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Distribution of acid sites and differential heat of NH_3 chemisorption on some aluminas and zeolites

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The distribution and the strength of acid sites in some aluminas and zeolites were obtained from microcalorimetry measurements of ammonia adsorption. They were compared to the results of FTIR of adsorbed CO and of $^1H \rightarrow ^{27}Al$ cross-polarization (CP) MAS NMR using chemisorbed ammonia as proton reservoir. FTIR of CO adsorption yields the numbers of Lewis sites and CP MAS NMR gives the coordination of surface aluminum. In spite of the variety of catalysts and of acidity encountered, interesting correlations were found with both the energy of adsorption and singularities in the microcalorimetric titration. In particular, in zeolites a clear difference exists in the distribution of the Lewis and Brønsted acid site strengths with respect to the amount of irreversibly adsorbed NH_3.

Keywords: ammonia; heat of chemisorption; Lewis acid sites and Brønsted acid sites

1. Introduction

The main purpose of the present note is to compare the distribution with coverage of differential heats of adsorption (ΔH_a) in catalysts on which the number and the nature of the acid sites have been studied separately by two spectroscopic techniques. The differential heats of adsorption (ΔH_a) of basic molecules on acid surfaces have been used to estimate the acid strengths and the variation of ΔH_a with coverage as a measurement of the acid strength distribution [1,2–7]. Since the interest here is in measuring a relatively large spectrum of acidity, ammonia, which has a "moderate" pK_a (ref. [1, table II]), has been chosen for this study. In addition, it is likely to meet the requirement clearly defined by Dumesic et al. [7], namely,

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that the diffusion of the base cannot prohibit the achievement of the thermodynamic equilibrium between the probe and the acid sites within the time-scale of the microcalorimetric measurements.

The calorimetric data will be compared to the absolute number of acid sites measured by the infrared (IR) spectroscopy study of CO adsorbed at low temperature and the nature (Lewis or Brønsted) of the active sites investigated by nuclear magnetic resonance (NMR). The detailed NMR and IR studies are reported separately [8,9]. For sake of clarity, we will nevertheless summarize briefly the main findings. First, the coordination of the acid site can be observed by $^{1}H \rightarrow {}^{27}Al$ cross-polarization (CP) magic angle spinning (MAS) NMR if chemisorbed ammonia acts as the proton reservoir. This technique shows that two kinds of Lewis sites exist on aluminas as well as on alumina debris present as non-framework aluminum (NFAl) in thermally or steamed activated zeolites. One of these sites has a distorted tetrahedral configuration: the isotropic chemical shift of the ^{27}Al resonance is 58 ppm (the observed chemical shift is 52 ppm at 11.4 T). The second one has a pentahedral symmetry with an isotropic chemical shift ca. 41 ppm (the observed chemical shift is about 35 ppm). In the zeolites the Brønsted site is, of course, the bridging Si–OH–Al hydroxyl. On this site, NH_3 chemisorption leads to the formation of an ammonium cation close to the negatively charged Al framework tetrahedron, Al_F^{IV}, which becomes detectable by CP.

Second, IR spectroscopy of CO adsorbed at low temperature yields quantitative information on the absolute number of sites, while the NMR technique gives only the relative distribution among the various sites.

It is well documented that the vibrational spectrum of CO chemisorbed on Lewis sites contains stretching bands attributable to various configurations [10–12]. It was shown [9] that the two strong Lewis sites corresponding to a CO stretch ca. 2190 cm^{-1} (L_1) and to a CO stretch ca. 2210 cm^{-1} (L_2) which exist on aluminas are also detectable in NFAl in zeolites. The chemisorption energy of CO on L_1 is about 25 kJ/mol while it is about 40 kJ/mol on L_2.

There are, of course, several ways to measure quantitatively the number of Brønsted sites. The most accurate one is probably through the deconvolution of the ^{29}Si MAS NMR peak in its Q^4(Si–nAl) components, leading to the Si/Al_F^{IV} ratio. Then, knowing the chemical composition, the number of Al_F^{IV} sites is computed.

In summary, since the amounts of Lewis and Brønsted sites and their nature are known, this paper will compare these data to the distribution of the differential heat of NH_3 adsorption with coverage.

2. Experimental

Three aluminas, including one commercial γ-alumina and two aluminas rich in pentacoordinated aluminum called superfive and surperfive (2.8) aluminas, and three zeolites which include an ultrastable Y (USY), a steamed H mordenite (VG3) and a H-ZSM5 were used for this study. Detailed information on the preparation procedure of these samples (except H-ZSM5) can be found in refs. [8,9]. It should be emphasized that the very same samples were used for the spectroscopic investigations. The H-ZSM5 was provided by PQ (ID# CBV3020). This sample has not been studied so far, except by ^{27}Al CP MAS NMR using chemisorbed NH_3 as proton reservoir (unpublished data).

The aluminas were activated at 600°C and the zeolites at 500°C before NH_3 adsorption and microcalorimetric measurements. The adsorption isotherms were carried on at 115°C. Two sets of measurements were performed: the pressure in the first isotherm was increased up to $P/P_0 \approx 3 \times 10^{-3}$ step by step. Then, the sample was outgassed at 115°C for 4 h and the second adsorption isotherm was run up to the point where it became parallel to the first one. The difference between both isotherms is the amount of irreversibly adsorbed NH_3 (at 115°C). The heat of chemisorption will be plotted with respect to a degree of coverage which is the amount of NH_3 adsorbed divided by the amount of irreversibly adsorbed NH_3. Details on the microcalorimetric apparatus can be found in refs. [1–7]. Table 1 contains the main parameters of interest for the comparison with the heats of adsorption of NH_3 and the NH_3 adsorption isotherms.

3. Results

The variations of the differential heats of adsorption with coverage are shown in figs. 1–3. The differentiation between aluminas and zeolites is evident. On the aluminas ΔH_a decreases logarithmically with the coverage. This is the classical case for an heterogeneous surface on which the adsorption isotherm belongs to the Freundlich type [13,14],

$$\Theta = (P/P_0)^{1/m}$$

with $m > 1$.

Table 1

Surface characteristics: A: N_2 BET (aluminas) or Langmuir (zeolites) surface area; L_1 number of Lewis sites with tetrahedral coordination and L_2, number of Lewis sites with pentahedral coordination obtained from CO chemisorption; Al_F^{IV}, tetrahedral framework aluminum obtained from ^{29}Si MAS NMR; Irr. NH_3, irreversibly chemisorbed NH_3

Sample	A ($m^2\ g^{-1}$)	L_1 ($\times 10^{20}/g$)	L_2 ($\times 10^{20}/g$)	Al_F^{IV} ($\times 10^{20}/g$)	Irr. NH_3 ($\times 10^{20}/g$)
γ-Al_2O_3	268	1	0.22	–	1.7
superfive	360	0.68	0.27	–	1.87
superfive (2.8)	360	$(L_1 + L_2) \approx 1.2$		–	1.95
VG3	500	1.2	0.53	8.4	4.7
USY	750	$(L_1 + L_2) \approx 0.9$		17	4.83
H-ZSM5	430	n/a	n/a	3.46	3.98

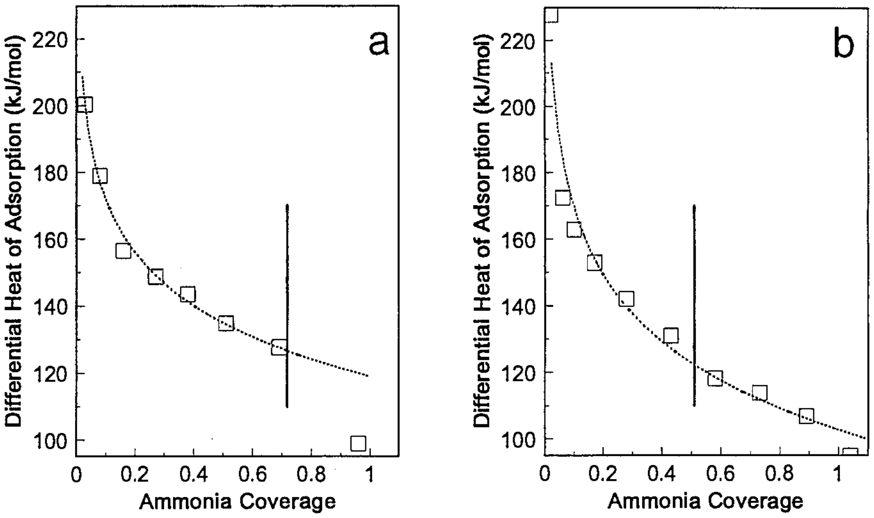

Fig. 1. Differential heats of adsorption (kJ mol^{-1}) versus degree of coverage obtained: (a) for a γ-alumina and (b) for an alumina rich in pentacoordinated aluminum (superfive). In all figures the degree of coverage is calculated with respect to the irreversibly chemisorbed NH_3 (left on the surface after outgassing overnight at 115°C). In all figures the vertical bar indicates the degree of coverage corresponding to the total amount of strong Lewis sites.

On the zeolite an initial logarithmic decrease is followed by a pseudo-linear variation similar to that leading to a Temkin isotherm [16]. The linear decrease is often attributed to the repulsion between chemisorbed species. The parameters of the Freundlich or Temkin equations are shown in table 2. It is interesting to observe

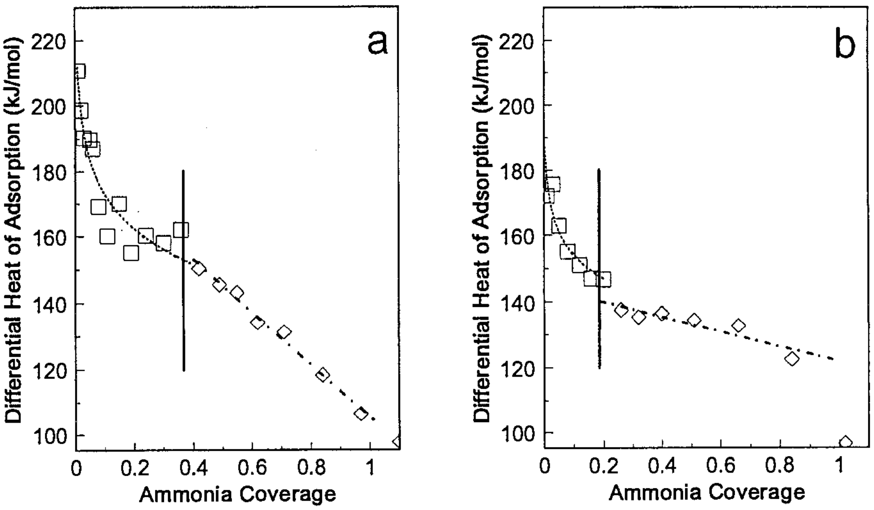

Fig. 2. Differential heats of adsorption (kJ mol^{-1}) versus degree of coverage obtained: (a) for a steamed H mordenite (VG3) and (b) for ultrastable Y. See additional comments on fig. 1.

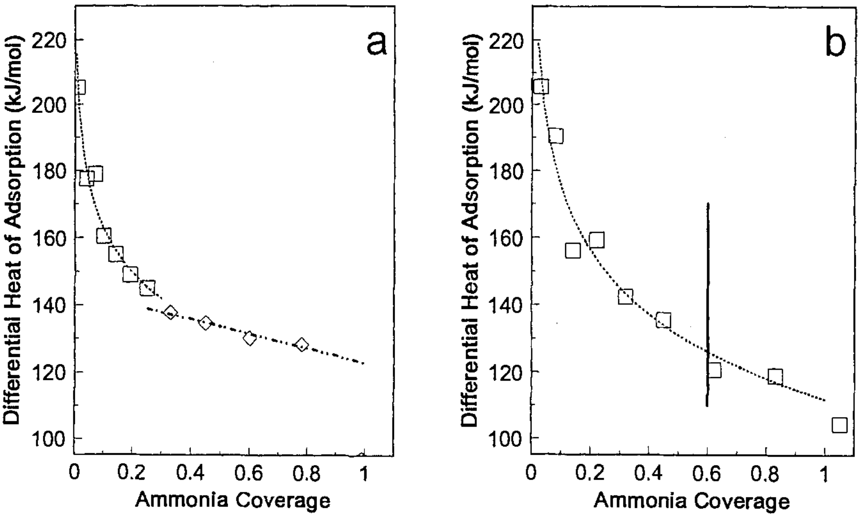

Fig. 3. Differential heats of adsorption (kJ mol^{-1}) versus degree of coverage. (a) H-ZSM5 and (b) an alumina (superfive 2.8) poorer in pentacoordinated aluminum than the sample shown in fig. 1b. See additional comments on fig. 1.

that the differential heats of adsorption for the six samples studied here are larger or equal to 110 kJ mol^{-1} for $\Theta \leqslant 1$. In other terms, molecules with differential heats of adsorption smaller than 110 kJ mol^{-1} are not retained on the surface under vacuum at 115°C.

On the aluminas, the irreversibly adsorbed NH_3 represents an average surface density of 0.56 sites per nm^2. Since according to Knözinger and Ratnasamy [15] in aluminas there are about 8 aluminum per nm^2, less than 10% of them are used as Lewis sites. The maximum differential heats of adsorption on aluminas is the lowest (~ 200 kJ mol^{-1}) for the γ-alumina, the highest (~ 230 kJ mol^{-1}) for the superfive alumina and intermediate for the superfive (2.8) alumina. This sequence is also that of the relative abundance of pentacoordinated aluminum on the surface [8]. When $\Theta = 1$, the differential heats of adsorption scale in the opposite order (see

Table 2
Numerical parameters (kJ mol^{-1}) obtained from points fitting in figs. 1–3

Sample	Fig.	Freundlich $\Delta H_a = a - b \ln \Theta$		Temkin $\Delta H_a = A - B\Theta$	
		a	*b*	*A*	*B*
γ-Al_2O_3	1a	119.0	23.0	–	–
superfive	1b	102.7	29	–	–
superfive 2.8	3b	112	27.5	–	–
VG3	2a	137.5	15.5	185.1	79.6
USY	2b	130.3	10.3	144.4	22.6
H-ZSM5	3a	119.1	19.0	144.4	21.6

parameter a in table 2), e.g. being the largest on γ-alumina and the lowest on the superfive alumina. These values are in general agreement with those shown in the literature (ref. [7] and references therein).

Thus, the alumina which has the highest relative content in pentacoordinated aluminum also has the largest distribution of acid strengths, measured by the differential heat of adsorption. Otherwise, since the density of state $(d\Theta/dE)$ decreases linearly with coverage in a Freundlich isotherm, there is no singularity in the distribution of the sites with respect to their strengths.

The ratios $(L_1 + L_2)/NH_3$ (see table 1) are 0.72, 0.52 and 0.61 for γ-Al_2O_3, superfive and superfive (2.8) aluminas, respectively. The corresponding values of Θ are shown by vertical bars in figs. 1a, 1b and 3b. It is interesting to observe that these bars intercept the distribution curves at nearly constant values of the heat of adsorption, namely, 125 ± 2 kJ mol^{-1}. Thus, the "strong" Lewis sites observed by the CO adsorption on aluminas have an acid strength, defined by the differential heat of ammonia chemisorption, larger than the differential heat corresponding to the irreversibly adsorbed NH_3 at 115°C.

As far as the zeolites are concerned, the evolution of ΔH_a versus coverage contains two well-differentiated regions. The first which encompasses an energy range from ~ 210 to about 140 kJ mol^{-1} extends almost exactly up to the value of Θ corresponding to the total number of Lewis sites $(L_1 + L_2)$ obtained from the CO FTIR technique. On H-mordenite, Spiekwak et al. [7] have observed a plateau with a nearly constant heat of chemisorption of 155 kJ mol^{-1} extending up to 800 μmol/g^{-1}. On HY Macedo et al. [16] have observed that after steaming the plateau is preceded by a relatively steep decrease of the differential heats of chemisorption from ~ 230 to ~ 180 kJ mol^{-1}. The three H zeolites studied here have been purposedly treated in such a way as to contain a noticeable amount of extra-framework alumina and for each of them we observed the initial logarithmic decrease, as on the aluminas. Hence, we conclude that on these zeolites, the first step of the microcalorimetric titration concerns the Lewis sites. Hence, the second step corresponding to the Temkin isotherm ought to be the titration of the Brønsted sites.

For USY, between $\Theta \approx 0.18$ to $\Theta \approx 1$, the differential heat decreases slowly from ~ 140 to ~ 120 kJ mol^{-1}. For VG3 mordenite it decreases steeply from ~ 150 to 105 kJ mol^{-1} between $\Theta = 0.37$ and 1. The HZSM5 behaves as USY. The relatively large distribution of Brønsted acid strength could be explained by a repulsion between chemisorbed species. A high Si/Al ratio does not rule out this explanation because interactions between Brønsted and Lewis sites are also possible. This is especially true for VG3, where there is a large number of highly dispersed Lewis sites [9]. The distribution of Lewis and Brønsted sites is very different for these three zeolites. As easily calculated from the results in table 1, if the difference between the amount of irreversibly adsorbed NH_3 and $(L_1 + L_2)$ is the amount of Brønsted sites titrated by NH_3, the ratio of this amount to the number of Al_F^{IV} is 35 and 23% for VG3 and USY, respectively, but it must be close to 100% for H-ZSM5. In VG3 and USY a part of the Brønsted sites are not available to NH_3 or "neutralized" by non-framework debris. Macedo et al. (ref. [16, fig. 1]) have shown that in USY the amount of strong Brønsted sites is rather low.

4. Conclusions

Microcalorimetric titrations of aluminas and zeolites by ammonia have shown interesting correlations with the study of the nature of the Lewis sites by NMR and of their number by CO FTIR.

(1) The numbers of Lewis sites obtained from the intensities of the CO stretch near 2190 cm^{-1} and near 2210 cm^{-1} match well the titration of the most energetic sites in zeolites.

(2) The solids with the highest energetic sites are also those in which the relative amount of pentacoordinated aluminum is the highest.

(3) The distribution of the sites with respect to the differential heats of NH_3 adsorption is exponential for the Lewis sites (Freundlich isotherm) and linear (Temkin isotherm) for the Brønsted sites.

The significance of the differential heats of adsorption for Brønsted and Lewis sites is not easily comparable. For the former it is the difference between the enthalpy of dissociation of the acid hydroxyl and the enthalpy of protonation of ammonia. For the Lewis site the differential heat of adsorption represents the energy associated with the transfer of electron density towards an electron deficient, coordinately unsaturated site, and probably an energy term related to a relaxation of the strained surface.

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