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Influence of calcination procedure on the catalytic property of sulfated zirconia

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Calcination parameters, such as atmosphere, duration and catalyst bed depth have a marked influence on the catalytic and spectroscopic properties of sulfated zirconia. Sulfated zirconia calcined in nitrogen or synthetic airflow, in deep bed, exhibited comparable activity in *n*-butane isomerization at 373 K, which suggests that oxygen is not necessary for formation of active sites. Catalysts calcined in shallow bed are catalytically inactive. Thus, the bed depth is concluded to be crucial for the formation of active sites. The samples calcined in shallow bed possessed lower sulfate content and the S = O stretching vibration was located at lower frequency. Calcination in the presence of water vapor also led to lower catalytic activity, sulfate content, and BET area. Extended calcination reduced gradually the activity and the sulfate content, which underlines the labile property of the active sites. A new interpretation of the function of the calcination step is proposed and compared with models described in the literature.

KEY WORDS: calcination procedure; catalyst bed depth; calcination atmosphere; calcination duration; sulfated zirconia; *n*-butane isomerization.

1. Introduction

Due to increasingly strict environment legislation, solid acids are promising alternatives for liquid acid catalysts used in industrial processes. Sulfated metal oxides, especially sulfated zirconia, which is active for alkanes activation at low temperature, have been studied for more than two decades and the results have been reviewed [1–8]. However, several topics, such as the structure of the active sites, the acid strength and the mechanism of alkane isomerization are still subject of debate.

The procedure for sulfated zirconia synthesis has been originally derived from the study of the anion effect on TiO_2 [9]. The influence of the preparation parameters, i.e., zirconium precursor, sulfation agent and sulfation procedure, and calcination temperature has been extensively studied [10–12]. However, despite the large amount of investigations, no general consensus on the more suitable preparation method has been reached.

In order to induce catalytic activity, a final calcination step at high temperature has been recognized as crucial in the conventional preparation method, where an amorphous zirconium hydroxide is sulfated with a liquid agent, such as H_2SO_4 or $(NH_4)_2SO_4$ solution. Calcination transforms the sulfated-promoted amorphous zirconium hydroxide into sulfated zirconia crystallized into the thermodynamically unstable, but catalytically active, tetragonal/cubic forms. Morterra *et al.* showed that a final calcination step at temperature above 823 K is necessary to induce catalytic activity also for samples obtained by sulfation of zirconia already crystallized into the tetragonal or cubic structure by formation of solid solution with Y_2O_3. Based on IR measurements with CO at low temperature, the authors suggested that one of the crucial function of calcination is the partial removal of sulfate groups, which renders strong Lewis acid sites accessible to the reactants [13,14]. We have recently questioned this interpretation [15]. In fact, we showed that when sulfation is performed using gaseous SO_3 instead of a traditional liquid sulfating agent, a final calcination step is not required to achieve high catalytic activity in *n*-butane isomerization at 373 K. This sulfation method proved to be effective when applied to a broad variety of already crystallized samples, whatever the structure and the presence/absence of sulfate species. Based on these results, accompanied by IR spectroscopic measurements and mechanistic study [16], we suggested that the main function of the calcination step is to decompose the sulfating agent into SO_3 which interacts with zirconia forming labile sulfated species, mostly under form of pyrosulfate groups. These groups have been identified as the active species for alkane activation via stoichiometric oxidative dehydrogenation [16].

A few parameters involved in the calcination step have been thoroughly discussed, often with contradictory results. Thus, for example, Morterra *et al.* claimed that an extension of the calcination beyond 4 h does not affect the final catalytic performance [13], while Fărcaşiu *et al.* reported that a correlation between calcination

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temperature and calcination duration exists, the same results being obtained by extended calcination procedure at lower temperature [5].

Other parameters involved in the calcination procedure have been mostly disregarded. For example, if we exclude the recent publication by Hahn *et al.* [17], the catalyst amount and the thickness of the calcination bed have not been taken into account.

In the present work, we investigate the influence of calcination parameters on spectroscopic features and catalytic activity of sulfated zirconia. Calcination atmosphere, catalyst bed depth and calcination duration were chosen to elucidate the function of calcination, providing insight into the formation of active sites.

2. Experimental

2.1. Catalyst preparation

Sulfated-doped zirconium hydroxide was purchased from Magnesium Electron Inc. (XZO 1077/01). All the sulfated zirconia samples investigated in this study were obtained by heating the parent material up to 873 K with a ramp rate of 10 K min^{-1}. However, various atmospheres (synthetic air or nitrogen), catalyst amounts and calcination durations were applied, as specified below.

About 20–30 g of the as-received sample was calcined in a quartz boat in a quartz tube for 3 h at 873 K with a flow (200 ml min^{-1}) of nitrogen, synthetic air or water vapor saturated air. The corresponding samples are referred to as SZ-DN, SZ-DA and SZ-DAW, respectively. The letter "D" in the catalyst name means "deep bed".

To calcine the sample in a shallow bed, around 0.1–0.2 g of sulfated zirconia precursor were dispersed on the bottom of a quartz boat and heated at 873 K for 3 h under 200 ml min^{-1} nitrogen or synthetic air. The obtained samples are referred to as SZ-SN and SZ-SA, respectively, where "S" denotes that the calcination was performed with a shallow bed.

In order to investigate the influence of the calcination duration, four samples were calcined in deep bed in synthetic air flow (200 ml min^{-1}) at 873 K for 1, 3, 5 and 10 h. The corresponding samples are referred to as SZ-DA-*n* where *n* indicates the calcination duration expressed in hours.

2.2. Catalyst characterization

The sulfate content of the catalysts was determined by ion chromatography as described in literature [18]. About 0.02 g of sulfated zirconia was suspended in NaOH 0.1 N and the solution was filtered with a 0.45 μm filter. The sulfate content was determined by using a Metrohm 690 ion chromatograph equipped an IC anion column.

BET surface area and pore size were determined by nitrogen physisorption using a PMI automated BET-sorptometer.

The XRD patterns of the sulfated zirconias were collected in *Philips X'Pert-1* XRD powder diffractometer using CuK_α radiation. The average particle size was obtained from the peak of $2\theta = 30°$ with the equation $L = k^*\lambda/(B^*\cos\theta)$, where $k = 0.9$ and $\lambda = 1.54051$.

IR spectra of the samples were collected using a Bruker IFS 88 spectrometer with a resolution of 4 cm^{-1}. Self-supporting wafers with a density of 5–10 mg cm^{-2} were prepared by pressing the sample. The wafers were placed into a stainless steel cell with CaF_2 windows, gradually heated up with 10 K min^{-1} to 673 K in He flow (10 ml min^{-1}), and activated at that temperature for 2 h. A spectrum was recorded after stabilization of the temperature at 373 K.

The gases evolved during calcination of the sulfate-promoted zirconium hydroxide were analyzed in a vacuum system equipped with MS by heating the sample with 10 K min^{-1} up to 873 K (3 h).

2.3. Butane isomerization

n-Butane isomerization was carried out in a quartz micro tube reactor (8 mm i.d.) under atmospheric pressure. 0.2 g of sulfated zirconia pellet (355–710 μm) were loaded into the reactor and activated *in situ* at 673 K for 2 h in He flow (10 ml min^{-1}). The catalyst was then cooled to 373 K and the reactant mixture (5% *n*-butane in He, total flow of 20 ml min^{-1}) was flown through the catalyst bed. Before to be mixed with He, *n*-butane (99.5%, Messer) was passed through an olefin trap containing activated HY zeolite (20 g) for the removal of the olefin impurities. No traces of butenes were detected in the reactant mixture after purification (detection limit 1 ppm). The reaction products were analysed using an on-line HP 5890 gas chromatograph equipped with a capillary column (Plot Al_2O_3, 50 m × 0.32 mm × 0.52μm) connected to a flame ionization detector (FID).

3. Results

3.1. Characterization

Sulfate content, BET area, pore size and particle size are reported in Table 1. All the samples presented a BET area between 137 and 205 $\text{m}^2\ \text{g}^{-1}$, and pore size between 2.5 and 3.4 nm, which indicate that the calcined sulfated zirconias are mesoporous with irregular pores.

The particle sizes of the sample calcined with shallow bed sample are larger than those of the corresponding samples calcined with deep bed.

The sulfate content of the samples calcined in air and in nitrogen for 3 h in deep bed (SZ-DA and SZ-NA) was approximately 6 wt% SO_4^{2-}while for the shallow bed

Table 1
Property of sulfated zirconia samples

Sample	BET area ($m^2 g^{-1}$)	Pore size (nm)	Particle size (nm)	Sulfate content SO_4^{2-}wt%
SZ-DA	180	3.2	9.1	6.2
SZ-DN	178	3.0	9.0	6.0
SZ-DAW	137	3.4	9.7	4.9
SZ-SA	–	–	12.7	3.9
SZ-SN	–	–	13.1	3.9
SZ-DA-1	160	2.5	9.3	6.5
SZ-DA-3	180	3.2	9.1	6.2
SZ-DA-5	158	2.5	8.9	5.7
SZ-DA-10	205	2.5	9.1	5.2

samples, the sulfate content was only 4 wt%. This shows that the calcination of small amounts of samples results in a more strong release of sulfur containing compounds during thermal treatment. The sulfate content on the sample calcined in the presence of water vapor was lower (5 wt%) than that of the corresponding sample calcined in dry atmosphere. As shown in figure 1, a longer calcination step progressively reduced the amount of sulfur retained on the catalyst surface from 6.5 wt% after 1 h calcination to 5.2 wt% for 10 h calcination.

All the sulfated zirconia samples had tetragonal structure.

The gases evolved during calcination were analyzed by mass spectroscopy. First, the dehydroxylation of zirconium hydroxide to amorphous zirconia was observed, associated with the water peak at 403 K (figure 2, curve a). Mass 80, corresponding to SO_3, was not detected. However, it must be noted that SO_3, even if it evolved, most likely would not be detected because it could decompose to SO/SO_2 and oxygen [19,20]. Therefore, mass 48, corresponding to SO, was taken as indicative of the release of sulfur containing compounds. As shown in figure 2 (curve b), two peaks with maxima at 403 and 853 K were observed. The former is assigned to ammonium sulfate decomposition, the latter to sulfated zirconia decomposition. At the final calcination temperature of 873 K, sulfur was still released from the sample. To elucidate this phenomenon, a higher amount of sulfated zirconia precursor was calcined. As shown in figure 2 (curve c), the SOx evolution decreased only when, after 3 h calcination, the sample was cooled down.

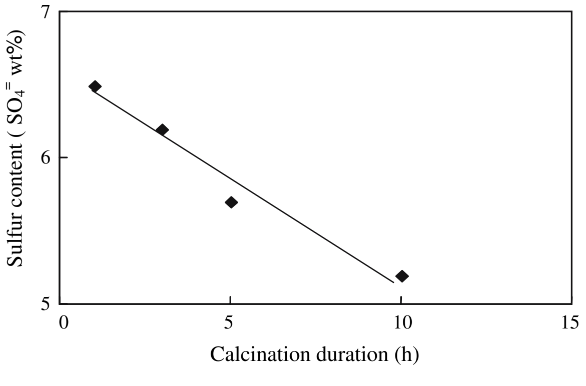

Figure 1. Sulfate content versus calcination duration for SZ-DA-*n* samples (*n* = 1, 3, 5, 10 h calcination).

The IR spectra of the calcined samples normalized by the wafer thickness are depicted in figure 3. In the region of the hydroxyl group vibrations, two bands at 3633 and 3745 cm^{-1} were observed (figure 3(a)). Their intensity was higher for the sample calcined in shallow bed (SZ-SA) than for that calcined in deep bed (SZ-DA). In the region of S=O stretching vibration (1300–1450 cm^{-1}, figure 3(b)), the maximum of the band was located at a rather high wavenumber for SZ-DA (1402 cm^{-1}) with respect to SZ-SA (1396 cm^{-1}). Additionally, the band was less intense than that of SZ-SA. The IR spectrum of the sample calcined in deep bed for 10 h (SZ-DA-10, figure 3(a′)) had slightly more intense OH groups than that of SZ-DA-3. However, for the three samples, SZ-DA-3, SZ-DA-10 and SZ-DAW, the band corresponding to the S=O stretching vibration presented the same intensity and positions (figure 3b′).

3.2. Catalytic performance

Skeletal isomerization of *n*-butane at 373 K was used as model reaction to investigate the catalytic performance. In figure 4, the activity profiles of the sulfated zirconias calcined in air and in nitrogen, with deep and shallow bed, are compared. The two samples calcined for 3 h in deep bed exhibited almost the same catalytic activity in spite of the calcination atmosphere (synthetic air or nitrogen). However, calcination in shallow bed, in both synthetic air and nitrogen, led to completely inactive samples.

As shown in figure 5, the presence of water vapor during calcination inhibited the catalytic activity by a factor of three. Longer calcination duration also had a negative effect on the catalytic activity (figure 6).

For all the active samples, the selectivity of isobutane was approximately 96 wt% at conversion below 5 wt%, by-products being propane and pentanes (n-to iso-pentane ratio 1:4).

4. Discussion

In the standard preparation procedure sulfated zirconia is obtained by sulfation of an amorphous zirconium hydroxide with a liquid agent (mostly H_2SO_4 or $(NH_4)_2SO_4$), followed by calcination at relatively high temperature. Although this calcination step has been recognized to be necessary to induce catalytic activity, the mechanism of formation of the active sites during calcination is not well understood. To trace the sequence of transformations occurring during calcination, we

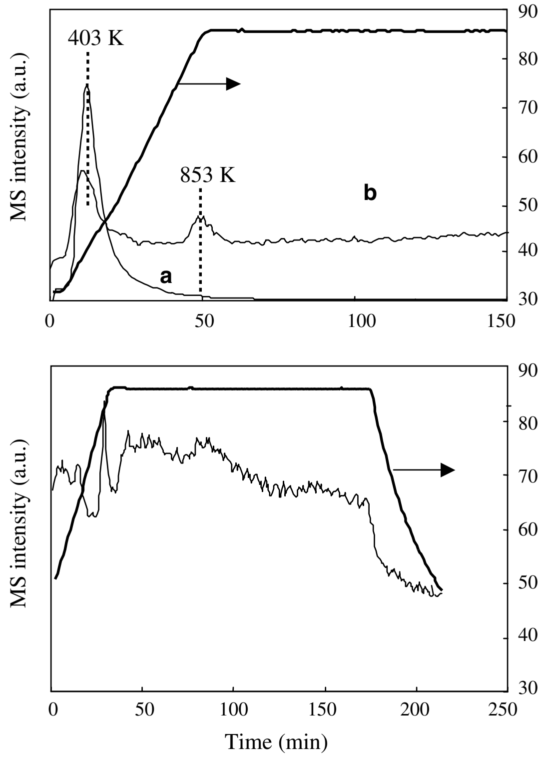

Figure 2. Profile of gas evolved during calcination with respect to time (and temperature): (a) m/e = 18, (b) m/e = 48; (c) m/e = 48 (higher amount of catalyst).

identified by MS the gases evolving, while increasing the temperature. Water was released already at low temperatures with a maximum at 403 K, which is due to the dehydroxylation of zirconium hydroxide to zirconia. Besides water, sulfur oxides (m/e = 48 for SO, m/e = 64 for SO_2) were detected. The first broad TPD peak is attributed to the decomposition of ammonium sulfate to ammonia and SO_3, in parallel to the water release. The absence of the signal m/e 80, corresponding to SO_3, is speculated to be due to the decomposition of SO_3–SO/SO_2 and oxygen, either following evolution and/or in the MS chamber [19,20]. At around 853 K a second sharp peak corresponding to sulfur oxide species was observed. According to the literature, during calcination of zirconium hydroxide or sulfated zirconium hydroxide, an exotherm was observed at high temperature, which was assigned to a "glow phenomenon" related to the crystallization of the amorphous sample [19–21]. This exothermic process would increase the temperature of the catalyst bed and, thus, cause the sulfur oxides release corresponding to the peak observed at 853 K. After reaching the final calcination temperature of 873 K, a slight and continuous release of SO_x was observed. This result, which was confirmed by the decreasing residual sulfate content observed with prolonged calcination, indicates that the sulfate species are, at least partially, temperature-labile.

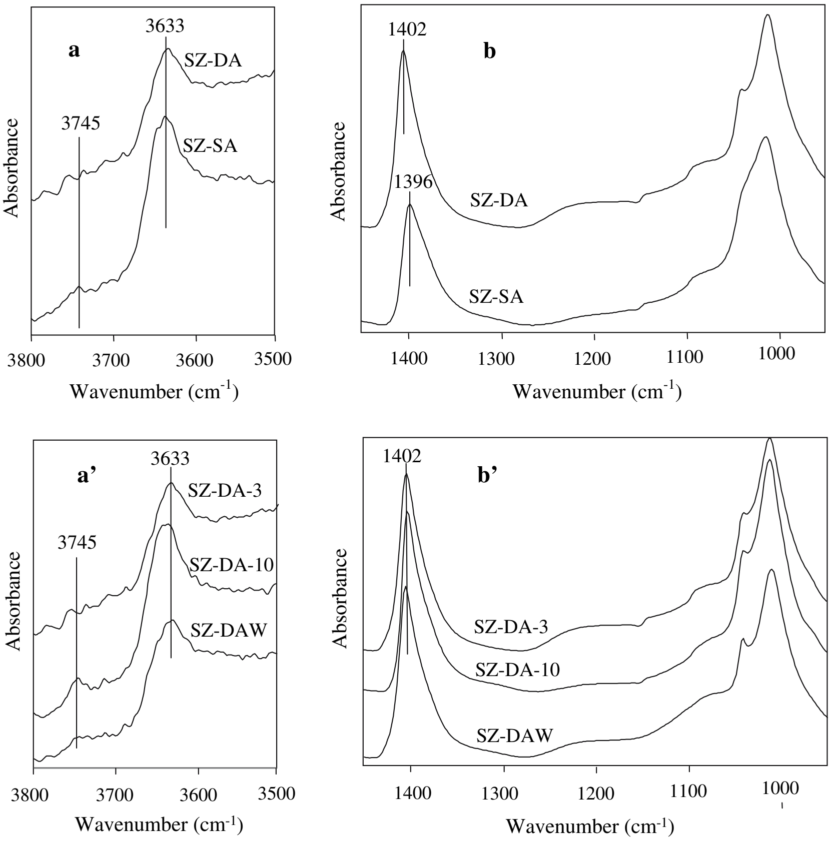

Figure 3. IR spectra. a and a′: hydroxyl stretching vibration region; b and b′: sulfate stretching vibration region.

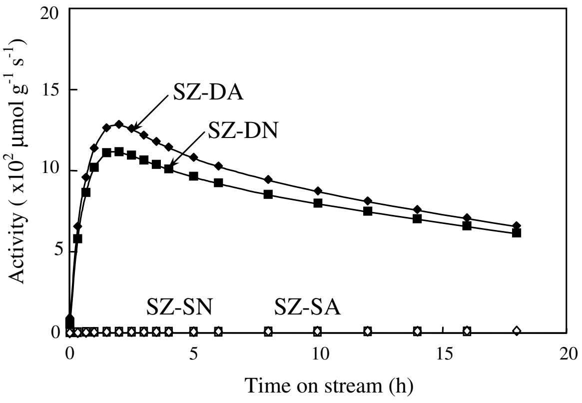

Figure 4. *n*-Butane reaction rate versus time on stream on sulfated zirconia: (◆) SZ-DA and (■) SZ-DN, (◇)SZ-SA and (□) SZ-SN.

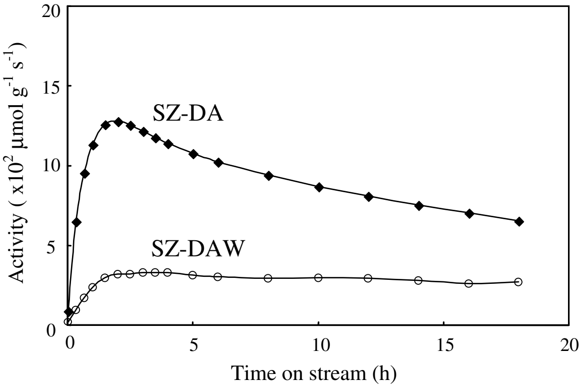

Figure 5. *n*-Butane reaction rate versus time on stream on sulfated zirconia: (◆) SZ-DA and (○) SZ-DAW.

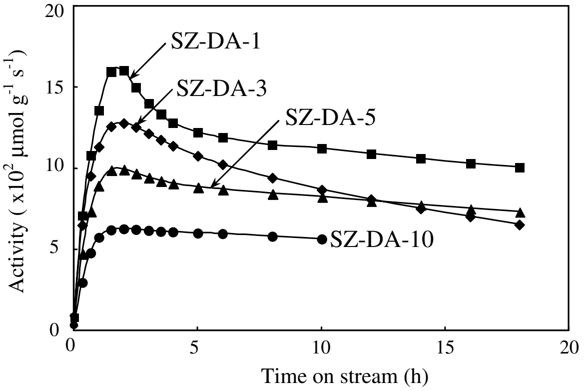

Figure 6. *n*-Butane reaction rate versus time on stream on sulfated zirconia: (■) SZ-DA-1, (◆) SZ-DA-3, (▲) SZ-DA-5, (●) SZ-DA-10.

As prolonged calcination also led to samples progressively less active in *n*-butane isomerization, the labile sulfate species are concluded to be involved in the catalytic process. On the other hand, IR characterization showed that the calcination duration does not affect the structure of the sulfated groups, as indicated by the constancy of the wavenumber corresponding to the stretching of the S = O bond.

The labile nature of the active surface sulfate has also been demonstrated by studying the effect of the calcination temperature [22,23]. In this regard, higher calcination temperatures resulted in samples with lower sulfate surface density and lower activity for *n*-butane isomerization.

Shallow and deep bed calcinations were performed under exactly identical conditions (atmosphere, increasing temperature rate, final temperature and duration), except a single parameter, i.e., the catalyst bed thickness. Thus, in the shallow bed procedure, the catalyst was spread in a thin layer, while in the deep bed calcination the catalyst had a bed depth of a few centimeters. The catalyst calcined in deep bed was active in *n*-butane isomerization, while the shallow bed catalyst was completely inactive.

This pronounced effect of the bed depth on the catalytic activity not only indicates that active sulfate species are labile, but also suggests that active sites are formed during calcination by decomposition of the sulfating agent and readsorption of the formed species on the zirconia surface. In fact, the failure in obtaining active samples upon calcination in shallow bed could be attributed to the easy escape of the sulfur containing species from the catalyst bed. This is confirmed by the lower sulfur amount detected in the shallow bed sample with respect to the corresponding deep bed, a parity of calcination atmosphere and duration.

Having hypothesized that the readsorption of sulfur species obtained by decomposition of the sulfating agent could be responsible for the generation of the active sites, the question has to be asked then, which nature these species could have. In a previous study, we have demonstrated that active sulfated zirconia can be obtained by sulfation with gaseous SO_3 of an already crystallized zirconia sample, without a final calcination step [15]. This method was successfully applied to a broad variety of zirconia samples, whatever the crystallographic structure and the absence/presence of sulfates. These results strongly suggest that the adsorption of SO_3 is responsible for the formation of the active sites. Therefore, we infer that in the conventional preparation method using liquid sulfation agents such as H_2SO_4 or $(NH_4)_2SO_4$, the calcination step is required to decompose the sulfation agent into SO_3 which, after chemisorption on zirconia, leads to the active sites.

The detrimental effect of water vapor in the carrier gas indicates that the atmosphere significantly affects the effectiveness of SO_3 interaction with zirconia surface. In this respect, water molecule will compete with SO_3 to interact with the zirconia surface. The lower sulfur content of the sample calcined in the presence of water also confirmed the inhibiting effect of water on SO_3 deposition on zirconia.

This is also supported by the IR bands observed in the region corresponding to hydroxyl stretching vibration. Two bands at 3747 and 3633 cm^{-1} were observed, which have been assigned to terminal and bridging hydroxyl groups, respectively [24,25]. The normalized area of the most intense of band (3633 cm^{-1}) was higher for the shallow bed samples than for the samples calcined in deep bed. This suggests that the active sulfate species are, at least partially, on top of Lewis acid sites, which, in hydrated state, are covered by hydroxyl groups. The lower sulfate content and the higher intensity of OH band at 3633 cm^{-1} for sample SZ-DA-10 with respect to SZ-DA-3 are in agreement with the above conclusions.

All the calcined samples investigated showed a characteristic IR band between 1300 and 1410 cm^{-1} which has been assigned to the stretching of the double bond $S=O$ [26,27]. For all the samples active in *n*-butane isomerization (SZ-DA, SZ-DA-10, SZ-DAW) this band showed a pronounced maximum at 1402 cm^{-1} while for the inactive samples obtained by calcination in the shallow bed (SZ-SA and SZ-SN) the component at high frequency was missing. Thus, we conclude that IR band at high frequency is a fingerprint of the active species involved in alkane activation. These results confirm our previous findings [15]. Based on DFT calculation and vibrational frequencies calculation we showed that these active species are mostly under form of pyrosulfate groups, which activate butane at low temperature through oxidative dehydrogenation [16].

Morterra *et al*. showed that a final calcination step at temperature above 823 K is necessary to induce catalytic activity even though the samples have been obtained by sulfating, with either H_2SO_4 or $(NH_4)_2SO_4$, zirconia already crystallized into the tetragonal or cubic active structures by formation of solid solution with Y_2O_3 [13,14]. Based on IR measurements with CO at low temperature, the authors suggested that one of the crucial functions of the calcination step is the partial removal of sulfate groups which renders strong Lewis acid sites accessible to the reactants. In this context, it is noteworthy to observe that our interpretation of the calcination function could justify the induction of catalytic activity observed by Morterra after calcination, while the formation of LAS could just be a marginal phenomenon not directly related to the onset of catalytic activity.

Thus, during calcination the sulfated zirconia precursor undergoes several transformations. Firstly, the amorphous zirconium hydroxide releases water and, simultaneously, ammonium sulfate decomposes to ammonia and SO_3. SO_3 interacts, at least partially, with zirconia while ammonia leaves the catalyst. At higher temperature, the amorphous zirconia crystallizes into the meta-stable tetragonal structures with high BET area. At the same time, sulfate species are partially released as SO_3. If the calcination is performed with deep bed, the gaseous SO_3 has the chance to be readsorbed on the sample. This process renders the sample active for skeletal isomerization of short alkanes. On the other hand, if the calcination is performed in shallow bed, SO_3 easily escapes and the final sample is completely inactive in alkane activation. The active sulfate species, mostly under form of pyrosulfate species, are unstable at high temperature, and the continuous release of SO_3 occurring during the isothermal calcination at 873 K results in a progressive decrease of catalytic activity.

In such transformations oxygen is not necessary and, thus, for the same catalyst bed depth, the sample calcined in flowing nitrogen exhibits almost the same catalytic activity of the sample calcined in air.

5. Conclusions

The catalytic activity of sulfated zirconia in *n*-butane skeletal isomerization at 373 K strongly depends not only upon the calcination temperature but also on other parameters involved in the calcination procedure such as catalyst bed depth and duration. On the other hand, the calcination atmosphere does not affect markedly the final performance. We can conclude the following:

1. Gaseous oxygen is not necessary for the formation of active sites during calcination.
2. Calcination in shallow bed catalyst leads to a lower sulfate content and to a completely inactive sample, because SO_3, formed during calcination by decomposition of the sulfating agent, easily escapes from the catalyst.
3. Prolonged calcination results in lower catalytic activity associated with lower sulfate content.
4. Calcination in water saturated synthetic air is less effective for the formation of active sites due to the competition between moisture and SO_3 for adsorption on zirconia.

The formation of active sites is ascribed to the interaction of gaseous SO_3 with the zirconia surface, which is formed by decomposition of the sulfating agent during calcination. The active species are pyrosulfate groups which activate short alkanes by oxidative dehydrogenation.

Acknowledgments

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References

[1] X.M. Song and A. Sayari, Catal. Rev. Sci. Eng. 38 (1996) 329.
[2] K. Arata, Appl. Catal. A Gen. 146 (1996) 3.
[3] T.-K. Cheung and B.C. Gates, Top. Catal. 6 (1998) 41.
[4] V. Adeeva, H. Liu, B. Xu and W.M.H. Sachtler, Top. Catal. 6 (1998) 61.
[5] D. Fărcaşiu and J.Q. Li, Appl. Catal. A Gen. 175 (1998) 1.
[6] Z. Hong, K.B. Fogash and J.A. Dumesic, Catal. Today 51 (1999) 269.
[7] G. Yadav and J.J. Nair, Micropor. Mesopor. Mater. 33 (1999) 1.
[8] T. Yamaguchi, Appl. Catal. A Gen. 222 (2001) 237.
[9] K. Tanabe, M. Itoh, K. Morishige and H. Hattori (1976), in: *Preparation of Catalysts*, eds. B. Delmon, P. Jacobs and G. Poncelet (Elsevier, Amsterdam) p. 65.
[10] T. Yamaguchi, K. Tanabe and Y.C. Kung, Mater. Chem. Phys. 16 (1986) 67.
[11] J.R. Sohn and H.W. Kim, J. Mol. Catal. 52 (1989) 361.
[12] M.-T. Tran, N.S. Gnep, G. Szabo and M. Guisnet, Appl. Catal. A Gen. 171 (1998) 207.
[13] C. Morterra, G. Cerrato and M. Signoretto, Catal. Lett. 41 (1996) 101.
[14] C. Morterra, G. Cerrato, G. Meligrana, M. Signoretto, F. Pinna and G. Strukul, Catal. Lett. 73 (2001) 113.
[15] X. Li, K. Nagaoka, R. Olindo and J.A. Lercher, J. Catal. 238 (2006) 39.
[16] X. Li, K. Nagaoka, L.J. Simon, R. Olindo, J.A. Lercher, A. Hofmann and J.A. Sauer, J. Am. Chem. Soc. 127 (2005) 16159.
[17] A.H.P. Hahn, R.E. Jentoft, T. Ressler, G. Weinberg, R. Schlögl and F.C. Jentoft, J. Catal. 236 (2005) 324.
[18] P. Canton, R. Olindo, F. Pinna, G. Strukul, P. Riello, M. Meneghetti, G. Cerrato, C. Morterra and A. Benedetti, Chem. Mater. 13 (2001) 1634.
[19] S. Chokkaram, R. Srinivasan, D.R. Milburn and B.H. Davis, J. Colloid Interface Sci. 165 (1994) 160.
[20] R. Srinivasan, R.A. Keogh, D.R. Milburn and B.H. Davis, J. Catal. 153 (1995) 123.
[21] R. Srinivasan and B.H. Davis, J. Colloid Interface Sci. 156 (1993) 400.
[22] R.A. Comelli, C.R. Vera and J.M. Parera, J. Catal. 15 (1995) 96.
[23] F.R. Chen, G. Coudurier and J.F. Védrine, J. Catal. 143 (1993) 616.
[24] W. Hertl, Langmuir 5 (1989) 96.
[25] A.A. Tsyganenko and V.N. Filimonov, J. Mol. Struct. 19 (1973) 579.
[26] T. Yamaguchi, T. Jin and K. Tanabe, J. Phys. Chem. 90 (1986) 3148.
[27] M. Waqif, J. Bachelier, O. Saur and J.C. Lavalley, J. Mol. Catal. 72 (1992) 127.