Physico-chemical features and catalytic activity of sulfated zirconia prepared by sol–gel method. The role of the solvent evaporation step

Stefano Melada [a], Michela Signoretto [a,*], Silvia A. Ardizzone [b] and Claudia L. Bianchi [b]

[a] *Department of Chemistry, University of Venice, Calle Larga St.Marta 2137, I-30123 Venice, Italy*
E-mail: miky@unive.it
[b] *Department of Physical Chemistry and Electrochemistry, University of Milan, Via Golgi 19, I-20133 Milan, Italy*

Received 27 March 2001; accepted 4 June 2001

ZrO_2–SO_4 powders have been prepared by following a single-step sol–gel preparative route using zirconium propoxide as the starting compound. Sulfuric acid was employed both as the sulfating agent and as the catalyst of the polycondensation reaction in the gel formation. Two different series of dried precursors were obtained by either evaporating the solvent in an oven at 100 °C (xerogels) or in supercritical conditions (aerogels). All the samples were calcined at three temperatures (470, 550, and 630 °C) for the same time length (5 h). The powders were characterized for phase composition–crystallinity, surface area–porosity, sulfur content and surface state (XPS). The catalytic activity of the calcined samples was tested in the isomerization of n-butane in a continuous system at 150 °C in absence of H_2 and 250 °C in presence of H_2. The role played by the conditions of the solvent elimination, at the end of the sol–gel reaction, in affecting the physico-chemical and catalytic properties of the powders is discussed.

KEY WORDS: sulfated zirconia; sol–gel route; n-butane isomerization

1. Introduction

In recent years great interest was devoted to the search for new solid catalysts which might replace strongly acidic homogeneous catalysts for different reactions and, mainly, for the isomerization of alkanes. Sulfated zirconia (SZ) has proved to be very efficient especially in the case of the isomerization of n-butane showing both good selectivity and lower temperature performance with respect to previous catalysts [1,2]. SZ has consequently been the object of extensive research both applied and fundamental and, in some cases, even contradictory data were reported in the literature. The presence of controversial evidence concerning the features of SZ can be related to the fact that even slight modifications in the preparation procedure of these compounds may provoke relevant variations in the final features of the products, and eventually in their catalytic performance [3–8].

A common feature in the preparation of these compounds is a stepwise procedure consisting in the impregnation of aqueous H_2SO_4 or $(NH_4)_2SO_4$ on previously precipitated $Zr(OH)_4$, followed by drying and calcination. These multistep procedures necessarily involve the presence of numerous variables which may not be easily controlled provoking lack of reproducibility in the sample features. For example, in the case of hydrothermal precursor precipitations, even slight variations of the composition of the precipitating mixture (*e.g.*, pH) provoke relevant modifications in the phase composition of ZrO_2, these in turn implying differences in specific surface area, degree of hydration and surface electrification [9].

More recently sol–gel routes, which employ as starting compounds zirconium alkoxides, have been proposed to prepare SZ catalysts [10–12]. In these preparations sulfates can be added by washing thoroughly at room temperature the hydrous zirconia with a sulfuric acid solution [13]. This leads to adsorption of the sulfate anions on the surface of zirconia. A second sulfate introduction method uses the incipient wetness impregnation of ammonium sulfate onto the hydrous zirconia drying to 110 °C [3] yielding final products with essentially the same features. Alternatively, a zirconia-sulfate co-gel is formed by including sulfate ions during the gelation step [14]. In this one-pot preparation the H_2SO_4 is at the same time the sulfating agent and hydrolysis polycondensation catalyst.

In these preparations, after the polycondensation reaction the excess solvent can be eliminated by either evaporation in an oven at 100 °C or under supercritical conditions. The first procedure is obviously simpler and easily performed but it might lead to samples showing surface contamination by the organic component. Consequently the choice of how to perform this latter step is not trivial, especially in the case of a catalyst where the surface state is ruling the reactivity. Further the solvent elimination route might affect not only the surface features but also the bulk and morphological characteristics of the powders.

The aim of this work was actually to compare the physico-chemical properties (structure, surface area, sulfur

---

[*] To whom correspondence should be addressed.

1011-372X/01/0900-0199$19.50/0

content) and the catalytic activity in the isomerization of *n*-butane of two series of samples, xerogels and aerogels, prepared by a common single-step sol–gel route and calcined at three increasing temperatures to evidence the effects provoked by the sole variation of the solvent elimination conditions.

2. Experimental

2.1. Sample preparation

SZ xerogel (X) and aerogel (A) were prepared by the sol–gel technique using zirconium *n*-propoxide, $Zr(OPr)_4$, as a precursor. Initially, a solution is prepared by mixing $Zr(OPr)_4$ (57 ml, 70% solution in *n*-PrOH), an amount of sulfuric acid (1.5 ml), and *i*-PrOH as the solvent (37 ml). To this solution water dissolved in *i*-PrOH (100 ml) is added dropwise with stirring. The molar ratio $H_2O/Zr(OPr)_4$ was 14.

Drying of the gel can be carried out either by evaporation in air for 43 h by increasing the temperature from 40 to 100 °C to obtain the xerogel, or by removing *i*-PrOH under supercritical conditions ($P = 60$ bar, $T = 250$ °C) to obtain the aerogel. In the supercritical drying the gel was placed in an autoclave and flushed with nitrogen at 5 bar, to prevent evaporation of the solvent. Then pressure and temperature were raised above the critical point of the solvent. After a period of thermal equilibration (1 h), the pressure was isothermally relaxed at a constant rate. To remove residual alcohol, the autoclave was flushed again with nitrogen and subsequently cooled to room temperature (25 °C). Then the samples were calcined at 470, 550, and 630 °C for 5 h in an oven open to the atmosphere.

2.2. Sample characterization

Surface area and pore size information was obtained from nitrogen adsorption/desorption isotherms at −196 °C in a Coulter SA 3100 analyzer.

Mesopore size distributions were calculated using the Barrett, Joyner and Halende (BJH) method. Assessments of microporosity were made from *t*-plot constructions, using the Harkins–Jura correlation with *t* as a function of p/p_0.

The nature of gel before calcination and the nature of the crystalline phase after calcination were ascertained by X-ray diffraction patterns obtained using a Siemens D500 diffractometer.

The amount of sulfate before and after calcination was determined by ion chromatography (IEC) after dissolution of the materials [15].

Thermal analysis was performed on the non-calcined samples in order to obtain information on the loss of sulfur, water, and carbonaceous residues and phase transitions involved in the calcination step. DTA/TG analyses were conducted on a Netsch instrument.

XPS spectra were obtained using an M-probe apparatus (Surface Science Instruments). The source was monochromatic Al K_α radiation (1486.6 eV). A spot size of 200×750 μm and a pass energy of 25 eV were used. The energy scale was calibrated with reference to the $4f_{7/2}$ level of a freshly evaporated gold sample, at 84.00 ± 0.1 eV, and with reference to $2p_{3/2}$ and 3s levels of copper at 932.47 ± 0.1 and 122.39 ± 0.15 eV, respectively; 1s level hydrocarbon–contaminant carbon was taken as the internal reference at 284.6 eV. The position and FWHM of the C 1s line were checked carefully for every independent determination. The accuracy of the reported binding energies (BE) can be estimated to be ±0.2 eV.

The *n*-butane isomerisation reaction was carried out at atmospheric pressure at 150 and 250 °C. The feed was dependent on the reaction temperature and the type of catalyst. At 150 °C the feed was composed by a mixture of *n*-butane and helium ($C_4H_{10}/He = 1/4$) and at 250 °C by *n*-butane and hydrogen ($C_4H_{10}/H_2 = 1/4$). Prior to the reaction, all catalysts (0.5 g) were activated in dry air (50 ml/min) at 450 °C for 90 min. Isobutane was analyzed on line by gas chromatography.

Reaction rates were defined as mole of *n*-butane converted per m^2 of catalyst per unit of time.

3. Results and discussion

Table 1 reports the surface areas and the pore volumes of the two series of samples as a function of the calcination temperature. The first striking difference appears from the comparison between the areas of the two uncalcined precursors. The area pertaining to the xerogel is about three times larger than the one of the aerogel. Further, also the trend with the temperature of the two series is different. The xerogels show a sharp and continuous decrease in surface area with the temperature, the more so in the lower temperature region. The aerogels, instead, exhibit an almost invariant pattern and only the highest calcination temperature provokes a slight decrease in area. In the case of the aerogels, the supercritical evaporation conditions adopted presently are rather severe. In fact the removal of *i*-PrOH as the supercritical fluid requires to reach relatively high temperature and pressure (*i.e.*, 250 °C and 60 atm). The adoption of combined high pressure and temperature imposes almost totally the

Table 1
Surface and bulk structure characterization of the samples. A = amorphous, T = tetragonal, and M = monoclinic. Symbols in parentheses indicate an amount <10%.

Sample	Surface area (m^2/g)	Pore volume (ml/g)	Crystal phase
SZX	437	0.7537	A
SZX470	242	0.5261	A
SZX550	179	0.4575	T (A)
SZX630	136	0.3637	T (M)
SZA	151	0.1442	T + M
SZA470	148	0.1672	T + M
SZA550	144	0.1694	T + M
SZA630	110	0.1795	T + M

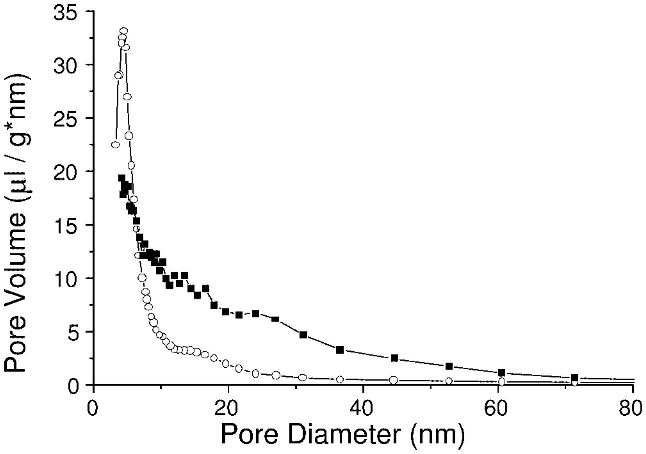

Figure 1. Pore size distribution curves for the aerogel (○) and the xerogel (■) samples calcined at 630 °C.

features of the samples during the solvent elimination making the effects of the mere calcination temperature almost un-appreciable. Strukul *et al.* [11] have reported similar effects for sol–gel SZ samples dried in supercritical conditions and have invoked the occurrence of a sort of "homogenizing effect" during the solvent supercritical elimination. The present larger values of the xerogels surface areas are, instead at variance with the results by Strukul *et al.*, who report for calcined xerogels surface areas which are lower than the ones of the relative aerogels. The present larger areas of the xerogels are to be related, in the first instance, to the highest porosity of the powders with pores prevailingly in the mesopore region (figure 1).

Vicarini *et al.* [16] have reported a similar comportment for sol–gel samples dried at room temperature (xerogel) or in supercritical conditions (aerogel) when the $H_2O/Zr(OPr)_4$ ratio is > 4 and the solvent is benzene. They found that, in the case of the aerogel samples, an increased $H_2O/Zr(OPr)_4$ ratio, in the reacting mixture, enhances not only Ostwald ripening and coalescence-coarsening, resulting in narrower and almost symmetric pore size distribution, but also segregation–crystallization.

A higher crystallinity of the aerogels, with respect to the xerogels, can be observed also in the present case. The xerogels (figure 2) appear to be amorphous for temperatures up to around 500 °C and then, for higher temperatures, they crystallize to the tetragonal form, showing a minor monoclinic component only at 630 °C. The variations of the structural features of the xerogels with the temperature of calcination are in agreement with the major part of literature results. In fact the "doping" of zirconia with sulfates is generally reported to reduce the crystallite sizes and to stabilize the tetragonal polymorph. The aerogels appear to be crystalline even at the lowest temperature and the crystal phase composition is unaffected by the calcination treatment (figure 3), the only effect being a slight increase in the crystallite size. The most striking difference between the highest temperature aerogels and xerogels is the major presence of the monoclinic component in the aerogels. This occurrence is definitely unusual for SZ even in the case of aerogels. The formation of the monoclinic form seems to be in the present case promoted by the high ratio $H_2O/Zr(OPr)_4$ and by the high pressure adopted in the supercritical evaporation procedure.

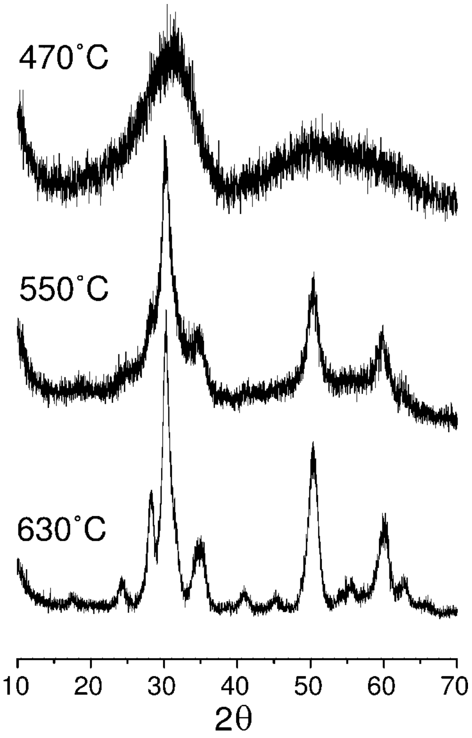

Figure 2. XRD spectra of calcined xerogels.

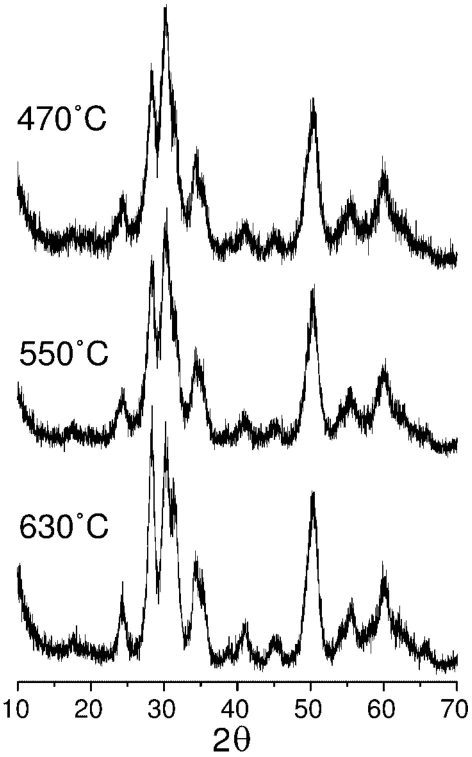

Figure 3. XRD spectra of calcined aerogels.

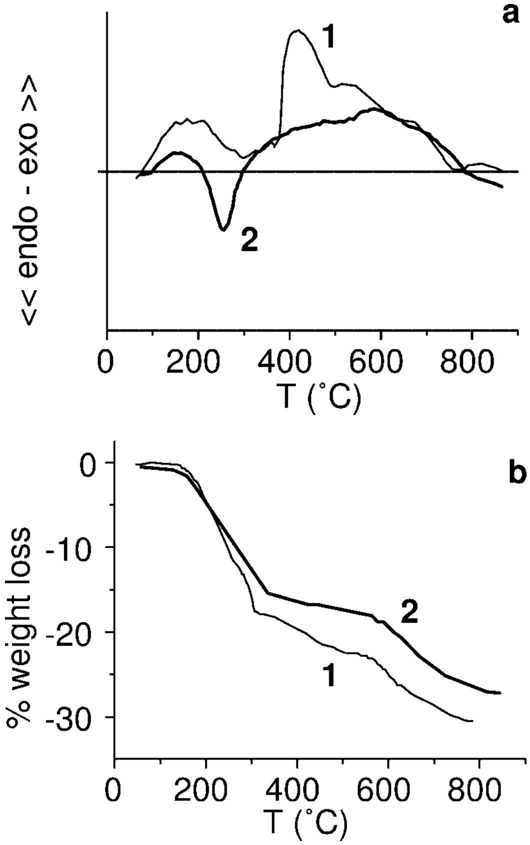

Figure 4. (a) DTA curves for SZX (1) and SZA (2). (b) TGA curves for SZX (1) and SZA (2).

The effect of the "homogenizing effect" in the aerogel synthesis can be observed also by thermal analysis (figure 4). The DTA and TG curves for the aerogel precursor are very smooth and only two weight loss peaks can be observed in the DTG curve. The first centered at 100 °C (11%) is endothermic and can be attributed to water loss, the second, broader, is the sulfur loss centered at 650 °C (7%). One can observe also a little but continuous loss of weight from 200 to 650 °C (5%) associated to an exothermic effect. This is probably due to the loss of carbonaceous species and weakly bound sulfur at the oxide surface.

By contrast, the thermal curves for the xerogel are more complicated, but this is an obvious consequence of the more crowded surface of this sample. Here we note a double consecutive loss of weight at low temperature: DTG peaks centered at 180 °C (12%) and 240 °C (4%), the first with a weak heat absorption and the second showing a strongly exothermic peak (loss of carbon). Then from 250 to 650 °C – where there is the sulfate loss peak (7%) – three, partially overlaid, exothermic peaks can be observed. The first and the second (respectively centered at 290 and 450 °C) can be attributed to the loss of the more tightly bound organic species and sulfur, in fact they are associated with a weak weight loss. The third peak, centered at 570 °C and associated with no weight loss, could be the transition from amorphous to tetragonal polymorph. This interpretation can explain the different behavior for the two series of calcined samples. The xerogel weight loss (30%) is bigger than that of aerogel (23%) because of the former more encumbered surface; this is a consequence of the solvent evaporation conditions.

Table 2
Sulfate contents on the surface and in the bulk using different methods.

Sample	$\%SO_4$ before activity test			$\%SO_4$ after activity test	
	SO_4 (wt%) by XPS	SO_4 (wt%) by IEC	SO_4/nm^2 by IEC	SO_4 (wt%) by IEC	SO_4/nm^2 by IEC[a]
SZX	–	10.44	1.50	–	–
SZX470	18.7	7.63	1.98	7.45	1.93
SZX550	14.8	7.55	2.65	7.37	2.58
SZX630	10.1	5.28	2.44	3.90	1.80
SZA	–	9.67	4.02	–	–
SZA470	17.2	7.82	3.31	6.91	2.93
SZA550	15.6	7.10	3.09	5.32	2.32
SZA630	10.1	3.58	2.04	3.43	1.96

[a] Surface areas used in calculation are that of samples before the activity test, because we did not measure areas on exhausted samples.

In table 2, a summary of some analytical and morphological properties of the samples is shown. A strong decrease in the actual amount of sulfate retained by the samples, after evaporation of solvent, with respect to the nominal sulfate content (16.4 wt% with respect to ZrO_2) can be appreciated.

The sulfur content, as a percent weight, shows, for both series of samples, a continuous decrease with the temperature of calcination as could have been expected on the grounds of the progressive elimination of sulfur observed for SZ samples by TGA [17], as previously mentioned and also reported by numerous literature results [7]. The aerogel precursor contains a lower amount of sulfur, as a percent weight, with respect to the xerogel and the effects of the calcination at increasing temperature are less appreciable than for the xerogels. These effects can be attributed, as already seen, by analogy with the trends of the surface areas, to the severe "uniforming" conditions adopted during the solvent elimination. Due to the larger values of the xerogels surface areas the surface density of sulfates are lower for the xerogels than for the aerogels; in the case of these latter samples the surface density is of about 3 SO_4 groups/nm^2, which is rather close to 4, the value estimated for the monolayer coverage of the surface by sulfates.

Survey XPS spectra were recorded for all samples. No significant presence of impurities was observed, except for the contaminant carbon. The regions of Zr 3d, O 1s, S 2p and C 1s were specifically investigated. The spectrum of S 2p was, in the case of all samples, regular and showed no peculiarities. The peak was fitted by a single component yielding a BE (169.0 eV) in agreement with the one relative to sulfur in sulfates [18] and with previous results relative to sulfated zirconia samples [5,17,19]. For all samples the zirconium peak showed the regular 3d doublet, with BE (182.2 and 184.6 eV) in agreement with literature data for Zr(IV) in the oxide [18]. The regularity of the Zr 3d doublet in the case of sulfated zirconia samples is not a general feature. In the case of samples sulfated by impregnation with either sulfuric acid or ammonium sulfate even important distortions of the doublet were observed, especially in the case of sam-

Table 3
XPS atomic ratios for calcined samples.

Sample	S/Zr	C/Zr
SZX470	0.24	1.10
SZX550	0.19	0.95
SZX630	0.13	0.50
SZA470	0.22	0.78
SZA550	0.20	0.57
SZA630	0.13	0.43

ples calcined at temperatures lower than 500 °C [17,19,20]. Considering the comparison between the atomic ratios between sulfur and zirconium it can be observed (table 3) that the ratios decrease with the temperature as expected and as already commented, in this paper, concerning the bulk sulfur content (table 2). The values relative to the two series of samples (xerogels and aerogels) do not show appreciable differences.

The oxygen 1s peak showed, as expected [17], the presence of more than one component, the main at lower BE (530.0 eV) due to oxygen in the oxide lattice and two further components respectively due to surface OH groups and to oxygen in sulfates. In the case of the C 1s peak only the component at 284.6 eV is present (–CH– species). On this basis, the occurrence of oxygen-containing carbon species and oxygen-containing organic contaminants (BE above 284.6 eV) can be excluded. This observation in the case of sol–gel samples prepared from an aqueous organic mixture is very relevant; in fact it allows one to exclude an appreciable organic contamination of the surface arising from the oxide preparation route, often suggested in the literature in the case of these preparations [21]. In the present case presumably the lack of appreciable organic contamination of the surface can be traced back to the high water/zirconium ratio adopted in the precipitation. The atomic ratios C/Zr, reported in table 3, decrease with the temperature of calcinations for both series due to the progressive combustion of organic species and are larger in the case of xerogels.

The reactivity of SZ samples (aerogel and xerogel) in the isomerization of n-butane was initially checked at 150 °C in the absence of hydrogen. The results obtained for the catalysts are summarized in figure 5 where the activity (expressed μmol isobutane formed/h m^2) *vs.* time is reported. The type of profile shows fast decay of activity during the reaction, probably due to a partial deactivation process. The reaction appeared to be sensible to temperature variations.

When the reaction is carried out at 250 °C in H_2 (figure 6), after an initial decay of activity, the catalysts remain stable for long time on stream. An important reason for deactivation of SZ catalysts is generally considered to be the formation of oligomeric species on the active sites. When hydrogen is present, catalytic reduction of carbonaceous residue occurs.

It can be noted that only the samples calcined at the highest temperature are active, whereas the samples calcined at low temperature exhibit only an initial activity. This is in agreement with a previous finding by Morterra *et al.* [22] in the case of a SZ catalyst, prepared by sulfating a crystalline tetragonal zirconia sample. Catalytic activity is induced by the calcination step; in fact, during the heating, the selective elimination of sulfates from some specific (defective) terminations of the zirconia crystallites occurs, these positions belonging to the high-symmetry crystal planes.

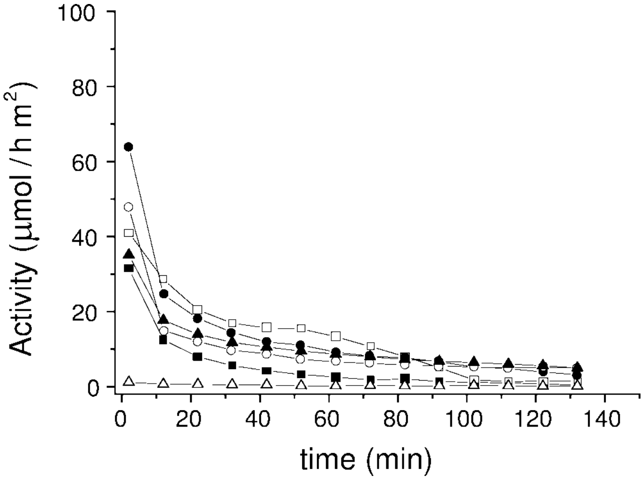

Figure 5. Catalytic activity for n-butane isomerization tests at 150 °C in helium flow. Empty signs stand for xerogels and full signs for aerogels ((□, ■) sample calcined at 630, (○, ●) at 550 and (△, ▲) at 470 °C).

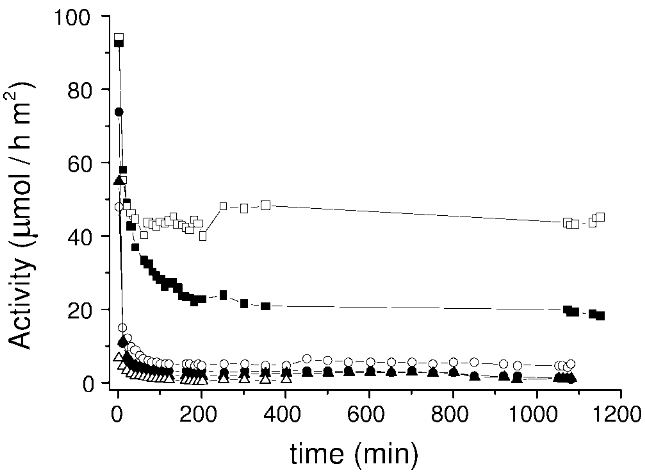

Figure 6. Catalytic activity for n-butane isomerization tests at 250 °C in hydrogen flow. Empty signs stand for xerogels and full signs for aerogels ((□, ■) sample calcined at 630; (○, ●) at 550 and (△, ▲) at 470 °C).

Between the two samples calcined at 630 °C, the xerogel exhibits the best catalytic activity. A possible explanation for the different activity shown by xerogel and aerogel samples calcined at the highest temperature can be found in the different crystalline zirconia polymorph present in the samples. In fact it has been reported that a stable tetragonal or cubic zirconia phase [23] seems to be a necessary structural condition to obtain SZ systems catalytically active in the isomerization reaction of light n-alkanes. Only in a few cases it was claimed that SZ systems, where the zirconia is present in monoclinic phase, may lead to catalytic performances comparable to those of tetragonal SZ catalysts [24,25].

4. Conclusion

This work shows that catalytically active SZ systems can be obtained by a sol–gel method. The catalytic activity of the xerogel samples turns out to be far the highest with respect to the aerogel samples. A possible explanation for the different activity can be found in the different crystalline zirconia polymorph present in the samples, in particular the major presence of the monoclinic component in the aerogel samples. The formation of the monoclinic forms seems to be in the present case promoted by the high ratio H_2O/ $Zr(OPr)_4$ and by the high pressure adopted in the supercritical evaporation procedure.

We find also that only the samples calcined at the highest temperature are active whereas the samples calcined at low temperature exhibit only an initial activity.

References

[1] K. Arata, Adv. Catal. 37 (1990) 165.
[2] M. Hino and K. Arata, J. Chem. Soc. Chem. Commun. (1980) 851.
[3] C. Morterra, G. Cerrato, F. Pinna, M. Signoretto and G. Strukul, J. Catal. 149 (1994) 181.
[4] J.M. Parera, Catal. Today 15 (1992) 481.
[5] K. Ebitani, J. Konishi and H. Hattori, J. Catal. 130 (1991) 257.
[6] K. Ebitani, H. Konno, T. Tanaka and H. Hattori, J. Catal. 135 (1992) 60.
[7] B.H. Davis, R.A. Keogh and R. Srinivasan, Catal. Today 20 (1994) 219.
[8] T. Yamaguchi, Appl. Catal. 61 (1990) 1.
[9] S. Ardizzone and C.L. Bianchi, J. Electroanal. Chem. 465 (1999) 136.
[10] D.A. Ward and E.I. Ko, J. Catal. 157 (1995) 321.
[11] G. Strukul, M. Signoretto, F. Pinna, A. Benedetti, G. Cerrato and C. Morterra, in: *Advanced Catalysts and Nanostructured Materials* (Academic Press, New York, 1996).
[12] M. Signoretto, F. Pinna, G. Strukul, G. Cerrato and C. Morterra, Catal. Lett. 36 (1996) 129.
[13] D. Fărcaşiu and J.Q. Li, Appl. Catal. 175 (1998) 1.
[14] D.A. Ward and E.I. Ko, J. Catal. 150 (1994) 18.
[15] C. Sarzanini, G. Sacchero, F. Pinna, M. Signoretto, G. Cerrato and C. Morterra, J. Mater. Chem. 5 (1995) 353.
[16] M.A. Vicarini, G.A. Nicolaon and S.J. Teichner, Bull. Soc. Chim. Fr. 5 (1970) 1651.
[17] S. Ardizzone, C. Bianchi and E. Grassi, Colloids Surf. 135 (1998) 41.
[18] J.F. Moulder, W.F. Stickle and K.D. Bomben, *Handbook of X-ray Photoelectron Spectroscopy* (Perkin–Elmer, Eden Prairie, 1992).
[19] S. Ardizzone and C.L. Bianchi, Appl. Surf. Sci. 152 (1999) 63.
[20] S. Ardizzone, C.L. Bianchi and M. Signoretto, Appl. Surf. Sci. 136 (1998) 213.
[21] S. Ardizzone, Chim. Ind. 81 (1999) 599.
[22] C. Morterra, G. Cerrato and M. Signoretto, Catal. Lett. 41 (1996) 101.
[23] C. Morterra, G. Cerrato, F. Pinna and M. Signoretto, J. Catal. 157 (1995) 109.
[24] T. Riemer, D. Spielbauer, M. Hunger, G.A.H. Mekhemer and H. Knözinger, J. Chem. Soc. Chem. Commun. (1994) 1181.
[25] A.F. Bedilo, A.S. Ivanova, N.A. Pakhomov and A.M. Volodin, J. Mol. Catal. A 158 (2000) 409.