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Platinum–sulfated–zirconia. Infrared study of adsorbed pyridine

Chunjie Zhang [a], Raul Miranda [b] and Burtron H. Davis [a]

[a] *Center for Applied Energy Research, University of Kentucky,*
3572 Iron Works Pike, Lexington, KY 40511, USA
[b] *Department of Chemical Engineering, University of Louisville,*
Louisville, KY 40292, USA

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Pyridine adsorption on sulfated zirconia (SO_4^{2-}–ZrO_2) provides evidence for infrared bands characteristic of both Brønsted and Lewis acid sites. Samples treated at 100°C retain water and have a higher fraction of Brønsted acidity than when the sample is treated at 400°C. The fraction of Brønsted acid sites observed for SO_4^{2-}–ZrO_2 is the same in the presence or absence of supported Pt. Based on pyridine adsorption, exposure to gaseous hydrogen at 100 or 150°C did not significantly alter the fraction of Brønsted acid sites following the exposure to hydrogen.

Keywords: pyridine adsorption; sulfated zirconia; infrared; acid sites

1. Introduction

Sulfated zirconia (SO_4^{2-}–ZrO_2) has generated much interest recently because the material has significant catalytic activity for the conversion of hydrocarbons at low (25–200°C) temperatures (see, for example, refs. [1–8]). The material has been considered to be a superacid (see, for example, ref. [9]); however, it has also been claimed that the acidity of SO_4^{2-}–ZrO_2 is no stronger than that of 100% H_2SO_4 [10].

The nature of the acidity 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). A descriptive indication of the type of acidity can be obtained from the IR spectra of adsorbed molecules, in particular, pyridine or carbon monoxide. Arata [9] summarized results for the adsorption of pyridine on Pt–SO_4^{2-}–ZrO_2 that were obtained in earlier studies [12,13]. The band for pyridinium ion at 1540 cm^{-1} provides a measure for the Brønsted acid sites and the band for coordinately bonded pyridine at 1440 cm^{-1} is representative of the Lewis acid sites. These authors 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 a concomitant decrease in the 1440 cm^{-1} band, indicating that Lewis sites are converted to Brønsted sites upon the adsorption of water.

Ebitani et al. [4] obtained spectra of pyridine adsorbed on Pt–ZrO_2, SO_4^{2-}–ZrO_2 and Pt–SO_4^{2-}–ZrO_2. After in situ treatment (the temperature was not given but it appears to be 600°C) for 3 h, the sample was exposed to 2–3 Torr of pyridine at 150°C for 15 min, and then evacuated at this temperature for 15 min. The spectra indicate that the surface acid sites for Pt–ZrO_2 and Pt–SO_4^{2-}–ZrO_2 are mostly Lewis sites and that SO_4^{2-}–ZrO_2 possesses Brønsted acid sites. From temperature desorption profiles, the authors concluded that the Lewis acid sites of the Pt–SO_4^{2-}–ZrO_2 surface are stronger than those of either Pt–ZrO_2 or SO_4^{2-}–ZrO_2.

Yamaguchi et al. [14,15] reported infrared spectra of adsorbed pyridine to show that the catalysts evacuated at 500°C possess only Lewis acidity; no Brønsted acidity was found. Bensitel et al. [16] reported that, in agreement with Tret'Yakov et al. [17] but contrary to Nakano et al. [18], they never observed the appearance of bands characteristic of the pyridinium ion on ZrO_2. Bensitel et al. [16] did not observe the formation of the pyridinium ion on their SO_4^{2-}–ZrO_2 samples; furthermore, these authors did not observe an increase in the number of acid sites due to sulfation but they did find that the strength of some of the Lewis sites increased. For the adsorption of CH_3SH, Bensitel et al. [16] observed that this molecule dissociated on ZrO_2 but not on SO_4^{2-}–ZrO_2, where it was present mainly as a coordinated form. They deduced that sulfate ions occupied basic oxygen ions which would normally dissociate CH_3SH. Recently, Morterra et al. [19] reported that all of the surface acidity determined by pyridine adsorption is essentially of the Lewis type.

Waqif et al. [20] reported that on pure metal oxides or on metal oxides with a small amount of sulfate (about 2%), the pyridinium ion was not observed; however, it is likely that their sample was prepared from calcined ZrO_2 rather than by adding sulfate to the hydrous oxide as is usually done. These authors reported that sulfidation increased the stretching frequency of the CO species coordinated on the SO_4^{2-}–ZrO_2 relative to that of ZrO_2 alone, indicating an increase of the Lewis acid strength.

Nascimento et al. [21] prepared a series of catalysts with a range of sulfur contents by varying the concentration of the sulfuric acid solution used to prepare the catalyst and the temperature at which the catalyst was calcined. They found that the ratio of Brønsted/Lewis acid sites increased with increasing sulfur content. Brønsted sites are formed in larger amounts than Lewis sites for sulfur contents higher than the value of sulfate that corresponded to a monolayer.

Ebitani et al. [4] found that the surface acidic properties of ZrO_2 containing both Pt and SO_4^{2-} were modified by the presence or absence of hydrogen. The impact of hydrogen was dynamic, and the generation or elimination of protonic acid sites followed the addition or removal of hydrogen. Acidity was followed by observing the appropriate infrared bands of the adsorbed pyridine after treating the sample in situ in the IR cell in a hydrogen flow at 350°C for 2 h. These infrared results are surprising, since exposure of a SO_4^{2-}–ZrO_2 catalyst to hydrogen gas in this temperature range is considered by many to result in the conversion of the sulfur to hydrogen sulfide which results in the elimination of sulfur from the catalyst. Apparently this was not the case in the study by Ebitani et al. [4]. These authors viewed the generation of the protonic acid sites to involve dissociative adsorption of the hydrogen molecule on Pt, spillover of the H atom onto the SO_4^{2-}–ZrO_2 surface, and electron transfer from the H atom to Lewis acid sites leaving H^+ on the surface. Reversal of this spillover reaction results in the loss of Brønsted acid sites.

We have made extensive studies of the preparation of ZrO_2 and have developed procedures to control the crystal phase of the calcined material [22–31]. The extent of SO_4^{2-} adsorption on the dried gel has been investigated as well as the decomposition of the hydrous SO_4^{2-}–ZrO_2, identifying the weight loss, the phase transformations and the gases evolved during the heating using combined TGA/DTA/MS [32,33]. Other studies defined the activity of the Pt–SO_4^{2-}–ZrO_2 catalysts, derived from precursors containing an initial SO_4^{2-} content in the range of 3–14 wt%, for the conversion of hydrocarbons [34,35]. XAFS data indicated that Pt in these samples was present in the metallic form after calcination in air for 2 h at 725°C [35]. Our studies indicate that an aged catalyst retained the hydrogenation function (Pt) and that the acid function was responsible for the aging [37]. 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. Since these hydrocarbon conversions are effected in the presence of hydrogen, it was desirable to learn whether the presence of hydrogen increases the number of Brønsted acid sites as indicated in some of the studies cited above.

2. Experimental

2.1. CATALYST PREPARATION

Zirconia was prepared through the rapid precipitation from a zirconium oxynitrate solution by adding an excess of ammonium hydroxide to a pH of 10.5 [38,39]. 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 H_2SO_4 and stirring the suspension for an hour [32]. In a typical sulfate adsorption experiment, 10 g of the zirconia powder were suspended in 60 ml of a 1 N (or other concentration as needed) sulfuric acid solution, and equilibrated for an hour at room temperature. The contents were then filtered, washed twice with distilled water and dried at 110°C overnight in air. The samples were analyzed for their sulfur content using a Leco SC-432 Sulfur Analyzer. Pt–SO_4^{2-}–ZrO_2 was prepared by immersing SO_4^{2-}–ZrO_2 into an aqueous solution of H_2PtCl_6 (0.1026 g Pt/ml) that was stirred for a few hours, the solid collected and then dried overnight at 353°C under vacuum. The final Pt concentration in the Pt–SO_4^{2-}–ZrO_2 catalysts in this study was a nominal 1 wt%.

Before conducting the adsorption studies, all samples (ZrO_2, SO_4^{2-}–ZrO_2 or Pt–SO_4^{2-}–ZrO_2), were calcined in air at 625°C for 2 h.

Zirconia samples containing different sulfate levels (0 wt%, 1.17 wt%, 9.87 wt% and 13.62 wt%), with and without 1% Pt, were used in this study. The sample preparations and experimental conditions are summarized in table 1. The samples are identified by the initial sulfate content; however, following calcination at 625°C for 2 h all samples approach a similar sulfur content (about 1–1.5 wt%) [32].

2.2. FT-IR EXPERIMENTAL

The types of acid sites on zirconia catalysts were determined by adsorption of pyridine. The investigation was conducted in a Perkin-Elmer FT-IR spectrophotometer (model 1720) with a Sprouse Scientific Systems, Inc. data acquisition system. A diffuse reflectance IR cell, equipped with an environmental chamber, allowed exposure of the sample to high vacuum, or gas flow, and to the desired temperature during these IR studies.

For these investigations, the zirconia catalyst was first pretreated in situ under vacuum for an hour at room temperature and then purged with dry helium for 30 min at room temperature. After this initial in situ pretreatment, different experimental conditions were adopted for different purposes of this study. For example, the influence of the water remaining in the sample on the type of acid sites was determined by increasing the temperature of the sample to 100°C for 2 h. Pyridine was adsorbed from a helium flow at 100°C and then the sample was heated stepwise to 200, 300 and 400°C, recording a spectrum at each temperature. The sample was held at each temperature until a constant intensity of the peaks in the OH region was obtained (about 2 h). For other experiments, the sample would be heated at

Table 1
Percentage of acid sites on the SO_4^{2-}–ZrO_2 catalysts that are of the Brønsted type [a]

Pretreat. temp. (°C)	Post-treat. temp. (°C)	Brønsted acid sites, % of total			
		SO_4^{2-} (wt%) = 0	= 1.17	= 9.87	= 13.6
100	100	0	47	98	98 (97) [c]
100	400	0	49	93	95 (89) [c]
400	100	42	– (45) [b]	63	68 (70) [c]
400	400	46	– (52) [b]	80	83 (64) [c]

[a] All samples were calcined at 625°C, exposed to air prior to the pretreatment in situ at 100 or 400°C prior to pyridine adsorption.

[b] SO_4^{2-} content of the precursor before 650°C calcination.

[c] Numbers in parentheses are for Pt containing material.

100, 200, 300 or 400°C in flowing helium following the initial pretreatment at room temperature prior to adsorbing pyridine.

To determine if the presence of hydrogen affects the distribution of the acid sites, a SO_4^{2-}–ZrO_2 sample, with or without Pt, was heated to 400°C under helium and maintained at this temperature for 2 h. The sample was then exposed to hydrogen at atmospheric pressure at either 100 or 150°C until a constant background was recorded over the 600–4 000 cm^{-1} range.

Pyridine adsorption was accomplished by injecting 2 μl of pyridine into a helium flow while the cell temperature was held at 100°C. IR spectra were recorded at 100°C after allowing an hour for equilibrium, and after each subsequent heating period at 200, 300 and 400°C.

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} (fig. 1).

3. Results

3.1. EFFECT OF MOISTURE

It is reported [9] that Lewis and Brønsted sites on the present type of catalysts easily interchange during adsorption or desorption of water. To investigate the influence of moisture on the types of acid sites, zirconia catalyst samples were evacuated at different temperatures in the FT-IR sample cell.

Before the injection of pyridine, the catalyst sample was heated at 100 or 400°C under helium. The data (fig. 2) show that Brønsted acid sites are dominant in the samples derived from the higher sulfate precursors ($\geqslant 9.87\%$) evacuated at 100°C,

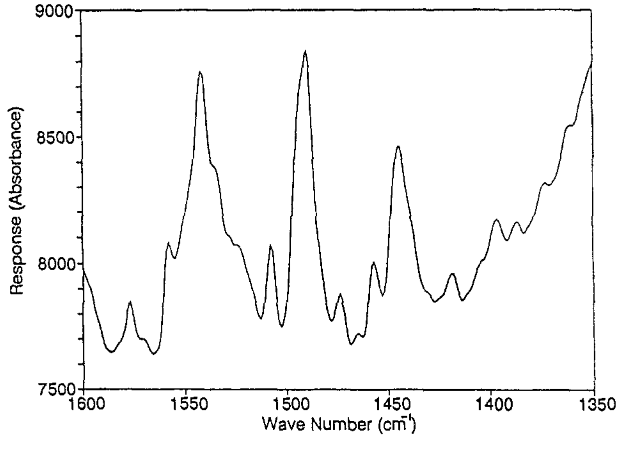

Fig. 1. FT-IR spectrum of pyridine adsorbed on a SO_4^{2-}–ZrO_2 catalyst at 100°C (without Pt, initial SO_4^{2-} content was 9.87 wt%).

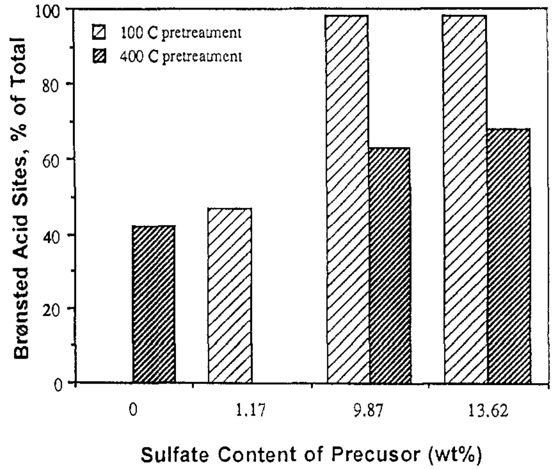

Fig. 2. Effect of the evacuation temperature on the distribution of the acid sites for SO_4^{2-}–ZrO_2 samples (without Pt, initially calcined at 625°C for 2 h and then exposed to the atmosphere).

comprising more than 95% of the total acid sites. When the samples are evacuated at 400°C, the percentage of Brønsted acid sites is lower, and accounts for 60–70% of the acid sites present in catalysts derived from the higher sulfate precursors. For the precursors with lower sulfate content, the Brønsted and Lewis acid sites are present in about equal amounts, whether the pretreatment was conducted at 100 or 400°C. Thus, the results show that, most probably, some acid sites are transformed from Brønsted to Lewis sites by heating at the higher temperature.

The two samples prepared from the higher sulfate precursors will retain about 1 ± 0.2 wt% S (3% SO_4^{2-}); however, the sample prepared from the lower sulfate (1.17 wt%) will contain less than 1 wt% S following calcination. Therefore, it appears that there is a limiting number of Lewis acid sites on the zirconia and for the materials containing 1 wt% S (presumably distributed between the bulk and surface) there are sufficient surface sulfate groups to eliminate essentially all surface Lewis acid sites.

The percentage of Brønsted (98%) acid sites is higher if the evacuation at 400°C follows pyridine adsorption at 100°C than if the pyridine injection is at 100°C after evacuation at 400°C. After pyridine has been adsorbed on a Brønsted acid site at the lower temperature, it is difficult to either eliminate or the Brønsted acid site to transform it to a Lewis acid site.

3.2. EFFECT OF SULFATE CONTENT

To investigate the role of sulfate content of the catalyst precursor on the characteristics of the surface acid sites, zirconia catalysts obtained from precursors of four different sulfate contents were used in the FT-IR experiments. An increase in the sulfate concentration in the precursor increases the percentage of Brønsted acid sites in the calcined catalyst (fig. 3). When the sulfate concentration in the precursor reaches a certain level (in this study about 10%), the fraction of Brønsted acid sites approaches a constant value; thus, the 9.87 and 13.6% sulfate containing precursors have about the same fraction of Brønsted sites following calcination at 625°C, exposure to air and then evacuation in situ at 100°C. For samples prepared from the precursors with the lower sulfate concentrations, about half of the acid sites are Brønsted sites.

3.3. EFFECT OF CALCINATION AND PLATINUM

Calcined and non-calcined zirconia catalyst samples were examined to define the effect of calcination on acid sites. The adsorption of pyridine indicates that there are few acid sites on uncalcined catalysts and calcination introduces some acid sites. Although it was not possible to obtain quantitative FT-IR data to define the increase in acid sites, the trend that local acid sites increase after calcination is apparent.

Superacid SO_4^{2-}–ZrO_2 is claimed to be a very active catalyst for paraffin isomerization. However, the activity of the catalyst may decrease rapidly during the reaction because of the formation of coke. It has been reported [4] that the addition of a noble metal, such as Pt, Rh and Ni, to the SO_4^{2-}–ZrO_2 catalyst leads to better catalytic performance for isomerization reactions. Among these noble metals, Pt supported on SO_4^{2-}–ZrO_2 has led to the highest activity. The presence of Pt is also claimed to generate Brønsted acid sites. In this study, pyridine was adsorbed at 100°C on SO_4^{2-}–ZrO_2 and Pt–SO_4^{2-}–ZrO_2 catalysts obtained from a common precursor. The data in fig. 4 show that there is no difference in the distribution of

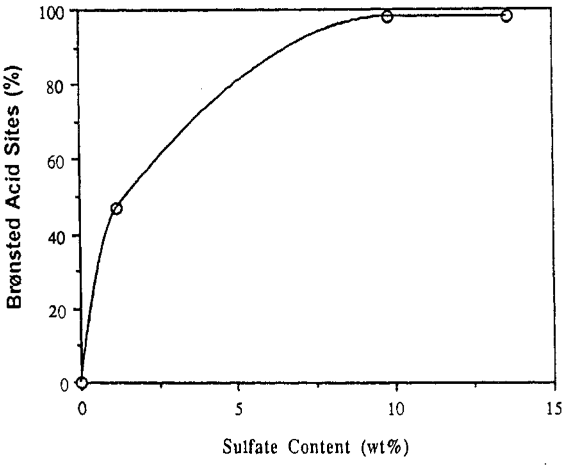

Fig. 3. Effect of sulfate content on the percentage of Brønsted acid site on SO_4^{2-}–ZrO_2 catalysts derived from precursors containing various SO_4^{2-} levels (samples calcined at 625°C, exposed to the atmosphere and then heated at 100°C).

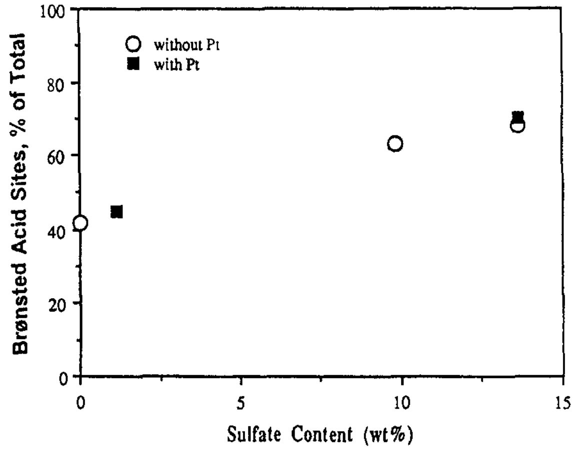

Fig. 4. Comparison of the percentage of Brønsted acid sites on SO_4^{2-}–ZrO_2 catalysts with and without Pt (samples evacuated at 400°C).

Brønsted and Lewis acid sites for the SO_4^{2-}–ZrO_2 with and without Pt, provided the catalysts are not heated at or above 400°C after pyridine adsorption. However, from the FT-IR data it was found that when the evacuation temperature was increased to 400°C, the percentage of Brønsted acid sites of the Pt containing catalyst was lower than that of the corresponding catalyst sample that did not contain Pt. For example, the SO_4^{2-}–ZrO_2 catalysts obtained from the 13.6% sulfate precursor had 83% Brønsted acid sites following evacuation at 400°C, whereas the catalyst containing Pt had, following the same treatment, only 64% Brønsted acid sites. In spite of the uncertainties in quantitatively defining the amount of each type of acid site, the data indicate that the presence of Pt does not increase the fraction of the Brønsted acid sites.

3.4. H_2 PRETREATMENT EFFECT

The role of gas phase hydrogen for the isomerization of hydrocarbons has been studied by many workers [6–8,34,40]. It has been reported that "hydrogen spillover" occurs for the Pt–SO_4–ZrO_2 catalysts and that this forms protonic acid sites to enhance the catalytic activity for the isomerization reactions [4].

The effect of hydrogen on the characteristics of the acid sites in Pt–SO_4^{2-}–ZrO_2 and SO_4^{2-}–ZrO_2 was investigated by exposing the materials to hydrogen at one atmosphere at different temperatures after the catalysts had been evacuated at 400°C for an hour to eliminate moisture. It was observed that the spectra taken before and after exposing the sample to hydrogen were about the same. After the hydrogen pretreatment at 100 or 150°C, 2 μl pyridine was injected into the gas stream to adsorb onto the zirconia catalysts, and a spectrum was again recorded. The Brønsted–Lewis acid site distribution for the Pt–SO_4^{2-}–ZrO_2 catalysts following the hydrogen treatment was about the same as for catalysts that were not pretreated with hydrogen (fig. 5). Hydrogen pretreatment at 150°C did not make a significant difference in the acid site distribution between Pt–SO_4^{2-}–ZrO_2 and SO_4^{2-}–ZrO_2 catalysts, as has been reported [4,41].

4. Discussion

The infrared spectra of pyridine adsorbed on Pt-containing SO_4^{2-}–ZrO_2 indicate that both Brønsted and Lewis acid sites are present on these materials. This conclusion is in agreement with that reported by Morterra et al. [19,42]. However, there is a major difference between the samples used in this study and those reported by Morterra et al. In the present study, the sulfate was added by adsorption on the gel that had been dried at 110°C, whereas the samples prepared by Morterra et al. involved a precalcination at 200°C followed by impregnation by an incipient wetness technique. Following the impregnation the present samples were calcined in air at 625°C, whereas most of the samples in the study by Morterra et al. were calcined at 400°C. The pre-drying or precalcination step greatly impacts the amount of sulfate adsorbed onto the ZrO_2 [32]. Morterra et al. [41] concluded that Brønsted acidity is only a minor component of the total acidity when the sample is activated at medium (400°C) temperatures. Thus, data of Morterra et al. are consistent with those of Bensitel et al. [16] but not with our results.

The structural characteristics of the samples reported by Morterra et al. [41] are unusual. They report that sulfation affects the starting ZrO_2, and that amorphous hydrated ZrO_2 crystallizes upon sulfation to produce the monoclinic phase at ambient temperature (i.e., the usual step that forms the microcrystalline tetragonal phase is skipped entirely). This is at variance with the report of others; for example, Wen et al. [6] report that only the tetragonal phase is present following

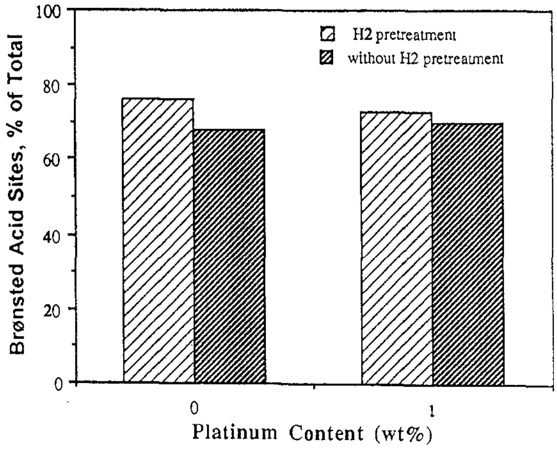

Fig. 5. Effect of H_2 pretreatment on the percentage of Brønsted acid sites Pt–SO_4^{2-}–ZrO_2 catalyst (13.62 wt% sulfate in the precursor).

calcination of sulfated zirconia at 400°C. We likewise find that sulfate stabilizes the tetragonal phase of zirconia and assists in retaining a high surface area [30]. The inhibition to phase transition has been confirmed by recent in situ X-ray diffraction studies [43].

These and earlier results make it clear that at least four major factors impact the type of acid sites detected on SO_4^{2-}–ZrO_2: (a) the time and highest pretreatment temperature of the hydrous ZrO_2 prior to sulfate impregnation; (b) the calcination temperature of the SO_4^{2-}–ZrO_2; (c) the highest temperature the sample is treated to in situ in the infrared instrument; and (d) the order in which evacuation and pyridine addition are performed. An in situ treatment at 400°C is not adequate to eliminate Brønsted acid sites. The fraction of Brønsted sites is lower when the sample is evacuated at 400°C prior to adsorbing pyridine at 100°C than if pyridine is adsorbed at 100°C prior to heating to 400°C.

In summary, the present data indicate that hydrous ZrO_2 sulfated to various levels contain about equal percentages of Brønsted and Lewis acid sites measured after a 400°C in situ heat treatment. This is significant since the materials used in characterization studies are usually treated in situ in the reactor at 400°C or lower, and the catalytic studies usually utilize materials that have been heated at temperatures higher than 400°C. The fraction of Brønsted acid sites is essentially the same whether Pt is present or not. Treatment with hydrogen at temperatures of 100 or 150°C does not increase the fraction of Brønsted acid sites over that obtained by heating the sample at the same temperature in helium. The catalysts pretreated in situ at 400°C have a high fraction of acid sites that are of the Brønsted type; however, catalysts treated only at these low temperatures are less active than when pretreated at higher temperatures [44]. Characterization data following pretreatment at these lower temperatures may therefore not provide data concerning the catalytic sites that have high activity for hydrocarbon concision.

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