

NOTES

Ammonia Adsorption on a Decationized Y Zeolite

Aluminosilicates in both the amorphous and crystalline form exhibit acidic sites responsible for catalytic reactions involving adsorbed intermediates behaving like carbonium ions. The nature of these acidic sites remains a matter of active discussion. Yet, the very high cracking activity of certain zeolites has now been very well established. For instance, a Y zeolite related to faujasite can have most of its sodium cations exchanged for ammonium ions; the ammonium ions can then be decomposed thermally to ammonia and protons that stay behind in the form of infrared-active OH groups (1, 2). Such materials have been called decationated (1) or decationized (2) zeolites, and their cracking activity has been reported to be 6400 times higher than that of a standard silica-alumina gel (3).

This striking difference in catalytic behavior between materials of similar chemical composition but different structure is one of the most exciting discoveries in recent catalytic work. Without taking a position on the nature of the acidic sites responsible for this difference between gels and crystalline materials, we decided to attempt a gross characterization of their surfaces by adsorbing a molecule which is bound, without discrimination, by various kinds of acidic sites. Such a molecule is ammonia, and the work presented in this note was prompted by an elegant study of Clark and co-workers (4, 5), who studied in great detail the equilibrium between gaseous ammonia and ammonia adsorbed on a series of silica-alumina gels of various chemical composition. It seemed interesting to compare enthalpies and entropies of

adsorption as reported for gels with the corresponding quantities observed on a decationized Y zeolite in the hope that such a comparison might help in the understanding of catalytic behavior.

EXPERIMENTAL

Ammonia and nitrogen were obtained from The Matheson Company. The ammonia, stated to be 99.98% pure, was used without further purification. Nitrogen was passed through an efficient liquid nitrogen trap before use. The adsorbent was purchased from the Linde Company as SK-40, the powder form of Na-Y.

First an $\text{NH}_4\text{-Y}$ sieve was prepared by exchanging Na-Y overnight at 50°C in a 2.77 N NH_4Cl solution containing 20 excess equivalents of NH_4^+ per equivalent of Na⁺ in the SK-40 sample. After filtration the exchanged zeolite was washed free of chloride with warm distilled water and then dried in air at room temperature for 24 hr. The decationized zeolite was then prepared by heating $\text{NH}_4\text{-Y}$ *in situ* to temperatures above 360°C (1). A chemical analysis of $\text{NH}_4\text{-Y}$ gave a unit cell composition of $\text{Na}_{18}(\text{NH}_4)_{41}(\text{AlO}_2)_{59}(\text{SiO}_2)_{133} \cdot n\text{H}_2\text{O}$.

Adsorption was studied gravimetrically with a Cahn Electrobalance, Model RG 2000, connected to a Leeds and Northrup Speedomax H recorder. The balance was encased in a large aluminum vacuum chamber attached to a gas-handling system. The quartz sample bucket was hung on a fine Nichrome wire into a quartz furnace tube which extended 45 cm below the base of the aluminum chamber. A thermocouple well extended upwards 12 cm from the

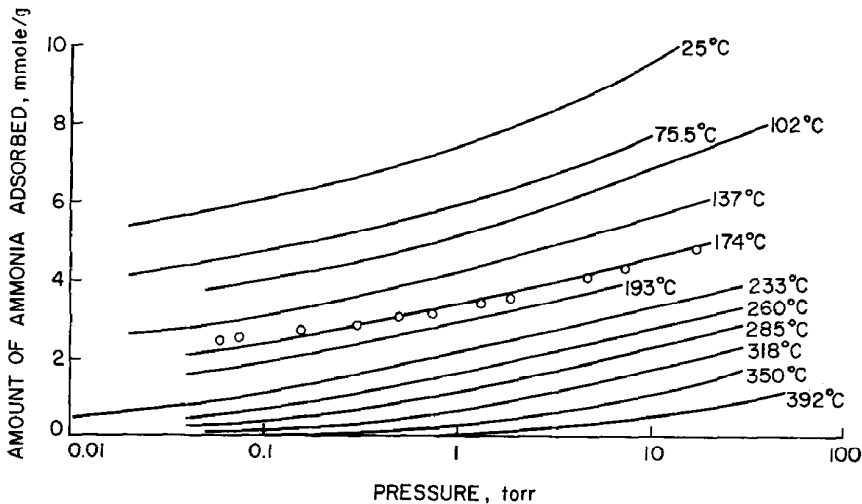


Fig. 1. Adsorption isotherms of ammonia on decationized Y zeolite.

lower end of the furnace tube so that the tip of the thermocouple was 5 to 10 mm below the sample bucket. The pressure in the system was measured with an NRC Alphatron gauge, Model 530, which had been calibrated against McLeod gauges.

The vacuum system consisted of a mechanical pump and an oil diffusion pump equipped with a large nitrogen trap. An ultimate vacuum of 10^{-6} torr was obtained. Extreme precautions were taken to eliminate traces of oil and grease from the

aluminum balance chamber and the quartz furnace tube.

The weight change during outgassing of the fresh sample was followed closely. For a loosely stacked 0.1 g sample of the wet zeolite in a quartz bucket, the first 2 hr of pumping at room temperature resulted in about 50% of the final, total weight loss. The temperature was then gradually raised to 100°C , held at 100°C for 2 hr and then increased at the rate of $50^{\circ}\text{C}/\text{hr}$ to 390°C . A sample was considered

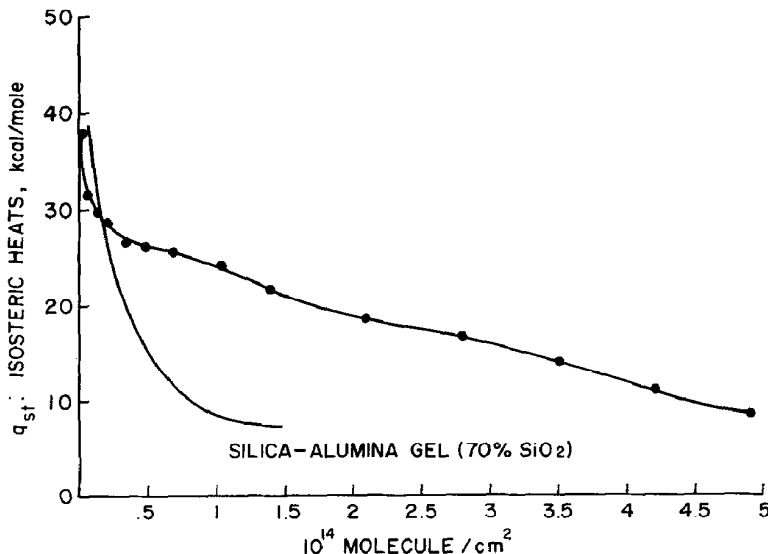


Fig. 2. Isothermic heats of ammonia on decationized Y zeolite.

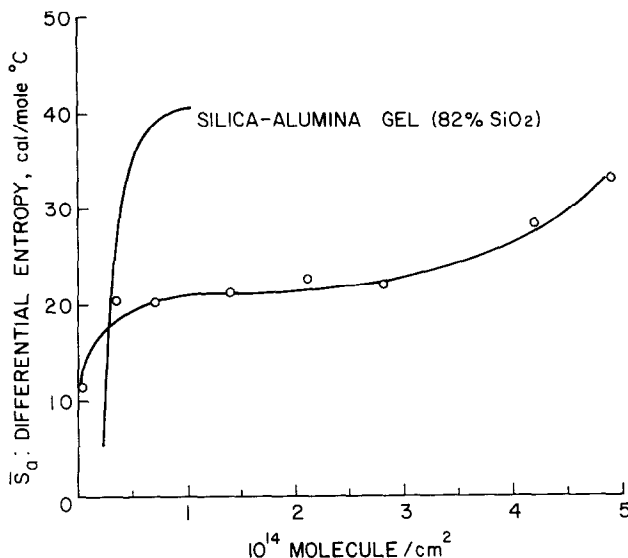


Fig. 3. Differential entropy of ammonia on decationized Y zeolite.

completely outgassed when a steady weight was observed at 390°C and 10⁻⁶ torr. The data for the isotherms were all based on the dry weights of the samples. However for their discussion in this note, it will be convenient to refer amounts adsorbed not to unit weight but to unit surface for comparison with the data of Clark *et al.* on silica-alumina gels (4, 5). For this purpose, nitrogen adsorption data at liquid nitrogen temperature were fitted to a Langmuir isotherm. The fit was excellent and gave for the decationized zeolite a surface area of 850 m²/g if it is assumed, as usual, that the cross-sectional area of a nitrogen molecule is 16.2 Å².

RESULTS AND DISCUSSION

Ammonia adsorption isotherms were obtained on the decationized samples between 25° and 390°C and at pressures from 10⁻² to 50 torr. These conditions are very similar to those of Clark, Holm, and Blackburn (4): 100° to 400°C and 10⁻³ to 20 torr. All isotherms in the present work were reversible within the accuracy of the temperature control, which was within ±3°C. Reproducibility of amounts adsorbed at a given temperature was within 10% at high pressures and somewhat poorer at low pressures. At high temperatures, equilib-

rium was achieved within a few minutes for all pressures, but it took about half an hour to reach equilibrium at low pressures and low temperatures. Blank measurements on the sample bucket and the balance parts were made for all temperatures and pressures studied. It was found that the blank correction reached its maximum at 0.1 torr regardless of temperature. The magnitude of the correction was such that it became important only at temperatures above 300°C and pressures below 10 torr.

All the isotherms are shown in Fig. 1, where experimental points have been omitted because of crowding except for one typical curve at 174°C. From the data isosteric heats, q_{st} (Fig. 2), were readily calculated from Clapeyron-Clausius plots and differential entropies of ammonia in the adsorbed state, \bar{S}_a (Fig. 3), were obtained by means of the relation

$$\bar{S}_a = (-q_{st}/T) + R \ln (p^\circ/p) + S_g^\circ$$

where p° is the standard pressure (1 atm) at which the entropy of gaseous ammonia, S_g° , is evaluated. In both Figs. 2 and 3, curves of q_{st} and \bar{S}_a are drawn for silica-alumina gels of a composition as close as possible to that of the decationized zeolite. These curves are taken from those avail-

able in the paper of Clark, Holm, and Blackburn (4).

At first glance the gel and crystalline materials appear strikingly different. Thus q_{st} falls precipitously on silica-alumina gel from values in the vicinity of 40 kcal/mole on a bare surface to values less than 10 for a surface coverage as low as 1×10^{14} molecule/cm². By contrast, on the zeolite, q_{st} starts at about the same value as on the gel but, after an initial drop to 28 kcal/mole at a surface coverage of 0.1×10^{14} molecule/cm², q_{st} falls very slowly and practically linearly to reach a value of 10 kcal/mole at a coverage corresponding to about 5×10^{14} molecule/cm². It is interesting to note that, according to the chemical analysis of the decationized zeolite, the number of protonic sites should be 2.4×10^{14} /cm². It is clear therefore that the values of q_{st} shown in Fig. 2 must correspond to several forms of adsorbed ammonia. Similarly, as seen in Fig. 3, \bar{S}_a rises very rapidly with coverage for the gel; it stays almost constant on the zeolite after a rapid initial increase until a coverage between 2 and 3×10^{14} /cm² is reached. It then increases further to values close to those found on the gel material. Interpretations of surface entropies, in the absence of knowledge of type of adsorption, are fraught with difficulties and will not be pursued any further since the considerations of Holm and Clark (5) may well apply *mutatis mutandis* to the present data.

Instead, let us focus attention on the isosteric heats. We believe that a significant result is the absence on the zeolites of surface sites capable of binding ammonia more strongly than silica-alumina gels. If then the superior catalytic cracking activity of the crystalline material is due to its possessing stronger acid sites, these are

either sites of a type which do not interact strongly with ammonia, or there are very few of these sites. Both explanations appear unlikely. In fact, closer examination of the two curves of Fig. 2 reveals that they are *qualitatively* very similar. The quantitative difference is that there are many more surface sites capable of binding ammonia with neither too large nor too small energies on the crystalline than on the gel sample. Whether this suffices to explain the superior catalytic activity of the decationized zeolite or whether some alternative explanation must be invoked must be decided by further work.

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