ELSEVIER

Catalysis Today 62 (2000) 255–268

CATALYSIS TODAY

www.elsevier.com/locate/cattod

n-Butane and *n*-pentane isomerization over mesoporous and conventional sulfated zirconia catalysts

M. Risch[1], E.E. Wolf*

Department of Chemical Engineering, University of Notre Dame,
Centre for Catalysis & Reaction Engineering, Notre Dame, IN 46556, USA

Abstract

Activity results for *n*-butane and *n*-pentane isomerization activity on a mesoporous and conventional sulfated zirconia are presented as a function of pretreatment and reaction conditions. During both reactions, rapid deactivation occurs followed by a low residual activity. The activity is shown to be a strong function of the extent of hydration of the catalyst. Regeneration in oxygen must be followed by a step that results in the rehydration of the catalyst to recover the original activity. The optimal activities of both a conventional and a mesoporous sulfated zirconia catalysts also depend on the drying procedure used. A two-site model consisting of Lewis and Bronsted active sites is proposed to explain the two regimes of deactivation observed on these catalysts. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Sulfated zirconia; Mesoporous; *n*-Butane isomerization; *n*-Pentane isomerization

1. Introduction

The application of sulfated zirconia (SZ) to the isomerization of hydrocarbons was first reported by Holm and Bailey [1], and has been the subject of many investigations thereafter [2,3]. The isomerization of *n*-butane has been extensively studied using conventional SZ as a catalyst, because SZ was first considered to be a solid superacid [4]. However, more recent studies have shown that the catalyst most likely does not possess superacid strength [2,3]. Moreover, the reaction has been shown to proceed via a less energy intensive bimolecular mechanism on the catalyst surface [5,6,40]. Although SZ is not a solid superacid, it is still catalytically active for *n*-butane isomerization at low reaction temperatures, which is especially desirable because *i*-butane is thermodynamically favored at lower reaction temperatures. The *n*-pentane isomerization reaction has been previously studied by several authors [8,9] on SZ and on WO_xZrO_2 [10,11]. There is a consensus that while *n*-butane isomerization is a bimolecular reaction, *n*-pentane isomerization is a monomolecular reaction. The addition of promoters such as Mn and Fe, greatly promoted the activity whereas the addition of Pt decreases the rate of catalyst deactivation.

SZ is typically prepared by contacting an amorphous hydrous zirconia powder with a solution of sulfuric acid or ammonium sulfate followed by calcination at temperatures varying from 500 to 650°C. Surface areas for active SZ range between 100 and 120 m^2/g and it has been observed to be catalytically active when the zirconia exists in the tetragonal crystalline phase [4]. Preparations of high surface area catalysts using surfactant assisted synthesis similar

---

* Corresponding author.
E-mail address: wolf.1@nd.edu (E.E. Wolf).

[1] Present address: Exxon Chemical Co. BCIT, 4500 Bayway Dr. PO Box 4900, Baytown, TX 77522-4900, USA.

PII: S0920-5861(00)00427-2

to those used to prepare MCM-41 [12,13] have also been reported for mesoporous SZ [14–17]. However, the hexagonal pore structure was lost upon calcination prior to catalytic testing [13] or has activity similar or decayed to values lower than the conventional sample after 70 min. Knowles and Hudson [18,19] reported a synthesis of mesoporous zirconia from a zirconyl chloride source with surface areas of approximately 300 m^2/g, but no catalytic activity was reported. Several authors, as well as results in our group, have found that when attempting synthesis with surfactant assisted methods, the structure collapsed upon attempts to remove the surfactant either by solvent extraction or calcination [15–17]. While attempting modifications of the synthesis reported by Knowles and Hudson [18,19], we observed that a high surface area zirconia could be formed in the absence of surfactant by refluxing a solution of zirconyl chloride and ammonium hydroxide at high pH. Here we report the results of the synthesis, characterization and activity of a higher surface area SZ catalyst prepared from the digestion of freshly precipitated hydrous zirconia under reflux at 90°C.

The *n*-butane reaction conditions and procedure utilized in this work were initially chosen to match those reported by Corma et al. [20]. Much of the current literature focuses on determining the mechanism of the reaction and its means of initiation. Typical conditions consist of low temperatures and dilute feed streams. However, the work of Corma et al. [20] was aimed at exploring the activity of the material as a function of its physical characteristics such as surface area and sulfur content. The objective of this work was to study the effect of pretreatment and reaction conditions on the activity and deactivation of the mesoporous SZ prepared by the reflux method. Reactions at temperatures of 150 and 250°C were studied. These temperatures are typical for *n*-butane and *n*-pentane isomerization over conventional SZ catalysts [2,3,7,8]. The activity of these conventional catalysts has been reported to be directly affected by pretreatment procedures [21,22]. Specifically, we report here results of the pretreatment on the activity of the mesoporous and conventional SZ catalysts. A model of the catalyst deactivation based on two sites is also presented. The effect of the addition of Pt to the catalyst was also investigated.

2. Experimental

2.1. Catalyst preparation

Details regarding the catalysts synthesis and characterization have been previously reported elsewhere [23], hence only a brief description is presented here. The conventional preparation [20] involves adding slowly 28–30% ammonia to 100 ml of a 0.4 M solution of zirconyl chloride (Aldrich) under vigorous stirring until the target pH of 10.0 was attained. Preparations at other pH values gave similar results [23] so only the sample obtained at pH = 10 was used in this work. Two methods of digestion were used. In the conventional method, the resulting slurry was stirred for 1 h at ambient temperature and then allowed to digest unstirred and covered with a watch glass for 20 h. In the new method, referred to as the reflux method, the pH adjusted precipitated slurries were stirred under reflux at 90°C during the 20 h digestion period. In both cases, the hydrous zirconia was recovered via vacuum filtration and washed with excess water to eliminate chloride ions, and then dried at 100°C.

Sulfate addition to zirconia powders to prepare active catalysts was by incipient wetness. Incipient wetness impregnation was used to control the amount of sulfate added. The catalyst was spread evenly in an evaporating dish and a sulfuric acid solution containing the desired amount of sulfate and the predetermined amount of water (distilled and de-ionized) was added drop-wise via a pipette. The catalyst was then dried at 110°C.

2.2. Catalyst characterization

The catalysts were characterized by X-ray diffraction (XRD), BET surface area, N_2 adsorption isotherms, and scanning electron microscopy (SEM) (see Ref. [23] for details).

X-ray photoelectron spectroscopy (XPS) measurements were conducted in a Kratos SAM-800 spectrometer with Mg Kα radiation. The C 1s, Zr 3d, S 2p, and O 1s, were analyzed. The reported binding energies were referenced to the C 1s binding energy of 284.6 eV. Quantification of the relative amounts of S, and Zr was performed using the peak heights and correction factors at the binding energies corresponding to their oxidized states: S^{6+} (∼170.0 eV), and Zr^{4+}

(~182.5 eV). Sulfur analysis was performed by Galbraith Laboratories (Knoxville, TN).

2.3. Catalytic activity

Catalytic activity was measured during n-C_4 and n-C_5 isomerization in a $\frac{3}{8}$ in. ID, 19 in. long quartz fixed bed reactor with a K type thermocouple located in the center of the catalyst bed. Depending on conditions 2 g or 1 g of catalyst, sieved to 20×40 mesh size was loaded in the reactor. The reactor was heated with a furnace controlled by an Omega temperature controller. The effluent lines were wrapped in heating and insulating tapes and kept at a temperature of 110°C to avoid condensation of heavier reaction products in the lines. The flow of gases was controlled by electronic mass flow controllers (Brooks 5850). The catalyst was activated in situ by heating to various temperatures and then cooling to reaction temperature under a dry stream of nitrogen (20 cc/min) or streams containing controlled amounts of water vapor.

For n-C_4 isomerization, the reaction was conducted at a WHSV of 1.5–3.0 h^{-1} using 20 ml/min 99% n-butane and a catalyst bed of 2 or 1 g. Impurities in the feed consisted of isobutane and trace amounts of propane. The reactor feed or effluent was analyzed using a Varian 3300 gas chromatograph using a 7 ft 0.19% picric acid on Graphpac packed column (Alltech) and a FID detector. The column was held at 50°C for 4 min and then heated at a rate of 25°C/min to a final temperature of 100°C and maintained until all C_5 species were eluted.

For n-C_5 isomerization He, flowing at a rate of 20 cc/min, was passed through a saturator containing n-pentane maintained at 0°C by an ice bath. These conditions result in an n-pentane partial pressure of approximately 0.2 atm and a WHSV of 0.6 h^{-1}. The reaction was run for 1 h and samples were taken for every 5 min after the reaction was initiated. The same analytical system was used for the n-pentane isomerization reaction but the column was held at 100°C.

Air, nitrogen, and oxygen were first passed through an Alltech gas purifier consisting of $CaSO_4$ and molecular sieve 5A columns in series. Ultrahigh purity helium was used as the carrier gas and as a diluent gas for reaction studies and was passed through an Alltech Oxygen Trap. n-Butane was employed in its received form.

Table 1
Texture and XRD results for SZ catalysts

	Conventional	Reflux
Total surface area (m^2/g)	117	269
Average pore diameter	43.7	66.6
Total pore volume (cc/g)	0.13	0.45
Mesopore pore volume	0.098	0.400
Micropore pore volume	0.031	0.071
XRD	Tetragonal reflection	Broad, low-intensity reflection

3. Results

3.1. Catalysts characterization

A detailed presentation of the texture and diffraction properties of the catalysts has been presented in Ref. [23], and the main results are summarized in Table 1. Briefly the mesoporous material prepared by the reflux method exhibits surface area in excess of 500 m^2/g prior to calcination, and in excess of 200 m^2/g after calcination. The XRD diffraction patterns of the mesoporous material contained only broad low-intensity reflections in place of the distinct (1 1 1) reflection of tetragonal zirconia characteristic of the conventional sample. The pore volume is larger by a factor of three for the mesoporous materials versus the conventional material, and the average pore diameter is larger by a factor of two in the mesoporous material. SEM micrographs show two distinct morphologies: the conventional material consists of large particles whereas the mesoporous material exhibits a morphology showing smaller particles.

3.2. Catalysts activity

3.2.1. n-Butane isomerization

Activity measurements were performed to compare the activity of the mesoporous catalyst with the conventionally prepared material. At first, reaction conditions were extended from the work of Corma et al. [20]. In these initial experiments, 2 g of catalyst was loaded into the reactor and activated by calcining in situ to 550°C for 3 h. The catalyst was cooled to the reaction temperature of 250°C in 1 h under 20 cc/min dry N_2 flow. The reaction was conducted at a WHSV of 1.5 h^{-1} by passing a stream of n-butane at 20 cc/min through the reactor. Fig. 1a shows the

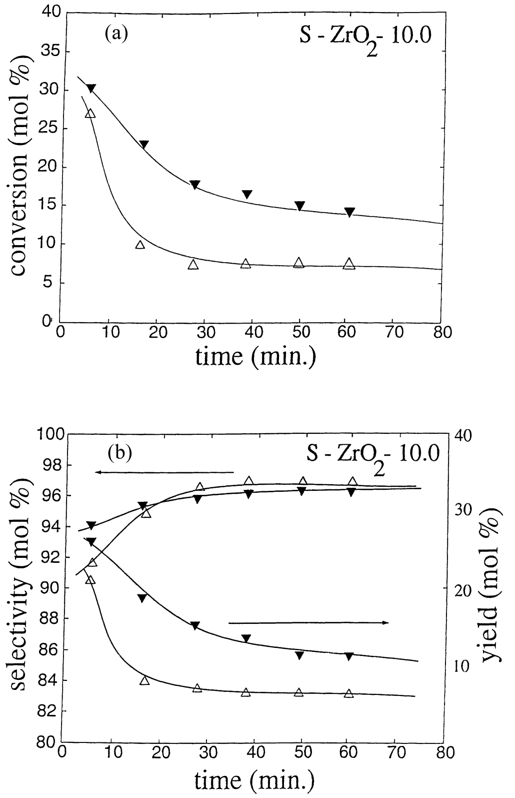

Fig. 1. (a) *n*-Butane conversion versus time, (b) isobutane selectivity and yield for a conventional catalyst and mesoporous catalyst. Reaction temperature = 250°C, WHSV = $1.5\,h^{-1}$.

conversion versus time on stream for the conventional and mesoporous catalyst prepared at pH 10. The data of the conventionally prepared catalyst agree very well with the published data of Corma et al. [20]. The initial conversion ($t = 5$ min) of around 30% decays to approximately 10% after 1 h on stream. The mesoporous catalyst is more active for *n*-butane isomerization achieving approximately a 50% higher activity after 1 h. The isobutane selectivity of the mesoporous catalyst is comparable to the conventional catalyst (Fig. 1b). However, higher yields of isobutane are still realized due to the increased conversion. The results obtained at pH of 8.4, 9, and 11.4 are similar to those shown in Fig. 1. The *i*-butane/*n*-butane ratio obtained at 5 min time on stream were 0.3 for the conventional and 0.35 for the mesoporous catalysts. These ratios are lower than the thermodynamic equilibrium ratio of the two components equal to 1.4, showing that the experimental reaction results are not limited by thermodynamic constraints.

These preliminary activity results clearly show that under these conditions the mesoporous material is catalytically active for the isomerization of *n*-butane. However, the XRD results of the mesoporous catalysts [23] show no sharp peaks and only a broad hump indicating that they do not have long-range order tetragonal phase crystallinity. The tetragonal phase has been previously associated with the activity of conventionally prepared SZ [24,25]. The results obtained on the mesoporous SZ indicate that either the crystallites are too small to be seen in the XRD results, or that long-range order tetragonal crystallinity is not a requirement for catalytic activity on the SZ catalysts. The crystallization of the zirconia from an amorphous state to the tetragonal phase on conventional catalysts could simply be a consequence of the preparation method of the catalyst, i.e. the calcination step, instead of a requirement for catalytic activity.

For these samples, sulfur was introduced by the immersion method. The sulfur content of the conventional catalyst was 3.24 wt.% sulfur, while the mesoporous material contained 4.45 wt.% S (all % refer to atomic weight). The mesoporous catalyst, with over twice the surface area compared to the conventional material prior to sulfating and calcining, exhibits only an increase of approximately 37% in sulfur content from the identical immersion treatment in sulfuric acid. To test catalysts with similar sulfur content, a new set of catalyst samples was prepared using incipient wetness. The same nominal amount of sulfur of 4.4% was loaded onto the conventional and mesoporous catalysts. SZ catalysts described in the literature typically contain 1–5 wt.% S [2,3,26]. After activation by calcination at 550°C in air for 3 h, sulfur analysis indicated a loading of 3.7 wt.% for the conventional material and 3.3 wt.% for the mesoporous material. These catalysts were used in the subsequent studies.

3.2.1.1. Regeneration of sulfated zirconia catalysts.

The presence of water on conventional SZ catalysts has been suggested to contribute to its unique activity at low reaction temperatures [27,28]. We observed a similar hydration effect on the mesoporous catalysts upon regeneration after reaction at 150°C. Li and Gonzalez [29] have determined that calcining a deactivated conventional SZ catalyst in oxygen at 450°C

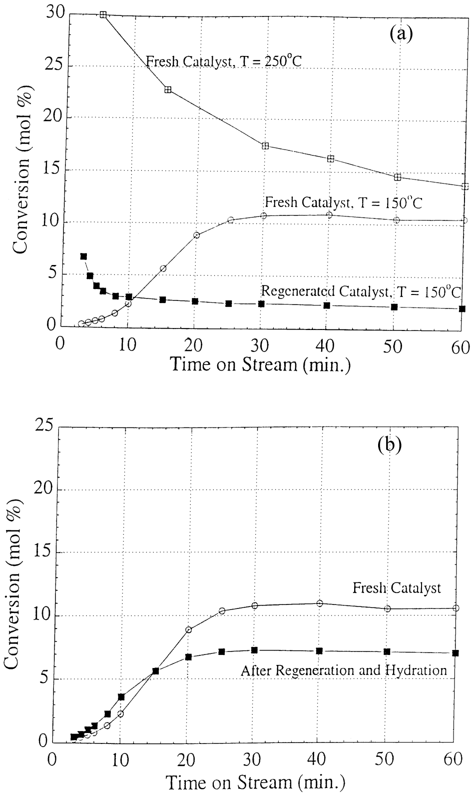

Fig. 2. Fresh mesoporous catalyst and regenerated mesoporous catalyst at $T = 150°C$: (a) after calcining in situ under oxygen at 500°C, (b) after calcining under oxygen at 500°C and rehydration. The fresh mesoporous catalyst at $T = 250°C$ is also shown. WHSV $= 1.5\,h^{-1}$.

is critical in regaining the original activity. Calcining in nitrogen to even a higher temperature of 550°C did not regain the activity of the fresh catalyst. Fig. 2a shows conversion versus time results at 150°C for the mesoporous catalysts pretreated at 400°C. The data from Fig. 1 at 250°C is included for comparison. The conversion versus time results for both the fresh mesoporous catalyst and the regenerated catalyst are quite different at 150°C than at 250°C. After reaction at 150°C, the mesoporous catalyst was regenerated by heating it in oxygen from the reaction temperature to 500°C in 1 h, and maintaining this temperature for an additional hour. Afterwards, the catalyst was cooled back to 150°C and the reaction procedure was repeated. The effluent of the reactor was monitored during regeneration in an IR cell employed as a detector, which permitted to follow CO_2 and H_2O evolution. A plot of the intensity of the strongest peak of each species (CO_2 and H_2O) and the reactor temperature versus the heating time (not shown) show that the removal of carbonaceous deposits from the catalyst as CO_2 starts at about 350°C and it reaches a maximum at 500°C. Regeneration is complete after 1 h at 500°C. Water is also evident during regeneration, and its presence could be attributed to either the combustion of the partially hydrogenated carbonaceous surface species or further dehydration of the catalyst's surface.

The conversion of the fresh catalyst at 150°C shows a long induction period at this temperature, unlike the high conversion followed by rapid deactivation observed at 250°C (Fig. 1). Such induction periods have been observed on conventional SZ catalysts at low reaction temperatures [30]. The induction period has been hypothesized to be caused by a build up of reaction intermediates on the catalyst surface [31]. It is important to note the difference in activity profiles between the fresh catalyst and its regenerated form at 150°C. The regeneration procedure in oxygen leads to a change in the catalyst's activity profile. Instead of an induction period, the regenerated catalyst rapidly deactivates to a much lower activity than the fresh catalyst. While higher initial activity is attained in the regenerated catalyst, its long term activity is lower.

An additional regeneration experiment was run in which the mesoporous catalyst, after the regeneration step at 500°C in oxygen and cooling to room temperature, was exposed to a stream of nitrogen that passed through a saturator containing water at room temperature for approximately 3 h. The original experimental reaction procedure, including pretreatment heating to 400°C, was repeated after this hydration step. Fig. 2b shows that the activity profile at 150°C was regained, although not completely, after regeneration and hydration. It follows that rehydration of the catalyst is necessary after a regeneration procedure in order to regain its original activity. Regeneration at 500°C and direct cooling to the reaction temperature clearly leads to a rapidly deactivating and thus less active catalyst than regenerating at 500°C followed by exposure to water. The work by Li and Gonzalez [29] shows that the initial activity of a conventional SZ can be regained after regeneration, their regenerated catalyst was exposed to the atmosphere overnight, presumably as a means of rehydrating the catalyst. However, these authors do not explicitly indicate the necessity of this hydration step in order to regain the same catalytic activity.

To verify the effect of hydration on pretreatment, experiments were conducted on the mesoporous material using the same catalyst bed at 200 and 250°C after calcining in oxygen at 500°C, and calcining in oxygen at 500°C followed by a hydration step. In both cases, the hydrated forms are more active and the induction period observed at the lower reaction temperatures is not present at 200 and 250°C. Only deactivation is apparent as the induction period happens much faster at these elevated temperatures. Similar observations have been reported for *n*-butane isomerization over conventional SZ [29,32]. These results indicate the unique effect of water on the catalyst's activity. In the subsequent comparisons between the mesoporous and conventional catalysts, a regeneration procedure of calcining in oxygen to remove the carbonaceous deposits followed by a hydration step was employed.

3.2.1.2. Effect of pretreatment procedure. Dumesic and co-workers [33,34] and Song and Kidd [22] have independently examined the effect of water content on the activity of conventional SZ catalysts in *n*-butane isomerization. By varying the pretreatment drying temperature on conventional SZ catalysts prior to reaction to obtain various states of hydration these researchers reported that an intermediate drying temperature was necessary to achieve maximum activity.

Fig. 3 shows the results of thermogravimetric analysis experiments similar to that of Dumesic and co-workers [33,34] and Song and Kidd [22]. However, unlike the data of these authors, the effects of cooling the catalyst are also shown. Results are shown for both the conventional and the mesoporous catalyst with similar sulfur contents. The amount of water on the solids in the temperature range from room temperature to 500°C is reported as μmol of water per gram of catalyst. These values were calculated from the difference of the weights of the catalyst at a certain temperature to its weight at 500°C. Each point was allowed to equilibrate for 1 h so that a constant weight was obtained. Extra dry nitrogen, containing only about 8 ppm water, was passed through an Alltech dryer containing calcium sulfate and zeolite 5A prior to passing it over the sample.

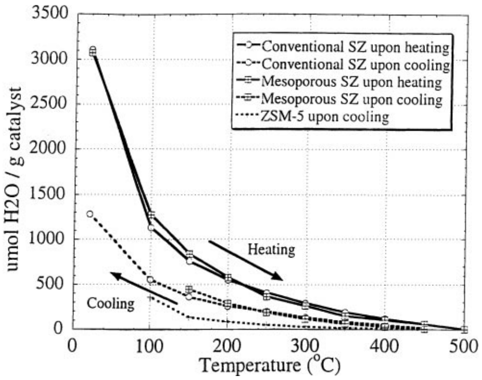

Fig. 3. Thermogravimetric analysis of conventional and mesoporous SZ during heating and cooling. Water adsorption onto zeolite ZSM-5 upon cooling is also shown.

Upon heating, water is lost as previously reported. The values of water content upon heating are higher than those reported by Kobe et al. [34] for a commercial MEI catalyst. However, they are similar to those reported by Song and Kidd [22] who prepared their own conventional catalysts in the same manner as the catalysts used in the experiments displayed in Fig. 1. Upon cooling, there is a significant amount of water that is re-adsorbed onto the surface, especially in the 100–250°C range where reactions on SZ are commonly studied. Interestingly, even though the mesoporous catalyst has over twice the surface area of the conventional catalyst, they both show almost identical water desorption and adsorption profiles. The weight gain attributed to water re-adsorption for a ZSM-5 zeolite, under identical conditions is shown for comparison.

To investigate the effect of cooling and thus water uptake, two different cooling periods were used after the catalyst was first pretreated at 400°C in a dried nitrogen stream passing through a dryer (Alltech). In the first case the reaction was run within 20 min after cooling to 150°C from the pretreatment temperature (rapid cool). In the second case the catalyst was cooled slowly over a period of 1 h and maintained at the reaction temperature of 150°C for 1 h prior to reaction under the nitrogen flow (slow cool). The rapidly cooled catalyst has a high activity initially and deactivates within 10 min to a lower, more sustained activity. However, the catalyst that was equilibrated with the dry nitrogen stream prior to reaction instead, shows much lower initial activity and an induction period prior to a sustained residual activity that is only slightly lower than the rapidly cooled case. These results indicate that the re-adsorption of water significantly affects the active sites responsible for the activity at early times on stream on the conventional catalyst. The results are consistent with the effects of adsorbed water observed in the regeneration studies of the mesoporous catalyst (Fig. 2). Thus, it is evident that the pretreatment temperature and the rate of cooling are important and must be well defined to obtain reproducible results. The reactions must be run on equilibrated catalysts that have achieved steady-state levels of hydration thus insuring that the active state of the catalyst is not changing when reaction measurements are initiated.

The effect of the pretreatment drying temperature on the mesoporous catalyst in comparison to the conventional catalysts was examined next for the reaction temperature of 150°C at WHSV of $3\,h^{-1}$. The optimum pretreatment temperature of 300°C agrees with the published reports for the conventionally prepared catalysts. The results differ in that induction periods are observed rather than just deactivation as reported by Kobe et al. [33,34]. For the mesoporous catalyst, a higher temperature of 400°C, instead of 300°C for the conventional catalyst, leads to the higher activity. Pretreatment drying at 500°C was also performed and led to lower activity than that obtained when the catalyst was pretreated at 400°C. These are clearly hydration effects since the two catalysts have similar sulfur contents. Despite having over twice the surface area, the maximum conversion attained by the mesoporous catalyst at 150°C, approximately 2.5%, is significantly lower than the maximum conversion obtained over the conventional catalyst, approximately 8.0%. In addition, the induction period on the mesoporous catalyst is much longer compared to that on the conventional catalyst.

The optimal pretreatment drying temperature for each catalyst was used to evaluate their activity at the reaction temperature of 250°C used in the preliminary activity studies. Likewise, the conventional catalyst was dried at its optimum pretreatment drying temperature of 300°C. The mesoporous catalyst was also dried at the optimum temperature for the conventional catalyst (300°C) as well as at 400°C. Fig. 4 shows that both conventional and mesoporous catalysts with similar sulfur content have no induction period at this higher temperature, and deactivate as in Fig. 1. Fig. 4 shows that, in contrast to the results in Fig. 1, the conventional catalyst dried at 300°C exhibits *similar* activity as the mesoporous catalyst dried at 300 and 400°C. The mesoporous catalysts dried at 400°C shows only 1–2% higher conversion than the other two catalysts. Isobutane selectivities are similar with the conventional catalyst being incrementally (1–2%) higher. A pretreatment temperature of 300°C, while optimal for the conventional catalyst, results in a slightly less active mesoporous catalyst. Similar results on a mesoporous catalysts with 4.4% S shows that the increased sulfur content does not lead to a significant increase in conversion at the optimal pretreatment conditions. The hydration effects appear to be more important than sulfur content (Fig. 1).

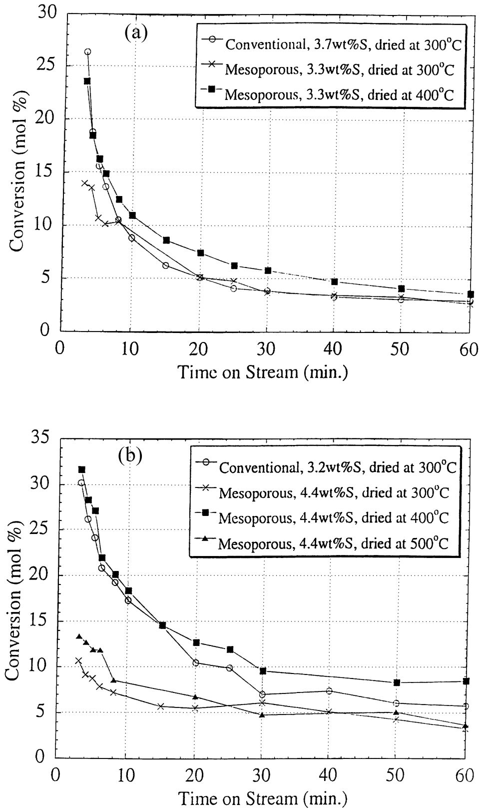

Fig. 4. Conversion of *n*-butane at $T = 250°C$ over both conventional and mesoporous catalysts pretreated at their optimum drying temperatures, 300 and 400°C.

3.2.2. *n-Pentane isomerization*

3.2.2.1. Unpromoted sulfated zirconia. The isomerization of *n*-pentane was first studied on the conven-

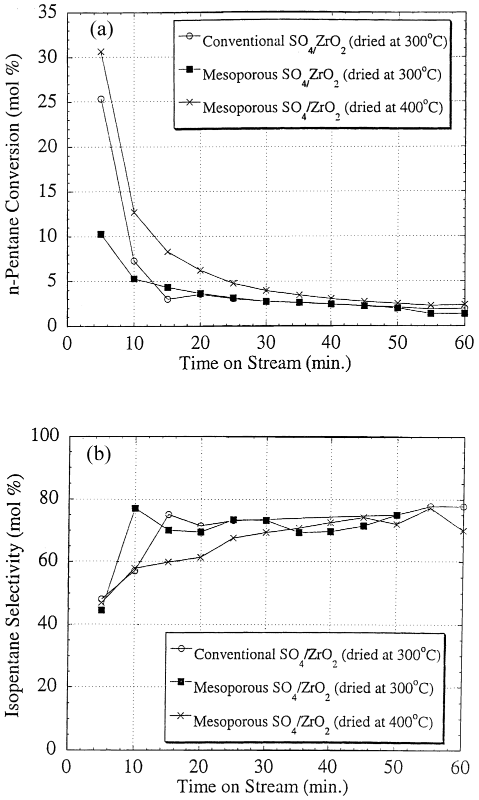

Fig. 5. (a) Conversion of *n*-pentane and (b) selectivity to isopentane versus time on stream on conventional and mesoporous SZ. Reaction temperature = 250°C.

tional and mesoporous catalysts prepared with 4 wt.% sulfur loadings. The pretreatment temperatures found to be optimal for *n*-butane isomerization [23] were used: 300°C for the conventional catalyst and 400°C for the mesoporous catalyst. In addition, the mesoporous catalyst was also pretreated at 300°C. The results are plotted in Fig. 5a and b in terms of *n*-pentane conversion (5a) and selectivity to isopentane (5b) versus time on stream. Both the mesoporous and conventional SZ catalysts are active for *n*-pentane isomerization. As in the case of *n*-butane isomerization, initial conversion is high but then the catalysts quickly deactivate to a much lower conversion within 20 min. When the mesoporous catalyst is pretreated at the same temperature as the conventional catalyst, 300°C, it yields a lower conversion at 5 min on stream as compared to when it is pretreated at 400°C. Selectivities to isopentane increase with decreasing conversion in all these runs and level off at approximately 75%.

The mesoporous catalyst exhibits a higher activity for *n*-pentane isomerization compared to the conventional catalyst, when pretreated at 400°C. The *n*-pentane conversion on the mesoporous catalyst is higher than that on the conventional catalyst by roughly a factor of two up to 20 min on stream. Thereafter, the conversion obtained on the two catalysts begins to converge and the differences in conversion appear only slight after 1 h. After less than 15 min on stream, both conventional and mesoporous catalysts dried at 300°C yield similar conversion. In the *n*-butane isomerization reaction, the mesoporous catalyst was much less active than the conventional catalyst when pretreated at 300°C.

3.2.2.2. Platinum promoted sulfated zirconia. Although the mesoporous catalyst is initially more active the rapidly deactivating nature of the SZ catalysts negate the expected benefit of increased surface area of the mesoporous catalysts. It was therefore decided to study the reaction in the presence of Pt, which has been used as a stabilizing promoter during *n*-butane isomerization [35], to investigate if the mesoporous catalyst could sustain its increased initial activity.

Conventional and mesoporous SZ catalysts were both prepared with 4 wt.% sulfur loading as in previous experiments. Platinum was loaded onto the catalysts via the incipient wetness technique using a solution of H_2PtCl_6. An amount corresponding to 1 wt.% Pt was added and the catalysts were then calcined at 550°C, in flowing air for 3 h. The same reaction conditions were used as previously, except for a reduction step in which the catalyst was exposed to a stream of 20 cc/min hydrogen at the reaction temperature after pretreatment drying and prior to reaction. Also, hydrogen was used as the carrier gas instead of He. Reactions were run on both catalysts after pretreatment at their optimal drying conditions and pretreatment was also performed at 500°C to investigate its effect with platinum present. Fig. 6a and b show the results for these experiments for the conventional and mesoporous catalysts, respectively.

The results are quite different for the Pt loaded catalyst from those of the unpromoted catalysts. In the case of the Pt promoted catalysts, on both mesoporous and conventional catalysts, the rapid initial deactivation is

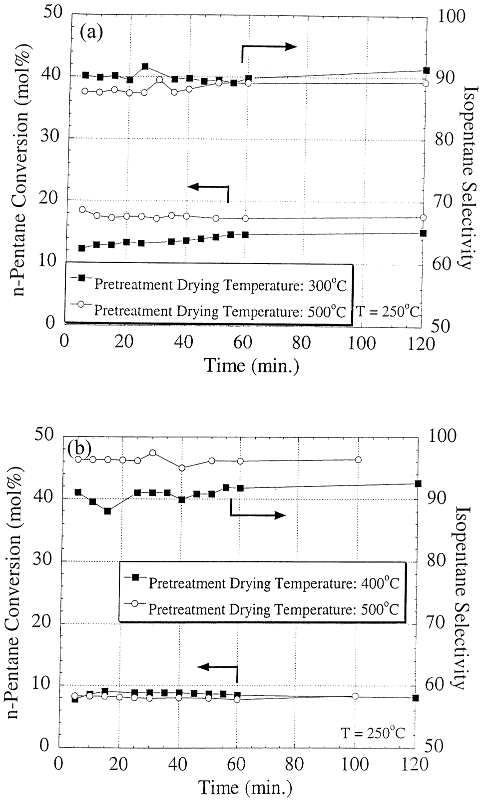

Fig. 6. Conversion of *n*-pentane and selectivity to isopentane on platinum promoted (a)conventional SZ and (b) mesoporous SZ pretreated at different temperatures. Reaction temperature = 250°C.

not detected. Instead the initial activity is lower but it is almost constant conversion throughout the run. On the conventional catalyst, pretreatment at 500°C leads to the more active catalyst while on the mesoporous catalyst the activities are similar between the two pretreatment temperatures.

The effect of amount of Pt promoter concentration on the mesoporous catalyst was also investigated since the mesoporous catalyst has twice the surface area of the conventional catalyst. A mesoporous catalyst with the same sulfur loading of 4 and a 2 wt.% Pt loading was prepared and its activity measured after a pretreatment drying temperature of 500°C. The results obtained (not shown) at the higher Pt did not result in an increase in conversion, although the selectivity to isopentane increased from around 95 to 100%. An extended reduction at 300°C led to a slight increase in the activity of the catalyst and reduction at higher temperatures for extended periods of time produced even less active catalysts.

To study the effect of sulfur loading mesoporous catalysts with sulfur loadings of 2, 3, 4, 6, and 10 wt.% were prepared by adding the necessary amount of 0.5 M H_2SO_4 to incipient wetness on the hydrous zirconias. All of the catalysts with varying sulfur loadings were prepared with 1 wt.% Pt. At low sulfur loadings of less than 2%, the surface areas measure around 100 and 300 m^2/g for the conventional and mesoporous catalysts, respectively. For S loadings of 3 and 4% the areas are 330 and 260 m^2/g for the mesoporous catalysts and 100 and 65 m^2/g for the conventional catalyst, respectively. The trend is that the BET areas decrease with increased sulfur loading. Similar results on the effect of S loading on the surface area were reported by Farcasiu et al. [25] on conventional SZ catalysts. XRD patterns, indicative of the tetragonal phase of zirconia (not shown here), show that the extent of crystallization decreases in the conventional catalyst with increasing S loading, in agreement with literature reports [36,37]. The XRD patterns of all of the mesoporous catalysts prepared with varying sulfur content show only a broad hump in the location of the (1 1 1) tetragonal phase. This indicates that either the crystallites are very small not detectable by XRD or that they exhibit short-range order. The higher sulfur loading does not have an effect as extensive on the crystal structure as was seen in the conventional catalysts. Due to their means of preparation, the mesoporous catalysts crystallize to a lesser extent than their conventional counterparts. Since the addition of the sulfate decreases any crystallization that does occur, these XRD patterns all appear very similar. The decrease in extent of crystallization with increasing sulfur content is expected based on the results of the conventional catalyst. Only one peak corresponding to platinum species is observed on the 4 wt.% sulfur catalyst prepared by adding the platinum prior to calcination at 550°C.

XPS was used to obtain S/Zr and Pt/Zr atomic ratios of elements on the surface of the catalysts. These ratios are summarized in Table 2 for the conventional and mesoporous catalysts, respectively, with 3 and 4% S. In the case of 3 wt.% S, the S/Zr ratio decreases slightly from the conventional to the mesoporous catalyst, from 0.091 to 0.078. However, for a loading of 4 wt.% S, this ratio increases from 0.100 to 0.145.

Table 2
S/Zr and Pt/Zr atomic ratios as determined by XPS on the conventional and mesoporous catalysts at similar sulfur loadings (Pt added after calcination)

	3% S conventional	3% S mesoporous	4% S conventional	4% S mesoporous
S/Zr	0.091	0.078	0.1	0.145
Pt/Zr	0.013	0.011	0.015	0.013
C_5 conversion (%)	16	15.8	11	13.5

The addition of platinum either prior to or after calcination at 550°C does not affect this ratio to a significant extent. The Pt/Zr ratios on the mesoporous catalysts are approximately constant for all the catalysts, at a value of around 0.012. Thus, XPS did not detect a significantly higher fraction of the Pt on the surface of the catalysts on which Pt was placed after calcination at 550°C.

The Pt/Zr ratios are similar for all the catalysts listed in Table 2. The mesoporous catalyst contains more surface sulfur and surface platinum species due to its higher surface area. Thus the conventional catalysts with identical sulfur loadings as the mesoporous catalysts must possess a higher fraction of the sulfate species below the surface.

The C_5 conversion at 250°C after 1 h on stream for the catalysts with 3 and 4 wt.% S and 1% Pt added after calcination at 550°C are also listed in Table 2. The conversion is roughly constant throughout the run as shown in Fig. 6 and the selectivity varied from 96 to 99% on these catalysts. The conversion is similar for the 3% S loaded mesoporous and conventional catalysts, and slightly higher on the mesoporous form for the 4% S loaded catalysts. So it appears that the increase in sulfur loading does not correlate with activity.

4. Discussion

The discussion will focus first on rationalizing the *n*-butane isomerization results, followed by discussion of the results on *n*-pentane isomerization.

One of the factors that affected the activity of both the mesoporous and conventional catalysts is the water content. The active sites on SZ catalysts have been proposed to be a combination of Lewis and Bronsted acid sites located around the sulfate groups that are bonded to the zirconia surface. The relative amounts of these two acid sites have been determined to be a function of the extent of hydration on the catalyst surface. The data of Song and Kidd [22] show that the concentration of Bronsted acid sites decreases with increasing drying temperature while the population of Lewis acid sites increases. The most active catalyst was found by Song and Kidd [22] to possess roughly a one to one ratio of the two types of acid sites after drying at an intermediate temperature (ca. 300°C). Both types of acid sites have been reported to contribute to the catalyst's activity in *n*-butane isomerization. Pinna et al. [36] have illustrated that the Lewis acid sites play a dominant role in the catalytic activity for *n*-butane isomerization. The involvement of Bronsted acid sites in *n*-butane isomerization has been verified by Xu and Sachtler [37]. Yaluris et al. [21] have suggested the Lewis acid sites may be involved in generating the initial high activity observed in *n*-butane isomerization, but determined that Bronsted acidity is a requirement for longer term activity.

The results of the regeneration studies on the mesoporous catalysts can also be explained by a two site mechanism consisting of both Lewis and Bronsted acid sites formed by two states of hydration. Song and Kidd [22] showed that a catalyst treated at high temperature increases its Lewis acidity at the cost of its Bronsted acidity resulting in a higher initial activity but rapid deactivation to a lower residual activity. Accordingly, the rehydration step after the regeneration procedure that regains the initial activity profile is necessary to restore the original ratio of Bronsted to Lewis acid sites on the surface. The two-site model is also consistent with the observation that an optimal state of hydration exists for both the conventional and mesoporous catalysts that results in their highest activity. According to the TGA results obtained on both catalysts, identical amounts of water were desorbed during heating of these two catalysts. Thus, the higher pretreatment drying temperature for the mesoporous catalysts shows that a higher extent of dehydration is necessary to obtain its optimal activity. Based on two active sites model, this suggests that there are less Lewis acid sites per square meter on the surface of the mesoporous catalyst, and that the higher drying temperature is necessary to expose these sites. An excessively high pretreatment temperature on the mesoporous catalyst decreases activity, presumably due to loss of the Bronsted acid sites. Comparison of the two catalysts pretreated at the same temperature does not compare the two in their most active state. In addition, the catalysts must be allowed to equilibrate in the cooling gas stream to further insure that comparisons between the catalysts as well as kinetic activity measurements are made with a catalyst surface that is in equilibrium state with respect to water content.

Lewis acid sites on SZ have been described as coordinatively unsaturated Zr^{4+} centers [37,38]. Previously, we proposed that during the preparation of the mesoporous catalysts [23] a higher extent of polymerization of the zirconia network occurred, which could effectively decrease the amount of coordinatively unsaturated Zr^{4+} centers. It is possible that the preparative route to prepare mesoporous zirconia, although effective in obtaining a higher surface area material, is counterproductive in creating a catalytically active material. A higher concentration of fully coordinated Zr^{4+} cations, and thus fewer Lewis acid sites, may result from the reflux procedure used to prepare the mesoporous catalyst.

The induction period, which has been attributed to a build up of reaction intermediates on the surface, appears to be more important at low temperatures such as 150°C than at 250°C [28,31]. These reaction intermediates subsequently react with one another via a bimolecular mechanism involving a C_8 carbocation intermediate to form isobutane. The induction period and catalyst decay overlap and result in a maximum in conversion. The longer induction period observed on the mesoporous catalyst at 150°C as compared to the conventional catalyst could be due to the high surface area mesoporous SZ. In the mesoporous material, assuming fewer unsaturated Zr^{4+} centers exist, the active sites are not as close to one another as they are on the conventional catalyst. The slower build up of surface intermediates appears to be negated by catalyst deactivation occurring at a similar rate, leading to the lower conversion as compared to the conventional catalyst at 150°C.

The other factor involved in the formation of active sites is the sulfur content since the Lewis and Bronsted acid sites are located around the sulfate groups on the catalyst surface. Therefore, the sulfate loading should correlate to an extent to the amount of acid sites on the catalyst and with the catalysts activity. XPS results of the conventional and mesoporous catalysts with similar sulfate content, 3.7 wt.% ($120\,m^2/g$) and 3.3 wt.% ($300\,m^2/g$), respectively, show similar S/Zr ratios of 0.084 on the conventional SZ, and 0.081 on the mesoporous catalyst. This indicates that in the mesoporous catalyst the sulfate species are mainly on the surface and there are more of them in the mesoporous catalysts than in the conventional catalyst due to its higher surface area. Even though, according to XPS results the higher surface area, mesoporous catalysts possess more than twice the surface sulfate groups per gram of catalyst, the large increase in surface sulfate species does not lead to proportional increases in activity in *n*-butane isomerization. Farcaciu et al. [25] has suggested that active sites might also be formed on the conventional SZ catalysts by inductive effects of sulfate species below the surface. It is possible that the higher amount of sulfate groups that resides in the subsurface of the conventional catalyst as compared to the mesoporous catalyst creates an increased number of surface active sites not directly related to the surface sulfate species. Even though more surface sulfur is exposed in the case of the mesoporous catalyst, a higher concentration of active sites per square meter of catalyst surface might be present on the conventional catalyst due to the presence of subsurface species.

The above arguments supporting a two-site model were taken a step forward and a detailed model of the reaction was developed incorporating two sites and a bimolecular mechanism. A schematic diagram of the reaction pathway is shown in Fig. 7. Details of the mathematical treatment are beyond the scope of this paper and will be published separately although details are available in Ref. [39]. The reaction pathway incorporates S_1 and S_2 sites representing Lewis and Bronsted sites and the bimolecular reaction between adsorbed butane in both S_1 and S_2 sites which determines the initial activity as well as the bimolecular reaction on S_2 sites which determines the residual activity. In addition, adsorbed butane forms irreversibly adsorbed carbonaceous species that deactivate the surfaces by blocking available sites. The reaction

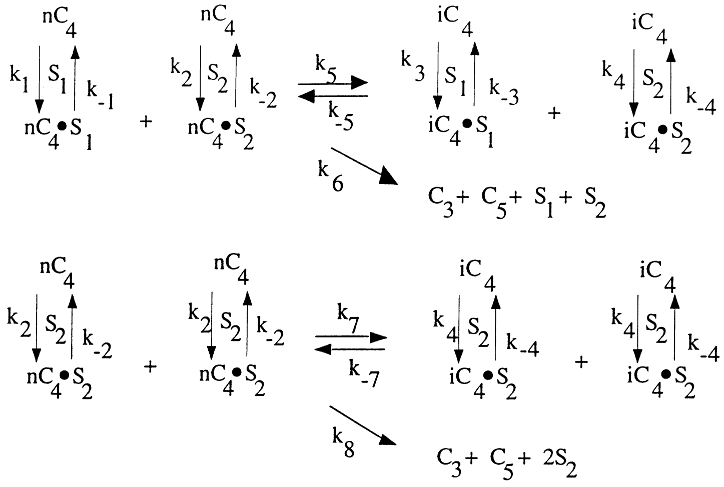

Fig. 7. Schematic diagram for a two-site model. S_1: Lewis sites and S_2: Bronsted sites.

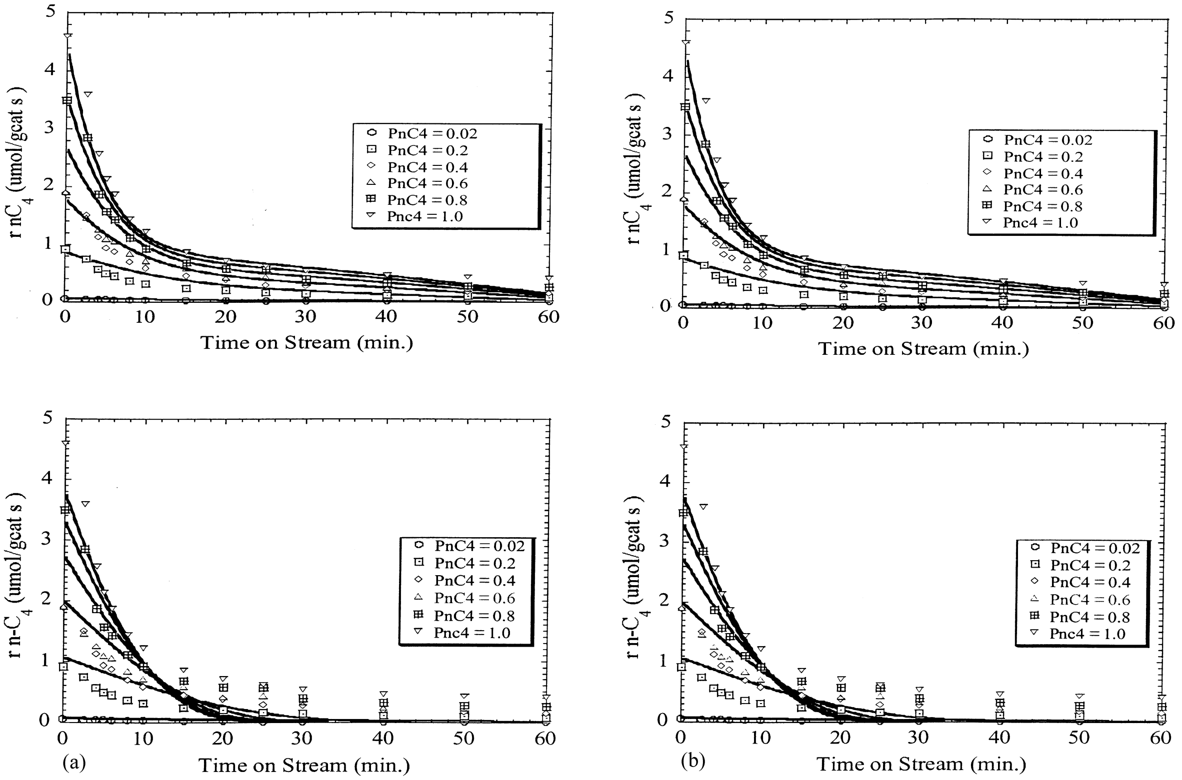

Fig. 8. Comparison of experimental data to deactivation modeling results: (a) two-site independent model, (b) one-site model.

scheme was incorporated in a kinetic model that was solved for an isothermal plug flow reactor for the gas phase combined with steady-state surface balances for the solid catalyst. In addition to the reaction scheme presented in Fig. 7 other reaction pathways involving a single site, and the two sites with independent reaction in S_1 and S_2 sites, were also considered. Fig. 8a shows that the two site kinetic model fits well the experimental kinetic results in terms of deactivation rates versus time on stream. The single-site model did not agree with the results and the two-site model with independent activity rendered a higher residual of the least-squares between model and experimental results as shown in Fig. 8b. In addition, the two-site model accounts for the effect of the addition of Pt, which lowered the initial activity and resulted in an almost constant activity as it also occurs in *n*-pentane isomerization. For the Pt loaded SZ, by eliminating the S_1 sites from the model it was possible to fit very well the model to the experimental results (not shown). While kinetic modeling is not a proof that the kinetic pathway presented in Fig. 7 represents the actual reaction mechanism, it shows that the two-site model is consistent with the experimental observations.

The two-site model previously discussed for *n*-butane isomerization also explains the trends observed during *n*-pentane isomerization although in this case the reaction is known to be unimolecular and thus it must proceed independently in each site. The *n*-C_5 isomerization reaction exhibits the same trends regarding pretreatment and deactivation than the *n*-C_4 reaction. The initial activity of the unpromoted mesoporous catalyst was higher at 400°C than the conventional catalysts. In the case of the Pt promoted catalyst, the rapid initial deactivation is not observed but the activity remains constant throughout the run. Matsuhashi et al. [35] have reported that Lewis acid sites are converted into Bronsted acid sites upon exposure to hydrogen in the presence of platinum. If the high activity at early times on stream on the unpromoted catalyst was most likely the result of Lewis acid sites, the data in Fig. 6 with lower conversions are in agreement with these reports. Thus, the non-deactivating reactions on the platinum promoted catalysts appear to occur only on the Bronsted acid sites, although they may be initiated in some manner by residual Lewis sites. The lower initial activity is not a result of an inhibition of the reaction mechanism because, as previously discussed, this reaction is monomolecular in nature

5. Conclusions

The activity of the mesoporous and conventional SZ catalysts is a combined effect of the degree of hydration and the active sulfate species that generate the active acid sites. The experimental trends can be explained both qualitatively and quantitatively by a two-site model consisting of Lewis sites (initial activity), and Bronsted sites (residual activity). Optimal activity can be obtained on mesoporous SZ by heating to an intermediate pretreatment drying temperature prior to reaction. This pretreatment temperature is higher than that required for conventional SZ. Possible reasons for these activity results on the mesoporous catalyst as compared to the conventional catalyst are that a different degree of hydration is needed to establish the optimal population of Lewis and Bronsted acid sites resulting from a lower amount of subsurface sulfate species, or a combination of both.

Unpromoted mesoporous SZ is shown to attain higher initial conversions of *n*-pentane to isopentane than conventional SZ. Pretreament effects and deactivation similar to those observed for *n*-butane isomerization were also found during *n*-pentane isomerization on unpromoted SZ. The two-site model argued to be valid for *n*-C_4 isomerization also explains the trends in pretreatment observed in *n*-C_5 isomerization, although in this case the reaction is monomolecular and proceeds independently in the two sites.

The addition of 1 wt.% platinum slows the deactivation rate over both forms of SZ. However, the platinum promoted catalysts pretreated in hydrogen do not exhibit the higher initial activity of the unpromoted catalyst, instead it shows a constant residual activity throughout the run. The Pt promoted mesoporous SZ has similar activity than the conventional catalysts indicating that the number of residual sites are the same on both catalysts.

Mesoporous SZ may serve well in other applications as a support for other catalytically active components or in reactions involving larger hydrocarbon molecules to decrease diffusional effects. In addition, loading mesoporous SZ with promoters such as Fe and Mn, used with conventional SZ, may lead to higher activity. The increased surface area could support larger loadings of these promoters that may prove beneficial in hydrocarbon conversion reactions.

Acknowledgements

The partial financial support for MR from the Texaco and DuPont fellowships funded by the Texaco and DuPont Foundations are gratefully acknowledged.

References

[1] V.C.F. Holm, G.C. Bailey, U.S. Patent 3,032,599 (1962), to Phillips Petroleum.
[2] B.H. Davis, R.A. Keogh, R. Srinivasan, Catal. Today 20 (1994) 219.
[3] X. Song, A. Sayari, Catal. Rev. Sci. Eng. 38 (1996) 329.
[4] M. Hino, S. Kobayashi, K. Arata, J. Am. Chem. Soc. 101 (1979) 6439.
[5] R.A. Comelli, C.R. Vera, J.M. Parera, J. Catal. 151 (1995) 96.
[6] H. Liu, V. Adeeva, G.D. Lei, W.M.H. Sachtler, J. Mol. Catal. A 100 (1995) 35.
[7] S. Rezgui, R.E. Jentoft, B.C. Gates, Catal. Lett. 51 (1998) 229.
[8] T. Tatsumi, H. Matsuhashi, K. Arata, Bull. Chem. Soc. Jpn. 69 (5) (1996) 169.
[9] H. Liu, G.D. Lei, W.M.H. Sachtler, Appl. Catal. A 146 (1996) 165–180.
[10] M. Scheithauer, T.K. Cheung, R.E. Jentoft, R.K. Graselli, B.C. Gates, H. Knozinger, J. Catal. 180 (1998) 1.
[11] J.G. Santiesteban, J.C. Vartuli, S. Han, R.D. Bastian, C.D. Chang, J. Catal. 168 (1997) 431.
[12] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgens, J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 108346.
[13] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 359 (1992) 710.
[14] U. Ciesla, S. Schacht, G.D. Stucky, K.K. Unger, F. Schuth, Angew. Chem. Int. Ed. Engl. 35 (1996) 539.
[15] F. Schuth, Ber. Bunsenges Phys. Chem. 99 (1995) 130.
[16] G. Larsen, E. Lotero, M. Nabity, L.M. Petkovic, D.S. Shobe, J. Catal. 164 (1996) 246.
[17] Y.-Y. Huang, T.J. McCarthy, W.M.H. Sachtler, Appl. Catal. A 148 (1996) 135.
[18] J.A. Knowles, M.J. Hudson, Chem. Commun. (1995) 2083.
[19] J.A. Knowles, M.J. Hudson, J. Mater. Chem. 6 (1996) 89.
[20] A. Corma, M.I. Juan-Rajadell, J.M. Lopez-Nieto, A. Martinez, C. Martinez, Appl. Catal. A 116 (1994) 151.
[21] G. Yaluris, R.B. Larson, J.M. Kobe, M.R. Gonzalez, K.B. Fogash, J.A. Dumesic, J. Catal. 158 (1996) 336.
[22] S.X. Song, R.A. Kidd, J. Chem. Soc., Faraday Trans. 94 (9) (1998) 1333.
[23] M. Risch, E.E. Wolf, Appl. Catal. A 72 (1998) L1.
[24] C. Morterra, G. Cerrato, F. Pinna, M. Signoretto, J. Catal. 157 (1995) 109.
[25] D. Farcasiu, J.Q. Li, S. Cameron, Appl. Catal. A 154 (1997) 173.
[26] K. Arata, Adv. Catal. 37 (1990) 165.
[27] C.R. Vera, J.M. Parera, J. Catal. 165 (1997) 254.
[28] C. Morterra, G. Cerrato, F. Pinna, M. Signoretto, G. Strukul, J. Catal. 149 (1994) 181.
[29] B. Li, R.D. Gonzalez, Appl. Catal. A 165 (1997) 291.
[30] J.E. Tabora, R.J. Davis, J. Catal. 162 (1996) 125.
[31] M.A. Coelho, W.E. Alvarez, E.C. Sikabwe, R.L. White, D.E. Resasco, Catal. Today 28 (1996) 415.
[32] T.-K. Cheung, J.L. D'Itri, B.C. Gates, J. Catal. 151 (1995) 464.
[33] M.R. Gonzalez, J.M. Kobe, K.B. Fogash, J.A. Dumesic, J. Catal. 160 (1996) 290.
[34] J.M. Kobe, M.R. Gonzalez, K.B. Fogash, J.M. Kobe, J.A. Dumesic, J. Catal. 164 (1996) 459.
[35] H. Matsushashi, H. Oikawa, M. Tanaka, React. Kinet. Catal. Lett. 65 (2) (1998) 253.
[36] F. Pinna, M. Signoretto, G. Strukul, G. Cerrato, C. Morterra, Catal. Lett. 26 (1994) 339.
[37] B.-Q. Xu, W.M.H. Sachtler, J. Catal. 165 (1997) 231.
[38] M. Signoretto, F. Pinna, G. Strukul, P. Chies, Cerrato, S. DiCero, C. Morterra, J. Catal. 167 (1997) 522.
[39] M. Risch, Ph.D. Thesis, University of Notre Dame, Notre Dame, IN, 1999.
[40] H. Liu, V. Adeeva, G.D. Lei, W.M.H. Sachtler, J. Mol. Catal. A 146 (1996) 165.