# Synthesis Gas Production in Oxy-Carbondioxide Reforming of Methane Over Perovskite Catalysts

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Abstract-- Consuming two major greenhouse gases, carbon dioxide  $(CO_2)$  and methane  $(CH_4)$ , to produce synthesis gas, which is a mixture of carbon monoxide (CO) and hydrogen  $(H_2)$ , carbondioxide reforming of methane shows significant environmental and economic benefits.

Recently the development of Oxy-CO<sub>2</sub> reforming of methane (OCM) has been investigated to produce syngas. OCM consists of both exothermic partial oxidation of methane and endothermic CO<sub>2</sub> reforming of methane , which is expected to increase the energy efficiency of the process and also to adjust the  $H_2$ /CO ratio of syngas for particular applications. However,

the process has not found wide industrial application due to severe catalyst deactivation, basically caused by carbon formation. Therefore, it is of great interest to develop stable catalysts without severe deactivation.

This review paper is mainly focused on the development of perovskites to achieve stable operation for  $oxy-CO_2$  reforming of CH<sub>4</sub>. The use of precursors such as perovskite like oxides ABO<sub>3</sub>, in which A-site cation is a rare earth and/or alkaline earth and B-site cation is a transition metal has increased recently for methane reforming. Perovskites not only fulfill the stability requirements for these reactions, but also by further reduction of B-site cations which remain distributed in the structure, they form well dispersed and stable metal particle catalysts.

Keywords-- Oxy-CO<sub>2</sub> reforming, perovskites, syngas.

## I. INTRODUCTION

The demand of syngas in both academic and industrial fields has increased due to its potential in many

applications such as Fischer-Tropsch process, in which syngas is converted into a series of liquid hydrocarbon fuels, or its direct conversion as a reactant to dimethyl ether or methanol for petrochemical industries.

Syngas can be produced in many ways, such as through steam reforming (SR), autothermal reforming of methane (ARM), dry CO<sub>2</sub> reforming of methane (DRM) and partial oxidation of methane (POM) . Each of the process described above shows different advantages and limitations, such as  $H_2$ /CO ratio, energy efficiency, catalytic activity and stability. Recently the development of CO<sub>2</sub> reforming of methane has been investigated to produce syngas. [1]

Moreover, the rapid catalyst deactivation due to coke formation is a serious concern especially for nickel metal catalyst. The use of perovskite material as the catalyst could potentially overcome this problem due to its well-defined structures, which produces highly-dispersed metallic particles to promote high activity which suppresses coke formation and enhances catalytic stability[2].

# **II. SYNTHESIS GAS PRODUCTION**

Two major processes for syngas production are steam reforming and Partial oxidation of methane (POX).  $CO_2$ reforming of methane is an environmentally beneficial production route. The source of syngas and their applications are shown in Table 1. In addition, syngas can be converted to ethylene, acetic acid, phosgene and acetone by exothermic reactions. Pure carbon monoxide is mainly used for the production of acetic acid, formic acid, polyurethane, polycarbonates and methylacrylates. Steam reforming, partial oxidation and  $CO_2$  reforming can be combined to adjust H<sub>2</sub> to CO ratio[3].

#### TABLE I

#### SOURCES OF SYNGAS AND APPLICATIONS [3].

H <sub>2</sub> /CO Ratio	Reaction	Applications
1	CO <sub>2</sub> Reforming of	Oxoalcohol,
	methane	polycarbonates,
		formaldehyde
		production,
		iron ore reduction
2	Partial oxidation of	Methanol synthesis,
	methane	Fischer-Tropsch
		synthesis
3	Steam reforming of	H <sub>2</sub> production
	methane	e.g. for ammonia
	and the WGS	synthesis
	reaction	

A) Steam Reforming

Steam reforming shown in Equation 1 is the most widely used reaction to produce syngas. The process conditions are usually 15-30 bar and 850-950 °C. All group VIII metals have good activity in steam reforming. Rhodium and ruthenium are the best but poorly available and expensive, thus nickel is the most common catalyst metal. Supports for the catalyst metal are oxide materials with low surface area such as MgO and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, which are stable under high temperatures and with steam. Due to the high temperatures involved and the presence of steam, sinterization of the active metal species and coke formation lead to catalysts deactivation and in some cases to plugging of the reactor. Methane conversion to syngas and  $H_2$  based in steam reforming occurs by the two following reactions[12].

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 (H^2_{298K} = 206 \text{ kJ/mol}) - (1)$$

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$$CO + H_2O \leftrightarrow CO_2 + H_2 (H^{\circ}_{298K} = -41 \text{ kJ/mol}) - (2)$$

These reactions produce syngas with a  $H_2/CO \ge 3$  ratio.

### B) Partial Oxidation

Syngas can be produced by partially oxidating methane (Equation 2). Non-catalytic process is performed at 1077-1527 °C and 1-140 bar. Catalytic reaction is carried out at lower temperatures between 727-927 °C. There are two possible reaction pathways for catalytic partial oxidation. In the indirect pathway methane is first combusted to carbon dioxide and water ( $\Delta H^{0}_{298K}$  = -802 kJ/mol) and then the remaining methane is reformed to syngas. Another way is the direct conversion to carbon monoxide and hydrogen. The major operation problem in partial oxidation is the hot spot formation due to the exothermal nature of the reaction. Thus, the coupling of partial oxidation with endothermic reforming reactions is attractive[6].

$$CH_4 + 0.5 O_2 \rightleftharpoons 2H_2 + CO; \Delta H^0_{298K} = -36 \text{ kJ/mol} - (2)$$

## C) Carbondioxide Reforming

 $CO_2$  reforming can be economically advantageous over the other syngas production ways depending on the required H<sub>2</sub> to CO ratio. For example, if ratio of 0-0.5 is needed, CO<sub>2</sub> reforming is preferred. For a ratio of 0.5-0.9, CO<sub>2</sub> reforming competes with the partial oxidation of bitumen. The major problem in CO<sub>2</sub> reforming is the carbon deposition on the surface of the catalyst. Advantage over steam reforming is lower remaining of methane, which is up to 2% unreacted methane with steam reforming.

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 (H^0_{298K} = 247 \text{ kJ/mol}) \quad - \quad (3)$$

#### D) Combined CO<sub>2</sub> Reforming And Partial Oxidation

One of the most serious problems in CO<sub>2</sub> methane reforming is catalysts deactivation by coke. Since the reaction is endothermic. proceeds high temperature. it at thermodynamically analysed coke formation. Recently, CO<sub>2</sub> reforming of methane combined with partial oxidation has been studied. Oxygen addition to these reactions reduces carbon deposition on the catalyst surface and increases methane conversion. Simultaneously, economical advantages are obtained by the appropriate combination of highly endothermic processes with the exothermic partial oxidation of methane by decreasing the energetic requirements of the reaction. The combine reaction then emerges as an interesting alternative since it improves the temperature control of the reactor and reduces formation of cold points. Besides, it allows the production of syngas with a broad range of H<sub>2</sub>/CO ratios by manipulating the relative concentrations of O<sub>2</sub> and  $CO_2$  in the feed[10].

The simultaneous oxidative and  $CO_2$  reforming reaction of methane notably diminished coke formation, increasing the

syngas production. The addition of oxygen to the  $CH_4 + CO_2$  system decreases the reaction temperature and energy consumption, indicating that the partial oxidation (exothermic) reaction promotes the dry (endothermic) reaction In addition, the  $H_2$  to CO ratio can be controlled between 1.0 and 2.0 by changing the ratio of oxygen and carbon dioxide.

# III. PEROVSKITE

A perovskite is any material with the same type of crystal structure as calcium titanium oxide (CaTiO3 Chemical compound and Mineral species), known as the perovskite structure . The perovskite structure is a highly versatile and widespread mineral form, of great importance in nature and technology. Perovskites take their name from this compound, which was first discovered in the Ural Mountains of Russia by Gustav Rose in 1839 and is named after Russian mineralogist, Count Lev Aleksevich von Perovski, who discovered the naturally occurring mineral calcium titanate (CaTiO3) (1792-1856)[15].

# A) Crystallography

The general chemical formula for perovskite compounds is ABX3 or ABO<sub>3</sub>, where 'A' and 'B' are two cations of very different sizes, and X or O is an anion that bonds to both. The 'A' atoms are larger than the 'B' atoms. The ideal cubic-symmetry structure has the B cation in 6-fold coordination surrounded by an octahedron of anions (B surrounded by six oxygens in octahedral coordination) and the A cation in 12-fold cuboctahedral coordination (A coordinated by 12 oxygen). The relative ion size requirements for stability of the cubic structure are quite stringent so slight buckling and distortion can produce several lower-symmetry distorted versions in which the coordination numbers of A cations, B cations or both are reduced[15].



Figure 1. Perovskite structure  $ABO_3$ . The red spheres are oxygen atoms, the deep blue are smaller (Ti+4) metal cations (B-site) and the green(blue) are the larger (Ca+2) metal cations (A-site)[15].

A ion can be rare earth, alkaline earth, alkali and other large ions such as Pb+2, Bi+3 that fits in to the dodecahedral site of the framework. The B ion can be 3d, 4d and 5d transition metal ions, which occupy the octahedral sites (surrounded by six oxygen atoms in octahedral coordination). Large classes of perovskite-like materials are comprised of layers such as alkaline earth oxides. Perovskite compounds can also tolerate significant partial substitution (A and/or B with metals (A', B' correspondingly) of different oxidation states) and nonstoichiometry while still maintaining the perovskite structure. Metal ions having different valence can replace both A and B ions. This may generate a non-integral number of oxygen atoms. Because of their varied structure and composition, perovskites have been considered as prototype material for fundamental areas of solid state chemistry (redox reactions), physics, catalysis, solid oxide fuel cells, oxygen separation membranes, chemical sensors for the detection of humidity alcohol and gases such as oxygen, hydrocarbon and nitric oxide[15].

#### **IV. PREPARATION OF CATALYSTS**

#### A) Preparation of Catalyst by the Sol Gel Method

All the La-Co oxide catalysts were prepared by sol-gel method as follows.

The solutions of  $La(NO_3)_3.6H_2O$  and  $Co(NO_3)_2.6H_2O$  were prepared separately and then mixed in a volume proportion corresponding to the final composition of the catalysts to be o<u>bt</u>ained.

The required amounts of the precursor salts  $[La(NO_3).6H_2O]$  and  $Co(NO_3)_2.6H_2O]$  along with citric acid were dissolved in water at an equivalent ratio of 1:1 (metal cations:citric acid). The Ethylene Glycol solution was added drop-wise to the nitrate solution and they were agitated for 15 min and color of the mixture is dark red. The resulting solutions were heated to 80 °C to form a viscous gel which finally yield a solid precursor upon slow solvent evaporation at that temperature for several hours. This gel was dried in an oven, with the temperature increased slowly up to 100 °C and maintained there overnight, to produce a solid amorphous citrate precursor which color is pink. The resulting precursor was milled and then calcined in air at 700 °C to 750 °C for 5 h in order to achieve the corresponding perovskite structure in the samples[3].

#### B). Preparation Of Catalyst By The Co-Precipitation Method

All the La-Co oxide catalysts were prepared by Coprecipitation method as follows.

The solutions of La(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O and Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O were prepared separately and then mixed in a volume proportion corresponding to the final composition of the catalysts to be obtained. The resulting solution was stirred and heated in a beaker. The aqueous 1 M Na<sub>2</sub>Co<sub>3</sub> solution was added dropwise to the nitrate solution under vigorous stirring until pH 1 was attained at room temperature. The precipitate was allowed to age for 1-hr at room temperature with stirring. The excess solution was removed by filtration. The precipitate was washed by double distilled water at a room temperature followed by several times by double distilled water at room temperature in order to remove the sodium salts. The drying was carried out at 100  $^{\circ}$ C for overnight. This material was the catalyst precursor, which was crushed to a fine powder and subsequently the catalyst was produces by calcinations in the presence of air at 700  $^{\circ}$ C for 5-hr[5].

# V. CATALYST CHARACTERIZATION

The optimum catalyst is the one that provides the necessary combination of properties (activity, selectivity, lifetime, ease of regeneration and toxicity) at an acceptable cost. Suitable promoters are frequently added to obtain adequate performance. They may either modify the catalyst structure, so improving stability, or enhance the catalytic reactions to give better activity or selectivity. However, the nature of the active species is always the most important factor. .A heterogeneous catalyst is a composite material, characterized by:

1. The relative amounts of different components (active species, physical and/or chemical promoters, and supports);

- 2. Shape
- 3. Size
- 4. Pore volume and distribution;
- 5. Surface area.

Following methods for catalyst characterization are discussed as below[3].

# A). Atomic Absorption Spectroscopy

Atomic spectroscopy is the determination of elemental composition by its electromagnetic or mass spectrum. The study of the electromagnetic spectrum of elements is called Optical Atomic Spectroscopy. Electrons exist in energy levels within an atom. These levels have well defined energies and electrons moving between them must absorb or emit energy equal to the difference between them. In optical spectroscopy, the energy absorbed to move an electron to a more energetic level and/or the energy emitted as the electron moves to a less energetic energy level is in the form of a photon[3].

# B) Scanning Electron Microscopy

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity[4].

#### 1) Physisorption Analysis

Measurements of gas adsorption isotherms are widely used for determining the surface area and pore size distribution of solids. The use of nitrogen as the adsorptive gas is recommended if the surface areas are higher than  $5m^2/g$ . The first step in the interpretation of a physisorption isotherm is to identify the isotherm type. This in turn allows for the possibility to choose an appropriate procedure for evaluation of the textural properties. Non-specific Brunauer-Emmett-Teller (BET) method is the most commonly used standard procedure to measure surface areas, inspite of the oversimplification of the model on which the theory is based. 4

The BET equation is applicable at low p/po range and it is written in the linear form

$$p/{n^{a}(po-p)} = {1/(n^{a}_{m}C)} + {(C-1)/n^{a}_{m}C}$$

Where p is the sample pressure,

po is the saturation vapour pressure,

na is the amount of gas adsorbed at the relative pressure p/po,

nam is the monolayer capacity

C is the so- called BET constant

Equation can be applied for determining the surface areas and pore volumes from adsorption isotherms. The pores are usually classified according to their widths as micropores (diameter less than 2 nm), mesopores (diameter between 2 and 5)

Several approaches have been developed to assess the microand mesoporosity, and to compute pore size distribution from the adsorption-desorption data. All of these involve a number of assumptions, e.g. relating to pore shape and mechanism of pore filling[4].

# 2) Chemisorptions Analysis

Chemisorption measurements were carried out in order to determine the dispersions metal particles, monolayer capacities and the amount of active metal in the catalysts[4].

# C) X-Ray Diffraction

X-ray scattering techniques are a family of non-destructive analytical techniques which reveal information about the crystallographic structure, chemical composition, and physical properties of materials and thin films. These techniques are based on observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy. Xray crystallography is a method of determining the arrangement of atoms within a crystal, in which a beam of Xrays strikes a crystal and diffracts into many specific directions. From the angles and intensities of these diffracted beams, a crystallographer can produce a three-dimensional picture of the density of electrons within the crystal. From this electron density, the mean positions of the atoms in the crystal can be determined, as well as their chemical bonds, their disorder and various other information. This technique used to estimate the total coke content after the catalytic reaction[5].

# D) Temperature Programmed Reduction (Tpr/Tpo)

Temperature-programmed reduction (TPR) is a technique for the characterization of solid materials and is often used in the field of heterogeneous catalysis to find the most efficient reduction conditions, an oxidized catalyst precursor is submitted to a programmed temperature rise while a reducing gas mixture is flowed over it. A simple container (U-tube) is filled with a solid or catalyst. This sample vessel is positioned in a furnace with temperature control equipment. A thermocouple is placed in the solid for temperature measurement. To remove the present air the container is filled with an inert gas (nitrogen, argon). Flow controllers are used to add hydrogen (for example, 10 Vol -% hydrogen in nitrogen). The composition of the gaseous mixture is measured at the exit of the sample container with appropriate detectors (thermal conductivity detector, mass spectrometer). Now, the sample in the oven is heated up on predefined values. Heating values are usually between 1 K/min and 20K/min. If a reduction takes place at a certain temperature, hydrogen is consumed which is recorded by the detector. In practice the production of water is a more accurate way of measuring the reduction. This is due to the potential for varying hydrogen concentrations at the inlet, so the decrease in this number may not be precise, however as the starting concentration of water will be zero, any increase can be measured more accurately. The amount of metal (Ni) in the solids was determined by atomic absorption spectrometry, using SHIMADZU equipment. All promoted and unpromoted catalysts were characterized for their structures before the dry reforming reaction using an X-Ray diffractrometer (XRD, Philips PW 1830) equipped with a CuKa source having a scanning range 20-100 Bragg's angle. The surface of the calcined catalyst was 4nalysed by Scanning electron microscope (SEM)[8].

# VI. SUMMARY

The simultaneous  $CO_2$  reforming and partial oxidation of methane, commonly called oxy-CO<sub>2</sub> reforming of methane is carried out by passing a mixture of CO<sub>2</sub>, CH<sub>4</sub> andO<sub>2</sub>. There is influence of temperature, space velocity and O<sub>2</sub>/CH<sub>4</sub> ratio in the feed on the conversion, H<sub>2</sub> selectivity, H<sub>2</sub>/CO ratio and net heat of reaction ( $\Delta$ Hr). There is no carbon deposition on the catalyst in Oxy-CO<sub>2</sub> reforming.

Effect of temperature: There is influence of temperature on the catalyst performance in the  $Oxy-CO_2$  reforming of methane. The  $O_2$  conversion is not influenced by the reaction temperature but the conversion of CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub> selectivity and H<sub>2</sub>/CO ratio at the high space velocity and the net heat of reaction are strongly influenced by the temperature.

With the increasing temperature:-

- [1] The conversion of  $CH_4$  or  $CO_2$  is increases.
- [2] The H<sub>2</sub> selectivity increases significantly.
- [3] The H<sub>2</sub>/CO ratio for the high space-velocity decreases, but that for the low space-velocity does not have any effect.
- [4] The net heat of reaction ( $\Delta$ Hr) is increased or the process exothermicity is decreased appreciably.

In general, the  $Oxy-CO_2$  process is less exothermic or more endothermic at the higher temperatures, at the lower space velocity and/or for the lower concentration of  $O_2$  in the feed. The process can therefore be made mildly exothermic, mildly endothermic or thermo-neutral by controlling the process parameters, particularly the reaction temperature and/or are the concentration of  $O_2$  in the feed.

In the simultaneous  $CO_2$  reforming and partial oxidation of methane, both the H<sub>2</sub>/CO product ratio and the process exothermicity or endothermicity can be controlled by manipulating the process condition, particularly the reaction temperature and/or the relative concentration of  $O_2$  in the feed. The simultaneous oxidative and  $CO_2$  reforming reaction of methane notably diminish coke formation, increasing syngas production. The addition of oxygen to the  $CH_4 + CO_2$  system decreases the reaction temperature and the energy consumption, indicating that the partial oxidation (exothermic) reaction promotes the dry (endothermic) reaction.

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