High catalytic activity of isolated Pt atoms of Ni-Pt alloy for CO_2 hydrogenation

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Abstract: Tiny amount of Pt was added into Ni/Al_2O_3, resulting in a unique structure with isolated Pt atoms surrounded by Ni atoms. $Ni-Pt/Al_2O_3$ exhibited higher activity for CH_4 formation than bare Ni/Al_2O_3 in CO_2 hydrogenation, although only CO was evolved on bare Pt/Al_2O_3. The FT-IR spectroscopy using CO as a probe revealed that isolated Pt atoms were negatively charged by the electron donation from surrounding Ni atoms. These surface isolated Pt atoms caused the higher TOF of CH_4 than bare Ni/Al_2O_3.

Keywords: alloy catalyst, isolated Pt species, CO_2 hydrogenation, CO adsorption

1. Introduction

Alloy catalysts have been known to exhibit unique properties which are different from the catalytic behavior of their monometallic catalysts, while the reaction mechanisms on the alloy catalysts have not been elucidated fully yet [1]. Ni/Al_2O_3 and Pt/Al_2O_3 catalysts show high activities for CH_4 and CO formations in CO_2 hydrogenation, respectively [2]. It is expected that the alloy catalysts based on Ni and Pt have a unique geometric and electronic structure, resulting in different selectivity from that on each monometallic catalyst because of the unique adsorption properties of intermediate species in CO_2 hydrogenation. To investigate the catalytic behavior of alloy catalysts, we studied CO_2 hydrogenation over Ni-Pt alloy catalysts supported on Al_2O_3 with various composition ratios of Ni/Pt.

2. Experimental

Ni-Pt alloys were prepared on a γ-Al_2O_3 powder (Catalysis Society of Japan, JRC-ALO-7) by an impregnation method using $Ni(NO)_3$ and $Pt(NO_2)_2(NH_3)_2$ as precursors. The loading amount of Ni and Pt were 1.0 mmol g_{cat}^{-1} with various molar ratios (Ni:Pt = 100:0, 95:5, 75:25, 50:50, 25:75, and 0:100). After the impregnation, the catalysts were calcined at 773 K for 5 h, and then grained and sieved to 25~50 mesh. 100 mg of catalysts were pretreated at 1173 K for 1 h under 5 % of H_2 flowing at a rate of 50 mL min^{-1}. CO_2 hydrogenation was carried out in a fixed bed flow reactor at ambient pressure. The catalytic activity test at elevated temperature was performed in the 50 mL min^{-1} of mixture gas flow containing 10 % of CO_2 and 40 % of H_2 in He balance. FT-IR spectra of $Ni-Pt/Al_2O_3$ under 0.08 Torr of CO at 303 K were recorded after in-situ H_2 pretreatment at 873 K for 1h.

3. Results and discussion

The metallic Ni and Pt peaks appeared in the XRD patterns of reduced Ni/Al_2O_3 and Pt/Al_2O_3 samples, respectively. In the case of $Ni-Pt/Al_2O_3$, the metallic Ni peaks gradually shifted to low angle with increasing molar ratio of Pt. The lattice parameters estimated from the peak positions followed Vegard's law, suggesting that the solid solution of Ni-Pt alloy was formed. **Figure 1** shows the yields of CH_4 and CO in the CO_2 hydrogenation. Ni/Al_2O_3 catalyst exhibited the activity for CH_4 formation mainly at less than 673 K, while CO was generated as a main product over Pt/Al_2O_3. At more than 773 K, the CH_4 formation over Ni/Al_2O_3 was suppressed by reaching the equilibrium. $Ni-Pt/Al_2O_3$ containing 5 mol% of Pt (hereinafter, $Ni_{95}Pt_5/Al_2O_3$) showed higher yield of CH_4 than Ni/Al_2O_3 with keeping the high selectivity toward CH_4 evolution (ca. 97 % at 523 K). $Ni_{75}Pt_{25}/Al_2O_3$, which contained the higher molar ratio of Pt than

$Ni_{95}Pt_5/Al_2O_3$, showed the lower yield of CH_4 than Ni/Al_2O_3. In contrast, much higher amount of CO was evolved over $Ni_{75}Pt_{25}/Al_2O_3$ than that over Ni/Al_2O_3 and $Ni_{95}Pt_5/Al_2O_3$, resulting in the low selectivity toward CH_4 evolution (ca. 50 % at 523 K). **Figure 2** shows the FT-IR spectra of $Ni\text{-}Pt/Al_2O_3$ under 0.08 Torr of CO as a probe at 303 K. The weak bands appeared at 2057 cm^{-1} and 1970 cm^{-1} in the FT-IR spectra of Ni/Al_2O_3, which were assigned to ν(CO) stretching mode of linear-CO and bridge-CO species on metallic Ni, respectively. Pt/Al_2O_3 showed a strong band at 2090 cm^{-1} and weak band at 1850 cm^{-1}. In the case of $Ni\text{-}Pt/Al_2O_3$, a strong band was observed between the bands of linear-CO on Ni/Al_2O_3 and Pt/Al_2O_3 ($Ni_{95}Pt_5/Al_2O_3$: 2079 cm^{-1}, $Ni_{75}Pt_{25}/Al_2O_3$: 2082 cm^{-1}). These strong bands were assigned to ν(CO) stretching mode of linear-CO on metallic Pt because of the similar desorption property as Pt/Al_2O_3. The peak shift to low frequency in the spectra of $Ni\text{-}Pt/Al_2O_3$ than that of Pt/Al_2O_3 suggested that Pt atoms of Ni-Pt alloy were negatively charged by electron donation from Ni atoms, which was consistent with the XANES results. The absorption edge of Pt L_{III}-edge XANES spectra gradually shifted to high energy with increasing molar ratio of Ni because of high electron density of 5d orbital of Pt. Additionally, these EXAFS spectra of $Ni_{95}Pt_5/Al_2O_3$ suggested that Pt atoms were surrounded by Ni atoms. The average particle size of $Ni_{95}Pt_5/Al_2O_3$ catalyst (d = 9 nm) was smaller than that of Ni/Al_2O_3 catalyst (d = 27 nm) from TEM images. The turnover frequency (TOF) of CH_4, namely, the number of moles of CH_4 by the moles of surface metal atoms by seconds (1.9×10^{-7} s^{-1}) over $Ni_{95}Pt_5/Al_2O_3$ was higher than that over Ni/Al_2O_3 (1.3×10^{-7} s^{-1}). It is suggested that the surface isolated Pt species contributes to improve the TOF of CH_4.

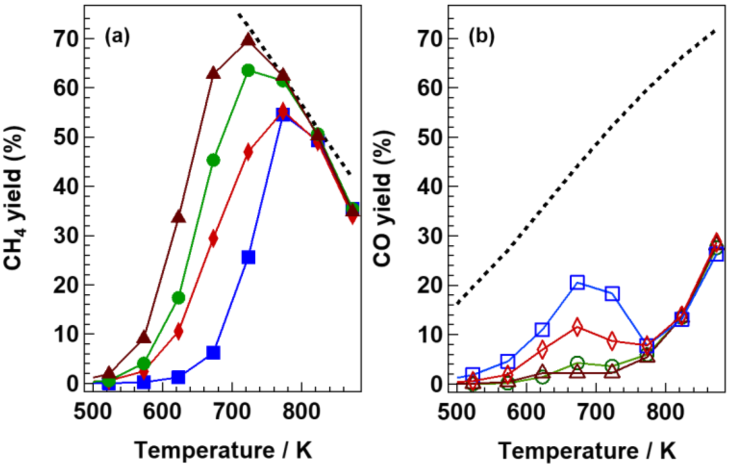

Figure 1 Yield of (a) CH_4 and (b) CO for CO_2 hydrogenation over $Ni\text{-}Pt/Al_2O_3$. Closed and open circles: Ni/Al_2O_3, triangles: $Ni_{95}Pt_5/Al_2O_3$, rhombus: $Ni_{75}Pt_{25}/Al_2O_3$, squares: Pt/Al_2O_3.Dashed line is equilibrium conversion of each reaction. $m_{catalyst}$ = 100 mg, 10 % CO_2 and 40 % H_2 in He (total flow rate = 50 mL min^{-1}).

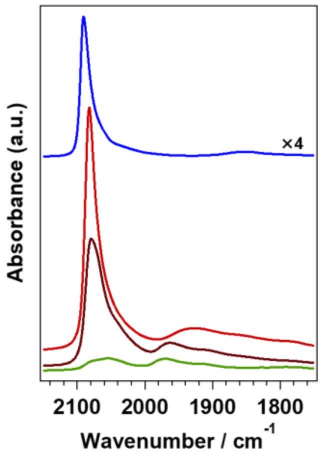

Figure 2 FT-IR spectra of $Ni\text{-}Pt/Al_2O_3$ under 0.08 Torr of CO. In order from the bottom to the top, the spectra of Ni/Al_2O_3, $Ni_{95}Pt_5/Al_2O_3$, $Ni_{75}Pt_{25}/Al_2O_3$ and Pt/Al_2O_3 are shown.

4. Conclusions

$Ni_{95}Pt_5/Al_2O_3$ exhibited the higher activity for the CH_4 formation than Ni/Al_2O_3 in the CO_2 hydrogenation. In contrast, the CO yield over $Ni_{95}Pt_5/Al_2O_3$ was as low as that over Ni/Al_2O_3, although only CO was generated on bare Pt/Al_2O_3. FT-IR and XAFS spectra revealed that isolated Pt atoms were formed on the surface of $Ni_{95}Pt_5/Al_2O_3$ with electron donation from surrounding Ni atoms to Pt atoms. We concluded that the unique surface structure of Ni-Pt alloy that isolated Pt atom surrounded by Ni atoms, caused the high TOF of CH_4 as compared to Ni/Al_2O_3.

References

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