NEW DEVELOPMENTS AND APPLICATION IN CHEMICAL REACTION ENGINEERING

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Preface

This Proceedings of APCRE'05 contains the articles that were presented at the 8th Asia-Pacific Chemical Reaction Engineering Symposium (APCRE'05), held at Gyeongju, Korea between June 12 and June 15, 2005, with a theme of "New Opportunities of Chemical Reaction Engineering in Asia-Pacific Region". The authors were invited to submit their manuscripts during the APCRE'05 at Gyeongju. It was understood that every manuscript should be reviewed by two experts in the corresponding area and, if accepted, the manuscripts will be published in the book series "Studies in Surface Science and Catalysis" by Elsevier BV early in 2006.

Following the tradition of APCRE Symposia and ISCER, the scientific program encompassed a wide spectrum of topics, including not only the traditional areas but also the emerging fields of chemical reaction engineering into which the chemical reaction engineers have successfully spearheaded and made significant contributions in recent years. Indeed, APCRE'05 focused on the following areas and naturally the articles are classified into the same areas as in the APCRE'05:

- Biological and Biochemical Reaction Engineering
- Catalysis and Catalytic Reaction Engineering
- Chemical Reaction Engineering in Microelectronics
- Environmental Reaction Engineering
- Fluidized Bed and Multiphase Reactors
- Fuel Cells and Electrochemical Reaction Engineering
- Micro-reaction Technology
- Modeling, Simulation and Control of Chemical Reaction Systems
- Nano Materials Synthesis and Application
- Novel Reactors and Processes
- Polymer Reaction Engineering

Out of 284 papers presented at APCRE'05, 190 papers have been accepted after a cautious review process and included in this Volume. In addition, six plenary lectures and 11 invited lectures are placed in two separate chapters in the front. One
author was allowed to have no more than four articles in the Proceedings. The articles were contributed by chemical reaction engineers and scholars from academic and R&D sector as well as from industrial sector, representing 16 countries not only from the Asia-Pacific region but from the western hemisphere.

We would like to express our sincere gratitude to all the authors for their valuable contribution and to the members of the Organizing Committee for sparing their valuable time and efforts to carry out the review process so successfully. We hope that this Proceedings may serve as noticeable references for the scientific and industrial communities in the years to come, contribute to make an overview of new developments and application in chemical reaction engineering, and allow chemical reaction engineering to make its full contribution to further advancement of respective countries in the Asia-Pacific region and other parts of the world.

Hyun-Ku Rhee
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December 20, 2005
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Selective Conversion of Methane to C2 Hydrocarbons using Carbos Dioxide as an Oxidant over CaO-MnO/CoO2 Catalyst

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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 CH4 conversion and C2 hydrocarbon yield, which may be due to the synergistic effect among CO2, CaO and MnO in the catalyst. The C2 hydrocarbons selectivity and yield ≤ 75.6% and 3.9%, respectively were achieved over the 12.8CaO-6.4MnO/CoO2 catalyst. The catalyst showed a good stability for 20h time on stream in the CO2 OCM process.

1. INTRODUCTION

Direct conversion of methane to ethane and ethylene (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 where the process utilizes CO2 as the feedstock in an environmentally-benefiting chemical process. Carbon dioxide rather than oxygen seems to be an alternative oxidant as methyl radicals are induced in the presence of oxygen. Basicity, reducibility, and ability of catalyst to form oxygen vacancies are some of the physio-chemical criteria that are essential in designing a suitable catalyst for the CO2 OCM process [2]. The synergism between catalyst reducibility and basicity was reported to play an important role in the activation of the carbon dioxide and methane reaction [2].

In this paper, the selective conversion of methane to C2 hydrocarbons over ternary CaO-MnO-CoO2 catalysts in the CO2 OCM process are presented. The synergistic effect within catalyst reducibility and distribution of basic sites are highlighted. The most promising catalyst was then tested towards its stability.

2. EXPERIMENTAL

The first ternary metal oxide catalyst of CaO-MnO-CoO2 was prepared by simultaneous impregnation method, while the second ternary metal oxide of CaO-MnO-CoO2 catalyst was prepared by combination of co-precipitation and impregnation method. The catalysts composition used in this paper were based on multi response optimization result [3]. TG-TPR was carried out using Micromeritics 2900 TPD/TPR equipped by TCD. A catalyst amount of
about 0.05 g was purged with Ar (25 cm$^3$ min$^{-1}$) at 773 K for 1 h and was cooled down to room temperature. The flow of 6% H$_2$ in Ar (25 cm$^3$ 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$^{-1}$. CO$_2$-TPD was carried out using Micromeritics 2900 TPD/TPR equipment by TCD. The catalyst samples of about 0.05 g each were initially calcined at 1073 K in a flow of argon (25 cm$^3$ min$^{-1}$) for 1 h. The chemisorption of CO$_2$ was carried out at 373 K by flowing CO$_2$ (25 cm$^3$ min$^{-1}$) for 1 h. The excess of CO$_2$ was purged in a flow of Ar (25 cm$^3$ min$^{-1}$) for 1 h. The sample was then heated at 1223 K at a linear heating rate of 5 K min$^{-1}$ in a flow of Ar (25 cm$^3$ min$^{-1}$). The amount of H$_2$ uptake and the amount of CO$_2$ desorbed in both characterizations were detected using TCD. The performances of the catalysts were tested using a fixed-bed quartz reactor at the following conditions: reaction temperature = 1123 K; CH$_4$/CO$_2$ = 1/2; feed flow rate = 100 ml min$^{-1}$; catalyst loading = 2 g. Before reaction, the catalyst was recalcined at 1123 K in air flow for 1 h and was flushed with high purity nitrogen at 1123 K for another 1 h. The products and the unreacted gases were analyzed by an online GC equipped with a thermal conductivity detector and ORAPAK-Q packed-column.

3. RESULTS AND DISCUSSION

3.1. Catalyst Characterization

The H$_2$-TPR peaks of CeO$_2$-based catalysts are presented in Fig. 1. The reduction of CeO$_2$ appears at about 300 °C and two broad peaks are observed at about 540 (weaker intensity) and 770 °C [4]. The TPR peak at 540 °C is assigned to the reduction of surface-capping oxides of ceria [4], while the peak at 770 °C is attributed to the reduction of bulk oxides of CeO$_2$. This reduction is associated to an increased reducibility of the bulk mixed oxides, which is evident in Figs. 1(c) and 1(d) as the H$_2$-TPR peaks shift from 770 °C to 750 °C and 740 °C for the CaO-MnO/CoO catalysts, respectively. The introduction of manganese strongly modifies the reduction behavior of CeO$_2$ by shifting the most peak of H$_2$ consumption to a lower temperature [5]. The TPR peak shifts show that the reducibility of both catalysts is different. The promotion of Ce$^{3+}$ reduction is related to higher mobility of oxygen from chemisorbed CO$_2$ due to the introduction of manganese. The reduction of surface capping oxygen of CaO-MnO-CoO catalyst shifted to higher temperature (from 540 to 580 °C) due to strong interaction effect of MnO, and CeO$_2$-support. The interaction also generates a new strong H$_2$-TPR peak at about 510 °C which is attributed to reduction of Mn$_3$O$_4$, or MnO to Mn$_2$O$_3$. Meanwhile, the new small peak is also appeared at about 398 °C due to the interaction effect. The H$_2$-TPR spectra as depicted in Fig.1 reveal that the CaO-MnO-CoO catalyst has moderate reducibility with high medium and strong basic sites (CO$_2$-TPD). It shows that the CaO-MnO-CoO catalyst has higher MnO$_2$ content (than the CaO-MnO-CoO catalyst) as indicated by high intensity of TPR peak at 540 °C. The very small peak within the temperature range of 300-400 °C indicates that the catalyst synthesis method brings about a little proportion of Mn$_2$O$_3$ in the surface of CaO-MnO-CoO catalyst which may be due to the formation of solid solution of Ca$_2$Mn$_3$O$_8$. The strong H$_2$-TPR peak at about 510 °C is assigned to the reduction of Mn$_3$O$_4$, or MnO to Mn$_2$O$_3$, while the peak at about 580 °C is attributed to the final reduction from Mn$_2$O$_3$ to MnO. The color change of the catalyst from black to brown and/or grey during the reaction is in agreement with the results of H$_2$-TPR peaks [6].

The CO$_2$-TPD curves demonstrating the basic strength distribution of different CeO$_2$-based catalysts are presented in Fig. 2. From the figure, the distribution of basic sites for each catalyst indicates that the basicity and base strength distributions are significantly influenced by CaO and its interaction with MnO in the CeO$_2$-based catalysts. The
CO2-TPD spectra obviously exhibit that the CaO/CoO catalyst gives the largest number of very strong basic sites, followed by CaO/MnO-CoO and CaO-MnO-CoO catalysts. According to Figs. (2b-d), the doping CaO on the CoO-based catalyst 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 CoO catalyst [7]. The CO2-TPD spectra in Figs. 2(c) and 2(d) show different peaks giving to the total number of medium and strong basic sites. Impregnation of calcium and manganese nitrate solutions to the CoO catalyst lead to higher distribution of medium and strong basic sites rather than when the MnO-CoO solid solution is used as the support. The CO2-TPD peak of medium basic sites becomes more intense significantly for CoO-MnO and CaO-MnO-CoO catalysts, but not for CaO-MnO-CoO catalyst.

3.2 Catalyst Activity and Correlation with Catalyst Basicity and Reducibility

The screening results of CO2-based catalysts over binary and ternary metal oxides in Table 1 indicate that the 12.8CaO-6.4MnO-CoO catalyst is the most potential [8] with CH4 conversion, C2 selectivity and yield being 51.7%, 74.6%, and 3.9%, respectively. Addition of CaO to the pure CoO catalyst results in a significant increase in the C2 hydrocarbon selectivity. The enhancement in the C2 yield is possible due to the synergistic effect of MnO and CoO, where the reducibility of the catalyst is increased as revealed in the H2-TPR results (Fig. 1). Our present study indicates that there exists a correlation between basic sites distribution, catalyst reducibility and catalytic activity toward C2 hydrocarbons production as exposed in CO2-TPD result (Fig. 2). The CaO species is suggested to play an important role in CO2 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 C2 hydrocarbons [2,9]. The MnO species evidently increases the reducibility of CoO due to increasing oxygen mobility of the CoO-Catalyst which enhances its reducibility and produces more oxygen vacancies [2]. The catalyst also shows high stability during 20 h time on steam for CO2 OCM as revealed in Fig. 3.

Previously, we performed single- and multi-response optimization works in order to address optimal catalyst composition (%CaO and %MnO) and optimal operating conditions (temperature and CO2/CH4 feed ratio) [5]. The maximum C2 selectivity and yield of 76.6% and 3.7% respectively were achieved in multi-response optimization over the 12.8CaO-6.4MnO-CoO catalyst corresponding to the optimum reactor temperature being 1177 K and CO2/CH4 ratio being 2 [5]. The recent contribution on the catalytic technology of CO2 OCM was
developed by He et al. [11] using nano-CeO$_2$/ZnO catalyst achieved C$_2$ yield 4.8% and selectivity 83.6% at 1098 K. Due to still low yield in CO$_2$ OCM, further improvements are required including the exploitation of some non-conventional technologies.

Table 1. Catalysts performance results of CO$_2$-based catalysts [3,8]

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CH$_4$ conversion (%)</th>
<th>C$_2$ selectivity (%)</th>
<th>C$_2$ yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$</td>
<td>13.2</td>
<td>9.1</td>
<td>1.2</td>
</tr>
<tr>
<td>12.8CeO$_2$/CeO$_2$</td>
<td>2.7</td>
<td>75.0</td>
<td>2.0</td>
</tr>
<tr>
<td>6.4MnO$_2$/CeO$_2$</td>
<td>8.8</td>
<td>3.1</td>
<td>0.3</td>
</tr>
<tr>
<td>12.8CeO$_2$/6.4MnO$_2$/CeO$_2$</td>
<td>5.3</td>
<td>62.2</td>
<td>3.3</td>
</tr>
<tr>
<td>12.8CeO$_2$/6.4MnO$_2$/CeO$_2$</td>
<td>5.1</td>
<td>75.6</td>
<td>3.9</td>
</tr>
</tbody>
</table>

Fig. 3. Stability test of 12.8CeO$_2$/6.4MnO$_2$/CeO$_2$ catalyst in CO$_2$ OCM reaction

4. CONCLUSIONS

Addition of CeO and MnO to the CeO$_2$ catalyst increased the CH$_4$ conversion and C$_2$ hydrocarbons yield in CO$_2$ OCM. The enhancement may be due to the synergistic effects between highly number of medium and strong basic sites and high reducibility of catalyst. The 12.8CeO$_2$/6.4MnO$_2$/CeO$_2$ catalyst exhibited better performance and high stability for the CO$_2$ OCM process.

REFERENCES
Hensin H.
Hardiman K.M.
Haroot T.
Havil J.
Hayashi H.
Huang S.-J.
Huang S.-W.
Huang T.
Huang Y.-H.
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