

Selective Conversion of Methane to C₂ Hydrocarbons using Carbon Dioxide as an Oxidant over CaO-MnO/CeO₂ Catalyst

Nor Aishah Saidina Amin* and Istadi[§]

Chemical Reaction Engineering Group (CREG), Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia, 81310 UTM Skudai, Malaysia

ABSTRACT

Carbon dioxide rather than oxygen seemed to be an alternative oxidant for the catalytic reaction of methane to produce C₂ hydrocarbons via oxidative coupling of methane (CO₂ OCM). The proper amount of medium and strong basic sites and the reducibility of the catalyst enhanced the C₂ hydrocarbon selectivity and yield, which may be due to the synergistic effect of CeO₂, CaO and MnO in the catalyst. The C₂ hydrocarbons selectivity and yield of 75.6% and 3.9%, respectively were achieved over 12.8CaO-6.4MnO/CeO₂ catalyst. The catalyst showed a high stability for 20 h time on stream in the CO₂ OCM process.

1. INTRODUCTION

The direct conversion of methane to ethane, ethylene and acetylene (C₂ hydrocarbons) has a large implication towards the utilization of natural gas in the gas-based petrochemical and liquid fuels industries [1]. CO₂ OCM process provides an alternative route to produce useful chemicals and materials using CO₂ as the feedstock and making use of CO₂ for environmentally-benign chemical process. Carbon dioxide rather than oxygen seems to be an alternative oxidant as methyl radicals are induced in the presence of oxygen in the gas phase. Basicity, reducibility, and catalyst ability to form oxygen vacancies are some of the physico-chemical criteria of a promising catalyst for the CO₂ OCM process [2]. It is believed that the synergism of reducibility and catalyst basicity plays an important role in the activation of carbon dioxide and methane [2].

In this paper, the selective conversion of methane to C₂ hydrocarbons by CO₂ OCM process and the stability test of CaO-MnO/CeO₂ catalyst are presented. H₂-TPR and CO₂-TPD were used to characterize basicity and reducibility of the catalyst. The synergistic effect of catalyst reducibility and distribution of basic sites are highlighted.

2. EXPERIMENTAL

The first ternary metal oxide catalyst of CaO-MnO/CeO₂ was prepared by simultaneous incipient wetness impregnation method, while the second ternary metal oxide of

* Corresponding Author. E-mail: noraishah@fkkksa.utm.my. Tel. +607-5535588, Fax. +607-5581463

[§] Present Address: Chemical Reaction Engineering & Catalysis (CREC) Groups, Dept. of Chemical Engineering, Diponegoro University, Semarang, Indonesia

CaO/MnO-CeO₂ catalyst was prepared by combination of co-precipitation and incipient wetness impregnation method. The catalysts composition used in this paper were based on multi-responses optimization [3]. H₂-TPR was carried out using Micromeritics 2900 TPD/TPR equipped by TCD. The catalyst amount of about 0.05 g was purged with Ar (25 cm³ min⁻¹) at 773 K for 1 h and cooled down to room temperature. The flow of 6% H₂ in Ar (25 cm³ min⁻¹) was then switched into the system, and the sample was heated up to 1223 K from room temperature at a rate of 5 K min⁻¹. CO₂-TPD was carried out using Micromeritics 2900 TPD/TPR equipped by TCD. The catalyst samples of about 0.05 g each were initially calcined at 1073 K in a flow of argon (25 cm³ min⁻¹) for 1 h. The chemisorption of CO₂ was carried out at 373 K by flowing CO₂ (25 cm³ min⁻¹) for 1 h. The excess of CO₂ was then purged in a flow of Ar (25 cm³ min⁻¹) for 1 h. The sample was then heated to 1223 K at a linear heating rate of 5 K min⁻¹ in a flow of Ar (25 cm³ min⁻¹). The amount of H₂ uptake and the amount of desorbed CO₂ in both characterizations were detected using TCD. The performances of the catalysts were tested using a fixed-bed quartz reactor at the following conditions: reactor temperature = 850 °C; CH₄/CO₂ = 1/2, feed flow rate = 100 ml min⁻¹; catalyst loading = 2 g. Before reaction, the catalyst was recalcined at 850 °C in air flow for 1 h and was flushed with high purity nitrogen at 850 °C for another 1 h. The products and the unreacted gases were analyzed by an online GC equipped with a thermal conductivity detector and PORAPAK N packed-column.

3. RESULTS AND DISCUSSION

3.1. Catalyst Characterization

The H₂-TPR peaks of CeO₂-based catalysts are presented in Fig. 1. The first low temperature peak located at about 500 °C is assigned to the reduction of the most easily reducible surface-capping oxygen of ceria, while removal of the bulk oxygen of ceria is indicated at about 800 °C [4]. This reduction is associated to an increased reducibility of the bulk mixed oxide, which is evident in Figs. 1(c) and 1(d) as the H₂-TPR peaks shift from 770 °C to 740 °C and 730 °C for the CaO-MnO/CeO₂ and CaO/MnO-CeO₂ catalysts, respectively. The manganese introduction strongly modifies the reduction behavior of CeO₂ by shifting the main H₂ consumption to a lower temperature [5]. The promotion of Ce⁴⁺ reduction can be related to a higher mobility and diffusion of bulk oxygen from chemisorbed CO₂ due to introduction of manganese into CeO₂ lattice. The H₂-TPR spectra as depicted in Fig.1 reveal that the CaO-MnO/CeO₂ catalyst has moderate reducibility with high medium and strong basic sites (CO₂ TPD). It is shown that the CaO/MnO-CeO₂ catalyst has higher MnO₂ content than the CaO-MnO/CeO₂ catalyst as indicated by high TPR peak at 390 °C. The H₂-TPR peak at about 510 °C is assigned to the reduction of Mn₂O₃ or MnO₂ to Mn₃O₄, while the peak at about 590 °C corresponded to final reduction from Mn₃O₄ to MnO. The change in the catalyst color from black to brown and/or grey after the catalyst testing suggested that the oxidation state of manganese oxide has been changed during the reaction from mixed MnO₂ and Mn₂O₃ to Mn₃O₄ and/or MnO [6].

The CO₂-TPD curves demonstrating the base strength distribution of different CeO₂-based catalysts are presented in Fig. 2. From the figure, the difference in the distribution of basic sites for each catalyst indicates that the basicity and base strength distributions are significantly influenced by CaO and by the addition of MnO_x in the CeO₂-based catalysts. The CO₂ TPD spectra obviously exhibit that the CaO/CeO₂ catalyst gives the largest number of very strong basic sites, followed by CaO/MnO-CeO₂ and CaO-MnO/CeO₂ catalysts. According to Figs. 2(b-d), the deposition of CaO on the CeO₂-based catalysts results in the creation of a large number of medium, strong and very strong basic sites at the expense of the weak basic sites as

compared to the pure CeO_2 catalyst [7]. The CO_2 -TPD spectra in Figs. 2(c) and 2(d) show different peaks owing to the total number of medium and strong basic sites. Impregnation of calcium and manganese nitrate solutions to the CeO_2 catalyst leads to higher distribution of medium and strong basic sites rather than when the MnO-CeO_2 solid solution is used as the support. The CO_2 -TPD peak of medium basic sites becomes more intense significantly for CaO/CeO_2 and CaO-MnO/CeO_2 catalysts, but not for CaO/MnO-CeO_2 catalyst.

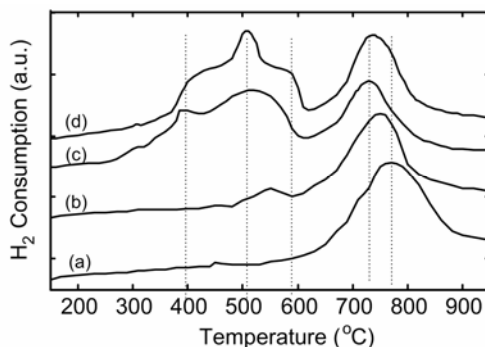


Fig. 1. H_2 -TPD spectra of different catalysts. (a) CeO_2 ; (b) 12.8CaO/CeO_2 ; (c) $12.8\text{CaO}/6.4\text{MnO-CeO}_2$; (d) $12.8\text{CaO-6.4MnO/CeO}_2$

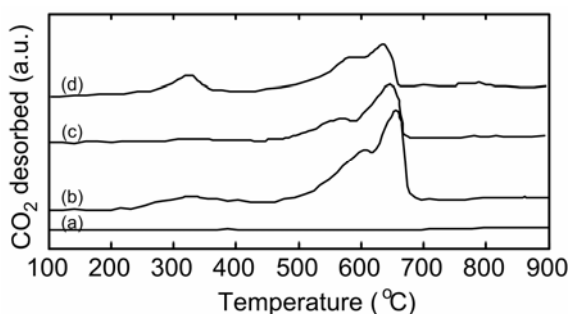


Fig. 2. CO_2 -TPD spectra of different catalysts. (a) CeO_2 ; (b) 12.8CaO/CeO_2 ; (c) $12.8\text{CaO}/6.4\text{MnO-CeO}_2$; (d) $12.8\text{CaO-6.4MnO/CeO}_2$

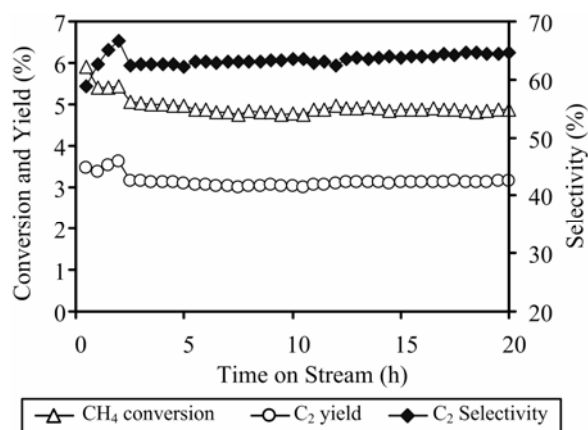
3.2. Catalyst Activity and Correlation with Basicity and Reducibility of the Catalyst

The screening results of CeO_2 -based catalysts as presented in Table 1 over binary and ternary metal oxides reveals that the $12.8\text{CaO-6.4MnO/CeO}_2$ catalyst is the most potential for the CO_2 OCM process [3,8]. Addition of CaO to the pure CeO_2 catalyst results in a significant increase in the C_2 hydrocarbon selectivity. The enhancement in the C_2 yield is possibly due to the synergistic effect of MnO and CeO_2 where the reducibility of the catalyst are increased as revealed in H_2 -TPR results (Fig. 1), which in turn enhance the oxygen vacancies formation. Our present study indicates that there exists a correlation between basic sites distribution, catalyst reducibility and catalytic activity toward C_2 hydrocarbons production as exposed in CO_2 -TPD result (Fig. 2). The CaO species is suggested to play an important role in CO_2 chemisorption on the catalyst surface due to the role in distribution of medium and strong basic sites of the catalyst [9,10]. Proper amount of catalyst basicity, particularly medium and strong basic sites, greatly enhances the selectivity to C_2 hydrocarbons [2,9]. The MnO species evidently increases the reducibility of CeO_2 due to increasing oxygen mobility of the CeO_2 catalyst which enhances its reducibility and produces more oxygen vacancies [2]. The catalyst also shows high stability during 20 h time on stream for CO_2 OCM as revealed in Fig. 3.

Table 1

Catalysts performance results of CeO₂-based catalysts [3,8]

| Catalysts | CH ₄ conversion (%) | C ₂ selectivity (%) | C ₂ yield (%) |
|---------------------------------|--------------------------------|--------------------------------|--------------------------|
| CeO ₂ | 13.0 | 19.4 | 2.5 |
| 12.8CaO/CeO ₂ | 2.7 | 75.0 | 2.0 |
| 6.4MnO/CeO ₂ | 8.8 | 3.1 | 0.3 |
| 12.8CaO/6.4MnO-CeO ₂ | 5.3 | 62.2 | 3.3 |
| 12.8CaO-6.4MnO/CeO ₂ | 5.1 | 75.6 | 3.9 |

Fig.3. Stability test of 12.8CaO-6.4MnO/CeO₂ catalyst in CO₂ OCM reaction

From single-response optimization using Response Surface Methodology, the maximum C₂ hydrocarbons selectivity and yield of 82.62% and 3.93%, respectively were achieved [3]. Meanwhile, the maximum C₂ selectivity and yield of 76.6% and 3.7%, respectively were achieved over 12.8% CaO-6.4% MnO/CeO₂ catalyst at the optimum reactor temperature being 1127 K and CO₂/CH₄ ratio being 2 [3].

4. CONCLUSIONS

Addition of CaO and MnO to the CeO₂ catalyst resulted in a significant increase in the C₂ hydrocarbons selectivity and yield. The enhancing effect may be due to the synergistic effects of high distribution of medium and strong basic sites and high reducibility of the catalyst. The 12.8CaO-6.4MnO/CeO₂ catalyst showed better performance and stability for the CO₂ OCM process.

REFERENCES

- [1] T. Suhartanto, A.P.E. York, A. Hanif, H. Al-Megren and M.L.H. Green, *Catal. Lett.*, 71 (2001) 49.
- [2] Y. Wang and Y. Ohtsuka, *J. Catal.*, 192 (2000) 252.
- [3] Istadi, N.A.S. Amin, *Chem. Eng. J.*, 106 (2005) 213.
- [4] M. Boaro, M. Vicario, C.D. Leitenburg, G. Dolcetti, A. Trovarelli, *Catal. Today*, 77 (2003) 407.
- [5] J. Kaspar, P. Fornasiero, M. Graziani, *Catal. Today*, 50 (1999) 285.
- [6] L.E. Cadus, O. Ferretti, *Appl. Catal. A*, 233 (2002) 239.
- [7] Y. Wang, Y. Ohtsuka, *Appl. Catal. A*, 219 (2001) 183.
- [8] Istadi and N.A.S. Amin, *J. Nat. Gas Chem.*, 13 (2004) 23.
- [9] V.R. Choudhary, S.A.R. Mulla, B.S. Uphade, *Fuel*, 78 (1999) 427.
- [10] Y. Wang, Y. Takahashi and Y. Ohtsuka, *J. Catal.*, 186 (1999) 160.