

Relation between the Hydroxylation State of Zirconia, the Sulfate Promotion Method, and the Catalytic Activity of SO_4^{2-} - ZrO_2 Catalysts

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$\text{Zr}(\text{OH})_4$ samples were prepared from ZrOCl_2 and ZrCl_4 ; they were calcined at temperatures between 100 and 620°C and were sulfated with H_2SO_4 solutions. The catalytic activity in *n*-butane isomerization of these samples (at 300°C, 1 atm, and $\text{WHSV} = 2.5 \text{ h}^{-1}$), previously activated in air at 620°C is not well correlated with their textural properties or the SO_4^{2-} concentration.

$\text{Zr}(\text{OH})_4$ samples calcined at temperatures higher than 375°C are crystalline and adsorb SO_4^{2-} groups, but which are not active catalytically. The catalytic activity decreases with the calcination temperature in a similar way as the OH groups (determined by chlorination) are eliminated, forming less reactive surface groups. When the crystalline samples are sulfated with H_2SO_4 vapors, catalytically active materials are produced, irrespective of the crystalline state.

The drastic sulfation overcomes the inertness of the crystalline surface and catalytic active sites for *n*-butane isomerization are produced. This *in situ* resultation may also compensate the sulfur losses during the reaction. © 1997 Academic Press

INTRODUCTION

Two statements are repeatedly found in the literature of oxoanion promoted ZrO_2 catalysts for acid catalyzed hydrocarbon reactions, concerning its crystalline structure and the catalytic activity: (i) The promotion (with SO_4^{2-} or other dopants, e.g., WO_3) must be performed on amorphous zirconium hydroxide; promoted crystalline samples are inactive (1). (ii) For SO_4^{2-} - ZrO_2 , the tetragonal structure is the dominant crystalline phase present in catalytically active materials (2). Apart from these and related to the sulfate content of the catalysts, (iii) there is a growing concern over the sulfur losses of SO_4^{2-} - ZrO_2 catalysts occurring during the activation and reaction, which may hamper the long-range activity of the catalyst. Statements (ii) and (iii) are reexamined in this work and evidence for its refutation is provided. A practical solution for (iii) is also devised.

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A thorough study of the effects of the calcination of zirconia gels previous to the sulfation with H_2SO_4 in solution was undertaken. It comprised the monitoring of common properties (pore volume, specific surface area, crystalline structure, crystallite size, sulfate content, and catalytic activity) and other ones not previously studied (surface OH content and surface charge in solution) in their evolution with the calcination temperature. Surface OH content and reactivity were probed by chlorination, while the surface charge was measured by "fast" potentiometric titration. The latter special focus on the surface chemical changes permitted monitoring of the dehydroxylation/oxolation surface process taking place along with the calcination. The surface oxolation appears irreversible and a chemical inertness at room temperature was observed.

In order to study the conditions for the attack of the surface oxo groups, both chlorination and sulfation under drastic conditions were attempted. In the last case, SO_4H_2 in the vapor state as the sulfating agent and high temperatures were used. The method, however aggressive, proved effective in promoting activity in crystalline monoclinic zirconia samples. It has *a priori* one attractive feature: it allows the resultation without unloading the catalyst. Nevertheless, the conditions must still be tempered and optimized in order to prevent the deterioration of the porous structure of the catalyst.

METHODS

Different zirconia samples were prepared using different precursors and following different synthesis routes. A schematic description can be found in Table 1.

Zirconia Gels

They were prepared by hydrolysis in water of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (Strem, 99.99%) (sample ZO1) and ZrCl_4 (Aldrich, 99.9%) (sample ZCl), followed by precipitation with NH_4OH (Merck, 37%) up to pH 10. The gels were then washed and dried overnight. A detailed description

TABLE 1
Description of Samples and Analysis Performed

Sample	Preparation	Analysis
ZO1	Zr(OH) ₄ from ZrOCl ₂ · 8H ₂ O calcined at T = 100–200–300–400–620°C for 3 h	XRD, textural
ZCl	Zr(OH) ₄ from ZrCl ₄ calcined at T = 100–250–375–500–600°C for 3 h	XRD, textural
ZO1-S	Samples ZO1, sulfated in 1 N H ₂ SO ₄ for 2 h	SO ₄ ²⁻ content, catalytic test
ZCl-S	Samples ZCl, sulfated in 1 N H ₂ SO ₄ for 1 h	SO ₄ ²⁻ content, catalytic test
ZO1-S-CT	Samples ZO1-S, after the catalytic test	SO ₄ ²⁻ content, textural
ZO2-Cl	Zr(OH) ₄ from ZrOCl ₂ · 8H ₂ O calcined at T = 100–200–300–400–500–600°C for 3 h, chlorinated with SOCl ₂ (liq), 25°C	Cl content
ZB-Cl	Zr(OH) ₄ from Zr(<i>n</i> -But-O) ₄ , Cl free, calcined at T = 100–250–400–500–600°C for 3 h, chlorinated with SOCl ₂ (liq), 25°C	Cl content
ZB-RCl	Idem ZB, chlorinated under reflux with SOCl ₂	Cl content
ZO3 ⁶⁰⁰ -VPC	ZrO ₂ from ZrOCl ₂ · 8H ₂ O calcined at 600°C 3 h, treated with CCl ₄ (vap) at 300–375–450–525–600°C.	XRD, Cl content
ZO4 ⁶⁰⁰ -VPS	Idem ZO3, treated with H ₂ SO ₄ vapors (instead of CCl ₄) at different temperatures	catalytic test, SO ₄ ²⁻ content

Note. In every case, the temperature of calcination of the gel is included in the sample name as a superscript, e.g., ZCl⁶⁰⁰. Idem for chlorination and sulfation temperatures (VPC, VPS).

of the method can be found elsewhere, either for samples ZO1 (3) or ZCl (4). Portions of the gels were calcined in a muffle at different temperatures (see Table 1) for 3 h.

Samples ZO1 and ZCl were analyzed by XRD in order to determine the crystal structure and the crystal size. The radiation used was CuK α filtered with Ni. The crystal size was determined with Scherrer's formula, with Lorentz correction factor and without corrections for network tensions. Textural properties were determined in a Quantachrome Nova-1000 sortometer, by adsorption of nitrogen at 77.4 K. The specific surface area (Sg) was determined by the BET method using four points of the adsorption branch of the isotherm, at p/p_0 values of 0.10, 0.15, 0.20, and 0.25. The pore volume was determined by nitrogen adsorption at $p/p_0 = 0.99$. The pore distribution was determined by the BJH method using the desorption branch of the nitrogen isotherm.

Precalcined Zirconia Gels Sulfated in Solution

Samples ZO1-S and ZCl-S were generated by sulfation of samples ZO1 and ZCl, after calcining at different temperatures (see Table 1). After the calcination and before sulfation the samples were allowed to rehydrate overnight in contact with room humidity. The method of sulfation consisted in the dipping of the samples in 1 N H₂SO₄ for 1 or 2 h (samples ZCl-S or ZO1-S, respectively), without agitation. The sulfated samples were subjected to the catalytic test of isomerization of *n*-butane. A quartz reactor operating under isothermal conditions and atmospheric pressure was

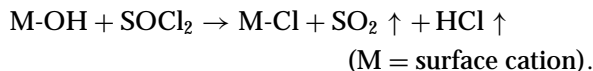
used. The reactor had a diameter of 1 cm approximately and a length of 45 cm. A 35–80 mesh fraction of the catalyst was loaded for the reaction (0.5 g), and supported over a porous glass disk in the middle of the reactor. The effluents of the reactor were analyzed in a gas chromatograph connected "on line." The chromatographic column was dimethylsulfonate supported on Chromosorb P, packed in a 6-m long, 1/8-in. external diameter steel tube. The isomerization of *n*-butane comprised the following steps: (i) activation at 620°C in air flow (10–12 ml/min) for 3 h and (ii) a reaction at 300°C for 3–4 h with an 8 ml/min flow of pure *n*-butane (Matheson 99.99%) and WHSV = 2.5 h⁻¹. The sulfate content and textural properties were determined before and after the catalytic test.

Assessment of OH Groups in Precalcined Zirconia Gels

Experiments of chlorination of samples ZO2 and ZB were conducted in order to assess the quantity and reactivity of the surface hydroxyls on the samples calcined at different temperatures. Many methods of characterization of surface groups have been used in the past. They comprise basically two types: spectroscopic (IR, NMR) and chemical. The latter is used extensively for quantitative determinations. Chlorination, etherification, fluorination, and reactions with organometallic compounds are the most common (5). Chlorination reactions are adopted in this work, for convenience. The determination of surface Cl in catalysts is reliable and reproducible, and the stoichiometry of reaction with the hydroxyl groups is expected to be 1 : 1,

a fact not found with other polydentate ligands (notably, SO_4^{2-}).

The reacting agent used, thionyl chloride (SOCl_2), is one of the most commonly used, because it decomposes giving only gaseous products:



The HCl adsorbed on the support is removed by thorough degassing. After the chlorination treatment all samples were heated *in vacuo* at 100–200°C for 1 h to remove the adsorbed products. Two kinds of samples were used in the chlorination experiments. Samples ZO2 were prepared from $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in the same way as samples ZO1. In order to avoid the interference of chloride ions retained in the matrix of the gel, samples ZB were prepared by hydrolysis of zirconium *n*-butoxide (Strem, stabilized solution, 70% in *n*-butanol). The butoxide was first dissolved in an organic solvent (*n*-butanol or hexane) for 2 h under agitation. Then the dissolved alcoxide was hydrolyzed by adding distilled water in excess (water/alcoxide > 20–30). The gel was then filtered and dried overnight. Samples ZO2 and ZB were first calcined at different temperatures (see Table 1) in a muffle for 3 h.

After this treatment the samples were allowed to rehydrate in contact with the ambient atmosphere. Then they were chlorinated at room temperature by means of a solution of SOCl_2 dissolved in benzene (1 : 4). The samples were immersed for 72 h. Then they were filtered, washed with hexane and dried at 110°C. The samples were always handled and stored in humidity-free vessels, since the Cl attached to the surface could be hydrolyzed. Finally, the samples were degassed and their specific surface area was measured. The samples calcined at 100°C were degassed at 100°C for 2 h, and the samples calcined at greater temperatures were degassed at 200°C for 1 h.

Chlorination with thionyl chloride at room temperature is found to produce a replacement of a fraction of all the available hydroxyl groups, while full replacement is said to be accomplished under reflux conditions (5). Such a treatment was also applied to samples ZB, reflux heating the solution (70–80°C) for 8 h. The method for the determination of chlorine is thoroughly depicted in Ref. (6). The Cl content was considered equal to the content of surface reacting OH groups.

To assess the influence of the calcination on the adsorptive properties in solution, potentiometric titrations were performed on dried and calcined gels. Since retained anions affect the adsorption behavior of surfaces, a gel dried at 100°C prepared from Zr *n*-butoxide (ZB^{100}) was taken as the reference for the uncalcined samples. In the case of calcined samples, gels heat treated at 600°C prepared from ZrOCl_2 (ZO1^{600}) and ZrCl_4 (ZCl^{600}) were used. It was con-

sidered that no surface chlorine was present in these calcined samples.

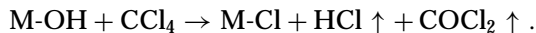
The equipment for potentiometric titrations consisted of an Altronix SX-II pH-meter coupled to a glass electrode. Acid and base titrating solutions HNO_3 and KOH were added with a microburet to a 0.1 *N* KNO_3 electrolyte solution containing the sample. The titrations were conducted in an inert atmosphere of nitrogen. This gas was also bubbled in the solution prior to the titration in order to desorb CO_2 . The surface charge was determined by subtracting the values of added base or acid between the titration of the sample and the blank experiment (electrolyte solution without the solid). More details can be found in Ref. (7). The surface charge was calculated with the expression:

$$\alpha = FV(C_b - C_a - (\text{OH}^-) - (\text{H}^+))/S,$$

where F = Faraday's constant, V = volume, S = surface of the sample, C_b = concentration of added base; C_a = concentration of added acid; (OH^-) , (H^+) = equilibrium concentration of OH^- and H^+ ions.

Vapor Phase Treatments

Portions of the dried gel were calcined at 600°C for 3 h in a muffle furnace (samples ZO3^{600} and ZO4^{600}). XRD analysis was performed in order to determine the crystal structure. To test the reactivity of the surface, chemical attacks under aggressive conditions were used: chlorination with CCl_4 and sulfation with H_2SO_4 . It has been reported (5) that CCl_4 at 150–350°C produces an incomplete chlorination (25%) of surface groups on silica; however, at 400°C siloxane bridges are opened; and a maximum chlorination is obtained at 600°C. Mc Daniel (7) reports that chlorination of silica with CCl_4 begins at 300°C and that siloxane bridges are opened at $T > 500^\circ\text{C}$. The reaction is



The temperatures of chlorination used were 300, 375, 450, 525, and 600°C. Pure CCl_4 (Mallinckrodt, 99%) at a rate of 3.9 ml/h was injected over a glass wool plug at the inlet of a quartz reactor. A flow of nitrogen (30 ml/min) carried the reactive, which vaporized rapidly in the first inlet portions of the reactor; 1-g samples were supported over a fritted glass slab in the middle of the reactor. The chlorination was conducted for 40 min; no reactive was injected during the cooling and heating ramps; and a flushing with nitrogen for 15–20 min was performed after the chlorination was finished. The samples were then dried and the specific surface area was measured.

Samples ZO3^{600} were also sulfated in the vapor phase. For this purpose a solution of H_2SO_4 5 *N* was injected in a nitrogen stream in the same way described above (3.9 ml/h, 40 min). The temperatures of sulfation were 300, 375, and 400°C; 1-g samples were also used. The sulfated samples

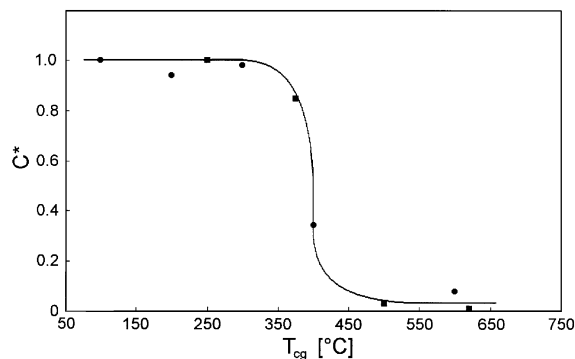


FIG. 1. A dimensional initial conversion (C^*) as a function of calcination temperature: C^* = (initial activity/maximum initial activity in a series); T_{cg} = temperature of calcination of the gel (before the sulfation); samples ZO1-S, ■; samples ZCl-S, ●.

were examined by XRD and their catalytic activity in the reaction of isomerization of *n*-butane was tested.

RESULTS

General Properties

Figure 1 shows the adimensional initial conversion as a function of the calcination temperature. The maximum values of conversion for samples ZO1-S and ZCl-S were 30% and 20%, respectively. The active samples deactivated rapidly, conversion being practically nil after 3 h of time-on-stream. Isobutane was the main product (85–90% selectivity) while propane was the main secondary one. A first search for a correlation of the activity pattern with variations in other properties can be done by inspecting the results for the textural properties of the calcined gels, their crystallinity, and the sulfate content of the sulfated samples.

As shown in Tables 2 and 3, the samples began to crystallize below 400°C. At 400°C crystals of 100 nm are present, with a mixture of structures T and M. Higher temperatures of calcination produce the growth of the crystals and the stabilization of the monoclinic phase after calcining at 600°C.

TABLE 2

Crystal and Textural Properties of Samples ZCl

Sample	S_g (m ² /g)	D_{pw} (Angstrom)	V_p (μl/g)	Structure	R1 (nm)	R2 (nm)	Rm (nm)
ZCl ¹⁰⁰	259.39	—	—	Amorphous	—	—	—
ZCl ²⁰⁰	280.89	29.3	206	Amorphous	—	—	—
ZCl ³⁰⁰	236.44	30.9	183	Amorphous	—	—	—
ZCl ⁴⁰⁰	110.18	48.8	139	T+,M-	129	82	100
ZCl ⁶⁰⁰	33.83	149.9	101	M	1570	1250	1410

Note. S_g , specific surface area; D_{pw} , Wheeler's pore diameter; V_p , pore volume; T, tetragonal; M, monoclinic; R1, crystal size calculated over the peak $2\theta = 28^\circ$; R2, crystal size calculated over the peak $2\theta = 34^\circ$; RM: $(R1+R2)/2$.

TABLE 3

Crystal and Textural Properties of Samples ZO1

Sample	S_g (m ² /g)	D_{pw} (Angstrom)	V_p (μl/g)	Structure
ZO1 ¹⁰⁰	262.13	22.711	298	Amorphous
ZO1 ²⁵⁰	235.44	25.145	296	Amorphous
ZO1 ³⁷⁵	120.14	46.722	281	T,M
ZO1 ⁵⁰⁰	66.50	74.850	249	T+,M-
ZO1 ⁶⁰⁰	39.48	102.67	203	M

Note. Notation as in Table 2.

The pore volume diminishes 30% in the case of samples ZO1 and 50% for samples ZCl. For both samples the specific surface area is reduced from 260 m²/g to 30–40 m²/g. The continuous drop in these values is more drastic at temperatures higher than 400°C, in coincidence with the process of crystal growth.

Typical BJH pore size distributions (samples ZO1) are plotted in Fig. 2. Zirconias were essentially mesoporous materials. At low temperatures of calcination, when no crystallization has taken place a peak of micropores at 25–30 Å and a zone of mesopores at 100–400 Å can be seen. Micropores sinter slowly and completely disappear at 600°C, contributing to increase the mesopore volume. Samples ZCl were more microporous, displaying a peak at 25–30 Å. Calcination at 600°C increases mesoporosity, with a wide maximum

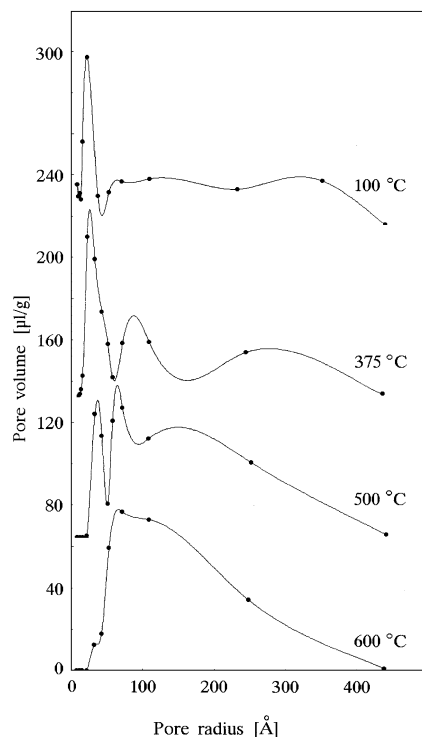


FIG. 2. BJH distribution of samples ZO1 (from oxychloride, calcined at different temperatures).

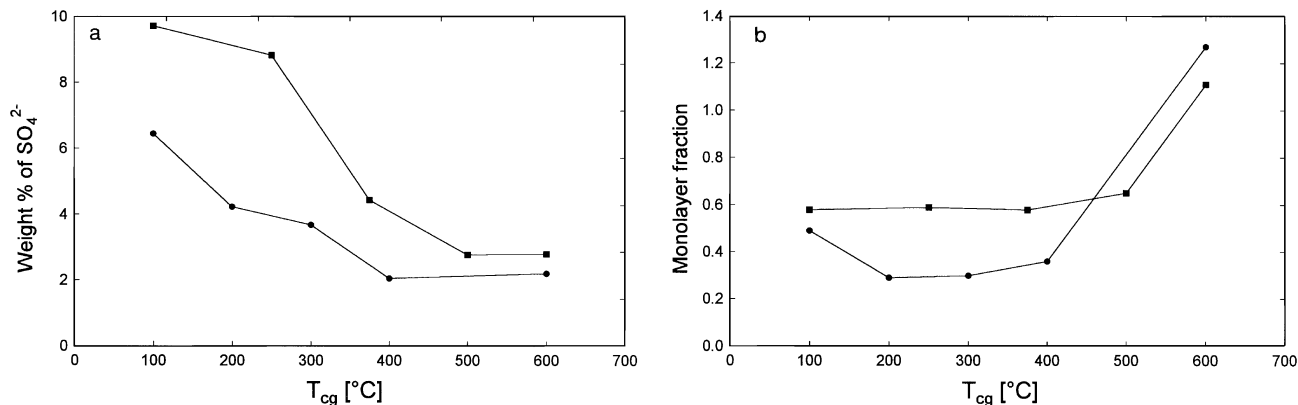


FIG. 3. (a) Weight% of sulfate as a function of the calcination temperature (T_{cg}): ZOI-S (from oxychloride), \blacksquare ; samples ZCl-S (from chloride), \bullet . (b) Fraction of sulfate monolayer as a function of the calcination temperature (T_{cg}). (Sulfate monolayer = 4 SO_4^{2-} groups/nm².) ZOI-S (from oxychloride), \blacksquare ; Sampels ZCl-S (from chloride), \bullet .

at 150–200 Å. For both samples, the loss of surface is higher than the loss of pore volume, due to the collapse of pores in the micropore range, which contribute largely to the total area. A fraction of the micropores merges to form mesopores with no loss of volume.

Table 4 shows the textural properties of samples ZOI-S-CT. During the catalytic test samples ZOI-S suffer the effect of sintering during the activation step at 620°C. Coking during the reaction is not expected to reduce the pore volume, since the coke deposit on $\text{SO}_4^{2-}\text{-ZrO}_2$ amounts to 1% approximately (2). Samples calcined at 100 and 250°C previous to sulfation display a more resistant area under calcination at 620°C, displaying final values of 125–137 m²/g; for these samples the reduction of pore volume is 20–30%. Apparently, the sulfate ion acts as textural stabilizer preserving part of the microporous volume.

For both ZOI and ZCl samples, the constant C in the BET equation increased after calcination. It was 50–60 at 100–200°C and 80–100 at 600°C. This indicates that the heat of adsorption of nitrogen increases when the surface is treated at high temperatures, a fact addressed either to the creation of new adsorption sites or an increase in the surface energy.

For both samples ZOI and ZCl, the initial crystal habitat is a mixture of phases T and M. The thermodynamically stable M phase is stabilized upon calcination at higher temperatures. There seems to be a coincidence between the

onset of the crystallization process and the drop in conversion, but there is no correlation with the evolution of other textural properties. In the case of surface area, while the activity drops to practically null values at high temperatures ($T_{cg} > 400^\circ\text{C}$), S_g does not.

The sulfate contents for samples ZOI-S and ZCl-S are plotted in Fig. 3. The samples differ in the time of sulfation (1 and 2 h) and in the precursor used in their synthesis. They display a common decrease in the mass content as T_{cg} increases (Fig. 3(a)). The results of surface sulfate density are somewhat different (Fig. 3(b)). For both samples, the density is lower than the monolayer value, for T_{cg} lower than 600°C. At this temperature of calcination, zirconia samples exhibit an enhanced capacity for the adsorption of anions. The sulfate surface density is stabilized at lower values after the treatment at high temperatures during the catalytic test, as shown in Fig. 4. A content of about 0.5 monolayers is retained in samples ZOI-S-CT. The patterns of catalytic activity and sulfate content are not well correlated. Mass percentages of sulfate do not decrease to such an extent

TABLE 4

Textural Properties of Samples ZOI-S-CT

Sample	S_g (m ² /g)	D_p Wheeler (Å)	V_p (μl/g)
ZOI ¹⁰⁰ -S-CT	125.36	33.39	209
ZOI ²⁵⁰ -S-CT	137.23	33.81	232
ZOI ³⁷⁵ -S-CT	114.95	51.29	284
ZOI ⁵⁰⁰ -S-CT	44.01	88.99	196
ZOI ⁶⁰⁰ -S-CT	38.13	102.25	195

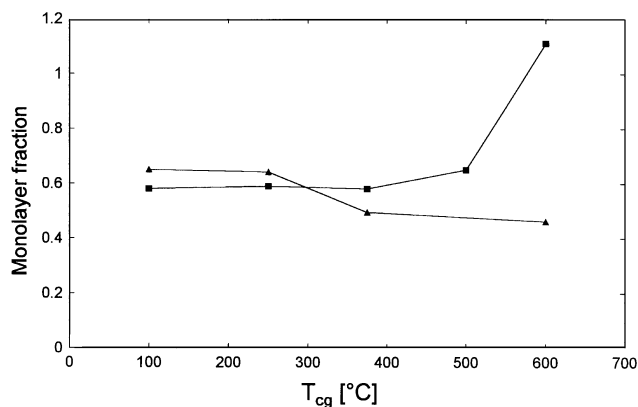


FIG. 4. Sulfate content of samples ZOI-S, prepared from oxychloride, calcined at different temperatures and sulfated: before catalytic test, ZOI-S-CT, \blacksquare ; after catalytic test, ZOI-S-CT, \blacktriangle .

which could explain the total loss of activity. Furthermore, sulfate surface densities can remain (after activation) at a half monolayer value or more for any T_{cg} value.

Assessment of Surface OH Groups

Zirconia gel has an isoelectric point of 6–7, typical of amphoteric transition oxides (6, 9). Chlorine free zirconia, prepared from *n*-butoxide, has a ZPC of 7.0. Samples prepared from chlorided precursors always display lower values of ZPC, due to the presence of chloride ions retained in the gel matrix. Therefore, for the comparison of adsorptive properties in solution, a sample prepared from *n*-butoxide is taken as reference material of the dried gel state. Besides, during the calcination at high temperatures chloride ions are removed nearly completely (9). Remaining ions after calcination at 600°C are expected to be in the bulk and not in the surface due to the enhanced surface ionic diffusion during the sintering processes.

The results of surface charge are plotted in Fig. 5. A first effect induced by the calcination is clearly the shift of the ZPC from a value of 7.0 to a value of 4.0. Many authors have studied independently the relation between the ZPC and the previous history of the sample and indicate that treatments leading to bulk or surface dehydration result in more acid values of ZPC (8). In the zone of anion adsorption ($\text{pH} < \text{PZC}$) there is a growth in the surface charge in relation to the noncalcined sample, in this case, for values of $\text{pH} < 3$. An increase in the surface charge indicates a corresponding increase in the number of adsorption sites, or a greater polarizability of the surface sites, induced by the heat treatment. The increased anion adsorption can be related to the higher contents of sulfate anion previously recorded.

Samples calcined at different temperatures were chlorinated in order to measure their OH content. The blanks before chlorination had a water content of 10–13%. The

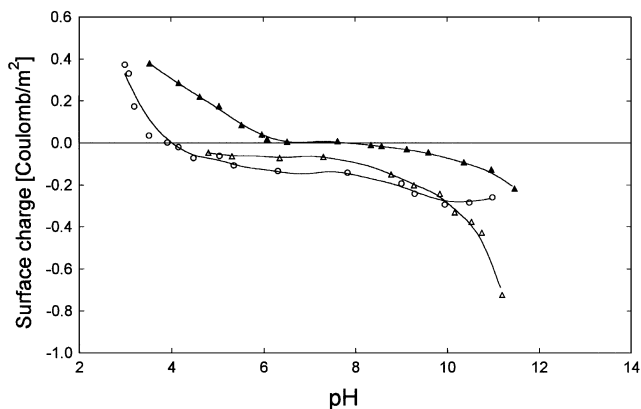


FIG. 5. Potentiometric titration curves of fresh and calcined zirconia gels: \blacktriangle , zirconia gel prepared from *n*-butoxide, dried at 100°C (ZB¹⁰⁰); \triangle , zirconia prepared from oxychloride, calcined at 600°C (ZO₂⁶⁰⁰); \circ , zirconia prepared from chloride, calcined at 600°C (ZC¹⁶⁰⁰).

TABLE 5

Specific Surface Area of Samples ZO₂-Cl and ZB-Cl (after Chlorination) and Cl Content of Samples ZO₂ (before Chlorination)

Sample	Cl content (%) (before chlorination)	Sg (m ² /g) (after chlorination)
ZO ₂ ¹⁰⁰ -Cl	1.42	206.25
ZO ₂ ²⁰⁰ -Cl	1.04	209.21
ZO ₂ ³⁰⁰ -Cl	0.96	173.94
ZO ₂ ⁴⁰⁰ -Cl	0.68	147.15
ZO ₂ ⁵⁰⁰ -Cl	0.57	120.73
ZO ₂ ⁶⁰⁰ -Cl	0.31	23.22
ZB ¹⁰⁰ -Cl	—	44.55
ZB ⁴⁰⁰ -Cl	—	55.60
ZB ⁵⁰⁰ -Cl	—	38.00
ZB ⁶⁰⁰ -Cl	—	20.38
ZB ²⁵⁰ -RCl	—	62.60
ZB ⁴⁰⁰ -RCl	—	27.84
ZB ⁵⁰⁰ -RCl	—	32.91
ZB ⁶⁰⁰ -RCl	—	20.37

chlorine content is detailed in Table 5. As we can see the samples before being chlorinated with SOCl₂ have retained Cl. This ion is fairly persistent. In principle, the Cl ion can be incorporated in the bulk or retained on the surface. It has been argued (9) that incorporation in the bulk is not likely because the ionic radius of Cl⁻ is bigger than the radius of oxygen. Therefore, the higher fraction would be on the surface. However, the more persistent chlorides, found after calcination at 500 and 600°C must be present in the bulk, since they persist after the crystallization process, in which the ionic surface diffusion must be high. Then, the surface chlorine of the blanks was estimated by subtracting the content at 500°C, taken as the initial bulk chlorine content.

The quantity of OH replaced by Cl decreases with calcination (Fig. 6) and is remarkably low on the samples calcined at 400, 500, and 600°C. In the case of samples ZO₂-Cl

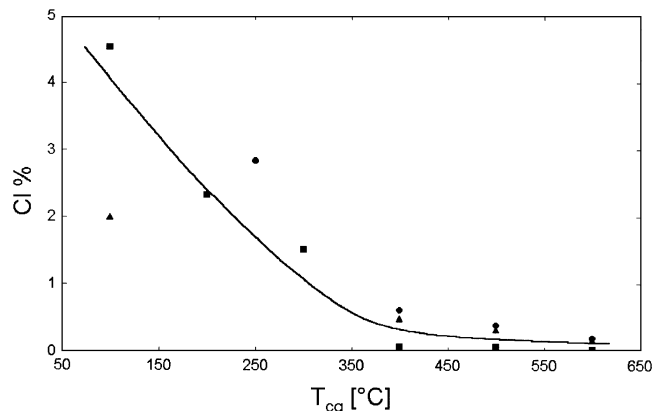


FIG. 6. Cl content (%) of samples treated with SOCl₂ in liquid phase: \blacksquare , ZO₂-Cl; \blacktriangle , ZB-Cl; \bullet , ZB-RCl.

calcined at these temperatures there is practically no Cl grafted. The heat treatment seems to produce an extensive dehydroxylation, accompanied by a surface passivation which makes it inert to the attack by SOCl_2 .

Surface chlorine densities were also calculated and were related to the OH density. For comparison, a rough estimation of the maximum content of OH groups ($\delta_{\text{OH}}^{\text{M}}$) was done by assigning a number equal to the number of surface cations, theoretically estimated to be of $8 \text{ Zr}/\text{nm}^2$ (6, 10). The maximum experimental OH densities were 40–45% $\delta_{\text{OH}}^{\text{M}}$ ($\text{ZO}2^{100}\text{-Cl}$, $200 \text{ m}^2/\text{g}$), 95% $\delta_{\text{OH}}^{\text{M}}$ ($\text{ZB}^{100}\text{-Cl}$, $44.5 \text{ m}^2/\text{g}$) and 100% $\delta_{\text{OH}}^{\text{M}}$ ($\text{ZB}^{250}\text{-RCl}$, $62.6 \text{ m}^2/\text{g}$). The higher surface Cl density in ZB may be addressed to a higher surface OH content of zirconias prepared from alcoxides (11).

Vapor Phase Treatments

The attack with CCl_4 vapors indicated that the inertness of the surface was broken under this more aggressive conditions (Fig. 7). Samples $\text{ZO}3\text{-VPC}$, which were crystalline and of similar nature than previous samples calcined at 600°C ($\text{ZO}2^{600}$), showed a chlorine intake of 4–7% (2.0–3.0 Cl/nm^2 , i.e., 25–37% $\delta_{\text{OH}}^{\text{M}}$). It must be recalled that the Cl intake in $\text{ZO}2^{400}\text{-Cl}$, $\text{ZO}2^{500}\text{-Cl}$, and $\text{ZO}2^{600}\text{-Cl}$ was practically zero. Plotted values correspond to the chlorine incorporated (the value of the blank has been subtracted, 0.1% at 600°C). The amount of chlorine retained can be considered as the resultant of an equilibrium between the Cl grafted and that removed by the high temperatures. The maximum Cl surface density is somewhat lower than the maximum obtained for $\text{ZO}2\text{-Cl}$ samples.

Vapor-phase sulfation in turn, succeeded in producing active samples in the catalytic test. The results plotted in Fig. 7 show that the samples have a maximum initial activity when they are activated by calcination at $650\text{--}700^\circ\text{C}$ in the catalytic test. Temperatures higher than 700°C must produce decomposition of surface sulfate, as is the case with common $\text{SO}_4^{2-}\text{-ZrO}_2$ catalysts. The XRD spectrum of the

sulfated samples was similar to the corresponding nonsulfated samples, and no new peaks related to bulk sulfates were detected. The samples were mainly monoclinic. Although they were active, the samples deactivated rapidly. The sulfate content of the sample sulfated at 300°C was 1.72% or $2.68 \text{ SO}_4^{2-}/\text{nm}^2$.

The obtention of mainly monoclinic active samples in a way resembles some results obtained by Morterra *et al.* (12). They synthesized $\text{SO}_4^{2-}\text{-ZrO}_2$ from Zr isopropoxide and obtained some samples which were mainly monoclinic after the crystallization. Comparing with other samples, they concluded that the maximum acidity was obtained for crystalline materials irrespective of their crystalline state.

DISCUSSION

The results show that there is a strong influence of the temperature of calcination of the gels before the sulfation over the catalytic activity of $\text{SO}_4^{2-}\text{-ZrO}_2$, when sulfation is accomplished by the common method of impregnation with aqueous H_2SO_4 at room temperature. The calcination temperature of 400°C establishes a sharp limit between active and inactive samples. There is no correlation with the textural properties modified by the calcination, since no parameter diminishes to nearly null values as the catalytic activity does. Crystallization seems to be related to the onset of catalytic inactivity, although it does not determine an accurate sufficient condition. Gels calcined at temperatures near the limit ($375\text{--}400^\circ\text{C}$), crystallized to a certain extent and still showed some catalytic activity. Nevertheless, crystallization does diminish the number of active sites produced by sulfation.

Variation of the quantity of surface OH groups, as measured by chlorination with SOCl_2 , offers a better explanation. Sulfate anions, in order to become anchored to the surface of zirconia and form sulfo bridges, need the presence of adjacent hydroxyls. Therefore, the depletion of surface OH groups hampers the possibilities of sulfo bridge formation. Calcination is thought to produce a progressive oxolation in the bulk and on the surface; the process that becomes accelerated and massive in the temperature interval corresponding to the "glow exotherm," $420\text{--}470^\circ\text{C}$ (13), as detected by DTA-DSC experiments. Oxolation on the surface produces oxo bridges, which must be rather inert species, in analogy with other M-O-M groups, such as the siloxane groups in silica. In the latter, oxo bridges are formed reversibly at low temperatures of calcination; at higher temperatures, siloxane groups are permanent. This is due to the need of a reorientation of the coordination tetrahedron of Si. Such reorientation does not seem necessary in the case of zirconia, since Zr has octahedral or near octahedral coordination in the oxide; therefore, the formation of oxo bridges seems favored. The oxo bridges on zirconia seemed to be inert and would not rehydrate under mild conditions,

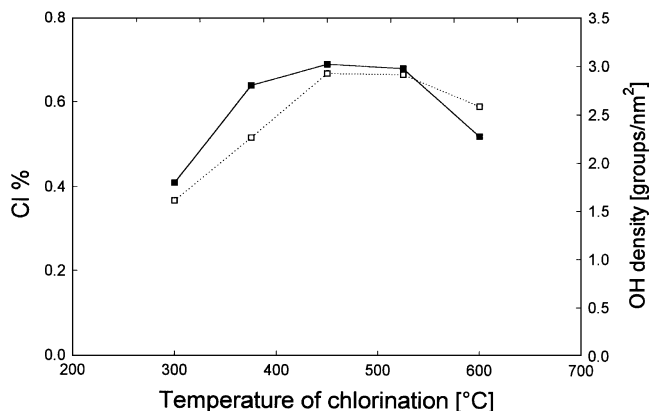
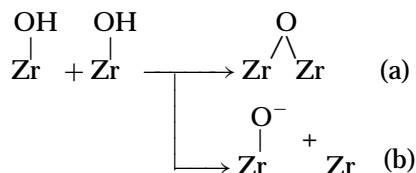


FIG. 7. Cl content of samples $\text{ZO}3^{600}\text{-VPC}$ (from oxychloride, calcined at 600°C) treated with CCl_4 vapors: ■, Cl%; □, OH density.

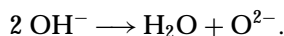
as was revealed by the chlorination of calcined samples with thionyl chloride.

The necessity of OH groups for the grafting of sulfate and the formation of acid sites has been previously hinted by Chen *et al.* (14), although no surface reactions were depicted. For zirconia sulfated in the form of Zr(OH)₄, they posed a two-step process in which the sulfate first displaces two OH groups of the framework and then upon calcination at T > 400°C acid sites are formed upon oxolation.

The presence of oxo bridges on the surface of zirconia has already been mentioned by Bianchi *et al.* (15). Thiel and Madey (16) have highlighted the fact that many oxide systems (titania, tungsten bronzes, PbO, NiO) do not rehydroxylate after they have crystallized and only display dissociative chemisorption of water in the presence of defects. Orlando *et al.* (17), by means of an *ab initio* quantum mechanical model of tetragonal zirconia, have shown that associative and dissociative chemisorption of water on crystalline zirconia involve similar energies. They estimated a rather high value for the activation energy between the two states of water. It is also well known that at sufficiently high temperatures, dehydroxylation produces Lewis acid-base pairs at the surface which act as catalytic active sites in many reactions. Therefore, we can envisage two kinds of groups appearing at high temperatures (see below). The stability or the appearance of (a) or (b) depends on the temperature of activation. The sustained drop of the OH density during our chlorination studies with SOCl₂, may indicate that (a) proceeds from the early stages of calcination:



Lewis sites (b) require rather high temperatures at which practically all the water is eliminated from the surface (18). Both (a) and (b) can be depicted by the schematic reaction:

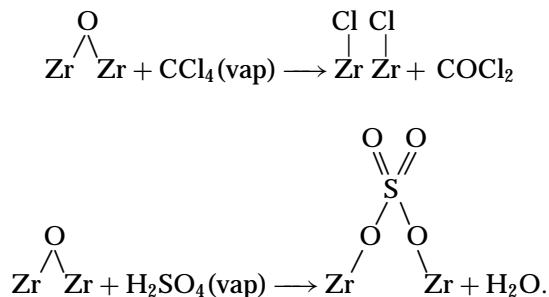


In the comprehensive review of Parks (8) on the ZPC (zero point of charge) of many oxide systems, the ratio (O²⁻/OH⁻) is said to have influence on the position of the ZPC. Higher ratios produce the shift of the ZPC to acid values of pH. Surface oxygen would produce a strong polarization of the free surface groups involved in amphoteric reactions with the solvent. This shift in ZPC for calcined samples was certainly observed in our potentiometric titrations, with a difference of three points with respect to noncalcined samples.

Now we have a hypothetical scheme to explain the observed pattern of catalytic activity. Calcination at temperatures higher than the "glow exotherm" produces a nearly

complete depletion of surface OH groups. The oxo bridges formed are inert and do not react under mild conditions; they do not rehydrate in the presence of water and do not react with sulfate anions to form sulfo bridges. At temperatures of calcination near but lower than 400°C the content of OH groups is low but enough to produce a minimum amount of active sulfates, which contribute substantially to the conversion of *n*-butane. Samples with a small fraction of sulfate monolayer are found to be as much active as samples with a half monolayer or more (19). At temperatures greater than 400°C the dehydroxylation is completed and practically no active sites are formed by sulfation in solution. However, chemically inert, crystalline zirconia calcined at 600°C seems to have similar or enhanced properties of adsorption. The observed contents of retained sulfate and the variation in the value of the C constant of the BET equation confirm this statement. Although calcination is generally thought to diminish the heterogeneity of gels and the number of adsorption sites, a more energetic surface may be produced if a new phase is produced. Holmes *et al.* (20) have found that the appearance of the monoclinic habitat upon calcination of zirconia results in a material with much higher surface energy; a difference in the heat of immersion of 300 Erg/cm² was found. Ardizzone and Bassi (21), while performing potentiometric titrations of zirconia, found that zirconia heat treated at 800°C differed from samples calcined at 200°C in the mechanisms of charge formation, the magnitude of the surface charge, and the sensibility to the concentration of electrolyte.

The surface inertness of crystalline calcined zirconia was found to be overcome when more aggressive conditions of reactions were used. Both chlorination and sulfation when performed in the gas phase, at high temperatures, seemed to produce the reopening of the oxo bridges, incorporating chlorine in one case and yielding active sulfate species in the other. The latter can be supposed to be sulfo bridges, to which the appearance of catalytic activity in SO₄²⁻-ZrO₂ is customarily related:



The evolution of the activity of the crystalline samples sulfated in vapor phase, when activated at high temperatures in air, is similar to that observed in SO₄²⁻-ZrO₂ catalysts sulfated in the traditional way, having a maximum at 650–700°C (Fig. 8). Higher temperatures produce a steep

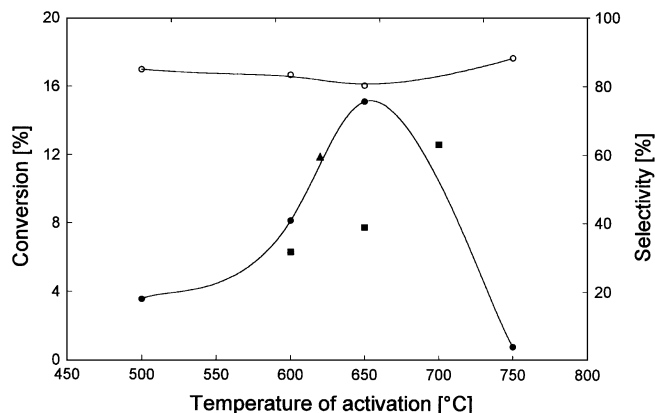


FIG. 8. Catalytic activity for the isomerization of *n*-butane of samples ZO_4^{600} sulfated in the vapor phase as a function of the activation temperature in the catalytic test. Activity: ●, ZO_4^{600} -VPS³⁰⁰ (calcined at 600°C, sulfated at 300°C); ■, ZO_4^{600} -VPS³⁷⁵; ▲, ZO_4^{600} -VPS⁴⁰⁰. Selectivity to *i*-butane: ○, ZO_4^{600} -VPS³⁰⁰.

activity drop that is surely related to the decomposition of surface sulfur species.

CONCLUSIONS

The variation of the catalytic activity of SO_4^{2-} - ZrO_2 with the temperature of calcination of zirconia gels before the sulfation in solution, does not correlate well with any textural or crystal property, or the sulfate content.

The adverse effect of calcination at $T > 400^\circ\text{C}$ of gels before sulfation, is not directly related to the crystallinity of zirconia. In fact, under certain conditions of preparation, crystalline materials can be effectively promoted to produce active catalysts in isomerization of *n*-butane.

The cause of the ineffective promotion by the customary sulfation in solution, when applied to crystalline materials, is explained by the disappearance of surface OH groups, which is practically complete at 500°C when the material has crystallized. OH groups would condense forming oxo bridges that would be inert to the attack by sulfuric acid in solution under mild conditions.

Sulfate contents cannot be related directly to the activity. Samples calcined at $T > 500^\circ\text{C}$ have an adsorption strength for sulfate anions that is equal to or higher than amorphous zirconia gels.

The density of surface OH groups and/or their reactivity seems to depend on the precursor used in the preparation of the gel. In any case, the density of chlorinated surface groups is always lower or equal to the surface cationic density ($8 \text{ Zr}/\text{nm}^2$). Samples prepared from oxychloride show a maximum of 3–3.7 OH/nm² titratable by chlorination

in solution at room temperature or chlorination in vapor phase.

The surface chemical inertness of zirconia after calcination at $T > 400^\circ\text{C}$, is rationalized in terms of the appearance of oxo bridges. This inertness can be overcome by the attack of some reactives, e.g., CCl_4 and H_2SO_4 , in vapor phase and at high temperatures. The more aggressive conditions are thought to produce the reopening of the oxo bridges.

Sulfation of zirconia with sulfuric acid in the vapor phase is posed as an alternative, however drastic, method of promotion of crystalline materials. An attractive feature of the method is that it enables the *in situ* resulfation of catalysts between reaction periods, thus allowing for a compensation of sulfur losses.

Predominant monoclinic zirconia can be promoted by vapor phase sulfation and turned active in isomerization of *n*-butane, suggesting that active catalysts need no specific crystalline phase.

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