JOURNAL OF CATALYSIS **164,** 459–466 (1996)
ARTICLE NO. 0402

Effects of Water on the Performance of Sulfated Zirconia Catalysts for Butane Isomerization

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Received May 7, 1996; revised August 28, 1996; accepted September 3, 1996

The activity, selectivity, and rate of deactivation of sulfated zirconia catalysts for isomerization of *n*-butane at 423 K depend on the temperature at which the catalyst is dried following initial calcination and exposure to air. The optimum drying temperature for the sample of this study is 548 K. The addition of 75 μmol/g of water to a sample dehydrated at 773 K restores high catalytic activity. Excessive catalyst hydration leads to low catalytic activity by causing extensive hydrogen bonding at the active sites. Changes in catalytic activity with drying temperature are not directly related to a transformation of Brønsted to Lewis acid sites. Rather, the surface sulfate species may participate in butane isomerization via a reduction–oxidation cycle, and water may promote the catalytic activity by altering the oxidation–reduction properties of the surface sulfate species.

INTRODUCTION

Sulfated metal–oxide catalysts are active for the low-temperature isomerization of hydrocarbons, and the most-studied of these catalysts is sulfated zirconia, which is active for butane isomerization at temperatures below 520 K (1–10). While the need for strong acidity appears to be important for the reaction to occur (6, 11, 12), the nature of the active sites is not yet understood. Some researchers propose that the active sites are Lewis acid centers (2, 3, 7–10, 13–18), and others suggest that Brønsted acid sites are the primary catalytic species (11, 12, 19, 20). Furthermore, some researchers report that a combination of both types of sites is needed for the catalyst to be active (4, 5, 21, 22).

Recently, Babou and co-workers have proposed that a combination of Brønsted acid sites and surface-bound water is needed for catalytic activity (9, 23). It has also been found that various factors affect the isomerization activity of sulfated zirconia catalysts, such as preparative methods, sulfur content, degree and type of crystallinity, and calcination temperature (1, 2, 4–6, 12, 17–19, 21, 24–28). Therefore, it has been difficult to document the effects of water on catalyst performance. Furthermore, several research groups (7, 29, 30) have shown that water may serve as a poison of the active sites. These researchers, along with other research groups (7, 9 18, 25, 27), have suggested that water serves to transform active Lewis sites into inactive Brønsted acid sites.

In the present study, we have used reaction kinetics studies of butane isomerization and water adsorption/desorption experiments to examine the effects of water on the catalytic activity of a sulfated zirconia catalyst. We show that small quantities of water are necessary for high catalytic activity of sulfated zirconia catalysts, providing insight into the nature of the active catalytic sites.

EXPERIMENTAL

The sulfated zirconia catalyst used in this study was obtained from Magnesium Elektron, Inc., in the form of sulfated zirconium hydroxide. The catalyst was prepared by heating it to 848 K in a stream of dry oxygen (100 cm^3/min/g cat) over a period of 1.5 h, followed by continued treatment at that temperature for 2 h. After calcination, the catalyst was stored in a desiccator for later use. The calcined catalyst has a sulfur loading of 1.8 wt% (Galbraith Laboratories), corresponding to a sulfate concentration of 560 μmol/g. The BET surface area after this treatment is 98 m^2/g.

Reaction kinetics measurements for *n*-butane isomerization were conducted in a quartz flow reactor 1.0 cm in diameter. The reactor was loaded with a mixture of 200 mg of catalyst and 100 mg of quartz particles. Kinetics measurements were initiated by flowing a mixture of ca. 10% *n*-butane (AGA, 99.5% purity, instrument grade) in He (Liquid Carbonic) over the catalyst at 423 K. The predominant impurity in the butane feed was isobutane (0.36%), with trace quantities of propane and pentanes. Butene impurities in the *n*-butane feed were about 1300 ppm. Both gases were purified by an oxygen absorbent trap (Alltech), and water impurities were removed by molecular sieve traps at 77 K for He and at room temperature for *n*-butane. Reaction products were analyzed using a Hewlett Packard 5890 gas chromatograph, containing a 7.3 m 5% DC-200

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Chromosorb P-AW column held at 323 K, and equipped with a flame-ionization detector.

Prior to reaction kinetics measurements, the catalyst was treated by heating at ca. 9 K/min in flowing He (65 cm^3/min). To study the effect of the drying temperature on catalytic activity, kinetics experiments were performed in which the catalyst was heated to a temperature between 423 and 773 K, held at that temperature for 1 h, and then cooled to 423 K for kinetics measurements. The catalysts used in these experiments will be denoted as SZ-*t*, where *t* is the drying temperature in K.

Experiments were also performed to study the effect of hydration of a previously dehydrated catalyst. The catalyst was first heated to either 673 or 773 K in flowing He and dried at that temperature for 1 h. After cooling to 423 K, the cell was connected (without exposure to the atmosphere) to a vacuum manifold and evacuated to a pressure of ca. 2 mPa. Water vapor was then dosed onto the catalyst sample at 423 K and allowed to equilibrate for 30 min. The quantities of water dosed onto the sample ranged from 24 to 150 μmol/g of catalyst. After equilibration, the cell was connected to the gas-handling system and purged with He for 5 min before beginning the kinetics experiments.

In separate experiments, dehydrated catalysts were fully hydrated with excess water to probe the reversibility of the rehydration process. In particular, samples were dried in He or O_2 at a temperature between 673 and 773 K, cooled to 423 K, and exposed to ca. 300 μmol/g of water. After equilibration for 30 min at 423 K, the sample was heated to 588 K and dried for 1 h, after which it was cooled to 423 K and reaction kinetics data were collected. These samples will be referred to as SZ-*t*/*G*, where *t* is the dehydration temperature and *G* is the carrier gas.

The amount of water removed at different drying temperatures was measured using a Cahn C-2000 microbalance. The sulfated zirconia sample (225 mg) was heated in ca. 100 cm^3/min of dry He to various temperatures. After drying at a certain temperature for 1 h, the sample was isolated in 1 atm He to allow for measurement of its change in mass. The sample was again exposed to flowing He and heated to a higher temperature, where its new mass was determined; this procedure was repeated at various temperatures between 423 and 773 K. The sample was then cooled to the various drying temperatures, where the mass of the dehydrated catalyst was measured to determine the extent of buoyancy effects on the previous mass measurements.

RESULTS

Deactivation Behavior

Measurements of catalytic activity reported in this paper were determined from the net formation of products and are given in terms of nmoles of *n*-butane converted per second per gram of catalyst. The initial sampling in these experiments occurred after 3 min on stream. All the reaction studies displayed first-order deactivation, as evidenced by the linearity of the semi-log plot of activity versus time on stream shown in Fig. 1 for the SZ-523 sample. We denote this first-order deactivation behavior as the "standard" activity, as noted in a previous study (11). The standard activity can thus be described by the relation

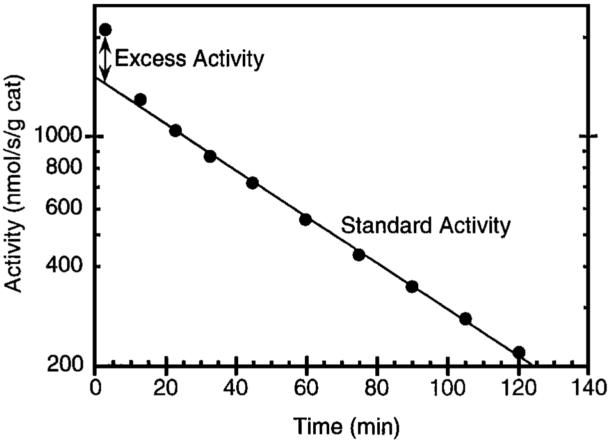

FIG. 1. Semi-logarithmic plot of activity vs. time on stream for the SZ-523 sample.

$$A = A_S\, e^{-k_S(t-3)}, \tag{1}$$

where A_S is the initial standard activity, and k_S is the deactivation constant. Various samples, however, exhibited an initial activity higher than that expected from the deactivation described by Eq. (1). This "excess" activity is defined as

$$A_E = A_o - A_S, \tag{2}$$

where A_E is the excess activity observed at 3 min on stream and A_o is the overall activity observed at that time.

Effect of Drying Temperature

Semi-log plots of catalytic activity versus time-on-stream are shown in Fig. 2 for catalysts dried at different temperatures. Figure 2 shows that intermediate drying temperatures lead to a more active catalyst. The slope of the deactivation profile (k_S) also appears to be a function of the drying temperature, with catalysts dried at higher temperatures appearing to deactivate at a faster rate.

Figure 3 shows the initial activities (A_o, A_S, and A_E) of the sulfated zirconia catalyst dried at different temperatures. The initial overall activity is highest after drying at 548 K (2470 nmol/s/g), and the initial standard activities (A_S) follow a similar trend. The excess activity is present only over a limited range of drying temperatures (523–588 K).

All samples dried between 423 and 623 K displayed an initial selectivity for isobutane in the range of 89–91%, with the selectivities decreasing slightly as the drying

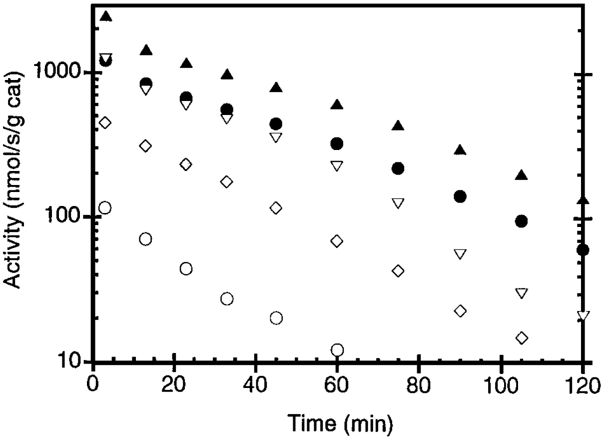

FIG. 2. Semi-logarithmic plots of activity vs. time-on-stream for the (●) SZ-473, (▲) SZ-548, (▽) SZ-623, (◇) SZ-673, and (○) SZ-773 catalysts.

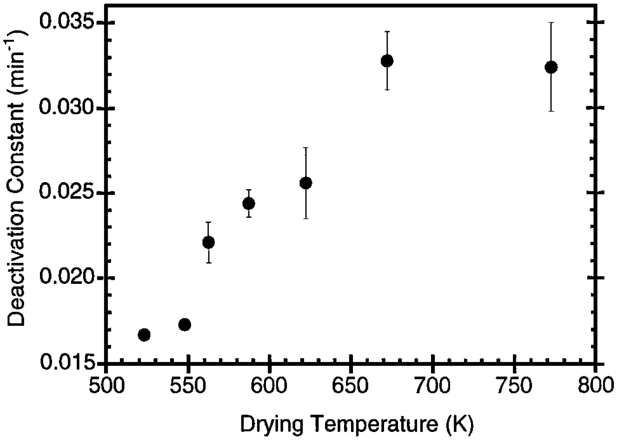

FIG. 4. Deactivation constants vs. drying temperature. Error bars reflect the range of possible deactivation constants taken between 20 and 80 min on stream.

temperature was increased. The selectivity of the SZ-673 sample was slightly lower (87%), while the selectivity for the SZ-773 catalyst was significantly lower (78%). While the major reaction product was isobutane, all catalysts studied also produced propane, isopentane, and *n*-pentane. The isopentane-to-*n*-pentane ratio was about 4.5. Comparable rates of production of the disproportionation products (propane and pentanes) were observed. The only other products observed were 2,2-dimethylbutane and 2-methylpentane, which were observed for the samples dried between 548 and 588 K and had initial selectivities to either species of about 0.13%.

The deactivation constant, as defined by Eq. (1), was determined by linear regression of the data collected between 20 and 80 min on stream. Shown in Fig. 4 are the deactivation constants (k_S) for catalysts dried above 473 K. The error bars reflect the largest and smallest values of the deactivation constants for each experiment. It can be seen that the deactivation constant increases as the drying temperature is increased.

Rehydration of Dried Catalysts

Hydration experiments were conducted by dosing water at levels from 24 to 146 μmol/g onto a sample dried at 773 K. Semi-log plots of the catalytic activity of these catalysts versus time on stream are shown in Fig. 5. The initial activity is a strong function of the amount of water added to the dehydrated sample, while the slope of the deactivation profile (k_S) appears to be a weak function of the amount of water adsorbed.

The relation between initial activity and amount of water adsorbed is shown in Fig. 6. Adding small quantities of water to the dried catalyst leads to a marked increase in catalytic activity, and maximum activity appears to occur at about 75 μmol/g. The highest initial activity measured for these

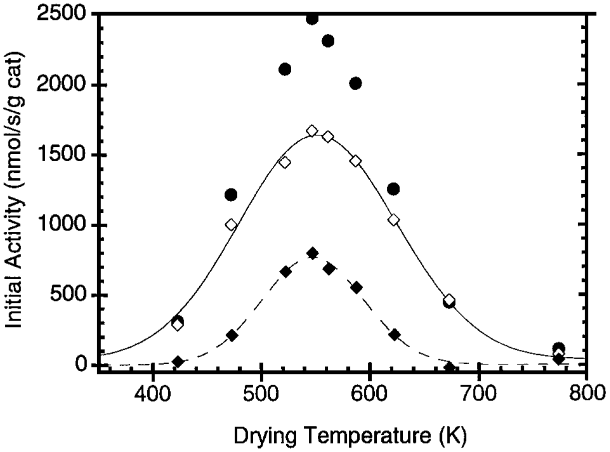

FIG. 3. Initial activity vs. drying temperature. Shown are the measured initial activities A_o (●), the predicted initial standard activity A_S (◇), and the predicted initial excess activity A_E (◆).

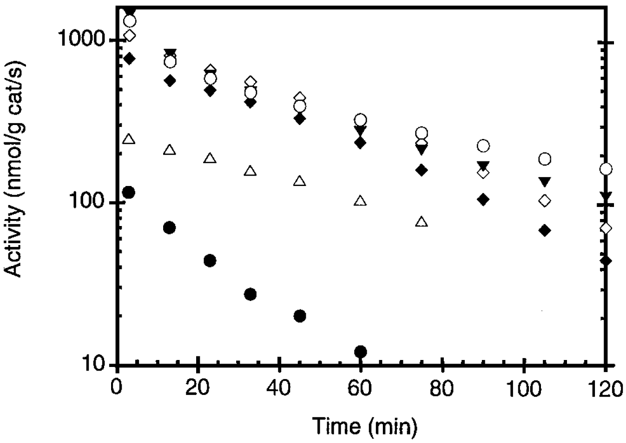

FIG. 5. Semi-logarithmic plots of activity vs. time-on-stream for samples dried at 773 K and rehydrated with (●) 0, (◆) 24, (◇) 54, (▼) 74, (○) 101, and (△) 146 μmol/g of water.

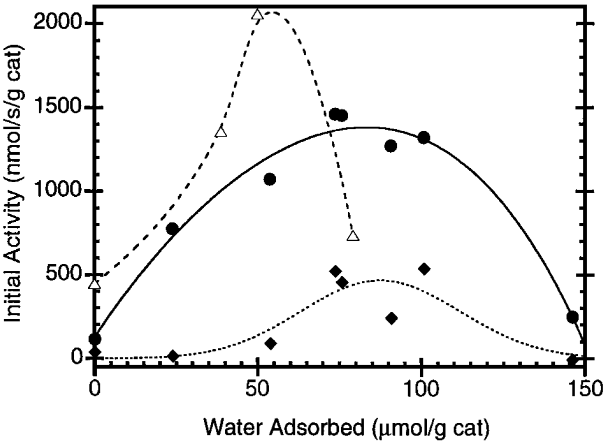

FIG. 6. Initial activity vs. quantity of water used to rehydrate a sample dried at 773 K. Shown are the measured initial activities A_o (●) and the predicted initial excess activity A_E (◆). Also shown is the initial activity (△) vs. the quantity of water used to rehydrate a sample dried at 673 K.

samples was 1460 nmol/s/g, corresponding to about 60% of the maximum activity observed during the drying studies (2470 nmol/s/g after drying a fresh sample at 548 K). The initial selectivity for isobutane was 78% for the dehydrated SZ-773 sample. The partially hydrated samples exhibited initial selectivities of 90 to 92%, and the selectivity was 86% after addition of 146 μmol/g of water. Thus, for both the drying and hydration studies, catalysts which were highly dehydrated exhibited lower selectivities than did those catalysts with intermediate hydration states. In addition, catalysts that were highly rehydrated also displayed decreased selectivity to isobutane.

Also shown in Fig. 6 are the initial activities observed when a sample dried at a lower temperature, SZ-673, is rehydrated. A maximum in activity appears with about 50 μmol/g of hydration; the maximum activity is 2060 nmol/s/g, which is 83% of the maximum achievable activity. Thus, when the catalyst is dehydrated at lower temperature, a larger fraction of the activity is recoverable through partial hydration, and a smaller extent of water addition is required to achieve optimum catalytic activity.

Deactivation constants (k_S) for the hydrated SZ-773 catalysts are shown in Fig. 7. The deactivation constant decreases with the addition of 24 μmol/g of water, and it changes little with the further addition of water. Thus, it appears that the addition of small amounts of water to a dehydrated catalyst decreases the rate of catalyst deactivation.

Further experiments were conducted in which an SZ-773 sample was allowed to deactivate for 5 min, after which it was hydrated with 73 μmol/g of water in the fashion described previously. The resulting activity increased from 260 to 1110 nmol/s/g, a value more similar to the 1460 nmol/s/g achieved by rehydrating an SZ-773 sample with 75 μmol/g of water. In separate experiments, an SZ-773 sample was allowed to deactivate for 5 min, after which ~10 cm^3/min

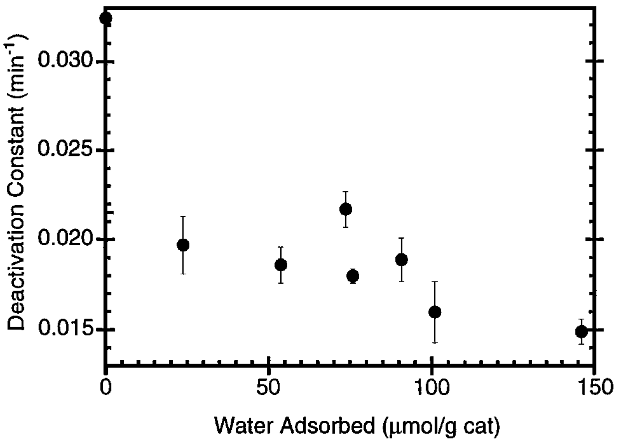

FIG. 7. Deactivation constants vs. quantity of water used to rehydrate a 773 K-dried sample. Error bars reflect the range of possible deactivation constants taken between 20 and 80 min on stream.

of O$_2$ was passed over the catalyst for 30 min. No increase in activity was observed following this oxygen treatment.

Reversibility of Rehydration

Approximately 60% of the maximum achievable activity is restored through hydration of a catalyst initially dehydrated at 773 K, while about 83% is restored by hydrating a catalyst initially dehydrated at 673 K. To test the reversibility of rehydration, the catalyst was dried under He at 673, 723, and 773 K, and under O$_2$ at 773 K. The catalysts were then cooled to 423 K and fully rehydrated, after which they were dried at 588 K before kinetics studies were conducted at 423 K. Semi-log plots of the catalytic activity versus time-on-stream are shown in Fig. 8. The standard activity does

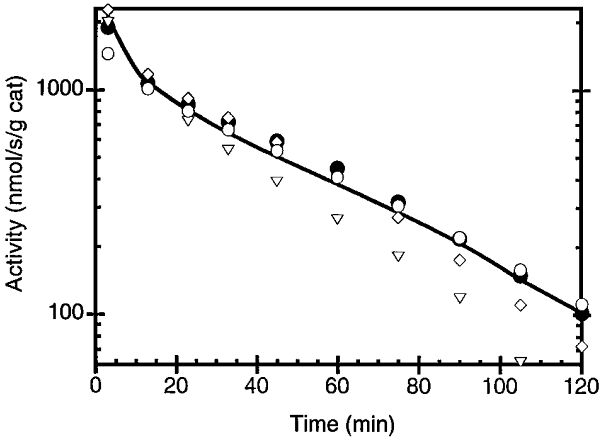

FIG. 8. Semi-logarithmic plot of activity vs. time-on-stream for catalysts dried between 673 and 773 K, rehydrated at 423 K, and then dried at 588 K. Shown are the (●) SZ-773/O$_2$, (◇) SZ-673/He, (▽) SZ-723/He, and (○) SZ-773/He samples. The line is an interpolated fit of the SZ-588 data, which was obtained by drying a fresh catalyst at 588 K without any dehydration–rehydration cycle.

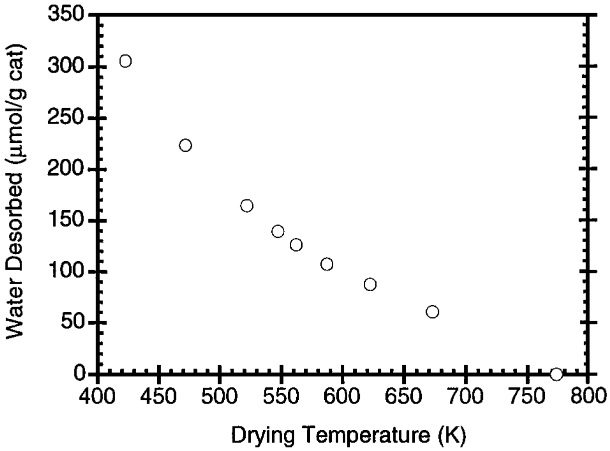

FIG. 9. Amount of water removed from a fresh sample dried at various temperatures. The quantity of water removed is given as the difference between the catalyst mass after being dried for 1 h at a given temperature and its mass after being dried for 1 h at 773 K.

not appear to be affected by the drying conditions. The initial activities for SZ-723/He (2000 nmol/s/g), SZ-673/He (2280 nmol/s/g), and SZ-773/O_2 (1900 nmol/s/g) are similar to the initial activity of the SZ-588 sample (2010 nmol/s/g). However, the SZ-773/He sample displays an initial activity of only 1450 nmol/s/g, and this value is similar to the maximum activity attainable through hydration of the SZ-773 catalyst (1460 nmol/s/g). Therefore, it appears that unless the drying occurs in an oxidizing environment, structural or chemical changes take place at temperatures above 723 K that cannot be restored by full rehydration of the catalyst at 423 K.

Water Removed during Drying

Figure 9 shows the results of microgravimetric measurements of the extents of water removal versus drying temperature. The values given for each temperature are the weight loss between a catalyst dried at that temperature and a catalyst dried at 773 K. In the range of drying temperatures used here, water should be the primary species removed from the catalyst (31). Maximum catalytic activity for a fresh catalyst is observed at a drying temperature of about 548 K (Fig. 3), and Fig. 9 indicates that 140 μmol/g of water are removed between 548 and 773 K.

DISCUSSION

The observed changes in catalytic activity as sulfated zirconia is dried at different temperatures may be caused by various factors, including conversion of Brønsted acid sites to Lewis acid sites, removal of surface-bound water, dehydration of nonacidic surface hydroxyls, or rearrangements of sulfate groups. We have found in the present study that similar activity and deactivation characteristics are observed for a fresh catalyst dried at different temperatures and for a highly dehydrated catalyst after rehydration. This similarity is most evident when comparing the trends in initial catalytic activity shown in Figs. 3 and 6. Therefore, our results indicate that the effects on catalytic activity caused during the drying process can be reversed by addition of water at 423 K. Accordingly, the effects of drying at progressively higher temperatures are most probably caused by the removal of water from the catalyst. Previous infrared spectroscopic studies of the sulfated zirconia catalyst suggest that the removal of water, upon drying from 588 to 773 K, does not significantly alter the concentration of Brønsted acid sites on the catalyst used in this study (32). This result suggests that the decrease in catalytic activity observed experimentally for a sulfated zirconia catalyst dried at 773 K compared to a catalyst dried at 588 K is not related to conversion of Brønsted acid sites to Lewis acid sites.

It appears that catalyst deactivation is affected by the hydration state of the catalyst, since Fig. 4 shows that the rate of catalyst deactivation increases as the temperature of drying is increased, and Fig. 7 shows that addition of small amounts of water decreases the deactivation rate. Various reports in the literature have suggested that deactivation is due to sulfate reduction (16, 33) or to coke formation (5, 18, 34, 35). In this respect, we have shown elsewhere that the insertion of a bed of mordenite to remove olefin impurities in the feed stream significantly reduces the rate of catalyst deactivation (36, 37). This result suggests that olefin impurities in the feed are a significant source of deactivation, and it appears that the addition of water may thus suppress the decomposition of these olefin impurities on the active sites.

The low catalytic activity observed on sulfated zirconia dried at 773 K is not caused by rapid coke formation on the surface sulfate species (i.e., during the initial exposure of active sites to reactant species), because high catalytic activity could be restored via hydration of SZ-773 after 5 min on stream. In these experiments, hydration of SZ-773 with 73 μmol/g of water after 5 min on stream resulted in an increase in catalytic activity from 260 to 1110 nmol/s/g, a value that is similar to 1460 nmol/s/g achieved by rehydrating an SZ-773 sample with 75 μmol/g of water. Furthermore, addition of water onto fully deactivated catalysts (dried at 588 K) did not restore catalytic activity. In addition, the low catalytic activity observed on sulfated zirconia dried at 773 K is not caused by rapid reduction of the surface sulfate species, because an SZ-773 sample deactivated for 5 min and subsequently oxidized with O_2 did not exhibit any increase in activity after the oxidizing treatment. These results suggest that dehydrated sites do not deactivate faster than hydrated sites, but rather they are less active or inactive.

The results of the present study show that while small quantities of water serve to promote the catalytic activity, larger amounts of water on sulfated zirconia poison the catalyst; similar results have been reported in the literature.

For example, Arata reported that for a catalyst calcined at 923 K, a maximum in isomerization activity was attained after drying the sample at 623 K (25). Babou *et al.* have suggested that the surface sites on sulfated zirconia may need small quantities of water to be active (9, 23). Arata and Hino, studying the benzylation of toluene over a sulfated alumina catalyst, observed a maximum in activity when the catalyst was dried at 563 K (24). Hindin and co-workers noticed that an optimum isomerization activity of a silica–alumina catalyst was achieved with the addition of small quantities of water (38). Most researchers, however, have only observed the poisoning effect of water on sulfated zirconia (7, 29, 30), most likely because the promotional effects of water are apparent only at low extents of surface hydration.

This research has shown that larger amounts of water poison the active sites. ^{2}H solid-state NMR (39) and infrared (32, 40) spectroscopic evidence have shown that strong hydrogen bonding is observed after all the sites have become hydrated. This extensive hydrogen bonding may decrease the reactivity of the active sites, in a similar fashion as we have shown that adsorbed ammonia poisons active sites (11, 20).

The results of ammonia poisoning experiments presented elsewhere (11, 20) show that a sulfated zirconia catalyst dried at 423 K has about 70 μmol/g of active acid sites, while our hydration studies show that about 75 μmol/g of water are needed to promote a sulfated zirconia catalyst dried at 773 K. This similarity between the numbers of acid sites and water-adsorption sites suggests that these sites may be related. After drying the catalyst at temperatures exceeding 548 K, it is unlikely that significant amounts of molecular water exist on the catalyst surface. It has been shown elsewhere that the initial heats of rehydration of the catalyst are higher than 120 kJ/mol (32, 40), and these higher heats are typical for dissociative adsorption of water to form surface hydroxyl groups (32, 40–43). Essentially identical heats of adsorption were measured for the adsorption of water on zirconia (44), which suggests that water adsorbs onto the zirconia support rather than onto the sulfates or acid sites. In addition, it has been shown that surface rehydration alters neither the number nor the strength of the acid sites, as revealed by microcalorimetric and infrared spectroscopic measurements of ammonia adsorption (32, 40). Infrared spectroscopy has shown that the addition of water to a dehydrated catalyst did not convert Lewis acid sites to Brønsted sites (32). These results suggest that rehydration does not alter the acid character of the catalyst, but instead serves to promote the existing acid sites. Thus, our studies indicate that the active sites for butane isomerization require an optimum state of hydration as well as an acidic component.

Our results indicate that only 60% of the catalytic activity lost upon drying the catalyst in He at 773 K could be restored upon complete rehydration and subsequent drying at 588 K. In contrast, most of the catalytic activity can be restored when the catalyst is dried in He at 673 or 723 K, or when it is dried in O_2 at 773 K. Thus, it appears that chemical changes occur when drying in He at temperatures above 723 K, and these changes are not completely reversed with the addition of water at 423 K. These effects seem to be more important for the excess activity (A_E), as the standard activity (A_S) is less sensitive to the treatment cycle of drying followed by rehydration. We speculate, therefore, that the species responsible for excess activity are less stable than are the species responsible for standard activity, as the former deactivate faster and are less readily regenerated by rehydration. Furthermore, as Figs. 3 and 6 indicate, excess activity only appears under a restricted range of pretreatment conditions.

Several recent papers have presented results which describe oxidative properties of sulfated zirconia catalysts (45, 46), thus suggesting that sulfate species may participate in butane isomerization via a reduction–oxidation cycle which activates the alkane, allowing the acidic function to isomerize the activated butane (47). Accordingly, activation of butane may take place via reduction of the surface sulfate species, followed by transfer of a C_4H_x species ($x = 8$ or 9) to a Brønsted acid site. The C_4H_x species associated with the acid site may then react with another C_4H_x species to form a C_8 species, which has been proposed by various authors (35, 48–53) to be a reactive intermediate in butane isomerization and disproportionation. This C_8 intermediate would undergo a methyl shift followed by β-scission to give an *i*-C_4 species that would lead to isobutane via the reverse of the aforementioned reactions. These reactions would return the sulfate species to their original oxidation state and thereby complete the catalytic cycle for butane isomerization. Integration over time of the activity plots for the SZ-548 sample shows that, on average, there are 67 turnovers per water-adsorption site (75 μmol/g) before the catalyst is fully deactivated, which suggests that butane isomerization is a catalytic process (in contrast to a stoichiometric process).

^{2}H NMR experiments (39) suggest that the activation of butane at 423 K does not necessarily involve Brønsted acid sites, because the Brønsted acid sites of an SZ-588 sample did not undergo H–D exchange at 423 K with d_{10}-*n*-butane. Similarly, Gates and co-workers (54), in comparing the products of the reaction of *n*-butane over iron- and manganese-promoted sulfated zirconia with those formed over H-ZSM-5, suggested that the catalytic properties of the modified sulfated zirconia at lower temperatures may not be attributed solely to acidity. In addition, while Fig. 8 reveals that the standard activity of fully rehydrated catalysts is not affected by the initial drying conditions, the excess activity is lower when dried under nonoxidizing conditions. Thus, drying under O_2 prior to rehydration preserves the sites responsible for excess activity, suggesting that the pathway for activation of butane may involve a redox mechanism.

In this respect, the hydrocarbon species formed during reduction of the surface sulfate groups could be alkoxyl or surface–ester species (55–57). Water may alter the oxidation-reduction properties of surface sulfate species, thereby lowering the energy barrier through which the catalytic cycle must proceed. An examination of the effect of hydration on the partial charge associated with the sulfur atom of the surface sulfate species (58) indicates that as hydration increases, the heat of reduction of the sulfate may decrease by as much as 100 kJ/mol, and this variation is sufficient to account for the observed promotional effects of water addition to sulfated zirconia catalysts.

CONCLUSIONS

The activity, selectivity, and rate of deactivation of sulfated zirconia catalysts for *n*-butane isomerization at 423 K depend upon the state of hydration of the catalyst. Our sulfated zirconia catalyst exhibits optimum activity after being dried at 548 K, while the activity of a catalyst dried at 773 K is optimized after being rehydrated with 75 μmol/g of water. The isomerization selectivity reaches at maximum value near 90% at the optimum state of catalyst hydration. Excessive catalyst hydration leads to low catalytic activity by causing extensive hydrogen bonding at the active sites. The rate of catalyst deactivation increases as sulfated zirconia becomes more dehydrated. Optimum hydration of the catalyst may decrease the rate of catalyst deactivation by suppressing the decomposition of impurity olefins on the active sites. Furthermore, we suggest that surface sulfate species may participate in butane isomerization via a reduction–oxidation cycle. Water promotes the catalytic activity by altering the oxidation–reduction properties of the surface sulfate species, thereby lowering the energy barrier through which the catalytic cycle must proceed.

ACKNOWLEDGMENTS

This work was supported by the Office of Basic Energy Sciences of the Department of Energy. For providing graduate fellowships, we thank the Wisconsin Alumni Research Foundation (JMK), the Amoco Oil Company (MRG), and the National Defense Science and Engineering Program (KBF). We also extend our most grateful appreciation to Robert Larson and Carolina Hartanto for their assistance in helping to perform the experiments described in this paper. Finally, we thank Manuel Natal-Santiago and Professor Juan de Pablo for discussions regarding the oxidation–reduction properties of sulfate species.

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