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n-Butane isomerization on sulfated zirconia: active site heterogeneity and deactivation

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Abstract

The fast deactivation of sulfated zirconia (SZ) has limited its use in commercial processes such as *n*-butane isomerization. In order to investigate this deactivation, steady-state isotopic transient kinetic analysis (SSITKA) was utilized to study in situ changes in surface kinetic parameters for *n*-butane isomerization on a widely studied SZ at 150°C. Approximately 20% of the sulfate species was found to be *n*-butane adsorption sites, but only 1–2% of the sulfate species appeared to adsorb active surface reaction intermediates. The decrease in catalytic activity during deactivation could be attributed to the loss of active sites. The change in $\mathrm{TOF}^*_{\mathrm{ITK}}$ (TOF based on an average residence time of active surface intermediates) and the regeneration characteristics of the SZ catalyst suggest a possible active site heterogeneity. It appears that the high initial activity and the fast deactivation for TOS $\leq$ 100 min were mainly due to the presence and deactivation of the more active sites, respectively. Following the loss of the more active sites, the less active sites provided the majority of the catalytic activity observed for TOS $\geq$ 100 min. The less active sites appeared to be more easily regenerated than the more active sites as the catalytic activity at TOS $\geq$ 100 min was recovered following regeneration at 315°C. Loss of active sites due to sulfur loss or migration seems unlikely. Site blockage by coke/oligomer formation appeared to be a significant contributor for catalyst deactivation for *n*-butane isomerization on SZ. The impact of sulfur reduction on catalyst deactivation cannot be ruled out at this point.

Keywords: *n*-Butane isomerization; Solid acids; Metal oxides; Sulfated zirconia; Deactivation of sulfated zirconia; Isotopic transient kinetic analysis; SSITKA; Surface reaction parameters; Active intermediates concentration

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1. Introduction

Metal oxides, such as ZrO_2, Al_2O_3, and TiO_2, have been shown to be acid catalysts. Sulfation has been shown to enhance the acidity of many metal oxides [1,2]. Sulfated zirconia (SZ) was labeled a solid “super” acid [3–7] when it was shown to be active for *n*-butane isomerization at room temperature while other solid acids such as acidic zeolites required temperatures above 300°C for similar catalytic activity [8–14].

The high catalytic activity of SZ for *n*-butane (n-C_4) isomerization has prompted much research into the impact of the physical and chemical characteristics of SZ on the reaction. These investigations have been reviewed in a number of papers in the literature [14–18]. Many parameters have been found to impact the catalytic activity of SZ. Catalyst preparation and pretreatment conditions determine the sulfur content, total surface area, crystallinity of ZrO_2, and the concentra-

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tions of Lewis and Bronsted acid sites [12,13,19–27]. Addition of promoters, such as Fe and Mn, has been shown to increase the catalytic activity [28–33]. The reactant stream composition has also found to have a large impact. The presence of olefin impurities enhances the initial catalytic activity but also increases catalyst deactivation [34,35]. H_2 in the feed stream can reduce the rate of catalyst deactivation, especially in the presence of Pt promoter [36–38], but, in addition, decreases the catalytic activity [39–41]. It is interesting to note that the factors that enhance the catalytic activity also increase the rate of catalyst deactivation.

SZ deactivation during n-C_4 isomerization can be severe. The catalyst can lose up to 50% of its initial activity during the first 45 min time-on-stream (TOS). Understanding the deactivation mechanism for *n*-butane isomerization on SZ is essential in commercializing SZ or SZ-based catalysts for *n*-butane isomerization and other hydrocarbon conversion processes.

The earlier studies suggested four mechanisms for catalyst deactivation. The first mechanism involves coke and/or oligomer formation on the catalyst surface [8,42]. The second mechanism is the migration of sulfur from the surface into the bulk of the ZrO_2 [15]. The third and fourth suggested mechanisms for the catalyst deactivation involve loss [43] and reduction [43,44] of sulfur, respectively. The catalyst may be regenerated in air by burning-off the coke/oligomer or by re-oxidizing the reduced sulfur.

In a recent publication [45], we reported on the first in situ measurements of surface kinetic parameters for *n*-butane isomerization on SZ utilizing steady-state isotopic transient kinetic analysis (SSITKA). This paper focuses on relating the observed changes in surface reaction parameters determined by SSITKA with the proposed deactivation mechanisms of SZ.

2. Experimental

2.1. Catalyst preparation and characterization

Detailed descriptions of catalyst preparation and characterization can be found in [45]. In short, the SZ catalyst was prepared by calcining sulfate-doped zirconium hydroxide (MEI, Flemington, NJ) at 600°C for 2 h in a high temperature oven. The total surface area of fresh SZ was determined to be 94.2 m^2/g (Micromeritics, Norcross, GA). The sulfur and carbon contents were determined at Galbraith Laboratories (Knoxville, TN). XRD of the fresh and used catalysts was done with a Philips X'Pert X-ray diffractometer equipped with a Ni filter utilizing monochromatized Cu Kα radiation.

2.2. n-Butane isomerization

Butane isomerization was carried out in a quartz microreactor with an inner diameter of 10 mm. The catalyst weight used was varied from 0.1 to 0.4 g in order to vary space time between 0.01 and 0.06 s. The calcined SZ catalyst was loaded into a reactor and pretreated in situ prior to isomerization. Three pretreatment temperatures (250, 315 and 450°C) were tested for optimum isomerization activity. The SZ catalyst was heated to the desired pretreatment temperature at 10°C/min in flowing air (30 cm^3/min, Praxair, UHP) and held at that temperature for 4 h before being cooled to the desired reaction temperature. n-C_4 was supplied as 5 mol% n-C_4 in He (Praxair, 99.95% purity). The n-C_4 mixture was passed through a bed of H-mordenite at room temperature to reduce the concentration of olefin impurities to below 100 ppm. The n-C_4 mixture was mixed with additional He (Praxair, UHP), further purified with an Alltech Gas Purifier packed with Drierite and 5 A molecular sieve, to achieve the desired n-C_4 concentration of 2.5 mol% at a total flow rate of 30 cm^3/min. The total pressure was kept constant at 1.5 atm throughout the study. The effluent from the reactor was analyzed using a Varian 3700 gas chromatograph (GC) equipped with an FID and a 6 ft 80/100 mesh Porapak Q column.

A step-change was made between n-$^{12}C_4$ and $^{13}CH_3(^{12}CH_2)_2{}^{13}CH_3$($n$-$^{\dagger}C_4$) without disturbing the other reaction conditions. Samples of the effluent were collected using a VICI 32-port valve. The collected effluent samples were separated in an 18 ft 80/100 mesh Porapak Q column held at 130°C using a carrier gas of 8.5 mol% H_2 in He. The separated effluent samples were converted to methane (CH_4) using the carrier gas as a source of H_2 in a hydrogenolysis unit (HU) consisting of 10 g of 5 wt.% Pt/SiO_2 at 250°C and then differentially introduced to a Balzers-Pfeiffer Prisma 200 amu mass spectrometer (MS). The MS data were collected with a Pentium II PC connected to the MS and using Quadstar software. More detailed descriptions of the equipment and the preparation method, and characterization of Pt/SiO_2 can be found in [46] and [47], respectively.

3. Results

The impurities in the n-C_4/He mixture were mainly butene, *iso*-butane, and *iso*-pentane. *iso*-Pentane and *iso*-butane concentrations were below 20 and 200 ppm, respectively. It is well known that the presence of olefin impurities increases not only the initial isomerization activity, but, more importantly, also increases the rate of catalyst deactivation [34,35]. With the H-mordenite olefin trap in place, butene concentration was kept below 20 ppm. The effluent analysis has been corrected for these impurities.

The pretreatment of the SZ catalyst at 315°C resulted in the highest activity for isomerization (Fig. 1). This is in agreement with literature reports that there is an optimum activation (drying) temperature for isomerization on SZ [13,17,19,21,24]. While the activation temperature of 315°C may not be the absolute optimum for this SZ catalyst, the isomerization activity and selectivity of SZ activated at 315°C is characteristic of this catalyst system.

The BET surface area of the fresh calcined SZ catalyst was determined to be 94.2 m^2/g within the range of reported values [14,21]. The slight differences among the BET surface area reported in the literature for SZ prepared from the same catalyst precursor is probably due to differences in the calcination procedures used in the various studies. XRD spectra of the fresh and used catalyst are shown in Fig. 2. The XRD spectra only exhibit the tetragonal phase of ZrO_2 for both the fresh and used catalyst. No significant change in crystallinity was observed after 300 min of reaction. No sulfur compounds were detected due to the low sulfur content. The sulfur and carbon contents of the SZ at various TOS are listed in Table 1. The sulfur content of the SZ remained relatively constant at 1.6 ± 0.1 wt.%. An increase in carbon content was observed with TOS with a significant increase between 150 and 300 min TOS.

Fig. 3 shows the isomerization activity on 0.2 g of SZ over 400 min TOS. The initial rate of n-C_4 conversion, measured at 5 min TOS, was 1.34 μmol/(g s) with 86% of product being *iso*-C_4. Other byproducts of isomerization were propane (C_3) and pentane (C_5) with a trace of butene. A fast initial deactivation was observed during the first 45 min TOS. The first-order deactivation rate constant, k_d, defined by Eq. (1) [48] was ca. 0.033 min^{-1}.

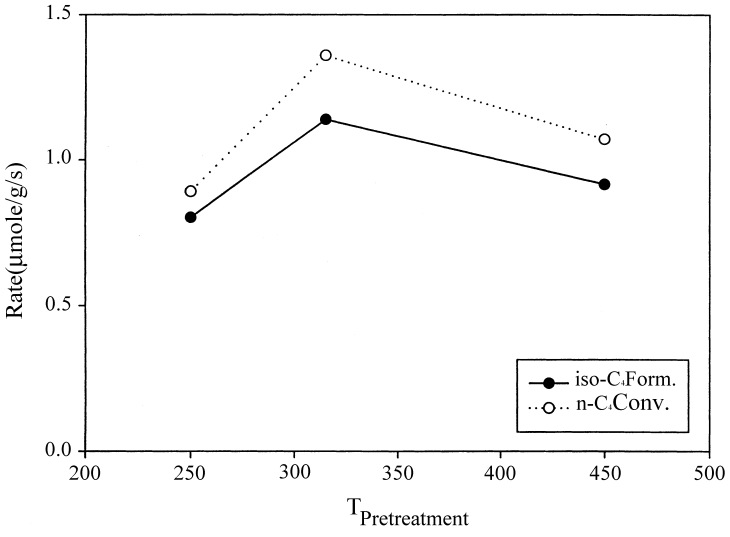

Fig. 1. Effect of pretreatment temperature on the initial isomerization activity ($T = 150°C$, $P = 1.5$ atm, n-$C_4 = 2.5$ mol%, $W_{cat} = 0.2$g, TOS = 5 min).

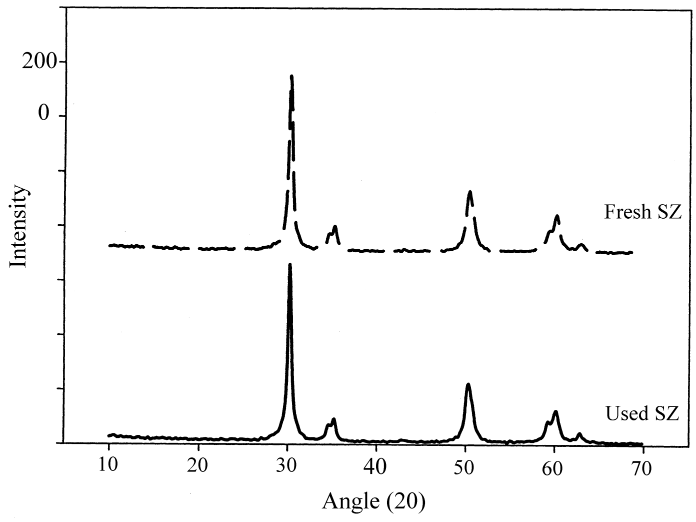

Fig. 2. XRD spectra of the fresh and used SZ catalyst.

Table 1
Sulfur and carbon contents of SZ

	Fresh	45 min TOS	150 min TOS	300 min TOS
Sulfur (wt.%)[a]	1.6	1.5	1.6	1.5
Carbon (wt.%)[a]	–	0.18	0.15	0.70

[a] Analysis error: ±0.1 wt.%.

$$\text{rate} = \text{rate}_0 \exp(-k_d t) \tag{1}$$

After the fast initial deactivation, the isomerization activity declined at a lower rate, k_d ca. 0.005 min^{-1}, to reach a rate of n-C$_4$ conversion of 0.05 μmol/(g s) at 300 min TOS. The *iso*-C$_4$ selectivity increased with TOS to a selectivity greater than 95% after 45 min TOS.

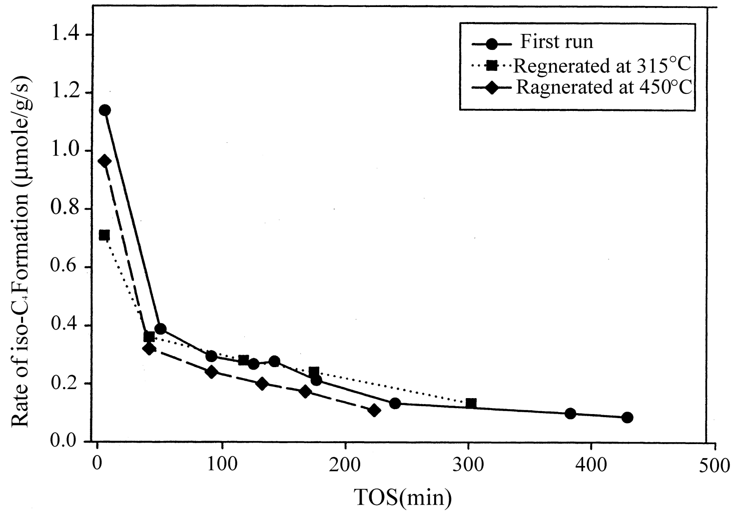

Fig. 3. Isomerization activity at 150°C of the fresh and regenerated SZ catalyst.

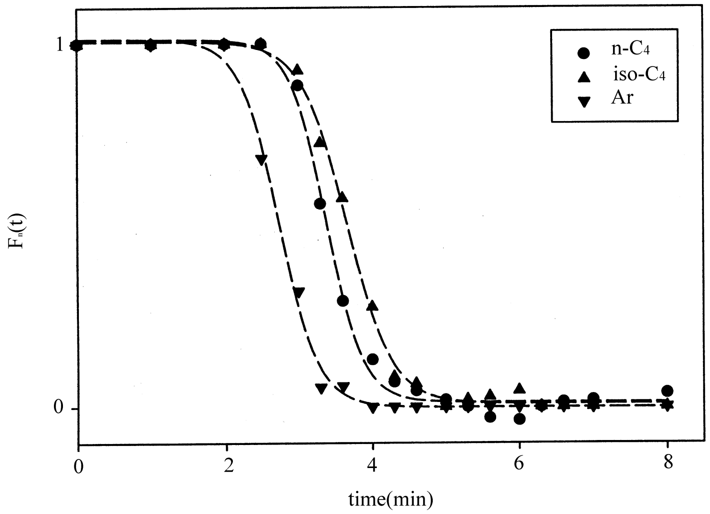

Fig. 4. Typical normalized isotopic transients: *n*-butane isomerization at 150°C for 30 min TOS.

After 500 min of reaction, the catalyst was regenerated using the pretreatment procedure. The isomerization activity of the regenerated catalyst is also shown in Fig. 3. The initial activity of the regenerated catalyst was lower than that of the first run catalyst; however, the activity duplicated that of the first run catalyst after 60 min TOS. Following regeneration at 450°C, the SZ recovered more of its initial activity than when regenerated at 315°C.

Typical normalized isotopic transients are shown in Fig. 4. The 15 points were obtained by analysis of effluent in each auto-sampler loop. The continuous transient was obtained by fitting a sigmoidal curve. $\tau_{iso\text{-}C_4}$ is determined by the area between the isotopic transients of *iso*-C_4 and Ar, the inert tracer, thereby subtracting out the effect of gas phase hold-up in the system.

Figs. 5 and 6 show the changes in average surface residence time ($\tau^*_{iso\text{-}C_4}$) and the concentration ($N^*_{iso\text{-}C_4}$) of the most active surface intermediates leading to *iso*-C_4 with TOS. $N^*_{iso\text{-}C_4}$ was determined by multiplying the rate of *iso*-C_4 formation by $\tau^*_{iso\text{-}C_4}$ [45]. $\tau^*_{iso\text{-}C_4}$ increased from 30 to 100 min TOS, and was relatively constant after 100 min TOS. $N^*_{iso\text{-}C_4}$ decreased significantly with increasing TOS. The asterisk (∗) indicates that these surface kinetic parameters have been corrected for interparticle readsorption of *iso*-C_4. This is done by extrapolating $\tau_{iso\text{-}C_4}$ measured at various space times to zero space time [5].

Unlike *iso*-C_4, readsorption of *n*-C_4 in the catalyst bed appeared to be insignificant. The high partial pressure of *n*-C_4 in the catalyst bed most likely increased the competition for adsorption sites and, thus, reduced the probability of *n*-C_4 readsorption. As discussed earlier, because the experimental techniques cannot determine the fraction of *n*-C_4 adsorbed on the catalyst surface, the measured value of $\tau_{n\text{-}C_4}$ cannot be used to characterize adsorption kinetics of *n*-C_4 on the catalyst. However, the measured value of $\tau_{n\text{-}C_4}$, in the range 25–30 s, indicates the presence of reversible chemisorption of *n*-C_4 rather than chromatographic separation due to physisorption in the catalyst bed. It may appear at first glance that the isotopic transients of *n*-C_4 and *iso*-C_4 are similar in Fig. 4, however, $\tau_{n\text{-}C_4}$ was ca. 25 s smaller than the measured values of $\tau_{iso\text{-}C_4}$ — greatly exceeding the maximum experimental error of 4 s. Fig. 7 shows the change in $N_{n\text{-}C_4}$ with TOS. $N_{n\text{-}C_4}$ was an order of magnitude larger than $N^*_{iso\text{-}C_4}$, and varied between 100 and 73 μmol/g over the TOS studied.

Surface coverages, θ, of *n*-C_4 and *iso*-C_4 were calculated using $N_{n\text{-}C_4}$, $N^*_{iso\text{-}C_4}$, and sulfur content, and are given in Table 2. $\theta_{n\text{-}C_4}$ ranged between 0.2 and 0.15. $\theta_{iso\text{-}C_4}$ at 30 min TOS was an order of magnitude lower than $\theta_{n\text{-}C_4}$ at ca. 0.022, and decreased to

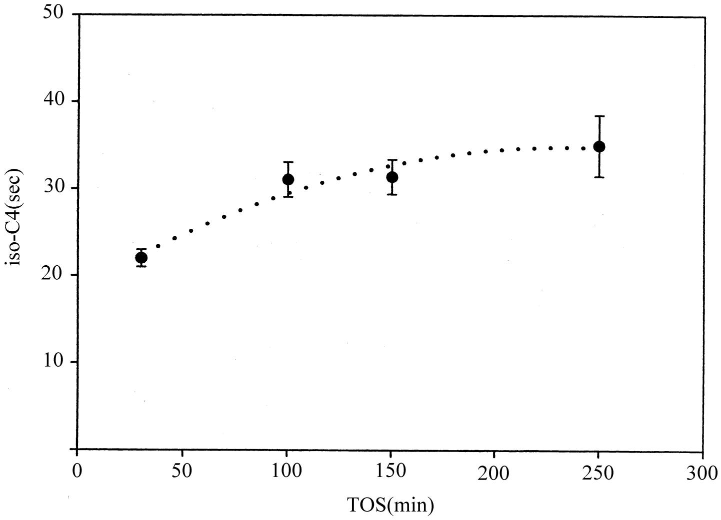

Fig. 5. Average residence time of active surface intermediates ($\tau^{*}_{iso\text{-}C_4}$) vs. TOS.

ca. 0.008 at 250 min TOS. Since it is highly likely that not all the sulfur was on the surface, the θ's represent maximum values relative to surface sulfur.

Table 3 lists the turnover frequencies (TOFs) at various TOSs. Since most studies in the literature vary in the sulfur content of SZ used, the activity constant, k_{sulfur}, based on the total sulfur concentration is often reported (Eq. (2)) [22], where

$$R_{iso\text{-}C_4} = k_{\text{sulfur}} N_{\text{sulfur}} \tag{2}$$

Then, it is useful to compare the TOFs based on the total sulfur concentration, $\text{TOF}_{\text{sulfur}}$, simply calculated by dividing the rate of *iso*-C_4 formation by the total sulfur concentration (Eq. (3)).

$$\text{TOF}_{\text{sulfur}} = \frac{R_{iso\text{-}C_4}}{N_{\text{sulfur}}} = k_{\text{sulfur}} \tag{3}$$

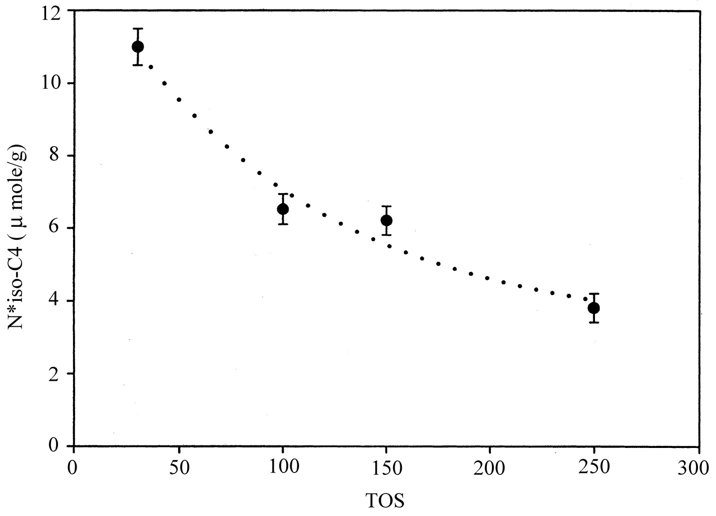

Fig. 6. Concentration of active surface intermediates ($N^{*}_{iso\text{-}C_4}$) vs. TOS.

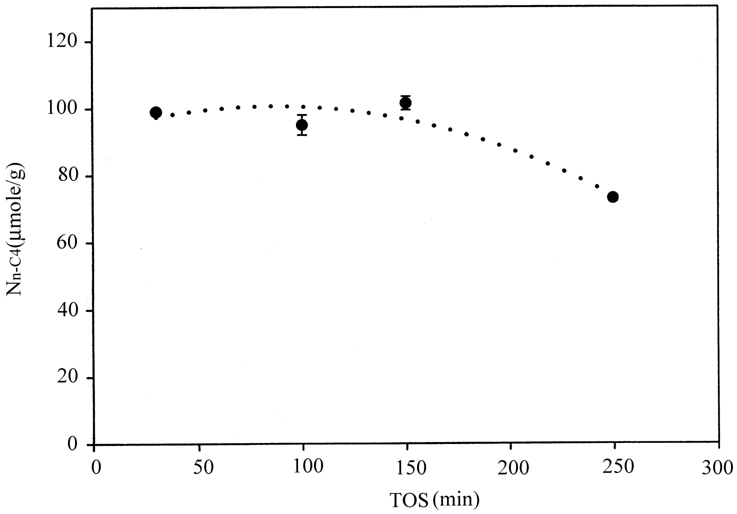

Fig. 7. Concentration of n-butane reversible adsorption sites ($N_{n\text{-C}_4}$) vs. TOS.

Similar to metal catalysis, a more accurate value of the true TOF can be estimated using $\tau^*_{iso\text{-C}_4}$ ($\text{TOF}^*_{\text{ITK}}$, Eq. (4)) [49]. This is because $\text{TOF}^*_{\text{ITK}}$ is based on the experimentally determined number of active intermediates rather than on all "hypothetical" sites, which in the case of SZ is truly hypothetical. This form of TOF is given by

$$\text{TOF}^*_{\text{ITK}} = \frac{R_{iso\text{-C}_4}}{N^*_{iso\text{-C}_4}} \approx \frac{1}{\tau^*_{iso\text{-C}_4}} \qquad (4)$$

Since not all potentially active sites may be occupied by intermediates under a given set of reaction conditions, $\text{TOF}^*_{\text{ITK}}$ represents a minimum value of the "true" site TOF (rate/site).

Table 2
Surface coverage based on sulfur content[a]

TOS (min)	$\theta_{n\text{-C}_4}$ [b]	$\theta_{iso\text{-C}_4}$ [c]
30	0.20	0.022
100	0.19	0.013
150	0.21	0.013
250	0.15	0.008

[a] $\theta_i = N_i/N_s = N_i/(493\ \mu\text{mol sulfur g}_{\text{cat}})$.
[b] Max error = ±0.006.
[c] Max error = ±0.0001.

Table 3
Turnover frequency

TOS (min)	$\text{TOF}_{\text{sulfur}}$ ($10^{-4}\ \text{s}^{-1}$)[a]	$\text{TOF}^*_{\text{ITK}}$ ($10^{-2}\ \text{s}^{-1}$)[b]
5	27.6	–
30	6.3	4.5
100	4.6	3.2
150	4.1	3.2
250	2.2	2.9

[a] $\text{TOF}_{\text{sulfur}}$ = rate of iso-C_4 formation/(493 μmol sulfur g_{cat}); Max error = ±5%.
[b] $\text{TOF}^*_{\text{ITK}} = 1/\tau^*_{iso\text{-C}_4}$; Max error = $\pm 0.002\ \text{s}^{-1}$.

4. Discussion

In Table 4, the initial activity and $\text{TOF}_{\text{sulfur}}$ obtained from this study are compared with data from the literature for similar catalysts [10,22,24,40]. $\text{TOF}_{\text{sulfur}}$'s were calculated using the concentrations of total sulfur and reported initial activities (Eq. (3)). All data are for reaction on unpromoted SZ at 150°C in the absence of H_2 while the partial pressure of n-C_4 varied. In general, the initial $\text{TOF}_{\text{sulfur}}$'s are in good agreement in the range between 1×10^{-3} and $7 \times 10^{3}\ \text{s}^{-1}$. The slight differences among the initial activities as well as among $\text{TOF}_{\text{sulfur}}$'s can be attributed to differences in catalyst preparation, pretreatment conditions, the partial pres-

Table 4
Comparisons of initial activity and TOF

Reference[a]	Sulfur (wt.%)	$P_{n\text{-C}_4}$ (atm)	Activity (μmol/(g s))	$\text{TOF}_{\text{sulfur}}$ ($10^{-3}\,\text{s}^{-1}$)
This study	1.6 ± 0.1	0.04	1.4 ± 0.07	2.76 ± 0.14
Fogash et al. [10]	1.80	0.10	2.0	3.56
Nascimento et al. [22]	1.55	1.00	0.63	1.30
	1.99	1.00	4.16	6.69
Corma et al. [25]	2.40	1.00	1.36	1.81
Tran et al. [40]	2.00	0.10	0.58	0.93

[a] Reaction conditions: Fogash et al. [10]: $T = 150°\text{C}, P = 1.0\,\text{atm}, n\text{-C}_4/\text{He} = 1/9$; Nascimento et al. [22]: $T = 150°\text{C}, P = 1.0\,\text{atm}, \text{WHSV} = 2\,\text{h}^{-1}$; Corma et al. [25]: $T = 150°\text{C}, P = 1.0\,\text{atm}, W/F = 39\,\text{g}_{\text{cat}}\,\text{h/mol}_{\text{C}_4}$; Tran et al. [40]: $T = 150°\text{C}, P = 1.0\,\text{atm}, n\text{-C}_4/\text{N}_2 = 1/9$.

sures of n-C_4 used, and the concentration of olefin impurities present. Differences in catalyst preparation (incorporation of sulfate, calcination and pretreatment conditions) affect not only the crystallinity of SZ but also determines the ratio of Bronsted/Lewis acid sites. It is well known that the partial pressure of n-C_4 has an effect on the isomerization activity. An increase in the partial pressure of n-C_4 increases the initial activity but may also increase the rate of deactivation in the presence of olefin impurities [34,35]. The presence of olefin also affects the activity of SZ, presumably by assisting in the initiation process [14,34]. Therefore, the differences observed in activity and $\text{TOF}_{\text{sulfur}}$ among these studies are reasonable. In the studies with lower $\text{TOF}_{\text{sulfur}}$'s, it is also possible that a smaller fraction of sulfur was available as active sites; whereas in the studies with higher $\text{TOF}_{\text{sulfur}}$'s, a larger fraction of sulfur may have been on the surface of SZ enhancing either the concentration of active sites or the site activities.

Interestingly, $\theta_{n\text{-C}_4}$ indicates that, under the reaction conditions used, only a small fraction (∼20%) of sulfur in the catalyst was utilized in the reversible adsorption of reactant (Table 2). The number of sulfate species that participated in the adsorption of surface reaction intermediates was an order of magnitude smaller (∼2%) than that utilized in adsorption of the reactant. Often a large fraction of adsorbed reactants do not become reactive intermediates and may simply desorb before the transformation can take place. This is often observed in reactions on supported metal catalysts [50]. Therefore, the large difference between $\theta_{n\text{-C}_4}$ and $\theta_{iso\text{-C}_4}$ is not unexpected.

It has been determined via ammonia adsorption that the acid sites on typical SZ catalysts vary in their differential heat of ammonia adsorption ($\Delta H_{\text{ads,NH}_3}$) in the range between 70 and 170 kJ/mol [10,25,51]. Of those different types of acid sites, acid sites with $\Delta H_{\text{ads,NH}_3} \geq 125\,\text{kJ/mol}$ have been suggested to be responsible for the isomerization activity of SZ [10,25,51]. Sites with $\Delta H_{\text{ads,NH}_3} \geq 140\,\text{kJ/mol}$ (the so-called "strong" acid sites) have been proposed to be the main reason for the high initial activity and deactivation [10]. Acid sites with $125\,\text{kJ/mol} \leq \Delta H_{\text{ads,NH}_3} \leq 140\,\text{kJ/mol}$ (the so-called "intermediate" acid sites), on the other hand, are suggested to be the main contributors to the later decreased activity and slow steady deactivation of the catalysts [10,51]. These acid sites typically have been reported to constitute 27–29% of the total acid sites. It has been determined that approximately 12–17% of sulfate species are utilized in the formation of the acid sites with strong and intermediate acid strengths (5–10% for strong acid sites and 7% for intermediate sites) [10].

Based on the present research, there seems to be a fairly good agreement between the hypothetical fraction of sulfur species related to the strong and intermediate acid strength acid sites (∼17% of total sulfur) on a typical SZ catalyst and the hypothetical fraction of sulfur species involved in adsorption of the reactant ($\theta_{n\text{-C}_4}$, ∼20% of total sulfur) for the SZ utilized in this study. This suggests that the n-C_4 adsorption sites may, at reaction conditions, consist of the strong and intermediate acid sites present on SZ.

Acidity characterization of the strong and intermediate acid sites on SZ is useful. Microcalorimetry of NH_3 appears to be a more reliable method of acidity characterization since it does not involve heating to temperatures where the surface structure of the SZ may change and where some sulfur may be driven-off of the surface. However, recent work by Gao and coworkers [51,52] raises an important question regarding the relationship between the NH_3 adsorption characteristics and the catalytic activity of SZ-based catalysts. Comparison of the concentrations of intermediate acid sites and the catalytic activities of sulfated or persulfated zirconia-based catalysts suggests no correlation between these measurements. Because of this new evidence and the controversies surrounding the accuracy and meaning of acidity measurements, this study does not repeat acidity characterization of the SZ utilized in this study. However, the MEI SZ studied here has been extensively characterized in other studies [8,10–14,20,25,34,35,48]. The relationship between acidity, activity, and surface reaction parameters of SZ will be addressed in a future publication.

In the presence of site heterogeneity, the sites with higher site activity tend to deactivate at a faster rate. This is especially true where the mechanism for the formation of products includes inherent deactivation steps. This behavior is observed in the present study. The high initial activity was accompanied also by a higher deactivation constant, k_d. $\mathrm{TOF}^*_{\mathrm{ITK}}$ sheds more light onto this. $\mathrm{TOF}^*_{\mathrm{ITK}}$ decreased from 30 to 100 min TOS, but was relatively constant after 100 min TOS. This suggests that at TOS $\geq$ 100 min, the active sites were relatively more homogeneous with lower site activity (less active sites). At 30 min TOS, the active sites consisted of two (or more) types of sites with different site activities. The presence of the more active sites (with higher site activity) was reflected in the higher $\mathrm{TOF}^*_{\mathrm{ITK}}$.

More supporting evidence can be obtained from the normalized isotopic transients. Deviation from linearity of a semi-log plot of the normalized isotopic transient is an indication of the presence of site heterogeneity [53]. The fast initial decrease in the isotopic transient of the product is due to the fast reaction and, hence, isotope replacement on the more active sites. The change in the slope of the isotopic transient at longer times is a result of slower isotope replacement on the less active sites. The observed change in the slope of the normalized isotopic transient at 5 min TOS, unlike at 150 min TOS, suggests the presence of active site heterogeneity at 5 min TOS (Fig. 8).

These results suggest the following: (a) the active sites during the initial period of isomerization consisted of sites with at least two different average site activities, (b) deactivation of the possibly smaller concentration of the more active sites contributed to the fast initial deactivation of SZ, (c) after the fast deactivation of the more active sites, most of the active sites that participated in reaction were the less active sites, and (d) the steady decrease in activity following the initial deactivation was due to the loss/deactivation of less active sites.

The isomerization activity after regeneration at 315°C gives more insights into the deactivation of SZ (Fig. 3). The initial isomerization activity after regeneration was ca. 50% of the initial activity of the fresh SZ catalyst. With increase in TOS, the rate of *iso*-C_4 formation on the regenerated catalyst duplicated the values of the fresh catalyst at the same TOS. This suggests that by heating the catalyst under O_2 (i.e., air), these deactivated sites became active again. The significant difference only in the initial activities of the fresh and the regenerated catalysts suggests that the sites less easily regenerated may be the more active sites.

There are four proposed mechanisms for the deactivation of an SZ catalyst during *n*-C_4 isomerization [15]: (a) site blockage by coke/oligomer formation, (b) sulfur migration from surface to bulk of the ZrO_2, (c) sulfur reduction, and (d) sulfur loss. If deactivation is due to the loss of active sites by either coke/oligomer formation and/or sulfur reduction, treating in O_2 (regeneration in air) can recover the lost active sites. It is necessary to note, however, that for a regeneration of only 4 h at temperature of 315°C, it is possible that not all the coke/oligomer was able to be burned-off nor all reduced sulfur re-oxidized. The active sites lost via sulfur loss or migration are probably not able to be recovered by treating the catalyst in air. The role of above-proposed catalyst deactivation mechanism is easily linked to loss of acid sites (which adsorbs the active surface intermediates). However, this impact on loss of sites which generate butene (probably required to form the active surface intermediates) requires more attention. It is important to understand the role of olefin generation, via a redox mechanism as proposed by Ghenciu and Farcasiu [54], in order to elucidate the nature of high *n*-butane isomerization activity on SZ. The role of catalyst parameters and

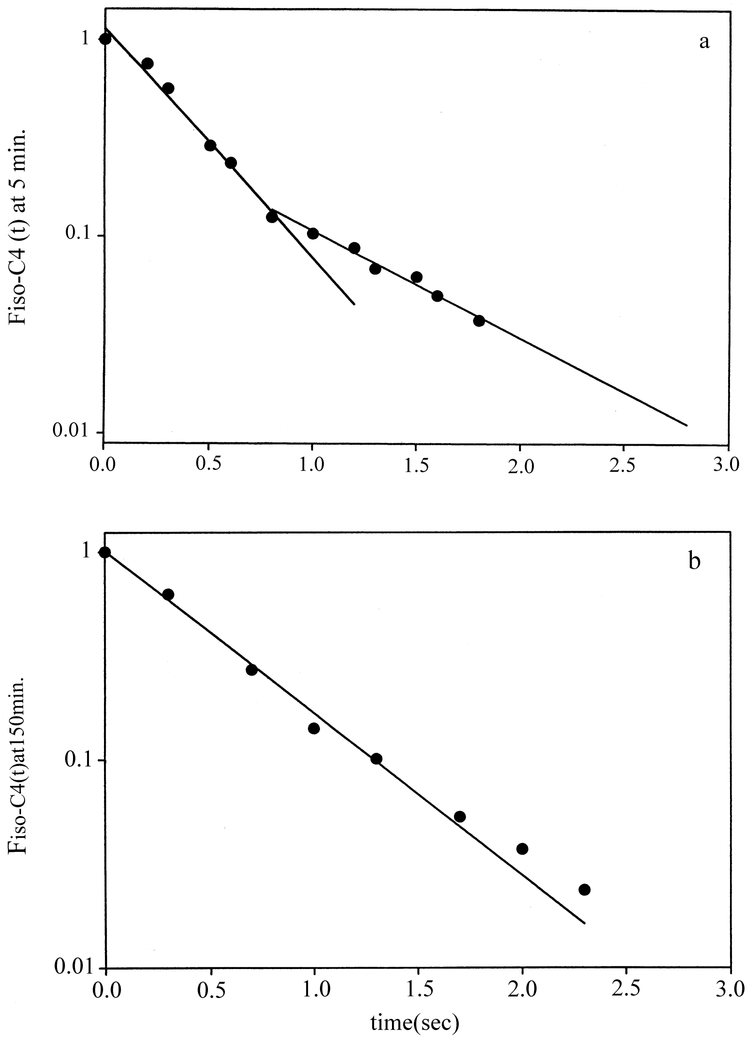

Fig. 8. Normalized isotopic transients of active surface intermediates leading to *iso*-butane (F_n) at (a) 5 and (b) 150 min TOS.

reaction conditions on the olefin generation ability of SZ will be the focus of a future publication.

Recovery of the isomerization activity and no significant change in surface kinetic parameters ($\tau_{iso\text{-}C_4}$ and $N_{iso\text{-}C_4}$) at TOS $>$ 100 min after regeneration of the catalyst (not shown) suggests that the dominant mechanisms for loss of less active sites were the reversible mechanisms, i.e., site blockage by coke/oligomer formation and/or sulfur reduction. A large increase in the carbon content between 150 and 300 min TOS (Table 1) suggested that catalyst deactivation via coke/oligomer formation may have played a significant role for the less active sites. Loss of active sites via sulfur reduction cannot be ruled out.

The large difference in the initial isomerization activity of the fresh and regenerated SZ indicates that the regeneration condition was not sufficient to recover all of the deactivated active sites, especially the more active sites. Sulfur loss did not appear to have taken place for the SZ catalyst (Table 1). Coke/oligomer formation, sulfur reduction, and sulfur migration need to be considered for the deactivation of these sites.

Table 5
Active sites on SZ

	More active	Less active
Activity	High initial	Steady state
Deactivation	Fast initial	Slow
Regeneration	Possible at high temperature	Possible at lower temperature
Possible deactivation mechanisms	Coke/oligomer formation, sulfur reduction	Coke/oligomer formation, sulfur reduction

It is interesting to study the impact of temperature on the regeneration ability of SZ, since others [21,26] have reported full recovery of deactivated sites when SZ was pretreated and regenerated at higher temperature of 450°C. As shown in Fig. 3, more but not all of initial activity was recovered with an increase in regeneration temperature to 450°C. It is likely that more of the coke/oligomer on the catalyst surface was able to be removed at a higher regeneration temperature. The oxidation of reduced sulfur could also be more favorable at a higher regeneration temperature. But at the same time, one must consider possible changes in catalyst characteristics (e.g., loss of hydroxyl groups and decomposition of sulfate species) which can affect the catalytic activity of the catalyst. The increase in initial activity following higher regeneration temperature suggests that loss of the more active sites may be significantly affected by coke/oligomer formation and/or sulfur reduction.

There is little known about the migration of sulfur and its impact on the catalytic activity of SZ. Arata and Hino [17] reported that sulfur is present as $SO_4{}^{2-}$ on the surface of SZ. Chen et al. [55] and Farcasiu et al. [56] reported that some fraction of sulfur can be incorporated into the bulk of metal oxide, especially when the sulfur loading is relatively high (>3 wt.%). Interestingly, Farcasiu et al. [56] concluded that sulfate does not have to be on the surface but rather should be located near the surface for methylcyclopentane (MCP) isomerization. For the SZ used in this study, it is most likely that a large portion of the sulfur was located on the surface of SZ since the sulfur content was low.

5. Conclusions

n-Butane isomerization on the SZ appeared to proceed on active sites with a range of average site activities (Table 5). Initially, both more and less active sites are suggested to have been present and to have contributed to the isomerization activity of SZ. The significant initial decrease in isomerization activity was mainly due to the loss of more active sites. At higher TOS, the isomerization primarily accomplished by the remaining less active sites. The deactivation of the less active sites was slower and was reflected in a lower deactivation constant, k_d. The impact of regeneration temperature on recovery of initial activity indicates that the deactivated more active sites were more difficult to regenerate than the deactivated less active sites. Also, the obtained results suggest that the dominant deactivation mechanisms were loss of active sites by blockage of sites by coke/oligomer and, possibly, sulfur reduction.

The fraction of sulfate species possibly utilized as n-C_4 reversible adsorption sites ($\theta_{n\text{-}\mathrm{C}_4} = N_{n\text{-}\mathrm{C}_4}/[\text{total sulfur}]$) was determined to be only ∼0.2. Even lower amounts of sulfate species apparently participated in the active reaction sites during n-C_4 isomerization ($\theta_{iso\text{-}\mathrm{C}_4} = 0.02\text{–}0.01$). It is important to be able to relate these adsorption sites of both the reactant and the active surface intermediates to the acid sites of the SZ. $\theta_{n\text{-}\mathrm{C}_4}$ showed good correlation with the hypothetical fraction of sulfate species forming acid sites with strong and intermediate acidity reported in the literature. However, the relationship between the active reaction sites and the acid sites of SZ appear to be complex. This issue will be the focus of future work.

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