

Catalytic Cracking of Methane, Methanol, and Ethanol by Ceria

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Abstract: In the present work, the catalytic cracking of methane, methanol, and ethanol with ceria (CeO_2) was investigated using temperature-programmed reaction (TPR_X) and isothermal reaction at 900°C . Ceria showed a reasonable activity in conversion of hydrocarbons to hydrogen, carbon monoxide, and carbon dioxide with only small amounts of carbon deposition observed compared to conventional $\text{Ni}/\text{Al}_2\text{O}_3$ even though the methanol and ethanol were fed. In addition, from the catalytic cracking of methanol and ethanol using ceria, hydrogen can be produced continuously without any requirement of oxidants due to the oxygen storage capacity of CeO_2 . Oxygen atom from methanol and ethanol can oxidise the reduced state of ceria, CeO_{2-x} , from the cracking reaction and recover the oxidised state of ceria, CeO_2 . However, the catalytic cracking reactivity of CeO_2 remains too low due to its low specific surface area. The use of synthesized high surface area CeO_2 improves the performance of ceria toward this reaction. The catalytic cracking of hydrocarbon elements by high surface area CeO_2 will be studied and presented in our next publication.

Keywords: Ceria, Cracking, Methane, Methanol, Ethanol.

Introduction

The green house effect and environmental crisis are among the critical global concerns. Combustion processes have been used to generate energy for more than a century. Although the combustion is a well-developed and cost-effective process, the main disadvantage is the unwanted by-products such as NO_x or CO_x , which could lead to the green house effect. The Solid Oxide Fuel Cell (SOFC) is an energy conversion unit which generates electrical energy and heat with greater energy conversion efficiency and lower pollutant emission than combustion processes [1]. This type of fuel cell is normally operated at high temperature, between 700°C to 1100°C [2]. Several hydrocarbon elements such as methane, methanol, or ethanol can be used as a fuel for SOFC. As an SOFC is operated at such a high temperature, these hydrocarbons can be reformed effectively by either catalytic steam reforming or partial oxidation to produce a H_2/CO rich gas, which is eventually used to generate electricity and heat. A partial oxidation process has advantages concerning the start-up, load changes, and the simpler set-up of the reformer [3], however, it has rather low system efficiency and provides low H_2 production content compared to a steam reforming process. Therefore, the partial oxidation process is preferred in small systems or portable application [4], while steam reforming is preferred in systems where high efficiencies are required. SOFC systems using hydrocarbons as the fuel normally consist of two main parts: the reformer and fuel cell sections. Hydrocarbon is firstly reformed at the reformer where H_2 and CO are produced and consequently used to generate electrical energy at the fuel cell section. These two parts can be coupled in the same unit called internal reforming as shown in Fig. 1. This way is expected to simplify the system design [2]

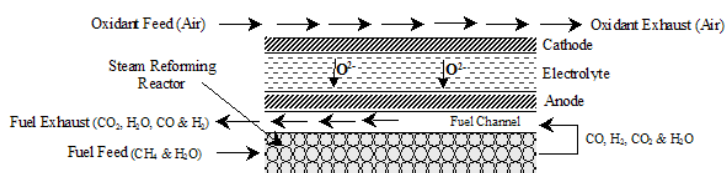


Fig. 1 Schematic diagram of SOFC with indirect internal reformer [2].

The reforming is currently carried out over Ni catalysts. Nevertheless, the endothermic reforming reaction over this catalyst is predicted to be too fast for the internal reforming operation which requires very large dilution [5], and carbon deposition always occurs [6]. A novel reforming catalyst with less activity and more resistant to carbon formation is required to improve the heat management in SOFCs [2, 5]. It is well established that ceria-based materials have been applied as the catalysts in a wide variety of reactions involving oxidation or partial oxidation of hydrocarbons (e.g. automotive catalysis). Cerium oxide (CeO_2) can provide a high oxygen storage capacity (OSC), which is beneficial in oxidation processes. It has been reported that the gas-solid reaction between CeO_2 and CH_4 produces synthesis gas with a H_2/CO ratio of two according to the following reaction [7, 8]: $\text{CeO}_2 + n\text{CH}_4 \rightleftharpoons \text{CeO}_{2-n} + n\text{CO} + 2n\text{H}_2$ (1)

Only a relatively low amount of carbon formation was observed from the reaction [9]. Moreover, it has been reported that the use of ceria as the internal reforming catalyst can prevent the local cooling spot at the entrance of the reformer due to its lower reactivity than conventional Ni catalyst [9]. Therefore, ceria would be a good candidate for use as a catalyst for hydrogen production.

In order to investigate the use of ceria for hydrogen production from several hydrocarbons, the gas-solid reactions between CeO_2 with methanol and ethanol were investigated and compared to that with methane. These experiments were carried out using a temperature programmed (TP) technique, which is described in the experimental section.

Experimental

Experimental Set-up

The investigation of gas-solid reaction between CeO_2 and hydrocarbons, was carried out in an experimental reactor system which was specially constructed as follows. This experimental set-up was designed to allow measurements under both transient and steady state conditions. Fig. 2 shows the flow sheet of this reactor system. All tubing was 1/8" or 1/16" AISI-316 stainless steel with unidirectional valves installed for each stream prior to mixing of gases. All auxiliary equipment such as non-return valves, three-way valves, elbows, reductions, expansions and on-off valves were also stainless steel (from Swagelok). This system consists of three main sections: feed, reaction, and analysis sections. The main obligation of the feed section is to supply CH_4 to the reaction section. After reaction, the gas mixture was transferred via trace heated lines to the analysis section, which consisted of a mass spectrometer (MS) and a gas chromatography (GC).

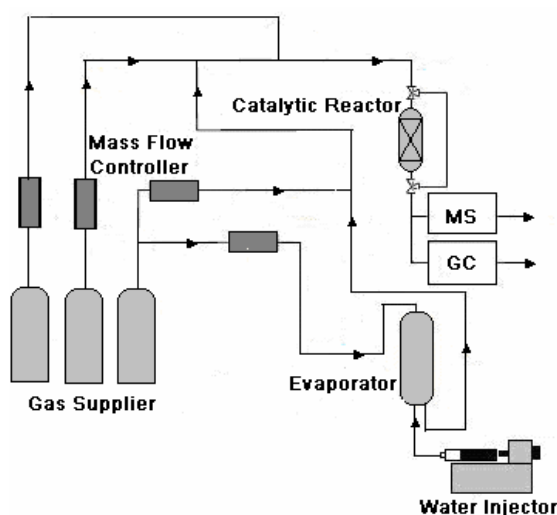


Fig. 2 The reactor system in this study.

Temperature programmed techniques (TP)

In the present work, temperature programmed technique (TP) was applied for studying the gas-solid reaction. Temperature Programmed Reaction (TPR_x) was used to investigate the reaction of methane, methanol, and ethanol with the surface of catalyst. 5% Methane, Methanol, and Ethanol in helium gas with the total flow rate of 100 ml min^{-1} was introduced into the system, while the operating temperature increased from room temperature to 900°C at the rate of 10°C/min . Then, the system was cooled down to room temperature under Helium flow. After the TPR_x experiment, the carbon deposited on the catalyst was investigated using a temperature programmed oxidation (TPO). 10% Oxygen in helium with the total flow rate of 100 ml min^{-1} was introduced to the system, after a He purge. Similar to the TPR_x experiment, the temperature was increased from room temperature to 900°C at the rate of 10°C/min .

Material Preparation

Undoped ceria was prepared by precipitation of cerium hydroxide ($\text{Ce}(\text{OH})_4$) from cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.0%) - Fluka). Cerium nitrate was diluted to 0.1 M and stirred by a magnetic stirrer (100 rpm) at room temperature. Cerium hydroxide was then precipitated by addition of 0.4 M ammonium hydroxide solution during stirring. The final pH of the solution was in the range of 7.0-7.5. Stirring was continued for another 3 hours to ensure that the reaction was complete. The precipitate was then filtered and washed with deionised water and ethanol to prevent an agglomeration of particles. The sample was dried overnight in an oven at 110°C . This

precipitated cerium hydroxide was then calcined in air at 900°C to convert to ceria (CeO_2). The calcination temperature was 900°C, as this is the maximum temperature used for all experiments in this work.

Catalyst Characterisation

Both fresh and spent catalysts were characterised using a particle size analysis (BET). The specific surface areas (SSABET) of all material powders were determined using the Brunauer-Emmett-Teller (BET) method with nitrogen as the adsorbate at its normal boiling point (77 K). Samples were degassed to 0.1 Pa for 4 hours at 200°C prior to nitrogen adsorption.

Results and Discussion

Gas-solid reaction between CeO_2 and hydrocarbons

Temperature-programmed using 5% methane, methanol, and ethanol in helium (temperature-programmed reaction (TPRx)) were carried out over CeO_2 . For methane, as shown in Fig. 3, the dissociative methane adsorption occurred at temperature above 800°C. Hydrogen was produced from the cracking of methane, while CO and CO_2 were also generated from the gas-solid reaction of CeO_2 and methane. This result is in good agreement with the previous studied by E. Ramirez et al. [10] who tested the gas-solid reaction between methane and Gd- CeO_2 .

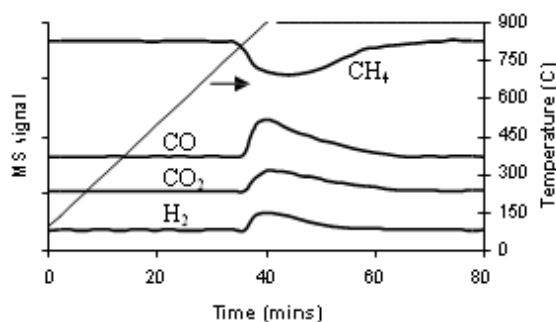


Fig. 3 TPRx of 5% methane in helium on CeO_2 .

Fig. 4 and 5 present the gas-solid reaction between CeO_2 with methanol and ethanol respectively. Unlike the cracking of methane, hydrogen can be produced by the cracking of both methanol and ethanol continuously without any addition of oxidants. This could be due to the oxygen storage capacity of CeO_2 because this catalyst acts as a local source or sink for oxygen involved in reactions taking place on its surface. Oxygen atom from methanol and ethanol can oxidise the reduced state of ceria, CeO_{2-x} , from the cracking reaction and recover the oxidised state of ceria, CeO_2 . The cracking of methanol on the surface of CeO_2 occurred at 600°C, whereas the cracking of ethanol occurred above 750°C. CO, CO_2 and CH_4 were also produced from the cracking together with hydrogen. However, the production of methane decreased when the operating temperature is higher than 850°C. This is due to the possible cracking of methane to CO, CO_2 , and H_2 .

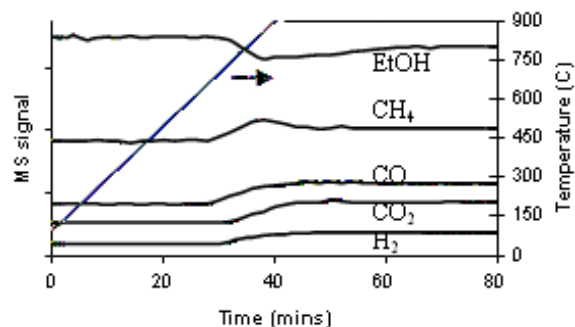
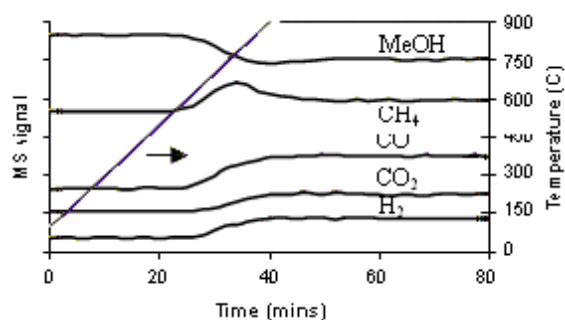


Fig. 4 TPRx of 5% methanol in helium on CeO_2 . **Fig. 5** TPRx of 5% ethanol in helium on CeO_2

At isothermal condition, 900°C, slight deactivation was observed. These are mainly due to sintering on the surface of CeO_2 , according to the BET measurement as presented in Table 1.

Table 1 BET measurement of CeO_2 before and after reaction

Reaction	Specific surface area ($\text{m}^2 \text{g}^{-1}$) before the reaction	Specific surface area ($\text{m}^2 \text{g}^{-1}$) after the reaction
CH_4 cracking	8.4	6.2
MeOH cracking	8.4	6.5
EtOH cracking	8.4	6.1

For comparison, the cracking of methane, methanol, and ethanol on conventional 5% $\text{Ni}/\text{Al}_2\text{O}_3$ (from Aldrich) were carried out. The catalyst was firstly reduced with 5% hydrogen in helium at 300°C for 6 h before studying. As seen in Fig. 6, 7, and 8 the dissociative hydrocarbons (methane, methanol, and ethanol) adsorption occurred at temperature above 550°C. However, as also seen from Fig. 7 and 8, the production of hydrogen from the cracking of methanol and ethanol are not permanent.

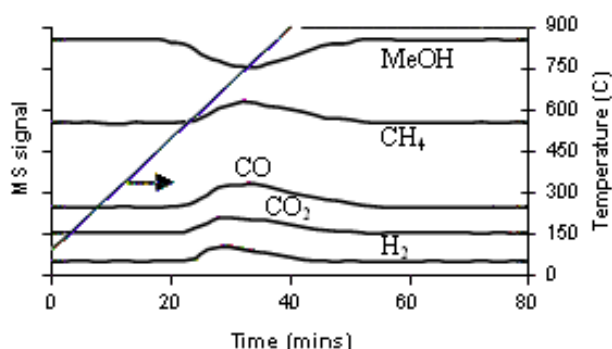
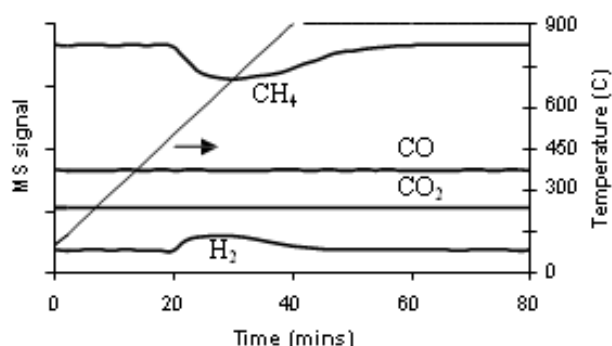


Fig. 6 PRx of 5% methane in helium on $\text{Ni}/\text{Al}_2\text{O}_3$. **Fig. 7** TPRx of 5% ethanol in helium on $\text{Ni}/\text{Al}_2\text{O}_3$.

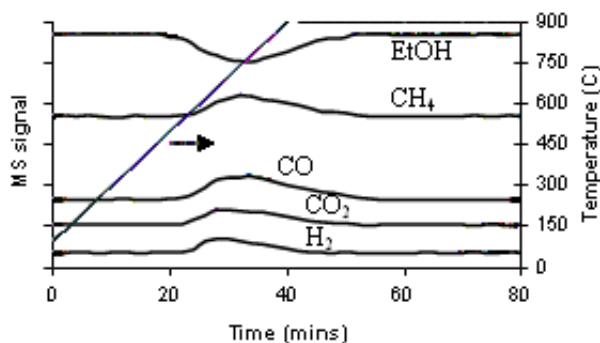


Fig. 8 TPRx of 5% ethanol in helium on Ni/Al₂O₃.

Apparently, the carbon deposition occurs on the surface of Ni/Al₂O₃ after exposure in dry hydrocarbon condition. The amounts of carbon formation on the surface of CeO₂ and Ni/Al₂O₃ after exposure in dry methane, methanol, and ethanol conditions are then studied and will be presented in the next section.

Resistance toward carbon formation

After the temperature-programmed adsorption, the system was cooled down to room temperature under helium flow. The carbon deposited on the catalyst was then investigated by the temperature-programmed oxidation (TPO). 10% Oxygen in helium with the total flow rate of 100 ml min⁻¹ was introduced into the system, after a He purge. Fig. 9, 10, and 11 presents the comparison TPO results between Ni/Al₂O₃ and CeO₂ fueled by methane, methanol, and ethanol respectively.

The figure indicates that a substantial quantity of carbon did indeed on the catalyst surface especially for Ni/Al₂O₃. The amount of carbon formation on the surface of catalyst, which was determined by measuring the CO and CO₂ yields from TPO, is presented in Table 2.

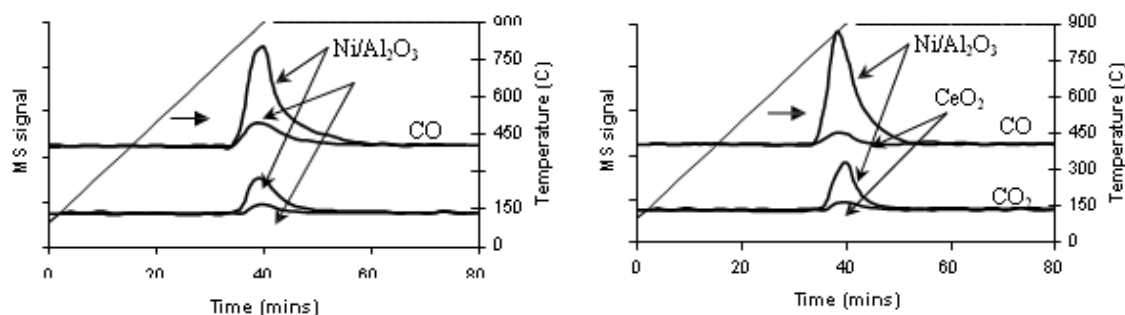


Fig. 9 TPO after exposure with 5% methane in helium. Fig. 10 TPO after exposure with 5% methanol in helium.

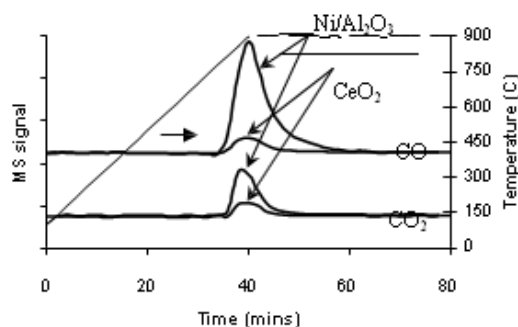


Fig. 11 TPO after exposure with 5% ethanol in helium.

Table 2 Amount of carbon formation on the surfaces of CeO₂ and Ni/Al₂O₃ after the cracking reaction

Catalyst	Reaction	Carbon formation (monolayer)
CeO ₂	CH ₄ cracking	0.14
	MeOH cracking	0.10
	EtOH cracking	0.18
Ni/Al ₂ O ₃	CH ₄ cracking	2.23
	MeOH cracking	2.31
	EtOH cracking	2.28

Using a value of 0.026 nm^2 for the area occupied by a carbon atom in a surface monolayer of the basal plane in graphite [10], the quantities of carbon deposited over CeO₂ range from approximately 0.14 monolayers fueled by methane to 0.18 monolayers fueled by ethanol. For Ni/Al₂O₃, much higher amount of carbon depositions were observed, they are in the range of 2.23 to 2.31 monolayers.

Conclusion

CeO₂ can be used as the catalyst for cracking of methanol and ethanol. Hydrogen can be produced continuously from this reaction without the requirement of any oxidant due to the oxygen storage capacity of CeO₂, as oxygen atom from methanol and ethanol can oxidise the reduced state of ceria, CeO_{2-x}, from the cracking reaction and recover the oxidised state of ceria, CeO₂. Moreover, it is also observed that only a few amount of carbon deposition was formed on the surface of CeO₂ compared to conventional Ni/Al₂O₃ even though methanol and ethanol were fed.

However, due to its low specific surface area, the reactivity over CeO₂ might be too low for commercial application. The use of synthesis high surface area CeO₂ may solve this problem. The cracking of methanol and ethanol by high surface area CeO₂ will be studied and presented in our next work.

Acknowledgements

The financial support from The Thailand Research Fund (TRF) and the National Metal and Materials Technology Center (MTEC) is gratefully acknowledged.

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