Syngas production from methane using ion transport oxides

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SYNGAS PRODUCTION FROM METHANE USING ION TRANSPORT OXIDES

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Abstract

Hydrogen will be an ideal clean energy carrier in the future if the Proton Exchange Membrane (PEM) fuel cell becomes economically available for automobile and domestic applications. Hydrogen at present is being produced in large quantities at a reasonable cost for industrial purposes. However, the challenge with tomorrow's hydrogen is the high cost of distributing hydrogen to dispersed locations. One solution to overcome this hurdle is through distributed small-scale hydrogen production.

In this study, a new process which is potential for small-scale H_2 production is implemented for the distributed hydrogen/synthesis gas production with the use of Ion Transport Oxides (ITOs). A simple cyclic reaction is proposed, where suitable candidates to be used in this system are determined. The ITOs were made to undergo reaction directly with methane at high temperature ranging from 800 to 950°C, forming hydrogen/syngas ($H_2 + CO$) in the production step (generation step) and these reduced oxides are recovered by air in the re-generation step. The overall equation for the reaction is $CH_4 + \text{air} \rightarrow CO + H_2 + N_2$.

The study covered three different categories of ion transport oxides namely the ABO_3 perovskite-type structure $La_{1-x}A_xBO_3$ perovskites-type oxides (A= Ba, Ca, Mg, and Sr while B=Cr and Fe), K_2NiF_4 structure $La_2Ni_{1-x}M_xO_4$ (M= Fe, Co and Cu with $x=0, 0.3, 0.5$) $La_{2-y}Ln_yNiO_4$ (Ln= Gd, Ce and Sr with $y=0.2, 0.6, 1.0$) and the fluorite-type structure, Gd, Sm and Y doped CeO_2 . The oxides were characterized by specific surface area measurements (BET), Scanning Electron Microscope (SEM), X-ray diffraction (XRD) and temperature programmed reduction (TPR). Subsequently, the catalytic properties of the oxides were studied by Temperature-Programmed Surface reaction (TPSR) and temperature-programmed oxidation (TPO) and catalytic activity measurements.

XRD analysis confirmed the formation of the respective ABO_3 perovskite structure, K_2NiF_4 structure and fluorite-type structure after high temperature calcination. The reducibility of the oxides is greatly affected by A- and/or B-site dopant and B- site ion type. Results showed that for both ABO_3 and K_2NiF_4 structured perovskite oxides, Sr is a good dopant to increase the oxygen content of the oxides and to reduce the generation temperatures. Subsequently, it was demonstrated that oxide ion removability either during reduction with H_2 or during partial oxidation with CH_4 is promoted if ceria is doped by Gd, Sm or Y.

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Abbreviations

AE	Alkaline earth metals
BET	Brunauer, Emmett and Teller
CeO₂	Cerium oxide
Ce₂O₃	Cerium (III) oxide
CH₄	Methane
CO	Carbon monoxide
CPO	Catalytic Partial Oxidation
CPOM	Catalytic Partial Oxidation of Methane
DOE	Department of Energy
EDX	Electron Dispersive X-ray
GC	Gas Chromatograph
GDC	Gadolinium Doped Ceria
ITOs	Ion Transport Oxides
LaACrO₃	AE doped Lanthanum Chromite oxide
LaCrO₃	Lanthanum Chromite oxide
LaAFeO₃	AE doped Lanthanum Ferrite oxide
LaFeO₃	Lanthanum Ferrite oxide
LSM	Lanthanum Strontium Manganate
LSCM	Lanthanum strontium manganese chromite
MS	Mass Spectrometer
NH₄OH	Aqueous Ammonia
ORC	Oxygen release capacity
OSC	Oxygen storage capacity
RT	Room Temperature
SEM	Scanning Electron Microscope
SMR	Steam Methane Reforming
Syngas	Synthesis gas
TCD	Thermal Conductivity detector
TE	Transition metals
TPO	Temperature Programmed Oxidation
TPR	Temperature Programmed Reduction
TPSR	Temperature-Programmed Surface Reaction
XPS	X-ray Photo-electron Spectroscopy
XRD	X-Ray Diffraction
YSZ	Yttrium-Stabilized Zirconia

CHAPTER 1:

Introduction

1.1. Overview

Hydrogen is not a natural energy source since it is not an abundant natural resource; however, it can be useful as a clean energy carrier with high enthalpy value [1]. It is regenerative and environmentally friendly. A transition from fossil fuels to hydrogen as a major fuel in the next 50 years could increase energy security and reduce environmental pollution. Due to growing interest in environmentally benign and energy-saving technologies, development in the field of distributed hydrogen production have been considerably intensified during the last decade. In particular, conversion of natural gas (methane) to hydrogen is considered to be a critical intermediate step in the drive to make viable the large scale production of hydrogen as a fuel for commercial and industrial use especially for the use in fuel cell [2]. Current commercial production of H_2 from natural gas involves primarily either steam methane reforming (SMR) or catalytic partial oxidation (CPO) which are some of the few synthetic gas manufacturing processes available in the hydrogen production economy as highlighted in [3]. In general, these technologies, though highly optimized over years of development, remain too expensive for large-scale production of H_2 , if H_2 is to be competitive with the current fuels. One way to overcome this is to distribute small-scale hydrogen production [4].

The challenge with tomorrow's hydrogen is the high cost of distributing hydrogen to dispersed locations. Today, global energy requirements are mostly dependent on fossil fuel which makes up about 80% of the present world energy demand. Eventually, this

will lead to the predictable depletion of limited fossil energy resources. Evidently, the utilization of fossil fuels are causing global climate change mainly due to the emission of pollutants like CO_x , NO_x , SO_x , C_xH_x , soot, ash, droplets of tars and other organic compounds into the atmosphere as a result of their combustion. Hydrogen, which has been suggested as the main energy source of the future could offer an answer to the threat of global climate change and help avoid the undesirable effects of the use of fossil fuels. Although it is estimated that hydrogen is more expensive than fossil fuels, hydrogen from renewable energy resources is a virtually inexhaustible, environmentally benign final energy source that could meet most of our future energy needs while avoiding the environmental costs and health problems associated with fossil fuels. Indeed, the demand of hydrogen for the production of hydrogen fuel cell is growing as the number of emission sources increases, contributing to rising levels of pollutants such as carbon monoxide and carbon dioxide gases, which in turn leads to the increase in global temperature. Not only is hydrogen gas an ideal clean energy source with high heating value, it is also regenerative and environmentally friendly.

Currently, there are three key challenges facing hydrogen economy:

- (i) produce more hydrogen at lower price;
- (ii) create effective hydrogen storage; and
- (iii) fabricate affordable $\text{H}_2\text{-O}_2$ fuel cells.

Hydrogen at present is being produced at large quantities at a reasonable cost for industrial purposes. However, the challenge with tomorrow's hydrogen is the high cost of distributing hydrogen to dispersed locations. One solution to overcome this hurdle is through distributed small-scale hydrogen production. The United States Department of

Energy (DOE) recommends small-scale direct hydrogen production using natural gas reforming [5]. Small-footprint plants for hydrogen are expected to be demonstrated in 2011 while in 2015 fueling park-commercial production of hydrogen from natural gases are targeted to reduce the cost of hydrogen by 25% [6].

Ninety five percent of hydrogen today is produced from natural gas by steam methane reforming. However, steam methane reforming is highly endothermic and requires superheated steam to convert methane and water vapour into hydrogen and carbon monoxide. Therefore, a large reactor is needed which leads to a large consumption of energy. In addition, it does not readily scale down to small scale production. Catalytic partial oxidation of methane is an attractive alternative. It is a process whereby hydrogen is produced through partial combustion of methane with oxygen gas to yield carbon monoxide and hydrogen [7]. In this process, heat is produced in an exothermic reaction and there is less energy consumption. Moreover, the reactor needed for the process is small thus a more compact design is possible. From an economic evaluation, the technology based on catalytic partial oxidation was found to be cheaper than steam methane reforming and the emission of CO_x to the atmosphere was much lower for catalytic partial oxidation. Therefore, catalytic partial oxidation is a promising alternative for distributed hydrogen production.

Effective technologies for the hydrogen production from natural gas via catalytic partial oxidation are developed for reducing the cost of production. One strategy to reduce the hydrogen production cost is to use air instead of pure oxygen as a raw material for the oxidation of natural gas. Membrane reactors which can combine the catalytic partial oxidation reaction and air separation in a single unit operation are one of the

approaches for this strategy. This approach however is not free of problems as the membranes require very high oxygen permeability and must be chemically and mechanically stable. As a result, materials which could fit into these requirements will be extremely difficult to locate.

On the other hand, a number of oxides available may have high oxygen permeability at high temperatures but under harsh environment, their performance may deteriorate as they are being deactivated. Such situation occurs when one side of the membrane is exposed to air and the other side to the syngas mixture; the oxides may undergo phase transitions and finally decompose, limiting the usefulness of such materials in commercial applications. Additionally, it is difficult to manufacture the membrane reactor without cracks and pin-holes, which requires good matching of thermal expansion coefficients of the membrane. Moreover, a long induction period of more than 20 hours is normally needed for the oxygen permeation rate to reach steady state [7].

Therefore, this research project is aimed at developing a new technology for distributed hydrogen production in which Ion-Transport Oxides (ITO) are synthesized using two different techniques for the partial oxidation of methane at a lower temperature to produce hydrogen gas. The reduced oxides are then recovered by air in the regeneration step. The main advantage of this new technology is its great flexibility as the restrictions derived from the membrane mechanical and chemical stability, as well as the manufacturing process of the membrane reactor, can be ignored. Moreover, since the reaction occurs between methane and lattice oxygen in the absence of gaseous oxygen, the risk of explosion which may be caused by mixtures of methane and pure oxygen will

be minimal. The selectivity of carbon monoxide and hydrogen is expected to be higher than conventional catalytic partial oxidation since further oxidation of carbon monoxide and hydrogen to carbon dioxide and water, is limited without the presence of gaseous oxygen.

1.2. Objective

This project and its research area are aimed at identifying suitable ITOs candidates for the purpose of designing a novel operation system that can perform at high effective productive level and at mild operating conditions. The candidates selected must have high oxygen species content. These oxide candidates must be able to achieve high methane conversion, high hydrogen selectivity and high hydrogen productivity. Through this project, it is hoped that catalysts can be developed with effective preparation method to fulfill the above target.

1.3. Scope

There are three aspects to this project involving the production of syngas:

1. Identifying potential ITOs candidates i.e. the ABO_3 perovskite type oxides, fluorite-type oxides and K_2NiO_4 structure oxides which are suitable to form syngas through partial oxidation reaction with methane.
2. Preparation of these potential ITOs through different synthesis routes.
3. Performing characterization and activity tests on the synthesized oxides.

The research carried out in the course of this project is confined to experimentation and characterization, in which the relationship between the physical properties of oxide materials (GDC, LSM, etc) and the catalytic property are established.

1.4. Synopsis of Chapters

The report is organized as follows:

1. Chapter Two covers mainly on the literature review of the past study and findings of other researchers on the area of the syngas production from natural gas in particular the commonly and widely used gas i.e. methane. Subsequently, the principles, theories and synthesis routes related to the ion transport oxides that are of interest to the current project scope.
2. Chapter Three describes the materials, the equipment and synthesis routes that have been used to prepare and test the test samples. In addition, it also includes the experimental procedures for both the catalytic activity and characterization tests.
3. Chapter Four, Five and Six present the data collected from the various tests conducted and discussions on the tabulated results of the prepared ion transport oxides. The focus of Chapter Four is on the $\text{La}_{1-x}\text{AB}_x\text{O}_3$ oxides while Chapter Five concentrates on the doped La_2NiO_4 at both A- and B-sites. Chapter Six reviews on the Fluorite type doped commercial CeO_2 oxides.
4. Chapter Seven brings to a close of the past two years research work with a summary of what was accomplished and the information that can be drawn

from the results obtained. Subsequently, an outline is drawn for future work that can be carried out with the useful findings from this project.

CHAPTER 2:

Literature Review

2.1. Hydrogen Production from Methane

In this section, some of the ways to produce hydrogen are described, including both their benefits and short-comings. Based on these, a novel technology of producing hydrogen is put forward with the aim to overcome the bottlenecks of the former methods discussed.

2.1.1. Steaming Methane Reforming (SMR)

Steam methane reforming (SMR) (Eq. (1)) is a well established, commercialized process, which is most commonly used for the large synthesis gas production [8]. As shown in Figure 2.1, the main process step involves reaction of steam with a hydrocarbon over a catalyst at around 750°C-800°C to form hydrogen and carbon monoxide [9-12]. In order to obtain acceptable reaction rates a catalyst (for example: Pd/ZnO catalysts) is required to accelerate the process. Even more, the catalyst should be stable under the rather extreme conditions under which high CH₄ conversions can be reached at high temperatures. However, there is a high probability of unwanted side reactions involving carbon deposition. To obtain pure hydrogen, purification steps in the downstream of the SMR plant are necessary to remove undesired compounds of this nature.

Although SMR is extremely productive, this reaction is highly endothermic, requiring superheated steam making energy consumption very extensive. Moreover, a large reactor is needed for this process such that the construction costs become high. Thus it cannot be scaled down to smaller production. Consequently, this reaction also emits high CO_x content, a pollutant to the atmosphere.

Figure 2.1: Schematic diagram of steam reforming process [13].

2.1.2. Dry reforming (Reforming of Methane with CO₂)

An alternative way to reforming CH₄ with H₂O (steam), is to reform using CO₂. The overall reaction equation (Eq. (2)) for the dry reforming of methane over La_{1-x}Sr_xNiO₃ catalyst, as it is usually termed, is:

One attraction of dry reforming process is due to its environmental friendliness, since the greenhouse gas CO₂ is consumed instead of being produced. Also, by adding a certain amount of CO₂ to the feed gas for conventional reforming with steam, it is possible to adjust the H₂/CO ratio at a range from 1:1 to 3:1 to meet specific usage [14, 15, 16].

2.1.3. Catalytic Partial Oxidation of Methane (CPOM)

The catalytic partial oxidation process (Eq. (3)) has captured wide attention as a noteworthy method that can drastically reduce production costs in the future. In CPOM, the reaction is exothermic, and energy consumption is lower than in the endothermic reaction of steam reforming [17, 18]. Since the reaction speed is rapid, the reactor is extremely small, and in comparison to the non-catalytic partial oxidation process, there is no generation of soot or other unnecessary byproducts. A major difficulty with this process lies in the consumption of large quantities of expensive pure oxygen. However, comparing with the conventional steam reforming method, catalytic partial oxidation of methane (CPOM) is more energy efficient and can be carried out at lower investment, and will produce synthesis gas with a H_2/CO ratio of 2 [13, 19]. In general, the mechanism of CPOM involves the conversion of CH_4 to CO_2 and H_2O followed by the reforming of the remaining CH_4 with steam and CO_2 to produce H_2 and CO . Catalysts such as Nickel, Cobalt, and Platinum are used for this process.

Distributed generation of hydrogen from CPOM of natural gas provides a cost reduction of 20-30% as compared with other available ways. Emission of CO_x to the atmosphere was significantly reduced, approximately 60%, as compared to Streaming Methane Reforming.

As observed, not many studies have been completed on the economy of the catalytic partial oxidation method due to the fact that the technology is still young and under development. Also, it is difficult to obtain a picture of it in its fully completed form.

Nevertheless, in the prefaces of various research reports, it is always pointed out that the catalytic partial oxidation method is superior to other conventional methods in terms of economical view and that great expectations have been pinned on its development.

2.1.4. Methane Oxidation Using Oxygen-Permeable Ceramic Membranes

Technologies for hydrocarbon oxidation using ceramic mixed-conductive membranes permit the integration of oxygen separation, steam reforming and partial oxidation into a single step for natural gas conversion. The dense ceramic membranes use air as the oxidant for methane conversion reactions, thus eliminating the need for an expensive oxygen separation unit. Oxygen is transported across the ceramic material in the form of oxygen anions, instead of oxygen molecules, for the oxidation of methane to produce syngas. In addition, the presence of active oxygen species (O^{2-} , O^-) at the membrane surface may improve the selectivity of methane oxidation reactions [7, 20].

The suggested reaction process involves applying an oxygen partial pressure difference to the membrane tube by exposing one side of the membrane tube to air and sweeping the other side of the tube with methane gas. The main disadvantage of using such ceramic membranes is that they undergo phase transitions and decompose easily, therefore limiting the usefulness of such materials in commercial applications.

2.1.5. Novel technology

The main concept of this simple yet novel technology is to allow ion transport oxides (ITOs) to react with methane under suitable conditions to produce syngas in the production (generation) step. Reduced oxides are recovered by air under suitable conditions in the re-generation step. The generation and re-generation steps continue, forming a cyclic operation as shown in Figure 2.2.

Production/Generation Step

Re-Generation Step

Figure 2.2: A cyclic operation of generation and re-generation to produce syngas.

Production/Generation step

In this step, methane gas and argon (carrier gas) are passed through the loosely packed ITO (as indicated by the orange color block in Figure 2.2). The temperature is gradually increased to initiate the reaction. During reaction, syngas (CO and H₂) is produced as shown in equation Eq. (4).

At high temperature (above 800°C), rapid oxygen ion transport is realized via oxides vacancies or oxygen interstitial migration. The lattice oxygen (O^{2-}) from ITO oxidizes methane to CO and H_2 under suitable conditions. The suitable conditions include having sufficient energy to break the C-H bond in methane and adequate methane flow through the ITO (Figure 2.3) in order for CPO reaction to take place. The bonding energy of C-H is 415.8 KJ/mol.

Figure 2.3: Illustrating the reaction mechanism between methane and the lattice oxygen in ITO. The latter (O^{2-}) forms covalent bond with carbon to give carbon monoxide.

Re-generation step

In this re-generating step, air (an electron acceptor) is passed through the reduced ITO. O_2 , being one of the main components of air recovers the oxides. N_2 , the other main component of air passes through the loosely packed ITO. There is no H_2 being produced in this step.

The combination of one generation and re-generation test forms a complete cycle. This cyclic novel operation system can continue as long as suitable conditions exist.

Advantages of the novel technology

In this technology, the production cost is greatly reduced with the use of air in place of pure oxygen as a raw material. In addition, what makes this methane conversion process a novel technology is its great flexibility. The restrictions derived from the membrane mechanical and chemical stability, as well as the membrane-reactor manufacture [21], can be released. Since the reaction occurs between methane and lattice oxygen in the absence of gaseous oxygen, there is no risk of explosion which may be caused by mixtures of methane and pure oxygen. The selectivity of CO and H₂ is expected to be higher than conventional Catalytic Partial Oxidation (CPO) since further oxidation of CO and H₂ (to CO₂ and H₂O) is limited without the presence of gaseous oxygen. As such, the life span of the ITOs will be longer and its potential value can be fully utilized.

2.2. Ion-Transport Oxides (ITOs) for the Novel Technology

The materials to be used in the novel technology must possess high oxygen mobility and oxygen content for the reaction with methane to form syngas under suitable conditions. One of the most promising candidates is the oxides which fall under the main group of Ion Transport Oxides (ITOs).

Ion transport oxides generally refer to the oxides with the perovskite-structure ABO₃ (e.g. CaTiO₃), perovskite-related tetragonal structure K₂NiF₄ (e.g. La₂CuO₄) or ceria-based fluorite type structure, which contains mobile oxygen ions. Excess oxygen ions can potentially be compensated for via several mechanisms, involving cation anisette, oxygen vacancies or oxidized lattice oxygen ions. ITOs possess highly symmetrical

structure, relatively large unit cell free volume and disordered oxygen vacancies [22]. The highest ionic conductivities for oxides are obtained in lattices in the absence of strain where isolated oxygen vacancies dominate.

Rapid oxygen ion transport is another characteristic of these oxides group that will allow high ion mobility leading to high oxide ion conductivity. The overall transport was found to be controlled by an oxygen exchange reaction at the grain boundaries. The movement of oxygen ion through the lattice is important for catalytic reactions at the surface.

Another feature of the ITOs is that it allows doping with different metals group according to the desired end product. The main parameter in determining both the concentration of the dopant and the mobility of oxides vacancies in the doped oxides is the concept of matching radius. The cations display minimum disruption of lattice structure when their radius is close to that of the ion they are displacing. For example; the radius of Ca^{2+} ion is the closest to that of La^{3+} ion in $\text{La}_{0.7}\text{Ca}_{0.3}\text{CrO}_3$. This will result in lattice without strain, leading to higher oxide vacancy mobility. The ionic radii of several potential elements are listed in Table 2.1.

Table 2.1: Ionic radii of cations with different coordination numbers [23].

Cation	La^{3+}	La^{3+}	Ba^{2+}	Mg^{2+}	Ca^{2+}	Ca^{2+}	Sr^{2+}	Sr^{2+}	Al^{3+}	Ce^{4+}	Ce^{4+}
Ionic radius (10^{-10}m)	1.03	1.36	1.35	0.72	1.00	1.34	1.18	1.44	0.54	0.87	0.97
Coordination number	6	12	6	6	6	12	6	12	6	6	8

In the next section, the three main categories of Ion Transport Oxides (ITOs) which are namely the perovskite- type ABO_3 , Ceria based fluorite-type and K_2NiF_4 structure will be described in greater details.

2.2.1. ABO_3 Perovskites

In the past years, perovskite-type oxides ($\text{ABO}_{3-\delta}$), perovskite-like oxides ($\text{A}_2\text{BO}_{4-\delta}$), and layered perovskite oxides (e.g. $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$) have been investigated extensively and intensively for the total oxidation of carbon monoxide and hydrocarbons [24-28]. This is because they show promises for many practical catalytic applications. These compounds are also suitable for fundamental studies of catalysis for the following reasons: (1) they are all of well defined structure, so that information on the solid-state and surface chemistry can be obtained without difficulty in using various analytical instruments, and (2) the oxidation states of the transition metals and the solid defect structures can be controlled in a systematic way by changing the constituent elements A or B and the conditions of preparation, so that they can be used as model compounds for investigating the role of defects in catalysts. Therefore, the amount of non-stoichiometric oxygen content and the redox ability determine the catalytic property of the perovskite. By partial substitution of ions in site A and/or site B, one can regulate the amount of oxygen non-stoichiometry and the valence distribution of the B-site ion. The controllable physicochemical properties of these catalytic materials make them useful models for the study of specific reactions. In the cubic ABO_3 lattice (Figure 2.4), the A-site ion is 12-fold coordinated and the B-site ion is 6 fold coordinated with O^{2-} ions. The A and O form a cubic closest packing, and B is contained in the octahedral voids in the packing. In

order for the ions to be in contact with each other in the ideal cubic structure, $r_A + r_O$ must be equal to $\sqrt{2}(r_B + r_O)$, where r_A , r_B , r_O are the ionic radii of the A, B and oxygen ions [29]. From this relation Goldschmidt defined a tolerance factor as shown in Eq. (6).

$$t = \frac{(r(A) + r(X))}{\sqrt{2}(r(B) + r(X))} \quad (6)$$

The perovskite structure is stable within the range $0.8 < t < 1.0$, and $r_A > 0.090$ nm, $r_B \geq 0.051$ nm [25]. A great many elements can form ideal or modified perovskites depending on the tolerance factor. The stability range allows a plethora of chemical compositions for the perovskite oxides, and depending on the valency of the cations the combinations $A^{1+}B^{5+}O_3$, $A^{2+}B^{4+}O_3$ and $A^{3+}B^{3+}O_3$ are all possible. Also, partial substitution of any or both of the A and B cations for A' and B' can be used to form species like $(A_xA'_{1-x})(B_xB'_{1-x})O_3$, or even more complex compositions. Likewise, A' and B' can be of the same or a different valency as the A and B ions.

Figure 2.4: Unit cell of the ABO_3 perovskite structure. The A cations occupy the larger spaces in the 12-fold oxygen coordinated holes; the B cations occupy the much smaller octahedral

holes (sixfold coordination). Full or partial substitution of the A or B cations [30].

The formation of the $\text{ABO}_{3\pm x}$ perovskites is mainly governed by the ability of the transition metal at the B-site to take several oxidation states and several co-ordinations although oxygen vacancies are more common than oxygen excess (i.e. cation vacancies), there are a few systems showing apparent oxygen excess, including $\text{LaCrO}_{3+\lambda}$.

It is a well known fact that the LaMO_3 systems comprise a rich family of compounds that exhibit high oxygen ion conductivity and find use in solid oxide fuel cells [31]. The LaCrO_3 oxide is known to be an orthorhombic derivative of the perovskite structure (Figure 2.5). Electron hole formation is favored in oxidizing atmosphere and is compensated by La or Cr vacancies. The electrical conductivity can be increased by lower valence substitution on either the La^{3+} or Cr^{3+} sites, resulting in an increase in the electron hole concentration [32].

Figure 2.5: Crystal structure of the rhombohedral phase of LaCrO_3 .

Although LaCrO_3 -based materials are in general poor SOFC anodes due to the poor catalytic activity for the oxidation of hydrogen and hydrocarbon fuels [33, 34] their properties can be improved to a great extent with suitable dopant candidate under

elevated temperature. This is owing to the fact that they have high electrical conductivity and good stability under high operating temperature and in corrosive environments. It has also been widely researched and published that incorporation of dopant ions to parent LaMO_3 oxides is crucial for promoting catalytic activity and high ionic conductivity [35-38]. Sfeir et al. [39, 40] studied the thermodynamic stability and the catalytic activity of the $(\text{La}_x\text{A}_{1-x})(\text{Cr}_x\text{B}_{1-x})\text{O}_3$ system ($\text{A}=\text{Ca}$, Sr and $\text{B}=\text{Mg}$, Mn , Fe , Co , Ni) as the alternative anode materials under simulated SOFC operation conditions. Ca and Sr substitution at the A-site improves the catalytic activity, and for B-site substitution, Co and Mg show an inhibiting effect while Mn , Fe , Ni improves the activity. Tao and Irvine [41, 42] studied the performance of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.25}\text{Mn}_{0.5}\text{O}_3$ (LSCM) as anode for direct methane utilization in SOFCs. Also the Lanthanum chromite based oxides were shown to have very low activity towards carbon deposition [43, 44].

Perovskite-type nanocrystalline LaFeO_3 is an interesting material in which the amounts of adsorbed and lattice oxygen under different compacting pressures change dramatically. This LaFeO_3 perovskite catalyst which exhibits excellent redox property, high oxygen mobility, and thermal stability are of practical interest for electro-ceramic applications in catalysis. The importance of these materials is mainly due to a wide variety of applications in catalysis [45], as active catalysts for oxidation or reduction of pollutant gases [46, 47], as electrode materials in solid oxide fuel cells [48, 49, 50] or materials for technological chemical sensors: oxygen sensor electrodes chemical sensors for the detection of humidity, alcohol, gases [51, 52], and oxygen permeating membranes [53]. LaFeO_3 oxide is also known to show high catalytic activity for the complete oxidation of hydrocarbons, and thus can replace noble metals as combustion catalysts

[54]. Improved catalytic performance can be obtained from nanoparticles of LaFeO_3 , which have much larger surface area than bulk materials.

Ionic conductivity of ABO_3

The conductivity of perovskite-type ABO_3 highly depends on occupied species in the crystal lattice of the constructed elements. The optimum oxide ion conductor should be found among the $\text{A}^{3+}\text{B}^{3+}\text{O}_3$ type of perovskites. This is because of the lowest oxide-B-ion interaction, giving rise to highest oxide vacancy mobility. The perovskite structures with transition metal in B site easily make the oxygen vacancies, because the B ions can take several valence states.

Perovskites based on LaBO_3 (B is Al, In, Sc, Y) have low oxygen ionic conduction. Sr^{2+} is one of the best alkaline earth dopants used to increase oxygen deficiency in LaAlO_3 . The oxygen ionic transport of $\text{La}_{1-x}\text{MnO}_3$ with ($x = 0.0 - 0.18$) is ranged from 3.0×10^{-5} to 5.0×10^{-5} at 1273K. The partial ionic conductivity of perovskite phases, derived from LaBO_3 at 800 °C is shown in Table 2.2.

The highest oxide ion conductivity in perovskites was found in Sr and Mg doped LaGaO_3 . This is achieved by substituting lanthanum with alkaline earth elements or incorporating divalent metal cations such as Mg^{2+} , into the gallium sub-lattice in order to increase the oxygen vacancy concentration and having the least lattice distortion at the same time. The maximum ion transport is found in $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-\delta}$ (LSGM), where $x = 0.10-0.20$ and $y = 0.15-0.20$. At 700 to 950 °C, the oxygen ion transference number of LSGM ranges from 2.2×10^{-3} to 1.5×10^{-2} [55]. The oxygen ion conductivity of

$\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.8}$ (LSGM) is 0.15 S/cm at 800°C [56]. At 800 to 950 °C, the oxygen ion transference number of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}(\text{Al},\text{Cr})\text{O}_{3-\delta}$ is from 10^{-4} to 10^{-2} .

Table 2.2: Partial ionic conductivity of perovskite phases, derived from LaBO_3 ($B = \text{Al}, \text{In}, \text{Sc}$) [41].

Composition	Temperature (°C)	Conductivity (S cm^{-1})
$\text{LaSc}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$	800	2×10^{-4}
$\text{La}_{0.9}\text{Sr}_{0.1}\text{AlO}_{3-\delta}$	800	2×10^{-3}
$\text{La}_{0.9}\text{Sr}_{0.1}\text{ScO}_{3-\delta}$	800	7×10^{-3}
$\text{La}_{0.9}\text{Sr}_{0.1}\text{InO}_{3-\delta}$	800	7×10^{-3}
$\text{La}_{0.9}\text{Sr}_{0.1}\text{Al}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$	800	2×10^{-4}
$\text{La}_{0.9}\text{Sr}_{0.1}\text{Sc}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$	800	5×10^{-4}
$\text{La}_{0.9}\text{Sr}_{0.1}\text{In}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$	800	9×10^{-4}

Doping Effect on ABO_3

High electrical conductivities can be obtained by doping with alkaline earth metal (AE) element. In addition, carbon deposition can be suppressed by the use of alkaline oxides or rare earth oxides in catalysts [57, 58]. Although the AE-doping can control thermal expansion behavior for LaCrO_3 and LaFeO_3 , the heavy doping causes a large thermal expansion under a reducing atmosphere [59]. However the AE doping is also indispensable in obtaining a dense LaCrO_3 and LaFeO_3 body. Therefore, the AE-dopant content in the lanthanum chromites must be well-controlled such that the amount can strike a balance between both the properties [60].

2.2.2. Fluorite type Ceria-based oxides

CeO_2 and CeO_2 containing materials have been studied as catalysts, structural and electronic promoters used for heterogeneous catalysis over past years. Cerium based oxides with metal doping have also been widely investigated for their potential applications especially in solid oxide fuel cells, nonvolatile memories, oxygen permeation membranes and magnetic memory media. It has been shown that cerium oxide having a fluorite structure promotes oxygen storage and release to enhance oxygen mobility, forming surface and bulk vacancies to improve the catalyst redox properties of the composite oxide when it is associated with transitional metal oxides [61-63]. This interesting property of cerium oxide (CeO_2) in its ability to release and absorb oxygen during alternating redox conditions could enable it to function as oxygen buffer in many applications. The concentration of oxide ion vacancies can be increased with the addition of rare earth oxides and yttria which are highly soluble in ceria, to a level of about 40% or more [64], but the fluorite-related structure must be maintained. The amount of isolated oxide vacancies reaches a maximum in the maximum doping range. At higher doping level, there will be structure re-arrangement, resulting in a decline of surface vacancies and a reduction in reactivity of the sample. Dopants like Gd_2O_3 , Y_2O_3 , Sm_2O_3 and CaO give the highest maximum conductivities [65]. Thus the properties of the oxygen vacancies, e.g., local atomic structure and chemical environment, and binding energies, can in principle be controlled by the choice of dopants [66].

T.S. Zhang had investigated the ionic conductivity of different doping of CeO_2 (e.g. Ca^{2+} , Sr^{2+} , Y^{3+} , La^{3+} , Gd^{3+} , Sm^{3+} and dopant concentration of 1- 4. The highest level of oxygen ionic transport is found in $\text{Ce}_{1-x}\text{M}_x\text{O}_{2-\delta}$, where $\text{M} = \text{Gd}$ or Sm and $x = 0.10$ to

0.20. It is generally accepted that Gd^{3+} and Sm^{3+} - doped CeO_2 exhibit the highest conductivity due to the small association enthalpy between dopant cation and oxygen vacancy in the fluorite lattice. The oxygen ion transference number of ceria-based oxides and Yttria Stabilized Zirconia (YSZ) was almost unity at 600°C to 800°C , whereas that of pure ceria was only about 0.4 [67]. Under oxidizing condition, $\text{Ce}(\text{Zr})\text{O}_{2-\delta}$ has a oxygen ion transference number of 0.8 at 950°C [68].

In addition, it is well known that the addition of CeO_2 as a promoter in the common automotive catalysts (so-called three way catalysts) allows the catalyst to operate over a wide range of air to fuel ratios. In other words, CeO_2 can provide oxygen for oxidizing CO and hydrocarbons under rich fuel conditions and remove it from the exhaust gas phase for reducing NO under lean fuel conditions: this is called the oxygen storage capacity [69-72]. Besides, CeO_2 is known to enhance CO and NO conversion [73-75], promote a low-temperature water-gas shift [74], stabilize noble metal dispersion [76], and minimize the thermally induced sintering of alumina supports.

Special attention also has been focused in recent years on the preparation of ceria, structurally doped with ZrO_2 . It has been reported that the thermal stability, redox properties and catalytic activity of these materials are strongly enhanced in comparison with pure CeO_2 [77-81]. A quantitative estimation of the amount of oxygen released and regained in the reduction-oxidation cycle showed that the bulk of the support material was involved [82]. It was found that the incorporation of Zr^{4+} into the lattice of CeO_2 strongly favored the creation of structural defects, and resulted in the acceleration of oxygen diffusion in the bulk. A correlation between phase modification and redox behavior of $\text{CeO}_2\text{-ZrO}_2$ solid solutions was studied in references. It was concluded that a

cubic lattice favors oxygen diffusion in comparison with a tetragonal one. To stabilize the cubic modification of $\text{CeO}_2\text{--ZrO}_2$ solid solutions, a high ceria content (>50 mol%) is required.

2.2.3. K_2NiF_4 structure like Oxides

Among the attractive alternatives to the mixed conductors having perovskite or related perovskite structure is the K_2NiF_4 structure [83]. This structure consists of layers of ABO_3 separated by A-O layers in which it is possible to incorporate excess oxygen in the unusual form of an interstitial species. This excess of oxygen provides an attractive alternative to the vacancy-based conduction mechanism present in the perovskite and fluorite oxides where the dopant–vacancy interaction can limit the observed conductivity. Compared to these latter oxides, this layered structure has a particular interest because it allows great flexibility in the oxygen stoichiometry [84–89]. For Catalytic Partial Oxidation of Methane, several perovskite-type precursors were used such as Ni-based and Co-based catalysts [90]. It was reported that Ni-based catalysts were more active than Co-based catalysts. Among the perovskite catalysts tested, La_2NiO_4 , a K_2NiF_4 -type perovskite oxide exhibits a rather high activity and stability. In addition, it also possesses appreciable oxygen permeability at elevated temperature [84, 91].

Takehira et al. [92] reported that Ni supported on perovskites like $\text{Ni}_{0.2}/\text{ATiO}_3$ (A:Ca, Sr or Ba), which were prepared by solid phase crystallization, showed good activity and selectivity as well as very low coke formation. Also, Tsipouriari et al. [93, 94] investigated the partial oxidation of methane to synthesis gas over a $\text{Ni}/\text{La}_2\text{O}_3$ catalyst and observed that CH_4 conversion and H_2 selectivity were close to thermodynamic

predictions. However, Ni catalysts suffer from the problem of coke formation. To inhibit carbon deposition, one must keep the size of the metal clusters smaller than the critical size needed for coke formation.

For an application in SOFC devices, $\text{La}_2\text{NiO}_{4+\delta}$ oxides are of significance because of their mixed conductivity due to the incorporation of additional oxygen on the interstitial sites. In particular, the oxygen ionic diffusion is some orders of magnitude higher than in perovskite. As shown in Figure 2.6, an important feature of this structure La_2NiO_4 is that it can accommodate both oxygen vacancies and excess oxygen atoms in interstitial positions between the layers, tetrahedrally coordinated by La^{3+} cations. In $\text{La}_2\text{NiO}_{4+x}$ at ambient temperature, x can be as high as 0.18 and in $\text{Pr}_2\text{NiO}_{4+x}$, the maximum value of x is 0.22. Even at ambient temperature, the oxygen interstitials are mobile enough to permit determination of the oxygen excess phase behavior by electrochemical oxidation in an aqueous KOH electrolyte. At higher temperature, the diffusivity increases though this is offset by the decrease in the concentration of oxygen interstitials. However, recent studies on La_2NiO_4 oxide showed that the electrical conductivity of this oxide is quite low [95]. It was also found that although the La_2NiO_4 catalyst exhibited excellent catalytic activity and stability, the specific surface area of these catalysts did not meet the requirements for industrialization.

Figure 2.6: The La_2NiO_4 unit cell without octahedral canting. The interstitial defect site is shown along with an outline of the tetrahedral La coordination environment. The interstitial site is also tetrahedrally coordinated by apical oxygen ions [96].

2.3. Synthesis Routes

The properties of ceramics are greatly affected by the characteristics of the powder, such as particle size, morphology, purity and chemical composition. Using chemical methods, e.g., co-precipitation, sol-gel, hydrothermal and colloid emulsion technique have been confirmed to efficiently control the morphology and chemical composition of prepared powder. Water-based chemical methods offer numerous advantages like being environmentally benign, using cheap and easy to handle starting products and low production cost, uncomplicated equipment, while requiring only a low energy input. Moreover they allow the easy tailoring of synthesis parameters throughout the whole process, which may be exploited to achieve a more precise control of composition, shape and size of the resulting material. Thus this session will be looking

into various synthesis routes commonly used in the researcher field where the preparation of ion transport oxides are concerned.

2.3.1. Solid State Reaction

Solid-state synthesis is the old conventional way to prepare powder chemically in the absence of a solvent. Solid-state reactions are generally consist of three types [97]:

- Reactions between neat reactants
- Reactions between supported reagents on solid mineral supports in “dry media” by impregnation of compounds on silica, alumina, or clays
- Phase-transfer catalysis (PTC) conditions in the absence of organic solvent, i.e., when a liquid reagent acts both as a reacting and an organic phase. This method is specific for anionic reactions as it involves “anionic activation”.

Since these solventless reactions often involve extreme conditions which are high temperature and/or high pressure, solvothermal techniques are considered part of the solid-state tool kit. Ultimately, solid-state synthesis is used where other techniques will not suffice: the production of bulk crystals, refractory ceramics, solid solutions, and glasses. This synthesis route is used to create the unique compositions and morphologies needed to generate the desired attributes in scintillation crystals, piezoelectrics, and other advanced materials. The absence of solvents coupled with the high yields and short reaction times often associated with this conventional reaction make their simple procedures very attractive for synthesis.

2.3.2. Co-Precipitation

Although chemical reactions for material synthesis can be carried out in the solid, liquid, or gaseous phase, it is advantageous to carry out these reactions in the liquid or gaseous states. Diffusion of matter in the liquid or gas phase is typically many orders of magnitude larger than in the solid phase, thus synthesis of nano-structured materials can be carried out at lower temperatures.

Precipitation is the synthesis of particles in a solution occurs through a chemical process. And in many cases, when a mixture of two or more than components is used, the chemical process is often term as “co-precipitation”. A general setup of the reflux experiment is graphically illustrated in Figure 2.7. The reactants are introduced into a solution after which the addition of reagents such as reducing and oxidizing agents chemical reactions occur and the solution becomes supersaturated with the product. The supersaturation drives the chemical system beyond the minimum free energy configuration. Thus, in order to restore the thermodynamic equilibrium of the system, product falls out of solution in solid particle form. Two types of precipitation often occur, homogenous and heterogeneous. Homogenous precipitation does not involve any foreign species while heterogeneous precipitation allows precipitation on foreign particles.

The physical appearance of precipitates is dictated by the level of supersaturation. Low supersaturation levels give small, compact, and well formed particles while that of high levels give large and dendritic particles. Even higher levels of supersaturation give compact, but agglomerated, clumped particles. When particles are formed nearly at the same time, a narrow size distribution is achieved. Homogenous precipitation requires

proper concentrations of reagents, while heterogeneous precipitation occurs if foreign matter is present in the solution. Heterogeneous precipitation results in large particle sizes.

Figure 2.7: Schematic of steps in the preparation of supported catalysts by precipitation alkali solution [98].

In addition, the precipitant obtained can differ according to the precipitating agents used in which two of the more commonly used type are the carbonate and oxalate respectively. The oxalate co-precipitation is an appropriate method for the synthesis of precursors in particular for superconducting materials. As shown in Table 2.3, the optimum pH value for the quantitative oxalate co-precipitation was established at 3.0 – 3.5, at the optimum oxalic acid concentration of 0.1M.

Table 2.3: Optimum pH-values for the oxalates precipitation [99].

$C(H_2C_2O_4) \text{ mol}\cdot\text{l}^{-1}$	0.05	0.1	0.2	1.0
Cu^{2+}	1.2-1.6	2.1-2.3	0.8-1.3	0.7-0.8
Ca^{2+}	>4.9	>4.8	>4.4	4.1-4.3
Sr^{2+}	>5.1	>5.7	4.7-5.2	4.2-4.9
Ba^{2+}	>4.7	>4.5	3.7-4.5	2.8-3.3
Pb^{2+}	1.5-3.0	1.5-2.3	1.3-2.2	0.8-1.5
Y^{3+}	1.0-1.5	0.9-1.4	0.7-1.2	0.4-0.8

In the aqueous synthesis method, water is usually used as a solvent. Water, due to its high permittivity, is an excellent solvent for both polar and ionic compounds. Precious elemental metal powders for electronic applications are prepared by adding liquid reducing agents to aqueous solutions of respective salts at adjusted pH levels. Nano-structured amorphous alloys, crystalline alloys, and composites can also be prepared using aqueous methods.

With this easy and simple method for preparation of catalysts is that it is highly desirable to obtain uniform and finely divided deposits, which translate to a high surface area catalyst of high activity. This wet chemical method has several advantages over conventional ceramic method for the preparation of the ceramics. These include fine particle size, high surface area, high reactivity and compositional homogeneity. Subsequently, this simple co precipitation method is attractive for large-scale powder production because of good stoichiometric, controlled homogeneous mixing on the atomic scale and less time consumption compared to other techniques [100-102]. The only drawback of this method is that all the phases of the components used should have similar solubility products.

2.3.3. Hydrothermal Synthesis

Hydrothermal synthesis is a process that utilizes single or heterogeneous phase reactions in aqueous media at elevated temperature and pressure to crystallize anhydrous ceramic materials directly from solutions. This aqueous chemical process can be easily differentiated from other processes, such as sol-gel and co-precipitation, by the temperatures and especially the pressures involved. The temperatures lie between the boiling point of water and its critical temperature (374°C), whereas pressures can go as high as 15 MPa [103, 104]. The calcination step required by earlier techniques is eliminated and many of the other steps employed in the previous wet methods can be used in hydrothermal processes. This synthesis technique offers a low-temperature, direct route to oxide powders with a narrow size distribution avoiding the calcinations step. Other advantages are the use of inexpensive raw materials such as oxides, hydroxides, chlorides and nitrates, control of the particle size, stoichiometry, particle shape in some cases, elimination of impurities associated with milling and achievement of very fine and highly reactive anhydrous crystalline powders.

The process involves heating metal salts, oxides or hydroxides as a solution or suspension in a liquid (or sodium hydroxide solution) at controlled temperature and pressure for about 20 hours. In the case of using metal salts as the starting material, the purpose of the sodium hydroxide solution is for the precipitation of metal hydroxides. The precipitation reaction can be represented by the overall equation (Eq. (7)):

where “ M^{z+} ” represents the metal ion. The metal hydroxides will then further react with one another to form the composite oxide. The product is then washed by de-ionized water to get rid of ions in the solvent and other impurities. Fairly well-dispersible ceramic nano-particles are obtained after drying the washed product in air or oven.

2.3.4. Sol-gel Synthesis

The aqueous solution-gel route combines the advantages of economical and ecological benign solvents and metal salts with the more general advantage of sol-gel synthesis, i.e. the composition homogeneity of the end product [105]. The route has already proven its success for the production of various multi-metal oxides [106-108]. The chelating ligands added completely prevent the hydrolysis and condensation of the metal ions. This hydrolysis and condensation are likely to occur in aqueous solution when high valent metal ions are present. After solvent evaporation a glasslike amorphous gel is aimed at, retaining the homogeneous molecular mix of the species in the solution. In the next step the homogeneous gel is calcined in order to obtain the desired oxide phase. Besides being a successful method to synthesize homogeneous multi-metal oxides, the aqueous solution-gel method has been applied to produce nano-particles [109, 110].

The principal advantages of sol-gel processing include the ability to achieve oxygen and ionic stoichiometry during the formation reaction, to synthesize complex composition single phase materials, to form higher purity products through the use of high purity reagents, and to provide coatings over complex geometries including the insides of tubes. Another advantage of the even elemental distribution within the gel is that unlike solid state synthesis, sol-gel processing does not require any grinding

procedures to achieve homogeneous single-phase ceramics, thereby avoiding a potential source of contamination and dust particles, which can be hazardous. However, these advantages are to put in balance with the raw materials high cost, the long processing time involved, the non-uniformity of the films, and the formation of cracks upon drying.

2.3.5. Citrate Gel (Penchini) Method

The Citrate Gel Method utilize poly-chelates between the C=O ligands of citric acid (CA) and metal ions [111]. The chelate undergoes polyesterification on heating with a polyfunctional alcohol, e.g., ethylene glycol (EG). Further heating produces a viscous resin, and a rigid transparent, glassy gel. Mixtures of different metal ions become immobilized in an early stage of the formation of this rigid network. This greatly reduces the risk of segregation into different oxide compositions during subsequent calcinations.

CHAPTER 3:

Experiment Methodology

3.1. Overview of Experiment

The overall view of the experiment aspect of the project is illustrated in Figure 3.1. The precursors are the starting materials which are normally the raw materials which have been commercially produced. The catalysts are prepared by adopting the conventional solid state method of ball milling, incipient impregnation, co-precipitation and sol-gel preparation methods. The catalysts were subsequently screened for their activity in methane and air combustion, followed by a series of catalyst characterization whereby the physical properties of the catalysts were determined.

Figure 3.1: Flowchart of synthesis and characterization of the powders.

3.2. Synthesis of Catalysts

All the samples used in the experiments are in powder form. The conditions under which some of them are prepared are stated.

- **ABO₃ Perovskite - type Oxides**

Prepared by ball milling method
Calcined at 1200°C and hold for 5 hours

- **K₂NiF₄ - type Oxides**

Prepared by ball milling method
Calcined at 1000°C and hold for 5 hours

- **Fluorite - type oxides**

CeO_2 { commercial – SigmaAldrich }
 Gd_{10}C { commercial – SigmaAldrich }
 $\text{Ce}_{0.85}\text{Sm}_{0.15}\text{O}_2$ { commercial – SigmaAldrich }
 $\text{Ce}_{0.85}\text{Y}_{0.15}\text{O}_2$ { commercial – SigmaAldrich }

Various techniques of catalysts preparation are applied. The techniques attempted are the conventional solid state reaction, co-precipitation, impregnation (incipient wetness) and sol-gel preparation methods.

3.2.1. Solid State Preparation

Lanthanum oxide and the alkaline earth metal oxide, all of Analytical Reagent grade having purity > 99%, were used as initial materials for preparation of the $\text{La}_{1-x}\text{A}_x\text{BO}_3$ with A= Ba, Ca, Mg, Sr, and B=Cr or Fe powders and slightly modified composition for $\text{La}_{1-x}\text{Sr}_x\text{BO}_3$. The series of powder were prepared following solid-state synthesis which involved weighing out stoichiometric ratios of the precursor powder,

subjecting them to hand grinding, then ball- milling them in iso-propanol after which by calcining at high temperature. The processing steps were: ball milling for 5 hours, calcining at 1200°C for 5 hours after which mixing the calcined products either by rolling or grinding for better homogeneity and purity.

3.2.2. Sol-gel Synthesis

Different stoichiometric amount of the precursors, namely $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and La_2O_3 with the various dopant precursors were dissolved completely in de-ionized water to form mixed metal solution. After which both citric acid and ethylene glycol were added to the metal ions mixture. The molar amounts of citric acid and ethylene glycol were 1.5 times that of the total metal ions. Then, the final mixed solution was heated to 60°C with constant stirring. After the removal of water through evaporation, a translucent green gel was formed. Next, the cogel obtained was aged and dried in a beaker at room temperature (RT) for 1 day. Subsequently, the sol-gel was then calcined at 400°C for 2 hrs and continuously at 800°C for 2 hr. This sol-gel-generated catalysts formed are of high purity and there can be excellent control of the composition of the resulting mixed oxide pigments.

3.2.3. Calcination using the furnace

Calcination is a process where by the prepared catalyst is subjected to high temperatures under air and hydrogen, but below its melting point or fusing point, to bring about thermal decomposition or a phase transition in its physical or chemical constitution. The purpose of using air is to burn off any impurities while hydrogen is used to reduce

the any metal compounds to the free metal. In normal practice, the catalyst will be calcined during the preparation stage. However, the catalyst that has been prepared during the training will only be calcined before the experiment in the furnace. This ensures that the catalyst will be free from any impurities and as such, the level of activity recorded can be attributed to the method of preparation and not due to the impurities.

3.3. Characterization Techniques

Below are descriptions on the principles of various equipments that are used to carry out the characterization tests of the samples synthesized in this work.

3.3.1. Surface area and Pore size analyzer (BET)

The surface area of a material is determined by the surface area and pore size analyzer. The “Brunauer, Emmett and Teller” (BET) method is used for determining the effective surface of solids materials with complicated shapes, such as porous powders, by using adsorbed gas molecules as rulers. The observation of so-called adsorption and desorption isotherms is used to determine the amount of gas molecules adsorbed to a surface^a. BET is made of a sample chamber, where one can put the sample to be measured that is in powder form. The attached powder placed in a glass tube is connected to a gas inlet, a vacuum pump and a (electronic) barometer.

The surface specific surface area of the calcined powders in this project were determined by Brunauer, Emmett and Teller (BET) single point method using N₂ as the adsorbate under high vacuum at 200 °C (Autosorb-6B Quantachrome Instruments SEA

^a website: www.bbc.co.uk/dna/h2g2/A845723

Di with specifications provided in Table 3.1). Prior to the analysis, the sample was degassed to eliminate volatile adsorbents on the surface at 200°C for 5 hours. Based on the Brunauer-Emmett-Teller (BET) theory, the sample surface area is the product of the cross-sectional area of adsorbent molecules with an estimation of number of molecules.

Table 3.1: Specifications of QUANTACHROME Autosorb-6.

Pressure	Range: 0 - 1,000 torr	Range: 0 - 10 torr
Accuracy	0.001 x full scale	0.0015 x reading
Linearity: 0.05% full scale	0.0005 x full scale	0.0015 x reading
Minimum resolvable pressure:	0.015 torr	0.0002 torr
Minimum resolvable relative pressure (P/P₀):	0.00002 nitrogen	2.6 x 10 ⁻⁷ nitrogen 7.6 x 10 ⁻⁵ krypton
Ultimate Vacuum	Less than 0.001 torr	Less than 10 ⁻⁵ torr
Sorbate Gas	Nitrogen	
Surface Area Range	Less than 0.0005 m ² /g with Kr to no known upper limit Less than 0.05 m ² /g with N ₂ to no known upper limit	
Pore Analysis	Less than 0.0001 cc/g detectable limit 3.5 - 4000Å pore diameter range with nitrogen	

3.3.2. Gas Chromatography (GC)

Gas Chromatography shown in (Figure 3.2) is used to qualitate and quantitate individual components in a mixture^b. In gas chromatography, the sample is firstly converted to the vapor state (if it is not in gaseous state) by injection into a heated port. It is then carried by a gas stream (the mobile phase) through a column which contains an immobilized stationary phase. The mobile phase in GC does not interact with molecules

^b website: teaching.shu.ac.uk/hwb/chemistry/tutorials/chrom/gaschrom.htm

of the analytes. Gas chromatographic separation occurs because of components' differential distribution between the stationary & mobile phase. In our study, the mobile phase of GC we used is Argon which is chemically inert.

Retention time is used for peak identification. It is absolute in most of cases, unless there are two peaks with exactly same retention time under same analysis conditions. For quantitative analysis, amount of a given components in a mixture is determined by analysis chromatographic data which is in the form of peak height or peak area. Ideally, every peak should be totally resolved from any neighboring peaks. It is difficult to determine the size of the peak accurately when there is co-elution or other anomalies in the chromatographic data.

Figure 3.2: Schematic Diagram of GC^c.

The detector provides a signal that is proportional to the concentration. The signal is displayed as a peak on the chromatogram. The following relationship can be established:

$$\text{Concentration of component} = \frac{\text{detector response for component} \times \text{area of peak for component}}{\text{area of peak for component}}$$

^c website: ull.chemistry.uakron.edu/analytical/GD/

In our experiment, GC (model: Shimadzu GC-8A Gas Chromatograph System Detector) was used to determine the concentration of the converted syngas (H_2 , CO and CO_2) evolved from the reaction with the ITOs and methane under high operating temperature. The retention times for different products are varies from 7.15 min to 13.44 min. However, GC cannot be used to analysize gas composition along with the temperature change. Therefore, mass spectrometer is used in order to find out the reaction production as the temperature changes.

3.3.3. Mass Spectrometer (MS)

Mass spectrometry, or commonly known as mass spectroscopy, is an instrumental approach that allows for the measurement of the mass-to- charge ratio of ions ^d. A typical mass spectrometer comprises five parts: a vacuum system, a sample introduction device, an ionization source, a mass analyzer and an ion detector. The mass spectrometer determines the molecular weight of chemical compounds by ionizing, separating, and measuring molecular ions according to their mass-to-charge ratio (m/z) and recording their relative abundance by measuring intensities of ion flux. The ions are generated in the ionization source by inducing either the loss or the gain of a charge (e.g. electron ejection, protonation, or deprotonation). Once the ions are formed in the gas phase they can be electrostatically directed into a mass analyzer, separated according to mass and finally detected. The result of ionization, ion separation, and detection is a mass spectrum that can provide molecular weight or even structural information^e. MS (Hiden HPR – 20

^d website: en.wikipedia.org/wiki/Mass_spectrometry

^e website: chemguide.co.uk/analysis/masspec/howitworks.html

QIC Bench Top Gas Analysis System) was used in analysis of all the generation and re-generation testing of the samples.

3.3.4. Scanning Electron Microscope (SEM) with electron dispersive

SEM is a type of electron microscope capable of producing high resolution images of a sample surface. SEM images have a three-dimensional appearance and are useful for judging the surface structure of the sample^f. As suggested by its name, SEM makes use of electrons to obtain surface images of samples. SEM electrons are emitted from a tungsten cathode and are accelerated towards an anode. Tungsten is used because it has a high melting point and lowest vapor pressure of all metals, thereby allowing it to be heated for electron emission. The electron beam is focused by one or two condenser lenses into a very fine focal spot sized ranging from 1 nm to 5 nm. The beam passes through pairs of scanning coils in the objective lens, which deflect the beam over the area of the sample surface. This produces electrons, which are then detected to produce an image. Besides this, it also produces back-scattered electrons which may be used to detect contrast between areas with different chemical compositions. These can be observed especially when the average atomic number of the various region different. This image can be used to determine the crystallographic structure of the specimen the resolution of SEM can be as high as 1.2 nm due to the shorter wavelength of the electrons.

The equipment SEM is usually coupled with an EDX which utilizes x-rays to determine the elemental composition of the samples. The surface morphology of the samples prepared was investigated using a JEOL JSM LV5600 SEM or LEICA S360

^f website: en.wikipedia.org/wiki/Scanning_Electron_Microscope

SEM analyzer. A small amount of less than 10 milligram of sample was coated with gold using the sputter coater before being placed into the SEM chamber. Microscopic qualitative and quantitative element analysis can be conducted by the characteristic X-rays emitted from the element present in the samples with the energy dispersive and the wavelength dispersive spectroscopy attachments^g.

3.3.5. X-ray diffraction (XRD)

XRD makes use of x-rays to hit a sample at a range of angles of incidence specified by the user. A detector will then be used at the other end to receive the diffracted x-rays (Figure 3.3). At particular angles of incidence, the x-rays with the wavelength of 1.54 Å will exhibit positive interferences and a peak will show at the detector. This angle will be dependent on the crystal structure of the sample. The relationship can be related by the following equation, commonly known as Bragg's Law (Eq. (8))^h.

$$n\lambda = 2d \sin\theta \quad (8)$$

Where:

n = an integer

d = distance between atomic layers in the sample

θ = angle of incidence

λ = wavelength of x-ray used

^g website: en.wikipedia.org/wiki/Scanning_Electron_Microscope

^h website: www.hmi.de/bereiche/SF/SF3/methods/xrd

Figure 3.3: Schematic diagram of X-ray diffraction on a sampleⁱ.

The obtained x-ray diffraction diagram will then be compared to a data base to identify the sample crystal structure. The drawback of this technique is that if the database does not contain the required data, then it would not be possible to identify the crystal structure of the sample. XRD can be used to perform another task. One can calculate the estimated size of the particles from the XRD diagram through the use of Scherrer's Equation (Eq. (9))^j.

$$D \approx \frac{0.9 \lambda}{\beta \cos \theta} \quad (9)$$

Where: D = estimated particle size

θ = angle of incidence

β = full width at half maximum intensity of peak

λ = wavelength of x-ray

This equation provides a relatively good approximation of the particle size but it is unable to determine the size of deposited metal on the support. However, it is a good alternative to Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM).

ⁱ website: xraydiffrac.com/xraydiff.html

^j website: csam.montclair.edu/earth/eesweb/gorring/geos443/443notes/xray.Html

Phase identification and crystal structures of the prepared doped oxides were investigated at room temperature by means of the powder diffraction technique using Bruker XRD D8 Advance Diffractometer, operating at 40kV and 30 mA with a Cu-K α radiation and a Ni filter with Laser wavelength of 1.54 Å. The intensity data were collected at 25°C over a 2θ range of 10° to 90° with a scan speed of 5°/min (2θ) and a scan step of 0.02° (2θ) and the counting time 1.0s, with the counting peaks being approximated by the Lorentzian shape.

3.3.6. Temperature Programmed Reduction (TPR)

Temperature-programmed reduction (TPR) was carried out according to the following procedure. The sample (50 mg) was heated from RT to 300°C at a rate of 10°C /min in a flow of He (20 ml/min), and was kept at this temperature for 30 min. The sample was then cooled to RT and the carrier gas was switched to a 5% H₂ / 95% Ar mixture with a flow rate of 50ml/min. Then the sample was held at this temperature for 30min. A linear rise in temperature from RT to 900°C at a rate of 10°C /min was adopted. The amount of hydrogen consumption was measured by means of a thermal conductivity detector (TCD). The amount of H₂ uptake in the TPR was estimated from integrated peak areas by comparison with those obtained using the data from calibrated H₂ gas as standard.

Linear heating rates are controlled by a powerful, compact temperature controller. The reaction between the sample and reducing gas is monitored by a highly stable thermal conductivity detector (TCD) which consists of an electrically-heated wire or thermistor. The temperature of the sensing element depends on the thermal conductivity

of the gas flowing around it. Changes in thermal conductivity cause a temperature rise in the element which is sensed as a change in resistance. Therefore, the final result will be a plot of intensity which is the change in resistance versus time or temperature of the reactor system.

There are three things to note where TPR analysis is concerned. Firstly is the difference in reduction temperature of the noble metal and the non-noble metal. Second would be the area under a TPR curve which represents the total hydrogen consumption, and is commonly expressed in number of moles of H_2 consumed per mole of metal atoms, H_2/M . Thirdly, the TPR pattern of the bimetallic catalyst shows that the bimetallic combination is reduced at lower temperatures.

TPR-TGA

The oxygen content was determined through temperature programmed reduction (TPR) followed by thermo-gravimetric analysis (TGA). Instead of air, the reactor was filled with a mixture of 5% H_2/Ar , maintaining a flow of 140 ml/min. TGA was used to measure the weight changes during reduction reaction. The temperature was then linearly increased with a heating rate of $10^\circ C/min$, hold for 10min at $100^\circ C$ to remove excess moisture, and then up to $900^\circ C$. The amount of sample used is 25 mg.

3.4. Evaluation Techniques

In this study, Temperature Programmed Reduction (TPR), Generation (TPSR) and Re-generation Test coupled with Mass Spectrometry and Gas chromatography were employed to study catalytic activities of the lattice oxygen present in the ITOs.

3.4.1. Activity measurement

Activity measurements were carried out in a continuous-flow fixed bed quartz micro-reactor (inner diameter = 10.3 mm, outer diameter = 12.0 mm) at atmospheric pressure packed with 250 mg samples which were sieved to a grain size of 180/300 μm . The samples were kept still in the middle of the quartz tube by means of quartz wool wads. A gas mixture of 5% CH_4 in Ar (carrier gas) with a total flow rate of 100 ml/min was passed through the sample in the quartz tube. The sample temperature was raised at a constant rate of $10^\circ\text{C}/\text{min}$ from 50°C to 850°C at which it is hold for a period of time (15 to 30 min). The reaction products were detected by an online gas chromatography on a Shimadzu GC-2010 equipped with both a thermal conductivity detector (for H_2 , CO , CH_4 , CO_2 , Ar and N_2) and a flame ionizing detector (for C_xH_y and other products). Ar was used as the internal standard.

The conversion of CH_4 , the selectivity of CO and H_2 are defined as follows according to Eqs. (1), (2) and (3), respectively:

$$X_{\text{CH}_4} = \frac{\text{Mol}_{\text{CH}_4\text{in}} - \text{Mol}_{\text{CH}_4\text{out}}}{\text{Mol}_{\text{CH}_4\text{in}}} \times 100\% \quad (1)$$

$$S_{\text{CO}} = \frac{\text{Mol}_{\text{COout}}}{\text{Mol}_{\text{CH}_4\text{converted}}} \times 100\% \quad (2)$$

$$S_{\text{H}_2} = \frac{\text{Mol}_{\text{H}_2\text{out}}}{\text{Mol}_{\text{CH}_4\text{converted}}} \times 100\% \quad (3)$$

where “*Mol*” represents number of moles tabulated based on the area of the gas detected with conversion factor tabulated from universal gas was taken into account. Calculations were done based on detected three main gases (CH_4 , CO and H_2) only.

3.4.2. Generation (TPSR) and Re-generation Test (TPO)

TPSR (H_2 Generation test)

Temperature-Programmed Surface Reaction (TPSR) shown in schematic in Figure 3.9 is performed to determine the temperature at which hydrogen, carbon monoxide and other byproduct gas is evolved from the reaction with methane and the ITO. The outlet gas is analyzed by an on-line Mass Spectrometer which can be used to study the activity of syngas and other gases (by-products) produced during the generation reaction. The concentration of gases as a function of gas molecule mass in the scan analogue mode or monitor the intensity versus time are recorded. The products from the reaction are less volatile. Therefore, a mass spectrometer is used to analyze the gas products instead of using gas chromatography.

This TPSR reaction takes place in a quartz tube micro-reactor system, which is similar to the temperature programmed oxidation (TPO) that is of the precedent step to TPSR. The sample, sieved to a grain size of 180/300 μm , was introduced into an open quartz capillary dimension of inner diameter = 1.6 mm, outer diameter = 1.8 mm (for MS analysis), to form a 5 to 15 mm long bed corresponding to 100 mg or 250 mg respectively of the sample. The samples were kept still in the middle of the capillary by means of quartz wool wads. One end of the capillary was mounted on the goniometer

head of the mass flow meter and connected to the line coming from the gas mixing device, while the other faced the MS sampling capillary. A gas mixture of 5% methane in helium or argon (carrier gas) with a total flow of 100 ml/min, was passed through the sample in the quartz tube. The sample temperature was raised at a constant rate of $10^{\circ}\text{C}/\text{min}$ from 50°C to 850 or 900°C at which it is hold for a short period of time. The temperatures at which hydrogen gas was evolved from the oxidation of methane, and the activity of the other gases (by-products) produced were analyzed by an on-line Mass Spectrometer.

Figure 3.4: Schematic diagram of the experimental set-up for TPSR.

Regeneration / Temperature-Programmed Oxidation (TPO)

Temperature-Programmed Oxidation (TPO) is the replica process of TPSR except for the difference in the inlet gas. Unlike TPSR, in TPO a mixture of oxygen and helium is used as the supply gas for the sample to undergo oxidation reaction. All the other testing parameters and the experimental settings however remain the same as before. And for re-generation test, it is ideal to let the sample heated up at a slower rate and hold at high temperature of 800°C or 900°C for 30 minutes. Subsequently, the same sample is used to undergone each cycle of generation and re-generation test. There is no change made to the sample holder or the sample during the cycles of testing.

Cycle of Generation (TPSR) and Re-generation Test (TPO)

The aim is to test these samples on their ability to be generated and re-generated repetitively under methane and air atmosphere respectively. Usually, the selected samples showed promising results from the generation and reducibility tests. The cycle of testing can range from three to ten, depending on the results obtained in each cycle.

CHAPTER 4:

Syngas Production by Catalytic Partial Oxidation of Methane over (La_{x-1}A_x) BO₃ (A = Ba, Ca, Mg or Sr; B = Cr or Fe) Perovskite-type Oxides

4.1. LaCrO₃ and LaFeO₃

ABO₃ oxides containing transition metals are orthorhombic derivatives of the perovskite structures. They normally exhibit high oxygen ion conductivity and high catalytic activity for the complete oxidation of hydrocarbons, and thus can replace noble metals as combustion catalysts [112, 113, 114, 115]. The oxidation of these hydrocarbons is found to occur on the ABO₃ oxide surface by means of an interfacial catalytic mechanism, in which the adsorbed oxygen is partly consumed and regenerated during a continuous oxygen adsorption. Several ABO₃ (A = La) oxides have shown to be good catalysts for the partial oxidation of methane to syngas. Among them La_{0.2}Sr_{0.8}Fe_{0.6}Co_{0.4}O₃ coupled with an Rh reforming catalyst could give 98% CH₄ conversion and 90% CO selectivity at 1023K [116]. LaFeO₃ based oxides have been reported as high temperature oxygen sorbent, offering significant promise for air separation [117]. In addition, ABO₃ oxides have been considered as alternative SOFC electrode materials. LaBO₃ (B=Cr, Fe) oxides, in particular the LaFeO₃ perovskite-type oxide, are of practical interest for electro-ceramic applications due to their attractive mixed conductivity displaying ionic and electronic defects [5, 118]. LaCrO₃ perovskites, with good stoichiometric compositions, are also attractive due to their chemical stability under oxidizing or reducing atmospheres at high temperature, and their very low activity towards carbon deposition [119]. However, both LaFeO₃ and LaCrO₃ are known to be poor SOFC anodes due to their poor catalytic activity for the oxidation of hydrogen and

hydrocarbon fuels [120, 121]. Electrochemically speaking, the anode's job is to use the oxygen ions that diffuse through the electrolyte to oxidize the hydrogen or hydrocarbon fuel. The catalytic activity of LaFeO₃ and LaCrO₃ can be highly improved by partial substitution with metals on A- and/or B-sites, causing only small changes in the average structure. It has also been widely published that incorporation of dopant ions to the LaCrO₃ (or LaFeO₃) oxides is crucial for promoting catalytic activity and high ionic conductivity [122, 123, 124, 125].

Thus in view of these favorable properties of LaCrO₃ and LaFeO₃, the La ions in these ABO₃ oxides have been doped with an alkaline earth metal to achieve better performance in particular to the oxygen storage ability. The La_{1-x}A_xCrO₃ and La_{1-x}A_xFeO₃ oxides (A=Ba, Ca, Mg and Sr) were synthesized by conventional ball milling of La, A(Ba, Ca, Mg or Sr), Cr/Fe nitrates, and then, further heating to 1200°C in air for 2 hours. They were characterized by XRD, BET, SEM, TPR and tested for their activity during catalytic partial oxidation of methane at selective operation temperatures.

4.2. Characterization Studies

4.2.1. BET and SEM

The results of the BET measurements for the perovskites-type oxides are listed in Table 4.1 below. All the BET surface areas of the La_{1-x}A_xBO₃ oxides are rather small, 3 - 5 m²/g for the LaAFeO₃ oxide series, and 2 - 3 m²/g for the LaACrO₃ series.

Table 4.1: Summary of the BET surface area results of the doped (La_{1-x}A_x) BO₃ perovskites-type catalysts

Surface area(m ² /g)		Surface area (m ² /g)	
LaCrO ₃	2.39	LaFeO ₃	2.99
(La _{0.7} Ba _{0.3})CrO ₃	2.57	(La _{0.7} Ba _{0.3})FeO ₃	3.72
(La _{0.7} Ca _{0.3})CrO ₃	3.21	(La _{0.7} Ca _{0.3})FeO ₃	4.76
(La _{0.7} Mg _{0.3})CrO ₃	2.76	(La _{0.7} Mg _{0.3})FeO ₃	5.02
(La _{0.75} Sr _{0.25})CrO ₃	2.78	(La _{0.75} Sr _{0.25})FeO ₃	4.97

As shown in Figures 4.1 and 4.2, the LaCrO₃ and LaFeO₃ particles are mainly made up of big spherically shaped particles. The particle size ranges from 150 to 250 nm on average. Signs of particle aggregation are noted in both figures. This observation is in line with the theory as the samples were synthesized using the conventional solid state reactions in which such clustering of particles is common. The SEM morphology illustrated in the figures was also found in all other eight doped LaACrO₃ and LaAFeO₃ oxides, with particle size of approximately 150-250 nm.

Figure 4.1: SEM image of the LaCrO₃ oxide prepared from the solid state reaction between lanthanum oxide and chromium oxide at 1200°C.

Figure 4.2: SEM image of the LaFeO₃ oxide prepared from the solid state reaction between lanthanum oxide and iron oxide at 1200°C

4.2.2. X-ray Diffraction (XRD) Analysis

The crystalline structures of freshly prepared LaACrO₃ and LaAFeO₃ oxides are shown in Figures 4.3 and 4.4 respectively. Basically, no secondary phase is found in Figure 4.3 for the LaACrO₃ samples although a very small shift to larger diffraction angle is observable for La_{0.75}Sr_{0.25}CrO₃ (Pattern 1 in Figure 4.3), indicating the lattice distortion due to Sr substitution. Sr²⁺ ion is slightly larger than La³⁺ ion in size (0.144 vs. 0.136 nm). For the LaAFeO₃ oxide series, Fe₂O₃ phase is observed in all doped samples, with the Fe₂O₃ content slightly higher in the samples containing Sr and Ba dopant (Patterns 1 and 4 in Figure 4.4). This could perhaps give explanation to the presence of three H₂ reduction peaks noted in TPR analysis (vide infra). Additional phase of La₂O₃ is also observed in Sr doped LaFeO₃ oxide (Pattern 1 in Figure 4.4). Nonetheless, the peaks of LaFeO₃ oxide are present in all the patterns in Figure 4.4.

Figure 4.3: XRD patterns of the freshly prepared LaACrO₃ oxides series:

1. La_{0.75}Sr_{0.25}CrO₃; 2. La_{0.7}Mg_{0.3}CrO₃; 3. La_{0.7}Ca_{0.3}CrO₃; 4. La_{0.7}Ba_{0.3}CrO₃; and 5. LaCrO₃.

Figure 4.4: XRD patterns of the freshly prepared LaAFeO₃ oxides series:

1. La_{0.75}Sr_{0.25}FeO₃; 2. La_{0.7}Mg_{0.3}FeO₃; 3. La_{0.7}Ca_{0.3}FeO₃; 4. La_{0.7}Ba_{0.3}FeO₃; and 5. LaFeO₃.

4.2.3. Temperature Programmed Reduction (TPR) Analysis

The mobility of lattice oxide ions in the LaABO₃ samples was investigated with the H₂ temperature-programmed reduction (TPR). Figure 4.5 shows the reduction profiles of the LaACrO₃ and LaAFeO₃ oxides (A = Mg, Ca, Sr and Ba respectively). The TPR graphs were plotted over the range of ramping time against both the intensity (hydrogen consumption) and the temperature of the reduction reaction.

All samples studied exhibited one or more peaks corresponding to the amount of hydrogen consumed by the samples. The undoped LaCrO₃ and LaFeO₃ oxides exhibit peaks of lower intensity with maximum H₂ consumption at around 620 and 660°C respectively. With AE metals dopants, there are two or more consecutive reduction peaks at lower temperature observed for both LaACrO₃ and LaAFeO₃ oxides.

For LaACrO₃ oxides, the undoped LaCrO₃ oxide exhibit a very broad peak of very low intensity, indicating the difficulty in removing oxide ions from undoped LaCrO₃. All dopants can largely enhance the oxygen ion mobility, and consume much more H₂ to remove them than undoped LaCrO₃. Mg²⁺ dopant produces three distinctive reduction peaks at 300, 450 and 550°C, as well as a high temperature peak at 800°C. Ba²⁺ peaks at slightly higher temperatures, 400, 500 and 600°C. Ca²⁺ and Sr²⁺ doping both result in higher H₂ consumption than that of Mg and Ba. For these two dopants, there is peak overlapping phenomenon observed in the lower temperature range which gave a higher amount of H₂ consumption. The peak area of the La_{0.7}Ca_{0.3}CrO₃ TPR profile is the largest. The low temperature reduction is evident between 300 and 500°C while the high temperature reduction occurs at 700°C with noticeably high H₂ consumption. For the Sr²⁺

doped sample, there are significantly two large peaks overlapping to form one single peak of high intensity at around 570°C.

Undoped LaFeO₃ oxide produces a peak of low intensity at 650°C in Figure 4.5 b. Again Sr doping results in large amount of H₂ consumption, peaked at 400, 560 and 890°C. The Ca and Mg have only one reduction peak in the 600-800°C region while Ba produces H₂ peak, with relatively low intensity, at 340, 500 and 700-850 °C. The hydrogen reduction at higher temperature regions may correspond to the presence of Fe₂O₃ and La₂O₃ phase due to the doping by Sr and Ba (refer to XRD analysis in section 4.2.2).

Figure 4.5: TPR profiles, showing the intensity, temperature and time on stream at which H₂ is consumed from the reaction between H₂ and LaABO₃ samples : (a) LaACrO₃ (b) LaAFeO₃ oxides. The flow rate was 50 mL/min of 5% H₂/Ar, and the weight of each sample is 50 mg. The temperature was raised at a rate of 10 °C/min from RT to 900 °C.

The total amount of hydrogen consumed per mole of catalysts for LaACrO₃ and LaAFeO₃ oxides during TPR was calculated by integration of the respective TPR profiles as shown in Table 4.2. With the assumption that one mole of hydrogen will react with one mole of oxygen species to form water, the area under the graph gives an estimation of the amount of oxygen species that has reacted in the reaction. The values for the hydrogen consumption indicate that the accessibility of the oxygen lattice ions differ between the oxides, assuming that a higher consumption implies the accessibility of more lattice O²⁻.

Table 4.2: Summary of the number of mole of H₂ being consumed per mole of ABO₃ samples derived from the TPR results for the LaACrO₃ and LaAFeO₃ oxides.

Sample	No of mol of H ₂ Consumed per mol of Catalyst
LaCrO ₃	0.08
(La _{0.7} Ba _{0.3})CrO ₃	0.27
(La _{0.7} Ca _{0.3})CrO ₃	0.60
(La _{0.7} Mg _{0.3})CrO ₃	0.20
(La _{0.75} Sr _{0.25})CrO ₃	0.38
LaFeO ₃	0.12
(La _{0.7} Ba _{0.3})FeO ₃	1.03
(La _{0.7} Ca _{0.3})FeO ₃	1.11
(La _{0.7} Mg _{0.3})FeO ₃	1.26
(La _{0.75} Sr _{0.25})FeO ₃	1.37

As illustrated, the ratio of hydrogen required for the reduction of the LaCrO₃ series to the number of moles of catalyst is much lower than that of the LaFeO₃ series. The results obtained are justifiable as Fe is rather more reducible than the Cr oxides. In comparison, pristine LaCrO₃ and LaFeO₃ have the smallest H₂/cat (molar ratio) which suggested that both precursors have the least amount of O²⁻ species. The highest value for the amount of O²⁻ species reacted is 1.37 which was achieved by the Sr²⁺ doping. This implies that La_{0.75}Sr_{0.25}FeO₃ possesses the largest amount of oxygen species that can react with H₂ or with CH₄ during the CPO reaction, having the highest reducibility among the two series of doped perovskites. Also, Sr is the best dopant for both the LaCrO₃ and LaFeO₃ series to remove more O²⁻ species for a better CPO reaction with methane. It is evident that although the LaAFeO₃ oxide series have bigger peaks with much higher hydrogen consumption, the O²⁻ species in the LaCrO₃ oxide series are able to react at lower temperatures so that they are more movable and easily reactive.

As discussed above from the TPR analysis, the distinctive reduction peaks at different temperatures could signify that there exist various types of O²⁻ species which

participate in the reaction with H₂ at different mobility under different temperature. These peaks with maxima at the temperatures in the range of between 250 and 900°C could indicate the increased mobility of lattice oxygen ions by A-site doping with the AE metals. This doping effect is most evident with Ca and Sr dopants in the respective doped series. It is evident that although the LaAFeO₃ series have bigger peaks with much higher hydrogen consumption, the O²⁻ species in the LaCrO₃ series are able to react at lower temperatures so that they are more movable. Evidently, A-site Sr²⁺ and Ca²⁺ doping disturbs the lattice structure mostly so that more oxygen ions become movable at lower temperatures. Thus the overall reducibility increases in the order of LaCrO₃ < LaFeO₃ < (La_{0.7}Ca_{0.3})CrO₃ < (La_{0.7}Mg_{0.3})CrO₃ < (La_{0.7}Ba_{0.3})CrO₃ < (La_{0.75}Sr_{0.25})CrO₃ < (La_{0.7}Ba_{0.3})CrO₃ < (La_{0.7}Ca_{0.3})CrO₃ < (La_{0.7}Mg_{0.3})FeO₃ < (La_{0.75}Sr_{0.25})FeO₃.

4.3. Catalytic Studies of LaACrO₃ and LaAFeO₃ oxides

The above LaACrO₃ and LaAFeO₃ oxides prepared were respectively used as a catalyst to react with CH₄ for the H₂ generation in the first step. The oxygen-depleted catalysts were then recovered by the reaction with air. The studies of these two reactions are reported in the following sections.

4.3.1. H₂ Generation Step

4.3.1.1. Methane Reaction with La_{1-x}A_xBO₃ (B= Cr and Fe)

The temperature programmed reaction (TPRa) profiles of 5% CH₄/Ar over LaACrO₃ and LaAFeO₃ perovskites oxides series are respectively illustrated in Figures 4.6 (a) and (b), in which the mass spectroscopic (MS) signal of H₂ is plotted as a function

of reaction temperature. The reaction may occur following the equation: $\text{CH}_4 + \text{O}^{2-} \rightarrow \text{CO} + \text{H}_2$. The CO and other by-products (CO_2 , H_2O , unreacted CH_4 and Ar) are not shown in the figure. The samples were heated at $10^\circ\text{C}/\text{min}$ from RT to 950°C .

Figure 4.6: The TPR profiles, showing the temperature at which H_2 is produced from the reaction between CH_4 and AE doped LaABO₃ catalysts: (a) LaACrO₃ (b) LaAFeO₃ oxides. The flow rate was 100 ml/min of 5%CH₄/Ar, and the weight of each

sample was 100 mg. The temperature was raised at a rate of 10 °C/min from RT to 950 °C.

From the summarized data based on TPR profiles in Figures 4.6 (a) and (b), it is noted that most of the H₂ peaks appear at around 850°C with the lowest desired peak at around 800°C. Both the undoped LaCrO₃ and LaFeO₃, being very stable oxides, require comparatively high temperatures (900°C and 950°C, respectively) to produce maximum amount of H₂. In contrast, by A-site doping both the LaACrO₃ and LaAFeO₃ oxide series were able to produce H₂ maximum peak at lower temperature than 900°C. Evidently, with the addition of AE metal dopants, the temperatures needed for the reaction to take place are reduced. This phenomenon is in line with the crystal structure analysis as well as the H₂ TPR results where the H₂ consumption peak shifted to lower temperature compare to the undoped oxides.

For the LaACrO₃ series, most of the H₂ peaks appear at around 800°C with La_{0.75}Sr_{0.25}CrO₃ having the highest intensity and lowest H₂ evolution temperature at 810°C. As for the LaAFeO₃ series, most of the H₂ peaks appear at around 850°C, with the Sr²⁺ doped oxide, La_{0.75}Sr_{0.25}FeO₃, having the highest intensity which is similar to the trend observed in the LaACrO₃ series. The peak intensity for La_{0.75}Sr_{0.25}FeO₃ seems to be higher than La_{0.75}Sr_{0.25}CrO₃. Among all the LaABO₃ oxides, only the La_{0.75}Ca_{0.25}CrO₃ profile gave two separate H₂ peaks. This observation could be due to the fact that there exist two well-separated strong peaks in H₂ TPR profile for La_{0.75}Sr_{0.25}CrO₃ (Figure 4.5(a)) which means that some O²⁻ species in the La_{0.75}Sr_{0.25}CrO₃ sample are of higher mobility whereas the others require a higher temperature to be removed. The pristine LaCrO₃, LaFeO₃, Mg²⁺- and Ba²⁺- doped LaFeO₃ show H₂ peaks at increasing

temperature range. In other words, this would mean that the oxygen species present in these oxides need much higher activation energy as provided by heating to higher temperature to initiate the catalytic partial oxidation with methane.

4.3.1.2. Activity Measurement

By using gas chromatography for on-line outlet gas analysis, CH₄ conversion, H₂ selectivity, and the H₂/CO ratio in the outlet gas stream could be measured and calculated based on Equations 1 to 3 defined in earlier section in chapter 3.4.1 on activity measurement. These data were obtained at 850°C in the 5% CH₄-95% Ar gas stream with GHSV of 750 h⁻¹, and shown in Figures 4.7 to 4.10.

As seen in Figure 4.7 (a), the CH₄ conversion on the LaACrO₃ oxide series is relatively low (<12%) but remains to be fairly steady. The undoped LaCrO₃ oxide yields the lowest value of 4% while the highest CH₄ conversion is 12% produced by Sr dopant. Though the CH₄ conversion decays at the first 70 mins, it remains the highest at the end of the test (8% at 130 min) for LaSrCrO₃. The La_{0.7}Ca_{0.3}CrO₃ oxide displays steady CH₄ conversion of 10% in the first 80 min, after which it drops to 4%. The Ba and Mg doped LaCrO₃ oxides are seen to have initial CH₄ conversion of 11% and 8% respectively. While the Mg dopant continues to convert CH₄ at a decreasing rate to 7%, the Ba dopant converts CH₄ at a constant rate of 5% from 40 min onwards.

LaAFeO₃ oxides have much higher amount of CH₄ converted which ranges from 10% of the undoped LaFeO₃ to 70% for the Ca doped LaAFeO₃ oxides (Figure 4.7 (b)). For undoped LaFeO₃ conversion of CH₄ remains steady and low (<8%) over the whole period of time. It takes 20 min for La_{0.7}Ca_{0.3}FeO₃ to reach a maximum of 70% CH₄

conversion while Sr takes 40min to convert 60% of CH₄, Ba take 60 min to achieve CH₄ conversion of 45%, and Mg dopant take 120 mins to reach a high conversion of 65%. LaAlFeO₃ oxides are not stable for long hour operation maybe because of carbon deposition (as seen from the sample appearance after reaction and also from SEM results) resulting from methane cracking or CO disproportionation catalyzed by Fe. Ca and Sr dopants have been shown to promote O²⁻ removal evidently (See Figure 4.5 (b)) so that they are more unstable than other LaAlFeO₃ oxides.

Figure 4.7: CH₄ conversion of LaABO₃ oxides during the partial oxidation of 5% CH₄ at 850 °C GHSV of 750 h⁻¹: (a) LaACrO₃ and (b) LaAFeO₃ oxides respectively.

As illustrated in Figure 4.8 (a), the H₂ concentration for raw LaCrO₃ and Ba-doped LaCrO₃ are basically constant at 0.5 and 0.8% correspondingly. Sr dopant has 2.4% of H₂ concentration, which however begins to decline to a steady value of 1.0% from 80th min of the reaction onwards. The Ca dopant shows rather high yield of H₂ production, which decreases gradually from 2.25% to 1.5% in the first 60 min on stream, and then remains steadily at the 1.5% in the next 80min. Mg dopant displays comparable falling trend from a value of 2.25% to 1.0%.

The LaACrO₃ oxides exhibit similar trends for CO yield in terms of output concentration to the above shown H₂ concentration (see Figure 4.8b). Both the pristine LaCrO₃ and Ba-doped oxide display stable CO yield at 0.2%. The Sr dopant decreases the CO concentration from initial 1.0 to 0.3% in the first 40 min which then rise to 0.4% by the end of 110 min. The Mg doped oxide shows similar trend but at a lower value between 0.6 and 0.2%. The Ca dopant drops from a 0.7% of CO yield from 0.3 the 60th min. In the next 60 min, the activity of Ca dopant remains steady and hence CO production maintains at 0.3 till the end of 140 min on stream time.

Figure 4.8: The catalytic activity of LaACrO₃ oxides during the partial oxidation of 5%CH₄ at 850°C with GHSV of 750 h⁻¹: (a) H₂, and (b) CO selectivity.

LaAFeO₃ oxides show increasing trend for H₂ concentration with reaction time (Figure 4.9 (a)). For LaFeO₃ the H₂ production increases to 2% in the 90th min after which remains at that value over the holding time of 140 min. The Sr doped oxide displays rather a steady increasing H₂ production in the first 60 min to give a peak at 10% which maintains for another ten min and further holding decreases to 1%. The Ba dopant follow similar trend with a gradual increase to 7%, and decreases to 1% in the next 80 min holding time. The La_{0.7}Ca_{0.3}CrO₃ increases from initial value of 3% to 9% in the 60 min stream on line time. The Mg dopant takes a longer time to be activated to give a raise from 0 to 11% in the 120th min.

In Figure 4.9 (b), the undoped LaAFeO₃ shows exceptionally steady CO concentration of approximately 0.5% throughout the 140 min. Similarly, Mg doped oxide has CO concentration in the range of 0.2 to 3% within 120 min. Ca dopant gives a peak of 2.5% CO production in the 30 min timeframe while Sr and Ba dopants also produce

peak at 2.8% CO concentration in the time frame of 40 and 80 min respectively. This relatively short duration of CO production for LaAFeO₃ (A = Ca, Sr, and Ba) oxides could indicate that CH₄ may not react with lattice oxide to form CO or/and CO₂ since CO₂ production in these tests was found to be in relatively low quantity too. Rather, CH₄ cracking might take place on reduced iron, forming carbon deposition, and slow down the CH₄ conversion.

Figure 4.9: The catalytic activity of LaAFeO₃ oxides during the partial oxidation of 5%CH₄ at 850 °C with GHSV of 750 h⁻¹: (a)H₂ and (b)CO selectivity.

The ratio of H₂ to CO for both oxide series are illustrated in Figures 4.10 (a) and (b) respectively. The H₂ to CO molar ratio for the undoped LaCrO₃ and LaFeO₃ samples is approximate at a value of 2 which is the theoretical value derived from Equation 1, CH₄+ O²⁻ → CO + 2H₂. Doping can generally enhance this ratio. LaMgCrO₃, LaSrCrO₃, LaMgFeO₃, LaBaFeO₃ and LaSrFeO₃ are seen to maintain the H₂/CO ratio steady at various levels between 2 and 6 within 80 min testing.

Figure 4.10: H₂/CO ratio of LaABO₃ oxides during the partial oxidation of 5%CH₄ at 850°C GHSV of 750 h⁻¹: (a) LaACrO₃, and (b) LaAFeO₃ oxides.

Thus it can be concluded that with the presence of alkaline earth metals there is improvement in both the CH₄ conversion and syngas concentration. The selectivity of H₂ was found to be 100% while that of CO was nearly 100%. The LaAFeO₃ oxides are found to be active in the oxidative conversion of methane to syngas as the CH₄ conversion and syngas concentration remained steady during the experimental period of 140 min. Among the doped LaACrO₃ series, Ca²⁺ doped oxide yielded better activity and syngas concentration. Despite having a slightly low methane conversion of 10%, La_{0.7}Ca_{0.3}CrO₃ outperformed the rest giving a high steady concentration: 2.25% for H₂ and 0.7% CO. Methane conversion of 12% with 2.25% H₂ and 1% CO concentration was achieved by La_{0.75}Sr_{0.25}CrO₃. For the doped LaFeO₃ series, CH₄ conversion is normally high, but decays fast. Similar dopants - Ca²⁺ and Sr²⁺, outperformed the rest. La_{0.7}Ca_{0.3}FeO₃ gave a 70% of CH₄ conversion with H₂ 10% and CO 2.5% within 50 mins, while La_{0.75}Sr_{0.25}FeO₃ achieved a 65% CH₄ conversion, 10% H₂ selectivity, and 2.8 %

CO selectivity within 50 mins. In short, Ca and Sr are the best dopants for both LaCrO₃ and LaFeO₃, regardless of the stability.

4.3.2. Re-regeneration of the LaABO₃ in O₂

The reduced oxides which have undergone reaction in methane at 950°C are re-oxidized in O₂ in the regeneration step at temperatures ramping up to 950°C at 10°C/min. In this way, the lost lattice oxygen can be supplemented, and the crystal framework of oxides can be recovered. Figures 4.11 and 4.12 display the O₂, CO and CO₂ MS profiles obtained from regeneration testing. It is noted that at the trough of every O₂ peak, there exist a big CO₂ peak and a small CO peak. The fact that these three trough/peaks occur at the same temperature would indicate the oxidation of carbon deposition by O₂.

Figure 4.11: The MS profiles for re-regeneration testing of the reduced La_{0.7}Ca_{0.3}CrO₃ in O₂ where the peaks of O₂, CO₂ and CO are indicated. The flow rate was 100 mL/min of 5%O₂/He, and the weight of each sample is 100 mg. The temperature was raised at a rate of 10 °C/min from RT to 950 °C.

Figure 4.12: The MS profiles for re-generation testing of the reduced $\text{La}_{0.75}\text{Sr}_{0.25}\text{FeO}_3$ in O_2 where the peaks of O_2 , CO_2 and CO are indicated. The flow rate was 100 mL/min of 5% O_2 /He, and the weight of each sample is 100 mg. The temperature was raised at a rate of 10 °C/min from RT to 950 °C.

The regeneration of reduced LaABO₃ oxides was confirmed by XRD analysis. The undoped LaCrO₃ and LaFeO₃ oxides are used as the example, and the XRD patterns at various testing stages are shown in Figures 4.13 and 4.14 correspondingly. Figure 4.13 shows the presence of secondary phases (La_2O_3 and LaCrO_4) in addition to the LaCrO₃ oxide after it has undergone reaction in CH_4 . However, after oxidation in O_2 at high temperatures in the regeneration step, all the secondary phases disappear, and high crystalline structure of LaCrO₃ is observed. The decomposition of LaCrO_4 may explain the intensity increase in the O_2 profile as seen in Figure 4.11. Figure 4.14 shows no presence of the La_2O_3 nor FeOx phase. The LaFeO₃ crystalline structure could be maintained during the reaction step, though the intensity of the respective LaFeO₃ peaks is decreased due to the reaction. And it can be totally recovered by the oxidation. Also, it was proven in the XRD patterns of the rest eight AE doped LaACrO₃ and LaAFeO₃

oxides that similar recovery of their respective ABO₃ crystalline structures in O₂ was possible.

Figure 4.13: XRD patterns of the LaCrO₃ samples. (a) Fresh sample calcined at 1200°C in air for 5 h, (b) after reaction in 5%CH₄/Ar (from RT to 900°C), (c) after regeneration in 5%O₂/He (from RT to 950°C).

Figure 4.14: XRD patterns of the LaFeO₃ samples. (a) Fresh sample calcined at 1200°C in air for 5 h, (b) after reaction in

*5%CH₄/Ar (from RT to 950°C), (c) after regeneration in
5%O₂/He (from RT to 950°C).*

4.4. Discussion

In this study, pure LaFeO₃ and LaCrO₃ are partially substituted with Alkaline Earth elements i.e (Ba, Ca, Mg and Sr) in the A-position of the LaBO₃ perovskite-type structure. Borchert and Bearns [126] indicated that the doping of perovskites with lower-valent ions give an increase in the oxygen ion conductivity, corresponding to an increase in oxygen vacancy concentration while that of the higher-valent ions have the opposite effect. The AE metals ions (A²⁺) replacing La³⁺ ions in the crystal lattice will cause charge compensation via Cr³⁺ to Cr⁴⁺, or O²⁻Fe³⁺ to O⁻Fe³⁺ respectively. Therefore, the resultant lattice oxygen produced from the charge compensation and lattice distortion will act as the extra oxidant for the partial oxidation of methane (POM) in the production of syngas. Therefore higher conversion rate is generally observed on the (La_{1-x}A_x)BO₃ with A= Ba, Ca, Mg and Sr while B= Cr or Fe. The AE cation incorporated oxides exhibited better catalytic performance than the corresponding pristine LaCrO₃ and LaFeO₃ oxides.

In doped oxides, the matching radius is the main parameter in determining the mobility of oxides vacancies. The cations display minimum disruption of lattice structure when their radius is close to that of the ion they are displacing. As a result, there is less strain on the lattice, leading to more oxide vacancy mobility and higher ionic conductivity. The AE metal ions: Ba²⁺, Mg²⁺, Ca²⁺ and Sr²⁺ display minimum distortion of lattice structure because their radii are close to La³⁺ (Table 4.3). Among these cations, the radius of Ca²⁺ is the closest to that of La³⁺ ion. This will result in lattice having least strain, leading to least resistance to oxide vacancy movement. Hence, comparing the

doping effect of AE metal ions, Ca²⁺ and Sr²⁺ are found to be the best doping ion. This is in agreement with the results obtained for the TPR and generation testing.

Table 4.3: Ionic radii of cations with different coordination numbers [23].

Cation	La ³⁺	La ³⁺	Ba ²⁺	Mg ²⁺	Ca ²⁺	Ca ²⁺	Sr ²⁺	Sr ²⁺
Ionic radius (10 ⁻¹⁰ m)	1.03	1.36	1.35	0.72	1.00	1.34	1.18	1.44
Coordination number	6	12	6	6	6	12	6	12

All the doped oxides display promising results even after having undergone repetitive process of generation and regeneration reactions. In this study, the overall performance of the series of doped LaFeO₃ is much better than that of the series of doped LaCrO₃ oxides: LaAFeO₃ > LaACrO₃. The results may be partly related to the slightly larger surface area of LaAFeO₃ (see Table 4.1).

4.5. Conclusion

In summary, syngas production via partial oxidation of methane by alkaline earth metal doped LaACrO₃ and LaAFeO₃ oxide series have been shown to be feasible. Doping of these two LaBO₃ oxides with AE metals generally increases the mobility of lattice oxygen ions so that they can be reduced by hydrogen, or react with methane at lower temperatures than pristine LaCrO₃ and LaFeO₃ oxides. The structure and activity of the oxides can be recovered by oxidation in O₂ at 950°C, in which the deposited carbon can be burned off, and lost lattice oxide ions in the reduced oxides can be supplemented. It is worthy to note that the sample exhibits stable activities during the repeated cycles of reaction-generation testing. Results show that LaAFeO₃ series yield better performance than the LaACrO₃ series. (La_{0.75}Sr_{0.25})FeO₃ show superior performance with 65% of CH₄

conversion, 10 % H₂ and 2.8% CO concentration at 850°C with full 100% H₂ selectivity . It possesses the largest amount of removable lattice oxide ions among all the LaABO₃ samples tested. It can be easily reduced at temperature as low as 400°C in H₂, with a high mole ratio of 1.37 (H₂ consumed /catalyst used). The H₂ evolution temperature for LaSrFeO₃ in reaction with methane is 850°C. This is a promising catalyst for syngas production via the reaction of methane with ion-transport-oxides.

CHAPTER 5:

Syngas Production by Catalytic Partial Oxidation of Methane over A-and B-site Doped La_2NiO_4 Perovskite-related Oxides

5.1. $\text{La}_{2-y}\text{Ln}_y\text{NiO}_4$ ($\text{Ln}=\text{Gd, Ce, Sr, } y = 0.4, 0.6, 1$) and $\text{La}_2\text{Ni}_{1-x}\text{M}_x\text{O}_4$ ($\text{M}=\text{Fe, Co, Cu, } x = 0, 0.3, 0.5$) Oxide Series

Oxides with the perovskite-related K_2NiF_4 structure can be used in applications that require mixed electron-ion conductivity such as oxygen separation membranes and electrodes in solid oxide fuel cells [127, 128, 129, 130]. This kind of material can accommodate a wide variety of oxygen stoichiometry by introducing excess oxygen into interstitial sites of the structure. This high concentration of oxygen excess can offer the possibility of rapid oxygen transport (via oxygen migration) in the ceramic material at relatively low temperatures. One commonly known oxide with this perovskite related K_2NiF_4 structure would be the oxygen-hyperstoichiometric La_2NiO_4 which is of significant interest for high-temperature electrochemical applications. The crystal lattice of La_2NiO_4 can be described as a succession of LaNiO_3 perovskite layers separated by LaO rocksalt layers. As a consequence of their layer framework, La_2NiO_4 oxides can accommodate both oxygen vacancies and excess oxygen atoms in the interstitial positions between the layers, tetrahedrally coordinated by La^{3+} cations. It has been reported that La_2NiO_4 possesses appreciable oxygen permeability at elevated temperatures [131] where at higher temperature, the diffusivity of oxygen increases though this is offset by the decrease in the concentration of oxygen present in the interstitial position.

It is well known that A-site cations strongly affect the mobility of the oxygen ion in the ABO_3 bulk phase. Conversely, chemical properties, including catalytic activity for the oxidative reactions is normally dependent on the nature of the B-site cation.

In view of these considerations, La_2NiO_4 was doped at B site to obtain $\text{La}_2\text{Ni}_{1-x}\text{M}_x\text{O}_4$ oxides and A-site to obtain $\text{La}_{2-y}\text{Ln}_y\text{NiO}_4$ oxides. Fe, Co and Cu which are traditional catalysts for methane activation were introduced as B-site dopants in place of Ni. The dopants such as Gd, Ce and Sr which are commonly known for their effectiveness and potential values in hydrogen production and SOFC applications were made to partially replace La^{3+} ions at the A-site of pure La_2NiO_4 . The $\text{La}_2\text{Ni}_{1-x}\text{M}_x\text{O}_4$ ($\text{M}=\text{Fe}, \text{Co}, \text{Cu}, x=0, 0.3, 0.5$) oxides have been prepared by conventional ball milling methods as described in synthesis section in Chapter 3 while the $\text{La}_{2-y}\text{Ln}_y\text{NiO}_4$ ($\text{Ln}=\text{Gd}, \text{Ce}, \text{Sr}, y=0.4, 0.6, 1$) oxides were synthesized though citric acid assisted sol-gel method. The doping effect of these six metals on the La_2NiO_4 crystal structure and their catalytic activity for selective partial oxidation with methane for syngas ($\text{H}_2 + \text{CO}$) production was studied. The catalysts were characterized by means of XRD, BET, SEM, TPR and catalytic activity measurements.

5.2. Methane reaction with undoped La_2NiO_4

Catalytic partial oxidation of 10% CH_4 /95%Ar over undoped La_2NiO_4 has been performed from room temperature to 800°C, and the MS signals of outlet gases are displayed in Figure 5.1. Small amount of H_2 starts to evolve at the temperatures as low as 575°C, and reaches maximum peak at 660°C. At this H_2 maximum production

temperature (660°C), there is relatively low CO peak detected with some traces of H_2O production, while the signal of CO_2 is too weak to observe under the same magnitude.

Figure 5.1: The MS profiles of the catalytic partial oxidation of 10% CH_4 over pure La_2NiO_4 .

The XRD patterns of the freshly prepared, post-reaction and regenerated samples are shown in Figure 5.2. The XRD pattern of the freshly prepared sample is identical to that of a tetragonal K_2NiF_4 structure, revealing the formation of La_2NiO_4 . The La_2NiO_4 structure disappeared and $\text{La}(\text{OH})_3$ formed after the reaction with methane as shown in the above figure. A comparison of the catalysts before and after the reaction shows that the crystal sizes of the catalysts undergo changes after the reaction in CH_4 atmosphere. This is expected because of the structural breakdown of the perovskites, resulting from their reduction by the H_2 and CO produced in the methane conversion reactions, followed by re-crystallization of their reduction products (La_2O_3 and partially and/or completely reduced Ni oxide species). Ni or NiO should also be present in the reduced sample although they may not be detected by XRD analysis. The formation of the $\text{La}(\text{OH})_3$ phase is probably due to hydrolysis of La_2O_3 by water produced during the reaction. However,

the original La_2NiO_4 structure can be recovered by heating the post-reaction sample in air at 800°C (Fig. 5.2 after regeneration). The recovered oxide was found to show the same activity in the reaction with methane, giving the same MS/TPSR profiles as those in Figure 5.1.

Figure 5.2: XRD patterns of (a) freshly prepared La_2NiO_4 sample; (b) the La_2NiO_4 sample after the temperature programmed surface reaction (TPSR) with $10\%\text{CH}_4/\text{Ar}$ (from RT to 800°C), (c) after regeneration in $5\%\text{O}_2/\text{Ar}$ (from RT to 800°C).

In addition to these favorable results, La_2NiO_4 catalyst was found to have a specific surface area of $6.66\text{ m}^2/\text{g}$ which is larger than that of its precursor $\text{Ni}/\text{La}_2\text{O}_3$ ($4.4\text{ m}^2/\text{g}$) [132]. With these encouraging results, modification of the La_2NiO_4 at either the A- or the B-site was done in an attempt to lower the H_2 production temperature and to achieve better yield of syngas in particular H_2 . The results are presented in the following sessions below.

5.3. B-site doped La_2NiO_4 : $\text{La}_2\text{Ni}_{1-x}\text{M}_x\text{O}_4$ (M=Fe, Co, Cu, $x=0, 0.3, 0.5$)

5.3.1. Effect of B-site doping on La_2NiO_4 crystal structure

The XRD patterns of freshly prepared $\text{La}_2\text{Ni}_{1-x}\text{M}_x\text{O}_4$ (M=Fe, Co and Cu) oxides are displayed in Figures 5.3- 5.5 respectively. The effect of varying amount of Fe, Co and Cu doping respectively at the B-site on the crystalline structure of La_2NiO_4 oxide is studied here.

It can be observed from Figure 5.3 that the impurities start to appear when Fe content increases from 0.1 to 0.3. With the amount of Fe doping ≥ 0.3 , the K_2NiF_4 structure begins to collapse. As shown in Figure 5.3(b) the (113) and (020) peaks are shifted to lower diffraction angle with increasing Fe substitution due to the distortion of the lattice. As a result, there exist two new phases, La_2O_3 ($2\theta \sim 30^\circ$) and $\text{La}_3\text{Ni}_2\text{O}_7$ ($2\theta \sim 32.4^\circ$) when Fe doping > 0.3 .

Figure 5.3: XRD patterns of freshly prepared $\text{La}_2\text{Ni}_{1-x}\text{Fe}_x\text{O}_4$ catalysts (where $x=0, 0.1, 0.3, 0.5$ in patterns 1-4 respectively): (a) from 20 to 70° (b) from 30 to 35° of 2θ .

In comparison with the Fe doping, the structure change observed in Figure 5.4 is even more evident for Co doped samples. The characteristic patterns of K_2NiF_4 structure starts to change, and the intensity of the main peaks reduces with low amount of Co content at 0.1. The K_2NiF_4 structure collapses when the doping content of Co increases to ≥ 0.3 . Subsequently, the phases of La_2O_3 and $\text{La}_3\text{Ni}_2\text{O}_7$ are also seen in the $\text{La}_2\text{Ni}_{1-x}\text{Co}_x\text{O}_4$ samples as consistent with the results from the Fe dopant.

Figure 5.4: XRD patterns of fresh $\text{La}_2\text{Ni}_{1-x}\text{Co}_x\text{O}_4$ catalysts (where $x=0, 0.1, 0.3, 0.5$ in patterns 1-4): (a) from 20 to 70° (b) from 30 to 35° of 2θ .

As shown in Figure 5.5, for Cu doped samples, there is no presence of additional peaks or break down of the La_2NiO_4 crystal structure. Contrary to the previous two dopant oxide series, the $\text{La}_2\text{Ni}_{1-x}\text{Cu}_x\text{O}_4$ oxides remain unchanged, retaining the original K_2NiF_4 structure with increasing Cu doping content up to 0.5. However, translation of the (113) and (020) peaks to the left is noted with the Cu doping content of 0.1. The shifting of La_2NiO_4 peaks are caused by the distortion of the lattice due to introduction of dopant

Cu ion into the lattice structure. This would imply that among the three dopants, only Cu doping does not have significant effect on the crystalline structure of the precursor except for the shifting phenomenon observed in all the three varying amount of Cu dopants. This may be because the ionic radii of Cu^{2+} (73pm) is more close to that of Ni^{2+} (70pm), than Co^{2+} (74pm) and Fe^{2+} (78pm).

Figure 5.5: XRD patterns of fresh $\text{La}_2\text{Ni}_{1-x}\text{Cu}_x\text{O}_4$ catalysts (where $x=0, 0.1, 0.3$, and 0.5): (a) from 20 to 70° (b) from 30 to 35° of 2θ .

5.3.2. H_2 Temperature Programmed Reduction (TPR) analysis

The reduction behavior of $\text{La}_2\text{Ni}_{1-x}\text{M}_x\text{O}_4$ catalysts were studied by means of temperature-programmed reduction (TPR) technique, as shown in Figures 5.6 to 5.8. Typically, the reduction was carried out in a gas stream of 5% H_2 /95%Ar from RT to 800°C and held for 15 min. The peaks found in the plotted graphs indicate the temperature at which the maximum amount of H_2 is consumed by the oxide samples during the reaction with reducing gas, H_2 . The $\text{La}_2\text{Ni}_{1-x}\text{M}_x\text{O}_4$ oxides being perovskite-

related oxides were generally reduced in two zones: the first in the range of 300–500°C and the second in the range of 500–750°C.

For the TPR profile of the pristine compound La_2NiO_4 , three peaks of varying intensity are observed. Beside the big peak at 675°C, there are peaks at 420 and 520°C. Compared with the TPR spectrum of NiO as disclosed in [133], the peak at about 420°C is assigned to the reduction of NiO. The peak at around 675°C and the shoulder at 520°C could be related to the reduction of surface and bulk La_2NiO_4 , respectively. It was reported by B.S. Liu [134] that when the reduction was stopped at first stage, the oxide still maintained the K_2NiF_4 structure. It is only when the reduction was completely finished at the second stage then the K_2NiF_4 structure collapsed. Therefore, the first and second reduction stage can be attributed to the reduction of surface NiO/active oxygen species and the lattice oxygen of La_2NiO_4 , respectively.

For the Fe doped $\text{La}_2\text{Ni}_{1-x}\text{Fe}_x\text{O}_4$ oxides, Fe doping causes a slight upward shift of the second peak (larger peak) towards a higher temperature. The increment in Fe content did not cause a significant shift in the reduction temperatures.

Figure 5.6: TPR profiles of ball mill $\text{La}_2\text{Ni}_{1-x}\text{Fe}_x\text{O}_4$ catalysts. The flow rate was 50 ml/min of 5% H_2/Ar , and the weight of each

sample is 50 mg. The temperature was raised at a rate of $10^\circ\text{C}/\text{min}$ from RT to 800°C .

For the Co doped $\text{La}_2\text{Ni}_{1-x}\text{Co}_x\text{O}_4$ oxides, the Co doping causes a slight shift of the two temperature zones towards higher temperatures as illustrated in Figure 5.7.

Figure 5.7: TPR profiles of ball mill $\text{La}_2\text{Ni}_{1-x}\text{Co}_x\text{O}_4$ catalysts. The flow rate was 50 ml/min of 5% H_2/Ar , and the weight of each sample is 50 mg. The temperature was raised at a rate of $10^\circ\text{C}/\text{min}$ from RT to 800°C .

In comparison, Cu doping causes the temperature of the second peak (larger peak) to shift to a lower temperature as illustrated in Figure 5.8. This phenomenon is clearly seen in the case of $\text{La}_2\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_4$ (Fig. 5.8 (4)), where the high-temperature peak at 675°C is shifted to lower temperature (by 125°C) while the low temperature one shifted to 400°C . Therefore it can be concluded that with an increase in Cu content, the reduction temperature of $\text{La}_2\text{Ni}_{1-x}\text{Cu}_x\text{O}_4$ decreases and the oxide can be reduced at a narrower

temperature range. It is interesting to note that the Cu dopant changes the La_2NiO_4 structure less, but reduces the oxides easier than Fe and Co dopants.

Figure 5.8: TPR profiles of ball mill $\text{La}_2\text{Ni}_{1-x}\text{Cu}_x\text{O}_4$ catalysts. The flow rate was 50 mL/min of 5% H_2/Ar , and the weight of each sample is 50 mg. The temperature was raised at a rate of 10 °C/min from RT to 800 °C.

5.3.4. Catalytic Partial Oxidation of Methane over $\text{La}_2\text{Ni}_{1-x}\text{M}_x\text{O}_4$ (H_2 generation test)

The catalytic partial oxidation in 10% CH_4 over doped $\text{La}_2\text{Ni}_{1-x}\text{M}_x\text{O}_4$ ($\text{M}=\text{Fe}$, Co and Cu) perovskites-related oxides are tested by temperature-programmed surface reaction (TPSR) with on-line MS analysis. The H_2 MS profiles are displayed in Figure 5.9 for the three dopants Fe, Co and Cu respectively. The data of these MS profiles are summarized in Table 5.1.

Table 5.1: A summary of the MS profile results obtained for the $\text{La}_2\text{Ni}_{1-x}\text{M}_x\text{O}_4$ catalysts after CPO in 10% CH_4/Ar (100ml/min flow rate) heated from RT to 800°C.

Ball Mill Sample	H ₂ Evolution Temp	Presence of CO	Presence of CO ₂	Presence of H ₂ O
La_2NiO_4	650°C	✓	Nil	✓
$\text{La}_2\text{Ni}_{0.9}\text{Fe}_{0.1}\text{O}_4$	680°C	✓	Nil	✓
$\text{La}_2\text{Ni}_{0.7}\text{Fe}_{0.3}\text{O}_4$	660°C	✓	Nil	✓
$\text{La}_2\text{Ni}_{0.5}\text{Fe}_{0.5}\text{O}_4$	680°C	✓	Nil	✓
$\text{La}_2\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}_4$	685°C	✓	✓	✓
$\text{La}_2\text{Ni}_{0.7}\text{Co}_{0.3}\text{O}_4$	710°C	✓	✓	✓
$\text{La}_2\text{Ni}_{0.5}\text{Co}_{0.5}\text{O}_4$	675°C	✓	✓	✓
$\text{La}_2\text{Ni}_{0.9}\text{Cu}_{0.1}\text{O}_4$	700°C	✓	Nil	✓
$\text{La}_2\text{Ni}_{0.7}\text{Cu}_{0.3}\text{O}_4$	740°C	✓	✓	✓
$\text{La}_2\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_4$	810°C	✓	✓	✓

Figure 5.9: The MS profiles, showing the temperature at which H_2 is produced from the reaction between CH_4 and $\text{La}_2\text{Ni}_{1-x}\text{M}_x\text{O}_4$ catalysts: (a) with Fe doping (b) with Co doping and (c) with Cu doping. For each dopant the H_2 peak is dependent on the doping content, which is labeled with various colors. The flow rate was 100 ml/min of 5% CH_4/Ar , and the weight of each sample was 100 mg. The temperature was raised at a rate of 10 °C/min from RT to 800 °C.

The results both from Figure 5.9 and Table 5.1 demonstrated that the undoped La_2NiO_4 was able to produce maximum H_2 quantity at a relatively low temperature of

650°C, with simultaneous production of CO and H_2O . The addition of the three transition metal dopants to the pristine La_2NiO_4 oxide, basically, does not reduce the temperature of H_2 evolution. In contrast 10% Cu doping shifts it to 710°C, 10% Co shifts it to 680°C while 10%Fe shifts to 675°C. With an increase in Cu doping content to 50% of substitution, the maximum H_2 evolution temperature is increased to 810°C. In the earlier section, Cu doping shifted the H_2 TPR peak to a lower temperature. This signifies that Cu is easily reduced under H_2 environment, but is not active in catalyzing the reaction between CH_4 and O^{2-} . Contrary to the behavior of Cu dopant, the CH_4 reaction with the Fe- and Co-doped La_2NiO_4 oxides did not show a linear correlation with the dopant content (seen in Figure 5.10). Nevertheless the overall trend in Figure 5.10 demonstrates that B-site doping with Fe, Cu and Co dopants has negative effect on the catalytic partial oxidation of CH_4 . With these dopants, the H_2 evolution temperature is shifted to a much higher values, instead of the desired easy removal of oxide ions.

Figure 5.10: The maximum H_2 evolution temperature as a function of Cu, Co and Fe doping level respectively for the catalytic partial oxidation of CH_4 over the $\text{La}_2\text{Ni}_{1-x}\text{M}_x\text{O}_4$ catalysts.

5.4. A-site doped La_2NiO_4 : $\text{La}_{2-y}\text{Ln}_y\text{NiO}_4$ ($\text{Ln} = \text{Gd, Ce, Sr}$, $y = 0.4, 0.6, 1$)

5.4.1. Effect of A-site doping on La_2NiO_4

The XRD patterns of freshly prepared $\text{La}_{2-y}\text{Ln}_y\text{NiO}_4$ perovskite-like oxides are displayed in Figures 5.11 to 5.13, in which the effect of different amount of Gd, Ce and Sr A-site dopants on the crystalline structure of La_2NiO_4 is clearly shown.

The perovskite-like K_2NiF_4 crystal structure of La_2NiO_4 is confirmed by the XRD pattern in Figure 5.11(4). Gd_2NiO_4 is known to have identical XRD pattern since its crystalline structure is the same as that of La_2NiO_4 . Doping with $y < 0.6$ mol% Gd does not change the La_2NiO_4 structure. (Figures 5.11 (2) and (3)) The La_2NiO_4 crystal structure is damaged only when $y > 1$ mol%, i.e. 50% La ions are replaced by Gd ions, as shown in Figures 5.11(1) for $(\text{LaGd})\text{NiO}_4$. The crystalline $\text{La}(\text{OH})_3$ and La_2O_3 phases becomes detectable in Figures 5.11 (1).

Figure 5.11: XRD patterns of the $\text{La}_{2-y}\text{Gd}_y\text{NiO}_4$ catalysts.

XRD patterns in Figure 5.12 illustrate that La_2NiO_4 is very sensitive to Ce doping. The impurity phase, Ce_7O_{12} may start to appear with as small as $y = 0.2$ mole% Ce doping, though La_2NiO_4 structure is basically maintained. When doping content increases to $y \geq 0.6$, the destruction of the perovskite-like K_2NiF_4 structure phase gradually takes place. The Ce_7O_{12} peaks become very strong, and weak NiO peaks are also observable at $y = 0.6$ and 1.0 mole% Ce doping (Figures. 12 (1) and (2)). The structural instability and the presence of the impurities phases in LaCeNiO_4 might explain the low hydrogen TPR peaks (around 600°C compared with 712°C of non-doping sample) of LaCeNiO_4 samples in the following session. NiO can be reduced by H_2 at 400°C .

Figure 5.12: XRD patterns of $\text{La}_{2-y}\text{Ce}_y\text{NiO}_4$ catalysts.

XRD patterns of the $\text{La}_{2-y}\text{Sr}_y\text{NiO}_4$ oxides (where $x=0.2, 0.6, 1$) are shown in Figure 5.13. The original structure of La_2NiO_4 together with some quantity of La_2O_3 phases is detected when 0.2 of Sr is added. On the other hand, as the doping amount increases to 0.6 and 1.0 respectively, the crystal structure approaches to that of

$\text{La}_{1.5}\text{Sr}_{0.5}\text{NiO}_4$ without the presence of any La_2O_3 impurity. These observations imply that Sr ions are successfully doped into the structure. However, the decrease in the peak intensity and the shift in the peak position (see the inset) indicate that the crystallinity becomes poorer with increasing doping content.

Figure 5.13: XRD patterns of $\text{La}_{2-y}\text{Sr}_y\text{NiO}_4$ catalysts.

5.4.2. Catalytic Partial Oxidation with Methane (H_2 generation test)

The results of CPO reaction with CH_4 over the doped $\text{La}_{2-y}\text{Ln}_y\text{NiO}_4$ ($\text{Ln}=\text{Gd}$, Ce and Sr while $y=0.2$ and 0.6) perovskites-like oxides are shown in Table 5.2. The temperature-programmed surface reaction (TPSR) MS profiles (in terms of H_2 signal) are plotted in Figure 5.14.

Table 5.2: A summary of the TPSR results obtained for the $\text{La}_{2-y}\text{Ln}_y\text{NiO}_4$ catalysts after generation test in 10% CH_4/He (100ml/min flow rate) heated from RT to 800°C.

Sol-gel Sample	H_2 Evolution Temp	Presence of CO	Presence of CO_2	Presence of H_2O
La_2NiO_4	650°C	✓	Nil	✓
$\text{La}_{1.8}\text{Gd}_{0.2}\text{NiO}_4$	701°C	✓	✓	✓
$\text{La}_{1.4}\text{Gd}_{0.6}\text{NiO}_4$	767°C	✓	✓	✓
$\text{La}_{1.8}\text{Ce}_{0.2}\text{NiO}_4$	620°C	✓	✓	✓
$\text{La}_{1.4}\text{Ce}_{0.6}\text{NiO}_4$	605°C	✓	✓	✓
$\text{La}_{1.8}\text{Sr}_{0.2}\text{NiO}_4$	708°C	✓	✓	✓
$\text{La}_{1.4}\text{Sr}_{0.6}\text{NiO}_4$	560°C, 710°C	✓	✓	✓

Figure 5.14: The TPSR H_2 profiles show the temperature at which H_2 is produced from the reaction between CH_4 and $\text{La}_{2-y}\text{Ln}_y\text{NiO}_4$ catalysts: (a) with Gd doping (b) with Ce doping and (c) with Sr doping. The doping content is labeled for various colors. The flow rate was 100 ml/min of 5% CH_4/Ar , and the weight of each sample is 100 mg. The temperature was raised at a rate of 10 °C/min from RT to 800 °C.

As listed in Table 5.2 H_2 is generated at 650°C for undoped La_2NiO_4 . For Gd doped oxides ($y = 0.2$ and 0.6 mol%), the maximum quantity of H_2 are produced at much higher temperature, 700 and 767 °C for $y = 0.2$ and 0.6 mole%, respectively, with low intensities. (Figure 5.14) As noted in the previous section 5.4.1, the Gd-doped samples

basically maintain the original K_2NiF_4 structure (Figure 5.11, $y < 0.6$). The structural stability may provide the explanation for the poor performance under CH_4 at 770°C .

For the Ce doped oxides, the H_2 release temperature is reduced to $600\text{--}620^\circ\text{C}$ but with low intensities (Figure 5.14). This is in good agreement with the XRD analysis in Figure 5.12 where Ce_7O_{12} and NiO may result from the Ce doping. NiO can be reduced by H_2 at 420°C while CeO_2 at $500\text{--}750^\circ\text{C}$. It was noted that the amount of CO_2 increased with Ce content, implying that the Ce doping enhanced the mobility of lattice oxide ions.

In Figure 5.14, the H_2 TPSR curves for 0.6 and 1.0 mole% Sr doped samples are rather different from other doped samples. The MS profile of the H_2 production for 0.2 mol% Sr is peaked at 708°C with medium intensity. However both $\text{La}_{1.4}\text{Sr}_{0.6}\text{NiO}_4$ and $(\text{LaSr})\text{NiO}_4$ give a relatively strong peak at 560°C , followed by a broad peak around 700°C . Since XRD patterns in Figure 5.13 reveal the maintenance of K_2NiF_4 structure, and the diffraction peak shifts, the two H_2 TPSR peaks could imply the presence of both interstitial and normal oxide ions. The H_2 released around 560°C is presumed to be produced by interstitial oxygen, which can be easily extracted from the perovskite like structure at low operating temperature. This interstitial oxygen peak, which is of very high intensity in the sample prepared by sol-gel method, can also be found in some samples prepared by ball-milling methods, but with comparatively lower intensity, indicating that sol-gel method is particularly suitable for preparing the interstitial K_2NiF_4 structure. The 0.6 Sr doping sample that underwent H_2 generation reaction which gave an early H_2 peak of 560°C was analyzed with XRD. The perovskite-like K_2NiF_4 structure with lower intensity was detected, which confirms the existence of interstitial oxygen. Also, the reaction with CH_4 at the low operating temperature (560°C) only weakened the

crystallization of the perovskite structure but do not cause any change in the stability of the structure. In short, with increasing the Sr doping, the reactivity of $(\text{La}_{2-y}\text{Sr}_y)\text{NiO}_4$ for hydrogen evolution is enhanced significantly while the K_2NiO_4 -type structure remains. This is a good phenomenon as this will allow the catalysts to be able to regenerate at a lower temperature during its application.

Figure 5.15 summarizes the A-site doping effect. On the contrary to the B-site doping, there is linear relationship between the amount of dopants and the H_2 evolution temperature. As the doping quantity “y” increases from 0 to 0.2-0.6, the H_2 evolution temperature increases for Gd dopant, whereas it decreases for Ce dopant. Sr dopant outperforms the Gd and Ce dopants. The H_2 evolution temperature increases first with increasing y from 0 to 0.2, but then decreases to 550°C when $y = 0.6$ and 1.

Figure 5.15: The maximum H_2 evolution temperature as a function of Gd, Ce and Sr doping level respectively for the catalytic partial oxidation of CH_4 over the $\text{La}_{2-y}\text{Ln}_y\text{NiO}_4$ catalysts.

Hence from the summarized data, it can be concluded that 0.6-1 mol percent of Sr dopant at A-site has the most desirable effect on the catalytic partial oxidation of CH_4 , shifting the H_2 evolution temperature to a much lower range (from 650°C to 550°C). The $\text{La}_{2-y}\text{Sr}_y\text{NiO}_4$ ($y = 0.4, 0.6, 1$) oxides were hence further studied in more details.

5.5. $\text{La}_{2-y}\text{Sr}_y\text{NiO}_4$ ($y = 0.4, 0.6, 1$) oxides

5.5.1. BET Measurements

BET results of the $\text{La}_{1-y}\text{Sr}_y\text{NiO}_4$ catalysts are shown in Table 5.3 below. The comparison reveals that the surface areas of $\text{La}_{1-y}\text{Sr}_y\text{NiO}_4$ catalysts perovskites-like oxides are significantly larger than the pristine precursor La_2NiO_4 with an increase in Sr content. With the increased surface area, there will be more active sites generated for catalytic reactions to take place. Thus this may help in increasing the reaction rate and lower the operating temperatures at which the hydrogen peaks occur for the generation reaction in the syngas production.

Table 5.3: A summary of the BET surface area results of the $\text{La}_{1-y}\text{Sr}_y\text{NiO}_4$ catalysts.

Sample	Surface area(m^2/g)
La_2NiO_4	6.67
$\text{La}_{1.8}\text{Sr}_{0.2}\text{NiO}_4$	7.57
$\text{La}_{1.4}\text{Sr}_{0.6}\text{NiO}_4$	17.87
LaSrNiO_4	19.98

5.5.2. TGA Analysis

TGA analysis was carried out on the $\text{La}_{2-y}\text{Sr}_y\text{NiO}_4$ catalysts under 5% H_2 to measure the weight lost during the reduction reaction. The results are summarized in Table 5.4. The thermal analyses reveal a three-step weight loss for $y = 0.2$ and 0.6 while two-step for $y = 1.0$ with corresponding TGA curves. It is possible that during the heating of nickelates interstitial oxygen ions leave the compound lattice at lower temperatures and cause the occurrence of the first oxygen desorption peaks in the range of 200-500°C. After reaching some lower oxygen over-stoichiometry the further allocation of oxygen apparently occurs accounting for the removing of oxygen from its regular positions. Oxygen allocated in this case causes the appearance of oxygen desorption peaks in the temperature range 650-850°C shown in Table 5.4. The trend observed is that the weight lost increases linearly with increasing Sr content. Since the weight lost is mostly due to the consumption/desorption of oxygen during heating, it would mean that the removable oxygen content increases with the amount of Sr doping at A-site. Although a higher amount of weight loss would be desirable as it would signify the presence of abundance of O^{2-} for reaction with CH_4 , lower H_2 operating temperature must be taken into account as well. The 0.6 mol% Sr doped oxides generally gave 3% weight loss throughout all the temperature range. As such, this $\text{La}_{1.4}\text{Sr}_{0.6}\text{NiO}_4$ oxide proves to fit the requirements both for large quantity of O^{2-} lattice and for low H_2 evolution temperature.

Table 5.4: Summary of TGA data of $\text{La}_{2-y}\text{Sr}_y\text{NiO}_4$ ($y=0.2, 0.6, 1$) oxides.

Sr content	Weight lost at different steps			Total weight loss
0.2	0.85% (200-350°C)	0.80% (350-450°C)	4.26% (650-700°C)	5.88%
0.6	2.39% (200-350°C)	3.75% (500°C)	3.30% (700-800°C)	9.45%
1.0	5.61% (100-500°C)		7.37% (800-850°C)	12.98%

5.5.3. Temperature Programmed Reduction (TPR) Analysis

The removable oxygen content of the $\text{La}_{1-y}\text{Sr}_y\text{NiO}_4$ samples was also determined through H_2 temperature programmed reduction (TPR). The peaks in the TPR graphs in Figure 5.16 indicate the temperature at which the maximum amount of H_2 is consumed by the samples during the reaction with the doped $\text{La}_{1-y}\text{Sr}_y\text{NiO}_4$ catalysts.

As mentioned in earlier section, for La_2NiO_4 catalyst, there are a total of three peaks observed at 420°C (small peak), 520°C (shoulder peak) and 675°C (big peak) respectively. The peak at about 400°C is assigned to the reduction of NiO according to the TPR spectrum of NiO. The peak at around 675 °C and the shoulder at 520 °C could be caused by the reduction of surface and bulk La_2NiO_4 respectively.

All samples studied exhibited two or more peaks over the two temperature range (300-500°C and 550-750°C) corresponding to the maximum amount of H_2 used by the doped samples. The distinctive reduction peaks at different temperatures could signify that there exist various types of O^{2-} species which participate in the reaction with H_2 at different mobility under different temperature. These peaks with maxima at the

temperatures in the range of between 300 and 800°C could indicate the increased mobility of lattice oxygen ions with an increase in Sr doping content.

In agreement to the TGA analysis in Section 5.5.2, the TPR profiles show that with the increase of Sr^{2+} content, the number of oxygen vacancies and the extent of lattice distortion increase. This arises as Sr^{2+} has a larger ionic radius than that of La^{3+} [$\gamma_{\text{Sr}^{2+}}$ (0.144 nm) > $\gamma_{\text{La}^{3+}}$ (0.136 nm)], while on the other hand as Sr content increases, the concentration of Ni^{4+} decreases with a corresponding increase in Ni^{2+} . Since $\gamma_{\text{Ni}^{2+}}$ (0.069 nm) > $\gamma_{\text{Ni}^{4+}}$ (0.048 nm), an increase in the lattice parameters is expected. In addition, due to charge balancing compensation, caused by substitution of Sr^{2+} for La^{3+} , there is formation of an oxygen vacancy.

With 0.2 of Sr doping, the two low-temperature TPR peaks of the pristine La_2NiO_4 oxide shift to the lower temperature range, 320 and 435°C respectively, and the H_2 consumption intensity of all three peaks, including that at 675°C, increases. This would suggest the positive influence of Sr dopant on the oxide as the reduction temperature of both NiO and La_2NiO_4 was lower with higher H_2 consumption. When the quantity of Sr was raised from 0.2 to 0.6, the reduction temperature of the consumed H_2 was reallocated to two lower temperatures at 370°C and 615°C respectively with much higher H_2 consumption value of 1.33 mole H_2 per mole of the oxide. $(\text{LaSr})\text{NiO}_4$ exhibits a singular narrow sharp peak at 350°C with a small shoulder at 390°C while the second peak at 440°C becomes broad with relatively large area. The high-temperature peak at 620°C is very weak in intensity. The sharp lower range reduction peak suggests that the Ni^{4+} present was unstable and of low amount. The shoulder peak which is consecutively next to this sharp peak could indicate the first appearance of reactive oxygen lattice. The

fact that the dominant peak occurred at 440°C could mean that there are more of surface oxygen lattice than that of the bulk.

Figure 5.16: TPR profiles, showing the temperature at which H_2 is consumed from the reaction between H_2 and $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ catalysts. The flow rate was 50 mL/min of $5\%\text{H}_2/\text{He}$, and the weight of each sample is 50 mg . The temperature was raised at a rate of 10°C/min from RT to 800°C .

The total amount of hydrogen consumed per mole of catalysts for this A-site Sr doped oxides during TPR was calculated by the integration of the respective TPR profiles as shown in Figure 5.14. A summary of amount of hydrogen consumption of all the samples during TPR testing was given in Table 5.5. The values for the hydrogen consumption indicate that the accessibility of the oxygen lattice ions differ between the oxides, assuming that a higher consumption implies the accessibility of more oxygen lattice, O^{2-} .

Table 5.5: A summary of the number of mole of H_2 being consumed per mole of Catalyst used tabulated from the TPR results for the $\text{La}_{1-y}\text{Sr}_y\text{NiO}_4$ catalysts.

Sample	Sr Content	No of mol of H_2 Consumed per mol of Catalyst
La_2NiO_4	0	0.75
$\text{La}_{1.8}\text{Sr}_{0.2}\text{NiO}_4$	0.2	1.03
$\text{La}_{1.4}\text{Sr}_{0.6}\text{NiO}_4$	0.6	1.33
$\text{La}_2\text{SrNiO}_4$	1.0	1.01

The hydrogen consumption may proceed according to the equation: $\text{O}^{2-} + \text{H}_2 \rightarrow \text{H}_2\text{O} + (\text{vacancy})^{2-}$. It is established that with Sr dopant, La_2NiO_4 oxides are more readily reducible. In comparison, the raw undoped La_2NiO_4 has the smallest H_2/cat ratio which suggested that this precursor oxide has the least amount of O^{2-} species reactable. A large area under the graph and high H_2/cat (molar ratio) is more desirable as it represents more number of moles of O^{2-} species in the sample that has reacted with the reducing gas. The optimum amount of O^{2-} species reacted is 1.33 which was achieved by the 0.6 mol percent of Sr^{2+} doping. This would suggest that $\text{La}_{1.4}\text{Sr}_{0.6}\text{NiO}_4$ possesses most quantity of oxygen species that can take part in the reaction with H_2 . Evidently, A-site Sr^{2+} doping, ideally with 0.6 mol percent of it disturbs the lattice structure mostly so that more oxygen ions become movable at lower temperatures. Alternatively LaSrNiO_4 could be a good choice too, since 1 mole of H_2 can be consumed per catalyst at temperatures below 500°C .

5.5.4. Catalytic Activity Analysis

Based on the results discussed in earlier sections, catalytic activity measurements have been done over the $\text{La}_{1.4}\text{Sr}_{0.6}\text{NiO}_4$ oxide which has shown superior performance among its relative oxide group. A small amount of catalyst (500mg) was tested under 9% CH_4 at 850°C with 5080 h^{-1} GHSV. The sample exhibited rather high methane conversion (35%), high H_2 production (75%), and 10% CO within the 22 min of the reaction time. However, the results reveal that the catalyst has poor stability as its activity and selectivity decreased pronouncedly with an increase in time-on-stream, indicating their fast deactivation during the catalytic process. The time-on-stream activity and selectivity data for the catalysts is included in Figure 5.17.

The $\text{La}_{1.4}\text{Sr}_{0.6}\text{NiO}_4$ oxide was chosen for studying the effect of operating temperature on the catalytic partial oxidation of methane using oxygen lattice from the oxide. Partial oxidation reaction of methane at 850°C can achieve a conversion of 35% while at 750°C on the same sample a lower conversion 16% was measured (Figure 5.18). This is probably due to the higher oxide ion mobility at 850°C. However, at 750°C the conversion of methane starts declining at 10 min of reaction while at 850°C it reaches maximum value at 22 min. This is understandable since at higher temperatures more oxide ions could be removed and react with methane.

The results indicate that not only the conversion but also the concentration, in other words concentration for both H_2 and CO is increased with increasing reaction temperature from 750°C to 850°C. The increase in the concentration is consistent with the fact that the formation of H_2 and CO in the oxidative conversion of methane is

thermodynamically favored at the higher temperatures. This is because of the fact that the oxygen lattice from the bulk diffuses to surface with very high active energy.

Figure 5.17: Catalytic Partial Oxidation of $\text{La}_{1.6}\text{Sr}_{0.4}\text{NiO}_4$ at 850°C using 110ml/min of $9\% \text{CH}_4$.

Figure 5.18: Catalytic Partial Oxidation of $\text{La}_{1.6}\text{Sr}_{0.4}\text{NiO}_4$ at 750°C using 110ml/min of $9\% \text{CH}_4$.

5.5. Discussion

La_2NiO_4 with A site doping $\text{La}_{2-y}\text{Ln}_y\text{NiO}_4$ ($\text{Ln} = \text{Gd}, \text{Sr}, \text{Ce}$, $x = 0.4, 0.6, 1$) and B site doping $\text{La}_2\text{Ni}_{1-y}\text{M}_y\text{O}_4$ ($\text{M} = \text{Cu}, \text{Co}, \text{Fe}$, $y = 0, 0.3, 0.5$) were prepared by citric acid assisted sol-gel method and solid state reaction respectively. The A and B -site doping effect on the La_2NiO_4 crystal structures and catalytic activity for the selective partial oxidation of methane for syngas ($\text{H}_2 + \text{CO}$) production have been studied.

B-site doping with transition metals Fe, Co and Cu exhibits negative effect on the reduction of H_2 production temperature. The maximum evolution of H_2 temperature increases from 650 to 810°C with increasing Cu doping content from 0 to 0.5, while, there is no linear correlation for that of Co and Fe doped La_2NiO_4 oxides.

Doping A site with Gd, Ce and Sr achieves mixed effects on the H_2 production temperature. While Gd dopant brings about similar reverse effect as seen with Cu dopant at B-site, the Sr and Ce dopants display positive outcome on the catalytic reactions conducted by shifting H_2 evolution temperature to a lower range. Thus among the 6 doping elements tested in this study, only Sr and Ce dopants at A-site were found to be able to lower the methane activation temperature of La_2NiO_4 . Other doping elements, i.e. Cu, Fe, Co and Gd played the reversed role. The doping effect on the perovskite-oxide methane activation ability is correlated to the oxygen content and mobility in their K_2NiF_4 structure.

The reduction behavior of M ($\text{M} = \text{Fe}, \text{Cu}, \text{Co}$) and Sr doped La_2NiO_4 were studied by means of a TPR technique. The perovskite-related oxides were generally reduced in two zones: the first in the range of 300°C – 500°C and the second in the range of 500°C –

750°C. This affirmed the presence of both interstitial and bulk oxygen species in the doped oxides. The TPR profiles of the B-site doped $\text{La}_2\text{Ni}_{1-x}\text{Co}_x\text{O}_4$ oxide series showed that all the three dopants (Fe, Cu and Co) seem to have little or no effect on the original pristine La_2NiO_4 . There is practically no significant improvement on the reduction peaks nor the amount of H_2 being consumed. However Sr doped La_2NiO_4 displayed notable performance. Subsequently, the poor performance of these dopants could be explained from the XRD patterns of freshly prepared doped samples. Basically the doped oxides the K_2NiF_4 structure could not be preserved and well maintained under the influence of increasing dopant content of the elements: Fe, Co, Cu, Gd and Ce. With exception to Sr dopant, of the perovskite-like K_2NiF_4 structure started to change and the intensity of the main peaks became lower with worst scenario having the entire K_2NiF_4 structure collapsed. Correspondingly, the K_2NiF_4 crystal structure was stable under different quantity of Sr doping with only peak shift.

Among $\text{La}_{1.4}\text{Sr}_{0.6}\text{NiO}_4$ oxide tested under 9% CH_4 at 850°C with 5080 h^{-1} GHSV yielded 35% CH_4 conversion with selectivity of 75% H_2 and 10% CO at 22 min of the time-on-stream. Also it was found that increase in reaction temperature could increase both the conversion but selectivity of both H_2 and CO.

5.6. Conclusions

Therefore it can be concluded that A-site doping has positive effect on the pristine La_2NiO_4 oxide but the B-site doping produce a conflicting results. Among many doping elements tested in this study, only Sr and Ce were found to be able to lower the methane activation temperature of La_2NiO_4 . The Sr doping at A-site achieved significant

enhancement of catalytic performance in term of lowest H_2 evolution temperature (550°C) and H_2/cat consumption mol ratio (1.33). The $\text{La}_{1.4}\text{Sr}_{0.6}\text{NiO}_4$ catalyst yielded the best performance. Other doping elements, i.e. Cu, Fe, Co and Gd played the reversed role. The doping effect on the perovskite-oxide methane activation ability is correlated to the oxygen content and mobility in their K_2NiF_4 structure.

CHAPTER 6:

Hydrogen Production by Catalytic Partial Oxidation of Methane over Doped Commercial CeO₂ Oxides

6.1. Overview of Gd, Sm and Y doped Commercial CeO₂ Oxides

High surface area Ceria and Ce-containing mixed oxides have attracted much attention as oxidation catalysts because of their unique redox properties (oxygen storage capacity - OSC) and textural properties. As well known, the most interesting property of ceria is its ability to act as an oxygen buffer with respect to the reaction environment. That is ceria is easily reduced and able to shift rapidly between the +3 and +4 state and vice versa. This is owing to the fact that it has a fluorite-like cubic structure in which each cerium site is surrounded by eight oxygen sites in fcc arrangement and each oxygen site has a tetrahedron of cerium sites. However, pure CeO₂ is seldom used since it is known to have poor thermal stability [135, 136, 137, 138]. Besides, the surface redox chemistry of ceria is known to be sensitive even at low temperatures to crystal structure defects. This is due to the changes in pore structure and in crystallite growth. Thus this disadvantage of Ceria can be fine tuned by substituting some of the Ce cations with ions of different size and/or charge [139, 140]. Additionally, doping with lower valent cations is known to decrease the expansion and contraction of ceria during reduction and oxidation [141]. Studies have shown that ceria modified by low-valence cations (Sm, Bi etc.) possess a good ionic conductivity, while the addition of yttrium which are highly soluble in ceria, to a level of about 40% or more [142], can increase the concentration of oxide ion vacancies. The incorporation of rare earth metal gadolinium (Gd³⁺) into ceria is found to stabilize the fluorite structure and increase the oxygen mobility due to formation of oxygen vacancies [143]. Additionally, these dopants (Gd₂O₃, Y₂O₃, and

Sm₂O₃) have shown to give the highest maximum conductivities [144] due to the small association enthalpy between dopant cation and oxygen vacancy in the fluorite lattice.

Thus in consideration of these, nano-crystalline CeO₂, and Gadolinium, Samarium, Yttrium doped CeO₂ which are commercially produced have been used in our study in this chapter. The samples presented in this chapter consist of pure CeO₂, Ce_{0.9}Gd_{0.1}O₂ (CGO), Ce_{0.85}Sm_{0.15}O₂ (CSO) and Ce_{0.85}Y_{0.15}O₂ (CYO) respectively. These four oxides are investigated by XRD, BET, TPR analyses and catalysis activity evaluation.

6.2. Catalytic Activity Studies

6.2.1. Catalytic Partial Oxidation with Methane (Generation test)

The doped oxides were made to undergo catalytic partial oxidation (generation test) in 5%CH₄-95%Ar from RT to 850°C. The results obtained are presented as graphs of MS profiles where the temperature range was plotted against the intensity, at which syngas (H₂ + CO) and other by products (H₂O, CO, CO₂) are being produced. The peak which is significant to our findings would be that of syngas that shows the temperature at which most of the respective H₂ and CO evolves. It is noted that in all the graphs of the doped commercial CeO₂ series for the generation test, the intensity of H₂ peak is higher than the CO peak. These results are in good accordance with the theory (CH₄ + O²⁻ → 2H₂ + CO) where the ratio of H₂ to CO is ideally 2. Here, we present the H₂ evolution peak of the all four catalysts over the range of temperature which they are heated to in Figure 6.1 as a summarized data.

All the doped oxides display single hydrogen peak with exception to that with Yttrium dopant. The 2 H₂ peaks observed in Yttrium dopant could be due to presence of different active O²⁻ species in which some are released at relatively lower temperature whereas others require a higher temperature (>850°C) to be activated for the CPO reaction with CH₄. The un-doped CeO₂ being a very stable oxide, requires comparatively high temperatures (850°C) to reach its peaks. However, with the addition of dopants (Gd, Sm and Y), H₂ peaks begin to appear at much lower temperature with the lowest desired peak at around 570°C. Even though Gd dopant enables production of H₂ at 805°C, the intensity of its H₂ peak is lowest among the series. Conversely, the Y and Sm doped CeO₂ oxide shows potentially increasing trend of H₂ production while the maximum operating temperature was hold at 850°C for sometime. This could imply that the O²⁻ species present needs high activation energy (>850°C) to be able to dissociate from the fluorite lattice. Among all the doped oxides, Yttrium doped oxide exhibited lowest H₂ evolution temperature of 570°C indicating that more lattice oxygen present at low temperature where the mobility of oxygen ions is high thus reduces the temperature for the partial oxidation reaction.

Figure 6.1: MS profiles, showing peak at which H₂ is produced from the CPO reaction between CH₄ and doped CeO₂ catalysts. The flow rate was 100 ml/min of 5%CH₄/Ar, and the weight of each sample is 100 mg. The temperature was raised at a rate of 10 °C/min from RT to 850°C.

6.2.2. Activity Measurements

Figure 6.2 illustrates the activity measurement during the partial oxidation of 5%CH₄/ Ar reaction at 850°C over pure CeO₂, CGO, CSO and CYO catalysts respectively with GHSV of 681 h⁻¹. As defined in earlier chapter by equation 1 to 3, the amount of CH₄ converted and the syngas concentration ratio in the outlet gas stream were measured and tabulated. It can be seen that the catalytic activity of doped CeO₂ is better than that of undoped with the highest CH₄ conversion of 20% as compared to 5% of the latter due to availability of more lattice oxygen and thus increase in oxygen mobility.

Figure 6.2: Catalytic activity of doped CeO₂ oxides during the partial oxidation of methane at 850 °C: (a) CH₄ conversion and (b) H₂/CH₄ ratio respectively.

The conversion of CH₄ for the Gd doped CeO₂ oxide is relatively stable (15%) over the range of holding time. However, the other three oxides do not show similar stable activity. The Y dopant have highest amount of CH₄ converted (20%) which could only remain steady over a short period of time. In comparison, the ratios of H₂/CH₄ (ideal = 2) which correspond to concentration of H₂ produced to CH₄ consumed, were in good agreement with that of CH₄ conversion and exhibit similar variations with time. Again, it is observed that Gd and Y dopant give the best results of 0.4 mole of H₂ produced per mole of CH₄. These facts may mean that most of CH₄ was converted to carbon deposition, other form of hydrocarbon (C_xH_y) and water on these doped oxides. Thus the overall catalytic activity can be arranged in this ascending order of CeO₂ < CSO < CYO < CGO. Subsequently it can be concluded that with Yttrium and

gadolinium doped to CeO₂ oxides, the performance is better, yielding 20% CH₄ conversion and 40% H₂ selectivity.

6.3. Structural Studies

6.3.1. Doping Effect on Fluorite Type structure

Figure 6.3 to 6.6 display the diffractogram of undoped CeO₂, CGO, CSO and CYO at different conditions: before reaction, after generation (CPO in CH₄) and after regeneration (in O₂). According to the XRD data measured, all the diffraction lines of the four catalysts could be indexed to the fluorite structure of ceria. Basically the oxides retain the structure of pure CeO₂, with no indication of any other phases. For the undoped CeO₂ and CGO, reaction with CH₄ caused the intensity of the respective ceria peak to decrease. Conversely in CSM and CYO, it was observed that the intensity of peaks were halved with the width of peaks widen and d-spacing doubled. However, recovery of all the four oxides is possible with regeneration at 850°C in air. After oxidation in air, all the structures of reduced oxides are recovered and revert back to the original fluorite-type crystalline frame-work which is same as before any reaction. Thus, the doping effect of these metals (Gd, Sm and Y) on the fluorite type CeO₂ oxide is that it allows the cations in the oxides to possess oxygen transfer capacity by being able to access a variable valence number under both reducing and oxidizing conditions without any re-constructive phase transitions. The difference in charge is compensated by the formation of oxygen vacancies [145]. Hence the consistencies in the results in retaining the Fluorite type Ceria structure indicate that the phase structures of the doped CeO₂ oxides are not affected by CPO or high reacting temperatures. The remarkable structural stability of the series of oxides to sustain its stable fluorite structure is highly desirable.

Figure 6.3: XRD patterns of CeO_2 catalyst. (a) Fresh sample commercially produced, (b) after generation in 5% CH_4/Ar (from RT to 850°C), (c) after regeneration in 5% O_2/Ar (from RT to 850°C).

Figure 6.4: XRD patterns of $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$ catalyst. (a) Fresh sample commercially produced, (b) after generation in 5% CH_4/Ar (from RT to 850°C), (c) after regeneration in 5% O_2/Ar (from RT to 850°C).

Figure 6.5: XRD patterns of Ce_{0.85}Sm_{0.15}O₂ catalyst. (a) Fresh sample commercially produced, (b) after generation in 5%CH₄/Ar (from RT to 850°C), (c) after regeneration in 5%O₂/Ar (from RT to 850°C).

Figure 6.6: XRD patterns of Ce_{0.85}Y_{0.15}O₂ catalyst. (a) Fresh sample commercially produced, (b) after generation in 5%CH₄/Ar (from RT to 850°C), (c) after regeneration in 5%O₂/Ar (from RT to 850°C).

6.3.2. Surface Morphology

The morphology of the transition metal doped CeO₂ oxides synthesized commercially is illustrated in Figure 6.7. Generally all the oxides display homogeneous clusters of spherical crystals with fine particle of size < 100 nm.

Figure 6.7: SEM morphology of commercial produced doped CeO₂ oxides (a) CeO₂, (b) Ce_{0.9}Gd_{0.1}O₂, (c) Ce_{0.85}Sm_{0.15}O₂ and (d) Ce_{0.85}Y_{0.15}O₂ oxides with different magnifications.

As these powders are commercially produced, the parameters of the resultant powders have been modified to give much finer powders with a narrow particle size distribution and a larger surface area ultimately. The BET areas are fairly similar for all samples with the values between 189 and 230 m²/g as presented in Table 6.1. Thus there is not much significant noted for both the surface area and morphology of the catalysts.

Table 6.1: A summary of the surface area BET results of the doped CeO₂ samples.

Samples	Surface area of samples(m ² /g)
CeO ₂	194.0
Ce _{0.9} Gd _{0.1} O ₂	189.3
Ce _{0.85} Sm _{0.15} O ₂	209.6
Ce _{0.85} Y _{0.15} O ₂	226.1

6.3.3. Temperature Programmed Reduction (TPR) Analysis

The capabilities of the oxides to store pure oxygen are measured by means of the temperature-programmed reduction (TPR) in 5%H₂/95%Ar. The temperature programmed reduction profiles of the tested catalysts are presented in Figure 6.8 and the correspondent H₂ consumptions per mole of catalysts are shown in Table 6.2. The TPR graphs were plotted over the range of time stream against both the intensity of the consumed H₂ peak and the range of temperature over which the reaction took place.

As shown, the reduction profile of CeO₂ consists of two peaks located at calcination temperature of 530°C and 770°C respectively. These are the well-known two peaks profile associated with, respectively, reduction at the surface and in the bulk of CeO₂ [146, 147]. The first peak originates from reduction of easily reducible surface cerium and the second is due to reduction of the innermost layer of CeO₂ to Ce₂O₃ [148].

Similar to the TPR Profile of the pure CeO₂, all three doped oxides exhibited H₂ consumed peaks over two temperatures ranges at low temperatures (450-500) and high temperatures (740-805) respectively. The presence of the dopants (Gd, Sm and Y) clearly promotes the reduction of the surface oxygen species as documented by the shift of the original low temperature peak of CeO₂ to below 530°C. The low temperature reduction is strictly related to the extent of surface area. In fact, under reducing conditions the CeO₂ surface is poorly stable [149], leading to a surface area collapse in the course of the initial TPR experiment [150]. This results in loss of metal and/or CeO₂ interactions as detected by the low temperature TPR peak. The results showed that the reduction behavior of CSO and CYO is nearly identical over the same range of temperature with the latter oxide having higher H₂ consumption at a slightly higher reduction temperature. It can be seen that in CYO and CSO oxides, more surface reduction took place as compared to the bulk reduction, which is indicated by the larger H₂ peak in the lower temperature range than that in the higher temperature range. This implies that more O²⁻ lattice is found on the oxide surface than in the bulk structure. Conversely, for CGO oxide, more active reduction took place in the bulk than on the surface.

Figure 6.8: TPR profiles, showing the intensity, temperature and time on stream at which H₂, is consumed from the reaction between H₂ and doped CeO₂ catalysts. The flow rate was 50 mL/min of 5%H₂/Ar, and the weight of each sample is 50 mg. The temperature was raised at a rate of 10 °C/min from RT to 850°C.

The total amount of hydrogen consumed during TPR was calculated by the integration of the profiles. As seen from the calculated amount of mole of the H₂ adsorbed per mole of catalyst reacted, the Gd, Sm and Y dopants have positive effects on the pristine CeO₂. The tabulated ratios are relatively small compared to the ideal ratio of 2. This suggests that even though the samples were readily reduced at the lower temperature range, only small amount of O₂ species was reacted. Nevertheless it should be noted that this CeO₂ oxide series is meant to be used as the active phase on which other potential metal oxides will be doped.

Table 6.2: A summary of the number of mole of H₂ being consumed per mole of Catalyst used tabulated from the TPR results for the doped CeO₂ oxides.

Sample	No of mol of H ₂ Consumed per mol of Catalyst
CeO ₂	0.14
Ce _{0.9} Gd _{0.1} O ₂	0.27
Ce _{0.85} Sm _{0.15} O ₂	0.16
Ce _{0.85} Y _{0.15} O ₂	0.34

6.4. Conclusion

Synthesis gas production from partial oxidation of methane over the commercially produced Ceria-based materials, Ce_xM_{1-x}O₂ where M = Gd, Sm, Y with variation of x factor from 0.1 (Gd) to 0.15 (Sm and Y) have been tested under redox atmosphere at high heating temperature of 850°C. Doping pure CeO₂ with these 3+ cations (valency lower than +4) was proven to introduce oxygen vacancies in the fluorite crystal structure of the ceria. It was demonstrated that oxygen exchange either during reduction with H₂ or during partial oxidation with CH₄ is promoted if ceria is modified by presence of Gd, Sm and Y respectively. The doped oxides were found to possess large surface area, with small narrow particle size. There is no difference in the morphological properties of the doped and undoped cerium. The XRD patterns of the oxides at different stage of testing demonstrated the remarkable structure stability of the doped CeO₂ oxides to sustain its stable fluorite structure under high reacting temperatures (850°C) and redox atmospheres.

The pristine CeO₂ requires comparatively high temperatures at 850°C to produce a full H₂ peak. With addition of metal dopants, the production temperature of syngas of CPO reaction is fairly reduced. The lowest H₂ evolution temperature is achieved by Y dopant at 570°C and 850°C respectively.

The yttrium and gadolinium doped CeO₂ oxides exhibited better catalytic performance, yielding 20% CH₄ conversion and 40% H₂ selectivity. CGO show good activity stability which remained steady over the period of 110 min time range in CH₄ at 850°C.

As observed with TPR profile and the H₂/Catalyst mole ratio, it is evident that addition of dopants lowers the reduction temperature of CeO₂ while increasing hydrogen consumption. It has been found that the doping of CeO₂ with low amounts of Gd, Sm and Y modifies redox behavior, leading to an enhancement of both bulk and surface ceria reduction at low temperature. The greatest enhancement was observed for the Y doped sample where the oxygen storage capacity was increased by as much as twice.

All in all, the results obtained for the catalytic tests (TPSR and activity testing) and that of characterization tests (BET, SEM, XRD and TPR) are in good agreement with each other. The ascending order of performance of the oxides are pristine CeO₂ < 0.15Sm < 0.1Gd < 0.15Y.

CHAPTER 7:

Conclusions & Future Work

7.1. Conclusions

Catalytic partial oxidation of methane (CPOM) over three categories of Ion Transport Oxides for syngas production in a fixed-bed reactor is presented in this thesis. The results presented in this thesis are obtained from three categories of Ion Transport Oxides, which are namely the oxides with the ABO_3 perovskite-type structure, the K_2NiF_4 structure and that of fluorite-type CeO_2 structure. For the former category, the $LaCrO_3$ and $LaFeO_3$ oxides were doped with alkaline earth metals (Ba, Ca, Mg and Sr) at A-site while the dopants for latter group of La_2NiO_4 oxides at both A- and B-site were transition metals (Gd, Ce, Sr, Fe, Co and Cu). The last category is made up of oxides with CeO_2 structure that consists of commercially produced Gd, Sm and Y doped CeO_2 .

The sole oxidant for this simple CPOM reaction would be the lattice oxygen which is present in the ITOs materials instead of the gaseous oxygen. It was found that under an appropriate reaction conditions, methane can be oxidized by perovskite type oxides (as an oxygen donor material), and the consumed lattice oxygen can be recovered in a reoxidation procedure through exposure to air. It was demonstrated in this work that synthesis of syngas (H_2 and CO) by using the lattice oxygen of the catalyst is possibly applicable. For syngas production in particular useful hydrogen, this new route is superior to POM in terms of stability, safety, ease of operation, optimization, and cost efficiency.

Through our research work, it was found that the doped samples under all the three categories gave a relatively small and narrow particle size distribution of 250nm in average. In addition, the doped oxides exhibited remarkable structural stability. XRD

analysis confirmed of the formation of the ABO_3 perovskite structure after the high temperature calcinations. The perovskite-type, K_2NiF_4 structure and fluorite framework were all conserved and recovered after reoxidation in air. This proves to show that the synthesized oxides are essentially durable under the present reaction conditions.

For the Polycrystalline alkaline earth metal cation incorporated oxides performed much better than the corresponding raw lanthanum chromite and ferrite oxides, yielding high methane conversion of more than 70% to syngas at much lower H_2 evolution temperature at 850°C . Doping LaCrO_3 and LaFeO_3 with these AE metal series generates active sites, resulting in apparent improved catalytic performance. The overall performance of the series of doped LaFeO_3 is much better than that of the series of doped LaCrO_3 oxides and the order of catalytic reactivity is $\text{LaFeO}_3 > \text{LaCrO}_3$.

In the latter group of LaACrO_3 oxides, the Ca-substituted oxide outperformed the other oxides. The Ca^{2+} doped LaCrO_3 was found to possess the largest surface area among its oxide group, providing largest reaction site. It also has the ability to be highly reduced by CH_4 at an operating temperature of 838°C and possesses high oxygen species content as shown by the 3 consecutive sharp peaks under TPR graph. In the former group of doped LaFeO_3 oxides, $\text{La}_{0.75}\text{Sr}_{0.25}\text{FeO}_3$ gives the best results. It yields good performances for both the generation test under methane and TPR testing under hydrogen giving a relatively low temperature of 850°C and 403°C respectively. The results are in good agreement with the catalytic activity test. $\text{La}_{0.75}\text{Sr}_{0.25}\text{FeO}_3$ also consume 1.37 H_2 per mole of oxide with 10 % H_2 and 2.8% CO concentration concentration at 850°C with full 100% H_2 selectivity which is the best among the tested $\text{La}_x\text{A}_{1-x}\text{FeO}_3$ oxides. Thus all in all, it can be concluded that the $\text{La}_{0.7}\text{Ca}_{0.3}\text{CrO}_3$ and $\text{La}_{0.75}\text{Sr}_{0.25}\text{FeO}_3$ are promising

catalysts for syngas production via the methane and ITO reaction.

A series of La_2NiO_4 catalysts doped at both A- and B-site with transition metals were prepared by citric acid assisted sol-gel method and solid state reaction respectively. The oxide series generally consist of $\text{La}_{2-y}\text{Ln}_y\text{NiO}_4$ ($\text{Ln} = \text{Gd}, \text{Sr}, \text{Ce}, x = 0.4, 0.6, 1$) and $\text{La}_2\text{Ni}_{1-y}\text{M}_y\text{O}_4$ ($\text{M}=\text{Cu}, \text{Co}, \text{Fe}, y=0, 0.3, 0.5$) catalysts. The catalytic performance of these doped oxides for the partial oxidation of methane to synthesis gas was evaluated.

Out of the 6 doping elements tested in this study, only Sr and Ce dopants at A-site were found to lower the methane activation temperature of La_2NiO_4 . Other doping elements, i.e. Cu, Fe, Co and Gd played the reversed role. In addition, there is practically no significant improvement on the reduction peaks nor the amount of H_2 being consumed for TPR testing. However Sr doped La_2NiO_4 displayed notable performance. Subsequently, the poor performance of these dopants could be explained from the XRD patterns of freshly prepared doped samples. The doping effect on the perovskite-oxide methane activation ability is correlated to the oxygen content and mobility in their K_2NiF_4 structure. Basically the doped oxides the K_2NiF_4 structure could not be preserved and well maintained under the influence of increasing dopant content of the elements: Fe, Co, Cu, Gd and Ce. With exception to Sr dopant, of the perovskite-like K_2NiF_4 structure started to change and the intensity of the main peaks became lower with the worst scenario having the entire K_2NiF_4 structure collapsed. Correspondingly, the K_2NiF_4 crystal structure was stable under different quantity of Sr doping with a peak shift only.

Thus it is demonstrated that better catalytic performances can be achieved using the perovskite La_2NiO_4 as catalysts precursor with Sr and Ce doped at A-site. Among all

the 19 catalysts tested, a significant enhancement of catalytic performance in term of lowest H_2 evolution temperature ($550^\circ C$) and H_2 /cat consumption mole ratio (1.33), was achieved by Sr doping (La:Sr= 1.4:0.6) at A-site. The $La_{1.4}Sr_{0.6}NiO_4$ catalyst yielded the best performance.

Commercially produced Ceria-based materials, $Ce_{0.9}Gd_{0.1}O_2$, $Ce_{0.85}Sm_{0.15}O_2$ and $Ce_{0.85}Y_{0.15}O_2$ displayed high oxygen mobility under both oxidizing and reduction atmosphere at high heating temperature. Undoped CeO_2 requires comparatively high temperatures at $850^\circ C$ to reach produce H_2 peak. With the addition of the transition metal, the temperatures needed for the CPO reaction to take place are fairly reduced. The doped oxides possess large surface area, with small narrow particle size and show structure stability under high reacting temperatures. However, under CH_4 atmosphere these oxides do not show good catalytic activities with the exception for GDC which remained stable over the time range with methane conversion of 15%.

All in all, the results obtained for the catalytic tests (TPSR and activity testing) and that of characterization tests (BET, SEM, XRD and TPR) are in good agreement with each other. The best performance was demonstrated by the CeO_2 oxide with 0.1 Gd and 0.15 Yttrium doping. Unlike the results presented in previous chapters, the results for the doped CeO_2 oxides in this chapter are limited. As this is the preliminary stage in search of oxides with fluorite type structure to act as precursors, it is still early to come to a conclusion on them. Thus the results discussed are not conclusive and require more detailed work.

7.2. Future work

This project is a pioneer project to investigate the potential ion transport oxides ITOs with high content of oxygen lattice that will give high conversion of methane into syngas and at the same time reduce the operation temperature for this syngas production from methane gas. Thus a lot of trials were done to achieve the possible feasible experimental settings. The three categories of oxide series reported in this work exhibited a variety of interesting properties, and the ITOs presented in this thesis are far from fully characterized, thus offering many possibilities for continuing studies. Further investigations of the other oxide series under these three categories with respect to the oxygen content and morphology are just one of the possible routes for future works. Also, the oxide materials were tested in small quantity of a few milligrams due to constraints in the laboratory equipments. Therefore, catalytic testing with the use of large quantity of sample could be carried out.

In addition, not only the perovskite products, but also the precursors and the synthesis methods hold challenges for the future work. To our knowledge, apart from the three categories of oxide series prepared, it would be interesting to prepare single crystal for structure determination of the other precursors. Moreover, there is a wide range of interesting ITOs, not only as precursor in materials synthesis, and the preparation and characterization of new related perovskite-type oxides would be worthwhile. Subsequently, a few of the synthesis routes that are being considered are micro-wave preparation and spray pyrolysis technique. Also, one simple way to enhance better application of powder for reaction is to coat them onto monolith or other support to

provide better adhesive and prevent any contamination, and pressure during reaction. An additional way to optimize the catalysts is through combining both the A- and B- site doping. The reaction pathway can be studied by identifying the active center and correlating both the bulk transfer and surface exchange of oxygen to the activation of CH_4 . And in the future work, surface analysis should be considered to be of more importance than the bulk analysis. Optimize the reaction condition by providing a shorter enthalpy path and lowering the activation energy.

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