

# Elucidation of *n*-Butane Isomerization on Sulfated Zirconia Using Olefin Addition

Sonia Hammache and James G. Goodwin, Jr.<sup>1</sup>

Department of Chemical Engineering, Clemson University, Clemson, South Carolina 29634-0909

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Olefin formation appears to play a key role in *n*-butane isomerization on sulfated zirconia (SZ). In order to better understand the pathway of the reaction, 1-butene (1-C<sub>4</sub><sup>=</sup>) was added during reaction at low and at high reaction temperatures. Olefin addition, even at the lowest 1-C<sub>4</sub><sup>=</sup>/*n*-C<sub>4</sub> ratio, decreased the activity of the catalyst at 250°C, did not eliminate the reaction induction period, and contributed to catalyst deactivation from the beginning of the reaction. However, it shifted the maximum activity to lower time-on-stream (TOS). Butene added for only 90 s at the beginning of the reaction deactivated the catalyst in a manner similar to that in the case where it was added continuously during all TOS. Isotopic transient kinetic analysis (ITKA) showed that although more intermediates were initially formed on the surface with olefin addition, this positive effect was quickly overwhelmed by the negative effect of olefin concentration on deactivation. The positive impact of butene on the reaction was able to be more clearly seen at a lower reaction temperature (150°C) when deactivation was not as severe. The positive impact was manifested by an increase in the 5-min TOS reaction rate. Olefin addition also did not eliminate the induction period for reaction at this temperature. Even for these reaction conditions, catalyst deactivation was significant after 30 min TOS due to coke/oligomer formation. The increase in the reaction rate with the addition of olefin was due to an increase in the concentration of surface intermediates; no effect was seen on the average surface residence time for reaction, suggesting that the additional sites created were identical to those formed in the absence of added olefin. Butene added for only 2 min at the beginning of the reaction increased the activity of the catalyst during the next 250 min of reaction time, long after the olefin feed was terminated. Each added 1-butene molecule, thus, contributed to greater *n*-butane isomerization for many reaction cycles (ca. 700) beyond its elimination from the reactant stream, suggesting that it may have been instrumental in the formation of the additional active sites observed. © 2002 Elsevier Science (USA)

**Key Words:** sulfated zirconia; isomerization; *n*-butane isomerization; reaction mechanism; isotopic transient kinetic analysis; butene addition; induction period.

## INTRODUCTION

The regulations imposed on the concentration of aromatics contained in gasoline have created the need to replace them with other more environmentally friendly high-octane species. Isomerization of C<sub>4</sub> to C<sub>7</sub> linear paraffins is useful for this purpose. Halogen-containing catalysts are currently used commercially to catalyze these reactions; however, due to the high corrosivity of the process, the need exists to replace them. Zeolites were first considered as an alternative, but they were not suitable due to their low activities at low reaction temperatures, a favorable thermodynamic domain for isoparaffin formation (1–3). Sulfated zirconia (SZ) has been shown to be a possible alternative isomerization catalyst, particularly for *n*-butane isomerization. It has a high activity even at low temperatures and a high selectivity to isoparaffins. UOP currently licenses a commercial process using SZ for *n*-alkane isomerization. Although *n*-butane isomerization on SZ has been widely studied, despite extensive research done by many groups (1, 4, 5) to clarify the reaction mechanism, the nature and the role of the active sites are still largely unknown. A better understanding of the reaction mechanism and the active sites could lead to a better catalyst design without the rapid deactivation exhibited by SZ.

Two reaction pathways (a monomolecular and a bimolecular) have been hypothesized for *n*-butane isomerization on SZ. Garin *et al.* (6) reported that they found *n*-butane isomerization on SZ at 250°C to occur via a monomolecular pathway in the presence of a large excess of hydrogen. The monomolecular pathway has to pass through a protonated cyclopropyl cation and an energetically unfavorable primary carbenium ionlike species prior to the formation of an isobutyl carbocation that is able to desorb from the surface of the catalyst as isobutane (7, 8). Matsushashi *et al.* (9) found that the mechanism of *n*-butane isomerization changed with TOS—starting out with a monomolecular pathway and switching to a bimolecular one later. However, the passage through a primary carbenium ion contradicts the low activation energy found for this

<sup>1</sup> To whom correspondence should be addressed. Fax: (864) 656-0874. E-mail: james.goodwin@ces.clemson.edu.

system at low temperature (10). Most evidence, thus, suggests that a bimolecular mechanism plays the primary role in *n*-butane isomerization on SZ at the typical reaction conditions used (11–23). The use of  $^{13}\text{C}$ -labeled *n*-butane showed that the reaction is bimolecular on SZ both at low and at high temperatures (1). It involves formation of a secondary carbenium ion and an olefin, oligomerization of the two  $\text{C}_4$  species to form an adsorbed  $\text{C}_8$  intermediate, and subsequent isomerization and  $\beta$ -scission of the  $\text{C}_8$  intermediates to form the products (11–23). Furthermore, it has been found that this bimolecular reaction mechanism does not change with TOS and catalyst deactivation (12).

Considering that the reaction probably follows a bimolecular pathway in most cases, important questions arise as to the role of the olefin during the reaction and its fate. It has been suggested that the olefin, present as impurity in the feed stream, participates in the formation of the  $\text{C}_8$  active surface intermediates and increases the initial catalytic activity for *n*-butane isomerization on SZ (1, 13, 23–27). In addition, lower deactivation rates have been found when the olefin was removed from the feed stream (1, 28). Coke and/or oligomer formation appears to be the main cause of catalyst deactivation, accelerated by the presence of unsaturated hydrocarbons, which are known to form coke more readily than paraffins. Tábora and Davis (22) looked into the impact of butene addition during an *n*-butane isomerization run at 60°C. They introduced *trans*-butene after 350 min time-on-stream (TOS) and noticed an increase in the activity. The resulting excess in the formation of isobutane was around 10 mol of isobutane formed for every mol of butene introduced. Similarly, Coelho *et al.* (29) found that the addition of 1-butene at the beginning of reaction at 100°C increased the activity of the catalyst.

As to the probable formation of the olefin on SZ during *n*-butane isomerization (necessary for the bimolecular mechanism to occur), several suggestions have been made. It has been suggested that butene might be formed by dehydrogenation of *n*-butane via a redox process (30, 31). Others have proposed that Brønsted (32, 33) or Lewis (34–36) acid sites are important in the formation of the olefin. But evidence in many studies has suggested that the presence of both types of acid sites on SZ is necessary in order for the reaction to proceed (35, 37).

It would thus appear that the olefin (as an impurity or formed from *n*-butane) plays a critical role in *n*-butane isomerization on SZ. The purpose of this study was to investigate the effect of 1-butene addition on the activity of SZ, on the surface reaction parameters, and on the deactivation characteristics with the aim of delineating the role of the olefin during the reaction. Utilizing isotopic transient kinetic analysis (ITKA) during *n*-butane isomerization permitted us to determine the surface kinetic parameters and how they were affected by the addition of 1-butene.

## EXPERIMENTAL

### *Catalyst Preparation and Characterization*

Sulfate-doped zirconium hydroxide  $[\text{Zr}(\text{OH})_4]$  precursor was obtained from Magnesium Elektron, Inc. (MEI, Flemington, NJ). It was calcined at 600°C for 2 h under static air to form SZ. The sulfur content (determined by Galbraith Laboratories, Inc.) and its BET surface area (determined by Micromeritics) were measured for the calcined catalyst. They were found to be of 1.7 wt% and 92.4  $\text{m}^2/\text{g}$ , respectively. XRD detected only  $\text{ZrO}_2$  and that it was present in the tetragonal phase (38). The carbon contents of the used catalysts were determined by Galbraith Laboratories. The catalyst formulation and pretreatment were chosen to provide a catalyst with characteristics similar to those in a broad range of previous studies reported in the literature.

### *Reaction Rate Analysis*

*n*-Butane isomerization was carried out in a quartz fixed-bed microreactor with an inner diameter of 10 mm under differential conditions with a maximum conversion of 18%. Precalcined SZ (0.2 g) was loaded in the reactor and pretreated *in situ* at 315°C for 4 h under a flow of 30  $\text{cm}^3/\text{min}$  of air (UHP, National Specialty Gases) prior to reaction. The pretreated catalyst was cooled to the reaction temperature, which was either 150 or 250°C, under air. It was purged with a flow of He (UHP, National Specialty Gases) prior to the introduction of the reactant stream to the reactor. The total flow rate and the reaction pressure were kept constant at 30  $\text{cm}^3/\text{min}$  and 1.5 atm, respectively. A gas mixture containing 5% *n*-butane/1% Ar/He (UHP, Hollox) was used, and Ar was present in the gas mixture as an inert tracer. This gas mixture was then diluted by a stream of He so that the reactant mixture to the reactor always contained 2.5% *n*-butane. In the case where 1- $\text{C}_4^-$  (1% 1- $\text{C}_4^-$ /He UHP, Hollox) and/or  $\text{H}_2$  (UHP, Hollox) was added, the flow of the stream of He was reduced in order to keep the concentration of *n*- $\text{C}_4$  constant at 2.5% of the final mixture. During the addition of  $\text{H}_2$ , a constant ratio of  $\text{H}_2/n\text{-C}_4 = 1.7$  was used. The small amount of olefin impurity in the *n*-butane stream was eliminated by the use of an olefin trap (a bed of H-mordenite) held at room temperature. The composition of the reactor effluent was analyzed using a Varian 3700 GC equipped with a 12-ft 15% Squalane CP-AW-DMCS/Chromosorb 80/100 mesh column and an FID. Changes in reaction rate during the initial period of reaction were followed using a 34-port VICI autosampling valve to collect 16 samples. This permitted study of the reaction induction period. The concentrations of the paraffinic impurities present in the effluent stream (i.e., ethane, propane, and pentane) were subtracted from the concentrations of the products prior to proceeding to the kinetic analysis. The time considered as the beginning of the reaction was when a switch was made from the

pretreatment gas to the reactants. The reproducibility of the experiments was ca. 5%.

### Isotopic Transient Kinetic Analysis (ITKA)

A detailed schematic of the ITKA system can be found elsewhere (39). Isotopic switches between two reactant streams containing either  $^{12}\text{C}_4\text{H}_{10}$  ( $n\text{-C}_4$ ) or  $^{13}\text{CH}_3(^{12}\text{CH}_2)_2^{13}\text{CH}_3$  ( $n\text{-}^*\text{C}_4$ ) were made without disturbing the other reaction conditions. The 34-port VICI valve was used to collect 16 samples of the effluent during a 5-min period in order to capture the isotopic transient. Most of the data points are taken in the first 2 min. The collected effluent samples were subsequently separated in the GC at  $35^\circ\text{C}$  using 8.5 mol%  $\text{H}_2$  in He as the carrier gas. Before being introduced into a Pfeiffer–Balzers Prisma 200 amu mass spectrometer (MS), the separated effluent samples were converted to methane ( $\text{CH}_4$ ) using the carrier gas as a source of  $\text{H}_2$  in a hydrogenolysis unit that consisted of 10 g of 5 wt% Pt/ $\text{SiO}_2$  at  $250^\circ\text{C}$ . The MS data were collected and treated with a Pentium II PC equipped with Quadstar software.

## RESULTS

### $n$ -Butane Isomerization at $250^\circ\text{C}$

The variations in the rate of formation of iso- $\text{C}_4$  with TOS on SZ at  $250^\circ\text{C}$  in the presence and in the absence of added 1-butene are shown in Fig. 1. A reaction temperature of  $250^\circ\text{C}$  has typically been used in studies of  $n$ -butane isomerization on SZ. In the absence of 1-butene, the formation rate of isobutane at 5 min TOS was  $0.99 \mu\text{mol/g cat/s}$ . Most studies have reported the first reaction data point at 5–15 min TOS, considering that a measure of the “initial” rate. For the case where there was an addition of 1-butene, the reaction rate at 5 min TOS was at the lower values

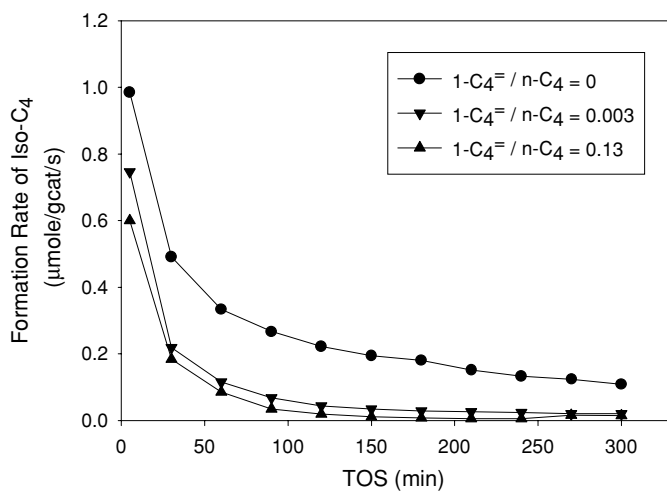


FIG. 1.  $n$ -Butane isomerization activity at  $250^\circ\text{C}$  in the presence and in the absence of added 1-butene.

TABLE 1

Carbon Content on SZ after 300 Min of Reaction at  $250^\circ\text{C}$

1-C <sub>4</sub> <sup>*</sup> /n-C <sub>4</sub> ratio	$k_d$ (min <sup>-1</sup> )		Carbon content (wt%) at 300 min TOS <sup>c</sup>
	5–30 min <sup>a</sup>	Steady state <sup>b</sup> (>90 min)	
0	0.01	0.004	0.16
0.003	0.03	0.005	0.78
0.13	0.04	0.009	1.4

<sup>a</sup> Error =  $\pm 0.003$ .

<sup>b</sup> Error =  $\pm 0.001$ .

<sup>c</sup> Error =  $\pm 0.1$  wt%.

of 0.74 and  $0.6 \mu\text{mol/g cat/s}$  for 1-C<sub>4</sub><sup>\*</sup>/n-C<sub>4</sub> ratios of 0.003 and of 0.13, respectively. Thus, the 5-min activity was lower when the higher concentration of butene was added. The activity of SZ decreased rapidly with TOS in all cases. After 100 min TOS, the activity leveled out close to a zero value when butene was added. The values of the deactivation rate constant (13),  $k_d$ , show that added olefin increased the deactivation rate as a function of the amount added (Table 1). The carbon content analysis after 300 min TOS revealed a greater amount of carbon deposited in the presence of butene, increasing as the olefin/paraffin ratio increased (Table 1). The carbon analysis confirms that the lower activity resulting from the addition of butene was probably due to coke/oligomer formation.

The selectivity of the catalyst for isobutane changed upon addition of the olefin. Typically, on SZ, in the absence of the olefin addition, isobutane selectivity increases with TOS. However, upon addition of 1-butene, it decreased with TOS, and the decrease was more pronounced for the higher concentration of the olefin (Fig. 2). More hexane, pentane, and heptane were formed as the reaction proceeded with time in those cases.

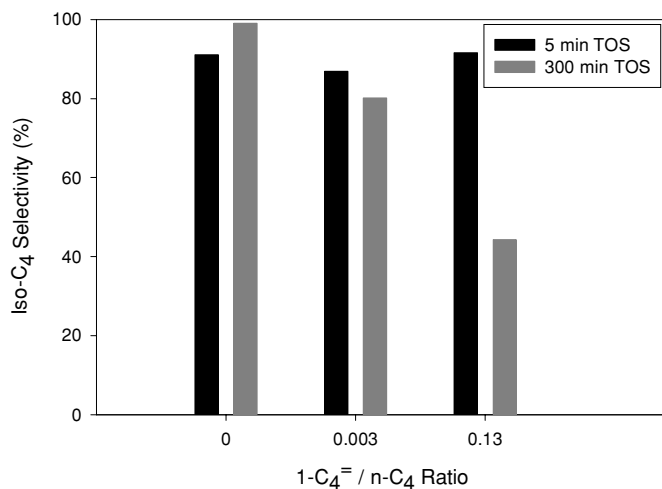


FIG. 2. Variation of isobutane selectivity with olefin addition at  $250^\circ\text{C}$ .

Although most studies in the past have focused on catalyst activity after 5–15 min of reaction, it is well known that the reaction on SZ goes through an induction period (40). Given the important role of the olefin in the isomerization mechanism and its ease in facilitating coke formation, one might ask whether its impact during the induction period could overshadow any effect afterward.

In order to investigate this impact, we measured the activity of the catalyst during the first 5 min of reaction (TOS = 0–5 min). Using the autosampling valve, 16 samples were collected during the first 5 min and were subsequently injected into the GC for analysis. These results as well as those for longer TOS are shown in Fig. 3. The activity of the catalyst went through an induction period in all cases. It reached a maximum at ca. 2 min TOS in the cases of  $1-C_4^-/n-C_4 = 0$  or 0.003. For the highest ratio,  $1-C_4^-/n-C_4 = 0.13$ , the maximum was reached earlier, at ca. 1 min. The availability of the olefin accelerated the reaction and allowed it to start quicker; however, it also accelerated the deactivation rate. These results during the induction period, thus, show the positive (increase in the isomerization rate during the first 1 min TOS) and the negative (increase in the deactivation rate apparent after 1 min TOS) effects of olefin addition that occur simultaneously.

ITKA was carried out for *n*-butane isomerization in the presence and in the absence of the olefin at 250°C. Previous work in our laboratory has shown the impact of readsorption of iso-C<sub>4</sub> on the kinetic parameters (39). A single measurement of average surface residence time ( $\tau_{\text{iso-C}_4}$ ) may lead to an error in the interpretation of the results. In order to remedy the impact of readsorption, the kinetic parameters were measured at different space times (by varying the catalyst weight from 0.2 to 0.5 g) and extrapolated to zero space time to determine a more exact value of average  $\tau_{\text{iso-C}_4}$ ,  $\tau_{\text{iso-C}_4}^*$  (41). The concentration of surface intermedi-

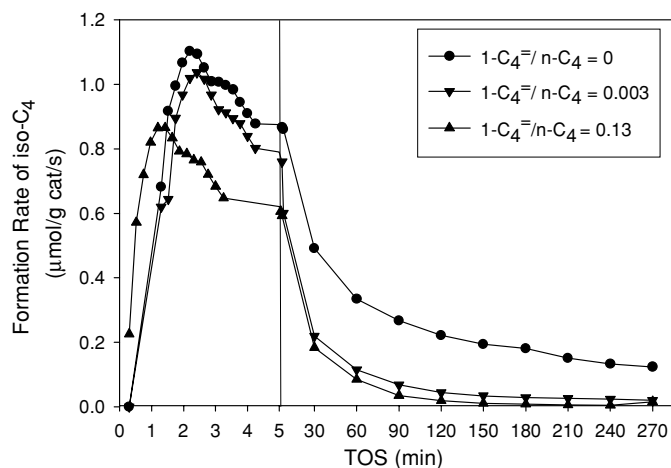


FIG. 3. Induction-period profile at 250°C in the presence and in the absence of added 1-butene.

TABLE 2

Effect of Olefin Addition on Kinetic Parameters of SZ at 250°C at 5 Min TOS<sup>a</sup>

Olefin exposure	Rate <sub>iso-C<sub>4</sub></sub> <sup>b</sup> (μmol/g/s)	$\tau_{\text{iso-C}_4}^*$ <sup>c</sup> (s)	$N_{\text{iso-C}_4}^*$ <sup>d</sup> (μmol/g)	$N_{n-C_4}$ <sup>e</sup> (μmol/g)
0	0.99	6.3	6.3	17.3
90 s at <i>t</i> = 0	0.58	20.2	11.7	19.9
Continuous	0.75	21.1	15.7	21.0

<sup>a</sup> Space time = 0.02–0.05 s; olefin/paraffin = 0.003.

<sup>b</sup> Max error = 5%.

<sup>c</sup>  $\tau_{\text{iso-C}_4}$  corrected for product readsorption by extrapolation to 0 space time using five measurements. Max error = ±15%.

<sup>d</sup>  $N_{\text{iso-C}_4}^* = R_{\text{iso-C}_4} \times \tau_{\text{iso-C}_4}^*$ . Max error = ±19%.

<sup>e</sup> No significant readsorption in catalyst bed.  $N_{n-C_4}$  = flow rate<sub>*n*-C<sub>4</sub></sub> ×  $\tau_{n-C_4}$  = (2.55 μmol/g/s) ×  $\tau_{n-C_4}$ . Max error = 17%.

ates leading to isobutane,  $N_{\text{iso-C}_4}^*$ , was calculated as (42)

$$N_{\text{iso-C}_4}^* = \tau_{\text{iso-C}_4}^* \times r_{\text{iso-C}_4},$$

where  $r_{\text{iso-C}_4}$  is the formation rate of isobutane. The reciprocal of  $\tau_{\text{iso-C}_4}^*$  is related to the average site TOF. The reversible adsorption of *n*-butane is not greatly affected by readsorption (probably due to its high concentration), and, consequently,  $\tau_{n-C_4}$  does not have to be corrected.

Table 2 shows the kinetic parameters of the reaction at 250°C in the presence and in the absence of added olefin. With continuous addition of butene, the value of  $\tau_{\text{iso-C}_4}^*$  was dramatically increased. In parallel, an increase in  $N_{\text{iso-C}_4}^*$  was also exhibited, related to an increase in the number of active sites—or at least to a higher occupancy of the active sites. However, the increase in the number of active intermediates was not able to compensate for the increase (decrease) in surface residence time (site TOF), resulting in less overall activity. The increase (decrease) in  $\tau_{\text{iso-C}_4}^*$  (site TOF) was probably due to a greater deactivation of the most active sites in the presence of added olefin. Within experimental error, no significant change occurred in the value of  $N_{n-C_4}$ .

Due to the very negative impact of added olefin on the activity of SZ, we also introduced butene to the reactant stream for only 90 s at the beginning of the reaction and then discontinued its addition. The variation in the formation rate of iso-C<sub>4</sub> with TOS is given in Fig. 4. A continuous exposure to the olefin, as seen previously, decreased the activity of the catalyst. However, the effect of only 90 s of olefin exposure on the activity of SZ was even more interesting. A more significant decrease in the activity was seen even though the olefin addition had been terminated after only 90 s. ITKA after 5 min TOS showed that 90 s of exposure to the olefin resulted in the same effect on  $\tau_{\text{iso-C}_4}^*$  as continuous addition, without increasing the concentration of surface intermediates as much (Table 2). This resulted in the lower apparent activity seen.

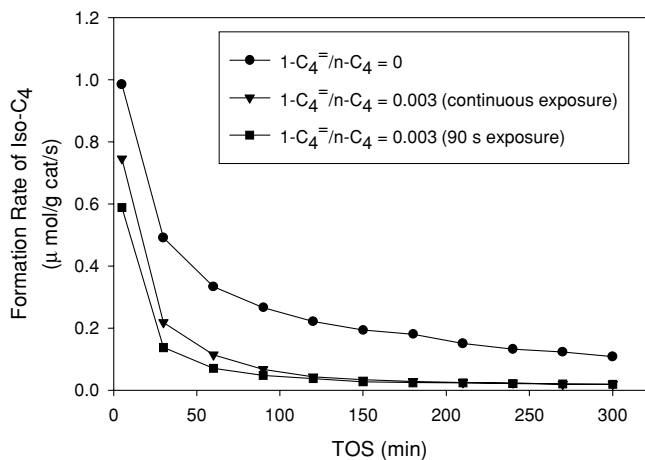


FIG. 4. Effect of 90 s vs continuous exposure to added 1-butene on the activity of SZ at 250°C.

The effect of concomitant addition of H<sub>2</sub> and 1-butene was also studied (Fig. 5). In the absence of added olefin, as reported in the literature (15, 20, 43, 44), H<sub>2</sub> decreases the 5-min activity of SZ but increases catalyst stability. In the case of either continuously added olefin or short (90 s) exposure, H<sub>2</sub> had almost no impact on the activity of SZ except at steady state, where the formation rate of iso-C<sub>4</sub> in the case of a short exposure to the olefin was slightly higher, suggesting that H<sub>2</sub> did perhaps decrease the amount of coke formed on the surface of the catalyst (Fig. 4 vs Fig. 5).

#### *n*-Butane Isomerization at 150°C

In order to reduce the deactivation effect of olefin addition on SZ (so dominant at higher temperature) and better explore the role of olefin in reaction, olefin addition was also studied at the lower reaction temperature of 150°C. Figure 6 shows the impact of the olefin on the activity of the catalyst at this temperature. Contrary to what was seen

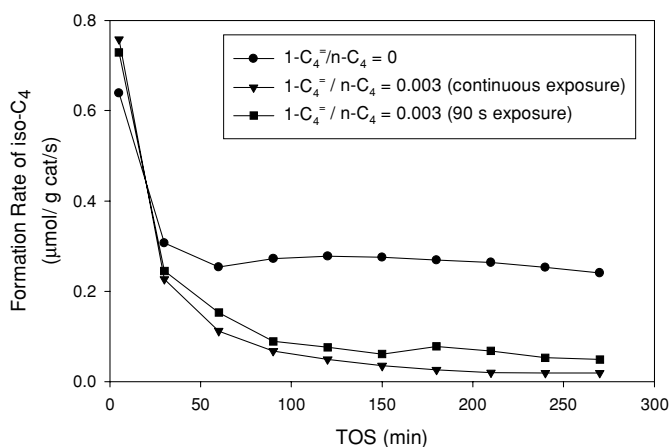


FIG. 5. Effect of H<sub>2</sub> on *n*-butane isomerization in the presence and in the absence of added 1-butene at 250°C.

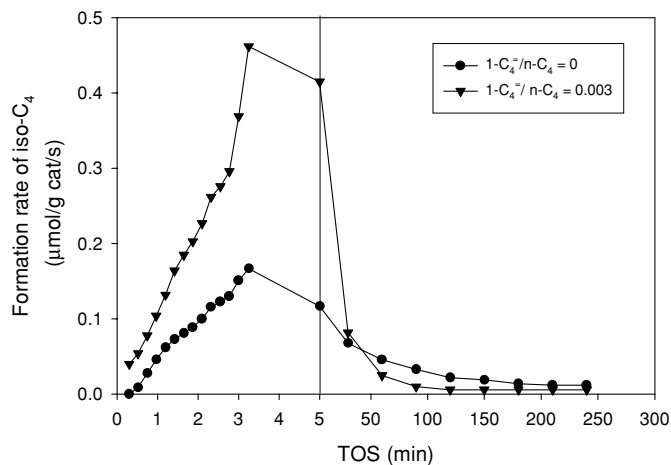


FIG. 6. *n*-Butane isomerization activity at 150°C in the presence and in the absence of 1-butene.

for reaction at higher temperature, in this case, added olefin (1-C<sub>4</sub><sup>-</sup>/n-C<sub>4</sub> = 0.003) clearly had a promoting effect on the 5-min reaction rate by increasing it by almost a factor of 3 at the maximum. As can also be seen in Fig. 6, the reaction went through a longer induction period than at 250°C. However, due to the promoting action of the olefin on deactivation, at 60 min of reaction the catalyst had a much lower activity in the presence of the olefin than in its absence. Moreover, the catalyst was much darker with the addition of olefin after ca. 4 h TOS, a proof of formation of additional coke on its surface. The variation in the selectivity with TOS in the presence and in the absence of the olefin was not greatly affected by the reaction temperature, being similar to the variation seen at higher temperature (Fig. 7).

In order to minimize deactivation due to olefin addition, the olefin was also added to the reactant stream for only 120 s at the beginning of the reaction (Fig. 8). In this case, the catalyst did not have as high a 5-min activity as in the

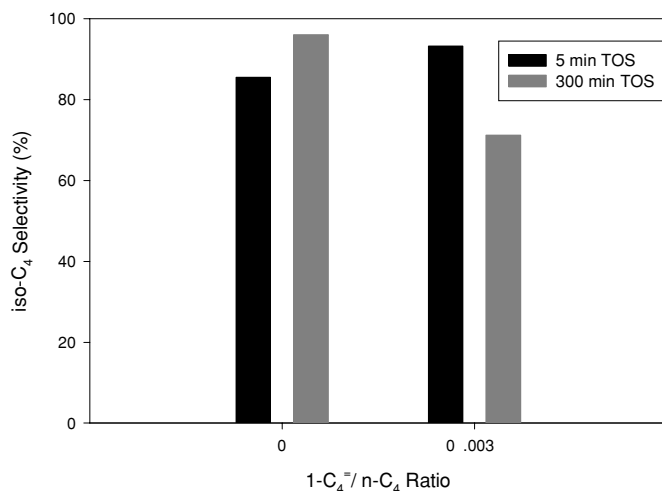


FIG. 7. Variation of isobutane selectivity with olefin addition at 150°C.

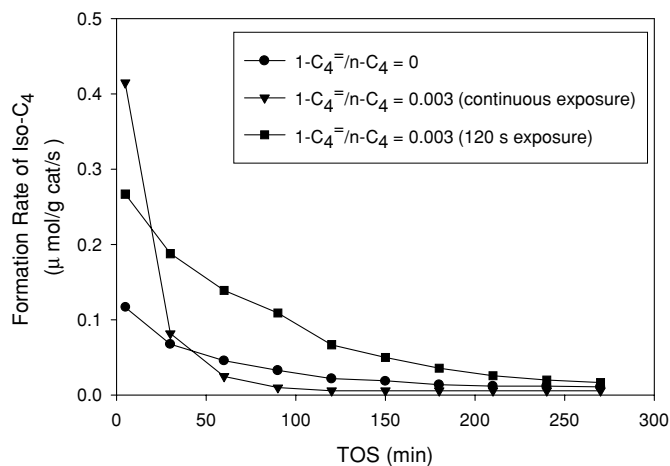


FIG. 8. Effect of 120 s vs continuous exposure to added butene on the activity of SZ at 150°C.

case where butene was fed continuously. However, the activity was much higher than in the case where no olefin was added. More interesting, the activity of SZ following exposure to only 120 s of olefin addition was more stable and remained significantly higher after 30 min TOS than that in the absence or in the continuous presence of added olefin.

ITKA results show that similarly to the case at 250°C, continuous addition of the olefin increased the concentration of surface intermediates by almost a factor of 3 at 150°C (Table 3). However, the negative impact on the site activity (related to the reciprocal of  $\tau_{\text{iso-C}_4}^*$ ) was nonexistent at 5 min TOS since no change in the average surface residence time was determined. The 120-s olefin addition increased the concentration of surface intermediates as well, although the addition had been terminated 3 min prior to the isotopic tracing measurements. It also did not affect the average surface residence time.

The previous reaction runs were repeated in the presence of H<sub>2</sub>. The results are summarized in Fig. 9. H<sub>2</sub>, in the

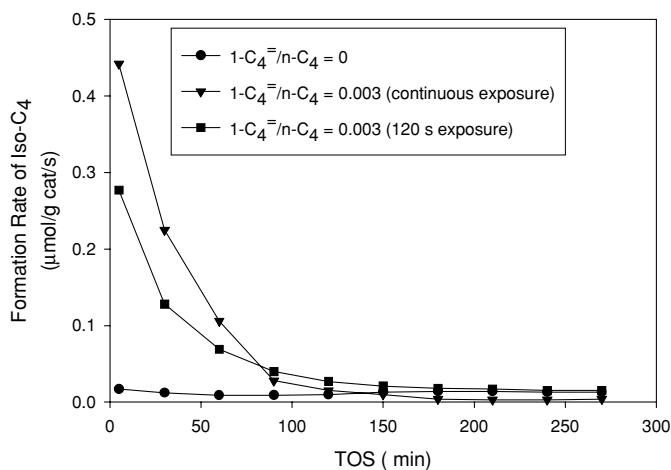


FIG. 9. Effect of H<sub>2</sub> on *n*-butane isomerization in the presence and in the absence of added 1-butene at 150°C.

absence of 1-C<sub>4</sub><sup>-</sup>, decreased considerably the activity of SZ. The decrease was much more significant than at 250°C. In the presence of a continuous feed of olefin, H<sub>2</sub> did not have an impact on the reaction rate at 5 min TOS. However, it did decrease the rate of deactivation of SZ after 30 min TOS compared to the case where no H<sub>2</sub> was added. When only a small amount of the olefin was added for 120 s at the beginning of the reaction run, H<sub>2</sub> addition did not have an effect on the activity of SZ at 5 min TOS. However, as the reaction proceeded, the activity decreased more significantly than in the absence of H<sub>2</sub> (Fig. 8 vs Fig. 9).

### DISCUSSION

Since the olefin is apparently an intermediate in *n*-butane isomerization, an increase in its amount should result in an increase in the activity of the catalyst. However, its impact would not be limited only to an increase in the reaction rate since olefins are well known to be good coke/oligomer precursors. Our results are in agreement with reports in the literature that olefins present as impurities in *n*-butane increase the deactivation rate (13, 23). The lower activities after 5 min TOS on addition of the olefin at 250°C (Fig. 1) were due to the increased formation of coke/oligomer on the SZ surface (45), as shown by carbon analysis of SZ measured at the end of reaction (Table 1). The reaction exhibited an induction period, apparently necessary to prepare the active sites for reaction (Fig. 3). The addition of the olefin, hypothesized intermediates in the reaction mechanism, from time = 0 did not eliminate the induction period. However, a subtle impact on the induction period can be seen at high 1-C<sub>4</sub><sup>-</sup>/*n*-C<sub>4</sub> ratio (0.13). The faster start in the reaction and the shorter induction period suggest to us that the presence of the olefin at high concentration accelerated the reaction process. Unfortunately, the positive impact of the olefin seen in a faster start in the reaction was

TABLE 3

Effect of Olefin Addition on Kinetic Parameters of SZ at 150°C at 5 Min TOS<sup>a</sup>

Olefin exposure	Rate <sub>iso-C<sub>4</sub></sub> <sup>b</sup> (μmol/g/s)	$\tau_{\text{iso-C}_4}^*$ <sup>c</sup> (s)	$N_{\text{iso-C}_4}^*$ <sup>d</sup> (μmol/g)	$N_{n\text{-C}_4}$ <sup>e</sup> (μmol/g)
0	0.12	12.1	1.4	16.9
120 s at <i>t</i> = 0	0.27	11.5	3.9	17.2
Continuous	0.41	10.5	4.3	17.9

<sup>a</sup> Space time = 0.02–0.05 s; olefin/paraffin = 0.003.

<sup>b</sup> Max error = 5%.

<sup>c</sup>  $\tau_{\text{iso-C}_4}^*$  corrected for product readsorption by extrapolation to 0 space time using five measurements. Max error = ±15%.

<sup>d</sup>  $N_{\text{iso-C}_4}^* = R_{\text{iso-C}_4} \times \tau_{\text{iso-C}_4}^*$ . Max error = ±19%.

<sup>e</sup> No significant readsorption in catalyst bed.  $N_{n\text{-C}_4}$  = flow rate<sub>*n*-C<sub>4</sub></sub> ×  $\tau_{n\text{-C}_4}$  = (2.55 μmol/g/s) ×  $\tau_{n\text{-C}_4}$ . Max error = 17%.

countered by the negative impact of the olefin in increasing coke/oligomer formation on the surface of the catalyst. The deactivation effect could be seen as soon as 1 min TOS in the case of the high  $1-C_4^-/n-C_4$  ratio. The activity was not able to reach an activity similar to the case where no olefin was added because of the increased deactivation. At a low concentration of added olefin ( $1-C_4^-/n-C_4 = 0.003$ ), the induction period looked almost the same as in the absence of added olefin (Fig. 3). Once again increased deactivation more than compensated for any increase in activity. The results with olefin addition lead us to believe that the need to form the olefin during the initial reaction is possibly not the sole reason for the existence of the induction period.

ITKA done at 5 min TOS in the case of  $1-C_4^-/n-C_4 = 0.003$  gave us more insight into how the added olefin affected the kinetic parameters of the reaction. The added olefin increased the concentration of surface intermediates, supporting the idea that it is an intermediate in the reaction mechanism and that it participates in the formation of isobutane. On the other hand, the olefin increased more significantly the average surface residence time for reaction, resulting in an overall decrease in the formation rate of isobutane (Table 2). The increase in the average surface reaction residence time on addition of the olefin (Table 2) was probably due to a faster initial deactivation of the most active sites. Yaluri *et al.* (46) determined that the strong acid sites are highly active but deactivate very rapidly during the first 30 min. The intermediate acid sites, the main contributors to the long-term activity of SZ, deactivate more slowly and possess a lower activity. In agreement with this work, a previous study in our lab demonstrated the heterogeneity of the active sites on SZ by means of ITKA (38). It was found that the sites with a higher activity deactivated rapidly initially, leaving only the less active sites after 100 min TOS.

Addition of 1-butene caused the selectivity to isobutane to decrease with TOS (Fig. 2). There are two possible reasons for this decrease: a high participation of the less active sites after the deactivation of the most active sites (46), or involvement of the coke/oligomer formed on the surface of SZ in the formation of more pentane, hexane, and heptane. Nonetheless, this behavior was not seen in the case of 90 s of exposure to butene even though the catalyst had a type of deactivation similar to that in the case of continuous exposure; the variation in the selectivity was similar to when no olefin was added (not shown).

The positive impact of the olefin seen at 150°C (Fig. 6) is due in part to the less dominant effect of deactivation at lower temperature and possibly in part to the lower ability of SZ by itself to generate as much olefin at this temperature, since dehydrogenation is more favored at higher temperature (47). However, long-term deactivation was still much greater than in the absence of added olefin. The increase in activity detected during the initial reaction period cannot be explained solely by the conversion of added olefin

to additional products. The amount of added olefin was around  $0.01 \mu\text{mol/g cat/s}$ ; it would have increased the rate of formation of isobutane only from 0.12 to ca.  $0.13 \mu\text{mol/g cat/s}$ , rather than the  $0.46 \mu\text{mol/g cat/s}$  actually seen, had all the added 1-butene gone simply to form product.

Similarly to the behavior seen at high temperature, and even though the added olefin increased the formation rate of isobutane, it did not eliminate the induction period. As was the case at 250°C, this suggests that the presence of the induction period is not due only to olefin formation. Furthermore, if olefin formation were the only reason for the presence of the induction period, one would expect to see a significant decrease in the average surface residence reaction time on olefin addition at 150°C (Table 3), where deactivation is less significant—something that was not observed. The value of the average surface residence time remained essentially unchanged. Clearly, from ITKA results (Table 3), we can see that the increase seen in the 5-min activity on addition of butene was due mainly to a significant increase in the concentration of surface intermediates.

To expand our understanding of the system and to reduce the impact of deactivation, we introduced the olefin at low and at high reaction temperatures for only a short period of time, as stated in the previous section. Addition of butene for only 90 s at 250°C did not improve the activity of SZ at 5 min TOS (Fig. 4) but rather decreased it. The decrease in the reaction rate at 5 min and at higher TOS was due mainly to deactivation of the most active sites during the initial 90 s, as evidenced by a higher average surface residence time, similar to that in the case of continuous exposure to butene. The nonavailability of added olefin after 90 s of exposure at 250°C resulted in a lower rate than when olefin was added continuously, since deactivation of the most active sites had already occurred. The loss of the most active sites might be due to the formation of coke for even a short exposure time to the olefin. Li and Gonzalez showed that a very small amount of carbon deposited on the surface of SZ can be enough to deactivate it (48). Even though added butene increased the concentration of surface intermediates, this could not compensate for the loss of the most active sites. The negative impact of butene is so prevailing at 250°C that even the presence of  $H_2$  could not prevent the added olefin from deactivating the catalyst (Fig. 5).

As mentioned previously, the lower reaction temperature of 150°C allowed us to better see the impact of added olefin on the desired reaction. On addition of 1-butene in a trace amount for 120 s at the beginning of the reaction at 150°C, an increase in the reaction rate during all TOS occurred long after the olefin feed had ceased (Fig. 8). The increase noticed in the activity of SZ reveals a long-term effect of the olefin on the catalyst. Tábora and Davis (22) found that the ratio of the excess amount of iso- $C_4$  produced/added *trans*- $2-C_4^-$  was around 10 when the olefin was pulsed into the *n*-butane reactant stream. In our case, the excess amount

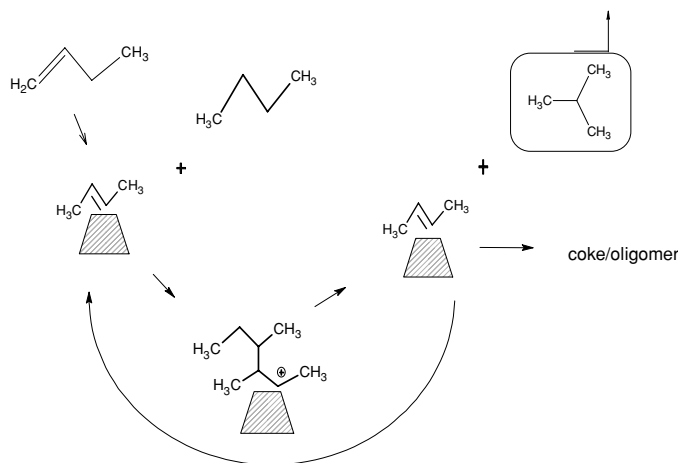


FIG. 10. Schematic of hypothetical *n*-butane isomerization reaction pathway.

of isobutane formed and the ratio of the excess in iso-C<sub>4</sub> produced/added 1-C<sub>4</sub><sup>+</sup> on addition during only 120 s of 1-butene were determined from time = 0 to the end of the reaction period (270 min). They were found to be around 836 μmol/g cat and 700, respectively. The result of this calculation cannot be compared exactly to that given in Ref. (22) due to the different reaction temperatures used and the different methods of olefin addition. Nevertheless, despite the different reaction conditions used, both studies found that the added butene caused an increase in reaction rate that lasted longer than the feed time of the butene. These results suggest that each molecule of added butene caused the formation of multiple isobutane molecules. However, addition of H<sub>2</sub> along with butene inhibited the promoting effect of butene once its feed was terminated (Figs. 8 and 9).

Based on the reaction rate in the presence and in the absence of 1-butene and the ITKA results, a schematic of the effect of added olefin on the reaction pathway (Fig. 10) is proposed. Since added butene was not detected at the exit of the reactor, we conclude that butene adsorbs irreversibly on surface sites. For the rest of the discussion we refer to these sites where olefin adsorbed as “olefin-modified” sites.

It has been proposed that SZ has a bifunctional character: an initiation step that consists of a one-electron oxidation of the hydrocarbon to form carbenium ions, and an acid-catalyzed reaction of the intermediates (31, 49). Various studies have led to the conclusion that Brønsted acid sites (32, 33), Lewis acid sites (36, 50), or a combination of both Brønsted and Lewis acid sites (35, 37) are responsible for the isomerization step.

It had been shown (51) that CO adsorbs on the coordinatively unsaturated surface cations, Zr<sup>+4</sup>, that act as Lewis acid sites. Thus, Pinna *et al.* (36) used CO poisoning in an attempt to show the importance of Lewis acid

sites in *n*-butane isomerization. Addition of CO to the reactant stream completely inhibited the reaction. However, Adeeva *et al.* (33) suggested that CO inhibits the reaction not because it adsorbs on Lewis acid sites but because it interacts with the carbenium ions formed on the catalyst. They investigated the effect of CO addition during *n*-pentane isomerization on HY, which contains an insignificant amount of Lewis acid sites and a important amount of Brønsted acid sites. They noticed that CO eliminated the reaction even though it was not a Lewis acid site-catalyzed reaction (33). Morterra *et al.* (52) pursued further the issue of Lewis acidity in a later study and found an increase in the concentration of Zr<sup>+4</sup> cations (Lewis acid sites) with an increase in the pretreatment temperature of the catalyst prior to the reaction. At first, an increase in the number of Lewis acid sites resulted in an increase in the activity; however, as the concentration of Lewis acid sites increased, due to higher pretreatment temperatures, the activity of SZ decreased. The authors proposed that both Lewis and Brønsted acid sites must be present on the catalyst for *n*-butane isomerization to occur. Clearfield *et al.* (53) had earlier also reached the same conclusion and proposed a model to describe the active site.

As to the type of sites on which butene reacts, we can only speculate on their nature based on our current kinetic and isotopic results. Butene adsorbed on SZ undoubtedly formed carbenium ions, a result similar to the previous proposition that addition of alkene can generate carbenium ions during acid-catalyzed reactions (49). A preliminary study in our laboratory of the addition of CO, known to adsorb on Lewis acid sites (51), in the presence and in the absence of added butene suggests that Lewis acid sites are not involved in the formation of the olefin-modified sites (54). The carbenium ions may have been formed on Brønsted acid sites by protonation of butene (55). What we can conclude based on the present and previous (11, 12) results is that the olefin-modified sites react with *n*-butane to form adsorbed C<sub>8</sub> species. After isomerization and β-scission of the C<sub>8</sub> intermediates, formation of isobutane and regeneration of the olefin-modified sites occur, with the olefin-modified sites able to be involved in the reaction with *n*-butane once more (in fact, for ca. 700 turnovers at 150°C). Fogash *et al.* (56), in their study of isobutane isomerization in the presence and in the absence of olefin impurities in the reactant stream, proposed a mechanism for the reaction that follows a catalytic cycle. Their proposition was that the olefin formed during the reaction is regenerated and participates in further oligomerization. The results from the current study clearly demonstrate this cycling of the olefin; although, if it desorbed and re-adsorbed, it would be unlikely to participate in so many turnovers in a differential reaction. Thus, it is likely that the olefin does not desorb between turnovers, leading to our conclusion of fairly stable olefin-modified sites.



It has been suggested that SZ, unlike PtSZ, does not generate the olefin during all TOS (1) and a small concentration of the olefin has to be built up during the initial TOS for the reaction to follow the cycle (57). From this study, ITKA results show that the higher activity at 150°C after termination of the olefin feed was due to an increase in the concentration of surface intermediates that must have been directly related to the "olefinic" species or olefin-modified sites formed from the added butene (Table 3).

In light of those results and our hypothesis, one can come back to the induction period and try to explain its presence in a more logical way. It has been proposed that this induction period is necessary to form olefinic intermediates prior to the isomerization reaction proceeding on FeMnSZ (29, 40). Furthermore, it was found that when 1-butene was injected at the beginning of the reaction on FeMnSZ, the induction period was shortened significantly (29). Fogash *et al.* (56) proposed that during isobutane isomerization, the olefin is first formed and then adsorbs on Brønsted acid sites. This later proposition is supported by our preliminary studies using CO poisoning of SZ (54).

Resasco and co-workers have suggested that the induction period noticed during *n*-butane isomerization in the absence of added olefin may be due to the formation and accumulation of the reaction intermediates on SZ (29). Though the limiting step may be the formation of the active sites, oligomerization cannot be ruled out. Coelho *et al.* (58) concluded that dehydrogenation of the paraffin was not the rate-determining step and proposed that the limiting step occurred later in the reaction, once the olefin was formed. However, the oligomerization step is clearly accelerated in the presence of a high concentration of olefin (57, 59). Adding small amounts of butene to the reaction mixture at 150°C in this study clearly rapidly increased the number of active surface intermediates/sites and, consequently, the rate of reaction (Fig. 6). Since olefin addition in this study did not eliminate the induction period, the formation of olefin may not be the only reason for the presence of this induction period, since initiation involves both butene and carbenium ion formation. However, this argument is not totally conclusive, since only a small amount of butene was added (0.01  $\mu\text{mol/g cat/s}$ ) due to the more rapid deactivation when much larger amounts were added. Consequently, the amount added may not have been significant enough to immediately saturate the potential surface sites. Added butene has two major effects on the reaction: (i) it increases the concentration of carbenium ions and the participation of those carbenium ions in the formation of isobutane multiple times, and (ii) it modifies but does not eliminate the induction period.

### CONCLUSIONS

Olefin addition during *n*-butane isomerization on SZ allowed us to reach a better understanding of the reaction

mechanism and the different ways the olefin affects reaction. Olefin addition at 250°C, either continuously or for a short time, had a dual effect on the reaction rate: it increased the rate of formation of isobutane on SZ due to an increase in the concentration of surface intermediates,  $N_{\text{iso-C}_4}^*$ , and it increased the deactivation rate. When butene was added for a short time, the increase in the concentration of surface intermediates,  $N_{\text{iso-C}_4}^*$ , was lower compared to the case where butene was added continuously and this resulted in a lower overall activity.

The promoting effect of olefin addition on isomerization could be seen more easily at 150°C, where deactivation was less prominent, and this effect was manifested in an increase in the 5-min reaction rate due to an increase in the concentration of surface intermediates. Added olefin did not have any significant impact on the intrinsic activity of the sites at 5 min TOS, as determined by ITKA.

Butene, added for only 120 s at the beginning of the reaction at 150°C, increased the activity of the catalyst during all TOS. Our results are in agreement with those of Tábora and Davis (22), who also found that each added butene molecule caused multiple isobutane molecules from the *n*-butane reactant. These results suggest that added butene adsorbs on SZ to form "olefin-modified" sites, probably carbenium ions, which are involved in the formation of multiple isobutane molecules from the *n*-butane reactant. We determined the ratio of excess isobutane formed/added 1-butene to be ca. 700 during 270 min of reaction at 150°C following cessation of butene addition.

The availability of the olefin in the reactant stream did not prevent the reaction from requiring an induction period at either 150 or 250°C. The continued need for the induction period in the presence of added olefin suggests that the induction period seen in *n*-butane isomerization on SZ may not be only due to the initial dehydrogenation of *n*-butane. The formation of olefin-modified sites on the catalyst may also be a concomitant cause for the induction period.

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