

Selective Poisoning and Deactivation of Acid Sites on Sulfated Zirconia Catalysts for *n*-Butane Isomerization

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Reaction kinetics measurements, selective poisoning, and microcalorimetry were used to study the activity, selectivity, and deactivation of acid sites on a sulfated zirconia catalyst for *n*-butane isomerization at 423 K. The sulfated zirconia catalyst has a distribution of acid site strengths, containing 50 $\mu\text{mol/g}$ of strong acid sites characterized by heats of ammonia adsorption from 125 to 165 kJ/mol. The strongest acid sites (heats from 145 to 165 kJ/mol) are responsible for the high initial activity of the catalyst, but these sites deactivate rapidly under reaction conditions. The acid sites exhibiting heats from 125 to 145 kJ/mol are less active than the stronger sites, but deactivate more slowly. Weaker sites have low activity and deactivate more rapidly after the intermediate sites are deactivated or poisoned. Brønsted acidity is necessary for extended catalytic activity, although Lewis acid sites may play a role in generating the initial high activity. Acid sites with heats of ammonia adsorption from 125 to 165 kJ/mol show good selectivity for production of isobutane (ca. 93%), while sites with heats from 120 to 125 kJ/mol show lower isobutane selectivity (ca. 80%). © 1996 Academic Press, Inc.

INTRODUCTION

The isomerization of light *n*-paraffins in the petroleum industry has become more important in recent years due to environmental legislation. Several catalytic systems have been considered for these reactions, including H-mordenite and H-MFI-based catalysts, as well as liquid and solid acids generally considered to be superacidic. A superacid is defined as a material with acidity stronger than 100% H_2SO_4 (1). Strongly acidic materials are useful as catalysts for isomerization reactions because they can operate at low temperatures where formation of branched isomers is favored thermodynamically. Authoritative reviews of these superacidic materials and the reactions they catalyze have been published by Olah *et al.* (2), Arata (3), Tanabe *et al.* (4), and Yamaguchi (5).

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Sulfated metal oxides have attracted considerable interest because they are more environmentally benign and more active for the transformation of hydrocarbons at low temperatures than current systems (3). In particular, sulfated zirconia has been studied for the isomerization of *n*-butane to isobutane, a hydrocarbon used in the production of oxygenates and alkylates. Measurements of acid strength using Hammett indicators and studies of the catalytic activity of sulfated zirconia for hydrocarbon reactions at low temperatures (4, 6, 7) have indicated that this catalyst may be superacidic. Several factors have been found to be important in determining the activity of sulfated zirconia catalysts, including the preparation method, sulfate loading, activation temperature, and moisture content of the catalyst (4, 7–12). While both Brønsted and Lewis acid sites have been suggested to be important for catalytic activity (8, 13, 14), the roles of these sites in determining the activity, selectivity, and deactivation of the catalyst have not been elucidated.

In a recent study (15), we used microcalorimetric measurements of the differential heats of ammonia adsorption to probe the strength of acid sites of sulfated zirconia catalysts. In conjunction with infrared spectroscopic experiments, we found that strong Brønsted and possibly Lewis acid sites were present on the sulfated zirconia catalysts studied. In the present paper, we investigate the catalytic properties for *n*-butane isomerization of the acid sites characterized in our earlier work.

METHODS

The sulfated zirconia catalyst studied was provided by MEI (Flemington, NJ) in the form of a sulfated $\text{Zr}(\text{OH})_4$ precursor. This catalyst precursor was heated to 848 K in 1.5 h and maintained at this temperature for 2 h in 100 cm^3 (NPT)/min of dry O_2 per gram of catalyst. After activation, the catalyst was removed from the reactor and stored in a desiccator. The catalyst, in the form of sulfated ZrO_2 , had a BET surface area of 98 m^2/g and a sulfur loading of 1.8 wt% (Galbraith Laboratories); this loading corre-

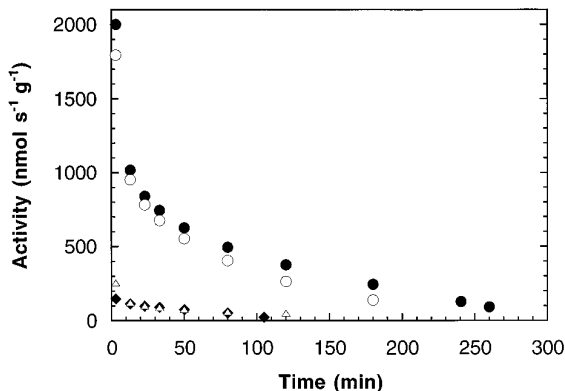


FIG. 1. Effect of drying conditions on sulfated zirconia activity for *n*-butane isomerization at 423 K. Activity with time on stream after drying in He at 588 K (●), in H₂ at 588 K (○), in He at 773 K (◆), and in O₂ at 773 K (△).

sponds to 560 $\mu\text{mol/g}$ of sulfur. For the surface coverage of the sample, 1.0 $\mu\text{mol/g}$ corresponds to 6.1×10^{15} sites/ m^2 .

The details of the reaction kinetics measurements of *n*-butane isomerization over sulfated zirconia are reported elsewhere (15). Typically, 500 mg of catalyst and ca. 250 mg of quartz particles were loaded in a quartz reactor and dried for 1 h at 588 K in 65 $\text{cm}^3(\text{NPT})/\text{min}$ of flowing, dry He (Liquid Carbonic). The reaction kinetics measurements were conducted at 423 K with a weight-hourly space-velocity (WHSV) of *n*-butane equal to 2.1 h^{-1} (10% *n*-butane, AGA 99.5% purity instrument grade, in dry He with a total flow rate of 65 $\text{cm}^3(\text{NPT})/\text{min}$). The major impurities in the *n*-butane feed were isobutane and traces of propane, for which the kinetics data were corrected. The reaction products were analyzed with a Hewlett Packard 5890 gas chromatograph equipped with a 24 ft 5% DC-200 Chromosorb P-AW column, held at 323 K, and flame ionization and thermoconductivity detectors.

Reaction kinetics studies were conducted using catalysts that were selectively poisoned by adsorbing specific amounts of ammonia (8–69 $\mu\text{mol/g}$ of catalyst). The catalyst was first dried in flowing He, as described above, and a specific amount of ammonia was then dosed onto the sample at room temperature. The temperature was subsequently raised to 573 K for 1 h to allow for equilibration of ammonia on the catalyst, and reaction kinetics measurements were initiated after cooling the catalyst to the reaction temperature of 423 K.

Microcalorimetric studies of ammonia adsorption were performed at 423 K using a Tian Calvet-type heat-flux calorimeter connected to a gas-handling system and volumetric system equipped with a Baratron capacitance manometer for precision pressure measurements. The detailed procedures followed for these measurements are described elsewhere (15).

RESULTS

Figure 1 shows the activity versus time on stream of the MEI sulfated zirconia catalyst for isomerization of *n*-butane at 423 K. The catalyst is active initially, but it deactivates rapidly and shows low activity after 4–5 h on stream. Catalytic activity measurements were subsequently made for samples poisoned with specific amounts of adsorbed ammonia. The amounts of ammonia used to poison this catalyst were based on the results of microcalorimetric studies of ammonia adsorption on this sulfated zirconia catalyst. The differential heat distribution for ammonia adsorption up to a coverage of 250 $\mu\text{mol/g}$ has been reported elsewhere (15). For comparison with the kinetics data in the present paper, we present in Fig. 2 the microcalorimetric data for ammonia adsorption on the MEI sulfated zirconia catalyst dried at 588 K. The microcalorimetric data show that the sulfated zirconia catalyst has a distribution of acid site strengths. This catalyst contains about 50 $\mu\text{mol/g}$ of strong acid sites with heats of ammonia adsorption equal to 125–165 kJ/mol. A collection of 25 $\mu\text{mol/g}$ of weaker acid sites appears to exist with heats between 120 to 125 kJ/mol, followed by a gradual decrease in the heat of adsorption at higher ammonia coverages. The acid sites with heats of ammonia adsorption below ca. 120 kJ/mol have negligible catalytic activity for *n*-butane isomerization (15). Based on these results, the catalyst was selectively poisoned with various amounts of ammonia to probe the relationship between acid-site strength and catalytic properties for *n*-butane isomerization.

Figure 3 shows semilogarithmic plots of catalytic activity versus time on stream for catalysts selectively poisoned by adsorbed ammonia. Significant regions of these plots are linear and can thus be described by a first-order deactivation relation

$$R = R_0 \exp(-kt) \quad (1)$$

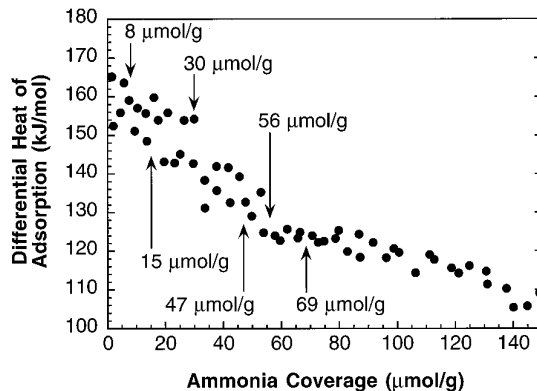


FIG. 2. Differential heats of ammonia adsorption on sulfated zirconia at 423 K.

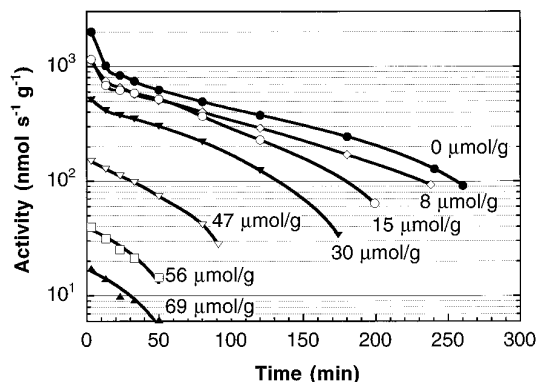


FIG. 3. Catalytic activity versus time on stream for *n*-butane isomerization at 423 K over sulfated zirconia catalysts selectively poisoned with 0 (●), 8 (◇), 15 (○), 30 (▼), 47 (▽), 56 (□), and 69 (▲) $\mu\text{mol/g}$ of NH_3 .

where R_0 and R are the initial and subsequent rates of the isomerization reaction, and k is the rate constant of deactivation.

The deactivation curve of the unpoisoned catalyst indicates the existence of two deactivation regimes. The catalyst deactivates rapidly during the first few minutes of reaction. Because this regime has essentially been eliminated by the time of the second kinetics measurement (ca. 10 min), a value of k cannot be determined for the first deactivation regime. The subsequent rate of deactivation can be characterized by a deactivation constant of k between 0.007 and 0.011 min^{-1} for most of the reaction time. The rate of deactivation increases at the final stages of the reaction. Exact measures of the deactivation constant are difficult since the value of k varies slightly depending on the section of the deactivation curve to which Eq. [1] is applied. For this paper, k is taken as the average of the deactivation constants determined from activities measured between 10 and 90 min on stream, neglecting the point measured at 10 min if regression analysis suggests that it falls within the first deactivation regime. Using these criteria, the value of k for the unpoisoned catalyst is 0.010 min^{-1} .

As shown in Fig. 3, selective poisoning with adsorbed ammonia changes the activity of the catalyst for *n*-butane isomerization. The initial activity is reduced significantly when the first 8–15 $\mu\text{mol/g}$ of strong acid sites are selectively poisoned with ammonia. However, the deactivation curves are still characterized by rapid initial deactivation followed by a region of slower deactivation that can be described by Eq. [1]. Upon poisoning the first 30 $\mu\text{mol/g}$ of strong acid sites with NH_3 , the first regime of initial rapid deactivation is essentially eliminated. After poisoning with 47 $\mu\text{mol/g}$ of ammonia, which corresponds to 8.4% of the total sulfur on the surface, the initial activity is an order of magnitude lower than that of the unpoisoned catalyst. Progressively larger NH_3 doses of 56 and 69 $\mu\text{mol/g}$ lead to further decreases in catalytic activity.

While the first 30 $\mu\text{mol/g}$ of ammonia decrease the activity, the deactivation constant is not affected. When more than 30 $\mu\text{mol/g}$ of ammonia are adsorbed, the deactivation rate increases, until 56 $\mu\text{mol/g}$ of ammonia are adsorbed, at which point the deactivation rate becomes constant. At the final stage of catalyst deactivation by selective poisoning, the rate of deactivation is greater ($k = 0.022 \text{ min}^{-1}$) than it is for the fresh catalyst.

The reaction selectivity data versus time on stream are shown in Fig. 4 for the MEI catalyst poisoned with different amounts of ammonia. After a short initial period, the selectivity to isobutane is about 93% for the unpoisoned catalyst. Similar isobutane selectivities have been reported for sulfated zirconia catalysts by Yori *et al.* at 573 K (13), Corma *et al.* at 423 K (16), and Chen *et al.* at 473, 523, and 573 K (10). The selectivity remains high during most of the reaction, and it decreases slightly at the latter stages of catalyst deactivation. The main side-products observed include propane, isopentane, and *n*-pentane. Some branched hexanes in trace amounts were also observed, but only at short times on stream when the catalyst was most active. The C_5 isomers appear to be near thermodynamic equilibrium, since the ratio of isopentane to *n*-pentane in the product stream has a value of 3.6 ± 0.4 and is independent of conversion (the equilibrium constant at 423 K is equal to 5.12). The addition of up to 30 $\mu\text{mol/g}$ of NH_3 leads to only slight decreases in the isobutane selectivity. However, the selectivity decreases significantly with further increases in the NH_3 coverage. The selectivity to isobutane becomes as low as 74% for the catalyst that was poisoned with 69 $\mu\text{mol/g}$ of NH_3 .

Figure 5 shows the ratio of propane to pentane produced over selectively poisoned sulfated zirconia catalysts. For the unpoisoned catalyst, the ratio of C_3 to C_5 species indicates a slightly higher selectivity for propane at short times

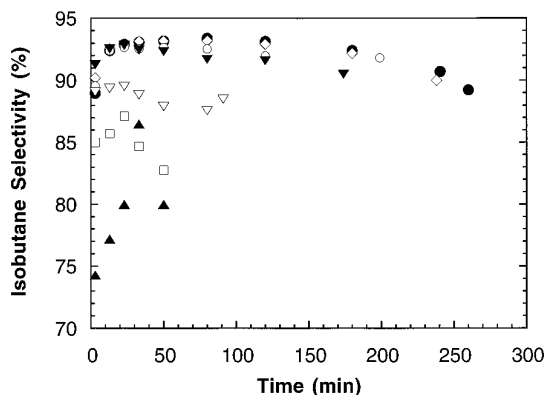


FIG. 4. Isobutane selectivity versus time on stream during *n*-butane isomerization at 423 K over sulfated zirconia catalysts selectively poisoned with 0 (●), 8 (◇), 15 (○), 30 (▼), 47 (▽), 56 (□), and 69 (▲) $\mu\text{mol/g}$ of NH_3 .

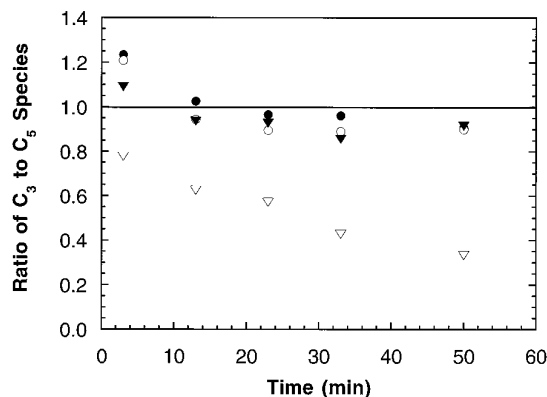


FIG. 5. Ratio of propane versus pentane versus time on stream during *n*-butane isomerization at 423 K over sulfated zirconia catalysts selectively poisoned with 0 (●), 15 (○), 30 (▼), and 47 (▽) $\mu\text{mol/g}$ of NH_3 .

on stream. The selectivity for propane decreases with time in favor of formation of the pentanes; this trend continues over the course of the reaction. However, the C_3 -to- C_5 ratio remains close to unity. The ratio of C_3 to C_5 species decreases for the catalyst poisoned with ammonia at a level of 47 $\mu\text{mol/g}$. The measurement of this ratio at higher ammonia coverages is difficult because the activity of the catalyst is low and we are limited by the sensitivity of the analytical instruments.

Figure 1 shows the activity versus time on stream of sulfated zirconia after different treatments. The catalyst treated in H_2 at 588 K exhibits a uniform 10% decrease in the activity compared to the catalyst dried at the same temperature in He. The activity of the catalyst treated in O_2 or He at 773 K is lower by an order of magnitude compared to drying at 588 K. The catalyst treated in He at 773 K seems to exhibit initial activity that is lower than the initial activity of the catalyst dried in O_2 at the same temperature; however, the two catalysts exhibit similar activity for the remainder of the time on stream.

The effects of changing the carrier gas from He to H_2 for *n*-butane isomerization studies are shown in Fig. 6. The initial activity of the catalyst in the presence of H_2 is about a factor of 5 lower than in the presence of He. However, catalyst deactivation is significantly slower in H_2 . The deactivation constant for the slow deactivation region is about 0.004 min^{-1} when H_2 is used as the carrier gas compared to a value of 0.010 min^{-1} for He.

DISCUSSION

The existence of superacidity for sulfated zirconia catalysts appears to be a matter of disagreement in the literature. For example, measurements using Hammett indicators give values of acid strength for sulfated zirconia higher than 100% H_2SO_4 ($H_0 = -11.9$) (5, 6, 17, 18). Corma *et*

al. (16, 19) used temperature-programmed desorption of NH_3 to characterize sulfated zirconia, and they observed an ammonia desorption peak at 813 K, higher than a similar desorption peak at 748 K observed for NH_3 on H-mordenite; they attributed this peak to superacidic sites. Lin and Hsu (20), using temperature-programmed desorption of a series of different bases, found that sulfated zirconia catalysts have stronger acid sites than unpromoted zirconia catalysts. Riemer *et al.* (21) used results from ^1H MAS NMR to suggest the presence of highly acidic protons on sulfated zirconia. However, Kustov *et al.* (22) studied the infrared shifts of the hydroxyl groups on sulfated zirconia after benzene adsorption and concluded that the Brønsted acid sites on sulfated zirconia are not stronger than sites observed on strongly acidic zeolites such as H-ZSM-5. Babou *et al.* (23) suggest that while the acidity of sulfated zirconia is similar to that of sulfuric acid, these acid sites are not really superacidic.

Our microcalorimetric results for ammonia adsorption indicate that sulfated zirconia has strong acid sites that adsorb ammonia with heats as high as 165 kJ/mol. This initial heat for ammonia adsorption is similar to values reported for other solid acidic materials such as H-mordenite (24), H-ZSM-5 (24), USY zeolites (25), and alumina (26, 27) that have been studied using the same technique. These catalysts are considered to be strong acids but not superacids; therefore, our microcalorimetric data suggest that while sulfated zirconia is a strong acid, it is not a superacid, at least as defined by the heat of ammonia adsorption. We realize that the heat of ammonia adsorption is a function of several interaction energies, as discussed by Gorte and co-workers (28, 29), and this heat may not necessarily provide a true scale for assessing acid strength.

Selective poisoning experiments provide further insight into the effects of acid strength on the activity and deactivation of the catalytic sites. Experiments where 8, 15, or 30 $\mu\text{mol/g}$ of ammonia were dosed onto the catalyst (see Fig.

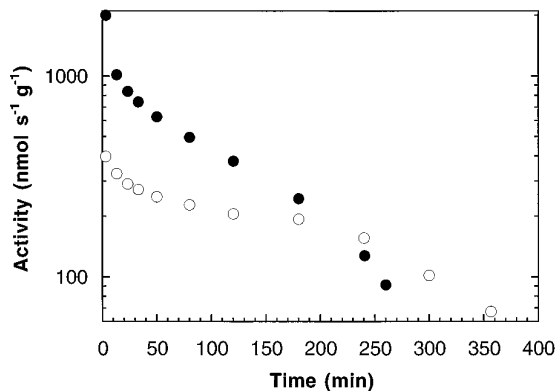


FIG. 6. Catalytic activity with time on stream for *n*-butane isomerization over sulfated zirconia catalyst using He (●) or H_2 (○) as carrier gas.

3) indicate that the high initial activity and rapid deactivation of the catalyst seem to be related to the strongest 25 $\mu\text{mol/g}$ of acid sites (145–165 kJ/mol). Infrared spectroscopic studies (15) suggest that while some of these sites may be Lewis acid sites, most are Brønsted acid sites. The kinetics measurements over the sulfated zirconia catalyst selectively poisoned with 30 and 47 $\mu\text{mol/g}$ of ammonia show that while acid sites with heats of 125–145 kJ/mol do not show initial high activity, these sites contribute to long-term catalytic activity. Selective poisoning with 56 and 69 $\mu\text{mol/g}$ of ammonia shows that weaker acid sites (heats of 120–125 kJ/mol) have low catalytic activities.

Deactivation during the course of the reaction appears to affect the catalytic sites in order of decreasing acid strength. Specifically, comparison of the deactivation curve of the unpoisoned catalyst to those of the selectively poisoned catalysts shows that the active sites lost during deactivation are the same sites poisoned during the selective poisoning with ammonia. Therefore, the highly active sites that deactivate rapidly are also the acid sites poisoned first by ammonia.

The deactivation curves of the catalysts poisoned with less than 30 $\mu\text{mol/g}$ of ammonia indicate that there appear to be two contributions to the overall activity; we will denote these as “standard” and “excess” activities. The standard activity is present at all levels of deactivation and has a behavior that can be described by Eq. [1]. The initial standard activity, R_0 , can be determined by extrapolating to zero time the linear portions of the curves in Fig. 3. The second contribution, the excess activity, is the additional activity that the catalyst exhibits at the beginning of the reaction. The excess activity is determined by subtracting the standard initial activity, R_0 , from the total initial activity. Thus, during the early stages of the reaction, both standard and excess activity are present, whereas the catalyst deactivates according to Eq. [1] for times longer than approximately 10 min. Figure 7 shows the initial total, standard, and excess activities for sulfated zirconia catalysts poisoned with various amounts of ammonia.

The data in Figure 7 show that the standard initial activity, R_0 , decreases continuously with ammonia coverage. Thus, it appears that essentially all of the acid sites with heats higher than 125 kJ/mol possess standard activity. When the strongest sites are selectively poisoned with 8 or 15 $\mu\text{mol/g}$ of NH_3 , the excess catalytic activity is reduced, and it is eliminated when the catalyst is poisoned with 30 $\mu\text{mol/g}$ of NH_3 . The excess activity is also eliminated when the catalyst is first exposed to reaction conditions for *n*-butane isomerization. After this initial loss of excess activity, all of the acid sites with heats higher than 125 kJ/mol deactivate in a manner consistent with Eq. [1].

The standard turnover frequency for isobutane production can be estimated by dividing the change in the value of R_0 by the change in the amount of adsorbed ammonia.

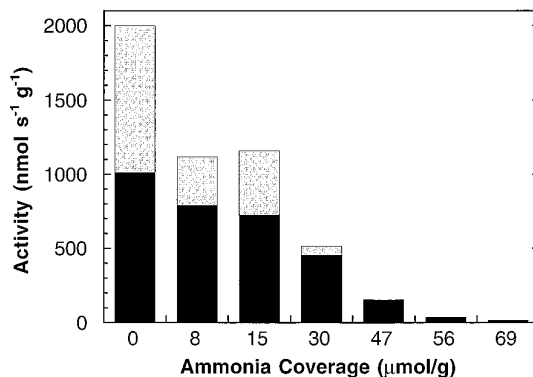


FIG. 7. Standard (black) and excess (gray) initial activities with NH_3 coverage for *n*-butane isomerization over sulfated zirconia at 423 K. The total initial activity is the sum of the standard and excess activities. All activities are calculated at 3 min on stream.

This standard turnover frequency is equal to approximately 0.02 sec^{-1} for each of the ammonia doses up to 47 $\mu\text{mol/g}$. Selective poisoning with 56 and 69 $\mu\text{mol/g}$ of ammonia shows that weaker acid sites (heats of 120–125 kJ/mol) have lower catalytic activities, with the sites poisoned by the last dose of ammonia having standard turnover frequencies near 0.002 sec^{-1} .

Significant debate about the nature of the active sites on sulfated zirconia catalysts can be found in the literature. Various researchers have reported that strong Lewis acid sites are generated on zirconia during sulfation (5, 30–32). Brønsted acid sites may also be formed on the catalytic surface; the presence of Brønsted acidity largely depends on the sulfate loading (14, 30, 33) and the hydration state of the catalyst (3, 9). Brønsted acid sites can be converted to Lewis sites by catalyst dehydration at progressively higher temperatures (3, 9, 34, 35). The importance of Lewis acid sites in the catalytic activity of sulfated zirconia catalysts seems to be widely accepted (4, 8, 13, 35–37). In fact, Yamaguchi and co-workers (5, 38, 39) and others (4, 36, 37) suggest that only Lewis acid sites are necessary for catalytic activity. However, some cooperative action between the two types of acid sites may exist. Nascimento *et al.* (8) observed a relationship between the catalytic activity of sulfated zirconia and the ratio of Brønsted to Lewis acid sites measured by infrared spectroscopy. A maximum in the activity was observed at a ratio equal to unity. Recently, Ward and Ko (14) also reported a relationship between catalytic activity and the ratio of Brønsted to Lewis acid sites. These authors reported that a sulfated zirconia catalyst having only Lewis acidity was not active for *n*-butane isomerization.

Our results demonstrate the role of Brønsted acid sites in catalytic activity under our experimental conditions. The results of infrared spectroscopic studies of adsorbed ammonia reported elsewhere (15) indicate that less than 5 $\mu\text{mol/g}$

g of the strong acid sites on our catalyst dried at 588 K are Lewis acid sites. Thus, the sites responsible for the excess activity are predominantly Brønsted acid sites. Furthermore, the acid sites with heats from 125 to 145 kJ/mol are Brønsted sites, and these remain active and provide the standard activity even after the strong acid sites are completely poisoned with ammonia. The role of the Lewis acid sites is still uncertain; their function may be to enhance the activity of Brønsted sites by increasing the acid strength via inductive effects (34, 35) or other cooperative action.

Additional mechanistic details of the Brønsted acid-catalyzed isomerization are suggested by the product distribution. We have observed the formation of C₃ and C₅ species, as well as traces of C₆ species. This distribution of products suggests a mechanism involving C₈ and C₉ intermediates formed via oligomerization/cracking. In a related system, iron–manganese sulfated zirconia, a bimolecular *n*-butane isomerization mechanism involving C₈ species has recently been proposed by Zarkalis *et al.* (40) as well as by Adeeva *et al.* (41). The same idea of a C₈ mechanism was proposed earlier by Hilaireau *et al.* (42). On the other hand, Garin *et al.* (43) have suggested a monomolecular mechanism involving self-isomerization of *n*-butane over sulfated zirconia.

As shown in Fig. 5, the C₃ to C₅ ratio for the unpoisoned catalyst remains near unity for most of the time on stream, pointing towards the possibility of a C₈ intermediate formed from two C₄ molecules. At short times on stream, however, a ratio of C₃-to-C₅ species greater than unity was observed. As suggested by Cheung *et al.* (44), this ratio may result from the elimination of C₅ species via additional oligomerization/cracking. The pentane species produced at short times on stream due to the excess activity may combine with C₄ species to give C₉ intermediates, which crack to C₃ and C₆ species. The C₆ carbenium ions can yield hexanes or additional propane.

Except for the initial lower selectivity at short times on stream, the selectivity is a weak function of the acid strength of the active sites (Fig. 4). Significant reductions in isobutane selectivity and the propane-to-pentane ratio are observed only after the strong acid sites have been poisoned by ammonia at a level of 47 μmol/g. Our data suggest that the weakest acid sites are less selective for isobutane formation; this occurs because the more active sites are apparently more effective for the skeletal isomerization of butane than are the weakest acid sites, which are more active towards the β-scission reactions responsible for the C₃ and C₅ products.

While the selective poisoning experiments provide insight to the nature of the activity of sulfated zirconia, the origin of its deactivation during *n*-butane isomerization has not been clearly established. Several researchers have suggested that the loss of isomerization activity may be related to the reduction of sulfur (13, 45). Our experiments,

however, suggest that this is not the dominant cause of deactivation. The observed decrease in catalytic activity (Fig. 1) when the catalyst is dried at 773 K instead of 588 K cannot be explained by a reduction in the oxidation state of the surface sulfur, because the activity is decreased in a similar manner when the catalyst is dried in O₂ or He at 773 K. The decrease in activity is more likely due to a loss of water or hydroxyl groups from the surface (46). Loss of sulfur is also an improbable explanation for the decrease in catalytic activity because the calcination temperature of the catalyst is 848 K, higher than our drying temperature. Furthermore, when we treated the sulfated zirconia catalyst at 588 K in H₂, we observed a decrease in catalytic activity by only about 10%. The catalyst maintained both the excess and standard activities. Therefore, if the initial rapid loss of excess activity is due to reduction at 423 K of the sulfated species, then the mechanism of the reduction would appear to be related to the isomerization reaction and the acid strength of the active site.

In addition, many researchers have suggested that coke formation is the primary mode of deactivation (10, 44, 47, 48). Indeed, infrared spectroscopy of our catalyst has shown the presence of coke and coke precursors on the surface after deactivation (49).

Many research groups have observed a stabilization of the catalytic activity by H₂ at high partial pressures (10, 13, 14, 47). Ward and Ko (14) observed a deactivation profile for the reaction of *n*-butane in H₂ over sulfated zirconia aerogels that is similar to the catalyst deactivation profile reported here. Yori *et al.* (13) also observed rapid initial deactivation followed by catalyst stabilization in the presence of H₂. Garin *et al.* (47) and Chen *et al.* (10), however, reported that the catalytic activity first increases during reaction and then stabilizes at higher values. Our results indicate that H₂ increases the life of the catalyst, but it suppresses the initial catalyst activity (Fig. 6), although the hydrogen pressures used in our experiments are lower than the pressures used in the aforementioned studies. Hydrogen may increase the catalyst life by reducing the accumulation of carbonaceous species on the surface. The causes of the decrease in the initial catalytic activity by H₂ are not clear. It has been proposed (47) that hydrogen may inhibit initiation processes in the reaction mechanism. In this respect, Ghenciu *et al.* (50) have suggested that these initiation processes may involve oxidation-reduction reactions.

In separate experiments, we have observed an increase in the deactivation constant from 0.010 to 0.022 min⁻¹ as the WHSV was increased from 2.1 to 5.7 h⁻¹. This behavior suggests that a product of the reaction (e.g., isobutane) acts to stabilize active sites downstream; therefore, in a larger catalytic bed (hence a smaller space velocity) more active sites would be stabilized, leading to a reduction in the rate of deactivation.

CONCLUSIONS

The MEI sulfated zirconia catalyst employed in this study has a distribution of acid strengths active for *n*-butane isomerization at 423 K. About 25 $\mu\text{mol/g}$ of sites have an acid strength corresponding to a heat of ammonia adsorption equal to about 145–165 kJ/mol, and these strong acid sites are highly active but deactivate rapidly. These sites contribute both excess and standard activity to the total catalytic activity observed. The next 25 $\mu\text{mol/g}$ of acid sites have heats of ammonia adsorption equal to 125–145 kJ/mol, and these intermediate-strength acid sites display standard activity and deactivate more slowly. The following 25 $\mu\text{mol/g}$ of sites have heats of ammonia adsorption in the range of 120–125 kJ/mol, and these weaker acid sites deactivate more rapidly and exhibit low activity. Sites with heats of ammonia adsorption lower than 120 kJ/mol have negligible activity for *n*-butane isomerization under the conditions of the present study. Brønsted acid sites are responsible for the standard activity, and Lewis acid sites may play a role in generating excess activity. The strong and intermediate-strength acid sites show good selectivity for production of isobutane, while weaker acid sites show lower isobutane selectivity.

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