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Infrared Study on the Adsorbed State of Ammonia on Heteropoly Compounds

INTRODUCTION

A heteropoly compound is one of the strongly active acid catalysts which can be used for several acid catalyzed reactions (*1*). One property of heteropoly compounds as a solid acid catalyst is that there are acid sites on the surface as well as in the bulk. The other property of these catalysts is that nitrogen compounds such as pyridine and ammonia are easily adsorbed as a pseudo-liquid phase in the bulk (*2*, *3*).

Kim *et al.* (*4*) reported that there was no correlation between the adsorbed amounts of pyridine and those of ammonia on heteropoly compounds. They suggested that ammonia could be adsorbed on an acid site of a heteropoly compound as well as on a metal cation. The adsorption of ammonia as an amine structure on copper containing heteropoly compound was discussed by Saito *et al.* (*5*). However, a systematic study on the adsorbed state of ammonia on the heteropoly compound was not reported.

This paper reports an investigation of the infrared spectra of ammonia adsorbed on a heteropoly compound to illustrate the possible states of the adsorbed ammmonia.

METHODS

Reagent grade 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$, abbreviated HTP) obtained from Wako Pure Chemicals was used to prepare heteropoly compounds containing metal cations (CaTP, SrTP, PbTP, BiTP, MgTP, CoTP, FeTP, NiTP, and CuTP) by the double decomposition of the acids and metal carbonates as described by Tsigdinos (*6*). An infrared cell, described elsewhere (*7*), was used to study the adsorbed state of ammonia. A silicon wafer was used to support the heteropoly compound, as in the infrared study of zeolite (*7*). Sample specimens were prepared by placing a few drops of a water suspension of heteropoly compound on the silicon wafer and drying. The sample wafer was then placed in a sample cell and the cell evacuated at 130°C for 2 h until about one molecule of water per Keggin anion remained (*3*). The heteropoly compound sample was then exposed to ammonia gas at 8 kPa for 30 min at 25°C. IR spectra were taken on a Jasco A-302 spectrophotometer after gaseous ammonia was removed by evacuation at 25°C for 40 min. A matched infrared cell containing a bare silicon wafer was used as a reference to compensate for absorption on the support. The absorbance in digitalized form was recorded on a Jasco DP-330 data processor. The IR spectra of the evacuated samples at 80, 150, and 300°C were also obtained at room temperature. The absorption spectra in the region 1700–950 cm^{-1} were deconvoluted with a computer by the simplex method to obtain several independent absorption bands.

RESULTS AND DISCUSSION

Figure 1 shows the typical infrared spectra of ammonia adsorbed on heteropoly compounds. The spectra, although limited to the range 1700–330 cm^{-1}, showed changes due to the adsorption of ammonia. The bands at about 3000 cm^{-1} related to OH stretching were too broad to discuss quantitatively, however. The dotted lines represent the spectra for the heteropoly compounds evacuated at 130°C for 2 h. The characteristic bands of the heteropoly compounds, 1080(P–O), 980(W=O), 895(W–

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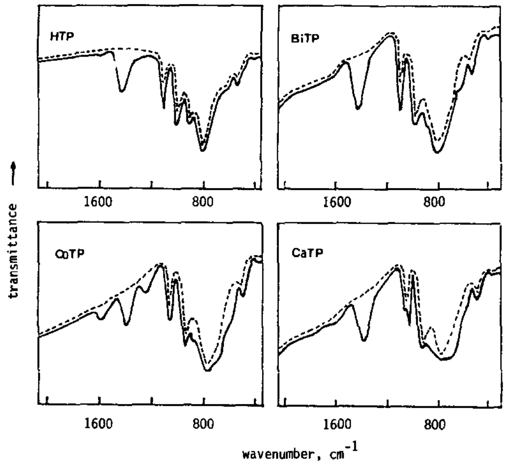

FIG. 1. Typical IR spectra of ammonia adsorbed on heteropoly compounds. (---) Evacuated at 130°C. (—) Exposed to ammonia and evacuated at 25°C.

O–W), and 805(W–O–W) cm^{-1} shown here compare very well with those of a similar previous study (*8*).

The spectra of ammonia adsorbed on heteropoly compounds show in general several new bands at 1600, 1400, 1190–1240, 1030–1070, and 500–950 cm^{-1}. Only the band at 1400 cm^{-1} appeared with HTP. The three bands at 1600, 1400, and about 1200 cm^{-1} were observed on CoTP. On CaTP, bands at 1400 and at about 1050 cm^{-1} were observed. The intensities of the absorption bands at 500–950 cm^{-1} are strong on CaTP and BiTP.

When the evacuation temperature is increased, the intensities of the absorption bands are reduced. Although the wavenumbers for the absorption bands are slightly different depending on the cation of the heteropoly compound, the bands at about 1600, 1400, 1200, 1080, and 1050 cm^{-1} are designated bands I, II, III, IV, and V, respectively. Bands I, II, III, and V are caused by the adsorbed ammonia and band IV by the P–O bond of the heteropoly compound (*8*). The area of band IV was proportional to the amount of heteropoly compound which might presumably have the same extinction coefficient for the P–O vibration of all heteropoly compounds. The specific areas of bands I, II, III, and V are defined as the band areas divided by the area of band IV in order to normalize the band area to the same amount of heteropoly compound.

The specific absorption band areas obtained at varying evacuation temperatures are listed in Table 1. The decreases in spe-

TABLE 1

The Specific Area of the Absorption Bands of Ammonia Adsorbed on Heteropoly Compounds

Heteropoly compound	Evacuation temperature (°C)	Specific band area			
		I	II	III	V
SrTP	25	0.33	3.73	—	1.23
	80	0.11	2.14	—	0.89
	150	0.08	0.81	—	0.23
	300	0.04	0.05	—	—
CaTP	25	0.33	3.52	—	0.99
	80	0.25	2.46	—	0.81
	150	0.09	0.81	—	0.08
	300	0.08	0.18	—	—
PbTP	25	0.64	5.10	—	0.85
	80	0.43	4.57	—	0.74
	150	0.16	1.76	—	0.07
	300	0.15	0.78	—	—
HTP	25	0.55	1.88	—	0.06
	80	0.03	1.29	—	0.01
	150	0.02	1.07	—	—
	300	0.01	1.06	—	—
BiTP	25	0.03	1.70	—	0.29
	80	0.02	1.26	—	0.19
	150	0.01	1.08	—	0.07
	300	0.01	0.92	—	—
MgTP	25	0.26	0.35	0.43	0.11
	80	0.09	0.27	0.14	0.07
	150	0.04	0.24	0.05	0.02
	300	0.01	0.16	—	—
FeTP	25	0.08	1.98	0.14	0.12
	80	0.04	1.47	0.03	0.07
	150	0.03	1.05	0.02	—
	300	0.02	0.60	0.02	—
CoTP	25	0.28	1.16	0.29	0.08
	80	0.13	0.88	0.13	0.05
	150	0.09	0.63	0.07	0.01
	300	0.03	0.27	0.01	—
NiTP	25	0.28	0.37	0.13	—
	80	0.16	0.28	0.07	—
	150	0.10	0.22	0.05	—
	300	0.09	0.17	0.03	—
CuTP	25	0.14	0.34	0.16	—
	80	0.10	0.18	0.11	—
	150	0.04	0.16	0.03	—
	300	0.02	0.15	0.01	—

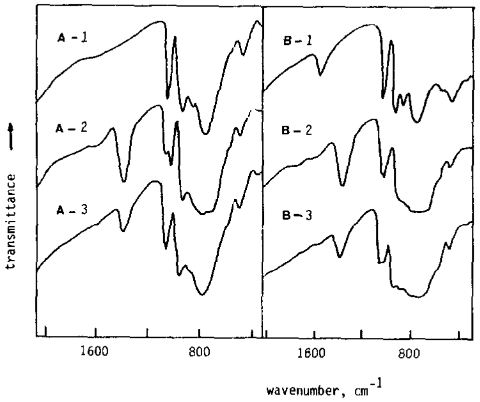

FIG. 2. IR spectra of ammonia adsorbed on SrTP. (A) Evacuated at 130°C (A-1), exposed to ammonia and evacuated at 25°C (A-2), and evacuated at 150°C (A-3). (B) Nontreated (B-1), exposed to ammonia and evacuated at 25°C (B-2), and evacuation at 150°C (B-3).

cific band area were different depending on the cations of the heteropoly compound. The decreases in the specific areas of bands II and V are different from those of the other bands. On HTP, FeTP, and BiTP, band II is predominant, while other bands are negligible. Band V has a high intensity on CaTP, SrTP, and PbTP evacuated at 25°C, but disappears readily after evacuation at 150°C. The specific areas of bands I and III show the same decreases in the spectra of ammonia-adsorbed MgTP, CoTP, NiTP, and CuTP. This indicates that the absorption bands I and III are caused by the same adsorbed state of ammonia. The decreases in bands I and III are quite different from those of bands II and V.

Therefore, ammonia can be thought to be adsorbed on heteropoly compound in three different states. The first is the absorption band at 1400 cm^{-1} (band II), the second is at about 1600 (band I) and 1200 cm^{-1} (band III), and the third is at about 1050 cm^{-1} (band V). Absorption band II was assigned to the ammonia adsorbed on the Brønsted acid site of a heteropoly compound by Misono (*9*). As band II at 1400 cm^{-1} is clearly observed in ammonium chloride due to ammonium ion (*10*), it is reasonable to belive that band II is caused by the ammonia adsorbed on the Brønsted acid site as ammonium ion.

Absorption bands I and III are observed with heteropoly compounds containing Ni^{2+}, Co^{2+}, Cu^{2+}, and Mg^{2+}. They are known to be the cations which can form an amine complex (*10*). The IR absorptions of deformation vibrations of octahedral amine complexes, δ_a(HNH) and δ_s(HNH), are reported to appear at about 1600 and about 1200 cm^{-1}, respectively. Therefore these bands are assigned to be the amine complex of adsorbed ammonia on a metal cation.

Absorption band V is observed with all heteropoly compounds on which ammonia is adsorbed. The intensity is weak except with SrTP, CaTP, PbTP, and BiTP. Evacuation at elevated temperatures sharply decreases the intensity of band V. On heteropoly compounds evacuated at 150°C, band V disappears. The IR spectra of ammonia adsorbed on SrTP before exposure to ammonia with and without evacuation at 130°C to remove water are shown in Fig. 2. Band V for ammonia adsorbed on dehydrated SrTP is stronger and more easily desorbed by evacuation at 150°C. This obviously indicates that the adsorption of ammonia is affected by the water content of heteropoly compound. Therefore, the third state of adsorbed ammonia as indicated by band V might be the sorbed ammonia in the bulk phase.

The acid strengths of heteropoly compounds (*11*) and the specific band areas of II

TABLE 2

Acid Strength of Heteropoly Compounds and the Specific Area of Band II after Evacuation at Varying Temperatures

Heteropoly compound	Acid strength[a] H_0	Specific band area 25°C	150°C	300°C
HTP	−8.2	6.88	1.07	1.06
BiTP	−5.6	1.70	1.08	0.92
PbTP	−0.5	5.10	1.76	0.78
CaTP	+1.5	3.52	0.81	0.18
SrTP	+1.5	3.73	0.81	0.05
MgTP	+2.4	0.35	0.24	0.16

[a] Saito, N., Park, N. C., Niiyama, H., and Echigoya, E., *J. Catal.* **95**, 49(1985).

at varying evacuation temperatures are listed in Table 2. There is no relationship between acid strength and the specific band area of II for evacuation at 25°C. There is a strong correlation between the specific band area of II evacuated at 300°C (with the exception of MgTP) and acid strength. This may be due to the desorption of ammonia adsorbed weakly on a Brønsted acid site. The specific band area of II (1400 cm^{-1}) after evacuation at the proper temperature is related to the acidic property of the heteropoly compound.

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