

THE EFFECT OF OXYGEN IN CARBON DIOXIDE REFORMING OF METHANE OVER A RH(5 wt%)/ Al_2O_3 CATALYST

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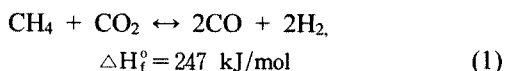
(received January 2002, accepted August 2002)

Abstract: The effect of oxygen in carbon dioxide reforming of methane to eliminate the green house gas over a Rh(5 wt%)/ Al_2O_3 catalyst was discussed based on the results of reaction in a fixed bed reactor under atmospheric condition and also on analysis results by SEM, FT-IR, and XRD. The added oxygen with 6.0 mol% of the feed did not only enhance the catalytic activity, but also seemed to almost completely prevent the carbon deposition on the Rh(5 wt%)/ Al_2O_3 catalyst surface. It could be suggested that the oxygen stimulates redispersion of Rh by providing oxidative atmosphere.

Key Words: carbon dioxide reforming, methane, oxygen, redispersion, Rh/ Al_2O_3

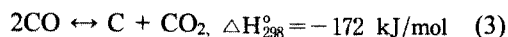
INTRODUCTION

The reduction of the green house gases such as carbon dioxide and methane is an urgent task for the earth. So far, in order to resolve this problem, the reforming of carbon dioxide of methane to syngas has been studied by many researchers.¹⁻³⁾



By utilizing this reaction, it is expected not only to reduce the green house gases but also to reuse carbon resources for a feedstock of petrochemicals.^{4,5)} However, in order for this reaction to occur, temperatures of 973~1,073 K or higher⁶⁾ are required, and the catalytic methane decomposition reaction (2) or Boudouard

reaction⁷⁾ (3) occurs on the catalyst surface as follows :

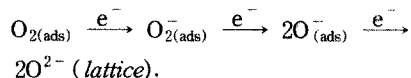


Rostrup-Nielsen et al.⁸⁾ and Tsang et al.⁹⁾ suggested that carbon deposition should be an inevitable problem in carbon dioxide reforming of methane to syngas. Gronchi et al.¹⁰⁾ proposed that the specific carbon deposition rate should be 20~30 times greater in the presence of Rh/ La_2O_3 than Rh/ SiO_2 . Zhang and Verykios¹¹⁾ suggested that three types of carbonaceous species, C_α , C_β , and C_γ can be found to exist on Ni catalysts. Scientists^{12,13)} in the world have made every effort to reduce carbon deposition on the catalysts, but it has remained unsolved yet. In addition, the oxygen species transform upon adsorption on a metal oxide according to the follow scheme :

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It could be suggested that the gaseous oxygen after adsorption change to the active species, O^- or O^{2-} , and then activate the metal oxide catalyst. This study attempts to investigate the effect of oxygen in carbon dioxide reforming over a Rh(5 wt%)/ Al_2O_3 catalyst by conducting catalytic measurements, SEM, FT-IR, and XRD analyses.

MATERIALS AND METHODS

Catalyst Preparation

The catalyst used in this study was Rh(5 wt%)/ Al_2O_3 (Aldrich products). It was calcined in an electric furnace (Eyela, TMF-1000, Japan) under air for 5 hours at 1,023 K. Then, it was ground to the size between 150 and 200 mesh.

Catalytic Reaction

The catalytic reaction was carried out under atmospheric pressure in a fixed bed flow reactor. A quartz tube of 6 mm inside diameter was used as the reactor. The catalyst powder of 2.0×10^{-5} kg was held on quartz wool. The CO_2/CH_4 molar ratio, temperature, and contact time of reactant gas were 1 mol $\text{CO}_2/\text{mol CH}_4$, 1023 K, and 6.34×10^{-5} kg-cat · s/mL, respectively. The reactor was maintained at a desired temperature with an accuracy of ± 1 K by a K-type thermocouple and PID-controller. The composition of reactant gas was controlled by a pressure regulator attached to each gas cylinder and then by each mass flow meter. The effluent was analyzed with an on-line G.C. (Shimadzu Co., Model 14B, Japan) with a thermal conductivity detector using Porapak Q and Molecular sieve 5 A columns in parallel. The fresh catalyst was reduced in hydrogen with a flow rate of 4.17×10^{-1} mL/s at 773 K for 5 hrs, then the temperature was increased to 1,023 K at a rate of 4.88 K/s. After reduction, the reacting gases were introduced. The yields are defined to analyze the activity of the

catalysts as follows :

% yield of carbon monoxide = (moles of carbon monoxide product/input moles of methane and carbon dioxide) $\times 100$,

% yield of hydrogen = (moles of hydrogen product/2*input moles of methane) $\times 100$.

Catalyst Characterization by SEM, FT-IR, and XRD

Morphology of catalysts was observed by using a SEM (Hitachi, S-4700, Japan). The infrared spectra were obtained by the transmission mode using FT-IR (Bomen, DA-8, Canada) spectroscopy. X-ray powder diffraction was carried out by a Rikagu X-ray diffraction equipment at 34 kV and 40 mA using the $\text{CuK}\alpha$ radiation.

RESULTS AND DISCUSSION

Figure 1 shows the effect of oxygen in carbon dioxide reforming of methane over the Rh(5 wt%)/ Al_2O_3 catalyst. It clearly shows that the addition of oxygen with a flow rate of 2.0×10^{-2} mL O_2/s to the reactants enhances the catalytic activity significantly. The enhancement of the activity was repeatedly observed by adding the oxygen again after stopping the oxygen flow. In addition, Figure 1 showed that

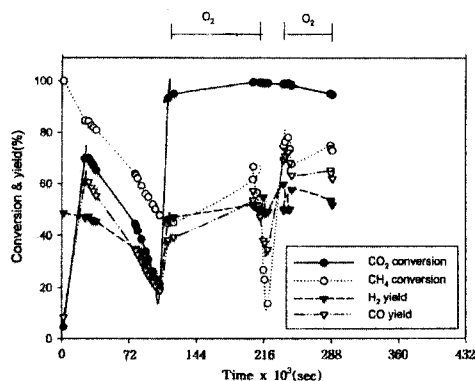


Figure 1. The effect of oxygen addition in CO_2 reforming of CH_4 over Rh(5 wt%)/ Al_2O_3 catalyst : Temp., 1023 K; W/F, 6.34×10^{-5} kg-cat · s/mL; 1 mol $\text{CO}_2/\text{mol CH}_4$.

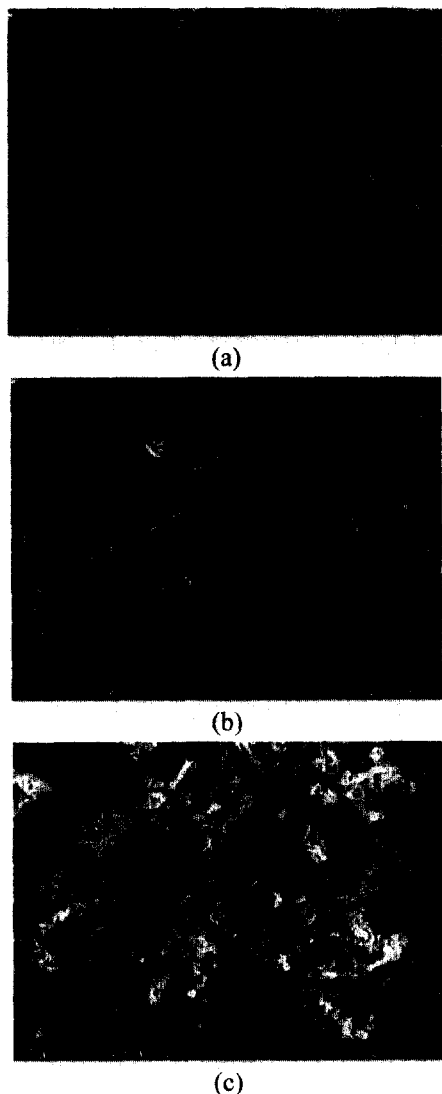


Figure 2. Scanning electron micrographs of Rh(5 wt%)/Al₂O₃ catalyst: (a) before reaction, (b) after reaction with addition of oxygen, (c), after reaction without addition of oxygen.

after 2.0×10^{-2} mL O₂/s of oxygen was added to the reactants, conversion of CH₄ and CO₂ and yield of CO and H₂ increased sharply. The phenomenon like this was considered occurring partial oxidation of CH₄ (4) with carbon dioxide reforming (1).

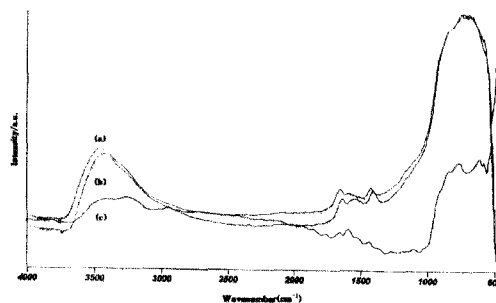
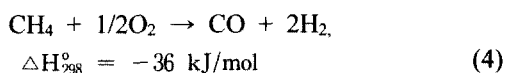


Figure 3. FT-IR spectra of Rh(5 wt%)/Al₂O₃ catalyst : (a) after reaction with oxygen, (b) before reaction, (c) after reaction without oxygen.

Scanning electron micrographs of the Rh(5 wt%)/Al₂O₃ catalyst are presented in Figure 2. It was observed that the Rh(5 wt%)/Al₂O₃ catalyst before reaction has small particles of Rh uniformly distributed on the catalyst surface. However, the Rh(5 wt%)/Al₂O₃ catalyst after reaction without oxygen showed that "tube", "filamentous", and "encapsulate" type carbon was deposited on the catalyst surface, but after reaction with oxygen the carbon deposition was barely seen on the catalytic surface up to 80 hours. Figure 3 shows FT-IR spectra for the Rh(5 wt%)/Al₂O₃ catalyst before reaction and after reaction without oxygen and with oxygen, 2.0×10^{-2} mL O₂/s. FT-IR spectra before reaction and after reaction with oxygen, 2.0×10^{-2} mL O₂/s were similar, but after reaction without oxygen it was quite different from the others. The absorption band of C-O or C-C were assigned in $1,242 \sim 810 \text{ cm}^{-1}$ region. The C=O absorption band appeared at $1,634 \text{ cm}^{-1}$, CH₃ absorption band was assigned at $1,404 \text{ cm}^{-1}$, and that of C=C was assigned at $1,573 \text{ cm}^{-1}$. Also, the asymmetrical stretching absorption band of CH₃ assigned at $2,925 \text{ cm}^{-1}$ was observed weakly. The absorption band of OH was assigned at $3,433 \text{ cm}^{-1}$. These results suggest that the addition of oxygen, 2.0×10^{-2} mL O₂/s to the reactants keeps particularly the steady state of -OH, CH₃, and C=O adsorbed on the catalyst surface as well as the elimination of carbon on the catalyst surface, and thus increases the catalytic activity. Hence,

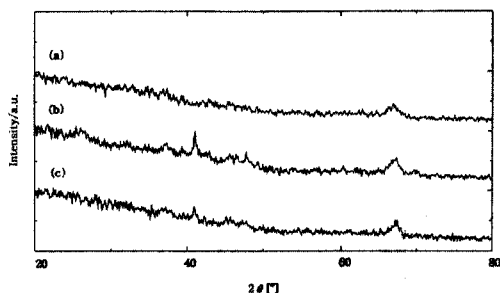


Figure 4. XRD patterns of Rh(5 wt%)/Al₂O₃ catalyst : (a) before reaction, (b) after reaction without oxygen, (c) after reaction with oxygen.

the following reaction scheme may be proposed.

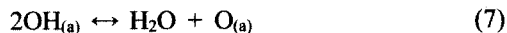


Figure 4 shows the XRD spectra of the Rh(5 wt%)/Al₂O₃ catalyst before and after reaction without and with oxygen. XRD peaks observed after reaction without oxygen were the Rh(111) plane at $2\theta = 40.9^\circ$ and Rh(200) plane at $2\theta = 47.7^\circ$, respectively, but the XRD pattern after reaction with oxygen showed only the Rh(111) peak at $2\theta = 40.9^\circ$ which was smaller than that after reaction without oxygen, and the Rh(200) peak did not appear. In addition, the XRD pattern before reaction did not show any Rh crystalline phases - the amorphous X-ray. Figure 5 shows scanning electron micrographs of Rh(5 wt%)/Al₂O₃ catalyst before reaction and after reaction with oxygen. It seemed that noble metal particles of Rh dispersed well in the Al₂O₃ matrix owing to the addition of oxygen. It is considered that the crystalline phases were not formed by sintering between Rh metals, but the amorphous phases were

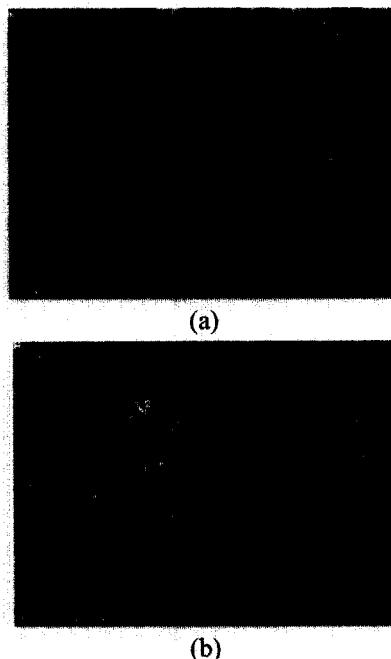


Figure 5. Scanning electron micrographs of Rh(5 wt%)/Al₂O₃ catalyst : (a) before reaction, (b) after reaction with addition of oxygen.

formed by redispersion of very small Rh metals. In addition, Ruckenstein¹⁴⁾ proposed that the redispersion could be stimulated by oxidative atmosphere, whereas the sintering could be stimulated by reductive atmosphere. It could be suggested that the oxygen stimulate redispersion of Rh by providing oxidative atmosphere, i.e. $2\text{Rh}^0 + 3\text{O}_2 + [*] \rightarrow 2\text{Rh}^{+3} + 3[\text{O}^{2-}]$, and thus the catalytic activity could be increased. In addition, it is considered that the redispersion¹⁵⁾ should occur because the surface free energy of Rh on Al₂O₃ under oxidizing conditions decreased.

ACKNOWLEDGEMENTS

This study is supported by Yosu National University through research fund (2000 year).

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