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The locus of sulfate sites on sulfated zirconia

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The surface of sulfated zirconia was probed using X-ray photoelectron spectroscopy. It was observed that the entire inventory of sulfur could be completely removed by sputtering the surface using an argon beam. Calibration using a $TiO_2(110)$ standard resulted in a surface concentration of 2.85 sulfur atoms/nm^2. This is in reasonable agreement with a value of 4.15 sulfur atoms/nm^2 based on sulfur analysis on the assumption that all of the sulfur was located at the surface. These results suggest that most, if not all, of the sulfur is near or at the surface. When charging was taken into account, we observed that the oxidation state of sulfur did not change following catalyst deactivation during the isomerization of *n*-butane. We also determined that the entire inventory of sulfur was present as SO_4^{2-}. These results reinforce previous studies suggesting that catalyst deactivation occurs as the result of carbon deposition and not a change in the oxidation state of sulfur.

KEY WORDS: sulfated zirconia; X-ray photoelectron spectroscopy; sulfur.

1. Introduction

Sulfated zirconia catalysts are usually prepared by a sequential impregnation method [1]. The zirconia is first prepared either by the calcination of the hydroxide, or by a sol–gel method using an appropriate alkoxide precursor [2]. The dried catalyst is then impregnated using either H_2SO_4 or $(NH_4)_2SO_4$. In previous catalyst deactivation studies using DRIFTS, Li and Gonzalez [3] found that approximately 14% of the total sulfate groups are catalytically active in the isomerization of *n*-butane to isobutane. Similar results using transient kinetic studies were reported by Soo *et al.* [4]. Using calorimetric methods, Yaluris *et al.* [5] and Marcus *et al.* [6] determined that the number of sites exhibiting strong heats of adsorption for pyridine was only a small fraction of the total number of available adsorption sites. A question immediately arises regarding the location of both the active and the inactive sulfate groups with respect to the surface of the catalyst. Several possibilities exist. If all of the sulfate groups are located on the surface, only a small number of these sites must be active in catalyzing the isomerization on *n*-butane. We have shown in a previous study that the isomerization activity is a strong function of the H_2SO_4 strength used in the impregnation step [6]. A maximum in the catalytic activity was observed when the concentration of the acid was 0.5 N. Surprisingly, this maximum in activity was coincidental with a local minimum in the surface area of the catalyst. Very strong acid concentrations result in a sharp decrease in surface area and a relatively low isomerization activity. We have also observed that an optimum in the Brønsted/Lewis acid ratio is approximately 0.5 [7]. This result has also been observed by Ward and Ko [8].

The possibility that sulfate groups can be distributed throughout the surface and the bulk cannot be excluded. If this is the case, then one might arrive at the obvious conclusion that surface sulfate groups are active whereas bulk sulfate species are inactive. Certainly the use of infrared spectroscopy cannot provide an answer to this important problem regarding the nature of what constitutes an active surface site. In order to search for an answer, we have resorted to X-ray photoelectron spectroscopy (XPS), which is much more surface sensitive. In order to bind a larger number of active sulfate sites to zirconia we must obtain a better idea as to their location on the surface. XPS can also provide additional information regarding the oxidation state of sulfur. If the sulfate groups were present primarily in the bulk, changes in binding energies would not be sensitive to XPS. On the other hand, if the active sulfate groups are all on the surface, shifts in binding energies might readily be detected.

2. Experimental

2.1. Sample preparation

Sulfated zirconia was prepared by a two-step sol–gel synthesis method shown in figure 1 [1]. In this method, zirconium oxide was first prepared using *n*-propoxide (Alfa Chemical, reagent grade) as a precursor. The precursor was dissolved in 2-propanol (CEM reagent grade) to make a 5 wt% Zr(*n*-propoxide)$_4$ solution. The

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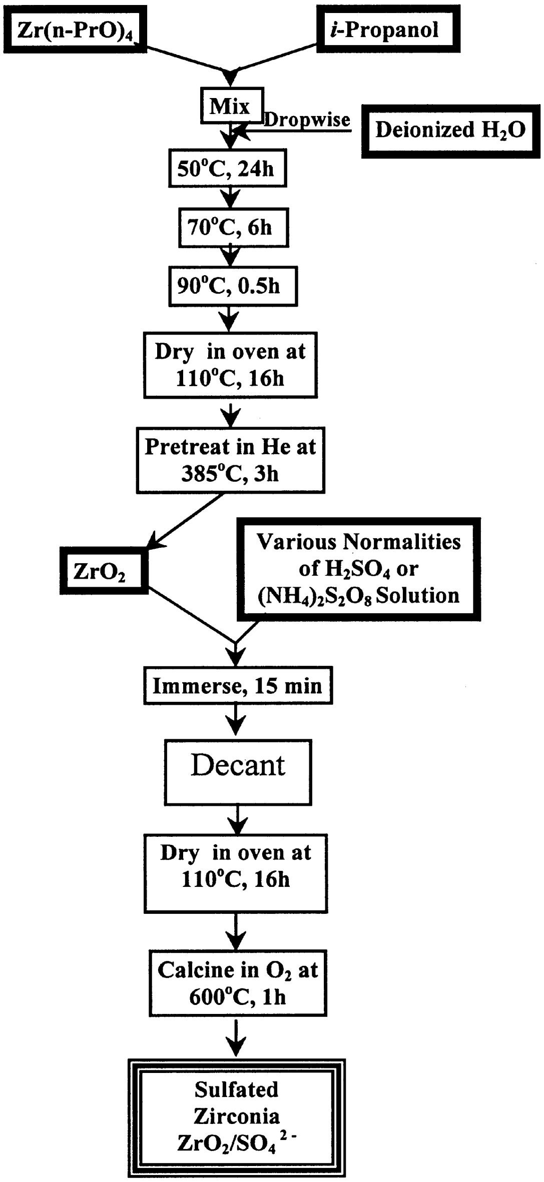

Figure 1. The two-step sol–gel preparation method for sulfated zirconia.

sample was then maintained at 50 °C and stirred for 24 h. The temperature was increased to 70 °C and then maintained at that temperature for 6 h to complete the synthesis. The solvent was removed by increasing the temperature to 90 °C for 30 min. The sample was dried in an oven for 16 h at 110 °C. The resulting xerogel was then ground using a mortar and pestle and pretreated in flowing He (30 ml/min) at 385 °C for 3 h. The pretreated zirconia was then sulfated using the desired concentration of H_2SO_4. The concentration of the H_2SO_4 used in this study was 0.5 N. A 1 g amount of zirconia was immersed in 15 ml of the acid solution for 15 min. The supernatant was then decanted and the sample was redried overnight at 110 °C. The resulting sulfated zirconia was calcined at 600 °C in flowing O_2 (20 ml/min) for 1 h and stored in a vial under ambient conditions. This particular H_2SO_4 concentration was chosen because in a previous study it was shown to have the highest activity in the isomerization of *n*-butane.

Surface areas and pore size distributions were obtained using a Coulter Omnisorb 100 instrument. The range of the P/P_0 values for the BET surface areas was 0.05–0.25. This is the range of the isotherm in which the monolayer is formed. The range of P/P_0 values used to calculate the pore size distributions was 0–1, *i.e.*, the entire isotherm.

The sulfur content analysis was performed by the Galbraith Laboratory (Knoxville, TN). A combustion method using a Leco induction furnace was used.

2.2. XPS

X-ray photoelectron spectroscopy was performed on a fresh and on a completely deactivated sample of sulfated zirconia. The deactivated sample had been reacted for 3 h under *n*-butane. A VG Michrotech XR3E2 X-ray source and Specs Phobios hemispherical energy analyzer were used. The powder samples were pressed into pellets and mounted on a tantalum sample holder. The sample was then introduced into an ultrahigh vacuum chamber and the surface was irradiated with Mg K 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. The surface of the catalyst was sputtered with argon ions for 15 min to remove the first few layers from the surface. The sample was then retested. Knowing the energies that the electrons from the different energy levels of various elements have, the elements on the surface of the catalyst and in some cases their oxidation states can be found. Because the mean free path of electrons in solids is very small, the detected electrons originate from only the top few atomic layers.

In order to quantify the sulfur at the surface of the catalyst, it was necessary to use a reliable standard, which could be compared with that of the sulfur signal obtained on the actual catalyst. This was accomplished by depositing sulfur at 350 °C on $TiO_2(110)$ according to a procedure described by Hebenstreit *et al.* [9]. This procedure results in a (4×1) overlayer which corresponds to a sulfur concentration of 5.12 s atoms/nm^2. This overlayer was also verified by STM [9]. By taking the ratio of the signals from the catalyst sample and from the standard, the concentration of sulfur on the surface of the catalyst can be obtained.

3. Catalytic test reactions

3.1. Isomerization of n-butane

The reaction was performed in a single-pass, downward-flow, quartz microreactor under atmospheric pressure and isothermal reaction conditions. Prior to performing a reaction, water was back-added to the catalyst by venting it to the atmosphere for 16 h. This step was necessary in order to restore Brønsted acidity to the catalyst. Immediately prior to reaction the catalyst was heated to 500 °C at 5 °C/min in N_2 (20 ml/min). The catalyst was then cooled to the reaction temperature, 200 °C. This catalyst pretreatment resulted in an optimum Brønsted/Lewis ratio of 0.5. This ratio was determined using pyridine adsorption by a DRIFTS technique, which has been described in detail in a previous paper [7]. A mixture of 10% *n*-butane with a balance of N_2 was passed through the reactor at a constant flow rate of 20 ml/min. Product gas analysis was performed by gas chromatography.

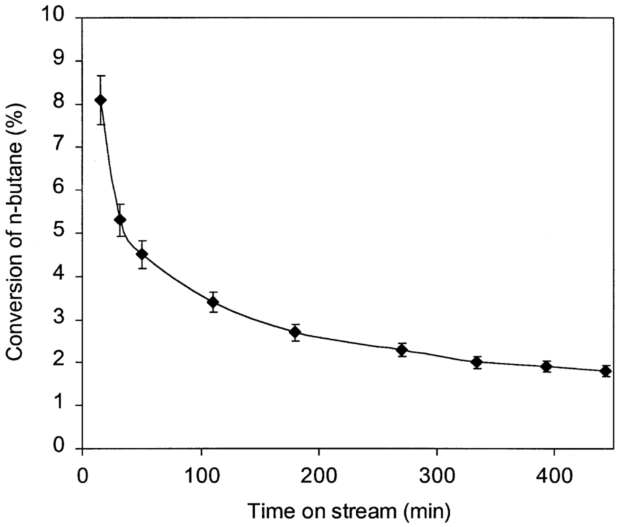

Figure 3. The percentage conversion of *n*-butane over time for 0.5 N sulfuric acid catalyst, with an olefin trap used to filter olefin impurities. The reaction temperature was 200 °C.

4. Results

4.1. Physical properties

For the sulfated zirconia catalyst prepared using a sulfuric acid concentration of 0.5 N, a surface area of 151 m^2/g was obtained. The average pore diameter was 44 nm and the pore volume was 0.37 ml/g. The sulfur content for this catalyst was 3.32%.

4.2. Catalytic activity

The conversion of *n*-butane was measured at 150 and 200 °C. The conversions are shown in figure 2. At both temperatures the catalyst deactivates rapidly and is completely deactivated after 3 h on-stream. A major cause of this deactivation can be linked to olefin impurities in the feed. The main impurities are linear olefins, which are precursors to the formation of coke [6]. The amount of butenes in the feed increases with age in the gas tank. The concentration of these impurities can be reduced considerably by adding an activated mordenite trap in the line. The percentage conversion of *n*-butane at 200 °C over time using a mordenite trap is shown in figure 3. Because *n*-butene is an intermediate in the isomerization of *n*-butane, a decrease in its concentration will have a negative effect on the overall conversion. This is clearly shown in figure 3. However, because the formation of coke, which is a secondary reaction, also decreases, the catalyst still shows considerable activity after 3 h on-stream. On the assumption that the rate of deactivation is first-order in the rate of isomerization, the first-order deactivation rate constant can be calculated. It was found to decrease from 0.02 min^{-1} without the mordenite trap to 0.007 min^{-1} [6] with the trap in the line. The catalyst could be completely regenerated by burning off the coke in air at 400 °C.

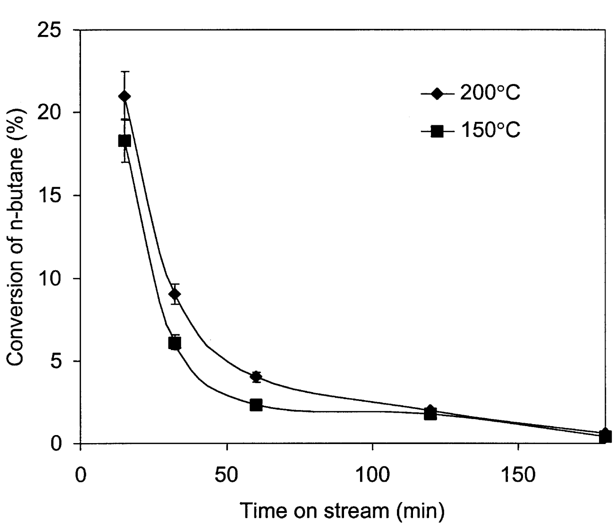

Figure 2. The percentage conversion of *n*-butane over time for 0.5 N sulfuric acid catalyst at reaction temperatures of 150 and 200 °C.

4.3. XPS

X-ray photoelectron spectroscopy was performed on a fresh and on a completely deactivated sample of sulfated zirconia made with 0.5 N sulfuric acid solution. The catalyst was deactivated by exposing it to *n*-butane until the isomerization activity was essentially zero. This was usually observed following reaction at 200 °C for approximately 3 h. An overview of the spectrum for the fresh sample is shown in figure 4. This spectrum is a plot of the signal intensity over the measured range of binding energies. The characteristic peaks for various elements were found in the XPS Handbook [10]. This spectrum shows three characteristic peaks for zirconium: a small peak at about 430 eV, which represents the 3s electron; a large doublet at 343 and 330 eV, which represents the $3p_{1/2}$ and $3p_{3/2}$ electrons, respectively; and another large doublet at 181 and 179 eV which

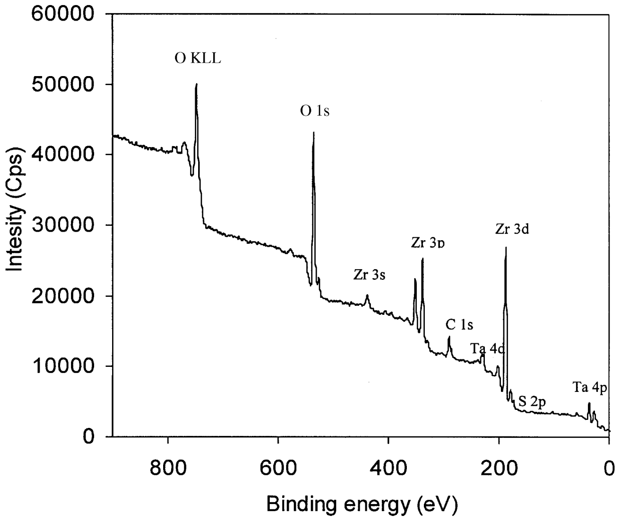

Figure 4. The XPS spectrum of a fresh sulfated zirconium catalyst made with 0.5 N sulfuric acid.

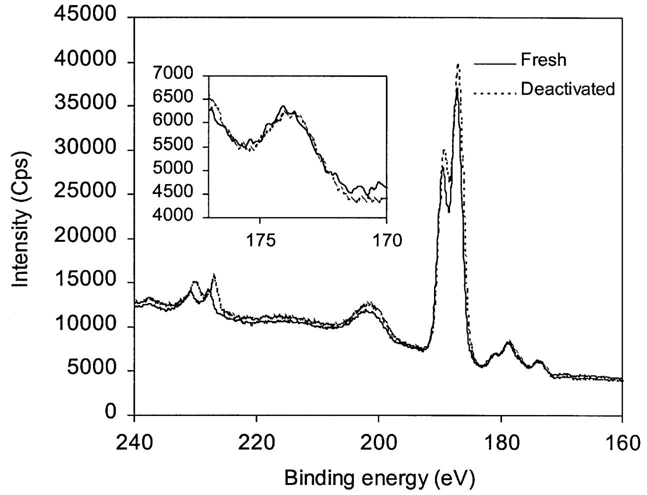

Figure 6. Enlargement of the XPS spectra of the zirconium and sulfur region for the fresh and deactivated 0.5 N sulfuric acid sulfated zirconia catalysts.

represent the $3d_{1/2}$ and $3d_{5/2}$ electrons, respectively. This spectrum also shows two distinct oxygen peaks, the oxygen 1s at 531 eV and the peak at 780 eV, which is an Auger series (KLL). The Auger series are a group of lines that are representative of Auger transitions. This spectrum also shows a small peak for the carbon 1s at 285 eV, a very small peak for the sulfur 2p at 165 eV and some small peaks for tantalum (which is the material from which the sample holder is made) at 230 and 24 eV. It is important to note that carbon is always present in the XPS background spectrum. It is not possible to distinguish between carbon deposited as the result of catalyst deactivation and background carbon in the XPS instrument.

Figure 5 shows the shift in the oxygen peak between the three samples. This shift is due to the electric charging of the samples. In order to compare the spectra visually this shift must be corrected for. The oxygen peak can be used as a standard to line up the plots and normalize the three spectra. Figure 6 shows the zirconium and sulfur region of the fresh and deactivated catalysts. The two sulfur peaks line up almost exactly, showing no noticeable differences. The fact that the two peaks are almost identical means that the oxidation state of the sulfur does not change as a result of deactivation. Figure 7 shows the same range as the previous figure but in this figure the fresh sample before and after sputtering are compared. Sputtering the surface of the sample with argon ions removes the first few monolayers of the sample. The sputtered sample shows no peak for sulfur. This must mean that all of the sulfur is removed by sputtering. Therefore, it can be concluded

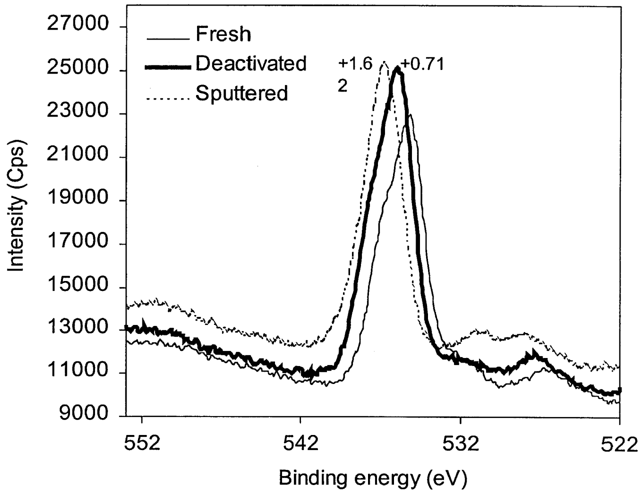

Figure 5. XPS plot of the oxygen 1s region of deactivated, fresh, and fresh-sputtered 0.5 N sulfuric acid sulfated zirconia catalysts. The shifts used to align the spectra are shown. Deactivation studies were performed by exposing the catalyst to the reaction mixture at 200 °C for 3 h.

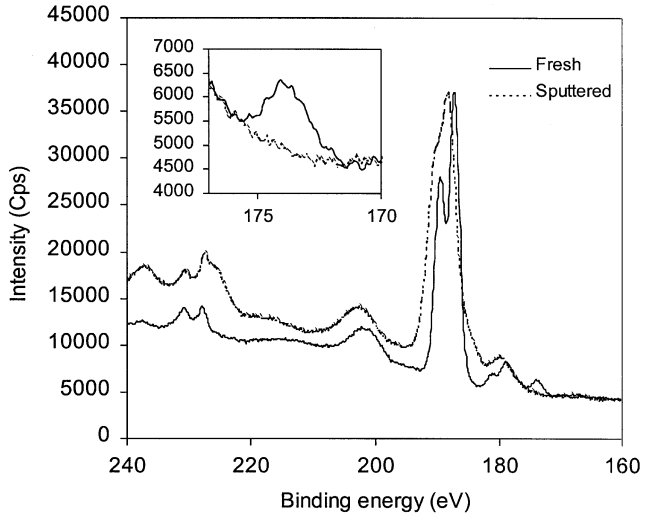

Figure 7. Enlargement of the XPS spectra of the zirconium and sulfur region for the fresh and fresh-sputtered 0.5 N sulfuric acid sulfated zirconia catalysts.

that most of the sulfur resides at or close to the surface of the catalyst.

A straightforward calculation using the measured BET surface area and the sulfur content of the catalyst shows that if all shows that if all of the sulfur is located on the surface, the sulfur surface density would be 4.15 sulfur atoms/nm^2. In order to check the validity of this assumption, the integrated signal corresponding to the standard and to the catalyst were measured. The average of the two measurements on the fresh and the deactivated catalysts was 3547 counts/eV/sec. For the sulfated $TiO_2(110)$ standard it was 6361 counts/eV/s. Hence the XPS spectra for the ZrO_2 catalyst corresponds to $3547/6361 \times 5.12$ sulfur atoms/nm^2) or 2.85 sulfur atoms/nm^2. This number is fairly close to the 4.15 sulfur atoms/nm^2 calculated on the assumption that all of the sulfur is located at or near the surface.

The peak position of the XPS 2p peak is at 168.5 eV. According to the XPS Handbook [10], this means that the sulfur is in the SO_4^{2-} form.

5. Discussion

In discussing the results, it is useful first to outline how the percentage of active sulfur is arrived at. In a previous study we showed that following complete catalytic deactivation, a temperature-programmed desorption study using nitrogen as the carrier gas resulted in two desorption maxima [6,7,11]. The low-temperature maximum is centered at 600 °C while the high-temperature desorption peak occurs at 900 °C. For a fresh catalyst, not subjected to deactivation by reaction, only a single maximum is observed. Using infrared spectroscopy it is possible to show that the low-temperature maximum includes CO_2 and SO_2 while the high-temperature maximum contains only SO_2 [11]. Using a method described in the literature it is possible to separate and to quantify both the CO_2 and the SO_2 from the low-temperature maximum [11]. When this low-temperature sulfur is removed by heating the catalyst in nitrogen to 600 °C, the catalyst is totally inactive for the isomerization of *n*-butane. The activity could not be restored regardless of catalyst manipulation. By burning of the CO_2 in an oxygen carrier at 400 °C the carbon which is deposited on the active sites can be selectively removed and the full initial activity is restored. Integration of the SO_2 maxima shows that the most active catalyst has a percentage of this active sulfur of about 14%.

The results of this study strongly suggest that most, if not all, of the sulfur is located at the surface of the catalyst and that it is present as SO_4^{2-}. The observation that 14% of this sulfur is catalytically active suggests that if a change in the oxidation state of the sulfur were to occur as a result of reaction, a shift in the XPS spectrum corresponding to at least part of the 2p surface sulfur peak should be observed. Because no such shift was observed, we must conclude that a change in the oxidation state of sulfur does not occur as a result of deactivation. When surface charging is taken into account, the XPS 2p spectra of sulfur for the fresh and the deactivated samples are identical. The possibility of re-oxidation of sulfur on the deactivated catalyst by exposing it to air prior to placing it in the XPS chamber cannot be totally ruled out. However, we discount it for two reasons. Activation of the sulfur on a fresh catalyst requires a calcination temperature of 600 °C in oxygen. It is therefore unlikely that a deactivated catalyst can be re-oxidized at room temperature. Additionally, the active isomerization site corresponding to the deactivated catalyst is covered by carbon, making re-oxidation unlikely.

From the above discussion, it is clear that there are two different sulfate species on the surface of sulfated zirconia. The observation that only one SO_2 desorption maximum is observed from a fresh catalysts also tells us that the two different sulfate species do not differ appreciably in binding energy. We also know that the normality of the sulfuric acid solution used to impregnate the zirconia is an important variable in maximizing the fraction of active sulfate groups. We suspected, as have others [12], that the active sulfate species is actually a dimer. However, in a recent study currently in press, we prepared sulfated zirconia using ammonium peroxodisulfate [$(NH_4)_2S_2O_8$] in place of H_2SO_4. The thought here was that the use of a dimer might lead to an increase in the number of active sites. However, isomerization activities were very similar to those obtained using H_2SO_4. We also observed that very little isomerization activity was observed until the concentration of the sulfuric acid used to impregnate the zirconia approached 3 N. The activity rapidly increased to a maximum at 5 N and then declined at higher acid strengths. This observation suggests that perhaps initial adsorption occurs on isolated sites. Further sulfate adsorption occurs at these isolated sites with the result that a dimer may be formed, resulting in the formation of an active site. Further sulfate adsorption results in a higher concentration of surface sulfate groups, which appear to have a lower isomerization activity. In other words, it makes very little difference whether the sulfate is added in the form of a dimer precursor or as sulfuric acid. When the concentration of these sites exceeds approximately 14% of the surface, additional surface sulfate groups act as “spectator” species.

6. Conclusions

XPS studies show that for solid acid catalysts prepared by the impregnation of zirconia with sulfuric acid, most if not all of the sulfate groups are present on the surface. However, only a small percentage of these are responsible for the isomerization activity.

XPS clearly shows that a change in the oxidation state of sulfur does not occur as a result of *n*-butane isomerization.

All of the surface sulfate is present as SO_4^{2-}. This includes both the active and the inactive sulfur.

Deactivation occurs primarily as the result of carbon deposition on the active sites. Because carbon is always present as backgound noise in the XPS spectrum, it is not possible to obtain much information regarding the type of carbon present.

Acknowledgments

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