DOE/ER/13183--10

Progress Report to the Department of Energy

July 1, 1994 – June 30, 1995

Thermodynamic and Kinetic Aspects of Surface Acidity

(DE-FG02-84ER13183)

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Environmental concerns have created the need for selective catalysts that increase the yield of desirable products (*e.g.*, isobutylene from hydrocarbon cracking units) or reduce the production of polluting byproducts. The development of selective catalysts may be facilitated by understanding the chemical factors controlling the rates of the various catalytic cycles available to the reactants and products. During the past year we have continued our studies of catalytic cracking of isobutane and 2-methyl-hexane over various USY-zeolite catalysts. In particular, we have developed a kinetic model for isobutane cracking over calcined and steamed Y-zeolite catalysts based on carbocation surface chemistry. The model utilized 21 reaction steps, initiation, oligomerization, β-scission, olefin desorption, isomerization, and hydride ion transfer, which adequately described the formation of all major products. We estimated kinetic parameters using transition state theory, the Evans-Polanyi correlation, and gas phase thermodynamic data. To relate gas phase calculations to the catalyst surface, we introduced a parameter ΔH_+, which is the heat of stabilization of a carbenium ion relative to the heat of stabilization of a proton in the zeolite framework. The model provided a good description of the experimental data for calcined and steamed catalysts with physically realistic kinetic parameters. The main difference between the two catalysts

was the higher value of ΔH_+ for the steamed catalyst. This indicates that steaming decreased the Brønsted acid strength of the catalyst.

We subsequently described the activity and selectivity of isobutane cracking on Y zeolite-based catalysts in terms of catalytic cycles composed of initiation, β-scission, oligomerization, olefin desorption, isomerization, and hydride ion transfer reactions involving carbenium ions. Olefin desorption and isomerization reactions are at quasi-equilibrium, with the former reactions determining the surface carbenium ion coverages. Microcalorimetric measurements of ammonia adsorption show that catalyst steaming leads to a decrease in the number and strength of acid sites. Decreasing the strength of Brønsted acid sites results in decreasing surface carbenium ion coverages and the rates of all reactions. The hydride ion transfer reactions are affected most by catalyst steaming, leading to lower paraffin selectivities. Lower temperatures and higher conversions increase carbenium ion coverages and favor hydride ion transfer cycles, leading to higher paraffin selectivities.

We have extended our kinetic model based on carbenium and carbonium ion surface chemistry for isobutane cracking to describe 2-methyl hexane cracking over USY-based catalysts. The overall chemistry of the major catalytic cycles is the same for isobutane and 2-methyl hexane cracking, although additional reaction pathways are available for the larger 2-methyl hexane molecule. Paraffins and olefins with three or more carbon atoms can be produced from 2-methyl hexane by cycles that include both initiation and hydride ion transfer reactions and the paraffin to olefin ratio can not be greater than 1. By allowing us to build catalytic cycles, such models help identify similarities and differences in reactivity patterns for various reactants.

During the past year we have broadened our studies of catalyst acid and basic properties to include alumina-supported metal oxides. These studies have involved the oxides of potassium, magnesium, lanthanum, tin, and europium supported on γ-Al2O3. We used microcalorimetric measurements of ammonia and carbon dioxide adsorption to determine the numbers and strengths of acid and base sites, respectively, at various loadings of these basic oxides on alumina. In addition, we used FTIR spectroscopy to probe the type of acid and base sites by monitoring the states of adsorbed ammonia and carbon dioxide at different adsorbate coverages and loadings of basic oxides on alumina. Furthermore, we developed luminescence techniques to probe the chemical environment of europium cations on oxide surfaces, and we compared the structural and chemical information obtained by this new technique with results from Mössbauer spectroscopy. In short, we have found that the electronegativities of these various basic oxides determine their effectiveness in neutralizing the acid sites on alumina at low loadings and in forming basic sites on alumina at higher loadings.

During the past year we also extended our studies of catalyst acidity funded by the Department of Energy to investigate the acidity of a sulfated zirconia catalyst and its role in the isomerization of normal butane. We have characterized the strength distribution of acid sites present on the surface by measuring the heat of ammonia adsorption versus adsorbate coverage. These measurements allow comparisons to be made with criteria established through past experimentation with zeolites and other acidic solids.

Figure 1 shows representative microcalorimetric results of NH_3 adsorption at 423 K on a sulfated zirconia catalyst (provided by MEI). The acid strength distribution that is evident from these measurements may be an indication that the active sites have several different structures or different configurations on the surface. The catalyst contains approximately 25 μmol/g of strong acid sites, having differential heats of NH_3 adsorption in the range of 140-165 kJ/mol. This catalyst also contains 25 μmol/g of acid sites with intermediate strength, giving differential heats of NH_3 adsorption equal to 125-140 kJ/mol. A further region of acid site strength 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 NH_3 coverage. Figure 2 shows microcalorimetric results of NH_3 adsorption at 473 K on this sulfated zirconia catalyst. From the differences in the heats of NH_3 adsorption between the two temperatures, it is apparent that differentiation between the different acidic sites of the catalyst within the first 100 μmol/g is more pronounced at 423 K. Thus, the adsorption temperature of 423 K represents the best compromise between achieving good equilibration of the gaseous probe molecule with the sulfated zirconia catalyst and yet also achieving more selective adsorption on the stronger acid sites.

Reaction kinetic measurements for *n*-butane isomerization were conducted by flowing a mixture of *ca.* 10% *n*-butane in He over the sulfated zirconia catalyst at 423 K. The reaction products were subsequently analyzed using a gas chromatograph. Figure 3 shows the rate of *n*-butane conversion versus time over the fresh catalyst and over samples selectively poisoned with varying amounts of NH_3. These selective poisoning experiments were guided by our microcalorimetric measurements of the heats of NH_3 adsorption versus adsorbate coverage. Figure 3 shows that the active sites for *n*-butane isomerization are essentially fully poisoned by

70 μmol/g of adsorbed NH_3. This coverage corresponds to those sites having differentials heats of NH_3 adsorption greater than 125 kJ/mol (Fig. 1). The catalyst has high initial activity but rapidly deactivates extensively, showing little activity after 4-5 hours on stream.

Figure 4 presents a semilog plot of catalytic activity versus time. The sulfated zirconia catalyst shows two main regions of deactivation prior to selective poisoning with NH_3. The first region is characterized by rapid initial deactivation, and the second region corresponds to the subsequent slower deactivation period. The initial rapid deactivation period is selectively eliminated by adsorbed NH_3, and this region is no longer evident after poisoning with 30 μmol/g of NH_3. The region of slower deactivation is progressively reduced with additional poisoning by adsorbed NH_3, until essentially all activity for the isomerization of *n*-butane has been eliminated by 69 μmol/g of NH_3.

Figure 5 shows the positions of the poisoning amounts used in the kinetic studies on the microcalorimetric results of NH_3 adsorption at 423 K on sulfated zirconia. The most active acid sites, as deduced from the first region of the catalyst deactivation which is eliminated by poisoning with 30 μmol/g of NH_3, have differential heats of adsorption near 150-165 kJ/mol. The second deactivation region corresponds to those sites with differential heats between 125-140 kJ/mol.

Figure 6 shows the selectivity for isobutane for the fresh catalyst and the catalyst with varying degrees of poisoning. The selectivity remains high during the reaction and decreases only when extensive poisoning by NH_3 has occurred. Selectivities of *ca.* 93% are observed for the fresh catalyst as well as catalysts poisoned with up to 47 μmol/g of NH_3.

The selectivities for isobutane are lower for catalysts poisoned with more than 47 μmol/g of NH_3.

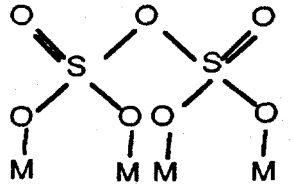
Treatment of the catalyst in flowing O_2 at 588 K recovers less than 40% of the activity of the fresh catalyst, while oxidation at 773 K and subsequent rehydration leads to recovery of 90% of the initial activity. Effects of drying the catalyst at different temperatures prior to reaction kinetics studies were also examined. It was found that drying at 773 K in O_2 or He prior to reaction reduced the catalytic activity by an order of magnitude, compared to the activity observed after drying at 588 K. Also, substitution of H_2 for He as the carrier gas in our kinetics studies reduced the initial activity of the catalyst by approximately 50%, whereas the presence of H_2 increased the long term activity of the catalyst.

Infrared spectroscopy of adsorbed NH_3 was used to provide insight into the nature of the acid sites present on the surface. Figure 7 shows infrared spectra of ammonia adsorbed onto sulfated zirconia dried at 588 K. The adsorption of 5 μmol/g NH_3 results in the appearance of a band at 1600 cm^{-1}, attributed to ammonia coordinatively bound to Lewis acid sites. A band at 1440 cm^{-1} due to ammonium ions associated with Brønsted acid sites also appears. It may be concluded, therefore, that the sites of strongest acid strength (heats near 160 kJ/mol for NH_3) are Lewis acid centers, although the total number of these sites is less than 5 μmol/g. Further adsorption of incremental amounts of ammonia and ultimate exposure to 40 Torr NH_3 (not shown) causes an increase in the intensity of the band assigned to ammonia on Brønsted acid sites. These latter sites are associated with hydroxyl groups on the surface of the metal oxide, as evidenced by a suppression of the 3620-3660 cm^{-1} region concurrent with the appearance of ammonium ions.

Infrared bands in the region of 1370-1410 cm^{-1} are assigned in the literature to the asymmetric stretching of S=O groups on the surface of sulfated zirconia. The electron-withdrawing capacity of these bonds results in electron-deficient zirconium cations which are responsible for the strong acidity of this material. In a sulfated zirconia catalyst containing a distribution of acid strengths, one may expect a band in this region to be the sum of components resulting from various sulfate groups on the catalyst. The interaction of a base probe molecule with a sulfate group on the surface shifts the S=O stretching to a lower frequency.

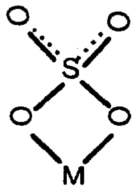
The first 25 μmol/g of ammonia adsorbed on sulfated zirconia causes a growth in a broad band at 1300 cm^{-1} while suppressing a band centered at 1400 cm^{-1}. This band at 1400 cm^{-1} for S=O stretching has been assigned by several researchers to polysulfate complexes, e.g.,

pyrosulfate



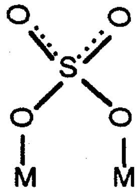
Uptake of an additional 25 μmol/g NH_3 shifts to 1300 cm^{-1} a band at 1380 cm^{-1} resulting from the following bidentate sulfate species:

chelating bidentate
sulfur complexes



or

bridged
bidentates



As mentioned above, reaction kinetics studies suggest that sulfated zirconia dried at 773 K possesses an initial activity for *n*-butane isomerization that is one order of magnitude lower than for a sample dried at 588 K. Infrared spectra of adsorbed ammonia, shown in Figure 8, reveal that the acid sites of a catalyst dried at the higher temperature are primarily Lewis acid centers. Various researchers have shown, through infrared spectroscopy of adsorbed pyridine, that a reversible transformation of Lewis acid sites to Brønsted acid sites occurs upon hydration of the sample.

The differential heats of H_2O and NH_3 adsorption onto a sulfated zirconia sample dried at 588 K are shown in Figure 9. Values for water adsorption are higher than heats for ammonia adsorption; however, the two sets of results exhibit the same trend with increasing adsorbate coverage. The initial heat of water adsorption is approximately 200 kJ/mol, a value that is approximately a factor of two higher than the value expected for water adsorption on a zeolite of comparable acid strength. Such a large release of heat upon hydration indicates a structural rearrangement, most likely the formation of new hydroxyl groups on the surface. It has been suggested in the literature that Lewis acid sites are important for the reaction, and the observation of a small number of very strong Lewis acid sites on the sample dried at 588 K is, therefore, significant.

Finally, we are continuing our studies of Brønsted acid sites using deuterium NMR techniques. We have used various deuterated hydrocarbons to identify experimental conditions under which the Brønsted acid sites can be selectively deuterated, while not reacting with non-acidic O-H groups. These studies are now being extended to sulfated zirconia catalysts.

Future Work

During the next year we will extend our studies of catalytic cycles for hydrocarbon cracking over USY-zeolite catalysts to include hydrocarbon reactions at lower temperatures on sulfated zirconia catalysts. These studies will allow us to begin to build bridges between the catalytic behavior of acidic zeolite catalysts and sulfated zirconia catalysts that may have super-acidic properties.

Our studies will also address the nature of the structural transformations occurring during exposure of sulfated zirconia catalysts to water will be studied through the use of infrared spectroscopy. In addition, reaction kinetics experiments will be conducted to assess the effect of hydration on catalytic activity for *n*-butane isomerization. Using a procedure similar to that employed in the ammonia poisoning experiments, water will be incrementally adsorbed onto a sulfated zirconia catalyst dried at 773 K. The partially rehydrated catalyst will then be examined spectroscopically and any activity enhancements will be detected kinetically.

After we have completed our microcalorimetric, spectroscopic and kinetics studies of our sulfated zirconia catalysts, we will examine different aspects of promoted sulfated zirconia systems. In particular, differential heats of adsorption will be measured for sulfated zirconia catalysts promoted with Pt, Mn, and /or Fe. These studies of promoted sulfated zirconia should help explain differences in the activities observed for these samples. Investigation into the nature of the deactivation phenomena, whether through coking, reduction, or a combination of both, will be performed through coke-burning studies. By burning the coke at different deactivation times, it should be possible to elucidate the method(s) of catalyst deactivation.

Finally, it is important to note that our studies to date strongly suggest that the presence of adsorbed ammonia and water species on the surface of sulfated zirconia have dramatic effects on the catalytic properties for *n*-butane isomerization. Adsorption of water may be used to activate a sample dried at a high temperature, while ammonia adsorption may be employed to selectively poison its acid sites. Key insight can be gained into the nature of the active centers by combining kinetics experiments with microcalorimetric and infrared spectroscopic studies. Our research group is in a unique position in the application of this powerful approach. In this way, the goal of designing acidic catalysts with desired activity, selectivity, and stability may be approached.

Publications during the past year

Methylamine Synthesis over Solid Acid Catalysts: Calorimetric and Infrared Spectroscopic Studies of Adsorbed Species, Journal of Catalysis, 146, 257 (1994), with D.T. Chen, L. Zhang and Chen Yi.

Microcalorimetric Studies of Ammonia Adsorption on γ-Al_2O_3, HNa-Y Zeolite, and H-Mordenite, Catalysis Letters, 23, 207 (1994), with B. E. Spiewak, B. E. Handy, and S. B. Sharma.

Microcalorimetric and Infrared Spectroscopic Studies of γ-Al_2O_3 Modified by Tin Oxides, Catalysis Letters, 26, 247 (1994), with J. Shen, Chen Yi and R.D. Cortright.

Methylamine Synthesis over Solid Acid Catalysts: Reaction Kinetics Measurements, Journal of Molecular Catalysis, 93, 337 (1994), with D.T. Chen, L. Zhang, J.M. Kobe, and Chen Yi.

Microcalorimetric and Infrared Spectroscopic Studies of γ-Al_2O_3 Modified by Basic Metal Oxides, Journal of Physical Chemistry, 98, 8067 (1994), with J. Shen, Chen Yi and R.D. Cortright.

Synthesis and Acid/Base Properties of Magnesium-Aluminum Mixed Oxides Obtained from Hydrotalcites, Langmuir, 10, 3902 (1994), with J. Shen, J. M. Kobe, and Yi Chen.

Catalytic Cycles and Selectivity of Hydrocarbon Cracking on Y-zeolite-based Catalysts, Industrial and Engineering Chemistry Research, 33, 2913 (1994), with G. Yaluris, R.J. Madon and D.F. Rudd,

Characterization with Deuterium NMR of Brønsted Acid Sites and Silanol Species in Zeolites, accepted in Journal of Physical Chemistry, with J.M. Kobe, T.J. Gluszak, and T.W. Root.

Isobutane Cracking over Y-zeolites: Part 1. Development of Kinetic Model, accepted in Journal of Catalysis, with G. Yaluris, J.E. Rekoske, L.M. Aparicio, and R.J. Madon.

Isobutane Cracking over Y-zeolites: Part 2. Catalytic Cycles and Reaction Selectivity, accepted in Journal of Catalysis, with G. Yaluris, J.E. Rekoske, L.M. Aparicio, and R.J. Madon.

Studies of the Surface Structures and Acid/Base Properties of Supported Europium Oxides, accepted in Journal of Physical Chemistry, with Jianyi Shen, M. J. Lochhead, K. L. Bray, and Yi Chen.

Characterization and Selective Poisoning of Acid Sites on Sulfated Zirconia, submitted to Catalysis Letters, with K.B. Fogash, G. Yaluris, M.R. Gonzalez, P. Ouraipryvan, D.A. Ward, E.I. Ko, and J.A. Dumesic.

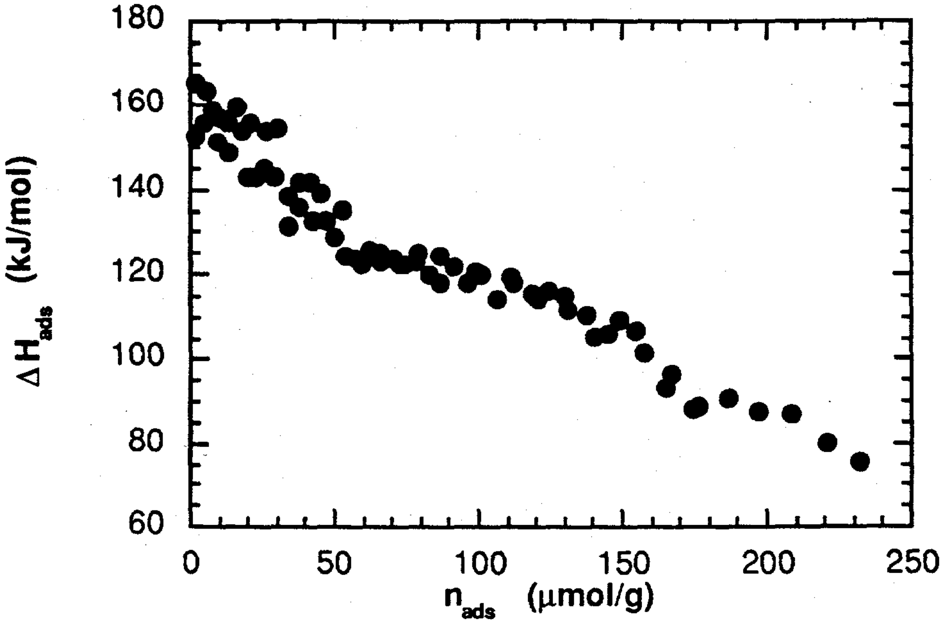


Figure 1. Differential heat of NH_3 adsorption versus adsorbate coverage (µmol/g) at 423 K. The sample was dried under vacuum at 588 K.

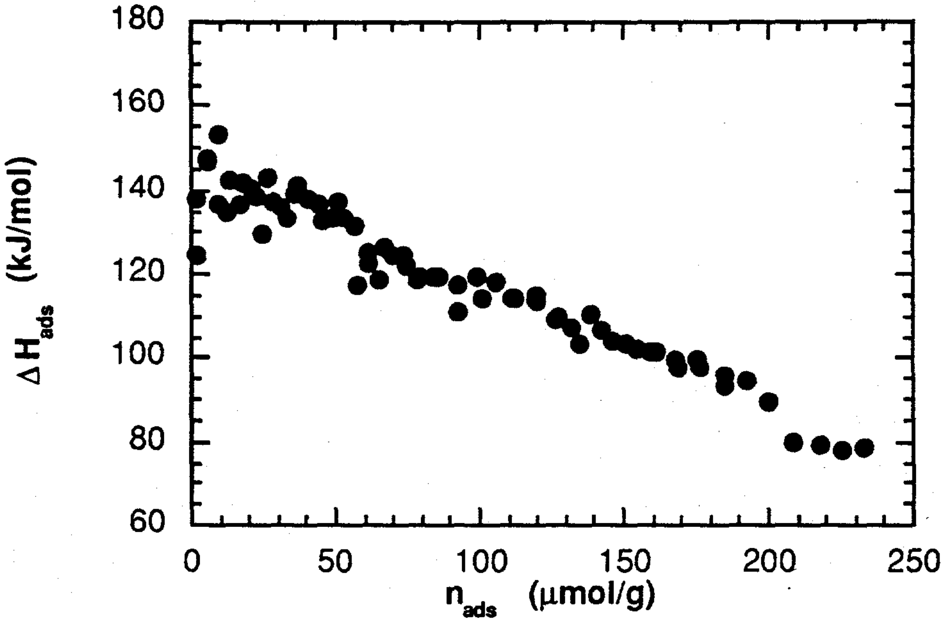


Figure 2. Differential heat of NH_3 adsorption versus adsorbate coverage (µmol/g) at 473 K. The sample was dried under vacuum at 588 K.

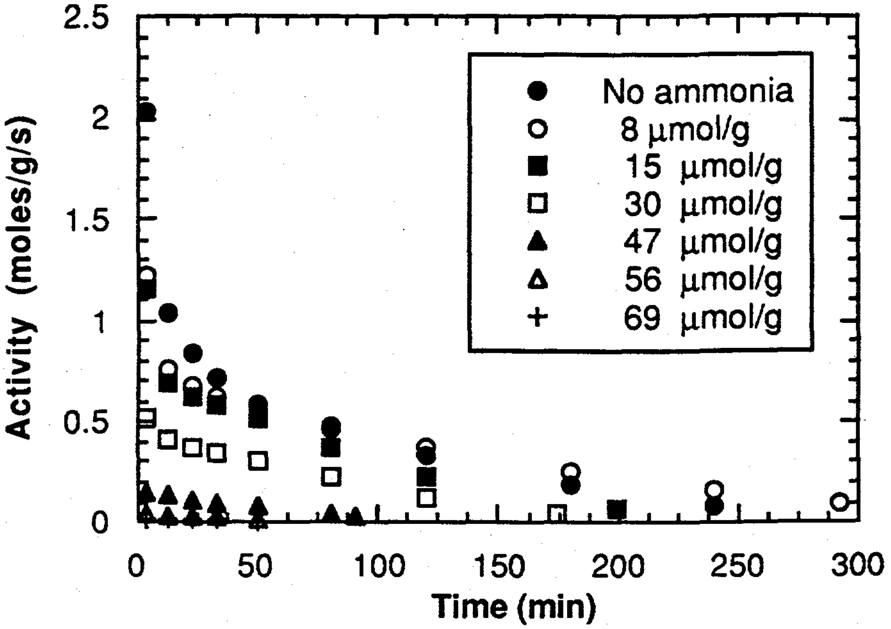


Figure 3. Rate of *n*-butane reaction at 423 K over sulfated zirconia poisoned to various degrees. Before reaction, the sample was dried at 588 K under flowing helium.

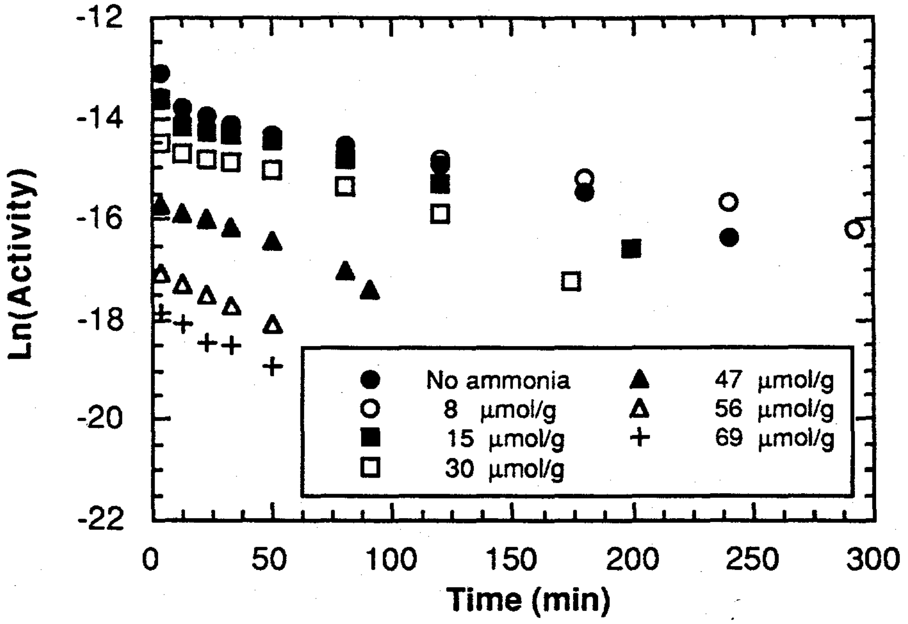


Figure 4. Logarithmic Rate of *n*-butane isomerization at 423 K versus time for fresh and poisoned sulfated zirconia catalyst. Before reaction, the sample was dried at 588 K under flowing helium.

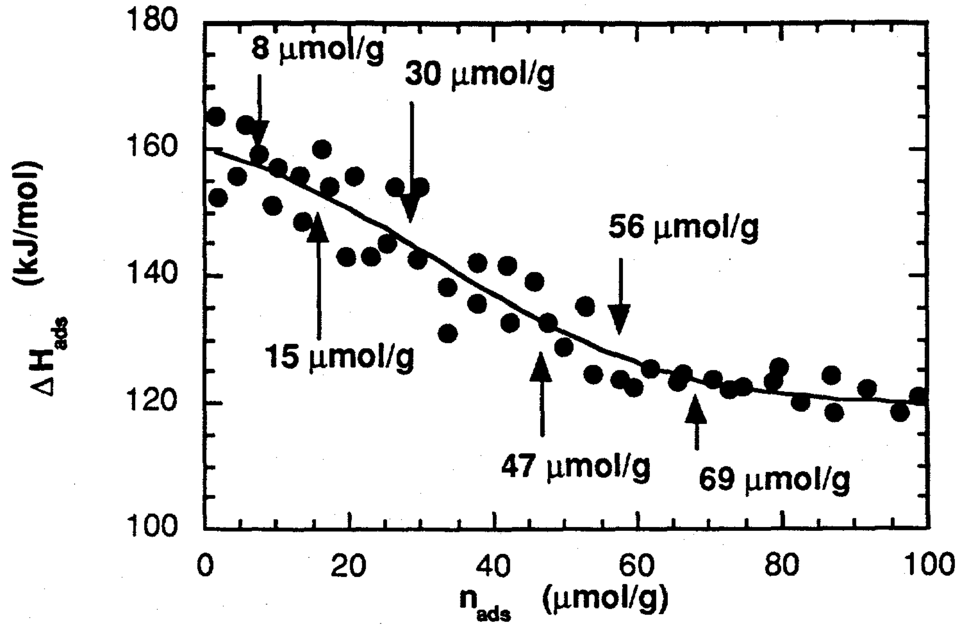


Figure 5. Differential heat of NH_3 adsorption versus adsorbate coverage (μmol/g) at 423 K showing poisoning divisions for a sample dried at 588 K.

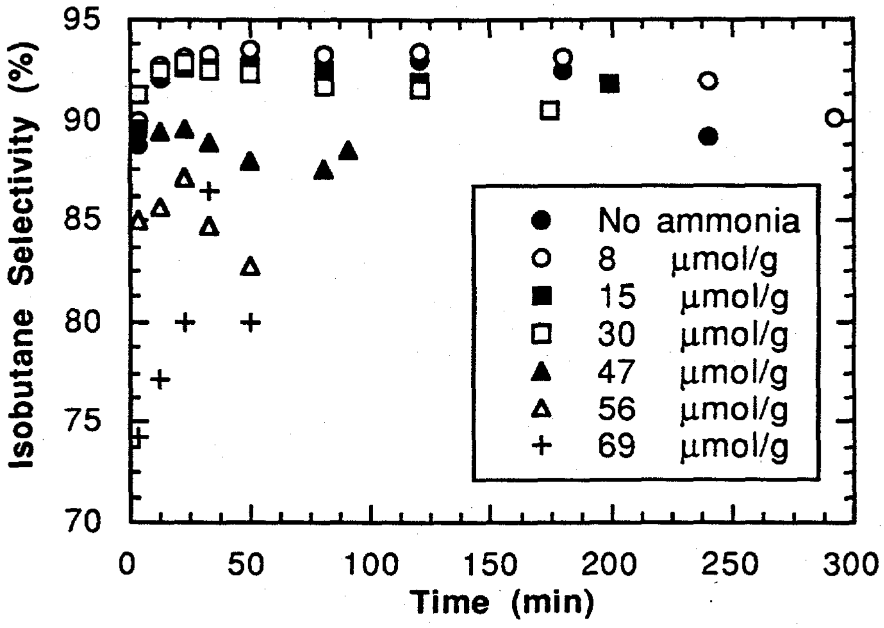


Figure 6. Selectivity for isobutane over time for a sulfated zirconia catalyst poisoned with ammonia to various degrees. Each sample was dried under flowing helium at 588 K before experimentation.

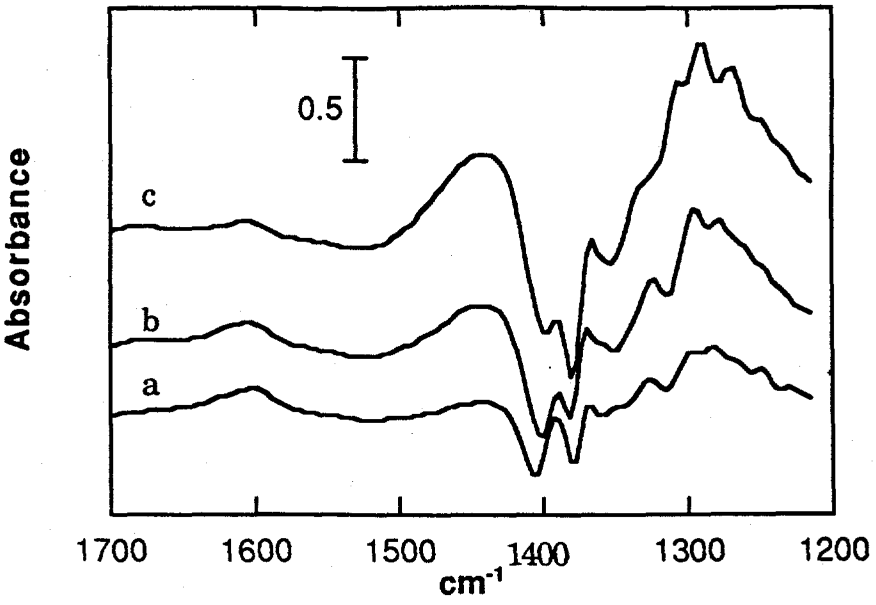


Figure 7. Infrared spectra of NH_3 adsorbed on sulfated zirconia dried at 588 K. Coverages of 5μmol/g (a), 25 μmol/g (b), and 50 μmol/g are shown. Absorbance scales are provided on the figure. The absorbance of the clean sample has been subtracted from all spectra.

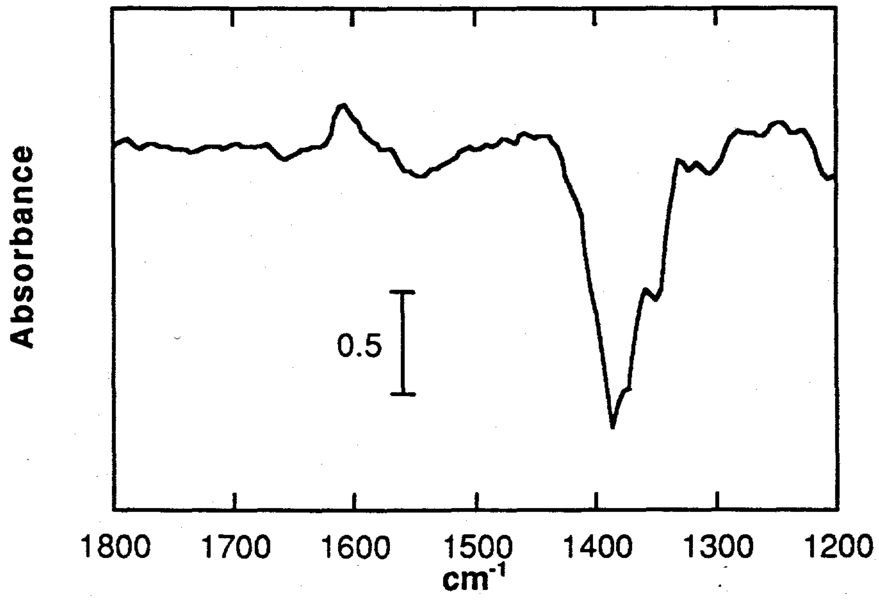


Figure 8. Infrared spectrum of sulfated zirconia dried at 773 K, after exposure to 40 Torr NH_3. Absorbance scales are provided on the figure. The absorbance of the clean sample has been subtracted.

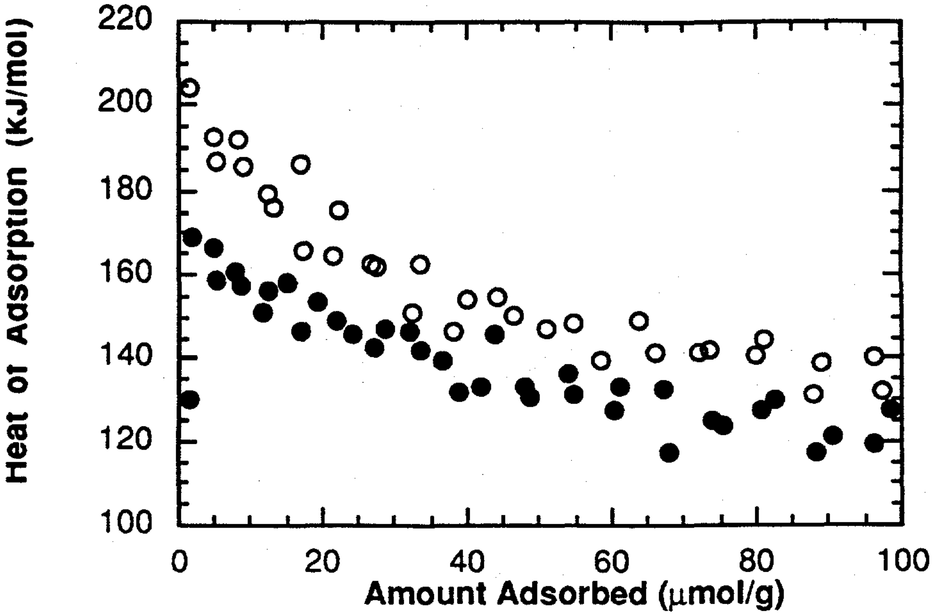


Figure 9. Differential heats of NH_3 (•) and H_2O (o) adsorbed on sulfated zirconia at 423 K. The sample was dried under vacuum at 773 K.