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NOTE

Improving the Selectivity of NH_3 TPD Measurements

The NH_3 TPD method, widely employed in characterizing the acidity of solid catalysts, is lacking in selectivity, because ammonia can titrate acid sites of any strength and type; moreover, it can be adsorbed by hydrogen bond or dipolar interactions. Physisorbed NH_3 can be eliminated by adsorption at high temperature; however, the problem of discriminating between different types of acid sites by TPD has not yet been resolved. Moreover, in some cases a further problem arises from superposition of peaks, so that a mathematical treatment is required for resolution (1).

A way of improving this method could be to promote selective desorption after the sample has been saturated with ammonia. This could be achieved, for example, by treating the material with a substance that can give rise to competitive adsorption with ammonia, such as water. It may be presumed that the effect of a treatment with water vapor would be selective displacement of ammonia, according to the relative affinities of ammonia and water for different adsorbing sites. By observing modifications of TPD peaks caused by such a treatment, one could gain information on the nature of adsorbing sites. Moreover, such at treatment could be also advantageous in resolution of peaks, as it should speed up desorption of physisorbed NH_3. In order to test this hypothesis, different catalytic materials, well known for their acidic properties, were subjected to NH_3 TPD measurements, following a conventional procedure which was modified by addition of a "water treatment." The materials include zeolites, metal oxides, and a metal acid phosphate.

An H-ZSM-5 (Si/Al ratio = 250) was obtained by ion exchanging a laboratory synthesized Na-ZSM-5 (2) with NH_4Cl solution and calcining at 550°C for 12 h. H-mordenite (Si/Al ratio = 16) was obtained from a natural mordenite (3) by the same procedure. γ-Al_2O_3 (type CK 300) was supplied by AKZO Chemie; it had a surface area of 180 m^2/g. TiO_2 "Eurotitania" was supplied by Tioxide Specialties Ltd.; it was 99.9% anatase and had a surface area of 120 m^2/g. A mixed tin–zirconium phosphate of formula $Sn_{0.5}Zr_{0.5}(HPO_4)_2 \cdot H_2O$, synthesized as described in (4), was calcined at 550°C for 20 h; its surface area was 75 m^2/g.

TPD tests were carried out in a conventional flow apparatus. The sample (0.04 g) was treated at 500°C in helium flow for 1 h; after cooling to 20°C it was saturated with a 1% NH_3/He mixture. Then the following purging treatment was applied at $T = 20$°C: 1 h in helium, 1 h in a 0.6% water vapor/helium mixture, and 1 h in helium flow. The flow rate was 100 cm^3/min in every case. The water vapor/helium mixture was obtained with a saturator kept at 0°C. In some cases, the water treatment was protracted for longer periods. After the purging treatment, desorption of ammonia was effected by heating to 800°C at a rate of 10°C/min, in helium flow of 30 cm^3/min. The concentration of NH_3 in the effluent from the cell was measured by a TCD detector. A water trap (KOH on ceramic wool) was located before the detector. The repeatability of concentration measurements was verified within 3%. For comparison, tests were made in the same conditions as above, but bypassing the water saturator: these tests are referred to as "conventional TPD measurements" in the following.

The results obtained with H-ZSM-5 are reported in Fig. 1. The conventional measurement gives the spectrum a, which shows a high temperature peak, with maximum at 350°C, and a low temperature peak, with maximum at 148°C. Similar results were already observed for H-ZSM-5 zeolites (5–9). The high temperature peak is related to protonic acidity, while the low temperature peak is probably due to ammonia coordinated to aluminium species or adsorbed by hydrogen bridging bonds (5, 8, 10). From the high temperature peak it can be calculated a concentration of 6.3×10^{-5} mole NH_3/g of zeolite, that is comparable with the concentration of protonic sites expected on the basis of the Si/Al ratio, 6.7×10^{-5} mol/g. The spectrum obtained after water treatment (curve b) shows that the low temperature peak has been completely removed, while the high temperature one has not been affected at all. By prolonging the water treatment (3 h), a spectrum identical to b was obtained. Thus, the treatment appears effective for discriminating the peak of protonic acidity from peaks due to different interactions.

The results obtained with H-mordenite are shown in Fig. 2. The conventional TPD gives rise to two peaks, with maxima at 157° and 465°C respectively, and a small shoulder at 655°C (curve a). According to literature data (11) only the peak at $T = 465$°C is attributable to protonic acidity. It corresponds to 6.4×10^{-4} mol/g, which is somewhat lower than the value expected on the basis of the Si/Al ratio, 9.5×10^{-4} mol/g. It is possible that some dealumina-

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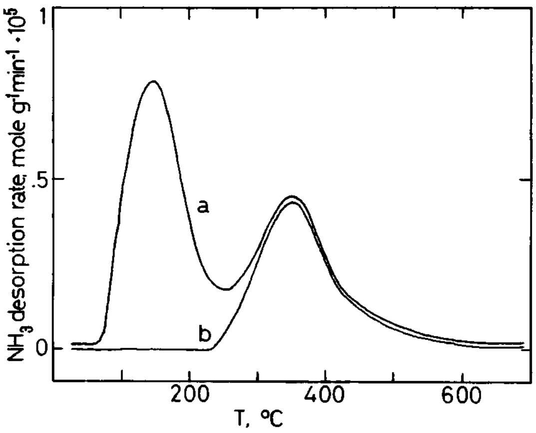

FIG. 1. NH_3 TPD spectra of H-ZSM-5: a, conventional measurement; b, after 1 h water treatment.

tion, with resulting loss of protonic acidity, occurred during the previous calcination of the zeolite. The water treatment (curve b) removes the low temperature peak, and also the small signal at $T = 655°C$, while the peak of protonic acidity remains unaltered. Again it has been observed that prolonging the purging treatment does not modify the TPD spectrum. Thus, for H-mordenite also the water treatment allows a clear separation of the peak of protonic acidity. The signal at $T = 655°C$, which is suppressed by the water treatment, could be due to strong Lewis acid sites, which are present in H-mordenite (12, 13).

It is interesting to study the behavior of materials characterized by a different type of Brønsted acidity, that is, layered acid phosphates containing HPO_4 groups. A mixed Sn/Zr hydrogen phosphate has been selected because of its high surface area (4). Since this material was treated at 550°C for 20 h before TPD tests, only surface HPO_4 groups are available for adsorption, while internal sites are eliminated: thus, complicating effects due to intercalation are avoided (4, 14). Results of TPD tests on this material are reported in Fig. 3. The spectrum of the conventional measurement (curve a) shows a peak with maximum at 175°C and a long tail, extending to 600°C. This result is typical of layered metal phosphates and is explained by the presence of Brønsted acid sites of different strength (4, 15). The amount of desorbed NH_3, 2.5×10^{-4} mol/g, corresponds to 2.0×10^{14} molecule/cm^2, that is, about half the theoretical concentration of surface HPO_4 groups, 4.4×10^{14} site/cm^2 (4). It is possible for this type of materials that the surface concentration of HPO_4 groups is lower than that of the idealized structure (4, 15). The water treatment causes a 25°–30° shifting of the curve to higher temperatures (curve b), without changing the amount of desorbed NH_3; also the shape of the curve is not significantly modified by this treatment. A longer water treatment (3 h) gives a spectrum identical to curve b. Two interpretations may be given for these results: one is that the water treatment removes ammonia from some weak sites and, at the same time, generates new strong acid sites, so that the two effects compensate each other; the other is that no ammonia is removed nor any new sites generated, but the desorption peak is simply shifted to higher temperatures in the presence of water. This shifting could be explained by stabilization of adsorbed NH_3, due to hydration of NH_4^+ ions. On account of the strict equivalence of the peaks, the latter interpretation seems more acceptable. This means that water cannot displace ammonia in this material from acid sites of any strength.

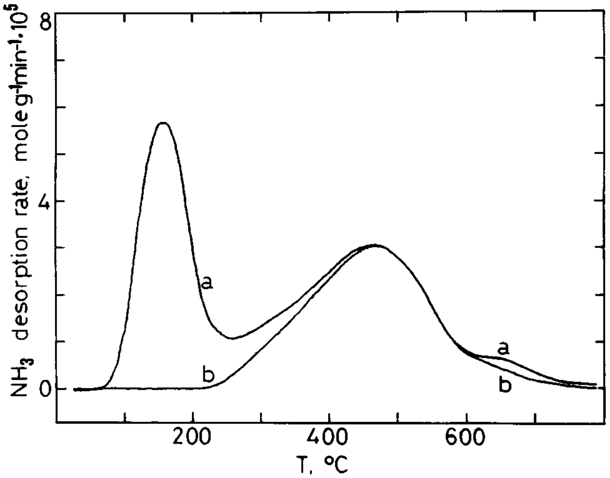

FIG. 2. NH_3 TPD spectra of H-mordenite: a, conventional measurement; b, after 1 h water treatment.

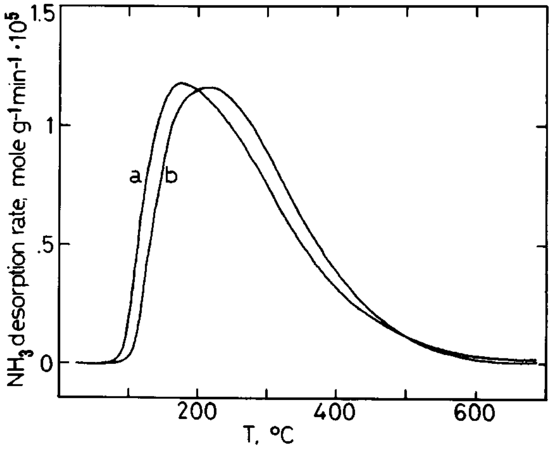

FIG. 3. NH_3 TPD spectra of acid Sn/Zr phosphate: a, conventional measurement; b, after 1 h water treatment.

Further, let us examine the behavior of materials characterized by Lewis type acidity. Active forms of alumina, when treated at temperatures higher than about 400°C (but lower than the temperature range of transition to α-Al_2O_3), contain acid sites consisting of c.u.s. Al^{3+} ions, whose strength

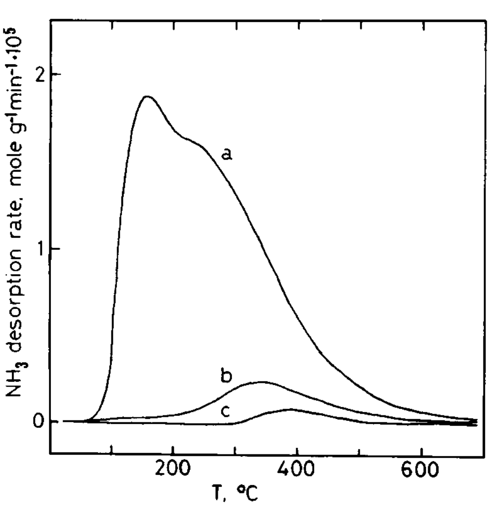

FIG. 4. NH_3 TPD spectra of γ-Al_2O_3: a, conventional measurement; b, after 1 h water treatment; c, after 3 h treatment.

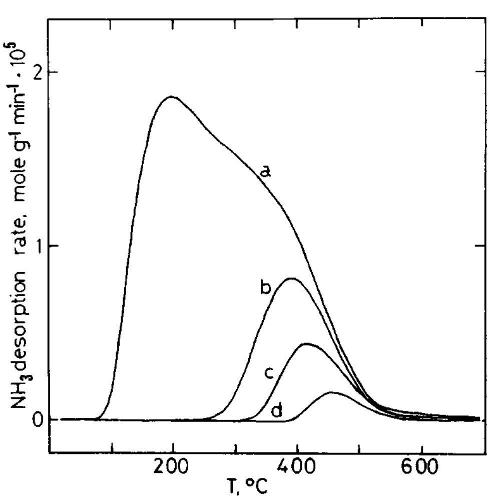

FIG. 5. NH_3 TPD spectra of TiO_2 anatase: a, conventional measurement; b, after 1 h water treatment; c, after 3 h treatment; d, after 8 h treatment.

is variable in a wide range (16, 17). On the other hand, no Brønsted acid sites of appreciable strength have been detected in γ-Al_2O_3 (18).

The spectra obtained with γ-Al_2O_3 are reported in Fig. 4. Without any water treatment (curve a) NH_3 TPD gives rise to a low temperature peak, with maximum at 158°C, and a shoulder at 245°C, with a tail extending to 600°C. The spectrum points to a wide distribution of strengths of acid sites. The total amount of desorbed NH_3 is 4.3×10^{-4} mol/g, corresponding to 1.5×10^{14} molecule/cm^2, which is the order of magnitude of acid site concentration of γ-Al_2O_3 (16). When the water treatment is applied, most NH_3 is removed (curve b): the residual peak at $T = 337$°C corresponds to a concentration of 0.4×10^{-4} mol/g. This residual NH_3 is removed by a longer water treatment: in fact, a 3 h treatment leaves only traces of NH_3 (curve c). Thus, in the case of γ-Al_2O_3, it is impossible to discriminate between different acid sites because ammonia bonded to acid sites of any strength is removed by water in reasonable times.

Titanium dioxide is another Lewis acid material. Acid sites on the surface of TiO_2 anatase have been identified as unsaturated Ti^{4+} ions; Brønsted acid sites are absent (19–22).

As shown in Fig. 5, the TPD spectrum of TiO_2 anatase consists of a peak with maximum at 195°C and a large shoulder at about 360°C (curve a). The total amount of desorbed NH_3 is 4.7×10^{-4} mol/g, corresponding to 2.3×10^{14} molecule/cm^2: this value is about one half the theoretical concentration of c.u.s. Ti^{4+} ions (23) and is close to the saturation value observed with other basic molecules, such as methanol (24). The spectrum indicates the presence of at least two types of NH_3 adsorbing sites, which could correspond to the two types of Lewis sites detected by other authors (19, 23). After the standard water treatment (curve b) the low temperature peak is absent while the high temperature one is reduced in intensity, amounting to 1.1×10^{-4} mol/g. After 3 h treatment (curve c) the ammonia peak is reduced to 0.6×10^{-4} mol/g; after 8 h (curve d) the signal is further reduced to 0.2×10^{-4} mol/g. Therefore, the behavior of TiO_2 is similar to that of Al_2O_3, but the displacement of ammonia from TiO_2 occurs in longer times, probably due to higher acid strength.

The results of this work can be briefly summarized. When the water purging treatment was applied to materials characterized by Brønsted acidity, desorption spectra showed little or no alteration of the peaks of protonic acidity, while other peaks were easily removed. On the other hand, when the same treatment was applied to Al_2O_3 or TiO_2, which were characterized by c.u.s. ions acidity, all ammonia peaks were gradually eliminated in a period of a few or several hours. Note that in these oxides there are sites which desorb ammonia at temperatures comparable with those of the stronger acid sites of zeolites; so the different behaviors of the materials seem not to be related to the strength, but rather to the type of acid–base interaction. It is possible to explain why ammonia bonded to protonic sites is stable in the presence of water, because ammonia is a stronger Brønsted base than water. As regards interactions with Lewis acid sites, no general scale of basic strength is available: however, considering the chemistry of Al^{3+} and Ti^{4+}, in particular the low stability of NH_3 complexes, it is not surprising that the coordination of water on these ions is preferred to that of ammonia. This result, of course, cannot be generalized, for other cations may show different behavior.

In conclusion, the procedure studied in this work could represent a simple way of improving the selectivity of the ammonia TPD method by making it possible to discriminate protonic from other acid sites and, in some cases, to exclude the presence of protonic acidity. Presumably, the method could be also advantageous for resolution of peaks in more complex spectra than those observed in this study.

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