Adsorption Behavior of CO Over Cu-Pd Bimetallic Nanoparticles Supported on SiO_2 Investigated by Infrared Spectroscopy

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Abstract: The adsorption of CO over Cu-Pd bimetallic nano-particles supported on SiO_2 was investigated by infrared spectroscopy. The infrared spectra clearly show that the unusable adsorption behavior of CO over the Cu-Pd bimetal nano-particles at the coverage below 5 % when Cu (10 wt%)-Pd (Cu:Pd=10:1) was applied as catalyst. Here, CO adsorbed over Cu ad-atom first, then migrated to Pd ad-atom and stabilized. If the coverage of CO increased over 5 %, the adsorption of CO proceeded over Cu atom. The states of SiO_2 supported Cu-Pd bimetal nano-particles were discussed on the basis of the infrared spectroscopic investigation.

Keywords: Cu-Pd/SiO_2, CO adsorption, Infrared spectroscopy.

1. Introduction

Metal catalysts are generally applied as supported metal, where metal nano-particles are dispersed over support materials with high surface area such as SiO_2 and activated carbon. The supported metals are play as the active center of the catalyst. In order to improve the supported metal catalysts, addition of promoters are often performed and among them addition of metal atom to form supporting bimetallic nanoparticle is one of the effective methods. Bimetallic nano-particles are reported to exhibit characteristic features as not only catalysts but also the surface phenomena on the basis of the electric and geometric interactions caused by the addition of different metal. Surface states of the supported bimetal are significant for the catalytic performance. However, limit number of techniques can be applied to analyze the surface directly in an atomic level. Infrared spectroscopic technique is one of them and can examine the states of first layer of the surface through the state of the adsorbed species, such as adsorbed CO.

In this study, we investigate the surface state of SiO_2 supported Cu-Pd bimetallic catalysts from the examination of the states of adsorbed CO by infrared spectroscopy. Here we report the adsorption behavior of CO over the Cu atom influenced by the addition of Pd as well as the formation of on-top CO over Pd atom on the special site consist of Cu-Pd on the bimetallic nano particle.

2. Experimental

The catalysts of Cu-Pd/SiO_2 used in this study were prepared by impregnation method. SiO_2 was dispersed in the $Cu(NO_3)_2$ and $PdCl_2$ mixed aqueous solution and dried and calcined at 723 K in air for 2 h. The prepared Cu-Pd/SiO_2 precursor (ca. 20 mg) was pressed into self-supporting pellet with 20 mm in diameter and set in an *in situ* IR cell. The IR cell was connected to iso-volumetric closed gas circulation system. The pressure of the system was precisely measured at the range of 10^{-3} Torr (1Torr=133.32 Pa) with using capacitance manometer to know the pressure change by the adsorption. The pellet was oxidized under O_2 at 523 K for 10 h and then reduced under H_2 for 2 h in the cell as pretreatment to become the precursor to Cu-Pd/SiO_2. The characterization of prepared Cu-Pd/SiO_2 was carried out by TEM-EDS.

The infrared spectra were recorded with an FT-IR. The spectra were normally measured with 100 scans at 4 cm^{-1} resolution. The spectra of adsorbed species were shown after rationing the background spectra of the catalyst to the spectra containing the adsorbed species.

3. Results and discussion

The Cu(10 wt%)-Pd(1:0.1)/SiO_2 catalyst was used in this study. From the TEM-EDS examination, homogeneously dispersed fine metal particles, which are consist of the homogeneous mixture of Cu and Pd with approximately 20 nm in diameter, over the SiO_2 support are clearly observed. This indicates that Cu-Pd bi-metallic particles supported over SiO_2 were applied to the present study.

Figure 1 shows the time dependence infrared spectra of adsorbed CO over the Cu-Pd/SiO_2 under the equilibrium pressure at 0.037 Torr at 298 K. If the small amount of CO introduced in the system, CO rapidly adsorbed over the surface to give the infrared band at the 2122 cm^{-1}. The band can be attributed to ν(CO) of CO adsorbed on Cu atom. As also shown in Fig.1, the intensity of the band decreases with passing time and instead of the band at 2122 cm^{-1}, new band produces at 2067 cm^{-1}, the intensity increases with passing time and finally the band at the 2122 cm^{-1} completely displaced to the band at 2067 cm^{-1}. These results suggest that, at the low coverage of CO, CO adsorbed on Cu atom first and then transformed to adsorbed CO on Pd atom. Under the series of transition, the pressure of CO in gas phase did not change essentially, so that the amount of adsorbed CO did not change under the transformation. From the results, unusual adsorption behavior of CO can be clearly confirmed over Cu-Pd bi-metallic system supported over SiO_2. The unusual adsorption behavior probably originated with the state of the adsorption site formed by the Cu and Pd.

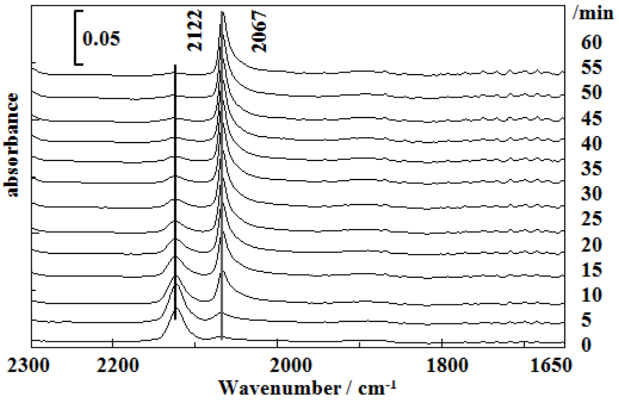

Figure 1. Time dependence infrared spectra of absorbed CO over Cu(10 wt%)-Pd(1 : 0.1)/SiO_2 at 298K under the equilibrium pressure at 0.037 Torr

Figure 2 shows the infrared spectra of CO adsorbed on the Cu-Pd/SiO_2 surface at 298 K at various equilibrium pressures. As shown in Fig.2, the band at 2063 cm^{-1} attributable to ν(CO) of the adsorbed CO on Pd atom was observed at the equilibrium pressure up to 0.078 Torr. The band at 2114 cm^{-1}, attributable to ν(CO) of the adsorbed CO on Cu atom, was observed at the equilibrium pressure over 0.078 Torr the intensity of the band at 2114 cm^{-1} saturates at the equilibrium pressure at 1.9 Torr. The amount of adsorbed CO was also evaluated. The value over Cu(10 wt%)-Pd(1:0.1)/SiO_2 was 87 μmol/g-cat, while Cu(10 wt%)/SiO_2 was 11 μmol/g-cat. From the result, the amount adsorbed CO increased markedly by introducing Pd. From Fig.2, these phenomena were probably caused by increasing the adsorption sites of CO over Cu in the supported Cu-Pd particles by the influence of introducing Pd atom in Cu nano-particles.

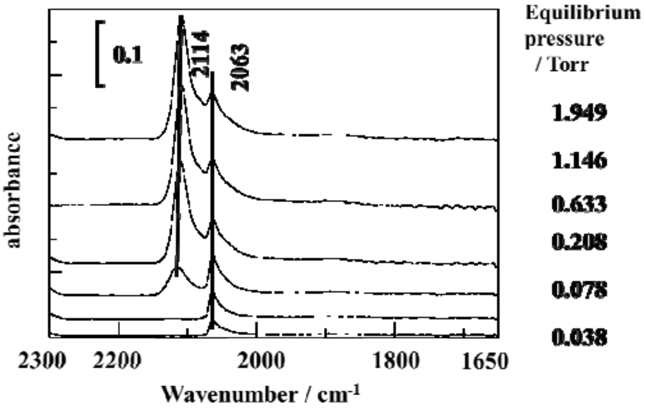

Figure 2. Infrared spectra of adsorbed CO over Cu(10 wt%)-Pd(1:0.1)/SiO_2 at 298 K at various equilibrium pressures

4. Conclusions

Pd atom in Cu-Pd bi-metal particles plays two kinds of significant roles to the bimetallic particles as adsorbent of CO, where one is the formation of characteristic adsorption site at which unusual adsorption behavior of CO can be observed and the other is chemically activation of the bi-metal particle to improve the capability of CO adsorption on surface Cu atom.