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Relationship between acid strength and framework aluminium content in dealuminated faujasites

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Calorimetric measurements of the chemisorption heats of ammonia were used to investigate the acid strength of dealuminated Y-zeolites. Our measurements show that the number of very strong acid sites rises, passes through a pronounced maximum and then decreases with increasing aluminium content in the framework. The results are in good agreement with literature data and prove the validity of the concept of the aluminium topological density of zeolites given by Barthomeuf.

Keywords: Zeolite catalysts; zeolite acidity; acid strength; adsorption calorimetry; ammonia chemisorption; aluminium topological density

1. Introduction

The importance of acid sites in reactions over zeolitic catalysts is well established. Generally accepted is as well that not only the concentration of these sites but also their acid strength and their distribution determine the catalytical properties of the zeolites investigated. From many experimental and theoretical investigations on the acidity of faujasites with different aluminium content of the framework it was concluded that the number of bridging hydroxyl groups increases with rising number of Al atoms in the lattice. In contrast to it, the dependence of the acid strength on the aluminium content is more complicated. From theoretical considerations [1,2] an increasing acid strength with decreasing number of aluminium atoms is expected on the one hand whereas from studies of the Al topology in the framework a vulcano shape curve was derived for the number of strong sites [3].

The experimental determination of the acid strength is difficult. Most methods used allow only a qualitative judgement upon the acid strength of the solids.

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Quantitative results of the strength of the acid sites (and also the number) are obtained from calorimetric measurement of the chemisorption heats of basic molecules at elevated temperatures.

In order to study the acidity of often catalytically used zeolites we measured the chemisorption of ammonia on dealuminated HY, H-ZSM-5 and H mordenites with a broad range of Si/Al ratios. The zeolites were characterized using many physico-chemical methods. The results of the acid strength investigations for the HY molecular sieves are presented, following the representation of a multitechnique study of the Y zeolite acidity in ref. [4].

2. Experimental

The aluminium deficient faujasites were prepared by a thermochemical procedure described in ref. [4]. The Al-content of the framework was calculated from ^{29}Si MAS NMR and IR measurements [4].

Differential molar heats of ammonia were measured at 423 K using a Calvet-type microcalorimeter connected to an adsorption unit. All samples were evacuated (at 673 K and $p < 1$ mPa) for about 15 h. The adsorption equilibrium was controlled as well by pressure measurements as by following of the thermokinetic curve.

3. Results and discussion

The number of acid sites was derived from the curves of the chemisorption heats. Earlier we showed [5] corresponding with literature data [6,7], that the heats of ammonia chemisorption (interaction with acid sites) on zeolites exceed the value of 80 kJ/mol and that during the chemisorption every ammonia molecule interacts with only one of those (Brønsted) sites. Therefore, the total number of acid sites is found as the amount of ammonia molecules adsorbed with a chemisorption heat $Q > 80$ kJ/mol. Al deficient Y zeolites may contain Lewis sites especially if they were prepared by a thermochemical procedure. Often these Lewis sites are identified with the extraframework alumina species. As was shown in ref. [4], the extraframework aluminium was removed by acid leaching. Therefore, the number of Lewis sites should be very small. Having in mind that the extraframework alumina possess only a weak acidity we conclude that the calorimetric measurement of the heats of ammonia chemisorption include only the Brønsted sites.

The heat curves (possessing a stepwise character for aluminium-rich zeolites) may be interpreted by the assumption that the acid sites exist in distinct groups of different acid strength and that these interact with ammonia molecules consecutively. In accordance with the three steps found in the heat curves also

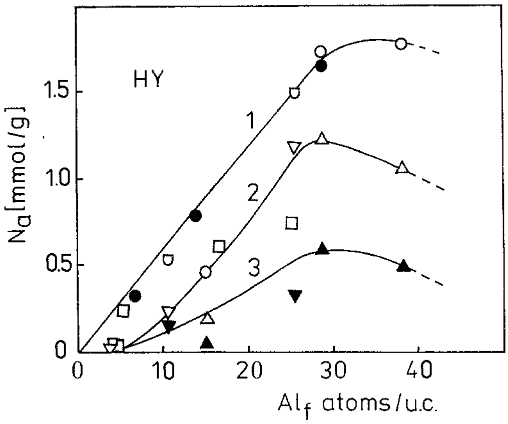

Fig. 1. Concentration of the acid sites in dependence on the number of Al_f atoms per unit cell. Curve 1: total number of acid sites with $Q > 80$ kJ/mol, (●) TPD, (○) own calorimetric, (Ū) calorimetric data from ref. [8]; curve 2: number of acid sites with $Q > 100$ kJ/mol, (△) own calorimetric data, (▽) calorimetric data from ref. [8]; curve 3: number of acid sites with $Q > 120$ kJ/mol, (▲) own calorimetric data, (▼) calorimetric data from ref. [8], (□) calorimetric data from ref. [9].

three groups of sites with different acidity were chosen $N_a^1 > 80$ kJ/mol; $N_a^2 > 100$ kJ/mol; $N_a^3 > 120$ kJ/mol.

The in this way found concentration of acid sites with different acid strength is plotted in fig. 1 against the number of aluminium atoms in the elementary cell. Calorimetric data of ammonia adsorption from literature [8,9] are also included as well as own TPD results from ref. [4]. Curve 1 corresponds to the total number of acid sites in dependence on the content of framework aluminium (Al_f) in the unit cell. It follows that with increasing number of Al_f atoms also the concentration of the acid sites rises (almost linearly) up to about 30 Al atoms in the elementary cell. Although no samples with more than 40 Al atoms/u.c. were investigated calorimetrically, we expect that HY zeolites with a large aluminium content will show no higher but a lower concentration of the total number of acid sites. This dependence is not unexpected and was noted by other authors [3,4]. From fig. 1 follows that the calorimetric results given by Klyachko and Mishin [8] are in good coincidence with our data, having in mind, that the dealumination and the measurements were not performed under the same conditions. In contrast to it the results of calorimetric measurements by Auroux and co-workers [9] show a systematic deviation to a higher concentration of acid sites. Nevertheless, they confirm the course of the curve of the strong acid sites in dealuminated HY zeolites in dependence on the aluminium content. Curve 2 as well as curve 3 of fig. 1 are characterized by a maximum. The abscissa values of both maxima are the same and correspond to an Al content of the framework of about 28–30 (and a Si/Al ratio of 5.4–5.9).

Comparing the curves of fig. 1 with the corresponding curves of dealuminated H mordenites [10], it is found that the concentration of the very strong acid sites also proceeds through a maximum. The abscissa of the maximum derived for H mordenites corresponds to an Al content of 4.6/u.c. and a Si/Al ratio of 9.5. We must therefore conclude that not the number of aluminium atoms in the framework (or the Si/Al ratio) but the crystal structure determines the maximum in the number of strong acidic sites of the molecular sieve investigated.

Studying the influence of the zeolite structure on the acidity Barthomeuf [3] considered recently the topological aluminium density TD_{Al} of a series of zeolites, including faujasites and mordenites. She defined a limit value of the topological aluminium density named limit TD_{Al}. Below the limit value no Al atom (of a SiOHAl configuration) has another Al atom as a next nearest neighbour and as a consequence all Brønsted sites possess a strong acidity, i.e. a high acid strength. Therefore, the number of strong acid sites increases with rising number of (isolated) Al atoms in the lattice. Above the limit TD_{Al} (and hence the corresponding limit Si/Al) Al atoms exist in the second coordination sphere. In this case not all Brønsted sites have a strong acidity and the concentration of the strong acid sites decreases with increasing Al content of the framework. As a consequence the curve of the concentration of strong acid sites in dependence on the Al content of the framework should pass through a maximum. Barthomeuf found that the lim TD_{Al} values differed for the zeolites investigated [3].

Under the assumption that the limit value of the aluminium topological density TD_{Al} of faujasites (determined experimentally) is the same for any aluminosilicates she was able to calculate the limit Si/Al value for many zeolites. For faujasites Barthomeuf [3] found experimentally a value of limit

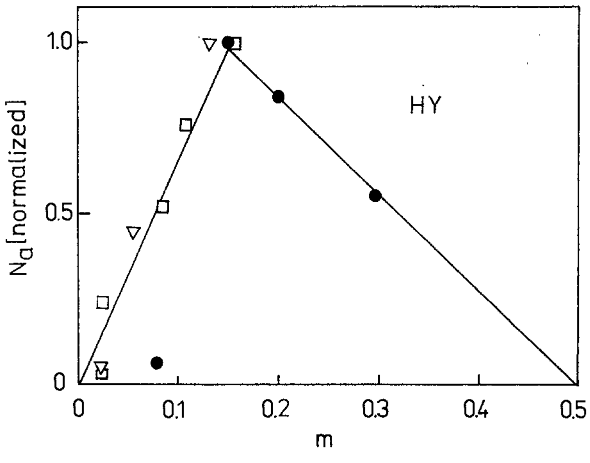

Fig. 2. Normalized concentration of the very strong acid sites ($Q > 120$ kJ/mol) in dependence on the aluminium molar fraction of HY zeolites. (●) Own calorimetric data; (▽) calorimetric data from ref. [8]; (□) calorimetric data from ref. [9].

$TD_{Al} = 2.65 \times 10^{-2}$ which corresponds to a limit Si/Al = 5.8. This agrees very well with our finding of limit Si/Al = 5.6 for the HY zeolites investigated. (A similar good agreement was found for H mordenites: predicted value by Barthomeuf [3] limit Si/Al = 9.4; experimentally from our measurements [10] obtained limit Si/Al = 9.5).

In fig. 2 the calorimetrically measured concentrations of very strong acid sites ($Q > 120$ kJ/mol) are plotted against the aluminium molar fraction m = Al/Al + Si of the dealuminated HY zeolites. Included are calorimetrical results given by Klyachko and Mishin [8] and Auroux and co-workers [9]. Their data (as well as our) are normalized in order to compare properly the experimental results. The coincidence between the three sets of measurements is very good. The abscissa value of the maximum corresponds to limit $m_{\mathrm{NNN}} = 0.150$ (m_{NNN} is the aluminium molar fraction at which exists no next nearest neighbour Al atom) which is also in good agreement with the predicted value (by Barthomeuf [3]) of $m_{\mathrm{NNN}} = 0.146$. (For H mordenites we found [10] a limit $m_{\mathrm{NNN}} = 0.096$ which has to be compared with a value given by Barthomeuf [3] of limit $m_{\mathrm{NNN}} = 0.096$ proving an excellent agreement.)

4. Conclusion

Overall the results of the calorimetric investigations of the ammonia chemisorption demonstrate that:

(i) the concept of the aluminium topological density by Barthomeuf [3] is very useful for studies of the acidity of zeolites;

(ii) the model of isolated aluminium atoms as the sites of the strong Brønsted acidity is justified.

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