n-butane isomerization on sulfated zirconia: isotopic transient kinetic analysis of reaction at the site level

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By using SSITKA (steady-state isotopic transient kinetic analysis), n-butane (n-C_4) isomerization on sulfated zirconia (SZ) has been studied for the first time at the site level. Accurate measures of the average residence time and the concentration of the most active surface intermediates leading to isobutane (iso-C_4) were able to be determined. As has previously been observed, a fast initial deactivation of the catalyst followed by a slow steady-state deactivation was observed over 400 min time-on-stream (TOS). It was shown that even though a large amount ($\sim$100 μmol/g) of n-C_4 ($N_{n\text{-C}_4}$) was adsorbed on the catalyst, the concentration of active surface intermediates leading to iso-C_4 ($N^*_{\text{iso-C}_4}$) was only $\sim$10 μmol/g at 30 min TOS. The continuous decrease in $N^*_{\text{iso-C}_4}$ indicated that the decrease in catalytic activity was due to loss of active sites. An increase in the average residence time of active surface intermediates leading to iso-C_4 ($\tau^*_{\text{iso-C}_4}$) was observed only between 30 and 100 min TOS. This suggests a possible presence of two types of active sites for n-C_4 isomerization on SZ under the reaction condition studied. It is suggested that the more-active sites contributed to the high initial activity, while the majority of active sites after 100 min TOS were the less active sites.

Keywords: n-butane isomerization, solid acids, metal oxides, sulfated zirconia, isotopic transient kinetic analysis, SSITKA

1. Introduction

Butane is an important chemical in the chemical and petroleum industries [1,2]. n-butane (n-C_4) can be added to gasoline for volatility control. Alkylation of isobutane (iso-C_4) with C_3 and C_4 alkenes is an important reaction in the production of gasoline alkylates. Iso-C_4 can also be converted to isobutylene for use in methyl *tert*-butyl ether (MTBE) synthesis. Iso-C_4 is the more valuable chemical of the two butane isomers because the availability of iso-C_4 from natural sources is far below its industrial demand. Therefore, most iso-C_4 is produced from n-C_4 via isomerization. The commercial process involves promoted Pt/Al_2O_3 catalysts [3]. Due to the presence of Pt, the catalysts are very sensitive to sulfur in the feed stream. Also, water is reported to be a poison for the catalyst.

In search of new catalysts for n-C_4 isomerization, researchers have studied inorganic solid acids such as zeolites and metal oxides [4,5]. Among these catalysts, sulfated zirconia (SZ) has been shown to produce iso-C_4 with a selectivity greater than 90% at 150 °C and 1 atm. The nature of the active sites on SZ catalysts and the reaction mechanisms have been studied extensively using various techniques such as FTIR, TPD, XRD, and isotope labelling. Recent reviews of butane isomerization on SZ and characteristics of SZ are available in the literature [4,6–8]. The important factors for n-C_4 isomerization activity on SZ include sulfur content, total surface area, calcination temperature, water content, ratio of Lewis-to-Brønsted acid sites, and presence of promoters such as Fe and Mn. Although these parameters can be adjusted to increase the overall activity and selectivity towards iso-C_4, the fast rate of deactivation has been a limitation for the use of SZ catalysts commercially.

A fast deactivation of SZ has been observed at the beginning of the reaction (<50 min time-on-stream (TOS)) during which time the catalyst loses up to 50% of its initial activity. This is followed by a more steady and slower deactivation with TOS, a pseudo-steady state. It is of interest to elucidate how the catalyst deactivates with TOS.

Steady-state isotopic transient kinetic analysis (SSITKA) is one of the most powerful reaction techniques used in heterogeneous catalysis [9]. SSITKA is based on the simple fact that there is no isotope effect for molecules with mass greater than hydrogen. A step change between two reactant streams containing different isotopes of the reactant(s) does not disturb surface reaction and allows for the determination of concentration (N_i [=] moles of surface intermediates of product i/W_{cat}) and average surface residence time (τ_i) of the most active surface intermediates. To date, SSITKA has been extensively used for reactions involving relatively simple molecules, such as methanation, methanol synthesis, ammonia synthesis, and ethane hydrogenolysis. Applications of SSITKA to monitor larger hydrocarbon products during Fischer–Tropsch synthesis have also been reported [10,11]. However, the limitation of SSITKA for reactions involving larger molecules lies with mass spectrometry used in isotope analysis [12].

This paper reports the results of a study of n-butane isomerization using SSITKA.

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2. Experimental

2.1. Catalyst preparation

Sulfate-doped zirconium hydroxide ($Zr(OH)_4$) was obtained from Magnesium Elektron, Inc. (XZ0682/01, Flemington, NJ). Sulfated zirconia (SZ) was prepared by calcination of the sulfate-doped $Zr(OH)_4$ at 600 °C for 2 h in a high-temperature oven.

2.2. Surface area and sulfur content

The BET surface area of the fresh calcined SZ catalyst was determined using N_2 adsorption by Micromeritics (Norcross, GA). The sulfur content of the fresh calcined SZ catalyst was determined by Galbraith Laboratories, Inc. (Knoxville, TN).

2.3. X-ray diffraction (XRD)

The crystallinity of fresh calcined SZ catalyst was studied using a Philips X'Pert X-ray diffractometer. The diffractometer utilized monochromatized Cu K_α radiation and a Ni filter, and was operated at 40 kV and 30 mA. The range of the spectra in 2θ was from 10° to 70°. The scanning rate was 0.5°/min (2θ).

2.4. n-butane isomerization

Butane isomerization was carried out in a quartz microreactor with inner diameter of 10 mm. The catalyst weight used was varied between 0.1 and 0.4 g in order to vary space time between 0.01 and 0.06 s. The calcined SZ catalyst was loaded in a reactor and pretreated *in situ* prior to isomerization. The SZ catalyst was first heated to the pretreatment temperature of 315 °C at 10 °C/min in flowing air (30 cm^3/min, Praxair, UHP) and then 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). 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 5A 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 foot 80/100 mesh Porapak Q column.

2.5. SSITKA system setup

The limitation on SSITKA, requiring modifications for this study, was simply due to the limitation of mass spectrometry. The larger molecules involved in this study, C_3 to C_6, fragment in the mass spectrometer (MS) during ionization. Overlapping fragments are convoluted in the intensity measured at various m/e rendering isotope analysis difficult. To overcome this limitation, GC separation and hydrogenolysis of the hydrocarbons to methane were incorporated in the SSITKA system.

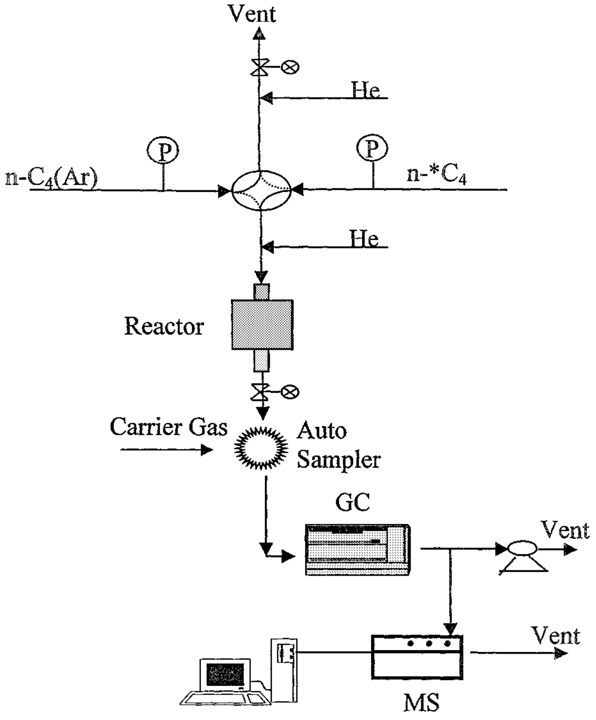

Figure 1. Schematic of the SSITKA system.

A schematic of the modified SSITKA system is shown in figure 1. A step-change was made between n-$^{12}C_4$ and $^{13}CH_3(^{12}CH_2)_2{}^{13}CH_3$ (n-$^*C_4$) without disturbing the other reaction conditions. Samples of the effluent were collected using a VICI 32-port valve (16 loops). The collected effluent samples were separated in an 18 foot 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, using the carrier gas as a source of H_2, was converted to methane (CH_4) in a hydrogenolysis unit (HU) consisting of 10 g of 5 wt% Pt/SiO_2 at 250 °C and then was differentially introduced to a Balzers–Pfeiffer Prisma 200 amu mass spectrometer (MS). The MS data was collected with a Pentium II PC connected to the MS using Quadstar software. More detailed descriptions of the equipment and the preparation method and characterization of Pt/SiO_2 can be found in [12,13], respectively.

3. Results and discussion

The impurities in the n-C_4/He mixture were mainly butene, isobutane, and isopentane. Isopentane and isobutane 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, increases the rate of catalyst deactivation [2,14–20]. With the H-mordenite olefin trap in place,

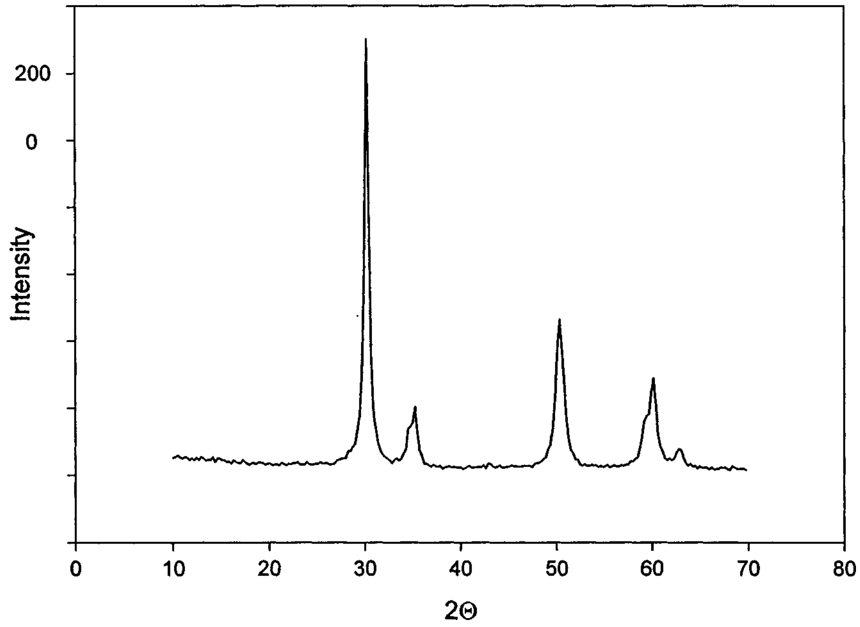

Figure 2. XRD spectrum of the fresh calcined SZ catalyst.

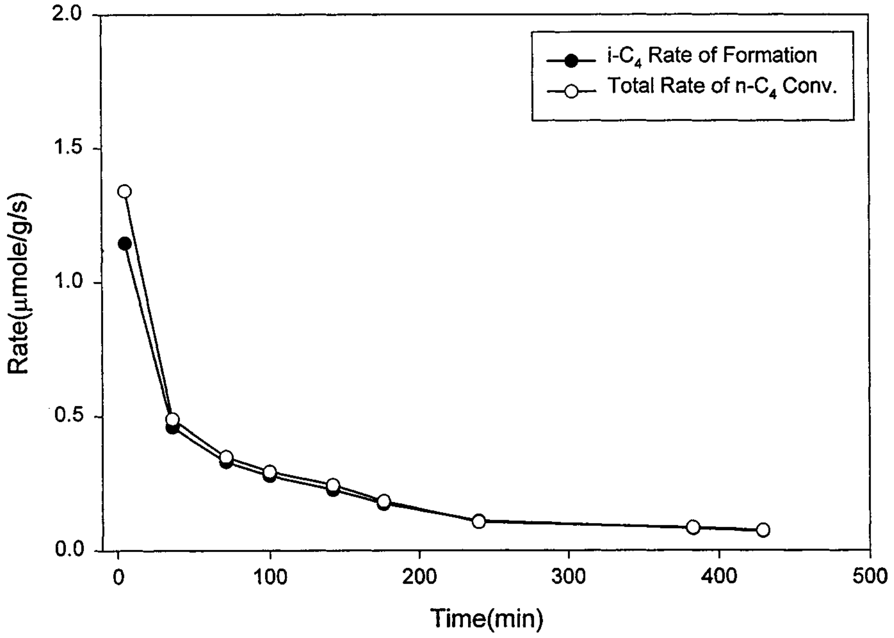

Figure 3. Isomerization activity of the SZ catalyst at 150 °C.

butene concentration was kept below 20 ppm. The effluent analysis has been corrected for these impurities.

The sulfur content of the fresh calcined SZ catalyst was 1.6 ± 0.1 wt%. The BET surface area of the fresh calcined SZ catalyst was determined to be 94.2 m^2/g. An XRD spectrum of the fresh catalyst is shown in figure 2. The XRD spectrum exhibits only the tetragonal phase of ZrO_2. No sulfur compounds were detected due to the low sulfur content.

Figure 3 shows the isomerization activity on 0.2 g of SZ at 150 °C over 400 min time-on-stream (TOS). No heat or mass transfer limitations were detected while varying the reaction temperature between 130 and 170 °C. The apparent activation energy of isomerization, based on the initial isomerization activities, was ca. 7.9 ± 0.8 kcal/mol. This is in close agreement with the reported values of E_{app} between 8.9 and 10.7 kcal/mol [12,21,22]. 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. By-products of reaction 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}, given by Fogash et al. [14],

$$\text{rate} = \text{rate}_0 \exp(-k_{\mathrm{d}}t), \qquad (1)$$

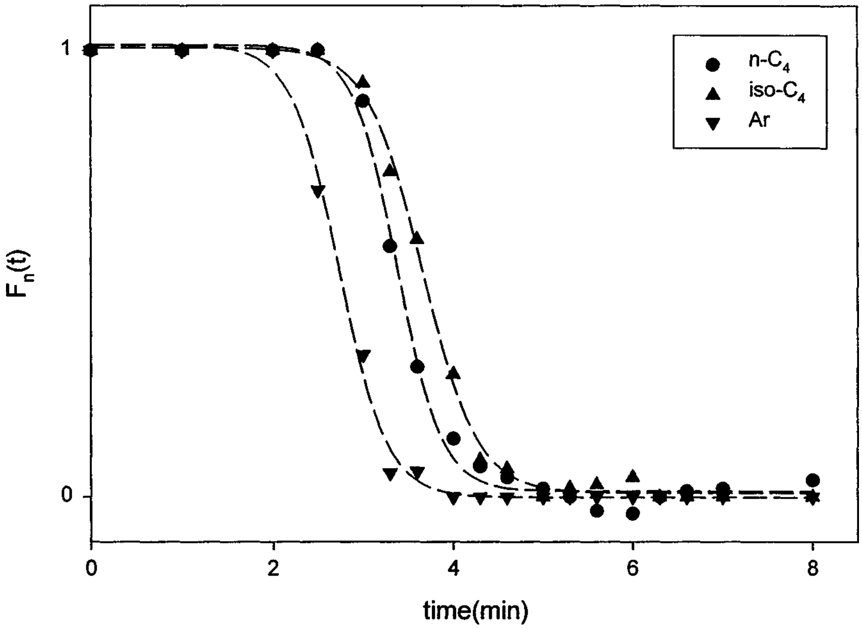

Figure 4. Normalized isotopic transients at 150 °C (TOS = 30 min, $W_{cat} = 0.2$ g).

was ca. 0.033 min^{-1}. After the fast initial deactivation, the isomerization activity declined at a lower rate, with 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. These results are consistent with those reported by others [7,8,16,20] for this reaction system.

Hong et al. [23] have reported formation of H_2 during the initial phase of isomerization. H_2 formation is proposed to be linked to the dehydrogenation of butane to butene which initiates the isomerization of butane [19,23]. In this study, the effluent from the reactor was directly injected into the MS via differential pumping during the first 100 min TOS. Unlike the results from Hong et al. [23], no measurable amount of H_2 was detected during this period.

Figure 4 shows an example of the normalized isotopic transients ($F_{n,i}(t)$ of component i, where i is the inert tracer (Ar), n-C_4, or iso-C_4) following a step change during SSITKA. The points were determined using the results from each sample loop and a line was fitted through the points using a sigmoidal equation. The average residence time of the surface intermediates leading to iso-C_4 ($\tau_{\text{iso-C}_4}$) is calculated by integrating the area between the normalized transients of iso-C_4 and of Ar:

$$\tau_{\text{iso-C}_4} = \int_0^{\infty} \left[F_{\text{n,iso-C}_4}(t) - F_{\text{n,Ar}}(t)\right] \mathrm{d}t. \tag{2}$$

The concentrations of these surface intermediates leading to iso-C_4 ($N_{\text{iso-C}_4}$) can be mathematically calculated using equation

$$N_{\text{iso-C}_4} = \tau_{\text{iso-C}_4} R_{\text{iso-C}_4}, \tag{3}$$

where $R_{\text{iso-C}_4}$ is the rate of iso-C_4 formation. Details on SSITKA can be found in a review by Shannon and Goodwin [9].

Figures 5 and 6 show the changes in $\tau_{\text{iso-C}_4}$ and $N_{\text{iso-C}_4}$ with TOS. These results would appear at first observation to suggest that the decrease in the isomerization activity is due to decreases in both $\tau_{\text{iso-C}_4}$ and $N_{\text{iso-C}_4}$. While the decrease in the concentration of the active surface intermediates with TOS is reasonable, the decrease in $\tau_{\text{iso-C}_4}$ is unexpected. A decrease in the average residence time of surface intermediates leading to iso-C_4 ($\tau_{\text{iso-C}_4}$) would mean that the average isomerization activity of the intermediates (related to site TOF) increased with TOS. The apparent decrease in $\tau_{\text{iso-C}_4}$ measured with TOS is an undesirable result due to product readsorption in the catalyst bed, and must be corrected before interpretation is attempted.

The impact of readsorption of a product on SSITKA has been found to be significant for a number of reactions [9,24–26] and can lead to wrong interpretation of results. Thus, it is important to understand the impact of product readsorption and to subtract out this effect prior to elucidating the role of the catalyst and reaction parameters on catalytic activity. Readsorption of a product can result in an overestimation of average residence time of the surface intermediates leading to that product [24]. The presence of product readsorption can be identified by plotting τ measured at various space times. Figure 7 shows $\tau_{\text{iso-C}_4}$ measured at 30 min TOS for various space times. The presence of iso-C_4 readsorption in the catalyst bed is clearly indicated. The effect of iso-C_4 readsorption on the measured value of $\tau_{\text{iso-C}_4}$ is a function of iso-C_4 partial pressure in the catalyst bed; hence, the decrease in $\tau_{\text{iso-C}_4}$ with TOS (figure 5) as the production rate of iso-C_4 decreased. A decrease in the partial pressure of iso-C_4 in the catalyst bed decreases the competition between iso-C_4 molecules for readsorption sites. This, in turn, increases the probability of a given iso-C_4 molecule readsorbing in the catalyst

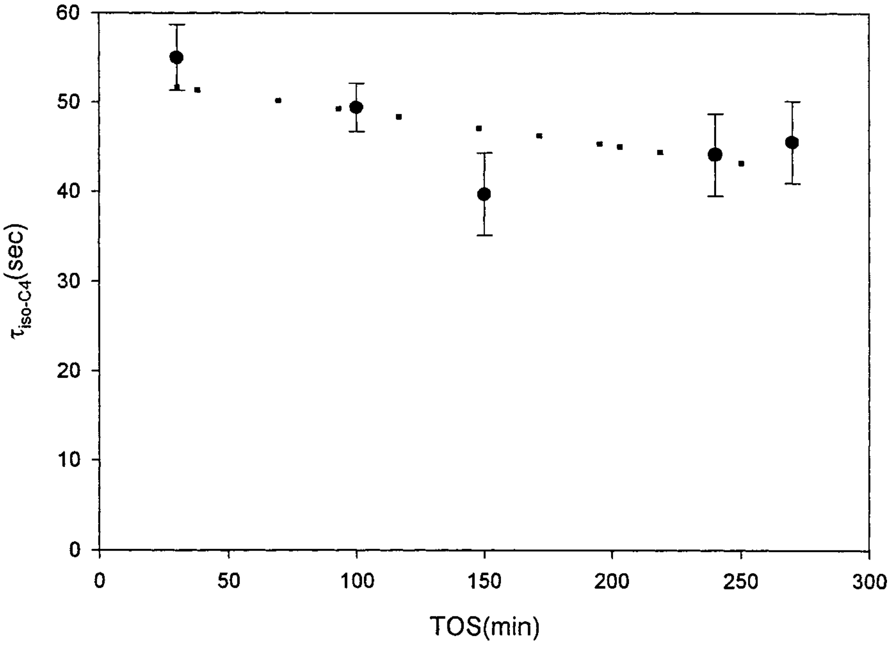

Figure 5. Average surface residence time of iso-C_4 vs. TOS at 150 °C.

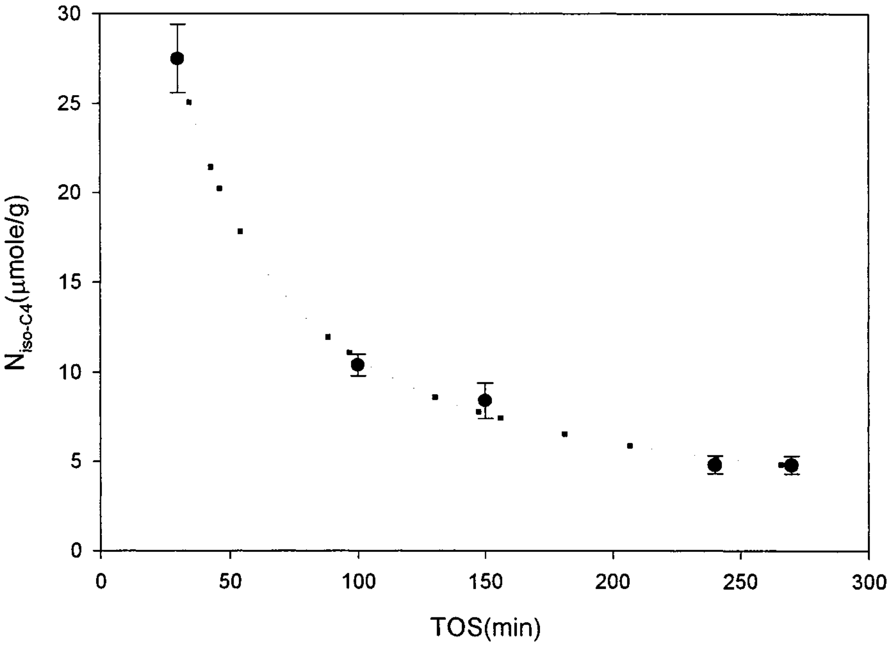

Figure 6. Concentration of surface intermediates leading to iso-C_4 vs. TOS at 150 °C.

bed. Thus, at higher partial pressures of iso-C_4, the "closer" the τ measured is to the true average surface reaction site residence time. As in the case for the surface residence time of intermediates during methanol synthesis [24], the $\tau_{\text{iso-C}_4}$ extrapolated to zero space time, $\tau^*_{\text{iso-C}_4}$, represents the average reaction site residence time of surface intermediates leading to iso-C_4 corrected for interparticle readsorption.

Figure 8 shows the changes in $\tau^*_{\text{iso-C}_4}$ with TOS. The $\tau^*_{\text{iso-C}_4}$ increased approximately 30% from 30 to 100 min TOS. However, $\tau^*_{\text{iso-C}_4}$ was relatively constant within the experimental error for TOS $\geqslant$ 100 min. This suggests that the change in the estimated average site activity (related to $1/\tau^*_{\text{iso-C}_4}$), specifically, the decrease in average site activity, occurs only during the first 100 min TOS.

Figure 9 shows the change in concentration of surface intermediates for iso-C_4, $N^*_{\text{iso-C}_4}$, over the TOS studied. $N^*_{\text{iso-C}_4}$ was determined by multiplying the rate of iso-C_4 formation with $\tau^*_{\text{iso-C}_4}$ [24]. The decrease in $N^*_{\text{iso-C}_4}$ with increasing TOS and with decreasing rate of isomerization suggests that the deactivation of SZ is primarily due to loss of active sites.

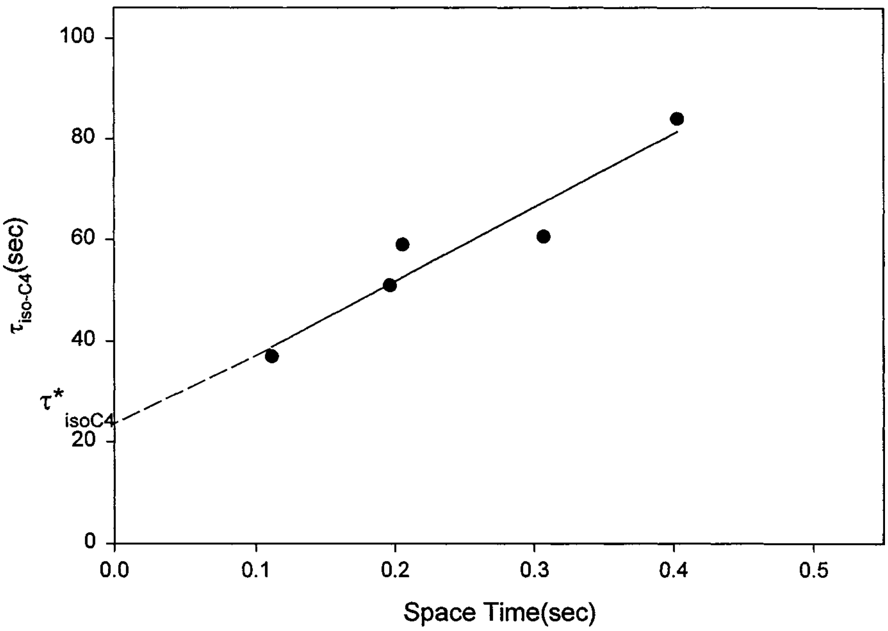

Figure 7. Average surface residence time at various space times at 150 °C (TOS = 30 min).

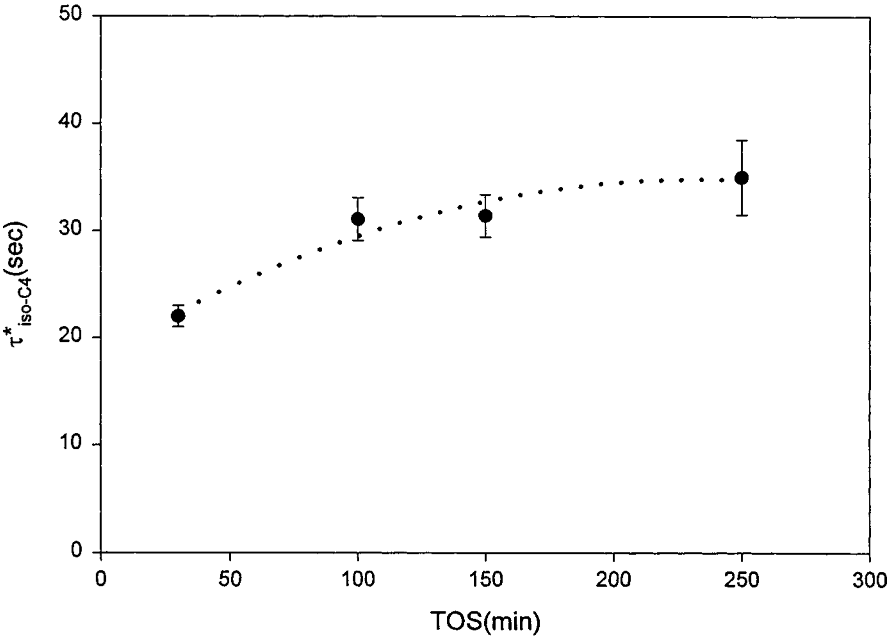

Figure 8. Corrected average surface residence time of iso-C_4 vs. TOS at 150 °C.

It is interesting to note that, while $N^*_{\text{iso-C}_4}$ continuously decreased with TOS, a significant change in $\tau^*_{\text{iso-C}_4}$ was observed only during TOS $\leqslant$ 100 min. These results suggest a possible presence of active site heterogeneity on SZ under the reaction conditions studied.

If one assumes that there are two different types of active sites with different average site activities, the sites with higher site activity can be designated as the "more active sites" and the sites with lower site activity as the "less active sites". In case of such site activity heterogeneity, the more active sites tend to deactivate at a faster rate than the less active ones. This is especially true where the mechanism for product formation includes steps leading to deactivation. Assuming there are two different types of active sites on SZ, the following hypothesis can be made with the aid of SSITKA results. The smaller $\tau^*_{\text{iso-C}_4}$ at TOS $<$ 100 min reflects a higher average site activity than at TOS $\geqslant$ 100 min. The higher average site activity is due to presence of both the more active sites as well as the less active one. After TOS $\geqslant$ 100 min, the larger and relatively constant $\tau^*_{\text{iso-C}_4}$ suggests that the average site activity has decreased and most of the active sites remaining are the less active one. The continuous decrease in $N^*_{\text{iso-C}_4}$ with TOS suggests loss of these active sites as well with deactivation.

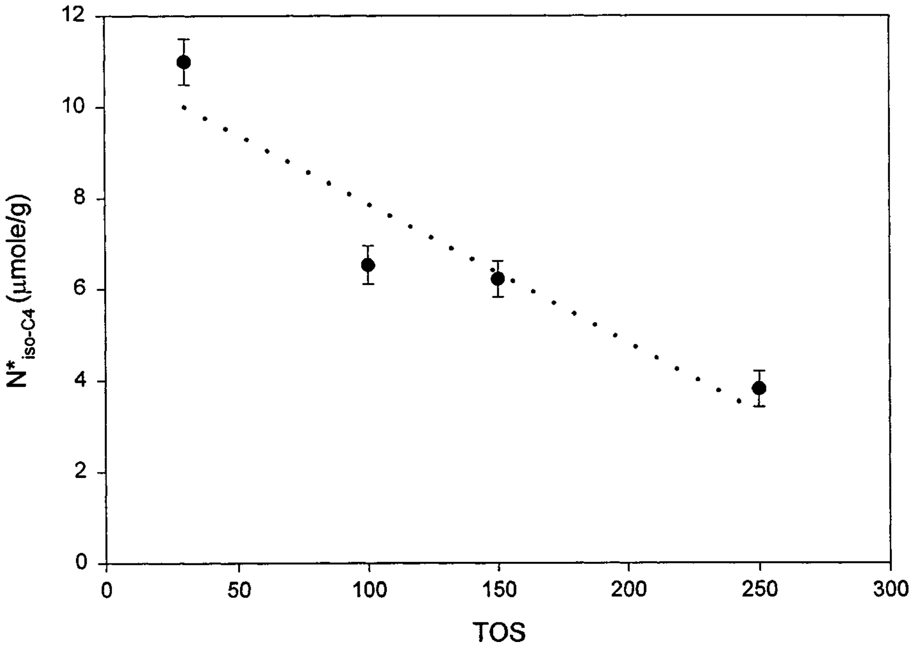

Figure 9. Corrected concentration of most active intermediates leading to iso-C_4 vs. TOS at 150 °C.

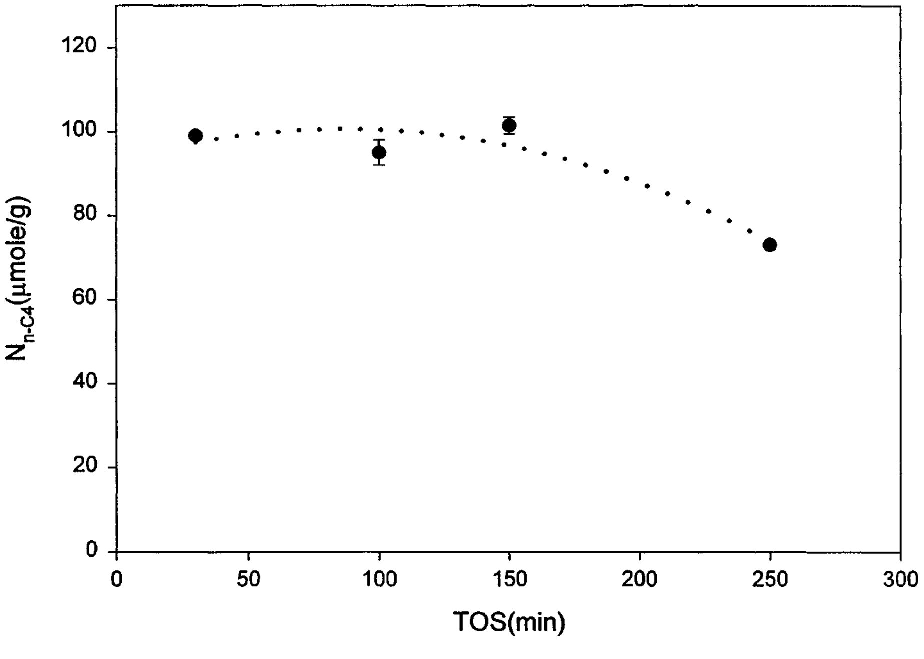

Figure 10. Concentration of adsorbed n-C_4 vs. TOS at 150 °C.

It is important to note at this point that τ of a reactant is different from τ of a product. Every product formed has been an active surface intermediate and has, thus, definitely resided on the surface on the catalyst. Therefore, τ of a product reflects the average residence time of surface intermediates leading to the product. However, since τ of an adsorbate is an average value, it is averaged over all reactant molecules whether they adsorb or not. Since one cannot know the true fraction of reactant adsorbed during passage through the catalyst bed, a τ measured for a reactant can only be used to determine the concentration of that reactant adsorbed [27]. The $\tau_{n\text{-}C_4}$ measured in this study indicated no significant readsorption of n-C_4 in the catalyst bed probably due to the high partial pressure of n-C_4.

Figure 10 shows the change in $N_{n\text{-}C_4}$ with TOS. $N_{n\text{-}C_4}$ varied between 100 and 73 μmol/g over the TOS studied. This suggests that the concentration of n-C_4 adsorption sites was not significantly affected by the deactivation of SZ via loss of concentration of active reaction sites. The large difference between $N_{n\text{-}C_4}$ and $N^*_{\text{iso-}C_4}$ suggests that only a small fraction of n-C_4 adsorption sites acted as active reaction sites.

4. Conclusion

n-butane isomerization on sulfated zirconia has been successfully studied using SSITKA following modification to the traditional SSITKA system and methodology. In particular, product (iso-C_4) readsorption in the catalyst bed had to be taken into account in the analysis of the isotopic tracing results. After correction for product readsorption, the results indicate that the decrease in catalytic activity of SZ with TOS was due mainly to a loss in active sites (intermediates) as indicated by the decrease in $N^*_{\text{iso-C}_4}$. Compared to the concentration of active reaction intermediates ($N^*_{\text{iso-C}_4}$), that of reactant adsorption was an order of magnitude larger and no significant decrease was observed during deactivation. The changes in the corrected residence time of active surface intermediates ($\tau^*_{\text{iso-C}_4}$) over the TOS studied suggest possible site heterogeneity. The results suggest that for TOS $\leqslant$ 100 min, the active sites consist of both the more and less active sites. But the loss of more-active sites during this period results in presence of mainly less-active sites at TOS $\geqslant$ 100 min.

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