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Influence of ZrO_2 Crystalline Structure and Sulfate Ion Concentration on the Catalytic Activity of SO_4^{2-}–ZrO_2

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The catalytic behavior of SO_4^{2-}–ZrO_2 in the *n*-butane isomerization reaction was studied. Both ZrO_2 crystalline structure and SO_4^{2-} concentration were analyzed. ZrO_2 samples were obtained from $ZrCl_4$ in different reaction media, thus allowing us to obtain tetragonal and monoclinic phases separately. The SO_4^{2-} concentration over ZrO_2 was the same by sulfating amorphous or crystalline materials. The sulfate addition over amorphous $Zr(OH)_4$ generated strong acid sites, which are active in *n*-butane isomerization. The catalytic activity showed a maximum at calcination temperatures between 873 and 893 K, where the Lewis acidity is higher. The tetragonal phase is present under these conditions, as shown by XRD patterns. The same results were obtained with samples synthesized from another precursor. Coke deposition or water presence produced catalyst deactivation. © 1995 Academic Press, Inc.

INTRODUCTION

Zirconium oxide, ZrO_2, is a very interesting material because of its thermal stability, its mechanical properties, and its basic, acidic, reducing, and oxidizing surface properties (1). Zirconia exhibits three different crystalline isomorphs: monoclinic (M), stable at temperatures below 1373 K; tetragonal (T), stable between 1373 and 2173 K; and cubic (C), stable above 2173 K (2). Nevertheless, the T and C forms can be generated and maintained as metastable structures at much lower temperatures than those mentioned above (3).

Zirconia can be prepared from different precursors such as $ZrOCl_2 \cdot 8H_2O$ (4, 5), $ZrO(NO_3)_2 \cdot 2H_2O$ (6, 7), Zr isopropoxide (8, 9), and $ZrCl_4$ (10, 11). The addition of the sulfate ion, SO_4^{2-}, to zirconia produces a very strong acid (12–14), which can catalyze reactions demanding high acidity, such as alkane isomerization (15–17). Also, the addition of the sulfate ion gives zirconia a higher stability, producing an increase in the temperature of the amorphous phase organization as well as in the stability of the T phase produced (18, 19). The same effect of phase stabilization was obtained by the addition of some oxides, such as Y_2O_3 and La_2O_3 (20).

Ishida *et al.* (21) stated that the T phase is the catalytically active one in SO_4^{2-}–ZrO_2. The activity of this catalyst in *n*-butane isomerization reaches a maximum when it is calcined at 893 K (17), the T crystalline structure being present (22).

There is a lack of information in the literature regarding the relation between the catalytic activity, the crystalline structure, and the SO_4^{2-} concentration. This paper studies the effect of sulfate ion addition to zirconia samples, which are synthesized from $ZrCl_4$ in different reaction media, in order to obtain separately the different crystalline structures. X-ray diffraction and differential thermal analysis techniques are used for the sample characterization, SO_4^{2-} concentration is measured, and catalytic performance is evaluated. These results are compared with those of zirconia synthesized from $ZrOCl_2 \cdot 8H_2O$. The influence of both the crystalline structure and the sulfate concentration over the *n*-butane isomerization reaction is analyzed.

EXPERIMENTAL

Catalyst Preparation

Different precursor salts and different synthesis routes were used to obtain ZrO_2 samples. The zirconium tetrachloride derived ones were prepared by adding $ZrCl_4$ (Johnson Matthey Electronics, 99.5 + %) in a properly chosen medium. The appearance of a specific crystalline structure upon calcination was determined by the type of solvent used, distilled water or an *n*-propanol : water (50 : 50) solution. The relative quantities of reactants used for the hydrolysis step were $ZrCl_4 : H_2O = 1:6$ and $ZrCl_4 : n\text{-PrOH} : H_2O = 1:10:10$; the pH values of these initial solutions were 1.65 and 0.85, respectively. $ZrCl_4$ undergoes hydrolysis to zirconium oxihydrate with a high exothermicity; therefore, it was poured onto the solution in small quantities, slowly and with energetic stirring; the

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addition was completed in 20 min. The Zr(OH)$_4$ precipitation was performed by the addition of a NH$_4$OH solution (28% NH$_3$) in the proportion of 3 ml per gram of ZrCl$_4$, finishing the addition in 25 min. At the end of this step, the pH values of aqueous or alcoholic–aqueous medium were 9.40 and 9.20, respectively. The large excess of base ensured the total precipitation of the Zr(OH)$_4$ hydrogel. The suspension thus obtained was reflux heated for 6 h, cooled to room temperature, and aged for 12 h. Then, it was filtered and thoroughly washed with deionized–bidistilled water until no chloride ion was detected in the washing liquid. The wet solid was dried under vacuum for 3 h and then in stove at 383 K for 12 h. The Zr(OH)$_4$ samples synthesized in aqueous medium were designated as I, and the ones produced in alcoholic–aqueous medium, as II. The Zr(OH)$_4$ sample, derived from ZrOCl$_2$ · 8H$_2$O (Merck, 99%) and designated as X, was prepared following a technique described elsewhere (23).

Samples I and II were sulfated in two ways: before calcination, with the substrate in a supposedly fully hydroxilated state; and after calcination, in the form of crystalline ZrO$_2$. For sulfation the sample was dipped in a 1 *N* solution of H$_2$SO$_4$ for 1 h and without stirring. This acid concentration has been previously reported as the optimum one (23, 24). The ratio of the acid solution and the dried solid used was 15 ml/g. Then, the sulfated samples were filtrated and dried for 12 h at 383 K.

Catalyst Characterization

The ZrO$_2$ and SO$_4^{2-}$–ZrO$_2$ samples, calcined at different temperatures for 3 h, were characterized by X-ray diffraction (XRD) and differential thermal analysis (DTA). The XRD analyses were made using a Rich–Seifert Iso-Debyeflex 2002 diffractometer. DTA tests were performed in a Shimadzu DT-30 thermal analyzer. The analysis conditions were detailed in a previous work (22).

The sulfate concentration in the samples, expressed as SO$_4^{2-}$ wt%, was measured following a technique previously reported (25). The sample was first attacked with an acid mixture (HI, CH$_3$COOH, H$_3$PO$_2$) in absence of oxygen, being heated at 388 K and maintained for 2 h. The H$_2$S produced by SO$_4^{2-}$ reduction was withdrawn in a NaOH solution, being titrated with Hg acetate.

Catalytic Test

The catalytic behavior of the sulfated samples in the *n*-butane isomerization reaction was studied. A fixed-bed quartz reactor operating in a continuous flow, at the atmospheric pressure and under isothermal conditions, was used. For the test, 500 mg of sample sieved to 35–80 mesh was calcined at different temperatures in an air stream for 3 h. After cooling to 573 K in nitrogen flow, a stream of pure *n*-butane (8 ml min^{-1}) was fed during the 4 h of reaction. Reactant and reaction products were analyzed by on-line gas chromatography, using a 6-m-long, 1/8-in-O.D. column, packed with 25% dimethylsulfolane on Chromosorb P and operating at room temperature.

TABLE 1

Crystalline Structure of Zirconia and Sulfated-Zirconia Samples Obtained by Different Synthesis Routes and Calcined at Different Temperatures (T_c)

	Samples					
T_c (K)	I	SO$_4^{2-}$–I	II	SO$_4^{2-}$–II	X	SO$_4^{2-}$–X
633	A	A	A	A	A	A
663	T	A	M	A	M, T	A
753	T	A$_m$, T	M$_m$, T	A$_m$, T	M, T	A$_m$, T
793	T	A$_m$, T	M$_m$, T	A$_m$, T	M, T	A$_m$, T
813	T	T	M$_m$, T	T	M, T	T
833	T	T	M$_m$, T	T	M, T	T
893	T$_m$, M	T	M$_m$, T	T	M$_m$, T	T
933	M$_m$, T	T	M$_m$, T	T	M$_m$, T	T
1123	M$_m$, T	T$_m$, M	M$_m$, T	T$_m$, M	M$_m$, T	T$_m$, M

Note. I, starting material ZrCl$_4$ added to aqueous medium; II, ZrCl$_4$ added to alcoholic–aqueous medium; X, starting material ZrOCl$_2$ · 8H$_2$O and aqueous medium; SO$_4^{2-}$, sulfated sample; A, amorphous; T, tetragonal; M, monoclinic; m, main component.

Carbon deposited on the catalyst at the end of the catalytic test was determined by a combustion–volumetry method.

RESULTS

XRD and DTA Characterization

XRD results are summarized in Table 1. In samples I, the T phase was the first to appear after calcining at 663 K being amorphous at lower temperatures. The T phase persisted alone upon calcination up to 833 K. At 893 K the transformation of the T phase into the M phase began. The proportion of the M phase was larger at higher temperatures. Finally, at 1123 K, practically only the M phase was present.

The samples II were monoclinic after calcining at 663 K and amorphous at lower temperatures. Between 753 and 933 K both T and M phases were present. At 1123 K, practically only the M phase remained.

Samples X did not yield a single phase upon calcination. A mixture of the T and M phases was observed along all the temperature range. At 1123 K, practically only the M phase was present.

The three sulfated samples, obtained after sulfating the amorphous, noncalcined hydrous zirconia specimens synthesized by methods I, II, and X, showed similar behavior. SO$_4^{2-}$–I, SO$_4^{2-}$–II, and SO$_4^{2-}$–X began to crystallize

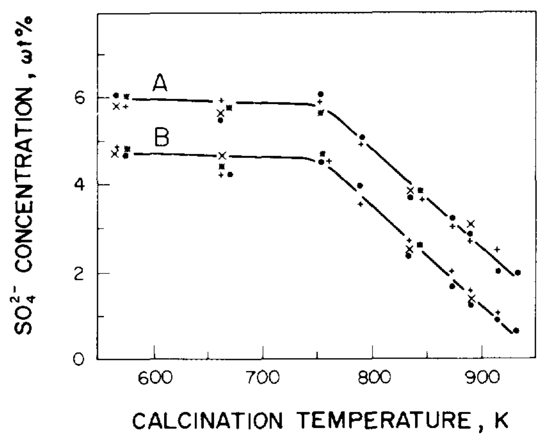

FIG. 1. Concentration of SO$_4^{2-}$, in weight percent, on SO$_4^{2-}$–ZrO$_2$ as a function of calcination temperature: (A) after 3 h calcination; (B) after 3 h calcination and 4 h reaction at 573 K. (●) Sample I dried at 383 K and treated with H_2SO_4. (+) Sample II dried at 383 K and treated with H_2SO_4. (×) Sample I dried at 383 K, calcined at 663 K, and then treated with H_2SO_4. (*) Sample II dried at 383 K, calcined at 663 K, and then treated with H_2SO_4.

at about 753–793 K. The T structure alone was obtained between 813 and 933 K. At 1123 K, the M phase appeared in a small proportion. Then, the presence of SO$_4^{2-}$ induced the formation of the T structure, which was stabilized in a broad temperature range.

In order to complement the XRD tests, several samples were characterized by DTA. The results confirm temperature ranges at which the phase transformations shown by XRD take place.

Measurement of SO$_4^{2-}$ Concentration

The SO$_4^{2-}$ concentration on ZrO$_2$ after calcination at different temperatures and at the end of the *n*-butane isomerization reaction, when calcining at these temperatures, was analyzed. The following substrates were sulfated: samples I calcined at 663 K, i.e., crystalline T zirconia [SO$_4^{2-}$–I(ca)]; samples II calcined at 663 K, i.e., crystalline M zirconia [SO$_4^{2-}$–II(ca)]; and samples I and II only dried at 383 K, i.e., amorphous zirconia [SO$_4^{2-}$–I and SO$_4^{2-}$–II, respectively]. The different sulfated samples were calcined at temperatures between 573 and 933 K, and their catalytic activities for *n*-butane isomerization were measured along with the sulfate ion concentration, before and after the reaction.

Figure 1 shows the SO$_4^{2-}$ concentration after the calcination step and at the end of the reaction as a function of calcination temperature. Samples I and II, sulfated over crystalline or amorphous structures, showed practically the same behavior. The SO$_4^{2-}$ concentration before and after the reaction in this calcination temperature range showed the same qualitative pattern, being always lower at the end of the reaction. The reaction was carried out at 573 K, a temperature lower than the calcination ones. During the catalytic test, the loss of SO$_4^{2-}$ was verified bubbling the reactor outlet in H_2O_2 and NaOH solutions, where SO$_4^{2-}$ was always detected. Calcination temperatures below 753 K did not greatly modify the SO$_4^{2-}$ content, which was 5.5–6.1% after the calcination step and 3.7–4.5% at the end of the reaction, for all samples. Calcination temperatures above 753 K produced an important decrease in the SO$_4^{2-}$ load, being 3.7% when calcining at 893 K and 2.2% after the reaction, and 2.0% and 0.9%, respectively, when the calcination was performed at 933 K. A sample calcined at 1273 K during 3 h gave 0.1% of SO$_4^{2-}$.

TABLE 2

Carbon Deposited at the End of the Isomerization Reaction on SO$_4^{2-}$–I Samples Calcined at Different Temperatures (T_c)

T_c (K):	793	833	893	913	933
Carbon (%):	1.0	1.1	1.2	1.0	1.0

Note. T_{reaction} = 573 K; P = 0.1 MPa; feed, *n*-C$_4$.

The increase in calcination temperature produced a slight decrease in the specific surface area which was 117 and 104 m^2 g^{-1} by calcining at 663 and 893 K, respectively. The sulfate content was 5.7 and 3.0% after calcining at these temperatures. Consequently, the sulfate concentration also decreased in terms of SO$_4^{2-}$ groups per unit surface area when calcination took place at temperatures higher than 753 K.

Catalytic Test

The SO$_4^{2-}$–I and SO$_4^{2-}$–II samples, obtained by sulfating the amorphous Zr(OH)$_4$, were calcined at temperatures between 793 and 933 K, and their catalytic activities were tested. All the samples showed an important deactivation during the first 60 to 90 min. A very noticeable carbonaceous deposit on the catalyst was obtained at the end of the test, as seen in Table 2, and the catalysts showed a black color. The reaction products were always ethane, propane, *i*-butane, and pentanes. The specific rate of *n*-butane isomerization and the selectivity values for SO$_4^{2-}$–I calcined at 893 K are shown in Table 3. At the initial time (first analysis at 5 min), the rate per residual sulfur atom is almost an order higher than the one obtained at the end of the reaction test (240 min).

Figure 2 shows the *n*-butane conversion and the selectivity to *i*-butane as a function of the calcination temperature at two values of time-on-stream, 5 and 150 min. The catalytic samples exhibit the same behavior. In Fig. 2A, at 5 min. on stream, there was a large increase in the *n*-butane conversion, 6 to 47%, for calcination at 833 and

TABLE 3

Specific Rate and Selectivity Values of SO_4^{2-}–I Samples for the *n*-Butane Isomerization Reaction

Time-on-stream (min)	Specific rate ($\times 10^2$)[a]	Selectivity (%)				
		C_1	C_2	C_3	*i*-C_4	C_5
5	1.874	0.3	0.7	30.7	59.2	9.1
240	0.262	0	0.3	6.4	89.0	4.3

Note. $T_{calcination} = 893$ K; $T_{reaction} = 573$ K; $P = 0.1$ MPa.

[a] Molecules of *n*-C_4 converted per second and residual S atom.

873 K, respectively. In addition, the selectivity to *i*-butane decreased from 83 to 60%. The maximum of activity lies between 873 and 893 K. In Fig. 2B, for longer times on stream, e.g., 150 min, no significant differences were produced by the different calcination temperatures, the *n*-butane conversion being always approximately 2–4% and the selectivity to *i*-butane, 90%.

The conversion and selectivity values of the SO_4^{2-}–X sample, prepared from $ZrOCl_2 \cdot 8H_2O$, corresponding to the calcination at 893 K are included in Fig. 2. These values fitted both the activity and selectivity curves obtained with the samples synthesized from $ZrCl_4$, viz. SO_4^{2-}–I and SO_4^{2-}–II.

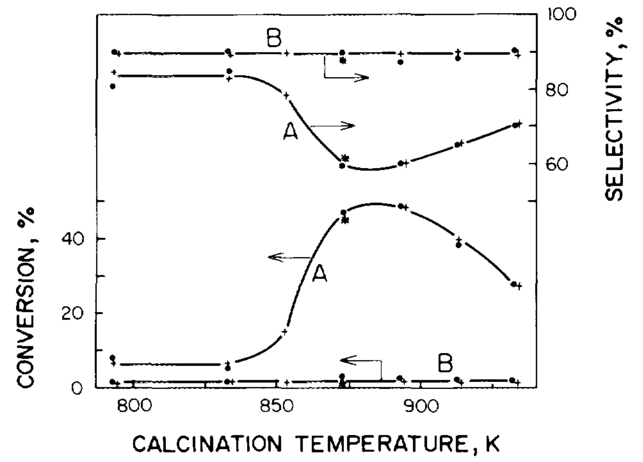

FIG. 2. Conversion of *n*-C_4 and selectivity to *i*-C_4 as a function of calcination temperature: (A) at 5 min time-on-stream; (B) at 150 min time-on-stream. (●) SO_4^{2-}–I. (+) SO_4^{2-}–II. (*) data for SO_4^{2-}–X.

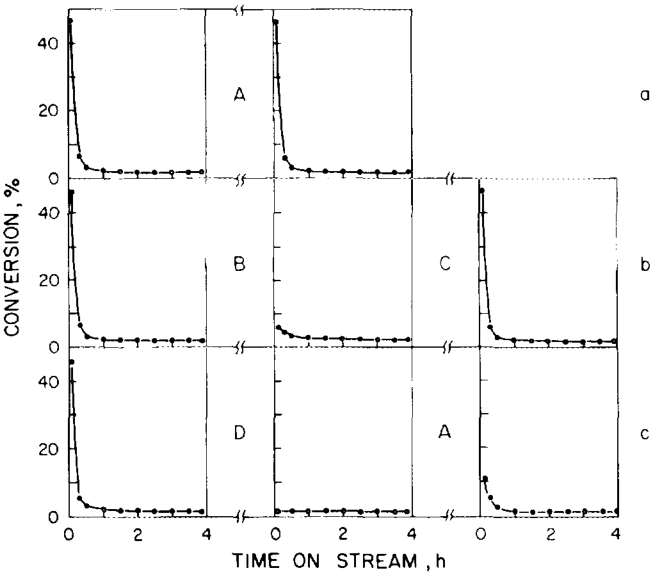

FIG. 3. Conversion of *n*-C_4 as a function of time-on-stream; three catalytic tests (a, b, c) with different intermediate treatments. Reaction step conditions: 4 h with pure *n*-C_4 at 573 K. Intermediate treatments: (A) 2 h with dry air flow at 773 K; (B) exposure to wet atmosphere and then 2 h with dry air flow at 773 K; (C) 2 h with dry air flow at 893 K; (D) 2 h with H_2 flow at 773 K.

Figure 3 shows the *n*-C_4 conversion on catalytic activity tests with different intermediate steps. In Fig. 3a, after 4 h of reaction the catalyst was regenerated by means of an 8 ml min^{-1} air flow at 773 K for 2 h. Thereafter, the reaction was started again, the initial activity being completely recovered. At the end of this reaction step, the carbon deposited was 1.0%. In Fig. 3b, after 4 h of isomerization reaction, the catalyst was taken from the reactor and exposed to the atmosphere. Subsequent regeneration at 773 K, as in the former case, produced only a partial recovery of the initial activity, being the *n*-butane conversion about 7% at 5 min on stream. Then, a new calcination in air flow at 893 K completely restored the initial activity. In Fig. 3c, after the reaction, a reduction treatment with hydrogen flow at 773 K for 2 h was performed; then, the catalytic activity was not recovered. The regeneration at 773 K for 2 h allowed a partial restoration of the initial activity. After this reaction step, the SO_4^{2-} concentration measured was 0.4% and the carbon deposited, 1.1%. XRD analysis showed that the crystalline structure did not change after the reaction or during any of the previous treatments; spectra always showed the presence of the T phase. On the contrary, the SO_4^{2-} concentration decreased during these experiments.

The catalytic behavior of the SO_4^{2-}–I(ca) and SO_4^{2-}–II(ca) samples, obtained by sulfating materials previously calcined at 663 K and having crystalline T and M structures, respectively, was also evaluated. After calcination at temperatures between 663 and 893 K, the samples behaved similarly. There was practically no catalytic activity. At 5 min of time-on-stream, the conversion was about 2–4%, and at 150 min it was only 0.1–0.2%. After the reaction, the carbonaceous deposit was very small and the catalyst showed a gray color. In order to analyze the effect of calcination and reaction steps over the crystalline structure, the samples were characterized by XRD before and after the reaction. Spectra of the SO_4^{2-}–I(ca) samples calcined at different temperatures showed the T phase, which was already present before the calcination and remained all throughout the calcination and reaction steps; no traces of M phase were detected. For SO_4^{2-}–II(ca) samples, the M phase, the starting isomorphs, remained unchanged without the appearance of other phases.

DISCUSSION

ZrO_2 is a very weak acid material, inactive for the *n*-butane isomerization reaction. The SO_4^{2-} addition promotes its acidity, being SO_4^{2-}–ZrO_2 a superacid. This is due to the inductive effect of the S═O groups that produces an electronic deficiency markedly increasing the Lewis acidity of the Zr cations (20). Two types of Lewis sites are produced; the more abundant are the less energetic (26). Figure 1 shows that sulfating either amorphous [samples SO_4^{2-}–I and SO_4^{2-}–II] or crystalline materials, with T structure [SO_4^{2-}–I(ca)] or M structure [SO_4^{2-}–II(ca)], the same SO_4^{2-} concentration is obtained, and it is a function of the calcination temperature. Then, the difference in amorphous and crystalline materials and different crystallographic phases, with their different coordination number of Zr, densities, and crystal size (2), does not modify the SO_4^{2-} amount deposited on ZrO_2, depending on parameters such as the SO_4^{2-} source and its concentration, as reported before (12, 23, 24). Calcination temperatures above approximately 753 K produce a large decrease in SO_4^{2-} concentration. During the *n*-butane isomerization reaction, all the samples lose sulfur, in spite of the fact that this reaction takes place at a lower temperature (573 K) than the previous calcination. Similar results in methanol dehydration were found by Waqif *et al.* (14), and they considered that some species present in the reaction favor the transformation of the covalent bonds of SO_4^{2-} into less stable ionic bonds. Working with SO_4^{2-}–Fe_2O_3, Lee *et al.* (27) found that *n*-butane decomposes surface SO_4^{2-} at about 573 K. Then, under our reaction conditions, a certain amount of SO_4^{2-} is decomposed and leaves the catalyst surface. This decomposition is not produced at the same temperature under the oxidizing condition of calcination. The SO_4^{2-} lost should be less energetically bounded and not important in the catalytic activity, because it is possible to recover the initial activity after the reaction test, as shown in Fig. 3.

There is no agreement in the literature with regard to the nature of the active sites. Morterra and Marchese (28) stated that water is completely eliminated from the ZrO_2 surface at 873 K; Mukaida *et al.* (24) considered that the more active sites are produced at high temperatures. According to Yamaguchi *et al.* (7), when calcining SO_4^{2-}–ZrO_2 the acidity is only of Lewis type. By IR spectroscopy, Nascimento *et al.* (29) found that the maximum in activity corresponds to the presence of both Brønsted and Lewis acid sites. Prior to their IR analysis, several samples that had been previously calcined at higher temperatures and stored in air without specific care were calcined at 723 K. It is possible that the Brønsted acidity that they found was produced by the water readsorption from the atmosphere during the storage and was not eliminated by calcining only at 723 K. Morterra *et al.* (9) considered that only Lewis acidity is present on the dehydrated sample. In a recent paper, Morterra *et al.* (30) studied the influence of sulfate concentration on SO_4^{2-}–ZrO_2. They found that at low SO_4^{2-} coverages (below 2 S atoms per nm^2, corresponding to the completion of an average half-monolayer of SO_4^{2-}) the acid sites are of Lewis type, and that at higher SO_4^{2-} concentrations (above 2 S atoms per nm^2) Brønsted-type acidity appears. There is a partial transformation of Lewis into Brønsted acidity when water is present. These authors found that calcining hydrated SO_4^{2-}–ZrO_2 at 773 K, about 50% of the potential Brønsted acidity is lost; when calcining at 823 K, almost all of this acidity is lost, and it is entirely lost when a temperature of approximately 873 K is reached. At this temperature, only Lewis acidity is present. These authors also found that sulfates responsible for Brønsted acidity are the thermally most labile fraction of the surface sulfate layer. In our experiments, by calcining at temperatures below 753 K, a concentration of 2.9–3.3 S atoms per nm^2 was obtained, thus allowing us to consider that both Brønsted and Lewis acidities are present, as stated by Morterra *et al.* (30). When calcining at 893 K, the concentration was approximately 2 S atoms per nm^2, only Lewis acidity being present in this case. Furthermore, in our catalytic tests the calcination was performed in the same reactor before the run; then, by calcining above 873 K, as water was eliminated, only Lewis acidity could be present.

Our results in *n*-butane isomerization tests at 5 min time-on-stream with samples SO_4^{2-}–I and SO_4^{2-}–II, obtained by sulfating amorphous $Zr(OH)_4$, give a specific rate of reaction between 0.1×10^{-2} and 0.5×10^{-2} molecules of *n*-C_4 converted per second and residual sulfur atom, when calcining at temperatures lower than 853 K or higher than 913 K. The catalytic activity shows a maximum at calcination temperatures between 873 and 893 K, the specific rate being approximately 1.9×10^{-2} molecules of *n*-C_4 converted per second and residual sulfur atom. Both SO_4^{2-}–I and SO_4^{2-}–II samples and the SO_4^{2-}–X one show the same behavior. This is due to the fact that all sulfated samples have the same tetragonal crystalline structure, in spite of the different preparation methods, as shown by the XRD diagrams. Other authors also found a maximum in catalytic activity with the calcination temperature, at 873 K in the 1-butene isomerization (1) and at 893 K in the *n*-butane isomerization (17). In our case, the increase in catalytic activity coincides with the increase in Lewis acidity due to the loss of water; simultaneously, there is a decrease in the acidity produced by the SO_4^{2-} lost and a slight decrease in specific surface area. The decrease in catalytic activity could be caused by the acidity decrease produced by the SO_4^{2-} lost. Then, the maximum in catalytic activity seems to derive from a compensation between the Lewis acidity and the acidity loss produced by SO_4^{2-} removal.

In our experiments with intermediate steps (Fig. 3), the regeneration with air flow at 773 K allows the catalyst to recover the initial activity. The catalyst deactivation is due to a carbonaceous deposit that is produced by polymerization on the active Lewis sites. The catalytic activity is recovered by burning off this deposit. When the catalyst is withdrawn from the reactor and left to the atmosphere, the regeneration with air at 773 K does not restore the initial activity. Then, if water is adsorbed over the catalyst surface, it will be necessary to calcine at 873 K to regenerate the Lewis sites and to restore the initial activity. When hydrogen was passed at 773 K during the regeneration step, the initial activity was not recovered. XPS analysis showed that most of SO_4^{2-} was reduced to S^{2-}; sulfur analysis at the reactor outlet showed that part of it left the catalyst surface as H_2S. When air is fed, the activity is partially recovered because S^{2-} is oxidized to SO_4^{2-}. During the catalytic test at 573 K, *n*-butane reduces SO_4^{2-} and all the samples lose sulfur. At higher reaction temperatures, the reduction is more rapid and, when feeding *n*-butane at 773 K, a large H_2S production is observed while the SO_4^{2-} concentration on the catalyst decreases rapidly.

SO_4^{2-}-I(ca) and SO_4^{2-}-II(ca), obtained by sulfating the T and M structures produced by calcination, have the same SO_4^{2-} concentration as SO_4^{2-}-I and SO_4^{2-}-II, but are practically inactive in the *n*-butane isomerization. The specific rate of reaction was an order lower than the one obtained with the sulfated amorphous samples. Then, the presence of SO_4^{2-} is not sufficient to produce an active catalytic material; even these materials present strong acidity (14, 30).

CONCLUSIONS

The catalytic activity of SO_4^{2-}-ZrO_2 for *n*-butane isomerization is higher in the region where the Lewis acidity is higher. The SO_4^{2-} presence is necessary to generate the strong acid sites, but it is not sufficient to give catalytic activity. In fact, the SO_4^{2-} addition must be done to the amorphous $Zr(OH)_4$. In this case, after calcination, the tetragonal structure is always obtained, and the catalytic activity is independent of the precursor salt and of the $Zr(OH)_4$ preparation method. Water or carbonaceous deposits, which decrease the Lewis acidity, produce a catalyst deactivation.

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