THE PARTIAL COMBUSTION OF METHANE TO SYNGAS OVER PRECIOUS METALS AND NICKEL CATALYSTS SUPPORTED ON Υ-AL₂O₃ AND CEO₂
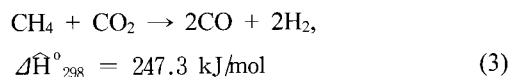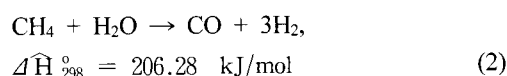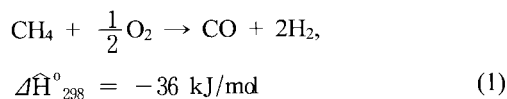
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Abstract : The catalytic activity of precious metals(Rh, Pd, Pt) and nickel catalysts supported on Υ-Al₂O₃ and CeO₂ in the partial combustion of methane(PCM) to syngas was investigated based on the product distribution in a fixed bed flow reactor under atmospheric condition and also on analysis results by SEM, XPS, TPD, BET, and XRD. The activity of the catalysts based on the syngas yield increased in the sequence Rh(5)/CeO₂≥Ni(5)/CeO₂>>Rh(5)/Al₂O₃>Pd(5)/Al₂O₃>Pt(5)/Al₂O₃>Ni(5)/Al₂O₃. Compared to the precious catalysts, the syngas yield and stability of the Ni(5)/CeO₂ catalyst were almost similar to Rh(5)/CeO₂ catalyst, and superior to these of any other catalysts. The syngas yield of Ni(5)/CeO₂ catalyst was 90.66% at 1023 K. It could be suggested to be the redox cycle of the successive reaction and formation of active site, Ni^{2+} and the lattice oxygen, O^{2-} produced due to reduction of Ce^{4+} to Ce^{3+}.

Key Words : Partial Combustion of Methane, Precious Metal Catalyst(Rh, Pd, Pt), Ni Catalyst, CeO₂, Al₂O₃, Redox cycle

INTRODUCTION

Methane, the main component of natural gas, is the one of alternative clean energy sources for petroleum and coal, and is a greenhouse gas.[1] A strategy for using methane is to convert methane into synthesis gas, H_2 and CO, by one method among the partial combustion, steam reforming, and CO_2 reforming as follows.

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2,$$
$$\Delta \hat{H}^{\circ}_{298} = -36 \ kJ/mol \tag{1}$$

$$CH_4 + H_2O \rightarrow CO + 3H_2,$$
$$\Delta \hat{H}^{\circ}_{298} = 206.28 \ kJ/mol \tag{2}$$

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$$CH_4 + CO_2 \rightarrow 2CO + 2H_2,$$
$$\Delta \hat{H}^{\circ}_{298} = 247.3 \ kJ/mol \tag{3}$$

This is expected not only to be used as a feedstock for products such as dimethylether, ethylene, and methanol,[1-3] but also to reduce the greenhouse gas. The PCM to synthesis gas has advantages due to exothermicity and suitable H_2/CO molar ratio compared to steam reforming from industrial point of view. Many studies have been reported concerning the PCM based on the precious and non-precious metal catalysis.[4-7] The catalysts based on the precious metal(Rh, Pd, Pt) and non-precious metal(Ni, Co, Fe) for PCM have shown the high activity, but the fast deactivation of the catalysts occurred due to a deposition[1,8] of inactive carbon on the catalyst surface. Therefore, the recent studies[9-13] of catalyst for PCM have been focussed on bet-

ween high activity and thermal stability by using the precious metal and non-precious metal impregnated on the various supports such as Υ-Al₂O₃, SiO₂, CeO₂, and MgO, etc. Thevenin et al.[13] reported that the presence of foreign ions such as Ba and La, etc. in Pd supported Υ-Al₂O₃ structure had a strong influence with respect to the stabilization of alumina when submitted to a temperature as high as 1273 K in PCM.

Especially, it has been known that ceria was very important as support or promoter due to redox properties, oxygen storage capacity, and thermal resistance.[14-15] Damyanova and Bueno[16] reported that addition of cerium oxide into Al₂O₃ supported Pt resulted in improvement of catalytic performance for reforming of methane with CO_2. Craciun et al.[17] suggested that the presence of CeO_2 as a promoter conferred high catalytic activity to the alumina-supported Pd catalysts used for methane steam reforming. Shan et al.[10] reported that the highest catalytic activity for methane combustion on $Ce_{0.7}Ni_{0.3}O_2$ catalyst was attributed not only to the highly dispersed Ni species but also to the more active oxygen species formed. Pengpanich et al.[5] proposed that the $Ni/Ce_{0.75}Zr_{0.25}O_2$ catalysts were found to resist to coke formation more than the Ni/ZrO_2 due to high degrees of metal dispersion and surface oxygen mobility. It is predicted that the properties of catalyst such as activity, stability, and the resistence of coke formation will be enhanced by impregnating the precious metals(Rh, Pd, Pt) and nickel on to CeO_2 in the PCM.

This study investigated the yield of methane to syngas over precious metals(Rh, Pd, Pt) and nickel catalysts supported on Υ-Al₂O₃ and CeO_2 by conducting catalytic activity experiments, and the active sites of economical and a excellent catalyst among the tested catalysts by SEM, XPS, BET, TPR, and XRD analysis.

MATERIALS AND METHODS

Catalyst Preparation

The commercial Pd(5) and Rh(5) catalysts supported on Al₂O₃ (Adrich products) 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, Al₂O₃ (Adrich products) catalyst impregnated with $H_2PtCl_6 \cdot xH_2O$ (Adrich products) and Al₂O₃ (Adrich products) catalyst impregnated with $Ni(NO_3)_2 \cdot 6H_2O$ (Adrich products) were prepared as previous study.[1] $Rh(5)/CeO_2$ and $Ni(5)/CeO_2$ catalysts were prepared by coprecipitation method. Reagents were extra pure grades. The $Ce(NO_3)_3 \cdot 6H_2O$ (Junsei chemicals) as supporter and $RhCl_3 \cdot 6H_2O$ (Adrich products), $Ni(NO_3)_2 \cdot 6H_2O$ as precursor were homogeneously mixed with deionized water by a stirrer, respectively and then precipitated 0.1N NH_4OH. The solution was filtered and then the precipitate was entirely dried at 393 K in a oven for 24 hr, followed by the calcination in an eletric furnace (Eyela, TMF-1000, Japan) under air for 5 hr at 1023 K. Then, it was ground to the size between 150 and 200 mesh.

Catalyst Characterization

Morphology of catalysts was observed by using a SEM (Hitachi, S-4700, Japan) at 1.33 x 10^{-7} kPa and 15kV. X-ray powder diffration was carried out on a Rikagu X-ray diffraction equipment(D/Max Uitima III, Japan) at 40kV and 40mA using the CuKα radiation. The BET surface area was obtained by nitrogen adsorption at 77.2 K using a Micrometrics ASAP 2020 instrument. The sample was degassed at 1.34 x 10^{-5} kPa before measurements. The XPS spectra were recorded with a VG-Scientific ESCALAB 250 spectrometer with monocromatized Al Kα X-ray source of 1486 eV. Temperature programmed reduction(TPR) response was obtained with G.C.(Shimadzu Co., Model 14B, Japan) with a TCD, using a H_2/Ar flow with 5mol% H_2 and a heating rate of 4.7 K/sec from 317 K upto 1123 K.

Reaction Procedure

The catalytic reaction was carried out under atmospheric pressure in a fixed bed flow reactor.

The inside diameter and length of quartz tube reactor were 6 x 10^{-3} m and 3 x 10^{-1} m, respectively. The catalyst powder of 3 x 10^{-5} kg was held on quartz wool. The CH_4/O_2 molar ratio, temperature, and contact time of reactant gas were 1 kmol CH_4/kmol O_2, 1023 K, and 6.01 x 10 kg-cat · sec/m^3, respectively. The reactor was maintained at a desired temperature with an acuracy 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 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 5A columns in parallel. The fresh catalyst was reduced before exposing reactant in hydrogen flow of 0.4 ml/sec at 773 K for 5hr, then the temperature was increased to 1023 K at a rate of 4.88 K/sec. After reduction, the reacting gases were introduced. The yield were defined to analyze the activity of the catalysts as follows :

% yield of carbon monoxide = (moles of carbon monoxide product/input moles of methane) × 100,

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

RESULTS AND DISCUSSION

Figure 1 and Figure 2 show yield of PCM to syngas over precious metals(Rh, Pd, Pt) and nickel catalysts supported on Υ-Al₂O₃ and CeO₂. It clearly shows that the activity of the catalyst based on the syngas yield increased in the sequence Rh(5)/CeO₂ ≥ Ni(5)/CeO₂ >> Rh(5)/Al₂O₃ > Pd(5)/Al₂O₃ > Pt(5)/Al₂O₃ > Ni(5)/Al₂O₃. Compared to the precious catalysts, the syngas yield and stability of the Ni(5)/CeO₂ catalyst were almost similar to Rh(5)/CeO₂ catalyst, and were superior to them of any other catalysts. The syngas yield of Ni(5)/CeO₂ catalyst were 90.66% at 1023 K. The syngas yield of the only carrier (CeO₂) was 0.69% at 1023 K.

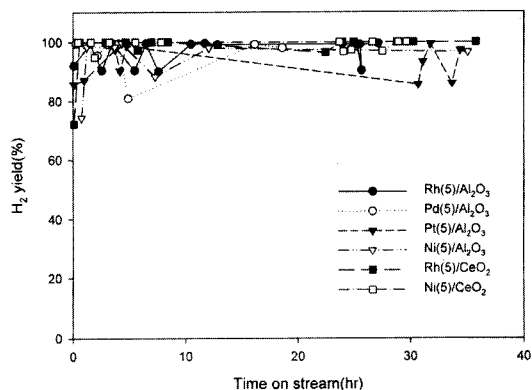
Figure 1. H₂ yield vs. time on stream over precious matals and nikel catalysts supported on carrier (Al₂O₃ and CeO₂): T, 1023K; CH₄/O₂ molar ratio, 1 kmolCH₄/kmolO₂; W/F, 6.01×10 kg-Cat.sec/m³.
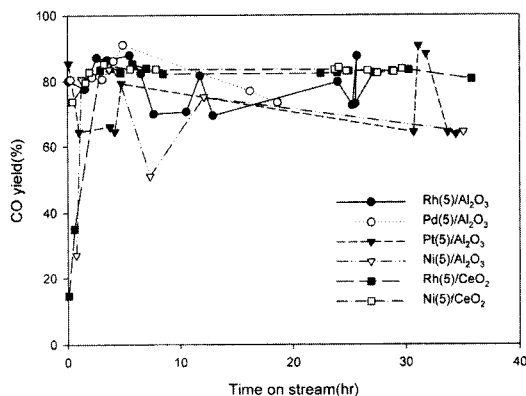

Figure 2. CO yield vs. time on stream over precious matals and nikel catalysts supported on carrier (Al₂O₃ and CeO₂): T, 1023K; CH₄/O₂ molar ratio, 1 kmolCH₄/kmolO₂; W/F, 6.01×10 kg-Cat.sec/m³.

SEM photographs of the Ni(5)/CeO₂ catalyst are presented in Figure 3. It is observed that the Ni(5)/CeO₂ catalyst before reaction has nano particles of Ni uniformly distributed on the surface catalyst. However, the Ni(5)/CeO₂ catalyst after reaction showed to be aggregation of the Ni particles by sintering, and also carbon deposited on the surface of the Ni(5)/CeO₂ catalyst was not observed.

Figure 4 shows the XRD specrta of the the Ni(5)/CeO₂ catalyst before and after reaction. XRD peaks observed before and after reaction except the Ni(011) plane at 2θ = 44.4[°] are
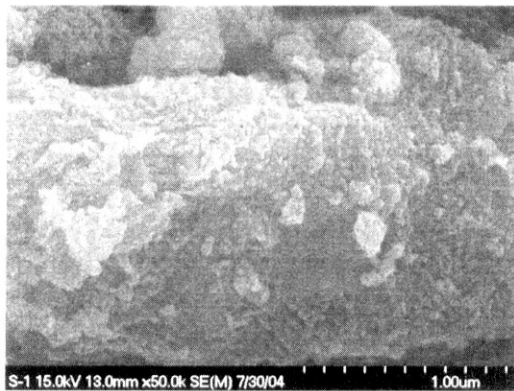
(a)
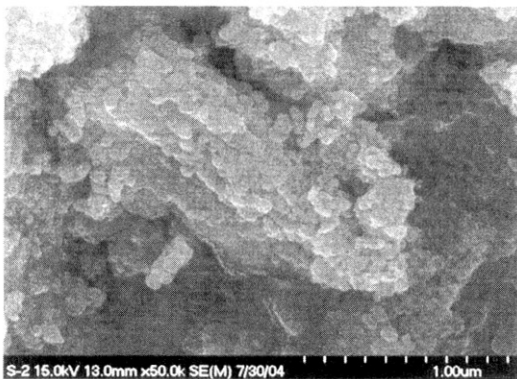
(b)

Figure 3. Scanning electron micrographs of Ni(5)/CeO₂ catalyst before and after reaction : (a), before reaction ; (b), after reaction.
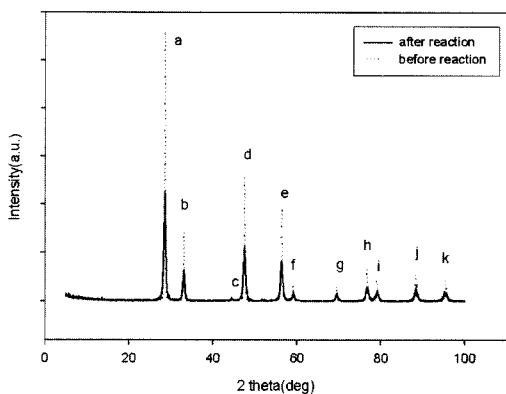

Figure 4. XRD patterns of Ni(5)/CeO₂ catalyst before and after reaction: a, CeO₂(111); b, CeO₂(200); c, Ni(011); d, CeO₂(220); e, CeO₂(311); f, CeO₂(222); g, CeO₂ (400); h, CeO₂(331); i, CeO₂(420); j, CeO₂(422); k, CeO₂(511).

Table 1. BET surface area of Ni(5)/CeO₂ catalyst before and after reaction

before reaction	after reaction
34.5 m²/g	7.3 m²/g

diffraction peaks of typical CeO_2. In addition, the width and intensity of XRD diffraction peaks before reaction show smaller and stronger than them after reaction. It prove that particles before reaction should be small, and the any crystallines of solid solution by interaction of Ni and CeO_2 are not in being. BET surface area of Ni(5)/CeO₂ catalyst before and after reaction were represented in Table 1. They were 34.5 m²/g and 7.3 m²/g, respectively.

BET surface area before reaction was 4.7 times of it after reaction. This means the aggregation of particles of Ni(5)/CeO₂ catalyst by sintering after reaction.

Figure 5 shows TPR profile of the calcined Ni(5)/CeO₂ catalyst. TPR profile for Ni(5)/CeO₂ catalyst clearly shows a main peak at 699 K owing to the reduction of bulk Ni and surface oxygen(O^{2-} or O^-).[16] The shoulder of TPR profile beween 904 K and 998 K contributes to the TPR bulk reduction of CeO_2 by elimination of lattice O^{2-} anions.[16] The TPR profile above 988 K was known to the reduction of bulk CeO_2.[18] Moreover, Jacobs et al.[18] reported that the bulk CeO_2 is assigned to reduction at close to 1023 K.
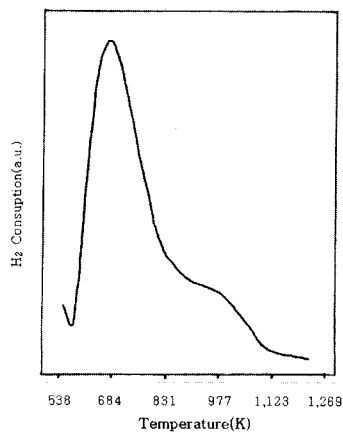

Figure 5. TPR profile of Ni(5)/CeO₂ catalyst before reaction.

Figure 6(a) shows XPS spectra of Ce 3d core electrons levels for reduced Ni(5)/CeO₂ catalyst. The two main $3d_{3/2}$ features at 900.0 and 903.1 eV corresponds to Ce^{4+} and Ce^{3+} components, respectively.[17-20] The $3d_{5/2}$ features at 882.0, 884.9, 897.9 eV corresponds to Ce^{4+}, Ce^{3+}, Ce^{4+} components, respectively.[17-20] The XPS spectra of O 1s core electrons levels for reduced Ni(5)/CeO₂ catalyst is shown in Figure 6(b) Two different oxygen components were found at 529.6 and 531.1 eV. The main peak at 529.6 eV can be assigned to lattice O^{2-}.[16] The shoulder peak at 531.1 eV is due to adsorbed molecular oxygen(O₂), adsorbed mononuclear oxygen(O⁻), and OH-groups.[11] Figure 6(c) shows XPS spectra of Ni 2p core electrons levels for reduced Ni(5)/CeO₂ catalyst. The Ni $2p_{3/2}$ profile displayed the broad peak between 851.7 and 854.2 eV. The peaks at 851.7 eV is assigned to Ni^o elements.[21] The peaks at 854.2 eV is assigned to Ni^{2+} ions.[21] These could be implied that reactants of CH₄ adsorbed on the Ni^{2+} active sites reduced of Ni^{2+} to Ni^o, and then discharge 4 electrons, and the electrons promote a reduction of Ce^{4+} to Ce^{3+} ions in the PCM to syngas over Ni(5)/CeO₂ catalyst. The gas phase oxygens contribute to supply lattice oxygen, O^{2-} produced by oxygenate ceria of insufficient electrons due to reduction of Ni^{2+} to Ni^o. It could be proposed that the catalysis of PCM to syngas should be continued to occur by Redox cycle as follows :

$$2Ni^{2+} \rightarrow 2Ni^o - 4e^- \quad (4)$$

$$2Ce^{4+} + 2e^- \rightarrow 2Ce^{3+} \quad (5)$$

$$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-} \quad (6)$$

Figure 7 shows redox cycle of Ni(5)/CeO₂ catalyst. In addition, it can be suggested that the formation of lattice oxygen, O^{2-} plays an important role to enhance the syngas yield and stability of Ni(5)/CeO₂ catalyst.
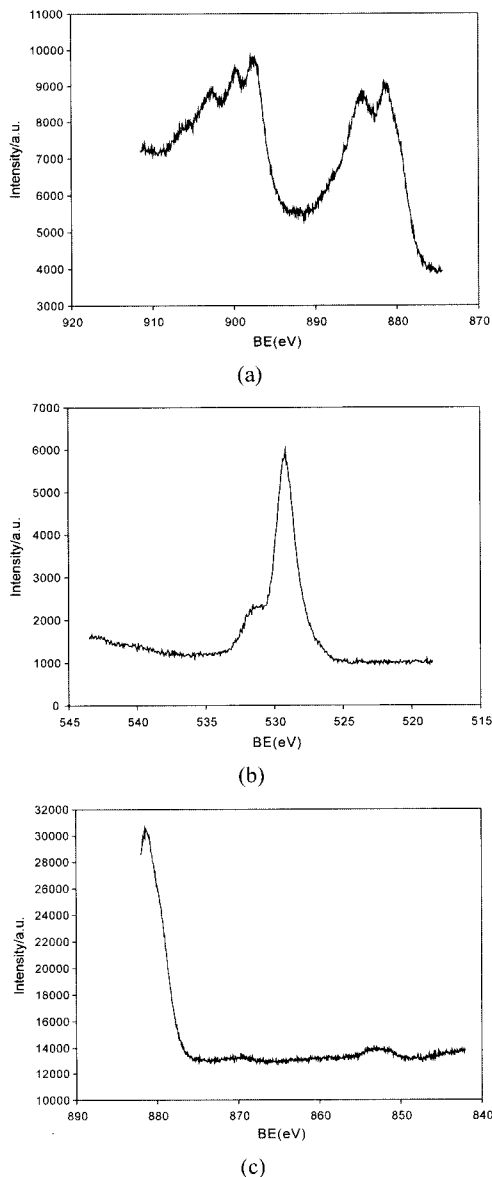

(a)

(b)

(c)

Figure 6. XPS spectra of Ce 3d, O 1s, and Ni 2p core electrons levels for reduced Ni(5)/CeO₂ catalyst: (a), Ce 3d; (b), O 1s; (c), Ni 2p.

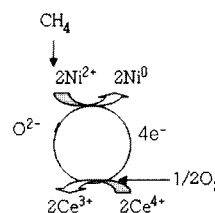Figure 7. Redox cycle of Ni/CeO₂ catalyst in the partial combustion of methane.

ACKNOELEDGEMENTS

CONCLUSIONS

The partial combustion of methane(PCM) to syngas was conducted on the precious metals (Rh, Pd, Pt) and nickel catalysts supported on γ-Al_2O_3 and CeO_2 in a fixed bed flow reactor. The syngas yield and stability increased in the sequence $Rh(5)/CeO_2 \geq Ni(5)/CeO_2 >> Rh(5)/Al_2O_3 > Pd(5)/Al_2O_3 > Pt(5)/Al_2O_3 > Ni(5)/Al_2O_3$. The promoter of Ni(5) impregnated CeO_2 due to high syngas yield and stability can be substituted for the noble metals (Rh, Pd, Pt) in PCM to syngas. The syngas yield of $Ni(5)/CeO_2$ catalyst was 90.66% at 1023 K. It enhanced the syngas yield and stability of $Ni(5)/CeO_2$ catalyst to fomnate the redox cycle of successive reaction active sites (Ni^{2+}), and lattice oxygen (O^{2-}), due to reduction of Ce^{4+} to Ce^{3+}.

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