7.1 (appendix to chapter 4). Thus, the physisorption energy is not expected to influence the activation energy barriers significantly. The reaction energy

reported in this investigation is the difference in the energy of the system consisting of physisorbed methane on the surface, referred to as IS, and the system consisting of the fragments of dissociation in the co-adsorbed state, referred to as FS. The activation energy barrier for the dissociation of methane on Cu(111) surface was calculated to be $169.8 \text{ kJ mol}^{-1}$ and this compares well with the reported value of $170.8 \text{ kJ mol}^{-1}$ in the literature.⁵⁴ The activation proceeds via a single copper atom and the products of dissociation, CH_3 and H , are both chemisorbed at the hollow sites on the copper surface, as shown in Fig. 4.2a. The reaction is highly endothermic, in agreement with literature,⁵⁴ with the reaction energy of 87.2 kJ mol^{-1} .

Fig. 4.2 Representation of the initial state (IS), transition state (TS) and final state (FS) corresponding to dissociation of methane a) by oxidative addition of copper on Cu(111) surface; b) in a pathway involving synergistic roles of dissociatively chemisorbed surface oxygen and copper atom on Cu(111) surface; and c) in a pathway involving synergistic roles of the under coordinated copper (Cu_3) and lattice oxygen (O_3) atoms on CuO(111) surface. The peach color represents copper, red represents oxygen, grey represents carbon and white represents hydrogen atoms.

Two distinct reaction mechanisms were investigated for the activation and dissociation of methane on the chemisorbed oxygen containing Cu(111) surface and on CuO surfaces. The chemisorbed oxygen at the fcc hollow site of Cu(111) can abstract the hydrogen of methane with cooperative assistance from a surface copper atom. The result is the formation of surface O-H and CH₃ species as shown in Fig. 4.2b. Details of the mechanism will be discussed in section 4.3.2. The calculated activation energy barrier of 133.1 kJ mol⁻¹ is in excellent agreement with the experimentally determined values of 123 ± 27 kJ mol⁻¹.⁵³ The reaction energy comes down to 41.1 kJ mol⁻¹ on chemisorbed oxygen containing Cu(111) compared to 87.2 kJ mol⁻¹ on clean Cu(111) surface.

On CuO(111), CuO($\bar{1}11$), CuO(01 $\bar{1}$) and CuO(010) surfaces, the under-coordinated lattice oxygen (O₃/O₂) abstracts the hydrogen of methane, with cooperative assistance from the under-coordinated surface copper (Cu₃) atom, forming the surface O-H and CH₃ species. The IS, TS and FS for dissociation of methane by this mechanism on CuO(111) is shown in Fig. 4.2c. Corresponding structures on the remaining CuO surfaces are similar and are presented in Fig. 7.3 (appendix to chapter 4). The activation energy barrier for the dissociation of methane was calculated to be 76.6 kJ mol⁻¹ on CuO(111), 90.2 kJ mol⁻¹ on CuO($\bar{1}11$), 95.3 kJ mol⁻¹ on CuO(01 $\bar{1}$) and 60.3 kJ mol⁻¹ on CuO(010). The calculated activation barrier on CuO(111) surface is in agreement with the experimentally determined activation barrier of 69 kJ mol⁻¹ and 96 kJ mol⁻¹ for the oxidation of methane on CuO nanowires and supported CuO nanoparticles respectively.⁷² The activation barriers for the dissociation of methane in this mechanism are reported in Table 4.1 with indicator ‘1’ against each surface.

The mechanism of activation on all these surfaces was observed to involve the under-coordinated Cu-O pair and this is responsible for the low barriers as shall be explained in section 4.3.2.2. The low activation barriers on these CuO surfaces suggest CuO to be a much more efficient catalyst than copper. Moreover, the activation barrier on CuO(010) and CuO(111) surfaces is relatively close to that reported for more active metals like Ni, Pd and Ru, which are between 60 and 70 kJ mol⁻¹.⁶² The reaction energy to form stable fragments of dissociation, CH₃ and H, co-adsorbed on these surfaces was calculated to be 3.4 kJ mol⁻¹ on CuO(111), 20.9 kJ mol⁻¹ on CuO($\bar{1}11$), 2.9 kJ mol⁻¹ on CuO(01 $\bar{1}$) and -58.4 kJ mol⁻¹ on CuO(010). These values are considerably lower than

that on clean and chemisorbed oxygen containing Cu(111) surfaces. The reaction energy for dissociation of methane on each of these surfaces are reported in Table 4.1 with indicator ‘1’ against each surface.

Table 4.1 Reaction pathways, activation barriers and energetics for dissociation of methane on Cu and CuO surfaces, along with the configuration of the TS and FS. 1 and 2 on the surfaces indicate the dissociation mechanism involving the Cu-O pair and only oxygen atoms respectively. FS1 refers to the configuration with both the fragments of dissociation, CH₃ and H, co-adsorbed on the surface, FS gas refers to the configuration with H on the oxygen and CH₃ in the gas phase and FS2 refers to the configuration resulting from chemisorption of CH₃ from the gas phase on the surface. (Cu) refers to top site of Cu, (Cu-h) refers to hollow site of Cu(111), (O) refers to oxygen and (gas) refers to gas phase.

Surface	TS configuration	Activation energy barrier (kJ mol ⁻¹)	FS1/ FS gas configuration	ΔE reaction (kJ mol ⁻¹)	FS2 Configuration	ΔE reaction (kJ mol ⁻¹)
Cu(111)	CH ₃ (Cu)-H(Cu-h)	169.8	CH ₃ (Cu-h)-H(Cu-h)	87.2	-	-
O on Cu(111)-1	CH ₃ (Cu)-H(O)	133.1	CH ₃ (Cu-h)-H(O)	41.1	-	-
O on Cu(111)-2	CH ₃ (gas)-H(O)	144.9	CH ₃ (gas)-H(O)	142.9	CH ₃ (Cu-h)-H(O)	43.0
CuO(111)-1	CH ₃ (Cu)-H(O)	76.6	CH ₃ (Cu)-H(O)	3.4	-	-
CuO(111)-2	CH ₃ (gas)-H(O)	131.4	CH ₃ (gas)-H(O)	118.2	CH ₃ (O)-H(O)	-57.5
CuO($\bar{1}11$)-1	CH ₃ (Cu)-H(O)	90.2	CH ₃ (Cu)-H(O)	20.9	-	-
CuO($\bar{1}11$)-2	CH ₃ (gas)-H(O)	130.3	CH ₃ (gas)-H(O)	128.6	CH ₃ (O)-H(O)	-57.7
CuO(110) _o	CH ₃ (gas)-H(O)	109.1	CH ₃ (gas)-H(O)	97.1	CH ₃ (O)-H(O)	-110.3
CuO(01 $\bar{1}$)-1	CH ₃ (Cu)-H(O)	95.3	CH ₃ (Cu)-H(O)	2.9	-	-
CuO(01 $\bar{1}$)-2	CH ₃ (gas)-H(O)	117.4	CH ₃ (gas)-H(O)	106.4	CH ₃ (O)-H(O)	-85.2
CuO(010)-1	CH ₃ (Cu)-H(O)	60.3	CH ₃ (Cu)-H(O)	-58.4	-	-
CuO(010)-2	CH ₃ (gas)-H(O)	71.5	CH ₃ (gas)-H(O)	58.3	CH ₃ (O)-H(O)	-191.1

On the chemisorbed oxygen containing Cu(111) surface, methane activation may also proceed via the involvement of the chemisorbed oxygen alone, without the participation of the copper atom, as shown in Fig. 4.3a. The activation energy barrier in this case is 144.9 kJ mol⁻¹ and is slightly higher than in the case where both the copper and chemisorbed oxygen atoms participated (Fig. 4.2b). Similarly, the dissociation of methane on CuO surfaces could also proceed via the involvement of the under-coordinated lattice oxygen alone, without the participation of the surface copper atom. The TS for the dissociation catalyzed by lattice oxygen alone on CuO(111) is shown in

Fig. 4.3b. The TSs corresponding to the dissociation of methane on the other CuO surfaces are similar and hence shown in Fig. 7.4 (appendix to chapter 4).

Fig. 4.3 TS corresponding to the dissociation of methane in a pathway involving only hydrogen abstraction by a) dissociatively chemisorbed surface oxygen on Cu(111) surface and b) the under-coordinated lattice oxygen (O_3) atom on CuO(111) surface. The activation energy barrier for dissociation on each of the surfaces is indicated and the dissociating C-H bond is indicated by the red dotted arrow along with the bond length.

The activation energy barrier for the dissociation of methane by this mechanism on CuO(111) surface is 131.4 kJ mol⁻¹, while on CuO($\bar{1}11$) surface it is 130.3 kJ mol⁻¹; on CuO(01 $\bar{1}$) surface, 117.4 kJ mol⁻¹; on CuO(010) surface, 71.5 kJ mol⁻¹; and on CuO(110)_O surface, 109.1 kJ mol⁻¹. The activation energy barrier for the dissociation via this mechanism on all these surfaces is higher than when both the copper and lattice oxygen atoms are involved. The activation barriers on all the surfaces is presented in Table 4.1 with the indicator ‘2’ against the surface.

In each of these cases, where lattice oxygen alone activates methane, the dissociation results in a CH_3 radical which is not interacting with any surface species. The CH_3 radical formed by the dissociation of methane on chemisorbed oxygen containing Cu(111) and CuO(111) surfaces are shown in Fig. 4.4a and Fig. 4.4c respectively. The configurations on the other CuO surfaces are similar.

The generated methyl radicals may evolve directly to the gas phase, as it is not stabilized by any surface atom or may chemisorb on the surface. In oxidative coupling of methane on metal oxide catalysts, the oxygen species is believed to catalyze the dissociation of methane to form CH_3 radicals which are known to be precursors for the formation of C_2 hydrocarbons.³⁰ On chemisorbed oxygen containing surface, the CH_3 may chemisorb on the surface, adjacent to the H-O species as shown in Fig. 4.4b. On the CuO(111)

surface, the CH₃ may chemisorb on the under-coordinated lattice oxygen (O₃) atoms adjacent to the H-O species as shown in Fig. 4.4d. Fig. 4.4b and Fig. 4.4d indicate the difference in energy of the co-adsorbed species with respect to the configuration where CH₃ is in the gas phase. On all CuO surfaces, the co-adsorption of the CH₃ and H on adjacent under-coordinated lattice oxygen atoms is highly favourable. The reaction energy of the co-adsorbed configurations, where CH₃ is also on oxygen, with respect to the weakly physisorbed methane on the surface (IS) is reported in Table 4.1.

Fig. 4.4 Representation of the FS in dissociation of methane via hydrogen abstraction mechanism alone, leading to the formation of gas phase CH₃ radical and hydroxyl species on the surface on a) chemisorbed oxygen containing Cu(111) surface; and c) CuO(111) surface. Representation of the subsequent co-adsorption of CH₃ and H on the surface in a configuration with b) CH₃ on the copper atom and H on chemisorbed oxygen containing Cu(111) surface; and d) CH₃ and H on the adjacent under-coordinated lattice oxygen atoms (O₃) on CuO(111) surface.

4.3.2 Differences in methane activation mechanisms on clean Cu(111), chemisorbed O containing Cu(111), and CuO surfaces

Three distinct mechanisms for the activation of methane are as follows: 1) Copper single-site three-center: involving only copper atoms on Cu(111) surface; 2) Cu-O two-

site four-center: involving both the copper atom and chemisorbed oxygen/lattice oxygen on Cu(111)/ CuO surfaces, with the exception of CuO(110)_O; and 3) Oxygen single-site three-center: involving only the chemisorbed oxygen atom on Cu(111) and the lattice oxygen on the CuO surfaces. These mechanisms are discussed in detail in this section. Bader charges on all the reaction centers in the IS, TS and FS configurations along all reaction pathways on Cu, chemisorbed oxygen containing Cu, CuO(111), CuO($\bar{1}11$) and CuO(110)_O are reported in Table 4.2 and Table 4.3.

Table 4.2 Bader charges on the CH₃ group, H, surface Cu and O atoms on Cu(111) and CuO surfaces in the configurations corresponding to IS, TS and FS during methane dissociation in Cu/ Cu-O pair mediated mechanisms. ^{#1} represents average of the nine surface copper atoms; ^{#2}: average of the three copper atoms connected to the chemisorbed oxygen; ^{#3} : average of the two nearest copper atoms to methane; ^{#4}: average of the six copper atoms (Cu₃) on the surface of CuO(111) and CuO($\bar{1}11$); ^{#5}: average of the six four-coordinate copper atoms on the surface; ^{#6} : average of three copper atoms attached to CH₃; ^{#7}: average of the three copper atoms attached to hydrogen. ^{*1}: average of the six under-coordinated lattice oxygen atoms (O₃) on the surface of CuO(111) and CuO($\bar{1}11$).

IS				
Surface	CH ₃ (e)	H atom pointing to surface (e)	Surface Cu (e)	Surface O (e)
Cu(111)	-0.0455	0.0227	-0.011 ^{#1}	NA
O on Cu(111)	-0.133	0.1188	0.2460 ^{#2} /0.0076 ^{#3}	-0.9344
CuO(111)	-0.0279	0.087	0.8622 ^{#4} /1.0317 ^{#5}	0.9474 ^{*1}
CuO($\bar{1}11$)	-0.0062	0.1091	0.7941 ^{#4} /1.0466 ^{#5}	-0.8857 ^{*1}
TS				
Surface	CH ₃ (e)	Dissociating H (e)	Surface Cu (e)	Surface O (e)
Cu(111)	-0.2861	-0.0856	0.1657	N.A.
O on Cu(111)	-0.3504	0.4168	0.2364	-1.0069
CuO(111)	-0.229	0.4001	0.883/1.0276 ^{#5}	-0.9901
CuO($\bar{1}11$)	-0.2093	0.4163	0.8759/1.0302 ^{#5}	-0.9512
FS				
Surface	CH ₃ (e)	Dissociated H (e)	Surface Cu (e)	Surface O (e)
Cu(111)	-0.3096	-0.2683	0.1502 ^{#6} / 0.0864 ^{#7}	NA
O on Cu(111)	-0.3085	0.5997	0.2138 ^{#2} / 0.1336 ^{#5}	-1.1842
CuO(111)	-0.1384	0.5972	0.8859	-1.0921
CuO($\bar{1}11$)	-0.1048	0.6748	0.8707	-1.1341

Table 4.3 Bader charges on the CH₃ group, H, surface Cu and O atoms on Cu(111) and CuO surfaces in the configurations corresponding to IS, TS and FS during methane dissociation involving only the oxygen atoms. The FS has CH₃ in the gas phase and hydrogen chemisorbed on the surface oxygen as O-H. ^{#1} represents the average of the three copper atoms connected to the chemisorbed oxygen; ^{#2}: average of the six surface under-coordinated copper (Cu₃) atoms; ^{#3}: average of the six surface four-coordinated copper (Cu₄) atoms.

IS				
Surface	CH ₃ (<i>e</i>)	H pointing to the surface (<i>e</i>)	Surface Cu (<i>e</i>)	Surface O (<i>e</i>)
O-Cu	-0.0671	0.0552	0.2441 ^{#1}	-0.9336
CuO(111)	-0.0665	0.0546	0.8561 ^{#2} /1.0349 ^{#3}	-0.9565
CuO($\bar{1}11$)	-0.0127	0.0098	0.7908 ^{#2} /1.0458 ^{#3}	-0.8914
CuO(110) _O	-0.1227	0.117	1.0645 ^{#3}	-0.8354
TS				
Surface	CH ₃ (g) (<i>e</i>)	Dissociating H (<i>e</i>)	Surface Cu (<i>e</i>)	Surface O (<i>e</i>)
O-Cu	-0.1465	0.4357	0.2154	-1.0596
CuO(111)	-0.0466	0.4526	0.8395 ^{#2} /1.0161 ^{#3}	-1.0309
CuO($\bar{1}11$)	-0.0963	0.3451	0.7778 ^{#2} /1.0362 ^{#3}	-0.9426
CuO(110) _O	0.0023	0.4537	1.0591 ^{#3}	-0.9388
FS gas				
Surface	CH ₃ (g) (<i>e</i>)	Dissociated H (<i>e</i>)	Surface Cu (<i>e</i>)	Surface O (<i>e</i>)
O-Cu	0.0131	0.6178	0.1877	-1.2104
CuO(111)	0.0431	0.5657	0.8342 ^{#2} /1.0135 ^{#3}	-1.1304
CuO($\bar{1}11$)	0.0497	0.5701	0.7669 ^{#2} /1.0272 ^{#3}	-1.103
CuO(110) _O	0.0368	0.609	1.0579 ^{#3}	-1.0786

4.3.2.1 Single-site-three-centered mechanisms: activation by copper alone

The TS for dissociation of methane on Cu(111) surface, shown in Fig. 4.5a, represents a single-site-three-center mechanism. Here, the surface copper atom forms the active site, and the CH₃ group, the dissociating hydrogen, and the copper atom form the three reaction centers.

The homolytic dissociation of methane leads to both CH₃ and hydrogen forming bonds with the copper atom. Along the reaction coordinate from the IS to the TS, the CH₃ group and the dissociating hydrogen can be seen to gain charge of 0.24 *e* and 0.12 *e*, respectively, while the copper atom loses charge of 0.18 *e*. This, along with the close

interaction of the copper atom with both the fragments, suggests an oxidative addition process whereby the copper atom adds into the C-H bond of methane to form a three centered σ -complex $\text{CH}_3\text{-Cu-H}$ (Fig. 4.5a).

Fig. 4.5 TSs for the dissociation of methane on Cu(111) and CuO surfaces via different mechanisms. a) Copper single-site three-center mechanism on Cu(111) surface; b) Cu-O two-site four-center mechanism on chemisorbed oxygen containing Cu(111) surface; c) Cu-O two-site four-center mechanism on CuO(111) surface; and d) oxygen single-site three-center mechanism on CuO(110)_o surface. Bader charges on the different atoms/groups are indicated in green font. The dissociating C-H bond is indicated by the red dotted arrow, the active site/ sites and three/ four reaction centers are indicated by the numbers, and the charge transfer direction is indicated by the black dotted arrows.

A similar three centered TS, resulting from the oxidative addition on transition metal surfaces, has been reported for methane activation and dissociation.^{58,66} The charge transfer from copper to methane does not change the oxidation state of any copper atom on the surface completely or increase the charge on any copper atom by more than 0.2 e as the charge is redistributed within the atoms in the vicinity. The oxidative addition mechanism involving only the copper atom of the surface makes the interaction between the CH_3 and the hydrogen fragments at the TS repulsive, as can be seen by the positive

interaction energy of $\sim 32 \text{ kJ mol}^{-1}$ (Table 7.2 appendix to chapter 4). The repulsive interaction between the fragments could result in the large strain on the dissociating molecule, as can be seen from the C-H bond length of $1.8 \text{ \AA}$ in the TS (Fig. 4.5a). Bond lengths of all four C-H bonds and the six H-C-H angles of methane in the IS and TS on different surfaces are reported in Table 7.3 (appendix to chapter 4). The strain on the methane molecule and the nearly negligible stabilization of the TS make the copper single-site three-centered mechanism a very high barrier process.

4.3.2.2 Two-site-four-centered mechanism: activation by Cu-O pair and dipole-dipole stabilization of TS

When the chemisorbed oxygen and the copper atom on Cu(111), and the under-coordinated Cu-O pair on CuO surfaces participate in the dissociation, the TS features two active sites (marked 1 and 2 in Fig. 4.5b and Fig. 4.5c) and four reaction centers (marked 1-4 in Fig. 4.5b and Fig. 4.5c). The presence of chemisorbed oxygen on Cu(111) and of the lattice oxygen in CuO surfaces, facilitate the addition process described earlier by the simultaneous abstraction of the hydrogen of methane. This favours heterolytic dissociation of methane on these surfaces, as the lattice/ chemisorbed oxygen polarizes the C-H bond, while copper adds across it. On chemisorbed oxygen containing Cu(111), the CH_3 group at the TS is observed to gain charge of $0.22 e$ in the course of the dissociation while the hydrogen atom loses charge of $0.3 e$. However, there is negligible change in the charge on the copper atom and on the chemisorbed oxygen atom. Similarly, on CuO(111) surface, the CH_3 group is observed to gain charge of $0.2 e$ and the hydrogen atom loses charge of $0.31 e$. The change in charges on the copper and lattice oxygen atoms on the surface are negligible and this trend is observed on all CuO surfaces. The negligible change in charges on the copper and oxygen atoms of chemisorbed oxygen containing Cu(111) and CuO surfaces, when the charges on the CH_3 group and the hydrogen atom change, suggests a cyclic concerted charge transfer involving four reaction centers ($\text{Cu} \rightarrow \text{CH}_3 \cdots \text{H} \rightarrow \text{O} \rightarrow \text{Cu}$). The charge lost by the copper atom in forming the Cu-CH_3 is recovered when the chemisorbed oxygen/ lattice oxygen redistributes it among the connected copper atoms by accepting charge from the dissociating hydrogen. Such four-centered TS and concerted charge transfer interaction has been reported for chemisorbed oxygen and platinum atom mediated activation on Pt clusters⁵⁸ and for the lattice oxygen and palladium atom mediated activation on Pd

clusters.⁶⁶ Copper addition to the C-H bond and concerted hydrogen abstraction by the chemisorbed/ lattice oxygen is reminiscent of the ‘ σ bond metathesis’- like pathway reported on chemisorbed oxygen containing Pt clusters⁵⁸ and PdO clusters.⁶⁶ This four centered TS is much more stable than the three centered TS described earlier, as the four reaction centers carry complementary charges enabling dipole-dipole like interactions ((Cu δ^+ - CH $_3\delta^-$)---(O δ^- - H δ^+)). Dipole-dipole interactions have been reported to stabilize transition states and bring about favourable changes in the activation energy barriers.¹⁷⁴ The TS in the activation of methane involving only copper addition on Cu(111) is not stabilized by such interactions and thus has a much higher activation energy barrier.

The interaction between the CH $_3$ and hydrogen fragments at the TS changes from repulsive on clean Cu(111) to attractive on the chemisorbed oxygen containing Cu(111) and CuO surfaces, when both the copper and lattice oxygen atoms participate in the activation. This is evident from the negative interaction energy between these fragments as reported in Table 7.2 (appendix to chapter 4). The attractive interaction may also explain the much shorter dissociating C-H bond length of around 1.4 Å on these surfaces compared to 1.8 Å on clean Cu(111) surface (Table 7.3 appendix to chapter 4). Shorter dissociating C-H bonds imply lesser strain on the dissociating methane molecule. Thus, the dipole-dipole interaction stabilizes the TS by virtue of the substrate-adsorbate charge transfer interaction. This additionally enables favourable interaction between the dissociating fragments, thereby lowering the strain on the dissociating molecule. The latter two factors are key to lowering the activation energy barriers for the dissociation of molecules as per the activation strain model proposed by Bickelhaupt and co-workers.^{106,107}

In addition to the stabilization of the TS, the participation of both copper and oxygen atoms in the activation and dissociation also lends stability to the co-adsorbed products of the dissociation. The reaction energy for the dissociation of methane decreases from 87.2 kJ mol $^{-1}$ on Cu(111) to 41.1 kJ mol $^{-1}$ when both the copper and oxygen atoms participate in the activation on chemisorbed oxygen containing Cu(111). The significant decrease in the reaction energy due to the presence of the chemisorbed oxygen on the surface brings about a corresponding reduction in the activation energy barriers. This is in agreement with the proposition by Nørskov and co-workers⁶⁵ that for C-H activation,

the role of chemisorbed oxygen on metals is to alter the thermodynamics of the reaction and thereby the reaction barriers. The reaction energy is further lowered on the CuO surfaces when the Cu-O pair are involved in the activation. Fig. 4.6 shows the nearly linear correlation of the activation energy barriers and the reaction energies on these surfaces. This Brønsted-Evans-Polanyi (BEP) like relationship, typically observed in transition metal catalyzed dissociation reactions,^{175,176} exists for the CuO surfaces as well when both the copper and oxygen atoms participate in the dissociation of methane.

Fig. 4.6 Plot of the activation energy barrier for the dissociation of methane on copper and copper oxide surfaces against the corresponding reaction energy, suggesting a nearly linear correlation between the two quantities.

Fig. 4.6 suggests that the more favourable reaction energy on the CuO surfaces compared to chemisorbed oxygen containing Cu(111) and clean Cu(111) could be one of the reasons for the much lower activation energy barriers on oxide surfaces (Table 4.1). Among the CuO surfaces, CuO(010) exhibits the most favourable reaction energy due to the presence of the 2-coordinated surface lattice oxygen atoms and therefore exhibits the lowest activation energy barrier. It has been shown that for metal oxides, the dissociative chemisorption energy becomes a descriptor for the activation energy barrier only if the geometry of the TS resembles that of the FS.¹⁷⁷ The TS on the clean Cu(111), chemisorbed oxygen containing Cu(111) and CuO surfaces is ‘late,’ resembling the FS, with almost dissociated C-H bonds/ nearly formed O-H species (Fig.

4.2). This is in agreement with literature showing the TS for C-H bond activation on metals and chemisorbed oxygen containing metals to be ‘late’.⁶⁵ Thus, for the oxygen containing surfaces, with both the copper and oxygen atoms participating in the activation of methane, the activation energy barriers are influenced by the stabilization of the TS as well as that of the co-adsorbed products.

4.3.2.3 Single-site-three-centered mechanisms: activation by oxygen alone

The TS for methane dissociation by the chemisorbed oxygen on Cu(111) or by the under-coordinated lattice oxygen (O₃) alone on CuO surfaces (Fig. 4.5d), suggests a single-site three-center pathway. The chemisorbed oxygen or under-coordinated lattice oxygen (O₃) atom is the active site instead of the copper atom. The dissociating CH₃ fragment is not stabilized by any surface atom and thus forms a radical in this homolytic dissociation pathway. The formation of the methyl radical can be confirmed by the near planar sp² structure of the species in the gas phase FS (Fig. 4.4a and Fig. 4.4c) and the near neutral charge on the group (less than 0.05 *e*) on all the surfaces, as seen from the Table 4.3. Such hydrogen abstraction mechanism with relatively high barriers via the formation of a free methyl radical has been reported on oxygen saturated Pt⁵⁸ and Pd⁶⁶ clusters. Unlike the copper atom, the lattice oxygen (O₃) atoms adjacent to the one abstracting the hydrogen are unable to interact with the CH₃ group during the dissociation. On CuO(110)_O, the surface Cu atoms are 4-coordinate and thus are unable to participate in the ‘σ bond metathesis’ like two-site four-centered mechanism observed on the other CuO surfaces. The absence of synergy in this oxygen mediated single-site three-center pathway results in the activation energy barrier for the dissociation being much higher than the pathway involving the Cu-O pair of atoms (Table 4.1). The lattice oxygen on the CuO surfaces are more efficient in abstracting the hydrogen of methane compared to chemisorbed oxygen on Cu(111). Moreover, the activation by lattice oxygen alone on the CuO surfaces has barriers equivalent to or lower than the mechanism involving the Cu-O pair on chemisorbed oxygen containing Cu(111). This decisively shows that CuO surfaces are catalytically more active than clean and chemisorbed oxygen containing copper, irrespective of the nature of the activation mechanism.

Similar to the 2-site 4-center mechanism involving the Cu-O pair, the activation barriers for 1-site 3-center hydrogen abstraction by oxygen can be seen to have a correlation with the energy of the final state (H is chemisorbed on O and CH₃ is in the gas phase as shown in Fig. 4.4a and Fig. 4.4c), and this is shown in Fig. 4.7a. Since the CH₃ is in the gas phase with no significant interaction with any surface species, there exists a linear correlation between the activation barrier and the H chemisorption energy on the oxygen sites as shown in Fig. 4.7b. H chemisorption energy has been shown to be a suitable descriptor for estimating the reactivity of metal oxides for H abstraction reactions.^{178,179}

Fig. 4.7 Linear correlation of the activation barrier for the dissociation of methane in the H abstraction mechanism by oxygen with a) the reaction energy; and b) the H chemisorption energy on the corresponding oxygen sites. The final state in these cases corresponds to a chemisorbed H on the surface with CH₃ in the gas phase.

4.3.3 Nature/ characteristics of the surface sites and their implications for activation energy barriers and reaction energies

The charges on surface atoms and the bonding of metal and oxygen in chemisorbed oxygen containing Cu(111) and CuO surfaces have implications for the stabilization of the TS and the FS. Thus, these factors may not only dictate the reaction pathways on these surfaces but also influence the energetics. Dissociatively chemisorbed oxygen on Cu(111) is coordinately bonded to the surface and the surface essentially retains its metallic character. Bader charges on the surface copper atoms (except those connected to the O atom) are close to 0 suggesting the metallic nature of the surface (Table 4.2). As with most late transition metal oxides of the reducible kind,¹⁸⁰ the bonding in CuO

is known to be a mix of covalent and ionic¹⁸¹. Bader charges (Table 4.2) on the surface copper and oxygen atoms on the CuO surfaces suggest a fair degree of ionic character. The charge on the copper atoms coordinated with the chemisorbed oxygen in Cu(111) surface is $\sim 0.24 e$ and lower, and is much lower compared to $0.86 e$ and $0.79 e$ on the under-coordinated copper atoms in CuO(111) and CuO($\bar{1}\bar{1}1$) surfaces, respectively. The charge on the chemisorbed oxygen atom on Cu(111) is $-0.93 e$ while it is $-0.95 e$ and $-0.89 e$ on the under-coordinated surface lattice oxygen atoms of CuO(111) and CuO($\bar{1}\bar{1}1$), respectively. The strong dipole-dipole interactions that stabilize the TS on CuO(111) and CuO($\bar{1}\bar{1}1$) surfaces are a result of these complementary charges on the Cu-O site pairs and the resulting charge transfer described in section 4.3.2.2. The complementary charges on the four reaction centers in the TS and the FS on the CuO surfaces (Table 4.2) have higher magnitude, compared to chemisorbed oxygen containing Cu(111). Thus, the stabilization of the TS and the FS is expected to be greater on CuO(111) and CuO($\bar{1}\bar{1}1$) surfaces than on chemisorbed oxygen containing Cu(111). This may be the reason for the significantly lower activation energy barriers for the dissociation of methane on CuO surfaces than on chemisorbed oxygen containing Cu(111), in the Cu-O two-site four-center mechanism.

For chemisorbed oxygen on metal surfaces, the binding strength of oxygen on the surface has been shown to be a factor determining its ability to dissociate methane.^{62,178} The weaker the interaction of oxygen with the metal, the stronger will be its interaction with adsorbates and its ability to abstract hydrogen. For the surface lattice oxygen atoms of CuO surfaces, the binding energy of the lattice oxygen may be interpreted as the energy to insert an oxygen atom into an oxygen vacancy on the surface. The binding energy of the chemisorbed oxygen on Cu(111) and the under-coordinated surface lattice oxygen on the CuO surfaces were estimated based on the method suggested by Nørskov and co-workers¹⁸² using the reaction scheme

Where Cu/ Cu_nO_{n-1} is the clean Cu(111) surface/ CuO surface with one under-coordinated lattice oxygen vacancy, O-Cu is the chemisorbed oxygen containing Cu(111) surface, Cu_nO_n is the stoichiometric CuO facets and H₂ (g) and H₂O (g) are molecules in the gas phase. As per this scheme, large positive values indicate weaker

binding on the surface. These values as calculated from simulations implementation the GGA + U scheme with $U = 7$ and $J = 0$. Fig. 4.8 shows a nearly linear correlation of the lattice oxygen binding strength on the surface and the H chemisorption energy on those sites. The H chemisorption energies in this plot are also calculated from simulations implementing the GGA + U scheme with $U = 7$ and $J = 0$. The linear correlation in Fig. 4.8 confirms that the weaker the binding of the surface lattice oxygen, the stronger is its ability to chemisorb the products of the dissociation of methane.

Fig. 4.8 Linear correlation of the lattice oxygen binding strength on the different CuO surfaces and the H chemisorption energy on those sites. The oxygen binding energy is calculated as per the reaction scheme $\text{Cu/Cu}_n\text{O}_{n-1} + \text{H}_2\text{O}_{(g)} \rightarrow \text{O-Cu/Cu}_n\text{O}_n + \text{H}_{2(g)}$, where $\text{Cu/Cu}_n\text{O}_{n-1}$ is the clean Cu(111) surface/ CuO surface with one under-coordinated lattice oxygen vacancy, O-Cu is the chemisorbed oxygen containing Cu(111) surface, Cu_nO_n is the stoichiometric CuO surface and $\text{H}_{2(g)}$ and $\text{H}_2\text{O}_{(g)}$ are molecules in the gas phase.

During the activation of methane, the chemisorbed oxygen on Cu(111) can be seen to be pushed from its fcc hollow site towards the bridge site of the copper atoms opposite the CH_3 group (Fig. 4.5b). This is to accommodate the CH_3 at the copper site. The repulsion between the chemisorbed oxygen and CH_3 also elongates the Cu- CH_3 bond by $0.12 \text{ \AA}$ compared to the same on Cu(111). The dislodging of the chemisorbed oxygen from the Cu(111) fcc hollow site to the bridge site at the TS (Fig. 4.5b) is possible due to its relatively weak binding on the Cu(111) surface. The weak binding can be gauged by the binding energy of 84.8 kJ mol^{-1} . This explains why the promotional effect of

chemisorbed oxygen is observed only on inactive coinage metals where the binding of chemisorbed oxygen on the surface is weak, as shown by Xing *et al.*^{62,63} If the chemisorbed oxygen is strongly bound, it cannot be displaced from its hollow site position and thus it weakens the M-CH₃ (where M is a metal) interaction which is essential for the activation process.

4.3.4 Dissociation of chemisorbed CH₃ on CuO(111)

CuO(111) surface is the most stable surface which can be experimentally synthesized.⁸¹ Thus, subsequent dissociation of chemisorbed CH₃ species was investigated on it. The barrier for diffusion of CH₃ between the under-coordinated (Cu₃) atoms on CuO(111) was calculated to be 21 kJ mol⁻¹ and thus CH₃ migration from one copper atom to a free adjacent copper atom is highly possible. Thus, the dissociation of chemisorbed CH₃ is evaluated without the dissociated and co-adsorbed hydrogen at the adjacent under-coordinated lattice oxygen atom. The pathways of the dissociation of CH₃ which is chemisorbed on lattice oxygen atoms may be direct pathways for its oxidation to CO and CO₂, and these have not been investigated.

The activation energy barrier for the dissociation of CH₃, as depicted in Fig. 4.9a, is calculated to be 137.9 kJ mol⁻¹ and is much higher than that of the dissociation of methane. The barrier is comparable to that of the dissociation of CH₃ on Cu(111) reported in literature.¹¹⁰ The dissociation of CH₃ necessitates reorganization of the CuO lattice to enable CH₂ to form bonds with two adjacent copper atoms. This allows it to maintain the sp³ nature of the C center, as shown in Fig. 4.9a. The overall lattice reorganization and geometric constraint lead to a longer dissociating C-H bond of 1.57 Å at the TS. The dissociation of CH₂, bound to two copper atoms, has an even higher activation energy barrier of 186.2 kJ mol⁻¹ and the reaction scheme is shown in Fig. 4.9b. The barrier is nearly double that of the corresponding step on clean Cu(111) surface which is reported to be ~90 kJ mol⁻¹¹¹⁰. The resulting CH species is bound to two copper atoms and an adjacent lattice oxygen atom in a distorted tetrahedron. The significant lattice reorganization in this step could be a reason for the large activation energy barrier. Subsequent dissociation to C is not investigated due to the large barriers for the formation of surface CH species.

Fig. 4.9 Representation of the IS, TS and FS corresponding to a) the dissociation of chemisorbed CH_3 on $\text{CuO}(111)$ surface and b) the dissociation of chemisorbed CH_2 on $\text{CuO}(111)$ surface. The dissociating C-H bond at the TS is depicted by the red dotted arrow. The activation energy barrier and the reaction energy in each of the cases and the attachment of the different species on the surface are also shown.

4.4 Summary

Facile C-H bond activation of methane on different surfaces of copper oxide is reported, and contrasts between the two potential mechanisms for the dissociation on these surfaces are elucidated. When mediated by a pair of adjacent under-coordinated Cu-O surface sites, the strong C-H bonds of methane can be cleaved with an activation energy barrier of 76.6 kJ mol^{-1} on the stable $\text{CuO}(111)$ surface. High energy CuO surfaces may dissociate methane with lower activation barriers via the same mechanism, as seen from the example of $\text{CuO}(010)$ surface where the barrier is only 60.5 kJ mol^{-1} . The heterolytic C-H bond dissociation on the under-coordinated Cu-O site pairs on CuO surfaces proceeds via copper addition to the C-H bond of methane and the concerted hydrogen abstraction by the lattice oxygen. The CH_3 group, the dissociating hydrogen, and copper and oxygen atoms form a 4-centered TS which is stabilized by the dipole-dipole interaction $((\text{Cu}^{\delta+} - \text{CH}_3^{\delta-}) \cdots (\text{O}^{\delta-} - \text{H}^{\delta+}))$. This is facilitated by a concerted cyclic charge transfer process involving the four centers $(\text{Cu} \rightarrow \text{CH}_3 \cdots \text{H} \rightarrow \text{O} \rightarrow \text{Cu})$. These interactions also reduce the strain on the dissociating methane molecule and in turn lower the activation energy barriers. Similarly, the Cu-O pair on the chemisorbed oxygen containing $\text{Cu}(111)$ surface activates methane via the same two-site four-centered mechanism, but with a higher activation energy barrier of $133.1 \text{ kJ mol}^{-1}$. The

lesser extent of stabilization of both the transition state and the final state by dipole-dipole interactions, compared to that on CuO surfaces, is the reason for the higher barrier. Thus, CuO is found to be a much better catalyst for methane activation, compared to copper.

In contrast, the dissociation of methane on clean Cu(111) surface proceeds by a single-site three-centered mechanism involving only copper atom addition to methane. The homolytic dissociation of methane on Cu(111) makes it a high barrier process, with the activation energy barrier of $169.8 \text{ kJ mol}^{-1}$. With chemisorbed oxygen containing Cu(111) and the CuO surfaces, methane activation may also proceed by the involvement of only the oxygen species as active sites in a hydrogen abstraction mechanism, another single-site three-centered process. This pathway also has higher activation energy barrier compared to the concerted mechanism involving the Cu-O pair. Additionally, it leads to the formation of methyl radicals which may subsequently adsorb on the surface. The absence of stabilization of the TS in these two single active sites (Cu and O) and three-centered mechanisms is the prime reason for the considerably higher barriers for methane activation, compared to the two-site four-centered concerted copper addition and hydrogen abstraction mechanism. On CuO surfaces, the H chemisorption energy is an indicator of the reactivity of the surface for the dissociation of methane by H abstraction mechanism. The surface Cu-O bond strength determines the ability of the lattice oxygen to abstract and chemisorb hydrogen.

The successive dissociation of chemisorbed CH_3 on CuO(111) to CH_2 and further to CH have activation energy barriers of $137.9 \text{ kJ mol}^{-1}$ and $186.2 \text{ kJ mol}^{-1}$, respectively. The barrier increases progressively at each dehydrogenation stage and both values are much higher than that of the first C-H bond dissociation on CuO(111). This is in contrast to the dissociation on Cu(111) surface where the barrier for the first dissociation is high and it decreases progressively until the last dehydrogenation step to form carbon, which has the highest barrier among the four steps.⁵⁴ Single-site copper-oxo complexes in zeolites have been recently shown to be highly reactive in the homolytic dissociation of methane and its conversion to oxygenates like methanol.⁸² Thus, the CH_3 species chemisorbed on the CuO surfaces may undergo surface reactions and rearrangements with the lattice oxygen to generate oxygen containing species as well.

5 Insights into C-H activation on NiO surfaces: the role of nickel and lattice oxygen vacancies and of low valent dopants on reactivity and energetics

5.1 Introduction

Among the transition metal catalysts for methane activation and dissociation, Ni is arguably the most widely used catalyst as it is active and relatively inexpensive.²⁷ Experimental investigations suggest activation barriers of ~ 60 kJ mol⁻¹ on Ni(100) surface¹⁸³ and 70 ± 10 kJ mol⁻¹ on Ni(111) surface¹⁸⁴ with the trend of Ni(100) > Ni(110) $\sim$ Ni(111)¹⁸⁵ for methane activation efficacy. Density functional theory (DFT) based calculations estimated the activation energy barrier for dissociation of methane on Ni(111) surface to be ~ 90 kJ mol⁻¹ and this was found to agree with fitted experimental data which suggested a barrier of 87 kJ mol⁻¹.⁵² However, experiments in the early nineties suggested that the activity of nickel oxide, NiO(100) surface, is much lower than that of the metal itself and that the active sites for dissociation of methane on both these surfaces are the Ni atoms.⁷¹ First principles calculations with clean and oxygen containing nickel surfaces as well as NiO(100) surface showed that the presence of oxygen increases the activation barriers for dissociation of methane.⁶⁰ The activation energy barriers were shown to follow the trend NiO(100) (158.2 kJ mol⁻¹) > chemisorbed oxygen containing Ni(100) (130.2 kJ mol⁻¹) > Ni(100) (57.9 kJ mol⁻¹). Even in partial oxidation reactions of methane on Ni based catalysts, there is a dynamic equilibrium of the reduced Ni sites and oxidized NiO sites and the reduced Ni sites serve as active sites for the dissociation of methane.¹⁸⁶ All these studies point to an inhibiting role of oxygen in methane activation. Although NiO(100), the most stable surface of NiO, is relatively inert, NiO materials with larger surface exposure of high energy surfaces like NiO(110) have been shown to be highly active in lithium storage for lithium ion batteries.⁸⁴ This suggests that the high energy surfaces of NiO may exhibit higher activity towards methane dissociation as well.

Oxides of iron, nickel and copper have been recently used as the regenerative oxygen transfer material in the chemical looping combustion (CLC)^{68,69} process and NiO in particular has been of interest for the chemical looping reforming (CLR)¹⁸⁷ process. Synthesized NiO materials are known to have intrinsic Ni vacancy defects, making them

p-type semiconductors due to the generation of hole states.^{89,188} Intrinsic cation vacancies in oxides like MgO are known to generate O^- species which abstracts hydrogen from methane to form methyl radicals during the oxidative coupling process on these materials.⁷⁵ Intrinsic oxygen vacancy defects may also be present in the samples of NiO prepared under low oxygen concentrations.⁸⁸ Oxygen vacancies are known to be active sites for adsorption and dissociation of molecular oxygen in oxygen rich atmospheres, serving as active sites for oxidation reactions.¹⁸⁹ These Ni and lattice oxygen vacancy defects may have significant but different effects on the methane activation and oxidation processes. The activation barrier for the reduction of NiO with methane was reported to decrease from 155-171 kJ mol⁻¹ in the initial stages of reduction to around 80 kJ mol⁻¹ in the later stages.¹⁹⁰ Reduction of NiO with methane involves sequential dissociation/ oxidation of methane on the surface and subsequent evolution of H₂O and CO/ CO₂ gases, where the oxygen species is the lattice oxygen. The drop in NiO reduction barriers in the course of the NiO reduction with methane¹⁹⁰ suggests that the changes in structure and potential active sites during the reduction process influences the activation barriers for methane dissociation as well.

To get a better understanding of active sites, activation barriers, energetics, and descriptors for methane dissociation on NiO catalysts, the first C-H activation on defect free stoichiometric surfaces and on vacancy defect containing NiO surfaces were investigated. To compare the activity of different NiO surfaces, the most stable NiO(100) and the high energy NiO(110) surfaces were considered in their defect free stoichiometric form. To understand the effect and contribution of defects in NiO surfaces in methane dissociation, NiO(100) and NiO(110) surfaces with single Ni vacancy and NiO(100) surface with single lattice oxygen vacancy were considered.

Lithium and low valent dopants are known to increase the activity of non-reducible metal oxides for catalysis involving the lattice oxygen.^{73,74} Li doped MgO is known to be an effective catalyst to generate CH₃ species in the oxidative coupling process to convert methane to ethylene.^{30,75} Here the Li⁺O⁻ sites generated in the vicinity of the dopant in the oxidative coupling process are believed to be active sites for the abstraction of H from methane. NiO and MgO have the same rock salt structure and Li doped NiO can be easily prepared with varying amounts of Li substituting Ni atoms in the NiO

lattice.⁷⁶ However, NiO being a reducible oxide, is not efficient in the oxidative coupling process and leads to complete oxidation of methane under the typical oxidative coupling conditions.¹⁹¹ Li doped into NiO also generates hole states which are known to be localized on the O species rather than on Ni.¹⁹² These species themselves can be active sites for methane activation or can lead to lattice vacancy formation and subsequent molecular oxygen adsorption in oxidative conditions to form the Li^+O^- species, as proposed in literature⁷⁵. Thus, Li doped NiO(100) and NiO(110) surfaces were also investigated for methane activation. Experimental techniques to prepare Li doped NiO materials vary depending on desired properties and end use, and some of the methods for preparing such materials include sol-gel synthesis,¹⁹³ solid state reaction of Li and Ni salts/ compounds and heating,^{76,194} pulsed deposition and annealing,¹⁹⁵ wet impregnation of NiO with LiNO_3 and calcination,¹⁹¹ and so on.

The computational methods adopted for this investigation with the different simulation systems are discussed in section 5.2. Section 5.3.1 reports the activation barriers and energetics of methane dissociation mediated by the Ni-O pair on stoichiometric NiO(100) and NiO(110) surfaces. Section 5.3.2 reports the activation barriers and energetics for the dissociation of methane by the hydrogen abstraction mechanism involving the lattice oxygen alone and by the Ni-O pair on Ni vacancy and O vacancy containing NiO(100) surfaces. Section 5.3.3 reports the activation barriers and energetics for methane dissociation on Li doped NiO surfaces in both the mechanisms. Section 5.3.4 presents the activation barriers for the dissociation of methane on Ni vacancy containing and Li doped NiO(110) surfaces for comparison. Section 5.4.1 analyses and discusses the reason for large positive value of reaction energy on stoichiometric NiO surfaces using CH_3 and H chemisorption and co-adsorption energies. Section 5.4.2 discusses H chemisorption energy as a potential descriptor for the reactivity of the different NiO surfaces in the 4-centered mechanism as well as 3-centered H abstraction mechanism. Section 5.4.3 discusses the origin of differences in H chemisorption energy on different lattice oxygen sites. The key results and conclusions are summarized in section 5.5.

Schematic representation of the three different mechanisms for methane dissociation on transition metal and metal oxide surfaces with differences in active sites and number of reaction centers is given in Fig. 5.1 below.

Fig. 5.1 Schematic representation of the mechanisms of dissociation of methane on a) a transition metal surface where the metal atom is the single active site, forming three reaction centers together with CH_3 and H; b) a transition metal oxide surface involving the cooperative roles of the M-O pair as the active site, forming four reaction centers together with CH_3 and H; and c) a transition metal oxide surface involving only the lattice oxygen as the active site, forming three reaction centers together with CH_3 and H.

5.2 Computational methods and systems

The simulations were performed with the periodic plane-wave implementation of Density Functional Theory (DFT)^{121,122} using the ab-initio total-energy and molecular-dynamics program VASP (Vienna ab-initio simulation program) developed at the Fakultät für Physik of the Universität Wien.^{157,158} The GGA-PBE exchange correlation functional¹²⁷ within DFT and the Projector Augmented Wave^{159,160} (PAW) method for the treatment of the inner core, with a plane wave cut-off energy of 450 eV were used in all calculations. The nudged elastic band (NEB) method implemented in VASP was used to locate the transition states (TSs) for the dissociation of methane on the different surfaces. The TSs were further reconfirmed with vibrational frequency calculations, where one imaginary frequency confirmed the TS. Spin polarized calculations were performed for all simulations involving NiO due to its antiferromagnetic ordering.^{196,197} Since DFT cannot reproduce the electronic and magnetic properties of NiO due to the strongly correlated and localized 3d electrons in Ni,¹⁹⁷ the implementation of Hubbard

U correction in the form of GGA+U (LDAU in VASP) in the prescription by Dudarev *et al.*¹⁶⁴ was applied to all simulations. The effective U-J value of 5.3 which replicates experimentally observed band gap and magnetic moment of NiO, as reported in literature^{196,198}, was used for all the calculations. Bader charges^{165,166} on the different atoms were calculated.

Fig. 5.2 Atomic arrangement of stoichiometric, defective, and Li doped NiO surfaces. a) NiO(100) surface with 5-coordinate Ni-O pairs; b) NiO(110) surface with 4-coordinate Ni-O pairs; c) Top view of NiO(100) surface with a surface Ni atom vacancy; d) Top view of NiO(100) surface with a surface lattice oxygen vacancy; e) Top view of NiO(110) surface with a surface Ni atom vacancy; f) Top view of Li doped NiO(100) surface where one surface Ni atom is replaced by Li; and g) Top view of Li doped NiO(110) surface where one surface Ni atom is replaced by Li. Blue balls represent Ni atoms, red balls represent oxygen atoms and purple ball represents Li atom.

The bulk lattice constant of NiO was optimized to 4.205 Å which is close to the experimentally determined value of 4.176 Å¹⁹⁹, as reported in the literature. The non-polar NiO(100) surface is known to be quite inert²⁰⁰ and is the most stable surface with the lowest unit surface energy.⁸⁴ This surface is atomically flat, with 5-coordinate Ni-O

pairs on the surface as shown in Fig. 5.2a. The NiO(100) surface was modelled as a 4x3 super cell with 3 atomic layers and 10 Å of vacuum over the surface. The antiferromagnetic ordering was imposed in the alternate rows of Ni atoms. The atoms in the lowest layer were fixed during the simulations to represent the bulk, while all atoms in the remaining layers were completely relaxed in all simulations. 2x4x1 Monkhorst-Pack K-point mesh was used to sample the Brillouin zone. The non-polar NiO(110) surface is a much higher energy surface,⁸⁴ and mesoporous NiO materials having good catalytic properties exposing this facet have been synthesized.^{84,201,202} It has 4 coordinated Ni-O pairs arranged in sequence on the surface, forming ridges on the surface as shown in Fig. 5.2b. The NiO(110) surface was modelled as 2x4 super cell with 5 atomic layers and 10 Å of vacuum over the surface with the antiferromagnetic ordering in the alternate rows of Ni atoms. 4x2x1 Monkhorst-Pack K-point mesh was used to sample the Brillouin zone. To understand the role of vacancy defects in methane activation, both NiO(100) and NiO(110) surfaces with surface Ni vacancies as shown in Fig. 5.2c and Fig. 5.2e respectively were considered for simulations. The super cell dimensions were identical to those used in the case of stoichiometric clean NiO(100) and NiO(110) surfaces. To investigate the role of oxygen vacancy defects on methane activation, surface oxygen vacancy was also modelled on the NiO(100) surface as shown in Fig. 5.2d. To understand the effect of low valent dopants in activating the surface and thereby aiding in methane activation, Li doped NiO(100) and NiO(110) surfaces were modelled with the same supercell dimensions as those used for Ni vacancy containing surfaces. In the Li doped systems, one surface Ni atom was replaced by Li as shown in Fig. 5.2f and Fig. 5.2g.

5.3 Results

5.3.1 Dissociation of methane on stoichiometric NiO(100) and NiO(110) surfaces: Ni-O pair mediated mechanism, activation barriers, and energetics

Methane was found to weakly physisorb on the NiO surfaces investigated. The physisorption energies on the different surfaces are reported in Table 7.4 (appendix to chapter 5). Thus, the activation energy barriers reported here are calculated with respect to the reactant state corresponding to weakly physisorbed methane on the surfaces.

Methane activation on the stable NiO(100) surface was found to proceed via a transition state (TS) involving the 5-coordinated Ni-O pair as active sites with four reaction centers (CH₃, H, Ni and O) as shown in Fig. 5.3a. This heterolytic dissociation process leaves CH₃ on the Ni atop site and H on the lattice oxygen, forming a hydroxyl species, as shown in Fig. 5.3a. The 4-centered mechanism of methane activation (Fig. 5.1) on oxygen containing metal surfaces and metal oxide surfaces has been discussed in detail in the literature.^{58,66,203}

Fig. 5.3 The initial state (IS), transition state (TS) and final state (FS) corresponding to dissociation of methane involving the Ni-O pair on a) NiO(100) surface; and b) NiO(110) surface. The active sites are numbered as 1 and 2 and the reaction centers are numbered 1- 4. The activation energy barrier and the reaction energy (ΔE) corresponding to the dissociation in each of these cases are also indicated in the figures. Blue balls represent Ni atoms, red balls represent O atoms, grey balls represent C atoms and white balls represent H atoms.

In contrast, dissociation of methane on Ni(100) surface is homolytic with the Ni atom alone as the active site and leaves CH₃ on the Ni-Ni bridge site and H on the 4-fold hollow site. The scheme for dissociation of methane on Ni(100) surface is shown in Fig. 7.5a (appendix to chapter 5). The activation barrier for the 2-site 4-center mechanism of

dissociation of methane on NiO(100) was calculated to be 136 kJ mol⁻¹. This barrier is nearly twice that of the calculated activation barrier of 70.3 kJ mol⁻¹ on Ni(100) surface. In contrast to the observation here, it was shown that the most stable and dominant facet of CuO, CuO(111) surface, can activate methane with barrier less than half of that on Cu(111) surface.²⁰³ Thus, the presence of oxygen (chemisorbed or in the form of lattice oxygen) on active metals like Ni inhibits methane activation while the same on an inactive metal like Cu promotes methane activation, in agreement with literature.^{60,62}

The reaction energy (ΔE), calculated as the difference of energy of the dissociatively chemisorbed products (CH₃ and H) on the surface with respect to the weakly physisorbed methane on the surface gives a possible explanation for the large barrier for dissociation. On NiO(100) surface, ΔE for the dissociative chemisorption is 133 kJ mol⁻¹ while on Ni(100) it is -5.7 kJ mol⁻¹. The large positive value of ΔE on NiO(100) suggests extremely unfavourable chemisorption of the products of dissociation on the surface. The 5-coordinated Ni-O pairs on the surface exhibit very strong mutual interaction which is unfavourable to chemisorption of CH₃ and H on the surface. This is further discussed in section 5.4.1.

The NiO(110) surface is known to be a higher energy surface compared to NiO(100) and is catalytically more active.^{84,201,202} NiO(110) surface can dissociate methane in the Ni-O pair mediated 4-center mechanism with activation barrier as low as 64.2 kJ mol⁻¹ as shown in Fig. 5.3b. This barrier is marginally lower than that on Ni(100) surface making this a highly reactive surface for methane dissociation. The ΔE for the dissociative chemisorption of methane on NiO(110) is calculated to be 31.2 kJ mol⁻¹ and is more favourable compared to that on NiO(100) surface. The coordinative unsaturation of the surface Ni-O pairs, which are 4 coordinate on NiO(110) surface while they are 5 coordinate on NiO(100) surface, may be responsible for the favourable chemisorption of the products of dissociation. This is further discussed in section 5.4.1.

An alternate mechanism for dissociation of methane involves hydrogen abstraction from methane by the lattice oxygen atoms (shown in Fig. 5.1 and presented in section 5.3.2.). Here the lattice oxygen serves as the sole active site for the dissociation, without the participation of the metal atoms. We believe that this mechanism might not be relevant

for the stoichiometric NiO surface due to the strong Ni-O bonding and is discussed further in section 5.4.1.

5.3.2 Dissociation of methane on defective NiO(100) surfaces: Ni-O pair mediated and lattice oxygen mediated mechanisms, activation barriers, and energetics

Fig. 5.4 The IS, TS, and FS/ FS (gas) corresponding to the dissociation of methane on Ni vacancy containing NiO surfaces involving a) the Ni-O pair adjacent to Ni vacancy on NiO(100) surface; b) the lattice oxygen adjacent to Ni vacancy on NiO(100) surface; and c) the lattice oxygen two rows from Ni vacancy on NiO(100) surface. The active sites are numbered as 1 and 2 for the 4-center mechanism and it is numbered as 1 for the 3-center mechanism. Lattice oxygen atoms adjacent to the Ni vacancy are indicated as O1 and the lattice oxygen atoms away from the Ni vacancy are indicated as O2. Also shown in each of the cases are the activation energy barrier for dissociation and the reaction energy (ΔE) calculated with respect to the IS.

Activation of methane can proceed by the involvement of the Ni-O pair adjacent to the Ni vacancy, like that on stoichiometric surfaces, with a barrier of 94.6 kJ mol^{-1} as shown in Fig. 5.4a. The barrier in this 4-center process is much lower than the barrier on stoichiometric defect free NiO(100) surface (136 kJ mol^{-1}) and is comparable to that of 94.5 kJ mol^{-1} on Ni(111) surface (Fig. 7.5b appendix to chapter 5). The reaction energy for dissociation of methane on the Ni-O pair adjacent to the Ni vacancy on NiO(100) is favourable with value $-13.2 \text{ kJ mol}^{-1}$, suggesting strong chemisorption of the products of dissociation.

Since methane dissociation by hydrogen abstraction by the lattice oxygen adjacent to a cation vacancy has been reported for MgO,⁷⁵ dissociation of methane by H abstraction mechanism by the lattice oxygen on Ni vacancy containing surfaces was investigated. The activation barrier for the dissociation of methane in the H abstraction mechanism by the lattice oxygen next to Ni vacancy (O1 in Fig. 5.4b) was calculated to be 86.1 kJ mol^{-1} . This is a 3-center process with the lattice oxygen as the only active site as shown in Fig. 5.4b. The activation barrier in this 3-center mechanism is marginally lower than the 4-center mechanism involving cooperative roles of the Ni-O pair. H abstraction from methane by the lattice oxygen leads to the formation of a CH_3 radical species which is not stabilized by any surface atom as indicated by $\text{FS}_{(\text{gas})}$ in Fig. 5.4b. Thus we see that the existence of a Ni vacancy on the surface of NiO(100) improves the activity of the surface lattice oxygen atoms adjacent to it. This in turn lowers the barrier for methane dissociation in both, the 4-center cooperative mechanism as well as the 3-center H abstraction mechanism. Methane dissociation in actual reaction conditions may proceed by both these mechanisms with similar kinetic probabilities.

To understand if the improvement in activity of the surface lattice oxygen due to Ni vacancies is a localized phenomenon, methane dissociation on lattice oxygen away from the vacancy on NiO(100) surface was investigated. It was found that Ni vacancy on the surface increases activity not only of the lattice oxygen atoms in its immediate vicinity, but to a lesser extent, that of the oxygen atoms a few rows away from the vacancy. Methane dissociates by the H abstraction mechanism by lattice oxygen two rows away

from the Ni vacancy (O2 in Fig. 5.4c) with barrier of 116.2 kJ mol⁻¹. This barrier involving O2 lattice oxygen is higher than that with the O1 lattice oxygen (86.1 kJ mol⁻¹), but lower than that with the 4-center mechanism on stoichiometric defect free NiO(100) surface (136 kJ mol⁻¹). Trends in barriers on the O1 and O2 lattice oxygen sites will be discussed in section 5.4.2.

The dissociation of methane may proceed on the Ni-O pair adjacent to an oxygen vacancy on NiO(100) surface in the 4-centered mechanism with activation barrier of 120.4 kJ mol⁻¹ as shown in Fig. 5.5. This value is slightly lower than the activation barrier on the clean and stoichiometric NiO(100) surface. The reaction energy for this dissociation mechanism is rather high at 118.3 kJ mol⁻¹, suggesting unfavourable chemisorption of the products of dissociation on the surface. Thus, unlike the Ni vacancy, the single surface lattice oxygen vacancy does not significantly improve the activity of the surface for methane dissociation. Thus, Ni atoms near the single surface lattice oxygen vacancy may not be active sites for methane dissociation in an oxygen limited conditions.

Fig. 5.5 The IS, TS and FS corresponding to the dissociation of methane involving Ni-O pair adjacent to O vacancy on NiO(100) surface. The active sites are marked as 1 and 2 and the reaction centers are marked 1– 4. The activation barrier and the reaction energy (ΔE) corresponding to the dissociation is also indicated in the figure.

Creating Ni vacancies on NiO(100) surface can increase the activity of the surface lattice oxygen atoms to varying extents depending on their proximity to the vacancy and make them active sites for dissociation of methane in the H abstraction mechanism. However, systematic generation of Ni vacancy defects on the surface may not be a controllable and viable process to increase the activity of the relatively inactive NiO(100) surface.

5.3.3 Dissociation of methane on Li doped NiO(100) surfaces: Ni-O pair mediated and lattice oxygen only mechanisms, activation barriers and energetics

On NiO(100) surface, with one Ni atom replaced by Li, methane dissociation may proceed both by the 4-center and 3-center mechanisms. The Ni-O pair adjacent to the Li atom as shown in Fig. 5.6a can activate methane in the 4-center mechanism with barrier of $102.7 \text{ kJ mol}^{-1}$ while the Ni-O pair away from the Li atom as shown in Fig. 5.6b can activate methane with a barrier of $120.5 \text{ kJ mol}^{-1}$. The lattice oxygen adjacent to the Li atom (O1) as shown in Fig. 5.6c can activate methane by the 3-center H abstraction mechanism with a barrier of 89.3 kJ mol^{-1} while the O2 lattice oxygen shown in Fig. 5.6d can do so with a barrier of $110.2 \text{ kJ mol}^{-1}$. The IS and FS for this mechanism on this surface are similar to those depicted in Fig. 5.4 and hence not shown.

Fig. 5.6 TS for dissociation of methane on Li doped NiO(100) surfaces by a) the 4-center mechanism involving the Ni-O pair adjacent to Li atom; b) the 4-center mechanism involving the Ni-O pair away from Li atom; c) the 3-center H abstraction mechanism involving the lattice oxygen (O1) atom in the immediate vicinity of the Li atom; and d) the 3-center H abstraction mechanism by the lattice oxygen (O2) atom away from the Li atom. The activation barrier (E_a) for the dissociation of methane in each of these cases is also indicated in the figures.

The activation barriers for methane dissociation by both these mechanisms on the Li doped NiO(100) surfaces are lower than the barrier for dissociation on stoichiometric

clean NiO(100) surface. This reconfirms that Li doping increases the activity of the surface for catalysis.⁷⁴ Like the Ni vacancy on the surface, the effect of the surface Li atom in increasing the activity of surface lattice oxygen is not limited to the lattice oxygen atoms in the immediate vicinity of Li. The activation barriers for the dissociation of methane by both the mechanisms on Li doped NiO(100) are comparable to the corresponding barriers obtained on NiO(100) with Ni vacancy. The barriers for the dissociation of methane by hydrogen abstraction by the O1 and O2 lattice oxygen atoms on the Li doped and the Ni vacancy containing NiO(100) surfaces are also comparable. Thus, with respect to the kinetics of the dissociation process, the effect of Li doping may be viewed as equivalent to that of the Ni vacancies on the surface.

Fig. 5.7 Plot of the activation energy barriers for the dissociation of methane and the corresponding reaction energy involving the Ni-O pair mediated 4-center mechanism on different NiO surfaces.

Fig. 5.7 shows the activation energy barriers for the dissociation of methane in the 4-center mechanism involving Ni-O pairs on different NiO surfaces and the corresponding reaction energy upon co-adsorption of the products of dissociation. There seems to be a linear correlation between the activation barrier and the reaction energy for dissociation of methane on the Ni-O pairs on stoichiometric NiO(100) surface, Ni/ lattice oxygen vacancy containing NiO(100) surfaces and Li doped NiO surfaces. The linear

correlation between activation barrier and reaction enthalpy, popularly referred to as the Brønsted-Evans-Polanyi (BEP) correlation, is well established for transition metal catalysed reactions, making reaction enthalpy a descriptor for reactivity in such processes.^{175,176,204} The presence of a Ni vacancy on the NiO(100) surface makes co-adsorption of CH₃ and H significantly more favourable than on stoichiometric NiO(100) and lattice oxygen vacancy containing NiO(100) surfaces. Li doping has a similar effect on the energetics of the dissociation process. Another potential descriptor for reactivity for dissociation of methane in the 4-center mechanism on NiO surfaces is discussed in section 5.4.2.1.

5.3.4 Dissociation of methane on Ni vacancy containing and Li doped NiO(110) surfaces: lattice oxygen only mechanism, activation barriers, and energetics

In section 5.3.2 and 5.3.3, it was shown that the H abstraction mechanism for methane activation on Ni vacancy containing and Li doped NiO(100) surfaces has an activation barrier lower than that with the 4-center Ni-O pair mediated mechanism. Thus, the same H abstraction mechanism was evaluated on Ni vacancy containing and Li doped NiO(110) surfaces and is presented here for comparison. Ni vacancy on NiO(110) surface (Fig. 5.8) increases the activity of the lattice oxygen atoms around it as described earlier. Methane dissociation by the H abstraction mechanism involving the O1 lattice oxygen on NiO(110) surface (Fig. 5.8a) has an extremely low barrier of 46.3 kJ mol⁻¹. The TS for this mechanism is shown in Fig. 5.8a. The IS and FS for this mechanism on NiO(110) is similar to those depicted in Fig. 5.4 and hence not shown. The barrier in this 3-center dissociation mechanism involving only the lattice oxygen is lower than the activation barrier in the 4-center mechanism involving the Ni-O pair on stoichiometric defect free NiO(110) surface (64.2 kJ mol⁻¹). The O2 lattice oxygen on NiO(110) (Fig. 5.8b) abstracts H from methane with a barrier of 106.9 kJ mol⁻¹ and the trend in barriers will be discussed in section 5.4.2.

Fig. 5.8 TS corresponding to the dissociation of methane on Ni vacancy containing and Li doped NiO(110) surfaces by the 3-center H abstraction mechanism involving a) O1 lattice oxygen in the immediate vicinity of Ni vacancy; b) O2 lattice oxygen away from Ni vacancy; c) by O1 lattice oxygen in the immediate vicinity of Li; and d) by O2 lattice oxygen away from Li. The activation barrier for the dissociation in each of the cases is indicated in the figure.

On Li doped NiO(110) surface, the O1 lattice oxygen can abstract H from methane with activation barrier of 75.7 kJ mol⁻¹ as shown in Fig. 5.8c while the O2 lattice oxygen can do so with a barrier of 114.7 kJ mol⁻¹ as shown in Fig. 5.8d. These values are higher than the values calculated for methane dissociation on clean and stoichiometric NiO(110) surface as well as NiO(110) surface with Ni vacancy. Thus, the increase in activity of the surface lattice oxygen on NiO(110) due to Li doping is less pronounced than it is on NiO(100).

5.4 Discussion

5.4.1 Chemisorption and co-adsorption energies of CH₃ and H on NiO surfaces and large positive reaction energy on stoichiometric surfaces

In section 5.3.1, it was shown that the co-adsorption of the products of dissociation, CH₃ and H, on NiO(100) and NiO(110) are unfavourable with large positive energy values

with respect to weakly physisorbed methane. The chemisorption of these individual species on their corresponding sites also has large positive values of 177.9 kJ mol⁻¹ for CH₃ on the 5-coordinated Ni atom and 82.1 kJ mol⁻¹ for H on the 5-coordinated surface lattice oxygen on NiO(100) (Table 5.1). These values are calculated as per the reaction scheme, CH₄ (g)/ H₂ (g) + * → CH₃*/ H* + ½ H₂ (g) where * represents the NiO surface with the corresponding Ni or lattice oxygen sites. The large positive values of the chemisorption energies of CH₃ and H are testimony to very strong bonding between the Ni-O pairs. The energy to insert an oxygen atom into vacant lattice oxygen site or in other words, the surface lattice oxygen vacancy formation energy are indicative measures of the strength of Ni-O bond. The strong Ni-O bonding on NiO(100) can be inferred from the large negative value of -175 kJ mol⁻¹ for surface lattice oxygen binding strength (Table 7.5 appendix to chapter 5).

Table 5.1 Chemisorption energy of CH₃ and H on Ni and lattice oxygen atoms respectively on different NiO surfaces. Chemisorption energy is calculated as per the reaction scheme CH₄ (g)/ H₂ (g) + * → CH₃*/ H* + ½ H₂ (g) where * represents the NiO surface.

Surface	CH ₃ site description	Chemisorption energy (kJ mol ⁻¹)	H site description	Chemisorption Energy (kJ mol ⁻¹)	Co-adsorption energy CH ₃ -H (kJ mol ⁻¹)
NiO(100)	Ni	177.9	O	82.1	140.6
NiO(110)	Ni	182.1	O	-72.8	23.1
NiO(100)-Ni vacancy	Ni adjacent to vacancy	171.5	O adjacent to vacancy (O1)	-183.4	-10.8
NiO(100)-Ni vacancy	Ni away from vacancy	150.6	O away from vacancy (O2)	-119.7	45.9
NiO(110)-Ni vacancy	Ni adjacent to vacancy	127.3	O adjacent to vacancy (O1)	-208.9	-
NiO(110)-Ni vacancy	Ni away from vacancy	160.6	O away from vacancy (O2)	-131.4	-
NiO(100)-O vacancy	Ni adjacent to vacancy	121.4	O adjacent to vacancy	46.3	122.8
Li doped NiO(100)	Ni adjacent to Li	174.9	O adjacent to Li (O1)	-151.9	22.6
Li doped NiO(100)	Ni away from Li	173.9	O away from Li (O2)	-126.2	43.9
Li doped NiO(110)	Ni adjacent to Li	136.8	O adjacent to Li (O1)	-170.1	-
Li doped NiO(110)	Ni away from Li	153.2	O away from Li (O1)	-127.8	-

The co-adsorption energy of $140.6 \text{ kJ mol}^{-1}$ for CH_3 and H on NiO(100) surface (Table 5.1) has a value which is much smaller than the sum of their individual chemisorption energies of $177.9 \text{ kJ mol}^{-1}$ and 82.1 kJ mol^{-1} suggesting that the co-adsorption is favourable. This can be explained by the formation of acid-base pairs on the NiO surface due to the heterolytic bond dissociation of methane. The CH_3 bound to the Ni atom tends to be the base and the H bound to the lattice oxygen atom tends to be the acid. The acid-base pair formation and its effects on strengthening chemisorption on metal oxides have been extensively discussed by H. Metiu and co-workers.^{205,206} A similar acid-base pair effect strengthening co-adsorption of CH_3 and H on the Ni-O pair is observed on the stoichiometric NiO(110) surface (Table 5.1). The difference of the co-adsorption energy of $140.6 \text{ kJ mol}^{-1}$ on NiO(100) and that of 23.1 kJ mol^{-1} on NiO(110) can be attributed to the difference in the binding energy of H on the 5-coordinated (82.1 kJ mol^{-1}) and 4-coordinated lattice oxygen ($-72.8 \text{ kJ mol}^{-1}$) atoms. The binding energy of CH_3 on the 5-coordinated Ni atoms on NiO(100) and the 4-coordinated Ni atoms on NiO(110) surfaces are similar. This suggests that irrespective of the surface termination, the interaction of CH_3 with surface Ni atoms on NiO is weak. The stronger chemisorption of H on the 4-coordinated lattice oxygen on NiO(110) can be explained by the weaker Ni-O bonding where the oxygen binding strength was calculated to be $-72.2 \text{ kJ mol}^{-1}$ (Table 7.5 appendix to chapter 5) compared to $-175.9 \text{ kJ mol}^{-1}$ on NiO(100). The influence of lattice oxygen binding strength on H chemisorption energy is discussed further in section 5.4.3.

During H abstraction from methane, the CH_3 is in the gas phase with no significant interaction with any surface atom, while the dissociating H forms the surface hydroxyl species. Thus, instead of the reaction energy, involving both the CH_3 and H species, the chemisorption energy of the dissociated H alone is expected to influence the activation barriers. Thus, for metal oxides, a linear correlation of the activation barrier for dissociation of methane and the lattice oxygen-hydrogen bond strength is proposed in literature.¹⁷⁸ The large positive value of H chemisorption energy of 82.1 kJ mol^{-1} on the lattice oxygen of stoichiometric NiO(100) surface suggests that the lattice oxygen would be incapable of abstracting the H of methane without assistance from the metal atom. Because of the weak binding of H on the lattice oxygen of NiO(100), methane activation by the hydrogen abstraction mechanism involving only the lattice oxygen atom was not

investigated for stoichiometric NiO surfaces. Based on the analyses here, it is inferred that the activation of methane on stoichiometric NiO surfaces may proceed only through the 2-site- 4-center mechanism involving the Ni-O pair.

5.4.2 Descriptors for activation barriers

5.4.2.1 Descriptors for activation barrier in the 4-center Ni-O pair mediated mechanism on NiO surfaces

It was shown in sections 5.3.1 to 5.3.3 and in Fig. 5.7 that favourable chemisorption energy upon co-adsorption of the products CH₃ and H on the surface, in the Ni-O mediated 4-center dissociation process leads to lower activation barriers. The nearly linear correlation between the activation barrier and the reaction energy (BEP like relationship) for dissociation by the Ni-O pairs on different NiO(100) surfaces was depicted in Fig. 5.7. In transition metal catalysed reactions, the reaction enthalpy serves as a descriptor.^{175,176,204} Thus, the linear correlation of activation barrier and the reaction energy on NiO surfaces suggests that the reaction energy may serve as a descriptor for the 4-center Ni-O mediated dissociation of methane on NiO surfaces as well.

The chemisorption energy of CH₃ alone on the Ni sites on stoichiometric NiO(100), Ni vacancy containing NiO(100), and Li doped NiO(100) surfaces are not significantly different as can be seen from Table 5.1. However, there are significant differences in the H chemisorption energies on the lattice oxygen sites of these surfaces. This suggests that the contribution to favourable energetics is determined by the H chemisorption energy rather than the CH₃ chemisorption energy. On plotting the activation barriers for the dissociation of methane involving the Ni-O pair on these surfaces against the H chemisorption energies, there emerges two sets of nearly linear correlations, spanning two different ranges of H chemisorption energy as can be seen from Fig. 5.9. Large positive values of H chemisorption energies indicate very weak chemisorption and large negative values indicate very strong H chemisorption. The stoichiometric NiO(100), the lattice oxygen vacancy containing NiO(100) and the stoichiometric NiO(110) surfaces fall in the weak H chemisorption range while the Ni vacancy containing and Li doped NiO(100) surfaces fall in the strong H chemisorption range. A lattice oxygen vacancy leaves the surface richer in two electrons, making it a Lewis base, while a Ni vacancy and low valent dopant like Li make the surface deficient in electrons making them Lewis

acids.²⁰⁵ Thus for acidic and basic surfaces where the interaction of the metal with CH₃ is weak, separate linear correlations exist for the activation barrier for dissociation of methane in the 4-centered M-O mechanism and the H chemisorption energy. Additionally, it can be inferred that the H abstraction mechanism may not prevail near a single oxygen vacancy on NiO surfaces due to its Lewis base nature.

Fig. 5.9 Plot of the activation energy barrier for the dissociation of methane and the H chemisorption on the corresponding lattice oxygen on NiO surfaces when the dissociation proceeds in the 4-center Ni-O pair mediated mechanism.

5.4.2.2 Descriptor for activation barrier in the 3-center H abstraction mechanism on NiO surfaces

H chemisorption energy, or hydrogen addition energy as some call it, has been reported to be the descriptor for the reactivity of lattice oxygen in metal oxide mediated hydrogen abstraction reactions.¹⁷⁹ It can be seen from sections 5.3.2 to 5.3.4 that the activation barrier for the dissociation of methane in the H abstraction mechanism on different surface lattice oxygen sites on NiO(100) and NiO(110) surfaces with Ni vacancy and Li dopant are different. On NiO(100) surface with a Ni vacancy, the chemisorption energy of H on the O1 lattice oxygen (Fig. 5.4b) was calculated to be -183.4 kJ mol⁻¹ while that on the O2 lattice oxygen (Fig. 5.4c) was calculated as -119.7 kJ mol⁻¹ (Table 5.1). The

difference in H chemisorption energy explains the difference in activation barrier: O1 oxygen is 86.1 kJ mol⁻¹ and that on the O2 oxygen is 116.2 kJ mol⁻¹.

Fig. 5.10 Activation barrier for dissociation of methane and the H chemisorption energy on the corresponding sites on different NiO surfaces when dissociation proceeds by the 3-center H abstraction mechanism. The two quantities have a nearly linear correlation as can be seen from the plot. Refer Fig. 5.4, Fig. 5.6 and Fig. 5.8 for specification of lattice oxygen as O1 and O2 on different NiO surfaces.

A similar trend is observed with the hydrogen chemisorption energies on the two lattice oxygen sites (O1 and O2) on Li doped NiO(100) and the activation barriers on those sites as shown in Fig. 5.6 and was reported in section 5.3.3. The same trend is found applicable to Ni vacancy containing NiO(110) and Li doped NiO(110) surfaces as well, as reported in section 5.3.4 (Fig. 5.8). Fig. 5.10 shows a linear correlation between the H chemisorption energy on the lattice oxygen sites on different NiO surfaces and the activation barrier for H abstraction from methane on those sites, in agreement with literature.¹⁷⁸ The stronger the H chemisorption (large negative value) on the lattice oxygen, the more effective the oxygen is towards abstracting H from methane. The results here further reconfirm that H chemisorption energy is a suitable descriptor to describe the reactivity of surface lattice oxygen on metal oxide surfaces for methane activation.¹⁷⁸ Lattice oxygen O1 on NiO(110) surface has the strongest H chemisorption and it exhibits the lowest barrier in the H abstraction process.

5.4.3 Differences in H chemisorption energy on different lattice oxygen sites

It is known that H chemisorption strength on metal oxides is related to the basicity of their lattice oxygen.¹⁷⁹ For chemisorbed oxygen on metal surfaces, the strength of interaction of the oxygen with the surface has been shown to determine its basicity and thereby its ability to dissociate methane.^{62,63} Oxygen vacancy formation energy was suggested to be an indicator of the surface reducibility of the metal oxide and was proposed to be a descriptor for the reactivity of both reducible and non-reducible oxides for C-H bond dissociation.²⁰⁷ It was shown that the lattice oxygen binding strength on different CuO surfaces influences their ability to chemisorb hydrogen and thereby activate methane.²⁰³ The weaker the interaction of the lattice oxygen with the metal atoms on the surface, the greater is its basicity and the stronger the H chemisorption. The surface lattice oxygen on stoichiometric NiO(100) is very strongly bound as evident from the large negative value of binding strength of $\sim -176 \text{ kJ mol}^{-1}$. In contrast, the surface O1 lattice oxygen atoms on NiO(100) (Fig. 5.4b) and NiO(110) (Fig. 5.8a) surfaces are very loosely bound as can be seen from the large positive value of binding energy of $\sim 141 \text{ kJ mol}^{-1}$ and 151 kJ mol^{-1} respectively (Table 7.5 appendix to chapter 5). The O2 lattice oxygen atoms on NiO(100) and NiO(110) surfaces (Fig. 5.4c and Fig. 5.8b) are also loosely bound (70.3 kJ mol^{-1} and 0.2 kJ mol^{-1} respectively), although not as loosely as their O1 counterparts (Table 7.5 appendix to chapter 5).

Fig. 5.11 shows the oxygen binding strength of the different lattice oxygen atoms on the different NiO surfaces and the corresponding H chemisorption energy on those sites. The plot shows three sets of nearly linear correlations between these quantities as indicated by the black, blue and lilac lines. The points in black represent the stoichiometric NiO surfaces, the points in blue represent the Ni vacancy containing surfaces, and the points in lilac represent the Li doped surfaces. The stoichiometric surfaces lie to the far left-top of the plot where the strong binding of surface lattice oxygen makes H chemisorption very weak. The Ni vacancy containing surfaces, in contrast, lie to the far right-bottom of the plot where the extremely weak surface binding of the surface lattice oxygen allows very strong H chemisorption. In the middle lie the Li doped surfaces where the surface lattice oxygen atoms are loosely bound compared

to their stoichiometric counterparts, but more strongly bound compared to their Ni vacancy containing counterparts.

Fig. 5.11 Hydrogen chemisorption energy on different lattice oxygen sites and the binding strength of the corresponding surface lattice oxygen atoms on the NiO surfaces. Surface lattice oxygen atoms on the stoichiometric surfaces, represented by the black triangles, are very strongly bound while surface lattice oxygen atoms on the NiO surfaces with Ni vacancies are very loosely bound. Surface lattice oxygen atoms on the Li doped NiO surfaces have lattice oxygen binding strengths intermediate to that of stoichiometric and Ni vacancy containing surfaces. Also indicated in red font in brackets are the activation barriers (kJ mol^{-1}) for the dissociation of methane in the 3-center H abstraction process involving these lattice oxygen sites.

The plot also reports the activation barriers for the dissociation of methane in the 3-center H abstraction mechanism on these lattice oxygen sites. The values in the plot suggest that the binding strength of the surface lattice oxygen atom on the metal oxide surface indirectly determines the activation barriers in the H abstraction mechanism. The difference in binding energy of the O1 lattice oxygen to the surface on Ni vacancy containing NiO(100) and Li dopant containing NiO(100) surfaces is as large as $\sim 160 \text{ kJ mol}^{-1}$. However, the difference in H chemisorption energies on these same sites on these surfaces is $\sim 30 \text{ kJ mol}^{-1}$ (Table 5.1). A similar trend exists for the NiO(110) surface as well. The plot of the activation barriers by the H abstraction mechanism and the lattice

oxygen binding strength on the surface for the corresponding sites is shown in Fig. 7.6 (appendix to chapter 5). The deviations from the best fit line can be seen to be large. Thus, in estimating the reactivity of doped and vacancy containing surfaces, the H chemisorption energy on these surfaces is a better descriptor as compared to the lattice oxygen binding strength on the surface. Janik and co-workers have also commented on the possible deviations from linearity in the correlation of C-H activation barriers and surface reducibility of metal oxides.²⁰⁷

The average Bader charge on the four lattice oxygen atoms around a Ni vacancy on NiO(100) surface is calculated to be $-1.04 e$. This is lower than the average Bader charge of $-1.17 e$ on the remaining surface lattice oxygen atoms. The Ni vacancy leaves two holes localized on the oxygen atoms around the vacancy giving them negative charge with smaller absolute magnitudes. The presence of a low valent dopant like Li leaves a hole localized on the oxygen atoms in its vicinity. The average charge on the four surface lattice oxygen atoms around the Li atom on the Li doped NiO(100) surface is $-1.17 e$ and is similar to that on the remaining surface lattice oxygen atoms. Larger negative values of charge on the oxygen imply stronger bonding with the remaining atoms. Thus, surface lattice oxygen around a Li dopant are active but more strongly bound to the surface compared to those around a Ni vacancy. On the contrary, Li doping makes the strongly bound ($\sim -175 \text{ kJ mol}^{-1}$) surface lattice oxygen atoms on stoichiometric NiO(100) surface much weaker in their interaction with the surface ($-21.5 \text{ kJ mol}^{-1}$ and $-28.7 \text{ kJ mol}^{-1}$), making the surface more reducible.

5.5 Summary

Methane dissociation on the most stable surface of NiO, NiO(100), proceeds in a 2-site 4-center mechanism involving the 5-coordinated Ni-O pair as active sites. This process on a stoichiometric NiO(100) surface has high activation barrier and the dissociation is highly endothermic. On NiO(110), a higher energy surface of NiO, the activation barrier for dissociation with the same mechanism is less than half of the barrier on the stoichiometric NiO(100) surface. The difference in activation barriers is attributed to the difference in surface coordination of the Ni-O pair which are 5-coordinated on NiO(100) surface and 4-coordinated on NiO(110) surface. The coordinate unsaturation on

NiO(110) enables stronger chemisorption of the dissociated hydrogen on the 4-coordinated lattice oxygen which in turn lowers the barrier for dissociation.

The presence of a Ni vacancy on the surface dramatically decreases the activation barrier for dissociation of methane and improves the energetics of the process. The lattice oxygen atoms next to the Ni vacancy on NiO surfaces are extremely active and can abstract hydrogen from methane in a single active site 3-center mechanism. The dissociation of methane in the 4-center mechanism involving the Ni-O pair adjacent to the Ni vacancy have barriers similar to those of the 3-center mechanism or are marginally higher. The strength of hydrogen chemisorption determines the activation barriers in the H abstraction mechanism and there exists a linear correlation of two quantities. The strength of hydrogen chemisorption is determined by the lattice oxygen binding strength on the surfaces. Thus, there is an indirect linear correlation between the activation barrier for dissociation by H abstraction and the lattice oxygen binding strength on the surface. Ni vacancy containing surfaces are electron deficient and thus serve as Lewis acids which can very strongly bind Lewis bases like H to benefit from the acid – base interaction. This explains the strong H chemisorption on such surfaces. The binding of CH₃ with the Ni atoms on the NiO surfaces is weak and the key factors influencing the co-adsorption energy of CH₃ and H on the surface are the H chemisorption strength and the acid-base pair (CH₃-(Ni)--H-(O)) interaction. Thus, for the 4-centered Ni-O mediated mechanism of C-H activation, in addition to the reaction energy, H chemisorption energy serves as a descriptor for reactivity. The single lattice oxygen vacancy containing NiO(100) surface on the other hand is electron rich and thus does not benefit from acid-base pair interactions in accepting H on the surface. Thus, the reaction energy in the co-adsorption of CH₃ and H as well as the H chemisorption energy have positive values. This makes the activation barrier for dissociation on the Ni-O pair adjacent to the oxygen vacancy comparatively high.

Li doping on NiO surfaces have kinetic consequences similar to that of creating Ni vacancies. The activation barriers for dissociation by the 4-center mechanism involving the Ni-O pair and the 3-center H abstraction mechanism on the lattice oxygen adjacent to Li are comparable to those on the corresponding sites on a Ni vacancy containing surface. However, the H chemisorption strength on these Li doped surfaces are lower.

The surface lattice oxygen adjacent to Ni vacancy sites are extremely loosely bound compared to those adjacent to the Li. Thus, Li doping increases the activity of the surface lattice oxygen atoms, making the surface more reducible compared to stoichiometric defect free surfaces. The insights from the trends discussed here would serve as guidelines to screen metal oxides and doped metal oxide surfaces for their reactivity towards methane.

6 Conclusions and perspectives

This thesis establishes two novel bimolecular coupling induced dissociation mechanisms for the direct transformation of methane to C₂ hydrocarbons like ethane and ethylene. The mechanical impact induces vibrational excitation of the molecules and the C-C coupling facilitates the dissociation of the C-H bonds. The conventional chemistry of the transformation of methane to C₂ hydrocarbons revolves around the unimolecular dissociation of methane to form CH₃ radicals and the subsequent coupling of these radicals to form C₂ hydrocarbons. Mechanical impact induces vibrational excitation of the molecules, while vibrational pre-excitation of the molecules facilitates easy approach to inter-nuclear separation lower than 2 Å. The insights from this investigation have direct relevance to understanding the planetary phenomenon of the transformation of methane to larger hydrocarbons due to extremes of temperature and pressure that prevail. The frequent mechanical impact of vibrationally excited molecules at the prevalent high temperatures and pressures will initiate coupling induced dissociation pathways as described in chapter 2, transforming methane to larger hydrocarbons. This may also explain the abiogenic origin of petroleum on the earth.

To validate the mechanism presented here, for better estimates of the activation barrier for the concerted dissociation and coupling, product distribution upon dissociation and so on, crossed molecular beam experiments^{208,209} and molecular dynamics simulations have to be performed. As processes to commercially exploit collisional impact and coupling induced dissociation, methane cluster beam collision techniques can be designed, where, multiple internal collisions within the core of the clusters undergoing impact, lead to the formation of larger hydrocarbons.

Methane dissociation on nanoclusters of an inactive transition metal, Cu, is facile due to collisional impact and special electronic and morphological features of these clusters. Small 3-dimensional Cu nanoclusters, with delocalized electron density, exhibit potential for the controlled dehydrogenation of methane. The first dissociation step has low barriers and the barriers increase steeply in the subsequent elementary steps due to the energy penalty for reorganisation of the clusters. Impact induced vibrational excitation of methane leads to the formation of a molecular collision complex, a

precursor for dissociation, whose proximity to the products of dissociation along the reaction coordinate serves to significantly lower the free energy barrier for dissociation. Temperature influences activation free energy barriers for the dissociation of methane upon collision, suggesting that the entropic contributions play a significant role in determining the activation free energy barriers for dissociation. These results suggest that methane activation on other inactive catalytic materials should be revisited in the context of collisional impact and special morphologies. In the absence of directed collisional impact, where dissociation is merely catalytic on the clusters, the free energy barrier for the dissociation of methane is much higher. The formation of the precursor, the origin of the barrier for impact induced dissociation, and the influence of cluster reorganization on free energy barrier for complete dehydrogenation on the clusters may not be reflected in conventional density functional theory (DFT) based simulations. This investigation also lends support to the proposition of ‘copper vapour assisted’ dissociation of methane^{117,118} which allows direct synthesis of graphene on inert substrates in the chemical vapour deposition process.

The most stable and dominant oxide surfaces CuO(111) and CuO($\bar{1}\bar{1}\bar{1}$) of an inactive transition metal, Cu, are active for methane dissociation while the most stable oxide surface NiO(100) of an active metal, Ni, is inactive. The surface lattice oxygen alone on the different CuO surfaces is more active in dissociating methane compared to clean metallic copper. However, a mechanism involving the synergistic role of the Cu-O pair exhibits the lowest activation barrier for C-H dissociation, as the pair stabilizes both the transition state and the products of dissociation. NiO materials synthesised specially to expose the high energy surfaces like NiO(110) surface would be active for methane dissociation. The weak molecular interaction of methane with the third-row transition metal oxides compared to the formation of strong sigma complexes on the 4th and 5th row oxides^{67,155} implies that the surface lattice oxygen primarily determines their activity. A simple measure of the reactivity of the surface lattice oxygen atoms on these metal oxides is the H chemisorption energy, which in turn has direct correlation with the intrinsic metal-oxygen interaction. H chemisorption energy is a simple measurable/computable quantity and can be used to screen potential oxide surfaces for C-H bond activation or as oxidation catalysts. A similar evaluation process can be extended for the surfaces of other third row transition metal oxides as well. CuO

materials exposing CuO(010) and CuO(110) surfaces would be excellent oxidation catalysts. Li doping would be a practically relevant method to make NiO a better candidate for C-H dissociation and oxidation reactions compared to inducing Ni vacancies on the surface. Both Ni vacancies and Li dopant increases the reactivity of the surface by weakening the metal-oxygen interaction, making the lattice oxygen more active. The reactivity trend for the oxide surfaces investigated in chapters 4 and 5 would be relevant to X-H activation in general, where X can be C, S, O and N. Since the extent of promotional effect of Li in increasing the activity of surface lattice oxygen is different for NiO(100) and NiO(110) surfaces, quantitative relationships for such effects need to be derived to facilitate catalyst synthesis in specific morphologies.

In summary, this thesis presents a comprehensive understanding of the role and contribution of mechanical impact, and lattice oxygen, metal vacancy defects and low valent dopants in metal oxides towards C-H bond activation of methane. The various mechanisms of C-H bond activation, the activation barriers for the dissociation along these pathways, factors influencing the activation barriers and measures of reactivity of the catalytic surfaces have been detailed.

7 Appendices

7.1 Appendix to Chapter 3

7.1.1 Computational methods

7.1.1.1 Collision of methane on the clusters

The collision of methane on copper clusters was simulated using the technique of metadynamics.⁸⁰ The collective variable (CV) CV1 was chosen to be the distance between the carbon atom and one of the copper atoms of the copper clusters and CV2 to be the coordination number of carbon atom with all hydrogen atoms, calculated by a rational function.²¹⁰ The rational function has the form

$$CN_i = \sum_{j \neq 1}^{nlist} \frac{1 - (\frac{d_{ij}}{d_0})^p}{1 - (\frac{d_{ij}}{d_0})^{p+q}} \quad (\text{Eqn. 7.1})$$

where $nlist$ is the number of atoms in species j , d_{ij} is the actual distance between atoms of indices i and j , d_0 is the reference distance which was fixed at 1.6Å, the exponents p and q were set at 6 and 12 to ensure quick response of the function to changes in the coordination number. The C-H coordination number calculated using the above function for a methane molecule away from the clusters would be $(4 \times 0.91) \sim 3.6$. Constraints²¹⁰ were imposed in molecular dynamics on the distance between the carbon atom and the selected copper atom of the cluster to ensure that the methane molecule moves close to the cluster by restricting the exploration of phase space within 5 Å of each other.

Metadynamics was propagated with 20-50 intermediate molecular dynamics steps between each Metadynamics deposition step. The temperature for the fictitious dynamics of the collective variables was fixed at the same value as those chosen for the simulations with a window of 70-80% of the actual value. The fictitious dynamics of the collective variables were monitored to closely follow that of the actual dynamics by adjusting the mass and spring constants coupling the fictitious dynamics to actual dynamics.²¹¹ This was a standard practise in all Metadynamics simulations.

7.1.1.2 Dissociation of chemisorbed CH₃ on the clusters

Systems of CH₃ + H chemisorbed on the copper clusters of different sizes were optimized and equilibrated at 1273 K for a sufficient period in constant temperature molecular dynamics simulations using the Nosé-Hoover chain thermostat^{130,131}. The investigation of further dehydrogenation of chemisorbed methane was done using Metadynamics simulations employing two collective variables. The first collective variable was the average coordination number of the copper atoms of the clusters with the the hydrogen atoms and the second was the coordination number of the carbon atom with all the hydrogen atoms. The average coordination number of the hydrogen atoms with the copper atoms of the cluster is used, as each dissociated hydrogen atom can form multiple bonds with the copper atoms of the cluster depending on its ‘bridge site’ or ‘three-fold site’ position. Moreover, the dissociated hydrogen on the cluster is very mobile, exploring various sites on the cluster, changing the copper atoms to which it is coordinated. The average coordination of the hydrogen atoms number with the copper atoms of the cluster therefore gives a reasonable estimate of the hydrogen copper interaction and diffusion. A significant change in the value is noticeable with every C-H dissociation step which leaves another hydrogen on the cluster. The same rational function as described above was used in these simulations with the cut off distance of 2.2 Å for the Cu-H coordination number and 1.6 Å for the C-H coordination number. The Cu-H coordination collective variable accounts for the abstraction of hydrogen from the chemisorbed CH_x (x= 1-3) species by the cluster and the subsequent surface hopping of hydrogen on the cluster. The C-H coordination number collective variable accounts for dissociation of any of the C-H bonds. The other CPMD-Metadynamics parameters are the same as discussed above.

7.1.1.3 Dissociation of methane on Cu₈ cluster with pre-adsorbed CH₃ + H

A system consisting of chemisorbed CH₃ + H on Cu₈ cluster along with methane in the gas phase, at a distance of around 4 Å from the cluster, was optimized and the system was equilibrated at 1273 K for a sufficient period in constant temperature molecular dynamics simulations. The dissociation of methane on the such a Cu₈ cluster was then simulated using Metadynamics with two collective variables. CV1 was chosen to be the distance between the carbon atom of methane and one of the copper atoms of the copper

cluster (Cu atom not coordinated to CH₃ or H) and CV2 was chosen to be the coordination number of carbon atom of methane with all its hydrogen atoms (not including the chemisorbed hydrogen and hydrogen atoms of CH₃) calculated by the same rational function as above. Constraints were imposed in molecular dynamics on the distance between the carbon atom and the selected copper atom of the cluster to ensure that the methane molecule moves closer to the cluster by restricting the exploration of phase space within 5 Å of each other.

7.1.1.4 Coupling of CH_x on the clusters

Systems of two CH₃, two CH₂ and two CH, each chemisorbed on Cu₈ clusters were optimized and equilibrated at 1273 K for a sufficient period in constant temperature molecular dynamics simulations. The coupling of the respective CH_x (x= 1 to 3) species was simulated using Metadynamics simulations with two collective variables. The first collective variable was the distance between carbon atoms of the two CH_x species and the second collective variable was the average coordination number of carbon atoms of both CH_x with all the hydrogen atoms in the system using the rational function described in the beginning. The inclusion of the C-H coordination number collective variable allowed for the dissociation of methane along the coupling or prior to it. In the case of two CH₃ groups chemisorbed on the cluster at a distance away from each other, it can be calculated as $(3 \times 0.9 + 3 \times 0.9)/2 = \sim 2.7$. Similar calculations can be done for the systems with CH₂ and CH. Constraints were imposed on the distance between the carbon atoms during molecular dynamics to ensure that the CH_x groups move towards each other by restricting the exploration of phase space.

7.1.2 Results and discussion

7.1.2.1 CH₃ + CH₃

Two reactive pathways were observed for the two CH₃ species on the cluster. In the first pathway, one of the CH₃ groups underwent further dissociation before C-C coupling and formed a CH₂-CH₃ species attached to the cluster through the CH₂ moiety. The sequence is depicted in in Fig. 7.1a-c. The dehydrogenation of CH₃ and subsequent coupling was observed to have a free energy barrier of 165 kJ mol⁻¹. The other pathway involved the

formation and evolution of ethane to the gas phase as depicted in Fig. 7.1d-f. The free energy barrier for the coupling of methyl groups without further dehydrogenation was found to be around 70 kJ mol⁻¹. The barrier for diffusion of the methyl groups towards each other on the cluster was calculated to be between 60 and 80 kJ mol⁻¹.

The ELF isosurfaces of structures from the simulations investigating the coupling of two methyl groups on Cu₈ clusters, corresponding to the two pathways discussed above, are shown in Fig. 7.1. Fig. 7.1a, b, and c are from the trajectory which showed the formation of a C₂H₅ group attached to the cluster and Fig. 7.1d, e, and f are from the trajectory which showed the evolution of ethane. Fig. 7.1b shows the onset of the dissociation of the C-H bond of one of the methyl groups and the formation of the C-C bond, which is evident from the disynaptic attractor along the C-C axis. The C-C coupling is completed in the structure shown in Fig. 7.1c and is indicated by the characteristic attractor in the C-C axis. The resulting structure can also be seen to be strongly bound to the Cu cluster. Corresponding structures from the other pathway are shown in Fig. 7.1e and Fig. 7.1f. The structure in Fig. 7.1e can be seen to have the characteristic attractors along the C-C axis indicating the formation of C-C bond. However, the two methyl groups in Fig. 7.1e and the ethane formed in Fig. 7.1f do not show any signs of attachment to the Cu cluster, suggesting that the coupling is not completely mediated by the surface. The multicentre C-Cu bonding and the favourable alignment of the C-H bond towards the electron cloud in the cluster enabled the dissociation of the C-H bond in the former trajectory which did not happen along the dynamics in the latter.

Fig. 7.1 ELF isosurfaces corresponding to coupling of two CH_3 groups and the formation of C_2 hydrocarbons/ hydrocarbon intermediates on Cu_8 cluster from CPMD-Metadynamics simulations at 1273 K. a, b and c are snapshots from a simulation showing the formation of C_2H_5 bound to the cluster, and d, e and f are snapshots from a simulation showing the evolution of ethane to the gas phase. The dissociating C-H bond is indicated with a dotted red line and the significant attractors indicating C-Cu and C-C bonds are highlighted in each structure. The colour scheme for atoms is similar to that in Fig. 3.5.

7.1.2.2 $\text{CH}_2 + \text{CH}_2$ and $\text{CH} + \text{CH}$

The reaction of two CH_2 species resulted in the formation and evolution of ethylene to the gas phase with a free energy barrier of $\sim 70 \text{ kJ mol}^{-1}$, while the reaction of two CH groups resulted in the formation of C_2H_2 attached to the surface with a free energy barrier of less than 50 kJ mol^{-1} . The structures and bonding in these cases are depicted in Fig. 7.2 and analysed in the context of ELF isosurfaces in the paragraphs that follow. The formation of C_2H_2 on copper surfaces was investigated by Zhang *et al.*⁵⁴ using first principles molecular dynamics at 1300 K and was found to be an exothermic reaction with an activation energy barrier of $\sim 30 \text{ kJ mol}^{-1}$. However, they observed the C_2H_2 to desorb from the $\text{Cu}(100)$ surface within 4 ps of simulation time, contrary to the

observation on the Cu_8 cluster described here. Shibuta *et al.*²¹² reported the evolution of ethane and ethylene and formation of C_2H_2 attached to the copper surface resulting from reactions of CH_3 , CH_2 and CH groups on the surface based on their MD simulations. This is in agreement with our results on the Cu_8 cluster.

Fig. 7.2 ELF isosurfaces corresponding to coupling of CH_2 and CH groups and the formation of C_2 hydrocarbons on Cu_8 cluster from CPMD-Metadynamics simulations at 1273 K investigating. a, b, and c are snapshots from a simulation showing the formation and evolution of C_2H_4 into the gas phase, while d, e, and f are snapshots from a simulation showing the formation of C_2H_2 bound to the cluster. The significant attractors indicating C-Cu and C-C bonding are highlighted in each structure.

Fig. 7.2a, b, and c are ELF isosurfaces of structures from a simulation which showed the evolution of ethylene because of the coupling of two CH_2 groups on the Cu_8 cluster. The multicentre bonding of the CH_2 groups to the cluster is evident in Fig. 7.2a. Unlike in the case of CH_3 groups, formation of C-C bond between the two CH_2 groups seems to be partially mediated by the Cu cluster, as can be seen from the C-Cu bond attractor in Fig. 7.2b. Once the C-C coupling is completed, ethylene can be seen to evolve into the gas phase. The dumbbell shaped attractor at the centre of the C-C axis, as seen in Fig. 7.2c, is characteristic of a C-C double bond and confirms the formation and evolution of ethylene. Fig. 7.2d, e, and f are isosurfaces of structures from a trajectory showing the coupling of two CH groups on the cluster. The CH groups are typically observed to be in 3-fold sites, as confirmed by the 3 centre bonding in Fig. 7.2d. The

onset of coupling is depicted in Fig. 7.2e and it is to be noticed that the two carbon centres are strongly bound to the Cu cluster. The coupling in this case is seen to result in C_2H_2 which is bound to the cluster through both the carbon atoms, as can be seen from Fig. 7.2f, while the C-C bond in it retains a partial double bond character, as can be seen by the dumbbell like attractor along the C-C axis. C_2H_2 does not form ethyne and evolve to the gas phase.

From the ELF analysis of structures from four reaction pathways, as depicted in Fig. 7.1 and Fig. 7.2, the CH group is more strongly bound with the cluster through multicentre bonding throughout the trajectory, as compared to CH_2 and CH_3 . This explains the higher ($\sim 100 \text{ kJ mol}^{-1}$) free energy barrier for diffusion of the CH groups on the cluster than that for CH_2 and CH_3 groups ($\sim 60 \text{ kJ mol}^{-1}$) at 1273 K.

7.1.2.3 Comparison of different coupling pathways and implications for larger hydrocarbon/ graphene growth

The coupling pathway via the formation of C_2H_2 , is hypothesised to lead to the formation of larger hydrocarbons on the Cu surface.⁵⁴ Further addition of CH to C_2H_2 was also observed to be thermodynamically favourable with an activation energy barrier of $\sim 105 \text{ kJ mol}^{-1}$.⁵⁴ However, there is another report which suggests that C_2H_5 is the key intermediate species in the formation of larger hydrocarbons which subsequently dehydrogenate to form graphene on copper surface.²¹³ From calculations presented in chapter 3, the free energy barrier for the dissociation of methane and formation of chemisorbed CH_3 on the larger clusters is around 100 kJ mol^{-1} and can be easily overcome at temperatures over 1000 K. However, for a surface mediated/restricted growth of hydrocarbons, which could eventually serve as precursors for nano-carbon growth, direct coupling of two CH_3 groups may not be the likely pathway. The pathway via C_2H_5 involves barriers in excess of 160 kJ mol^{-1} and the pathway via C_2H_2 involves barrier between 160 and 190 kJ mol^{-1} . Formation of C_2H_2 also entails greater surface saturation of small clusters compared to C_2H_5 due to the presence of four surface hydrogens and C_2H_2 being bound to the cluster through both carbons. Thus, considering the free energy barriers involved in the formation process and the surface limitations of small clusters, it can be speculated that the C_2H_5 pathway would be dominant in the growth of larger hydrocarbon precursors on the clusters. Extending this to graphene

growth on copper surfaces, the C_2H_5 pathway would be dominant in the growth conditions with high hydrogen partial pressure. This is due to competitive saturation of surface sites by chemisorbed hydrogen from the carrier gas, which, along with the possibility of the competitive recombination, makes it more likely to leave a higher concentration of CH_3 on the surface, compared to CH_2 and CH . This is in agreement with reports which claim CH_3 to be a more dominant species compared to CH in graphene growth on Cu(100) surface at high partial pressure of hydrogen.²¹⁴

Direct coupling of CH_x ($x=1-3$) fragments on the clusters are facile processes with free energy barriers lower than 80 kJ mol^{-1} . The resulting C_2H_n species, except for the ones with $n=4$ and 6 , remain bound to the cluster. For formation of larger hydrocarbon precursors bound to the cluster, CH_3 groups with high mobility (free energy barrier for movement on the cluster is less than 70 kJ mol^{-1}) are likely to be the key species, under conditions of saturation of the cluster with chemisorbed hydrogen. However, under low cluster saturation, pathways involving the CH group are equally possible on these clusters at the temperatures considered.

7.2 Appendix to chapter 4

7.2.1 Results and discussion

7.2.1.1 Interaction of methane on Cu(111), chemisorbed oxygen containing Cu(111) and CuO surfaces

Table 7.1 Physisorption energy of methane on the clean Cu(111), chemisorbed oxygen containing Cu(111) and CuO surfaces calculated as per the equation $E_{adsorption} = E_{CH4-m} - (E_{CH4(g)} + E_{clean-m})$ where E_{CH4-m} is the energy of weakly physisorbed methane on the surface, $E_{CH4(g)}$ is the energy of a gas phase methane molecule and $E_{clean-m}$ is the energy of the clean surface.

Surface	Physisorption energy of methane (kJ mol ⁻¹)
Cu(111)	4.92
O on Cu(111)	2.27
CuO(111)	2.21
CuO($\bar{1}11$)	-1.02
CuO(110) _O	2.36

7.2.1.2 Dissociation of methane on CuO surface involving the synergistic roles of the under-coordinated Cu-O pair

Fig. 7.3 Representation of the IS, TS and FS corresponding to the dissociation of methane in 4-center pathway on CuO surfaces involving synergistic roles of a) the 3-coordinated Cu-O pair on CuO($\bar{1}11$) surface; b) the 3-coordinated Cu-O pair on CuO($01\bar{1}$) surface; and c) the 3-coordinated copper and 2-coordinated lattice oxygen on CuO(010) surface. The activation barrier for the dissociation of methane and reaction energy are also indicated in the figure. The peach color represents copper, red represents oxygen, grey represents carbon, and white represents hydrogen atoms.

7.2.1.3 Dissociation of methane on CuO surfaces by hydrogen abstraction by the under-coordinated lattice oxygen atom alone

Fig. 7.4 TS corresponding to the dissociation of methane in the H abstraction pathway on CuO surfaces involving a) the 3-coordinated lattice oxygen (O_3) on $CuO(\bar{1}11)$ surface; b) the 3-coordinated lattice oxygen (O_3) on $CuO(110)_O$ surface; c) the 3-coordinated lattice oxygen (O_3) on $CuO(01\bar{1})$ surface; and d) the 2-coordinated lattice oxygen (O_2) atoms on $CuO(010)$ surface. The activation barriers for the dissociation of methane are also indicated in each case.

7.2.1.4 Interaction energy of CH_3 and hydrogen at the transition state (TS), resulting from the dissociation of methane on Cu and CuO surfaces

The interaction energy of CH_3 and hydrogen fragments of methane at the TS, resulting from dissociation, is decomposed based on the scheme

$$E_{int} = E^{TS} - (E_{CH_3}^{TS} + E_H^{TS} - E_{surf}^{TS}) \quad (\text{Eqn. 7.2})$$

Where E_{int} is the interaction energy of the CH_3 and hydrogen species in the TS, E^{TS} is the total energy of the TS, $E_{CH_3}^{TS}$ is the energy of the CH_3 species on the surface at the TS without the hydrogen, E_H^{TS} is the energy of the hydrogen on the surface at the TS without the CH_3 species and E_{surf}^{TS} is the energy of the surface at the TS without both CH_3 and H. This scheme is based on the decomposition prescribed by Z-P Liu and P. Hu for ‘Late’ TS.²¹⁵ All the energy values were obtained from single point calculations without

optimization of geometry and are reported in Table 7.2. The positive values suggest repulsive interaction and negative values suggest attractive interaction.

Table 7.2 Interaction energy of the dissociating CH₃ and H fragments of methane at the TS on the clean and chemisorbed oxygen containing Cu(111), CuO(111) and CuO($\bar{1}\bar{1}\bar{1}$).

Surface	Interaction energy of CH ₃ with H (kJ mol ⁻¹)
Cu(111)	32.6
Chemisorbed O Cu	-123.8
CuO(111)	-101.1
CuO($\bar{1}\bar{1}\bar{1}$)	-78.9

7.2.1.5 Geometry of methane at the initial state (IS) and transition state (TS) on Cu and CuO surfaces

Table 7.3 The dimensions of the four C-H bonds and six H-C-H angles of methane as observed in the IS and the TS on Cu and CuO surfaces. CH n (n=1 to 4) refers to the C-H bonds of methane and HCH m (m=1-6) refers to the H-C-H angles of methane. The dissociating C-H bond length at the TS on each of the surfaces is highlighted in red and the H-C-H angles involving the dissociating C-H bond, suggesting deformation of methane, are highlighted in blue.

	IS									
Surface	CH 1 (Å)	CH 2 (Å)	CH 3 (Å)	CH 4 (Å)	HCH 1 (°)	HCH 2 (°)	HCH 3 (°)	HCH 4 (°)	HCH 5 (°)	HCH 6 (°)
Cu(111)	1.1	1.09	1.09	1.09	109.02	109.04	109.21	109.36	109.38	110.78
O on Cu(111)	1.09	1.09	1.09	1.10	110.49	108.81	109.18	109.13	110.28	108.89
CuO(111)	1.09	1.10	1.09	1.09	110.51	109.44	109.01	108.28	111.16	108.41
CuO($\bar{1}\bar{1}\bar{1}$)	1.10	1.09	1.09	1.09	107.51	110.15	107.50	109.87	110.81	110.86
CuO(011)	1.09	1.09	1.09	1.1	109.34	109.77	110.12	108.19	109.31	110.08
CuO(010)	1.09	1.09	1.10	1.10	108.51	109.12	111.42	108.53	108.67	110.59
	TS									
Cu(111)	1.80	1.09	1.09	1.09	105.30	82.01	134.53	111.31	108.69	110.70
O on Cu(111)	1.41	1.09	1.10	1.10	99.95	94.37	138.74	110.32	106.27	105.34
CuO(111)	1.37	1.09	1.09	1.09	92.78	96.56	138.37	107.46	108.46	111.45
CuO($\bar{1}\bar{1}\bar{1}$)	1.39	1.09	1.09	1.1	95.41	95.44	136.65	112.10	108.03	107.96
CuO(011)	1.42	1.09	1.09	1.1	94.419	98.922	136.17	106.92	107.39	111.93
CuO(010)	1.39	1.09	1.10	1.10	96.41	102.15	132.18	106.87	107.17	111.06

7.3 Appendix to chapter 5

7.3.1 Results

7.3.1.1 Interaction of methane with the NiO surfaces

Table 7.4 Physisorption energy of methane on different NiO surfaces calculated as per the scheme $\text{CH}_4(\text{g}) + * \rightarrow \text{CH}_4^*$ where $\text{CH}_4(\text{g})$ is a gas phase CH_4 molecule, * represent the NiO surface and CH_4^* represents physisorbed methane on the surface.

Surface	Physisorption energy (kJ mol^{-1})
NiO(100)	0.67
NiO(110)	-7.08
NiO(100)- Ni vacancy	2.39
NiO(100)- O vacancy	4.16
NiO(110)- Ni vacancy	6.05
Li doped NiO(100)	5.00
Li doped NiO(110)	-1.31

7.3.1.2 Dissociation of methane on Ni(100) and Ni(111) surfaces

Fig. 7.5 The IS, TS and FS for dissociation of methane involving a single Ni atom active site on a) Ni(100) surface; and b) Ni(111) surface. Dissociation on Ni(100) leaves the CH_3 on the Ni-Ni bridge site and H on the 4-fold hollow while dissociation on Ni(111) leaves the CH_3 and H on adjacent 3-fold hollow sites. The activation barrier for dissociation and reaction energy calculated as difference of energy of FS with respect to IS are also indicated. Blue balls represent Ni atoms, Grey represents C atom and White represents H atoms.

Dissociation of methane on Ni(100) and Ni(111) surfaces was investigated for comparison of the activation barriers with those on the NiO surfaces. The initial states (IS), transition state (TS) and Final state (FS) corresponding to dissociation of methane on Ni(100) surface is shown in Fig. 7.5a and the same on Ni(111) surface is shown in Fig. 7.5b. On the Ni(100) surface the final state with CH₃ on the Ni-Ni bridge site and H in the 4-fold hollow site was found to be the most stable. On Ni(111) surface the final state with both CH₃ and H on the adjacent 3-fold hollow sites was found to be the most stable.

7.3.1.3 Binding strength of surface lattice oxygen on different NiO surfaces

Table 7.5 Binding energy of surface lattice oxygen on different NiO surfaces, estimated as the energy in inserting an oxygen atom into a surface lattice oxygen vacancy on these surfaces as per the reaction scheme $\text{H}_2\text{O}_{(\text{gas})} + \text{Ni}_n\text{O}_{n-1} \rightarrow \text{H}_2_{(\text{gas})} + \text{Ni}_n\text{O}_n$, where $\text{Ni}_n\text{O}_{n-1}$ represents a NiO surface with a surface lattice oxygen vacancy and Ni_nO_n represents a stoichiometric NiO surface. Negative values indicate strong binding of lattice oxygen on the surface and positive values indicate weak binding.

Lattice oxygen on surface	O binding energy (kJ mol ⁻¹)
NiO(100)	-175.9
NiO(110)	-72.2
O ₁ on NiO(100)- (Fig. 5.4)	141.3
O ₂ on NiO(100)- (Fig. 5.4c)	70.3
O ₁ on Li doped NiO(100)- (Fig. 5.6c)	-21.5
O ₂ on Li doped NiO(100)- (Fig. 5.6d)	-28.8
O ₁ on NiO(110)- (Fig. 5.8a)	150.9
O ₂ on NiO(110)- (Fig. 5.8b)	0.2
O ₁ on Li doped NiO(110)- (Fig. 5.8c)	11.3
O ₂ on Li doped NiO(110)- (Fig. 5.8d)	-12.1

7.3.1.4 Activation barrier for H abstraction on NiO surfaces and lattice oxygen binding strength on the surface

Fig. 7.6 Plot of the activation barrier for dissociation of methane in the 3-center H abstraction mechanism by lattice oxygen sites on NiO surfaces and the binding energy of the corresponding surface lattice oxygen atoms on the surface.

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