

NOTES

Coadsorption of Ammonia and the Other Bulky Bases on Aluminium Phosphate

Ammonia and pyridine are commonly used as probe molecules to characterize surface acid properties, and these two molecules are believed to be adsorbed on the same sites regardless of the difference in the types and strength of acid sites. We wish to report that ammonia and pyridine are adsorbed on different sites on the aluminium phosphate surface, indicating the existence of two kinds of acid sites on the surface. By IR study of coadsorption of ammonia and pyridine, it is possible to distinguish one type from the other type. Bulky amines such as ethylamine, diethylamine, and triethylamine behaved just as pyridine in the coadsorption with ammonia.

Aluminium phosphate (AP) was prepared by addition of 10% $\text{NH}_4\text{OH}_{\text{aq}}$ to an aqueous solution containing $\text{Al}(\text{NO}_3)_3$ and H_3PO_4 . Detailed procedures are described in our previous paper (1). γ -Alumina was obtained by hydrolysis of aluminium isopropoxide.

The sample (20–30 mg) was pressed into a disk (20 mm dia.) and pretreated *in vacuo* at 923 or 1023 K *in situ* of the IR cell. The IR spectra were recorded on the JEOL JIR-40X FT-IR spectrometer.

Two kinds of bases were coadsorbed on AP or alumina as follows. Initially the sample was exposed to the vapor of one of the bases at 296 K (10 Torr, for 10 min), then evacuated at 296 K for 40 min. After recording the IR spectrum the sample was exposed to that of the other base and evacuated under the same conditions.

The total amounts of adsorbed bases are measured by an electrobalance or a quartz spring balance.

The IR spectra of ammonia and pyridine coadsorbed on AP evacuated at 1023 K are shown in Fig. 1. A and C show spectra of

adsorbed ammonia and pyridine, respectively. The bands due to NH_4^+ (1450 cm^{-1}) and the pyridinium ion (1550 cm^{-1}) are scarcely observed, suggesting no participation of Brønsted acid sites in the adsorption. B and D show the spectra of coadsorbed ammonia and pyridine. When ammonia was adsorbed first followed by pyridine adsorption (B), new bands due to adsorbed pyridine appeared although the bands assigned to preadsorbed ammonia scarcely changed. When pyridine was adsorbed first followed by ammonia adsorption (D), intensities of the bands assigned to adsorbed ammonia were essentially the same as those in spectrum A, but those of the bands assigned to adsorbed pyridine decreased to four-fifths as compared to spectrum C. These adsorption bands decreased in parallel with the increase in the evacuation temperature, and diminished on evacuation at 623–673 K. These facts suggest that there are two different types of adsorption sites on AP, where ammonia and pyridine are independently adsorbed on each site.

The results of the coadsorption of ammonia and ethylamine are shown in Fig. 2. Most of preadsorbed ammonia still remained after ethylamine adsorption (C), and the opposite situation was also observed (E). Similar results were obtained in the experiments of coadsorption of ammonia/diethylamine and ammonia/triethylamine. From these facts, the amines and pyridine seem to be adsorbed on the same type of adsorption sites. In fact, this interpretation was supported experimentally, that is, the displacement of preadsorbed triethylamine by pyridine occurred as shown in Fig. 3.

On the other hand, on alumina, no such

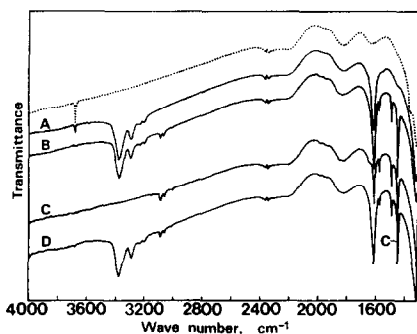


FIG. 1. Infrared spectra of ammonia and pyridine on aluminium phosphate evacuated at 1023 K. (A) Preadsorbed ammonia, (B) pyridine was added on A, (C) preadsorbed pyridine, (D) ammonia was added on C, (---) background. The same sample disk was used in all experiments.

different types of adsorption sites have been reported. According to Take *et al.* (2) most of the preadsorbed ammonia was displaced by pyridine, although a small fraction of preadsorbed ammonia was still adsorbed. They explained that the remaining ammonia exists in micropores where the larger molecule pyridine cannot enter. Figure 4 gives another type of evidence. In this coadsorption experiment ethylamine was employed instead of pyridine. Ammonia could not be adsorbed on ethylamine-pre-

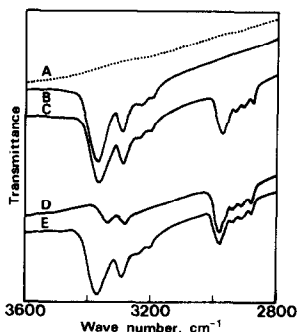


FIG. 2. Infrared spectra of ammonia and ethylamine on aluminium phosphate evacuated at 1023 K. (A) Background, (B) preadsorbed ammonia, (C) ethylamine was added on B, (D) preadsorbed ethylamine, (E) ammonia was added on D. The same sample disk was used in all experiments.

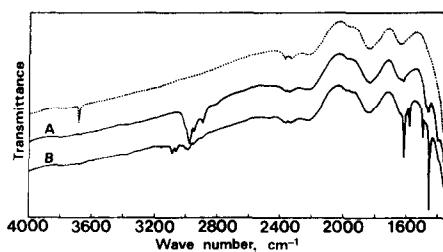


FIG. 3. Infrared spectra of pyridine and triethylamine on aluminium phosphate evacuated at 1023 K. (A) Preadsorbed triethylamine, (B) pyridine was added on B, (---) background.

adsorbed alumina, and almost all preadsorbed ammonia were displaced by ethylamine. These results indicate that most of the adsorption sites on alumina are evidently available for both ammonia and pyridine (or ethylamine).

The total amounts of adsorbed bases on AP at 296 K and the evacuation temperatures required to desorb half of them ($T_{1/2}$) are given in Table 1. Although there are no great differences among $T_{1/2}$ values, it is worth noting that both pyridine and ethylamine are desorbed at lower temperatures than ammonia. In the gas phase, the base strength of pyridine and the amines are sub-

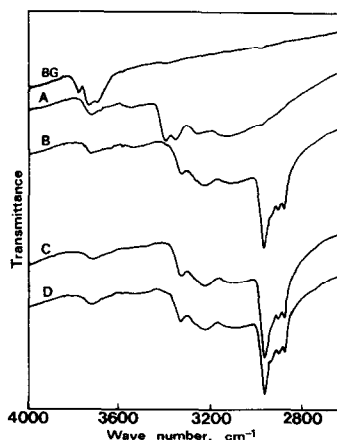


FIG. 4. Infrared spectra of ammonia and ethylamine on γ -alumina evacuated at 923 K. (A) Preadsorbed ammonia, (B) ethylamine was added on A, (C) preadsorbed ethylamine, (D) ammonia was added on C, (BG) background.

stantially greater than that of ammonia (3, 4). Therefore pyridine (or amines) should have been desorbed at a higher temperature than ammonia. This fact implies the existence of a special interaction between pyridine (or amines) and the surface of AP.

Figure 5 shows IR spectra of the gas phase and adsorbed pyridine. It is found that the bands due to ν -CH of adsorbed pyridine (3088 and 3065 cm^{-1}) are very weak compared with those of gas phase pyridine. This suggests that the hydrogen of adsorbed pyridine, which is considered to be positively charged, interacts with the surface, probably with a basic site.

It is quite difficult to give an explanation for the two different types of adsorption sites, since there has been no direct evidence for basic sites on AP. But we would like to suppose that there are two domains, one including acid sites alone and the other including acid-base pair sites. Pyridine or amines could take place on acid-base pair sites, where the basic site interacts with the H atom of the $=\text{N}-\text{CH}=\text{}$ group of the above molecules in cooperation with the bonding between the acid site and the N atom of the $=\text{N}-\text{CH}=\text{}$ group to strengthen the adsorption bond. On the other hand, ammonia would be adsorbed on the acid site alone. The reason why ammonia cannot be adsorbed on acid-base pair sites is given as follows. The acid strength of the acid-base pair site is so weak that weaker base ammonia cannot be adsorbed, because it has no such $=\text{N}-\text{CH}=\text{}$ group as pyridine. Here, one might have a ques-

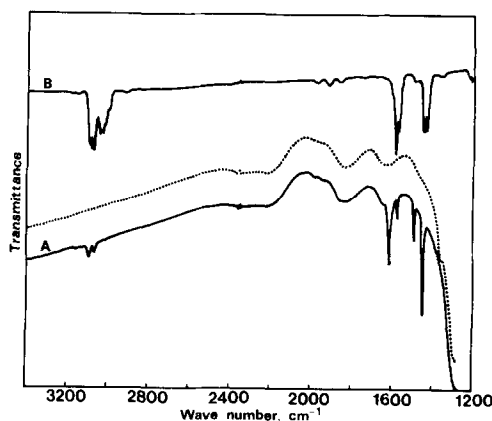


FIG. 5. Infrared spectra of adsorbed pyridine on aluminium phosphate evacuated at 1023 K (A), and gas phase pyridine (B). (---) Background of A.

tion about the inhibition of pyridine (or amines) adsorption on the acid site. We speculate that it would be caused by a steric hindrance, because pyridine (or amines) is a more bulky molecule than ammonia.

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TABLE I

Total Amounts of Adsorbed Bases at 296 K and Temperatures Required to Desorb Half of Them ($T_{1/2}$)

Base	mmol/g	$T_{1/2}$ (K)
Ammonia	1.05	344
Pyridine	0.69	341
Ethylamine	0.67	331

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