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Optimization of synthesis variables in the preparation of active sulfated zirconia catalysts

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The synthesis of a series of sulfated zirconia catalysts was optimized using the isomerization of n-butane as a reaction probe. The normality of the H_2SO_4 solution used in the sulfation step was found to be the most important variable. A systematic change in the concentration of the H_2SO_4 solution showed that the optimum acid concentration was 0.25 N. When a catalyst prepared with this acid concentration was used, the conversion of n-butane at 200 °C was 35% at 5 min t-o-s. This was close to the thermodynamic equilibrium value of 56% conversion. This maximum was coincident with a catalyst with the highest specific surface area. An increase in the concentration of the H_2SO_4 solution above 0.25 N resulted in a decrease in both surface area and zirconia crystallinity. XPS studies showed a linear relationship between the H_2SO_4 solution concentration and the surface sulfur concentration. Bulk concentrations were determined by elemental analysis. The surface area increased to a maximum for a H_2SO_4 concentration of 0.25 N, while the concentration of bulk sulfur continued to increase when the acid concentration was progressively increased to 2.00 N. The use of a mordenite trap in the reactant stream resulted in an increase in n-butane conversion and a decrease in the rate of catalyst deactivation. XPS studies showed that the sulfur was present as sulfate species and that the oxidation state was not affected by the reaction.

KEY WORDS: sulfated zirconia; n-butane isomerization; catalyst deactivation.

1. Introduction

The high activity of sulfated zirconia catalysts in the isomerization of straight chain hydrocarbons has been the subject of a large number of studies published during the last 25 years [1–18]. These studies include both promoted [11] and unpromoted catalysts [12–18]. A major problem with these catalysts is the rapid rate of deactivation, which they undergo under reaction conditions. Adding promoters such as Pt or Fe-Mo can substantially reduce this rapid rate of deactivation [11,19]. In these studies it has also been shown that when the calcination step is performed prior to the addition of Pt, deactivation can be reduced to a very low level [11]. The role of the noble metal in these promoted sulfated zirconia catalysts is to hydrogenate the olefinic species which are rapidly formed on the catalytically active sites. Because these olefinic species are precursors to the formation of oligomers and aromatic molecules, their elimination prevents, or at least retards, the coverage of the active sites by carbon. From this discussion, it should be apparent that the synthesis of an active sulfated zirconia catalyst should consist of two important steps. First, an active sulfated zirconia catalyst should be synthesized without the addition of promoters, which may obscure the reaction mechanism due to the dual nature of the acid-metal interaction. The second step in the synthesis should deal with the addition of promoters and the pretreatment of the catalyst in such a way that catalytic deactivation is minimized.

In several laboratories, including our own, studies have been performed in which an attempt has been made to understand the role of preparative variables in the absence of metal promoters. These studies include: the optimization of the Brønsted/Lewis ratio to give maximum conversion in the isomerization of n-butane [20], the role of surface area in the conversion of n-butane [18], the location of the active site [18], the fraction of surface sulfate sites that are catalytically active [17,21], the active phase of zirconia [22], the concentration of the sulfuric acid used in the sulfation step [18], the oxidation state of sulfur [23], the effect of adding an olefin trap prior to the reactor [16], the distribution of sulfate sites between the surface and the bulk [23], and the effect of pretreatment on catalytic activity [11].

In many of our studies we have noted that the normality of the sulfuric acid used in the sulfation step is the most important variable in the synthesis of an active hydrocarbon isomerization catalyst. It has an effect on the surface area, the phase of zirconia, the pore size distribution, the sulfur content of the catalyst and, of course, the catalytic activity. Because of this we have decided to perform a study in which the sulfuric acid

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concentration was varied over a wide range of normalities. The probe reaction was the isomerization of n-butane performed at 200 °C.

2. Experimental

2.1. Catalyst preparation

The sulfated zirconia samples were prepared by a two-step procedure which was similar to that described by Li and Gonzalez [12]. The first step in the synthesis involves the formation of a hydrous zirconia gel generated by the hydrolysis of a zirconium salt. The resulting xerogel is dried and pretreated in helium prior to the sulfation step. The sulfated gel is then dried again and calcined at high temperature.

In a typical preparation, 156.4 ml of i-propanol was mixed with 10.26 ml of a solution of the precursor, Zr(n-PrO)$_4$ (70 wt% zirconium n-propoxide, 30 wt% n-propanol). The alcoxide-alcohol solution was heated to 50 °C under continual stirring in a rotavapor. Deionized water was added in a dropwise manner (40 drops/min) until a total of 16.5 ml of water had been added. After 24 h at 50 °C, the temperature was increased to 70 °C and kept constant for a period of 6 h. Finally the solvent was removed by increasing the temperature to 90 °C and maintaining the mixture at that temperature for 30 min. The resulting gel was then dried in an oven at 110 °C for 16 h. Calculation shows that the water/zirconium molar ratio was equal to 40 and the percentage of Zr(n-PrO)$_4$ in the mixture Zr n-propoxide/n-propanol/i-propanol/water was 5 wt%.

The resulting xerogel was pretreated in helium (30 ml/min) for 3 h at 385 °C. It was then sulfated by immersion (1 g xerogel: 15 ml solution; 15 min) in a sulfuric acid solution of a given concentration (0.05–2.00 N). The supernatant was decanted and the sample was dried again in an oven for 16 h at 110 °C. The powder was calcined in an oxygen flow (20 ml/min, 1 h at 600 °C). Prior to storage, the sample was exposed to the atmosphere for a period of 16 h in order to adsorb moisture. The purpose of this step is to restore Brønsted activity.

The sulfated zirconia catalysts will be referred to as SZ*x*, where *x* denotes the normality of the sulfuric acid solution used in the sulfation step. A non-sulfated zirconia sample was prepared using the same procedure (except for the sulfation and the second drying steps).

2.2. Characterization

The crystal structures of the samples were analyzed by x-ray diffraction (XRD) using a Siemens D500 diffractometer with Cu Kα radiation (1.5418 Å). The zirconia crystalline phases (tetragonal and monoclinic) were identified by comparison with the diffractograms in the Powder Diffraction File. The percentage of monoclinic in the zirconia sample was calculated from the intensity of the main XRD signals by means of an empirical equation [24], while the crystallite average size was estimated from the peak width by the Scherrer equation, after taking into account Warren's correction for instrumental broadening [25].

The physical properties of the catalysts were studied by nitrogen adsorption/desorption measurements at −196 °C using a Micromeritics ASAP 2010 instrument. Prior to analysis, the samples were heated in vacuum at 200 °C. The specific surface area was determined from the adsorption data using the BET equation. The pore volume and the mesopore size distribution were obtained by the BJH method [26].

The sulfur content was assessed by a combustion method using a Leco induction furnace. The Galbraith Laboratory, (Knoxville, Tennessee) performed the analyses.

The nature of the surface sulfur was investigated by x-ray photoelectron spectroscopy (XPS). A VG Microtech XR3E2 x-ray source and a SPECS Phobios 100 hemispherical energy analyzer were used. The powder samples were fixed to a molybdenum sample holder with a vacuum-compatible adhesive conductive carbon fixture. Each sample was then introduced into an ultrahigh vacuum chamber and the surface was irradiated with Mg Kα x-rays (1253.6 eV). The energy of the electrons leaving the surface was measured. The spectrum was obtained as a plot of the number of detected electrons per second versus their kinetic energy. A software package (Casa XPS) was used to analyze the spectra.

2.3. Catalytic tests

The catalytic activity of the sulfated zirconia samples was studied using the isomerization of n-butane as a probe reaction. The catalytic runs were carried out in a tubular quartz reactor at atmospheric pressure and at a constant temperature (usually 200 °C, except for some runs at lower temperatures) in a constant flow (20 ml/min) of n-butane (10% in N_2). Prior to reaction, the catalyst was activated in a N_2 flow (20 ml/min), increasing the temperature up to 500 °C (heating rate 5 °C/min) and then reducing it to the reaction temperature. This catalyst activation schedule had been shown to give an optimum Brønsted/Lewis acid site ratio of 0.5 [12,20]. The reaction was stopped when the n-butane conversion became negligible (usually approximately after 150 min).

The reactions carried out in the presence of an olefin trap involved the use of a fixed bed of mordenite through which the reactant was passed prior to reaching the reactor. The mordenite was activated prior to reaction (N_2 flow 20 ml/min; 1 h at 200 ° to remove adsorbed water.

The gas mixture leaving the reactor was analyzed at 10-min intervals following a time on stream of 5 min.

The gas composition of the reaction mixture was obtained using an HP 5890A gas-chromatograph, connected to the reactor through a sampling valve and equipped with a Flame Ionization Detector (FID). The carrier gas was N_2 at a pressure of 20 psi; the column (Alltech Associates), packed with 20% squalane on chrom 60/80 mesh, had an outside diameter of 1/8'' and was 3 m long. The relevant temperatures during the analyses were: column 30 °C, injector 70 °C, FID 200 °C. The actual percentage composition of the gas mixture was calculated from the integrated areas under the peaks in the GC printout and the response factors were previously obtained using Scotty analyzed gas mixtures [27]. The conversion of n-butane and the selectivity to cracking, isomerization and alkylation products were calculated and reported as a function of time on stream.

Table 1
Textural properties of all the samples obtained by N_2 adsorption/desorption measurements

Sample	S_{BET} (m^2/g)	V_P (cm^3/g)	D_p(Å)
ZrO_2	19	0.08	187
SZ0.05	95	0.13	68
SZ0.10	127	0.20	78
SZ0.15	162	0.20	61
SZ0.20	170	0.22	64
SZ0.25	171	0.21	61
SZ0.30	165	0.22	65
SZ0.40	151	0.18	60
SZ0.50	148	0.21	71
SZ0.60	130	0.17	62
SZ1.00	86	0.12	74
SZ2.00	31	0.08	118

3. Results

3.1. Physical properties

The XRD patterns for the non-sulfated zirconia sample and for a series of sulfated zirconia catalysts are shown in figure 1. The pure zirconia sample is composed of a mixture of monoclinic and tetragonal phases. By considering the intensity of the peaks, the volume percentage of the monoclinic phase was calculated to be 40%. The average crystallite size, as calculated from the peak width by the Scherrer equation, was approximately 10 nm. As shown in figure 1, the sulfation step stabilizes the tetragonal phase, whatever the acid concentration. However, a loss in crystallinity with increasing H_2SO_4 solution concentration is also observed.

The nitrogen adsorption/desorption analyses provide information regarding the textural properties of the catalysts. The surface areas (S_{BET}), as calculated by the BET method from N_2 adsorption data are reported in table 1, together with the cumulative pore volume (V_p) and the average pore diameter (D_p), as obtained by the BJH analysis of the data. Sulfation generally increases the rather low surface area and pore volume of ZrO_2. An increase in the concentration of the H_2SO_4 results in an increase in the surface area of the sulfated zirconia. A maximum in both the surface area and the pore volume is obtained when the concentration of H_2SO_4 is about 0.25 N. A further increase in the concentration of H_2SO_4 results in a decrease in both the surface area and the pore volume.

3.2. Sulfur species on the surface

The content and the nature of the sulfur species in the bulk and on the surface of six SZ*x* samples were investigated by elemental analysis and by XPS. The samples were chosen so that the entire range of sulfuric acid concentrations was covered. The results of the bulk analysis (table 2) clearly show that an increase in the normality of the sulfuric acid solution results in an increase in the sulfur content of the catalyst without reaching a saturation point.

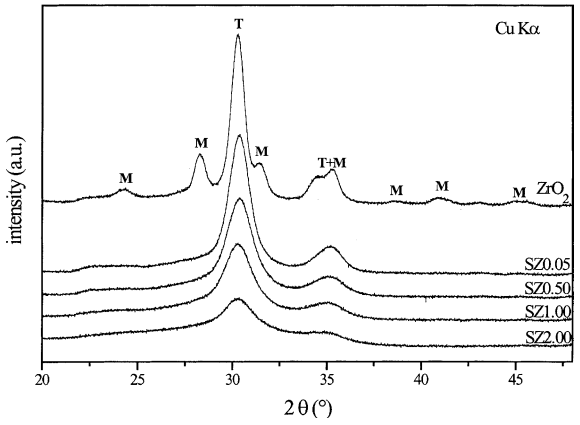

Figure 1. XRD patterns of ZrO2 and a series of SZ*x* samples. T and M indicate the characteristic signals for the tetragonal and monoclinc zirconia phases.

Table 2
Sulfur content (wt%) of a series of SZ*x* samples

Sample	wt% S
SZ0.05	1.08
SZ0.20	2.56
SZ0.25	2.61
SZ0.50	3.46
SZ1.00	4.75
SZ2.00	8.42

The XP spectrum of SZ2.00 is shown in figure 2. It is a plot of the signal intensity over the measured range of binding energies (BE). The peaks were assigned, using the library of the CasaXPS software and the XPS Handbook [28], to the elements present on the surface of the sample (Zr, O, S, C). The use of XPS to identify the presence of surface species is useful as it can also give valuable information regarding the oxidation state of the elements residing on or near the surface. The relatively large C 1s peak is due to the use of a carbon attachment between the sample and the sample holder. In order to correct for the shift due to sample charging, the position of the individual peaks was referenced to the C 1s peak of carbon for each of the samples studied. The BE values of the zirconium peaks are characteristic of ZrO_2, while the S peaks are consistent with the presence of sulfate species [28].

The XP spectrum of SZ2.00 for the Zr 3d ($3d_{3/2}$ and $3d_{5/2}$) and S 2p peaks is shown in figure 3. Using the area of the Zr 3d and the S 2p peaks, multiplied by the corresponding sensitivity factors, the relative amounts of the two elements on the surface can be calculated. As shown in figure 4, the results of this calculation, expressed as atom % S on the surface and reported as a function of the H_2SO_4 solution concentration, follow the same trend as the wt % S, obtained by bulk elemental analysis (table 2). An increase in the H_2SO_4 concentration results in an increase in the concentration of the sulfur both in the bulk and on the surface. This increase is very rapid for the more dilute solutions. However, at acid concentrations in excess of 0.25 N, the increase is nearly linear.

3.3. Catalytic results

The catalytic activity is expressed in terms of n-butane conversion and selectivity to cracking, isomeri-

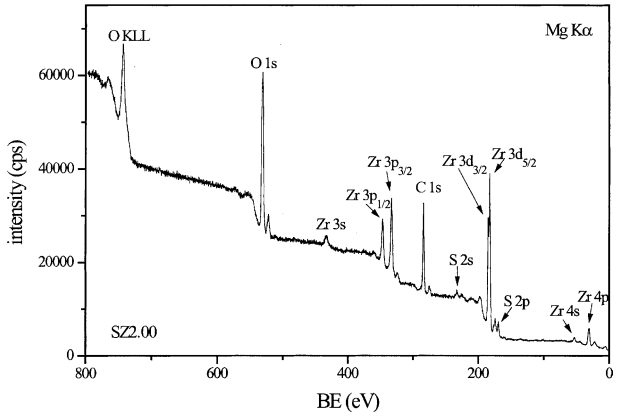

Figure 2. XP spectrum of SZ2.00.

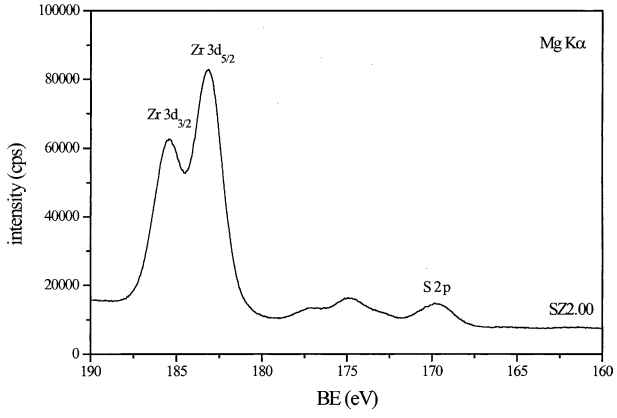

Figure 3. XP spectrum of SZ2.00 in the Zr 3d – S 2p region.

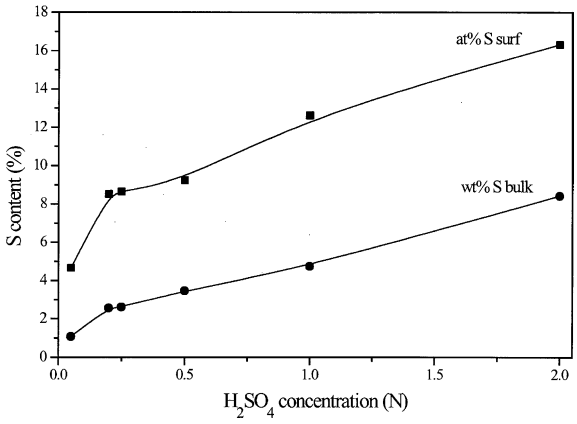

Figure 4. Sulfur content (■: at% on surface; ●: wt% in bulk) versus H_2SO_4 solution concentration.

zation and alkylation products (S_{cr} S_{iso}, and S_{alk}, respectively) as a function of time on stream (t-o-s). As an example, the results of three different runs on the SZ0.60 sample, performed at 200 °C in the absence of an olefin trap, are shown in figure 5. It is important to note that the thermodynamic calculations at 200 °C result in an equilibrium conversion of 56%. The almost perfect agreement between the data obtained for the three runs is apparent, which proves the excellent reproducibility of the catalytic tests. The initial conversion (at 5 min t-o-s) is approximately 30% (figure 5a). However, it rapidly decreases with t-o-s. After 1 h t-o-s it is approximately 6.5%. The selectivities as a function of t-o-s are shown in figure 5b. i-Butane is by far the most abundant product, with an average selectivity value of ca. 92%. Only during the first 15 min t-o-s, it is lower than 90%, but it rapidly increases to a steady state value of 92%. The selectivity plots for cracking and alkylation products are almost coincident, so that any differences in their respective selectivities are difficult to obtain. As expected, S_{cr} and S_{alk}, during the initial t-o-s, show a trend which is opposite to that of S_{iso}. After 30 min t-o-s, they approach a constant value of 4%.

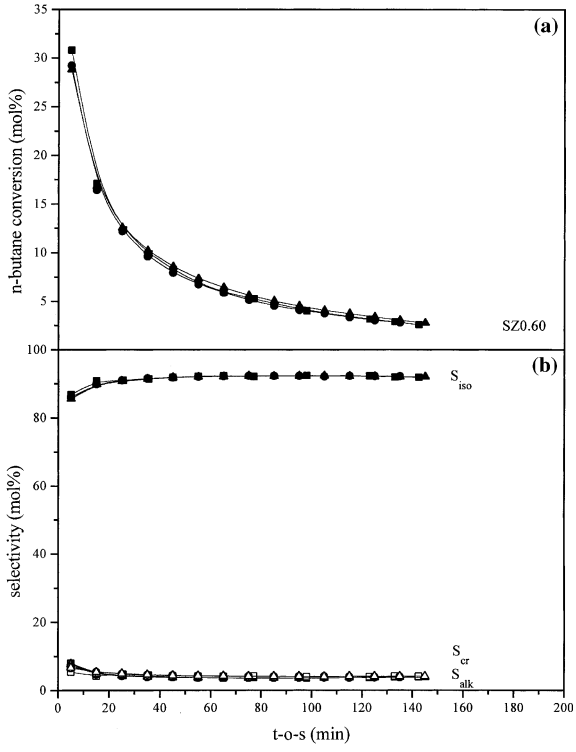

Figure 5. Conversion of n-butane (a) and selectivities (b) versus time on stream (t-o-s) for SZ0.60 at 200 °C. The symbols ●, ■, ▲ refer to three different runs. Black symbols: conversion and S_{iso}; grey symbols: S_{cr}; white symbols: S_{alk}.

Pure ZrO_2 was also studied and found to be completely inactive as a catalyst in the isomerization of n-butane. For the other sulfated zirconia samples, results similar to SZ0.60 (figure 5) were obtained. The trend of conversion and selectivity with t-o-s was essentially the same with any of the other catalysts studied as was also the product distribution following the first few minutes t-o-s. The only notable difference between the catalytic behavior of samples sulfated with different H_2SO_4 concentrations was in the conversion values. However, a larger rate of initial deactivation was obtained for the more active samples. Conversion, which at 5 min t-o-s could be higher than 35% (SZ0.20, SZ0.25, and SZ0.30), rapidly decreased. At 60 min t-o-s it was always below 10% and at 150 min t-o-s it was practically negligible (always lower than 3%). Selectivity results were quite independent of the catalyst tested and, therefore, independent of the concentration of the H_2SO_4 solution used in the preparation. Isomerization was always the prevailing reaction, while cracking and alkylation took place to almost the same limited extent. At the beginning of each run, a slight variation in the product distribution with t-o-s was observed: selectivities (average values at 5 min t-o-s: S_{iso} 86%, S_{cr} 7.5%, S_{alk} 6.5%) reached constant values (on average: S_{iso} 92%, S_{cr} 4%, S_{alk} 4%) after 30 min t-o-s. This suggests that cracking and alkylation preferentially occur on the more active sites, which are rapidly poisoned by coke deposition.

Looking at conversion and selectivity data at 15 min t-o-s one can make a comparison of the catalytic activity of the different samples. This is the time necessary to make sure that the system has been equilibrated. This also enables us to compare the experimental data to results previously obtained in our laboratory [12,14,18]. In table 3, the catalytic data at 15 min t-o-s are reported for all samples. Again, it should be noted that the effect of sulfation is not on the selectivity, but rather on the conversion of n-butane, which is clearly dependent on the concentration of H_2SO_4 solution used in the preparation. Interestingly, the conversion reaches a maximum when the acid solution concentration is approximately 0.25 N. Lower acid concentrations are not able to generate the optimum concentration of active sites. However, when the concentration of the H_2SO_4 solution is too high, the catalytic activity decreases, most probably because of the loss in crystallinity and the decrease in BET surface area caused by the treatment with concentrated acid solutions.

The dependence of n-butane conversion and of surface area on the normality of the H_2SO_4 solution is shown in figure 6. The two curves show a similar trend. A maximum in the surface area is obtained when a 0.25 N H_2SO_4 solution is used in the sulfation procedure. Correspondingly SZ0.25 also shows the highest catalytic activity.

3.4. Effect of a mordenite trap and temperature

In several catalytic runs, the use of mordenite as an olefin trap was tested. The reaction was performed at 200 °C on the same sulfated catalyst with and without a mordenite trap in the line. The conversion of n-butane obtained in these runs is shown in figure 7. A sulfated zirconia catalyst, which gave a somewhat lower butane conversion was used in this study primarily because an improvement in conversion would be easier to notice. Curve NM shows that in the absence of a mordenite trap the catalyst is not very active. The use of a mordenite trap activated in N_2 prior to reaction (curve AM) significantly results in an increase in the conversion. The regeneration of the mordenite trap (same conditions as the first activation) leads to very similar results (curve RM), while non-regenerated mordenite (curve NRM) is essentially inactive, the conversion being the same as without a mordenite trap. The use of the olefin trap also resulted in a small selectivity increase to i-butane by 2 mol%

Table 3
Conversion and selectivity values at 15 min on-stream

Sample	conv (mol%)	S_{iso} (mol%)	S_{cr} (mol%)	S_{alk} (mol%)
ZrO_2	0.0	-	-	-
SZ0.05	2.3	89.3	5.3	5.4
SZ0.10	11.5	90.4	4.5	5.1
SZ0.15	16.5	89.3	5.1	5.6
SZ0.20	20.6	89.9	4.7	5.4
SZ0.25	21.1	89.1	5.2	5.7
SZ0.30	20.7	89.2	5.1	5.7
SZ0.40	19.4	89.9	4.7	5.4
SZ0.50	19.2	89.1	5.2	5.7
SZ0.60	16.8	90.2	4.8	5.0
SZ1.00	14.3	90.7	4.3	5.0
SZ2.00	1.7	90.0	5.2	4.8

The effect of reaction temperature on conversion and selectivity was also studied. Some catalytic runs on the SZ0.20 catalyst were carried out at 150 °C and the results were compared to those obtained at 200 °C. As expected, n-butane conversion decreased with decreasing temperature (20.6 mol% at 200 °C and 14.2 mol% at 150 °C). On the other hand, selectivity to isomerization at 150 °C was somewhat higher than at 200 °C, S_{iso} reaching 94 mol%.

Of particular interest is the effect of reaction temperature in the presence of the mordenite olefin trap. The variation of n-butane conversion with temperature as a function of t-o-s is shown in figure 8. Although the

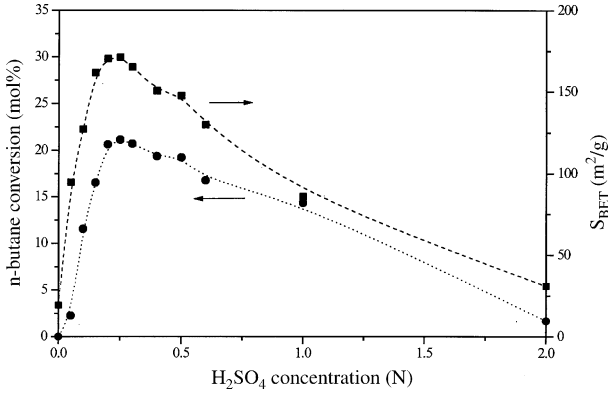

Figure 6. Surface area (S_{BET}) and n-butane conversion at 15 min t-o-s versus H_2SO_4 solution concentration.

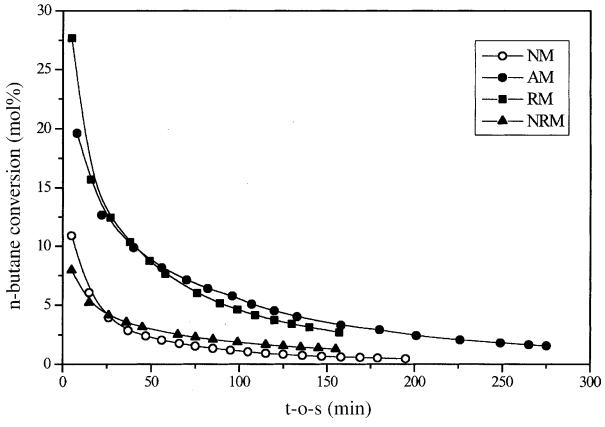

Figure 7. Conversion of n-butane versus time on stream (t-o-s) at 200 °C on a SZ*x* catalyst. NM, ○: No Mordenite; AM, ●: Activated Mordenite; RM, ■: Regenerated Mordenite; NRM, ▲: Non-Regenerated Mordenite.

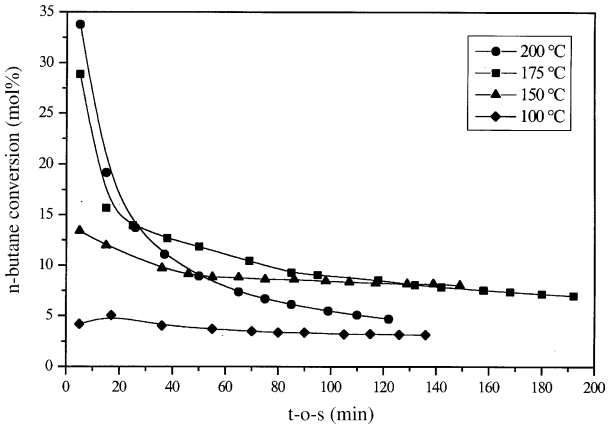

Figure 8. Conversion of n-butane versus time on stream (t-o-s) on a SZ*x* catalyst in the presence of the mordenite trap at different temperatures. ●: 200 °C; ■: 175 °C; ▲: 150 °C; ◆: 100 °C.

initial conversion decreases with decreasing temperature, an inversion is observed at increasing t-o-s. Deactivation is pronounced at 200 °C. However, it decreases substantially when the temperature is decreased. At 100 °C catalyst deactivation is non-existent. At t-o-s in excess of 50 min, n-butane conversion at 100 °C and 150 °C are essentially constant; however, at 175 °C and 200 °C deactivation is still observed. In addition to the decrease in the rate of deactivation, the selectivity to i-butane in the presence of a mordenite trap was observed to increase to a steady state value of 95 mol% at 100 °C.

4. Discussion

The presence of sulfate groups on the surface of zirconia is undoubtedly related to the catalytic activity of sulfated zirconia in the isomerization of straight chain hydrocarbons. XPS analysis clearly shows that the entire sulfur present on the surface is in the sulfate form. The concentration of these surface sulfate groups depends on the normality of the H_2SO_4 solution used in the sulfation step. This is evidenced by the observation that both the weight percentage of sulfur in the catalyst and the atom percent sulfur on the surface are nearly linearly related to the normality of the H_2SO_4 solution used in the synthesis (see figure 4). For very dilute solutions of H_2SO_4 the rate of increase in the sulfur content of both the catalyst and the surface was large. For acid concentrations in excess of 0.25 N the sulfur increase was considerably slower. However, the increase was close to being linear. Even an exposure of the catalyst to a 2.00 N H_2SO_4 solution in the sulfation step did not saturate the surface with sulfate groups.

The synthetic procedures used in this study have lead to the preparation of sulfated zirconia samples with excellent catalytic properties. In fact the highest conversion was obtained using the catalyst SZ0.25 (35%), which compares to a maximum possible conversion of 56% assuming thermodynamic equilibrium. Many parameters can be fine-tuned during the synthesis. Among them particular attention was given to the concentration of the sulfuric acid solution used in the sulfation step. The effect of this parameter is seen by looking at figure 6. An increase in the acid concentration results in an initial increase in the conversion of n-butane. A maximum conversion is reached at an acid concentration of 0.25 N. Higher acid concentrations have a detrimental effect on the catalytic activity. This decrease in conversion is related to a decrease in both the surface area and the crystallinity of the solid acid catalyst (BET and x-ray diffraction experiments) and occurs in spite of an increase in the sulfur content both in the bulk and on the surface (bulk elemental analysis and XPS). n-Butane conversion is reported as a function of the sulfur content in figure 9, where a maximum is clearly observed at 2.61 wt% sulfur. The same trend was found for the methylcyclopentane conversion in [29], which showed a maximum at a sulfur content approximately equal to 3 wt%.

For the present samples, the effect of the concentration of the surface sulfate groups on the catalytic activity is somewhat masked by that of surface area. However, a careful analysis of the experimental data shows that the rate at which the conversion increases with increasing surface area is greater than the rate at which it decreases with decreasing surface area. This is apparent when the conversion is plotted as a function of the surface area for increasing H_2SO_4 solution concentrations. This data is shown in figure 10. Two sets of data can be distinguished, depending on whether an increase in the H_2SO_4 concentration is accompanied by an increase (line *a*, H_2SO_4 concentration: 0.05–0.25 N) or a decrease (line *b*, H_2SO_4 concentration: 0.25–2.00 N) in both n-butane conversion and S_{BET}. A difference in the slope of the two lines confirms that although the conversion is primarily dependent on the surface area, the sulfur concentration on the surface is also important. Comparing two samples with a similar S_{BET}, the one prepared using the

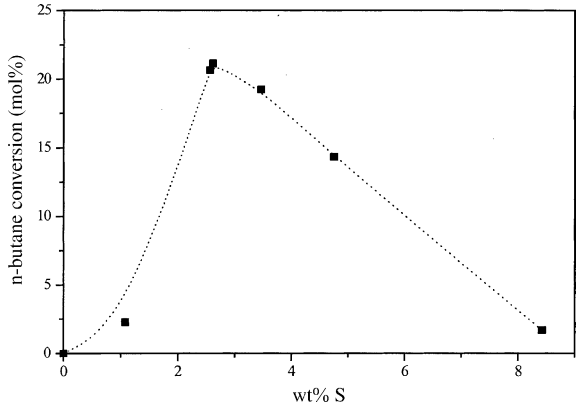

Figure 9. Conversion of n-butane at 15 min t-o-s versus sulfur content.

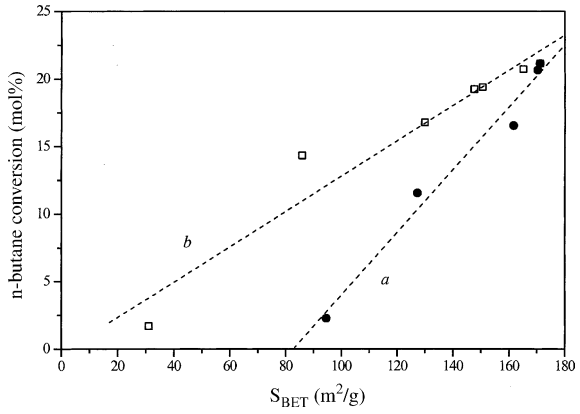

Figure 10. Conversion of n-butane at 15 min t-o-s versus surface area (S_{BET}) for all the SZx samples; a, ●: $x = 0.05–0.25$; b, □: $x = 0.25–2.00$.

highest acid concentration – and thus having the highest surface sulfate concentration – is the most active.

The effect of the gases used in the calcination step was also studied. The temperature program during the calcination step was as follows: (1) heating from RT to 600 °C at a rate of 10 °C/min; (2) isothermal heating at 600 °C for 1 h; (3) cooling to RT, at a rate of 10 °C/min. Oxygen, which was always used in the second step was generally introduced in the initial step of the calcination. Alternatively, N_2 could be used in place of oxygen in the initial step, followed by a switch to O_2 in the second step of the calcination. The choice between these two heating schedules was critical in the synthesis of an active catalyst as shown by the comparison between SZ0.25 and a sample obtained from the same batch using N_2 instead of O_2 during the heating step (SZ0.25 N). The low catalytic activity of SZ0.25 N (conversion at 15 min t-o-s: 1%) was, in all likelihood, due to both low surface area and low sulfur content. In fact, SZ0.25 N in comparison to SZ0.25 had approximately half of S_{BET} and only one third of the sulfur content. Actually these values were even lower than SZ0.05. This observation points to the need of using O_2 as opposed to an inert gas in the initial step of the calcination. The use of N_2 leads to an increase in temperature following the switch to O_2 at 600 °C. A peak temperature of 730 °C was actually recorded following the switch to O_2 before the temperature returned to 600 °C. This was due to the strongly exothermic nature of the combustion reactions of organics, which were suddenly exposed to O_2 at 600 °C. When O_2 was used in the initial step of the calcination, traces of organics were gradually burned off as the temperature was raised. The large spike in the temperature caused by the combustion of organics resulted in the loss of sulfur and also a decrease in S_{BET}.

Though based on the same general method, the synthetic procedure followed for the catalysts used in this study has undergone some modifications since it was first developed [12]. Even slight changes in the sulfation step, in the temperature control or in the calcination atmosphere can result in differences in the characteristic of the samples (especially S_{BET} and S content) and thus in their catalytic activity. This is why the comparison of the present data with those previously obtained in the same laboratory [12,18] is not immediate and one needs to be careful. The maxima in the surface area and in the n-butane conversion, found at a concentration of 0.25 N of the sulfuric acid solution for the present series of catalysts, was found for a catalyst prepared with 0.5 N H_2SO_4 by Li and Gonzalez [12]. Despite the difference in the concentration of H_2SO_4, the surface area (186 m^2/g) and the sulfur content (2.48 wt%) of that sample were quite similar to the values obtained for SZ0.25 and such similarity can actually explain the similar catalytic behavior. In general, comparing the entire set of results in [12] with the present ones, it seems that the trends in conversion and S_{BET} with H_2SO_4 concentration are exactly the same, but shifted so that the maximum in both curves occurs at a higher H_2SO_4 concentration. It is as if the, catalysts obtained by the present procedure retain the sulfate groups more effectively.

If we now consider the results obtained in the same laboratory by Marcus *et al.*[18], we can notice some interesting differences in both the present data and those in [12]. As in [12], the n-butane conversion has a maximum for the sample obtained with a 0.5 N H_2SO_4 solution, but the surface area is much lower (151 m^2/g). A careful analysis shows that, in terms of the surface area and the sulfur content, this sample is much more similar to the present SZ0.50 than to the one in [12] prepared with the same H_2SO_4 solution concentration (0.5 N). Also, the conversion is similar to that of SZ0.50 and lower than the maximum, obtained for SZ025. Actually, as for the present samples, lowering the sulfuric acid solution concentration in [18] resulted in an increase in S_{BET} and a maximum could be sensed in correspondence to a H_2SO_4 concentration of 0.25 N. The real difference between the present results and those in [18] is the trend followed by the n-butane conversion, which in [18] decreased rapidly with increasing surface area. Such a decrease in conversion in spite of an increase in S_{BET} could be explained by the drastic drop in S content observed for H_2SO_4 concentrations lower than 0.3 N [18], which is not observed for the present samples and that is likely to depend on the slight differences in the preparation procedure.

During the catalytic runs carried out at 200 °C in the absence of a mordenite trap, all the catalysts, regardless of initial conversion, showed a rapid rate of deactivation with t-o-s. Deactivation with t-o-s has been a major drawback to the commercialization of sulfated zirconia catalysts. In the current study, changes in the physical properties of the catalysts as a result of reaction could be ruled out. The XRD pattern of the deactivated catalyst was identical to that of a fresh catalyst as was also the surface area and the Brønsted/Lewis ratio of acid sites [20]. The percentage of sulfur

in the bulk and also on the surface showed no appreciable change as a result of the reaction. Likewise, XPS studies did not suggest a change in the oxidation state of sulfur as a result of the reaction.

Previous studies have shown that coke deposition on the active sites is the main culprit for the deactivation [21]. In the absence of a noble metal such as Pt, which will assist in hydrogenating olefinic residues, the catalyst is rapidly deactivated. Olefins can be introduced into the system by two different routes. Because the isomerization of n-butane is a bimolecular reaction [30, 31], olefins can be produced as secondary products during reaction. They can also be introduced as impurities in the feed stream. The use of a mordenite trap to exclude olefins from entering the reactor should therefore result in an increase in the conversion. When the reaction was performed at 100 °C in the presence of an olefin trap, practically no deactivation was observed as a function of time on stream. In addition to a decrease in the rate of deactivation, the selectivity to isomerization was observed to increase. Surprisingly, the reverse reaction, i.e., the isomerization of i-butane to n-butane, is not poisoned to the same extent as the forward reaction, presumably because i-butene is not a good precursor to coke formation [16].

5. Conclusions

The following important conclusions emerge from this study:

(1) The most important variable in the synthesis of an active sulfated zirconia catalyst is the concentration of the H_2SO_4 solution used in the sulfation step. The optimum acid concentration was found to be 0.25 N.
(2) The sulfur content of both the bulk and the surface were strongly related to the concentration of the H_2SO_4 solution used. Both were observed to increase linearly with acid concentration.
(3) Deactivation could be reduced through the addition of an olefin trap in the reaction line. Activated mordenite was found to work quite well as an olefin trap. When the reaction is performed in the presence of an olefin trap at 100 °C deactivation is reduced to a very low value.
(4) Attention needs to be paid in the calcination step to insure that temperature spikes due to the conversion of trace organics do not occur.
(5) The use of XPS can effectively be used to measure both surface concentrations and elemental oxidation states.

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