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**NANYANG
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UNIVERSITY**

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**INVESTIGATING METAL OXIDES FOR
C₁ CHEMISTRY: A COMPUTATIONAL
AND EXPERIMENTAL STUDY**

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**SCHOOL OF CHEMICAL AND BIOMEDICAL
ENGINEERING (SCBE)**

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C1 CHEMISTRY: A COMPUTATIONAL
AND EXPERIMENTAL STUDY**

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SCHOOL OF CHEMICAL AND BIOMEDICAL
ENGINEERING (SCBE)

A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of

Doctor of Philosophy

2018

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

20/4/2019

Date

Kartavya Bhola

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Authorship Attribution Statement

This thesis contains material from 2 papers published in the following peer-reviewed journals in which I am listed as an author.

Chapter 2 is published as Kartavya Bhola, Jithin John Varghese, Liu Dapeng, Yan Liu and Samir H. Mushrif, 'Influence of Hubbard U Parameter in Simulating Adsorption and Reactivity on CuO: Combined Theoretical and Experimental Study,' *J. Phys. Chem. C* 121, 39, 21343-21353, American Chemical Society."

The contributions of the co-authors are as follows:

- Dr. Samir Mushrif provided the project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The overall manuscript was revised by Dr. Samir Mushrif, and the experimental part was reviewed by Dr. Liu Yan.
- All the computational work in this study has been performed by me with the assistance of Dr. Jithin John Varghese on the initial computational system establishment.
- All the experimental work in this study has been performed by me with the assistance and guidance of Dr. Liu Yan and Dr. Liu Dapeng on the catalyst synthesis, experimental setup (FTIR), sample characterization (XRD, SEM, TEM).

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- Dr. Samir Mushrif provided the project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. It was refined by Dr. Quang Thang Trinh. The overall manuscript was revised by Dr. Samir Mushrif, and experimental part was reviewed by Dr. François Jérôme.
- All the computational work in this study has been performed by me with equal contribution from Dr. Quang Thang Trinh on the initial computational system establishment, geometric optimizations and XPS calculations.
- All the experimental work (Catalyst synthesis and characterization techniques) in this study has been performed by Dr. Prince Nana Amaniampong and Dr. François Jérôme.

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Abstract

With huge global natural gas reserves, coupled with depletion of fossil fuels, researchers are exploring potential technologies to convert methane into high value-added chemicals. Transition metal oxides (TMOs) are an important class of catalytic materials widely used in the direct and indirect catalytic methane conversion methods. Fundamental understanding of the reaction chemistry is crucial to the realization of commercial catalytic methane conversion processes. Computational tools like Density Functional Theory (DFT), and experimental surface characterization techniques like Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) and X-ray Photoelectron Spectroscopy (XPS), are often used independently by computational and experimental researchers, to provide insights into metal oxide catalyzed reaction mechanisms, pathways, and energetics.

Identifying realistic reaction intermediates and their corresponding IR and XPS spectral peaks presents a challenge for researchers to study complex catalytic reactions on TMO surfaces. DFT calculations are widely employed to assist in experimental analysis and provide mechanistic insights into reaction intermediates, and pathways for TMO catalyzed reactions. Localised nature of electrons leads to the strongly correlated nature of TMOs, and the standard approximations in the DFT exchange-correlation functional fail to describe these electron localizations accurately. DFT+U method is a widely used extension of DFT, where the Hubbard U term is an onsite potential that penalizes electron

delocalization, successfully describing such systems. This U-value is usually chosen based on its accuracy in reproducing bulk properties, however, using the bulk properties-based U-values in a locally changing surface reaction environment may not describe the surface reaction energetics correctly.

CuO is a widely-used TMO with applications in heterogeneous and environmental catalysis. In this thesis, two novel DFT+U approaches are developed with CuO as a model TMO and present methods for U-value determination that accurately capture the surface chemistry on TMOs. Both these approaches provide consistent U-values of 4-5 eV that accurately predicts the surface catalytic properties, as opposed to the widely used bulk property, optimized U-value of 7 eV that fails to correctly predict both surface reaction energetics and XPS shifts for CuO catalytic systems. In the first method, DFT+U calculations are performed to investigate the dissociative chemisorption of H₂ on CuO, and the appropriate U-value is determined from the comparison of DFT+U calculated adsorption enthalpies for different U-values with the experimental adsorption enthalpy. In the second method, comparison of experimental XPS shifts with DFT+U derived XPS shifts (for a range of surface moieties on the catalyst) for different U-values leads to the determination of the U-value. The second method not only benchmarks the U-value but also establishes unknown surface adsorbates, their configurations and predict their experimental XPS shifts synergistically, thus addressing the bottlenecks associated with the application of

integrated computational and experimental methods for studying TMO catalyzed reactions.

After establishing a robust DFT+U method that accurately captures surface chemistry on TMOs, the sequential activation of C-H bonds of methane on CuO is investigated using DFT+U and experimental FTIR study. The primary process and operational challenges for methane catalytic conversion over TMO surfaces are associated with the activation of the highly stable and weakly polarized C-H bonds of methane, which leads to the employment of high operating temperatures, consequently favoring undesired reactions, leading to a loss in activity, selectivity, and yield of desired products. In literature, the presence of moisture and surface hydroxyls on transition metal systems is known to reduce the barriers of various catalytic methane conversion reactions, but their role in TMO catalyzed reactions has not been investigated. The current thesis reveals that the presence of surface hydroxide species on CuO reduces the activation barriers associated with methane activation and dissociation. Experimental FTIR study was performed to investigate the reaction under dry and moisturized reaction conditions and revealed the presence of similar intermediates (methoxy, formic, CO₂, and surface hydroxyl species) under both conditions. Presence of surface hydroxide species even under dry conditions is predicted by DFT and confirmed by FTIR experiments, thus indicating that the C-H bond of methane may not be activated by CuO lattice oxygen directly but

gets oxidized with the formation of moisture and surface hydroxide species, henceforth reducing the C-H activation barriers.

In summary, this thesis reveals: (i) A novel surface reactivity based semi-empirical DFT+U approach that accurately describes surface catalytic reactions over TMOs and establishes the failure of widely applied bulk property optimized U-value to study these surface catalytic reactions, (ii) The Synergistic application of DFT and experimental XPS shifts to determine the reaction intermediates and surface species for TMO catalyzed reactions without any explicit knowledge of the U-value for respective TMO. This is the first study that integrates DFT and XPS methods to study TMO catalyzed reactions and addresses the bottleneck constraining the application of combined experimental and computational approaches to such systems. (iii) The promoting role of moisture and surface hydroxides in the activation and dissociation of methane from computational and experimental studies. This study provides evidence that even under dry conditions, lattice oxygen may not directly activate the C-H bonds of methane but indirectly via the formation of surface hydroxides formed on the surface. It also establishes that moisturized surface approach can lead to an increased lifetime of the catalysts due to water being the oxygen donor for the initial part of the methane activation.

1 Introduction

1.1 Methane: Occurrence, Chemistry, and Potential

Methane is the primary component of commercially exploitable resources like 1) natural gas (proved world reserves of ~186 trillion cubic metres¹), 2) shale gas (technically recoverable reserves estimated to be ~206 trillion cubic metres²), and 3) gas hydrates. Although methane is the simplest and the smallest of hydrocarbons, It is also the most abundant hydrocarbon on earth, with natural sources as well as ones that result from human activities. Its vast reserves found in crystalline hydrates exceed the amount of petroleum and conventional sources. As per U.S. Energy Information Administration³, Natural gas is the world's fastest-growing fossil fuel, increasing at 1.4% per year. In contrast, liquid's consumption rises at 0.7% per year and coal sees almost no escalation (0.1% per

Figure 1.1 World energy consumption in quadrillion Btu by energy source³ (reproduced with permission)

Despite these vast deposits, most of it is in remote areas like marine and offshore⁴, and consequently, it must be transported across vast distances to reach its markets. Thus, necessitating the transformation to liquids to capitalize on more facile transportation systems to distant end users. The immense potential of methane as a cheap feedstock to be converted to a variety of value-added chemicals remains hugely underutilized due to its direct consumption as a cleaner alternative fuel for industrial (including power generation), domestic and transportation applications.⁵ Both Methane, as well as gaseous emission products (CO₂ and CO) when it's used as a fuel, are greenhouse gases. Utilization of methane as a chemical feedstock is imperative, not only to replace and conserve the depleting conventional fossil fuels,⁶ but also to avoid the deleterious environmental effects on its release to the atmosphere due to its extremely potent greenhouse characteristics⁷. Therefore, methane conversion to more useful and easily transportable chemicals (liquid) is a priority in the current scientific community.

A methane molecule consists of a central carbon atom attached to four hydrogen atoms, forming a regular tetrahedron with a substantial bond dissociation energy of $\sim 440 \text{ kJ mol}^{-1}$, leading to high activation barriers associated with breaking of each C-H bond. The C-H bonds are very stable with a high enthalpy of dissociation with no net dipole moment due to molecular symmetry. It is resistant to most electrophilic and nucleophilic attacks, along with

being extremely weak acid with a very low proton affinity makes acid/base based catalytic activation difficult.⁸ Commercially viable and successful methane upgradation processes typically involve the capital-intensive indirect pathways like steam/ CO_2 reforming and partial oxidation to produce ‘synthesis gas’ or ‘syngas’ which is a mixture of CO and H_2 .⁵ Industrial hydrogen, ammonia, methanol, and its derivatives are typically obtained via the syngas route.⁹ Another commercial success involving syngas is the Fischer-Tropsch synthesis for the production of various liquid hydrocarbon equivalents of gasoline and diesel and higher alcohols.¹⁰ In spite of the success of these indirect routes for methane transformation, there is an intrinsic economic incentive to commercialize the direct pathways; direct oxidation to produce methanol/derivatives and oxidative/non-oxidative coupling to produce ethylene which is the most abundant commodity chemical by scale. Methanol/derivatives and ethylene/derivatives are currently produced both from conventional petroleum and coal-based feedstock as well as from gas-based feedstock. With such large demands and market potential for these bulk and commodity chemicals, there is an excellent opportunity to move towards the more sustainable methane driven market, replacing the conventional petroleum and coal-driven one. In addition to fuels and chemicals, methane is also a source gas to produce high-performance carbon nanomaterial graphene by chemical vapor deposition (CVD). The graphene-based electronics industry relying on monolayer/ bilayer graphene obtained from CVD of methane, evaluated at USD 58 million in 2013, is projected to grow to ~\$1.5 billion by 2020. Thus, methane utilization is an extremely lucrative

proposition considering the abundant availability of the resource and the massive demand for its derivatives. Hence, methane is an abundant hydrocarbon feedstock that has an immense potential that can be converted into value-added bulk chemicals and fuels, which are currently synthesized from conventional coal and oil/petroleum derivatives. This potential remains hugely underutilized and demands cheap, efficient and selective catalytic materials and technologies for selective and controlled activation of the strong C-H bonds of methane.

1.2 Catalytic CH₄ Conversion Methods: An Overview

Methane can be converted to a variety of chemicals by sequential dehydrogenation. As of today, commercial success for the use of methane to produce value-added chemicals has been achieved only with specific but indirect energy, and capital intensive pathways like steam/CO₂ reforming to generate synthesis gas, which is then converted to various value-added chemicals. Although more desirable reaction pathways and processes involving the direct conversion of methane to value-added chemicals through partial oxidation, and coupling have been established with proof of principle and have enormous potential, they have limited commercial success due to design, operational and economic challenges.

1.2.1 Indirect Methods for Methane Conversion

Although there are different approaches for employing methane as a raw material, the current process to utilize methane involves indirect pathways that convert it into another feedstock, i.e. synthesis gas which is a mix of CO and H₂, which is then converted to a variety of bulk chemicals like methanol¹¹, formaldehyde¹², olefins and other liquid fuels by Fischer-Tropsch synthesis method.¹³⁻¹⁵ Secondary products like olefins, gasoline aromatics, etc. can also be synthesized using primary products like methanol using technologies like methanol-to-olefins¹⁶, methanol-to-aromatics¹⁷, etc. The use of syngas for a particular synthesis application (Fischer-Tropsch synthesis, reforming, etc.) is dependent on the hydrogen/carbon monoxide (H₂/CO) ratio in the feed. In applications where syngas hydrogen/carbon monoxide (H₂/CO) ratio must be increased/adjusted to meet downstream process requirements, the syngas is passed through a multi-stage reactor containing shift catalysts to convert CO and water into additional H₂ and carbon dioxide (CO₂) according to the following reaction, which is also popularly known as the water-gas shift (WGS) reaction:

The shift reaction operates with a variety of catalysts between 200°C and 500°C at conditions different than the underlying chemical synthesis method (Fischer-Tropsch synthesis, reforming, etc). The equilibrium for H₂ production is favored by high moisture content and low temperature for the exothermic reaction. Normally, excess moisture is present in the scrubber syngas from slurry-fed

gasifiers sufficient to drive the shift reaction to achieve the required H₂-to-CO ratio. Fig. 1.2 shows the conventional and indirect methods for methane conversion. Although commercial, these processes require extremely high temperatures, and they are energy intense and expensive. Synthesis gas generation is mainly achieved by three ways, (i) Dry reforming (using CO₂), (ii) Steam reforming, and (iii) Partial oxidation of methane¹⁸. Methane steam reforming¹⁹ to generate synthesis gas mixtures is one of the most technologically advanced methods for indirect conversion of methane to fuels and chemicals, and is carried out at high temperatures of 700 – 1000 °C and pressures of 15-40 atm.²⁰ The partial oxidation of methane provides an optimal CO:H₂ ratio of 1:2 in the output stream (to be used for its conversion to various chemicals) and is mildly exothermic (making this route less energy and capital intensive) as well as has fast reaction rate and better product selectivity, thus giving excellent syngas yield.^{18, 21-23} However, the capital (high cost of pure O₂), operational and safety concerns (mixing of fuel and pure O₂) involving consumption of pure oxygen makes it inefficient. The similarities in the above reforming processes often lead to their combination into bi or tri processes to yield different CO: H₂ ratios in the output stream.²⁴

Figure 1.2 The conventional methane conversion route²⁵

1.2.1.1 Chemical Looping Concept for Synthesis Gas Generation

Since the biggest challenge in the partial oxidation of methane to synthesis gas using pure O_2 as an oxidizing agent is the safety and cost, the principles of chemical looping were introduced to this process. In this process, solid metal oxides are used as oxygen carriers for methane oxidation, and the spent catalysts (reduced metal oxides) are regenerated using gaseous oxygen, thus avoiding direct contact between the fuel and gaseous oxygen.²⁶

1.2.1.2 Chemical Looping Combustion & Chemical Looping Reforming

The introduction of chemical looping to methane conversion technologies paved the way for various new and prospective methods like Chemical Looping Combustion (CLC). It is used for power generation, where the oxygen carrier converts the methane to a mixture of CO_2 and H_2O (*cf* Fig 1.3). Two separate

Figure 1.3 Schematic of Chemical Looping Combustion (CLC) process

exhaust gas streams, consisting of CO_2 and H_2O only, allow CO_2 concentration without the need for costly separation processes. This ensures minimized energy losses with the CO_2 separation by avoiding oxidation of fuels with air (where other components of air also get oxidized leading to impurities in the product stream).²⁷ The total heat release from CLC is equal to that of direct combustion and, the remaining energy penalty to account for CO_2 compression and purification efforts, which is common for all other processes. This gas mixture of CO_2 and H_2O are further reacted with methane over reforming catalysts to produce synthesis gas.

The more preferred route to utilize chemical looping concept in methane oxidation is the direct generation of mixtures of CO and H_2 (with no CO_2 or H_2O) through chemical looping over metal oxides. This is referred to as Chemical Looping auto-thermal Reforming²⁸ (CLR). This process is similar to CLC, however, instead of just fuel, a combination of a fuel with steam is sent to the fuel reactor, and the reaction conditions are altered to induce reforming reactions and give the more desired product, syngas. In this process, the oxidizing agent (metal oxides) to fuel ratio is kept low to avert the formation of complete oxidation products (CO_2 and H_2O), thus generating the output gas stream rich in H_2 and CO .²⁹⁻³⁰ The significant advantage of this process lies in its heat balance, the heat needed for converting methane to synthesis gas is supplied without (i) costly pure O_2 production, (ii) without mixing of air with carbon-containing fuel gases, and (iii) without consumption of a portion of hydrogen gas produced in the process. Currently, autothermal reforming stands to be the only

commercialized method for syngas generation. The exothermic reactions in the air-reactor (oxidation of metal to metal oxide) provide the energy for the endothermic reactions in the fuel reactor (fuel oxidation and metal oxide reduction). The heat generated in the air reactor must be sufficient to fulfill the energy balance to avoid any external heat source. The excess heat needed for the fuel reactor is supplied by the temperature of the solid oxygen carriers, controlled by the amount transferred to the fuel cell. The syngas production step of any methane to chemical/fuel conversion is the most expensive step of the production chain.³¹

1.2.2 Direct Methods for Methane Conversion

To date, industrial routes for one step methane conversion to useful bulk chemicals and fuels is limited.³² Direct conversion of methane to liquid fuels and valuable chemicals like methanol, formaldehyde, etc. has attracted a lot of attention in the recent years. Various approaches like Thermal and catalytic pyrolysis of methane, dehydroaromatization, oxidative coupling of methane, partial oxidation of methane to C-1 oxygenates as well as new technologies involving around different processes like Plasma, halogenation, photocatalysis, membranes, etc. are proposed and tested (*cf* Fig. 1.4).³³⁻³⁴ These processes lead to the direct conversion of methane into Hydrocarbons C_{2+} , Hydrocarbons $CH_3-OH/COOH$ /aryl, and Formaldehyde.^{33, 35}

Figure 1.4 Pathways for the valorization of methane, showing direct conversion pathways

1.3 Transition Metal Oxides as Catalysts for C-H bond oxidation: Overview, Challenges, and Knowledge Gaps

For both the direct and indirect methods of catalytic methane conversion, gaining a fundamental understanding of the reaction chemistry is indispensable to the realization of the commercial transformation of methane to value-added chemicals and products. C-H bond activation/dissociation, identification of active sites of proven catalysts, screening and developing cheap and efficient catalytic systems continue to be among the most active pursuits and testing challenges of the catalysis community, as can be seen from the numerous expert reviews^{18, 36-43} on the topic over the last few decades.

Among the hundreds of catalysts and supports evaluated for their efficiency in methane oxidative conversion to partially oxygenated products (direct conversion routes) and synthesis gas generation (indirect conversion of methane), a majority of them fall under the category of Transition Metals and Transition Metal Oxides (TMOs). Both chemisorbed surface oxygen on the metal surface⁴⁴ as well as oxygen incorporated into the lattice of the metal oxide⁴⁵ have been shown to activate the C-H bonds of alkanes. Coordinatively unsaturated metal and oxygen pairs on the surface of TMOs are known to be active sites for many reactions involving alkane C-H activation. These coordinatively unsaturated atoms result from the creation of the oxide surface from the bulk oxide by cleavage of bulk and coordinatively saturated metal-oxygen bonds. Since the nature of surface metal and oxygen sites control the surface chemical properties of transition metal oxides, the cleavage plane, the surface structure, and the

termination play a unique role in these properties. For example, the less stable (101) facet of PdO is the most active surface for C-H dissociation of methane with extremely favorable reaction energy, while the more stable PdO(100) surface offers reasonable reaction energy but with high energy activation barrier for the dissociation. Catalytic properties of TMOs are primarily dependent on its surface characteristics such as, but not limited to, the degree of unsaturation of the surface, the surface acid-base characteristics, the adsorbate-surface interactions, the binding energy of lattice oxygen and the ease of vacancy formation and the presence of cationic and anionic vacancies⁴⁶. Hence, it is essential to study and understand the influence of surface characteristics on the catalytic activity of TMOs, to guide the design and development of efficient and novel TMO based catalysts for direct methane conversion to value-added chemicals.

In the process of oxidatively activating the strong C-H bonds over TMO surfaces, the primary challenge lies in the fact that the intermediates (desired products) are more reactive than CH₄ itself, and hence the reaction tends to go to completion with undesired products (CO or CO₂) being formed with higher selectivity. Direct TMO catalyzed the conversion of methane to oxygenates like methanol and oxidative coupling to ethylene are plagued by poor overall conversion and selectivity,⁴⁷⁻⁴⁸ making them commercially unviable. Some processes like the partial oxidation of methane to syngas enjoy limited commercial success partly for want of stable catalytic systems with sufficient lifetime, allowing controllable reaction at optimum conditions.¹⁸ Selectivity and

conversion of methane are sometimes also constrained by thermodynamics⁴⁹, and extreme reaction conditions may be necessitated for a favorable shift of the chemical equilibrium. Thus, virtually all commercial process involving methane conversion like reforming require high temperatures (≥ 700 °C) and operating pressures (vary according to the overall process integration), leading to higher equipment and operating costs. Thus, commercial utilization of methane is posed with challenges originating from both reaction chemistry as well as process and operational aspects.

Irrespective of the final product of methane oxidation, this dissociation process begin with methane's first activation. The first activation of methane on TMOs⁵⁰⁻⁵¹ gives rise to either generation of methyl radicals or surface stabilized methoxy species, which can further oxidize to CO/CO₂ via various reaction pathways involving partially oxygenated species like methanol, formaldehyde, formic acid. These partially oxygenated intermediates are of immense value, and if captured as a reaction product by altering the reaction kinetics (through initiators, novel catalysts or promoters), could address the high energy and cost challenges associated with direct and indirect pathways of methane oxidation. These subsequent activations of methane on TMOs are not widely investigated in the literature.

Water and OH species can be present on the transition metal oxide's surface either from the catalyst synthesis method or via the adsorption from moisture in the atmosphere.^{8, 28-30} These surface OH species can also be formed during the CH₄ activation reactions under dry conditions. They can significantly

influence the catalytic behavior by promoting the activation of C-H bonds of methane and other reaction intermediates. Surface hydroxide can act as Bronsted bases when bound to transition metals like Cu, Au, Ag and have shown to aid in the activation of C-H bonds.⁵² These adsorbed OH intermediates withdraw electron density from the metal to form negatively charged surface intermediates, thus behaving as a Bronsted base capable of activating the C-H bonds of methane.⁵³⁻⁵⁴ They may significantly influence the catalytic behavior by promoting the activation of C-H bonds of methane and other reaction intermediates on TMO surface as well. The selectivity towards partial oxygenates of methane (methanol and formaldehyde) as compared to CO/CO₂ was stated to be strong positive function of the amount of water vapor present in the system for methane oxidation on MoO₃/SiO₂.⁵⁵ Limited literature is available with respect to the mechanism of how moisture or surface hydroxide species (added externally or generated during the reaction) participate and affect the methane activation reaction energetics and barriers over Transition metal oxides. Thus, to address the challenges associated with methane activation over TMOs, it is crucial to study subsequent activations of methane as well as the role of moisture and surface OH species on the activation and dissociation in TMO catalyzed methane activation reactions. Insights provided from such mechanistic studies of reaction pathways can aid in improving the overall energy efficiency and reducing the capital costs associated with the state of the art CLC/CLR process (by lowering the temperatures and pressures employed for such operations) as well as in the synthesis of partially oxygenated products (by investigating the

rate-determining step, and the effect of promoters and initiators on different reaction pathways to bypass the expensive synthesis gas generation altogether).

Variety of experimental surface science techniques as well as computational tools are employed to develop understanding about the surface-active sites, reaction intermediates, pathways, energetics, and barriers involved in the oxidation of methane to partially oxygenated species. Both experimental and computational methods have their advantages, challenges, and limitations when applied to study reactions over TMOs.

1.4 Experimental Challenges in investigating TMO catalyzed reactions and the Role of DFT

Under reaction conditions, TMO surface experiences a dynamic environment due to various parallel and sequential reaction steps like adsorption/desorption, oxidation/reduction, and the diffusion of intermediates from one site to the other. These reactions get further complex with the participation and consumption of lattice oxygen as the reaction proceeds. Also, the intrinsic heterogeneity of the majority of the TMO catalytic systems leads to a wide range of active sites, each with their selectivity, reactivity and promoter effects. This makes it challenging for independent experimental surface characterization techniques to comment on mechanistic details of the reaction conclusively. More often than not, deductions of the reaction mechanism, active sites, etc. are constructed based on analysis of different independently performed surface characterization techniques. Moreover, the spectroscopic information obtained from a catalyst surface under

ex-situ conditions (before and after the reaction) is of limited relevance to study the reaction mechanism and pathways, since significant structural, physical and chemical changes can take place on the catalyst surface under reactions conditions, and these changes may further influence the course of reaction by altering the reaction mechanism, pathways and energetics.⁵⁶ A number of spectroscopic techniques, such as UV-VIS, NMR, EPR, IR etc., have already been adapted to study metal oxide catalysts under reaction conditions. It is beneficial to combine two or more of the above spectroscopic surface science techniques into one catalytic system to provide complementary information for the reaction under identical catalytic conditions. However, such combined operando and in-situ techniques have their own challenges. A major challenge for operando techniques is to discriminate between spectator species (bulk/gas phase/solvent species → noise) and active species (adsorbates, intermediates → interest species) in the system. Hence, the high spectrum contribution from the surrounding bulk phase dominates the signals of interest from the metal oxide surface and the interface, thus interfering with the observations from the catalytic surface reaction under study. Every spectroscopic technique has its own sensitivity and limitations. Another challenge is to decrease the time necessary for measuring reaction intermediates in an active catalytic reaction. An intelligent combination of two or more spectroscopic techniques, which provides complementary information on the reaction mechanism and surface moieties under reaction conditions must be chosen.⁵⁷⁻⁵⁸ Spectroscopic tools can be used to obtain valuable information on the behavior of a catalytic solid under reaction

conditions, affording a critical insight into the source of surface activity and oxide deactivation.⁵⁹ Despite the vast information obtained with these *in-situ* surface science techniques, it is still exhausting for the experimental researchers to associate spectrophotometric signals with respective surface species (and their adsorption configurations). This signal-to-species characterization becomes even more challenging in complex systems where multiple surface moieties may contest to provide a very close spectrophotometric response. For example, (i) in a FTIR spectra with various kinds of C-H or O-H stretching signals, it can be very difficult to establish these to individual structures or reaction intermediates for a complex system, and (ii) The C 1s core-level shifts in XPS spectra corresponding to different adsorbed hydrocarbon species can be too small to be resolved. Also, difficulty in deconvolution of spectrophotometric spectra increases with the increasing type of moieties, increasing contribution from bulk catalyst as well as gas phase species. Overcoming these experimental challenges requires the integration of advanced surface science experimental techniques with computational tools, which can deliver the necessary information to determine potential active sites, reaction intermediates, and pathways to design new heterogeneous catalysts.

Hence, computational techniques like Density Functional Theory (DFT) are extensively used as a complementary and predictive tool to investigate the structural, magnetic, and electronic properties of such systems. DFT is used to examine the electronic structure of TMO surfaces, active sites, adsorption configurations, reaction pathways and energetics, vacancy formation, coke

formation, and to identify and predict the elementary reaction steps which govern reaction rates and product selectivity on TMO catalyzed reactions. Computational methods coupled with experimental surface science techniques can provide mechanistic insights (i) by investigating novel catalysts and reaction paths that can oxidize methane at lower temperatures than the current methods, and thus reduce the operating costs for the current indirect methods (chemical looping combustion or chemical looping reforming), as well as, (ii) by exploring novel catalysts/promoters that can selectively activate the methane to partial oxidation products like methanol, formaldehyde etc.

1.5 Limitations of DFT to investigate TMOs

In strongly correlated systems like TMOs, due to the localized nature of electrons, the interelectronic interaction is strong, and dynamics of each electron is influenced by and correlated to all other electrons in the system. Strongly correlated systems are ones, where due to the localized electrons, the overall motion of a valence electron is influenced and correlated to all other electrons, and the extent of this electron-electron interaction determines the electron localization, which in turn determines the metallic or insulating nature of a system. Although DFT is widely used as a complementary and predictive tool to investigate the structural, magnetic and electronic properties of TMO, a few fundamental approximations of DFT fail to account for exchange and correlation effects, leading to difficulties in the description of electron localization in strongly correlated systems. In Kohn-Sham Density Functional theory⁶⁰ (KS-

DFT), the interacting many-particle system is modeled in terms of an auxiliary non-interacting particle system (Kohn-Sham system), such that the new effective potential (Kohn-sham potential, V_{KS}) reproduces its true electron density. The energy is calculated using series of one electron Kohn-sham equations:

$$\varepsilon_i \phi_i(\mathbf{r}) = \left[-\frac{\nabla^2}{2} + V_{KS}(\mathbf{r}) \right] \phi_i(\mathbf{r}) \quad (1)$$

Solved self-consistently with

$$\rho_0(\mathbf{r}) = \sum_{i, \text{Lowest } \varepsilon_i} |\phi_i(\mathbf{r})|^2 \quad (2)$$

, where the first term on the RHS of equation 1, represents the kinetic energy of the electron. $\phi_i(\mathbf{r})$ are the KS single-particle orbitals, ε_i are the KS eigenvalues, ρ is the electron density and V_{KS} is defined as

$$V_{KS}(\mathbf{r}) = V(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) \quad (3)$$

$$V_H(\mathbf{r}) = e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' \quad (4)$$

$$V_{XC}(\mathbf{r}) = \frac{\partial E_{XC}}{\partial n(\mathbf{r})} \quad (5)$$

, where $V(\mathbf{r})$ is the external potential of electron-nuclei interaction (equation 3), $V_H(\mathbf{r})$ is the potential of electron-electron coulomb interaction known as Hartree potential (equation 4). $V_{XC}(\mathbf{r})$ and $E_{XC}(\mathbf{r})$ (equation 5) are the exchange-correlation potential and energy respectively with the latter being the only unknown parameter required to solve the KS-DFT total energy equation. For such systems, the exchange-correlation (XC) functional approximations in DFT fall short to

accurately capture the exchange and correlation effects, leading to difficulties in accounting for electron localization. The description of the electron-electron interaction leads to a systematic difficulty for DFT calculations, arising from the unphysical interaction of an electron with itself, resulting into an over-delocalization of the electron density. For systems with highly delocalized electrons, the XC functional approximations like the Local density approximation (LDA) and the Generalized gradient approximation (GGA) perfectly cancel out the self-interaction errors (SIEs) arising due to the electron-electron repulsion term, hence correctly describing the electronic structure of systems like metals. However, in systems with strongly correlated electrons and localized states, unequal cancellations of these errors lead to over-delocalization of electrons and underestimation of the band gaps. Hence, a material being insulator or semiconductor could be incorrectly predicted to have a metallic ground state by DFT calculations. This inaccurate description of the electronic structure of strongly correlated materials with partially or entirely localized outer shell electrons is a long-standing challenge for DFT⁶¹.

1.5.1 Extension to DFT methods to describe correlated systems:

DFT+U

Over the years, numerous methods have been developed to treat SIEs and electron delocalization for strongly correlated systems such as self-interaction correction (SIC) methods⁶²⁻⁶³, DFT+U method, Hybrid functionals as well as more accurate, computationally expensive methods like Reduced Density Matrix

Theory⁶⁴ and Dynamical Mean Field Theory⁶⁵. Among these, two popular and widely used methods for catalytic surface applications are, (i) DFT+U, in which an onsite Coulomb correction potential, U , is introduced as an energy penalty on the delocalization of electrons, thus restricting the amount of delocalization done by standard DFT methods, and (ii) Hybrid functionals, which involve mixing of non-local (exact Fock exchange) and semi-local DFT exchange energy, in different percentages. Jacobs ladder⁶⁶ ranks the density functional approximations in order of increasing accuracy and sophistication, with Hartree approximation ($E_{xc}=0$) being the least accurate. Semi-local approximations like LDA and GGA, being more precise, occupy the initial levels of this ladder, whereas, non-local approximations like hybrid functionals belong to the higher levels because of their increased sophistication (and accuracy). DFT+U is the most widely used method to correct the self-interaction errors due to its (i) add-on nature, leading to easy implementation, (ii) easy inclusion and calculation for first and second derivatives of energy such as atomic forces, stresses and atomic force constants⁶⁷ (iii) marginal additional costs involved over standard DFT methods, making it computationally less demanding than other higher level functionals.

The DFT+U method to treat SIEs in strongly correlated systems was first established by Anisimov et al.⁶⁸. Dudarev et al.⁶⁹ bridged this orbital-dependent expression with the rotationally invariant functional proposed by Liechtenstein⁷⁰ and came up with the most extensively used form of DFT+U total energy calculations, which in its orbital form is

$$E_{GGA+U} = E_{GGA} + \frac{(\bar{U} - \bar{J})}{2} \sum_{\sigma} \left[\left(\sum_m n_{m,m}^{\sigma} \right) - \left(\sum_{m,m'} n_{m,m'}^{\sigma} n_{m',m}^{\sigma} \right) \right] \quad (6)$$

where $\bar{U}$ and $\bar{J}$ are the screened averaged on-site coulomb repulsion and exchange interaction parameters, respectively. The occupation number of a d-orbital is represented by n_m , with subscripts m, m' representing the angular momentum quantum number (-2 to +2) for different d orbitals with spin signified by $\sigma = (1 \text{ or } -1)$. In this approach, U_{eff} replaces $\bar{U} - \bar{J}$ as the overall net potential term. In other words, U_{eff} is the net penalty function which improves the occupancy of certain orbitals by forcing electron localization in the description of strongly correlated systems by DFT+U. From here onwards, U_{eff} is referred to as U.

Rohrbach et al.⁷¹ compared the DFT+U method for LDA and GGA functionals for a few transition metal sulfides (MnS, FeS) and stated that a larger U-value is required to compensate for the overbinding characteristic of the LSDA (Local spin-density approximation, an extension of LDA to include electronic spin), which leads to widening of the energy gap, in disagreement with the photoemission spectra. They concluded that DFT+U with GGA, to be a better descriptor for the functional.

1.5.2 Determining the U-value for TMOs

Although the physical interpretation of the U-value as an onsite potential to restrict the electron delocalization among the neighboring sites might be

straightforward, the parameter value can be either determined *ab initio* from DFT calculations, or more commonly selected in a semi-empirical way by its ability to computationally reproduce experimentally measured system properties such as band gap⁷², band structure⁷³, metal-metal or metal-oxygen bond distances⁷⁴, lattice parameters and magnetic moments⁷⁵. In the first approach, U value is computed using the second derivative of the DFT computed energy with respect to orbital occupations, rendering the DFT+U calculation completely *ab initio*. Amongst the most common *ab initio* methods used to determine the U value are constrained random phase approximation (cRPA)⁷⁶ and linear-response constrained DFT. Some discrepancies⁷⁷⁻⁷⁸ have been observed in the U value provided by both these methods, particularly towards the end of 3d metal series, even though theoretically they ought to give the same results. Although significant work⁷⁹⁻⁸¹ is being done in this approach to get a robust procedure to determine the U-value for transition metal compounds, the second approach based on the fitting of experimental data remains widely practiced and accepted. Although popular, the general observation in this approach is that no single U-value perfectly reproduces all the experimental bulk properties of a material. A U-value which either predicts one selected property of interest accurately or minimizes the overall error in predicting a combination of different properties is chosen, leading to different U values for the same TMO like CuO^{74, 82-83}. Capdevila-Cortada et. al.⁸⁴ have done significant work in evaluating the performance of DFT+U approaches in studying catalytic systems and also summarized U values available in the literature for different TMOs. Another

interesting aspect of this implementation is that all the properties mentioned above are the bulk properties of the system. Hence using the bulk-determined U -value in a locally changing surface environment, which involves structural transitions along a reaction coordinate or changing physical conditions, may cause significant errors in the calculated energetics^{75, 85-88}.

When a catalytic surface is formed, the breaking of z symmetry of the bulk phase leads to surface strains and different atomic coordination of the surface atoms from the bulk. This results in a difference in the electronic structure of the bulk and surface atoms. Studies have shown that the calculated band gap of bulk TMOs is always higher than that of surface TMOs.⁸¹ Hence, the bulk property determined U value should be of higher magnitude than the U value that describes surface properties correctly. Hubbard term U is an onsite potential that, when applied, restricts the over delocalization of electrons as done by standard DFT methods. The larger the U value, the more restricted would be the participation of these electrons in bonding with adsorbates on the metal center. The band gap broadens with the increase in U value, and the metals d orbitals would weaken the interaction between the frontier molecular orbits of adsorbate and metal oxide d -bands. This can have two effects on the prediction of adsorbate energies, (i) The adsorption energies for the species adsorbed on the metal center are underestimated by the higher U values due to higher restriction of electrons in bond formation, (ii) due to this increased band gap, the metal-oxygen bond of the lattice is also weakened, which leads to stronger adsorption of species on the surface oxygen, and hence overprediction of adsorption energies. Therefore, the

bulk optimized U values, which are larger than the surface property optimized U value, tend to over localize the electrons and hence predict the incorrect adsorption enthalpies for the reaction energetics and surface properties. Surface property based U value resets the correct delocalization of electrons to maintain the strongly correlated nature of TMOs and predict accurate surface energetics and properties.

The U-value for strongly correlated systems is also determined by fitting bulk redox energies instead of bulk structural or electronic properties. Wang et al.⁸⁵ determined the bulk experimental oxidation enthalpies (from the thermodynamic tables) for TMOs (FeO, NiO, MnO, etc.) and compared those with the theoretically computed enthalpies for incremental U values using DFT+U. Lutfalla et al.⁸⁶ measured the bulk reduction enthalpies of oxides of Ti, V, Mn, and Ce with H₂ and compared those with the reaction enthalpies computed systematically using DFT+U. Aykol et. al.⁸⁹ derived the local environment dependent (LD) U value based on the transition metal's oxidation states and coordinating ligand contributions, by comparing the DFT+U calculated energies with the experimental bulk reaction/formation energies (from thermodynamic tables) of 3d metals (Ti, V, Cr, Mn, Fe, Co and Ni) in their oxides and fluorides form. The U-value which replicated the bulk redox energies with sufficient accuracy was chosen to be the U-value for the TMO system. Curnan et. al.⁹⁰ calculated the U value based on its ability to accurately predict the relative experimental energy of ordering of various TiO₂ polymorphs.

Bennett et. al.⁹¹ showed that U-value affected adsorption energies of different species differently on CeO₂ and presented a theoretical model to predict the U-value based on the average change in the adsorption energy and its gradient for various probe molecules with respect to U. Based on the stationary points in the above model, adsorbates were split into four classes, with one extreme being the adsorptions which involved no orbital overlap or charge transfer, leading to no influence of U-value on the adsorption energies, while the other extreme involved reduction of the oxide surface by complete charge transfer and hence the adsorption energies had significant dependence on the U-value. They stated that the U-value influences the quantitative adsorption energy data, as well as the qualitative thermodynamic reaction profile.

Many similar studies^{75, 85, 87, 92} have been conducted for CuO as well. One of the widely accepted work is by Nolan et al.⁷⁵, where the U-value of 7 eV was shown to be consistent to match bulk properties like magnetic moment and the band gap of CuO. Another study by Maimaiti et al.⁸⁷ showed that the energetic preference of different vacancies (surface and subsurface) on CuO(111) was not influenced by U-value. Hence, they claimed that for CuO(111), the U-value of 7 eV described both, the electronic structure and reaction energetics correctly. It must be noted here that, although U-values did not alter the trend of energetic preference, it affected the energies of individual structures by different magnitudes. Song et al.⁹² studied the partial oxidation of propylene on CuO(111). They showed that U-value did not affect the adsorption energy of propylene and hence used the U-value of 4 eV (as predicted by Wang et al.⁸⁵ against bulk redox

energetics) for the entire oxidation reaction. It must be noted that the effect of U-value was evaluated only on the adsorption (physisorption) of propylene and not for the entire reaction.

The aforementioned literature on determining the U-value for TMOs has following limitations: (i) they investigated and focused only on bulk oxides without any consideration to surface chemistry and adsorbate-surface interactions during the course of the reaction. This was a result of the presumption that the U-value which described bulk properties correctly will predict the energetics of a surface chemical reaction correctly too. However, work done by Huang et al.⁸⁸ to determine the influence of U-value on CO adsorption on Cerium oxide showed that the inclusion of the adsorbate-surface interaction and adsorption configurations in the DFT+U calculations lead to a better and relevant estimate of U-value in catalysis applications involving strongly correlated systems. (ii) DFT computed energy values were compared to the thermodynamic enthalpy data taken from standard thermodynamic tables which are non-surface specific and ignore the role and influence of active surfaces in the reaction chemistry (e.g., lattice oxygen binding strength on different facets of CuO will affect reaction enthalpy when lattice oxygen is consumed in the reaction via the Mars van Kreevelan mechanism⁹³⁻⁹⁴). (iii) When a catalytic surface is formed, the breaking of z symmetry of the bulk phase leads to surface strains, defects, and a different atomic coordination from the bulk. Hence, surface magnetic properties are expected to differ from those of the bulk phase. TMOs being strongly correlated systems, the total atomic spin represents the spin of an ion better than

the individual electronic spin of the electrons⁹⁵. In literature, the effect of different magnetic spin ordering configurations on the surface reactivity has been overlooked. (iv) Along the reaction coordinate, the *d* band of the oxide becomes partially filled, and hence U-value may affect the computed adsorption energies differently. The underlying assumption that the same U-value being valid for two different oxidation states of the same transition metal might not be correct. (v) It is important to note that even when the reactant's binding energy is weakly affected by the U-value (reactant being physisorbed, weakly interacting or involving no or limited charge transfer), the adsorption energies of reaction intermediates or products, which involve complete charge transfer, vacancy formation and/or consumption of oxygen, might be strongly dependent on U. Hence, it is essential to carefully examine the nature of reaction on the oxide surface and choose a uniform U-value which represents reaction energetics for a TMO correctly.

It is also important to mention here that, in the current work, plane wave pseudopotential of DFT has been employed, which is the widely used method to study catalysis due to the periodic nature of catalytic TMO systems. As discussed in section 1.6.1, higher theory level methods, as well as all electron approach to DFT, would yield more accurate results for such strongly correlated systems, but the cost of calculations assisted with such systems is orders of magnitude higher.

1.6 Aims and Objectives of the thesis

The unifying theme of the present thesis is to implement appropriate theoretical and experimental methods to investigate the role of TMOs in C1 chemistry by addressing the challenges pertaining to experimental surface science and DFT techniques employed to study TMO catalyzed reactions.

The knowledge gaps in the literature, as identified and discussed in detail in the previous sections are (i) Challenges associated with independent experimental surface science techniques to investigate TMO catalyzed reactions (section 1.5), (ii) Limitations of DFT to examine TMOs and application of bulk property optimized U value to study TMO surface catalysis (section 1.6), and (iii) Absence of detailed mechanistic study of the role of moisture and surface OH species on methane dissociation on TMOs (section 1.4). Based on these knowledge gaps, the primary objectives of this thesis are:

- 1) Develop an appropriate semi-empirical DFT based method that incorporates an accurate theory level to describe the surface catalytic reactions over TMOs correctly;
- 2) Develop a novel, theoretical (DFT) and experimental toolbox to investigate *in situ* reactions, determine surface moieties and their adsorbed configurations for TMO surface catalyzed reactions.

3) Provide mechanistic insights and experimental evidence into Methane activation and dissociation on CuO and investigate the role of moisture and surface OH species to favorably alter the kinetics of the methane activation and dissociation on CuO.

1.7 Dissertation Overview

A flow-chart containing a thesis overview, addressed challenges, knowledge gaps in the literature, adopted methodology, conclusions from this thesis is presented in Fig. 1.5.

Following the introduction, relevant literature, knowledge gaps and thesis objectives presented in *Chapter 1*, *Chapter 2* of this thesis presents a combined theoretical and experimental benchmarking study to understand the influence of Hubbard U parameter in simulating adsorption and reactivity on CuO surfaces. It highlights the gap in the computational studies involving Transition Metal Oxides for surface catalysis application. It establishes the need for U value determination based on surface properties and characteristics as opposed to the bulk properties. It incorporates experimental techniques like chemisorption experiments as well as FTIR study reaction of H₂ with CuO to determine the U value for CuO. It also establishes a benchmarking method for U value determination which can be applied to any other strongly correlated system.

Chapter 3 of this thesis focusses on the comparison of experimental XPS and computationally generated XPS shifts to determine realistic surface moieties, establish their XPS shifts as well as determine the U value for CuO in a synergic manner. This technique establishes the base for combined experimental and theoretical studies for TMOs without any need for separate U value calculation.

Chapter 4 of this thesis investigates the sequential oxidation of methane on CuO(111) surface under dry as well as moisturized conditions to study the evolution and role of moisture and surface hydroxide species in activation of methane and determining mechanisms, activation barriers and the energetics of methane dissociation C-H bonds. It incorporates both computational tools like DFT and experimental FTIR methods to study the reaction under both dry and moisturized conditions.

Chapter 5 summarises the conclusions drawn from the work in the thesis and offers some perspectives on them.

Figure 1.5 Summary of the thesis and organization

2 The Influence of Hubbard U Parameter in Simulating Adsorption and Reactivity on CuO: A Combined Theoretical and Experimental Study

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Source: “Kartavya Bhola, Jithin John Varghese, Liu Dapeng, Yan Liu and Samir H. Mushrif, ‘Influence of Hubbard U Parameter in Simulating Adsorption and Reactivity on CuO: Combined Theoretical and Experimental Study,’ *J. Phys. Chem. C* 121, 39, 21343-21353, American Chemical Society.”

2.1 Introduction

Transition metal oxides (TMOs) are widely used in heterogeneous catalysis in various industrially important reactions owing to their low cost, high surface area, low toxicity, and easily tunable surface and structural properties. CuO has recently shown to be a suitable catalyst for methane C-H bond activation and for activating formyl C-H bond for the conversion of glucose to gluconic acid. Computational tools like Density Functional Theory (DFT), and experimental surface characterization techniques like Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) are often employed by computational and experimental researchers, to provide insights into metal oxide catalyzed reaction mechanisms, pathways, and energetics. Owing to the complex nature of catalytic reactions on TMO surfaces involving participation and consumption of surface lattice oxygen as well as the presence of a variety of intermediates along the

reaction coordinate, identifying realistic reaction intermediates and their corresponding Infrared (IR) spectra peaks presents a challenge for experimental researchers. DFT methods are widely used as complementary tools to provide mechanistic insights, reaction pathways and energetics for TMO catalyzed reactions.

As discussed in Section 1.6, Density Functional Theory (DFT) calculations, when implemented for such strongly correlated systems, the description of electron-electron interactions (in DFT) lead to a systematic error causing unphysical delocalization of electrons. DFT+U is one of the most widely used methods to correctly account for this electron delocalization, wherein an onsite Coulomb correction potential U is introduced as an energy penalty for the electron delocalization done by standard DFT methods. For DFT calculations, the U -value is typically chosen based on its accuracy to reproduce bulk physical or redox properties. However, chemical reactions on TMO surfaces usually involve complex surface-adsorbate interactions and using the bulk properties based U -values in a locally changing surface environment may not describe reaction energetics correctly. Hence, for the reasons stated above, considering the influence of surface characteristics (surface saturation, the binding energy of the lattice oxygen, acid-base characteristics, etc.) on the catalytic activity of TMOs, it becomes crucial to determine the U -value based on surface reactions, rather than using the bulk property-optimized U -value. In the present chapter, the dissociative chemisorption of H_2 on the CuO surface is investigated to determine

the U-value for surface catalytic reactions on CuO, taking into account complex surface-adsorbate interactions. Adsorption energies are measured experimentally using chemisorption experiments, and experimental surface characterization techniques are used to identify adsorption configurations. The reaction mechanism leading to the experimentally determined adsorption configuration is investigated computationally, and a U-value that correctly described the entire reaction energetics and adsorption energies over the CuO surface is identified.

In section 2.2, the computational and experimental methods used in the study are described, followed by CuO morphology and surface characterization results in section 2.3.1. In section 2.3.2, the rationale for choosing H₂ as a probe molecule is presented along with a model catalytic reduction reaction. In section 2.3.3, the experimental H₂ chemisorption energies on CuO is presented, and the possible H₂ adsorption configurations as computed by DFT calculations are discussed in section 2.3.4. In section 2.3.5, the equilibrium H₂ adsorption configuration along the reaction coordinate is identified by performing in-situ IR analysis of CuO catalyzed reduction reaction. In section 2.3.6, the effect of U-value on the adsorption enthalpy is discussed, and the range of U-values that accurately estimate the experimental chemisorption energy for CuO catalyzed surface reactions is presented. The conclusions from this work are summarised in section 2.4.

2.2 Computational and Experimental Methods

2.2.1 Computational Methods

All the calculations in the current work were performed using GGA⁹⁶ with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional implemented in VASP⁹⁷ with the periodic plane wave implementation within DFT^{60, 97}. The projector augmented-wave (PAW)⁹⁸⁻⁹⁹ scheme is employed to describe the inner core-valance interaction with a plane wave cut-off energy of 450 eV. For integration over the Brillouin zone, k points sampling of 4x4x1 within the Monkhorst-pack scheme is used. Integration is performed utilizing the tetrahedron method with Blöchl corrections. A four-layer CuO(111) slab with top three layers allowed to be fully relaxed is used to model the system; the number of slab layers and the density of k point grids were chosen to ensure the adsorption energies were well converged within 0.01 eV with respect to the computational setup discussed here. A vacuum region of 12 Å was wide enough to avoid interactions between different slabs. To ensure a high level of accuracy, energy convergence criteria of 10⁻⁶ eV per unit cell along with a minimization of interatomic forces to 0.01 eV/Å was employed. Since CuO is antiferromagnetic at its ground state, spin polarization for all simulations involving CuO was turned on.

In the current DFT+U benchmarking study, in order to eliminate the effect of different lattice parameters on reaction energetics, and keep the computational system in a close match to the experimental system, the lattice constants were fixed at the values obtained with U-value of 7 eV, as it showed excellent

agreement with experimental lattice parameters (a , b , c , β), interatomic distances⁷⁵ and reproduced experimental band gaps and magnetic moments⁷⁴. CuO has a monoclinic structure, and the lattice constants $a = 4.68 \text{ \AA}$, $b = 3.43 \text{ \AA}$, $c = 5.14 \text{ \AA}$, $\beta = 99.3^\circ$, as optimized by Varghese et al.⁹⁴ with the U-value mentioned above are used in this study. All the calculations have been done on CuO(111) as it is the most stable CuO facet followed by CuO(-111)³⁵. Both CuO(111) and CuO(-111) have similar geometric configuration and surface structure arrangement of Cu and O atoms. CuO(111) facet has been predominantly found in our as-synthesized sample of CuO, which is used for experiments in this work.

CuO(111) surface consists of a repeating surface atom arrangement of $O_3\text{-Cu}_3\text{-O}_4\text{-Cu}_4$ units (*cf* Fig. 2.1a), where the subscript denotes the coordination number of the individual atom. Although CuO is antiferromagnetic, different atomic magnetic spin configurations are possible while maintaining the antiferromagnetic behavior, such as line-by-line ordering (*cf* Fig. 2.1a, where alternate rows of Cu atoms have opposite magnetic spins) and bulk-like magnetic ordering (*cf* Fig. 2.1b, where alternate atoms of Cu in any particular row have opposite magnetic spins). Line-by-line magnetic spin ordering has been used in the current work. As per literature^{35, 74}, the bulk-like magnetic ordering (*cf* Fig. 2.1b) was only marginally stable than the line-by-line ordering (*cf* Fig. 2.1a) by $\sim 0.01 \text{ J/m}^2$, and both these magnetic orderings co-exist in a system. Their effect

on adsorption energies was also evaluated, and the calculated adsorption energies were unaffected by the change in these two magnetic order configurations.

Figure 2.1 The surface atomic arrangement on CuO(111) facet showing the repeating arrangement of O_3 - Cu_3 - O_4 - Cu_4 units, where the subscript denotes the coordination number of the respective atom. a) Line-by-line magnetic spin ordering (where the alternate rows of Cu atoms have opposite magnetic spins) b) Bulk-like magnetic spin ordering (where the alternate atoms of Cu in any particular row have opposite magnetic spins). The upward and downward arrows represent the positive and negative spin respectively. Peach and red balls represent Copper (Cu) and Oxygen (O) atoms, respectively.

The zero-point energy (ZPE) and entropic and enthalpic temperature corrections were calculated for gas phase molecules from thermodynamic tables and for adsorbed structures as per statistical thermodynamics, where molecular partition function describes each of these effects¹⁰⁰. For the adsorbed species, these effects arise only from the vibrational motion of the adsorbed atoms hence

we ignored the effects resulting from translational and rotational partition function. The enthalpic contribution from the surface (clean or adsorbed) was expected to be insignificant as compared to the adsorbate and did not include them in the vibrational analysis. In cases where the lattice oxygen dashed out of the surface and constituted a part of the adsorbed species or product, its enthalpic contribution was no longer excluded but was evaluated as a part of adsorbed species. The frequency analysis with finite difference approximations was performed with a displacement size of 0.01 Å, where atoms were individually displaced in each of the Cartesian direction.

Adsorption energy, E_{ads} , was calculated as follows, for a model adsorption reaction:

Using the expression,

$$E_{ads} = E_{A^*} - (E_* + E_{A(g)}) \quad (8)$$

, where E_{A^*} is the total energy of the system, E_* is the energy of the clean surface, and $E_{A(g)}$ is the energy of the isolated gas phase molecule $A(g)$. Since these energies are computed at 0 K, the ZPE and enthalpy temperature corrections $[H(T) - H(0)]$ to the computed reaction energies are added, as proposed by Irikura¹⁰⁰, to compare the computational adsorption energies with the experimental enthalpy data by the following equations

$$ZPE = \frac{1}{2} \sum_i h\nu_i \quad (9)$$

$$[H(T) - H(0)]_{vib} = RT \sum_i \left(\frac{h\nu_i}{kT} \right) \frac{e^{-\frac{h\nu_i}{kT}}}{\left(1 - e^{-\frac{h\nu_i}{kT}} \right)} \quad (10)$$

, Where h is the planks constant and ν_i is the computed frequencies of the system, k is the Boltzmann constant, and R is the ideal-gas constant. The surface coverage in the simulation is comparable to the experimental system. The net enthalpy of a reaction was calculated by

$$\Delta H = \Delta E_{Reaction} + \Delta\{ZPE + [H(T) - H(0)]\}_{Reaction} \quad (11)$$

2.2.2 Experimental Methods

CuO nanomaterial was synthesized by the precipitation method using NaOH solution as the precipitant. The concentrated NaOH solution, around 4M, was added dropwise to the $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ solution under continuous stirring at room temperature. The black precipitate appeared as soon as the basic solution was added. The resultant slurry was aged under stirring at ambient temperature for 5 h, and the final product was collected by vacuum filtration, washed with deionized water, dried at 60 °C and calcined at 350 °C for 4 hours.

Experiments to investigate the water evolution (possibly due to hydrogen chemisorption followed by CuO reduction) were carried out using a continuous fixed bed reactor under Temperature Programmed Surface Reaction (TPSR) mode, and products were monitored with a HPR 20 QMS Sampling System

(Hiden Analytical). During TPSR test, a low-temperature ramping rate of 5 °C/min was used and the dwelling time is 10 min at each temperature.

X-ray diffraction (XRD) patterns were recorded on a Bruker AXS D8 diffractometer under ambient temperature using CuK α radiation operated at 40 kV and 40 mA in the 2 θ range of 10°–80°, using a 0.05° step size of and a step time of 20 seconds at each point.

The morphology of the calcined catalyst was analyzed using a Field-emission scanning electron microscope (FE-SEM, Jeol JSM-6700) at an accelerating voltage of 5 kV. Further morphological information was acquired through transmission electron microscopy (TEM) observation using Tecnai G² TF20 S-twin microscopy operated at 200 kV. Samples were dispersed on carbon grids after sonicating the samples in ethanol for half an hour.

In situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) spectra were recorded on a Bio-Rad FT-IR3000 MX spectrometer equipped with a Harrick Praying Mantis DRIFTS cell connected to a liquid N₂ cooled mercury-cadmium-telluride (MCT) detector and a resolution of 4 cm⁻¹ with an accumulation of 64 scans in a single measurement. The catalyst was loaded into the reaction cell, and the reaction gasses were passed through the sample at a controlled flow rate. The background was recorded under Helium atmosphere at the reaction temperature. Background subtractions were performed for all spectra reported in the investigation.

Please note that the fresh catalyst was pre-treated before every reaction (MS and DRIFTS) in Helium at 350°C for 30 min to clean the surface and any morphology change in pre- and posttreatment of catalyst was not observed, assuring that the catalyst structure was not affected.

Chemisorption was carried out with a Micromeritics ASAP 2020C instrument through static measurement of H₂ chemisorption. The heat of adsorption was calculated from the isosteric curves using the Clausius-Clapeyron equation (Equation 12), a function of system pressure and the temperature.

$$\Delta H^{\circ}_{adsorption} = R \left[\frac{\partial(\ln P)}{\partial(1/T)} \right]_{\theta} \quad (12)$$

2.3 Results and Discussion

2.3.1 CuO morphology and surface characterization

The as-synthesized CuO was characterized using XRD (*cf* Fig. 2.2), and all the peaks in the spectra were representative of the monoclinic C/2c symmetry of cupric oxide¹⁰¹. The major peaks centered at $2\Theta = 35.5^{\circ}$ and 38.8° are indexed as CuO $[-1\ 1\ 1]$, and CuO $[1\ 1\ 1]$, respectively, and are characteristic of the pure phase monoclinic CuO crystallites. Furthermore, no side products such as Cu(OH)₂ and Cu₂O were detected from the XRD pattern, further indicating the synthesis of highly pure CuO nanostructures. The morphology of CuO nanoparticles was examined by SEM (*cf* Fig. 2.3a), and the particles had a cylindrical/ellipsoidal morphology, resembling nano-pellets. For detailed

morphological characterization, TEM and HR-TEM were employed. The TEM images of the as-synthesized CuO nanopellets (*cf* Fig. 2.3b) were consistent with the SEM observations and revealed the leaf-like morphology of the as-synthesized CuO. HRTEM was conducted and focused on different areas of the pellet surface, and lattice fringes with a d-spacing of 0.23 nm were typically observed, corresponding to the distance of the (111) plane of the monoclinic CuO as the most exposed surface in the as-prepared CuO and confirmed the crystalline nature of the as-synthesized morphology with the same crystallographic orientation. The same surface is used to model reactions in computational work.

Figure 2.2 X-ray diffractograms of as-synthesized CuO with signature peaks of copper (II) oxide.

Figure 2.3 Morphology characterization of the as-synthesized CuO a) SEM image depicting the nano-pellets morphology b) Bright field TEM image with HRTEM image insert for the nano-pellets depicting lattice fringes corresponding to the (111) facet.

2.3.2 Choice of probe molecule and model reduction reaction

Most of the catalytic applications of CuO, such as partial and complete oxidation and dehydrogenation of hydrocarbons (and oxygen-containing moieties) involve hydrogen abstraction, leading to both, the formation of adsorbed hydrogen species and the reduction of CuO. Hence, in this contribution, hydrogen was used as a probe molecule.

A typical hydrogen reduction reaction on a metal oxide can be broken down into the following elementary steps (Equations 13-16),

, where * denotes the various active surface sites. The elementary reaction steps are (i) H₂ adsorption on the surface to form molecularly adsorbed H₂^{*} (Equation 13), (ii) dissociation of H₂ to form different adsorbed H^{*} species (on surface metal or lattice oxygen centers) (Equation 14), (iii) reaction with surface hydroxyl species to form adsorbed (H-O_{Lattice}-H)^{*} species (Equation 15) (iv) desorption of H₂O, leaving the surface with one less oxygen per molecule of H₂ adsorbed (Equation 16).

2.3.3 Experimental adsorption energy measurements

Since to the best of our knowledge, enthalpy data of H₂ adsorption on copper oxide was not available in the literature; The H₂ adsorption energy on CuO was experimentally measured using chemisorption method. Before the measurements, mass spectrometry (MS) based TPR (CuO with H₂) was carried out to ensure that temperatures used for the chemisorption study won't lead to the loss of CuO reduction products, i.e., water. (Equation 16). The results showed H₂O peak evolution from 70 °C onwards, and hence the temperature range of 30-50° C was chosen for chemisorption studies. The enthalpy values for H₂ adsorption on the as-synthesized CuO was observed to be 42.2-60.8 kJ mol⁻¹, as summarized in Table 2.1.

This adsorption enthalpy could correspond to any of the surface species that are present during the adsorption reaction (Equations 13-15). Hence, to accurately compare the above experimental adsorption enthalpies to DFT calculated adsorption energies, it was essential to identify the equilibrium surface species and adsorption configurations along the course of the reaction.

Table 2.1 Enthalpy of H₂ adsorption (kJ mol⁻¹) for different adsorption coverages (Quantity of H₂ adsorbed per gram of CuO), as calculated using isosteric adsorption curves to solve Equation 12.

Quantity of H ₂ gas adsorbed (cm ³ /g STP)	Enthalpy of adsorption (kJ mol ⁻¹)
2.02	-60.83
2.13	-49.69
2.24	-50.42
2.36	-55.96
2.47	-52.66
2.58	-47.19
2.69	-42.18
2.80	-43.98

2.3.4 Theoretically predicted adsorption configurations

DFT calculations to evaluate different possible surface adsorption configurations along the course of the reaction were performed, and it was

noticed that H_2 preferred to dissociatively chemisorb on the CuO surface, which was also observed by Bersani et al.¹⁰². Due to the possibility of H_2 dissociation on different active sites of CuO(111) (*cf* Fig. 2.1), dissociated hydrogens, H^* , can occupy different adsorption configurations, as shown in Fig. 2.4; (i) under coordinated surface Cu_3 sites (*cf* Fig. 2.4a), (ii) under coordinated surface Cu_3-O_3 pair sites (*cf* Fig. 2.4b), (iii) under coordinated surface O_3 sites, forming 2 hydroxyl species involving lattice oxygen $H_{latticeO}^*$ (*cf* Fig. 2.4c), (iv) under coordinated surface O_3 site, forming a water-like structure involving lattice oxygen $(H-O_{Lattice}-H)^*$ (*cf* Fig. 2.4d). Since the under coordinated surface sites are the active sites of the CuO surface⁹³⁻⁹⁴, the H_2 dissociation products on the less active surface sites (saturated Cu_4 and O_4 surface sites) was not evaluated.

Figure 2.4 Different possible surface adsorption configurations for H_2 adsorption on CuO (111), where the two dissociated hydrogen atoms, H^* , occupy a) two under coordinated surface Cu_3 sites, b) under coordinated surface Cu_3-O_3 pair sites, c) under coordinated surface O_3 sites, forming two hydroxyl species involving lattice oxygen $H_{latticeO}^*$ d) under coordinated surface O_3 site, forming a water-like structure involving lattice oxygen ($H-O_{Lattice}-H$)*. Peach, red and white balls represent Copper (Cu), Oxygen (O) and Hydrogen (H) atoms respectively.

An initial free energy calculation at reaction temperatures for the four configurations mentioned above rendered H_2 dissociation on two Cu_3 atoms (*cf* Fig. 2.4a) and between Cu_3 - O_3 atoms (*cf* Fig. 2.4b) to be unfavorable irrespective of the U value chosen. Hence, only two of the H_2 adsorption configurations (*cf* Fig. 2.4c and 2.4d) were possible on the CuO (111) surface.

Figure 2.5 Surface adsorption configuration for H_2 adsorption on CuO , where the two dissociated hydrogen atoms, H^* occupy a single lattice oxygen, forming $(H-O_{Lattice}-H)^*$ configuration with $Cu-O$ bond length of $2.00 \text{ \AA}$ and, the $O-H$ bond lengths of 0.973 and $1.022 \text{ \AA}$ and HOH bond angle of 107.62° . Color code is the same as Fig. 2.4.

It is interesting to note that in the $(H-O_{Lattice}-H)^*$ configuration (*cf* Fig. 2.5), the lattice O atom, O_O (Kröger-Vink Notation) gets pulled out from the surface by $2 \text{ \AA}$, leaving a surface vacancy, V_O (Kröger-Vink Notation). Similar structures were also found by Maimaiti et al⁸⁷ and Bersani et al¹⁰². The formed water-like structure has the $O-H$ bond lengths of 0.973 and $1.022 \text{ \AA}$ and HOH bond angle

of 107.62° , as compared to a free gas phase water molecule with O-H bond lengths of $0.974 \text{ \AA}$ and HOH bond angle of 104.45° . These bond distances and angles did not change significantly for different U values.

2.3.5 Surface species characterization using DRIFTS

As discussed above, the dissociation of H_2 leads to various possible adsorption configurations, and to identify the adsorbed surface species along the reaction coordinate, *in situ* DRIFTS analysis of H_2 reaction with CuO surface at the chemisorption temperature of 40°C was carried out. The IR spectra were recorded at successive time intervals to gauge the evolution of various surface O-H species, and the reaction proceeded with the instantaneous evolution of a sharp peak (3595 cm^{-1}) in the O-H Stretching region, which was getting saturated at the reaction time of 4 minutes, as shown in Fig. 2.6. The other O-H stretching peaks at 3629 cm^{-1} and 3500 cm^{-1} (broad) started to develop at 4 minutes and continued to grow as the reaction proceeded. The wide band in the H-O-H bending region ($1450\text{-}1650 \text{ cm}^{-1}$) began to evolve slowly and did not saturate even after 27 minutes of the reaction. This confirmed the presence of H-O-H bond in the equilibrium adsorption configuration¹⁰³⁻¹⁰⁵.

To comment on the evolution of adsorption configurations and establish the IR spectra peak numbers to corresponding O-H bonds, an associated FTIR study consisting of two experiments was performed: (i) the activation of CH_4 on CuO, and (ii) the adsorption and splitting of H_2O on CuO.

Figure 2.6 In-situ DRIFT spectra at consecutive time intervals for H₂ (5% H₂/95% Ar) adsorption on CuO at a constant temperature of 40°C, shows a) O-H bond stretching region and b) H-O-H bond bending region. Symbols: (*) 3595 cm⁻¹; (#) 3629 cm⁻¹; (♦) 3500 cm⁻¹

In (i), methane was passed over dry CuO surface at the 300° C, which is high enough to activate the first C-H bond with energy barriers⁹⁴ of 76.6 kJ mol⁻¹, as per the following reaction:

* denotes the active surface site and $H_{LatticeO}^*$ denotes the hydrogen from C-H cleavage that is adsorbed on the O₃ site. An important point to note here is that even though the methyl species can further oxidize, each subsequent C-H activation will also lead to more $H_{LatticeO}^*$ species. Hence, the $H_{LatticeO}^*$ formed as the product of this reaction should be the predominant -OH species in the system at this temperature. This is consistent with the IR results as shown in Fig.

2.7a, where only one sharp O-H stretching peak was observed in the O-H stretching region at 3595 cm^{-1} , suggesting the splitting of methane C-H bond, as shown in equation 17.

Figure 2.7 DRIFT spectra for (a) activation of CH_4 on as-synthesized CuO and b) adsorption and splitting of H_2O on as-synthesized CuO. Symbols: (*) 3595 cm^{-1} ; (•) 3650 cm^{-1} ; (♦) 3250 cm^{-1} .

In (ii), dry helium was purged through a pre-moisturized CuO surface to remove any gas phase moisture and retain only the surface adsorbed H_2O . This sample was then heated at a temperature of 300°C , to initiate water splitting as per the following reaction:

, where * denotes the active surface site. $(\text{OH})_{\text{Cu}}^*$ denotes the OH species (where the oxygen is from the split water) adsorbed on the surface Cu_3 site and $\text{H}_{\text{LatticeO}}^*$ denotes the hydrogen from split water that is adsorbed on lattice O_3 site. IR spectra as shown in Fig. 2.7b clearly presented two sharp O-H stretching peaks ($\approx 3595\text{ cm}^{-1}$ and $\approx 3650\text{ cm}^{-1}$) and one broad O-H stretching peak (which corresponds to the hydrogen bonded -OH species¹⁰⁵).

By having common OH species in the products (Equation 17 and 18) and comparing the IR spectra (*cf* Fig. 2.7a and 2.7b), it is confirmed that the sharp peaks at 3595 cm^{-1} and 3650 cm^{-1} correspond to $H_{LatticeO}^*$ and $(OH)_{Cu\text{ site}}^*$ species respectively. The above insights about the frequencies of various O-H peaks and the corresponding surface species is applied to understand the IR spectrum of the H_2 reaction on CuO (*cf* Fig. 2.6) and it is concluded that:

- (i) Instantaneous evolution of sharp peak at 3595 cm^{-1} ($H_{LatticeO}^*$) established H_2 being dissociatively chemisorbed over two different lattice oxygens (*cf* Fig. 2.4c) as the first adsorption configuration
- (ii) The broad band in the H-O-H bending region ($1450\text{-}1650\text{ cm}^{-1}$) confirmed the presence of H-O-H bond in the equilibrium adsorption configuration and established the $(H-O_{Lattice}-H)^*$ configuration (*cf* Fig. 2.4d) as the equilibrium adsorption configuration. O-H stretching peaks at 3500 cm^{-1} (broad) and 3629 cm^{-1} correspond to the stretching vibrations of two O-H bonds of $(H-O_{Lattice}-H)^*$ configuration.

Based on the above, it is proposed that the H_2 adsorption is a series reaction with $H_{LatticeO}^*$ (*cf* Fig. 2.4c) being the first intermediate and $(H-O_{Lattice}-H)^*$ configuration (*cf* Fig. 2.4d) being the equilibrium adsorption configuration.

2.3.6 Comparison of experimentally measured and DFT+U calculated adsorption enthalpies

DFT+U calculations were performed for the adsorption of H_2 with systematic increments in U, to calculate the adsorption energy for both, the intermediate ($H_{latticeO}^*$) and equilibrium adsorption configuration ($(H-O_{Lattice}-H)^*$) on the surface and added the ZPE and enthalpy temperature correction factors to determine the enthalpy of adsorption. The influence of U-value on computed adsorption enthalpies is reported in Fig. 2.8. The calculated adsorption enthalpy differed by 40 kJ mol^{-1} & 100 kJ mol^{-1} (for the same range of U-values) for the intermediate (*cf* Fig. 2.8a) and for the equilibrium (*cf* Fig. 2.8b) configuration, respectively. The comparison of DFT+U calculated adsorption enthalpies to experimental chemisorption enthalpies is shown in Fig. 2.9, and it was observed that the U-value of 4.5-5.5 eV correctly estimates the experimental adsorption enthalpy. The influence of U-value on adsorption enthalpies is ascribed to the increase in electron localization with an increase in the onsite potential U. With more localization of electrons, their transfer between the surface and adsorbate is restricted, hence weaker adsorption is observed with each incremental U-value. Hydrogen chemisorption energy has been reported and accepted to be a suitable descriptor for the reactivity of metal oxide mediated hydrogen abstraction reactions in hydrocarbons^{50, 106-109}. Hence, due to the existence of this linear correlation between the activation barrier and H chemisorption energy, it is suggested that the above determined U value, 4.5 – 5.5 eV (based on hydrogen

adsorption enthalpies) would be appropriate to investigate hydrocarbon activation and oxidation on CuO too.

The bulk property optimized U-value of 7 eV which is widely used to model catalytic reactions over CuO, underestimated the experimental adsorption energies by 30 kJ mol⁻¹ (*cf* Fig. 2.9) and thus failed to predict the correct reaction energetics and adsorption energies. This underestimation of adsorption energies by U-value of 7 eV was a direct result of the over-localization of valence d-electrons due to the application of a larger U-value than required. It is a common practice to determine the U-value for a system in a semi-empirical way, through seeking agreement with available experimental measurements of certain bulk properties or bulk redox energies and using these bulk determined U values to evaluate surface reactions and energetics. It is shown that the bulk determined U-value and the U-value that determined the correct surface reaction energetics are different.

Figure 2.9 Variation of adsorption enthalpy with incremental U -values for DFT+ U calculations for a) H_{LatticeO}^* , intermediate adsorption configuration and b) $(H-O_{\text{Lattice}}-H)^*$ equilibrium adsorption configuration for H₂ adsorption on CuO. Peach, red and white balls represent Copper (Cu),

Figure 2.8 Comparison of DFT calculated adsorption enthalpies for the equilibrium configuration to the experimental adsorption enthalpies.

Table 2.2 Desorption energy (kJ mol⁻¹) of ($H-O_{Lattice}-H$)* adsorption configuration forming gas phase water for different U values.

U Value (eV)	Desorption Energy (kJ mol ⁻¹)
5	68.01
7	68.54

To determine the effect of U value on the desorption reaction, the desorption energy (equation 16) for the ($H-O_{Lattice}-H$) * configuration was calculated for the U-value of 5 and 7 eV and it was quantified that the choice of U-value does not affect the desorption energy, as shown in Table 2.2. This signifies that once the lattice oxygen has been consumed in the reaction, leaving a reduced (partially or fully) surface, the influence of the U value on the reaction energy is not significant. Hence, U value of 5 eV (from the range 4.5-5.5 eV) should be used for the entire surface catalytic reaction over CuO (111) surface. Hence, further emphasizing that the choice of U value (4.5-5.5 eV) not only replicates the adsorption energies but is able to correctly describe entire reaction energetics, including product desorption.

To investigate H-H lateral interaction and the effect of U value on it, hydrogen coverage in the first adsorption configuration ($H_{latticeO}^*$) was systematically increased and it was observed that lateral interactions are insignificant up to 4 chemisorbed hydrogens in the unit cell. The effect of lateral interactions with the

complete coverage of hydrogens on active O₃ sites (6 hydrogen atoms) is also only 7% of the total energy. It is also observed that these lateral interaction energies do not change with the change in U value.

The above work compares theoretical and experimental adsorption energies along with surface-adsorbate interactions with respect to different adsorption configurations on different surface-active sites. The U value range presented in the article is benchmarked with PBE exchange-correlation functional and does not change significantly with the addition of van der Waals corrections (long-range interactions between the adsorbate and transition metal oxide surface). The presented U value range correctly accounts for the excessive electronic delocalization in CuO catalyzed surface reactions, independent of the vdw interactions. Hence, this U value should, in principle, be valid for reactions where van der Waals interactions may affect reaction energies, although a separate benchmarking for choosing the correct vdw corrections to DFT functional may still be needed in such a case. This DFT+U benchmarking procedure covers the entire reaction coordinate from reactant chemisorption and splitting, surface species reaction, vacancy formation and product desorption. It includes the effects of different magnetic spin ordering configurations, the participation of lattice oxygen in the reaction, the surface reduction and change in oxidation state of surface atoms due to the vacancy and product formation. It provides a method to determine a U-value which is valid for the entire reaction over a TMO surface.

2.4 Summary and Conclusions

The current chapter presents a DFT+U benchmarking study for surface catalytic reactions over CuO surface, using H₂ as a probe molecule, combined with chemisorption experiments and surface and reaction species characterization using FTIR technique. CuO nano-pellets are synthesized using precipitation method with CuO(111) surface as the most exposed facet. The experimental H₂ adsorption enthalpy on as-synthesized CuO is observed to be 42.2-60.8 kJ mol⁻¹. Adsorption (dissociative) configurations along the reaction coordinate are determined by performing in-situ infrared analysis at adsorption temperatures. The systematic variation of U for DFT+U calculations shows that the U-value influences H₂ adsorption enthalpies up to 100 kJ mol⁻¹ for different adsorption configurations. For the IR validated equilibrium configuration, calculated adsorption enthalpies are compared with the experimental enthalpy of adsorption and conclude that a U-value of 4.5-5.5 eV correctly estimates the adsorption energetics. It is also shown that the U-value of 7 eV, as determined by fitting against various bulk properties of CuO, is an overestimation of the introduced energy penalty and leads to an underestimation of the adsorption energy. Although the benchmarking method uses H₂ as a probe molecule, the evaluated U value can be employed to other hydrocarbon-based surface catalytic reactions over CuO(111). This work establishes a benchmarking procedure that encompasses the effect of various surface-adsorbate interactions (dissociation, chemisorption, and desorption) and a dynamic surface environment to present a surface specific approach to determine the U-value for TMO catalyzed reactions.

This method can be applied to determine the appropriate U-value for other TMOs using a suitable choice of the probe molecule and experimental data to model and simulate their catalytic surface reactions accurately.

3 Synergistic application of XPS and DFT to investigate Metal Oxide Surface Catalysis

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3.1 Introduction

Transition metal oxides (TMOs) are widely used in the form of pure, supported, and zeolite incorporated structures as catalysts for various industrially important reactions like chemical looping combustion,^{27, 110} selective oxidation,¹¹¹⁻¹¹⁷ and dehydrogenation of hydrocarbons to produce multiple high-value chemicals.¹¹⁷⁻¹¹⁹ Catalytic performance of TMOs for a particular reaction or a product is an interplay between (i) surface characteristics, such as the degree of unsaturated sites, acid-base characteristics, facet distribution (presence of one or more dominant facets),^{51, 119} lattice oxygen binding energies, ease of vacancy formation, presence of cationic or anionic vacancies, and the type and degree of doping^{111, 116, 120} and, (ii) adsorbate-surface interactions. Presence of different kinds of metal and oxygen sites^{51, 113, 119, 121} adds to the limitations of experimental surface science techniques^{59, 122} in the identification and

quantification of the number of active sites,^{59, 122-124} subsequently making it challenging to determine the turn-over-frequency for metal oxides. As discussed in section 1.5, TMO catalyzed reactions are often complex, composed of multiple, series and parallel elementary reactions, leading to the dynamic environment of the surface under reaction conditions. This makes it difficult for standalone experimental surface characterization techniques to conclusively determine surface species and reaction intermediates under reaction conditions for this class of catalysts. Therefore, it is vital to develop novel approaches that integrate the surface sensitive experimental techniques and theoretical tools to gain a better understanding of the effects of surface characteristics on the catalytic activity of TMOs and to determine the surface species and intermediates, thus paving a way for the design and development of more active and selective TMO-based catalysts.

As discussed in section 1.6, when conventional DFT calculations are implemented for strongly correlated systems such as TMOs, the description of electron-electron interactions (in DFT) lead to a systematic error causing unphysical delocalization of electrons.¹²⁵ To overcome this shortcoming, DFT + U remains one of the most widely used methods to correctly account for this electron delocalization due to its add-on nature and marginally additional cost over standard DFT methods.^{69, 84, 126} However, determination of the appropriate U value for a TMO poses another challenge. In literature, the U value is determined either from first principles calculations (constrained random phase

approximation (cRPA)⁷⁶ or linear-response constrained DFT¹²⁷) or, more extensively from semi-empirical fitting against bulk physical or redox properties⁸⁴. These methods are mainly suited for bulk TMO applications and might not always be interchangeably used for surface catalyzed reactions, since the electronic properties of surface sites, and, even the surface compositions of metal oxides, could be very different from those of the bulk.^{59, 122} Huang et al¹²⁸ highlighted this inconsistency by using the U-value based on bulk properties for studying surface phenomena and also showed that the inclusion of adsorbate-surface interactions and adsorption configurations lead to an improved and relevant estimate of U-value (2 eV vs. 4-5 eV based on bulk properties of CeO₂). Our recent work, (presented in chapter 2 of this thesis) has also established that the bulk property optimized U value of 7 eV for CuO, fails to predict hydrogen chemisorption energy on CuO(111) by 30 kJ mol⁻¹.¹²⁷ Therefore, whilst coupling experimental and theoretical approaches (DFT+U) to provide mechanistic insights into TMO catalyzed reactions is vital for the development of novel heterogeneous catalysts, it is equally central to determine the appropriate U-value, based on TMO surface-dependent properties rather than its bulk properties.

X-ray photoelectron spectroscopy (XPS) with a small photoelectron penetration depth of ~ 5nm is one such surface-sensitive technique that is extremely responsive to changes in the chemical state and the environment of surface species,¹²⁹⁻¹³⁰ and can be used as a gauge to determine the U value for

TMOs. The chemical shift in the core level binding energies (CLBEs) is widely used to identify the structure and binding sites of the surface species.¹³⁰⁻¹³³ But, as discussed earlier, due to the dynamic nature of surface reactions and participation of surface lattice oxygen in the reactions, interpreting the XPS spectra for complex surface reactions on TMOs can be exhausting (difficulty in deconvolution increases with the increasing type of moieties, the contribution from bulk catalyst and gas phase species).

DFT can be employed to address this challenge in XPS spectral analysis to assist in the identification of adsorbates, and XPS spectral peak assignment for TMO catalyzed reactions. This combined XPS and DFT-computed XPS approach is evolving as a new characterization technique to study reaction mechanisms, identify stable intermediates, understand the nature of active sites and evaluate the catalyst performance, but, the current application is limited to systems where U value does not apply (non-semiconductors). Some excellent examples of this approach include the identification and quantification of surface intermediates during Guaiacol thermal decomposition on Pt(111) in the recent work by Hensley et. al.¹³⁴, the structural characterization of bimetallic Pd-Fe alloy catalyst for the conversion of furfural by Pinto et al.,¹³⁵ the detection of vacancy and substitution defects in a nitrogen-containing graphene-like matrix by Artyushkova et al.¹³⁶ and the insightful investigation into the electronic properties for self-assembled monolayer structures by Taucher et al.¹³⁷ It is expected that such integrated methods could also be extended for studying

heterogeneous catalysis over TMOs; however, the application of such combined approaches for TMO catalyzed reactions requires U value estimation for DFT+U so that predictions are accurate and reliable. Therefore, provided that the appropriate U value is known, theoretical (DFT computed XPS) methods could be extended to accurately interpret experimental XPS shifts and assign them to respective surface moieties to provide mechanistic insights into TMO catalyzed reactions, to guide the development of more active and selective TMO-based catalysts.

In the current chapter, taking CuO as a model TMO, an integrated experimental (XPS) and theoretical (DFT+U) approach is demonstrated to (i) determine the optimum U value for the TMO and, (ii) identify and assign adsorbate species to experimental XPS peaks. While the experimental XPS CLBE shifts are used to determine the appropriate U value for DFT+U calculations, DFT+U calculations, in return and concurrently, assist incorrect assignment of experimental XPS CLBE shifts to their respective adsorbates, establishing the synergistic nature of this approach. To the best of our knowledge, the current study is the first work of determining various surface species, their XPS BEs and the optimum U value for a TMO using XPS and DFT techniques simultaneously.

The experimental and computational methods used in the current work are presented in section 3.2, and CuO morphology and surface characterization results are presented in section 3.3.1. The experimental XPS binding energies and

chemical shift measurements are reported in section 3.3.2, followed by the discussion of computationally predicted surface species and their XPS shifts in section 3.3.3. The experimentally measured and DFT+U calculated XPS shifts and adsorbate structures are compared in section 3.3.4. Summary and conclusions from the current chapter are discussed in section 3.4.

3.2 Experimental and Computational Methods

3.2.1 Catalyst synthesis and characterization

Copper (II) Oxide Nanoleaves (CuO NLs) were synthesized *via* low frequency (20 kHz) ultrasonic irradiation method¹³⁸⁻¹⁴¹ and analytical grade of all the reagents were used without further purification. In a typical synthesis method, 40 mL of 0.25 M NaOH aqueous solution was added to 10 mL of 0.5 M Cu(NO₃)₂ aqueous solution and a sky-blue suspension was obtained. This suspension was subsequently exposed to low-frequency ultrasound irradiation. Ultrasound was generated by a Digital Sonifier S-250D from Branson (power of standby, $P_o = 27.0$ W; nominal electric power of the generator, $P_{elec} = 8.2$ W). A 3.2 nm diameter tapered microtip probe operating at a frequency of 19.95 kHz was used. The volume acoustic power of this system was $P_{acous.vol} = 0.25$ W.mL⁻¹ in water (determined by calorimetry measurements). The ultrasound probe was immersed directly in the reaction medium, and a Minichiller cooler (Huber) was used to control the reaction temperature at 25 °C. On completion of sonication at the desired time, the dark blue or black precipitates were washed thoroughly with distilled water and dried in an oven at 60 °C overnight. This method provides a

fast and efficient synthesis route to produce highly crystalline, pure, and uniform CuO 2D-nano leaves (NLs) at room temperature (25 °C), as well as involves short sonication synthesis time and the use of environmentally benign reactants. It does not require any surfactant, post-calcination treatment or template as usual, thus simplifying the downstream procedure.

Crystallographic analysis of the CuO NLs was performed using XRD measurements in 2θ mode on a Bruker AXS D8 diffractometer with $\text{Cu}_{K\alpha}$ ($\lambda = 0.154056 \text{ \AA}$) radiation at 40 kV and 20 mA. XPS was performed on a Thermo Escalab 250 spectrometer. The binding energy was calibrated using C1s (284.6 eV) as a reference. The as-synthesized CuO NLs morphology was also studied by SEM (JEOL JSM 6700F field emission), TEM and HR-TEM (JEOL JEM-2100F).

3.2.2 Computational Details

All the calculations in the current work were performed with the periodic plane-wave implementation of Density Functional Theory (DFT) using VASP (Vienna ab initio simulation package)¹⁴²⁻¹⁴³ with Projector Augmented Wave (PAW) scheme⁹⁸ (plane wave cut-off energy of 450 eV). Calculations were performed using DFT with Generalized Gradient Approximation (GGA). Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional⁹⁶ is widely used exchange-correlation functional to study transition metal oxide catalyzed reactions, and the same has been employed in our work. A k-points sampling of 4x4x1 within the Monkhorst-pack scheme is used for integration over the

Brillouin zone. Integration is performed utilizing the tetrahedron method with Blöchl corrections. The convergence criteria for total energy and interatomic forces was set to 10^{-6} eV per unit cell and 0.01 eV/Å, respectively. All the calculations were performed with spin polarization owing to the antiferromagnetic ground state of CuO.^{121, 127, 144-145}

All the calculations have been performed on the most stable and dominant exposed facet of as-synthesized CuO, CuO(111). The lattice parameters (a, b, c, β) for the monoclinic crystal structure of CuO are optimized for all different U values chosen in this study (ranging from 0 to 9 eV) and used for further calculations for the respective U values. The obtained lattice parameters are shown in Table 3.1. CuO(111) surface is modeled with a periodic slab structure with the vacuum thickness of 12 Å above the topmost layer to avoid interactions between different slabs. The structure used to model CuO(111) surfaces is illustrated in Fig. 3.1. The Cu 2p_{3/2} and O 1s core-level binding energies were calculated using DFT with the final state approximation as implemented in VASP.^{132-133, 146}

Table 3.1 Summary of the calculated Lattice Parameters (a, b, c, and β) for CuO at different U values

U	a (Å)	b (Å)	c (Å)	β (°)
0	4.4075	3.8648	5.1672	92.1597
3	4.4591	3.7635	5.1924	94.6419
4	4.5067	3.6956	5.1970	96.0963
5	4.5231	3.6636	5.1899	95.8377
6	4.5437	3.6302	5.1815	96.1702
7	4.5597	3.6059	5.1782	96.3385
8	4.5836	3.5723	5.1708	96.9091
9	4.5872	3.5590	5.1668	97.2440

Figure 3.1 Representation of the system used to model the CuO(111) surface, illustrating the Number of layers, Slab size and Vacuum thickness. The oxygen atom in the central layers representing the O_{bulk} is also marked in the figure. *Peach and red balls represent copper (Cu) and oxygen (O) atoms, respectively.*

Among the three types of magnetic ordering (bulk, line-by-line, and layer-by-layer) that can be assigned to CuO(111) structure, as described by Hu et al.,¹⁴⁵ the bulk-like magnetic configuration is the most stable arrangement, and therefore, used for all calculations in our study. Indeed, our test showed that the total energy for four layers CuO(111) p(4×2) slabs computed at $U = 7$ eV using bulk-like magnetic ordering is -0.36 eV and -2.39 eV more stable than the line-by-line and layer-by-layer configurations, respectively. The bulk-like magnetic arrangement of CuO(111) is illustrated in Fig. 3.2.

Figure 3.2 Magnetic arrangement for CuO(111), showing Bulk-like magnetic spin ordering (where the alternate atoms of Cu in any particular row have opposite magnetic spins). The upward and downward arrows represent the positive and negative spin, respectively. *Peach and red balls represent copper (Cu) and oxygen (O) atoms, respectively.*

3.2.2.1 Convergence test for parameters of the CuO model:

3.2.2.1.1 Slab size (geometry)

The convergence test to choose the slab size $p(a \times b)$ was performed by comparing surface lattice oxygen binding energy of the CuO(111) structure with the varying size of modeled slab¹⁴⁷. The binding energy of lattice oxygen is computed as the reaction energy of the following equation:

$$\Delta E = E(Cu_nO_{n-1}) + E(H_2O(g)) - E(Cu_nO_n) - E(H_2(g)) \quad (20)$$

$E(Cu_nO_n)$ and $E(Cu_nO_{n-1})$ are the computed total energies for clean CuO(111) surface and CuO(111) with one surface oxygen vacancy, whereas $E(H_2O(g))$ and $E(H_2(g))$ are the total energies for H₂O and H₂ in the gas phase, respectively. As can be seen from the data presented in Fig. 3.3, the converged slab size of (4×2) is used to model the CuO(111) surface in our study.

Figure 3.3 Convergence test for the CuO(111) slab size by calculating the binding energy of lattice oxygen (as the reaction energy for eq. 1). a) Reaction energy variation with increasing value of parameter a , keeping the parameter b constant, and b) Reaction energy variation with increasing value of parameter b , keeping the parameter a constant.

3.2.2.1.2 Number of layers

In contrast to the convergence test to choose the slab size, the number of layers (thickness of the model) has very little influence on the surface oxygen binding energy. However, the XPS core-level binding energy for atoms is very sensitive to the local environment, atomic arrangement and also changes with its depth in the slab/system (on the surface, inner layers and in bulk).^{132-133, 148-149} Therefore, it is important to model the slab thickness large enough to ensure that the atoms at the central layers are capable of representing the bulk site (to act as a reference for calculating core-level shifts). For systems with incremental slab layers, O 1s and Cu 2p_{3/2} surface core-level shifts were computed for the surface oxygen (saturated/4-coordinated, O_{sub}, and unsaturated/3-coordinated, O_{suf}) and copper (saturated/4-coordinated, Cu_{csa} and unsaturated/ 3-coordinated, Cu_{cus}) atoms with

reference to representative atoms at the center layer. The data is presented in Fig.

3.4

As is shown in Fig. 3.4, the computed Cu 2p_{3/2} surface core-level shifts (for both Cu_{cus} and Cu_{csa} sites) change very little with different numbers of CuO(111) layers. However, the O 1s surface core-level shifts (for both O_{suf} and O_{sub} sites) are quite sensitive to the number of layers and are only converged at the thickness of 7 layers. Therefore the structure of p(4×2) slab of CuO(111) surfaces with seven layers to model the synthesized CuO NLs catalyst and the O at the center layer (fourth layer from the topmost layer and is highlighted in Fig. 3.1) is used to represent the bulk Oxygen atom.

Figure 3.4 Convergence test showing the variation in calculated Surface core-level shift with the increasing slab thickness (number of layers) for different surface atoms, O_{sub}, O_{suf}, Cu_{csa}, and Cu_{cus}.

3.3 Results and Discussion

Figure 3.5 Characterization of 2D CuO nanoleaves prepared using the sonochemical method. a) XRD patterns; b) a high magnification SEM image with a low magnification TEM image inserted; c) high-resolution TEM image (HRTEM)

3.3.1 CuO morphology and surface characterization

The X-ray diffraction (XRD) patterns (*cf* Fig. 3.5a) revealed signature peaks attributed to the monoclinic $c/2$ symmetry crystal structure of CuO (JCPDS card No. 80-1917), with dominating peak at $2\theta = 38.6$ and 35.58° , which are characteristics for CuO(111) and CuO(-111) surfaces, respectively.^{112-113, 119} The morphology of the as-synthesized CuO was studied using a scanning electron microscope (SEM). A uniform leaf-like morphological structure (*cf* Fig. 3.5b)

was observed, which was strikingly consistent with the low magnification transmission electron microscopy (TEM) image (inset in Fig. 3.5b). High resolution TEM image (*cf* Fig. 3.5c) showed a clear and continuous lattice fringe with an inter-fringe d spacing of 0.234 nm (inset in Fig. 3.5c), characteristic for the [111] plane distance of monoclinic CuO^{113, 119} and confirmed the high-crystalline nature of the CuO 2D leaf-like morphology with CuO(111) as the dominant exposed facet. Owing to the sensitivity of core-level BEs towards the relative atomic arrangement and surface facets, it was crucial to obtain a single uniform facet exposed CuO(111). This also ensures that the measured experimental data for the as-synthesized CuO is comparable with theoretical data from DFT+U simulations using CuO(111) slab-modeled surface.

3.3.2 Experimental XPS B.E. measurements

XPS was performed on the as-synthesized CuO sample (*cf* Fig. 3.6). The XPS Cu 2p spectrum in Fig. 3.6a shows the peaks at 934.1 eV, and 954.2 eV which are assigned to Cu 2p_{3/2} and Cu 2p_{1/2}, CLBEs of CuO.^{119, 150} The appearance of shakeup satellite with peaks at ~942 eV and ~962 eV is also characteristic for the presence of Cu²⁺ and is unique for the Cu(II)O structure.¹⁵¹⁻¹⁵²

Figure 3.6 XPS spectra of CuO NLs. a) Cu p_{3/2} spectra and b) deconvolution of the O 1s spectra (showing 4 different peaks corresponding to the BEs of 529.7 eV, 531.4 eV, 533.2 eV, and 534.6 eV)

In our XPS analysis of the synthesized CuO sample, the strong shake-up satellites confirm the Cu (II) oxidation state and rule out the possibility of the existence of a Cu₂O phase. Furthermore, the Auger peak shape has also been analyzed, since an inspection of Auger peak-shape and position allows for the most accurate identification (Cu LMM level with BE of 915-918 eV). The Auger parameter recorded for the as-prepared CuO sample was 1851.3 eV with a Cu LMM of 917.1 eV (*cf* Fig. 3.7) which is a signature Cu LMM value for CuO. This value is strikingly consistent with literature reported values.^{151, 153}

Figure 3.7 Cu LMM Auger analysis of the as prepared CuO depicting the main peak position of Cu LMM at kinetic energy of 917.1 eV, a characteristic Cu LMM value for CuO.

The XPS O 1s spectrum is presented in Fig. 3.6b and the deconvolution of the spectrum show the presence of 4 different peaks with BEs of 529.7 eV, 531.4 eV, 533.2 eV, and 534.6 eV. The peak at 529.7 eV is assigned to the bulk lattice

oxygen of CuO, as established in the literature.^{119, 150-152, 154-157} Hence, with bulk lattice oxygen as the reference, the three shifts observed in the O 1s spectra are +1.7 eV, +3.5 eV, and +4.9 eV. These XPS shifts (and respective BEs) are widely detected in literature for CuO O 1s spectra, but the assignment of these BEs to surface moieties (and their adsorption configurations) is either not done or is inconsistent and disputed. For example, +1.7 eV shift can either correspond to the adsorbed oxygen species in molecular or dissociative form or hydroxyl species on the CuO surface,^{154, 156} +3.5 eV can correspond to surface hydroxyl or H₂O adsorbed on CuO,¹⁵⁴⁻¹⁵⁵ and +4.9 eV can correspond to H₂O or CO₂/CO₃²⁻ species adsorbed on CuO.¹⁵⁷⁻¹⁵⁹ This ambiguity limits the analysis and application of surface science techniques for TMO catalyzed reactions.

The current chapter focuses on these chemical shifts in binding energies of the core level electrons, with reference to the bulk oxygen CLBE and not on the absolute BE values due to, (i) the ability of DFT to compute the chemical shifts in BE of the core-level electrons accurately, and (ii) the sensitivity of BE core-level shifts to the change in the local reaction environment, adsorption sites and configurations. Therefore, the combination of experimental and theoretical XPS presented in this study benefits both theorists and experimentalists in this field by serving two purposes: estimation of the U value for a TMO and assignment of XPS peaks, in a synergistic manner.

3.3.3 Computationally predicted surface species and their XPS shifts and rationale behind selecting them

The exposure of as-synthesized CuO to air would allow the molecules from the atmosphere (mostly oxygen, water, and carbon dioxide), and their reaction products (like carbonates, bicarbonates, etc.), to interact and adsorb on the catalyst surface. Since the as-synthesized CuO surface may not be stoichiometric and may contain surface vacancies, all these probable adsorbates were examined (in different adsorption configurations), to the best of our ability, while considering both, perfect surface and surface with oxygen vacancies. The species considered in this evaluation are, (a) surface oxygen sites on perfect CuO(111), (b) surface oxygen sites with neighboring oxygen vacancy, (c) surface oxygen sites with neighboring copper vacancy, (d) adsorbed oxygen molecule in $\eta_1(\text{O})$ configuration, (e) adsorbed oxygen molecule on surface with oxygen vacancy, (f) adsorbed atomic oxygen, (g) adsorbed hydrogen, (h) adsorbed water on clean surface, (i) adsorbed water on the surface with neighboring oxygen vacancy, (j) surface hydroxyl, (k) adsorbed CO_2 in $\eta_2(\text{C},\text{O})$ configuration, (l) adsorbed CO_3 , (m) adsorbed HCO_3 , (n) adsorbed HCO_2 (resembling adsorbed HCO_3 , but with one oxygen being the surface lattice oxygen) species, (o) adsorbed NO, (p) adsorbed NO_2 and (q) adsorbed NO_3 as illustrated in Table 3.2, structures a-q. Structural details and the rationale behind selecting these moieties is discussed in the following subsections.

For the Cu 2p DFT XPS calculations, it was observed that the variation of Cu 2p CLBE shifts with reference to bulk Cu across different U values is extremely small (-0.11 eV and -0.12 eV for 3-coordinated Cu sites and -0.08 eV and -0.04 eV for 4-coordinated Cu saturated site at $U = 4.5$ and $U = 7$, respectively) and hence, the comparison of Cu 2p CLBE shifts might not be a suitable method for U value benchmarking.

Table 3.2 Structures and O 1s core level binding energy (CLBE) shifts with respect to the O 1s CLBE of bulk lattice Oxygen for different surface adsorbates on CuO(111) surface evaluated at (i) U value of 7 eV (highlighted in grey) (ii) at different U values (0 – 9 eV). If any of the three observed experimental shifts falls within the DFT calculated CLBE shift range, the DFT calculated shift range is highlighted in bold. Color code: peach, white, grey, and red balls represent Copper (Cu), Hydrogen (H), Carbon (C), and Oxygen (O) atoms respectively.

Structure	clean surface						O ₂ _vac		Cu ₂ _vac		O ₂ _ads - η ₁ (O)		O ₂ @O ₂ _vac		atomic O

	O ₁	O ₂	O ₁	O ₂	O ₁	O ₂	O ₁	O ₂	O ₁	O ₂	O ₁	O ₂	O ₁	O ₂	O ₁	O ₂
O 1s CLBE shift (eV)	-1.07	-0.39	-1.01	-2.09	+1.21	+0.74	+1.16	+0.88	-3.15							
Range for U = 0-9 ^b	-1.16 to -0.73	-1.09 to -0.71	-2.14 to -1.74	+0.66 to +1.87	+1.05 to +1.55	-3.50 to -1.96										
Structure	H _{ads}		H ₂ O _{ads}		H ₂ O@O ₂ _vac		OH-bridge		CO ₂ _ads - η ₂ (C,O)		CO ₃ _ads

	O ₁	O ₂	O ₁	O ₂	O ₁	O ₂	O ₁	O ₂	O ₁	O ₂	O ₁	O ₂				
O 1s CLBE shift (eV)	+2.02	+3.19	+3.11	-0.99	+1.42	+1.11	-2.32	-1.17								
Range for U = 0-9 ^b	+1.92 to +2.15	+2.98 to +3.37	+2.87 to +3.79	-1.34 to -0.15	+1.15 to +1.50	-2.59 to -0.93										
Structure	HCO ₃ _ads		HCO ₂ _ads		NO ₂ _ads		NO ₃ _ads

	O ₁	O ₂	O ₁	O ₂	O ₁	O ₂	O ₁	O ₂								
O 1s CLBE shift (eV)	+2.65	+0.46	+4.98	+2.52	+0.71	-1.66										
Range for U = 0-9 ^b	+2.36 to +3.74	+4.81 to +5.03	+1.97 to +2.91	+0.29 to +1.56	-1.03 to -0.23											

^b. For structures that have more than one type of Oxygen atom, the value is reported for O₁ only

3.3.3.1 Clean surface and surface with vacancies

The clean structure of CuO(111) involves different types of Cu and O atoms on the surface.^{51, 113, 119, 121, 144-145} There are two different types of surface Cu sites: the coordinatively saturated site where Cu is coordinated to 4 adjacent O atoms (Cu_{csa}) and the coordinatively unsaturated site where Cu is coordinated to only three adjacent O atoms (Cu_{cus}). The Cu_{cus} sites are widely reported as active sites for different reactions on CuO like oxidation,¹¹³ C-H activation, N-H oxidative coupling¹¹⁹, etc. Similarly, there are also two different types of surface O sites: the 4-coordinated site (O_{sub}) and the 3-coordinated site (O_{suf}), and the latter is also the active site for many reactions.^{51, 113, 119} The structure of clean CuO(111) surface is shown in Fig. 3.8a. Note that the O_{suf} and O_{sub} are denoted as O_1 and O_2 sites in the main text (Table 3.2, inset a)

Figure 3.8 Surface atomic arrangement of CuO(111) facet showing (a) Clean CuO(111), with 3-coordinated surface atoms (Cu_{cus} , O_{suf}) and 4-coordinated surface atoms (Cu_{csa} , O_{sub}), (b) CuO(111) surface with an Oxygen vacancy, and (c) CuO(111) surface with Cu vacancy on CuO(111) surface. *Peach and red balls represent copper (Cu) and oxygen (O) atoms, respectively.*

During the catalyst synthesis and reactions, surface vacancies can be generated and may alter the activity of the catalyst.¹⁶⁰⁻¹⁶⁴ This has been tested, and it is found that the coordinatively unsaturated sites (Cu_{cus} and O_{suf} sites) are

weakly bound to the surface (consistent with the study of Mamaiti et al.¹²¹) and two types of surface vacancies, namely Oxygen vacancy V_O (Kröger-Vink Notation) (*cf* Fig. 3.8b) and Cu vacancy, V_{Cu} (Kröger-Vink Notation) (*cf* Fig. 3.8c) can be formed on CuO(111) surface. In the current work, for the core-level shift calculations of systems containing vacancy, the core-level shifts of the O_{surf} site next to the vacancy are evaluated and reported.

3.3.3.2 Oxygen species

When the surface of CuO is exposed to the atmosphere, the O_2 molecule from the air can be adsorbed on the surface. The adsorption of O_2 on CuO(111) has been studied by DFT calculations and reported in the literature.^{145, 165} In line with that study, it is found that O_2 is strongly adsorbed on CuO(111) surface with the adsorption energy larger than 100 kJ/mol. There are two different configurations of O_2 adsorbed on CuO(111) surface: the di- σ structure where both two oxygen atoms are coordinated to surface Cu sites (*cf* Fig. 3.9a) and the top structure where only one O atom are coordinated to surface Cu site (*cf* Fig. 3.9b). Both these structures were also observed in the DFT study without using the Hubbard correction by Sun et al.¹⁶⁵ Our study show that the top site is ~ 12 kJ/mol more stable (computed at $U = 4.5$ eV, *cf* Fig. 3.9a,b), in consistence with the report by Hu et al.¹⁴⁵ Furthermore, the computed entropy at room temperature for the top-configuration (76.81 J/K.mol) is larger than the di- σ structure (49.18 J/K.mol), and therefore even if the O_2 adsorbs in the di- σ configuration at lower coverages, it can be converted to the top-configuration driven by the entropic difference

between those two configurations. The similar process was also reported for the conversion of di- σ to the top configuration for aldoses (glycolaldehyde, glyceraldehyde, and glucose) driven by the entropic driving force, as reported in our earlier study.¹⁴⁷

On defect containing CuO(111) surface with oxygen vacancy, O₂ adsorbs even stronger at the vacancy site, V_O (Kröger-Vink Notation) and the most stable configuration is presented in Fig. 3.9c. It is consistent with the observation reported by Sun et al.¹⁶⁵ The adsorbed O₂ is stable on clean CuO(111) surface (reported dissociated barrier is 269 kJ/mol) but could easily be dissociated into atomic adsorbed oxygen on defected CuO(111) with O vacancy, as was reported by earlier in a theoretical study¹⁶⁵ (reported activation barrier is only 77 kJ/mol) and in experiments.¹⁶⁶ In the latter scenario, surface atomic oxygen formed on CuO(111) surface and adsorbed most stable at the bridge site between two adjacent Cu_{cus} sites and the structure is illustrated in Fig. 3.9d, consistent with earlier reports.^{165, 167}

Figure 3.9 O_2 adsorption on $\text{CuO}(111)$ surface in (a) di- σ configuration; (b) top configuration and (c) at oxygen vacancy site of defected $\text{CuO}(111)$ surface. (d) Adsorption of atomic O on $\text{CuO}(111)$ surface. Adsorption energies computed at $U = 4.5$ eV are also indicated. *Peach and red balls represent copper (Cu) and oxygen (O) atoms, respectively.*

3.3.3.3 H-containing species:

Water and hydroxide species can be present on the CuO surface, either from the preparation method or via the adsorption from moisture in the atmosphere.^{127, 168-}

¹⁷⁰ However, the binding energy of water is within the magnitude of $\sim 60 \text{ kJ mol}^{-1}$

¹ and therefore H_2O can be considered to be physisorbed on $\text{CuO}(111)$ (*cf* Fig.

3.10a). However, the adsorption of H_2O at the oxygen vacancy site, V_{O} (Kröger-

Vink Notation) is stronger with the adsorption energy of $\sim 70 \text{ kJ/mol}$. The

configuration of H₂O adsorbed at Oxygen vacancy is also different since the H₂O is bent towards the surface forming H-bonding with the adjacent surface O_{suf} site (*cf* Fig. 3.10b). This H bonding configuration was also detected by FTIR analysis in our recent study.¹²⁷ Finally, the dissociation of H₂O on CuO(111) is quite feasible¹⁶⁸ with the computed activation barrier of 5 kJ mol⁻¹ (*cf* Fig. 3.10c), forming adsorbed OH and adsorbed H on the surface. In literature, the presence of OH on the surface of metal oxides are also detected from experiments.¹⁷⁰⁻¹⁷¹ There are two adsorbed configurations for surface OH on CuO surface: at bridge site (*cf* Fig. 3.10d) and top site (*cf* Fig. 3.10e), with the former is ~20 kJ mol⁻¹ more stable than the later and both these structures are considered for core-level shift calculations.

Atomic H adsorbs strongly at the 3-coordinated site O_{suf} site (*cf* Fig. 3.10f) are also widely reported in literature^{51, 113, 127, 145}. It is also important to mention that the hydrogens adsorbed on adjacent O_{suf} sites can react to form adsorbed H₂O, leading to popping out of the coordinated O_{suf} atom (resulting into O vacancy) (*cf* Fig. 3.10b), as observed by experimental¹²⁷ and theoretical studies.¹²¹

Figure 3.10 a) H₂O adsorption on clean CuO(111); (b) H₂O adsorption at oxygen vacancy on defected CuO(111) surface; (c) Transition state of H₂O dissociation on CuO(111); Adsorbed OH at (d) bridge site and (e) top site; (f) Adsorbed atomic H at surface O_{surf} site. *Color code: Peach, white, and red balls represent Copper (Cu), Hydrogen (H), and Oxygen (O) atoms respectively.*

3.3.3.4 Carbonaceous species

During the exposure of CuO(111) surface to the atmosphere, the atmospheric CO₂ molecule can be adsorbed on the CuO surface. There are two different configurations for CO₂ adsorption on CuO(111) surface, called $\eta_2(\text{C},\text{O})$ (*cf* Fig. 3.11a) and $\eta_3(\text{C},\text{O},\text{O})$ configurations (*cf* Fig. 3.11b). Both these structures are also reported in the literature.¹⁴⁴ Our study shows that the $\eta_2(\text{C},\text{O})$ is ~39 kJ/mol more stable than the $\eta_3(\text{C},\text{O},\text{O})$ configuration, consistent with DFT study of Mishra et al.¹⁴⁴ and therefore only the $\eta_2(\text{C},\text{O})$ configuration was chosen for core-level shift calculations.

Figure 3.11 CO₂ adsorption on clean CuO(111) in (a) $\eta_2(\text{C},\text{O})$ configuration and (b) $\eta_3(\text{C},\text{O},\text{O})$ configuration; (c) adsorbed bicarbonate HCO₃ on clean CuO(111) surface; (d) adsorbed HCO₂ on clean CuO(111) surface; (e) adsorbed HCO₃ at oxygen vacancy; (f) adsorbed carbonate CO₃; (g) Initial, transition and final states for the reaction CO₂ + H₂O = HCO₂ + OH. *Color code: Peach, white, grey, and red balls represent Copper (Cu), Hydrogen (H), Carbon (C), and Oxygen (O) atoms respectively.*

The adsorption of atmospheric CO₂ on metal oxide surfaces has been studied experimentally in literature¹⁷⁰⁻¹⁷⁴ and surface adsorbed bicarbonate and carbonate species were identified upon adsorption.

The time-dependent FTIR analysis in the studies by Gankanda et al.¹⁷⁰ and Tanvir et al.¹⁷⁴ have revealed the formation and presence of bicarbonate species upon the adsorption of CO₂ on CuO surface. Therefore different configurations of adsorbed HCO₃ on CuO(111) have been considered in our study, including the adsorption of HCO₃ on a clean surface (*cf* Fig. 3.11c), adsorption of HCO₂ on lattice oxygen (*cf* Fig. 3.11d) and adsorption of HCO₃ at oxygen vacancy (*cf* Fig. 3.11e). It is important to note that in structure (*cf* Fig. 3.11d), the adsorbate is HCO₂ but since it coordinates with the lattice oxygen, it resembles the structure of adsorbed HCO₃. The lattice oxygen in Fig. 3.11d might be popped out from the surface and forms the adsorption of HCO₃ at oxygen vacancy V_O (Kröger-Vink Notation) in Fig. 3.11e, but the later structure is ~20 kJ/mol less stable than the former, so only the structures in Fig. 3.11c and 3.11d are considered for core-level shift calculations. The study of the reaction mechanism for the formation of HCO₂/HCO₃ is beyond the scope of the current study and was not studied in detail. Nonetheless, HCO₂ is proposed to be formed from the reaction between adsorbed CO₂ and H₂O via the reaction: CO₂ + H₂O = HCO₂ + OH. The Initial state, transition state and final state of this reaction are presented in Fig. 3.11g with the activation barrier of 82 kJ mol⁻¹, which is feasible at room temperature.

Finally, since carbonate CO_3 , is another readily observed molecule upon the exposure of CuO to atmospheric CO_2 ,^{170, 173-174} the adsorption configuration of CO_3 is included for core-level shift calculations as well. Similarly, to the case of bicarbonate HCO_3 , in the most stable adsorption configuration of CO_2 (*cf* Fig. 3.11a) wherein the C atom coordinates to the lattice oxygen and hence it also resembles the adsorbed structure of carbonate CO_3 .

3.3.3.5 NO_x Species

The following reaction steps occur during the synthesis of CuO NLs via sonochemical method¹⁴¹ using $\text{Cu}(\text{NO}_3)_2$ as a precursor:

Where))) denotes sonication method

Therefore, adsorbed NO_3 could be present on CuO(111) surface in a noticeable amount. The structure of the adsorbed NO_3 is shown in Fig. 3.12a. Besides that, atmospheric NO_x species (NO and NO_2) could also adsorb on CuO(111) surface,¹⁷⁵ however, their adsorbed concentration should be quite small (atmospheric concentration ~ppb). NO adsorption is the most stable on CuO(111) in the top configuration (*cf* Fig. 3.12b) while NO_2 adopts the most stable bi-dentate configuration (*cf* Fig. 3.12c), which is consistent with the study of Cao et al.¹⁷⁵

Figure 3.12 Adsorption configuration for (a) NO_3 ; (b) NO ; (c) NO_2 in bidentate configuration *Color code: Peach, blue, and red balls represent Copper (Cu), Nitrogen (N), and Oxygen (O) atoms respectively.*

3.3.4 Comparison of experimentally measured and DFT+U calculated XPS shifts

Since the U value of 7 eV is most commonly established in the literature for CuO and obtained by semi-empirical fitting of bulk physical properties (band gap, magnetic momentum, and bulk lattice parameters),^{121, 144} the study was initiated with the computation of O 1s core-level shifts with reference to bulk lattice oxygen for the structures in Table 3.2 at U of 7 eV. However, none of the possible, proposed, or reported structures could reproduce any of the experimentally observed chemical shifts of +1.7 eV, +3.5 eV or +4.9 eV at this U value. This is in line with our recent benchmarking results where the bulk value optimized U value of 7 eV failed to predict the reaction energetics correctly.¹²⁷ In that study, the hydrogen chemisorption enthalpy computed at U value of 7 eV was higher than the measured experimental value by 20 - 40 kJ mol^{-1} and the U value between 4.5 to 5.5 eV was suggested as an appropriate value.

Since the widely applied U value of 7 eV fails to predict the experimentally observed O 1s core-level shift, the calculations (Lattice parameter, Geometry optimizations, and CLBE shifts) are extended for different U values ranging from 0 to 9 eV to gauge the effect of U value on the O 1s chemical shifts. The variation in O 1s chemical shifts for different U values (0 to 9 eV) is presented in Table 3.2. It is observed that the change in U value does not change a positive BE shift into negative and vice-versa. Since the experimentally observed O 1s core-level shifts are all positive (*cf* Fig. 3.2b), the structures associated with the negative shifts are not considered for further evaluation. Among the structures with positive shifts, adsorbed O₂ in $\eta_1(\text{O})$ configuration (structure d in Table 3.2 with DFT computed CLBE shift range from +0.66 to +1.87 eV) and adsorbed HCO₂ (structure n in Table 3.2 resembling adsorbed HCO₃ structure, but with one oxygen being the surface lattice oxygen and with DFT computed CLBE shift range from +4.81 to +5.03 eV) can reproduce the experimental shifts of +1.7 eV and +4.9 eV respectively. Both adsorbed H₂O on the surface at oxygen vacancy site (structure i in Table 3.2 with DFT computed CLBE shift range of +2.87 to +3.79 eV), and adsorbed bicarbonate, HCO₃ (structure m in Table 3.2 with DFT computed CLBE shift range of +2.36 to +3.74 eV) can reproduce the experimental shift of +3.5 eV. It is important to note here that in the process of U value estimation based on the experimental XPS spectral analysis, the surface species and their structures, and their respective XPS shifts have already been identified.

Finally, these four structures were investigated to estimate the appropriate U value that accurately reproduces the respective experimental XPS O1s CLBE shifts. The variation in CLBE shifts for these structures as a function of U value is shown in Fig. 3.13. As shown in Fig. 3.13a and 3.13b, for the O_2 adsorbed on CuO in the $\eta 1(O)$ configuration, and H_2O adsorbed at the surface oxygen vacancy site, V_O (Kröger-Vink Notation), the U value of 4~4.5 eV correctly predicts the experimental CLBE shift of +1.7 eV and +3.5 eV, respectively. Similarly, for adsorbed HCO_2 , and adsorbed HCO_3 , the U value of ~4 eV correctly predicts the CLBE shift of +4.9 eV and +3.5 eV, respectively (*cf* Fig. 3.13c and 3.13d). In this range of U values (4-4.5 eV), a single U value of ~4 eV gives the best prediction of experimental core-level binding energy shifts (+1.7 eV, +3.5 eV and +4.9 eV) and thus, in-turn of absolute binding energies (by adding the computed O1s chemical shifts to the binding energy of the bulk lattice oxygen, 529.7 eV) of 531.4 eV, 533.2 eV and 534.6 eV for all the four adsorbed moieties.

Figure 3.13 Variation of computed O 1s core-level binding energy shifts at different U values for (a) adsorbed O₂ in $\eta_1(\text{O})$ configuration, (b) adsorbed H₂O at oxygen vacancy site, (c) adsorbed HCO₂ (resembling adsorbed HCO₃), and (d) adsorbed HCO₃ on CuO(111) surface. Experimental values are shown as dash-lines. Color code for atoms is the same as in Table 3.2.

As mentioned earlier, the XPS peaks at 531.4 eV, 533.2 eV, and 534.6 eV are contested in literature to correspond to various possible adsorbates on CuO, and there exists an uncertainty in establishing these peaks to both, the type, and structures of surface species. This method eliminates this prevailing ambiguity in the assignment of XPS peaks to surface moieties as well as their respective

adsorption configurations, to assign the BEs (and shifts) to the respective structures. Thus, in parallel to the U value determination for CuO and identification of adsorbates and intermediates present in the system, the synergistic nature of this study also assists in peak identification for XPS spectral analysis.

Interestingly, it has to be noted that the appropriate U value range (from 4 to 4.5 eV) observed in this study is in reasonable agreement with the U value range (4.5 to 5.5 eV) based on the adsorption energy and FTIR measurements in our recent study.¹²⁷ Both these U value benchmarking methods (based on XPS and adsorption energy measurements) are very surface sensitive, and encapsulate the various surface-adsorbate interactions, electronic transitions, charge transfers, vacancy formation, lattice oxygen involvement in the reaction, partial surface reduction, and changes in oxidation state of atoms. This also re-establishes the necessity for the U value benchmarking to be based on surface properties of TMOs (and not on bulk properties) to accurately capture the changes in physical interactions, chemical states, and electronic transitions for both the adsorbate and catalyst surface.

3.4 Summary and Conclusions

In summary, this chapter demonstrates a synergistic application of XPS and DFT+U methods, in which the U value for a TMO is determined using the experimental XPS technique, and concurrently, the DFT+U calculations assist in

the identification of surface adsorbates and assignment of their respective XPS peaks. Based on the comparison of experimental XPS and DFT+U generated O 1s core level binding energy shifts of various possible molecules adsorbed on the as-synthesized CuO, the U value range of 4 to 4.5 eV captures the experimental XPS O1s core-level binding energy correctly, while the bulk property optimized and widely used U value of 7 eV fails for this task. It further validates that when the DFT + U method is applied to study surface reactions, pathways and energetics, the appropriate U value should be benchmarked based on surface sensitive techniques and experimental surface reaction data rather than employing the bulk property optimized U-value. The obtained U value range also establishes the adsorbate structures corresponding to the peaks in the XPS spectra as to O₂ adsorbed on CuO in the $\eta_1(\text{O})$ configuration (531.4 eV), H₂O adsorbed at the surface oxygen vacancy site (533.2 eV), adsorbed HCO₃ (533.2 eV) and adsorbed HCO₂ (534.6 eV), thus, invalidates the existing ambiguity and challenges associated with XPS spectral analysis (surface species identification and XPS peak assignment) for CuO. This work establishes a foundation for experimental and computational techniques to understand surface catalysis reactions over TMOs by eliminating the need of separate benchmarking beforehand, which is extremely beneficial for studying TMOs without any existing benchmarked U value. This can be extended to techniques like in-situ and temperature programmed XPS for identification of surface species present at reaction conditions throughout the course of the reaction. This type of concerted approach establishes the immense potential that combined experimental and

computational methods have for understanding surface catalysis, identification of reaction intermediates and pathways and design of heterogeneous catalytic processes, focused on TMOs.

With the accurate theory level and computational approaches to study TMO catalyzed surface reactions in place, we apply them to investigate the methane activation and dissociation on CuO surfaces with the aim to investigate the role of molecular moisture or surface OH species in methane activation and dissociation. Surface hydroxide can act as Bronsted bases when bound to transition metals like Cu, Au, Ag and have shown to aid in the activation of C-H bonds.⁵²⁻⁵⁴ Since, (i) Water and OH species can be present on the transition metal oxide's surface either from the catalyst synthesis method or via the adsorption from moisture in the atmosphere,^{8, 28-30} and can also be formed during the CH₄ activation reactions under dry conditions, and, (ii) Presence of these species may significantly influence the catalytic behavior by promoting the activation of C-H bonds of methane and other reaction intermediates on TMO surface as they do on the metal surface, we study the effect of water and surface hydroxyls on methane activation on CuO(111) in the next chapter.

4 Insights into the role of water and surface hydroxyls in C-H bond activation of methane on CuO(111)

4.1 Introduction

Most of the TMO catalyzed hydrocarbon oxidation reactions are believed to occur primarily via the Mars-Van Krevelen mechanism¹⁷⁶⁻¹⁷⁷ with nucleophilic oxidation¹⁷⁸ (consumption of lattice oxygen¹⁷⁹). As discussed in detail in section 1.4, coordinative unsaturated metal and oxygen atoms on the surface of transition metal oxides are known to be the active sites for reactions involving C-H activation of methane. Since the surface atomic arrangement of metal oxides depends on the cleavage surface or the exposed facets, the surface reactivity of metal oxides varies distinctly with surface structure and nature of surface atoms. Trends in reactivity of metal oxides across groups and periods may differ significantly. In TMOs, the overlapping 2p-orbitals of oxygen form the low energy valence band, which is highly populated; whereas the overlapping d orbitals of the transition metal form the conductance band, which is mainly responsible for their diverse electronic and magnetic properties. Unlike the homolytic bond cleavage typically observed on transition metal surfaces, the metal oxides are also shown to promote heterolytic cleavage of methane with the metal center adsorbing the CH₃ fragment and the oxygen adsorbing the dissociated hydrogen. Chemisorption energy of hydrogen is accepted to be a suitable descriptor for the reactivity of metal-oxide mediated hydrogen

abstraction reactions.^{50, 106-109} All these have significant effects in determining the efficacy of the metal oxide to activate C-H bonds in methane.

Experimental results suggest rare earth and transition metal oxides are effective catalysts to activate C-H bonds of methane. However, due to limitations associated with independent experimental surface science techniques to provide fundamental insights into these complex transition metal oxide catalyzed reactions (detailed discussion in section 1.5), computational investigations employing quantum mechanics based DFT approach complemented experimental observations and has shed some light on the active sites, mechanisms, and energetics of these surface reactions.

The first activation of methane on TMOs⁵⁰⁻⁵¹ gives rise to methyl species in the system, which can further oxidize to partially oxygenated species like methanol, formaldehyde, formic acid before converting to fully oxygenated products like CO/CO₂. Since the first activation of methane is usually the rate-limiting step, a large number of studies have studied the first activation of C-H bonds of methane,^{37, 44, 180-181} whereas subsequent activations of methane on TMOs are not widely investigated in the literature. It is crucial to study subsequent activations of methane not just from the methane partial oxidation perspective but also to develop understanding the role of surface-active sites in these oxidations.

Water and OH species can be present on the transition metal oxide's surface either from the catalyst synthesis method or via the adsorption from moisture in the atmosphere.^{8, 28-30} Surface hydroxide species can act as Bronsted bases when bound to transition metals like Cu, Au, Ag and have shown to aid in

activation of C-H bonds.⁵²⁻⁵⁴ The presence of a co-adsorbed surface hydroxide reduced the activation barrier for ethanol deprotonation on Au(111) in water by order of magnitude to 22 kJ mol⁻¹ compared to the barrier on a bare gold surface (204 kJ mol⁻¹)⁵². Presence of these surface OH species may influence the catalytic behavior by promoting the activation of C-H bonds of methane and other reaction intermediates on TMO surface as well. These surface OH species can also be formed during the CH₄ dissociation reactions under dry conditions or in the presence of moisture or steam as a reactant, from the C-H and O-H cleavage generating strongly bound dissociated H atoms on the catalyst surface. The generated surface hydroxyls, $H_{LatticeO}^*$ block the active, undercoordinated surface O₃ site. At sufficiently high coverages or reaction temperatures, these surface OH species can combine to form water, thereby generating oxygen vacancies and thus a partially reduced CuO structure, further influencing the reaction pathways and kinetics. The selectivity towards partial oxygenates of methane (methanol and formaldehyde) as compared to CO/CO₂ was stated to be a strong positive function of the amount of water vapor present in the system for methane oxidation on MoO₃/SiO₂.⁵⁵ It has been shown by a recent computational and experimental study that presence of surface hydroxide species $(OH)_{Cu\ site}^*$ on CuO, from the dissociation of H₂O₂, provides a lower energy pathway for glycerol oxidation, without utilizing the surface lattice oxygen, and lead to an increased conversion of glycerol(>70% vs. 10% in absence of surface OH species).¹⁸² Also, the presence of these surface OH species has shown to affect the product distribution and yield of the glycerol oxidation. It has been reported

that these surface hydroxide species $(OH)_{Cu\ site}^*$ can react with that H atom occupying the active surface O_3 site (surface hydroxyl species, $H_{LatticeO}^*$) easily with the barrier of 27 kJ mol^{-1} , to generate water and free the active sites on the CuO surface. Due to this interaction, the active O_3 site is regenerated and this contributes to the high conversion of glycerol, as is observed experimentally.¹⁸² There is limited literature available with respect to the mechanism of how moisture or surface hydroxide species (added externally or generated during the reaction) participate and affect the methane activation reaction energetics and barriers over TMOs. Reduction of methane oxidation barriers, if achieved with the presence of surface OH species, can lead to reduction in temperatures employed in the fuel reactor of CLC/CLR processes (thus improving the heat balance and overall efficiency of these process¹⁸³) as well as higher stability of the catalyst (due to low or no consumption of lattice oxygen in oxidation reactions).

Previous work⁵¹ has shown that an otherwise inactive metal Cu, when converted to its oxide, CuO, can activate C-H bonds in methane with three and four center mechanisms involving surface Cu & lattice oxygen extracting hydrogen from C-H bond. It is an extensively used and studied TMO, in both pure and supported forms. Recently, CuO in both pure and supported forms has been shown to activate the formyl C-H bond to convert glucose to gluconic acid⁹³,¹¹² for biomass oxidation reactions, and to be highly selective for desired products (imine derivatives) under solvent-free conditions by oxidative coupling of aromatic amines¹¹⁹. Use of low-valence dopants such as Cu, Zn, Mg (relative to

the primary oxide) in La_2O_3 has also shown to decrease the energy of oxygen vacancy formation as well as lower the first activation barrier for methane activation.¹⁸⁴⁻¹⁸⁵ These studies provide mechanistic insights into the C-H bond activation, which is central in paving the way for novel processes and catalysts to be used in value-added C_1 chemical processing.

Heterogeneous catalyst systems involving Cu-modified zeolites (via incorporation of Cu-oxo clusters) have been shown to be active for methane activation. One of the first studies to investigate Cu loaded zeolites for methane oxidation was studied by Groothaert et al¹⁸⁶. After oxidative activation of the copper-exchanged zeolite to form Cu-O-Cu species, catalytic methane oxidation is established in sequential steps involving activation of methane and desorption of products.¹⁸⁷ The formation of bis(μ -oxo)di Cu clusters (by reaction of Cu-ZSM-5 with oxygen) on Cu loaded ZSM-5 was confirmed by spectrophotometric techniques and proposed to be the active sites for conversion of methane to methanol. The role of active species (Cu-O-Cu) in Cu-exchanged mordenite(MOR) has also been examined for the selective oxidation of methane to methanol^{117, 188-189}. The active sites of Cu-exchanged zeolites and MOR successfully mimic the active site in the naturally occurring enzyme methane monooxygenase¹⁹⁰ (that successfully catalyzes methane to methanol in the presence of O_2). Recent studies have also confirmed the existence and selective synthesis of other active Cu-oxo species like well-defined trinuclear $[\text{Cu}_3(\mu\text{-O})_3]^{2+}$ clusters in Cu/MOR materials^{189, 191}. Several theoretical studies are exploring and providing insights into the selective oxidation of methane to

methanol in Cu exchanged zeolites and mordenite systems providing evidence into the bi or trinuclear metal-oxo centers being the responsible species for methane activation. Li et al. investigated the catalytic behaviour of transition metal ions and oxides clusters (including Fe, Cu etc.) introduced into mesoporous silica SBA-15, and reported CuO_x/SBA-15 to exhibit best catalytic performance for selective oxidation of methane to formaldehyde, with active sites being the reduced Cu species (which react with molecular oxygen to create active O* species) generated during the reaction.¹⁹²⁻¹⁹³ Although highly selective to partial dehydrogenated products, zeolite mediated methane conversion has its current limitations with respect to (i) the low compositional richness (amount of active metal centers with respect to total amount of catalyst), and (ii) product desorption step due to a) it's underlying hydrophilic nature leading to undesired oxidation reactions, as well as, b) a separate extraction process hindering the Cu-ZSM/MOR mediated methane to methanol conversion to be converted into a fully catalytic process¹⁹⁴.

Although all these studies that provide mechanistic insights into the C-H bond activation on pure, supported as well as zeolite incorporated Cu based catalysts highlight the unique nature of Cu-O bonds that play a vital role in the methane activation. The role of lattice oxygen, as well as surface OH species (generated intrinsically through dissociation of moisture or catalytic preparation or through C-H activation reactions) on the reaction energetics and pathways, are not understood. A detailed understanding of the role and contribution of lattice oxygen and surface OH species towards C-H bond dissociation will help in the

design of controlled oxidation reactions on these catalysts. Moreover, due to the presence of various surface species with similar (competing) spectrophotometric signals (e.g., different kinds of OH species in methane dissociation reaction have very similar FTIR signals), it becomes challenging for independent experimental techniques like FTIR to comment on the type of adsorbates and surface moieties. Based on the gaps identified above, DFT calculations are performed, coupled with experimental FTIR studies to investigate methane activation and dissociation to partial oxidation products over CuO surface. The reaction pathways to study the formation of surface OH species under dry and moisturized reaction conditions on CuO are investigated. Finally, the role of moisture as well as surface OH species on activation and dissociation of methane on CuO is examined. These insights from the current work would help in the fundamental understanding of the C-H bond activation on TMOs to design novel processes and catalysts for both the direct and indirect methods of methane oxidation.

The computational and experimental methods adopted for this investigation are discussed in section 4.2.1 and section 4.2.2, respectively. Section 4.3.1 reports the activation barriers, energetics and pathways of methane dissociation on CuO(111) surface under dry conditions. Section 4.3.2 reports the activation barriers, energetics and reaction pathways for the dissociation of methane on CuO(111) in the presence of molecular water. Section 4.3.3 investigates the formation of surface OH species in the presence and absence of moisture. Section 4.3.4 reports the activation barriers and energetics for methane dissociation on CuO(111) in the presence of surface hydroxides. Section 4.3.5 presents a

discussion of the role of moisture in both molecular and dissociated forms in comparison to surface mediated methane dissociation on CuO(111). In section 4.3.6 the surface characterization data for the as-synthesized CuO is presented. In section 4.3.7, various surface moieties present during the CuO catalyzed methane oxidation reaction under dry and moisturized conditions at 300 °C are identified by performing an in-situ IR analysis of the reaction at successive time intervals. The summary of this chapter is presented in Section 4.4.

4.2 Computational methodology and simulation systems

4.2.1 Computational Methods

All the calculations in the current work were performed using the PBE exchange-correlation functional of GGA⁹⁶ as implemented in VASP⁹⁷ with the PPW implementation within DFT^{60, 97}. The PAW⁹⁸⁻⁹⁹ scheme is used to describe the inner core-valance interaction with a plane wave cut-off energy of 450 eV. K points sampling of 4x4x1 within the Monkhorst-pack scheme is employed. A three-layer CuO(111) slab with top two layers allowed to be fully relaxed is used in the current study. A vacuum region of 12 Å was wide enough to avoid interactions between different slabs. Energy convergence criteria of 10^{-4} eV per unit cell along with minimization of interatomic forces to 0.2 eV/Å was employed. Since CuO is antiferromagnetic at its ground state, spin polarization

Figure 4.1 The surface atomic arrangement on CuO(111) facet showing the repeating arrangement of O₃-Cu₃-O₄-Cu₄ units, where the subscript denotes the coordination number of the respective atom. Peach and red balls represent Copper (Cu) and Oxygen (O) atoms, respectively.

was turned on. CuO(111) surface has a repeating surface arrangement of O₃-Cu₃-O₄-Cu₄ units (*cf* Fig. 4.1), where the subscript denotes the coordination number of the individual atom.

Similar to Chapter 1, the lattice constants were fixed as obtained with U-value of 7 eV, as it showed excellent agreement with experimental lattice parameters (a, b, c, β), interatomic distances⁷⁵ and reproduced experimental band gaps and magnetic moments⁷⁴. CuO has a monoclinic structure, and the lattice constants a = 4.68 Å, b = 3.43 Å, c = 5.14 Å, β = 99.3°, as optimized by Varghese et al⁹⁴ have been used in this study. All the calculations have been done on CuO(111) as it is the most stable CuO facet followed by CuO(-111)³⁵. CuO(111) facet has been predominantly found in the as-synthesized sample of CuO, which is used for experiments in this work.

Adsorption energy, E_{ads} , was calculated as follows, for a model adsorption reaction:

Using the expression,

$$E_{ads} = E_{A^*} - (E_* + E_{A(g)}) \quad (3)$$

, where E_{A^*} is the total energy of the system, E_* is the energy of the clean surface, and $E_{A(g)}$ is the energy of the isolated gas phase molecule $A(g)$.

4.2.2 Experimental Methods

CuO nanomaterial was synthesized by the precipitation method using NaOH solution as the precipitant. The concentrated NaOH solution, around 4M, was added dropwise to the $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ solution under continuous stirring at room temperature. The black precipitate appeared as soon as the basic solution was added. The resultant slurry was aged under stirring at ambient temperature for five hours, and the final product was collected by vacuum filtration, washed with deionized water, dried at 60 °C and calcined at 350 °C for 4 hours.

X-ray diffraction (XRD) patterns were recorded on a Bruker AXS D8 diffractometer under ambient temperature using $\text{CuK}\alpha$ radiation operated at 40 kV and 40 mA in the 2θ range of 10° – 80° , using a 0.05° step size of and a step time of 20 seconds at each point.

The morphology of the calcined catalyst was analyzed using a Field-emission scanning electron microscope (FE-SEM, Jeol JSM-6700) at an accelerating voltage of 5 kV. Further morphological information was acquired through transmission electron microscopy (TEM) observation using Tecnai G² TF20 S-twin microscopy operated at 200 kV. Samples were dispersed on carbon grids after sonicating the samples in ethanol for half an hour.

In situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) spectra were recorded on a Bio-Rad FT-IR3000 MX spectrometer equipped with a Harrick Praying Mantis DRIFTS cell connected to a mercury-cadmium-telluride (MCT) detector and a resolution of 4 cm^{-1} with an

accumulation of 64 scans in a single measurement. The catalyst was loaded into the reaction cell, and the fresh catalyst was pre-treated before every reaction (MS and DRIFTS) in Helium at 350°C for 30 min to clean the surface and any morphology change in pre- and posttreatment of catalyst was not observed, assuring that the catalyst structure was not affected. This was performed for both the dry and the moisturized conditions.

Post the Pretreatment of the catalyst in the DRIFT chamber, based on the reaction under study, different procedures were followed,

- (i) *Moisturized case:* He was bubbled through water at room temperature and then passed through the FTIR cell after the pretreatment. The FTIR measurements were performed to ensure that the water reached the catalyst surface. After 30 minutes of bubbling, dry He was purged for an hour to ensure none of the gas phase water is present in the system, and the same was verified using FTIR measurements. Post this, methane was introduced into the reaction chamber at the reaction conditions and the FTIR measurements were done at successive intervals.
- (ii) *Dry case:* It was ensured that none of the gas phase water or surface hydroxyls are present in the system by using FTIR measurements. Post this, methane was introduced into the reaction chamber at the reaction conditions and the FTIR measurements were done at successive intervals.

Throughout the work, the background was recorded under Helium atmosphere at the reaction temperature. Background subtractions were performed for all spectra reported in the investigation.

4.3 Results and Discussions

4.3.1 CuO(111) surface mediated methane activation

Methane adsorbs weakly on the CuO(111) surface with the adsorption energy of only about 4 kJ mol⁻¹. The reaction energy for the first activation is the difference in the energy of the physisorbed methane system, referred to as IS, and the dissociation products, referred to as FS (*cf* Fig 4.1 and Fig 4.2). As reported in earlier studies, two mechanisms are investigated for the first activation of methane on CuO(111) surface based on the surface sites that activate the C-H bond. C-H activation in methane (and other hydrocarbons) over popular transition metal oxides can proceed via the following mechanisms^{50, 94, 195}:

- i. **Three center or radical mechanism**, where only the undercoordinated lattice oxygen O₃ abstracts Hydrogen from the C-H bond, without any direct involvement of the surface Cu₃ atom. As shown in Fig. 4.2 FS, this leads to the formation of a CH₃ radical, and an H atom adsorbed on the undercoordinated lattice oxygen site O₃, (active site for the CuO (111) surface, *cf* Fig. 4.1). The activation barrier for the three center mechanism is 141.3 kJ mol⁻¹, generating methyl radicals. These radicals may evolve directly to the gas phase since there is no stabilization by any surface moieties or may adsorb on the CuO surface.¹⁹⁶ The CH₃ fragment can either adsorb on the surface undercoordinated Cu₃ (*cf* Fig. 4.2 FS2) or O₃ sites (*cf* Fig. 4.2 FS2'), with the latter being 60 kJ mol⁻¹ more stable.

- ii. **Four center or surface stabilized mechanism**, where the under coordinated lattice oxygen (O_3) abstracts the hydrogen with the involvement of the undercoordinated surface copper (Cu_3) atom, forming the surface hydroxyl, and adsorbed CH_3 species (*cf* Fig. 4.3). While the Cu_3 adds across the C-H bond, the O_3 polarizes the C-H bond leading to heterolytic dissociation of methane on surface.¹⁹⁶ The activation barrier for the four-center mechanism is 82.2 kJ mol^{-1} , with ΔE_{rxn} of 30 kJ mol^{-1} .

Figure 4.2 The initial state (IS), transition state (TS) and final states (FS, FS2 and FS2') corresponding to the dissociation of methane by 3 center or radical mechanism on CuO(111) surface. Activation energy barriers (kJ mol^{-1}) associated with the reaction are indicated in the figure. Peach, red, grey and white balls represent Copper (Cu), Oxygen (O), Carbon (C), and Hydrogen (H) atoms, respectively.

Figure 4.3 The initial state (IS), transition state (TS) and final state (FS) corresponding to dissociation of methane by 4 center mechanism involving synergistic roles of the under coordinated copper (Cu_3) and lattice oxygen (O_3) atoms on $\text{CuO}(111)$ surface. Activation energy barriers (kJ mol^{-1}) associated with the reaction are indicated in the figure. The color scheme is the same as in Fig 4.2

The barriers and reaction energy for the first activation of methane are different from the earlier reported values (E_a of 130 kJ mol⁻¹ of 3 center mechanism, E_a and ΔE_{rxn} of 76.6 kJ mol⁻¹ and 3.4 kJ mol⁻¹ for 4 center mechanism)¹⁹⁷ due to the inclusion of surface property determined U value of 5 eV in the DFT calculations to correct the self-interaction errors associated with transition metal oxides like CuO. Addition of this U value puts a penalty on the delocalization of the surface electrons of the transition metal, and hence, restricts their participation in bond formation between surface-adsorbates. This leads to the reduced binding energy of the reaction products in this case, and thus higher ΔE_{rxn} energies (30 kJ mol⁻¹ vs. 3.4 kJ mol⁻¹) are observed. The reaction energies are affected by higher magnitude than the activation barriers due to limited charge transfer between the surface and the adsorbate species in the transition state as compared to the fully adsorbed final state (introduction of U value → restriction of the electron in bond formation → low binding energies for FS → high reaction energy).

The CH₃ adsorbed on the Cu₃ site on the surface in the four-centered mechanism (*cf* Fig. 4.3) may also diffuse to the non-bonded under coordinated lattice oxygen (O₃) atom via a two-step mechanism with the barrier reported as 77.3 kJ mol⁻¹ previously.¹⁹⁷ Thus, under typical catalytic conditions of high temperature (> 800 K) for methane oxidation, the diffusion of CH₃ from Cu surface sites to under coordinated oxygen O₃ sites is highly probable. Also, the final state thus achieved with both CH₃ and hydrogen on adjacent under

coordinated oxygens is much more stable than the configuration in the first activation FS by 60 kJ mol⁻¹.

The hydrogen extracted from the methane molecule, which is also adsorbed on the undercoordinated O₃ atom, can also diffuse to the neighboring O atom (*cf* Fig. 4.4). The barrier for this diffusion is 92.5 kJ mol⁻¹, which is low enough to be achieved at the reaction conditions at which methane is oxidized. Thus, both the first activation products of methane can diffuse between the active

surface sites and hence for any further reactions; these products are being evaluated without being co-adsorbed adjacent to each other.

Figure 4.4 The initial state (IS), transition state (TS) and final state (FS) corresponding to the diffusion of surface hydroxyls, $H_{LatticeO}^*$ from one under coordinated surface O₃ atom to another. Activation energy barriers (kJ mol⁻¹) associated with the reaction are indicated in the figure. The color scheme is the same as in Fig 4.2

The dissociation of CH₃ chemisorbed on O is evaluated for further activation (*cf* Fig. 4.5 IS). The barrier for the dissociation is 154 kJ mol⁻¹ with reference to the CH₃ chemisorbed on O, with the reaction energy of 5.9 kJ mol⁻¹ (*cf* Fig. 4.5). The dissociation of CH₃ dictates a restructuring of the CuO surface to permit both H₂C- and oxygen to form bonds with the same Cu atom as noticed in the FS. This permits the system to preserve the sp³ nature of the C center as well as necessitates the lattice oxygen being pulled out from the surface (*cf* Fig. 4.5 FS). As the reaction proceeds, the lattice oxygen pops out of the surface forming HCHO adsorbed on the surface leaving behind a surface oxygen vacancy (*cf* Fig. 4.5 FS2) with ΔE_{rxn} of 38.8 kJ mol⁻¹. The calculated desorption energy for HCHO is 54.3 kJ mol⁻¹.

The desorbed formaldehyde can reabsorb on the CuO(111) surface and get oxidized further. The activation of this formyl C-H bond is evaluated on fresh CuO(111) surface. The $\Delta E_{\text{adsorption}}$ is 41 kJ mol⁻¹ in a η_1 configuration, where the formaldehyde oxygen is bonded to the surface Cu₃ site (*cf* Fig. 4.6 IS η_1). This adsorbed state then moves to a more stable state in η_2 configuration where the carbon is bonded to surface under coordinated oxygen O₃, and the formyl oxygen is bonded to surface Cu sites in a bridge configuration (*cf* Fig. 4.6 IS η_2). η_2 configuration is more stable than η_1 configuration by 71.4 kJ mol⁻¹.

Figure 4.5 The initial state (IS), transition state (TS), final states (FS,FS2) and desorbed state (FS_{desorbed}) corresponding to second activation of methane involving C-H bond dissociation of methyl fragment adsorbed on surface O₃ site on CuO (111) surface. Activation energy barriers (kJ mol⁻¹) associated with the reaction are indicated in the figure. The color scheme is the same as in Fig 4.2

One of the formyl hydrogens is activated by the surface under coordinated O₃ site with the barrier of 122.8 kJ mol⁻¹ (*cf* Fig. 4.6 TS) and the reaction energy of -73.4 kJ mol⁻¹. The oxygen atom of the resulting formate group can be hydrogenated back with the hydrogen abstracted from the carbon atom in the formaldehyde leading to the formation of formic acid. The Similar mechanism is observed for oxidation of glucose to gluconic acid on CuO where O₃ of copper oxide (CuO) nano leaves activate the formyl C-H bond in glucose and incorporates itself into the glucose molecule to oxidize it to gluconic acid.¹⁹⁸

Figure 4.6 The initial state with gas phase HCHO (IS0), adsorbed state in η_1 configuration (IS η_1), adsorbed state in η_2 configuration (IS η_2), transition state (TS), final state (FS) corresponding to activation of formaldehyde (third activation of methane) on CuO (111) surface. Activation energy barriers (kJ mol^{-1}) associated with the reaction are indicated in the figure. The color scheme is the same as in Fig 4.2

4.3.2 Investigating the role of moisture in methane activation

A water molecule can activate the C-H bond of methane via two pathways, either in molecular form (hydrogen shuttling mechanism) or in dissociated form (via the water dissociation products (surface OH species) on CuO surface). The second mechanism is discussed in section 4.3.3.1 and 4.3.4. In the hydrogen shuttling mechanism, the hydrogen from the C-H bond is abstracted by the oxygen of the water molecule, and, one of the two hydrogens of the water molecule is shuttled to the catalyst surface. There are two possible pathways for the shuttling mechanism for the first activation of methane. In the first pathway (*cf* Fig. 4.7), C-H bond of methane is activated only by the oxygen of the water molecule without assistance from the CuO surface, thus generating a methyl radical as a product (*cf* Fig. 4.7 FS). The barrier for the radical pathway is 137.7 kJ mol⁻¹.

In the second pathway (*cf* Fig. 4.8), C-H bond of methane is activated by the oxygen of the water molecule assisted by the CuO surface, thus generating adsorbed methyl species on Cu₃ of the catalyst surface (*cf* Fig. 4.8 FS). In this case, the TS is stabilized by the surface, and hence the barrier for the C-H bond activation is lower by 16 kJ mol⁻¹.

Figure 4.8 The initial state (IS), transition state (TS), , and final state (FS) corresponding to the first activation of methane by hydrogen abstraction mechanism involving only molecular water as a reactant (radical mechanism). Activation energy barriers (kJ mol^{-1}) associated with the reaction are indicated in the figure. The color scheme is the same as in Fig 4.2

Figure 4.7 The initial state (IS), transition state (TS) , and final state (FS) corresponding to the surface mediated first activation of methane involving molecular water as a reactant. Activation energy barriers (kJ mol^{-1}) associated with the reaction are indicated in the figure. The color scheme is the same as in Fig 4.2

In both the pathways, in the process of extracting the hydrogen from methane, water loses one of its hydrogens to the active surface undercoordinated O₃ site, thus generating a surface hydroxyl site as well as regenerating H₂O in the gas phase, as shown in Fig. 4.7 FS and Fig. 4.8 FS.

For the second activation of methane, the hydrogen shuttling mechanism for the activation of C-H bond of the methyl species adsorbed on CuO surface is investigated. C-H bond of the methyl species on the O₃ site is activated by the oxygen of the water molecule through hydrogen abstraction pathway with a barrier of 106.7 kJ mol⁻¹ (*cf* Fig. 4.9).

Figure 4.9 The initial state (IS), transition state (TS), and final state (FS) corresponding to the second activation of methane involving molecular water as a reactant. Activation energy barriers (kJ mol^{-1}) associated with the reaction are indicated in the figure. The color scheme is the same as in Fig 4.2

It is important to mention here that for both the first and second activation of methane involving water molecule, the transition state is entropically confined due to the presence of a gaseous molecule in the TS (cf Fig. 4.6 TS, Fig. 4.7 TS, Fig. 4.8 TS), which can lead to a possibly huge entropy loss from IS to TS.

4.3.3 The formation of surface OH species in methane activation

As discussed in section 1.4, OH species can be present on the catalyst surface either from the preparation method or via the adsorption and dissociation from moisture in the atmosphere. They can also be formed on the transition metal oxide's surface during the course of the CH₄ activation reactions. Before proceeding to investigate the role of surface OH species in methane activation, the feasibility of formation of surface OH species in the presence of moisture, and under dry conditions is studied.

4.3.3.1 Formation of surface OH species on CuO (111) in the presence of moisture: Dissociation of Water

The adsorption energy of water on CuO(111) is 56.2 kJ mol⁻¹ (*cf* Fig. 4.10 IS). The dissociation of H₂O on CuO(111) is feasible²⁸ with the computed activation barrier of 5 kJ mol⁻¹, leading to the formation of two kinds of surface OH species, (i) surface hydroxyls ($H_{LatticeO}^*$) and, (ii) surface hydroxides ($(OH)_{Cu\ site}^*$) (*cf* Fig. 4.10 FS). In literature, the presence of OH on the surface of metal oxides is also detected from experiments.³⁰⁻³¹ There are two adsorbed configurations for surface hydroxides ($(OH)_{Cu\ site}^*$) on CuO surface: at bridge site (*cf* Fig. 4.10 FS2) and at the top site (*cf* Fig. 4.10 FS), with the former being 21 kJ mol⁻¹ more stable than the later. Both these structures are considered to determine the first and second activation of methane.

Figure 4.10 The initial state with gas phase water (IS0), adsorbed state (IS), transition state (TS), final state with surface hydroxide in top configuration (FS), final state with surface hydroxide in bridge configuration on two surface Cu_3 sites (FS2) corresponding to activation of water on CuO (111) surface. Activation energy barriers (kJ mol^{-1}) associated with the reaction are indicated in the figure. The color scheme is the same as in Fig 4.2

4.3.3.2 Formation of surface OH species on CuO (111) under dry reaction conditions: Role of Lattice oxygen

As discussed in section 4.3.1 and 4.3.2, every activation of C-H bond of methane results in the formation of surface hydroxyls ($H_{LatticeO}^*$) species on the CuO surface. These surface hydroxyls ($H_{LatticeO}^*$) can also react to form a water molecule, $H_2O_{lattice}$, leaving an oxygen vacancy, V_O on the CuO surface. As depicted in Fig. 4.11, either of the surface oxygens (with hydrogens adsorbed on them) stretch out from the surface slightly, with a hydrogen atom from one surface hydroxyl ($H_{LatticeO}^*$) species migrates to the oxygen of the neighbouring surface hydroxyl ($H_{LatticeO}^*$) with the formation of an [O---H---O---H] complex with elongated O---H bond (*cf* Fig. 4.11 TS). Post this hydrogen transfer, the oxygen atom which lost the hydrogen settles back into the lattice, and the other Oxygen atom with 2 hydrogens adsorbed on it pops out of the surface leading to the formation of $H_2O_{lattice}$ (*cf* Fig. 4.11 FS), leaving a surface with vacancy, V_O . The barrier for the formation of $H_2O_{lattice}$ is 95.6 kJ mol^{-1} . This indicates that the formation of water on the CuO surface could be possible, even in dry conditions.

This water molecule can either desorb with the desorption energy of 71.4 kJ mol^{-1} (*cf* Fig. 4.11 FS_{desorbed}) or can further dissociate to form surface hydroxides $(OH)_{Cu\ site}^*$. An under coordinated lattice O_3 sites activates this O-H bond of $H_2O_{lattice}$, resulting into formation of a surface hydroxyl ($H_{LatticeO}^*$) and, a surface hydroxide $(OH)_{Cu\ site}^*$, as seen in the case of water dissociation on clean CuO(111) in section 4.3.3.1. The barrier for the dissociation of $H_2O_{lattice}$ is only 11.2

kJ mol^{-1} . Hence, presence and reaction of surface hydroxyls (H_{LatticeO}^*) species on the CuO surface can serve as the source of water as well as surface hydroxides ($(OH)_{\text{Cu site}}^*$) even in the dry reaction conditions (*cf* Fig. 4.11).

Figure 4.11 The initial state (IS), transition states (TS, TS2), final states (FS, FS2 and FS3), and desorbed state (FS_{desorbed}) corresponding to the reaction of two H_{LatticeO}^* to form water adsorbed next to a vacancy, $H_2O_{\text{Lattice}}^*$ and its further dissociation to form surface hydroxides $(OH)_{\text{Cu site}}^*$ species under dry conditions. Activation energy barriers (kJ mol^{-1}) associated with the reaction are indicated in the figure. The color scheme is the same as in Fig 4.2

4.3.4 Investigation of the role of surface OH species in methane activation

As discussed in section 4.3.3, Surface hydroxides $(OH)_{Cu\ site}^*$ can be generated both from the dissociation of water, as well as from the reaction of surface hydroxyls ($H_{LatticeO}^*$) under dry reaction conditions. These surface hydroxides can activate the C-H bonds of methane. The first activation of methane can proceed through the hydrogen abstraction mechanism, where the oxygen of the hydroxide activates the C-H bond of methane, generating a methyl radical and a water molecule (*cf* Fig. 4.12). The barrier for the gas phase hydrogen abstraction mechanism is 130.9 kJ mol⁻¹.

Figure 4.12 The initial state (IS) and transition state (TS) corresponding to the first activation of methane by surface hydroxides $(OH)_{Cu\ site}^*$ (radical mechanism). Activation energy barriers (kJ mol⁻¹) associated with the reaction are indicated in the figure. The color scheme is the same as in Fig 4.2

The activation of C-H bonds of methane can also occur via the involvement of both surface sites and the oxygen of surface hydroxide mediating the C-H bond cleavage. This can generate methyl species on undercoordinated surface O₃ (*cf* Fig. 4.13 IS'—TS'—FS') or Cu₃ sites (*cf* Fig. 4.13 IS—TS—FS). The surface hydroxide (OH)_{Cu site}^{*} converts to a top configuration (*cf* Fig. 4.13 IS and IS') for the activation of methane C-H bonds via this pathway. The barrier for the surface mediated activation with CH₃ adsorbed on the Cu₃ site in the final state (*cf* Fig. 4.13 FS) is 62.6 kJ mol⁻¹, which is similar to the calculated barrier

Figure 4.13 The most stable initial state (IS0), initial state for the first activation of methane (IS and IS'), transition states (TS and TS') and final states (FS and FS') corresponding to the surface mediated first activation of methane by surface hydroxides (OH)_{Cu site}^{*}. Activation energy barriers (kJ mol⁻¹) associated with the reaction are indicated in the figure. The color scheme is the same as in Fig 4.2

of 61.6 kJ mol^{-1} , for the pathway with CH_3 adsorbed on the O_3 site in the final state (*cf* Fig. 4.13 FS'). The reaction is highly exothermic for the latter case (*cf* Fig. 4.13 IS'—TS'—FS'), since the final state thus achieved with CH_3 adsorbed on the under coordinated oxygen O_3 is more stable than the CH_3 adsorbed on Cu_3 site, which is also observed in surface mediated first activation of methane as well (*cf* Fig. 4.3).

For the second activation of methane, the surface hydroxide $(\text{OH})_{\text{Cu site}}^*$ converts to a top configuration (*cf* Fig. 4.14 IS) for the activation of methyl C-H bonds, which is 41.8 kJ mol^{-1} less stable than the bridge configuration (*cf* Fig. 4.14 IS0). The Oxygen of the surface hydroxide extracts the Hydrogen from the methyl species with a barrier of 76.9 kJ mol^{-1} . This activation leads to CuO surface rearrangement with both Oxygen and Carbon attaching to the same surface Cu site as can be seen in both the TS and FS (*cf* Fig. 4.14). This ensures that carbon stays in its sp^3 configuration. This rearrangement also mediates the popping out of lattice oxygen leading to the formation of HCHO in FS2. The desorption energy for HCHO is 55.6 kJ mol^{-1}

Figure 4.14 The most stable initial state (IS0), initial state for the second activation of methane (IS), transition states (TS), final state (FS and FS2), and desorbed state (FS_{desorbed}) corresponding to the second activation of methane by surface hydroxides ($(OH)_{Cu\ site}^*$). Activation energy barriers (kJ mol^{-1}) associated with the reaction are indicated in the figure. The color scheme is the same as in Fig 4.2

4.3.5 Comparison of Dry and Moisturized surface activation

methane

As expected, the barrier for the first activation of methane is higher than the second activation for the reaction under all the three conditions, i.e. surface reaction, reaction with gas phase water, and reaction with surface OH (*cf* Fig. 4.15).

For all the C-H activations studied (first activation (3 and 4 centers), and second activation), the free energy barrier is substantially high for the mechanism involving molecular H₂O. This is due to the entropically constrained nature of the transition state with gaseous molecules (H₂O in the gas phase) leading to a higher drop in entropy, and thus a higher free energy barrier. Therefore, the trend for all the activation free energy barriers are H₂O(g) > Dry Surface & Surface OH.

Figure 4.15 Grouped column chart comparing the free energy activation barriers for first and second activation of methane under dry and moisturised conditions.

For the second activation barrier of methane, the contribution of entropy in the activation of C-H bond with molecular water is driving up its free energy barrier more as compared to the dry case due to entrapment of gaseous species in the TS. The inclusion of entropy in activation by surface hydroxide species is having the reverse effect on the barriers due to lattice oxygen popping out of the surface in the form an adsorbed water and thus increasing the entropy of the system (increase in entropy $\rightarrow$ positive $\Delta S \rightarrow$ more negative delta G at higher temperatures). Thus explaining the trend for the second activation free energy barriers $\text{H}_2\text{O(g)} > \text{Dry Surface} > \text{Surface OH}$.

It is evident from the above discussion that dissociated water in the form of surface hydroxide $(\text{OH})_{\text{Cu site}}^*$ species can reduce the barrier for first and subsequent C-H bond activations of methane. As discussed in the previous sections, these surface hydroxide $(\text{OH})_{\text{Cu site}}^*$ species can be present in the system due to (i) the low barrier of dissociation of water (supplied externally), as well as, (ii) generated during the course of the reaction under dry conditions (reaction of surface hydroxyls generated from activation of C-H bonds).

4.3.6 CuO morphology and surface characterization

The as-synthesized CuO was characterized using XRD, and all the peaks in the spectra were representative of the monoclinic $C/2c$ symmetry of cupric oxide⁶⁸. The morphology of CuO nanoparticles was examined by SEM and TEM (*cf* Fig. 4.16), and the particles had an ellipsoidal morphology, resembling nano-pellets or rice like structures. HRTEM was conducted and focused on different areas of the pellet surface, and lattice fringes with a d spacing of 0.23 nm were typically observed, corresponding to the (111) plane as the most exposed surface in the as-prepared CuO. The same surface is used to model reactions in the computational work.

Figure 4.16 Morphology characterization of the as-synthesized CuO a) SEM image depicting the nano-pellets morphology, b) Bright field TEM image with HRTEM image insert for the nano-pellets depicting lattice fringes corresponding to the (111) facet, c) X-ray diffractograms of as-synthesized CuO with signature peaks of copper (II) oxide.

4.3.7 Surface Species Characterization in Dry and Moisturised using DRIFTS

As discussed in the previous sections 4.3.1-4.3.4, methane oxidation on CuO, (i) can lead to various possible partially oxidized intermediates and species prior to the evolution of combustion products like CO₂, CO, and H₂O, (ii) can lead to the formation of surface hydroxide $(OH)_{Cu\ site}^*$ species even in the dry conditions, and (ii) the presence of water and surface hydroxide species in the system reduces the barriers for the first and second activation of methane. To investigate these findings, *in-situ* DRIFTS analysis of CH₄ reaction with CuO at the reaction temperature of 300 °C is carried out under both dry (absence of any form of external source of moisture or surface hydroxide species) and moisturized conditions (catalytic surface with abundant adsorbed water and hydroxide species). The IR spectra were recorded at successive time intervals to gauge the evolution of various surface species and the various interest regions (C-O stretching region, CO₂ stretching region, aldehydic/formic C=O stretching region, O-H stretching). These are discussed in the subsequent Sections 4.3.7.1 – 4.3.7.4.

4.3.7.1 HC-X stretching Region

Our calculations have shown that the first activation of methane results in CH₃-X (CH₃-Cu or CH₃-O, *cf* Fig. 4.2 FS2 FS2') species on the CuO surface, where CH₃ is most stable on the undercoordinated surface lattice oxygen O₃. Hence, any methane activation mechanism will involve methoxy species formation. The IR spectra of the HC-O stretching region for CH₄ reaction on CuO at 300°C under moisturized and dry conditions is shown in Fig. 4.17a and Fig. 4.17b respectively. As shown in these spectra, the absorbance peak around 1050 cm⁻¹ appears in the IR spectra for both, moisturized and dry reaction. This peak corresponds to the C-O stretch of methoxy species. Another observation is that the peak starts to appear earlier in the moisturized system (2-3 min) vs. dry system (4min), thus indicating lower kinetic barrier or lower induction times for methoxy species formation (first activation product). This validates with the lower activation barriers calculated using DFT for the first activation of methane in the presence of moisture and surface hydroxides.

Figure 4.17 DRIFT spectra at successive time intervals for the CH-X stretching region for (a) CH₄ oxidation on moisturized CuO at 300 °C and b) CH₄ oxidation on dry CuO at 300 °C. Symbols: (*) 1050 cm⁻¹.

4.3.7.2 Region for C=O stretching vibrations

Our calculations have shown that the second activation of methane results in the formation of formaldehyde (H₂C=O) on the CuO surface under both moisturized (*cf* Fig. 4.9 FS and Fig 4.14 FS) and dry conditions (*cf* Fig. 4.5 FS2). The IR spectra of the C=O stretching region for CH₄ reaction on CuO at 300°C under moisturized and dry conditions is shown in Fig. 4.18a and Fig. 4.18b respectively. As shown in the spectra, the absorbance peak around 1680 cm⁻¹ appears in the IR spectra for moisturized as well as dry reaction. The peak at 1680 cm⁻¹ corresponds to double bonded Carbon and Oxygen of aldehyde groups, and hence this peak is assigned to the C=O peak of the formaldehyde group. This validates the DFT computed reaction pathway for second activation of methane generating formaldehyde as an intermediate under both moisturized (*cf* Fig. 4.9 FS and Fig

4.14 FS) and dry conditions (*cf* Fig. 4.5 FS2). The peaks in both dry and moisturized cases appear at a similar time in the reaction (~ 2-3 min).

Figure 4.18 DRIFT spectra at successive time intervals for C=O stretching region for (a) CH₄ oxidation on moisturized CuO at 300 °C and b) CH₄ oxidation on dry CuO at 300 °C. Symbols: (*) 1680 cm⁻¹.

4.3.7.3 Region for CO₂ stretching vibrations

The IR spectra of the C=O asymmetric stretching region for CO₂ generated during CH₄ reaction on CuO at 300°C under moisturized and dry conditions is shown in Fig. 4.19a and Fig. 4.19b respectively. The doublet around 2350 cm⁻¹ is present in both dry and moisturized systems, and it corresponds to the asymmetric stretching mode of gas-phase CO₂. The peaks occur around the same time interval (~2 min) for both dry and moisturized cases. This confirms the

temperature used for the reaction (300 °C) is high enough for the complete oxidation of methane to CO₂.

Figure 4.19 DRIFT spectra at successive time intervals for CO₂ stretching region for (a) CH₄ oxidation on moisturized CuO at 300 °C and b) CH₄ oxidation on dry CuO at 300 °C. Symbols: (*) 2350 cm⁻¹.

4.3.7.4 Region for OH stretching

Our calculations presented in section 4.3.3 have shown that the surface hydroxide species can be formed on the CuO surface under both dry and moisturized conditions. The IR spectra of the O-H stretching region for CH₄ reaction on CuO at 300°C under moisturized and dry conditions is shown in Fig. 4.20a and Fig. 4.20b respectively.

In the FTIR study presented in chapter 2, section 2.3.5, by comparing the IR spectra of two different reactions of methane activation and water splitting (having common OH species in the products (Equation 17 and 18) and (*cf* Fig. 2.7a and 2.7b), it was established that the sharp peaks at 3595 cm^{-1} and 3650 cm^{-1} correspond to surface hydroxyl species, $H_{LatticeO}^*$ and surface hydroxide species $(OH)_{Cu\ site}^*$ respectively. These insights are applied to the IR spectra recorded for the methane reactions on moisturized and dry CuO surface (*cf* Fig. 4.20a and 4.20b) and provide the following observations:

1. IR spectra for the moisturized reaction shown in Fig. 4.20a presents two sharp O-H stretching peaks ($\approx 3595\text{ cm}^{-1}$ and $\approx 3650\text{ cm}^{-1}$) of similar intensity at time = 0, even before the methane induction to the chamber starts, thus confirming the presence of both $H_{LatticeO}^*$ and $(OH)_{Cu\ site}^*$ species from the splitting of water. This validates the low activation barrier reported for dissociation of water on CuO surface (section 4.3.1)
2. IR spectra for the moisturized reaction shows that both $H_{LatticeO}^*$ and $(OH)_{Cu\ site}^*$ peaks ($\approx 3595\text{ cm}^{-1}$ and $\approx 3650\text{ cm}^{-1}$) continue to increase in intensity as the reaction proceeds, with the peak at 3595 cm^{-1} increasing with higher intensity than the peak at 3650 cm^{-1} . This agrees with the higher number of $H_{LatticeO}^*$ being formed by C-H activation of Methane (and other reaction intermediates) than the $(OH)_{Cu\ site}^*$.
3. The broad peak around 3500 cm^{-1} in the IR spectra for moisturized reaction corresponding to stretching vibrations of hydrogen bonded O-H bonds and $(H-O_{Lattice}-H)^*$ starts to appear in the reaction. This is in

agreement with the C-H bond activation with surface $(OH)_{Cu\ site}^*$ species generating surface H_2O species, which again split to provide both $H_{LatticeO}^*$ and $(OH)_{Cu\ site}^*$ species.

4. The IR spectra in Fig. 4.20b for the dry reaction shows no presence of OH peaks in the OH stretching region at the start of the reaction, thus establishing that the system does not contain identifiable amounts of adsorbed water or adsorbed surface hydroxyls ($H_{LatticeO}^*$ and $(OH)_{Cu\ site}^*$) at the start of the reaction.
5. IR spectra for the dry reaction shows that $H_{LatticeO}^*$ peak ($\approx 3595\ cm^{-1}$) starts to appear first in the O-H region. This is in lines with the generation of $H_{LatticeO}^*$ as the product of the first activation of methane (section 4.3.1).
6. As the reaction proceeds, the peak corresponding the surface hydroxide $(OH)_{Cu\ site}^*$ ($\approx 3650\ cm^{-1}$) starts to develop in the dry reaction at about 4 minutes (*cf* Fig. 4.20b).
 - a. In the dry experiment, the C-H bonds of methane are only activated by the extraction of Hydrogen by the surface under coordinated O_3 sites, leading to the formation of only surface hydroxyl species. Hence the peak at $3650\ cm^{-1}$ corresponding to surface hydroxide species, could not be explained if only lattice Oxygen is involved in methane activation under dry conditions.
 - b. This peak indicates the formation of surface hydroxides $(OH)_{Cu\ site}^*$ as the reaction proceeds. This validates the findings

from section 4.3.3.2 regarding the generation of surface hydroxides from the reaction of surface hydroxyls under dry conditions.

- c. Thus, even under dry conditions, CuO(111) surface may only activate the C-H bonds of methane for the initial period only. In this induction period, enough $H_{LatticeO}^*$ are generated that react to form $H_2O_{lattice}$, that consequently dissociate to form surface hydroxides $(OH)_{Cu\ site}^*$. After this initial induction period, the dissociation of methane would proceed through activation via surface hydroxides, $(OH)_{Cu\ site}^*$ pathway, since the barriers reported for this pathway are the lower compared to the pathways where only surface-active sites activate methane C-H bonds (section 4.3.5).

Figure 4.20 DRIFT spectra at successive time intervals for O-H stretching region for (a) CH₄ oxidation on moisturized CuO at 300 °C and b) CH₄ oxidation on dry CuO at 300 °C. Symbols: (*) 3595 cm⁻¹, (+) 3650 cm⁻¹, (#) 3500 cm⁻¹.

7. The peaks in the O-H stretching region IR spectra for moisturized experiment develop faster than for the dry case (2 min vs. 3-4 min), indicating faster kinetics or fewer induction times in the presence of moisture as a promoter.

4.4 Summary

In summary, the reaction mechanism and various pathways for methane oxidation on CuO(111) surface under dry conditions as well as in the presence of moisture in the system were investigated. For the first activation of methane under dry conditions, the four-center mechanism ($E_a = 82 \text{ kJ mol}^{-1}$) has a lower barrier than the three center mechanism (141 kJ mol^{-1}). The surface hydroxyls $H_{LatticeO}^*$ generated during the C-H bond cleavage can diffuse on the surface with the barrier of about 92 kJ mol^{-1} . The second and third activation barriers for methane under dry conditions are $154.7 \text{ kJ mol}^{-1}$ and 122 kJ mol^{-1} respectively. The first and second activation barrier of methane with the presence of molecular water is 121 kJ mol^{-1} and 106 kJ mol^{-1} . Next, the formation of surface OH species from dissociation of moisture as well as under dry conditions from the participation of $O_{lattice}$ was evaluated. Due to the low barrier of water dissociation (5 kJ mol^{-1}) on CuO(111) as well as due to huge entropy entrapment associated with the transition states involving molecular water as a reactant, it was concluded that water would participate in the reaction in the form of surface hydroxides. Also, calculations were performed to investigate the formation of surface hydroxides on the surface under dry conditions and the mechanism was

revealed. Two surface hydroxyls react to form water with one of the lattice oxygen popping out from the surface with a barrier of $106.6 \text{ kJ mol}^{-1}$. This water can easily split on CuO surface with the low barrier of 11 kJ mol^{-1} , thus generating surface hydroxides. The first and second barrier in the presence of surface hydroxide species is 62 kJ mol^{-1} and 76 kJ mol^{-1} . The barriers in the presence of surface hydroxides are lowest as compared with both the dry cases and molecular water. FTIR experiments of methane reaction on CuO were performed at a temperature of 300°C and the subsequent spectra were recorded at successive time intervals for both dry and moisturized cases. The IR spectra confirms the presence of the methoxy (1050 cm^{-1}), Aldehyde C=O (1680 cm^{-1}), CO_2 (Doublet at 2350 cm^{-1}) and various surface O—H species (3500 cm^{-1} , 3595 cm^{-1} , 3650 cm^{-1}) for the reaction in both, the absence and presence of moisture. The time of first peak appearances in the IR spectra analysis for the moisturized reaction depicts it to be a bit faster and with slightly less induction times, indicating adsorbed water to be acting as an initiator. Also, the peak in the IR spectra of dry reaction confirms the formation of surface hydroxide $(\text{OH})_{\text{Cu site}}^*$ even without the presence of any water source in the system. These insights from the current work provide the computational and experimental evidence that even when methane reacts on CuO surface under dry conditions, the lattice oxygen does not directly activate the methane C-H bonds, but rather activates the C-H bonds in the form of surface hydroxide species. It also establishes that water in the form of the moisturized surface can not only can act as an initiator to reduce the induction time but also that such approach can lead

to an increase lifetime of the catalysts due to water being the oxygen donor for the initial part of the methane activation.

5 Conclusions and Future Perspectives

A large number of processes are widely investigated for the conversion of methane to value-added chemicals and fuels. Gaining a fundamental understanding of the reaction chemistry is indispensable to the realization of the commercial transformation of catalytic methane conversion to value-added products. Among the hundreds of catalysts and supports evaluated for their efficiency in oxidative methane conversion, the majority of them belong to the class of TMOs. Due to the challenges associated with the complexity of these systems, computational tools, and experimental surface characterization techniques are often employed independently by researchers, to provide insights into metal oxide catalyzed reaction mechanisms, pathways, and energetics.

This thesis presents a combined theoretical and experimental approach to investigate TMOs for C1 chemistry, where DFT computed, and experimental data are compared at each step to address the individual challenges associated with TMOs for both these approaches, i.e., U-value determination based on surface chemistry and difficulty in spectral peak identification. Using CuO as a model TMO, two novel DFT+U approaches are investigated, and the use of surface sensitive approaches for U-value determination for catalytic surface reactions over TMOs is established.

Chemisorption and FTIR based U-value determination approach takes into account the reaction energetics over TMOs surface, and the XPS based U-value determination approach is based on the characterization spectra and electronic

state of the species present on the TMO surface. Although both these DFT+U approaches incorporate the surface chemistry on TMOs, they are based on very different principles, the first one captures the reactions on TMO surface under *in situ* conditions, whereas the other one is based on a characterization method for the catalyst surface under *ex-situ* conditions. The robustness of these approaches is highlighted by the prediction of the same U-value for CuO by both these fundamentally different approaches, i.e., 4 – 5 eV. This U-value range is shown to correctly predict the surface associated properties like the O1s chemical shifts, the surface moieties (and their adsorption configurations) as well as the adsorption enthalpy of H₂ on CuO. It is demonstrated comprehensively that the commonly applied U-value of 7 eV (fitted against CuO bulk properties) fails to predict the experimental XPS shifts for the surface intermediates as well as the surface adsorption enthalpies. This provides evidence of the inability of the bulk property optimized U value to be applied to study surface reactions over TMOs. The XPS based DFT+U approach established in the current thesis is the first work of determining various surface species, their XPS BEs and the optimum U value for TMOs synergistically using XPS and DFT techniques. This novel approach can eliminate both computational (U-value) and experimental (complex XPS spectral analysis) bottlenecks associated with the combined application of these individual techniques, thus enabling their integration in the field of TMO surface catalysis. In whole, the DFT+U approaches elucidated in this thesis, encapsulates surface-adsorbate interactions, surface reactivity, and the dynamic surface

reaction environment and thus, delivers an appropriate U-value such that DFT calculations can be used to model reactions on metal oxide surfaces correctly.

After developing a robust method to capture surface chemistry on TMOs accurately, methane activation and dissociation are investigated over CuO(111) surface, under dry and moisturized conditions. It is revealed that the involvement of surface hydroxide $(OH)_{Cu\ site}^*$ species can reduce the barrier for first and second C-H bond activations of methane. These surface hydroxide $(OH)_{Cu\ site}^*$ species can be present due to the dissociation of water (supplied externally) as well as can be generated during the course of the reaction under dry conditions (reaction of surface hydroxyls generated from activation of C-H bonds). FTIR study under both dry and moisturized conditions, reveal the presence of first and second oxidation products (CH_3 -O, HCHO), CO_2 as well as different kinds of surface -OH species. FTIR investigations confirmed the formation of surface hydroxides, even in the absence of any moisture source in the system. It is revealed for the first time that even under dry conditions, the lattice oxygen may not activate the methane C-H bonds directly, but via the surface hydroxides formed on the surface. Promotional effect of moisturized surface approach in reducing the induction times for methane activation is established. It also recognized that water in the form of the moisturized surface can not only can act an initiator to reduce the induction time of the reaction but also that, such approach can lead to an increase lifetime of the catalysts due to water being the oxygen donor for the initial part of the methane activation.

In summary, this thesis focuses on (i) addressing one of the biggest and long-standing challenges for DFT methods to study TMO based catalytic systems. It establishes the importance of determining the U value based on surface properties as compared to conventional and widely practiced bulk property based U value determination. (ii) Establishing a novel computational and experimental XPS method to study surface moieties, their adsorbate configurations and predict their XPS shifts in parallel to determining the U value for respective TMO. This approach establishes the base for such experimental and computational integrated methods to study TMO catalyzed systems without prior knowledge or separate calculation for the respective U value. (iii) Establishing the formation and role of surface hydroxide species in methane activation and dissociation in the presence and absence of external moisture.

Some future research directions from the thesis can include (i) The extension of the DFT+U benchmarking approaches demonstrated in this paper (employing CuO as a model TMO) to other TMOs like NiO, Fe₂O₃, etc. thus providing more accurate comparative analysis for the performance of various TMO based systems, (ii) These integrated computational and experimental approaches can also be adjoined to other powerful and novel surface science techniques such as in-situ, operando and temperature programmed XPS, for more accurate determination and prediction of reaction mechanisms, pathways, active catalytic sites, and thus guide the design and development of efficient and novel TMO based catalysts. Integrated XPS and DFT for metal systems is one of the novel methods to study the surface catalytic reactions, and with the second approach

elucidated in this thesis, these integrated methods can now be extended to TMO based systems without the need of U value, (iii) With the establishment of the promoting role of surface OH species in the activation of C-H bonds of methane, further investigations can be done to examine the role of surface OH species on the reaction pathways and energetics on other catalytic reactions over CuO and other heterogeneous catalysts, (iv) Studying the CO and CO₂ formation pathways in methane oxidation is also vital in developing strategies and altering reaction conditions to suppress their formation. This is also important to control the CO/CO₂ ratio to further gain another control over the product distribution.

6 References

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