Influence of the Preparation and of the Activation Treatments on the Catalytic Activity of Mechanical Mixtures of Sulfated Zirconia and Pt/Al₂O₃

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Zirconium hydroxides with specific surface areas in the range of 60 to 300 m²/g were obtained by varying between 6 and 12 the final pH of precipitation of the gels and the nature of the precursor salt. These compounds were sulfated by impregnation with 15 and 35 ml of aqueous 0.5 M H₂SO₄. Their sulfur content was 3 to 5 wt%. Sulfation increases the thermal stabilities of the zirconias by nearly 200 K. The solids remain amorphous up to at least 673 K and then crystallize in the tetragonal and monoclinic phases. The properties of mechanical mixtures of the sulfated zirconias and a Pt/alumina catalyst were evaluated for the isomerization of n-hexane. The study of the conditions of activation show that the highest performances of these catalysts result from a pretreatment under hydrogen at 573 and 623 K when the amounts of H₂SO₄ added are, respectively, of 35 and 15 ml/g of zirconium hydroxide, whatever their specific surface areas. A close correlation is found between the activities of the catalysts and their specific surface areas. This suggests that the active sites are located at the low coordination sites of zirconia and that their efficiency increases with their dispersion. The acidity determined by IR spectroscopy of NH₃ adsorption is essentially of Lewis type after evacuation at 573 K. However, Brønsted acidity results from a reversible redox equilibrium between hydrogen and zirconia. The isomerization of n-hexane is considered to follow a classical bifunctional mechanism. © 1996 Academic Press, Inc.

INTRODUCTION

High catalytic activities for the isomerization reactions of alkanes are found with catalysts of sulfate-promoted metal oxides such as Fe₂O₃, TiO₂, and ZrO₂, due to the enhancement of their acidic properties. Superacid sites were even proposed (1–4). These originate from the introduction of sulfate ions exchanged on the support followed by a calcination at a judiciously chosen temperature (5, 6). This induces the transformation of the isolated sulfate ion to catalytically active sites whose structure has been extensively studied since the initial work of Hino *et al.* (2).

On very acidic sulfated oxides a strong band near 1400 cm^{-1} is observed by IR spectroscopy which is related to the high catalytic activity. The similarity of this band with those found in the covalent organic sulfates has led some authors to propose a bidentate sulfate structure with two S=O bonds where the metal cation of the oxide is a Lewis acid site (4–6). ^{18}O exchange studies led Lavalley *et al.* (7, 8) to propose the existence of a tricoordinated sulfate species with a single S=O bond which is transformed to a bidentate species upon water addition by the breaking of a M–O–S bond. This accounts for the high Brønsted acidity of these compounds due to the formation of SOH groups. Quantum chemical calculations show that the stronger acidity should be of the Brønsted type (9), and protons with an acid strength comparable to that of high-silica zeolites have indeed been observed on sulfated zirconia at 873 K and kept in air (10).

During catalytic reactions a rapid deactivation occurs which can be reduced by loading a metal, generally Pt, and using H₂ atmosphere (11–13). However, Garin *et al.* (14) stabilized the activity of the ZrO₂–SO₄$^{2-}$ compounds without a metallic function, by merely adjusting the hydrogen pressure.

Spectroscopic studies of the acidity of platinum sulfated zirconia catalysts have shown that Brønsted acid sites are generated when heating under H₂ flow with a concomitant decrease of Lewis acidity. The explanation involves the dissociation of molecular hydrogen on platinum and spillover of the hydrogen atoms on to the ZrO₂–SO₄$^{2-}$ surface (11). Due to this effect, the activity was proposed to be restricted to the interface between Pt and sulfated zirconia (12). A bifunctional mechanism was also claimed in other reports (15).

In addition to these determinations concerning the nature of the active sites, several studies have revealed the influences of the atmosphere and temperature of treatment, type of the oxide support, and amount of SO₄$^{2-}$ added, but the role of several other parameters is still not well understood. Moreover, the acid strength and stability of these

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catalysts are very dependent on their mode of preparation and on activation conditions. Usual activation includes a treatment in oxidizing atmosphere, but the influence of a pretreatment in a reducing atmosphere has been much less investigated.

This paper is devoted to study of the activation conditions of sulfated zirconia giving reproducible high catalytic activities. The influence of the dispersion of the sulfate entities on the catalytic activity and thermal stability was investigated. The enhancement in activity obtained by an increase of the dispersion of the acid sites is well known in solid acids such as zeolites and pillared clays (16, 17).

The sulfation of zirconia or titania is generally performed by adding aqueous sulfuric acid or ammonium sulfate. In the present work we chose to add different quantities of H_2SO_4 to zirconia supports of different surface areas. The catalytic test used the skeletal isomerization of hexane.

EXPERIMENTAL

Sample Preparation

$Zr(OH)_4$ compounds were obtained in aqueous media by hydrolysis of $ZrOCl_2$, $8H_2O$ or $ZrONO_3$, xH_2O salt solutions (0.4 M) with adjusted quantities of NH_4OH (6 M) (Table 1, in which Z-60, for instance, represents a solid with a surface area of 60 m^2/g). The precipitates were stirred for 12 h at ambient temperature, filtered, and washed with hot deionized water (340–360 K) to remove excess salts ($AgNO_3$ or $(NH_4)SO_4$ tests). The products were dried at 383 K for 24 h.

The sulfated compounds were obtained by impregnation of the dried supports prepared as described above with 0.5M H_2SO_4 solution (15 or 35 ml/g support) and further dried at 383 K for 24 h.

Catalytic Measurements

Catalytic properties were studied for n-hexane isomerization at atmospheric pressure in an all-glass microflow reactor with a fixed bed, using a mechanical mixture prepared by grinding 80 mg of sulfated zirconia and 160 mg

TABLE 1

Synthesis Conditions and Crystallographic State of the Zirconia Samples

Support	Precursor	Final pH of precipitation	Control of the pH during precipitation	Crystallographic state
Z-60	$ZrOCl_2$, $8H_2O$	6	No	Amorphous
Z-207	$ZrOCl_2$, $8H_2O$	12	No	Amorphous
Z-236	$ZrONO_3$, xH_2O	10	Yes	Amorphous
Z-300	$ZrOCl_2$, $8H_2O$	10	Yes	Amorphous

of Pt/Al_2O_3 catalyst (0.37% in weight Pt, H/Pt = 0.9). Hydrogen used as carrier gas was saturated with n-hexane whose partial pressure was 41 Torr and passed over the catalyst with a weight hourly space velocity (WHSV) of 0.8 h^{-1}. The analysis of the products was made on line with a Carlo Erba chromatograph equipped with an OV1 capillary column (50 m, 0.2 mm).

Characterization

The samples were characterized by X-ray powder diffraction (XRD), thermogravimetric analysis (TGA), nitrogen physisorption, and infrared spectroscopy.

Elemental analysis of S was performed on the solids by the Service Central d'Analyse CNRS (Solaize, France), by decomposition of the sample above 1273 K and potentiometric titration of SO_2 trapped in a solution.

X-ray diffraction patterns were recorded on a CGR Theta 60 instrument using Cu$K\alpha_1$ radiation. The crystal phases were identified using the ASTM 13-307 and 17-923 cards. The crystallite size (D_{111}) of the monoclinic and metastable tetragonal phases was determined from the (111) reflection by using the Scherrer relationship,

$$D_{111} = 0.91/(L^2 - d^2)^{1/2} \cos\theta,$$

where L is the width of the (111) peak at half maximum and d the width due to the broadening of the peak (reference $d = 0.133$ for mica).

The crystallization and the crystal phase transformation were studied by calcination of the samples *in situ* under air flow in an X-ray diffraction furnace CGR (système Barret-Gerard). The patterns were recorded every 50 K. The heating rate was 5 K/min.

TGA was carried out on a Setaram TG 85 1000°C microbalance operating in a flow of dry nitrogen (110 ml/min) at a heating rate of 2 K/min.

Specific surface areas and micropore volumes were obtained from the adsorption isotherms determined for N_2 at liquid nitrogen temperature using the BET and Dubinin equations.

IR spectra were measured at 2 cm^{-1} resolution on a Nicolet 320 FT-IR spectrometer. Self-supported wafers of about 20 mg/cm^2 were used. Ammonia was chosen as probe molecule to characterize the acidity. Infrared spectra were recorded at room temperature in all cases.

RESULTS

Characteristics of the Supports

All samples were in the amorphous state before calcination as shown, for example, in the X-ray diffractogram of Z-60 (Fig. 1). Their specific surface areas depend on the starting salt (chloride or nitrate) and whether the pH was thoroughly controlled during the NH_4OH addition
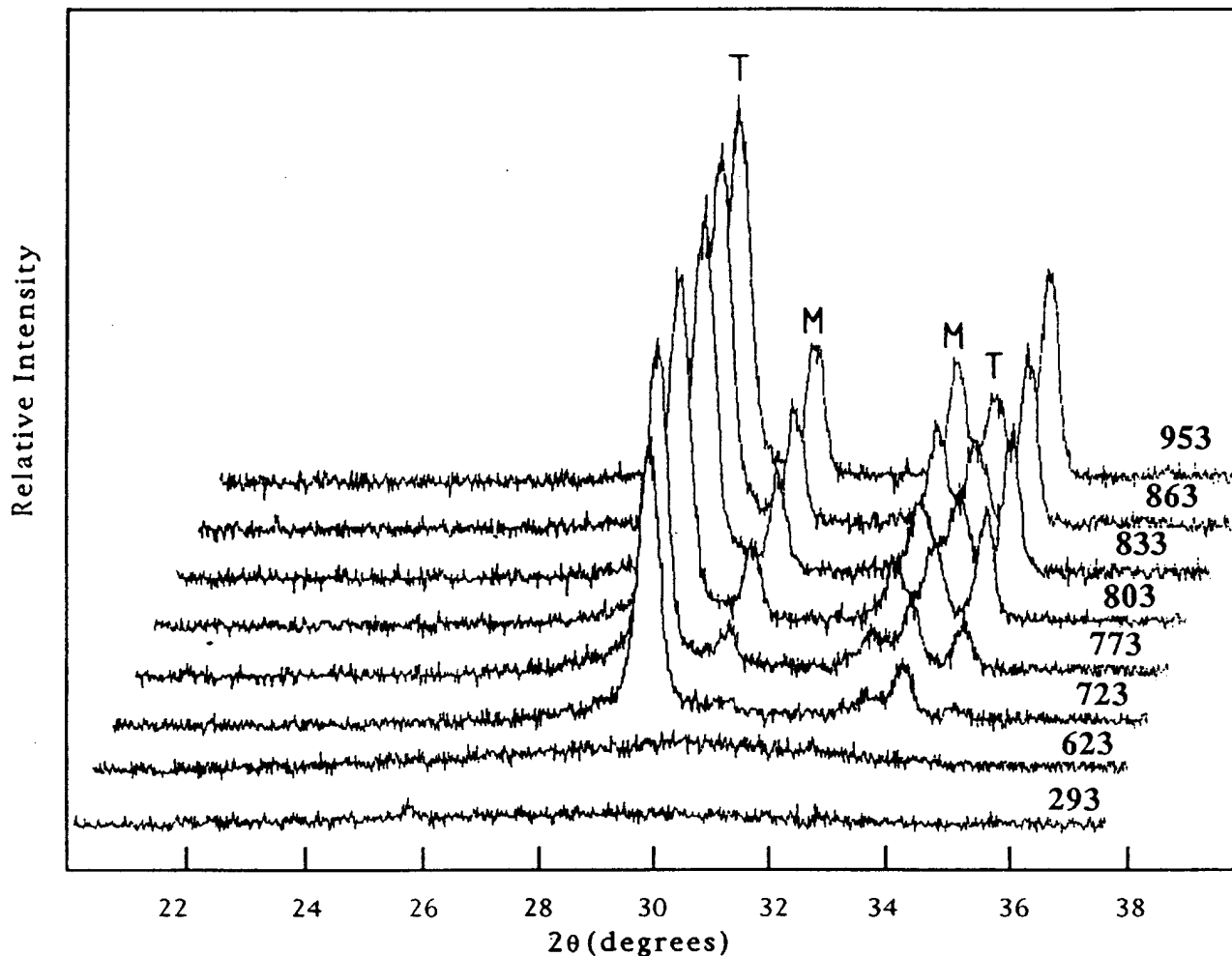
FIG. 1. XRD profiles of Z-60 calcined in the X-ray diffraction furnace at increasing temperatures. T, tetragonal phase; M, monoclinic phase.

(Table 1). They increase from 60 to 300 $m^2 g^{-1}$ with a related enhancement of the proportion of micropores (Table 2), representing 60% of the pore volume for the Z-300 support. Thermogravimetric analysis revealed a total weight loss in the range of 14 to 17% achieved at 773 K due to the dehydration and the dehydroxylation of the samples. An average composition of these precipitated gels between ZrO_2, $1.2H_2O$ for Z-207 and ZrO_2, $1.4H_2O$ for Z-60 was deduced, which is well under the value of $n = 2$ for $Zr(OH)_4$.

Upon thermal treatment crystallization occurs and the lines of the tetragonal and monoclinic phases successively appear in the X-ray diffractogram. A typical evolution of these patterns up to 950 K is reported in Fig. 1 for the Z-60 sample. The tetragonal phase is observed after calcination at 723 K and both the tetragonal and the monoclinic phases at 773 K in all samples. The relative amounts of these two phases at a given temperature also depends, as with the specific surface area, on the preparation conditions of the gels.

These phenomena are in accordance with the changes on thermal treatment described in the literature (18).

The tetragonal phase results from the topotactic crystallization of the amorphous gel. This metastable phase is indeed due to the lower surface energy of the related particles. When the temperature increase further, the tetragonal crystallites grow and reach the critical size, generally around 100 Å, where they transform to the more thermodynamically stable monoclinic phase (19, 20), therefore always of greater size than the former. For example, in the case of Z-236 calcined at 823 K the average sizes of the tetragonal and monoclinic crystals are respectively 100 and 140 Å. These phenomena induce a regular decrease of the specific surface areas from 236 to 21 m^2/g at 1023 K.

Characteristics of the Sulfated Samples

The sulfated samples prepared by the impregnation of Z-60, Z-236, and Z-300 with 35 ml of H_2SO_4 (0.5 M) and of Z-207 with 15 ml of H_2SO_4 (0.5 M) are hereafter denoted as SZ-60-35, SZ-236-35, SZ-300-35, and SZ-207-15 (Table 2).

TABLE 2

Preparation Conditions and SO_4^{2-} Content of the Sulfated Zirconia

| Support | Calcination temp. (K) | Specific surface area ($m^2 g^{-1}$) | Contribution of micropores (%) | H₂SO₄ added | | Catalyst | H₂SO₄ retained on the solid | |
				ml	μmol/m²		μmol/m²	wt%
Z-60	NC	60	25	35	292	SZ-60-35	16.2	9.6
Z-207	NC	207	45	15	36	SZ-207-15	4.4	8.9
Z-236	NC	236	58	35	74	SZ-236-35	7.5	17.3
Z-300	NC	300	60	35	58	SZ-300-35	5	14.7
Z-171	823	171		35	102	SZ-171-35	5.5	9.2
Z-40	Unknown	40		35		SZ-40-35	43.7	17.1

Note, NC, noncalcined.

The quantities of SO_4^{2-} ions retained, as determined by elemental analysis of S on the solids, are in the range from 8.8 to 17% in weight corresponding to surface densities in the range of 5–43 μmol/m² (Table 2). Therefore the density of SO_4^{2-} species decreases regularly from SZ-60 to SZ-236 and SZ-300 supports impregnated with the same amount of H₂SO₄ (35 ml). Its influence on the catalytic activity is, as previously reported, a main objective of the present study.

The stabilizing effect of the SO_4^{2-} ions on the zirconia support is illustrated in Fig. 2 where the X-ray diffraction patterns of Z-207 and SZ-207-1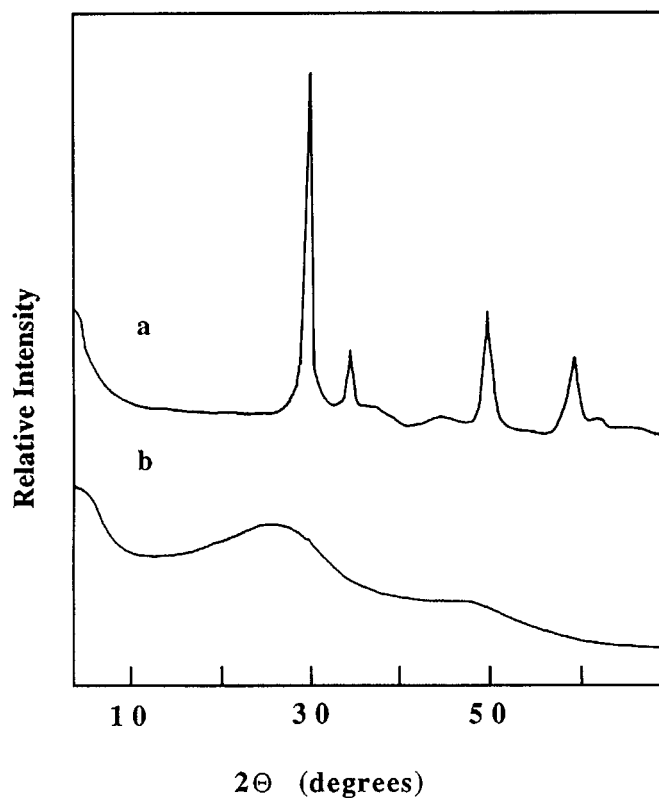5 after calcination at 620 K are reported. The sulfated sample (SZ-207-15) remains in the amorphous state while the parent zirconia (Z-207) support crystallizes in the tetragonal phase. An increase of nearly 200 K in the thermal stability has thus been clearly evidenced in all samples.

The TGA study of SZ-207-15 and SZ-236-35 (Fig. 3) shows that, in addition to the weight losses in two steps at low temperature attributed to the dehydration of the
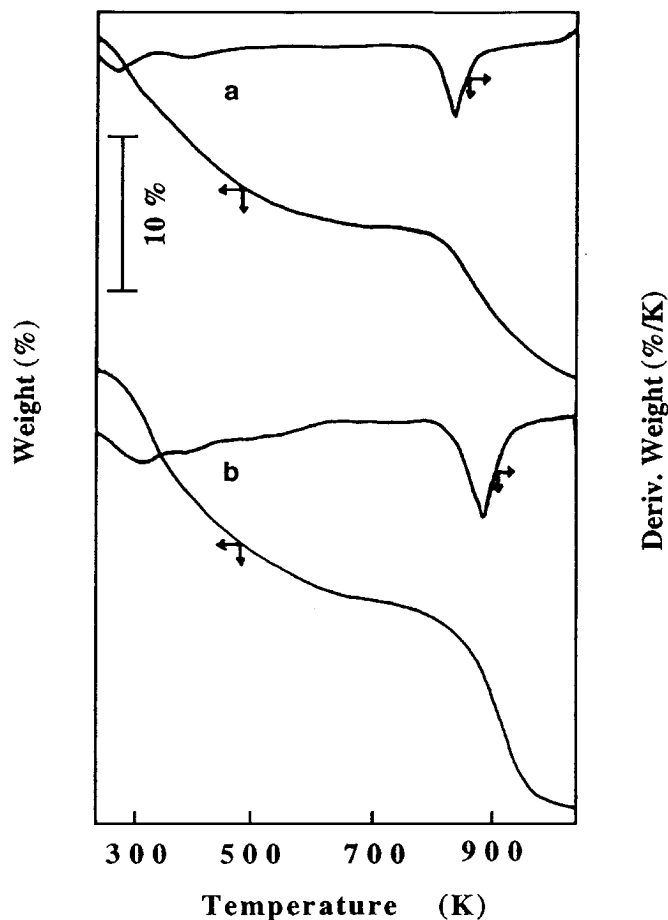

FIG. 2. XRD profiles of (a) the support Z-207 and (b) the sulfated SZ-207-15 sample, both calcined at 620 K.

FIG. 3. DTA–TGA curves of (a) SZ-207-15 and (b) SZ-236-35.

support, a third peak is detected at 890 and 923 K. The corresponding weight losses of 5.85 and 11% for SZ-207-15 and SZ-236-35 could be related to the decomposition with emission of SO_2 of the sulfate species deposited on these supports (respectively 8.9 and 17.3 wt%).

Chen *et al.* (21) provided evidence for the formation of Zr^{3+} species located at the surface of the crystallites after desorption at high temperature and described the decomposition of sulfates by the reaction

$$2Zr^{4+} + SO_4^{2-} \rightarrow 2Zr^{3+} + SO_2 + O_2.$$
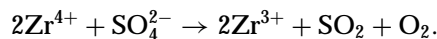
The amount of Zr^{3+} detected by ESR represents about 10^{-9} mol/g Zr^{4+}, which is to be compared with the present loss of 10^{-4} mol/g of SO_2. The formation of Zr^{3+} only cannot then account for the weight loss, and it can be proposed that part of the SO_2 is formed by the reaction

$$ZrSO_4H \rightarrow ZrOH + SO_2 + 1/2\,O_2,$$

which could explain desulfation without reduction.

Influence of the Pretreatment Conditions

As mentioned above, the properties of sulfated zirconia were evaluated in the metal–acid bifunctional isomerization of hexane using a mechanical mixture of the samples and Pt/Al_2O_3 as catalysts. In a previous study (22) the conversion of alkanes was investigated on mechanical mixtures of Pt/Al_2O_3 and dealuminated mazzite zeolites. The activity appeared to be controlled by the acid isomerization above $1\ m^2\ Pt/g$ of zeolite, for catalysts showing activities as high as 3.16×10^{-6} mol $sec^{-1}\ g^{-1}$. The present catalysts are slightly less active, so all the samples were tested as mechanical mixtures constituted by 160 mg Pt/Al_2O_3 and 80 mg ZrO_2/SO_4^{2-}, corresponding to $1\ m^2\ Pt/g$ zirconia.

A small deactivation was noticed with time on stream. All conversions were measured at the steady state achieved, under our experimental conditions, after 30–40 min. Isomerization selectivity is higher than 90% depending on the conversion level. The main products are isohexanes (2- and 3-methylpentane) with small amounts of 2,3-dimethylbutane and 2,2-dimethylbutane, not separated from 3-methylpentane.

Before testing, the catalysts were activated under a gas flow at a given temperature. The influence of a reducing or oxidizing atmosphere was particularly investigated. Two procedures were tested with Pt/SZ-207-15 catalyst:

Treatment A: a calcination under dry air at 573 K for 4 h followed by a treatment for 2 h at 673 K under H_2 stream (1 atm);

Treatment B: 2 h at 673 K under a hydrogen stream only.

As reported in Table 3, following the B treatment the activity is higher. A calcination step under dry air increases by nearly 30 K the threshold activity (arbitrarily fixed at

TABLE 3

Variations of the Activities of Pt/SZ-207-15 vs Temperature in the Reaction of Hexane after A and B Treatments

Reaction temperature (K)	Activities (10^{-7} mol g^{-1} s^{-1})	
	Treatment A	Treatment B
433	—	0.52
443	—	0.55
463	0.52	—
473	0.60	1.51
493	1.09	2.38

0.5×10^{-7} mol g^{-1} s^{-1}) of the same catalyst. The catalysts were consequently always heated under a hydrogen stream in the following experiments.

The influence of the activation temperature was in turn investigated using two samples impregnated with different amounts of SO_4^{2-}, Pt/SZ-207-15 and Pt/SZ-236-35, activated between 473 and 773 K under H_2 (Fig. 4). Their activities in the conversion of hexane at 463 K, both in the range of 0.5 to 1.7×10^{-7} mol g^{-1} s^{-1}, vary similarly with a net defined maximum after activation at 573 and 623 K for Pt/SZ-236-35 and Pt/SZ-207-15. Moreover, the same maximum activity of 1.7×10^{-7} mol g^{-1} s^{-1} is found in the two cases.

These studies on the activation conditions provided evidence that higher activities resulted from treatment under hydrogen. The catalysts have a similar behavior in the temperature range from 473 to 673 K. However, the maximum activity is observed at a different temperature when the content of SO_4^{2-} is varied. The shift is 50 K toward lower temperatures when the amount of H_2SO_4 used for impregnation increases from 15 to 35 ml/g of support.

Some knowledge on these systems could also be deduced from the structural changes observed during the activation and the catalytic reactions. The SO_4^{2-} content of the used catalysts initially reduced at the temperatures reported above are reported in Fig. 4. Fifty to 60 wt% of the SO_4^{2-} species are decomposed at 523 K, and then the amount decreases only slightly up to 673 K. Therefore, for a given sample, the changes in activity observed between 520 and 673 K are not related to those of the S content but probably to the nature of the sulfur species.

SO_4^{2-} species decomposed in great amount above 473 K during the catalytic reaction are therefore considerably less stable than previously reported in the TGA study where the corresponding peaks were found at 923 and 890 K for SZ-236-35 and SZ-207-15. This is due to the respective procedures involving a treatment under air during TGA and under hydrogen during catalytic reaction. In the former the SO_4^{2-} species are decomposed with emission of SO_2. In the latter a metal-catalyzed reduction of SO_2 can displace the equilibrium to lower temperatures. Whatever the
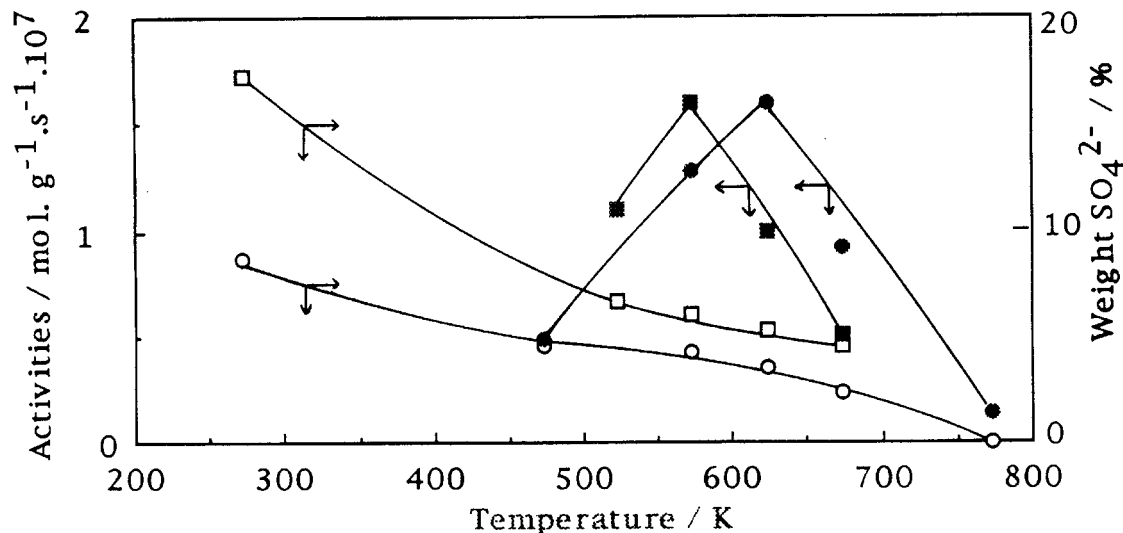
FIG. 4. Variations of the activity and of the SO_4^{2-} content of ($\bullet$)($\bigcirc$)Pt/SZ-207-15 and ($\blacksquare$)($\square$)Pt/SZ-236-35 vs activation treatment under hydrogen, in the reaction of hexane at 463 K.

procedure involved in the decomposition of SO_4^{2-}, enough sulfur remains on the zirconia to induce a doping effect. This is illustrated in Fig. 5, giving the X-ray diffraction patterns after catalytic reaction of Pt/SZ-207-15 activated at 673 and 773 K. Sulfated zirconia is still amorphous at 673 K and
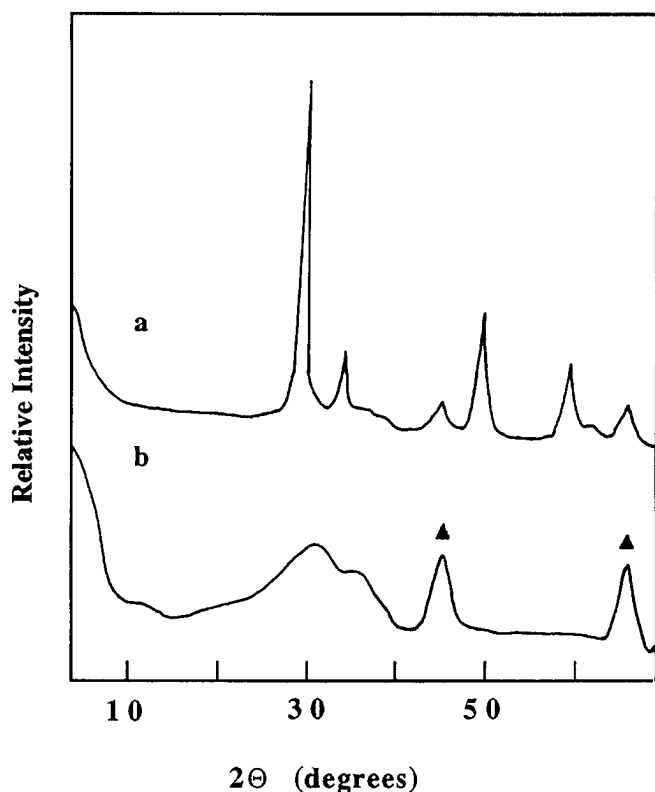
crystallizes above this temperature, as previously observed after calcination of the sulfated zirconia in air (Fig. 2).

Moreover, from the catalysis experiments in the conversion of hexane at 463 K reported in Fig. 4, it is also noticeable that Pt/SZ-236-35 and Pt/SZ-207-15 samples treated at 773 K are inactive. This could be attributed to the crystallization of the support discussed above. Arata (5) reported that superacid sites were not created by impregnation of sulfate ions on the crystallized oxides. This idea is reinforced by the comparison of the three catalysts Pt/SZ-300-35, Pt/SZ-171-35, and Pt/SZ-40-35.

SZ-171 is obtained using a tetragonal support prepared as described above by precipitation of $ZrONO_3$, xH_2O at pH 12, followed by a calcination at 823 K. SZ-40 is obtained using a monoclinic zirconia supplied by Degussa, the specific surface area of which is 40 m^2/g (Table 2). The activities of these catalysts for the isomerization reaction of hexane at 463 K are reported in Table 4.

The activities of Pt/SZ-300-35 and Pt/SZ-171-35 show that the support in the amorphous state gives the more active catalyst. The monoclinic support leads to a lower activity in spite of a high sulfur content.

FIG. 5. XRD profiles of Pt/SZ-207-15 activated under hydrogen at (a) 773 K and (b) 673 K after catalytic reaction of hexane. (▲) Pt/Al$_2$O$_3$ catalyst.

TABLE 4

Activities of Pt/SZ-300-35, Pt/SZ-171-35, and Pt/SZ-40-35 in the Reaction of Hexane at 463 K

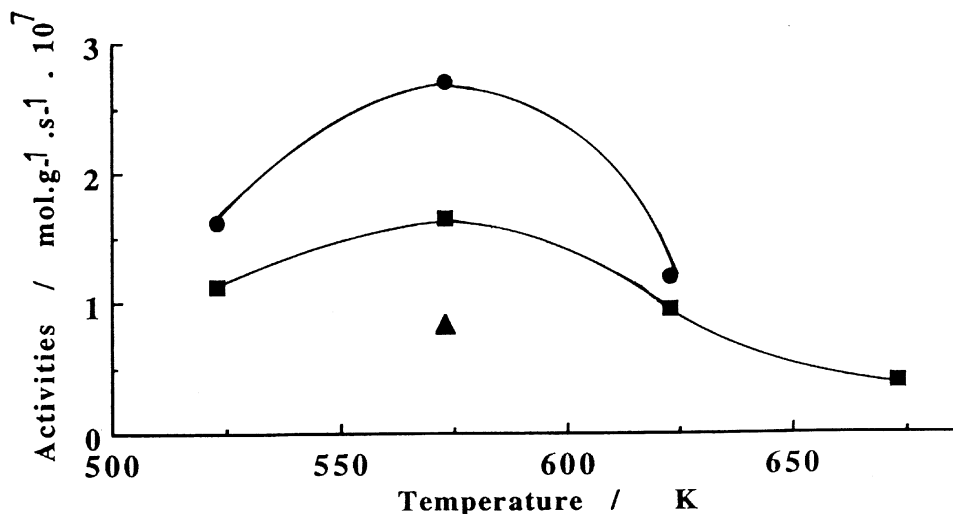| Samples	Crystallographic phase	SO_4^{2-} before activation (μmol/m^2)	Activity (10^{-7} mol g^{-1} s^{-1})
Pt/SZ-300-35	Amorphous	5	2.75
Pt/SZ-171-35	Tetragonal	5.52	1.58
Pt/SZ-40-35	Monoclinic	43.75	1

FIG. 6. Variations of activities vs temperature of pretreatment for (●) Pt/SZ-300-35, (■) Pt/SZ-236-35, and (▲) Pt/SZ-60-35 in the reaction of hexane at 463 K.

Influence of the Surface Area of the Zirconia

The activities of Pt/SZ-300-35, Pt/SZ-236-35, and Pt/SZ-60-35 catalysts with decreasing densities of SO_4^{2-} species were compared in the conversion of hexane at 463 K.

As previously shown, a weak maximum appears after treatment at the same temperature of 573 K with these supports impregnated with the same amount of 35 ml of H_2SO_4 (0.5 M) (Fig. 6). This result obtained with zirconia of different specific areas confirms that the optimal activation temperature is mainly related the quantity of H_2SO_4 added.

The respective activities of the three samples pretreated at 573 K were determined at different temperatures (Fig. 7).

The threshold activity is 30 K higher for Pt/SZ-300-35 than for Pt/SZ-60-35, and the activity of the former is then one order of magnitude higher at 473 K. The selectivities of the products obtained with Pt/SZ-300-35 and Pt/SZ-236-35 show that these catalysts have essentially an isomerization activity. Cracked products are obtained only at reaction temperatures above 463 K.

Infrared Study

An infrared study was performed on Pt/SZ-236-35 sample to characterize the sulfur species and define the nature of the acid sites using ammonia as probe molecule.
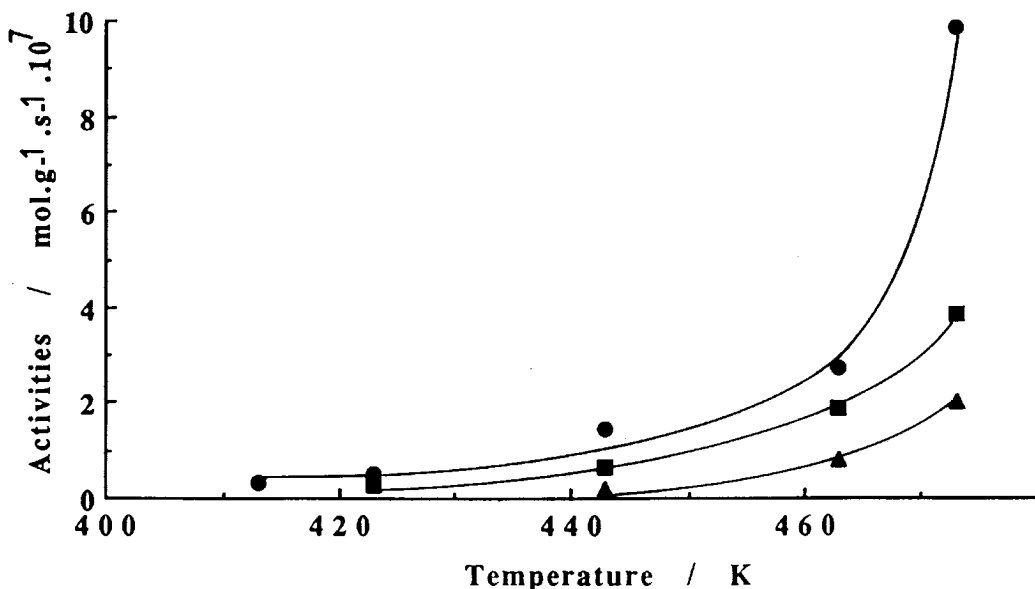

FIG. 7. Variations of activities vs reaction temperature in the reaction of hexane for (●) Pt/SZ-300-35, (■) Pt/SZ-236-35, and (▲) Pt/SZ-60-35 pretreated at 573 K.

The wafer was pretreated *in situ* at 573 K for 2 h in a hydrogen flow in the IR cell, as in the optimum activation treatment of the catalyst. The spectrum in the range from 1200 to 1800 cm^{-1} is reported in Fig. 8a. A band is observed at 1364 cm^{-1} ascribed to the fundamental frequency of the asymmetric stretching vibration of SO_4^{2-} anions. It is generally found between 1375 and 1390 cm^{-1} on several oxide supports (4). The low frequency shift of this band leads us to ascribe it to isolated surface SO_4^{2-} localized in a crystallographically defective configuration (23). These sites are
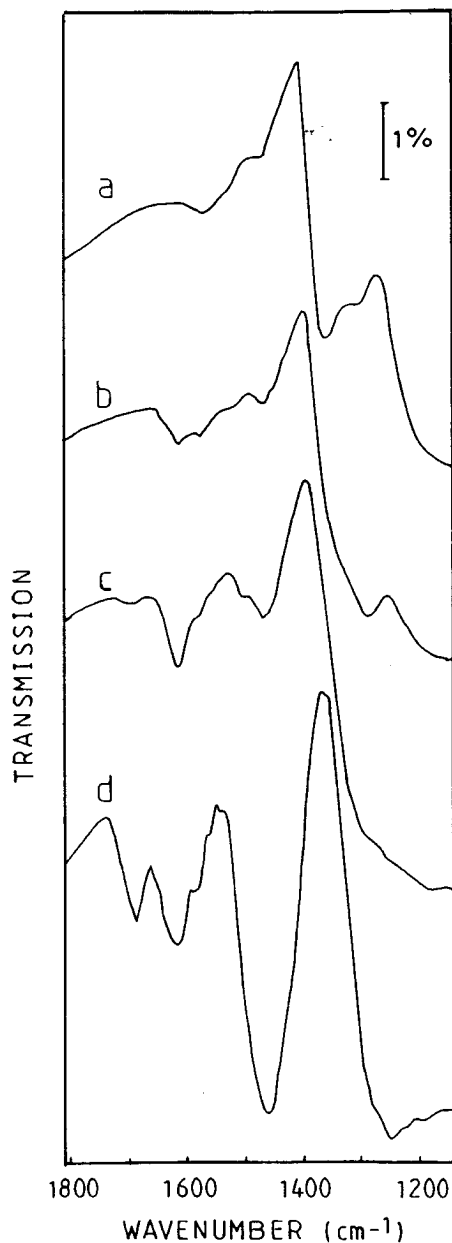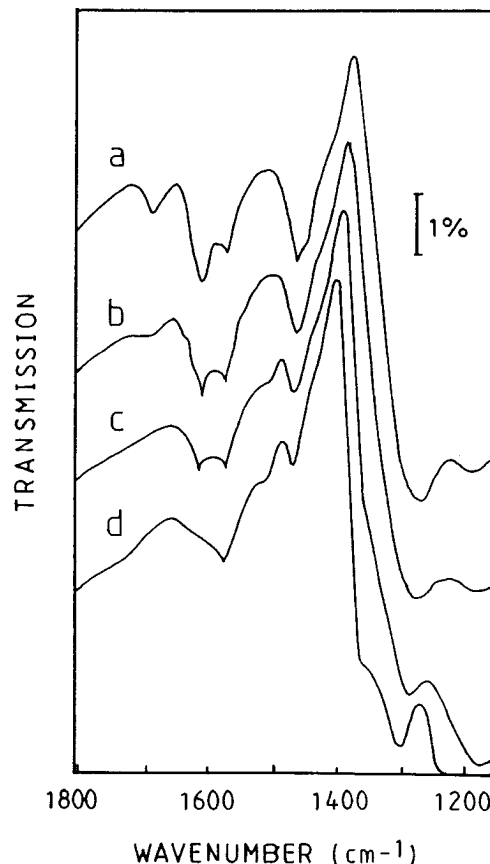

FIG. 9. IR spectra of Pt/SZ-236-35 outgassed at (a) 373 K, (b) 423 K, (c) 473 K, and (d) 573 K.

present in great amount in the samples with high specific surface areas.

Upon NH_3 adsorption the S=O peak of Pt/SZ-236-35 moves from 1364 to 1300 cm^{-1}, as observed by Lee and Park (24) for SO_4^{2-}–Fe_2O_3 catalysts. At the same time a broad band appears at 1618 cm^{-1} due to ammonia coordinated to Lewis acid sites (Fig. 8b). Therefore the mechanical mixture possesses only Lewis acid sites after activation in hydrogen.
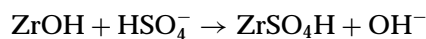
33 Torr of hydrogen was then introduced into the cell at ambient temperature (Fig. 8c). The intensity of the Lewis band increases and a new band related to ammonium ions chemisorbed on Brønsted acid sites appears at 1466 cm^{-1}. By heating at 463 K under hydrogen (Fig. 8d) the intensity of the Brønsted acid band increases greatly. At the same time the S=O stretching frequency is shifted to 1257 cm^{-1}.

An evacuation was performed on this sample up to 573 K (Fig. 9). Above 373 K, a great decrease of the Brønsted acidity and a shift of the S–O peak from 1257 to 1273 cm^{-1} is observed. NH_3 adsorbed on Lewis sites disappears after evacuation at 573 K where the S=O band returns to its original position of 1364 cm^{-1}. The peak at 1466 cm^{-1} characteristic of Brønsted acidity disappears after evacuation

FIG. 8. IR spectra of Pt/SZ-236-35 (a) treated 2 h under hydrogen at 573 K, (b) after NH_3 adsorption, (c) after introduction of 33 Torr of hydrogen, and (d) after heating at 463 K.
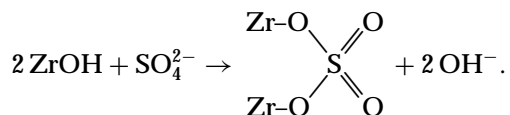
above 473 K. The surface sulfur species responsible for the initial Lewis acidity of these sulfated zirconia undergoes then reversible changes upon hydrogen adsorption.

DISCUSSION

The purpose of this work is to investigate the influence of preparation on the properties of sulfated zirconia, and some information can be obtained on the mechanism of incorporation of sulfur. Only a small fraction of the sulfate ions of the solution used for sulfation, about 5–10%, are trapped by the solid. The comparison of two samples SZ-207-15 and SZ-236-35, of comparable surface area and treated with different amounts of H_2SO_4, shows that the amount of sulfate retained by the solid increases with the concentration of acid. An equilibrium thus exists. Pure zirconia has a basic character (25) and is therefore an anion exchanger. Sulfate anions can be introduced by one of the two possible equilibria:

$$ZrOH + HSO_4^- \rightarrow ZrSO_4H + OH^-$$

or

$$2\,ZrOH + SO_4^{2-} \rightarrow \begin{matrix} Zr\text{–}O \\ \\ Zr\text{–}O \end{matrix}\!\!\!\diagdown\!\!\!\underset{O}{\overset{O}{S}}\!\!\!\diagup + 2\,OH^-.$$

This equilibrium is displaced in acid medium since OH^- anions are then neutralized by protons, and this accounts for the influence of the precursor, ammonium sulfate or sulfuric acid, reported by many authors (3, 5).

It can be pointed out that for a constant acid solution, the fraction of sulfate anions retained by noncalcined solids is higher for high surface areas and decreases when zirconia is calcined at 820 K. The basic sites of oxides are usually related to defects, edge or corner atoms, which are more numerous on small particles and disappear upon thermal treatment (26, 27). This proposal, established with MgO and CaO, would account for the influence of surface area on the sulfation of zirconia.

The acid strength of sulfated zirconia is still a matter of debate. A super-acid character evidenced by some authors (6, 11–13) was denied by other (28). The results reported in this paper show that the catalytic properties of sulfated zirconia are related to their preparation method and activating treatments. For zirconium oxide it was reported that acidic and basic properties change with the pretreatment temperature and that both the acid and basic sites of this oxide act in many catalytic reactions (29). When sulfate anions are introduced in variable amount onto zirconium oxide the properties of the acid catalysts thus obtained are related to the pretreatments.

The thermal pretreatment changes the amount of sulfate remaining at the surface and induces a decrease of the surface area and a crystallization of the oxide. Sulfation influences the structure of zirconia and increases its thermal stability by at least 200 K. This suggests that the SO_4^{2-} species may diffuse into the structure. Crystallization into tetragonal and monoclinic phases occurs after activation at 773 K. Indeed, most of the catalysts cited in the literature show a maximum in activity after a thermal treatment in air at about 823 K where they have been converted to the tetragonal and monoclinic forms, and it is then difficult to appreciate the importance of the original crystalline phase of zirconia for acid catalysis. By contrast, the catalysts of this work are active after reduction at lower temperatures and do not crystallize below 673 K. The comparison (Table 4) of an amorphous and a tetragonal ZrO_2 containing similar densities of sulfate anions shows that the nature of the crystalline phase has only a limited influence on catalytic activity.

For sulfated samples used as acid catalysts it seems now established that activity passes through a maximum as a function of the temperature of calcination, because an optimum amount of sulfate is required at the surface. In an oxidizing atmosphere the decomposition of sulfates occurs at relatively high temperature, about 873 K, according to several authors (5, 6). In H_2, however, sulfur is partially lost by reduction, and the optimum temperature of activation is then shifted to much lower values. Catalytic activity is not related only to the respective quantities of SO_4^{2-} retained by the support because catalysts with similar densities but prepared with 15 ml (Pt/SZ-207-15) and 35 ml of H_2SO_4 (Pt/SZ-300-35) show different behaviors. This might be related to the poisoning effect of SO_2 on the metallic function, but since rather similar quantities of SO_2 were released at 573 and 623 K for different quantities of H_2SO_4 added (35 and 15 ml) this hypothesis then appears less probable.

For a given catalyst the variation of activity for treatment temperatures between 473 and 673 K is accompanied by a smooth variation of the S content. These phenomena suggest that the increase in activity is related to a change in the nature of the sulfur species. For pretreatments in oxidizing atmosphere, Chen et al. (21) also reported previously that the nature of the sulfur species is more important than the S content for samples also prepared by impregnation with H_2SO_4 of noncalcined zirconia gels. Morterra et al. (23) have shown that the polynuclear sulfates are decomposed and yield some isolated sulfates when the calcination temperature of sulfated zirconia increases. This could account for the increase in activity observed in our case. On the other hand, when the calcination temperature increases further, the isolated sulfates such as the low coordination sites disappear and this could be easily related to the decrease in activity observed.

For a given quantity of H_2SO_4 impregnated onto zirconia the activity is higher for the higher values of the surface area. This suggests that the active species are preferentially formed at the low coordination sites located at defects, corners, and edges of the crystals. These sites are isolated and

in weak interaction, like acid sites in dealuminated zeolites, which is a favorable situation for high acidity.

The catalysts resulting from the mixture of platinum on alumina and sulfated zirconia are active for the isomerization of hexane. This can be considered as experimental evidence that the reaction obeys a metal–acid bifunctional mechanism involving successive steps on metallic and acid sites (30). The alkane dehydrogenates into olefin on Pt and then diffuses to the acid sites where isomerization occurs. The isomerized olefins are hydrogenated on the Pt sites and the alkanes are desorbed. It is well established that activity and selectivity in alkane hydroconversion on a bifunctional catalyst depend on the balance between the hydrogenating function and the acidic function (30). In the presence of Pt in excess the limiting step is the acid-catalyzed isomerization of the intermediate olefin. This mechanism implies a protonation of the olefin, and so should work better in the presence of protons. The original sulfated zirconia is a Lewis acid, but the partial reduction of zirconia assisted by the dissociation of hydrogen on Pt leads to its transformation into a Brønsted acid as revealed by IR spectroscopy. The following equilibrium is involved on the zirconia support:

$$Zr^{4+} + 1/2\,H_2 \rightarrow Zr^{3+} + H^+ \qquad [1]$$
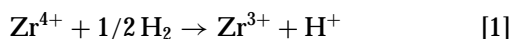
This is supported by the observation that the Brønsted acidity created by interaction with H_2 increases with the temperature of adsorption. The Brønsted sites are probably the active sites of the metal–acid bifunctional mechanism of the isomerization reaction.

However, in the absence of hydrogen, the number of acid sites resulting from hydration decreases with the temperature of evacuation (11) or shows a high thermal stability (31). Kustov et al. (10) reported that the intensities of the related bands started to decrease only after heating above 820 K. Here, Brønsted acidity decreases after evacuation above 473 K, which is far too low for dehydroxylation of the surface. A second mechanism accounting for this phenomenon is the reversal of equilibrium (1). In that case H^+ ions are reduced to H_2 and the surface is reoxidized. This equilibrium can account for the positive order relative to H_2 observed by Iglesia et al. (32), since in that case the activity would be proportional to the concentration of protons and thus to the pressure of hydrogen.

In conclusion, it can be remarked that these sulfated zirconias exhibit catalytic activities for n-hexane isomerization comparable to those of dealuminated mazzite (33) or BEA (34). Thus they appear to be strong acids, but not superacids, at least in our operating conditions.

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