

Tetragonal structure, anionic vacancies and catalytic activity of $\text{SO}_4^{2-}\text{-ZrO}_2$ catalysts for *n*-butane isomerization

Carlos R. Vera^a, Carlos L. Pieck^a, Kiyoyuki Shimizu^{b,*}, José M. Parera^a

^a Instituto de Investigaciones en Catálisis y Petroquímica (INCAPE) (FIQ-UNL, CONICET),
Santiago del Estero 2654, 3000 Santa Fe, Argentina

^b National Institute for Resources and Environment (NIRE) (AIST, MITI), 16-3 Onogawa, Tsukuba 305-8569, Japan

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Abstract

An assessment of the influence of the crystal structure, surface hydroxylation state and previous oxidation/reduction pretreatments on the activity of sulfate-zirconia catalysts for isomerization of *n*-butane was performed using crystalline and amorphous zirconia supports. Different sulfation methods were used for the preparation of bulk and supported $\text{SO}_4^{2-}\text{-ZrO}_2$ with monoclinic, tetragonal and tetragonal + monoclinic structures. Activity was important only for the samples that contained tetragonal crystals. The catalysts prepared from pure monoclinic zirconia showed negligible activity. $\text{SO}_4^{2-}\text{-ZrO}_2$ catalysts prepared by sulfation of crystalline zirconia displayed sites with lower acidity and cracking activity than those sulfated in the amorphous state. Prereduction of the zirconia samples with H_2 was found to greatly increase the catalytic activity, and a maximum rate was found at a reduction temperature of 550–600 °C, coinciding with a TPR peak supposedly associated with the removal of lattice oxygen and the creation of lattice defects. A weaker dependence of catalytic activity on the density or type of surface OH groups on zirconia (before sulfation) was found in this work.

A model of active site generation was constructed in order to stress the dependence on the crystal structure and crystal defects. Current and previous results suggest that tetragonal structure in active $\text{SO}_4^{2-}\text{-ZrO}_2$ is a consequence of the stabilization of anionic vacancies in zirconia. Anionic vacancies are in turn supposed to be related to the catalytic activity for *n*-butane isomerization through the stabilization of electrons from ionized intermediates. © 2002 Published by Elsevier Science B.V.

Keywords: Sulfate zirconia; Crystalline zirconia; *n*-Butane isomerization; Tetragonal structure; Oxygen vacancy

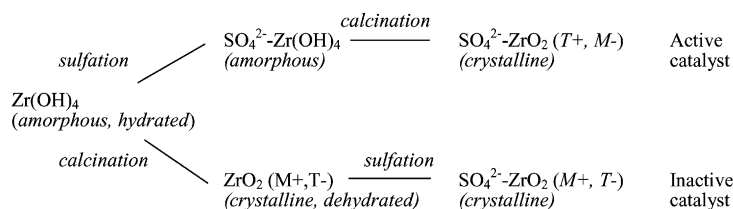
1. Introduction

Sulfate-promoted zirconia catalysts (SZ), which are active in the isomerization of *n*-butane, mainly have a tetragonal structure after calcination at high temperatures, and this structure is usually associated with catalytic activity. The sulfate ion produces a preferential stabilization of the tetragonal phase during calcination of sulfated Zr hydroxide gel, and the growth of

the monoclinic phase is highly inhibited [1–3]. Therefore, elucidation of the relationship between catalytic activity and the presence of a specific crystal phase is difficult. An assessment of the role of the crystal phase could be made if different crystalline monoclinic and tetragonal zirconia samples were sulfated and their catalytic activity compared. Zirconia gels calcined until crystallized and then doped with sulfate by impregnation in aqueous H_2SO_4 at room temperature, are practically inactive in *n*-butane isomerization (250–300 °C). The latter effect can be extended to other promoters of activity, like WO_3 , which needs to

* Corresponding author.

E-mail address: ksimizu@op.cao.go.jp (K. Shimizu).



Scheme 1.

be impregnated onto amorphous Zr(OH)_4 to produce active catalysts [4]. Failure to activate crystalline zirconia has prevented researchers from determining whether a specific crystalline form is necessary in active sulfated zirconia catalysts [2] (see Scheme 1) (sulfation: impregnation in H_2SO_4 solution at room temperature; calcination: in air at $T = 600\text{--}650^\circ\text{C}$; T: tetragonal; M: monoclinic).

Two main questions arise: (i) is the tetragonal phase specifically needed in active sulfate-zirconia materials, or can monoclinic materials also be active? and (ii) why does calcination (previous to sulfation) inhibit the formation of active sites? According to Vera [5], and Vera and Parera [6] the latter inhibiting process seems to take place in a narrow calcination temperature range, between 350 and 450°C , where a steep drop in catalytic activity takes place. At calcination temperatures (before sulfation) lower than 350°C , all catalysts are produced from amorphous, fully hydroxylated Zr(OH)_4 , that converts to the tetragonal phase after calcination at 600°C . At calcination temperatures higher than 450°C , all catalysts are inactive, mainly monoclinic, and are formed by sulfation of crystalline zirconia, which reportedly has a lower content of OH groups due to calcination. The results could be explained by a dehydroxylation process. During calcination OH groups would be depleted and upon sulfation no active sites would be formed due to an inappropriate OH configuration for condensation with sulfate [6].

A recent work by Stichert et al. [7] has reported the synthesis of monoclinic SZ catalysts active in $n\text{-C}_4$ isomerization which were synthesized in a novel one-step hydrothermal process. In this sense the answer to (i) would be that tetragonal structure is not needed in catalytically active SZ. However, the produced material had one-fourth of the catalytic activity

of tetragonal materials with a similar amount and type of acidity. The authors concluded that isomerization of $n\text{-butane}$ on tetragonal materials was favored by the arrangement of surface groups. Synthesis of active monoclinic SZ catalysts has only been reported in a few other articles [6,8,9]. In the first two [6,8] the catalysts had a non-negligible amount of tetragonal zirconia and in every case the activity of monoclinic catalysts was much lower than that of tetragonal SZ. In another report by Vera and Shimizu [10], fully tetragonal SZ materials were synthesized from hydrothermally aged zirconia and they were practically inactive in the reaction of $n\text{-C}_4$ isomerization despite enhanced stabilization of the T phase. As can be seen, the source of activity and its relation to the crystal structure is still a matter of debate.

In this study, we sought answers to questions (i) and (ii) above. We intended to determine clearly whether fully monoclinic materials could produce active catalysts for $n\text{-C}_4$ isomerization and also to clarify whether the deleterious effect of calcination of zirconia gels was due to irreversible crystallization into the monoclinic phase or to a reversible surface process, like dehydroxylation. For this purpose SZ catalysts with different proportions of the monoclinic (M) and tetragonal (T) phase, promoted in the amorphous and crystalline state, were tested in $n\text{-butane}$ isomerization and were further characterized by other techniques. For the promotion of crystalline zirconia a new method with a prereluction step was used.

2. Methods

In order to assess the influence of the crystalline phase, SZ catalysts with different crystalline phases were synthesized.

2.1. Preparation of unsulfated zirconia

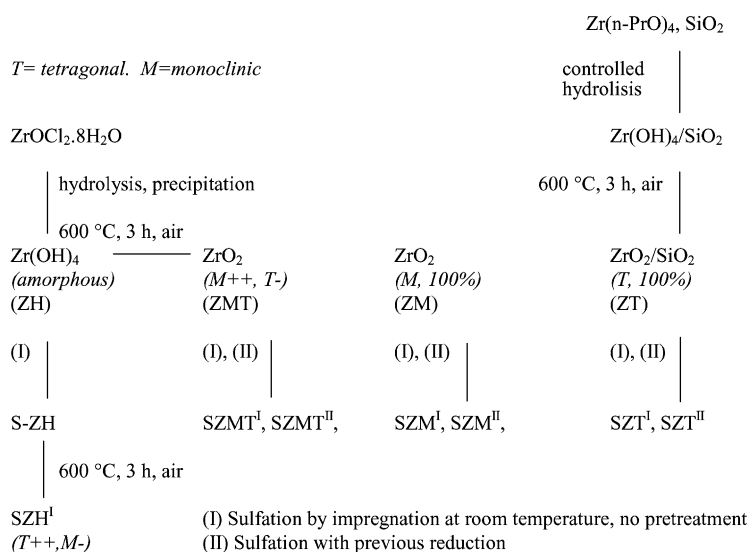
Amorphous zirconium hydroxide was prepared by precipitation from $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (Strem Chemicals, 99.9998%) with concentrated NH_4OH (Merck, 37%). The base was added until $\text{pH} = 10$ [11] and the gel was aged for 24 h at room temperature in its mother liquor. Then it was washed, filtered and dried at 110°C overnight (sample ZH). Crystalline fully monoclinic zirconia (ZM) was supplied by Strem Chem. (ZrO_2 , 99%). Part of the ZH batch was transformed into crystalline zirconia with a mixture of T and M phases (sample ZMT) by calcination in static air (3 h, 600°C) in a muffle oven.

The tetragonal zirconia phase is thermodynamically stable only at high temperatures ($T > 1150^\circ\text{C}$) and cannot be quenched [12]. It can be produced in *metastable* conditions at lower temperatures and in high proportion by aliovalent cation bulk doping [13,14], surface doping [14] or refluxing in basic media [15]. Fully fluoritic zirconia (tetragonal or cubic) can also be synthesized by supporting it on silica or alumina [16,17]. For the preparation of SZ catalysts with different crystal phases, bulk- or surface-doped zirconia samples are not good for comparison because foreign cations and anions obscure the results. Reflux-aged zirconia may also contain occluded

nitrogen compounds. For this reason, fully tetragonal crystalline ZrO_2 was prepared by supporting it on silica. Silica, sulfate-doped or free, has no catalytic activity for *n*-butane isomerization, the test reaction used here. In the synthesis we used a controlled hydrolysis of alkoxide in which the OH groups of the support react with the organic ligands of a metal alkoxide [16]. Zr *n*-propoxide (Fluka, 70% in *n*-propanol) was used as the precursor and *n*-hexane (Merck, min 99%) as the solvent. Silica from Morton-Thiokol (Alfa, wide pore, $300\text{ m}^2\text{ g}^{-1}$) was loaded with 21% Zr. After impregnation, the sample was hydrated by immersion in water for 8 h and then dried in a stove at 110°C overnight. Finally, it was calcined at 600°C in air for 3 h (ZT sample, expected to be fully tetragonal) (Scheme 2: (I) sulfation by impregnation at room temperature, no pretreatment; (II) sulfation with previous reduction).

2.2. Preparation of sulfated zirconia catalysts

Two different sulfation techniques were used. (I) Impregnation: samples of the ZH, ZMT, ZM and ZT batches were sulfated by wet impregnation at room temperature, dipping the sample in a solution of H_2SO_4 1 N (10 ml solution $\text{g}_{\text{cat}}^{-1}$) for 2 h. Then they were rinsed thoroughly, filtered and dried at 110°C in a stove. They were finally calcined at 600°C in



Scheme 2.

flowing air ($10 \text{ ml min}^{-1} \text{ g}^{-1}$) for 1 h to remove excess adsorbed sulfate. The catalysts obtained were called SZH^I, SZMT^I, SZM^I and SZT^I. (II) Sulfation of previously reduced zirconia: crystalline materials need a special sulfation method for promotion of catalytic activity because method (I) is normally not effective [6]. A new method was used here, based on some preliminary results obtained at our lab. Samples of ZMT, ZM and ZT were calcined in H₂ at 550 °C for 1 h; then they were cooled to about room temperature and immersed in 1 N H₂SO₄ (10 ml g^{-1} support) for 2 h. Finally they were filtered, dried and calcined as in (I). These catalysts were named ZMT^{II}, ZM^{II} and ZT^{II}.

2.3. Characterization

XRD spectra were recorded in a Shimadzu XD-1 diffractometer using Cu K α radiation filtered with Ni. Textural properties were measured in a Quantachrome NOVA-1000 sortometer; the specific surface area (S_g) was measured by the BET method and the pore distribution by the BJH method. Laser Raman spectra in the 100–900 cm^{-1} range were recorded in a JASCO TRS-600 SZ-P having a NEC Ar ion laser (514.5 nm, power = 40–50 mW). Acidity was measured by IR measurement of adsorbed pyridine. Pyridine adsorption was performed in glass equipment and monitored in the IR region of 1400–1600 cm^{-1} . Self-supporting circular wafers (2 cm diameter, 50 mg) of the catalysts were used, and vacuum treated in a cell with NaCl windows. Residual pressure was less than 1 mTorr. Temperature programmed reduction tests were performed in a Okhura 2002-S apparatus using a TCD detector, 200 mg of sample and a 10 °C min^{-1} heating ramp.

The isomerizing activity of the sulfated catalysts was measured by the test reaction of *n*-butane isomerization (300 °C, 1 atm). Since SZ deactivates rapidly, a pulse reaction system was chosen in order to collect accurate data corresponding to the first instants of time-on-stream (TOS) (0.5 ml *n*-C₄ per pulse, 8 ml min^{-1} N₂ carrier). Pure *n*-C₄ (Matheson, 99.99%) was used and before the reaction all samples were activated at 600 °C (air, 90 min, 10 ml min^{-1}). Because of the different available surfaces of the catalysts, some compensation was done. For SZH, SZT and SZMT, 300 mg were chosen. In the case of SZM, 1000 mg were used, because the catalyst had a very low area. In the case of SZT no correction was

performed, because the dispersion of the supported phase could not be assessed.

Fast potentiometric titrations (FPT) were used to measure the polarizability and O/OH ratio on the surface of the samples before sulfation. A description of the method can be found elsewhere [5,18]. A 0.1 M KNO₃ was used as electrolyte and HNO₃/KNO₃ and KOH/KNO₃ as titrating solutions. The samples tested were: ZMT, ZMT pretreated in H₂ (550 °C, 1 h, 10 ml/min $\text{g}_{\text{cat}}^{-1}$), ZMT pretreated in N₂ (550 °C, 1 h, 10 ml/min $\text{g}_{\text{cat}}^{-1}$). They were tested in two states, without and after rehydration. Non-rehydrated samples were stored immediately after the thermal treatments while rehydrated ones were allowed to rehydroxylate by immersion in water for 3 days. Then they were dried at 110 °C and stored. The relative abundance of OH group types was measured by IR absorption in the 3000–4000 cm^{-1} range. Equipment and sample preparation were the same as those used for acidity measurements. Probed samples were ZH, ZMT, ZM, SZH^I, SZMT^I, SZMT^{II} and SZM^I. The samples were evacuated (residual pressure < 1 mTorr) at 150, 300, 450 and 600 °C for 40 min before recording the spectrum.

3. Results and discussion

3.1. Textural results

The BET specific surface-area values of the samples can be seen in Table 1. Amorphous zirconium hydroxide (ZH) and calcined SZ sulfated in the amorphous state (SZH^I) had the highest areas of all samples and were the only sample with a meaningful amount of micropores. SZH^I: 5 vol.% micropores (radius < 25 Å), 75 vol.% mesopores (25 Å < radius < 250 Å), 20 vol.% macropores (radius > 250 Å). ZH: 12 vol.% micropores, 75 vol.% mesopores, 13 vol.% macropores. The addition of sulfate before calcination stabilized the surface of SZH^I which contributed to the inhibition of sintering and the conservation of part of the micropore volume.

In the absence of the surface stabilization effect of sulfate the area decreased upon calcination in air, as in the case of the ZMT sample. With this support the micropore volume was mostly lost (0.6 vol.%) and the final structure was mainly mesoporous (85 vol.%). The

Table 1
Specific surface area, pore radius and pore volume distribution of the supports and catalysts^a

Sample	Sulfur content (a.u.) (density) ^b	Specific surface area (m ² g ⁻¹)
ZH*	–	252.0
SZH ^I	475 (3.86)	123.0
ZMT	–	77.7
SZMT ^I	168 (2.31)	–
SZMT ^{II}	227 (3.24)	70.1
ZM*	0.0	23.0
SZM ^I	–	22.5
SZM ^{II}	–	21.0
Silica*	–	300.0
SZT ^I	–	125.0
SZT ^{II}	80	110.0

^a All catalysts were calcined in the last step of their preparation except for those marked with asterisks (*) which were only dried at 110 °C.

^b Area of the TPR peak between 400 and 700 °C; density is equal to sulfate groups per nm².

treatment with hydrogen on samples of ZMT (ZMT^{II}) reduced their area, although not to a great extent (about 10%).

3.2. Crystal structure

Fig. 1 shows XRD plots corresponding to the crystalline zirconia. Data for the ratio of intensities of the main peaks of the monoclinic and tetragonal phases, I^M/I^T (M: $2\theta \approx 28^\circ$; T: $2\theta \approx 30^\circ$) at different calcination stages and for zirconia with different sulfation

treatments is shown in Table 2. Samples of ZMT were mainly monoclinic (Fig. 1a) and the ratio of the main peaks of each phase was $I^M/I^T = 1.96$. The I^M/I^T ratio increased a little upon hydrogenation ($I^M/I^T = 2.25$, SZMT^{II}, Fig. 1c). Zirconia sulfated in the amorphous state and then calcined (sample SZH^I, Fig. 1b) was mainly tetragonal, with a ratio $I^M/I^T = 0.349$. The sample of commercial ZrO₂ (ZM) was 100% monoclinic with no tetragonal phase peak at $2\theta = 30^\circ$. Conversely, ZT calcined at 600 °C in air was completely fluoritic with no peak at $2\theta = 28^\circ$. An accurate identification of the structure of the supported zirconia crystallites was difficult because of the great similarity between the cubic and tetragonal phases. In any case, the stabilization of a fluoritic phase in the thermodynamic temperature range of monoclinic zirconia was clear and it was supposed to be related to the small crystal size of silica supported zirconia. Due to the different surface energy of the monoclinic and fluoritic phases of zirconia, as stated by Garvie [19], an energy barrier for the T → M transition exists for small particles (of high surface/mass ratio). The broad peak in the XRD spectrum indicated that the crystal size was much lower than in the case of the SZM and SZH^I samples. This was addressed to a big initial dispersion of the supported zirconia and the retard in crystal growth due to the interaction with the support. The dispersion was only indirectly assessed by the recording of XRD spectra. The crystals in SZT were detectable at temperatures of calcination higher than 500 °C, while crystallization of bulk Zr(OH)₄ into ZrO₂ is known to occur at 375 °C.

Table 2
Ratio of the intensities of the main XRD peaks of the monoclinic and tetragonal phases (I^M/I^T)

Sample		I^M/I^T
ZMT	Zirconia gel calcined at 600 °C 3 h in air	1.96
SZMT ^{II}	SMT reduced 3 h at 600 °C in H ₂ and then sulfated in solution 2 h (A)	2.24
	A calcined in air at 600 °C 1 h	2.04
	A calcined in air at 600 °C 3 h	2.14
	A calcined in air at 600 °C 8 h	2.00
SZMT ^I	ZMT sulfated in solution 2 h, then calcined in air at 600 °C 1 h (B)	1.94
	B calcined 3 h	2.03
	B calcined 8 h	2.10
SZH ^I	Zirconia gel sulfated in solution, then calcined in air at 600 °C 1 h (C)	0.35
	C calcined 3 h	0.32
	C calcined 8 h	0.27

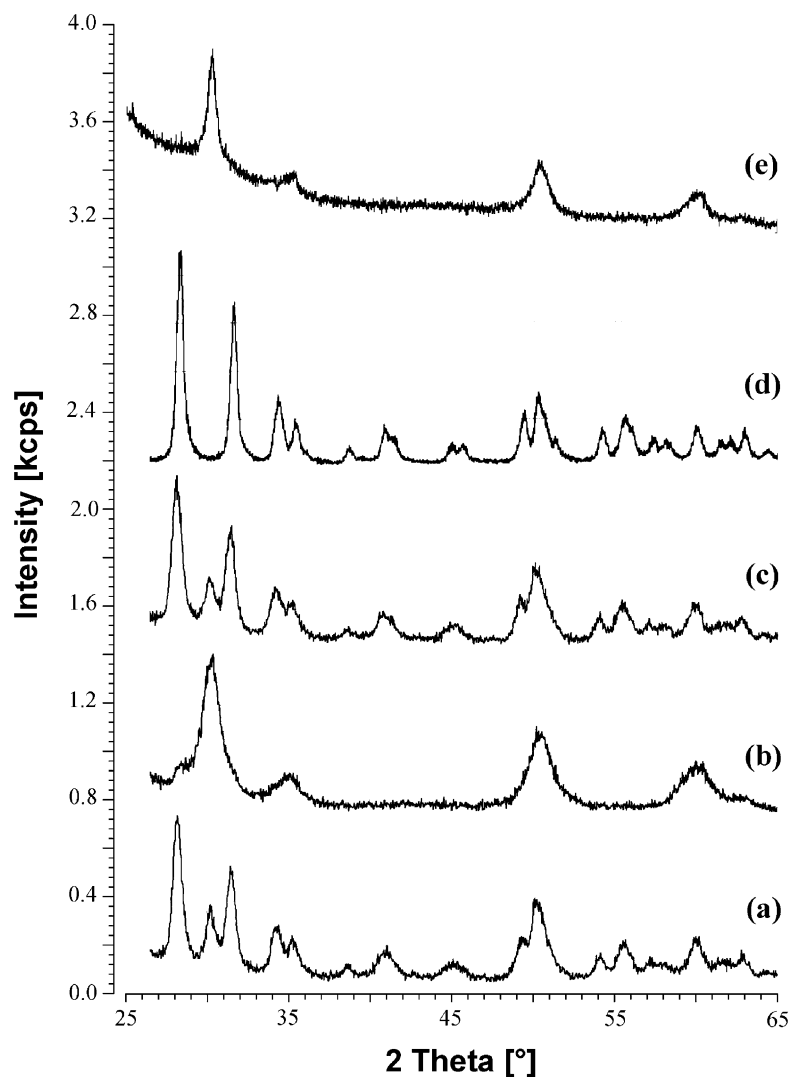


Fig. 1. XRD plots of zirconia samples: (a) ZMT, zirconia gel calcined at 600 °C in air; (b) SZH^I, sulfated zirconia gel calcined at 600 °C; (c) SZMT^{II}, zirconia ZMT treated with H₂ and sulfated; (d) ZM, commercial monoclinic ZrO₂; (e) ZT, zirconia on silica (intensity × 2).

A clear identification of the tetragonal phase present in the SZH^I, SZMT and SZT catalysts was done based on Raman spectra (not shown) and on published reports of Raman spectra of zirconia polymorphs [20,21]. The cubic phase has only one broad Raman band at about 490 cm⁻¹ which was absent in all the samples tested.

For zirconia sulfated in the amorphous gel state, the M/T ratio decreased continuously with calcination (from 0.35 to 0.27), indicating the dominant growth

of the T phase, though it is not thermodynamically favored at 600 °C. Sulfate grafted on crystalline zirconia by common sulfation at room temperature (SZMT^I) seemed not to introduce changes upon calcination; there was a growth of the monoclinic phase and a corresponding increase in the I^M/I^T ratio (from 1.94 to 2.10). However, when the sample was reduced before sulfation, there seemed to be a little growth of the T phase upon calcination, and the M/T ratio decreased (from 2.24 to 2.00).

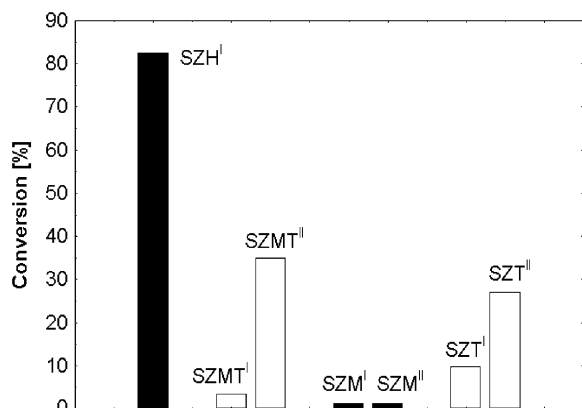


Fig. 2. Initial catalytic activity of sulfated zirconia catalysts (conversion of the first pulse).

3.3. Catalytic activity

Fig. 2 shows a plot of initial activity (conversion of *n*-C₄ in the first pulse) for the sulfated zirconia catalysts. SZH^I, promoted with sulfate in the state of amorphous gel, had the highest initial conversion. SZMT catalysts were almost inactive when promoted by common impregnation at room temperature (SZMT^I). However, ZMT supports became much more active (than SZMT^I) after they were reduced in hydrogen and sulfated (SZMT^{II}). In the case of the SZM catalysts, all samples displayed a very low activity level. This result was not due to the small surface area, because the mass of catalyst used was higher (3.3 times that of SZMT and SZH) and the total area was similar to that of SZMT. All sulfation methods were ineffective in producing active catalysts from purely monoclinic ZM zirconia (SZM^I, SZM^{II}).

SZT catalysts, which were completely tetragonal, were always active, although with a lower level than in bulk SZH^I. The lower activity was due to the small fraction of active phase present (21% Zr). When compared on a basis of equal content of zirconia, bulk and supported SZ catalysts had similar activity levels. For example, the conversion of SZT^{II} was about 30% that of SZH^I for a 20% content of zirconia. If we compare SZT^{II} and SZT^I we can see that SZT^I had a lower activity than SZT^{II}, an effect similar to but less pronounced than in the case of SZMT catalysts. It is noteworthy that SZT^I was active after sulfation at room temperature and with no special treatment. This

result could be attributed to the presence of a substantial amount of amorphous material which did not crystallize due to the interference of the support (then being converted to SZH^I-like material). Another possibility is that crystallinity is not an obstacle for the preparation of successful catalysis, unlike growth of the monoclinic phase (not present in SZT).

To further study the possibility that hydroxylation could play some role in the success of the sulfation method, ZM and ZMT were steamed before sulfation (a variation of method I) during 1 h at 100, 150 and 200 °C (10 ml min⁻¹ g⁻¹). The catalysts were then calcined at 600 °C in air before the run, like the rest of the samples, and their catalytic activity in *n*-butane isomerization was tested. The samples had a similar level of conversion at all steaming temperatures, which was smaller than those of samples sulfated with method (I) (SZMT = 0.98%, SZM = 0.95%). The low conversion was associated in part to a decrease in the total surface area (30% less than the original), but mainly to a different concentration of surface groups able to be converted into active sites upon sulfation. If total rehydration is supposed to have taken place during steaming, another process other than dehydroxylation should then be called upon for not producing active sites from air-calcined zirconia gels.

Fig. 3 shows plots of conversion and selectivity to *i*-butane as a function of pulse number for the most active catalysts. Bulk SZ sulfated in the amorphous state (SZH^I) not only had the highest activity but also the highest initial cracking activity. The zirconia catalysts sulfated in the crystalline state, SZMT^{II} and SZT, which were moderately active, had less cracking activity than SZH^I, a fact reflected in the higher selectivity to *i*-butane and the lower production of C₁–C₃ (not shown). In all cases apart from *i*-C₄, C₁–C₃ products appeared as a result of cracking and a little amount of C₅ coming from dismutation. Butane transformation over SZ catalysts has been reported to proceed through a C₈ adsorbed intermediate [22] which might be cracked (dismutated) to produce C₃ and C₅.

3.4. Temperature programmed reduction

At this point it is necessary to study in more detail the conditions that led to the enhancement of activity in the case of SZMT^{II} catalysts. Activity (initial values of conversion of *n*-butane) as a function of

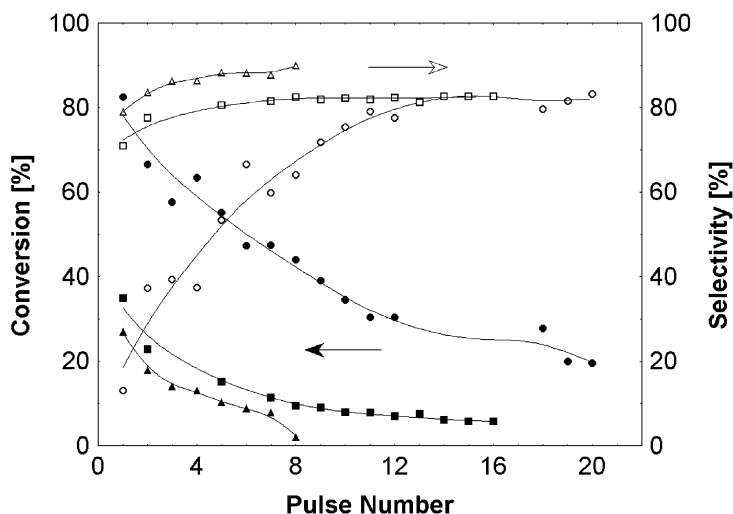


Fig. 3. Catalytic activity as a function of pulse number: (●, ○) SZH^I; (■, □) SZMT^{II}; (▲, △) SZT^{II} (conversion: black labels; selectivity to *i*-butane: hollow labels).

prereduction temperature was measured. Before the catalytic test (and after sulfation) all samples were activated at 600 °C in air. The existence and quantity of reducible species was assessed by TPR. Both results are included in Fig. 4. We can easily distinguish in the plot a volcano shape with one maximum value at 550–600 °C (corresponding to the conversion of SZMT^{II} of Figs. 2 and 3). Hydrogenation of ZMT at temperatures ≥ 400 °C promoted the formation of

active sites in SZMT^{II}, which was otherwise inactive. The volcano peak is fairly smooth and the samples reduced at 550–600 °C had similar conversion values.

The plot of the TPR test of the ZMT sample indicates the existence of two peaks at high temperatures, one at 550–600 °C and the other at 650–750 °C. The first one can be attributed to a surface process of lattice oxygen elimination (formation of anionic vacancies) and reduction of Zr⁴⁺ to Zr³⁺ [23]. The second

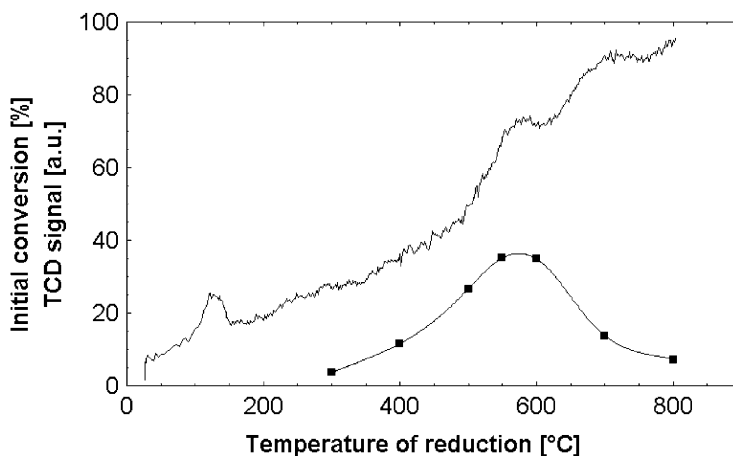


Fig. 4. Initial catalytic activity (conversion of the first pulse of SZMT^{II} (■)) as a function of prereduction temperature (before sulfation) and TPR plot of a ZMT sample.

one may be related to bulk reduction or hydrides formation. The low temperature peak at 120 °C is likely due to water desorption.

ZMT samples reduced at temperatures higher than 500 °C were always slightly gray, a color commonly associated with the formation of anionic vacancies having trapped electrons which are capable of absorbing light [24]. After sulfating and calcining at 600 °C in air, the original white color was recovered. Treatments of reduction in hydrogen at temperatures higher than 600 °C were not able to promote activity, indicating that the amount of reduction is also a sensitive parameter for activity promotion.

Trying to establish a relationship between the catalytic activity and the sulfur content of SZ catalysts is always misleading and is not attempted in this work. It has been demonstrated that a very small fraction of sulfur monolayer can contribute to almost all of the catalytic activity [25]. Sulfur contents before calcination generally amount to 0.5–1.1 monolayers (1 monolayer = 4 S nm^{-2}) and are stabilized at about half a monolayer after calcination at 600 °C [5,26]. Sulfur contents for some samples were indirectly assessed with the area of the 400–700 °C TPR peak due to evolved SO_2 [27] (see Table 1) and indicate a roughly similar sulfur density for SZH and SZMT.

3.5. Acidity

Acidity results are presented in Fig. 5. All catalysts had mainly Lewis acidity and the presence of Brønsted sites was negligible as it was inferred from the low area of the band due to adsorbed pyridinium ion ($1520\text{--}1560 \text{ cm}^{-1}$) for catalysts degassed at 150 °C (not shown). SZH^I had the highest total acidity ($180 \mu\text{mol Py g}_{\text{cat}}^{-1}$), followed by SZM^I ($34 \mu\text{mol Py g}_{\text{cat}}^{-1}$), SZMT^I ($20 \mu\text{mol Py g}_{\text{cat}}^{-1}$) and SZMT^{II} ($25 \mu\text{mol Py g}_{\text{cat}}^{-1}$). Fig. 5 is a plot of the percent distribution of the integrated absorbance of the peak associated to Lewis acid sites (coordinatively bound pyridine, $1430\text{--}1460 \text{ cm}^{-1}$) as a function of evacuation temperature. The plot shows that SZH^I also had the greatest fraction of Lewis sites that retained pyridine at $T > 400 \text{ °C}$ (77.6% strong sites). SZM^I had the lowest fraction (6.0%), while SZMT^I (19.1%) and SZMT^{II} (18.3%) had moderate fractions. In SZMT^{II}, the different sulfation treatment clearly increased the fraction of strong acid sites (relative to SZMT^I) as shown by the bigger peaks at higher temperatures of desorption.

The low fraction of Brønsted acid sites can be related to a low density of surface sulfate, as expected by the high temperature of calcination used (600 °C). According to Morterra et al. [26] strong Lewis sites

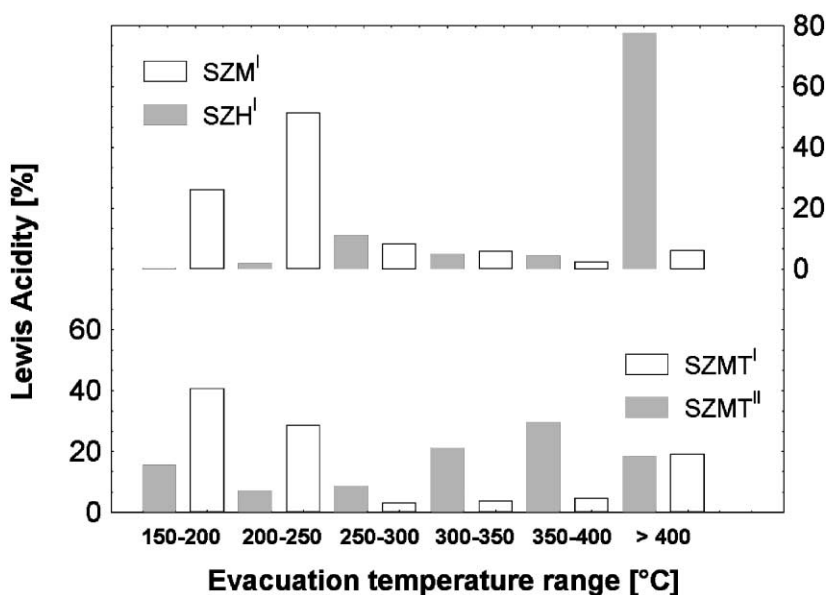


Fig. 5. Normalized distribution of Lewis acidity for different SZ catalysts as a function of evacuation temperature.

are first formed on zirconia lattice defective sites and they are thermally stable. These sites do not form protonic acidity. Conversely, sulfate groups linked to Brønsted sites are the most labile during calcination and would be mainly formed at high contents of sulfate [26]. At temperatures higher than 600 °C, practically no Brønsted sites are detected [28]. Thermal treatments that lead to removal of sulfate largely decrease the proportion of Brønsted sites while Lewis acidity is affected to a minor degree [27]. Only a very small fraction of sulfate groups is needed to produce much of the initial activity of SZ catalysts [25]. These could be the sulfate groups associated with strong Lewis acid sites that are formed by adsorption onto defective lattice sites.

3.6. IR absorption of OH groups

The 3200–4000 cm^{-1} IR range was scanned and the results can be seen in Fig. 6. Most samples were degassed at 300 °C, because in the early stages of the dehydration by evacuation at temperatures lower than 150 °C, and especially at room temperature, the high frequency spectral range (4000–2500 cm^{-1}) was dominated by a broad and unresolved absorption band at $\nu < 3600 \text{ cm}^{-1}$, due to OH stretching modes of both undissociated water molecules and OH species

interacting by H bonding. At degassing temperatures higher than 300 °C, depletion of OH groups began and information could be lost. Due to the possible differences in length of the optical path between different samples and the dehydroxylation effect of vacuum degassing, IR measurements were used only for assessing the relative abundance of OH group types and not for total OH content. The scale of the plots in Fig. 6 has been adjusted to obtain similar size spectra.

The ν_{OH} stretching range is 3000–3850 cm^{-1} and vibrations due to tricoordinated OH (3630–3720 cm^{-1}), dicoordinated OH (3740–3770 cm^{-1}) and monocoordinated OH (3770–3810 cm^{-1}) have been identified on zirconia [29,30]. Before being sulfated all the supports had a relevant fraction of tricoordinated OH groups, especially in the case of the zirconia gel sample (ZH). The other unsulfated supports (ZMT, ZMT^{II} and ZM) also had some monocoordinated OH groups, and this fraction was very important in the case of ZMT. Dicoordinated OH groups were absent on practically all the unsulfated supports and only a small fraction could be detected on ZM. The dominance of tricoordinated OH groups on the surface of zirconia has previously been stated [29]. The appearance of OH with lower coordination upon calcination may indicate that oxolation produces the rearrangement of the remaining adjacent groups which were

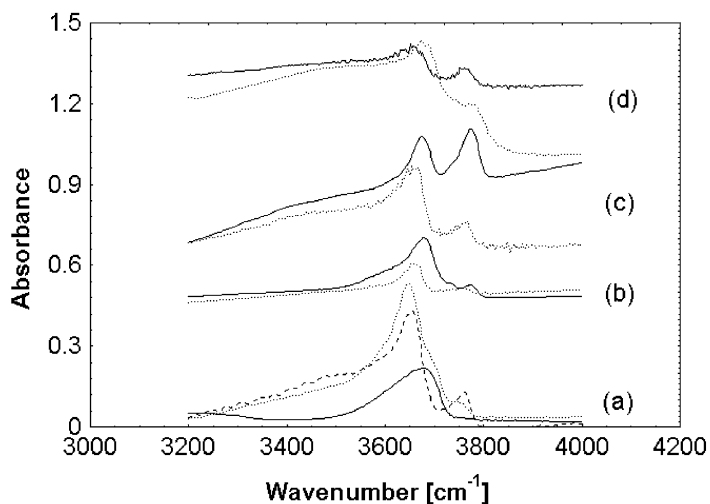


Fig. 6. IR spectrum of the absorption zone of OH groups. If a different value is not stated, an evacuation temperature of 300 °C applies: (a) zirconium hydroxide ZH (full line) and SZH^I evacuated at 300 °C (dotted line) and 375 °C (segmented line); (b) ZM (full line) and SZM^I (dotted line); (c) ZMT (full line) and SZMT^I (dotted line); (d) ZMT treated with hydrogen (full line) and SZMT^{II} (dotted line).

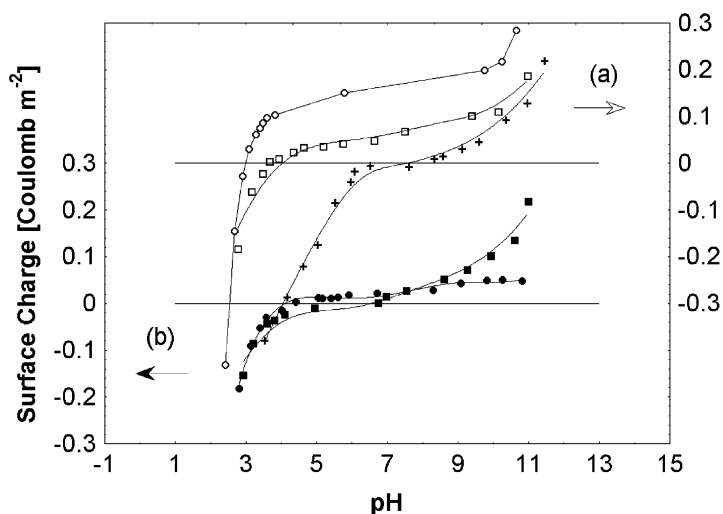


Fig. 7. Potentiometric titrations results. (a) Influence of heat treatments without rehydration: (+) ZH, (○) ZMT (ZH calcined in air at 600 °C), (□) ZMT treated with H₂ (550 °C, 1 h). (b) Influence of rehydration after the treatments: (●) rehydrated ZMT, (■) ZMT treated with H₂ and rehydrated.

not eliminated by calcination. On ZMT^{II} and ZM the more resistant OH groups are the tricoordinated ones which are dominant in these supports.

Upon sulfation the population of OH groups decreased (smaller area in the OH region) and the fraction of single OH groups increased. As was the case with the unsulfated supports, tricoordinated OH groups were the most abundant, a fact that can be seen in the results reported by other authors [31]. The increase in the fraction of single OH groups may be linked to the bonding of sulfate to two adjacent Zr cations of a tricoordinated OH group, leaving the third cation free for the formation of a single OH group. A small signal due to dicoordinated OH was seen on the SZH^I catalyst, but disappeared upon degassing at 375 °C.

3.7. Surface charge

The amount of surface OH groups were indirectly monitored by measuring the polarizability of the samples in order to check the influence of rehydration treatments. FPT in aqueous media were performed to assess the (O/OH) ratio. An increase in the ratio of surface oxygen to surface OH groups has been reported to decrease the isoelectric point (zero point of charge, ZPC) [32]. Surface oxygen would be formed

upon oxolation of adjacent OH groups and dehydroxylated samples would have a more acid and negatively charged surface in aqueous solution.

Fig. 7 shows the curves of surface charge as a function of pH for the different zirconia samples. Zirconia gel was amphoteric. Calcination in air followed by no rehydration produced a shift of the ZPC toward acid values (sample ZMT, a). A further calcination in hydrogen did not modify this behavior substantially, although there was a slight shift toward basic values of pH which could be due to rehydroxilation. Ardizzone et al. [33] have previously reported that calcination in H₂ produces a shift in the ZPC of zirconia.

For the samples rehydrated by immersion in water, the amphoteric character was recovered. Their polarizability was similar to that of fully hydrated zirconia. For the sample calcined in air the ZPC remained rather acidic, which may indicate the presence of higher amounts of remaining surface oxygen. For the samples calcined in hydrogen, the ZPC was about 7. It is also possible that during calcination coordinatively bound water (acting as a Lewis base) would be lost and replaced by some chemisorbed oxygen. In any case the original surface charge was recovered upon rehydration. Therefore one conclusion would be that calcination in air or hydrogen does affect the surface hydroxylation state or the (O/OH) ratio, but hydration

treatments restore the original ZPC (and OH surface density).

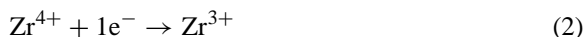
3.8. On the role of anionic vacancies in the stabilization of the T phase and the onset of catalytic activity

Promotion of crystalline zirconia calcined at high temperature in air by a common sulfation technique (wet impregnation at room temperature) is ineffective in producing catalytic activity for *n*-butane isomerization. Two different phenomena occurring during calcination could be made responsible for this effect: dehydroxylation of the surface and crystallization into the monoclinic phase. According to the data of this work it seems appropriate to disregard the importance of dehydroxylation. FPT experiments indicated that heat treatments in air increase the relative proportion of oxygen species in relation to OH species, but that this phenomenon is mostly reversed upon rehydration. If depletion of OH groups occurred in ZMT samples, it was not an obstacle for the onset of activity on SZMT^{II}. Steam rehydration of SZMT followed by sulfation produced no activity. Moreover, and according to our IR measurements, there was not a big difference in the relative abundance of coordination families of OH groups. Tricoordinated OH groups were the most abundant for practically all samples and the trend of increase of the monocoordinated fraction after sulfation was the same both for catalytically active (SZH^I) and inactive samples (SZM^I). The increase in catalytic activity seemingly does not depend on the hydroxylation state of the surface. In the case of the ZMT samples activated in the crystalline state by method (II), the promotion of activity must be related to phenomena other than rehydroxylation.

In the conditions of preparation of this work no active catalysts could be synthesized from monoclinic supports. It cannot be concluded that the tetragonal phase is the only catalytically active phase for SZ catalysts in highly demanding acid catalyzed reactions, because some isolated results of catalysts prepared under special conditions do exist [7,9]. Also, in our case prereluction in H₂ promoted the activity of catalysts with a mixture of M and T phases. We think that a comprehensive explanation of the (crystal phase: catalytic activity) relations found can be sought by

examining the similarities between prerelucted zirconia and the freshly precipitated zirconia gels.

Promotion of catalytic activity in SZMT^{II} was maximum at a prereluction temperature of 550–600 °C. The TPR hydrogen consumption peak in this range is attributed to the loss of surface lattice oxygen. Surface and bulk defective sites would be produced upon treatment at high temperatures in hydrogen as described by Eqs. (1)–(4):



Kröger–Vink notation was adopted. V_O^{••} denotes an oxygen vacancy with no electrons, V_O[•] a vacancy with one electron and V_O[×] is a vacancy with two electrons (and the same charge as the original site, O²⁻). Electrons may remain in the anion vacancy (producing V_O[×] and V_O[•] sites) or reduce a nearby Zr⁴⁺ cation to Zr³⁺. V_O[•] and Zr³⁺ are paramagnetic and have been detected in SZ catalysts by ESR techniques [34].

A new explanation in agreement with our experimental results is that anionic vacancies on the surface of the SO₄²⁻-ZrO₂ catalysts are needed to produce active sites for isomerization of *n*-butane. They would be present in the freshly precipitated gel and their concentration would be enhanced by reduction of crystalline samples at high temperature. We have already proposed a model to account for the possible role of these species in SZ catalysts [35]. The model postulates that anionic vacancies act as sites for charge stabilization. Charge transfer from neutral alkane molecules would be needed for the formation of carbenium ions and radical adsorbed species. A second role of the anionic vacancies, depending on their relative concentration, could be to act as promoters of n-type conductivity in the catalyst [36]. The narrowing of the band gap due to electron donation from the anionic vacancies would enable an easier charge transfer between intermediates through the conduction band of the crystal as it is also postulated in V₂O₅-WO₃/TiO₂deNO_x catalysts [37]. The role of anion vacancies could equally well be to induce strong local adsorption and significant C–H bond polarization. This would increase the

development of partial charge and potentially lower the energy barrier significantly for the transition state.

The posing of another classical model for active sites seems unlikely. Although the prereduction treatment did increase the proportion of Lewis sites with high acid strength (Fig. 6) a correlation between acidity and catalytic activity was not possible. The most active sample (SZH^I) had nearly only sites that desorbed pyridine at temperature >400 °C. SZM^I (catalytically inactive) had a small but non-null fraction of these sites. SZMT^I (inactive) and SZMT^{II} (active) had the same percent fraction.

Posing anionic vacancies as possible active centers for acid catalysis on SZ materials reconciles many results related to catalytic activity of active tetragonal materials, because the link between V_O species and the tetragonal structure has long ago been established. Oxygen vacancies have been reported to be necessary for the stabilization of the T phase of zirconia [13]. Osendi et al. [38] argued that nucleation of metastable tetragonal zirconia is favored by anionic vacancies with trapped electrons. Djuricic et al. [39] found that during crystallization at about 375 °C oxygen vacancies were produced on fired ZrO₂ gels, and they were filled upon heating in O₂ at higher temperatures. If heated in N₂ the oxygen loss increased and the T phase was further stabilized. Torralvo et al. [40] calcined ZrO₂ gels in air and N₂ and found a weight gain in the air-calcined samples, which started at 600 °C and continued up to 800 °C. The gain was attributed to the filling of V_O species.

Transformation of the metastable tetragonal phase towards the stable monoclinic phase seemingly takes place from the surface to the “bulk” by the adsorption of oxygen onto defective sites. Because sulfate is less labile than OH groups, occupation of these sites by sulfate bridges has been claimed to stabilize the tetragonal phase in sulfate doped zirconia [41]. Silver et al. [42] reported results of SO₃ adsorption over yttria doped ZrO₂ and they found that SO₃ was quantitatively adsorbed at surface vacancies as (ZrO)₃S=O.

Our proposed model of structural stabilization and generation of active sites for common SZ catalysts prepared by sulfation in the hydroxide state (SZH^I) is as follows: during the calcination of sulfated zirconia gels at temperatures in the “glow exotherm” after a fast oxolation and restructuring process, oxygen vacancies are produced in the network of SO₄²⁻-ZrO₂. These

vacancies very likely arise as a result of the presence of coordinatively unsaturated cations in the gel and formed during the fast polymerization of Zr(OH)₄. After sulfation, the anchored sulfate would produce a shift in the crystallization temperature, due to both the high thermal stability of sulfate and the introduction of stress in the crystal lattice (sulfate bridge is bigger than OH bridge). More important would be the stabilization of vacancies in the first layers of the zirconia crystals either by a distortion in the network imposed by the size of the ion or by a charge-compensating mechanism. The presence of vacancies would lower the average coordination number (CN) of Zr and then the T structure would be highly favored. Upon calcination in air, there would be no diffusion of oxygen into the network of crystalline zirconia, due to blockage by surface sulfate. ZrO₂ would then crystallize into the T phase.

With the model thus outlined we can now attempt to explain the different catalytic behavior of the samples studied.

3.8.1. ZH sample

Surface oxygen vacancies produced by polymerization of zirconia gel with Zr cations of abnormal coordination are stabilized by preferential sulfate chemisorption on these sites during impregnation with sulfuric acid. More defects in the bulk of growing crystals can be generated if the O/Zr ratio of the water-free gel is lower than 2 because O²⁻ diffusion from the surface is disturbed by sulfate.

3.8.2. ZMT sample

Particles in these samples are supposed to be formed by mainly monoclinic crystals with small T phase crystallites embedded in them. The surface is thought to be stoichiometric with CN = 7 and fully coordinated Zr linked to O and some surface OH groups. Upon treatment with H₂ at high temperatures, oxygen losses from the surface and first lattice layers would create anionic vacancies. The process should be favored near the T crystallites, where Zr is coordinated with CN = 8, producing in these zones a critical concentration of defects necessary for the appearance of catalytic activity. The final surface would be an array of Zr cations, O anions, OH groups and a small amount of vacant oxygen sites. The results of Table 2 indicate that T phase growth was seemingly favored

in this sample. The bias toward T phase might have been due to the stabilization of surface V_O species by sulfate.

3.8.3. ZT sample

The whole particle has Zr cations with CN = 8 probably with anionic vacancies in the bulk. The bias to the T phase is a result of the interaction with the surface of the silica support. The surface layers are thought to be enriched in oxygen with a diminished concentration of defects due to the calcination in air. Some catalytic activity is had with wet impregnation at room temperature. After reduction in hydrogen and sulfation (method II), the concentration of sulfate groups grafted onto anionic vacancies increases and so does the catalytic activity.

3.8.4. ZM sample

The whole particle is in seven-fold coordination and the Zr/O ratio is completely stoichiometric (0.5). Though some surface oxygen vacancies may be produced during sulfation by method (II) a meaningful amount cannot be produced, because oxygen removal needs the reconstruction of the network. No substantial catalytic activity appears. Another report relating the monoclinic structure and the activity of SZ should now be recalled. Similar Raman-UV bands are found on monoclinic zirconia and on coked, deactivated tetragonal SZ catalysts [43]. A similar electronic structure of surface Zr could appear during reaction upon changes in adjacent V_O^X , V_O^\bullet or $V_O^{\bullet\bullet}$ species.

We must remark that the presence of the tetragonal phase in active catalysts seems to be a *consequence* of the stabilization of anionic vacancies after oxoanion promotion of the amorphous zirconia gel. Catalytic activity is thought to be related to the presence of these defects but not to the tetragonal structure itself. The crystal phase is a *bulk* property and catalysis is related mostly to *surface* phenomena. The best counter-example is the tetragonal SZ catalyst which under certain synthesis conditions lacks catalytic activity. Fully tetragonal catalysts prepared by sulfation of gels refluxed at basic pH are inactive in n -C₄ isomerization [10]. Bulk SiO₂ doping of WO_x-ZrO₂ catalysts enhances the stability of the T phase but is completely deleterious to catalytic activity in n -C₄ isomerization [44].

4. Conclusions

Crystalline fully monoclinic zirconia could not be activated with sulfate to produce catalysts that had a meaningful activity level in isomerization of n -butane. Conversely, promotion of activity was greatly favored for tetragonal zirconia samples. Hydrogenation of zirconia at 550 °C, a treatment thought to increase the population of surface anionic vacancies, was found to enhance the formation of active sites on sulfated zirconia for the reaction of n -C₄ isomerization.

SZ catalysts prepared from crystalline zirconia had lower acidity and cracking activity than SZ catalysts prepared by sulfation of amorphous Zr(OH)₄. The catalytic inactivity of SZ catalysts produced by wet impregnation at room temperature of zirconia gels previously calcined in air at 600 °C seems to be due to a surface enrichment of a monoclinic-like, defect-free, stoichiometric zirconia layer.

There likely exists a close relation between the presence of crystalline defects, the stabilization of the tetragonal structure, and the onset of catalytic activity in SZ catalysts. Tetragonal structure in catalysts promoted in the state of amorphous gel is a consequence of the stabilization of anionic vacancies by sulfate. Catalytic activity is supposedly related to charge abstraction and stabilization from radicalar and ionic intermediates, a process enabled or enhanced by anionic vacancies in tetragonal zirconia catalysts.

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References

- [1] R. Srinivasan, Catal. Lett. 9 (1991) 1.
- [2] R.A. Comelli, C.R. Vera, J.M. Parera, J. Catal. 151 (1995) 96.
- [3] R.A. Comelli, C.R. Vera, J.M. Parera, Latin Am. Appl. Res. 24 (1994) 227.
- [4] K. Arata, M. Hino, in: M.J. Phillip, M. Ternan (Eds.), Proceedings of the 9th International Congress on Catalysis Calgary, Vol. 4, Chemical Institute of Canada, Ottawa, 1988, p. 1727.

- [5] C.R. Vera, Thesis, Universidad Nacional del Litoral, Argentina, 1995.
- [6] C.R. Vera, J.M. Parera, *J. Catal.* 87 (1997) 165.
- [7] W. Stichert, F. Schüth, S. Kuba, H. Knözinger, *J. Catal.* 198 (2001) 277.
- [8] C. Morterra, G. Cerrato, C. Emanuel, V. Bolis, *J. Catal.* 142 (1993) 349.
- [9] A.F. Bedilo, A.S. Ivanova, N.A. Pakhomov, A.M. Volodin, *J. Mol. Catal. A* 158 (2000) 409.
- [10] C.R. Vera, K. Shimizu, in: *Proceedings of the 82nd Japan Catalysis Conference, Matsuyama, Japan, 16–19 September 1998*, p. 272.
- [11] J.M. Parera, *Catal. Today* 15 (1992) 481.
- [12] P.D.L. Mercera, J.G. Van Ommen, E.B.M. Doesburg, A.J. Burggraaf, J.R.H. Ross, *Appl. Catal.* 79 (1991) 78.
- [13] P. Li, I.W. Chen, J.E. Penner-Hahn, *J. Am. Ceram. Soc.* 77 (1994) 118.
- [14] J.C. Yori, C.L. Pieck, J.M. Parera, *Catal. Lett.* 52 (1998) 3.
- [15] G.K. Chua, S. Jaenicke, *Appl. Catal. A* 163 (1997) 261.
- [16] C. Márquez-Alvarez, J.L.G. Fierro, A. Guerrero-Ruiz, J. Rodríguez-Ramos, *J. Colloids Interf. Sci.* 454 (1993) 159.
- [17] S. Damyanova, P. Grange, B. Delmon, *J. Catal.* 168 (1993) 421.
- [18] W. Stumm, J. Morgan, *Aquatic Chemistry*, Wiley/Interscience, New York, 1970.
- [19] R.C. Garvie, *J. Phys. Chem.* 69 (1965) 1238.
- [20] V.G. Keramidis, W.B. White, *J. Am. Ceram. Soc.* 57 (1974) 22.
- [21] C.M. Phillippi, K.S. Mazdiyasi, *J. Am. Ceram. Soc.* 54 (1971) 254.
- [22] C.R. Vera, C.L. Pieck, K. Shimizu, C.A. Querini, J.M. Parera, *J. Catal.* 187 (1999) 39.
- [23] F.R. Chen, G. Coudurier, J.F. Joly, J.C. Vedrine, *J. Catal.* 143 (1993) 616.
- [24] V.A. Shvets, A.V. Kuznetsov, V.A. Fenin, V.B. Kazansky, *J. Chem. Soc., Faraday Trans. I* 81 (1985) 2913.
- [25] J.C. Yori, J.M. Parera, *Appl. Catal. A* 151 (1995) 129.
- [26] C. Morterra, G. Cerrato, C. Emanuel, V. Bolis, *J. Catal.* 142 (1993) 349.
- [27] B.-Q. Xu, W.M.H. Sachtler, *J. Catal.* 167 (1998) 224.
- [28] M. Tran, N.S. Gnep, G. Szabó, M. Guisnet, *Appl. Catal. A* 207 (1998) 171.
- [29] T. Yamaguchi, Y. Nakano, K. Tanabe, *Bull. Chem. Soc. Jpn.* 51 (1978) 2482.
- [30] G. Cerrato, S. Bordiga, S. Barbera, C. Morterra, *Appl. Surf. Sci.* 115 (1997) 53.
- [31] V. Adeeva, J.W. de Haan, J. Jänchen, G.D. Lei, V. Schünemann, J.M. van de Ven, W.M.H. Sachtler, R.A. van Santen, *J. Catal.* 151 (1995) 364.
- [32] G.A. Parks, *Adv. Chem. Ser.* 67 (1967) 121.
- [33] S. Ardizzone, M.G. Cattania, M. Sarti, *Colloids Surf.* 68 (1992) 25.
- [34] D. Spielbauer, G.A. Mekhemer, E. Bosch, H. Knözinger, *Catal. Lett.* 36 (1996) 59.
- [35] C.R. Vera, J.C. Yori, J.M. Parera, *Appl. Catal. A* 167 (1998) 75.
- [36] A. Clark, in: *The Chemisorptive Bond, Electron-Bond Theory and the Ionic Bond*, Academic Press, New York, 1974, Chapter V, p. 74.
- [37] L.J. Alemany, L. Lietti, N. Ferlazzo, P. Forzatti, G. Busca, E. Giamello, F. Bregani, *J. Catal.* 155 (1995) 117.
- [38] M. Osendi, J.S. Moya, C.J. Serna, J. Soria, *J. Am. Ceram. Soc.* 68 (1985) 135.
- [39] B. Djuricic, S. Pickering, D. Mc Garry, P. Glaude, P. Tambuyser, K. Schuster, *Ceram. Int.* 21 (1995) 195.
- [40] A.J. Torralvo, M.A. Alario, J. Soria, *J. Catal.* 86 (1984) 473.
- [41] R. Srinivasan, T. Watkins, C. Hubbard, B.H. Davis, *Chem. Mater.* 7 (1995) 725.
- [42] R. Silver, C.J. Hou, J.G. Ekerdt, *J. Catal.* 118 (1989) 400.
- [43] C. Li, P.C. Stair, *Catal. Lett.* 36 (1996) 119.
- [44] R.A. Boyse, E.L. Ko, *J. Catal.* 179 (1998) 100.