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MICROCALORIMETRIC EVIDENCE OF THE NON-UNIFORM DISTRIBUTION OF ACID SITES IN A ZSM-TYPE ZEOLITE

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ABSTRACT

Calorimetric heats of adsorption of ammonia on a protonated ZSM zeolite at 416 K, plotted as a function of surface coverage, pass through a maximum which is explained by the unusual conjunction of three independent phenomena: (i) immobile adsorption, (ii) mass-transfer limitations, and (iii) preferential location of the most energetic acid sites in the internal pores of the zeolite structure.

INTRODUCTION

It is an experimentally observed fact that, when calorimetric heats of adsorption are determined by introducing successive doses of the adsorptive onto an energetically heterogeneous surface, the sites are preferentially covered by order of decreasing reactivity so that "differential" heats of adsorption ($\bar{Q}$) usually decrease with increasing coverage (θ). Low maxima in the ($\bar{Q}$ vs. θ) curves of differential heats of adsorption are found only in the case of physical adsorption when lateral attraction of adsorbate molecules can occur[1]. When external or internal mass-transfer limitations exist, a limited part of the whole adsorbing surface is accessible, at any time, to adsorptive molecules so that diffusional limitations usually smooth out details in the $\bar{Q}$ vs. θ curves and that the adsorbent surface then appears to be less energetically heterogeneous than it actually is[2]. Therefore maxima in the $\bar{Q}$ vs. θ curves always appear suspect in the case of chemisorption and, indeed, are likely to be the result of a faulty calorimetric procedure[3].

However, the purpose of this article is to describe such maxima in $\bar{Q}$ vs. θ curves, obtained when ammonia adsorbs at 416 K on a ZSM zeolite. It is also attempted to explain the appearance of the maxima and to relate them to the ZSM zeolite acid properties.

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EXPERIMENTAL

The ZSM zeolite samples were prepared according to a method described earlier[4]. Hydrogen forms were obtained by treatment with hydrochloric acid. X-ray diffraction patterns have allowed to check the cristallinity of the samples and to characterize their nature. NH_4-ZSM zeolite was prepared by contacting, four times consecutively, Na-ZSM zeolite with an ammonium nitrate aqueous solution at room-temperature for 1 h, and by washing it thereafter with distilled water. Chemical formulas of the H-ZSM and NH_4-ZSM zeolite samples are respectively: $Na_{0.05}$ $H_{4.7}$ $Al_{4.8}$ $Si_{91.2}$ O_{192}, 12 H_2O and $Na_{0.25}$ $NH4_{4.6}$ $Al_{4.8}$ $Si_{91.2}$ O_{192}, 14 H_2O. A sample of H-Z mordenite (Zeolon from Norton) was also used for the purpose of comparison (the mean diameter of the channels is 0.54 nm for H-ZSM and 0.62 nm for H-Z).

A heat-flow calorimeter of Tian-Calvet type, maintained at 416 K throughout this study, was used in connection with a volumetric apparatus equipped with a McLeod gauge. Operation of the calorimeter and its electrical calibration have been described earlier[2]. Sample weights were typically ~0.1 g and ammonia doses ~0.1 cm^3 NTP.

RESULTS AND DISCUSSION

Figure 1 reports the differential heats of adsorption of ammonia at 416 K on H-ZSM zeolite as they were recorded during two separate experiments with samples from the same batch of zeolite. In both cases, the samples were heated in vacuo

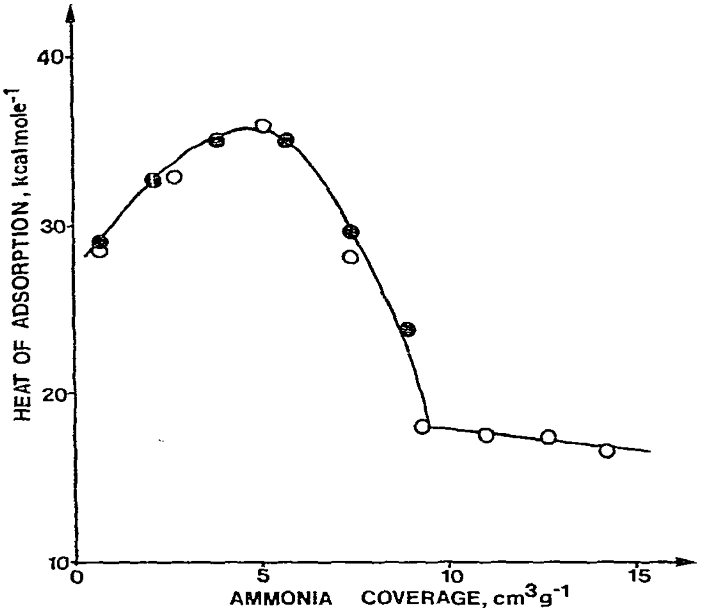

Fig. 1. Differential heats of adsorption of ammonia at 416 K on H-ZSM zeolite.

(10^{-5} torr)[5] for 6 h at 773 K before the calorimetric experiment. Adsorption of all doses of ammonia is a fast process. The final ammonia pressure, after the adsorption of the first doses, is always small, adsorption being then an irreversible process. However, when the cumulated surface coverage exceeds ~8 cm^3 g^{-1}, the final pressure after the adsorption of further doses steadily increases and adsorption is then reversible. Differential heats recorded during the irreversible adsorption of ammonia first increase with coverage, reach a maximum then decrease to the value for reversible adsorption. The two sets of data reported on Fig. 1 indicate the reproducibility of this unexpected behavior.

Apparently similar maxima reported earlier by Kervorkian and Steiner[6] and by Hsieh[7], also in the case of ammonia adsorption on acidic materials have been convincingly explained by the imperfect record, in a single-junction calorimeter with a low heat capacity, of the full heat liberated in very fast chemisorption processes[3]. The arrangement in a Tian-Calvet calorimeter makes such an instrumental artefact very unlikely since the active junctions of the thermocouples almost completely surround the calorimetric vessel and thus allow the quasi complete integration of the heat flux leaving the cell[2]. However, in order to definitely rule out the possibility of an artefact, the same experiment was repeated, the sample of H–ZSM zeolite being replaced by a sample of H–Z zeolite. Figure 2, which reports the results of this experiment, indicates that no maximum was recorded and that, therefore, the profile of the $\bar{Q}$ vs. θ curve in Fig. 1 is not the result of a calorimeter artefact.

The maximum must therefore be related to some peculiarity of the H–ZSM zeolite samples and the most likely explanation is that very reactive sites are not accessible to the adsorptive when the first doses are introduced but become progressively covered when further doses are added. This tentative explanation includes two separate hypotheses: (i) mass-transfer limitations must occur, and (ii) adsorption is immobile. Both invoked phenomena are temperature activated. In order to test

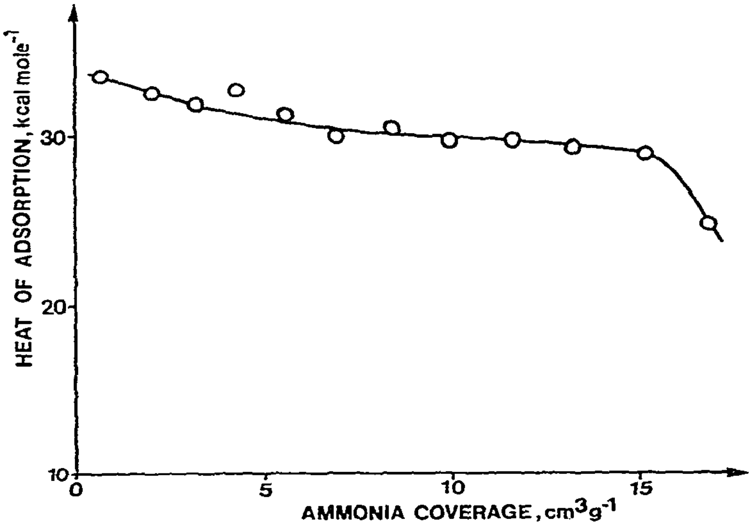

Fig. 2. Differential heats of adsorption of ammonia at 416 K on H–Z zeolite.

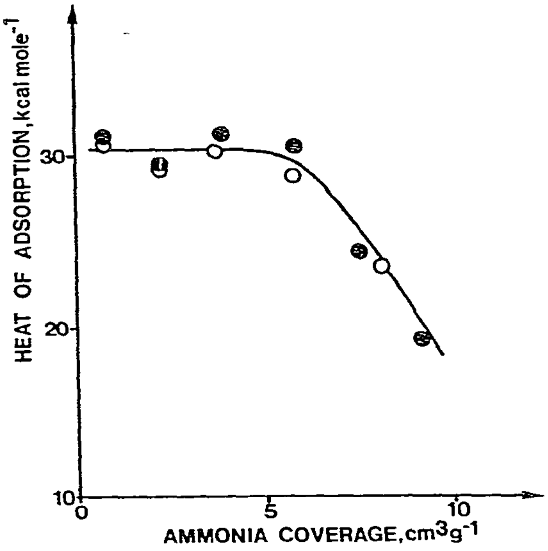

Fig. 3. Differential heats of adsorption of ammonia at 416 K on H–ZSM zeolite (see the text).

the consistency of the proposed explanation, the following experiment was performed.

A first dose of ammonia (of a volume similar to those utilized in the preceding experiments) was adsorbed on a fresh sample of H–ZSM zeolite, maintained as earlier in the calorimeter at 416 K. After adsorption was completed, however, the cell containing the sample was closed, disconnected from the volumetric line and heated at 523 K in a furnace for 2 h. It was then cooled down to 416 K, replaced in the calorimeter, connected again to the volumetric line and another dose of ammonia was introduced, the evolved heat being again measured calorimetrically. The same process (cell closure; heating at 523 K) was again carried out and the same procedure was repeated for all doses of ammonia. The calorimetric results of this experiment (repeated twice under identical conditions to ascertain its reproducibility) are presented in Fig. 3.

One of the experiments was carried out as long as reversible adsorption appeared. The maximum coverage for irreversible adsorption at 416 K deduced from Fig. 3 (~ 8 cm^{3}g^{-1}) is identical to that determined in the usual adsorption experiment (Fig. 1). Heating the sample several times at 523 K has apparently not modified its capacity for irreversible adsorption at 416 K. It has caused, however, a profound modification in the profile of the $\bar{Q}$ vs. θ curve: no maximum then appears (Fig. 3) and the plateau which is now recorded corresponds to sites which are approximately equivalent to those which reacted initially (i.e. for a small coverage) in the first experiment (Fig. 1). The high energy sites whose presence is demonstrated by the maximum in Fig. 1 must have therefore been covered by ammonia when the sample was heated out of the calorimeter, in the case of the experiment summarized in Fig. 3. Heating the sample at 523 K thus increases the surface mobility of preadsorbed ammonia so that it migrates and adsorbs on the most reactive sites, which were not readily accessible at 416 K, probably because of mass-transfer limitations. The most

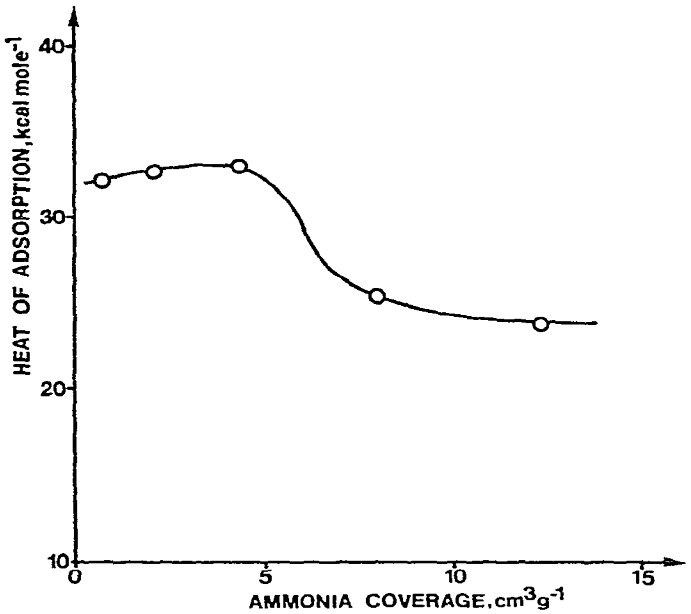

Fig. 4. Differential heats of adsorption of ammonia at 416 K on NH_4–ZSM zeolite.

accessible sites are then free once more and adsorb ammonia again when a new dose of adsorptive is introduced at 416 K, thereby producing the plateau in the $\bar{Q}$ vs. θ curve which appears in Fig. 3. The results of the experiments summarized in Figs. 1 and 3 therefore support the above-mentioned hypotheses and they indicate moreover that the most energetic acid sites are not readily accessible to ammonia molecules at 416 K. It is probable that these most energetic sites are located preferentially in internal pores of the H–ZSM zeolite structure.

The question then is to determine whether the non-uniform distribution of acid sites in the H–ZSM zeolite is an intrinsic property of this small-pore zeolite, or whether it is the consequence of the preparation or activation procedures, adopted in this study. A calorimetric study of the adsorption of ammonia at 416 K on a NH_4–ZSM was thus carried out, the sample being first heated under vacuum (10^{-5} torr) at 773 K for 6 h. The differential heats of adsorption then registered are presented in Fig. 4. As in the case of the previous experiments, adsorption is first irreversible (up to ~6 cm^{3}g^{-1}) then becomes reversible. In this case, however, there is no clear maximum in the $\bar{Q}$ vs. θ curve, the small increase observed being within experimental uncertainty. A comparison of Figs. 1 and 4, which both refer to protonated samples of ZSM zeolite, indicates therefore that the non-uniform distribution of acid sites in the case of the H–ZSM zeolite (Fig. 1) is not an intrinsic property of zeolites of this type but probably results from the pretreatment of the zeolite with hydrochloric acid.

CONCLUSIONS

The experiments reported in this article have demonstrated that the surprising increase of the differential heats of adsorption which is registered when the first successive doses of ammonia contact a sample of H–ZSM zeolite at 416 K is not caused by an instrumental artefact. It has been attempted to show that this increase is due to the unusual conjunction of three independant phenomena: (i) immobile adsorption, (ii) mass-transfer limitations, and (iii) preferential location of the most energetic acid sites in the internal pores of the zeolite structure. The last hypothesis has found further support in recent ESR experiments of benzene and naphthalene adsorption on the same H–ZSM zeolite[8], since the larger naphthalene molecule does not form a radical in this system, although its ionisation potential is lower than that of benzene, whereas the smaller benzene molecule forms radicals, since it can probably diffuse into the zeolite pores and meet the acidic centers. The non-uniform distribution of acid sites in H–ZSM is not, however, an intrinsic property of the small-pore ZSM zeolite but is probably caused by the hydrochloric acid treatment which was used to prepare the protonated H–ZSM sample.

REFERENCES

1 D. M. Young and A. D. Crowell, *Physical Adsorption of Gases*, Butterworths, London, 1962, p. 51.
2 P. C. Gravelle, *Adv. Catal.*, 22 (1972) 191.
3 F. S. Stone and L. Whalley, *J. Catal.*, 8 (1967) 173.
4 R. J. Argauer and G. R. Landolt, *U.S. Pat. 3,702,886*, 1972.
5 Throughout this article, 1 cal = 4.184 J; 760 torr = 101.325 kN m^{-2}.
6 V. Kervorkian and R. O. Steiner, *J. Phys. Chem.*, 67 (1963) 545.
7 P. Y. Hsieh, *J. Catal.*, 2 (1963) 211.
8 J. C. Vedrine, A. Auroux, V. Bolis, P. Dejaifve, C. Naccache, P. Wierzchowski, E. G. Derouane and J. H. C. Van Hoof, *J. Catal.*, in press.