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n-Butane isomerization on sulfated zirconia: How olefins affect surface intermediate concentration

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Abstract

Isotopic transient kinetic analysis (ITKA) was used to study the effect of various olefin additions (ethylene, propylene, 1-butene, and 1-pentene) on n-butane isomerization on sulfated zirconia (SZ) at 100 °C. Earlier work showed that the activity of this catalyst is enhanced not only by the addition of butene, but also by the addition of ethylene, propylene, and 1-pentene. This reaction activity enhancement observed for olefins other than butene was suggested to be due to the isomerization of n-butane via different oligomeric species. In this work, we show that at the maximum reaction rate after the initial induction period, the activity of the reaction sites appeared to be similar, regardless of whether they were activated by the various added olefins or by butene produced during reaction. The addition of butene was able to lower the average surface residence time of the active intermediates leading to isobutane ($\tau^*_{\mathrm{isoC_4}}$) at the very beginning of the reaction induction period, reinforcing an early suggestion that butene formation and accumulation of olefinic intermediates are required for the reaction. The improved isobutane formation rate caused by the addition of olefins was due to an increased concentration of surface intermediates leading to isobutane ($N^*_{\mathrm{isoC_4}}$). Any type of added olefin led to the formation/utilization of additional active olefin-modified sites (i.e., adsorbed carbenium ions on acid sites). A larger $N^*_{\mathrm{isoC_4}}$ was obtained compared with the reaction without olefin addition when the olefins were added only during the initial 2 min of reaction and then terminated. This suggests that most of the olefin-modified sites were probably formed by the addition of olefin at the early stages of the reaction. Those sites were able to integrate themselves into the reaction cycles and to persist for multiple turnovers.

Keywords: Sulfated zirconia; n-Butane isomerization; Olefin addition; Isotopic transient kinetic analysis; Active sites

1. Introduction

The structural isomerization of linear paraffins to branched ones is an important process in raising the octane number of gasoline. Most current commercial processes are based on the use of chlorinated Pt/Al_2O_3 that requires the continuous addition of chlorine. To make this process more environmentally friendly, heterogeneous strong acid catalysts that do not require the continuous addition of an undesirable chemical, such as chlorine, have been sought.

Modified zirconias have been shown to be very strong solid acids and much research has been conducted on these catalysts. One of the most active modified zirconias is sulfated zirconia (SZ), on which one current UOP-licensed process is based. Although SZ has high activity for alkane isomerization even at low temperatures [1], it also deactivates rapidly.

The mechanisms of alkane isomerization, particularly for n-butane isomerization, have been widely studied. Numerous studies have shown that an increase in SZ activity is manifested when butene is added [2,3] or is present as an impurity [4–7]. This result has led to a suggestion of a bimolecular mechanism that requires the formation of C_8^+ species via the oligomerization of butene and n-butane before isomerization and β-scission to form isobutane [2,3,5,8–12]. However, Li et al. [13] suggested that n-butane isomerization proceeds via a monomolecular pathway in which isobutane is formed by the skeletal isomerization of *sec*-butyl ion produced by a protonation of butene to *tert*-C_4^+ intermediates. An increase in the surface concentration of *sec*-butyl ions due to the presence of butene led to an enhanced reaction rate. Recently, we have put forth a new hypothesized mechanism based on the results that any olefin can

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enhance *n*-butane isomerization on SZ [14]. Not only butene, but also ethylene, propylene, and 1-pentene, would appear to be able to form active "olefin-modified sites," which have been suggested to be the main centers of reaction [2]. In this proposed mechanism, isomerization takes place by a monomolecular skeletal rearrangement of oligomeric species through protonated cyclopropane states [14]. These oligomeric intermediates are formed via oligomerization of olefin and an adsorbed carbenium ion, the so-called "olefin-modified site" [2]. The comprehensive mechanism, having attributes of both the previously hypothesized monomolecular and bimolecular pathways, is able to resolve all the disparate results in the literature.

It has been shown that the addition of butene does not have an impact on the average site activity of the SZ catalyst, because the average surface residence time of isobutane intermediates ($\tau^*_{\mathrm{isoC_4}}$) remained essentially unchanged for *n*-butane isomerization at 150 °C as determined by isotopic transient kinetic analysis (ITKA) [2]. The increase in the isobutane formation rate caused by the addition of butene at 150 °C was shown to be due to an increase in the concentration of surface intermediates leading to isobutane ($N^*_{\mathrm{isoC_4}}$). However, it is important to know the effects of adding ethylene, propylene, or 1-pentene on the surface kinetic parameters of *n*-butane isomerization. By determining the surface kinetic parameters using ITKA, a better understanding can be developed of how the addition of olefins influence reaction rate with TOS, since understanding what happens on the catalyst surface during the induction period is key to understanding how the catalyst works and how olefins influence activity and reaction. Although isotopic tracing measurements were carried out previously for *n*-butane isomerization with the addition of 1-butene [2], the surface reaction parameters during the reaction induction period or for reaction at 100 °C have not been reported. Therefore, in this work, ITKA was carried out for *n*-butane isomerization at 100 °C in the presence and absence of various added olefins (ethylene, propylene, 1-butene, and 1-pentene). The concentrations of surface intermediates and other surface kinetic parameters during the induction period of *n*-butane isomerization on SZ were measured and are reported herein.

2. Experimental

2.1. Catalyst preparation and characterization

The SZ catalyst was prepared by calcining a sulfate-doped zirconium hydroxide [$Zr(OH)_4$] precursor (XZ0 1249/01, obtained from MEI, Flemington, NJ) at 600 °C under static air for 2 h. It was then cooled to room temperature over a 4-h period. BET surface area of the calcined SZ catalyst using N_2 adsorption was determined with a Micromeritics ASAP 2010. The sulfur content was measured by Galbraith Laboratories, Inc. (Knoxville, TN). The crystallinity of the calcined catalyst was analyzed using a Philips X'Pert X-ray diffractometer with monochromatized CuK_α radiation and a Ni filter, operated at 40 kV and 30 mA.

2.2. Reaction rate analysis

The study of *n*-butane isomerization was performed in a quartz microreactor (8 mm i.d.). The reaction was carried out under differential reaction conditions with a maximum conversion <5% to minimize temperature and concentration gradients. The SZ catalyst (0.2 g) was pretreated in situ at 315 °C under 30 cc/min of dry air (National Specialty Gases, Zero Grade) for 4 h, where the temperature was ramped at 2 °C/min and held constant at 100 °C for 1 h before heating to 315 °C. Then the reactor was cooled down to 100 °C under air and flushed with He (National Specialty Gases, UHP) for 30 min before the reaction. Reactions were carried out at 100 °C and at a constant pressure of 1.5 atm, where reaction rates were affected by neither mass nor heat transfer limitations.

A trap containing 10 g of H-mordenite held at room temperature was used to remove any olefin impurities present in the *n*-butane feed. The impurities remaining in the *n*-butane feed after the trap were 1 ppm ethane, 17 ppm propane, and 90 ppm isobutane. The total flow rate of the reaction mixture was 30 cc/min (STP), containing 15 cc/min of 5% *n*-$^{12}C_4H_{10}$ + 1% Ar (balance in He) (National Specialty Gases) and 15 cc/min of He. The flow of pure He was reduced to maintain a constant concentration of *n*-butane when olefins (1% of $C_2^=$, $C_3^=$, 1-$C_4^=$, or 1-$C_5^=$ in He [National Specialty Gases, UHP]) were added to the feed stream. Ethylene was added to the reaction at the lowest olefin-to-paraffin (O/P) ratio of 0.003, due to its strong catalyst activation–deactivation response, whereas propylene, 1-butene, and 1-pentene were added at the optimum O/P ratio for maximum rate enhancement, as determined previously (0.009, 0.012, and 0.009, respectively) [3]. Reaction samples were analyzed using a Varian 3700 gas chromatograph equipped with a 12-ft 15% Squalane CP-AW-DMCS/Chromosorb 80/100-mesh column (Alltech) and a flame ionization detector. All experiments were reproducible within a maximum error rate of ±5%.

2.3. Isotopic transient kinetic analysis

For ITKA during the reaction, a Valco two-position valve with an electric actuator was used to switch between 5% *n*-$^{12}C_4H_{10}$ + 1% Ar in He and 5% $^{13}CH_3(^{12}CH_2)_2{}^{13}CH_3$ in He (Isotec, 99%) without disturbing the other reaction conditions. A trace of Ar was present in the *n*-$^{12}C_4H_{10}$ to measure the gas-phase holdup for the reaction system. A 34-port VICI autosampling valve was used to collect 16 effluent samples during the 2-min isotopic transient periods. Then the collected effluent samples were separated by a gas chromatograph with 24-ft 15% Squalane CP-AW-DMCS/Chromosorb 80/100-mesh column (Alltech) held at 27 °C. A thermal conductivity detector (TCD) was used for product analysis to prevent product destruction. H_2/He (8.5%) at a flow rate of 20 cc/min was used as the carrier gas in the GC column and as a source of H_2 for a hydrogenolysis unit in which the separated effluent was converted to methane (CH_4) after GC separation. The hydrogenolysis reactor containing 5 g of 5% Pt on Al_2O_3 was held at 250 °C. The product CH_4 was subsequently introduced into a Balzers–

Pfeiffer Prisma 200-amu quadrupole mass spectrometer (Pfeiffer Vacuum) via a 1/16-inch capillary tube with differential pumping. The MS data were collected by a personal computer using Balzers Quadstar 422 v 6.0 software. Surface kinetic parameters such as the average surface residence time (τ_{isoC_4} and $\tau_{n\text{-C}_4}$) were determined from the isotopic transients using ITKA data analysis software. The analysis method and system setup have been described previously [15,16].

We previously reported that, if not taken into account, the impact of isobutane readsorption on ITKA can cause an overestimation of the average residence time of surface intermediates leading to isobutane (τ_{isoC_4}), resulting in an overestimation in the concentration of surface intermediates for isobutane (N_{isoC_4}) [16,17]. Therefore, to correct τ_{isoC_4} for readsorption, experiments were performed at different space times by varying catalyst weight from 0.05 to 0.25 g, and the values of τ_{isoC_4} were measured. These values were then used to determine a corrected value of τ_{isoC_4}. The impact of reversible isobutane readsorption on τ_{isoC_4} was significant for every situation studied (not shown). By extrapolating to zero space-time, a better value for τ_{isoC_4} in the absence of readsorption effects was obtained, designated as $\tau^*_{\text{isoC}_4}$. Thus, the $\tau^*_{\text{isoC}_4}$ and $N^*_{\text{isoC}_4}$ values reported in this paper are essentially free from isobutane readsorption effects. $N^*_{\text{isoC}_4}$ was determined by multiplying the formation rate of isobutane by $\tau^*_{\text{isoC}_4}$ [16]. Unlike isobutane, the average residence time of n-butane ($\tau_{n\text{-C}_4}$) was essentially constant independent of space-time within the limits of experimental error (not shown). This indicates that reversible readsorption of n-butane was not an issue, possibly due in part to the relatively high partial pressure of n-butane, as was also suggested by Kim et al. [16]. Bajusz et al. [18] found that at relatively high partial pressures, the competition for adsorption increases. This in turn minimizes readsorption of the n-butane reactant molecules. Although clearly some n-butane had to adsorb on the reaction sites to form the isobutane product, much more (1–2 orders more) was able to adsorb and desorb reversibly from other sites without reaction.

3. Results and discussion

3.1. Catalyst characterization

The BET surface area and sulfur content of the fresh calcined SZ were measured as 137 m^2/g and 1.89 wt% (590 µmol sulfur/g), respectively. XRD analysis showed that ZrO_2 was present only in the tetragonal phase. No sulfur compounds were detected due to the low concentration of sulfur present.

3.2. The continuous addition of various olefins

It has been shown that the presence of 1-butene in the feed stream affects the behavior of n-butane isomerization on SZ by shortening the induction period and increasing the rate of catalyst deactivation [2,3,5]. Thus, ITKA was carried out for n-butane isomerization at 100 °C as a function of TOS in the presence of 1-butene at an O/P ratio of 0.012, which has been shown to be the optimum ratio to ensure a maximum enhancement in an isobutane formation rate [3]. The variations in isobutane formation rate, the average surface residence time of the intermediates leading to isobutane ($\tau^*_{\text{isoC}_4}$), and the concentration of active surface intermediates leading to isobutane ($N^*_{\text{isoC}_4}$) at 100 °C with TOS (corrected for readsorption) in the presence and the absence of 1-butene addition are shown in Fig. 1.

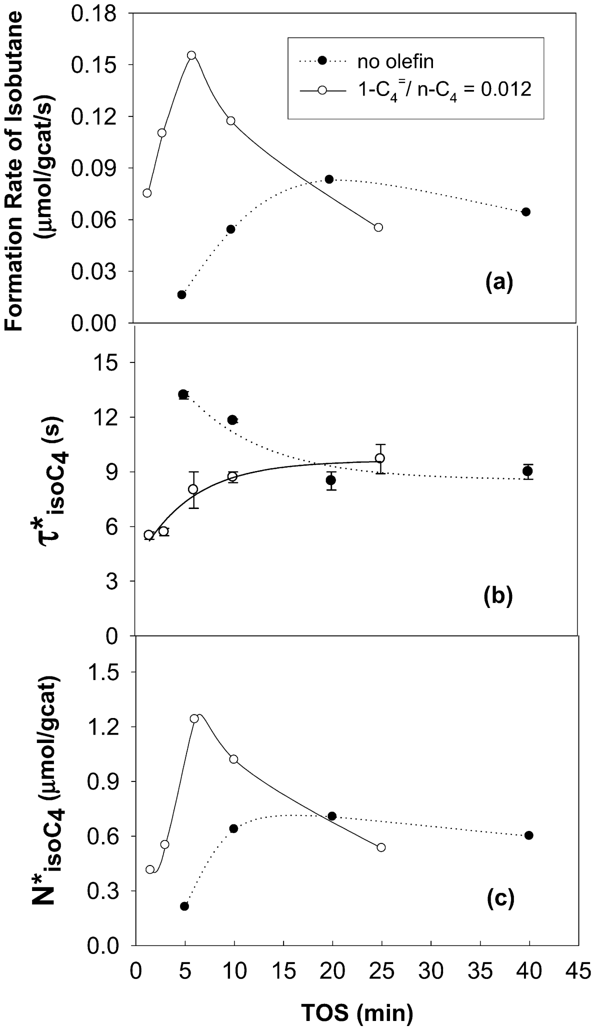

Fig. 1. The effect of continuous 1-butene addition (O/P ratio = 0.012) on the surface kinetic parameters with TOS at 100 °C.

In the absence of 1-butene addition, $\tau^*_{\text{isoC}_4}$ appeared to decrease somewhat with TOS before reaching a steady-state value of 8.5 s at 20 min TOS, where the maximum activity of the catalyst was exhibited (Fig. 1). This suggests that the average site activity of the catalyst ($\text{TOF}^*_{\text{ITK}}$, where $\text{TOF}^*_{\text{ITK}} = \text{rate}_{\text{isoC}_4}/N^*_{\text{isoC}_4} \approx 1/\tau^*_{\text{isoC}_4}$) increased at the beginning of reaction (the first 20 min TOS). The initial decrease in $\tau^*_{\text{isoC}_4}$ obtained when the catalyst was not exposed to added olefin is probably because of the greater amount of butene produced with TOS. Hammache and Goodwin [2] suggested that butene (added or formed) is able to adsorb on catalytic sites and form olefin-modified sites that contribute to isobutane formation. As was also suggested by others [2,3,5,7,13,19], n-butane isomerization on SZ requires some amount of butene to initiate the reaction.

Unlike without olefin addition, smaller $\tau^*_{\mathrm{isoC_4}}$ values at the very beginning of the induction period were observed when 1-butene was added to the reaction. $\tau^*_{\mathrm{isoC_4}}$ was 5.5 s at 1.5 min but increased rapidly up to 8 s at 6 min TOS. Adding 1-butene was able to lower $\tau^*_{\mathrm{isoC_4}}$, whereas deactivation of catalyst was not significant. This suggests that the presence of butene in the feed stream activated catalytic sites to promptly react with *n*-butane (or, rather, butene formed from *n*-butane). Butene formation has been suggested to occur via the oxidative dehydrogenation of *n*-butane by sulfate groups where the oxidizing and reducing species are SO_3 and SO_2, respectively [7,20]. However, $\tau^*_{\mathrm{isoC_4}}$ was observed to increase after the first 3 min of reaction. This was probably due to a higher participation of weaker acid sites in overall reaction as a result of rapid catalyst deactivation of the most active sites caused by the addition of 1-butene. Yaluris et al. [21] and Kim et al. [22] found that strong acid sites (i.e., sites with a higher activity contributing to a smaller $\tau^*_{\mathrm{isoC_4}}$) tend to deactivate at a faster rate compared with the less active sites. It has also been reported that the deactivation rate constant for 1-butene addition at 100 °C is 4 times higher than that for the reaction without 1-butene addition [3].

Fig. 1 clearly shows that the activity and deactivation behaviors of the catalyst (i.e., increase and decrease in the rate of isobutane formation) were due primarily to changes in $N^*_{\mathrm{isoC_4}}$. $N^*_{\mathrm{isoC_4}}$ was significantly larger with the addition of 1-butene than in the absence of the added olefin. The larger values for $N^*_{\mathrm{isoC_4}}$ observed from continuous addition of 1-butene (1.2 μmol/g at the maximum activity) compared with those in its absence (0.6 μmol/g) confirms the concept that the addition of butene increases the number of olefin-modified sites by forming or activating additional active sites. However, $N^*_{\mathrm{isoC_4}}$ went through a maximum value of 1.2 μmol/g at 6 min TOS and then decreased, just like the overall rate of isobutane formation. A loss of active sites by coke/oligomer formation has been reported to be the major cause of catalyst deactivation for *n*-butane isomerization on SZ [9,16,23,24]. In contrast, little significant change in $N^*_{\mathrm{isoC_4}}$ was observed after 10 min TOS for the reaction without added olefin, due to the lower catalyst deactivation rate at this low reaction temperature.

ITKA measurements were also made for reaction with the addition of ethylene, 1-propylene, and 1-pentene to study the effects of olefin type on the surface reaction parameters of the catalyst. Propylene, 1-butene, and 1-pentene were added at the optimum O/P ratios (0.009, 0.012, and 0.009, respectively) known to maximally enhance catalyst activity [3]. (Increasing the concentration of added olefins beyond these values only accelerates catalyst deactivation and lowers isobutane selectivity.) Ethylene was added at an O/P ratio of 0.003, because ethylene strongly promotes catalyst activation and deactivation. Fig. 2 shows that the activity of SZ for *n*-butane isomerization is increased by the addition not only of 1-butene but also of ethylene, propylene, and 1-pentene. The enhanced maximum activity of the catalyst was observed in varying degrees, depending on the type of olefin added. The increased activity for isobutane observed during the addition of various olefins was much greater than the simple conversion of the added olefin to isobutane. Adding ethylene significantly promoted the catalyst activity and significantly shortened the induction period, whereas adding propylene, 1-butene, and 1-pentene produced relatively comparable reaction rate profiles with a 6-min induction period at these reaction conditions before catalyst deactivation became dominant.

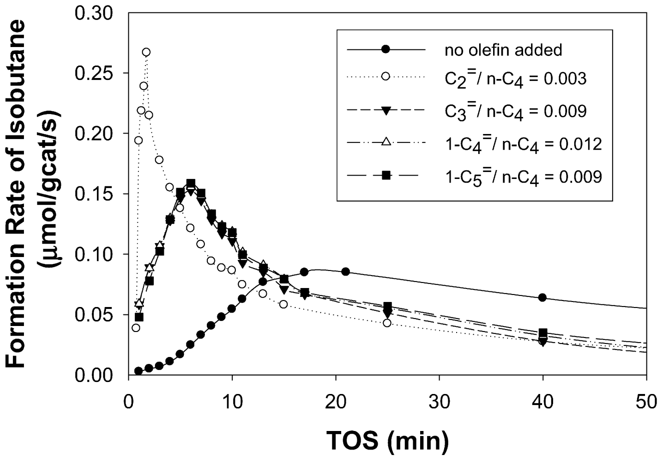

Fig. 2. The reaction rates at 100 °C when ethylene, propylene, 1-butene and 1-pentene were added continuously. (Reproduced from Ref. [14].)

As shown in Fig. 2, olefins influence the maximum catalyst activity to varying degrees. Thus, the ITKA study was performed at the maximum isobutane formation rate (i.e., 20, 1.5, and 6 min TOS for no olefin, ethylene, and propylene, 1-butene and 1-pentene addition, respectively) and the results are shown in Table 1. At the maximum reaction rate, $\tau^*_{\mathrm{isoC_4}}$ values were insignificant different among the reactions with and without olefin addition, showing relatively the same average site activity ($\mathrm{TOF}^*_{\mathrm{ITK}} \approx 1/\tau^*_{\mathrm{isoC_4}}$) regardless of whether the olefin-modified sites were formed by different added olefins or by butene produced during reaction. This reinforces the previous suggestion that any type of olefin (ethylene, propylene, and 1-pentene) besides butene is able to adsorb on the catalyst surface and form olefin-modified sites [14]. Such sites have been proposed to be main centers of reaction that could lead to the formation of oligomer when reacted with a butene (from *n*-butane) molecule. Those oligomeric species were hypothesized to be C_6^+, C_7^+, C_8^+, and C_9^+ due to the dissimilarity among the olefin-modified sites (i.e., C_2^+, C_3^+, C_4^+, and C_5^+ from addition of ethylene, propylene, 1-butene, and 1-pentene, respectively). However, it is hard to imagine that those sites were so similar when they were formed by different hypothesized oligomeric species. Considering the small change in $\tau^*_{\mathrm{isoC_4}}$ values, it appears that the activity of active sites modified by added ethylene was higher (i.e., $\tau^*_{\mathrm{isoC_4}}$ was lower) than in the absence of olefin addition. Only a relatively small difference in $\tau^*_{\mathrm{isoC_4}}$ was observed, because $\tau^*_{\mathrm{isoC_4}}$ is the average value for all of the active intermediates, including more than a third (0.7 vs 1.9 μmol/g) generated by butene from the *n*-butane reactant.

Obviously, the increase in $N^*_{\mathrm{isoC_4}}$ observed during reaction with added olefins appeared to be the main cause of the higher catalyst activities observed. As would be expected, $N^*_{\mathrm{isoC_4}}$ was most enhanced by the addition of ethylene. Adding ethylene was able to increase $N^*_{\mathrm{isoC_4}}$ to almost 3 times that extant in the

Table 1
The effect of the continuous addition of various olefins on surface kinetic parameters at 100 °C at maximum reaction rate

Olefin	O/P ratio	TOS (min)	$\text{Rate}_{\text{isoC}_4}$ [a] (μmol/(g s))	$\text{TOF}_{\text{sulfur}}$ [b] (10^{-4} s^{-1})	$N^*_{\text{isoC}_4}$ [c] (μmol/g)	$\tau^*_{\text{isoC}_4}$ [d] (s)	$\text{TOF}^*_{\text{ITK}}$ [e] (10^{-1} s^{-1})	$N_{n\text{-C}_4}$ [f] (μmol/g)	$\theta^*_{\text{isoC}_4}$ [g]/ sulfur (10^{-3})	$\theta_{n\text{-C}_4}$ [h]/ sulfur (10^{-2})
None	–	20	0.083	1.41	0.7	8.5	1.18	14.5	1.2	2.5
$C_2^=$	0.003	1.5	0.235	3.98	1.9	7.9	1.27	14.0	3.2	2.4
$C_3^=$	0.009[i]	6	0.152	2.58	1.2	8.0	1.25	14.0	2.1	2.4
1-$C_4^=$	0.012[i]	6	0.155	2.63	1.2	8.0	1.25	15.0	2.1	2.6
1-$C_5^=$	0.009[i]	6	0.159	2.69	1.3	8.3	1.20	14.8	2.2	2.5

[a] Max error = ±5%.
[b] $\text{TOF}_{\text{sulfur}} = \text{Rate}_{\text{isoC}_4}/(590\ \mu\text{mol sulfur/g})$; Max error = ±5%.
[c] $N^*_{\text{isoC}_4} = \text{Rate}_{\text{isoC}_4} \times \tau^*_{\text{isoC}_4}$; Max error = ±0.06 μmol/g.
[d] Corrected τ_{isoC_4} due to isobutane readsorption by extrapolating to zero space time; Max error = ±0.5 s.
[e] $\text{TOF}^*_{\text{ITK}} = 1/\tau^*_{\text{isoC}_4} = \text{Rate}_{\text{isoC}_4}/N^*_{\text{isoC}_4}$; Max error = ±0.007 s^{-1}.
[f] $N_{n\text{-C}_4}$ = flow rate n-C_4 (2.55 μmol/(g s)) $\times \tau_{n\text{-C}_4}$ (no significant readsorption of n-C_4 in the catalyst bed determined); Max error = ±0.6 μmol/g.
[g] $\theta^*_{\text{isoC}_4} = N^*_{\text{isoC}_4}/(590\ \mu\text{mol sulfur/g})$; Max error = ±0.0009.
[h] $\theta_{n\text{-C}_4} = N_{n\text{-C}_4}/(590\ \mu\text{mol sulfur/g})$; Max error = ±0.0012.
[i] The optimum olefin-to-paraffin ratio for the maximum isobutane formation rate.

absence of added olefin and 2 times that produced by the addition of any other olefin. Ethylene probably accomplished this by rapidly populating and forming a greater number of active sites on the catalyst surface as a result of a very high reactivity of the primary carbenium ion-modified site produced by the adsorption of ethylene. Table 1 also shows that the similarity in the isobutane formation rate enhancement caused by the addition of propylene, 1-butene, and 1-pentene was due to similar values of $N^*_{\text{isoC}_4}$. $N^*_{\text{isoC}_4}$ was observed to be similar probably because of a similar reactivity of these 3 olefins to form secondary carbocations on the acid sites. Although experiments with different olefin concentrations were not performed in this study, we believe, based on these results and those previously [3], that $N^*_{\text{isoC}_4}$ would decrease with higher olefin concentrations due to enhanced deactivation.

The $N^*_{\text{isoC}_4}$ value was observed to be very low compared with $N_{n\text{-C}_4}$ (the concentration of n-butane reversibly adsorbed), which was approximately 14.5 μmol/g of catalyst. Only a fraction of the total adsorption sites (1.2 μmol/g, or <10%) contributed to the formation of isobutane. $N_{n\text{-C}_4}$ was found to be relatively constant within the limits of experimental error and was not affected by the addition of any olefin. In addition, surface coverages of sulfur (assuming that all sulfur entities are accessible) by n-butane ($\theta_{n\text{-C}_4}$) and isobutane ($\theta^*_{\text{isoC}_4}$) are given in Table 1. It was found that probably only ca. 2.5% of sulfur loading was used in the adsorption of n-butane ($\theta_{n\text{-C}_4}$), which was an order of magnitude higher than $\theta^*_{\text{isoC}_4}$.

3.3. *Initial 2-min addition of olefins*

The positive effect on the formation rate of isobutane from continuous feeding of olefins to the reaction was overwhelmed long term by more rapid catalyst deactivation. To minimize this negative impact of olefin addition, propylene, 1-butene, and 1-pentene were added to the reaction at 100 °C for only the first 2 min of the reaction. The addition of ethylene during the initial 2 min of the reaction was not done in this study because ethylene considerably increased catalyst activity and significantly promoted catalyst deactivation in less than 2 min (see Fig. 2). The effect of an initial 2-min addition of the other various olefins on the formation rate of isobutane is shown in Fig. 3. Although the flow of olefin was introduced to the feed stream for only 2 min at the beginning of the reaction and then terminated, isobutane formation was still higher compared with that when no olefin was added. The initial 2-min addition of these three olefins also produced similar effects on catalyst activity as seen from continuous addition. To gain more insight into how olefins promote catalyst activity after their addition is terminated, ITKA measurements were made for the reaction at two different TOS (i.e., 5 min and at maximum catalyst activity) before significant catalyst deactivation.

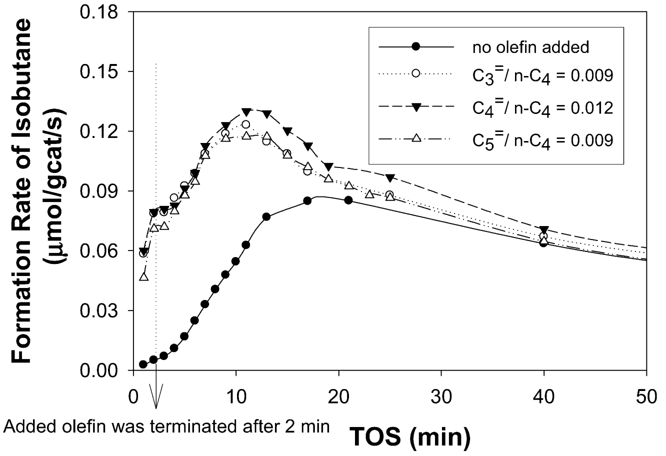

Fig. 3. The reaction rates at 100 °C when propylene, 1-butene and 1-pentene were added during the first 2 min of reaction at the optimum O/P ratio (O/P ratio = 0.009 for $C_3^=$ and 1-$C_5^=$, and 0.012 for $C_4^=$). (Reproduced from Ref. [14].)

A comparison of ITKA results at 5 min TOS and at maximum isobutane formation between the reaction with and without the initial 2 min addition of olefins (propylene, 1-butene and 1-pentene) is shown in Table 2. Adding olefin only during the initial 2 min of reaction resulted in the same effect on $\tau^*_{\text{isoC}_4}$

Table 2
The effect of initial 2 min addition of various olefins on surface kinetic parameters at 100 °C

TOS (min)	Olefin	O/P ratio[a]	$\text{Rate}_{\text{isoC}_4}$[b] (μmol/(g s))	$N^*_{\text{isoC}_4}$[c] (μmol/g)	$\tau^*_{\text{isoC}_4}$[d] (s)	$N_{n\text{-C}_4}$[e] (μmol/g)
5	None	–	0.016	0.2	13.2	14.3
5	$C_3^=$	0.009	0.092	0.8	8.2	16.8
5	1-$C_4^=$	0.012	0.091	0.8	9.1	14.5
5	1-$C_5^=$	0.009	0.088	0.7	8.3	15.0
20[f]	None	–	0.083	0.7	8.5	14.5
11[f]	$C_3^=$	0.009	0.123	1.1	9.1	15.3
11[f]	1-$C_4^=$	0.012	0.130	1.1	8.8	13.5
11[f]	1-$C_5^=$	0.009	0.117	1.0	8.2	14.4

[a] The optimum olefin-to-paraffin ratio for the maximum isobutane formation rate.

[b] Max error = ±5%.

[c] $N^*_{\text{isoC}_4} = \text{Rate}_{\text{isoC}_4} \times \tau^*_{\text{isoC}_4}$; Max error = ±0.04 μmol/g.

[d] Corrected τ_{isoC_4} due to isobutane readsorption by extrapolating to zero space time; Max error = ±0.3 s.

[e] $N_{n\text{-C}_4}$ = flow rate n-C$_4$ (2.55 μmol/(g s)) $\times \tau_{n\text{-C}_4}$ (no significant readsorption of n-C$_4$ in the catalyst bed determined); Max error = ±1 μmol/g.

[f] TOS at the maximum isobutane formation rate.

just like the continuous addition of olefins, regardless of the type of olefin. Taking into account experimental error, $\tau^*_{\text{isoC}_4}$ remained unchanged with TOS during the induction period for 2-min olefin addition. No differences in intrinsic site activity were seen among the reactions with the addition of these three olefins. These values ($\tau^*_{\text{isoC}_4}$) were similar to those seen when the catalyst was continuously exposed to added olefins within experimental error. This indicates that the average site activity was not influenced by either olefin type or the addition of olefin.

Similar values of $N^*_{\text{isoC}_4}$ appeared to be associated with the similar catalyst activities observed for reaction with an initial 2-min addition of propylene, 1-butene, and 1-pentene, but these values were slightly lower than those seen when olefins were added continuously. Similar to continuous 1-butene addition, ITKA done before the point at which catalyst deactivation became dominant showed that $N^*_{\text{isoC}_4}$ increased with TOS during the induction period for every olefin added. Although the isotopic tracing measurements were performed after olefin addition was stopped, a higher $N^*_{\text{isoC}_4}$ compared with that for the reaction without added olefin was obtained. This suggests that these additional active sites likely were activated by butene formed from n-butane or perhaps by olefins fed slowly during the first 2 min of reaction. Olefin-modified sites are known to be able to persist for multiple reaction cycles, producing a long-lasting impact of olefin addition on the catalyst. Each added butene molecule has been reported to result in more than 10–700 additional isobutane molecules, depending on reaction conditions [2,3,8]. Tabora and Davis [8] reported that at least 10 excess isobutane molecules were produced per molecule of added trans-2-butene on iron- and manganese-promoted SZ during n-butane isomerization at 100 °C; Hammache and Goodwin [2] found this value to be 700 when the reaction was carried out at 150 °C with the addition of 1-butene.

4. Conclusions

Our previous proposal [14] that the active sites for n-butane isomerization on SZ can be activated by any olefin has been strongly confirmed by a similar effect of adding olefins on surface reaction parameters, such as $\text{TOF}^*_{\text{ITK}}$ ($1/\tau^*_{\text{isoC}_4}$) and the concentration of active surface intermediates ($N^*_{\text{isoC}_4}$). At the maximum reaction rate, $\tau^*_{\text{isoC}_4}$ was observed to be essentially equal for all continuously added olefins (ethylene, propylene, 1-butene, and 1-pentene) within the limits of experimental error. An increased concentration of active surface intermediates leading to isobutane ($N^*_{\text{isoC}_4}$) with the addition of various olefins was shown to be the cause of the enhanced catalyst activity. $N^*_{\text{isoC}_4}$ was most increased by the addition of ethylene, resulting in the highest maximum formation rate of isobutane. The value of $N^*_{\text{isoC}_4}$ at the maximum rate was similar for the addition of propylene, 1-butene, and 1-pentene, resulting in similar rate maxima. As expected, the increase in $N^*_{\text{isoC}_4}$ caused by the initial 2-min olefin additions was lower than that with continuous olefin additions. However, although the olefin feed was terminated at least 3 min before the isotopic tracing measurements were made, the $N^*_{\text{isoC}_4}$ was still larger compared with that for the case without added olefin, regardless of the type of olefin added. This reinforces our previous suggestion that olefin-modified sites can be formed by adding any olefin at the beginning of the reaction induction period and persist for multiple reaction cycles. Certainly, the fact that the addition of 1-butene was able to lower the $\tau^*_{\text{isoC}_4}$ value at early stages of the induction period lends credence to the widely held belief that in the absence of added olefins, n-butane isomerization requires the formation of butene and an accumulation of surface intermediates to carry out the reaction.

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References

[1] C.Y. Hsu, C.R. Heimbuch, C.T. Armes, B.C. Gates, J. Chem. Soc. Chem. Commun. (1992) 1645.
[2] S. Hammache, J.G. Goodwin Jr., J. Catal. 211 (2002) 316.
[3] N. Lohitharn, J.G. Goodwin Jr., E. Lotero, J. Catal. 234 (2005) 199.
[4] V. Adeeva, G.D. Lei, W.M.H. Sachtler, Catal. Lett. 33 (1995) 135.
[5] H. Liu, V. Adeeva, G.D. Lei, W.M.H. Sachtler, J. Mol. Catal. A Chem. 100 (1995) 35.
[6] M.A. Coelho, W.E. Alvarez, E.C. Sikabwe, R.L. White, D.E. Resasco, Catal. Today 28 (1996) 415.
[7] X.B. Li, K. Nagaoka, L.J. Simon, R. Olindo, J.A. Lercher, A. Hofmann, J. Sauer, J. Am. Chem. Soc. 127 (2005) 16159.
[8] J.E. Tabora, R.J. Davis, J. Catal. 162 (1996) 125.
[9] T.K. Cheung, J.L. Ditri, B.C. Gates, J. Catal. 151 (1995) 464.
[10] S.Y. Kim, J.G. Goodwin Jr., S. Hammache, A. Auroux, D. Galloway, J. Catal. 201 (2001) 1.
[11] V. Adeeva, G.D. Lei, W.M.H. Sachtler, Appl. Catal. A Gen. 118 (1994) L11.

[12] S. Hammache, J.G. Goodwin Jr., J. Catal. 218 (2003) 258.
[13] X.B. Li, K. Nagaoka, L.J. Simon, R. Olindo, J.A. Lercher, J. Catal. 232 (2005) 456.
[14] N. Lohitharn, E. Lotero, J.G. Goodwin Jr., J. Catal. 241 (2006) 328.
[15] S.L. Shannon, J.G. Goodwin Jr., Chem. Rev. 95 (1995) 677.
[16] S.Y. Kim, J.G. Goodwin Jr., D. Galloway, Catal. Lett. 64 (2000) 1.
[17] S.H. Ali, J.G. Goodwin Jr., J. Catal. 171 (1997) 339.
[18] I.G. Bajusz, J.G. Goodwin Jr., D. Galloway, N. Greenlay, Langmuir 14 (1998) 1846.
[19] J.E. Tabora, R.J. Davis, J. Am. Chem. Soc. 118 (1996) 12240.
[20] D. Farcasiu, A. Ghenciu, J.Q. Li, J. Catal. 158 (1996) 116.
[21] G. Yaluris, R.B. Larson, J.M. Kobe, M.R. Gonzalez, K.B. Fogash, J.A. Dumesic, J. Catal. 158 (1996) 336.
[22] S.Y. Kim, J.G. Goodwin Jr., D. Galloway, Catal. Today 63 (2000) 21.
[23] B. Subramaniam, V. Arunajatesan, C.J. Lyon, Catal. Deact. 126 (1999) 63.
[24] S.Y. Kim, N. Lohitharn, J.G. Goodwin Jr., R. Olindo, F. Pinna, P. Canton, Catal. Commun. 7 (2006) 209.