

## INSIGHT MECHANISTIC STUDY OF SAMARIUM OXIDE BASED CATALYST IN METHANATION REACTION

(Kajian Mendalam Mekanistik Pemangkin Berasaskan Samarium Oksida dalam Tindak Balas Metanasi)

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### Abstract

An understanding of the mechanism of chemical reactions is needed to optimize the reaction process and improve performance. The adsorption of reactant molecules, formation of reaction intermediates, and finally the distribution of products depend on the composition and surface structure of the catalyst. This research work deployed Fourier transform infrared (FTIR), high performance liquid chromatography (HPLC), and gas chromatography (GC) to identify the mechanism of Sm/Mn/Ru (60:35:5)/Al<sub>2</sub>O<sub>3</sub> catalyst. The envisioned methanation reaction initially follows the Langmuir Hinselwood mechanism with the adsorption of CO<sub>2</sub> and H<sub>2</sub> gases on the catalyst surface. From the gaseous product, only methane peak was observed. Meanwhile, from the liquid product, methanol peak is observed at retention time 20 mins which accordance with standard methanol. Therefore, the final products acquired from the methanation reaction of Sm/Mn/Ru (60:35:5)/Al<sub>2</sub>O<sub>3</sub> catalyst are CH<sub>4</sub>, CH<sub>3</sub>OH and H<sub>2</sub>O.

**Keywords:** methanation, hydrogenation, samarium oxide, catalyst, mechanism

### Abstrak

Pemahaman kepada mekanisme tindak balas kimia adalah perlu untuk mengoptimumkan proses tindak balas dan meningkatkan prestasi. Penjerapan molekul reaktan, pembentukan perantaraan tindak balas, dan taburan produk pada asasnya bergantung kepada komposisi dan struktur permukaan pemangkin. Kerja penyelidikan ini menggunakan inframerah transformasi Fourier (FTIR), kromatografi cecair prestasi tinggi (HPLC), dan kromatografi gas (GC) untuk mengenal pasti mekanisma mangkin Sm/Mn/Ru (60:35:5)/Al<sub>2</sub>O<sub>3</sub>. Tindak balas metana yang dipostulatkan adalah mengikut mekanisma Langmuir Hinselwood yang pada mulanya melibatkan penjerapan gas CO<sub>2</sub> dan H<sub>2</sub> pada permukaan mangkin. Daripada produk gas, hanya puncak metana

diperhatikan. Manakala, daripada produk cecair, puncak metanol diperhatikan pada minit ke 20 masa tahanan mengikut larutan piawai metanol. Oleh itu, produk akhir yang diperoleh daripada tindak balas metana mangkin Sm/Mn/Ru (60:35:5)/Al<sub>2</sub>O<sub>3</sub> ialah CH<sub>4</sub>, CH<sub>3</sub>OH dan H<sub>2</sub>O.

**Kata kunci:** metanasi, penghidrogenan, samarium oksida, pemangkin, mekanisma

### Introduction

Nowadays, catalytic methanation reaction has been widely explored in order to convert CO<sub>2</sub> gas to CH<sub>4</sub> gas by reducing emission of greenhouse gases using metal oxide. The most conventional metal oxide catalyst used are nickel, cobalt, manganese, copper, iron and lanthanide element. The catalytic ability of metal oxide catalyst deteriorates after several hours of reaction time due to the carbon forming process. The formation of carbon can be avoided by adding a dopant to the metal oxide catalyst [1]. Rosid et al. revealed that dopants and metal-based oxides have varying functions in hydrogenation reactions [2]. The metal-based oxide incites the reaction via combining with CO<sub>2</sub> molecules to form carbonate species on the surface, while the dopant split the H<sub>2</sub> molecules and provides the H atoms required for further hydrogenation of the carbonate to form methane [3].

Carbon dioxide (CO<sub>2</sub>) adsorption happens during carbonate species and carrier-related formate formation in H<sub>2</sub> presence [4, 5]. Many studies have proposed varying CO<sub>2</sub> methanation mechanisms. The first proposed mechanism refers to CO<sub>2</sub> reaction in a carrier, while H (ads) species generated in metals yield formate intermediate (COOH) at the interface of metal support. The CO (ads) species generated by formate are hydrogenated to methane [6]. Meanwhile, on second proposed mechanism, CO<sub>2</sub> (ads) and O (ads) dissociated directly on the metal surface. Subsequently, CO (ads) become hydrogenated to CH<sub>4</sub>. The dissociation of CO (ads) denotes the rate determining step of the reaction [7].

Other than that, Marc. et al. also pointed out that the methanation process consists of three steps, of which the first step is to adsorb CO<sub>2</sub> on the catalyst chemically [8]. The second step is to separate CO<sub>2</sub> into surface-absorbed CO and O, and the final step is species reaction to separate it from H<sub>2</sub>. The particular

reaction process is known as Langmuir-Hinselwood mechanism [9]. However, most of the proposed mechanism involved alkaline earth metal and transition metal which showed the formation of carbonate and formate species during reaction. Therefore, in this study the mechanistic study has been conducted over lanthanide element, which is samarium oxide catalyst in order to identify the mechanism pathway and product formed during the reaction occur. This study was conducted using FTIR, GC and HPLC for identification of product and by-product formed in methanation reaction.

### Materials and Methods

#### Catalyst preparation

The catalyst was prepared by aqueous incipient wetness impregnation method. 5 g of samarium(III) nitrate was firstly weighed in a beaker and dissolved in a small amount of distilled water, then mixed together with a solution of RuCl<sub>3</sub>.xH<sub>2</sub>O and Mn(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O salts according to the desired ratio. The catalyst solutions were stirred continuously for 30 minutes before 7 g of alumina was added to it. After that, the coated alumina was aging at 80 – 90 °C for 24 hours followed by calcination at 1000 °C for 5 hours using a ramp rate of 10 °C/min to remove all the metal counter ions and water present in the catalyst. Lastly, the sample was labelled as Sm/Mn/Ru (60:35:5)/Al<sub>2</sub>O<sub>3</sub>. All chemicals used in this study were purchased from Sigma Aldrich.

#### Catalytic screening

A gas mixture consisting of CO<sub>2</sub> and H<sub>2</sub> with a molar ratio of 1: 4 was continuously passed through the catalyst at a flow rate of 50.00 cm<sup>3</sup>/min. Prior to starting the catalyst test, the reaction gas was introduced into the microreactor system without passing through the catalyst as a calibration. Then, the reaction gas was passed through a catalyst and the temperature is raised from room temperature (RT) to

400°C using FTIR Nicolet Avatar 370 DTGS spectrophotometer. The percentage of CO<sub>2</sub> conversion

calculation is shown in Equation 1.

$$\% \text{ of CO}_2 \text{ conversion} = \frac{\text{Peak Area of CO}_2 \text{ calibration} - \text{Peak Area of CO}_2 \text{ conversion}}{\text{Peak area of CO}_2 \text{ calibration}} \times 100 \quad (1)$$

### Mechanistic study

First, the catalyst was ground and placed in a glass tube, while air pre-treatment was executed for 30 minutes at 100 °C for catalyst sample activation. When the sample cooled to ambient temperature, H<sub>2</sub>/CO<sub>2</sub> gas was installed into the microreactor system with the temperature increased to 400 °C. The product stream was gathered in a sample cell equipped with a KBr window and scanned through an in-situ Nicolet Avatar FTIR 370 DTGS spectrophotometer. Then, FTIR was used to analyze the catalyst powder to identify adsorbed materials on the catalyst surface. The liquid product of the reaction and methanol standard were analyzed by HPLC (Rezex ROA-Organic Acid), and methanol was detected using a 300 mm × 7.8 mm ID column with a refractive index (RI) detector. Meanwhile, gas products were analyzed by Hewlett Packard 6890 series gas chromatograph with Flame Ionization Detector (FID) and methane production was determined using an Equation 2.

$$\% \text{ Yield of CH}_4 = \frac{[\text{CH}_4] \text{ from GC}}{\% \text{ Conversion of CO}_2} \times 100\% \quad (2)$$

### Results and Discussion

Marwood et al. and Sharma et al. confirmed the direct decomposition of CO<sub>2</sub> into CO and O [10, 11]. In this study, it seems that the direct decomposition of CO<sub>2</sub> is demonstrated. This proposal is very consistent with the fact that, as described by Solymosi et al. formate was not detected in excessive supports containing low concentrations of OH groups [12]. This was ascribed to hydrogen present in the reaction that hindered CO intermediates formation, thus yielding formate species.

### Products analysis

Potential Sm/Mn/Ru (60:35:5)/Al<sub>2</sub>O<sub>3</sub> catalyst reveal catalytic routes for methane as main product, methanol and water as a by-product. In this study, it seems that the direct decomposition of CO<sub>2</sub> is demonstrated. The FTIR spectrum of the gaseous product is presented in Figure 1. The spectrum shows that the peak is close to 2351 cm<sup>-1</sup> due to the CO<sub>2</sub> stretching mode. At the same time, the stretching mode of CH<sub>4</sub> band at the wavenumber of 3014 cm<sup>-1</sup> and C-H deformation mode at 1310 cm<sup>-1</sup> [13] can be clearly detected starting at 250 °C reaction temperature. From the figure, it can be observed that no methane peak was appeared at room temperature (RT) and 100 °C indicating the absence of methane gas produced during the reaction. When the reaction temperature was raised to 400 °C, the highest CH<sub>4</sub> gas was formed with around 69% detected by GC-FID. This show that methane formation is advantageous at high reaction temperature [14]. No band of 3300-3600 cm<sup>-1</sup> of water was observed in the FTIR spectrum because the silica trap system used in the reactor functions as adsorbed water. Interestingly, no CO intermediate was formed as there is no CO peak around 2080 cm<sup>-1</sup> was detected. This shows that CO<sub>2</sub> gas is directly converted into CH<sub>4</sub> gas without producing CO gas as an intermediate.

As can be observed in Table 1, no methane gas was formed at room temperature (RT) and 100 °C of reaction temperature which agreed with the absence of methane peak (~3000 cm<sup>-1</sup>) in FTIR spectra in Figure 1. However, when increasing reaction temperature to 200 °C, about 6% of CH<sub>4</sub> gas was formed from 65.52% of CO<sub>2</sub> conversion. This means that 59.09% of the reacted CO<sub>2</sub> was attained as a by-product. At a reaction temperature of 250 °C, the catalyst formed 20% CH<sub>4</sub> gas. Upon raising the reaction temperature to 400 °C (maximum value), the best 69% CH<sub>4</sub> gas was formed

as detected by GC-FID. Although CO<sub>2</sub> conversion is 100%, but the CH<sub>4</sub> gas formed only 69%. This might due to formation of methanol as side product for the catalysts (Refer Figure 2) as confirmed by HPLC analysis which showed the presence of peak at 20 minutes compatible with the retention time of standard

methanol. As qualitatively, the presence of methanol was confirmed in the water product. This is because the peak area of  $1.708 \times 10^6$  at 20.038 minutes coincided with the peak of standard methanol (not shown) at 19.122 minutes.

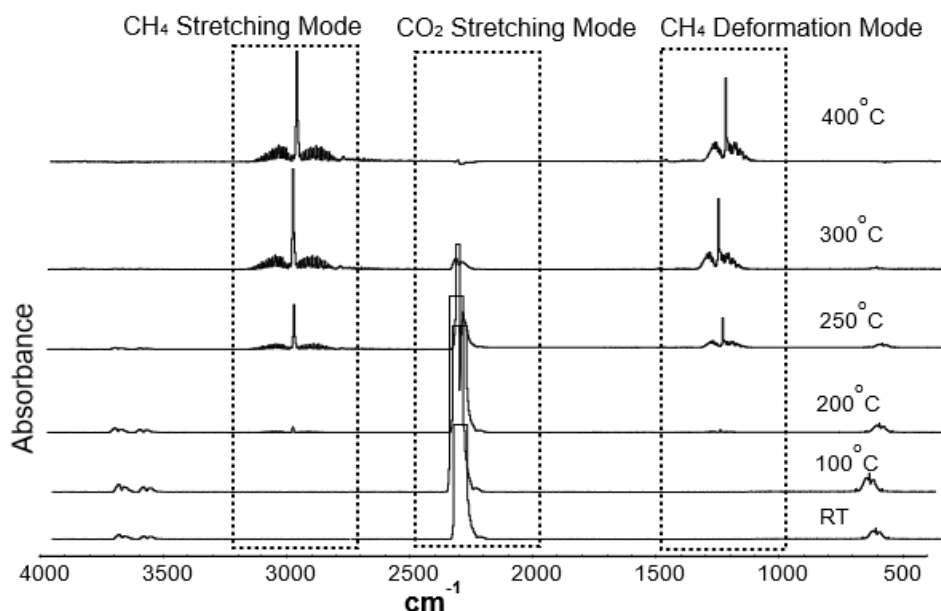


Figure 1. FTIR spectra of gaseous product at various reaction temperatures over calcined Sm/Mn/Ru (60:35:5)/Al<sub>2</sub>O<sub>3</sub> catalyst

Table 1. Product analysis via *in-situ* reactions during methanation for Sm/Mn/Ru (60:35:5)/Al<sub>2</sub>O<sub>3</sub> catalyst calcined on 1000 °C for 5 hours using GC-FID

Reaction Temperature (°C)	Converted CO <sub>2</sub> (%)*		Unreacted CO <sub>2</sub> (%)
	% Formation of CH <sub>4</sub> **	% Formation of H <sub>2</sub> O + with/without CH <sub>3</sub> OH***	
RT	-	0.00	100.00
100	-	0.31	99.69
200	6.43	59.09	34.48
250	20.85	71.67	7.48
300	31.11	65.67	3.22
350	48.91	49.95	1.14
400	68.87	31.13	-

\*Converted CO<sub>2</sub> and Unreacted CO<sub>2</sub> was determined from FTIR as in Equation 1

\*\*Formation of CH<sub>4</sub> was calculated from GC-FID as in Equation 2

\*\*\*The presence of CH<sub>3</sub>OH was confirmed with HPLC

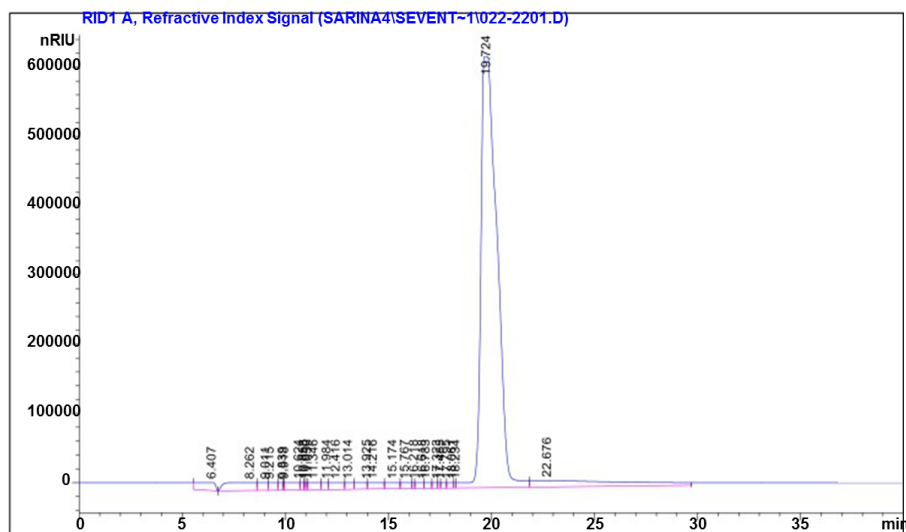


Figure 2. HPLC chromatogram of liquid product over calcined Sm /Mn/Ru (60:35:5)/Al<sub>2</sub>O<sub>3</sub> catalyst

### Methanation mechanism

The hydrogenation methanation adhered to the Langmuir-Hinshelwood mechanism, which reflected CO<sub>2</sub> and H<sub>2</sub> gases adsorption on the surface of catalyst. All CO<sub>2</sub> adsorption, dissociation, and reaction of the resolved species with H<sub>2</sub> had been established from in-situ FTIR experiments without any carbonate adsorption peak at 1760 and 1570 cm<sup>-1</sup>. The FTIR spectra for catalyst during reaction is depicted in Figure 3. The spectra exhibited two broad O-H peak around 3443 and 1637 cm<sup>-1</sup> corresponded to stretching and bending of adsorbed water on Al<sub>2</sub>O<sub>3</sub> support [15, 16]. According to Narain et al., a peak band was noted at 1639 cm<sup>-1</sup> for the similar temperature due to O-H bending derived from H<sub>2</sub>O [17]. Initially, CO<sub>2</sub> and H<sub>2</sub> molecules were drawn to the catalyst surface (Step I) and directly coordinated the C atoms to generate inorganic carboxylate as proposed in Figure 4. The peak at 1116 cm<sup>-1</sup> assigned to the CO species observed during the attachment of CO<sub>2</sub> to the catalyst surface at reaction temperature, 100°C [10]. This suggested the arrangement of C atoms attached to the catalyst surface (Step II). The adsorbed H<sub>2</sub> molecule was dissociated to

active H atom species, and this was followed by CO<sub>2</sub> gas dissociation, as reported by Haldor [18] in Step III. The continuous flow of H<sub>2</sub> gas on the catalyst connects with oxygen atoms at the lone pair of electrons with higher electronegativity to form water (step IVa). This was supported with intense peak in the FTIR at reaction temperature, 200°C. A little peak at 1397 cm<sup>-1</sup> was also observed at 200°C that correspond to the methoxy group (H<sub>3</sub>C-O) as suggested in step IVb. Solymosi et al. described the peak around 1397 cm<sup>-1</sup> on the catalyst surface foremost to the formation of methanol as a by-product [12]. When increased the reaction temperature to 250 – 300°C, the peak at 2892-2926 cm<sup>-1</sup> was appeared which suggested free carbon from step III react directly with hydrogen to produce methane (step V). The intensity of C-H peak decreased at 350°C indicating that almost all CH<sub>x</sub> was released as CH<sub>4</sub> gas. At a reaction temperature of 400°C, all peak C-H groups disappeared which resulted higher CH<sub>4</sub> formation at this reaction temperature with 69% as stated in Table 1. This signifying the conversion of all species to CH<sub>4</sub>, H<sub>2</sub>O, and CH<sub>3</sub>OH as the final yields.

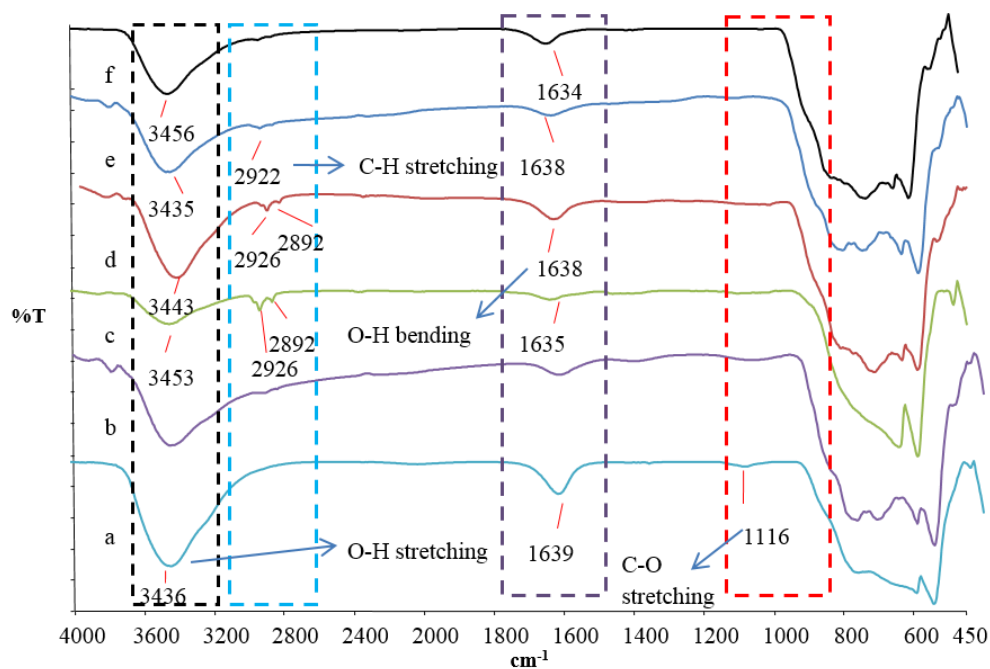


Figure 3. FTIR spectra of Sm/Mn/Ru (60:35:5)/Al<sub>2</sub>O<sub>3</sub> catalyst surface at (a) 100°C, (b) 200°C, (c) 250°C, (d) 300°C, (e) 350°C, and (f) 400°C reaction temperature

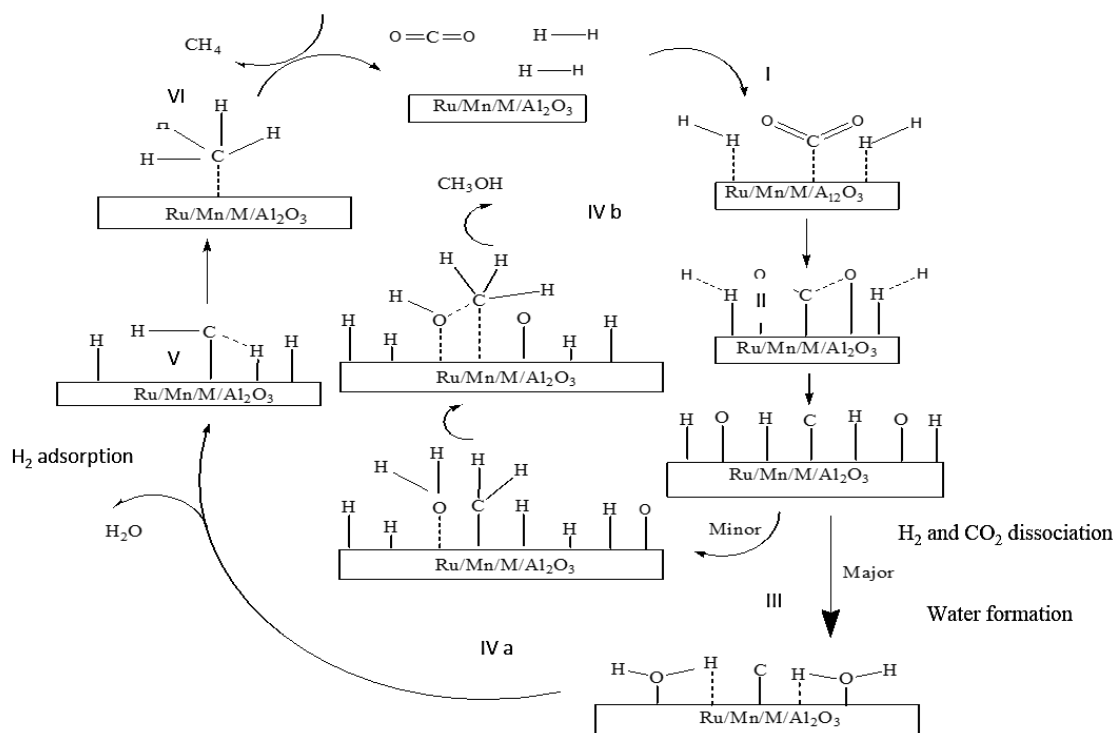


Figure 4. Proposed mechanism of M/Mn/Ru (60:35:5)/Al<sub>2</sub>O<sub>3</sub>, (M= Sm) calcined for 5 hours at 1000 °C

### Conclusion

This evaluation revealed compliance with the Langmuir Hinselwood mechanism, where CO<sub>2</sub> gas is first adsorbed, and then H<sub>2</sub>-reactive gas is adsorbed on the catalyst surface. Based on the mechanistic approach, CH<sub>4</sub> was formed at temperature of 250 °C and CO<sub>2</sub> peak was gradually decrease when the reaction temperature increased. The CO<sub>2</sub> conversion at 400°C is 100%, with CH<sub>4</sub> formation of 69%. The others percent conversion was side products which are water and methanol, as detected by HPLC.

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