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Quantitative determination of Brönsted acid sites on zeolites: a new approach towards the chemical composition of zeolites

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An original quantitative method based on H/D exchange between H_2O/D_2O molecules and the OH groups of different zeolites has been developed for the titration of the Brönsted acid sites present on the solid surface. The measured Brönsted acid sites density appears to be in good agreement with the theoretical amount estimated by the Si/Al ratio. In contrary to classical methods, this non-destructive anhydride method titrates the whole quantity of Brönsted acid sites of zeolites.

KEY WORDS: acid sites; titration; H/D exchange; zeolites; Brönsted acidity.

1. Introduction

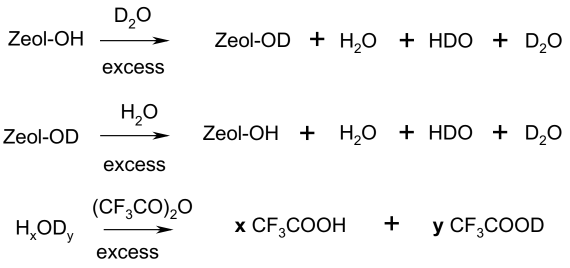
Zeolites have a well-defined three-dimensional porous structure arising from a framework of $[SiO_4^{4-}]$ and $[AlO_4^{5-}]$ tetrahedra linked together by all their corners. These primary building units are assembled so that each O is shared by two tetrahedra, thus creating an infinite lattice with identical unit cells in the manner that is common to all crystalline materials. Since the trivalent Al is bonded to four shared O-atoms, the residual charge on each AlO_4 unit is −1. Therefore, each alumina tetrahedron requires a +1 charge from a cation in order to maintain electrical neutrality throughout the structure: typically H^+ cations in acidic zeolites [1,2].

The chemical composition of a protonic zeolite can hence be represented by a formula of the type:

$$H_nAl_nSi_{x-n}O_y \cdot zH_2O \tag{1}$$

where x and y are typical features of the crystalline structure [3]. Since the pioneering work done by Haag *et al.* [4], where a linear dependence between cracking activity and Al content (or H content) has been observed, there has been a growing interest to determine the concentration of Brönsted acid sites [2,5]. This determination remains a non-trivial problem since the difficult estimation of absorption coefficients limits the use of IR and TPD measurements of different amines or ammonia lead sometimes to misinterpretation of the results [6].

Therefore, in relation to recent works done in our group on H/D exchange occurring between small alkanes and solid acids [7,8], we monitor here the exchange taking place between deuterated acid catalysts and water according to scheme 1.



Scheme 1. Set of H/D exchange steps between H_2O/D_2O and the OH groups of the zeolite.

2. Experimental

2.1. Materials

The BEA (Si/Al = 13.6), MOR (Si/Al = 5), EMT (Si/Al = 6.5) samples were provided by UOP. The ammonium NH_4-ZSM-5 zeolite (Alsi-Penta, Germany, Si/Al = 12.5) was calcined under air at 550 °C for 5 h to produce H-form. HUSY (Si/Al = 4.5, Petrobras, Brazil) and SAPO-5 (University of Leuven, Belgium) were received in their H-form. $H_3PW_{12}O_{40}$ (Fluka) was used as a probe to see whether this method is also applicable to other crystalline solid acids.

2.2. Experimental procedures

All the reactions were performed in an all-glass, grease-free, flow system with a U-shaped reactor as reported elsewhere [8]. The gas-pressure was regulated by means of a Brooks 5850E mass flow controller.

The catalyst (300 mg) was first activated under dry air flow (40 mL/min) at 450 °C for 1 h to desorb the water present in the void volume (corresponding to the z molecules in equation (1)) but without dehydroxylation

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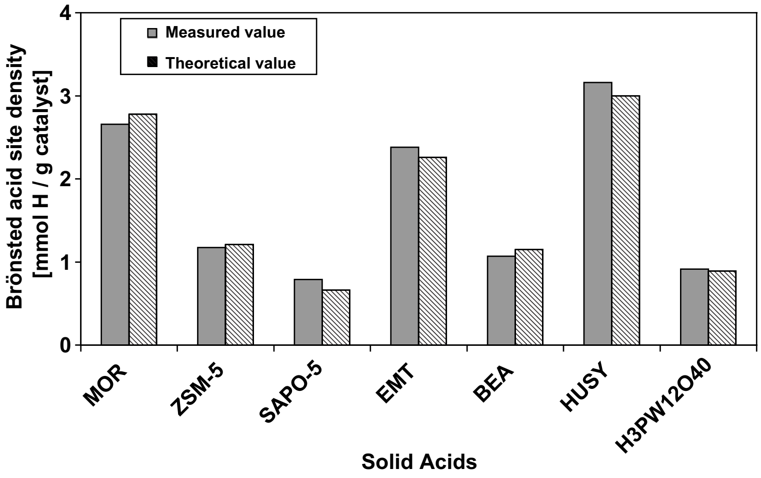

Figure 1. Measured and theoretical amount of Brönsted acid sites of different solid acids.

of the framework. The temperature of the catalyst was lowered to 200 °C for deuteration.

At first, the catalyst deuteration was performed at 200 °C by sweeping for 1 h 40 mL/min of dry N_2 previously bubbled at room temperature through a U-tube containing D_2O (about 0.05 g). Excess of D_2O was removed by flushing dry N_2 at 200 °C during 90 min.

The titration of the O–D sites was then performed by back-exchanging the deuterium present on the solid surface with distilled water (3% of H_2O in N_2 stream). This step is necessary since the trifluoroacetic anhydride usually contains 0.11 mmol of trifluoroacetic acid per gram of anhydride as controlled in blank experiment. For this reason, it is preferable to apply the anhydride method to the partially exchanged water obtained in the last step rather than after the deuteration step (scheme 1).

The partially exchanged water H_xOD_y, composed by H_2O, HDO and D_2O, was collected in a cold U-tube at −117 °C (ethanol melting point). The recovered H_xOD_y was weighed and chemically trapped by trifluoroacetic anhydride (used in twofold excess). The acid solution thus obtained was transferred under argon to a NMR tube for analysis. The amount of protonated and deuterated acids was determined by means of common ^{1}H and ^{2}D liquid NMR technique [8]. The spectra were recorded on a Bruker AM400 spectrometer (400 MHz) after addition of a $CDCl_3$ (10 wt%)/$CHCl_3$ mixture as reference.

The acid site density was then calculated based on the H/D ratio measured and the mass of H_xOD_y collected.

3. Results and discussion

Figure 1 shows the comparison between the measured amount of Brönsted acid sites by this method and the theoretical amount estimated by means of the Si/Al ratio [3].

The Brönsted acid sites density measured on all zeolite samples: MOR, MFI, SAPO, EMT, BEA and HUSY is in good agreement with the theoretical amount estimated by the Si/Al ratio (figure 1). Prior to the H/D exchange steps, the samples were calcined at 450 °C to prevent from the dehydroxylation of the framework. Brönsted acid sites appear to be equal in concentration to the framework aluminium content. By means of microcalorimetry, and the measurement of heats of ammonia adsorption, Gorte *et al.* have already observed the same trend for un-steamed zeolites [9].

So, this anhydride method can be used as a powerful tool to determine the whole quantity of Brönsted acid sites on zeolitic materials. Thus, by knowing the crystalline structure of any material, one is able to determine the number n of H atoms (regarding equation (1)) and therefore to estimate the Si/Al ratio, which is a key parameter for the study of the catalysis by zeolites [10,11].

As an example, 1.17 ± 0.05 mmol H/g_{zeolite} could be measured on a ZSM-5 sample (Si/Al = 12.5). This value corresponds to approximately 7 H atoms in the unit cell. By taken $x = 96$ and $y = 192$ from the atlas of zeolites for the MFI structure [3], a Si/Al = 12.7 is obtained corresponding to the value given by the manufacturer.

Figure 1 also presents the results for $H_3PW_{12}O_{40}$ heteropolyacid, which normally possess 0.89 ± 0.05 mmol H/g [12]. By applying the D_2O/H_2O isotopic exchange (activation of the catalyst was performed during 1 h at 300 °C under air to prevent from the decomposition of the Keggin structure), about 0.91 ± 0.05 mmol H/g were measured, which further demonstrates the reliability and the versatility of the anhydride method to other crystalline materials.

Gorte *et al.* have recently developed a method based on propylamine decomposition (via Hofmann elimination into propene and ammonia) for measuring Brönsted acid sites density at 200 °C [13]. Figure 2 presents

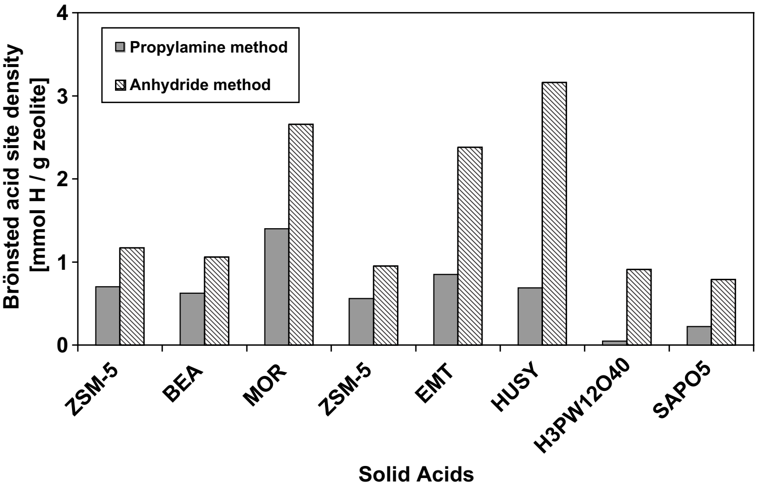

Figure 2. Comparison between the anhydride method and the propylamine method.

the results obtained with the two methods for different zeolites. The general trend observed is a lower amount of Brönsted acid sites titrated with the propylamine method (via measuring the propene released from the solid) compared to the anhydride method. While the former is based on a protonation of the alkylamine, which probably involves acid sites of sufficient strength, the latter does not discriminate between the H-atoms.

The main difference is observed for HUSY zeolite which presents theoretically 3.0 ± 0.1 mmol H/g zeolite; only 0.69 ± 0.05 mmol H/g were measured (each experiment has been repeated twice). In the important case of FAU-type zeolites, it is known that a great part of the charge-balancing hydroxyls are inaccessible to reactant molecules [5], so that the number of bridging OH groups is under-estimated by base adsorption. In fact, Tsutsumi and Nishimiya [14] have noticed that the number of Brönsted acid sites calculated from the heat curves of NH_3 adsorption plotted against the theoretical number of protons (Al content) per unit cell deviates from unity for the samples having low Si/Al ratios.

Moreover, almost no propene could be detected over the heteropolyacid indicating a stronger adsorption; $H_3PW_{12}O_{40}$ is known to be more acid than zeolites [15]. Thus, this probably led to oligomerisation reactions over the catalyst [16].

This work describes an innovative way for determining the chemical composition of both zeolitic materials and other crystalline solid acids like heteropolyacids. While other methods are restricted to the determination of Brönsted sites of sufficient acidity to protonate amines, this "anhydride method" based on D_2O/H_2O exchange steps opens the field of until now unreported determination of the whole Brönsted acid sites, and hence the chemical composition of zeolites. This technique offers a complementary measurement to the OH density that could be predicted from a knowledge of the Si/Al ratio in zeolites. Furthermore, the knowledge of the exact number of OH groups on zeolites can serve as a basis for the design of new kinds of "uniform single-site catalysts" [17]. Further studies are under progress to investigate the effect of different pre- or post-treatments of the zeolite structure.

4. Conclusion

This work reports a non-destructive method, based on H_2O/D_2O exchange steps, for characterising the surface of zeolites. Unlike other methods, limited by mass transfer constraints, the shape of the catalytic bed, or the need to reach a thermodynamic equilibrium between the basic probe and the solid surface, and which seek to discriminate between acidic and non-acidic protons, this technique counts the total number of Brönsted acid sites in zeolitic materials.

Moreover, this way of titration is easy, rather cheap, and essentially does not lead to the poisoning or destruction of the sample.

Acknowledgments

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