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Journal of Catalysis 218 (2003) 258–266

JOURNAL OF CATALYSIS

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Characteristics of the active sites on sulfated zirconia for *n*-butane isomerization

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Received 13 September 2002; revised 3 February 2003; accepted 18 February 2003

Abstract

n-Butane isomerization on sulfated zirconia (SZ) has been studied with the goal of increasing our understanding of the nature of the active sites and the role of the acid (Brønsted and Lewis) sites. Isotopic transient kinetic analysis (ITKA), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), butene addition, CO addition, and pretreatment of the catalyst at different temperatures have been used to investigate the nature of the active sites involved in the formation of reaction intermediates and of isobutane. It was found that CO, added from the beginning of the reaction, inhibited the formation of isobutane but it did not prevent formation of carbon from *n*-butane, resulting in a deactivation of the catalyst proportional with the exposure time to CO. Butene added for 2 min at the beginning of the reaction increased the reaction rate and was involved in the formation of isobutane during multiple turnovers as a result of creation of olefinic modified sites. Addition of CO (for different period of times) along with butene (for 2 min at the beginning of the reaction) did not prevent the formation of the olefinic modified sites when CO was added for a short time. However, such sites participated in the formation of isobutane only after the CO feed was stopped and it desorbed from the surface of the catalyst. These results indicate that Lewis acid sites are not involved in the formation of either deactivating carbon or the olefinic modified sites. Pretreatment of SZ at 500 °C improved the activity of SZ due to an increase in the concentration of surface intermediates, $N_{\text{iso-C4}}$, compared to when it was pretreated at 200 and 315 °C and the Brønsted/Lewis acid sites ratio was greater. The results of this study support the hypothesis that the "active centers" for reaction are probably a combination of Brønsted and Lewis acid sites.

Keywords: *n*-Butane isomerization; Sulfated zirconia; Butene addition; CO poisoning; Induction period; Activation temperature; Isotopic tracing

1. Introduction

After long debate, it has been determined that *n*-butane isomerization mainly follows a bimolecular mechanism [1–12] at both low and high temperatures [2], although some reaction may also occur by a monomolecular mechanism [13]. The bimolecular mechanism involves several steps: formation of butene as an intermediate, oligomerization of this olefin with *n*-butane to form an adsorbed C_8-intermediate, and finally isomerization and β-scission of the C_8-intermediate to form mainly isobutane [1–12].

The presence of butene plays an important role in enhancing both the activity and the deactivation rate of sulfated zirconia (SZ). On one hand, elimination of olefin impurities present in the reactant stream has been found to lead to a decrease in the initial activity; this led to the suggestion that butene participates in the formation of isobutane [14,15]. It has also been found that added olefin can lead to hundreds of additional turnovers per added butene molecule in the formation of additional isobutane [12,16]. On the other hand, the absence of olefin or the decrease in its concentration in the reactant stream has also been shown to improve the stability of the catalyst [17]—reasonable since olefins are known to be good coke/oligomer precursors.

Even though the reaction mechanism is now better understood, key questions about the nature of the active sites have not been totally answered. It has been variously suggested that Brønsted acid sites [18,19], Lewis acid sites [20,21], or a combination of both [22] play an important role in the formation of isobutane. It has also been proposed that the surface intermediates may be formed through an oxide mechanism [23,24].

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doi:10.1016/S0021-9517(03)00067-8

The dehydration level has been found to have a dual effect on the activity of SZ—both promoting and deactivating. Comelli et al. [25] showed that SZ pretreated around 600 °C, where Lewis acidity is dominant, has a higher isomerization rate than SZ pretreated at lower temperatures. Morterra et al. [26] proposed that Lewis acid sites are crucial for isobutane formation; although they did not exclude a role for Brønsted acid sites in the reaction. Song and Kydd [27] reported that an increase in the activation temperature caused a decrease in the Brønsted acid sites and an increase in the Lewis acid sites. These authors proposed that the sites involved in surface intermediate formation by protonation of butene are Brønsted acid sites. The adsorbed species resulting can be best described as alkoxy groups with a small positive charge that have transition states more positively charged and related to carbenium ions [28]. Because the exact nature of these surface species is not known, they will be referred to throughout this paper as "carbenium-like ions" where appropriate.

Gonzalez et al. [29] found that an increase in drying temperature resulted in a decrease in the activity of SZ as well as a decrease in the amount of Brønsted acid sites. They reported that the Brønsted acid sites were not converted to Lewis acid sites since no change in Lewis acidity occurred. However, in a later paper, Li and Gonzalez [30] reported a decrease in the Brønsted-to-Lewis acid site ratio when the drying temperature was increased and found that the ratio giving the optimum activity was 0.5. Other spectroscopic studies showed that introducing water vapor into the reactor converted Lewis acid sites to Brønsted acid sites [27]. It is obvious from these studies that the presence of some level of hydration is important for SZ to be active.

Pinna et al. [31] explored the importance of Lewis acidity in the formation of isobutane by adding CO addition to the reactant stream. The addition of CO, known to adsorb on the coordinatively unsaturated surface cations (cus) acting as Lewis acid sites [32], decreased the activity of SZ to almost zero [31]. Once the CO feed was stopped, CO rapidly desorbed from the surface of SZ and the activity returned to a similar level as before CO addition [31]. However, Adeeva et al. [18] disagreed with the interpretation of those results [31]. They suggested that CO may have the ability to inhibit the reaction without Lewis acid sites being involved in the formation of isobutane since the addition of CO during n-pentane isomerization on zeolite HY that contains mainly Brønsted acid sites inhibits reaction. They proposed that CO may interact with carbenium-like ions (surface butoxy groups) to form oxocarbenium ions on SZ, thereby disabling the formation of isobutane. Thus, the proposition that the Lewis acid sites are the main sites involved in the formation of isobutane is still debatable.

Although n-butane isomerization on SZ has been extensively investigated, important questions remain to be answered. Two of these questions are: (a) how the reaction intermediates are formed and (b) which sites are involved in their formation.

The purpose of this study was to investigate further the nature of the sites involved in the formation of isobutane on SZ using variation of pretreatment temperature, CO poisoning, and butene addition. Butene addition has been previously found useful in studying n-butane isomerization on SZ [16]. Utilizing isotopic transient kinetic analysis (ITKA) during n-butane isomerization and FTIR permitted us to determine changes in surface kinetic parameters and the acidity of the catalyst, respectively, as pretreatment temperature was varied.

2. Experimental

The sulfate-doped zirconium hydroxide [$Zr(OH)_4$] precursor used for this study was provided by Magnesium Elektron, Inc. (MEI, Flemington, NJ). It was calcined at 600 °C for 2 h under static air to form sulfated zirconia. Its sulfur content (Galbraith Laboratories, Inc.) and its BET surface area (Micromeritics) were determined after calcination and were found to be 1.7 wt% and 92.4 m^2/g, respectively. XRD analysis showed that ZrO_2 was in the tetragonal phase [33].

A detailed description of the reaction and the isotopic transient kinetic analysis systems can be found elsewhere [34]. Typically, the reaction was carried out in a quartz fixed-bed reactor (i.d. = 10 mm) loaded with 0.2 g of SZ. Prior to the reaction, the catalyst was pretreated in situ in the temperature range 200–500 °C for 4 h under a flow of 30 cc/min of air (UHP, National Welders) and then purged with He (UHP, National Welders) during 30 min at the reaction temperature, 150 °C. The reaction temperature of 150 °C was chosen for this study rather than 250 °C (typical for many studies) for two reasons: (1) the deactivation rate is not as significant at this temperature and (2) CO desorption is greater at higher temperature making it more difficult to study the effect of its adsorption on SZ. The total flow rate and the reaction pressure were kept constant at 30 cc/min and 1.5 atm, respectively. The reactant stream consisted of 5 vol% n-C_4/He (UHP, Hollox) (n-C_4 flow rate = 0.75 cc/min) plus an additional stream of He (UHP, National Welders). The partial pressure of n-butane was maintained at 0.04 atm. One percent 1-$C_4^{=}$/He (UHP, Hollox) and/or pure CO (UHP, Hollox) (14 cc/min) was added to the reactant stream without disturbing the partial pressure of n-C_4 by replacing some of the pure He stream. The olefin/paraffin ratio used, when butene was added, was equal to 0.003. An olefin trap (a bed of H-mordenite at 35 °C) was used to completely eliminate olefin impurities in the n-butane reactant stream. The composition of the reactor effluent was analyzed using a Varian 3700 GC equipped with a 12 foot 15% Squalane CP-AW-DMCS/Chromosorb 80/100-mesh column and an FID. The reproducibility of the results was found to be ca. ±5%. A 34-port VICI autosampling valve was used to collect 16 samples during the first 5 min of reaction, allowing us to investigate changes in the reaction rate during the induction period. The time for the reactants and products to reach the sampling valve after the switch from pretreatment gas to reactants was ca. 30 s.

For ITKA, isotopic switches between two reactant streams, containing unlabeled {$^{12}C_4H_{10}$ (n-C_4)} or labeled {$^{13}CH_3$ $(^{12}CH_2)_2$ $^{13}CH_3$ (n-$^*C_4$)}, were made without disturbing other reaction conditions. Samples from the product stream were collected in the 34-port VICI autosampling valve and subsequently separated in the GC column set at 35 °C. The effluent was sent to a hydrogenolysis unit (5 wt% Pt/SiO_2, at 250 °C) where the hydrocarbons were converted to methane. A 8.5 mol% H_2 in He was used as a carrier gas and as a source of H_2 for the hydrogenolysis. Effluent from the hydrogenolysis unit was fed to a Pfeiffer–Balzers Prisma 200 amu mass spectrometer, and data were collected by a Pentium II PC equipped with Quadstar software.

The in situ diffuse reflectance spectra of SZ were obtained using a Nexus fourier-transform infrared spectrometer equipped with a diffuse reflectance (DRIFTS) attachment along with a reaction chamber, both obtained from Harrick Scientific Corp. The Nicolet detector was cooled with liquid nitrogen and used at a resolution of 8 cm^{-1}. The catalyst was pretreated in situ in air prior to collecting the IR spectra. The pretreatment conditions used were chosen to be the same as those used in the reaction study. After pretreatment, the DRIFTS cell was purged with He for 30 min. Pyridine adsorption at 100 °C was carried out by injection of 50 µl of pyridine into a He flow upstream of the reaction chamber. The catalyst was then purged for 30 min under He. The spectra were taken at 2 min and at 80 min after the catalyst was purged.

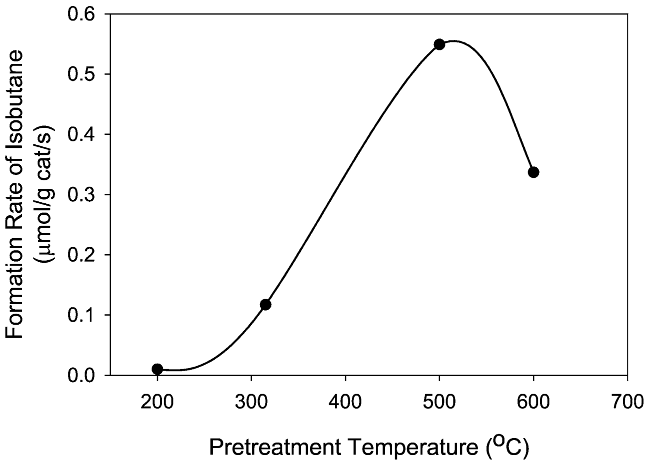

Fig. 1. Effect of pretreatment temperature on the n-butane isomerization activity of SZ at 5 min TOS at 150 °C in the absence of added butene.

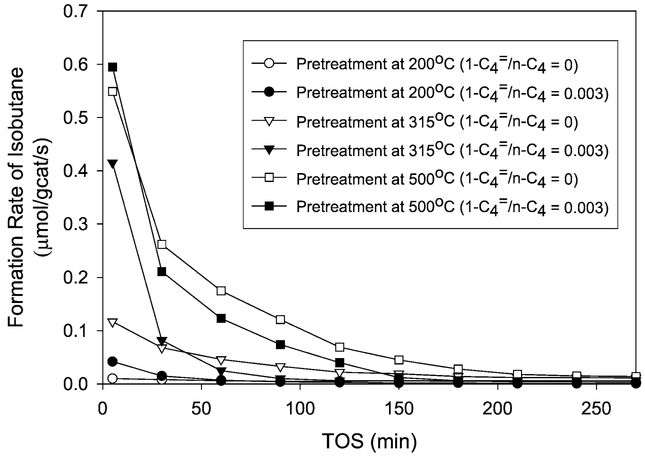

Fig. 2. Impact of pretreatment temperature on n-butane isomerization activity at 150 °C in the presence and in the absence of added 1-butene.

3. Results

3.1. Effect of pretreatment temperature

SZ is very sensitive to the preparation conditions and the activation procedure used prior to reaction. The activation temperature is one of the factors that have an important role in determining the acidity and, thus, the activity of the catalyst during n-butane isomerization [35–37] due to its hygroscopic property. The effect of pretreatment temperature (200, 315, 500, and 600 °C) on the rate of formation of isobutane on SZ in the presence and in the absence of added butene at 150 °C was investigated and the results are summarized in Figs. 1 and 2. The catalyst's activity went through a maximum (at 5 min TOS) with an increase in pretreatment temperature (Fig. 1). When pretreated at low temperature (200 °C), the catalyst had very low activity. Our results are in agreement with the work of Comelli et al. [25] who found a maximum activity when the catalyst was calcined between 500 and 520 °C. However, our results and those of Comelli et al. [25] are in contradiction with those Song and Kydd [27] who found that SZ had a higher activity when dried at 250 °C. These apparently contradictory results may be due to differences in drying procedure. It has been reported that there is always a presence of residual moisture during normal drying and reaction conditions [38]. An optimum dehydration level has also been reported to be necessary for SZ to achieve its optimum activity [27]. Although pretreatment temperature had an important effect on reactivity, it did not have a dramatic impact on the selectivity of the catalyst to isobutane. The variation in the selectivity with TOS was typical for SZ. The selectivity to isobutane was ca. 85% at 5 min and 90% at 300 min TOS for a pretreatment temperature of 315 °C. Pretreatment at 500 °C resulted in the selectivity to isobutane being 93 and 97% at 5 and 300 min TOS, respectively.

Olefin addition increased the rate of formation of isobutane at 5 min TOS for all pretreatment temperatures studied (Fig. 2), but, the 315 °C-pretreated catalyst showed the biggest response to olefin addition since it increased its activity by almost a factor of three. The increase in the rate of formation of isobutane was always orders of magnitude greater than the flow rate of added butene (ca. 0.01 µmol/(g_{cat} s)). However, the impact of butene addition

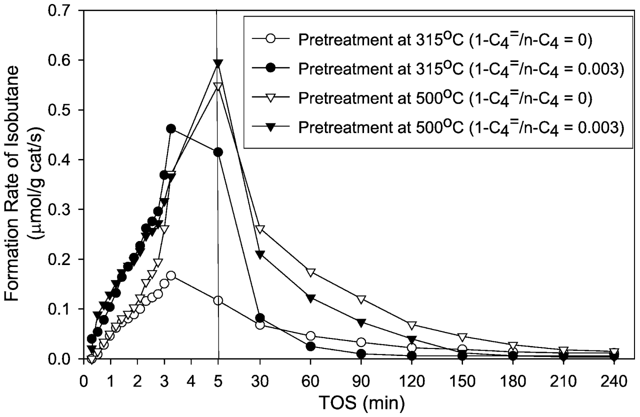

Fig. 3. Effect of pretreatment temperature on the reaction induction period profile at 150 °C in the presence and in the absence of added 1-butene.

was not limited to just increasing the formation rate of isobutane; it also increased the deactivation rate as well.

Since reaction on SZ has been found to exhibit an induction period during the first 5 min TOS and the induction period behavior contains important information, the variations in isobutane formation rate before 5 min TOS of the 315 °C- and the 500 °C-pretreated catalysts in the absence and in the presence of butene were also studied and are shown in Fig. 3. In all cases, the catalyst went through an induction period lasting 4–5 min. Neither the pretreatment of the catalyst at higher temperature nor the addition of butene eliminated the presence of this induction period, despite their positive impact on the performance of the catalyst. Added olefin appeared to have a major impact on the differently pretreated catalysts from the beginning of the reaction, causing the catalysts to develop higher activity faster. However, the maximum activity achieved for the 500 °C-pretreated catalyst was only slightly greater than when olefin was not added. The principal observed effect was an increase in the deactivation rate. This was probably the reason why the catalyst did not exhibit significantly higher activity than when no butene was added. On the other hand, olefin addition to the catalyst pretreated at 315 °C caused a significant increase in the maximum activity reached during the induction period. Butene addition did not appear to affect the time to maximum activity during the induction period for either pretreatment temperature.

Carbon content analysis results are given in Table 1. The 315 °C- and the 500 °C-pretreated catalysts had similar amounts of carbon deposited on their surfaces after 300 min TOS. The addition of olefin caused an increase in the amount of carbon on the catalyst, but the resulting content was essentially the same regardless of the pretreatment temperature.

Table 1
Carbon content on SZ after 300 min of reaction at 150 °C: effect of pretreatment temperature and continuous olefin addition during reaction

Pretreatment temperature (°C)	Carbon content at 300 min TOS[a] (wt%)
315	0.07
500	0.09
315 (with 1-$C_4^=$)	0.65
500 (with 1-$C_4^=$)	0.62

[a] Measured by Galbraith, Inc., using coulometric titration. Error = ±1% of the measurement.

Table 2
Effect of pretreatment temperature on 5-min TOS surface kinetic parameters of SZ for *n*-butane isomerization at 150 °C[a]

Pretreatment temperature (°C)	Rate$_{\text{iso-C4}}$[b] (μmol/(g s))	$\tau^*_{\text{iso-C4}}$[c] (s)	$N^*_{\text{iso-C4}}$[d] (μmol/g)
315	0.12	12.1	1.4
500	0.55	8.1	4.4

[a] Space time = 0.02–0.05 s.
[b] Max error = ±5%.
[c] $\tau_{\text{iso-C4}}$ corrected for product readsorption by extrapolation to 0 space time using 4 measurements based on varying catalyst loading in the reactor from 0.2 to 0.5 g. Maximum error = ±15%.
[d] $N^*_{\text{iso-C4}} = R_{\text{iso-C4}} \times \tau^*_{\text{iso-C4}}$. Max error = ±19%.

ITKA was used to explore the impact of pretreatment on the surface reaction kinetic parameters. Those parameters able to be determined by ITKA are the concentration of surface intermediates, $N_{\text{iso-C4}}$, and the average surface reaction residence time, $\tau_{\text{iso-C4}}$. More details about the use of ITKA and its application to the study of *n*-butane isomerization can be found elsewhere [34,39,40]. The effect of pretreatment on the surface reaction parameters for reaction at 5 min TOS in the absence of added butene, as determined by ITKA, is given in Table 2. Readsorption of isobutane has been shown to have an impact on surface residence time measured with ITKA. In order to overcome this limitation, surface residence times were measured at different space times and extrapolated to zero space time to determine a more exact value of average residence time, $\tau^*_{\text{iso-C4}}$ [34]. The concentration of surface intermediates was calculated then using the following formula,

$$N^*_{\text{iso-C4}} = \tau^*_{\text{iso-C4}} \times r_{\text{iso-C4}},$$

where $r_{\text{iso-C4}}$ is the formation rate of isobutane.

Pretreatment of the SZ catalyst at higher temperature increased significantly the concentration of surface intermediates, $N_{\text{iso-C4}}$, and decreased slightly the average surface residence time, $\tau_{\text{iso-C4}}$. The decrease in the average surface residence time is an indication that the average activity of the sites possibly increased slightly when the catalyst was pretreated at 500 °C, as opposed to when it was pretreated at 315 °C.

Pyridine, used as a probe molecule, adsorbs on both Brønsted acid sites and Lewis acid sites. When adsorbed on Brønsted acid sites, pyridine forms pyridinium ions and its characteristic bands appear at 1640, 1607, 1540, and 1490 cm^{-1} [41]. When adsorbed on Lewis acid sites, the adsorbed pyridine has bands at 1604, 1574, 1490, and 1445 cm^{-1} [30]. The DRIFTS results (not shown) indicate that, as the pretreatment temperature increased, the band representative of Lewis acid sites, 1445 cm^{-1}, increased as well while the band representative of Brønsted acid sites,

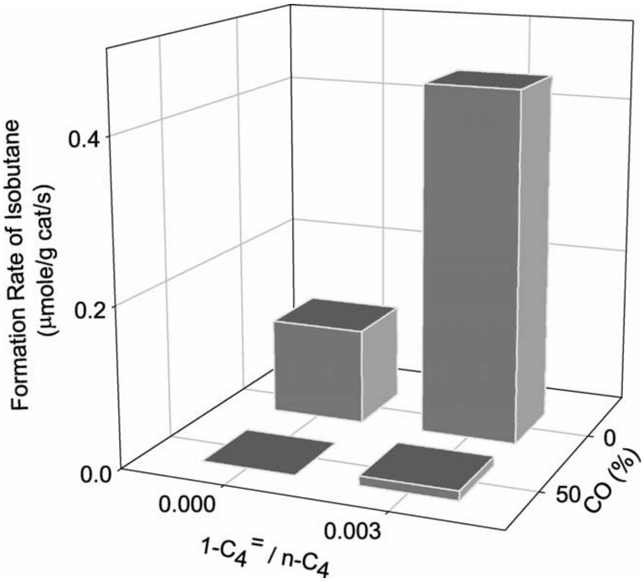

Fig. 4. Effect of continuous butene and CO additions on the isobutane formation rate at 5 min TOS (150 °C) for SZ pretreated at 315 °C.

1540 cm^{-1}, decreased. The ratio of Brønsted-to-Lewis acidity was determined from the spectra of the adsorption of pyridine on SZ using the method of Basila and Kantner [42]. The Brønsted/Lewis acid site ratio decreased with the increase in drying temperature as the Brønsted acid sites were converted to Lewis acid sites upon dehydration. When the catalyst was dried at 315 °C, the Brønsted/Lewis acidity ratio was ca. 0.3, versus 0.45 when dried at 200 °C. The DRIFTS cell used did not allow us to pretreat the catalyst over 400 °C; however, the results confirm that as the catalyst is dried at higher temperature the Brønsted/Lewis acidity ratio decreases. Li and Gonzalez [30] found that the ratio that gave the optimum activity was approximately 0.5 when SZ was pretreated between 375 and 400 °C. The difference in the ratio values seen from one study to another for a given drying temperature may be due to different catalysts being used as well as different amounts of residual moisture being present.

3.2. *Effect of CO addition*

The continuous addition of olefin to the reactant stream increases the performance of the catalyst by as much as a factor of three, as shown in Figs. 2 and 3. Fig. 4 shows the impact of continuous CO and olefin additions on the rate of formation of isobutane of SZ at 5 min TOS. For this study, 315 °C was chosen as a pretreatment temperature instead of 500 °C due to the fact that the impact of butene was more pronounced at the lower temperature. In the absence of added butene, the addition of CO to the reactant stream inhibited completely the rate of formation of isobutane and all other products (C_2, C_3, and C_5). However, the catalyst also had a negligible activity when both butene and CO were added since the rate detected was similar to the amount of butene added (0.01 µmol/g cat/s). This result is in agreement with what has been reported previously in the literature for CO addition (without butene addition) to n-butane isomerization on SZ at 150 °C [31]. The presence of CO, thus, prevented the reaction from taking place, both in the presence and in the absence of added butene. Therefore, the availability of the olefin had no significant impact on reaction in the presence of CO.

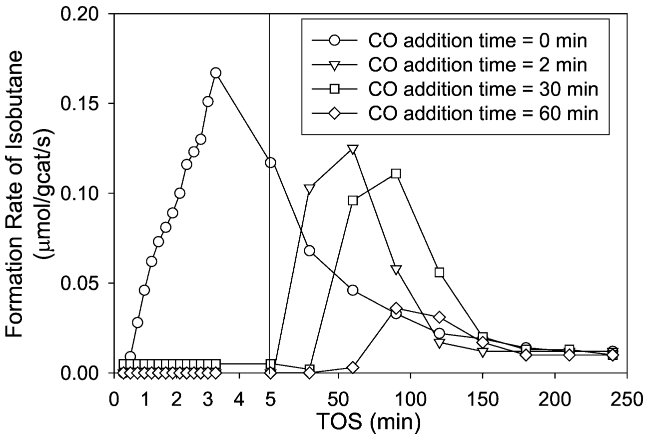

Fig. 5. Effect of CO exposure time on the rate of formation of isobutane at 150 °C for SZ pretreated at 315 °C in the absence of added 1-butene.

To investigate recovery of activity after CO exposure, CO was added to the reactant stream at the beginning of the reaction for different time periods, and then switched off and replaced with the same flow rate of He. Fig. 5 shows the impact of the time of CO addition on the rate of formation of isobutane in the absence of added butene. Introducing CO for 2 min at the beginning of the reaction inhibited temporarily the isomerization of n-butane. After termination of the CO feed, the activity recovered slowly to reach a maximum activity only about 75% of that of the fresh catalyst. For all cases where CO was added, it took approximately 40 min of reaction time after stopping CO addition for the catalyst to reach its maximum activity. As the time of CO addition was prolonged, the catalyst recovered less and less of its maximum activity. Even though CO inhibited formation of isobutane, it did not apparently inhibit irreversible deactivation of the catalyst.

Previous results have shown that butene addition during the first 2 min of reaction on SZ at 150 °C results in a lasting increase in catalyst activity [16]. The impact of exposure time to CO (2–60 min) on the rate of formation of isobutane when butene was added for only the initial 2 min at the beginning of the reaction was thus investigated. The results are shown in Fig. 5. As shown previously, CO inhibits the formation of isobutane in the absence and in the presence of added butene. After the CO feed was terminated, the catalyst recovered partially its activity, the maximum activity depending on the feed time of CO. Interestingly, the addition of CO for only 2 min did not completely inhibit the promoting impact of butene (also only added for the initial 2 min of reaction), although the impact on the formation rate of isobu-

Table 3
Carbon content on SZ after 30 min of reaction at 150 °C: effect of CO (for 30 min) and olefin (for 2 min) additions

$1\text{-}C_4^{=}/n\text{-}C_4$ for initial 2 min	CO added for initial 30 min	Carbon content at 30 min TOS[a] (wt%)
0	No	0.06
0	Yes	0.12
0.003	No	0.20
0.003	Yes	0.35

[a] Measured by Galbraith, Inc., using coulometric titration. Error = ±1% of the measurement.

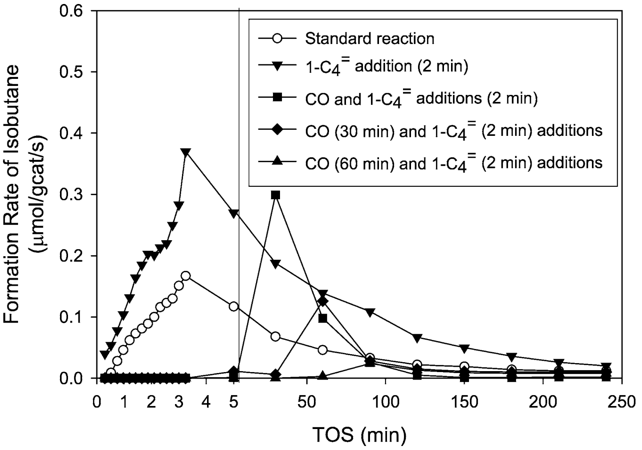

Fig. 6. Effect of CO exposure time on the rate of formation of isobutane at 150 °C for SZ pretreated at 315 °C when butene added for 2 min at the beginning of the reaction.

tane was not as great as when it was added without CO. The rate of formation of isobutane increased slowly upon termination of CO addition. The highest activity reached was 80% of the maximum activity when only butene was added for the initial 2 min. However, the catalyst deactivated more rapidly in this case. As the exposure time to CO increased, the promoting effect of butene diminished and the rate of reaction at a given TOS never exceeded that of the reaction with or without the addition of butene.

Carbon content analysis of SZ after 30 min TOS in the absence and in the presence of CO is given in Table 3. Although exposure to CO blocked the formation of isobutane, the amount of carbon formed on the surface of the catalyst was higher than the amount of carbon formed for the same TOS in the absence of CO, both in the presence and in the absence of added butene. Formation of carbon on the catalyst is known to be the most important factor for the deactivation of SZ. This explains why the maximum activity seen after CO exposure and termination in Figs. 5 and 6 was lower than for the catalyst not exposed to CO.

4. Discussion

Several hypotheses have been proposed to explain the formation of the reaction intermediates. It has been suggested that isomerization occurs by carbenium-like ion formation (a) on Brønsted acid sites by protonation of the alkane [43,44] or (b) on Lewis acid sites [45]. It has also been suggested that the mechanism on SZ is bifunctional [23,46], i.e., is a combination of partial oxidation of butane (the initiation step) and then acid-catalyzed reaction of the intermediates. Below, the role of Lewis and Brønsted acid sites in the formation of isobutane and coke on SZ will be discussed in light of the results from this investigation.

4.1. Carbon deposition

Considering that pretreatment at the higher temperature of 500 °C should have decreased the number of Brønsted acid sites but increased their average strength, it is surprising that there was no significant difference in the amount of carbon deposited during reaction for the two pretreatment temperatures (Table 1). Poisoning SZ with CO, known definitely to adsorb on Lewis acid sites, during n-butane isomerization did not prevent formation of coke on the catalyst (Table 3) even though no isobutane was produced. The longer CO was present in the reactant stream, the less activity was recovered after CO addition was terminated. Moreover, the amount of carbon formed in the presence of CO was higher than in its absence. That was true both in the presence and in the absence of added butene. Pinna et al. [31] found that, once the CO feed was stopped, the catalyst recovered its normal activity. However, in that study, CO was added once the catalyst reached its pseudo-steady state, namely a quasi-deactivated state. This may have been the reason the authors did not see further deactivation of the catalyst during CO addition. The results of CO poisoning under the conditions used in this study suggest that there was still reaction occurring on the catalyst, although not generating gaseous products.

The deposited carbon formed on SZ in the presence of CO during reactant flow could have derived from surface species formed on the catalyst. It has been suggested that the initiation step, i.e., formation of carbenium-like ions, involves a partial oxidation step [23] and does not involve an acid reaction. In the absence of CO, the carbenium-like ions formed would have participated in the formation of isobutane and would have also been the source of coke formation. However, when CO was added, the formation of products was inhibited allowing the surface species to form more coke, thus the unanticipated higher amount of coke formation in the presence of CO as opposed to in its absence. As expected, more carbon was deposited on SZ when butene was added, both in the presence and in the absence of CO, since butene is known to be a good coke/oligomer precursor. The formation of carbon on SZ would appear not to have required Lewis acid sites given that they were not available during CO addition. These results suggest that Lewis acid sites under our reaction conditions are not responsible for the formation of surface carbon.

4.2. Isobutane formation

The role of the acid sites in isobutane formation has been investigated and until now no consensus has been reached. In this study, CO poisoning inhibited the formation of isobutane (Figs. 4–6), in agreement with the results of Pinna et al. [31]. It has been shown that CO adsorbs on Lewis acid sites [32] and, thus, it would first appear from these results that Lewis acid sites are crucial in the isomerization of n-butane. However, as noted earlier, Adeeva et al. [18] proposed, based on results for CO poisoning of n-pentane isomerization on an HY catalyst containing primarily Brønsted acid sites, that CO, besides adsorbing on Lewis acid sites, can form oxocarbenium ions with surface butoxy groups, thus disabling the formation of isobutane. An interaction of CO and carbenium ions has also been reported in the Koch synthesis of carboxylic acid [47].

It was shown (Fig. 6) that the addition of butene alone for 2 min greatly increases the formation rate of isobutane. In a previous study [16], we have shown that addition of butene for only 2 min increases the activity of SZ and is responsible for ca. 700 reaction turnovers per molecule of added butene. In that study, we proposed that added butene forms “olefinic modified sites.” Addition of both butene and CO for only 2 min to the reactant stream gave us more insight into this issue (Fig. 6). Added butene did not improve the negligible activity in the presence of CO. However, once both CO and butene additions were terminated, the rate increased and reached a higher value than during standard reaction in the absence of both CO and butene additions. The higher maximum activity of SZ seen (than during standard reaction) following termination of both butene and CO addition after only 2 min suggests that the olefinic modified sites could be formed even in the presence of CO. This long-lasting promoting impact of added butene can be explained by the hypothesis of Adeeva et al. [18]. Added butene may have been converted to surface carbenium-like ions that interacted with CO. These carbenium-like ions would have been able to participate in the formation of isobutane once CO was removed, provided CO poisoning did not last too long. However, when CO was added for a longer time, the promoting impact of butene disappeared, most probably because the carbenium-like ions were eventually converted to coke (Table 3). These results suggest that Lewis acid sites are not involved in the formation of olefin-modified sites.

Pretreatment of SZ at high temperature has an impact on the acidity of SZ. DRIFTS results showed that as the pretreatment temperature went from 200 to 315 °C, the Brønsted/Lewis acidity ratio decreased from 0.45 to 0.3. Following this trend and as has been shown in the literature, pretreatment of SZ at higher temperatures would have decreased this ratio even more. The increase in activity seen upon pretreatment of SZ at 500 °C would, thus, have been caused by an increase in the Lewis acid sites or a decrease in the Brønsted acid sites. The ITKA results (Table 2) show that the increase in activity upon pretreatment at 500 °C was primarily due to an increase in the concentration of surface intermediates, $N^*_{\text{iso-C4}}$. The average surface residence time, $\tau^*_{\text{iso-C4}}$, did not significantly change, suggesting that the active sites were not significantly different after these two different pretreatments. The small difference seen in average site activity ($1/\tau^*_{\text{iso-C4}}$) could perhaps have been due to a small increase in average acid site strength. Any increase in $N^*_{\text{iso-C4}}$ did not lead to an increase in the carbon content as long as additional butene was not added (Table 1). The increase in activity would appear to have been due to an increase in the number of active sites. Moreover, the increase in pretreatment temperature increased the relative number of Lewis acid sites on SZ (DRIFTS results). This could suggest that the increase in the concentration of Lewis acid sites somehow caused the increase in activity.

It has been proposed that strong acid sites are the reason for the high activity of SZ and that those strong acid centers consist of Brønsted and Lewis acid centers [48]. The same study showed that the intermediate strength acid sites are only Brønsted acid sites. Other studies have suggested that Brønsted acid sites were needed for the high activity of SZ [36]. It has been found that a SZ catalyst dried at very high temperature, where only Lewis acid sites are present, has a very low activity [29]. It has also been reported that an optimum dehydration level is necessary for SZ to exhibit its highest activity [27], as we have also clearly shown in Fig. 1.

Our results do not reconcile with a model requiring only Brønsted acid sites or only Lewis acid sites. Our results as well as many in the literature suggest that most probably a combination of both Lewis and Brønsted acid sites is required for high activity [22] and that an optimum ratio of Brønsted/Lewis acid sites is needed. Based on our results, the best model in the literature to describe the active sites in our opinion is that proposed by Clearfield et al. [49]. This model (Fig. 7) proposes that both Lewis and Brønsted acid sites on SZ have simultaneously a role in isomerization. In this model, the noncalcined SZ (species I) contains two types of protons: as bisulfates and as hydroxy groups connecting two Zr ions. During calcination, water is removed to form species II and species III. The asterisks in the species II and III indicate Lewis acid sites. In structure II, the bisulfate does not change after dehydration of the hydroxide thus creating an S–O–H group with neighboring Lewis acid sites. The Lewis acid sites can impact the Brønsted acid site, S–O–H group, by electron withdrawal, thus weakening the SO–H bond. This results in stronger and more active Brønsted acid sites. CO when adsorbed on Lewis acid sites may affect the interaction of neighboring Lewis and Brønsted acid sites, resulting in lower activity on the Brønsted sites than when CO is not present.

5. Conclusions

In this study, both the impact of CO, known to adsorb on Lewis acid sites and to interact with carbenium-like ions,

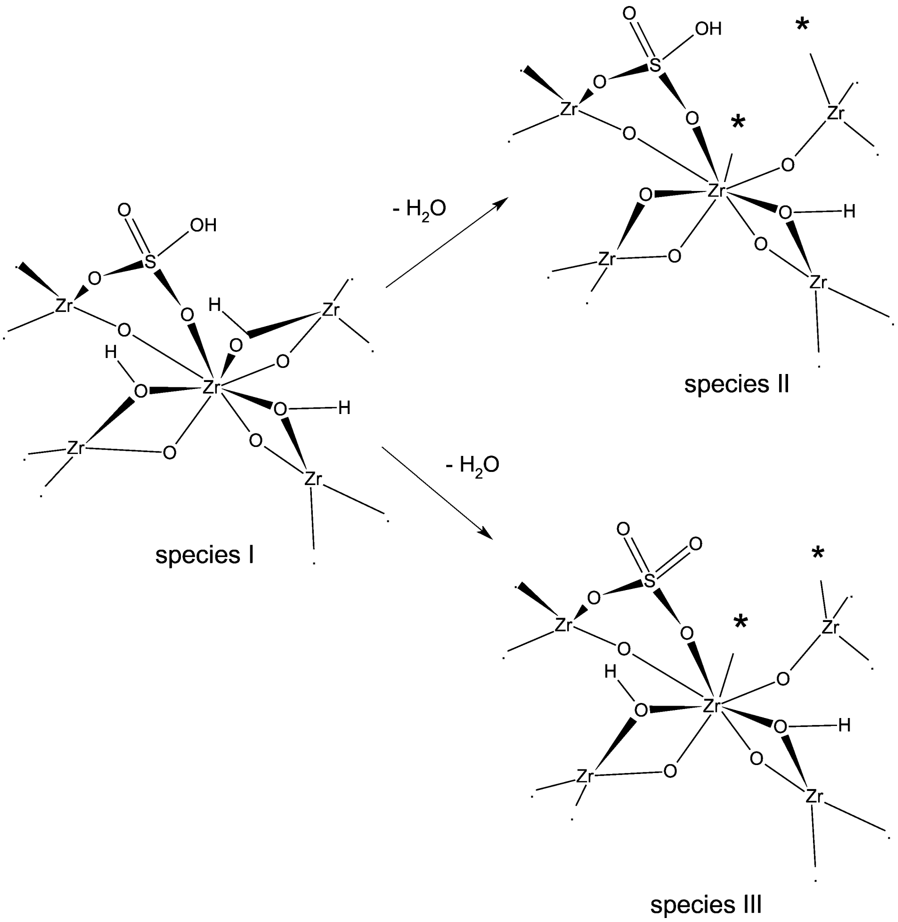

Fig. 7. Proposed model of Clearfield, Serrette, and Khazi-Syed (redrawn from Ref. [49]).

and the impact of the pretreatment temperature in the range 200–600 °C on the performance of SZ during *n*-butane isomerization were investigated in the absence and in the presence of added butene. Addition of CO to the reactant stream inhibited essentially completely the activity for *n*-butane isomerization of the catalyst both in the absence and in the presence of added butene, respectively. SZ recovered partially its activity once the CO feed was terminated. The deposition of carbon on SZ even during CO addition suggests that Lewis acid sites are not involved in the formation of coke.

The nonavailability of Lewis acid sites during CO poisoning did not eliminate the promoting long-term effect of added butene when both CO and butene were added for 2 min at the beginning of the reaction. A longer exposure to CO, however, eliminated the promoting impact of butene. Undoubtedly, CO interacted with the carbenium-like ions formed from added butene, thereby preventing further reaction with *n*-butane to form isobutane. Once CO addition was stopped and CO was able to desorb, these surface carbon-containing species were able to participate in the formation of isobutane—provided CO poisoning was discontinued before these species were converted to coke.

Activation of SZ at 500 °C improved its activity both in the presence and in the absence of butene compared to when it was activated at 200 °C or at 315 °C. The increase in activity was due to an increase in the concentration of surface intermediates, $N_{\text{iso-C4}}$. DRIFTS results showed that Brønsted acid sites were converted to Lewis acid sites and that the Brønsted/Lewis acid site ratio decreased upon increasing the drying temperature.

Although the Lewis acid sites do not appear to be the active sites for reaction intermediates, i.e., carbenium-like ions, their presence seem to be the cause for the significant activity of SZ as long as sufficient Brønsted acidity remains. The results of this study support the hypothesis that a combination of both Lewis and Brønsted acid sites constitutes the “active centers” for reaction on SZ. This synergetic interaction has been previously suggested [49] to be due to neighboring Lewis acid sites acting to modify Brønsted acid sites by electron withdrawal.

Acknowledgment

The authors acknowledge financial support of this work by the National Science Foundation (Grant CTS-9988412).

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