Catalytic properties of sulfated and non-sulfated ZrO_2–SiO_2: effects of the sulfation submitted before or after the calcination process, in the cyclohexene isomerization reaction

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Abstract

Catalytic properties of sulfated and non-sulfated ZrO_2–SiO_2 (14% molar in ZrO_2) for cyclohexene conversion (skeletal isomerization and hydrogen transfer) have been studied. The effects of the sulfation, submitted before or after the calcination process upon textural, morphological and surface acidity, have been studied. All these properties were correlated to explain catalytic behaviour of the non-sulfated and sulfated samples. It has been shown that catalytic activities were increased on sulfated samples, but at the same time products of the hydrogen transfer reaction seem to increased too, lowering the selectivity of the reaction; isomerization always predominates. For a given temperature, when sulfation process is submitted before calcination the catalytic activities are lower than those obtained when the sulfation is submitted after the calcination process. In summary, the effect of calcination temperature, the presence of sulphate groups on the surface and the sequence of the sulfation procedure (before or after the calcination process) seem to be important parameters on the catalytic properties for cyclohexene isomerization reaction exhibited by this kind of catalysts. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The catalytic properties of metal oxide surfaces are typically described in terms of acid–base properties. Some reactions require acid sites while others occurs on basic sites. Those oxides used as industrial catalysts are often multicomponent materials [1]. It has been found that the acid properties of mixed metal oxides can be varied by choosing different metal oxide constituents at different concentrations and by changing the treatment of the samples [1]. Thus, it appears that by properly choosing the aforementioned variables, mixed oxides could be used to develop new catalysts with desired acid properties.

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Zirconia, ZrO_2, is an important material that finds application in several fields, in particular has been reported as catalyst with specific catalytic activity for a wide range of reactions [2–7]. All this characteristic behaviour of ZrO_2 is considered due to the acid–base bifunctional catalysis. In a previous paper [8] we have shown the catalytic properties of ZrO_2–SiO_2 samples for the cyclohexene isomerization reaction. In that work it has been studied, the effects of calcination temperature and impregnation with sulphate groups upon the acid sites distribution and catalytic yield for the reaction. As conclusion we presented a correlation between calcination temperature and the presence of sulphate groups with the Brönsted/Lewis site ratio and as further instance with the development of the reaction.

In the present work we complete the previous study of the catalytic properties of ZrO_2–SiO_2 (14% molar in ZrO_2) for the same reaction. In this case sulfation has been submitted before the calcination process. Textural and surface acid properties have been compared with those exhibited by the catalysts studied in the previous reported paper [8].

2. Experimental

2.1. Sample preparation

Amorphous powder ZrO_2–SiO_2 (14% molar in ZrO_2) were processed by a sol–gel chemical route, as it is reported elsewhere [9]. At this ZrO_2 content, theoretically the system would be expected as zirconia particles homogeneously dispersed over the silica ones, forming a monolayer; on the contrary the resulting system is constituted by silica particles partially coated by zirconia [9,10]. The amorphous composite thus obtained was then submitted to a sulfation process following the procedure described in a previous paper [8]. Finally the sulfated sample was calcined at several temperatures (673, 773, 873 and 1073 K) for 2 h. We called these samples ZSS[T] with T being the calcination temperature (ZSS673, ZSS773, ZSS873 and ZSS1073). Samples studied in the previous paper will be here used as reference; they were called ZS[T] and ZS[T]S for ZrO_2–SiO_2 (14% molar in ZrO_2) calcined at various temperatures (773, 873 and 1073 K) for 2 h and for the same sample submitted to a further sulfation process, respectively.

2.2. Techniques

Specific surface area and pore size were obtained from N_2 adsorption–desorption isotherm at 77 K, using a Micromeritics ASAP2000 analyzer. Pore size distribution was calculated using the Barrett, Joyner and Halenda method, assuming cylindrical pore models [11].

X-ray powder diffraction diagrams were obtained in a Siemens D-501 diffractometer, using Ni-filtered Cu–Kα radiation.

Infrared spectra were recorded on a FTIR instrument (Bonem MB-100) equipped with diffuse reflectance (Spectra Tech. Collector). A resolution of 8 cm^{-1} with 250 scans was averaged to obtain a spectrum from 4000 cm^{-1} to 400 cm^{-1}. KBr were used as reference spectra.

Surface acidity was determined using pyridine (PY) and 2,6-dimethylpyridine (DMPY) adsorption. Samples were previously heated at 573 K under dried N_2 for 1 h and then sequentially cooled to 473 K, the catalyst remaining 30 min at this temperature. PY and DMPY were then introduced by bubbling a stream of dehydrated and deoxygenated N_2 (20 ml/min) through the liquid (298 K) and into the sample chamber containing the neat catalyst sample at 373 K for 1 h. After 1 h of adsorption, the system was flushed with N_2 to desorb the loosely bound PY and DMPY from the surface of the catalyst and the respective DRIFT spectra were recorded. The samples were then heated in N_2 stream to 473 K and 573 K and the respective DRIFT spectra were obtained. Samples were equilibrated at least 1 h at each temperature of reactant condition prior to spectra measurements.

Surface acidity (Lewis and Brönsted sites) was measured in a dynamic mode by means of the gas-phase adsorption of PY and DMPY molecules at 473–673 K using a pulse chromatographic technique according to a method described elsewhere [12].

Catalytic activity and selectivity for these samples in cyclohexene isomerization reaction was determined in a pulse microreactor (4 mm i.d.), with pulses of 1 μl of pure cyclohexene (supplied by Merck), connected to a gas chromatograph (HP 5890 II) with a FID detector using N_2 as carrier gas. A detailed description of the microreactor and the experimental procedure for measuring the catalytic activity have been given elsewhere [13]. Reaction products were characterised by gas chromatography–mass spectrometry.

3. Results and discussion

3.1. Textural properties

As it was previously reported [8], ZrO_2–SiO_2 (14% molar) system presents a crystallization effect centred around 1173 K from DTA–TGA profiles. It is also reported [14,15] that sulfation process produces a certain delay in the crystallization of these system. Thus, it was expected that sulfated samples used as catalysts in the present work remains amorphous at the temperatures of calcination lower than 1173 K. Fig. 1 shows the X-ray diffraction patterns of ZSS1073 and ZSS873 catalysts. At these calcination temperatures X-ray patterns of samples remains amorphous, so we may conclude that all catalysts studied here are in this structural form. However, it can be observed an initial crystallization peak centred at $2\theta = 30.2°$ for ZSS1073 that could correspond to the cubic/tetragonal crystal phase of ZrO_2.

Specific surface areas were calculated by means of the n-method (S_n) and BET method (S_{BET}). Regarding the obtained surface proper-
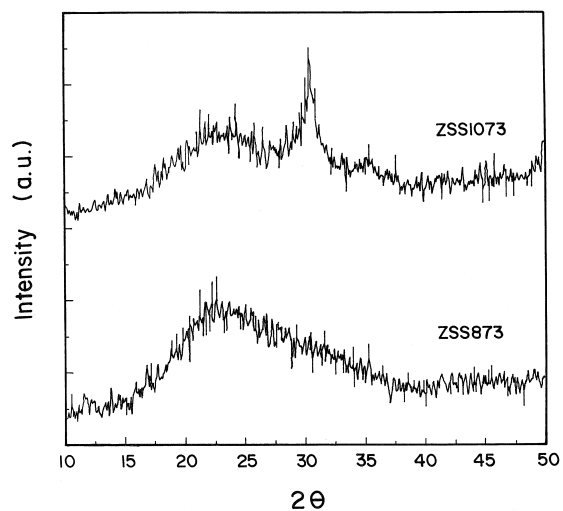

Fig. 1. X-ray diffraction diagrams of ZSS873 and ZSS1073 catalysts.

ties of these catalysts (Table 1), it should be noted that non-sulfated samples ZS[T], exhibited the higher surface area values if compared with the sulfated ones. According to results reported on Table 1, the following sequence for the BET surface areas can be proposed:

$$ZS[T] > ZS[T]S > ZSS[T]$$

The lower surface area value are obtained for the set of samples for which sulfation has been submitted before the calcination process, indicating that the sequence in the procedure is of great influence in textural properties of this

Table 1

Textural properties of ZrO_2–SiO_2 (14% molar) catalysts processed by different methods

Catalyst	S_{BET} / m^2 g^{-1}	S_n / m^2 g^{-1}	V_p / ml g^{-1}	r_p / nm
ZS773	400	381	0.64	3.2
ZS873	351	336	0.65	3.7
ZS1073	333	316	0.56	3.4
ZS773S	321	305	0.53	3.3
ZS873S	315	301	0.63	4.0
ZS1073S	318	309	0.57	3.6
ZSS673	259	249	0.56	4.3
ZSS773	249	236	0.53	4.3
ZSS873	252	240	0.53	4.3
ZSS1073	251	239	0.52	4.2

catalytic system. In the case of ZSS[T] samples it can be noticed that the increase in the calcination temperature does not produce significant differences between the values of surface areas. Therefore, the surface collapse observed for ZSS[T] set of catalysts, seems to be produced by the previous sulfation process rather than by latter calcination.

At the same time, no significant changes can be observed in the V_p and r_p values for all samples (Table 1).

3.2. Drift spectra

In Fig. 2 are shown IR spectra in the range 4000–3000 cm^{-1} for ZSS[T] samples. As can be observed, the IR spectra of these samples shows a sharp band centred at 3730 cm^{-1} and a wide band around 3540 cm^{-1}. The first one could be assigned to hydroxyl groups bounded

to Si atoms (silanol groups, Si–OH) [16,17]. The second region at lower wave number could be assigned to OH groups bounded to Zr atoms with different neighbouring environment, depending also on the Zr/Si ratio of the surface. This difference in the environment is caused by the heterogeneous surface composition that presents this samples inherent to the processed method.

It is worthy to note that for this series of sulfated catalysts, ZSS[T], the more affected bands by the calcination treatment are those ascribed to the hydroxyl groups linked to Zr^{4+} ions observed at around 3540 cm^{-1}. This fact indicates that the temperature effect is mainly observed in this OH groups. The same behaviour was observed for ZS[T] and ZS[T]S catalysts previously described [8], and could be explained assuming a great strength of Si–OH groups with respect to those linked to Zr^{4+}.
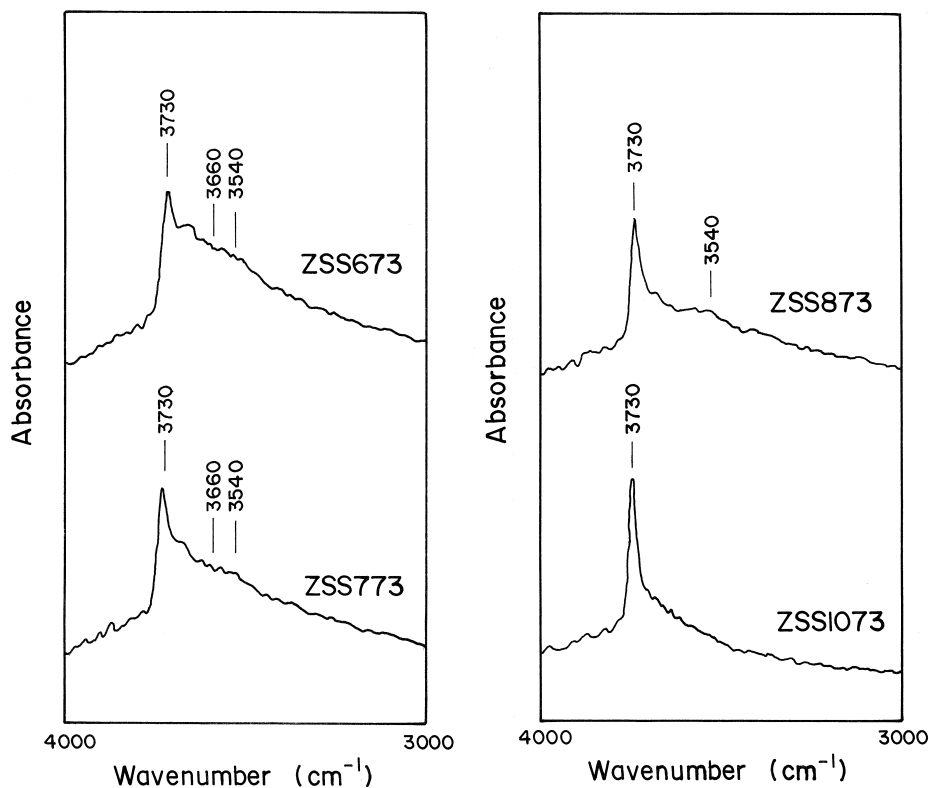

Fig. 2. DRIFT spectra of ZSS573, ZSS673, ZSS873 and ZSS1073 catalysts.

3.3. Surface acidity measurements

The surface acidity measurements were carried out by the adsorption of basic probe molecules. The most widely used basic molecules are PY and DMPY [18–24]. Table 2 shows quantitative results of the irreversible adsorption of PY and DMPY after evacuation at 673 K, in respect with the initial population at 573 K for ZrO_2–SiO_2 (14% molar) catalysts.

Regarding to ZSS[T] catalysts it can be noticed that the evolution of the basic molecule adsorption follows an increase till a calcination temperature of 773 K (Fig. 3). Beyond this temperature, the adsorption decreases gradually. It is worthy noting that both Brönsted and Lewis population follows a similar progress, indicating that after sulfation no new site is created. In other words, calcination affects, in the same way, both types of acid sites. The fact that as calcination temperature increases up to 773 K surface acidity begins to decrease could be explained as a partial decomposition of $SO_4^=$ groups [15,25]. On the contrary, while ZS[T] catalysts have mainly Lewis acidity, the ZS[T]S ones present a Brönsted acidity (Table 2). This fact represents a great difference between the three sets of catalysts with respect to the nature of their acid sites.

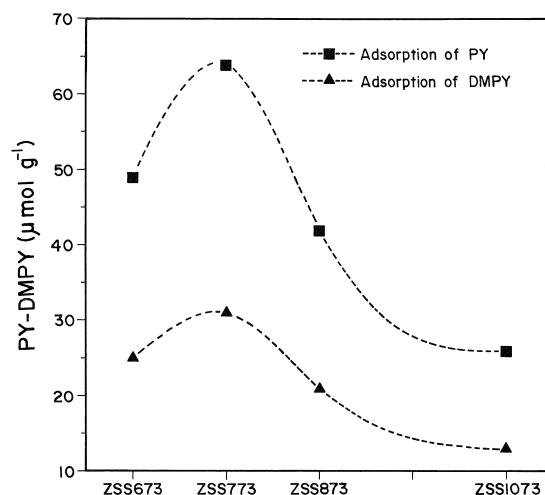We have not determined the amount of S species incorporated on the catalysts; only from

Fig. 3. Number of acid sites related with the adsorption of PY and DMPY over the surface of ZSS573, ZSS673, ZSS873 and ZSS1073 catalysts.
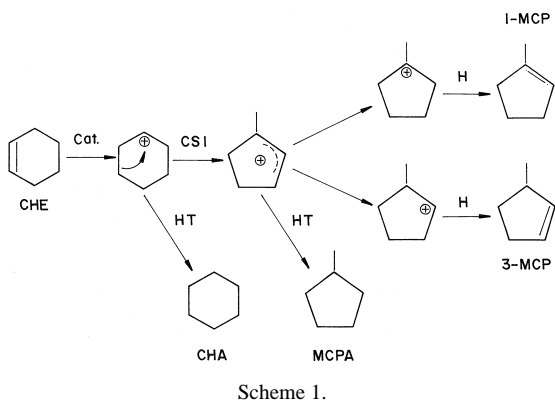
our DRIFT spectra of probe molecules (PY and DMPY) adsorbed on ZSS[T] samples (Fig. 3) can we follow the evolution of surface acidity with the calcination temperature that could be correlated with the amount of $SO_4^=$ anions present at the surface, thus providing qualitative (but not quantitative) evidence of the amount of S species adsorbed at the surface.

At the same time, we have not studied the thermal stability of S species on these catalysts because this study is beyond of the objective of the present paper. However, we have accepted results from the literature given by other authors [15,25] providing data that above 773K a partial decomposition of $SO_4^=$ groups occurs.

3.4. Catalytic activity measurements

The catalytic study of these samples were carried out by using the cyclohexene skeletal isomerization (CSI) reaction (Scheme 1). This reaction is a good test for the acid measurement of the protonic sites present in a catalyst [26–29].

The catalytic runs were carried out in the absence of diffusional influences through the choice of the suitable operating variables [8]. In the absence of mass transfer process, it is possi-

Table 2
Acid properties of ZrO_2–SiO_2 (14% molar) catalysts determined by PY and DMPY adsorption

Catalyst	(PY)/ (DMPY)	$(B)/(B+L)\times100 =$ $(DMPY)/(PY)\times10$
ZS773	5.3	18.7
ZS873	1.8	54.3
ZS1073	8.7	11.5
ZS773S	0.8	100.0
ZS873S	1.4	71.9
ZS1073S	1.9	51.3
ZSS673	1.9	52.0
ZSS773	2.1	46.9
ZSS873	2.0	50.0
ZSS1073	2.0	50.0

Scheme 1.

Table 3
Catalytic properties of ZrO_2–SiO_2 (14% molar) catalysts for cyclohexene skeletal isomerization (CSI) reaction

Catalyst	K_a /mol $(atm \cdot g \cdot s)^{-1}$	X_T /%	$\sigma_{X1/X3}$	S_{CSI}
ZS773[a]	46.9	14.2	2.9	86
ZS873[a]	3.1	3.9	2.1	87
ZS1073[a]	6.6	4.2	2.6	64
ZS773S[b]	518.1	39.6	4.7	66
ZS873S[b]	465.1	26.1	4.8	84
ZS1073S[b]	411.4	30.8	5.1	86
ZSS673[c]	222.3	20.6	3.6	96
ZSS773[c]	278.1	29.6	3.7	94
ZSS873[c]	97.1	14.6	3.4	99
ZSS1073[c]	8.1	1.9	2.3	94

[a] K_a at 523 K and X_T at 623 K.
[b] K_a at 523 K and X_T at 523 K.
[c] K_a at 573 K and X_T at 623 K.

ble to apply the Bassett–Habgood kinetic equation [30] for the first-order kinetic process in which the rate determining step is the surface reaction.

$$\ln[1/(1-X)] = RTk_a(W/F) \qquad (1)$$

where X is the conversion, k_a the apparent rate constant of the surface process, W the catalyst weight and F the flow rate of carrier gas. Thus, by plotting $\ln[1/(1-X)]$ vs. F^{-1} at various flow rates (20–40 ml/min) of N_2 carrier gas, a lineal representation is obtained (and also pass through the origin) indicating a good fit of data to the Bassett–Habgood equation.

In this way it was obtained the value of k_a (apparent rate constant) that gives a direct measurement of the degree of reaction.

Table 3 shows conversion and kinetic data for CSI reaction of cyclohexene for ZrO_2–SiO_2 (14% molar) catalysts. Experimental selectivities (S_{CSI}) and selectivity factors to 1-methyl-cyclopentene (1-MCPE) vs. 3-methylcyclopentene (3-MCPE) ($\sigma_{X1/X3}$ coefficient between 1-MCPE and 3-MCPE molar fractions) are also included in this table.

For the set of catalysts named ZSS[T] the hydrogen transfer reaction (HT) products cyclohexane CHA and methylcyclopentane MCPA is not observed (see Scheme 1). In contrast with the other two set of catalysts, for which the selectivity for HT reaction varies from 36% to 13%. The OPE (Optimum Performance Enve-

lope) plots for 1-MCPE and 3-MCPE present a good linear fitting (Fig. 4), indicating that they are stable primary products [31,32].
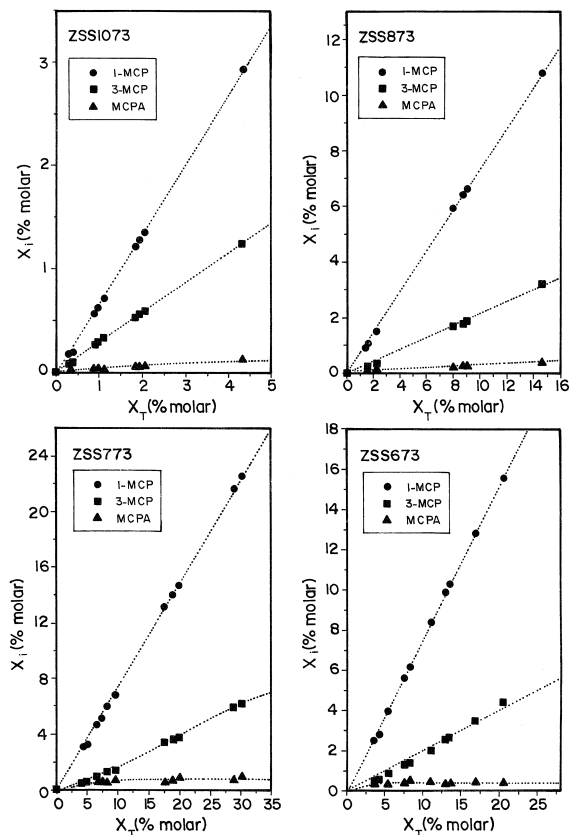

Fig. 4. OPE curves for the 1-MCP, 3-MCP and MCPA products vs. X_T for ZSS573, ZSS673, ZSS873 and ZSS1073 catalysts.

Regarding k_a and conversion (X_T) values it is worth noting that both parameters follow a similar behaviour to that of the acidity properties of these series; a maximum value of this parameters for ZSS773 catalyst is observed. Comparing these data with those obtained for ZS[T] and ZS[T]S catalysts it could be said that ZSS[T] present an intermediate behaviour between ZS[T] and ZS[T]S. Then, the order in reactivity of these series of catalysts for CSI reaction could be expressed in general terms as:

$$ZS[T] < ZSS[T] < ZS[T]S$$

This sequence in reactivity is in accordance with the sequence of Brönsted acid site population (Table 2), indicating that probably these type of acid sites are mainly responsible for the catalytic activity of the cyclohexene skeletal isomerization reaction.

With respect to the isomerization product selectivity ($\sigma_{X1/X3}$) it is observed (Table 3) the same sequence for ZSS[T] catalyst, i.e., a slight maximum value for ZSS773 catalysts. Again the factor selectivity ($\sigma_{X1/X3}$) presents an intermediate values between ZS[T] and ZS[T]S set of catalysts.

4. Conclusions

ZrO$_2$–SiO$_2$ (14% molar) processed by a sol–gel method has been used as isomerization catalyst. The effect of calcination temperature, the presence of sulphate groups on the surface and the sequence of the procedure have been studied.

As it was established in our previous work [8], the presence of sulphate groups enhances the surface acidity, specially Brönsted acid sites. When sulfation process is submitted before calcination (ZSS[T] catalysts), the Brönsted/Lewis ratio is constant, with a value of 50%. The total acidity leads to a significant decay with calcination temperature, being ZSS773 the sample that shows a higher acidity. This fact is explained as a partial decomposition of SO$_4^=$ groups up to 773 K.

Comparing surface acidity and catalytic properties of the ZSS[T] series of samples with ZS[T] and ZS[T]S series it could be deduced the following sequence for total acidity and degree of reaction:

$$ZS[T] < ZSS[T] < ZS[T]S$$

An additional difference, regarding the acidic properties is that not only the total acidity is different but the nature of acid site. Thus, meanwhile ZS[T] catalysts have a Lewis acidity and ZS[T]S a Brönsted one, the ZSS[T] serie has a Brönsted/Lewis ratio of 50%. For this latest serie the acidity lead to a gradual decrease as the calcination temperature increases probably due to a progressive elimination of sulphate groups by decomposition.

Catalytic activity for ZSS[T] catalysts (degree of reaction and total conversion) shows a similar behaviour as the acidic properties showing a maximum of these parameters for ZSS773 catalyst. The selectivity to 1-MCPE product is quite constant for the whole series showing a slightly higher value for ZSS773 catalyst. The selectivity for CSI reaction is about 96%, the parallel hydrogen transfer reaction for this series was not observed.

Acknowledgements

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