

CARBON NANOTUBES RESULTED FROM THE CARBON DIOXIDE REFORMING BY CATALYTIC PYROLYSIS TO REDUCE THE GREENHOUSE GAS

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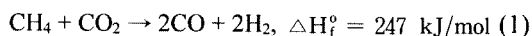
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Abstract : Carbon nanotubes formed in carbon dioxide reforming (CDR) by catalytic pyrolysis were discussed on the basis of analysis results by SEM, TEM, and FT-IR. The only active phases of Rh or Pd on Al₂O₃ matrix were responsible for making carbon nanotubes, and the whisker carbon was produced on Rh(5)/Ce(1)/Al₂O₃ and Rh(5)/La₂O₃ catalyst. The mechanism of carbon nanotubes growth was proposed that carbon formed by methane cracking and Boudouard reaction dissolve in the metal (Pd, Rh), and then the bulk and surface diffusion of dissolved carbon occur through the metal particle (Pd, Rh). The CDR by catalytic pyrolysis over Pd(5)/Al₂O₃ and Rh(5)/Al₂O₃ catalysts was suggested to be useful for the effective preparation of carbon nanotubes.

Key Words : carbon nanotubes, catalytic pyrolysis, CO₂ reforming, greenhouse gas

INTRODUCTION

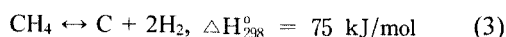
Carbon dioxide contributes to 61 percent effect¹⁾ among the greenhouse gas for the earth, and in the future its emission will increase continuously. In addition, methane, waste gas of filled-up-land is alternative energy resources of petrochemicals and is one of the greenhouse gas. In order to reduce concentration of carbon dioxide, the CDR (carbon dioxide reforming) of methane to syngas (CO + H₂), the basic chemicals of C₁ chemistry has been studied by many researchers.^{2~4)}



This would not make it possible only resolving the greenhouse effect problem, but also reusing carbon resources for a feedstock of petrochemicals.^{5~7)} However, Park *et al.*⁸⁾ reported that in order to enhance this reaction (1) and reduce water gas shift reaction (2), side reaction, high temperature of 973~1,073 K was required



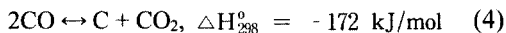
Moreover, the methane cracking (3) and the Boudouard reaction (4) to promote carbon formation on the catalyst surface under this reaction condition, these reactions are as follows :



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The highly active catalysts for the CDR by catalytic pyrolysis are generally known as the noble metals (Ir, Pd, Pt, Rh, Ru, etc.) and nickel metal.^{9,10)} Rostrup-Nielsen and Hansen¹¹⁾ and Tsang *et al.*¹²⁾ suggested that carbon deposition be inevitable problem in the CDR of methane to syngas. Zang and Verykios¹³⁾ suggested that three types of carbonaceous species, C_α , C_β , and C_γ be found to exist on nickel catalysts. Cardge *et al.*¹⁴⁾ and Bradford and Vannice¹⁵⁾ reported that nickel promoted catalyst produced the filamentous and encapsulated carbon on the catalyst surface, and Bradford and Vannice¹⁵⁾ proposed that noble metal promoted catalysts did not almost produce carbon on it. But, so far, the carbon species have not been reported based on the noble metal promoted catalyst. This study attempts to investigate carbon species and the reaction path of carbon formation with CDR by catalytic pyrolysis over noble metal (Pd, Rh) supported on metal oxide catalysts, and also by analysing the results by SEM, TEM, and FT-IR.

MATERIALS AND METHODS

Catalyst Preparation and CDR Reaction

The commercial Pd(5 wt%) and Rh(5 wt%) supported on Al_2O_3 (Aldrich product) catalysts were used as a catalyst in this study. A number in parenthesis is the amount of impregnation which is indicated to weight percent. In addition, La_2O_3 (Junsei chemicals) catalyst impregnated with $\text{RhCl}_3 \cdot 6\text{H}_2\text{O}$ (Aldrich product) and CeO_2 (Junsei chemicals) promoted Rh(5)/ Al_2O_3 catalyst were used. Reagent were extra pure grades. Lanthanum oxide and $\text{RhCl}_3 \cdot 6\text{H}_2\text{O}$, precursor and CeO_2 and Rh(5)/ Al_2O_3 were homogeneously mixed with deionized water by a stirrer. The solution was kept less than 373 K on a hot plate until water was completely evaporated, and then the paste was entirely dried at 393 K in an oven for 24 hr, followed by the calcination in an electric

furnace (Eyela, TMF-1000, Japan) under air for 24 hr at 1,023 K. Then, it was ground to the size between 150 and 200 mesh. The CDR by catalytic pyrolysis was carried out under atmospheric pressure in a fixed bed flow reactor. A quartz tube of 6 mm inside diameter was used as a reactor. The catalyst powder of 0.02 g was held on quartz wool. The molar ratio of CO_2 to CH_4 molar ratio was adjusted to one, and the temperature, and contact time of reactant gas were 1,023 K, and 6.34×10^{-5} kg-cat · sec/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 reactants purged with a pressure regulator attached to each gas cylinder and then the composition of reactants was controlled by each mass flow meter. The fresh catalyst was reduced before exposing reactant in hydrogen flow of 0.4 mL/sec at 773 K for 5 hr, then the temperature was increased to 1,023 K with a ramping rate of 4.88 K/sec.

Catalyst Characterization by SEM, TEM, and FT-IR

Morphology of catalysts was observed by using a SEM (Hitachi, S-4700, Japan) at 10^{-6} torr and 20 kV, and by using a TEM (Jeol, JEM-2000 FXII, Japan) at 10^{-5} Pa and 200 kV. The infrared spectra were obtained by the transmission mode using FT-IR (Bomen, DA-8, Canada).

RESULTS AND DISCUSSION

Scanning electron micrographs of Pd(5)/ Al_2O_3 and Rh(5)/ Al_2O_3 catalyst were presented in Figure 1. It was observed that Pd(5)/ Al_2O_3 and Rh(5)/ Al_2O_3 catalyst produced a lot of carbon nanotubes on catalyst surface. Figure 2 showed transmission electron micrographs of Pd(5)/ Al_2O_3 and Rh(5)/ Al_2O_3 catalyst after reaction. These clearly showed carbon nanotubes to be made well on the Pd(5)/ Al_2O_3 and Rh(5)/ Al_2O_3 catalyst. Scanning electron micrographs of Pd(5)/ Al_2O_3 and Rh(5)/ Al_2O_3 catalyst before

Figure 1. Scanning electron micrographs of carbon nanotubes formed on noble metal(Pd, Rh) supported on Al_2O_3 catalysts after CDR reaction: (a), Pd (5 wt%)/ Al_2O_3 ; (b), Rh(5 wt%)/ Al_2O_3 .

reaction were represented in Figure 3. It would seem that the noble metal particles of Pd or Rh diffused well on the Al_2O_3 carrier. In addition, the mechanism of carbon nanotubes growth was suggested that carbon formed by methane cracking (3) and Boudouard reaction (4) dissolve in the metal (Pd, Rh), and then the bulk and surface diffusion of dissolved carbon occur through the metal particle (Pd, Rh) in Figure 2 and 3. This is consistent with the mechanism of carbon growth given by Harris.¹⁶⁾

Figure 4 showed scanning electron micrographs of Rh(5)/Ce(1)/ Al_2O_3 and Rh(5)/ La_2O_3 catalyst. It was observed that the whisker carbon was produced on catalyst surface. These were convinced that carbon nanotubes produced only Pd or Rh catalyst supported on Al_2O_3 . Figure 5 showed FT-IR spectra for the Pd(5)/ Al_2O_3 and Rh(5)/ Al_2O_3 catalyst after reaction. It was

Figure 2. Transmission electron micrographs of carbon nanotubes formed on noble metal(Pd, Rh) supported on Al_2O_3 catalysts after CDR reaction: (a), Pd(5 wt%)/ Al_2O_3 ; (b), Rh(5 wt%)/ Al_2O_3 .

observed that FT-IR spectra of them were similar. The bending absorption band of CH_2 was appeared at 592 and 602 cm^{-1} , and the rocking absorption band of CH_2 was appeared at 734 and 745 cm^{-1} . The C-C stretching absorption band assigned in 988-1,243 cm^{-1} region, the twisting absorption band of CH_2 appeared 1,309 cm^{-1} , and the C=C absorption band appeared at 1,573 cm^{-1} , respectively. The asymmetrical stretching absorption band of CH_3 assigned at 2,925 cm^{-1} was observed weakly. These could be suggested that carbon nanotubes may be produced by sequence of methane cracking i.e. $\text{CH}_4 \rightarrow (\text{CH})_x \rightarrow \text{C}$.

The equilibrium constants for coking reactions over nickel catalysts were represented in Figure 6. Richardson¹⁷⁾ reported that the equilibrium constants of coking formation of methane cracking and Boudouard reaction were 1.15

Figure 3. Scanning electron micrographs of Pd(5 wt%)/Al₂O₃ and Rh(5 wt%)/Al₂O₃ catalysts before CDR reaction: (a), Pd(5 wt%)/Al₂O₃; (b), Rh(5 wt%)/Al₂O₃.

and -0.62 at 1,023 K, respectively, and also reported that in 873~1,023 K of reaction temperature, methane cracking dominated and reverse Boudouard reaction occurred, thermodynamically. In addition, Trvares *et al.*¹⁸⁾ suggested that the encapsulated carbon be produced in the mixture of CO/CO₂ gas, but the filamentous carbon be produced in the mixture of CH₄/H₂ gas. Claridge *et al.*¹⁴⁾ reported that carbon deposition did not occur on the pure alumina, but occurred on only metal. These convinced that carbon nanotubes could be made on the surface of Pd(5)/Al₂O₃ and Rh(5)/Al₂O₃ catalysts by methane cracking (3).

CONCLUSIONS

Carbon nanotubes were made on only

Figure 4. Scanning electron micrographs of whisker carbon formed on Rh(5 wt%)/Ce(1 wt%)/Al₂O₃ and Rh(5 wt%)/La₂O₃ catalysts after CDR reaction: (a), Rh(5 wt%)/Ce(1 wt%)/Al₂O₃; (b), Rh(5 wt%)/La₂O₃.

Pd(5)/Al₂O₃ and Rh(5)/Al₂O₃ catalysts in CDR by catalytic pyrolysis, and the whisker type carbon was made on Rh(5)/Ce(1)/Al₂O₃ and Rh(5)/La₂O₃ catalysts. The mechanism of carbon nanotubes growth was that carbon formed by methane cracking and Boudouard reaction dissolved in the metal (Pd, Rh), and then the bulk and surface diffusion of dissolved carbon occurred through the metal particle (Pd, Rh). The CDR by catalytic pyrolysis over Pd(5)/Al₂O₃ and Rh(5)/Al₂O₃ catalysts was useful for the effective preparation of carbon nanotubes.

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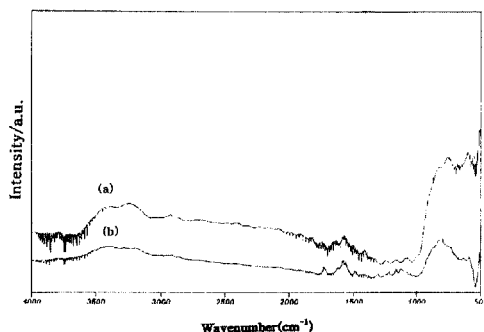


Figure 5. FT-IR spectra of noble metal(Rh, Pd) supported on Al_2O_3 catalysts after reaction: (a), Rh(5 wt%)/ Al_2O_3 ; (b), Pd(5 wt%)/ Al_2O_3 .

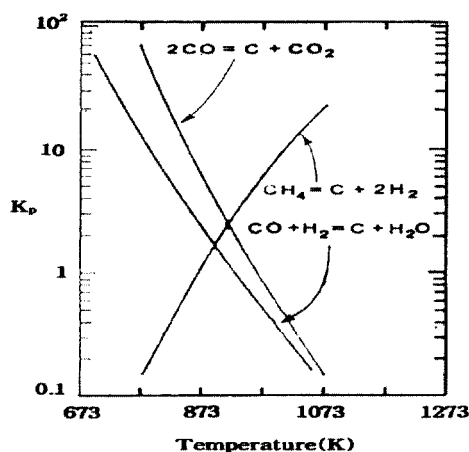


Figure 6. Equilibrium constants for coking reactions over nickel catalysts.⁽¹⁷⁾

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