Catalysis Letters 32 (1995) 241–251

Characterization and selective poisoning of acid sites on sulfated zirconia

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Received 7 December 1994; accepted 14 March 1995

Microcalorimetric measurements and infrared spectroscopy of ammonia adsorption were used to characterize the acidic properties of sulfated zirconia catalysts. Reaction kinetic measurements for *n*-butane isomerization were conducted over catalysts that were selectively poisoned with controlled amounts of ammonia. Initial heats of ammonia adsorption on the strong acid sites of sulfated zirconia were 150–165 kJ/mol, and these sites contain Brønsted acid and possibly Lewis acid centers. Sulfated zirconia samples that show high activity for the isomerization of *n*-butane possess Brønsted acid sites of intermediate strength, with differential heats of ammonia adsorption between 125 and 140 kJ/mol. The results of selective poisoning of sulfated zirconia with ammonia confirm that Brønsted acid sites of intermediate strength are active for *n*-butane isomerization at 423 K while not discounting a possible role of the stronger acid sites.

Keywords: infrared spectroscopy; microcalorimetric measurements; ammonia adsorption; acidic properties; sulfated zirconia catalysts

1. Introduction

Solid superacid catalysts have been studied for a variety of hydrocarbon conversion reactions, such as isomerization, alkylation, and cracking [1–4]. For example, sulfate-promoted zirconium oxides show activity for the isomerization of *n*-butane at temperatures near 420 K [5–12]. The activity of these sulfated zirconia catalysts depends on the preparation method, activation temperature, and sulfate loading of the catalyst [1–3]. While structures for the acidic surface sites have been postulated [13–17], the strengths of these acid sites have not been thoroughly examined. Therefore, we have employed microcalorimetry in the present study to measure

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the heats of ammonia adsorption on sulfated zirconia catalysts to determine the number and acid strength distribution of the acid sites. This approach has been used effectively in previous studies to probe the acidic properties of various metal oxides and zeolite catalysts [18–25]. Importantly, we have used the results of our microcalorimetric measurements of sulfated zirconia to selectively poison various acid sites for subsequent reaction kinetics studies of *n*-butane isomerization. This experimental approach provides information about possible relationships between acid strength and catalytic properties for these solid superacid catalysts.

2. Experimental

The preparation and catalytic properties of two of the sulfate-promoted zirconia samples examined in this study have been presented elsewhere [7]. Briefly, sulfate-promoted zirconia aerogels were prepared by a one-step sol–gel synthesis followed by supercritical drying with carbon dioxide. These samples were calcined in dry oxygen for 2 h at temperatures of 773 K (CMU1) and 848 K (CMU2). A third catalyst was provided by MEI Corporation in the form of a sulfated $Zr(OH)_4$ precursor. The MEI sample was heated to 848 K in flowing oxygen (100 cm^3/min) over a period of 1.5 h and then maintained at this temperature for 2 h. Table 1 lists some of the properties of these three catalysts. Sulfur loadings were determined by chemical analysis (Galbraith Laboratories).

Microcalorimetric studies of the adsorption of ammonia 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 design and operation of this apparatus have been described elsewhere [26]. The differential enthalpy changes of adsorption, ΔH_{ads}, versus adsorbate coverage were obtained by measuring the heat evolved from sequential doses of the adsorbate gas (2–10 μmol) onto the catalyst until the surface was saturated by adsorbed species. These values of ΔH_{ads} are negative, and it is convenient to define the heat of adsorption as being equal to $-\Delta H_{ads}$. Prior to microcalorimetric measurements, the catalysts were pelletized, evacuated to 10^{-4} Pa at 588 K for 1–2 h, isolated with 30–55 kPa of argon and equilibrated in the heat sink over night. The ammonia subsequently dosed onto the

Table 1
Properties of sulfated zirconia samples

Sample	Surface area (m^2/g)	Calcination temperature (K)	Sulfur (wt%)
CMU1	141	773	2.6
CMU2	110	848	2.2
MEI	98	848	1.8

catalysts was purified before use by successive freeze/pump/thaw cycles and kept under a dry ice/acetone bath during dosing.

Reaction kinetic measurements for *n*-butane isomerization were conducted on the MEI catalyst in a quartz flow-reactor 1.27 cm in diameter. Typically, the reactor was loaded with 0.5 g of catalyst and about 0.25 g of quartz particles to minimize channeling. The catalyst was first dried at 588 K for 1 h in flowing He (65 cm^3/min), and reaction kinetics measurements were commenced by flowing a mixture of ca. 10% *n*-butane (AGA, 99.5% purity, instrument grade) in He (Liquid Carbonic) over the catalyst at 423 K. Both gases were purified by an oxygen absorbent trap (Alltech). Water impurities were removed by molecular sieve traps at 77 K for He and at room temperature for *n*-butane. The reaction products were analyzed using a Hewlett Packard 5890 gas chromatograph, containing a 7.3 m 5% DC-200 Chromosorb P-AW column held at 323 K, and equipped with flame ionization and thermoconductivity detectors. The procedures for the kinetic experiments on the CMU samples have been reported elsewhere [7].

For selective poisoning experiments, a quartz reactor was used that allowed the catalyst to be isolated in dry He and moved from the microcalorimetric apparatus (where specific amounts of ammonia were dosed) to the reaction kinetics system (where *n*-butane conversion was studied). Ammonia was dosed onto the catalyst at room temperature, and the sample was subsequently heated to 573 K for 1 h to allow for ammonia equilibration on the various acid sites of different strength. The catalyst was then cooled to 423 K before starting reaction kinetics studies.

Infrared spectra of adsorbed ammonia were collected at room temperature using a Mattson Galaxy 5020 FTIR spectrometer. The MEI sample was pressed into a self-supporting pellet (18 mg/cm^2) at a pressure of ~ 70 MPa. Samples were loaded into a cell containing CaF_2 windows, followed by heating under vacuum, 10^{-4} Pa, at 588 K for 1 h. Known amounts of ammonia were then dosed into the cell at room temperature, followed by heating at 493 K to allow for ammonia equilibration on the sample. All spectra were collected at a resolution of 8 cm^{-1}.

3. Results and discussion

Fig. 1 shows microcalorimetric results of ammonia adsorption at 423 K on the MEI sample. The differential heat of adsorption decreases with increasing ammonia coverage, indicating a distribution of acid site strengths [22]. The presence of several plateaus of sites of similar acid strength is evident from these data. The MEI catalyst contains approximately 30 μmol/g of strong acid sites, having differential heats of NH_3 adsorption in the range of 150–165 kJ/mol. This catalyst also contains 40 μmol/g of acid sites with intermediate strength, giving differential heats of NH_3 adsorption equal to 125–140 kJ/mol. A further plateau can be distinguished at approximately 120 kJ/mol followed by a gradual decrease in the differential heat to a value of approximately 70 kJ/mol with increasing ammonia coverage.

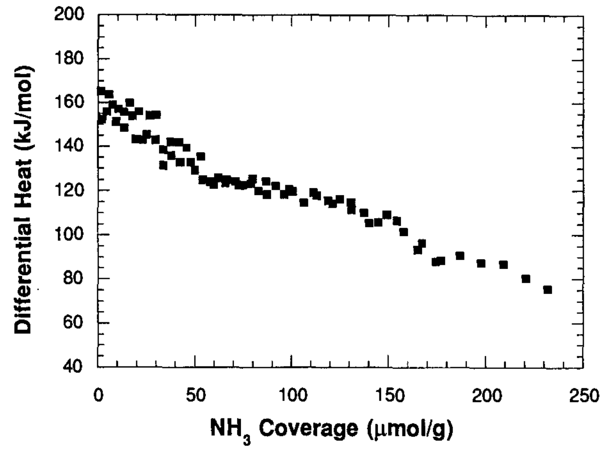

Fig. 1. Differential heat of NH_3 adsorption versus adsorbate coverage (µmol/g) at 423 K for (■) MEI sample.

Jin et al. [17] found that the saturation ammonia coverage was equal to ca. 260 µmol/g on a sulfated zirconia sample prepared using ammonium sulfate, and this value is similar to the total coverage shown in fig. 1 for the MEI sample. In addition, Corma et al. [27,28] detected between 10 and 30 µmol/g of strong acid sites in ammonia TPD studies of sulfated zirconia catalysts (corresponding to desorption at ca. 815 K) and this value is in agreement with the coverage found on the MEI sample for the strong sites with differential heats of ammonia adsorption between 150 and 165 kJ/mol.

Fig. 2 shows the differential heats of NH_3 adsorption versus adsorbate coverage on the CMU samples. Both CMU catalysts show similar numbers of strong acid sites with differential heats of NH_3 adsorption equal to 150–165 kJ/mol. However,

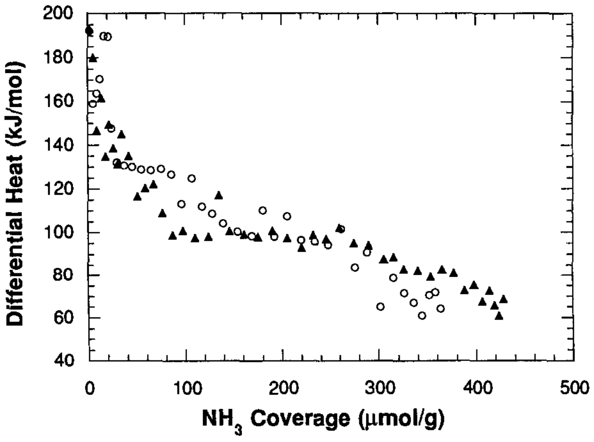

Fig. 2. Differential heat of NH_3 adsorption versus adsorbate coverage (µmol/g) at 423 K for (▲) CMU1 and (○) CMU2.

the CMU2 sample contains a larger number of acid sites with intermediate strength, having differential heats between 125 and 140 kJ/mol. Both CMU samples show similar behavior for values of the differential heat of ammonia adsorption lower than 125 kJ/mol, although the CMU1 catalyst possesses an extended coverage at 100 kJ/mol.

Fig. 3 shows plots of the differential heat of NH_3 adsorption versus adsorbate coverage per surface area (m^2) of catalyst. This figure shows that the CMU2 sample possesses 0.6 μmol/m^2 of sites with heats of adsorption between 125 and 140 kJ/mol, while the CMU1 sample contains fewer than 0.2 μmol/m^2 of these sites. In comparison, the MEI sample contains ca. 0.4 μmol/m^2 of these acid sites with intermediate strength. The MEI catalyst contains approximately 6 μmol/m^2 of acid sites, and the observed coverages and differential heats of ammonia adsorption are comparable to those observed on zirconia [25].

Fig. 4 shows the rate of *n*-butane conversion versus time over the fresh MEI catalyst and over an MEI sample that had been previously dosed with ca. 30 and 70 μmol/g of NH_3. This figure shows the active sites for *n*-butane isomerization on the MEI catalyst are within the 70 μmol/g of strong acid sites. This coverage corresponds to those sites which have differential heats for NH_3 adsorption greater than 125 kJ/mol (fig. 1). Furthermore, since evacuation of the sample does not remove the ammonia adsorbed on the acid sites with differential heats of ammonia adsorption higher than 100 kJ/mol, we can assume that the dosed ammonia remains on the surface of the catalyst during the isomerization reaction.

Histograms of the apparent distribution of acid site strengths are shown in fig. 5 for the three sulfated zirconia catalysts of this study. These histograms over the range of heats from 115 to 150 kJ/mol were obtained from the plots shown in fig. 3. The two materials that show high catalytic activity, CMU2 and MEI, each possess significant numbers of acid sites with intermediate strength. In contrast,

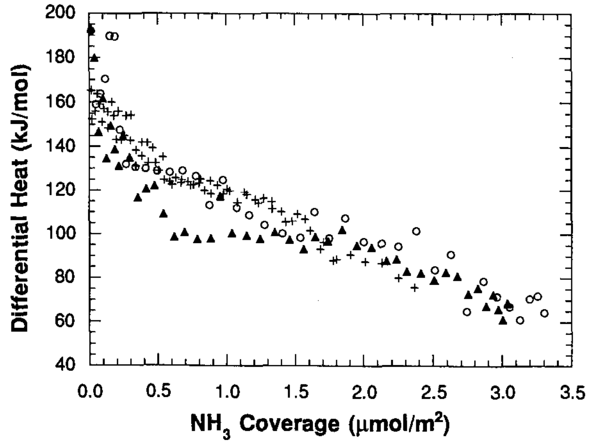

Fig. 3. Differential heat of NH_3 adsorption versus adsorbate coverage (μmol/m^2) at 423 K (▲) CMU1, (○) CMU2, and (+) MEI.

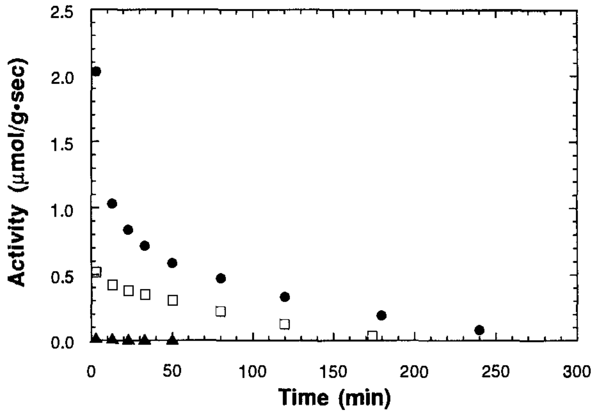

Fig. 4. Rate of *n*-butane isomerization at 423 K versus time for fresh MEI sample (●) and for MEI samples containing 30 μmol/g (□) and 69 μmol/g NH_3 (▲).

the CMU1 sample, which is inactive, does not have an appreciable concentration of acid sites with differential heats between 125 and 140 kJ/mol. While the CMU1 sample contains a large number of acid sites with heats between 115 and 125 kJ/mol, the selective poisoning results in fig. 4 suggest that these weaker acid sites are not active for *n*-butane isomerization at 423 K.

Fig. 6 shows infrared spectra of the MEI sample after exposure to specific amounts of ammonia. Upon admittance of ca. 5 μmol NH_3/g, an increase in absorbance is seen at 1600 cm^{-1} and at 1442 cm^{-1}. The appearance of the former band suggests that some of the ammonia may be coordinatively bound to Lewis acid sites [29–31]. Adsorption of additional amounts of ammonia results in growth of the band at 1442 cm^{-1}, indicating the formation of ammonium ions produced by protonation of NH_3 on Brønsted acid sites [31,32]. Most of the sites on the MEI sample are Brønsted acid centers, as evidenced by the dominance of the band at 1442 cm^{-1} upon saturation of the sample with ammonia. Also seen in the spectrum of the sample saturated with ammonia is an absorbance band at 1684 cm^{-1} due to hydrogen-bonded ammonium ions, the result of weak Brønsted sites on the surface [32,33]. In addition, saturation of the sample with ammonia leads to suppression of a band centered at 3640 cm^{-1}, which is attributed to the OH groups responsible for most of the observed Brønsted acidity [34]. In agreement with other authors [1,2,13,35], the absorbance near 1390 cm^{-1} is suppressed or shifted to lower frequencies upon adsorption of ammonia on the MEI sample. This band is believed to result from the stretching of covalent S=O double bonds on the original sample.

The combination of the microcalorimetric and infrared spectroscopic results for ammonia adsorption on the MEI sample indicates that the strong acid sites with differential heats near 150–165 kJ/mol consist of Brønsted and possibly Lewis acid centers, while sites with differential heats between 125 and 140 kJ/mol are mainly Brønsted acid centers. Thus, the 70 μmol/g of active sites for *n*-butane iso-

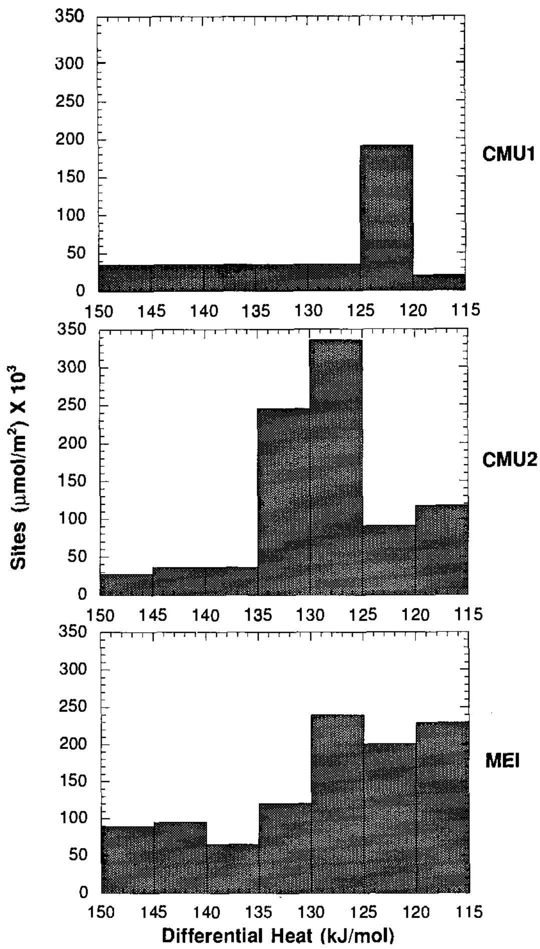

Fig. 5. Histograms of acid strength distributions for sulfated zirconia catalysts determined from plots of differential heats of NH_3 adsorption versus adsorbate coverage.

merization with differential heats of NH_3 adsorption above 125 kJ/mol exhibit Brønsted and possibly Lewis acidity.

Previous authors [1,11,12,36–43] have found that the relative amounts of Lewis and Brønsted sites on sulfated zirconia are dependent on the pretreatment conditions, such as calcination temperature, sulfate loading and drying temperature. For example, Brønsted acid sites seem to be favored for higher sulfate loadings [8,36,44]. Also, for certain sulfate loadings, higher drying temperatures decrease the number of Brønsted acid sites [36,44,45].

Morterra and co-workers [6,9,35,44,46] found mostly Lewis acidity on sulfated zirconia samples, although they allowed for the existence of Brønsted acidity for certain conditions such as higher sulfate loadings [44]. Furthermore, Morterra et al. [9] proposed that the presence of Lewis sites was vital for higher isomerization

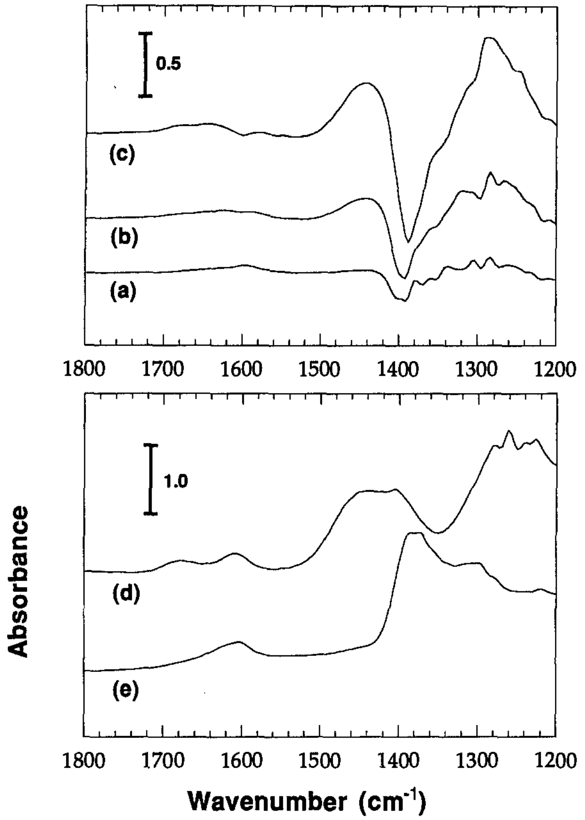

Fig. 6. Infrared spectra of NH_3 adsorbed on MEI at coverages of 4 μmol/g (a), 26 μmol/g (b), and 67 μmol/g (c). Also shown is a spectrum of the sample after exposure to 40 Torr NH_3 and evacuation at room temperature (d). The absorbance of the clean MEI sample (e) has been subtracted from spectra (a–c). Absorbance scales are provided on the figure.

activity, while not excluding the possible contribution from Brønsted acid sites. Specifically, Morterra et al. [47] suggested that Brønsted acid sites remaining following high temperature dehydration may be catalytically active. Yamaguchi et al. [16] found that catalysts evacuated at 773 K displayed only Lewis acid sites, and Jin et al. [17] also stated that some sulfated zirconia samples possess only Lewis acidity.

Lunsford et al. [48] used ^{31}P-NMR spectroscopy to probe the nature of the Lewis and Brønsted acid sites on sulfated zirconia catalysts. These authors found evidence for the existence of both Lewis and Brønsted acidity, and they suggested that Brønsted acid sites were needed for high catalytic activity. Waqif et al. [43] also found Lewis and Brønsted acidity on sulfated zirconia and suggested that the increase in the Brønsted acid sites came at the expense of the Lewis acid sites. Nascimento et al. [8] proposed that Brønsted and Lewis acid sites must both be present on the catalyst surface to generate superacidic properties. Chen et al. [11]

proposed that both strong Lewis and Brønsted acid sites are needed for *n*-butane isomerization. Riemer et al. [12] observed Brønsted acidity on a sulfated zirconia catalyst calcined at 873 K and which was active for isomerization of *n*-butane. In addition, Lewis acid centers were observed for this material using IR spectroscopy of adsorbed carbon monoxide. Arata [1], Sohn and Kim [37], Guo et al. [38], Ebitani et al. [39], Clearfield et al. [40] and Hino and Arata [42] observed both Lewis and Brønsted acid sites on various sulfated zirconia samples. Davis et al. [41] summarized the results of various investigators and concluded that Brønsted acidity likely exists on sulfated zirconia. Thus, our observation of both Lewis and Brønsted acidity on a sulfated zirconia sample that is active for the isomerization of *n*-butane appears to be in agreement with the literature.

Earlier kinetic studies on the CMU catalysts [7] have shown that the CMU2 sample is active for *n*-butane isomerization while the CMU1 sample is inactive. The microcalorimetric results in fig. 2 show that the plots of differential heat versus coverage for the samples are similar for differential heats higher than 140 kJ/mol. The primary difference in the plots of differential heat versus ammonia coverage for these two CMU catalysts is the larger number of acid sites with intermediate strength for CMU2, giving rise to heats between 125 and 140 kJ/mol. Furthermore, the CMU1 catalyst exhibits only Lewis acidity, while CMU2 catalyst exhibits both Lewis and Brønsted acidity [7]. Recalling the similarity in the histograms of the acid site strength distribution between the CMU2 and MEI samples (fig. 5), it appears that acid sites giving rise to differential heats of NH_3 adsorption between 125 and 140 kJ/mol for the CMU2 sample correspond to mainly Brønsted acid centers. The strength of the Brønsted site is important since the Brønsted sites with differential heats below 125 kJ/mol are not active, as shown by the selective poisoning studies. Therefore, it appears that the difference in the activity between the two CMU catalysts is due to the emergence of Brønsted acid sites for the CMU2 sample with differential heats of NH_3 adsorption between 125 and 140 kJ/mol. More generally, these Brønsted acid sites with differential heats of NH_3 adsorption between 125 and 140 kJ/mol are present both in the MEI and CMU2 materials, and both of these samples of sulfated zirconia are active catalysts for the isomerization of *n*-butane at 423 K.

The results of this study provide strong evidence that Brønsted acid sites with differential heats of NH_3 adsorption between 125 and 140 kJ/mol are involved in *n*-butane isomerization over sulfated zirconia catalysts. It is possible, however, that the strong Lewis acid sites present on these catalysts giving differential heats of NH_3 adsorption equal to 150–165 kJ/mol are also involved in the active sites. Specifically, we report elsewhere that small doses of ammonia (ca. 5 μmol/g) on the MEI catalyst decrease by a significant amount the initial activity for *n*-butane isomerization at 423 K [49]. In addition, catalytic activity for *n*-butane isomerization over a sulfated zirconia catalyst is strongly suppressed by the presence of CO in the reactor feed [6], and this molecule adsorbs more strongly on Lewis acid sites compared to Brønsted acid sites. However, as shown by the CMU1 sample, sulfated zirconia containing only Lewis acidity is not active for *n*-butane isomerization. Thus, it is possible that acid catalysts for *n*-butane isomerization may require a combination of strong Lewis acid sites with Brønsted acid sites of intermediate strength.

4. Conclusions

Initial heats of ammonia adsorption on sulfated zirconia catalysts were 150–165 kJ/mol. Sulfated zirconia samples that show high activity for the isomerization of *n*-butane possess acid sites of intermediate strength, with differential heats of ammonia adsorption between 125 and 140 kJ/mol. Infrared spectroscopic studies indicate that the strong acid sites are Brønsted and possibly Lewis acid centers, while the acid sites of intermediate strength are mainly Brønsted acid sites. The results of selective poisoning of the sulfated zirconia with ammonia indicate that Brønsted acid sites of intermediate strength are active for *n*-butane isomerization at 423 K while not discounting a possible role of the stronger acid sites.

Acknowledgement

We wish to acknowledge that this work was supported by the Office of Basic Energy Sciences of the US Department of Energy. In addition, we acknowledge the National Defense Science and Engineering Fellowship Program for providing a fellowship for KF. Also, we wish to acknowledge Robert Larson for assisting in the kinetic studies.

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