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# Syngas production from methane dry reforming over SmCoO<sub>3</sub> perovskite catalyst: Kinetics and mechanistic studies

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## ABSTRACT

The kinetics of the methane dry (CO<sub>2</sub>) reforming over the SmCoO<sub>3</sub> was investigated in the temperature ranged 973–1073 K by varying the CH<sub>4</sub> and CO<sub>2</sub> partial pressures. Based on detailed study of the reaction mechanism, a mechanistic model is proposed from which a kinetic model is derived. The mechanistic pattern assumes adsorption of CH<sub>4</sub> on reduced Co, followed by methane cracking and carbon deposition. CO<sub>2</sub> reacts with Sm<sub>2</sub>O<sub>3</sub> to form Sm<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> and the oxycarbonates react with carbon to produce CO. The power law and Langmuir–Hinshelwood kinetic model which is established on this mechanism were able to forecast the kinetic results.

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## Introduction

Methane (CH<sub>4</sub>) reforming with carbon dioxide (CO<sub>2</sub>) is gaining popularity because; it produces synthesis gas (mixture of H<sub>2</sub> and CO) with a theoretical ratio of unity. This ratio is ideal for methanol and Fisher Tropsch synthesis [1]. Synthesis gas is also considered as a possible substitute to conventional fuels and as a source of hydrogen for fuel cells once it undergoes

purification process [2,3]. Significantly, the reaction consumes two carbon containing gases that are naturally available and relatively inexpensive. These carbon compound; CO<sub>2</sub> and CH<sub>4</sub> are the main components of the greenhouse gases.

The reaction equilibrium of methane reforming with carbon dioxide can be written as:



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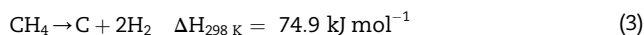
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which is dependent on the concurrent occurrence of the reverse water–gas shift reaction.



Due to its endothermic nature, methane dry reforming is favoured at high temperatures. However, high temperature promotes carbon formation from methane cracking, which leads to catalyst deactivation represented as:



Attempts have been made in previous works on methane dry reforming to develop catalyst with high activity and minimal carbon affinity. Supported noble metal catalysts have shown good activity and resistance to carbon, however these catalyst are not economically-viable because of their scarcity and high cost [4,5]. Supported nickel catalysts have also been widely employed due to their high activity in the methane reforming reaction at elevated temperature, but its major disadvantage remains its high affinity towards carbon [6,7].

Bradford [8] established a kinetic model for the  $\text{CH}_4$ – $\text{CO}_2$  reforming reaction that successfully describes the reaction kinetics over Ni/MgO and Ni/TiO<sub>2</sub> catalysts. The main assumptions of this model are that;  $\text{CH}_4$  and  $\text{CH}_x\text{O}$  decomposition's were the slowest kinetic steps,  $\text{CO}_2$  took part in the reaction mechanism through the reverse water–gas shift to produce surface OH groups, and subsequently the surface OH groups reacted with adsorbed  $\text{CH}_x$  intermediates to yield a formate-type intermediate,  $\text{CH}_x\text{O}$ , which eventually decomposed into  $\text{H}_2$  and  $\text{CO}$ .

Topalidis et al. [9] investigated the kinetics of interconversion of  $\text{CH}_4$  with  $\text{CO}_2$  over a 0.5%Pt/SrTiO<sub>3</sub> solid catalyst. Using the Langmuir–Hinshelwood kinetics, they arrived at the conclusion that the reactants adsorbed on distinct and discreet active sites of the catalyst. The study reiterated that the  $\text{CH}_4$  was weakly bound on the metallic phase while the  $\text{CO}_2$  was strongly bound on the oxidic phase of the catalyst [10]. Verykios [11] studied the kinetics of the reaction of  $\text{CO}_2$  reforming of methane over Ni/La<sub>2</sub>O<sub>3</sub> catalyst. A mechanistic model was proposed which assumed adsorption of  $\text{CH}_4$  on the metal, followed by decomposition and carbon deposition as the slowest step. Furthermore,  $\text{CO}_2$  reacted with La<sub>2</sub>O<sub>3</sub> to form La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> which was adjudged to be a fast step and the oxy-carbonates reacted with carbon at the Ni–La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> catalyst interface (slow step) to produce  $\text{CO}$ . Moradi et al. [12] carried out the kinetic investigation of  $\text{CO}_2$  reforming of  $\text{CH}_4$  over La–Ni based perovskite (LaNiO<sub>3</sub>). A mechanism was proposed which showed that  $\text{CH}_4$  reversibly adsorbs on the metallic site, leading to cracking of the adsorbed species. Also,  $\text{CO}_2$  was rapidly adsorbed on the La<sub>2</sub>O<sub>3</sub> site thereby generating oxy-carbonate, which in turn reacts slowly with carbon deposits on the Ni at the catalyst interface to form  $\text{CO}$ . Foo et al. [13] studied the performance of both Ce-promoted and unpromoted bimetallic Co–Ni catalyst supported on alumina. A dual site Langmuir–Hinshelwood mechanism was proposed with oxidation of carbon being the rate determining step. In a recent work [14] by our group, the mechanism of syngas production from  $\text{CO}_2$  reforming of methane over neodymium sesquioxide supported cobalt was investigated. The mechanism step involved reversible adsorption and activation of  $\text{CH}_4$

on the surface of the Co forming  $\text{H}_2$  and C, adsorption of  $\text{CO}_2$  on the Nd<sub>2</sub>O<sub>3</sub> basic site and gasification of the C deposited on the Co surface by the lattice oxygen from the adsorbed  $\text{CO}_2$ .

In this study, SmCoO<sub>3</sub> perovskite was synthesized by a sol-gel method and was used in the methane dry reforming reaction. The dependency of conversion of reactants, reactant consumption rate and product formation rate on temperature (973–1073 K) and reactants partial pressure (6.8–60.8 kPa) was investigated. Data obtained from this study were used to analyse and predict a reaction mechanism. The rate equation parameters were calculated using the Langmuir–Hinshelwood kinetics model. In addition, the activation energy and reaction order were obtained using the power law model and Arrhenius plot.

## Experimental

### Synthesis of SmCoO<sub>3</sub> perovskite catalyst

The citrate sol-gel method was employed in the preparation of SmCoO<sub>3</sub> perovskite catalyst following the previous procedures [7,15,16]. 2 M solution of citric acid (99.5% purity, anhydrous, Sigma Aldrich) was mixed with the Co metal nitrates (99.99% purity, Sigma Aldrich) in the ratio of 2:1. The Sm metal nitrates (99.99% purity, Acros Organics) was then added to the mixture and stirred at ambient condition until a clear solution was obtained. The solution was then stirred for 4 h at 353 K resulting in a gel form which was subsequently dried at 383 K to obtain xerogel powder. Subsequently, the powder catalyst was calcined at 1123 K, before being crushed and sieved to 140–250 μm for characterization and reaction studies.

### Characterization of catalyst

A Thermo Scientific acquisition analyser, equipped with a degasser station and surfer acquisition software (version 1.2.1), was employed to determine the textural properties of the catalyst. Brunauer–Emmett–Teller (BET) method using the N<sub>2</sub> multi-layer adsorption–desorption isotherm data for the determination of specific surface area, while the Barret–Joyner–Halenda (BJH) method was employed to determine the pore size distribution of the catalyst based on desorption data.

A TPDRO 110 apparatus furnished with thermal conductivity detector (TCD) was used to obtain the temperature programmed reduction profile (TPR). Pre-treatment was carried out under N<sub>2</sub> flow at a rate of 5 K min<sup>−1</sup> by flushing 50 mg of sample for 2 h at 393 K. Sample was then cooled to ambient temperature before being blanketed for duration of 1 h with 5% H<sub>2</sub> in N<sub>2</sub> flow (20 K min<sup>−1</sup>) up to the temperature of 1173 K.

$\text{CO}_2$ -temperature programmed desorption (TPD) and  $\text{NH}_3$ -TPD were also performed using the same equipment. Approximately 50 mg of fresh catalyst was charged into a quartz reactor tube, pre-treated in 20 ml min<sup>−1</sup> of N<sub>2</sub> flow at 313 K for 30 min and then cooled to ambient temperature. After pre-treatment, the test gases were adsorbed for 1 h at 393 K before being flushed with He for 30 min. Desorption was then performed by increasing the temperature from ambient

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