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An Infrared Spectroscopic Study of Acrylonitrile Adsorbed on Silica-Supported Copper Catalyst

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Adsorption state of acrylonitrile on Cu catalyst was studied by means of infrared spectroscopy. The C≡N stretching vibration of acrylonitrile adsorbed on Cu was appreciably shifted to lower frequency regions in comparison with that in liquid-state. The π-component coordination of cyano group in acrylonitrile with Cu surface site was suggested.

Acrylonitrile is a multifunctional molecule having single, double and triple bond and lone pair of electrons. It can therefore be presumed that there are many coordination models of acrylonitrile molecule on surface sites, i.e., with various metal cations and atoms the covalent coordination through electrons of N(2s) lone pair$^{1-3)}$ and σ- and π-component coordination through the C=C double bond$^{4-6)}$ of acrylonitrile. The π-component coordination through the C≡N triple bond of acrylonitrile with surface sites is still not completely elucidated.

Selective hydration of the C≡N triple bond of acrylonitrile leads to the formation of acrylamide, in which the metallic Cu is the most active catalyst among the metal elements of periodic table.$^{7)}$ In this communication the chemisorption of acrylonitrile on silica-supported Cu was investigated aiming to clarify the hydration mechanism of acrylonitrile to acrylamide.

The silica-supported Cu sample was prepared by an impregnation method. An aqueous $Cu(NO_3)_2$ solution was mixed with the SiO_2(Aerosil-380 supplied by Japan Aerosil Co.). The resulting slurry was dried in a vacuum disiccator at room temperature for 3 days and then calcined at 300 °C for 3 h. The amount of Cu loaded on SiO_2 was 10 % by weight. Infrared spectra of acrylonitrile adsorbed on Cu/SiO_2 were measured in a glass cell with CaF_2 windows, using a JEOR JIR-100 FT-IR spectrometer. A Cu/SiO_2 disk of ca. 20 mm of diameter was prepared by pressing 20 mg of powder under a pressure of 200 kg/cm^2. After the sample wafer was reduced in a stream of H_2 at 350 °C for 2 h, acrylonitrile vapor(70 Torr) was adsorbed at room temperature for 12 h and then evacuated for 3 minutes. Spectra were obtained by 40 scans at a resolution of 1 cm^{-1}. Infrared spectra of propionitrile adsorbed on Cu/SiO_2 sample were also measured by the same method described above. Ni/SiO_2 sample was also prepared by similar procedure as above.

The infrared spectra of acrylonitrile adsorbed on Cu/SiO_2, Ni/SiO_2, oxygen-treated Cu/SiO_2, and SiO_2 were shown in Fig. 1. The infrared spectrum of liquid acrylonitrile shows three characteristic absorption bands; C≡N stretching vibration

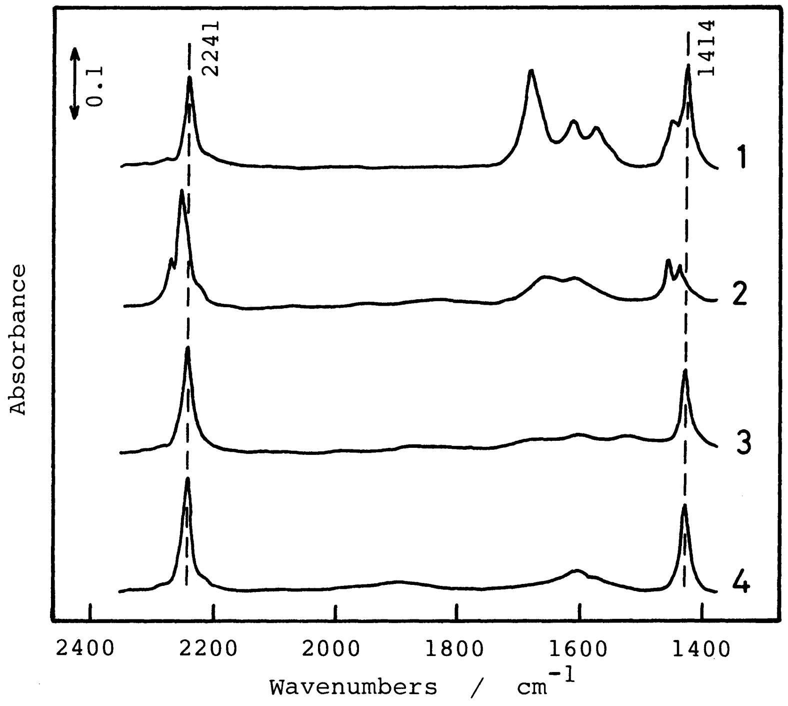

Fig. 1. Infrared spectra of acrylonitrile adsorbed on various samples:(1) Cu/SiO_2;(2) Ni/SiO_2;(3) Cu/SiO_2 treated with 80 Torr O_2 for 15 min at 100 °C;(4) SiO_2.

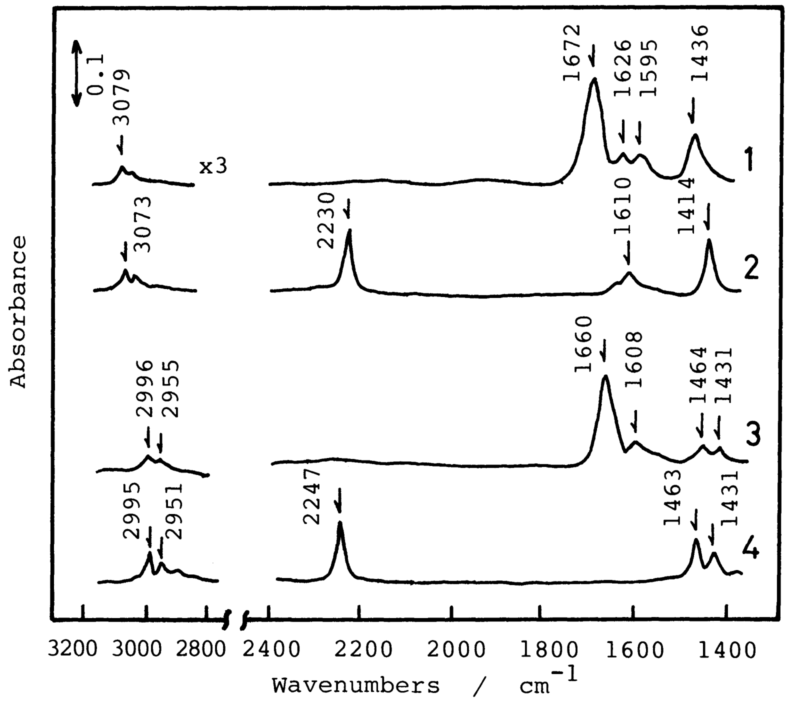

Fig. 2. Infrared spectra of acrylonitrile and propionitrile adsorbed on Cu surface and of liquid-state:(1) Adsorbed acrylonitrile(subtracted);(2) Liquid acrylonitrile;(3) Adsorbed propionitrile(subtracted);(4) Liquid propionitrile.

at 2230 cm^{-1}, C=C stretching vibration at 1610 cm^{-1} and CH_2 deformation vibration at 1414 cm^{-1}, respectively.[8)] By the adsorption of acrylonitrile on SiO_2 surface, the C≡N band shifted to a higher frequency(2241 cm^{-1}). This spectrum shows that the interaction between acrylonitrile and surface hydroxyl group on SiO_2 occurs through donation of the lone pair of electrons of nitrogen atom as reported in the previous paper.[9)] When acrylonitrile was adsorbed on Cu/SiO_2 four new absorption bands appeared in the range of 1680-1430 cm^{-1}. On the other hand, similar absorption bands of propionitrile appeared at 2247, 1446, and 1427 cm^{-1} on Ni/SiO_2 sample. This result indicates that the preferential coordination of C=C double bond in acrylonitrile occurs rather than C≡N bond and is in good agreement with that reported by Schrauzer.[10)] The same spectrum of acrylonitrile adsorbed on oxygen-treated Cu/SiO_2 and SiO_2 suggests that acrylonitrile does not adsorb on the oxidized surface of Cu. Because the four new absorption bands on Cu/SiO_2 were not observed on the other samples such as Ni/SiO_2 etc. and entirely different from the infrared spectra of hydration products such as acrylamide, they indicate the presence of adsorbed species of acrylonitrile on a Cu surface.

In order to assign the four new absorption bands the infrared spectrum of propionitrile adsorbed on Cu surface was examined. The subtracted spectra of both acrylonitrile and propionitrile adsorbed on Cu surface were shown in Fig. 2. The C≡N stretching vibration band of both nitrile compounds disappeared. Four absorption bands of acrylonitrile at 1672, 1626, 1595, and 1436 cm^{-1} and two new peaks of propionitrile at 1660 and 1608 cm^{-1} were detected.

In general, the stretching vibration band of C≡N triple bond of nitrile compounds appears sharply in the range of 2270-2220 cm^{-1}.[11)] As shown in Table 1, π-bonded C≡N stretching vibration band coordinated in organometallic complexes is shifted to lower frequency in the range of 2100-1700 cm^{-1}. Furthermore, azomethines having C=N double bond have the C=N stretching vibration bands in the range of 1680-1640 cm^{-1}. Consequently, the strong absorption bands appeared at 1672 and 1660 cm^{-1} correspond to the nitrile compounds adsorbed on a Cu surface in a state

Table 1. Characteristic infrared absorption bands of azomethines and π-coordinated nitriles

Compound	$\nu_{C=N}$ / cm^{-1}	π-Coordinated $\nu_{C≡N}$ / cm^{-1}	Ref.
$CH_3CH=NCH_3$	1673	----	12
$(CH_3)_2C=NCH_3$	1662-1649	----	
$(CH_3)_2C=NH$	1646-1640	----	
$Pt(CF_3C≡N)(PPh_3)_2$	----	1734(2271)[b)]	13
$Mn(CO)_3IL$[a)]	----	1973(2225)[b)]	14
$Mn(CO)_3(N≡CCH_2CH_2C≡N)Cl$	----	2068(2257)[b)]	15

a) L; o-cyanophenyldiphenylphosphine.

b) Infrared absorption bands of the oridinal cyano group were shown in parentheses.

of double bonding properties of cyano groups and the weak absorption bands at 1626 and 1608 cm^{-1} seem to be the sub-bands of them, respectively. It is considered that the peaks of acrylonitrile at 1595 and 1436 cm^{-1} are associated with the stretching vibration band of the C=C double bond and the deformation vibration band of CH_2, respectively, because their frequency bands are not observed in the case of propionitrile adsorption and the stretching vibration band of C-H of acrylonitrile is observed at 3079 cm^{-1}.

From the above results, it is suggested that acrylonitrile molecule will be adsorbed on Cu surface in the state of π-component coordination through the cyano group. This peculiar adsorption state of acrylonitrile on Cu is at least partly responsible for the excellent selectivity of the Cu catalyst on the hydration of acrylonitrile to acrylamide.

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