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# MODIFIED ZEOLITE ACIDITY AS KEY TO INTERPRETING MODIFIED CATALYTIC REACTIVITY
## A MICROCALORIMETRIC STUDY OF $NH_3$ SORPTION OVER BORON-IMPREGNATED ZSM-5.

Aline Auroux*, Moein B. Sayed, and Jacques C. Védrine
Institut de Recherches sur la Catalyse, CNRS
2, avenue A. Einstein, F.69626 Villeurbanne, France.

## ABSTRACT

The small, but strong base $NH_3$ has been applied to probe modified acidity of the small pore zeolite, ZSM-5, impregnated with boric acid in a microcalorimetric study. A combination of computer processed volumetric, calorimetric, and thermokinetic data allows to briefly describe the sorption process and identify modified zeolite acidity. The data have shown consistently that while zeolite sorption capacity towards $NH_3$ is slightly modified, the overall acidity is considerably reduced with increased content of the boron modifier.

## INTRODUCTION

The quantitative interpretation of the binding energy resulting from interaction of polar adsorbate, e.g. $NH_3$, with the zeolite structure is of considerable complexity. Barrer and Gibbon[1] have resolved part of this complexity. Because of its feature of measuring the energy of interaction, microcalorimetry has proved as a powerful technique, which differentiates complex surface acidity together with distributions of interaction strengths. Takahashi et al.[2] have applied this technique to characterizing the acidity of a variety of oxide and zeolite surfaces. $NH_3$ has proven useful in probing the acidity of zeolites, particularly those exhibiting small pores[3]. The aim of this study was to exploite the advantage of computer-processed microcalorimetry $NH_3$ adsorption to probe ZSM-5 boron modified acidity[4,5].

## EXPERIMENTAL

Dry and degassed $NH_3$ was used as the probe adsorbate. The adsorbent was· ZSM-5 ($(Na,K)_{0.3}H_{3.8}Si_{91.9}Al_{4.1}O_{192}$) modified by impregnation with boric acid[6]. Three modified samples, HZSM-5 (Δ, 0.3 wt % B ≅ 1.6 per u.c), $HZSM_2$-5 (▼, 0.6 wt % B), and $HZSM_3$-5 (⬤, 1.6 wt % B ≅ 8.5 per u.c), were derived from and compared with original $HZSM_0$-5 (O, 0 % B) zeolite. The zeolite samples (ca. 0.1 g) were pretreated at 1.33 mPa/673 K for 12 h, with the temperature increase being programmed as 2 K $min^{-1}$. $NH_3$ was then admitted in small doses (ca. 0.04 $cm^3$) onto the pretreated zeolite, with both $NH_3$ pressure and thermogram being monitored to identify equilibrium attainment. The heat of $NH_3$ sorption was followed (with facilities of automatization and computer-processing) both calorimetrically

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and volumetrically, using a Setaram Tian-Calvet microcalorimeter at 423 K up to a final pressure of ca. 133 Pa (1 torr)[4].

## RESULTS AND DISCUSSION

Three physico-chemical parameters can briefly describe the sorption process and precisely identify zeolite acidity.

### i- Volumetric Isotherm of $NH_3$ Sorption

Fig. 1 presents the isotherm of $NH_3$/ZSM-5. It is clear that increased zeolite modification contributes to an increased loss of $NH_3$ sorption. However, such a loss is not so pronounced as the loss of zeolite acidity, see below.

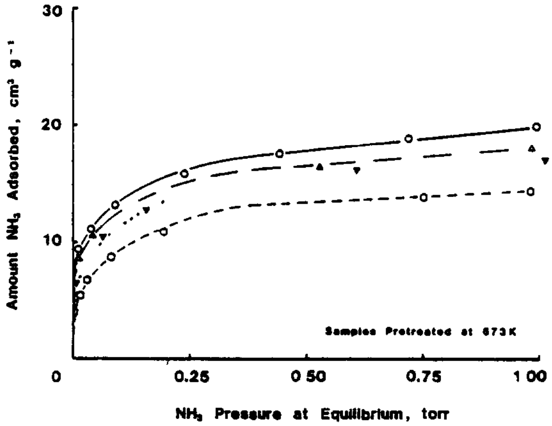


Fig. 1. Adsorption isotherm of $NH_3$/ZSM-5 at 423 K. For symbol significance in this Fig. and elsewhere, see experimental.

### ii- Differential Heat of $NH_3$ Sorption

The differential heat of adsorbed $NH_3$ (Fig. 2) may reveal two phenomena : A general loss of zeolite acidity and/or increased surface heterogeneity, which both become more pronounced for increasingly modified zeolites. While the former is reflected by the loss of sorbed $NH_3$ on the stronger sites evolving a heat $\geqslant$ 100 $kJ.mol^{-1}$, the latter is indicated in a differential heat of more systematic decrease rather than abrupt change with coverage. It has previously[7] been explained that systematic decrease of differential heat is a consequence of interaction of $NH_3$ with a variety of surface sites exhibiting different strengths. On the other hand an abrupt change is a consequence of the interaction with only two types of strong and weak acidic sites. The former yield upper heat level plateau, which abruptly changes to lower level, when interaction with the latter becomes dominant.

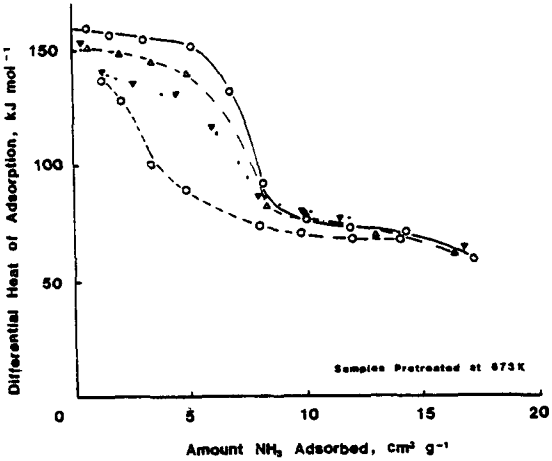
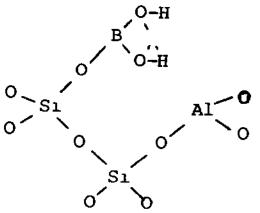


Fig. 2. Differential heat of $NH_3$/HZSM-5 at 423 K.

### iii- Evaluation of Strong Surface Acidity.

In this study, a valuable method of evaluating strong zeolite acidity is suggested, which is based on a thermokinetic parameter ($t_{1/2}$, half of the time consumed in evolving $NH_3$ thermogram) previously used by Della Gatta et al.[8] as a function of sorbate coverage to differentiate irreversible and reversible sorption processes. Since chemisorption is an irreversible process involving site activation and sorbate transformation from sorption site to a stronger one, longer-time and therefore broader thermogram distinguish such a process from quicker reversible physisorption process. This feature is exploited to follow $NH_3$ interaction change with coverage. As shown (Fig. 3), the sorption process starts slow and gets slower reaching a maximum, which is zeolite dependent, before a significant acceleration of the process upon approaching the physisorbed state at high coverages. The maximum is most probably indicative of maximum interaction with the zeolite, and therefore, a better defined value of acidity strength can be drawn. Provided that one $NH_3$ mol. interacts with one zeolite acidic site, the number of strong sites can be estimated directly from the amount of sorbed $NH_3$ defined by peak maximum. Fig. 3 provides with two important, modification-dependent, features : a- $NH_3$ sorption shifts from strong chemisorption for non-modified $HZSM_0$-5 to a process dominated by a more physisorption (shorter $t_{1/2}$) for more modified zeolites and b- acidity identification by this thermokinetic method while correlates well with other thermal method (Fig. 2), similar precise correlation is not provided by the volumetric (Fig. 1) methods, however similar zeolite sequence is given.



Surface boric anhydride

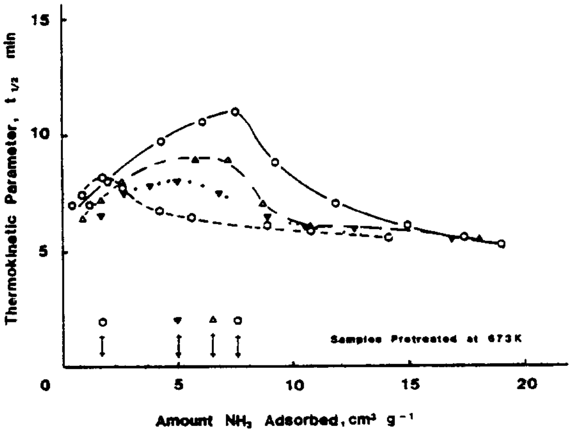


Fig. 3. Dependence of sorbate interaction strength ($t_{1/2}$) on $NH_3$ coverage.

Slight modification of zeolite sorption to $NH_3$ (Fig. 1) and drastic loss of overall zeolite acidity (Figs. 2,3) with increased zeolite modification can be demonstrated in the light of structural change induced by zeolite pretreatments for impregnated zeolites. Pretreatment at 673 K assists in condensing boric acid with zeolite Brønsted sites into the structure shown above[6]. Replacing strongly H-bonded boric protons for original strong Brønsted sites is origin of lowered zeolite acidity. Therefore, the resultant sites might sorb $NH_3$, but would not evolve heat $\geqslant$ 100 kJ.mol$^{-1}$.

The data of the present study reveal an acidity sequence correlating with modified catalytic reactivity shown for $CH_3OH$ conversion, toluene/$CH_3OH$ alkylation, and toluene disproportionation processes[6] ;

$$HZSM_0\text{-}5 > HZSM_1\text{-}5 > HSZM_2\text{-}5 > HZSM_3\text{-}5$$

which is clearly dependent on the zeolite modification by boron. The more modified zeolite is the less strong and more heterogeneous acidic surface.

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