

Infrared Study of Pyridine Adsorbed on Unpromoted and Promoted Sulfated Zirconia

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Infrared spectra of pyridine adsorbed on zirconia and Pt–zirconia exhibited bands consistent with Lewis acid sites. Sulfated zirconia, after heating at 400°C, exhibited bands indicating about equal amounts of Lewis (L) and Brønsted (B) acid sites; the B/L ratio decreased with increasing reactivation temperature to become essentially zero after reactivation at 600°C. In contrast, both Pt and Fe/Mn promoted sulfated zirconia exhibited B/L ratios that increased slightly with increasing reactivation temperature. It is proposed that pyridine reacts with a Lewis acid site to produce an adsorbed “pyridone-type” surface species with the concurrent generation of a proton. The superior performance of the promoted sulfated zirconia catalyst is believed to arise from its ability to generate Brønsted acid sites. © 1999 Academic Press

INTRODUCTION

Sulfated zirconia (SZ) has generated much interest because it has significant catalytic activity for the conversion of hydrocarbons at low temperatures (25–200°C) (for example, Refs. (1–8)). The material has been considered to be a superacid (for example, Ref. (9)); however, others claim that the acidity is no stronger than that of 100% sulfuric acid (10).

The acid type is also controversial (11). There are claims that the catalytic activity derives mainly, or completely, from protonic (Brønsted) acid sites. Other authors are equally convinced that the acid sites are aprotic (Lewis sites).

An identification of the type of acidity can be obtained from infrared spectra of adsorbed molecules, especially pyridine. The pyridinium ion displays a vibration at 1540 cm⁻¹ and provides a measure for the Brønsted acid sites. Coordinately bonded pyridine exhibits a band at 1440 cm⁻¹ which is representative of Lewis acid sites.

Arata (9) summarized some earlier results (12, 13) for the adsorption of pyridine on SZ containing platinum (Pt–SZ). Arata *et al.* (12, 13) reported an increase in the Lewis sites relative to the Brønsted sites as a result of heating

at high temperatures. However, if water was added to the sample following heating at a high temperature, the intensity of the 1540 cm⁻¹ band increased with concomitant decrease in the 1440 cm⁻¹ band, indicating that Lewis sites are converted to Brønsted sites upon the adsorption of water.

For pyridine adsorbed on pure zirconia, only bands for Lewis sites are observed (14, 15). Some authors have reported that only Lewis sites are present on promoted and unpromoted SZ (16–20). Bensitel *et al.* (16) did not observe an increase in the number of acid sites as a result of sulfation of zirconia but reported that the strength of some of the Lewis sites was increased. Other authors indicate that Brønsted sites are present on SZ. Nascimento *et al.* (21) found that the fraction of Brønsted sites increased with sulfur loading and that when the sulfur loading exceeds a monolayer the Brønsted sites exceed the Lewis sites. Tabora and Davis (22) found only Lewis sites on zirconia or Fe/Mn–zirconia but reported that the incorporation of sulfate to these two materials produced about equal amounts of Brønsted and Lewis sites following outgassing at 477°C. Our earlier results showed about equal amounts of Brønsted and Lewis sites on Pt–SZ following outgassing at 400°C even though only Brønsted sites were observed for a sample outgassed at 100°C (23).

Ebitani *et al.* (4) proposed that gaseous hydrogen impacted the Brønsted acidity of Pt–SZ. Brønsted acidity was proposed to develop from dissociative adsorption of hydrogen on Pt, spillover of the H atoms onto the SZ surface, and then electron transfer from the H atoms to Lewis acid sites left H⁺ on the surface. Reversal of this spillover reaction results in the loss of Brønsted acid sites.

Our activity studies indicate that an aged Pt–SZ catalyst retained the hydrogenation function and that the loss of the acid function was responsible for the catalyst aging (24). It was therefore desirable to define the types of acidity present in these catalysts following a pretreatment under conditions that are typical of those that produce a catalyst that is active for the conversion of hydrocarbons.

EXPERIMENTAL

Catalyst Preparation

Hydrous zirconia was prepared by rapid precipitation from a zirconium oxynitrate solution by adding an excess of ammonium hydroxide to a pH of 10.5 (25, 26). The resulting precipitate was filtered, washed, and dried at 110°C overnight. Sulfate adsorption on the dried zirconia sample was carried out by immersing the zirconia powder in H₂SO₄ and stirring the suspension for 4 h (27). In a typical sulfate adsorption experiment, 10 g of the zirconia powder were suspended in 900 mL of a 1 N sulfuric acid solution and stirred for 4 h at room temperature, filtered, and dried at 110°C overnight in air. The samples were analyzed for their sulfur content using a Leco SC-432 sulfur analyzer. Pt-SO₄²⁻-ZrO₂ was prepared by immersing SO₄²⁻-ZrO₂ into an aqueous solution of H₂PtCl₆ (0.10082 g Pt/mL) that was stirred for a few hours and the water removed. The sample was dried at 110°C overnight. The final Pt concentration in the Pt-SO₄²⁻-ZrO₂ catalysts in this study was a nominal 0.6 wt.%.

Before conducting the adsorption studies, all samples (ZrO₂, SO₄²⁻-ZrO₂, or Pt-SO₄²⁻-ZrO₂), were calcined in air at 600°C for 2 h.

Diffuse Reflectance Infrared Spectroscopy (DRIFTS)

DRIFTS was used to determine the relative amounts of Brønsted and Lewis acid sites (28). The DRIFTS cell (Harrick Scientific Corporation) was equipped with a heater and connected to a vacuum system. Temperature was monitored with a thermocouple placed in direct contact with the sample. Other modifications made to the cell and diffuse reflectance accessory were similar to those reported by Venter and Vannice (29).

Catalyst samples were initially calcined at 600°C then exposed to atmospheric moisture. Approximately 100 mg of sample was loaded into the DRIFTS cell for characterization. The sample was heated *in situ* to the desired temperature (400, 500, 600°C) under an oxygen purge. After 2 h the sample was cooled to 40°C. The purge gas was switched to dry argon (20 cc/min) and the sample reheated to the final pretreatment temperature for 2 h. After cooling to 40°C a background spectrum was collected. The sample was reheated under an argon purge to 150°C. The sample was then saturated with pyridine by directing the gas flow through a pyridine saturator for 10 min. The sample chamber was maintained at 150°C and purged with dry argon for 2 h at 150°C to remove any physisorbed pyridine, then cooled to 40°C to record the sample spectrum. Baseline corrections were performed on spectra and relative populations of Brønsted and Lewis acid sites were determined from absorbance bands observed at 1542–1545 cm⁻¹ (Brønsted) and 1448–1455 cm⁻¹ (Lewis). A fresh aliquot of sample was used for each pretreatment temperature.

Ultrahigh purity gases were obtained from Tri-State Oxygen and passed over molecular sieves prior to being used. Pyridine (Aldrich 99.9%) was degassed and stored in an inert atmosphere over molecular sieves.

Pyridine chemisorbs on Lewis and Brønsted acid sites. The bands at 1450 cm⁻¹ and 1545 cm⁻¹ (corresponding to Lewis and Brønsted sites, respectively) were integrated between 1420 and 1470 cm⁻¹ and between 1515 and 1565 cm⁻¹. In measurements for more than 200 catalyst samples, it has been found that the peak height ratios are essentially the same as the corresponding ratio of the integrated areas. Thus, in this study the ratios of Lewis–Brønsted acid sites are based on the ratios of the two peak heights.

RESULTS

The infrared spectra of zirconia samples are displayed in Fig. 1. As expected, only bands indicative of pyridine adsorbed on Lewis acid sites are observed in the IR spectra (Fig. 1). Furthermore, the number of Lewis sites appears to be nearly constant for each of the three outgassing temperatures. Spectra collected using Pt–ZrO₂ could not be distinguished from those of ZrO₂ (Fig. 2). Pt does not modify the type of acid sites that are present on zirconia. Both zirconia and Pt–zirconia possess predominantly Lewis acid sites. Pt–zirconia contains broad bands between 1625–1690 cm⁻¹. Furthermore, these peaks increase in intensity as the reactivation increases from the 400 to 500°C, then decrease after reactivation at 600°C. These vibrations are not observed for the zirconia or sulfated zirconia samples. Metal promoted sulfated zirconias exhibit an absorbance at 1640 cm⁻¹. Thus, the vibrations between 1625–1690 cm⁻¹ appear to be associated with the presence of Pt.

Spectra for a sulfated zirconia catalyst are shown in Fig. 3. Pyridine on sulfated zirconia displays a strong peak centered at about 1640 cm⁻¹ that is not observed in the

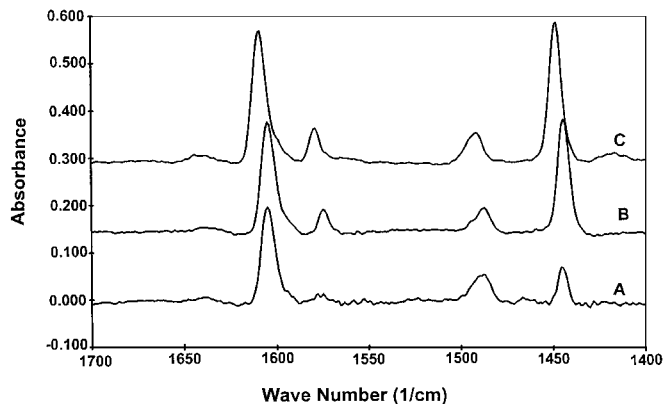


FIG. 1. The infrared spectra of pyridine adsorbed on zirconia (calcined at 600°C, monoclinic phase) following *in situ* evacuation at 400°C (A), 500°C (B), and 600°C (C).

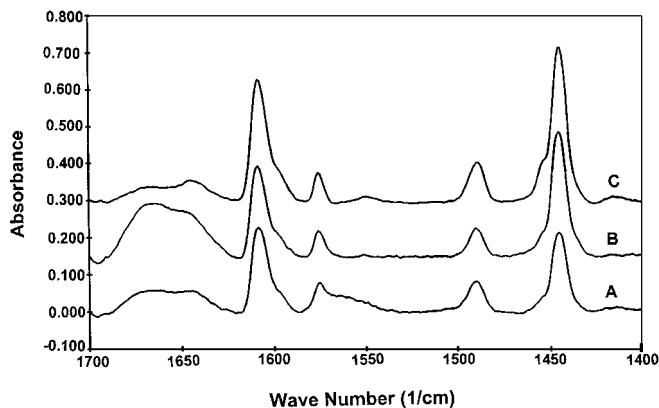


FIG. 2. The infrared spectra of pyridine adsorbed on Pt-zirconia (calcined at 600°C, monoclinic phase) following *in situ* evacuation at 400°C (A), 500°C (B), and 600°C (C).

spectra of zirconia or Pt-zirconia samples. This feature is attributed to Brønsted acidity as will be discussed below. Data for the sample reactivated at 400°C are similar to the results reported in our earlier infrared study (23). Both Brønsted and Lewis acid sites contribute to the band at 1490 cm^{-1} . Rosenthal *et al.* (30) found that the extinction coefficients for the Lewis-pyridine (Lpy) and Brønsted-pyridine (Bpy) bands were equal. While this does not require similar extinction coefficients for the 1450 and 1540 cm^{-1} bands, we assume this to be the case in the following. In both instances the sample contained, with this assumption, equal amounts of the Brønsted and Lewis sites. As anticipated, there is a decrease in the Brønsted-Lewis ratio as the sample is reactivated at higher temperatures (Fig. 4). Following reactivation at 600°C, sulfated zirconia contains little if any Brønsted acidity but does contain Lewis acidity. A direct comparison of the intensities of samples reactivated at different temperatures cannot be made since different portions of a common sample were used. However, it appears that the intensity of both the Brønsted and the Lewis

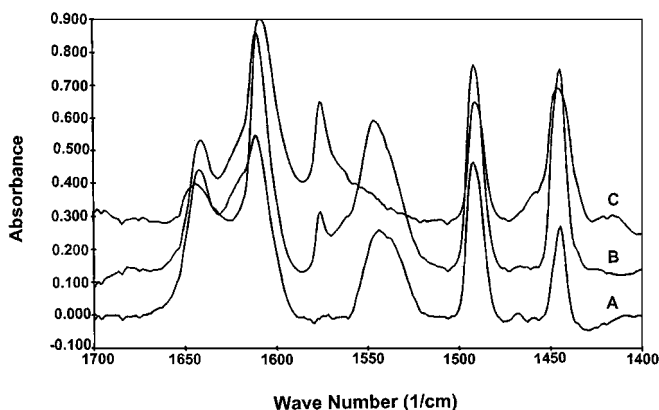


FIG. 3. The infrared spectra of pyridine adsorbed on $\text{SO}_4^{2-}\text{-ZrO}_2$ (calcined at 650°C, tetragonal phase) following *in situ* evacuation at 400°C (A), 500°C (B), and 600°C (C).

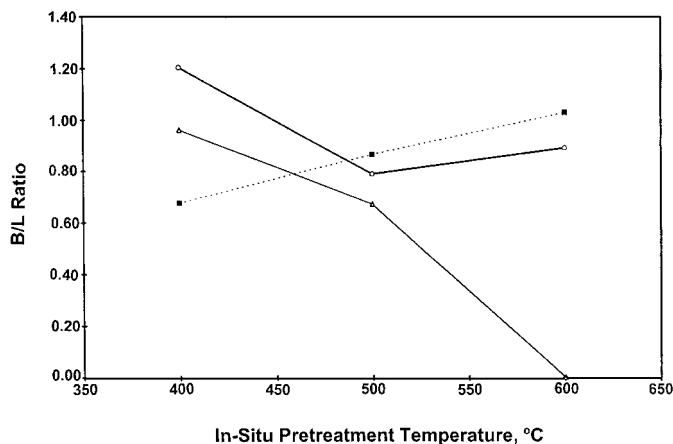


FIG. 4. Ratio of the Brønsted-Lewis acid-pyridine peak intensity for $\text{SO}_4^{2-}\text{-ZrO}_2$ ($\Delta\text{-}\Delta$), $\text{Pt-SO}_4^{2-}\text{-ZrO}_2$ ($\blacksquare\text{-}\blacksquare$), and $\text{Fe-Mn-SO}_4^{2-}\text{-ZrO}_2$ ($\circ\text{-}\circ$) following reactivation at 400, 500, and 600°C.

bands increases when the pretreatment temperature was increased from 400 to 500°C and then decreases upon reactivating at 600°C.

Spectra obtained for the Pt-sulfated zirconia (Fig. 5) are qualitatively similar to those of sulfated zirconia, but exhibit some differences. In contrast to sulfated zirconia, the intensity of the Brønsted-Lewis acid sites increases with increasing reactivation temperature for Pt-sulfated zirconia (Fig. 4). This is due to an increase in the intensity of the peak assigned to the Brønsted acid-pyridine complex, implying that platinum acts to increase the number of Brønsted acid sites with increasing reactivation temperature. As with the Pt-sulfated zirconia sample, a prominent peak centered at about 1640 cm^{-1} was observed and this band increases in intensity with increasing reactivation temperature.

Spectra for Fe/Mn-sulfated zirconia catalysts (Fig. 6) resemble those of Pt-sulfated zirconia. Even after reactivation at 660°C, approximately equal amounts of Brønsted and Lewis acid sites were observed. In addition, the 1640 cm^{-1} band was observed at all three reactivation temperatures.

For sulfated zirconia catalyst samples, the intensity of the 1640 cm^{-1} peak follows the concentration of the Lewis acid site-pyridine complex, as determined from this intensity of the 1544 cm^{-1} band (Fig. 7). The ratio of the intensity of the 1544 cm^{-1} and 1640 cm^{-1} bands is close to one and increases slightly with increasing reactivation temperature up to 500°C and then decreases to near zero following reactivation at 600°C. For the Pt-sulfated zirconia and the Fe/Mn-sulfated zirconia samples, the curves for the ratio of the Brønsted-Lewis acid sites with reactivation temperature mirrors the ratio of the Brønsted-Lewis peaks. Similarities between the curves shown in Figs. 4 and 7 suggest the 1640 cm^{-1} band is related to the sample's Brønsted acidity.

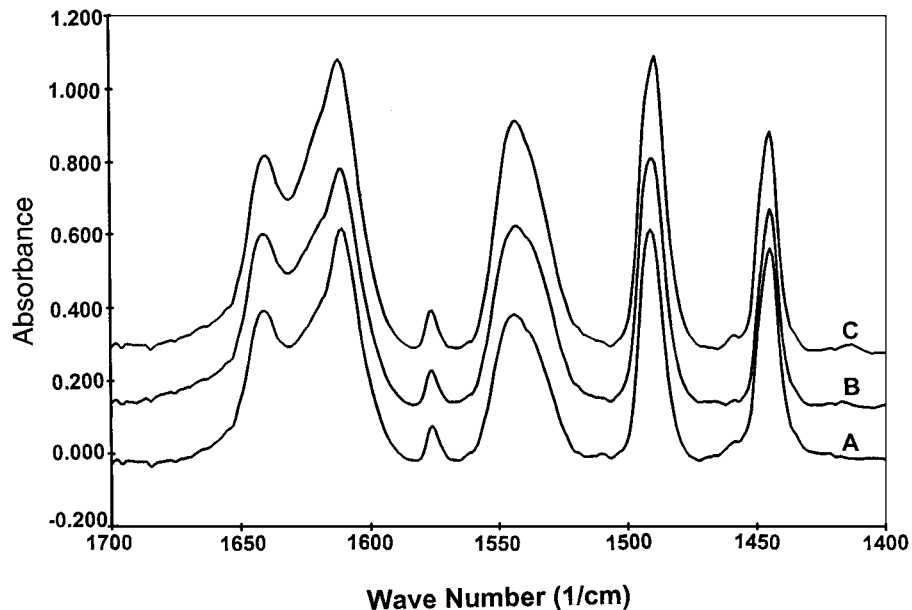


FIG. 5. The infrared spectra of pyridine adsorbed on Pt-SO₄²⁻-ZrO₂ (calcined at 650°C, tetragonal phase) following *in situ* evacuation at 400°C (A), 500°C (B), and 600°C (C).

DISCUSSION

Results obtained with zirconia and Pt-zirconia are as expected. Both samples have Lewis acid sites with little, if any, Brønsted acidity being detected by the infrared technique used in this study. There is some indication that pyridine interacts with Pt in Pt-zirconia. However, it is not possible to assign a definitive structure to this species.

Results obtained with the sulfated zirconia are consistent with previously reported data. Approximately equal amounts of Brønsted and Lewis acid sites are observed after activation at 400°C. Previous studies showed that exposing a sulfated zirconia sample to atmospheric moisture after initial activation at 650°C converted all of the acid sites into Brønsted sites (23). Reactivating sulfated zirconia at higher temperatures results in increased amounts

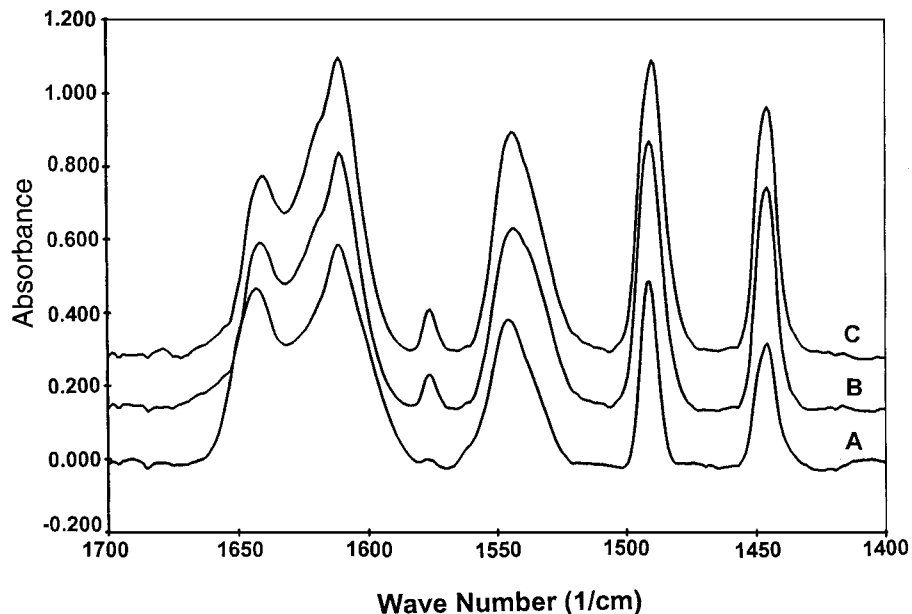


FIG. 6. The infrared spectra of pyridine adsorbed on Fe-Mn-SO₄²⁻-ZrO₂ (calcined at 650°C, tetragonal phase) following *in situ* evacuation at 400°C (A), 500°C (B), and 600°C (C).

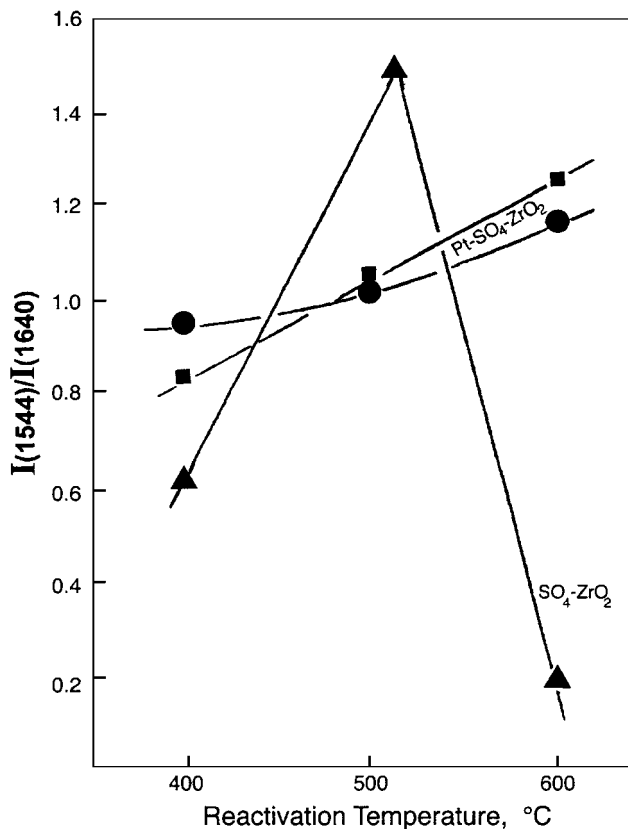


FIG. 7. Ratio of the intensity of the band centered at 1544 cm^{-1} (Brønsted)-intensity of the band centered at 1640 cm^{-1} for $\text{SO}_4^{2-}\text{-ZrO}_2$ (▲-▲), $\text{Pt-SO}_4^{2-}\text{-ZrO}_2$ (■-■), and $\text{Fe-Mn-SO}_4^{2-}\text{-ZrO}_2$ (●-●) following reactivation at 400, 500, and 600°C .

of Lewis acid sites. The Brønsted-Lewis acid site ratio is approximately 1 after reactivation at 400°C and then decreases as the reactivation temperature increases. The Brønsted-Lewis acid site ratio is essentially zero after the sample was reactivated at 600°C .

Results for sulfated zirconia are consistent with the adsorption-desorption of water as a controlling factor in determining the ratio of Brønsted-Lewis acid sites. Exposure of an activated sample to atmospheric moisture will saturate the surface with water. Adsorbed water presumably reacts with surface sulfate groups to produce a species that resembles adsorbed sulfuric acid. The fraction of water retained decreases as the reactivation temperature is increased. The infrared data are consistent with complete removal of water and Brønsted acidity after reactivation at 600°C . Likewise, temperature programmed thermal gravimetric analysis (tga) shows that the adsorbed water is removed from sulfated zirconia as it is heated to approximately 500°C . Heating to higher temperatures produces negligible weight loss by tga analysis, indicating all of the adsorbed water is removed by heating to 500°C (27).

Our previous studies show that the materials used in this study are active for hydrocarbon conversions after activa-

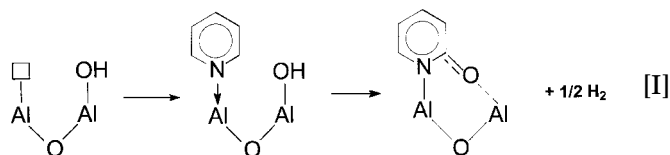
tion at 650°C (31, 32). Infrared data suggest that sulfated zirconia activated at 650°C should not contain a significant number of Brønsted acid sites, but would possess a significant amount of Lewis acid sites. This leads to the following possibilities: (1) Lewis acid sites are responsible for the catalytic activity, (2) the number of Brønsted sites responsible for the catalytic activity are too low to be detected by the i.r. technique, or (3) the true catalytic sites are generated during the induction stage of the hydrocarbon conversion. We now believe that the third scenario is the most plausible—catalytic sites are generated during the initial hydrocarbon conversion process.

It is surprising that the relative amounts of Brønsted acid sites increase with reactivation temperatures when the metal promoters (Pt or Fe/Mn) are present. Clearly, a sample heated at 500 or 600°C will contain less adsorbed water than one heated to 400°C . The role of water in acid catalysis has long been a concern and remains an unanswered question. A sulfated zirconia possesses only Brønsted acidity following exposure to atmospheric moisture (23) and this documents that water adsorbed on sulfated zirconia creates Brønsted sites. For this sample, the ratio of Brønsted to Lewis acid sites decreases as the reactivation temperature increases. In the current study, Brønsted sites are below the detection level following reactivation at 600°C ; however, Lewis acid sites are still present. If gases and/or apparatus were a source of water contamination during the measurement, the sulfated zirconia sample reactivated at 600°C should exhibit Brønsted as well as Lewis sites. Since the sample shows Lewis but not Brønsted acidity, it is concluded that the gases and equipment are dried sufficiently to prevent the formation of Brønsted acidity from moisture contamination. The results shown in Fig. 4 for sulfated zirconia were reproduced with two sample preparations as well as being duplicated with a common sample. Since a common procedure was used to obtain the infrared spectra for all samples, it is concluded that the data with the metal promoted samples are not due to the presence of traces of water and that the additional Brønsted acid sites present in the 500 and 600°C samples cannot be due to the presence of residual water. A process not involving water must therefore be responsible for the increase in the Brønsted acid site concentration.

From the data in Fig. 7, it appears the species responsible for the i.r. band centered at about 1640 cm^{-1} plays a role in the proton formation that leads to detection of Brønsted acidity. It is also evident that Pt or Fe/Mn enhances the formation of this species.

Knözinger and co-workers (33-35) also observed an infrared band centered at 1640 cm^{-1} on partially dehydroxylated alumina that contained both Lewis sites and OH groups. At room temperature pyridine was initially coordinated to unsaturated Al^{3+} sites. As the sample was heated above 350°C , they observed a strong band at 1634 cm^{-1} ,

indicating the alumina surface contained acid–base pairs. One schematic representation of these sites (labeled site II in Ref. (33) and X-site in Ref. (35)) is as shown at the left in Eq. [I] and its reaction with pyridine to form the pyridone species

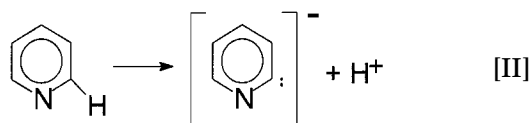


where \square indicates an anion vacancy. Knözinger and Müller (33) detected hydrogen in the infrared cell, which provides additional support for reaction [I]. The pyridone surface species has a [C---O---] stretching band at 1634 cm^{-1} . The above reaction is not restricted to the i.r. identification since it was established by chemical methods (33).

In earlier studies, it has been shown that once pyridine adsorbs on sulfated zirconia as well as Pt- or Fe/Mn-promoted sulfated zirconia, the chemisorbed pyridine does not desorb. Chemisorbed pyridine is not removed intact from the surface with programmed heating but only as a product of reaction with the sulfate group; thus carbon dioxide, water, and oxides of sulfur are observed as decomposition products. The irreversible adsorption is not limited to a strong base such as pyridine. Jatia *et al.* (37) reported that benzene chemisorbed at low temperatures did not desorb intact. Instead, benzene was removed from the surface as the oxidation product, CO_2 . Without question, activated sulfated zirconia or metal-promoted sulfated zirconia can react to irreversibly chemisorb hydrocarbons even at room temperature.

By analogy to Knözinger and co-workers' data (33–35), it is reasonable to assign the species responsible for the i.r. band centered at 1640 cm^{-1} to the structure shown in Eq. [I] except that the coordinatively unsaturated site resides on a Zr^{4+} rather than Al^{3+} . The reaction shown in Eq. [I] produces hydrogen which has not been observed when hydrocarbons interact with sulfated zirconia catalysts (38); rather, a proton, or a hydrogen species that can be converted to a proton, is generated. During the cracking of 2-methylbutane with a silica–alumina catalyst hydrogen was generated but even at high conversion levels hydrogen was not detected with the sulfated zirconia catalyst (38).

By analogy to Knözinger and co-workers (33–35), the reaction of the organic species can be written:

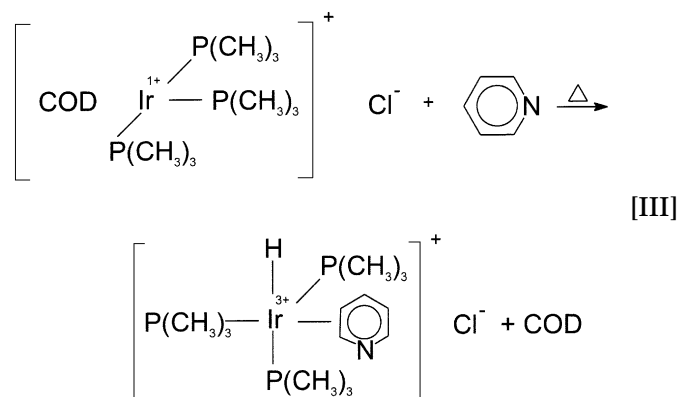


The structure of the site on the promoted or unpromoted

sulfated zirconia must be speculative. Zirconia differs from alumina since it has a much greater tendency to become deficient in oxygen when heated at high temperatures; for example, stoichiometries such as $\text{ZrO}_{1.99}$ are reasonable for zirconia heated to 600°C . This means that there will be more Lewis acid sites on the surface of zirconia than on alumina. Furthermore, to explain the present results requires that the promoter (Pt or Fe/Mn oxides) provide a porthole for the escape of oxygen from the surface so that more Lewis acid sites are present on the surface of the promoted material.

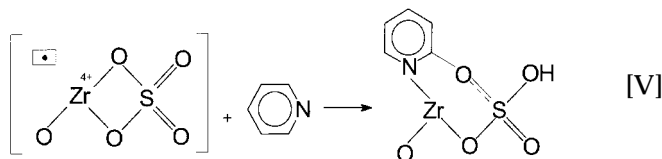
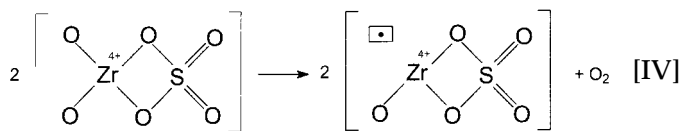
While there may be some question about the chemical state of the Pt in the surface layer, the bulk platinum promoter in a sulfated zirconia is considered to be present in the metallic state following heating at 650°C or higher (39–41). When a Pt–zirconia material is heated at 725°C in hydrogen, zirconium oxide is reduced to form metallic zirconium which subsequently forms an alloy with the metallic platinum. XRD data show that this Pt_3Zr alloy is stable upon cooling to room temperature in air and is only reoxidized to zirconium and metallic platinum after heating in air at about 400°C (41). While zirconia is slightly oxygen deficient when heated to 725°C , it is not reduced in hydrogen at this temperature to form metallic zirconium. Thus, there is direct experimental evidence to show that platinum functions as a porthole for the removal of oxygen from zirconia. This concept is utilized for writing equations shown below.

At first glance, the reaction of pyridine to form the pyridone compound may be surprising. However, the facile attack at the 2-position of pyridine is common in organo-metallic chemistry as illustrated by the following:

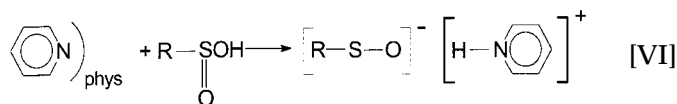


In this instance the Ir^{1+} complex is electron rich. The driving force for the reaction is the oxidation of Ir^{1+} to Ir^{3+} . In reaction [III], one may view the reaction of pyridine as the formation of the anion of pyridine, C_5H_5^- , and a proton, H^+ . The oxidation of Ir^{1+} to Ir^{3+} provides two electrons to convert the proton to the hydride ion in the coordination sphere. A similar reaction occurs with furan where the electron-rich Ir complex attacks at the α -position with the generation of a proton that is subsequently converted to a hydride ion (42).

A reaction that could account for our i.r. observations and the role of metal promoters would be:



This reaction must be followed by the migration of physically adsorbed pyridine to the newly generated acid site where it forms the pyridinium ion:



Since pyridine is adsorbed at 150°C and then subjected to a gas flow at this temperature, it is reasonable to expect sufficient amounts of physically adsorbed pyridine to be present to allow reaction [VI]. Reactions IV through VI will form one pyridinium ion for each pyridone surface species. This is consistent with the experimental results if the pyridinium surface ion and the pyridone-type surface species have similar extinction coefficients. This is a reasonable assumption since most investigators report that the extinction coefficients for the pyridinium surface ion and the Lewis acid site-pyridine complex have similar extinction coefficients (30).

Ebitani *et al.* (4) have used data from infrared studies of adsorbed pyridine to support the hydrogen spillover mechanism for the generation of Brønsted acidity. In their studies, they reduced Pt-SZ with gaseous hydrogen at various temperatures in the range 300–450°C and then exposed each sample to pyridine following reduction. They found that the amount of Brønsted acidity decreased while the amount of Lewis sites increased. This is not surprising since hydrogen reduction at high temperatures can remove sulfur, and thereby Brønsted acidity. Results of more importance to this study are when a sample was exposed to pyridine, then evacuated at 400°C for 15 min, and gaseous hydrogen was added to the infrared cell. The sample was heated in the presence of hydrogen at increasing temperature intervals to 350°C. As the temperature was increased the amount of Lewis acid sites decreased and the Brønsted sites increased. The authors attributed the generation of the

Brønsted sites to the adsorption of hydrogen on Pt where it underwent homolytic bond rupture followed by diffusion to a Lewis site where oxidation-reduction reactions led to the formation of a proton. It appears that at least two other explanations are equally or more plausible. First, it has been demonstrated experimentally that heating sulfated zirconia to higher temperatures in the presence of hydrogen generates water (27, 36, 43) and the water formed during the heating process would generate Brønsted acid sites. Second, the experiment conducted by Ebitani *et al.* (4), except for the higher hydrogen pressure, parallels closely those conducted with alumina by Knözinger and co-workers where they observed the formation of pyridone. Ebitani *et al.* (4) also reported that pentane skeletal isomerization occurred much more rapidly when hydrogen was present and this was consistent with their view of hydrogen spillover creating Brønsted acidity. However, Liu *et al.* (44) report just the opposite: increasing hydrogen partial pressure decreased the isomerization of *n*-pentane.

The data are conclusive that both hydrocarbon (benzene) and pyridine are irreversibly adsorbed on promoted and unpromoted sulfated zirconia (27, 36, 37) and does not desorb intact. For the conversion on *n*-pentane in the presence of excess "magic acid," HSbF₆, it was reported that *i*-butane was essentially the only product (45). This conversion is equivalent to a chemical reaction in which *n*-pentane reacts with the acid to produce *i*-butane and some C₁ species which remains fixed in the magic acid. Similar results have been obtained for the conversion of 2-methylbutane with promoted sulfated zirconia: 2-methylbutane produces *i*-butane as the dominant product and the C₁ species did not appear as methane or any other C₁-gaseous product (46). These results are consistent with, but do not require, a mechanism where the hydrocarbon reacts with the sulfate group to produce *i*-butane and an adsorbed cation species that is retained by the catalyst. This reaction would be equivalent to a chemical reaction in which the reactant was converted to a fragment which desorbed as a stable chemical compound and a fragment that remained attached to the catalyst as a cation that can serve as a Brønsted or Brønsted-like site.

SUMMARY

In summary, the current data show that only Lewis acid sites are present on calcined zirconia and Pt-zirconia samples. Based on the area of the 1450 and 1540 cm⁻¹ infrared bands of adsorbed pyridine and the assumption of equal absorption coefficients for these two bands, metal promoted or unpromoted sulfated zirconia has nearly equal amounts of Brønsted and Lewis acid sites. Unpromoted sulfated zirconia, calcined at 600°C, exposed to atmospheric moisture, and then reactivated at 400, 500, and 600°C, showed a decline in the Brønsted-Lewis acid site ratio which became essentially zero for the sample reactivated *in situ* at 600°C.

On the other hand, the Brønsted–Lewis acid site density for Pt and Fe/Mn promoted sulfated zirconia did not decrease for increasing reactivation temperature but actually showed a slightly higher value after heating at 600°C than at 400°C. While the assumption of equal absorption coefficients for the 1450 and 1540 cm⁻¹ infrared bands of adsorbed pyridine may not be correct, and deviation from equality will not alter the trends shown for the change in the Brønsted–Lewis acid site ratio with increasing reactivation temperature.

For the promoted and unpromoted sulfated zirconia, a band appears at 1640 cm⁻¹ which, based upon results obtained by Knözinger and co-workers (33–35), has been assigned to the formation of an adsorbed pyridone structure which results from the reaction of pyridine with a Lewis acid site to generate a proton. Based upon the observation that platinum “catalyzes” the hydrogen reduction of zirconia to produce zirconium metal that forms an alloy with platinum, it is proposed that the metal promoter serves as a “porthole” that facilitates the thermodynamic tendency for zirconia to become oxygen deficient at high temperatures. Thus, it is envisioned that the promoter serves to allow the formation of a greater oxygen deficiency and thereby a greater amount of Lewis sites. These Lewis sites are believed to be able to react with adsorbed hydrogen-containing molecules to produce Brønsted sites. This model is consistent with the infrared data for adsorbed pyridine.

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