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Hydrogen Exchange between Sulfated Zirconias and per Deutero-Benzene as Characterization of the Surface Acidity

Study by DRIFT and ^{1}H MAS-NMR Spectroscopies

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The surface acidity of sulfated zirconia has been investigated by diffuse reflectance IR and ^{1}H MAS-NMR spectroscopies. Both techniques give evidence of the existence of two types of acid sites: a weak acid characterized by an infrared band at 3630 cm^{-1} and an ^{1}H NMR resonance at 3.5 ppm relative to TMS, and a strong acid characterized by resonances at 3300 cm^{-1} in infrared and 5.8 ppm in ^{1}H NMR. The interaction of deuterated benzene with these solids also shows two types of acid sites: the weaker sites give hydrogen bonding with benzene, evidenced by a shift of the resonance frequency in infrared spectrometry. The presence of strong acid sites able to exchange protons with deuterated benzene has been ascertained by FTIR and NMR investigation of the adsorbed phase and by mass spectrometric analysis of the effluents. The catalytic properties in isomerization of *n*-hexane are correlated with the presence of these strong acid sites, the formation of which depends on the type of preparation of the catalyst. © 1997 Academic Press

INTRODUCTION

Sulfated zirconia has attracted interest since it has shown to present a strong acidity (1–5) and to be able to convert alkanes at low temperatures. Despite considerable efforts, the characterization of the protonic acidity of these solids is still disputed. Riemer *et al.* (6) analyzed sulfated zirconia by Raman and MAS-NMR spectroscopies. Protons considered as super acid were identified by an infrared band at 3640 cm^{-1}, and a NMR resonance at 5.85 ppm. The solids also showed two other NMR resonances at 1.6 and 3.86 ppm, previously assigned by Matiskhin *et al.* (7, 8) to terminal and bridging OH groups. The same view has been supported by Adeeva *et al.* (9), who attributed the acidity of sulfated zirconia to a NMR resonance at about 6 ppm, corresponding to an infrared band at 3630 cm^{-1}. The acid character of these species was checked by their shift upon adsorption of a weak base, CCl_3CN. The conclusion reached by these authors was that sulfated zirconia showed a relatively weak acid strength comparable to that of CsHY zeolites. Semmer *et al.* (10) applied to sulfated zirconia the method of investigation of the acid strength based on the NMR study of water adsorption, first described for zeolites (11). The results of broad line NMR experiments showed the formation of hydroxonium ions upon water adsorption. The ratio H_3O^+/SO_4 was equal to 1 when 2 moles of water were adsorbed per SO_4 species. The ionization coefficient, or number of hydroxonium ions formed per Brønsted acid site was found equal to 0.5, compared to 0.2 for silica rich zeolites, and 1 for Nafion.

Kustov *et al.* (12) observed by diffuse reflectance two infrared bands corresponding to acid hydroxyls: one at 3630 cm^{-1}, attributed to bridging hydroxyls, the acidity of which is increased by sulfation, and a broad band at about 3200 cm^{-1} corresponding to the stronger acid sites, identified to the OH group of SO_4H^-. Since this band is broad, the formation of hydrogen bonds by interaction with benzene gave little information because the band is then broader and disappears in the background. These hydroxyls reacted with ethylene at room temperature, and the rate of ethylene polymerization then observed was comparable to that measured with ZSM-5. Sulfated zirconia was then proposed to show the same acid strength as observed in zeolites. It can be pointed out in this respect that a broad band centered at 3250 cm^{-1} and associated to a NMR line at 7 ppm has also been reported on H-ZSM5 (13, 14).

The discrepancies existing in the literature on the acid strength of sulfated zirconia can in part stem from the different methods of characterization: acetonitrile, water, benzene have different basicities and therefore probe different sites. Catalyst preparation has also probably a great importance since the 3200 cm^{-1} band reported by Kustov *et al.*

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(12) was not observed in other works relative to infrared studiers of sulfated zirconias (8, 15–17).

We have recently reported that the catalytic properties for the isomerization of *n*-hexane on sulfated zirconias was very sensitive to the method of preparation. The strong acidity of these solids is reflected by the formation of 2,2-dimethylbutane. At equal conversion of 24%, the selectivity to 2,2-dimethylbutane changed, however, from 0.8% for a classical preparation in two steps (first precipitation of $Zr(OH)_4$ then sulfation) to 8.6% for a one step sol–gel synthesis (18). In order to determine if these different properties can be related to different protonic acidities, in situ diffuse reflectance studies were undertaken and the results are compared with those of MAS-NMR spectroscopy carried out in a controlled atmosphere.

EXPERIMENTAL

Catalyst Preparation

The preparation of the samples of sulfated zirconia is described in detail in (18). Two preparations were applied: in the first one zirconia is first obtained, by a sol–gel procedure, by hydrolysis of zirconium *n*-propylate in *n*-propanol by the additition of water. The gel is dried, then sulfated by treating with a 0.5 M solution of sulfuric acid, to obtain a solid referred to as SGZR-2. In the other cases, sulfuric acid is used as the catalyst in the sol–gel; the solution is made by mixing the propoxide, *n*-propanol, water, and sulfuric acid. The acid can be added either to the propoxide, as reported by Ward and Ko (19) which gives the sample referred to as SGZR-7, or to water in order to obtain a diluted solution which is mixed with the solution of propoxide in *n*-propanol, to obtain the sample SGZR-5.

SGZR-11 and SGZR-13 were prepared as SGZR-5 with different amounts of sulfuric acid in the solution; the latter were adjusted in order to obtain a nominal sulfur content of 5, 2.5, and 10 wt% in SGZR-5, SGZR-11, and SGZR-13, respectively. After drying the samples were calcined at 898 K in air, except SGZR-2 which was calcined at 923 K.

Infrared Spectrometry

The measurements were made using a Nicolet 550 instrument equipped with a MCT detector and a DRIFT cell (Spectratech) used in flow mode. The sample (about 15 mg) was used in the powder form after sieving to 60–80 mesh, calcined in situ in dry air, then kept in a flow of helium dried by a liquid nitrogen trap. In a typical experiment, a spectrum was taken at room temperature after sample calcination; then 5 μL of light benzene (C_6H_6, dried on zeolites) was injected in the inlet flow, and spectra were taken at different intervals of time; then several doses of deuterated benzene C_6D_6 were injected in the same way. Infrared spectra were continuously recorded (60 scans per spectrum). The gaseous effluents released by the catalysts were continuously monitored by on-line mass spectrometry at the reactor outlet.

MAS-NMR Measurements

All NMR spectra were measured at room temperature using a Bruker DSK-300 spectrometer with a special home built NMR probehead able to spin 5 mm sealed NMR tubes up to 4 kHz. The ^1H MAS-NMR spectra were obtained at an excitation frequency of 300.18 MHz and with a repetition time of 1 s, using about 3 kHz MAS speed and 90° pulses of 2.0 μs length. Chemical shifts were referenced to external tetramethylsilane (TMS). In all cases the background signal, measured under identical conditions with an empty rotor, was subtracted from the spectrum.

Before the NMR analysis, about 100 mg of solid were introduced in a 5 mm NMR tube and treated under vacuum, rising gradually the temperature over several hours up to 673 K, temperature which was maintained 2 h. The NMR tube was then sealed under vacuum.

Benzene-d6 samples: benzene-d6 was degassed at liquid nitrogen temperature to remove noncondensable gases. Afterwards the deuterated benzene was added to the different samples, previously pretreated at 673 K in vacuum as mentioned above, by exposure to 23 Torr of vapor pressure at room temperature. When the adsorption equilibrium had been reached, the samples were evacuated 10 min and the tubes sealed in vacuum.

n-Hexane Conversion

The samples were tested in the hydroconversion of *n*-hexane as mechanical mixtures of ZrO_2–SO_4^{2-} (100 mg) with Pt/Al_2O_3 (300 mg) as described previously (18). Pt/Al_2O_3 was prepared by ion exchange between H_2PtCl_6 and γ-Al_2O_3; it contains 0.37 wt% Pt with an accessibility of $H/Pt = 0.90$. This sample does not exhibit any activity for *n*-hexane conversion in the temperature range investigated, then the reaction is a bifunctional process controlled by acidity.

The reaction of *n*-hexane (nH, Carlo Erba >99%) with hydrogen (AGA, high purity grade >99.99%) was carried out at atmospheric pressure in a dynamic glass reactor. The partial pressure of nH was maintained at 6.04 kPa. The effluents were analysed by sampling on-line to a FID gas chromatograph equipped with a J & W capillary column (60 m × 0.5 mm i.d., DB1 apolar bonded phase).

Under these conditions the reaction rate is controlled by acidity. Since the acid sites are presumed to be related to sulfated species the activities are expressed here as turnover frequencies, i.e. number of molecules of *n*-hexane reacted per unit time and per S atom in the sample.

TABLE 1

Characteristics of the Sulfated Zirconias

Sample	Sulfur content (wt%) after calcination at		Surface area (m^2/g)	Turnover (h^{-1})	Selectivity 2,2-DMB
	393 K	898 K			
SGZR-2	5.9	1.0[a]	81	0.67	0
SGZR-5	3.15	1.8	88	10.6	11.1
SGZR-7	3.15	2	108	5.3	5.6
SGZR-11	2.15	1.01	66	0.72	5.15
SGZR-13	6.5	5.35	55	0.13	5.4

[a] After calcination at 923 K.

RESULTS AND DISCUSSION

The chemical analyses and surface areas of the samples are reported in Table 1. The amount of sulfur which can be retained by the zirconia gel depends on the concentration of sulfuric acid in the preparation; an equilibrium exists between the solution and the solid. There exists an optimum calcination temperature for catalytic activity, which is 898 K for the samples prepared in a one-step procedure and 923 K for the sample prepared classically in two steps. After this calcination significantly different amounts of sulfur are retained.

The DRIFT spectra of these samples, calcined in dry air at 773 K are reported in Fig. 1. In agreement with literature data (12), they present two types of isolated ZrOH groups characterized in the fundamental OH stretching region by the narrow IR-bands at 3765–3770 cm^{-1} and 3665–3670 cm^{-1}, and a broad band between 3200 and 3400 cm^{-1}, previously assigned to OH groups of a SO_4H species.

It can be noticed that this band is very weak on the samples showing a low activity for the isomerization of *n*-hexane:

(i) SGZR-2, prepared by the classical two-step procedure which yields a solid of lower activity (Table 1). The fact that no dibranched products are formed in that case also suggests a lower acid strength.

(ii) SGZR-13 prepared by the sol–gel method with high sulfur loading. In this second case polysulfates are likely to

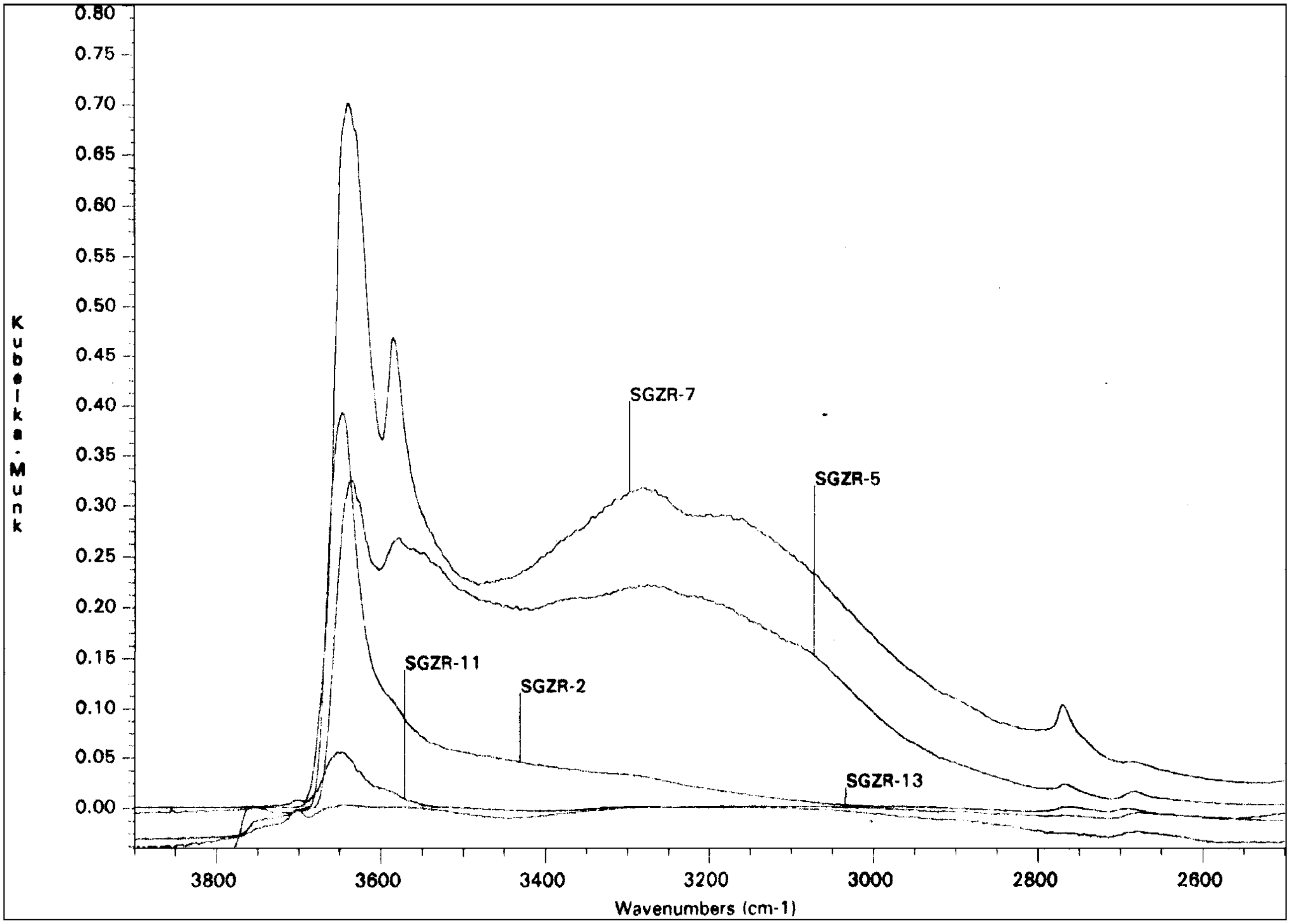

FIG. 1. DRIFT spectra at room temperature, of sulfated zirconias treated in a flow of dry helium at 773 K.

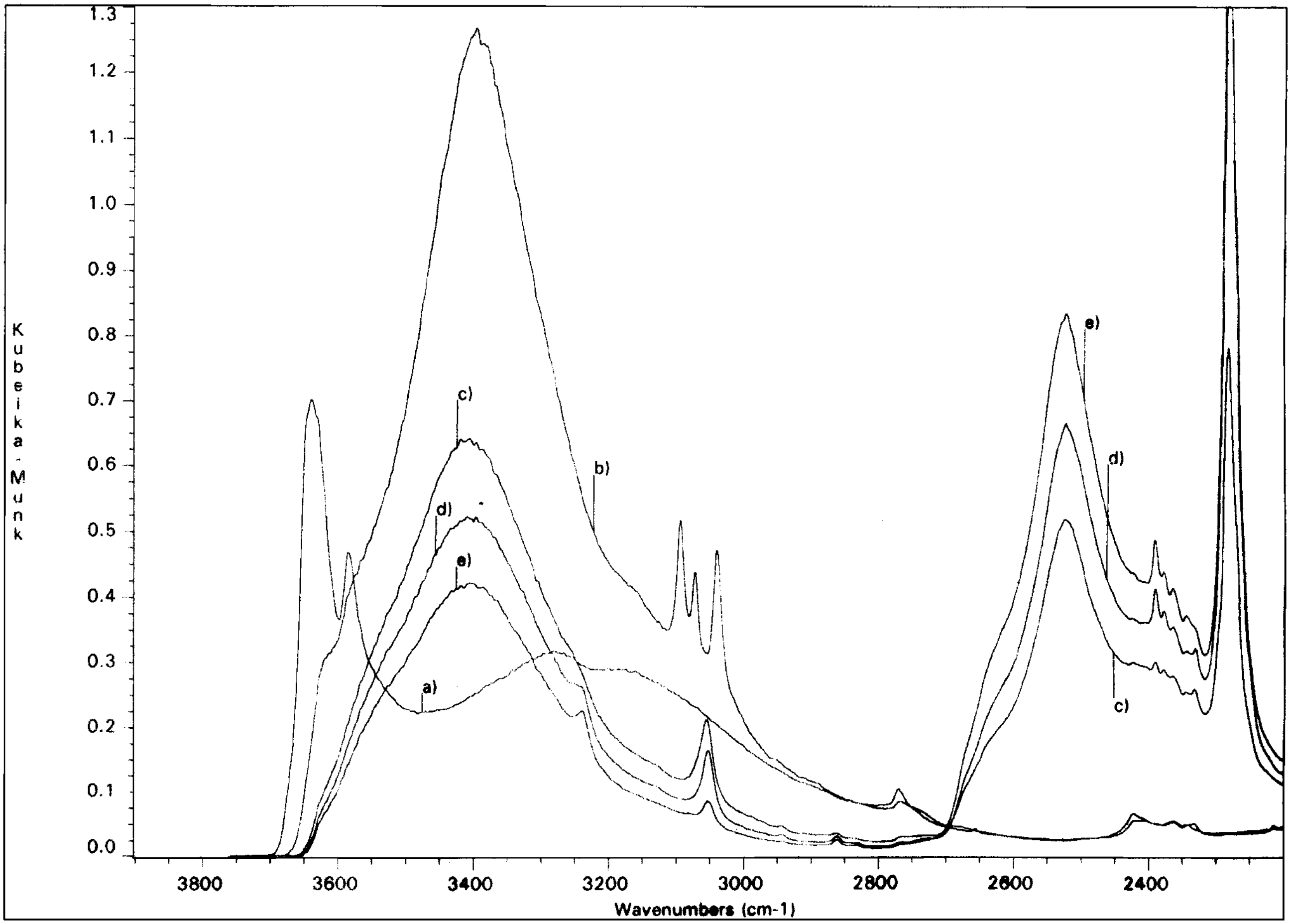

FIG. 2. DRIFT spectra of the SGZR-7 sample after activation in helium (a) and after introduction of (b) 5 μL of liquid C_6H_6 in the carrier gas; (c), (d), and (e) successive pulses of 5 μL of liquid C_6D_6.

exist, and Morterra *et al.* (20) have proposed that the acidity of these species is lower than that of sulfates.

(iii) SGZR-11 prepared by sol–gel with a low sulfur content.

This parallelism with catalytic activity for an acid catalysed reaction confirms the previous assignment of this band at 3200 cm^{-1} to an acid OH. The acid strengths associated with these different OH groups can be estimated by the extent of the interaction with a weak base such as benzene. The spectra obtained upon interaction of the solid (SGZR-7) with C_6H_6 or C_6D_6 are reported in Fig. 2. As reported previously, the intensity of the bands at 3600–3700 cm^{-1} decreases by interaction with C_6H_6 and a new broad band is formed around 3450 cm^{-1}, which corresponds to a band shift of 200–240 cm^{-1} on SGZR-5 and SGZR-7. Narrow bands are also observed in the region corresponding to aromatic CH vibrations (3000–3100 cm^{-1}). The eventual changes of the 3200 cm^{-1} band are here masked below the broad 3450 cm^{-1} band.

Upon adsorption of C_6D_6 the band at 3450 cm^{-1} decreases as a function of the amount of C_6D_6 injected, while an intense band develops in the region corresponding to OD groups in the 2500–2700 cm^{-1} range (spectra c–e). Taking into account the isotopic ratio 1.35, this OD band corresponds to the exchange of an OH band at 3350 cm^{-1}, therefore to the broad band, the intensity of which decreases upon interaction with deuterated benzene. A new band at 3065 cm^{-1} is characteristic of a partially exchanged benzene ring. These features clearly indicate that an H/D isotopic exchange occurs between the reactant and acidic OH groups of the solid. When deuterated benzene is pulsed first (Fig. 3), the same features are observed, with the development of the OD band at about 2500 cm^{-1} and the decrease of the OH bands. The OH bands can be restored by the injection of light benzene, with concomittent decrease in intensity of the OD bands; apparently the process is reversible.

Two different types of hydroxyls appear according to their interaction with benzene; the first one, associated with the band at 3640 cm^{-1}, gives simple hydrogen bonding, and shifts by about 200 cm^{-1} upon benzene adsorption. This OH is then acid, with an acidity corresponding to that of HX zeolites (21). The shift upon benzene adsorption is related to the amount of sulfur on the solid: SGZR-2 and 11 with lower

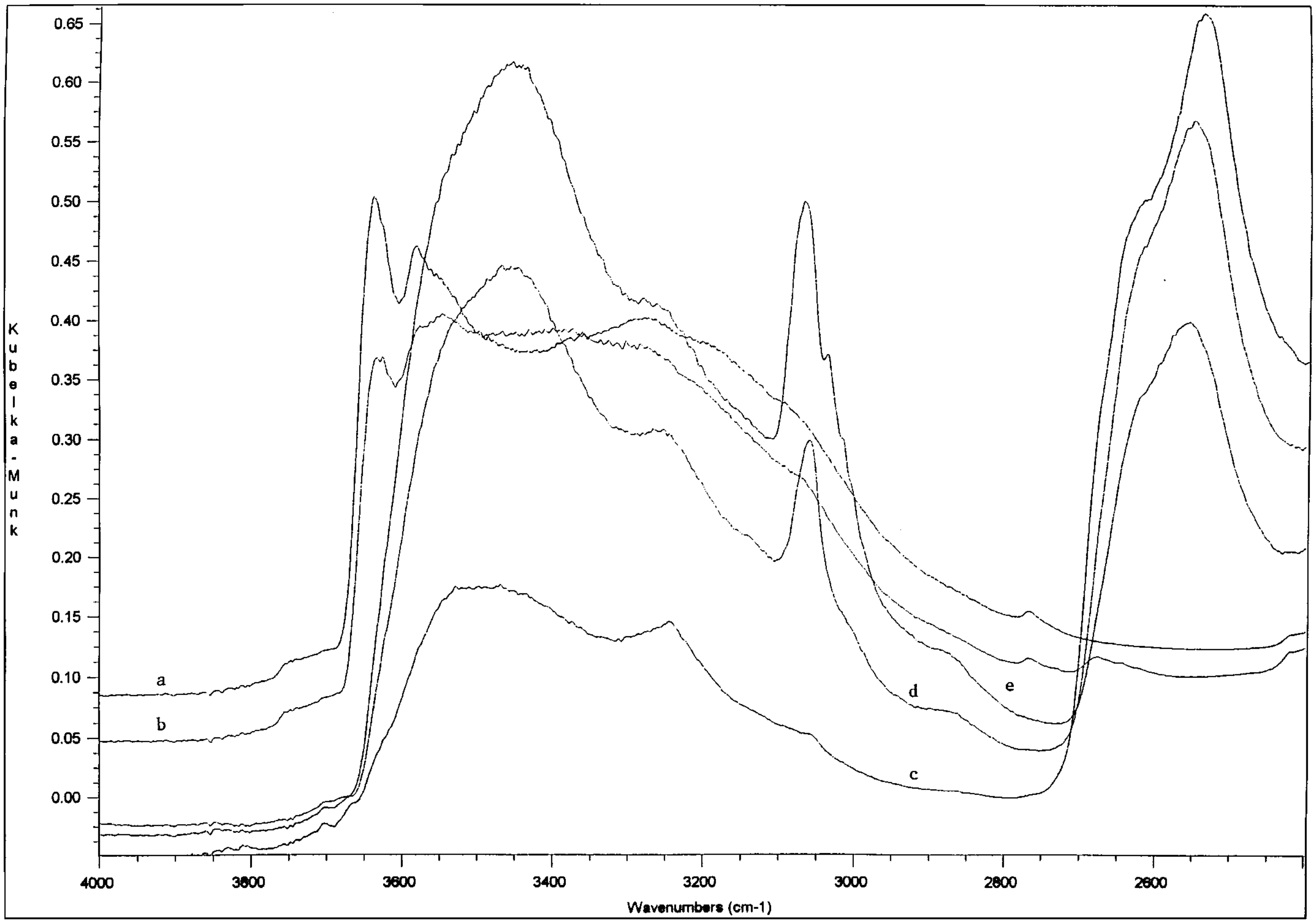

FIG. 3. DRIFT spectra of the SGZR-5 sample after activation in helium (a) and after introduciton of (b) and (c) two successive pulses of 5 μL of liquid C_6D_6 in the carrier gas; (d) and (e) successive pulses of 5 μL of liquid C_6H_6.

S loadings after calcination show smaller shifts (Table 2), but no large differences appear between these shifts. The second type of hydroxyl, associated with the band at 3200–3300 cm^{-1}, is able to exchange H with C_6D_6, which would involve protonation of benzene at room temperature.

A direct evidence that an isotopic exchange occurs between deuterated benzene and the surface can be found in the analyses of the effluents at the exit of the FTIR cell by mass spectrometry as illustrated in Figs. 4A and 4B for SGZR-11 and SGZR-5, respectively. Two main features are apparent:

TABLE 2

Shift of the OH Infrared Bands upon Adsorption of Benzene

	νOH (cm^{-1}) after		
Sample	Treatment in vacuum	Adsorption C_6H_6	$\Delta\nu$ (cm^{-1})
SGZR-2	3646	3467	179
SGZR-5	3633	3402	201
SGZR-7	3639	3395	244
SGZR-11	3640	3446	194
SGZR-13	3646	3420	226

(1) Concerning the adsorption of light benzene, calculated from the area of the outlet benzene peak (first peak on the left-hand side):

—on SGZR-11, only a small fraction (about 10%) of the first pulse of light benzene is retained by the catalyst when crossing the DRIFT cell (Fig. 4A).

—on SGZR-5 a large part of the pulse remains adsorbed by the catalyst (about 88%) (Fig. 4B).

(2) Concerning the isotopic exchange deduced from the isotopic composition of the deuterated benzene pulses at the reactor outlet (three last peaks in Figs. 4A and 4B and Table 3):

—on SGZR-11, a very small fraction of light C_6H_6 benzene (1–2%) is released suggesting a minor displacement of light benzene initially adsorbed by the perdeuterated C_6D_6 benzene. The occurrence of most of the deuterated benzenes (from $C_6H_3D_3$ to C_6HD_5) clearly indicates a process

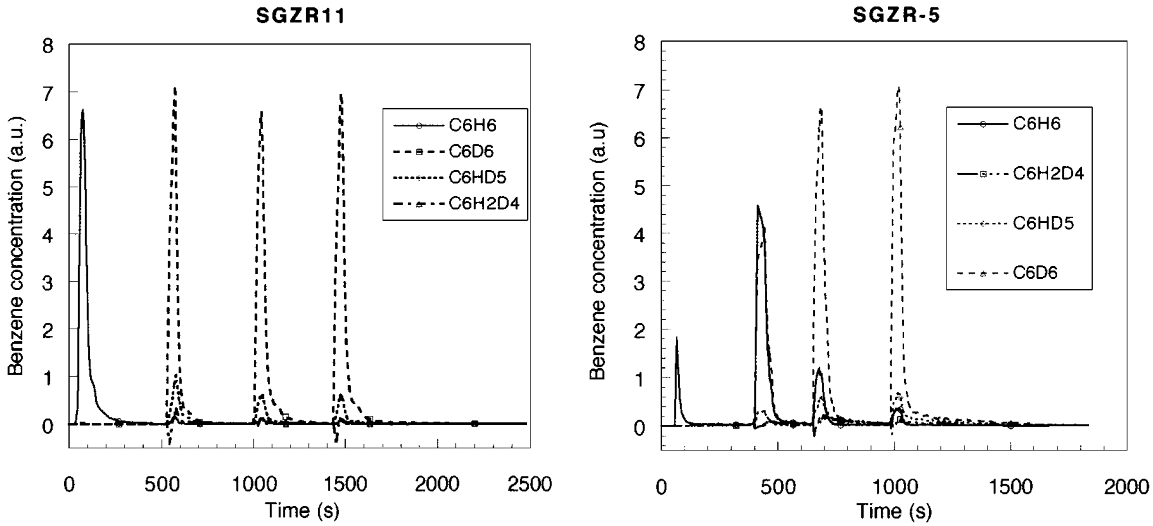

FIG. 4. Benzene concentrations in the effluents of the IR cell, in the case of (a) SGZR-11 and (b) SGZR-7.

of isotopic exchange between perdeutered benzene and a pool of hydrogens when the C_6D_6 pulses cross the catalyst bed. The extent of this exchange is evaluated to around 10% for the three C_6D_6 pulses. In addition, the distribution of the hydrogen atoms in the deuterated benzene molecules is found quite distinct from a statistical distribution and typical of a stepwise process of exchange such as:

$$C_6D_6 + H^+ \rightarrow C_6HD_5 + D^+.$$

On SGZR-5, a very large fraction of light benzene is displaced by the perdeuterated benzene pulses (but decreasing from pulse to pulse), as expected from the strong initial adsorption of light benzene. A similar process of isotopic exchange is also observed as previously, but to a larger extent (around 22% for the last pulse, i.e. when most of the initially adsorbed light benzene has been displaced and released into the gas phase).

The ^1H MAS-NMR spectra are reported in Fig. 5 for the five catalysts. These spectra show a principal broad resonance at about 5.8 ppm, with a shoulder at about 3.0 ppm and a weaker resonance at 1.1 ppm. Pure zirconium oxide shows mainly a broad resonance centered at 3.5 ppm. According to the results found in the literature (6–8), these signals can be assigned to the terminal OH (at 1.1 ppm), bridging OH (at 3.5 ppm) and acid OH bonded to sulfur at 5.8 ppm. The distributions of the different species on the four solids investigated here are reported in Table 4. All sulfated samples show the three different lines, but in agreement with the IR results, the amount of strong acid sites ($\delta = 5.8$ ppm) is lower on the SGZR-2 sample.

The ^1H NMR spectra recorded upon adsorption of benzene-d6 on these solids are reported in Fig. 6. A new line appears at $\delta = 7.2$ ppm which belongs to hydrogens in benzene, corroborating the former results of DRIFT spectrometry. The adsorption of deuterated benzene on pure

TABLE 3

Isotopic Composition and Extent of Isotopic Scrambling for the Various Benzene Pulses, Light and Deuterated, Introduced into the DRIFT Cell at 293 K over 15 mg of Calcined Sulfated Zirconia Samples

Sample	C_6H_6	C_6H_5D	$C_6H_4D_2$	$C_6H_3D_3$	$C_6H_2D_4$	C_6HD_5	C_6D_6	τ (%)
SGZr-11								
C_6H_6 peak	98.6	0.1	0	0	0	0	0.3	1.4
C_6D_6 peak 1	1.7	0	0	1.2	3.7	1.4	81.7	8.3
C_6D_6 peak 2	1.4	0	0	0.6	1.4	9.3	90.4	9.6
C_6D_6 peak 3	0.9	0	0	0.5	1.1	7.8	89.6	10.4
SGZR-5								
C_6H_6 peak	92.7	0	1.2	1.5	1.5	1.6	1.6	7.3
C_6D_6 peak 1	45.6	1.7	2	3.0	1.6	3.6	42.6	57.4
C_6D_6 peak 2	12.0	0.6	0	3.7	4.6	8.7	70.4	29.6
C_6D_6 peak 3	3.9	0	0	1.6	4.8	13.7	78.0	22.0

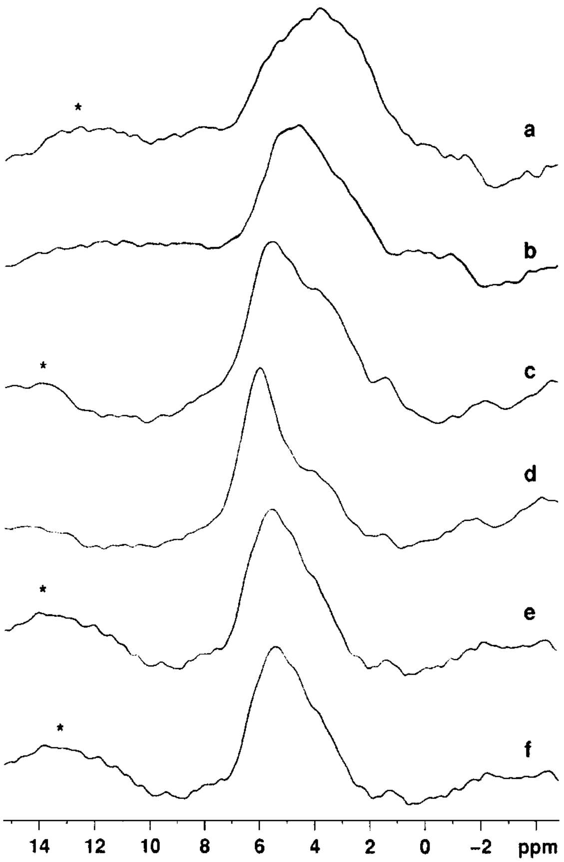

FIG. 5. ^{1}H MAS NMR spectra of samples after vacuum treatment: (a) ZrO_2; (b) SGZR-2; (c) SGZR-5; (d) SGZR-7; (e) SGZR-11; and (f) SGZR-13; * = rotation bands.

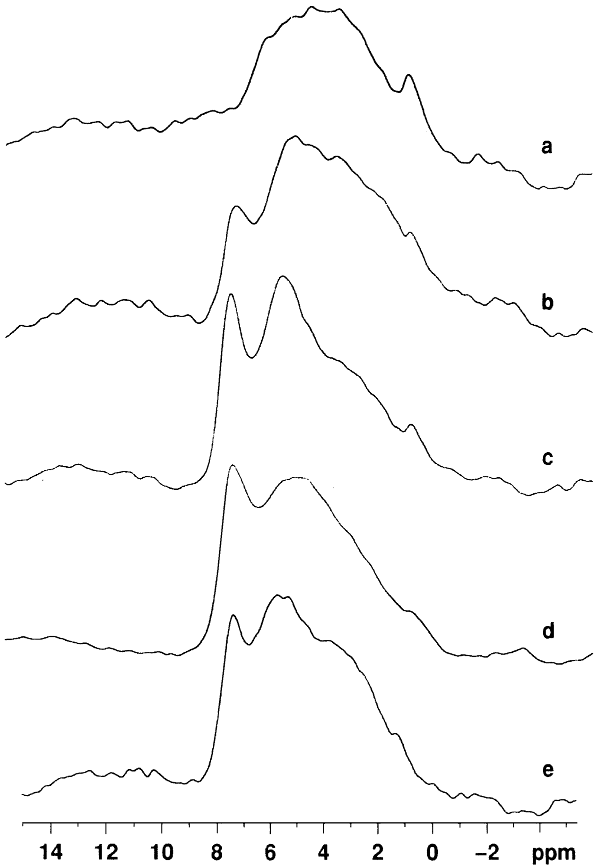

FIG. 6. ^{1}H MAS NMR spectra of samples after adsorption of per deutero-benzene. Treatment: (a) ZrO_2; (b) SGZR-5; (c) SGZR-7; (d) SGZR-11; and (e) SGZR-13.

ZrO_2 gives a band centered at 4.5 ppm, with a weak band at 1.1 ppm, and in that case the line at 7.2 ppm is not observed. Isotopic exchange is related to the presence of sulfates at the surface, that is to acidity.

The interaction of C_6D_6 with these solids therefore puts into evidence several types of acid hydroxyls: one of moderate strength, which gives an hydrogen bond with benzene; and a second one, much stronger, which gives hydrogen exchange with deuterated benzene. The occurrence of an isotopic H-D exchange upon adsorption of perdeutero benzene, which implies its protonation at room temperature, is confirmed by the different techniques used here. This strong acidity is related to the appearance of an infrared band at 3300 cm^{-1} and a NMR line at 5.8 ppm.

An interesting question is, which of these characterizations gives the better prediction of catalytic activity for parafin isomerization? NMR does show more intense lines for the most active SGZR-7 catalyst, but it cannot discriminate between this one and SGZR-11 and 13, which

TABLE 4

Distributions of the Different H Species on Four Different Preparations of Sulfated Zirconia

Sample	$\delta = 1.1$	$\delta = 3.5$	$\delta = 5.8$	%S
SGZR-2	22	49	28	1.0
SGZR-5	2	56	42	1.8
SGZR-7	2	37	61	2
SGZR-11	8	32	60	1.01
SGZR-13	4	39	57	5.35

TABLE 5

Distribution on the Products of Isomerization of *n*-Hexane at 423 K

		Selectivities				
Sample	Conv[a]	22DMB	23DMB	2MP	3MP	Cracking
SGZR-2	1.2	—	12	50.5	32.5	5
SGZR-5	37	11	13.7	45.7	25	4.4
SGZR-7	22.3	5.6	12.7	40.9	22.4	18.3
SGZR-11	11.5	5.2	13.8	48	26.7	6.2
SGZR-13	13.35	5.5	14.7	49.5	27.6	2.7

[a] Conversion after 10 min on stream: WHSV = 0.8 h^{-1}; $H_2/n\text{-}C_6 = 17$.

show activities lower by a factor of 50 for *n*-hexane isomerization. This is consistent with the fact that NMR lines are correlated with acidity only if H-bonding is suppressed (22). The results of DRIFT spectroscopy are more directly correlated with the activity in isomerization of *n*-hexane: the two samples exhibiting the 3300 cm^{-1} infrared band are 10 to 50 times more active than the samples which do not show this band. However, according to DRIFT data, SGZR-7 should be more active than SGZR-5. It appears that SGZR-7 deactivates faster than SGZR-5 and shows a higher selectivity for cracking at lower conversion (Table 4). This higher deactivation accounts for a lower rate of reaction after 10 min on stream.

In conclusion, it is interesting to compare the acidity of these systems to that of liquid super acids measured by their reactivity toward benzene. The formation of benzenium ion has been observed by NMR spectroscopy at 139 K (23), while it would be formed here at room temperature. The large difference in the reaction temperature is a further indication that sulfated zirconias are strong but not super acids.

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