Direct quantitative determination of surface Brønsted acidity of solids by H/D exchange using D_2O

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A highly flexible method for direct and quantitative determination of surface Brønsted acidity of solids in terms of number, type and strength of the acid sites based on quantitative H/D exchange kinetics between the acid solid and gaseous D_2O has been developed and applied to materials covering the whole range of acidity.

Here we report on a highly flexible method for direct and quantitative determination of surface Brønsted acidity of solids in terms of number, type and strength of the acid sites based on quantitative H/D exchange kinetics between the acid solid and gaseous D_2O.

Since solid acid catalysts are used extensively in the chemical industry, measuring the acidity of solids is of great interest and methods providing information on the number, type and strength of the acid sites are of the greatest importance for understanding their catalytic reactivity and behaviour. However, as underlined by several authors,[1–3] the reliability and the applicability of different methods suggested are questionable. Up to now, the most frequently used techniques have been based (i) on the measurement of catalytic activities directly related to the acidity of the solid. This method remains difficult to use for solid acids with a variety of different kinds of acid sites available at the surface and for which only one type of acid site is catalytically active; (ii) on the chemical adsorption of a basic compound, using its acid–base interaction with the acid solid. Among these techniques, one can note titration methods, such as the widespread Hammett colour indicator method.[4] Up to now, the adsorption of basic probe molecules, such as NH_3, pyridine, amines, … has been the most widely used method for obtaining Brønsted-site densities, usually coupled to techniques such as vibrational and Raman spectroscopy,[5–7] nuclear magnetic resonance, temperature programmed desorption and calorimetric measurements.

Unfortunately, the techniques based on the adsorption of basic molecules suffer from a large number of drawbacks making the results controversial.[1,3] Among the most important limitations mentioned in the literature, one can mention that adsorption of bases is generally not specific to Brønsted sites but also to Lewis sites, and that parasite reactions and phenomena not resulting from acid–base interactions can occur, thus disturbing the measurement and leading to incorrect determination.[8] IR spectroscopy of adsorbed bases often gives only semiquantitative measurements.[9,10] In addition, a complete characterization of Brønsted acidity (number, type and strength of acid sites) generally requires the coupling of several techniques rendering the acidity determination inflexible and difficult to perform in standard and suitable experimental conditions. Drawbacks and limitations are extensively summarized in recent and adequate books and reviews.[1–3]

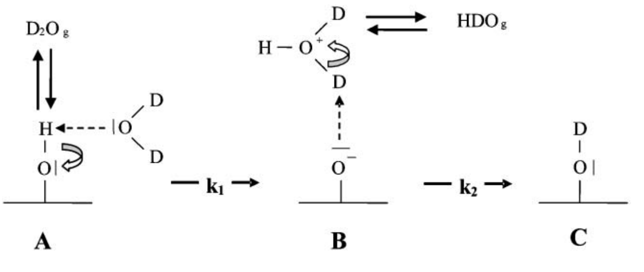
In the definition of Brønsted acidity, the solid is able to donate or at least partially transfer a proton, which becomes associated with surface anions. Our quantitative method for directly measuring the surface Brønsted acidities of solids is based on quantitative H/D exchange between the acid solid and gaseous D_2O and allows the determination of the acid strength as well as the number of Brønsted acid sites.

Experimentally, the solids were first pretreated under He at 300 °C for 1 h and subsequently submitted to a D_2O (3 vol.%)/He flow at 150 °C, leading to exchange of the hydron present on the solid surface with gaseous D_2O. The direct titration of the –O–H acid sites, *i.e.* the H/D exchange on Brønsted acid groups according to the reaction mechanism shown in Scheme 1, was *on-line* followed by mass spectrometry, using the m/z = 19 signal corresponding to HDO gas molecules in the outlet stream. Only a part of the total HDO exchanged molecules was dynamically and quantitatively analyzed in order to remain in the linearity domain of mass spectrometry analyses. Residual exchange of the micropilot was eliminated by subtracting from the experimental signal the exchange one obtained in a blank exchange experiment.

A reaction kinetic model has been proposed assuming a series of two consecutive first-order reactions, the integration of the differential kinetic equations leading to the B concentration as a function of time during the exchange.[11]

$$A \overset{k_1}{\rightarrow} B \overset{k_2}{\rightarrow} C$$

$$\mathrm{B}(t) = \frac{A_0 k_1}{(k_2 - k_1)}\left(\mathrm{e}^{-k_1 t} - \mathrm{e}^{-k_2 t}\right)$$



Scheme 1 Mechanism of the H/D exchange considering a series of two consecutive first-order reactions. k_1, k_2 are the reaction rate constants corresponding to the consecutive reactions involved, and used for kinetic modelling.

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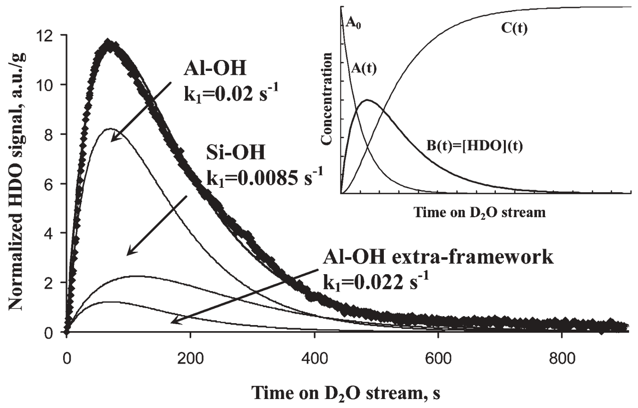

Fig. 1 Experimental concentration–time curve for HDO in the gas phase for a mordenite zeolite (normalized per weight unit). Inset: theoretical concentration–time curves corresponding to the kinetic model.

The theoretical concentration–time curves (inset, Fig. 1) corresponding to the assumed kinetic model show the evolution of A (–O–H) and C (–O–D) surface concentrations, which in parallel continuously decrease and increase respectively with time on D_2O stream. In this model, the B intermediate evolution is proportional to the recovered HDO signal measured in the gas phase, and the correlation between experimental and theoretical concentration–time curves (Fig. 1, *e.g.* using a mordenite) validated the model and the experimental procedure.

The previous kinetic model is also valid for each type *i* of surface Brønsted acidity with A_0^i, the number of surface Brønsted acid sites *i* and k_1^i, the reaction rate constant, defined as the rate constant of the first step of hydron abstraction and directly linked to the acid strength of sites *i*.

The acidity calibration curve (inset, Fig. 2) was built up using well-characterized zeolites, ZSM5, EMT and mordenite, with known Brønsted acidity,[12,13] after optimization of the exchange experimental conditions, to be sure that all the –O–H surface groups to titrate have been transformed into –O–D.

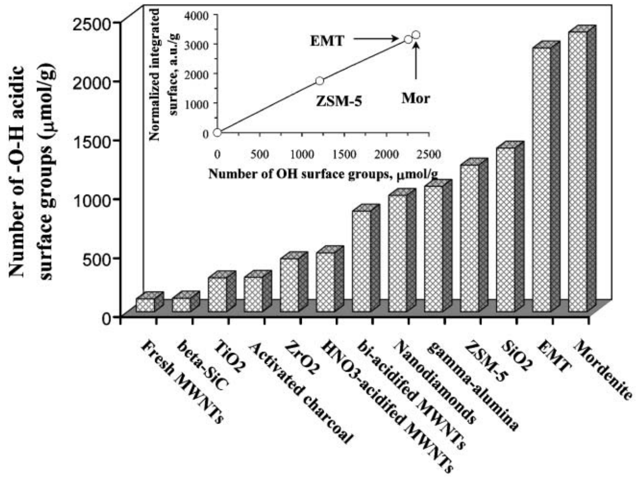

Fig. 2 Determination of the number of Brønsted acid sites of some oxide, carbide, carbon and zeolite catalysts and materials. Inset: calibration curve obtained with ZSM5, EMT and mordenite materials.

The reproducibility and the reliability of the method have been verified by reproducing the exchange experiments three times on each zeolite used for calibration (inset, Fig. 2). The calibration curve was built up plotting the normalised integrated HDO signal as a function of the number of –O–H surface groups of the three zeolites used for calibration.

Fig. 1 shows the example of a mordenite, for which three kinds of different Brønsted acidity, *i.e.* Al–OH (1520 μmol/g), Al–OH extra-framework (225 μmol/g) and Si–OH (630 μmol/g) have been determined by complementary methods.

The experimental exchange curve can be easily deconvoluted using an appropriate algorithm[14] into three contributions, each of them following the theoretical kinetic model. The total amount of each kind of Brønsted surface acidity, determined *via* the calibration curve, is in very good agreement with the known values for Al–OH, Al–OH extra-framework and Si–OH. The k_1 rate constants, directly linked to the acid strength and resulting from the deconvolution parameters are respectively, 0.02, 0.022 and 0.0085 s^{-1}.

This new method based on direct H/D exchange was applied to Brønsted acidity characterization of some catalysts and catalytic supports with weak, moderate and strong acidities. The number and strength of Brønsted acidities of γ-Al_2O_3, SiO_2, TiO_2, ZrO_2, AC (activated charcoal), β-SiC, nanodiamonds, multi-walled carbon nanotubes, *i.e.* MWNTs (fresh, HNO_3- and HNO_3/H_2SO_4-acidified[15]) were determined (Fig. 2). For each material, the number of total Brønsted acid sites was determined and after deconvolution, the number and strength of each kind of acidity, in the whole acidity range, from 98 μmol/g for low acidity fresh MWNTs to 2375 μmol/g for strongly acidic mordenite zeolite. Whatever the solid, the experimental curve deconvolution first led to the integrated surface of each type *i* of acidity and to the k_1^i rate constant linked to the strength of the type *i* of acid site. The quantification of the number of surface Brønsted acid sites (total and for each kind of acidity) was performed using the integrated surface *versus* the number of –O–H surface groups calibration curve.

In conclusion, this new method based on direct H/D exchange displays advantages when compared to conventional methods because it gives a direct measurement of the hydron lability and allows the determination of surface Brønsted acidity in the whole range of acidity, from very weakly acidic materials (*e.g.* carbonaceous solids) to highly acidic materials (*e.g.* acidic oxides or zeolites). There is also no restriction on the nature (carbon, carbide, oxide, sulfide, zeolites, …) and on the morphology (powder, grains, extrudates, nanotubes, …) of the material. Furthermore, this method is very flexible in terms of temperature, flow rate and solid weight thus allowing the determination of surface Brønsted acidity in similar conditions to those employed during the further use of the material. The material can be easily *in-situ* pre-treated under reactional flow or in reductive/oxidative/inert atmosphere, without being exposed again to air, thus giving information on the real "working surface".

In contrast to some recent and successful H/D exchange methods,[12,13] our technique has the advantage of being direct, and of allowing the determination of both number and strength of each kind *i* of surface Brønsted acidity. In addition, it is easy to use, rather cheap and non-destructive, a simple back-exchange with gaseous H_2O allowing the initial material to be recovered.

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