ELSEVIER

Catalysis Today 33 (1997) 303–312

CATALYSIS TODAY

Promotion of n-butane isomerization by hydroxyl groups on sulfated zirconia

Martín R. González [1], Kevin B. Fogash, Jeffrey M. Kobe, James A. Dumesic *

Department of Chemical Engineering, University of Wisconsin, Madison, WI 53706, USA

Abstract

Microcalorimetry, infrared spectroscopy, and reaction kinetics measurements were used to investigate the role of hydroxyl groups on sulfated zirconia in promoting n-butane isomerization at 423 K. The catalytic activity for a sample dried at 773 K is an order of magnitude lower compared to a sample dried at 588 K. However, the catalytic activity for the sample dried at 773 K is promoted by dosing approximately 75 μmol/g of water onto the surface at 423 K. Larger doses of water poison the catalyst. Dehydration of the catalyst did not alter the heats of adsorption of n-butane, isobutane, or ammonia. Water dissociates upon adsorption on the sample dried at 773 K, producing new hydroxyl groups which increase the extinction coefficient for infrared absorbance of ammonium ions. It is proposed that these hydroxyl groups may aid n-butane isomerization by stabilizing species on the surface and/or by suppressing the irreversible reduction of surface sulfur species.

1. Introduction

The isomerization of straight-chain paraffins to more highly branched species is beneficial for the production of cleaner-burning fuels. For example, n-butane, whose volatility requires its removal from gasoline, may be converted to isobutane, a valuable precursor to MTBE and other fuel additives. Sulfated zirconia catalysts are active for n-butane isomerization at low temperatures (e.g., 300 K) [1,2]. Evidence of unusually strong acidity on these catalysts, denoted as superacidity, has been reported by many researchers [2–7]. In addition, the presence of an additional non-acidic functionality which facilitates hydrocarbon rearrangement has also been proposed [8,9]. The origin of the observed superacidity of these materials, therefore, remains a subject of current research.

In the present study, the combination of microcalorimetry, infrared spectroscopy, and reaction kinetics experiments is used to characterize the sites on sulfated zirconia that are active for n-butane isomerization. The reaction is carried out over a catalyst prepared in two states of hydration, one which is active and one which is relatively inactive. A measure of the number of active sites is obtained by selective poisoning of the catalyst with adsorbed ammonia. Adsorption calorimetry is performed with ammonia to assess the strength distribution of the acid sites, and calorimetric studies of n-butane and isobutane adsorption are conducted to determine if the strength of interaction of the surface with

---

* Corresponding author. Tel.: +1-608-2621095; fax: +1-608-2625434.

[1] Present address: Amoco Petroleum Products, 150 W. Warrenville Rd, Naperville, IL 60566-7011.

PII S0920-5861(96)00156-3

these paraffins is related to the rate of isomerization. The role of adsorbed water in promoting the isomerization activity of sulfated zirconia is then investigated.

2. Experimental

The sulfated zirconia catalysts used in this study were prepared from sulfuric acid-treated zirconium hydroxide provided by MEI Corporation. The precursor was heated in flowing oxygen (100 cm^3/g min, NTP) from room temperature to 848 K over a period of 1.5 h. After calcination for 2 h at this temperature, the catalyst was transferred in air to a vial and stored in a desiccator. The calcined material contains 1.8 wt% sulfur, as determined by chemical analysis (Galbraith Laboratories). The BET surface area after this treatment is 98 m^2/g. Prior to subsequent experimental studies, the catalyst was dried for 1 h in flowing He (65 cm^3/min) at either 588 or 773 K to study the effect of moisture content. Experiments involving adsorption of water were conducted with the sulfated zirconia samples maintained at 423 K during exposure. Water was purified before use by successive freeze–pump–thaw cycles.

The isomerization of n-butane was carried out at 423 K using a gas composition of 10% n-butane (AGA, 99.5% purity, instrument grade) in He (Liquid Carbonic). A quartz flow-reactor 1.27 cm in diameter was loaded with approximately 0.2 g of catalyst and 0.1 g of quartz particles. This solid mixture was dried in flowing He (65 cm^3/min) for 1 h at 588 K (MEI-1) or 773 K (MEI-2). For the hydration experiments, the catalyst was dried at 773 K before adsorption of the indicated amount of water at 423 K.

Helium and n-butane were purified by oxygen absorbent traps (Alltech), and water impurities were removed by molecular sieve traps (13X) at 77 K and at room temperature for He and n-butane, respectively. The major alkane impurities in the n-butane feed were isobutane and propane, for which the kinetics data were corrected. The n-butane contained C_4-olefins at a level of approximately 1000 ppm. Reaction products were analyzed using a Hewlett–Packard 5890 gas chromatograph equipped with a flame ionization detector. The chromatograph contained a 7.3 m 5% DC-200 Chromosorb P-AW column held at 323 K. Catalytic activities and selectivities are calculated on the basis of hydrocarbon products detected in the reactor effluent.

Details of the selective poisoning of sulfated zirconia with ammonia have been presented elsewhere [10]. Specific amounts of NH_3 were adsorbed at room temperature on a catalyst dried at 588 K. The sample was then heated to 573 K and held at this temperature for 1 h to allow the ammonia to equilibrate with acid sites on the surface. Measurements of the rate of n-butane isomerization were initiated after cooling the catalyst to 423 K.

Microcalorimetric studies were performed using a Tian–Calvet type heat-flux calorimeter connected to a gas-handling system. The design of this apparatus and the procedure for its operation have been described elsewhere [11]. Experiments were conducted at 423 K for ammonia and water and at 308 K for n-butane and isobutane. Samples weighing approximately 0.6 g were pelletized and evacuated to 10^{-4} Pa at 588 K (MEI-1) or 773 K (MEI-2) for 1 h. Samples were then allowed to equilibrate overnight in the heat sink at the desired temperature under 30–55 kPa of argon before calorimetric measurements were taken. Differential heats of adsorption versus adsorbate coverage were obtained by measuring the energy evolved from sequential doses of the adsorbate gas (2–10 μmol) onto the catalyst. The enthalpy change associated with adsorption of the probe molecule is exothermic, and the heat of adsorption is defined as the absolute value of this quantity.

Infrared spectra were collected at room temperature using a Mattson Galaxy 5020 FTIR spectrometer. Samples were pressed into self-supporting pellets (18 mg/cm^2) at a pressure of ca. 70 MPa. Drying for 1 h at 588 K (MEI-1) or 773 K (MEI-2) was performed under vacuum (10^{-4} Pa) in a cell containing CaF_2 windows. During the adsorption of ammonia or water, the catalyst pellet was maintained at 423 K. All spectra were collected at room temperature at a resolution of 8 cm^{-1}.

3. Results and discussion

Fig. 1 shows the catalytic activity for n-butane isomerization of sulfated zirconia dried at 588 and 773 K, respectively. The activity of the catalyst dried at the lower temperature (MEI-1) is initially about 2.1 μmol/g · s. The activity decreases with time, at least in part, because of the formation of coke [12]. Some reduction of sulfur may also take place [13,14]. The selectivity of this catalyst for isomerization to isobutane is 92%, with the balance of the products consisting mainly of propane and isopentane.

In contrast to the MEI-1 sample, the catalyst dried at the higher temperature (MEI-2) shows low activity, initially converting n-butane at a rate of 0.12 μmol/g · s. The selectivity of this catalyst for isomerization is about 80%. After 1 h on stream, no measurable conversion of n-butane takes place over MEI-2.

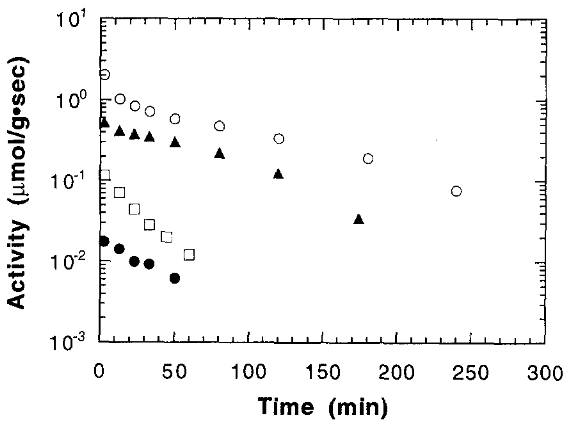


Fig. 1. Rate of n-butane isomerization at 423 K versus time on stream of MEI-2 (□), and MEI-1 containing adsorbed NH_3 at coverages of 0 μmol/g (○), 30 μmol/g (▲), and 69 μmol/g (●).

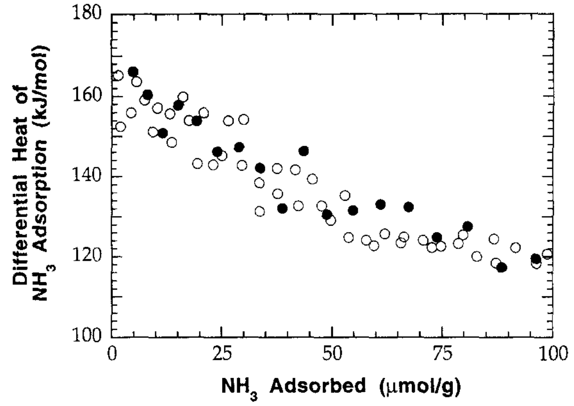


Fig. 2. Differential heat of NH_3 adsorption versus adsorbate coverage at 423 K on MEI-1 (○) and MEI-2 (●).

Also shown in Fig. 1 are rates of n-butane conversion over MEI-1 samples containing ca. 30 and 70 μmol/g of adsorbed NH_3. Ammonia is a strong base that preferentially adsorbs onto the strongest acid sites when allowed to equilibrate [15,16]. As shown in the figure, the uptake of 30 μmol/g of NH_3 causes a significant decrease in activity and the isomerization reaction over MEI-1 is effectively eliminated after the strongest 70 μmol/g of acid sites have been neutralized with ammonia. The strongest acid sites of MEI-1 are, therefore, implicated in the isomerization of n-butane. Moreover, a maximum of ca. 70 μmol/g of acid sites participate in the reaction. It should be noted that the MEI samples of this study contain 560 μmol/g of sulfur, and 1 μmol/g corresponds to 6×10^{15} sites/m^2.

Differential heats of ammonia adsorption at 423 K versus adsorbate coverage are shown in Fig. 2 for MEI-1 and MEI-2. The two samples show essentially the same behavior for differential heats of ammonia adsorption to a coverage of 100 μmol/g. The MEI-2 sample possesses strong acid sites even though it shows low activity. Microcalorimetric data for ammonia adsorption on MEI-1 have been previously reported [17].

Microcalorimetric measurements of ammonia adsorption have been successfully correlated with the acid strengths of silica–alumina [15] and H-ZSM-5 [18]. The initial heat of ammonia adsorption on these sulfated zirconia catalysts, ca. 165 kJ/mol, is comparable to values reported for H-mordenite [19], H-ZSM-5 [19], Y zeolites [20], and for alumina [20–22]. Thus, these sulfated zirconia catalysts do not appear to be superacidic, at least as measured by the heat of ammonia adsorption. Parillo et al. [23] have recently suggested that the differential heat of ammonia adsorption may not be a reliable measure of acid strength, since this heat has contributions from acidic as well as non-acidic interactions, i.e., the proton affinity of the acid site and the stabilization of the acid–base adduct on the surface, respectively.

The calorimetric results in Fig. 2 demonstrate that the differential heat of ammonia adsorption versus ammonia coverage is not sensitive to the temperature of vacuum dehydration within the range 588–773 K. Thus, a simple consideration of acid strength, as measured by the heat of ammonia adsorption, cannot account for the significant difference in the n-butane isomerization activity displayed by the catalysts dried at these two temperatures (Fig. 1). We suggest that the presence of acid sites is a necessary but not a sufficient condition for high catalytic activity for n-butane isomerization at the reaction conditions of the present study.

Fig. 3 shows heats of n-butane adsorption at 308 K on MEI-1 and MEI-2. For both samples, the initial dose of the probe molecule releases about 57 kJ/mol, a relatively large value when compared to the heat of condensation of n-butane (22 kJ/mol) [24]. The heat of adsorption decreases in a monotonic fashion with adsorbate coverage on both catalysts, reaching a value of approximately 38 kJ/mol after 35 μmol/g of n-butane are adsorbed. These data indicate that MEI-1 and MEI-2 exhibit similar strengths of interaction with n-butane. Thus, the relatively high isomerization activity of MEI-1 does not arise from an unusually strong affinity for the reactant molecule.

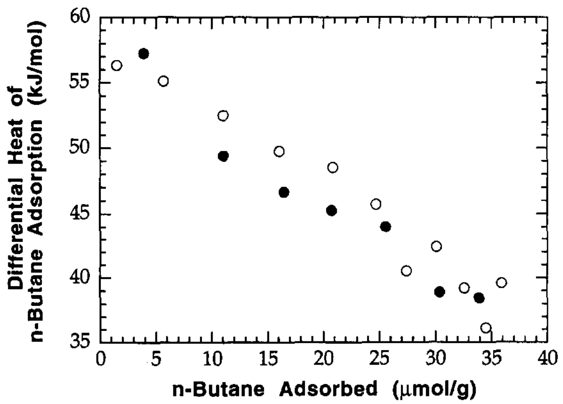


Fig. 3. Differential heat of n-butane adsorption versus adsorbate coverage at 308 K on MEI-1 (○) and MEI-2 (●).

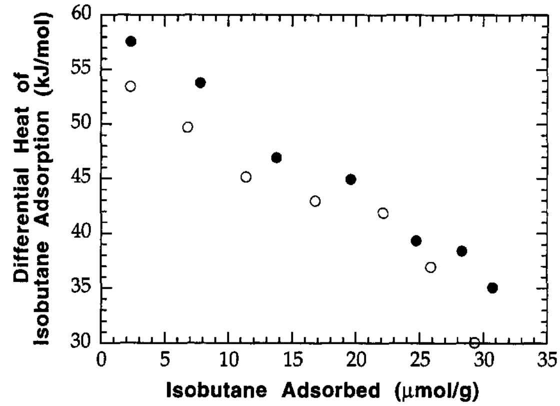


Fig. 4. Differential heat of isobutane adsorption versus adsorbate coverage at 308 K on MEI-1 (○) and MEI-2 (●).

Differential heats of isobutane adsorption at 308 K for both samples are shown in Fig. 4. The initial heat of isobutane adsorption on MEI-1 is about 54 kJ/mol, while that on MEI-2 is about 58 kJ/mol. For both samples, the heats decrease monotonically to approximately 35 kJ/mol at 30 μmol/g coverage. These data suggest that MEI-2 may adsorb isobutane slightly more strongly than MEI-1. Nevertheless, the difference between samples is small and cannot account for the observed difference in catalytic activity for n-butane isomerization.

Spectra of the hydroxyl-stretching region of MEI-1 and MEI-2 are displayed in Fig. 5. In agreement with other spectroscopic studies of sulfated zirconia [9,25–27], the strongest absorbance for both samples is seen at 3640 cm^{-1}.

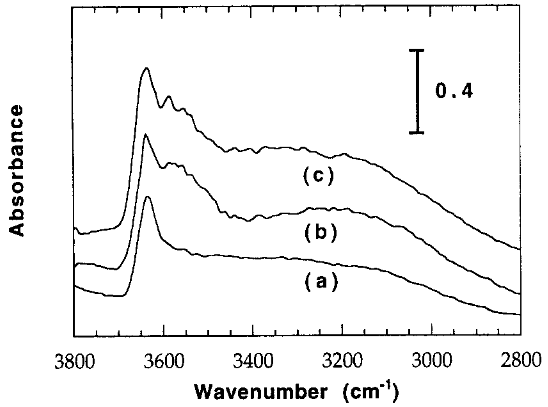


Fig. 5. Infrared spectra of MEI-2 (a), MEI-1 (b), and MEI-2 with 50 μmol/g of adsorbed H_2O (c). Absorbance scale is provided on the figure.

The intensity of this band is slightly higher on MEI-1 than on MEI-2. In addition to absorbance at this frequency, MEI-1 shows a broader band centered at approximately 3550 cm^{-1} and an extremely broad region extending from 2800 to 3400 cm^{-1}. These features are indicative of surface OH groups that are strongly hydrogen bonded to each other or to other groups on the surface [28]. Thus, the surface of the catalyst dehydrated at 588 K is populated by hydroxyl groups that are removed by drying at 773 K. Although these OH groups may be related to the higher activity for n-butane isomerization of MEI-1, they apparently do not affect the adsorption of n-butane, isobutane, or ammonia. Ammonia probably adsorbs on hydroxyl groups that give rise to the band at 3640 cm^{-1}. The presence of this type of OH group on both MEI-1 and MEI-2 would account for the similarity in NH_3 adsorption heats of these samples. Any new OH groups created by hydration of MEI-2 may be more weakly acidic than those hydroxyl species already present.

Also shown in Fig. 5, the spectrum of MEI-2 is rehydrated with 50 μmol/g of H_2O. The adsorption of water on the catalyst results in absorbance in the hydroxyl stretching region that is more similar to that of MEI-1. The new OH bands of the rehydroxylated MEI-2 do not appear to be as clearly defined as those of the MEI-1 sample, suggesting that the former may have a greater tendency toward hydrogen bonding.

A plot of the differential heat of water adsorption on MEI-2 is shown in Fig. 6. The initial heat of water adsorption on MEI-2 is approximately 205 kJ/mol, although sites are discernible that display varying strengths of interaction with the surface. The heat of water adsorption on MEI-2 is higher than that of ammonia adsorption for at least the first 100 μmol/g of adsorbed species. Because water is a weaker base than ammonia, the high differential heat of adsorption suggests that water probably dissociates on the surface, for example, by interacting with bridging oxygens to form new hydroxyl groups on the surface [29,30]. This conclusion is consistent with the higher OH concentration displayed by the MEI-1 sample in the infrared spectra of Fig. 5.

To investigate the effect of surface water content on the catalytic activity for n-butane isomerization, the MEI-2 sample was rehydrated incrementally with known quantities of water. Based on the behavior shown in Fig. 6 for the differential heat of water adsorption versus adsorbate coverage, reaction kinetics experiments were performed on formulations of MEI-2 titrated with approximately 25, 50, 75, 100, and 150 μmol/g of water. Fig. 7 shows

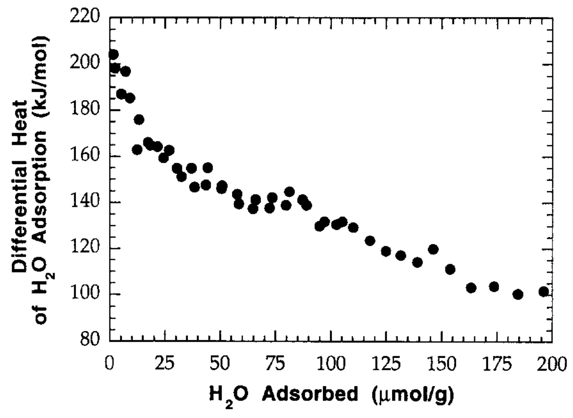


Fig. 6. Differential heat of H_2O adsorption versus adsorbate coverage at 423 K on MEI-2.

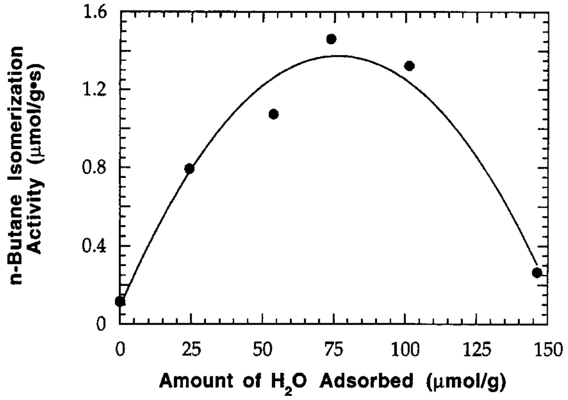


Fig. 7. Initial rate of n-butane isomerization at 423 K versus amount of H_2O adsorbed on MEI-2. All activities are calculated at 3 min on stream.

the initial rate of n-butane isomerization for each of the rehydrated catalysts. As described above, the n-butane isomerization activity of MEI-2 at 3 min on stream is 0.12 µmol/g · s, while the activity of MEI-1 is 2.1 µmol/g · s. Adding 24 µmol/g of H_2O to MEI-2 causes a significant increase in catalytic activity to a value of approximately 0.80 µmol/g · s. The promotional effect of water addition to MEI-2 continues until a maximum catalytic activity of 1.5 µmol/g · s is reached upon addition of 74 µmol/g of H_2O. Water acts as a poison at higher amounts on the catalyst. For example, the initial catalytic activity for n-butane conversion over MEI-2 after treatment with 146 µmol/g of water is only slightly higher than that of the original dehydrated catalyst.

The adsorption of large amounts of water onto sulfated zirconia has been shown in the literature to poison n-butane isomerization [31,32]. Importantly, the results of the present study indicate that water promotes n-butane isomerization over sulfated zirconia for moderate extents of catalyst hydration.

The results of Fig. 1 show that the MEI-2 sample exhibits an initial activity for isomerization that is an order of magnitude lower than the MEI-1 sample. Gravimetric measurements reported elsewhere [33] indicate that this increase in drying temperature leads to the removal of about 110 µmol/g of water from the catalyst. As seen in Fig. 7, the maximum rate of n-butane conversion observed during rehydration of the MEI-2 sample occurs for 74 µmol/g of H_2O, which corresponds to 67% rehydration of the catalyst. This treatment restores approximately 70% of the activity lost in the drying process at 773 K. The portion of the activity that is not regained may indicate that some of the dehydroxylation which occurs at 773 K is irreversible. For example, metal oxides dehydrated at high temperatures may possess annealed oxygen bridges which are rehydrated only by immersion in liquid water [28].

Fig. 8 shows infrared spectra of MEI-2 prior to and following rehydroxylation with 50 µmol/g of D_2O. As with H_2O addition (Fig. 5), a band centered at 3550 cm^{-1} appears, and absorbance in the 3400–2800 cm^{-1} region grows. The increase in intensity at 3640 cm^{-1} that accompanies water uptake is absent. Instead, two OD bands of approximately equal intensity arise at 2685 and 2665 cm^{-1}, corresponding to OH bands at 3670 and 3640 cm^{-1} that have been isotopically shifted by a factor of 1.37. The region below these new bands exhibits a weak increase in intensity, revealing the participation of OD groups in hydrogen bonding.

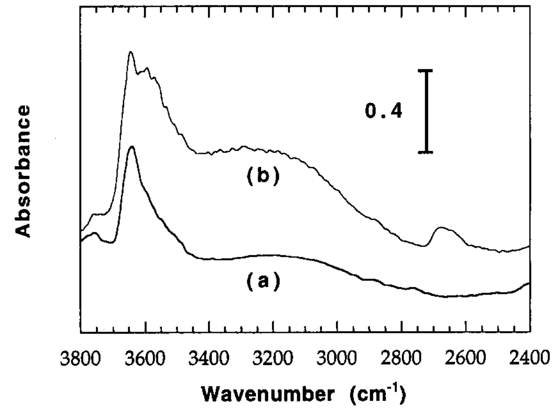


Fig. 8. Infrared spectra of D_2O adsorbed on MEI-2 at coverages of 0 µmol/g (a) and 50 µmol/g (b). Absorbance scale is provided on the figure.

Absorbance at 3670 cm^{-1} is commonly observed on zirconia in the absence of sulfate [25,27,34–37]. Thus, new Zr–OH groups similar to those present on zirconia are created by rehydration of MEI-2. Although this band was not observed when MEI-2 was treated with H_2O, the presence of this band may have been obscured by broader, more intense OH bands.

The spectra shown in Fig. 8 provide evidence for strong hydrogen bonding on the surface of sulfated zirconia. This hydrogen bonding includes participation not only of the new OD bands that appear when D_2O is added, but also the OH groups that are already present and whose hydrogen bonding is indicated by absorbance at 3600–2800 cm^{-1}. Moreover, it is likely that the two broad bands appearing in this region are due to OH groups which would absorb at 3640 and 3670 cm^{-1} were they not shifted by strong hydrogen bonding. Shifts on the order of 100 cm^{-1} are common upon the interaction of OH bonds with S=O bonds [38,39].

Fig. 9 shows the S=O stretching region of MEI-2 with 101 μmol/g of NH_3 adsorbed. The spectrum of the clean MEI-2 catalyst has been subtracted. This catalyst contains almost exclusively Brønsted acid sites, evidenced by the band near 1440 cm^{-1}. A weak band at 1600 cm^{-1} is also present, and may be due to coordinatively bound NH_3 or to the overtone of an OH bending mode occurring at about 800 cm^{-1} [40]. Uptake of the ammonia probe molecule causes intensity to diminish in the region 1370–1420 cm^{-1} while absorbance at 1280 cm^{-1} increases. This apparent shift of S=O stretching absorbance to lower frequencies is related to a withdrawal of electrons by adsorbed molecules [1,41,42]. Alternatively, such a shift may be indicative of increased hydrogen bonding [43].

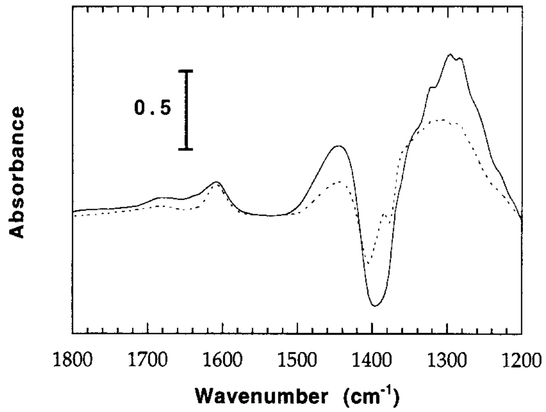


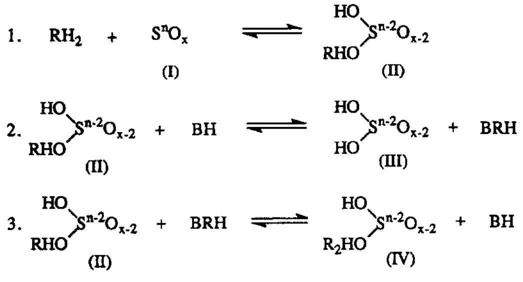
Fig. 9. Infrared spectra of an experiment in which the adsorption of 101 μmol/g NH_3 on MEI-2 (broken line) is followed by the adsorption of 49 μmol/g H_2O (solid line). The absorbance of the clean MEI-2 sample has been subtracted from all spectra. Absorbance scale is provided on the figure.

The spectrum of this MEI-2 sample containing 101 μmol/g of adsorbed NH_3 and subsequently exposed to 49 μmol/g of H_2O is also shown in Fig. 9. Surprisingly, the intensity of the 1440 cm^{-1} band increases when the catalyst is exposed to water. This change reflects an increase in the dipole moment of the ammonium ions on the surface, caused by a change in the electronic structure [44]. The stabilization of NH_4^+ by hydrogen bonding in polar solvents is well known [45]. We offer this experiment as further evidence that hydroxyl groups on sulfated zirconia interact with positively charged surface species, in a manner analogous to water molecules that stabilize ions in solution.

Several researchers have suggested that the reactive forms of hydrocarbons adsorbed on solid acids are covalent in nature and carry a positive charge only briefly while undergoing rearrangement [46–57]. The rate-limiting step for isomerization may be the rearrangement of a charged species, as in traditional carbenium ion chemistry [58]. Lowering the energy barrier for excitation from the covalent ground state to the charged excited state would increase the rate of isomerization. Accordingly, the newly formed OH groups on the rehydrated catalysts of the present study may lower the activation energy for rearrangement of n-butane. The strong hydrogen bonding seen in the infrared spectra of active samples, suggests that stabilization of reactive intermediates may be occurring in the same way that solvent molecules stabilize carbenium ions in liquid superacids. An investigation into the kinetics of butane isomerization as well as the deactivation for sulfated zirconia is presented elsewhere [59].

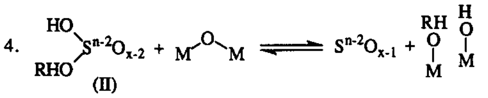
We have shown in this study that sulfated zirconia catalysts active for n-butane isomerization contain many non-acidic hydroxyl groups. Further, the acidity of sulfated zirconia as measured by the heat of ammonia adsorption is comparable to materials not generally considered to be superacidic. We may now propose that the unique catalytic properties of sulfated zirconia may be related to the combination of acid sites with sites capable of undergoing oxidation–reduction cycles, as suggested by TPD studies of bases on modified sulfated zirconia catalysts which revealed the presence of oxidized adsorbed species [52,60,61]. For example, a simple reaction scheme is shown schematically in Scheme 1, where S^nO_x is a surface sulfur oxide species and BH is a Brønsted acid site.

The oxidation state of sulfur in species (I) is $+n$ (e.g., $n = 6$), while the oxidation state is $+n - 2$ in species (II)–(IV). Accordingly, the activation of butane in step 1 takes place via reduction of sulfur, followed by the transfer of the C_4H_9 species (RH) to a Brønsted acid site (BH) in step 2. The olefinic species (R) associated with the acid site may then react with species (II) in step 3 to form a C_8 species that has been proposed by many authors [62–67] to be a reactive intermediate in butane isomerization and disproportionation. This C_8 intermediate undergoes a methyl shift followed by β-scission to give an i-C_4 species that leads to isobutane via the reverse of reactions 1–3.



Scheme 1.

The presence of hydroxyl groups on the surface can alter the rate of butane isomerization by interacting with and stabilizing various reaction intermediates (I)–(IV), as noted above. However, another important function of these hydroxyl groups may be to prevent the irreversible reduction of surface sulfur compounds such as species (II). For example, consider the following step:



where M–O–M represents a portion of the zirconia surface that has been dehydroxylated by removal of water at elevated temperatures (e.g., 773 K). Thus, the presence of the proper degree of hydroxylation would retard reaction 4, thereby preventing irreversible sulfur reduction. Further studies will be required to elucidate the important role of non-acidic hydroxyl groups in promoting the activity of sulfated zirconia catalysts for butane isomerization at low temperatures.

Acknowledgements

This work was supported by funds provided by the Office of Basic Energy Sciences of the US Department of Energy (DE-FG02-84ER13183). For providing graduate fellowships, we would like to thank Amoco Oil Company (MRG), the National Defense Science and Engineering program (KBF), and the Wisconsin Alumni Research Foundation (JMK). We gratefully acknowledge the help of George Yaluris, Robert Larson, Carolina Hartanto, and Daniel Stein in conducting these experiments. Finally, we wish to thank Manuel Natal-Santiago and Professor Juan de Pablo for discussions about the oxidation/reduction properties of sulfur.

References

[1] K. Arata, Adv. Catal. 37 (1990) 165.

[2] M. Hino and K. Arata, J. Chem. Soc., Chem. Commun. (1980) 851.

[3] K. Arata, M. Hino and N. Yamagata, Bull. Chem. Soc. Jpn. 63 (1990) 244.

[4] F.R. Chen, G. Courdurier, J. Joly and J.C. Vedrine, J. Catal. 143 (1993) 616.

[5] T. Riemer, D. Spielbauer, M. Hunger, G.A.H. Mekhemer and H. Knözinger, J. Chem. Soc., Chem. Commun. (1994) 1181.

[6] C.H. Lin and C.Y. Hsu, J. Chem. Soc., Chem. Commun. (1992) 1479.

[7] F. Garin, L. Seyfried, P. Girard, G. Maire, A. Abdulsamad and J. Sommer, J. Catal. 151 (1995) 26.

[8] T.K. Cheung, J.L. d'Itri and B.C. Gates, J. Catal. 153 (1995) 344.

[9] V. Adeeva, J.W. de Haan, J. Jänchen, G.D. Lei, V. Schünemann, L.J.M. van de Ven, W.M.H. Sachtler and R.A. van Santen, J. Catal. 151 (1995) 364.

[10] G. Yaluris, R.B. Larson, J.M. Kobe, M.R. González, K.B. Fogash and J.A. Dumesic, J. Catal. 158 (1996) 336.

[11] B.E. Handy, S.B. Sharma, B.E. Spiewak and J.A. Dumesic, Meas. Sci. Technol. 4 (1993) 1350.

[12] J.M. Kobe, K.B. Fogash, M.R. González and J.A. Dumesic, (1996) in preparation.

[13] J.C. Yori, J.C. Luy and J.M. Parera, Appl. Catal. 46 (1989) 103.

[14] F.T.T. Ng and N. Horvát, Appl. Catal. A 123 (1995) L197.

[15] N. Cardona-Martínez and J.A. Dumesic, J. Catal. 128 (1991) 23.

[16] P. Carniti, A. Gervasini and A. Auroux, J. Catal. 150 (1994) 174.

[17] K.B. Fogash, G. Yaluris, M.R. González, P. Ouraipryvan, D.A. Ward, E.I. Ko and J.A. Dumesic, Catal. Lett. 32 (1995) 241.

[18] D.J. Parrillo, R.J. Gorte and W.E. Farneth, J. Am. Chem. Soc. 115 (1993) 12441.

[19] S.B. Sharma, B.L. Meyers, D.T. Chen, J. Miller and J.A. Dumesic, Appl. Catal. A 102 (1993) 253.

[20] G. Yaluris, J.E. Reskoske, L.M. Aparicio, R.J. Madon and J.A. Dumesic, J. Catal. 153 (1995) 65.

[21] J. Shen, R.D. Cortright, Y. Chen and J.A. Dumesic, Catal. Lett. 26 (1994) 247.

[22] J. Shen, R.D. Cortright, Y. Chen and J.A. Dumesic, J. Phys. Chem. 98 (1994) 8067.

[23] D.J. Parrillo, C. Lee, R.J. Gorte, D. White and W.E. Farneth, J. Phys. Chem. 99 (1995) 8745.

[24] R.C. Weast, Handbook of Chemistry and Physics, 58th Ed. (CRC Press, Cleveland, 1977).

[25] L.M. Kustov, V.B. Kazansky, F. Figueras and D. Tichit, J. Catal. 150 (1994) 143.

[26] C. Morterra, G. Cerrato, F. Pinna and M. Signoretto, J. Phys. Chem. 98 (1994) 12373.

[27] E. Escalona Platero and M. Peñarroya Mentruit, Catal. Lett. 30 (1995) 31.

[28] L.H. Little, Infrared Spectra of Adsorbed Species (Academic Press, New York, 1966).

[29] D.J. Coster, J.J. Fripiat, M. Muscas and A. Auroux, Langmuir 11 (1995) 2615.

[30] B.V. Romanovskii, K.V. Topchieva, L.V. Stolyarova and A.M. Alekseev, Kinet. Catal. 11 (1969) 1525.

[31] C. Morterra, G. Cerrato, F. Pinna, M. Signoretto and G. Strukul, J. Catal. 149 (1994) 181.

[32] R.A. Keogh, R. Srinivasan and B.H. Davis, J. Catal. 151 (1995) 292.

[33] J.M. Kobe, M.R. González, K.B. Fogash and J.A. Dumesic, J. Catal. (1996) submitted for publication.

[34] F. Babou, G. Courdurier and J.C. Vedrine, J. Catal. 152 (1995) 341.

[35] M. Bensitel, O. Saur, J.C. Lavalley and G. Mabilon, Mater. Chem. Phys. 17 (1987) 249.

[36] J.C. Lavalley, M. Bensitel, J.P. Gallas, J. Lamotte, G. Busca and V. Lorenzelli, J. Molec. Struct. 175 (1988) 453.

[37] V. Bolis, C. Morterra, M. Volante, L. Orio and B. Fubini, Langmuir 6 (1990) 695.

[38] L.J. Bellamy, The Infrared Spectra of Complex Molecules (Chapman and Hall, New York, 1980).

[39] C.C. Chang, J. Catal. 53 (1978) 374.

[40] M.R. González, J.M. Kobe, K.B. Fogash and J.A. Dumesic, J. Catal. 160 (1996) 290.

[41] M. Bensitel, O. Saur, J.C. Lavalley and B.A. Morrow, Mater. Chem. Phys. 19 (1988) 147.

[42] C. Morterra, V. Bolis, G. Cerrato and G. Magnacca, Surf. Sci. 307–309 (1994) 1206.

[43] R. Langner and G. Zundel, J. Phys. Chem. 99 (1995) 12214.

[44] J.L.G. Fierro, In: ed. J.L.G. Fierro, Spectroscopic Characterization of Heterogeneous Catalysts, Vol. B (Elsevier, Amsterdam, 1990) Ch. 2.

[45] D.F. Shriver, P.W. Atkins and C.H. Langford, Inorganic Chemistry (Freeman, New York, 1990).

[46] A. Corma, Chem. Rev. 95 (1995) 559.

[47] R.A. van Santen and G.J. Kramer, Chem. Rev. 95 (1995) 637.

[48] J.W. Hightower and W.K. Hall, J. Phys. Chem. 72 (1968) 4555.

[49] M.T. Aronson, R.J. Gorte, W.E. Farneth and D. White, J. Am. Chem. Soc. 111 (1989) 840.

[50] C. Pareira, T. Kokotailo, R.J. Gorte and W.E. Farneth, J. Phys. Chem. 94 (1990) 2063.

[51] V.B. Kazansky, W.J. Mortier, B.G. Baekelandt and J.L. Lievens, J. Molec. Catal. 83 (1993) 135.

[52] A. Ghenciu, J.Q. Li and D. Farcasiu, In: 14th North Am. Meet. of the Catal. Soc., Snowbird, Utah, 1995.

[53] V. Bosacek, J. Phys. Chem. 97 (1993) 10732.

[54] V.G. Malkin, V.V. Chesnokov, E.A. Paukshtis and G.M. Zhidomirov, J. Am. Chem. Soc. 112 (1990) 666.

[55] A.G. Stepanov, K.I. Zamaraev and J.M. Thomas, Catal. Lett. 13 (1992) 407.

[56] N.D. Lazo, J.L. White, E.J. Munson, M. Lambregts and J.F. Haw, J. Am. Chem. Soc. 112 (1990) 4050.

[57] G.M. Kramer, G.B. McVicker and J.J. Ziemak, J. Catal. 92 (1985) 355.

[58] H. Pines, The Chemistry of Catalytic Hydrocarbon Conversions (Academic Press, New York, 1981).

[59] K.B. Fogash, R.B. Larson, M.R. Gonzalez, J.M. Kobe, and J.A. Dumesic, J. Catal. (1996) in press.

[60] E.C. Sikabwe, M.A. Coelho, D.E. Resasco and R.L. White, Catal. Lett. 34 (1995) 25.
[61] A. Jatia, C. Chang, J.D. MacLeod, T. Okubo and M.E. Davis, Catal. Lett. 25 (1994) 21.
[62] V. Adeeva, G.D. Lei and W.M.H. Sachtler, Catal. Lett. 33 (1995) 135.
[63] C. Bearez, F. Chevalier and M. Guisnet, React. Kinet. Catal. Lett. 22 (1983) 405.
[64] V. Adeeva, G.D. Lei and W.M.H. Sachtler, Appl. Catal. A 118 (1994) L11.
[65] T.K. Cheung, J.L. d'Itri and B.C. Gates, J. Catal. 151 (1995) 464.
[66] R.A. Asuquo, G. Eder-Mirth and J.A. Lercher, J. Catal. 155 (1995) 376.
[67] A.S. Zarkalis, C.Y. Hsu and B.C. Gates, Catal. Lett. 29 (1994) 235.