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# INFRARED STUDY OF AMMONIA AND PYRIDINE ADSORPTION ON V-Ti OXIDE

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Adsorption of ammonia and pyridine on V-Ti oxide with a low vanadium content (2 and 5 wt%) has been studied by IR techniques. V-Ti oxide shows both Brønsted and Lewis acidities. The nature of both acid sites and the difference between the acidities determined from ammonia and pyridine adsorption have been discussed.

Vanadium oxide catalysts in combination with various promoters are widely used for selective oxidation of hydrocarbon. Particularly, V-Ti oxide catalysts are well known because of their high selectivity and activity. The acid-base properties of V-Ti oxide have been discussed on the basis of the results of adsorption of various basic and acidic molecules on it. The results of IR studies of ammonia adsorption on unsupported and supported vanadium oxides show some contradiction concerning the nature of their acidity.1-5) In previous work,6) we studied the effects of the adsorption of acidic and basic molecules on alcohol oxidation over V-Ti oxide by IR techniques. In the present work, in order to clarify the surface acidity of V-Ti oxide, the adsorption of basic molecules on it has been studied by IR spectroscopy.

Two sets of vanadium-titanium oxide, V-Ti-2 and V-Ti-5 (2 and 5 wt% of $V_2O_5$, respectively), were prepared by impregnating the $TiO_2$ support (Degussa P25) with an oxalic acid solution of ammonium metavanadate followed by calcination at 383 K for 10 h. A disk of V-Ti oxide was degassed, oxidized at 673 K for several hours, degassed for 2 h at that temperature, and cooled to room temperature. After the introduction of a small amount of ammonia or pyridine (Py) infrared spectra were recorded. The BET surface areas were 42 and 48 $m^2g^{-1}$ for V-Ti-5 and V-Ti-2, respectively. The details of the apparatus and procedures were reported previously.7)

Figure 1 shows the typical spectra of $NH_3$ adsorbed on V-Ti-2 (dry V-Ti-2). The spectra in the region above 2000 $cm^{-1}$ could not be observed. Bands appeared at 1600 and 1439 $cm^{-1}$, which does not change on evacuation at 323 K, agree with those due to coordinately adsorbed $NH_3$ and $NH_4^+$ ion,1,3-5,8) respectively. In order to obtain information on the effect of surface hydroxyl groups, before the introduction of $NH_3$ V-Ti-2 disk was pretreated with water vapor at 523 K (wet V-Ti-2). The resulting spectra were also shown in Fig. 1. The $NH_4^+$ band is intensified as compared to that with dry V-Ti-2, suggesting that Brønsted (B)-acid site was enhanced by water pretreatment.

Figure 2 shows the IR spectra of $NH_3$ adsorbed on dry V-Ti-5. The $NH_4^+$ band is intensified with increasing the content of $V_2O_5$. In addition, a new band at 1483 $cm^{-1}$ appeared, being intensified with increasing the temperature of the disk. This band is tentatively assigned to $NH_2$ species,8) although the position of this band varies with metal oxides.8) Relative intensity of the $NH_3$ band to the $NH_4^+$ one is decreased with increasing the content of $V_2O_5$. This suggests that with V-Ti-2 the Ti ion also acts as L-acid sites. In the case of wet V-Ti-5 (Fig.2), this ratio was decreased. In addition, no $NH_2$ band was observed.

Similar experiments were carried out using Py instead of $NH_3$. With dry V-Ti-2 sharp bands at 1603, 1482, and 1440 $cm^{-1}$, together with weak bands at 1634, 1572, and 1534 $cm^{-1}$, appeared (Fig.3). On evacuation at 323 K the intensities of these bands were not changed significantly. These bands were not affected by water pretreatment (Fig.3). In the case of dry V-Ti-5 sharp bands at 1606, 1482, and 1440 $cm^{-1}$ and weak bands at 1634, 1573, and 1537 $cm^{-1}$ appeared (Fig.4). On evacuation at 323 K the intensities of these bands were not changed

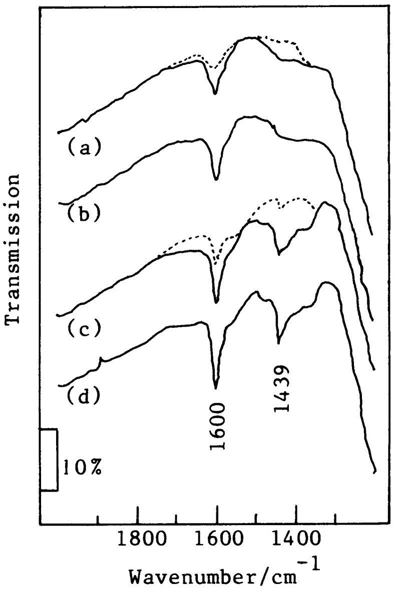


Fig. 1. IR spectra of $NH_3$ on V-Ti-2. After adsorption of $NH_3$ ($3 \times 10^{18}$ $m^{-2}$) on V-Ti-2, dry (a,b) or wet (c,d), followed by 1 h evacuation at; (a) 293 K; (b) 323 K; (c) 293 K; (d) 323 K. In Figs. 1-4 the dotted lines show background spectra.

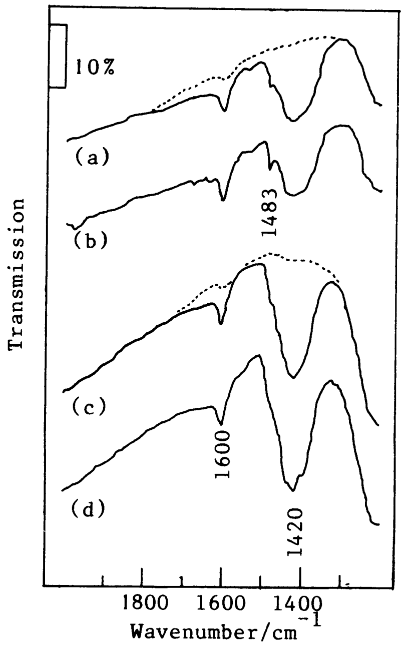


Fig. 2. IR spectra of $NH_3$ on V-Ti-5. Conditions are the same for Fig. 1.

significantly. The former and the latter group of the bands are characteristic of Lewis (L) coordinated Py (LPy) and pyridinium ions (BPy),[8] respectively. With wet V-Ti-5 the bands due to BPy are strengthened (Fig.4).

The results described above suggest that the acid sites of V-Ti oxide are characterized by both L and B acids. Since parent titania with or without water pretreatment showed no B acidities on the adsorption of $NH_3$ or Py, it is concluded that surface vanadate play a role as B sites, being in agreement with those in the literatures.[1,4,5] In addition, the difference in the position of the 8a mode of LPy on V-Ti-5 (1606 $cm^{-1}$) and $TiO_2$ (1602 $cm^{-1}$) suggests that the L-acid sites are associated with vanadium ion.[6]

It is possible to employ the IR spectra for Py on V-Ti oxide to estimate the number of B- and L-acid sites on V-Ti oxide. Such an estimation has been carried out from the relative intensities of the 1440 (LPy) and 1537 $cm^{-1}$ (BPy) bands on V-Ti-5 in previous paper.[6] The results show that ca. 80 and 20% of the acid sites on the V-Ti-5 is composed of L- and B-acid sites, respectively.

Although such a quantitative analysis was not undertaken for the adsorption of $NH_3$ on V-Ti-5 the results in Figs. 2 and 4 suggest that as compared to that with Py adsorption a much higher fraction of B-acid sites would be obtained from $NH_3$ adsorption. With dry V-Ti-5 $NH_3$ reacts with surface vanadate to form B-acid site together with $NH_2$ species, resulting in the increase in the fraction of B sites. Thus

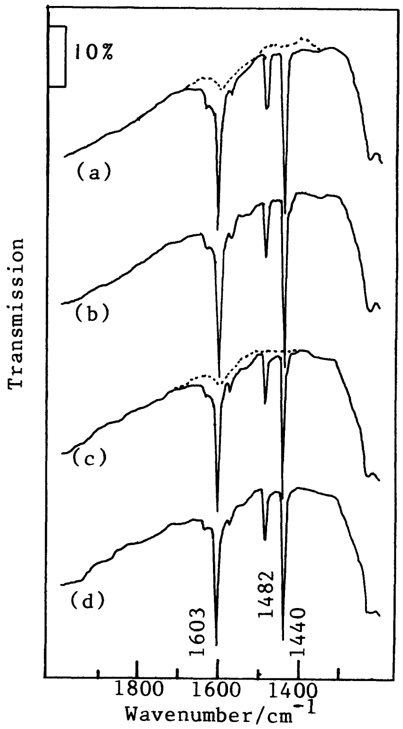


Fig. 3. IR spectra of Py on V-Ti-2. After adsorption of Py (1.2 x $10^{18} m^{-2}$) on V-Ti-2, dry (a,b) or wet (c,d), followed by 1 h evacuation at; (a) 293 K; (b) 323 K; (c) 293 K; (d) 323 K.

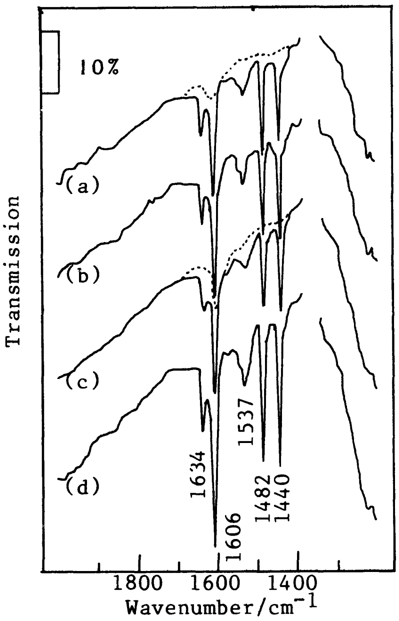
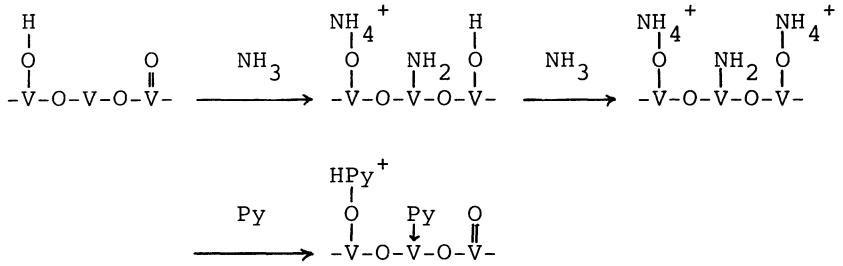


Fig. 4. IR spectra of Py on V-Ti-5. Conditions are the same for Fig. 3.

the adsorption of both bases on dry V-Ti oxide presumably takes place as follows:



In the case of wet V-Ti-5, the following explanation would be offered. No formation of $NH_2$ species with wet V-Ti-5 suggests that all the vanadium ions associated with $NH_2$ formation are converted to the V=OH species, which interact with $NH_3$ to form $NH_4^+$. On the other hand, with Py most of the V-OH species act as L-acid sites, although its small fraction having a strong acidity interacts with Py to form BPy. This explanation is supported by the fact that there is no difference between the amount of Py strongly adsorbed on both V-Ti-5 pretreated with water vapor at 423 and 673 K. In addition, Morterra et al.9) have reported that Py interacts with hydroxylated $TiO_2$ to displace hydroxyl groups, adsorbing on Ti ions.

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