Activation of sulfated zirconia catalysts Effect of water content on their activity in *n*-butane isomerization

Steven X. Song and Ronald A. Kydd

Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4



The effect of water content in sulfated zirconia catalysts on their activities for *n*-butane isomerization was investigated using catalytic testing, Fourier transform infrared (FTIR) spectroscopy and thermogravimetry analysis. It was found that minor amounts of water promote the catalytic activity while excess water diminishes it. The FTIR spectrum of pyridine adsorbed on the catalysts showed that a decrease in water content resulted in a decrease in Bronsted acidity with a concurrent increase in Lewis acidity. In the most active catalyst, approximately two-thirds of the acid sites are Bronsted sites, and the rest are Lewis sites; an appropriate amount of water is needed to produce this ratio. The Bronsted acid sites presumably contribute to the catalysis by protonating butene formed at redox sites on the catalyst to create carbocations. The high catalytic capability of the Bronsted acid sites requires the presence of adjacent Lewis acid sites, which withdraw electrons from bisulfate SO—H bonds through an induction effect, giving rise to more acidic protons.

Sulfated zirconia (SZ) has attracted extensive attention because of its strong acidity and high activity in light alkane conversions at relatively mild temperatures.¹⁻⁶ Much work has been devoted to studies of the preparation, characterization and application of this catalytic material. However, owing to the sensitivity of the material to the preparation and activation conditions, a number of themes concerning its physicochemical properties and catalytic reactivity still remain uncertain.⁶ One such example is the effect of the catalyst surface hydration on its reactivity. Both beneficial^{1,7} and detrimental^{2,8-11} effects of water have so far been reported in the literature. In addition, some authors also suggested that an intermediate water content is necessary for the catalyst to reach its maximum activity.¹²⁻¹⁷

The issue of the water effect is closely related to another important topic, which has been studied extensively but is still under debate, *i.e.*, the nature of the catalytically active acid sites. Most of the recent reports indicated the simultaneous presence of both Lewis and Bronsted acid sites and the reversible transformation between them upon hydration/ dehydration, in spite of the earlier studies which showed the existence of only Lewis acidity.^{18–21} Several authors came to contradictory conclusions about which type of acid site is responsible for the activity of sulfated zirconia. Some correlated the catalytic activity to Lewis acidity,^{8–11,22,23} whereas others emphasized the role of Bronsted acid sites.^{1,7,24–26} In addition, there is another proposal that attributes the activity to a synergistic effect between both types of acid sites.^{12,27–31}

Research into the water effect on the reactivity of sulfated zirconia catalysts is of significance. This is not only because many reactions (e.g., Fischer–Tropsch synthesis³² and those involving alcohols^{14,33,34}) over this type of catalyst may involve the formation of water as a by-product; such research can also help us understand the activation process of the catalysts. These types of catalyst are usually prepared by impregnating zirconium hydroxide powders with an aqueous solution of H_2SO_4 or $(NH_4)_2SO_4$ followed by drying and calcination in air. The calcined sample is usually cooled and stored in the ambient atmosphere before use, and may adsorb moisture from the atmosphere during its cooling and storage. An activation or pretreatment process is usually necessary prior to reactions to make the material catalytically active. Since the dryness of the catalyst strongly depends on the activation temperature, the question arises as to whether this dryness is the factor that determines catalytic activity, or

whether some other effect of the activation is important.

The objective of this work was to clarify the effect of water on the activity of sulfated zirconia catalysts. We carried out n-butane isomerization over sulfated zirconia catalysts activated in flowing dry air at various temperatures (150–500 °C) and thus having different water contents, and also characterized the acidity of these catalyst samples using infrared (IR) spectroscopy of adsorbed pyridine. A correlation between the catalytic results and the acidity measurements was attempted. We noticed that so far most of the reported IR data for acidity characterization were obtained over catalysts pretreated under vacuum at elevated temperatures, while most reaction studies were carried out over catalysts activated in an inert gas or dry air stream under atmospheric pressure at elevated temperatures. We believe that a correlation between acidity and activity data obtained using different activation conditions for each of these measurements is not appropriate because the different activations may lead to different dryness of the catalysts. Thus, in this work we used the same activation procedure for both catalytic experiments and acidity characterization.

Experimental

Sulfated zirconia catalysts used in this study were prepared using the conventional method. A 0.45 M solution of $ZrOCl_2 \cdot 8H_2O$ (600 ml) was hydrolyzed by dropwise addition of 75 ml aqueous ammonia (28–30 wt.% NH₃) with vigorous mechanical stirring to produce $Zr(OH)_4$ precipitate. After the hydrolysis, the pH of the mixture was about 9, and the mixture was stirred for another 30 min. The $Zr(OH)_4$ precipitate was then separated from the liquid by filtration and washed thoroughly with distilled water until no chloride ions were detected. The $Zr(OH)_4$ was then dried overnight and powdered to below 100 mesh. Sulfation was carried out by adding the $Zr(OH)_4$ powder to a 0.5 M solution of H_2SO_4 (1 g solid per 10 ml liquid) followed by stirring the mixture for 1 h. The solid was separated from the liquid by filtration without washing and then dried overnight.

The dried sulfated $Zr(OH)_4$ was calcined either *ex situ* or *in situ*. In the *ex situ* calcination, sulfated $Zr(OH)_4$ was calcined in a furnace at a given temperature (450-750 °C) for 3 h in static air and then cooled and stored under ambient conditions before being placed in the reactor. In the *in situ* calcination, sulfated $Zr(OH)_4$ was calcined in the reactor, in which

1333

the catalytic testing was to be done, at a given temperature (500-700 °C) for 3 h under flowing dry air (30 ml min⁻¹). The catalyst *ex situ* calcined at 620 °C for 3 h has a surface area of 77 m² g⁻¹.

n-Butane isomerization was carried out in a fixed bed downward-flow guartz reactor (9 mm id) at 90 °C under atmospheric pressure. The reaction feedstock was a mixture of nbutane (Instrument Grade, 99.5%) with helium (High Purity). Prior to the reaction, ex situ calcined catalyst samples were activated in the reactor at a given temperature (150-500 °C) for 2 h and cooled to reaction temperature in flowing dry air (30 ml min⁻¹). In situ calcined catalysts were cooled from the calcination temperature directly to the reaction temperature under the dry air stream; in this case, care was taken to prevent contact of the catalyst with moisture before activity testing. All the catalyst samples were purged with flowing helium (30 ml min⁻¹) at the reaction temperature for 10 min before being exposed to the reaction feedstock. The reaction products containing propane, isobutane, pentanes and unconverted *n*-butane were analyzed on-line using an HP 5890 gas chromatograph equipped with a stainless-steel column (3 mm od, 3 m long) packed with Porapak Q (80/100 mesh) and a flame ionization detector. In all experiments, the selectivity to isobutane was above 94%.

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 8000 FTIR spectrometer at 2 cm⁻¹ resolution using a liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector. SZ samples calcined at 620 °C were powdered below 200 mesh and pressed (3 \times 10⁸ Pa, 2 min) into self-supporting wafers (11 mg cm⁻², diameter = 13 mm). The activation of the samples was conducted in a quartz IR cell in the same way as for the catalyst activation in the catalytic testing. In brief, a wafer was heat-treated at a given temperature (150-500 °C) for 2 h and then cooled to room temperature, both steps being carried out in flowing dry air (130 ml min⁻¹). After 30 min purge of the IR cell with flowing helium (130 ml min⁻¹) at room temperature, an FTIR spectrum was recorded. The wafer in the cell was then heated to 100 °C in flowing helium and pyridine adsorption was performed by admitting a helium stream (80 ml min⁻¹) saturated with pyridine at room temperature into the cell for 30 min. The physisorbed pyridine was removed by purging the wafer at 100 °C with flowing helium (130 ml min⁻¹) for 2 h, and then another IR spectrum was recorded.

Thermogravimetry analysis (TG) was carried out using a Perkin-Elmer TGS-1 thermobalance. About 5 mg of SZ calcined at 620 °C was heated in a platinum pan under flowing dry air from room temperature to 800 °C at a rate of 20 °C min⁻¹, and the sample weight *vs.* temperature was recorded. In a separate experiment, in order to simulate the catalyst activation conditions used for the catalytic testing, an SZ sample was heat treated in the thermobalance under a dry air stream at incrementally increasing temperatures (150–550 °C) for 2 h, and the sample weight after the treatment at each temperature was monitored.

Results

Fig. 1 shows *n*-butane conversion *vs.* time on stream over SZ catalysts, which were first *ex situ* calcined at $620 \,^{\circ}$ C and then *in situ* activated in flowing dry air at temperatures from 150–500 $\,^{\circ}$ C. As the reaction was carried out at a low temperature, 90 $\,^{\circ}$ C, an induction period in which *n*-butane conversion increased with time on stream was observed in all the experiments. After the conversion reached a maximum, it started to decrease with the time on stream. Throughout this paper, we take the maximum *n*-butane conversion as a measure of the catalytic activity, rather than simply taking the conversion at some fixed time. The induction period in *n*-butane isomerization over SZ-based catalysts was usually ignored in studies



Fig. 1 *n*-Butane conversion *vs.* time on stream over SZ catalysts activated at various temperatures (indicated on the right-hand side of each curve). Before activation, the catalysts were *ex situ* calcined at 620 °C for 3 h. Reaction conditions: 90 °C, *n*-butane = 1 ml min⁻¹, helium = 22 ml min⁻¹, catalyst = 0.25 g.

using higher reaction temperatures (e.g., above $150 \,^{\circ}$ C) because it was too short to be observed at these reaction temperatures. It is seen from Fig. 1 that the induction period decreased with the increasing catalyst activation temperature from 150 to 250 °C and then stayed essentially unchanged at higher catalyst activation temperatures. It is also seen from Fig. 1 that the maximum *n*-butane conversion increased with the catalyst activation temperature from 150 to 300 °C and then decreased at higher catalyst activation temperatures. This is more clearly shown in Fig. 2(a). Fig. 2(b) shows the *n*-butane conversion data at a reaction temperature of 45 °C. Fig. 2 clearly indicates that there is an optimum temperature for catalyst activation, which in our study lies in the range 250–300 °C.

It is known that, among many factors, the water content of SZ catalysts is important in influencing their activity. The catalysts used in Fig. 1 and 2 were *ex situ* calcined at 620 °C for 3 h in static air in a furnace. The calcined catalysts were exposed to the ambient atmosphere during cooling and storage without any special protection. In the temperature range for the catalyst activation (150–500 °C), the sulfate ions will not be removed from the catalyst, but the water content in the catalyst (*i.e.*, catalyst dryness) will be affected by the temperature of activation; the higher the activation tem-



Fig. 2 Dependence of the catalyst activity on its activation temperature. The catalysts were the same as in Fig. 1. (a) Reaction conditions as in Fig. 1. (b) Reaction conditions: $45 \,^{\circ}$ C, *n*-butane = 1 ml min⁻¹, helium = 4 ml min⁻¹, catalyst = 0.3 g.

perature, the drier the catalyst. Therefore it is suggested that the change of n-butane conversion vs. the catalyst activation temperature is due to the change in the catalyst dryness.

To investigate the role of water, in a series of experiments we loaded sulfated $Zr(OH)_4$ samples into the reactor, calcined them *in situ* at various temperatures (500–700 °C), and then cooled them in a dry air stream to the reaction temperature (90 °C). Using this approach, the samples maintained the high degree of dryness reached during the high-temperature calcination because they did not have chance to adsorb moisture from the atmosphere. The reaction results are shown in Fig. 3(a). The *n*-butane conversion over the dry catalyst samples was very low. In contrast, the *ex situ* calcined SZ catalysts, which were wetted by atmospheric moisture during cooling and storage and then activated at 250 °C in dry air, exhibited much higher activity [Fig. 3(b)].

To clarify further the role of water in SZ catalysts, we carried out the following experiment. After sulfated $Zr(OH)_4$ samples (0.25 g) were *in situ* calcined at 620 °C in a dry air stream for 3 h and then cooled to 100 °C, a helium stream (22 ml min⁻¹) passing through a bubbler containing water at 11 °C was admitted into the reactor for 10 min. The wetted catalyst was then activated in a dry air stream at a certain temperature (150–500 °C) for 2 h and cooled to the reaction temperature (90 °C). The catalyst testing results over these



Fig. 3 Dependence of the catalyst activity on its calcination temperature. (a) In situ calcination. (b) $Ex \ situ$ calcination followed by activation at 250 °C in dry air. Reaction conditions as in Fig. 1.

catalysts were found to be similar to those over the *ex situ* calcined catalysts shown in Fig. 1. The maximum *n*-butane conversion vs. the activation temperature is depicted in Fig. 4, which closely resembles Fig. 2(a) with a minor difference believed to arise from the minor temperature difference between *in situ* and *ex situ* calcinations. The induction periods corresponding to the catalytic testing data in Fig. 4 varied from 38 to 48 min, depending on the catalyst activation temperature.

IR spectroscopy was performed to obtain an indication of the change of the catalyst acidity with the activation temperature. Consistent with the literature data, a band at 1300– 1400 cm⁻¹ was observed, which generally has been assigned to the asymmetric stretching of S=O double bonds. As shown in Table 1, the wavenumber at which the band appears strongly depends on the activation temperature: the higher the activation temperature, the higher the wavenumber. After pyridine adsorption, the band shifted to a lower wavenumber, with higher activation temperatures producing larger shifts.

IR spectroscopy of adsorbed pyridine provides information about Bronsted and Lewis acidities on the SZ catalysts. Both Bronsted and Lewis acid sites were observed in the range of activation temperature used in this study. An estimation of the acidity was performed based on the integrated molar absorption coefficients (IMACs) determined by Emeis,³⁵ which are considered to be the most reliable reported so far.³⁶ The IMACs of bands characteristic of pyridine adsorbed on Bronsted sites (1540 cm⁻¹ band) and Lewis sites (1445 cm⁻¹ band) are 1.67 cm μ mol⁻¹ and 2.22 cm μ mol⁻¹, respectively. Fig. 5 shows the dependence of the acidity on the activation temperature. As expected, an increase in activation temperature resulted in a decrease in Bronsted acidity with a concurrent increase in Lewis acidity. The total acidity also decreased with the increasing activation temperature (Fig. 5A).



Fig. 4 Dependence of the catalyst activity on its activation temperature. The catalysts were *in situ* calcined at $620 \,^{\circ}$ C for 3 h, hydrated at $100 \,^{\circ}$ C and activated in dry air at various temperatures. Reaction conditions as in Fig. 1.

 Table 1
 Effect of activation temperature on the IR band of the asymmetric stretching of S=O double bond

activation temperature/°C	S=O stretching frequency/cm ⁻¹	
	before pyridine adsorption	after pyridine adsorption
150	1301 (not well developed)	1300 (not well developed)
250	1317	1310
300	1334	1313
400	1365	1317
500	1387	1320



Fig. 5 Dependence of the catalyst acidity on catalyst activation temperature. Before activation, the catalysts were treated as described in the caption to Fig. 1.

Thermogravimetry data of SZ catalysts from our study and from the literature³⁷ indicate that during the thermal treatment below 500 °C, the weight loss of the samples is essentially due to its dehydration. The removal of sulfur species only occurs at temperatures higher than 550 °C. Therefore, as considered by Kobe et al.,¹⁶ we assume the catalyst activated at 500 °C contains no water, and the water contents of the catalysts activated at the lower temperature were calculated based on the weight difference between these samples and the one activated at 500 °C. The results are shown in Fig. 6. The catalyst dehydration occurred in three stages. In the first stage (below 220 °C), there was a fast dehydration due to the removal of physically adsorbed water. A comparison of Fig. 6 with Fig. 5 indicates that the removal of this portion of water does not strongly affect the Bronsted sites. During the second stage (220-400 °C), dehydration was slow, leading to a gradual decrease in Bronsted sites. In the third stage (400-500 °C), dehydration became faster, leading to a sharp decrease in Bronsted sites. A comparison of Fig. 2 with Fig. 5 and 6 indicates that the most active catalyst (calcined at 250-



Fig. 6 Water content of SZ catalysts activated at various temperatures. Before activation, the catalysts were treated as described in the caption to Fig. 1.

300 °C) contains about 200 $\mu mol~g^{-1}$ of water, and 67% of Bronsted sites out of the total acid sites.

Discussion

In the above, we have shown that the activity of SZ catalysts for *n*-butane isomerization strongly depends on their water content under their working conditions. In the present study, the catalyst water content was controlled by varying the activation temperature of the catalyst samples, which were calcined (ex situ or in situ) and then hydrated (by atmospheric moisture or by water from a bubbler). The activation temperatures were chosen so that the different catalyst drynesses could be obtained, but the sulfur species in the catalyst samples would stay intact. It was found in this study that minor amounts of water promote the catalyst activity while excess water diminishes it. This result is different from that reported by some other researchers, who found a poisoning effect of water on SZ catalysts,⁸⁻¹¹ but agrees with the data recently reported by Dumesic and co-workers.15-17 It is worth noting that the water content in working SZ catalysts is a function of a number of factors including their preparation method, calcination/activation conditions, and even the catalyst testing method. In addition, the promoting effect of water was only observed at a very low level of water content, which make its observation difficult. In the studies of water effect reported so far, different conditions for catalyst preparation, calcination/activation and catalytic testing were used. These differences may have caused the different observation in water effects previously reported.

Fig. 2 indicates that the tendency for the reactivity difference induced by the catalyst thermal pretreatment observed at two reaction temperatures (90 and 45 °C) is the same. In addition, Kobe *et al.*¹⁶ carried out reactions at a higher temperature (150 °C) and observed the same tendency as we have. Therefore, we believe that our conclusion about the water effect is appropriate, at least at reaction temperatures up to 150 °C.

Pretreatment (i.e., calcination and activation) of SZ is normally necessary to make the material catalytically active. For ex situ calcined samples, the purpose of the activation step is to achieve a preliminary surface dehydration. Then, can one consider that, if the surface dehydration achieved in a calcination step is maintained (e.g., for in situ calcination where the calcined catalyst is not exposed to the atmosphere), the catalyst will necessarily be effective?³⁸ The answer based on our data is no. Fig. 3(a) indicates that in situ calcined SZ catalysts without any hydration are inactive. In other words, an active SZ catalyst needs a certain degree of hydration. The cooling and storage of ex situ calcined samples provide a chance for the samples to adsorb moisture from the atmosphere. Once an appropriate water content in the catalyst is created by removal of excess water in activation, the catalyst becomes active [Fig. 3(b)]. In contrast, for in situ calcined catalyst, as the high degree of surface dehydration achieved in its calcination is maintained, the catalyst is inactive. Therefore, it is concluded that an activation step is needed for both ex situ and in situ calcined SZ catalysts to become active. For ex situ calcined samples, the activation is to remove excess water to reach an appropriate water content, whereas for in situ calcined samples, the activation is to add an appropriate amount of water to the samples to make them active.

The form of water in a SZ catalyst depends on the degree of its dehydration. According to Bolis *et al.*,³¹ upon contact with a highly dehydrated SZ where coordinatively unsaturated (cus) Zr^{4+} cations are present, H_2O may dissociate on very strongly acidic cus Zr^{4+} cations, giving rise to a surface OH group. Excessively adsorbed water may exist in the form of undissociated water molecules. We believe that heating a fully hydrated SZ sample involves first a fast removal of undis-

sociated water molecules at lower temperatures and then a slow elimination of surface OH groups at higher temperatures, as shown in Fig. 6. An active SZ catalyst should contain no undissociated water but possess strongly acidic OH groups.

During the preparation of this manuscript, the work by Dumesic and co-workers¹⁵⁻¹⁷ was published, which showed a similar effect of water content in SZ to that described above. These authors¹⁶ suggested that the changes in catalytic activity with drying temperature are not directly related to a transformation of Bronsted to Lewis acid sites, rather, the surface sulfate species may participate in butane isomerization via an oxidation-reduction cycle, and water may promote the catalytic activity by altering the oxidation-reduction properties of the surface species. In the present work, the FTIR spectrum of pyridine adsorbed on the catalysts shows that the decrease in water content resulted in a decrease in Bronsted sites with a concurrent increase in Lewis sites. The most active catalyst possesses an intermediate amount of Bronsted acidity. Therefore, we believe that the contribution of the catalyst acidity to the catalytic activity should not be ignored.

The acidity of SZ catalysts has been extensively studied.⁶ It has been observed that both Bronsted and Lewis acid sites can be present and their densities depend on, among many factors, the degree of dryness of the catalysts. The two types of acid sites are reversibly transformed upon hydration/dehydration. Our observation (Fig. 5) is in agreement with the literature data.

Significant change in the IR spectra in the range of S=O stretching frequency of sulfate ion was caused by activating SZ at different temperatures (Table 1). The band at 1300–1400 cm⁻¹ is attributed to the asymmetric vibration of S=O bonds of the bidentate sulfate ion coordinated to the metal cation.¹⁸ The band position relates to the strength of the Lewis acid sites of the metal cations in sulfated metal oxides. The higher the frequency of the asymmetric vibration of the S=O band, the stronger the Lewis acid sites.²⁶ It is seen from Table 1 that, with an increase in the activation temperature, this band shifted to higher frequencies, indicating that the Lewis acid sites were strengthened. When the catalysts were exposed to pyridine, the S=O bands shifted to lower frequencies; the stronger the Lewis acid sites, the larger the shift.¹⁸

A number of models have been proposed to describe the sulfate species on the catalyst surface. Of these models, the one proposed by Clearfield *et al.*²⁷ seems to correlate best with our experimental data. In this model (Scheme 1), the uncalcined catalyst (species I) contains protons as bisulfate and as hydroxy groups bridging two Zr ions. During calcination, water is lost to form species II and III. In both structures, Lewis acid sites are formed as indicated by asterisks, but in species II the bisulfate remains intact, which results in a



Scheme 1

Lewis acid site adjacent to an S-O-H group. These bisulfate groups act as highly acidic Bronsted sites because the neighboring Lewis acid sites tend to withdraw electrons from the bisulfate group, thus weakening the SO-H bond. It is inferred that the combination of the bisulfate protons with adjacent Lewis acid sites is responsible for the strong acidity. It is believed that the bisulfate protons act as active Bronsted acid sites. In catalyst samples with excess water, although the Bronsted acid sites are abundant, their strength is low because the adjacent Lewis acid sites are scarce. With the increasing activation temperature, more adsorbed water is removed and the strength of the Lewis acid sites is enhanced, which resulted in an increased electron-withdrawing ability of the Lewis acid sites. This, in turn, increases the strength of the Bronsted acid sites and thus the catalytic activity. When the catalyst is activated at progressively higher temperatures, the loss of the Bronsted acid sites becomes prodominent, and the drastic reduction of the amount of the Bronsted acid sites leads to a decrease of the catalytic activity.

In the above, we have discussed the importance of the catalyst acidity on the catalytic activity in *n*-butane isomerization. As to how the acidity contributes to the activity, there are different considerations. Some researchers believed that SZbased catalysts possess superacidity that can easily generate carbocations from butane molecules to initiate the reaction. However, this consideration has been challenged by several recent studies using various techniques for acidity characterization.^{13,39-43} which showed that the acid strength of SZ is only about equivalent to that of such zeolites as HY, ZSM-5, etc., which are not superacids. The exceptionally high activity of SZ catalysts stems from their ability to facilitate the formation of butene molecules.44,45 It was proposed that the catalyst acidity contributes to *n*-butane conversion by protonating the butene molecules formed to generate carbenium ions, which then either go through further transformations⁴⁶ or participate in a bimolecular reaction process in which the carbenium ions first react with butene molecules to form C₈ entities, which then go through skeletal rearrangement and β scission to form isobutane.44,47 The formation of butene, according to Ghenciu and Fărcașiu,46 may take place through a redox process involving a one-electron oxidation followed by trapping of the cation radicals on the surface, which leads to sulfite esters. The esters can either ionize to generate carbocations or eliminate to form butene. Therefore, the catalyst acidity contributes to the conversion of n-butane, not through direct activation of butane to create carbocations, but by protonating butene, which is formed from butane at a different type of sites (redox). Therefore, a synergism between the redox capability and the acidity of SZ catalysts can be visualized, and the Bronsted acid sites are essential for the protonation.

According to the synergistic reaction process, an induction period in which *n*-butane conversion increases with time on stream can be predicted in the early stages of the reaction.^{46,48} Indeed, an induction period was commonly observed in most of the studies of *n*-butane isomerization over Fe and Mn promoted SZ catalysts at low temperatures (usually below 100 °C). At relatively high reaction temperatures, it becomes too short to be observed. The induction period over unpromoted SZ catalysts was rarely reported in the literature because the reaction temperature used there was usually higher than 150 °C. In this work, we used a reaction temperature of \leq 90 °C. Clear induction periods were observed (Fig. 1), which are consistent with the proposal that butene is involved in the reaction.

Conclusions

It was shown in this work that small amounts of water increase the activity of SZ catalysts in *n*-butane isomerization,

while excess water diminishes it. Both Bronsted and Lewis acid sites were present on the active catalysts, and a decrease in water content resulted in a decrease in Bronsted acidity with a concurrent increase in Lewis acidity. In the most active catalyst, approximately two-thirds of the acid sites are Bronsted sites, and the rest are Lewis sites; an appropriate amount of water is needed to produce this ratio. We believe that the Bronsted acid sites (i.e., bisulfate protons) are primarily responsible for the formation of carbenium ions by protonating butene formed at redox sites on the catalyst. The butene and the carbenium ions react to form C8 entities which then go through skeletal rearrangement and β -scission to produce isobutane. According to the model of surface sulfate species proposed by Clearfield et al.,²⁷ the acid strength of the bisulfate protons depends on the number of adjacent coordinatively unsaturated acid sites (i.e., Lewis sites), which weaken the bisulfate SO-H bonds by withdrawing electrons from the bonds through an inductive effect.

We gratefully acknowledge financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC). S.X.S. is thankful to NSERC for awarding a Postdoctoral Fellowship.

References

- 1 K. Arata, Adv. Catal., 1990, 37, 165.
- 2 K. Tanabe, H. Hattori and T. Yamaguchi, Crit. Rev. Surf. Chem., 1990, 1, 1.
- 3 T. Yamaguchi, Appl. Catal., 1990, 61, 1.
- 4 B. H. Davis, R. A. Keogh and R. Srinivasan, *Catal. Today*, 1994, **20**, 219.
- 5 A. Corma, Chem. Rev., 1995, **95**, 559.
- 6 X. Song and A. Sayari, Catal. Rev.-Sci. Eng., 1996, 38, 329.
- M. Y. Wen, I. Wender and J. W. Tierney, *Energy Fuels*, 1990, 4, 372.
- 8 C. Morterra, G. Cerrato, F. Pinna, M. Signoretto and G. Strukul, J. Catal., 1994, 149, 181.
- 9 V. M. Mastikhin, A. V. Nosov, S. V. Filimonova, V. V. Terskikh, N. S. Kotsarenko, V. P. Shmachkova and V. I. Kim, J. Mol. Catal. A: Chem., 1995, 101, 81.
- 10 R. A. Keogh, R. Srinivasan and B. H. Davis, J. Catal., 1995, 151, 292.
- 11 R. A. Comelli, C. R. Vera and J. M. Parera, J. Catal., 1995, 151, 96.
- 12 J. H. Lunsford, H. Sang, S. M. Campbell, C-H. Liang and R. G. Anthony, *Catal. Lett.*, 1994, 27, 305.
- 13 F. Babou, B. Bigot, G. Coudurier, P. Sautet and J. C. Védrine, Stud. Surf. Sci. Catal., 1994, 90, 519.
- 14 D. Fraenkel, Abstr. Book, 14th North Am. Meeting Catal. Soc., Snowbird, UT, June 1995, p. T-48.
- 15 M. R. González, J. M. Kobe, K. B. Fogash and J. A. Dumesic, J. Catal., 1996, 160, 290.
- 16 J. M. Kobe, M. R. González, K. B. Fogash and J. A. Dumesic, J. Catal., 1996, 164, 459.
- 17 M. R. González, K. B. Fogash, J. M. Kobe and J. A. Dumesic, *Catal. Today*, 1997, **33**, 303.

- 18 T. Jin, T. Yamaguchi and K. Tanabe, J. Phys. Chem., 1986, 90, 4794.
- 19 T. Yamaguchi, K. Tanabe and Y. C. Kung, Mater. Chem. Phys., 1986, 16, 67.
- 20 M. Bensitel, O. Saur, J. C. Lavally and G. Mabilon, *Mater. Chem. Phys.*, 1987, 17, 249.
- 21 A. Corma, V. Fornés, M. I. Juan-Rajadell and J. M. López Nieto, Appl. Catal. A: Gen., 1994, 116, 151.
- 22 F. Pinna, M. Signoretto, G. Strukul, G. Cerrato and C. Morterra, Catal. Lett., 1994, 26, 339.
- 23 R. Srinivasan, R. A. Keogh and B. H. Davis, *Catal. Lett.*, 1996, **36**, 51.
- 24 D. A. Ward and E. I. Ko., J. Catal., 1994, 150, 18.
- 25 K. B. Fogash, G. Yaluris, M. R. González, P. Ouraipryvan, D. A. Ward, E. I. Ko and J. A. Dumesic, *Catal. Lett.*, 1995, **32**, 241.
- 26 K. Ebitani, J. Konishi and H. Hattori, J. Catal., 1991, 130, 257
- A. Clearfield, G. P. D. Serrette and A. H. Khazi-Syed, *Catal. Today*, 1994, **20**, 295.
 P. Nascimento, C. Akratopoulou, M. Oszagyan, G. Coudurier, C.
- Travers, J. F. Joly and J. C. Védrine, *Stud. Surf. Sci. Catal.*, 1993, **75**, 1185.
- 29 F. R. Chen, G. Coudurier, J-F. Joly and J. C. Védrine, J. Catal., 1993, 143, 616.
- 30 C. Morterra, G. Cerrato, V. Bolis, S. Di Ciero and M. Signoretto, J. Chem. Soc., Faraday Trans., 1997, 93, 1179.
- 31 V. Bolis, G. Magnacca, G. Cerrato and C. Morterra, *Langmuir*, 1997, 13, 888.
- 32 X. Song and A. Sayari, *Energy Fuels*, 1996, 10, 561.
- 33 M. Waqif, J. Bachelier, O. Saur and J-C. Lavalley, J. Mol. Catal., 1992, 72, 127.
- 34 M. Nita, H. Sakoh and K. Aomura, Appl. Catal., 1984, 10, 215.
- 35 C. A. Emeis, J. Catal., 1993, 141, 347.
- 36 T. Barzetti, E. Selli, D. Moscotti and L. Forni, J. Chem. Soc., Faraday Trans., 1996, 92, 1401.
- 37 R. Srinivasan, R. A. Keogh, D. R. Milburn and B. H. Davis, J. Catal., 1995, 153, 123.
- 38 C. Morterra, G. Cerrato and M. Signoretto, *Catal. Lett.*, 1996, **41**, 101.
- 39 B. Umansky, J. Engelhardt and W. K. Hall, J. Catal., 1991, 127, 128.
- 40 L. M. Kustov, V. B. Kazansky, F. Figueras and D. Ticht, J. Catal., 1994, 150, 143.
- 41 V. Adeeva, J. W. de Haan, J. Jänchen, G. D. Lei, G. Schünemann, L. J. M. van de Ven, W. M. H. Sachtler and R. A. van Santen, J. *Catal.*, 1995, **151**, 364.
- 42 V. Semmer, P. Batamack, C. Dorémieux-Morin, R. Vincent and J. Fraissard, J. Catal., 1996, 161, 186.
- 43 R. S. Drago and N. Kob, J. Phys. Chem. B, 1997, 101, 3360.
- 44 V. Adeeva, G. D. Lei and W. M. H. Sachtler, Catal. Lett., 1995, 33, 135.
- J. E. Tábora and R. J. Davis, J. Am. Chem. Soc., 1996, 118, 12240.
 A. Ghenciu and D. Fărcaşiu, J. Mol. Catal. A: Chem., 1996, 109, 273
- 47 J. E. Tábora and R. J. Davis, J. Catal., 1996, 162, 125.
- 48 M. A. Coelho, D. E. Resasco, E. C. Sikabwe and R. L. White, *Catal. Lett.*, 1995, **32**, 253.

Paper 7/06892A; Received 23rd September, 1997