CHEMISTRY LETTERS, pp. 1695-1698, 1986.

An Infrared Study of NO Adsorbed on SiO_2-Supported Fe, Co, and Ni Bimetallic Alloy Catalysts for CO Hydrogenation

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The electronic state of bimetallic system of Fe, Co, and Ni was investigated by infrared spectra of the bent- and linear-types adsorbed nitrogen monoxide. The conversion of CO was related with the absorbance of bent-type NO. The alloying of metals increased the absorbance of bent-type in accord with high CO conversion and high selectivity to higher hydrocarbons.

Infrared spectra of adsorbed CO has been widely used for studies on CO hydrogenation catalysts, however, the spectral observation sometimes encounters difficulties owing to the high reactivity of CO on the metal surfaces.[1,2] Electronic configuration of a nitrogen monoxide molecule resembles with that of a CO molecule except for one electron which is occupying the antibonding orbital of NO.[3] Since the wave number of N-O stretching mode for adsorbed NO is very sensitive to the electronic state of metal, nitrogen monoxide is well-suited as a probe molecule for an infrared study on metal catalyst. As for catalysts of Fischer-Tropsch synthesis, the IR bands of adsorbed nitrogen monoxide at 1790 and 1850 cm^{-1} on Co/Al_2O_3 catalyst were assigned to bent- and linear-type, respectively, by Niiyama et al.[4] Adsorbed NO on Ru/Al_2O_3 is converted in the presence of CO to M-NCO (isocyanate).[5] We have reported previously that the product distribution of CO hydrogenation over the bimetallic catalysts of Fe, Co, and Ni depends on metallic composition.[6] Mixing of metals brought about excellent activity for production of higher hydrocarbons. Adsorbed nitrogen monoxide was found to be so stable on this bimetallic system that its IR observation elucidated the electronic states of metal in the present study.

Table 1. Identification of adsorbed NO species over SiO_2-supported Fe, Co, and Ni bimetallic alloy catalysts

	Linear type (cm^{-1})	Bent type (cm^{-1})
Fe	1915	1827
Co	1880	1790
Ni	1875	1845
75Fe25Co	1888	1809
50Fe50Co	1882	1805
25Fe75Co	1880	1795
75Co25Ni	1883	1800
50Co50Ni	1865	1788
25Co75Ni	1875	1790
75Ni25Fe	1878	1827
50Ni50Fe	1874	1823
25Ni75Fe	——	1820

The supported bimetallic catalysts of Fe, Co, and Ni with total metal loading of 10 wt% were prepared by an incipient wetness technique.[6] Hereafter, metallic compositions in the catalysts are denoted as molar percentage of component metal (e.g., 75Ni25Co). Catalytic hydrogenation of carbon monoxide was carried out in a high pressure flow reactor. The reaction was normally performed at 523 K under 1.0 MPa. A gaseous mixture of H_2 (62 vol%), CO (33 vol%), and Ar (5 vol%) was fed to the catalyst bed at W/F=10 g-cat·h/mol where W is the catalyst weight and F is the total flow rate of reactants. Infrared spectra were recorded with a JASCO A-810 spectrometer. Catalyst powders, of which weights were 30 mg, were pressed into disc and were placed in the in-situ cell. Nitrogen monoxide (ca. 4×10^3 Pa) was introduced to the samples after evacuation at 673 K for 3 h and then evacuated again prior to the IR measurement. Disproportionation product of adsorbed NO such as NO_2 or N_2O could not be detected by IR. The dissociated nitrogen was not present on the surface, since the introduction of H_2 to the sample with adsorbed NO did not produce the N-H absorption band.

Adsorption of NO was observed for every catalyst of Fe, Co and Ni system by infrared spectroscopy, whereas its wave numbers and intensities were largely affected by metallic composition. Infrared spectra of NO adsorbed on 75Ni25Co are shown in Fig. 1. After adsorption at 373 K, two adsorption bands centered at 1790 cm^{-1} and 1875 cm^{-1} appeared, but both of them were weakened with rising evacuation temperature. Although the absorption band at 1875 cm^{-1} was still present even after evacuation at 573 K, that of 1790 cm^{-1} was almost disappeared. Two kinds of adsorbed NO, i.e., bent-type and linear-type, have been observed so far by IR measurement at 1720-1520 and 1900-1700 cm^{-1}, respectively. Bent-type (NO^-) is formed by electron donation from the metal to antibonding orbital of NO molecule, but linear-type (NO^+) is formed by electron withdrawal from NO. Adsorbed NO on Rh catalyst suggests that the bent-type NO is formed only on reduced Rh surface with electron donation, but the oxidized Rh surface only produces the linear-type NO.[5] The IR intensity of bent- and linear-type NO seems to reflect the number of electron-donating and electron-withdrawal sites, respectively. Since the bonding of N-O in bent-type NO is weaker than that in linear-type NO and its stretching band appears at low wave number, the absorption bands at 1875 and 1790 cm^{-1}

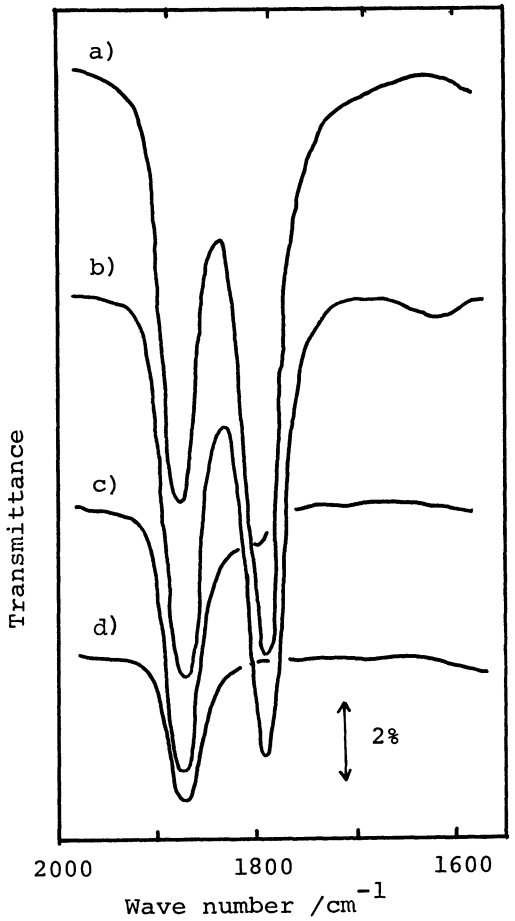

Fig.1. IR spectra of adsorbed NO over $75Ni25Co/SiO_2$ after evacuation.
a) at 297 K b) at 373 K
c) at 473 K d) at 573 K

for 75Ni25Co catalyst can be assigned to linear-type and bent-type NO, respectively. Metal-nitrogen bond for bent-type NO is easily dissociated and its desorption occurs at lower temperatures than that of linear—type NO on heating as was observed in Fig. 1. Infrared spectra of NO adsorbed on SiO_2-supported bimetallic catalysts of Fe, Co, and Ni are shown in Fig. 2 and the wave numbers at the peaks of NO bands are listed in Table 1. Two absorption bands, i.e., bent- and linear-types, were always observed by IR, but the adsorption types of NO do not reflect the oxidation state of metals, since a formation of oxides, except for the support oxide, cannot be detected from chemical shift of XPS for every catalyst.[7] We have reported previously that the amount of adsorbed H_2 or CO is not related with the surface area of exposed metal in the Fe-Co-Ni system. Alloying of Fe, Co, and Ni appears to affect the electronic state of metals and to produce several kinds of adsorption sites, which can be observed as two IR bands of adsorbed NO. The IR bands of bent- and linear-types NO on Fe-Co system tended to shift to low frequency with increasing Co content. This shift in absorption frequency with Co content suggests an increase in electron donation from metal to NO. In the Fe-Co system, the olefin selectivity was the highest and NO bands appeared at the lowest wave number on the single Co catalyst. High selectivity to olefins on this Fe-Co bimetallic catalyst can be explained by this increase of electron density. From this aspect, the effect of alloying Co with Fe resembled the promotion effect of alkali metal such as K. Although the wave number of each N-O band was hardly affected in the case of Co-Ni and Ni-Fe system, the intensity was greatly changed with the metal composition (Fig. 2). In Co-Ni system, the intensity of bent-type NO was significantly weakened with Ni content. In Fe-Ni system, the adsorption band of linear-type NO was

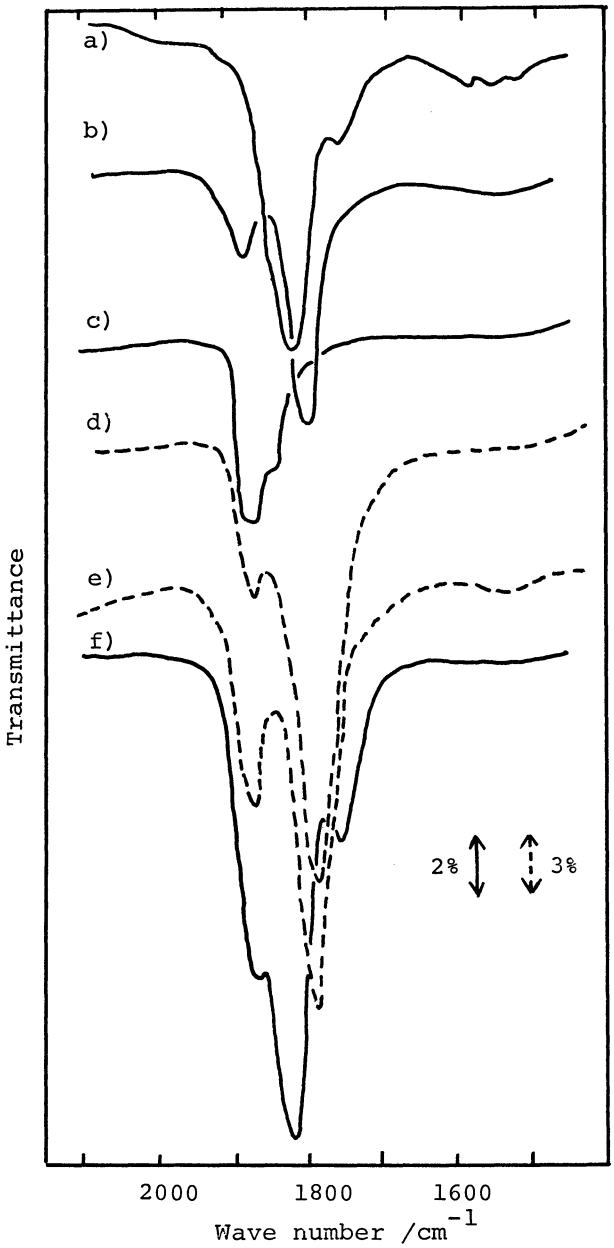

Fig.2. IR spectra of adsorbed NO over SiO_2-supported bimetallic alloy catalysts.
a)Fe b)Co c)Ni d)50Fe50Co e)50Co50Ni f)50Ni50Fe

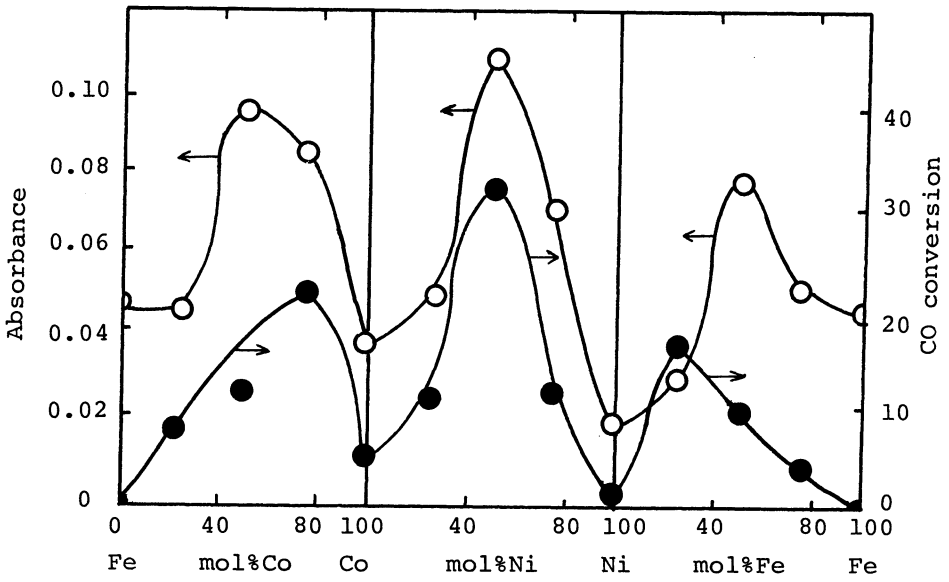

Fig.3. CO conversion and absorbance for bent-type adsorbed NO over bimetallic alloy catalysts as a function of composition.

weakened with increasing Fe content. The linear- and bent-type NO could not be observed on single Fe and Ni, respectively.

Changes in IR intensities with metal composition, which are very important information for the catalytic activity and selectivity for CO hydrogenation, should reflect the electronic state of metal. An extraordinary similarity was found between the change in absorbance of bent type band with bimetallic composition and the change in CO conversion as shown in Fig. 3. The catalytic activity was always enhanced by alloying of metals in accord with an increase in intensity of bent-type band. Thus, the bent-type NO seems to adsorb on the active site for CO hydrogenation. Hydrogen and carbon monoxide molecules are expected to be easily dissociated on the surface of electron donating metals because of occupation of antibonding orbitals of them. The amount of bent-type NO, which is formed by adsorption on donor metal, seems to be related with the number of active sites for CO hydrogenation. The intensity increase of bent-type band by alloying of Fe, Co, and Ni suggests that the alloying produces the active site for CO hydrogenation and the catalytic activity is regulated by the electron donation from metal surfaces.

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(Received July 7, 1986)