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New Methods for Quantitative Determination of Brønsted Acid Sites on Solid Acids: Applicability and Limits for Al_2O_3-Promoted SO_4^{2-}/ZrO_2 Catalysts

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Two quantitative methods, both based on H/D exchange, have been developed for the Brønsted acid sites titration on solid acids. The agreement between the results obtained with the two methods on unpromoted sulfated zirconia (SZ) is remarkable: 0.061 and 0.064 mmol of H/g of catalyst were respectively found with the first (anhydride method) and the second (isobutane method) method. Furthermore, the use of a small alkane as the probe molecule with the isobutane method gives us information about the capacity of the solid to activate an alkane. Nevertheless, this last method is hard to apply to very active catalysts such as 3% alumina-promoted sulfated zirconia (SZA3). Indeed, it was not possible in this case to find optimal temperature conditions, low enough to minimize secondary reactions such as isomerization or cracking and, at the same time, sufficiently high for an accurate quantitative H/D exchange measure. On the other hand, the anhydride method was always applicable to SZA*n* catalysts and the obtained results were very reproducible.

Key Words: **sulfated zirconia; alumina-promoted sulfated zirconia; acid sites titration; H/D exchange; alkane activation.**

1. INTRODUCTION

Solid acids have found widespread applications in many catalytic reactions concerning hydrocarbons, such as alkane or alkene isomerization, oligomerization, alkylation, and cracking.

Regarding the economic value of solid acid catalysts in the oil industry (1, 2), methods giving information about their acid sites (number, type, and strength) are of the greatest importance for understanding their catalytic activity.

However, as recently underlined in several reviews (3, 4), the reliability and the applicability of various suggested methods are questionable. The most frequently used techniques are based on the adsorption of basic compounds.

Calorimetric titrations with Hammett indicators suffer from a large number of limitations: the equilibrium is rarely achieved; non-acid sites may also produce the change of color; this method gives the sum of the amount of Brønsted and Lewis acid sites (3).

TPD of basic molecules may be misleading because reactions different from acid–base interactions often occur between the base probe and the solid surface. Furthermore, TPD of benzene or pyridine cannot be used to measure the acidity of sulfated zirconia or composite materials based on it (5).

Calorimetry has uncertainties due to thermal effects induced by interactions other than hydron transfer (6). In addition, acid–base interactions may involve more than one hydron transfer; thus, some molecules, treated as simple bases in calorimetric studies, were later proved by NMR to be, at least in part, diprotonated (6, 7).

Moreover, these methods give the total number of acid sites (Lewis and Brønsted) but do not differentiate between them. In those cases when only one of the two types of acid sites is catalytically active, the results from these methods do not correlate with catalytic activity.

IR spectroscopy of absorbed basic probes such as pyridine allows us to easily distinguish the two types, but only semiquantitative measurements are possible because the exact value of the extinction coefficient of these species is very seldom known (8). Besides, as recently reported by Morterra, this method has led to at least an overestimation of the Lewis acidity of SZ systems (9).

Therefore, in relation to our recent work on H/D exchange occuring between small alkanes and solid acids, we have developed two complementary methods of chemical titration of sites in solid acids. In our previous work (10–13) we used the regioselective H/D exchange to achieve qualitative comparisons between different solid acids under various conditions.

We monitor also the exchange taking place between the deuterated acid catalyst and water, describe the precise

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quantitative experimental procedure used, and discuss the feasibility and the limits of these methods.

2. EXPERIMENTAL

2.1. Catalyst Preparation and Materials

The alumina-promoted sulfated zirconia catalysts (ZSA*n*) were prepared by the co-precipitation method described in detail elsewhere (14). Briefly, a mixed solution of $ZrOCl_2 \cdot 8H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ was slowly added to aqueous ammonia under heavy mechanical stirring at room temperature. During the precipitation the pH value was kept constant at 8 by simultaneous addition of 10 N NH_4OH. The precipitate, as obtained, was thoroughly washed with distilled water and dried at 110°C for 20 h. Sulfation was carried out by incipient wetness impregnation with an aqueous 1.8 N $(NH_4)_2SO_4$ solution. The samples were dried again and then calcined at 650°C for 3 h under a dry air flow and stored under air.

As a reference, plain ZrO_2/SO_4 (ZS) was prepared in the same way, starting from the $ZrOCl_2 \cdot 8H_2O$ precursor. The promoted catalysts were labeled ZSA with a number *n* ($n = 1, 3, 5, 9, 15$) corresponding to the nominal alumina concentration as the molar percentage.

Nitrogen (purity 4 N, $H_2O < 5$ ppm) and isobutane (research quality, 99.95%) were purchased from Air Products. The purity of the hydrocarbon was checked by GC and the alkane was used without further purification. The natural abundance of deuterium in isobutane was measured by $^1H/^2H$ NMR (0.01% in methyl groups) and subtracted from the results obtained with SZA*n* catalysts.

Trifluoroacetic anhydride (99+%) was purchased from Aldrich.

Deuterium oxide (>99.90%) was purchased from sds France.

2.2. General Experimental Procedures

All the reactions were performed in an all-glass, grease-free, flow system with a downward reactor (Fig. 1).

The temperature was controlled with a thermocouple immersed in the catalytic bed and the gas pressure regulated with a Brooks 5850E mass flow controller.

Before each experiment, the apparatus was cleaned, flushed, and checked for leaks.

A blank experiment without catalyst was carried out under the same conditions used with SZA*n* catalysts to test the absence of exchange between D_2O and the glass apparatus.

2.2.1. Catalyst pretreatment. The catalyst (500 mg) was first activated under air flow (40 ml/min) at 450°C for 1 h and 30 min to eliminate hydrocarbon contamination. Then, it was flushed at the same temperature for 1 h with a stream of N_2 (40 ml/min) dried over molecular sieves (zeolite, 3 Å) and passed through a cold trap maintained at the liquid nitrogen temperature. The temperature of the catalyst was lowered to 200°C for deuteration.

2.2.2. Catalyst deuteration. 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 (T_3, Fig. 1).

The catalyst was heated again at 450°C and maintained at this temperature for 1 h to desorb any adsorbed D_2O. Then, the temperature was lowered to 200°C before use.

2.2.3. Acid sites titration by the trifluoroacetic anhydride method. The deuterated catalyst (cat-OD) was contacted at 200°C for 1 h with 40 ml/min of dry N_2 previously bubbled through a U tube (T_2, Fig. 1) containing distilled H_2O at room temperature (N_2 containing approximately 3% H_2O). Excess water was again removed by flushing the catalyst at 450°C for 1 h with dry N_2.

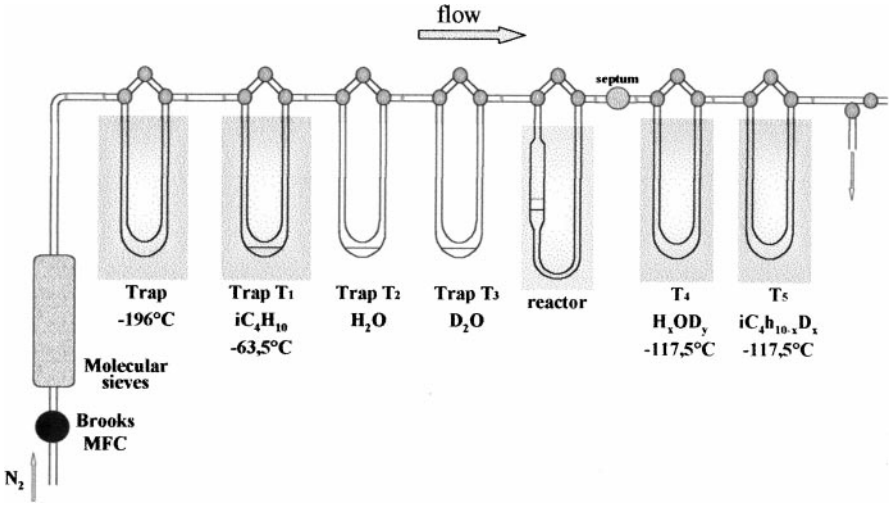

FIG. 1. All glass, grease-free, flow system.

During the H/D exchange and the flushing the partially exchanged water (H_xOD_y) was collected in a cold U tube (T_4, Fig. 1) at −117.5°C (ethanol melting point). Before and after these steps, the traps T_2 and T_4 were weighed to measure the exact amounts of H_2O used and H_xOD_y trapped. The material balance was found correct with an error of less than 5%.

An excess of trifluoroacetic anhydride (molar ratio $(CF_3CO)_2O/H_xOD_y$ about 1.5) was then added to trap T_4 with a syringe under argon.

The acid solution thus obtained was transferred under argon to a NMR tube for $^1H/^2H$ analysis. $^1H/^2H$ NMR spectra were recorded on a Bruker AM400 spectrometer (400 MHz) after addition of a $CDCl_3$(2 wt%)/$CHCl_3$ mixture as reference. The acid sites density was then calculated based on the H/D ratio determined by NMR and the weight of H_xOD_y condensed.

2.2.4. Acid sites titration by the isobutane method. The protonated catalyst (cat-OH) was again deuterated as described in Section 2.2.2 and then contacted at 180°C for 1 h with 20 ml/min of dry N_2 containing approximately 6% of isobutane, after bubbling through a U tube containing iC_4H_{10} maintained at the $CHCl_3$ melting point (−63.5°C). The catalyst was then flushed with dry N_2 at 180°C for 1 h. During H/D exchange and flushing, the partially exchanged alkane ($iC_4H_{10-x}D_x$, with $0 < x < 9$) was collected at the outlet of the reactor in a cold trap at −117.5°C. The traps T_1 and T_5 were weighed to know the exact amount of isobutane sent and collected. For the quantitative acid sites density determination ^1H and ^2H NMR spectra were recorded using, as a reference and internal standard, a mixture of $CDCl_3$ (3 wt%)/$CHCl_3$ and Freon 113 (CF_2Cl–$CFCl_2$) as the solvent.

3. RESULTS AND DISCUSSION

The two quantitative methods for Brønsted acid sites titration presented here are both based on the proton/deuterium exchange. The first method with H_2O titrates the amount of OD sites on the deuterated catalyst (anhydride method) and the second method measures the amount of deuterium transferred from the deuterated catalyst to isobutane (isobutane method). It is well known (15) that the number of OH sites on solid acids is very much dependent on the activation temperature of the catalyst. For this reason the catalyst pretreatment was always performed at 450°C to study the acid sites density under the same activation conditions as those used for the *n*-butane isomerization test for these catalysts (16).

Figure 2 illustrates the consecutive sequences of catalyst treatment and H/D exchange procedures used for plain SZ.

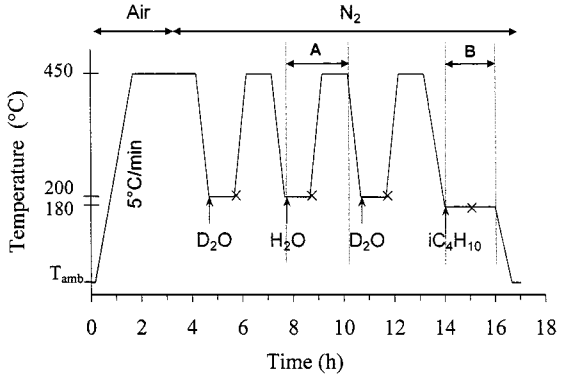

FIG. 2. Experimental procedure for the H/D exchange reactions on plain sulfated zirconia: (A) trapping of H_xOD_y; (B) trapping of $iC_4H_{10-x}D_x$.

3.1. Acid Sites Titration on SZ by the Trifluoroacetic Anhydride Method

At first, a very large excess of gaseous D_2O (about 0.05 g) was used to exchange the totality of the Brønsted acid sites present on the catalyst.

$$\mathrm{SZ{-}OH} \xrightarrow[\text{in excess}]{\mathrm{D_2O}} \mathrm{SZ{-}OD} + \underbrace{\mathrm{H_2O + HDO + D_2O}}_{\mathrm{H_{x'}OD_{y'}}\ (x' \ll y')} \quad [1]$$

The titration of the O–D acid sites was then performed by exchanging the deuterium present on SZ with distilled water [2] and trapping the recovered H_xOD_y by an acid anhydride [3a].

$$\mathrm{SZ{-}OD} \xrightarrow[\text{in excess}]{\mathrm{H_2O}} \mathrm{SZ{-}OH} + \underbrace{\mathrm{H_2O + HDO + D_2O}}_{\mathrm{H_xOD_y}\ (x \gg y)} \quad [2]$$

$$\mathrm{H_xOD_y} \xrightarrow[\text{in excess}]{(\mathrm{RCO})_2\mathrm{O}} x\mathrm{RCOOH} + y\mathrm{RCOOD} \quad [3a]$$

We tested three different anhydrides (trifluoroacetic, maleic, and phtalic). Both maleic and phtalic anhydrides were too little reactive toward water. Trifluoroacetic anhydride proved to be very suitable: its hydrolysis [3b] is fast and complete.

$$\mathrm{H_xOD_y} \xrightarrow[\text{in excess}]{(\mathrm{CF_3CO})_2\mathrm{O}} x\mathrm{CF_3COOH} + y\mathrm{CF_3COOD} \quad [3b]$$

Moreover, it does not contain hydrogen, which facilitates ^1H NMR analysis. Both ^1H and ^2H NMR spectra of the acid solution show only two narrow peaks corresponding to trifluoroacetic acid (δ 11.6) and the reference (chloroform, δ 7.26).

Nevertheless, we must note that trifluoroacetic anhydride is extremely reactive toward water and requires extreme protection from moisture. It contains usually about 0.11 mmol of trifluoroacetic acid per gram of anhydride as

controlled in a blank experiment. For this reason we preferred to apply the anhydride method to the titration of partially exchanged H_2O obtained in step [2] rather than to partially exchanged D_2O (step [1]). The acid site density thus obtained by application of the anhydride method is 0.061 mmol of H/g of SZ. The isobutane method described below gives a similar result.

3.2. Acid Sites Titration on SZ by the Isobutane Method

The second method used to determine the acid site density in SZA*n* catalysts is based on the amount of deuterium incorporated by an alkane during the H/D exchange reaction between the deuterated solid (1 g) and the alkane itself.

$$SZ{-}OD + iC_4H_{10} \rightarrow SZ{-}OH + iC_4H_{10-x}D_x. \qquad [4]$$

The exchange process was discussed earlier (10–13). The recovered alkane exchanges, in part, only its primary hydrons for deuterium. The regiospecific H/D exchange observed here in isobutane was rationalized by the catalytic cycle involving deprotonation and reprotonation (here redeuteronation) steps of a *tert*-butyl ion. The deuterated trimethyl carbenium ion is obtained specifically following Markovnikov's rule.

H/D exchange occurring between acidic catalysts and isobutane is very fast as it occurs with zeolites at temperature below 100°C in the absence of noticeable side reactions (10–13). Moreover, once the carbenium intermediate is generated from the starting alkane, due to the high proton mobility, all sites do not need to be strongly acidic as we have shown with HPAs (11); even residual D_2O will participate. For these reasons again it is important to stress the temperature at which the catalyst has been activated before measurements.

3.2.1. Temperature dependence of the H/D exchange rate. A preliminary study was performed to verify how long we had to contact the deuterated SZ catalyst with isobutane to recover all deuteron atoms present on it. Collecting the alkane at 10-min intervals directly in NMR tubes, we followed the time dependence of H/D exchange between isobutane and SZ-OD in the range 120–180°C. The results obtained at various temperatures, plotted in Fig. 3, show that at 120°C several hours are necessary to recover all deuterium from the catalyst and at 150°C 90 min is sufficent and that SZ contacted with isobutane was depleted of deuterium in about 1 h only at 180°C. To recover all exchanged isobutane, we flushed the catalyst with N_2 for 1 h more. This temperature is higher than that found in our previous studies on SZ synthesized in a similar way but activated at a lower temperature (200°C) (14). In this temperature range, we were not able to detect by GC any side reactions (isomerization or cracking) accompanying the H/D exchange process. Based on this preliminary study, the isotopic exchange reaction between deuterated sulfated zirconia and isobutane was performed at 180°C.

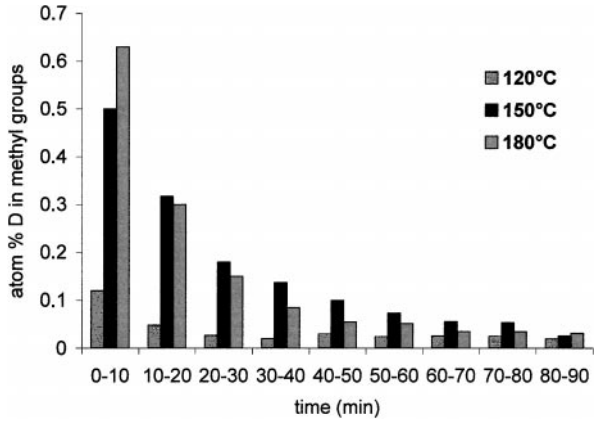

FIG. 3. Kinetic study of H/D exchange between isobutane and deuterated sulfated zirconia. Fraction collected as a function of time and temperature.

The acid sites density determined by the isobutane method gave 0.064 mmol of H/g of SZ after activation at 450°C.

In the present work, good agreement between the results obtained with the anhydride method and the isobutane method applied to plain SZ is remarkable: 0.061 and 0.064 mmol of H/g. In comparison with the results published previously in the literature, these values are in very good agreement with those reported by Mastikhin *et al.* (15a) for a SZ sample calcined at 600°C and evacuated at 400°C: 0.066 mmol of H/g ($C_{OH}/10^{20}$ g^{-1}). However, our values of acid sites density are higher than that (0.025 ± 0.003 mmol of H/g) measured by Xu and Sachtler (17) on a SZ catalyst calcined at the same temperature (650°C) but pretreated at slightly more severe conditions (evacuation at 450°C).

Whatever technique is used, it is essential when quoting the BAS density to indicate the pretreatment temperature of the catalyst before measurements. The values obtained for catalysts activated at 450°C are of the same order of magnitude as the strongest acid sites estimated by differential calorimetry (15e).

We have previously used the isobutane method in the past few years to make qualitative and quantitative comparisons between various solid acids and alkanes under various conditions. The quantitative results obtained for a series of acid solids (HBEA, SZ, HUSY, SAPO-5, and HZSM-5) are close to the Brønsted acid sites concentration determined by other experimental methods (13). In all these cases H/D exchange occurred in the absence of any detectable side reactions at around 200°C. Thus, H/D exchange in isobutane can be useful in comparing the acidity of solid acids, particularly if we want to know if the solid acids are sufficiently strong to activate saturated alkanes.

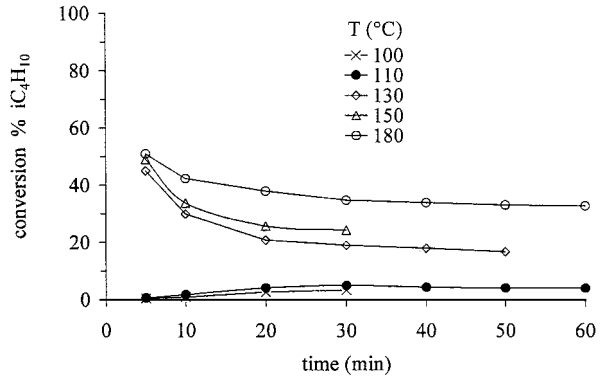

FIG. 4. Temperature effect on iC_4H_{10} conversion with SZA3 catalyst in the flow system.

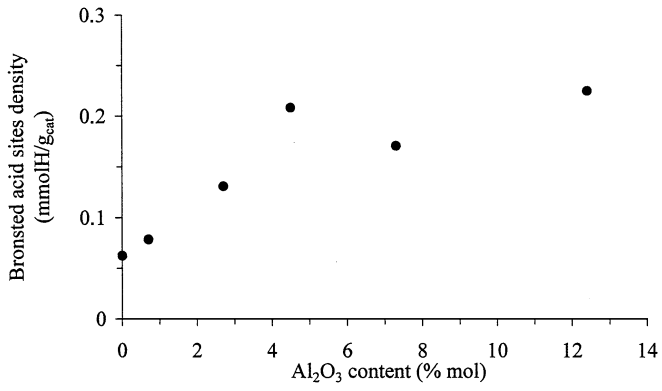

FIG. 5. Effect of alumina on Brønsted acid sites density in SZA.

3.2.2. The limits of the isobutane method for more active catalysts. The isobutane method however is not applicable to catalysts that are very active toward the isobutane molecule at low temperature. In fact, in the case of SZA3, it was not possible to find temperature conditions sufficiently low to minimize secondary reactions, such as isomerization and cracking, and at the same time sufficiently high for the quantitative calculation of the exchange.

To find a suitable temperature, we progressively lowered the reaction temperature until, at $T = 110$–100°C, the isobutane conversion was negligible (Fig. 4).

Then, to verify if it was possible, at this temperature (110°C), to recover quantitatively deuterium by isobutane, we passed for 2 h the gaseous alkane (5% v/v in N_2, 20 ml/min) over the catalyst (SZA3, 1 g). Isobutane, partially exchanged, coming out from the reactor was condensed at -117.5°C in three traps corresponding to the first hour, the subsequent 30 min, and the last 30 min. The content of three traps was analysed by $^1H/^2H$ NMR and the results showed that at 110°C the $^1H/^2H$ exchange rate between iC_4H_{10} and SZA3-OD was too slow to recover all deuterons present on the catalyst. Because of its very high activity compared to that of plain SZ, it was not possible to increase the temperature to increase the exchange. On the other hand, it was not possible to extend the duration of exchange in the flow system because the concentration of deuterons recovered would be too small to make an accurate NMR analysis.

To increase the exchange, without diluting the deuterons too much, we tested the reaction in recycling experiments: 15 ml of the alkane, added to a volume of 300 ml, were recirculated at a rate of 20 ml/min, on the catalyst (1 g) maintained at 100°C. Unfortunately, the side reactions are not any more negligible: after only 40 min about 12% of isobutane was converted.

At room temperature, after 22 h, this conversion was only 1%, but the $^1H/^2H$ exchange was far from being quantitative.

3.2.3. Acidity of alumina-promoted sulfated zirconia. The isobutane method is interesting because its results are in good agreement with those from other methods and because it allowed us to explore mechanistic aspects of alkane activation (in the absence of side reactions). However, it is not applicable to very active catalysts such as 3% alumina-promoted sulfated zirconia.

In that case we were obliged to use the anhydride method. To study the reproducibility of the results, we sent sequentially D_2O and H_2O three times, with intermediate drying at 450°C. The reproducibility of the results was excellent: the amounts of Brønsted acid sites obtained were 0.131, 0.129, and 0.133 mmol of H/g of SZA3.

The anhydride method was also applied to sulfated zirconia catalysts promoted with different amounts of alumina. The results are reported in Table 1 and shown in Fig. 5. The Brønsted acid sites density increases with alumina introduction and then seems to reach a nearly constant level at higher alumina contents (5–15%).

TABLE 1

Effect of Alumina on Brønsted Acid Sites Density in SZA

		Brønsted acid sites density (mmol of H/g)			
Catalyst	Al_2O_3 (mol%)	Isobutane method	Anhydride method		
SZ	0	0.061	0.064		
SZA1	0.7	—	0.078		
SZA3	2.7	—	0.131	0.129	0.133
SZA5	4.5	—	0.210	0.204	
SZA9	7.3	—	0.167	0.176	
SZA15	12.4	—	0.251	0.200	

4. CONCLUSION

We developed two new quantitative methods for titration of the BAS on solid acids, both based on H/D exchange. The agreement between the results obtained was excellent.

The use of a small alkane such as isobutane gives us information about the capacity of solid acids to activate the alkane. Unfortunately, this last method is difficult to apply to very active catalysts such as 3% alumina-promoted sulfated zirconia (SZA3) for which the isotope exchange is accompanied by substantial conversion of the alkane.

In contrast, the anhydride method is easy, rather cheap, and always applicable. Its results are very reproducible. It allowed us to study the effect of the amount of alumina in promoted sulfated zirconia catalysts on Brønsted acid sites density.

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