

# Effect of ceria and strontia over Ru/Mn/Al<sub>2</sub>O<sub>3</sub> catalyst: Catalytic methanation, physicochemical and mechanistic studies



Susilawati Toemen, Wan Azelee Wan Abu Bakar\*, Rusmidah Ali

Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM, Johor Bahru, Johor, Malaysia

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## ABSTRACT

The 65 wt% of ceria and strontia based catalysts prepared by impregnation with Ru/Mn/Al<sub>2</sub>O<sub>3</sub> were tested on its CO<sub>2</sub> methanation reaction under reducing pretreatment at 300 °C. The result obtained revealed that the addition of Ce to Ru/Mn/Al<sub>2</sub>O<sub>3</sub> has a positive effect on the activity and catalyst stability compared to the Sr containing catalyst. The CO<sub>2</sub> conversion over Ru/Mn/Ce-65/Al<sub>2</sub>O<sub>3</sub> achieved 97.73% with 91.31% of methane formation at a reaction temperature of 200 °C while, 73.10% conversion over Ru/Mn/Sr-65/Al<sub>2</sub>O<sub>3</sub> catalyst with 44.58% of methane yielded at reaction temperature of 210 °C. The characterization results obtained suggest that the CeO<sub>2</sub>, SrO<sub>2</sub>, RuO<sub>2</sub>, Mn<sub>2</sub>O<sub>3</sub> and orthorhombic Al<sub>2</sub>O<sub>3</sub> were the active species for both catalysts while, the presence of spinel compound, Sr<sub>4</sub>(Ru<sub>2</sub>O<sub>9</sub>) caused the reducibility and basicity of Ru/Mn/Sr-65/Al<sub>2</sub>O<sub>3</sub> catalyst decreased hence reduced the catalytic activity eventually. The mechanistic study showed it was depended on the type of catalysts as the CO<sub>2</sub> adsorbed on the Sr based catalyst tended to form monodentate carbonate at the initial state before forming the formate species when it was hydrogenated and finally releasing the methane. Meanwhile, the methane formation on Ce based catalyst involved the initially adsorption and dissociation of CO<sub>2</sub> into C and O adsorbed species before reacting with the adsorbed H<sub>2</sub> to form methane gas.

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## 1. Introduction

Metal oxides are among the most important and widely used catalyst. Metal oxides generally exhibit both electron and proton transfer abilities and can be used as catalysts in redox as well as acid–base reactions [1]. The usual traditional metal oxide catalyst used for industrial applications is nickel [2–4], one of the elements in Group VIII metals. It can give higher activity, but suffer severe carbon deposition at high reaction temperature. Even though, the noble metals such as ruthenium and rhodium act as more active catalysts than transition metal, but due to the price and limited availability of these materials they are rarely used [5].

Generally, the active catalyst for CO<sub>2</sub> methanation should have higher basicity and higher surface area with small particle sizes which highly dispersed on the catalyst surface. Therefore, the basic elements of alkaline earth metal (Sr) and rare earth metal (Ce) were chosen. A highly basic catalyst such as CeO<sub>2</sub> is proposed to enhance carbon dioxide adsorption and chemisorptions on the catalyst surface. It has excellent redox properties owing to the very

fast reduction of Ce<sup>4+</sup>/Ce<sup>3+</sup>, which is associated with the formation of oxygen vacancies at the surface [6]. It is well known that ceria can affect the thermal and structural stability of the catalyst support, the dispersion of supported metal and the decrease of carbon formation on the catalyst surface [7,8].

In addition, by incorporating the alkali modifier is said to be effective in improving a catalyst's behavior [9], enhance the acidic or basic character or impart thermal stability to the carrier [10]. Shen et al. [11] who studied on support modification with additives such as K<sub>2</sub>O, MgO, La<sub>2</sub>O<sub>3</sub>, and SnO<sub>2</sub> found that these additives influence the number and nature of basic or acid sites on the support. Besides, the presence of strontia and ceria as based catalyst are not being widely investigated by other researchers.

Supported bimetallic catalyst containing Mn and Ru had been studied on the hydrogenation of CO<sub>2</sub> [12]. It is an active catalyst for methanation process, but not cost effective material because of the expensiveness of Ru, consequently hardly applied for practical. In the present study, the supported mixed metal oxide catalysts made of Ru/Mn/Ce and Ru/Mn/Sr were prepared. Therefore, the aim of the present investigation is to elucidate the effect of ceria and strontia towards supported Ru/Mn catalyst on the catalytic activity, structure and physicochemical properties for CO<sub>2</sub> methanation reaction as well as its mechanistic study.

\* Corresponding author.

E-mail address: [wazelee@kimia.fs.utm.my](mailto:wazelee@kimia.fs.utm.my) (W.A.W. Abu Bakar).

## 2. Experimental

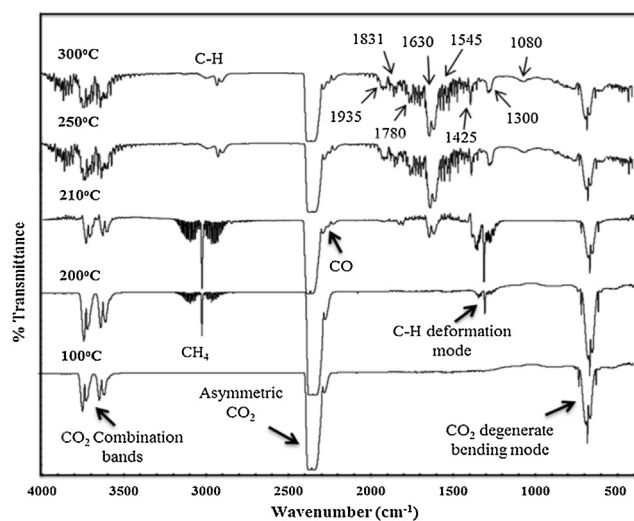
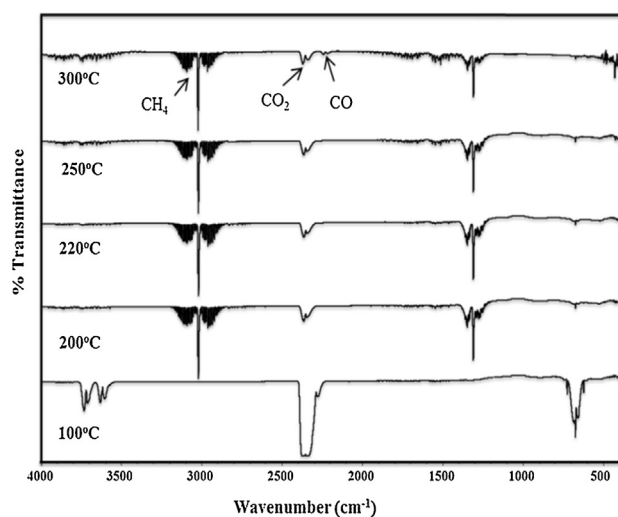
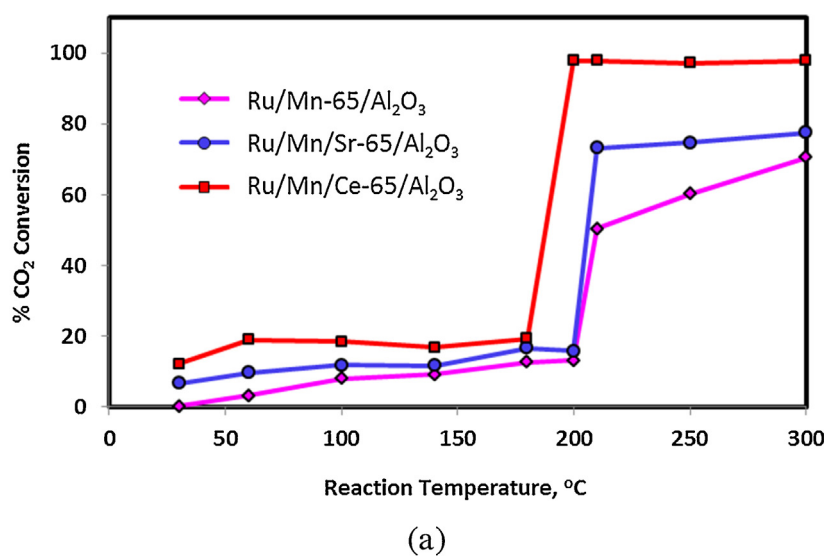
### 2.1. Preparation of catalysts

All the catalysts were prepared by aqueous incipient wetness impregnation method. 5 g of  $\text{Ce}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  obtained from MERCK was dissolved in 10 mL of distilled water. The mixed catalyst solution was prepared by mixing an appropriate amount of  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  (0.296 g) and  $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (3.969 g) (Sigma-Aldrich) with  $\text{Ce}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  solution according to its ratio. A homogeneous mixture was obtained by electromagnetic stirring at room temperature for 30 min. 10 g of alumina beads with a diameter of 3 mm were used as support material in this study. The support was immersed into the catalyst solution until the solution was evenly absorbed on the surface of the support. The coating process was repeated three times with drying at ambient temperature for every coating process. It was then aged inside an oven at 90 °C for 24 h, followed by calcination using a furnace in the air atmosphere at 1000 °C for 5 h 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 Ru/Mn/Ce-65/Al<sub>2</sub>O<sub>3</sub>

meaning that there is 65 wt% of Ce, 30 wt% of Mn and 5 wt% of Ru. Similar procedure was repeated for the Ru/Mn/Sr-65/Al<sub>2</sub>O<sub>3</sub> and Ru/Mn-65/Al<sub>2</sub>O<sub>3</sub> catalysts. The catalyst labelled as Ru/Mn-65/Al<sub>2</sub>O<sub>3</sub> was composed by 65 wt% of Mn and 35 wt% of Ru.

### 2.2. Catalytic activity measurement

The catalytic CO<sub>2</sub> methanation reaction was performed under atmospheric pressure in a fixed micro reactor and analyzed via online Fourier Transform Infra Red (FTIR) Nicolet Avatar 670 DGTS. The supported catalyst was placed in the middle of the glass tube made of Pyrex glass with diameter 10 mm and a length of 520 mm. It was then secured with glass wool at both ends. The reaction gas mixture consisting of CO<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub> (10/40/39/11) was passed continuously through the catalyst and was heated in an isothermal tube furnace. The total flow rate was set to 100 mL/min, while the weight hourly space velocity was kept fixed at 636 mL g<sup>-1</sup> h<sup>-1</sup>. The feed gas flow rate was adjusted with a mass flow controller and the reaction temperature was performed from 60 °C up to 300 °C with the increment temperature rate of 5 °C/min. Offline Gas Chromatography (GC) analysis (Hewlett Packard 6890 Series GC System)



**Fig. 1.** (a) Percentage conversion of CO<sub>2</sub> by using 10 g of catalysts dosage, (b) FTIR spectra of gaseous product at various reaction temperatures over Ru/Mn/Ce-65/Al<sub>2</sub>O<sub>3</sub> and (c) FTIR spectra of gaseous product at various reaction temperatures over Ru/Mn/Sr-65/Al<sub>2</sub>O<sub>3</sub>.

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