Acidity and Reactivity of Sulfated Zirconia and Metal-Doped Sulfated Zirconia

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Since its discovery, sulfated zirconia and metal-doped sulfated zirconia have been the subject of numerous reports on their catalytic activity. Their ability to perform low-temperature hydrocarbon isomerizations has led to claims that sulfated zirconia and metal-doped sulfated zirconia are superacids or at least very strong acids. This has led to many investigations on the acid strength of sulfated zirconia and metal-doped sulfated zirconia producing varying results. We report the use of cal-ad (which uses combined information from calorimetry and adsorption of pyridine onto the solid acid) to determine the acidity of sulfated zirconia and metal-doped sulfated zirconia. We find that sulfated zirconia has two types of acid sites: 24 μmol of a strong site, which has a strength of 31.2 kcal/mol, and 52 μmol of a weaker site of 25.8 kcal/mol, which places the acidity of sulfated zirconia lower than that of HZSM-5 (41 kcal/mol) and about the same as that of HY (34 kcal/mol). Doping sulfated zirconia with 0.2 wt % Pt does not change the acidity, but doping with iron and manganese (which increases the catalytic activity) results in a lower measured acidity, indicating that iron and manganese have occupied the strongest acid sites.

Introduction

Hino was the first to report that zirconium oxide modified with sulfate on the surface develops strong acidic properties and unique acid catalytic activity.[1] Since the original report, numerous studies using sulfated zirconia (SZ) as an acid catalyst have appeared. Its low-temperature activity for isomerization of hydrocarbons is well-documented and has led to reports claiming that SZ is a solid superacid[2] or at least a very strong solid acid. The early assessment of acidity is in part based on the product distribution of paraffin isomerization with SZ catalysis giving products typical of that from catalysis by sulfuric acid and a mechanism that involves the formation of carbenium or carbonium ions.

The direct measurement of the strength of a solid acid is much more elusive than measuring the strength of a liquid acid. Issues such as accessibility of sites and heterogeneity of the surface cause discrepancies in the different methods used to measure the acidity of solid acids.[3,4] Not surprisingly, the measurement of the acid strength of sulfated zirconia is the subject of many investigations producing varying results. Hammett indicators suggest a value of −14.5 to −16 on the Ho scale, making SZ more acidic than 100% sulfuric acid.[3] The use of Hammett indicators is considered unreliable by most investigators for the accurate measurement of solid acidity.[5] ^{1}H NMR and Raman spectroscopic studies led to the conclusion that SZ has superacidic protons,[6] and EPR studies[7] involving charge transfer complex formation using benzene as a probe have been interpreted to show that the acidity of SZ was greater than that of zeolite HY. Results from temperature-programmed desorption of NH₃[8] and other bases were attributed to superacidic acid sites.[9] Recently, microcalorimetric adsorption of gaseous NH₃ by solid SZ at 423 K was interpreted to involve very strong acid sites[10] that catalyze the isomerization of butane.

In contrast to the above conclusions, numerous investigators have claimed that SZ is not superacidic. Temperature-programmed desorption or methods based on desorption of weakly or strongly basic probes are reported to provide unreliable measures of acidity[11] because desorption channels for different probe molecules on SZ are very different. It is claimed[12] that none of the probes selectively probe only the acid site in desorption measurements. These observations were interpreted to indicate[11,12] that SZ and transition-metal-doped SZ's are not superacids. Infrared sifts of hydroxyl groups after benzene adsorption suggested that SZ acid sites are weaker than those found on HZSM-5.[13] Another study reported that SZ is not really superacidic[14] based on its high-temperature cracking activity. Changes in the NMR and FTIR upon adsorption of acetonitrile suggest that the acidity of SZ is similar to that of HY but less than that of HZSM-5 and is clearly not super-acidic.[15] A recent report indicates that the activity of SZ for alkane reactions is not related to acidity but is initiated by a one-electron oxidation of the hydrocarbon by sulfate to form a carbocation.[6,16] Surface binding is proposed to lead to a dramatic increase in the oxidizing ability of sulfate. The organic radical cation loses a proton and combines with the reduced sulfate radical to form a surface organic sulfate or alcohol. Transfer of a hydrogen atom from the organic radical cation leads to sulfite and the carbocation. Dehydrogenation of that alcohol can also generate alkenes which can be protonated to give a carbocation isomerization distribution in the products.

Doping of SZ with iron and manganese is reported to increase the activity of SZ for hydrocarbon cracking by increasing the solid's acidity.[20] On the other hand, it has been claimed that the activity of SZ doped with Fe and Mn is due to redox-active metal sites.[5,14]

Since the discovery of SZ, it has been reported that the acidic and catalytic properties depend on a number of preparative procedures including sulfation and the activation temperature. The proponents of superacidity often attributed results indicating SZ is not a superacid to differences in preparation. A detailed study of the preparation of SZ concluded that the sulfation procedure has no effect on the final SZ product.[17] It was further shown that the activation temperature effects the catalytic activity, but its effect on the acidity of SZ is not clear. Calcination of zirconia at 650 °C produces a metastable tetragonal phase and a stable monoclinic phase. Sulfation is reported to crystallize ZrO₂ at 550 °C and stabilize the tetragonal phase.

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It is generally accepted that SZ contains only a small number of the most acidic sites (which many claim to be superacidic), and this complicates the assessment of the acidity of these sites. The low site concentration in addition to perceived differences in preparative procedures has been used to rationalize differences in catalytic activity and measures of the acidity of SZ.

We report the use of results from a cal-ad titration of sulfated zirconia with pyridine to address this problem. Cal-ad differs from other solid acid characterization methods because it determines the number (n_i), equilibrium constants (K_i), and strengths (ΔH_i, enthalpy) of different acid sites on solids.[18,19] The subscripts i refer to the above quantities, where $i = 1$ would be the first site describing the strongest sites, $i = 2$ the next site, and so on. In the general area of donor−acceptor bonding, it has long been accepted that the appropriate measure of the strength of binding is the enthalpy of adduct formation. However, in any calorimetric or equilibrium measure that involves gas−solid equilibria, the enthalpies contain contributions from a donor−acceptor interaction as well as a dispersion component. The cal-ad measurements are carried out in a hydrocarbon solvent whose molecules are close in molecular mass to those of the donor[18,19] to cancel out the dispersion component. Thus, the cal-ad analysis provides a complete characterization of the acid strength for different sites and determines the number of acid sites of each strength, providing the most complete characterization of the acidity of SZ reported to date. The results from this measure of the acidity of SZ is used to compare it to other solid acids and to investigate the effects of preparative procedures and metal doping on the acidity.

Experimental Section

Catalyst Preparation. Zirconium sulfate was supplied by MEI in the form of sulfated $Zr(OH)_4$ precursor. This precursor was heated at different activation temperatures (600 and 300 °C) under dry air for 3 h. The catalysts have a sulfur loading of 1.6 wt %, which corresponds to 0.5 mmol of sulfur per gram of solid. Sulfated zirconia was doped with Pt by adding an aqueous solution of H_2PtCl_6 to the solid and evaporating to dryness. The loading of Pt after evaporation was 0.2 wt %. The Pt sulfated zirconia was activated at 600 °C in dry air for 3 h. A SZ sample doped with iron and manganese was prepared according to a reported procedure.[20]

Cal-ad Analysis. The calorimetric titration was carried out as described previously.[18] One gram of sulfated zirconia slurried in cyclohexane solution is reacted with pyridine while stirring. The cyclohexane and pyridine reagents used were distilled over P_2O_5 prior to use. After each injection of pyridine solution, the heat evolved is measured. This heat is then used to determine the enthalpy. In the cal-ad analysis an adsorption isotherm is measured over the range of base additions used in the calorimetric titration. The combined calorimetric and adsorption data are analyzed to produce K's (equilibrium constants), n's (moles of site), and ΔH's (enthalpies). Parameters from the fitting procedure were found by nonlinear regression analysis using a nonlinear least-squares simplex algorithm. The standard deviation is a maximum likelihood estimate and an unbiased minimum variance.[21] Errors in the experimental data were assigned by performing several calorimetry and adsorption experiments to determine the average deviation.

UV−vis Spectroscopy. Measurement of the free pyridine in solution in equilibrium with the sulfated zirconia in the calorimetric experiment was determined by UV−vis as described previously[18] using a Perkin-Elmer Lambda 6 UV/vis
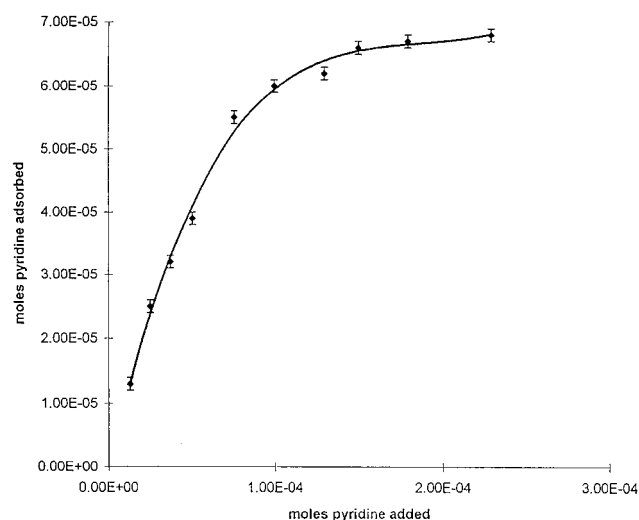

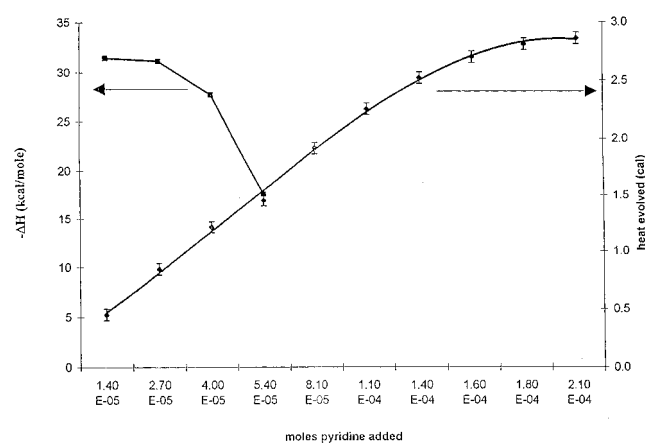**Figure 1.** Pyridine adsorption on sulfated zirconia.

Figure 2. Heat evolved and $-\Delta H_{ave}$ as pyridine is added to sulfated zirconia.

spectrophotometer. Suprasil quartz cells of were employed in the adsorption studies.

Alkylation of Isobutane with Butene. Alkylation of isobutane with 2-butene was performed in a batch reactor. The batch reactor was filled to a total volume of 12 mL with a 50:1 volume ratio of liquid isobutane to liquid 2-butene. One gram of sulfated zirconia or 1 mL of concentrated sulfuric acid was placed into the batch reactor with a stir bar prior to filling with reactants. The reaction was carried out a 0 °C with stirring for 30 min. Upon completion of the reaction the liquid product was filtered, and the products were analyzed using gas chromatography. Pentane is added to the reaction products as an internal standard for gas chromatographic analysis.

Isomerization of Pentane. The isomerization of pentane was performed in a batch reactor using 1 g of SZ and 3 mL of a 25% pentane solution in carbon tetrachloride. The reaction was stirred at 50 °C for the allotted time period, and products were analyzed by gas chromatography.

Results and Discussion

Cal-ad and Determination of Acidity. Figure 1 shows the results from adsorption measurements plotted as the moles adsorbed by the solid vs moles of pyridine added. Figure 2 shows the results from the calorimetric titration of SZ with pyridine, plotted as calories evolved, h', vs moles of pyridine added. For the first few injections of pyridine corresponding to less than 50 μmol, there is no free pyridine present in solution. The acid sites of the solid have totally complexed the pyridine.

Dividing h' for these additions by the moles of pyridine added produces molarity weighted averages of the enthalpies of binding to the sites to which the pyridine coordinates. The fraction of sites involved in binding changes for each addition as the strongest sites become saturated. The left axis of Figure 2 gives the average enthalpies for those additions in which 90% of the added pyridine is bound to the solid. The quantity of interest is the enthalpy of binding to the strongest site, not some average that is dependent on the magnitude of the equilibrium constants. This information can be provided by the full cal-ad analysis.

A dilute solution of pyridine was used in the calorimetric titration of SZ in order to avoid titration of all the strongest and some of the weaker acid sites with the first injection. A report has indicated that a very small concentration (<70 μmol/g) of sites exist on SZ which are active catalytically but which deactivate very quickly.[10] In our calorimetric titration the first injection of pyridine delivers 13 μmol of pyridine which is completely bound to the solid. With complete complexation of the first two additions of pyridine, we can divide h' by the moles added to get an average enthalpy of the sites titrated. The corresponding enthalpy for these 25 μmol of acid sites/g of SZ is only -31 kcal/mol, which is not superacidic. The $-\Delta H_1$ value of sulfated zirconia is less than that of HZSM-5 and about the same as that of zeolite HY as shown in Table 2. Since the average enthalpy of reaction for the first 13 μmol of pyridine added is the same as that for the addition of the second injection of 12 more μmol, we can place an upper limit on the small amount of a very strong site that could be present. Furthermore, since the h' value for the first injection is 0.463 $\pm$ 0.029, we can state that if superacidic sites are present (e.g., some with enthalpies above 50 kcal mol^{-1}), they would have to be present at concentrations of 2.5 μmol or less in order not to influence the average enthalpy of the first injection as compared to that of the second. An excess of 50 kcal/mol is a value we have chosen based on SGOAlCl$_2$, which is the strongest solid acid ($-\Delta H = 50$ kcal mol^{-1}) studied by cal-ad to date.[22] This solid acid catalyzes low-temperature cracking as well as the alkylation of isobutane and butene.

The above discussion indicated that average enthalpies result when h' is divided by the moles of base added and is typical of the literature procedures used to analyze gas–solid enthalpies and solution calorimetric data. Dividing h' by moles of base even at low base concentrations produces the enthalpy for the strongest site only if $K_1 \gg K_2$. Since n_2 is usually much larger than n_1, the differences in K's must be substantial to obtain an average enthalpy that is within 10% of that for site 1 by this approach. The average enthalpy problem is particularly critical in studies of gas–solid equilibria at elevated temperatures. If the two K's approach each other at elevated temperatures, average enthalpies will result. Unfortunately, there is no way to determine the extent of the averaging from enthalpy data alone. For example, the first two base additions in Figure 2 could be an average of 65–70% of -40 kcal mol^{-1} site and 30–35% of a -13 kcal mol^{-1} site. The average $-\Delta H$ would be 31 kcal/mol, and a large error results by assuming the average is the strong site. As site 1 is saturated, the average $-\Delta H$ decreases to that of site 2, and this would give rise to a curve like that shown in Figure 2.

The full cal-ad analysis produces meaningful equilibrium constants, enthalpies, and number of sites by simultaneously analyzing the data in Figures 1 and 2. Table 1 shows the ΔH, K, and n values determined from the cal-ad analysis of SZ. The $-\Delta H_{\text{AVG}}$ calculated from the first two injections of pyridine agrees with that of $-\Delta H_1$ from cal-ad, enabling us to conclude that $K_1 \gg K_2$, and $-\Delta H_{\text{ave}}$ for the first few injections is $-\Delta H_1$.

TABLE 1: Cal-ad Analysis of Sulfated Zirconia

$K_1 = 6.6 \times 10^9 \pm$	$K_2 = 3.0 \times 10^4 \pm$
7.9×10^8 L/mol	1.4×10^4 L/mol
$n_1 = 2.73 \times 10^{-5} \pm$	$n_2 = 5.52 \times 10^{-5} \pm$
2.6×10^{-6} mol/g	1.3×10^{-6} mol/g
$\Delta H_1 = -31.2 \pm 2.2$ kcal/mol	$\Delta H_2 = -25.8 \pm 2.4$ kcal/mol
$\Delta S_1 = -59.5$ cal/deg	$\Delta S_2 = -66.1$ cal/deg
$\Delta G_1 = -13.46$ kcal/mol	$\Delta G_2 = -6.1$ kcal/mol

TABLE 2: ΔH_1 Values for Other Solid Acids (Errors ± 1 kcal/mol)

solid acids	$-\Delta H_1$ (kcal/mol)	solid acids	$-\Delta H_1$ (kcal/mol)
SiO$_2$	12	SZ–Pt	30
HZSM-5[22]	41	SZ-300 °C	15
HY	34	SZ–Fe–Mn	26
SG–AlCl$_2$[21]	51		

The reported data for the $-\Delta H$ from the solid analysis of the calorimetric titration of pyridine with silica[18] and HZSM-5[21d] are summarized in Table 2. From these results one can place the acidity of the strongest sites of SZ as greater than silica gel but less than those of HZSM-5. These results are consistent with those obtained by NMR and FTIR adsorption of acetonitrile[15] and infrared adsorption of benzene.[13] Table 2 provides a scale of acidities of those solid acids which have been studied using the cal-ad technique. The cal-ad procedure allows the determination of not only the relative strength but also the number of sites and their equilibrium constants for adsorption of a probe molecule which is information that is not obtained by using other common techniques of acidity characterization. The cal-ad determination of the enthalpy of the donor–acceptor interaction of the solid acid with the basic probe pyridine supports the position that SZ is not a superacid and reinforces the suggested problems with other measurements suggesting superacidity.

A study involving selective poisoning of the acid sites on SZ by NH$_3$ concluded that there are 70 μmol/g of active acid sites[10] in the solid. Our cal-ad analysis n_1 sites plus n_2 sites gives us a total of 79 μmol/g of acid sites. This is in excellent agreement considering different samples were measured in different laboratories using different techniques. This provides a confirmation of the cal-ad method.

Calorimetry using a gaseous probe molecule such as NH$_3$ is a common method used to analyze solid acid acidity.[10,23] A recent report on the use of gaseous NH$_3$ calorimetry at 150 °C showed that two or three types of sites were present on SZ. The strongest sites had a strength of 34–39 kcal/mol, which is 3–9 kcal/mol higher than our reported value. Measurements on silica[24] and carbonaceous solids[25] show that there is a contribution (about 10 kcal/mol) from nonspecific dispersion force interactions when a gaseous probe is adsorbed on a solid. If one takes into account the 10 kcal/mol dispersion interactions in the gaseous NH$_3$ adsorption, then the results from cal-ad analysis agree quite well with the upper limit of strong acid sites found. The fact that the values are close at the lower limit is attributed to the effect of the high investigation temperature on the K's. At the higher temperature the K's approach one another, and therefore, site 1 is not being exclusively probed. The contribution from site 2 causes the measured enthalpy to be an average of site 1 and 2 and thus lower values are obtained.

The effect of activation temperature on the catalytic performance of SZ is widely documented.[26] In order to investigate the influence of the calcination temperatures on the acidity of SZ, a calorimetric titration of a sample calcined at 300 °C was carried out. Up to 13 μmol, UV spectroscopy of the solution shows that all of the pyridine added is coordinated to the solid. Up to 90% is absorbed for additions in the range 13–25 μmol

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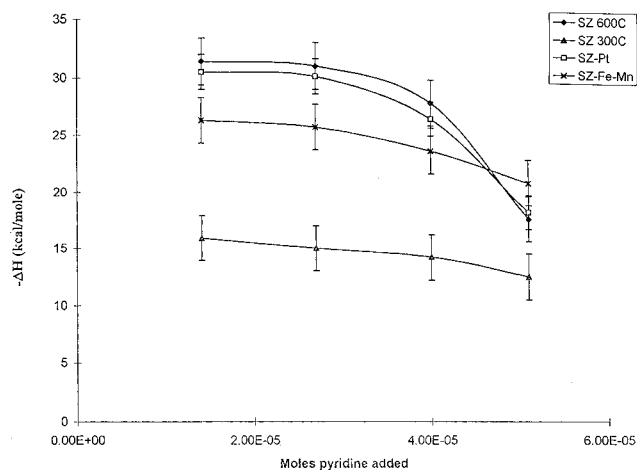*J. Phys. Chem. B, Vol. 101, No. 17, 1997* **3363**

Figure 3. Calorimetric titration of sulfated zirconia and metal-doped sulfated zirconia with pyridine.

of pyridine. Since our main interest in these materials is the strength of the strongest acid sites and since $-\Delta H_{AVG}$ is very low, a full cat-ad analysis was not carried out. Instead, the calorimetric data are used to calculate the average enthalpy h' divided by the moles of pyridine added, and the results are shown in Figure 3. Values of 15 kcal mol^{-1} are obtained for the first two pyridine additions corresponding to 25 μmol of pyridine added. Though this analysis does not give an accurate value for the strongest site, it does show that $-\Delta H_1$ considerably less than 32 kcal/mol, and it is clear from this result that the calcination procedure greatly influences the acidity of SZ. At calcination temperatures below 400 °C the SZ sample is amorphous. When the sample is activated at 500 °C, the SZ forms a tetragonal phase, and the catalytic properties are greatly enhanced. SZ in the amorphous phase may contain adsorbed water coordinated to the acid sites, and this causes the acidity of the sites to decrease.

The influence of 0.2 wt % Pt on the acidity of SZ, activated at 600 °C, was studied next. The calorimetric titration is shown in Figure 3. Again, all of the added pyridine is adsorbed up to 25 μmol of added pyridine and produces a $-\Delta H_{AVG}$ of 30.5 kcal mol^{-1}. Doping with platinum has had little effect on the acidity of the strongest sites of sulfated zirconia. The calorimetric titration curve for both sites is almost identical to SZ, suggesting platinum doping does not modify the acidity of SZ. The effect of Pt addition to SZ is known to enhance the activity of the catalyst for hydrocarbon isomerization reactions.[28,29] This could be due to the spillover effect of Pt when H_2 is used in the reactant feed. A similar increase in hydrocarbon isomerization activity is seen for Pt-doped HZSM-5.[30]

Relationships of Catalytic Activity and Acidity. We performed reactions with our sample of SZ which was activated at 600 °C to test the activity of the catalyst. As expected, the catalyst isomerized pentane at 50 °C, reaching 33% conversion of pentane after 30 h. This result is consistent with other literature reports on the activity of sulfated zirconia on light paraffin isomerization activity. The ability of sulfated zirconia to perform reactions yielding products expected from superacidic carbocation mechanisms has led to the labeling of SZ as a superacid. This result is in contrast to the acidity determined by cal-ad and will be addressed in further detail. The catalyst activated at 300 °C had no activity for pentane isomerization, which is consistent with its cal-ad analysis that places its acidity only slightly higher than that of silica gel. The decrease in the catalytic activity of samples calcined at 300 °C at the lower activation temperature may be due to the inability of the solid

to stabilize the one-electron transfer unless the tetragonal phase is present.

The description of SZ as having a small concentration of superacidic sites has often been invoked to explain the rapid deactivation of this catalyst. This explanation does not explain the catalytic reactivity of SZ in the isomerization of butane and pentane in recirculating reactors where the percent conversion is reported to increase at high temperatures with time on stream. Clearly, this is inconsistent with a superacid mechanism in which coking deactivates the strongest acid sites and should result in decreased activity if the number of sites is small. Perhaps more disturbing is the fact that additions of Fe and Mn have been reported to enhance the activity of SZ 3 times.[20,27] The addition of Pt to sulfated zirconia also increases its activity for hydrocarbon conversion reactions.[28,29] As shown in Figure 3, these additions are not enhancing the acidity of the SZ. It has been reported that SZ undergoes a one-electron-transfer mechanism rather than a traditional superacidic mechanism.[6] This would account for the catalytic properties and the moderate acidity. Farcasiu and Davis[14] report that the additions of Fe and Mn as well as Pt are aiding the reactions by modifying the one-electron acceptor ability of the sulfated zirconia catalyst.

The average enthalpy for the first two base additions of pyridine to Fe Mn SZ gives an average enthalpy of 26 kcal mol^{-1}. Clearly, the acidity is not increased, and no new strong acid sites are evident. To the contrary, doping leads to a decrease in the average enthalpy of the strongest sites. If doping does not influence the equilibrium constants and the enthalpy for site 2, the ΔH_{ave} suggests that practically none of the strong acid sites for SZ remain in the iron−manganese-doped sample. This indicates that the Fe and Mn may be deposited onto the strongest acid sites on SZ.

When SZ activated at 600 °C was tested for the alkylation of isobutane with 2-butene, no activity was found. This is significant since H_2SO_4, which is the benchmark for superacidity, catalyzes this reaction at the conditions used. One milliliter of concentrated sulfuric acid at these conditions produces large amounts of isooctane products. Alkylation of isobutane with butane is reported with SZ but in a flow reactor system at high temperatures and may involve a different mechanism for the reaction. Commercially, alkylation of isobutane is carried out at low temperatures using 100% sulfuric acid. The inability of SZ to perform this reaction at 0 °C is further evidence that the acid sites are not superacidic. This is consistent with our cal-ad results.

The results of these catalytic studies with cal-ad analyzed catalysts emphasize an important point. If superacidity or strong acidity is to be inferred from catalytic activity, it is essential to demonstrate that the reaction mechanism is indeed an acid-catalyzed mechanism. Otherwise, correlations of reactivity with acidity will fail.

Conclusion

Our findings show that a significant amount of superacid sites does not exist on SZ or metal-doped SZ. The calorimetric analysis indicates that the strongest acid sites on SZ are stronger than silica gel but weaker than HZSM-5. Furthermore, our results show that doping with platinum or iron and manganese does not increase the acidity of these materials.

The temperature of activation of SZ plays a role in determining both the acidity and the catalytic activity. The catalytic activity for hydrocarbon isomerization is well-documented, but the mechanism by which the transformation occurs is still in question. More research is necessary in this area to establish how SZ accomplishes the transformations. It is the conclusion

of this study that the mechanism is not based on the traditional carbenium ion mechanism because SZ is not a superacid. This example emphasizes the point that for correlations of the acid strength of catalysts with reactivity it is critical to be sure that the catalytic reactions proceed through a similar acid-catalyzed mechanism for all catalysts being compared.

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