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A comprehensive mechanistic pathway for *n*-butane isomerization on sulfated zirconia

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Abstract

This paper proposes a comprehensive mechanistic model for *n*-butane isomerization on sulfated zirconia (SZ) that accounts for the apparent contradictory results reported in the literature. The use of nonspecific olefins as molecular probes in *n*-butane isomerization has played a central role leading to this mechanistic proposal. The contradictory results in the literature have led various authors to conclude that the reaction occurs via a bimolecular mechanism, while others have suggested that a monomolecular pathway is dominant. The presence of butene is well known to lead to increased isobutane formation, suggesting a predominantly bimolecular route. However, we recently showed that the addition of other olefins (ethylene, propylene, isobutene, and 1-pentene) also promotes the reaction rate and modifies the induction period. These results indicate that not only C_4 olefins, but also any olefin with the ability to form carbenium ion species on the catalyst surface, can promote catalytic activity. Taking into account our latest experimental evidence, a reaction mechanism is proposed involving a *bimolecular pathway* with the characteristics of a *monomolecular pathway* (dual-nature mechanism) using "olefin-modified sites" as the main centers of reaction. The major observations made for the isomerization of *n*-butane (i.e., isotopic scrambling, nonspecific olefin activity promotion, high isobutane selectivity, and catalyst deactivation) are discussed in light of the proposed molecular pathway, and the seeming duality of the mechanism is addressed.

Keywords: Sulfated zirconia; *n*-Butane isomerization; Olefin addition; Mechanism of reaction

1. Introduction

The skeletal isomerization of *n*-alkanes plays an important role in the production of branched, high-octane hydrocarbons as a replacement for traditional tetra-ethyl lead additives. Sulfated zirconia (SZ) has gained much attention for the isomerization of *n*-butane because it exhibits high activity and selectivity toward isobutane even at low temperatures [1–3]. Initially, this was suggested to be related to the strong acidity of SZs, similar to that found for zeolites such as HY [1,4], but it has been shown that this is not the case. Zeolites, for instance, require much higher temperatures to achieve similar conversions [5,6]. It is possible that the catalytic ability of SZ for *n*-butane isomerization is related to its capacity to promote redox reactions of hydrocarbons (oxidative dehydrogenation), as some authors have recently suggested [7–10].

There is still much controversy about the mechanistic pathway operating for *n*-butane isomerization on SZ. Several researchers have suggested that the reaction proceeds through a monomolecular mechanism involving formation of a protonated cyclopropane ring on unpromoted SZ [2,11,12] and on Pt-SZ in the presence of H_2 [13–15]. The monomolecular pathway can satisfactorily explain the high selectivity toward isobutane, especially for short time on stream (TOS) and low conversion [2,12].

The other mechanism for *n*-butane isomerization on SZ suggested by numerous researchers is the bimolecular mechanism [16–23]. The bimolecular pathway is considered to occur via the formation of butene, which subsequently oligomerizes with adsorbed $C_4{}^+$ carbenium ions to produce $C_8{}^+$ oligomeric species. Under this hypothesis, it is assumed that a $C_8{}^+$ species undergoes isomerization and β-cleavage, leading to mainly isobutane and some disproportionation products. To date, however, just how the isomerization step of the $C_8{}^+$ oligomer oc-

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curs and how it leads mainly to isobutane have not been clearly explained in the literature.

The hypothesized bimolecular mechanism is supported especially by two facts: (1) the observation of disproportionation products, such as propane and pentanes, and (2) substantial isotopic scrambling for the reaction using 1,4-^{13}C *n*-butane, with the isobutane product containing an isotopic distribution between 0 and 4 ^{13}C atoms [17,20,24,25], which cannot be explained solely by a monomolecular route. In addition to these two important observations, recent experimental results have shown that the initial formation rate of isobutane is dramatically enhanced by olefins introduced at low concentrations in the reactant stream [16,21–23]. The activity-promoting effect of olefins occurs even when the added olefin is not butene, pointing to a nonspecific olefin rate enhancement for isobutane formation [23]. In addition, excess isobutane molecules are formed from each olefin molecule added [16,21,23], suggesting that active sites formed by olefin addition last for multiple turnovers. This evidence has led us to conclude that active sites probably can be best described as olefin-modified sites [21,23]. From our standpoint, this observation supports a bimolecular pathway requiring butene oligomerization before isomerization. A bimolecular pathway is also largely supported by the presence of an induction period, which has been hypothesized to result from the formation and accumulation of olefinic intermediates on the surface before isomerization [26].

Nevertheless, some authors have suggested that *n*-butane isomerization does not proceed through a bimolecular route exclusively. Matsuhashi et al. [2] concluded that *n*-butane isomerization occurs through a monomolecular pathway in the early stages of reaction before becoming a bimolecular pathway at long TOS. Li et al. [12] also proposed that the monomolecular isomerization pathway occurs at very low *n*-butane conversions, resulting in 100% isobutane selectivity. As conversion increases, the contributions from a bimolecular route become important, yielding disproportionation products.

Various studies have found that the reaction mechanism is dependent on reaction temperatures. According to Tran et al. [5], a diluting gas such as H_2 considerably decreases the formation rate of isobutane at low temperatures (150 and 200 °C), whereas there is no impact at 250 °C. This was taken as an indication that a bimolecular pathway is more pronounced at low temperatures, as was also suggested by a study using double-labeled ^{13}C butane by Echizen et al. [27], who found an increase in the monomolecular pathway for *n*-butane isomerization with increasing reaction temperature.

The work presented here is a continuation of our research on the effect of nonspecific olefin addition on the catalytic activity of SZ for *n*-butane isomerization and its relationship to the reaction mechanism. As reported previously, olefins, such as propylene, 1-butene, and 1-pentene, have a substantial impact on the induction period of *n*-butane isomerization on SZ in an indistinguishable way [23]. The main conclusion from that work was that olefin-modified sites, rather than purely Brønsted or Lewis acid sites themselves, may be at the center of catalytic activity for *n*-butane isomerization. The present work expands on the range of olefins that can affect the isomerization activity of SZ, including ethylene and isobutene. Conclusions based on these results lead us to a proposed mechanism exhibiting a duality between monomolecular and bimolecular routes that substantiates all of the major facts observed for *n*-butane isomerization. Thus, the issues of high selectivity, presence of disproportionation products, isotopic scrambling, catalyst deactivation, and the effect of nonspecific olefin addition on reaction activity can all be addressed within the context of our mechanistic proposal.

2. Experimental

2.1. Catalyst preparation and characterization

The SZ catalyst was prepared by calcining the sulfate-doped zirconium hydroxide [$Zr(OH)_4$] precursor [MEI (XZO 1249/01, Flemington, NJ)] at 600 °C under static air for 2 h. The BET surface area of the calcined SZ catalyst was determined using N_2 adsorption with a Micromeritics ASAP 2010 (Norcross, GA). The sulfur content was determined by Galbraith Laboratories (Knoxville, TN). The crystallinity of the calcined catalyst was studied using a Philips X'Pert X-ray diffractometer using monochromatized Cu-K_α radiation and a Ni filter, operating at 40 kV and 30 mA.

2.2. *n*-Butane isomerization

A quartz microreactor (8 mm i.d.) was used in this study. The reaction was carried out with a maximum conversion of <6% to operate under differential conditions. Before reaction, 0.2 g of the SZ catalyst was pretreated in situ at 315 °C under 30 cc/min of dry air (National Specialty Gases, Zero Grade) for 4 h. Then the reactor was cooled to the reaction temperature of 100 °C under air and flushed with He (National Specialty Gases, UHP) for 30 min. The total flow rate of the reactant stream was 60 cc/min (STP), consisting of 30 cc/min of 5% n-C_4 + 1% Ar in a balance of He (National Specialty Gases). The reaction pressure was kept constant at 1.5 atm. The flow of pure He was adjusted to maintain a constant flow rate of *n*-butane when olefin [1% of $C_2^=$, $C_3^=$, 1-$C_4^=$, iso$C_4^=$ or 1-$C_5^=$ in He (National Specialty Gases, UHP)] was added to the feed stream. Any olefin impurities from the *n*-butane cylinder were removed using a trap containing 10 g of H-mordenite held at room temperature. The impurities remaining in the *n*-butane feed were 2 ppm propane and 7 ppm isobutane.

In this study, various olefins ($C_2^=$, $C_3^=$, 1-$C_4^=$, iso-$C_4^=$, and 1-$C_5^=$) were added to the reaction stream to measure their effect on SZ activity. Ethylene was added to the reaction at the lowest olefin/paraffin (O/P) ratio of 0.003 due to the strong catalyst activation-deactivation response to this olefin, while isobutene was continuously added at 0.009. Other olefins ($C_3^=$, 1-$C_4^=$, or 1-$C_5^=$) were added at various O/P ratios (0.003–0.015). Reactions were carried out at 100 °C, where reaction rates were not affected by either mass or heat transfer limitations.

Reaction samples were collected using a 34-port VICI autosampling valve that could obtain up to 16 product samples to precisely study the induction period of 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 and a flame ionization detector. All major reaction products were identified using a known standard gas mixture. All experiments were reproducible within a maximum error of ±5%.

3. Results

3.1. Catalyst characterization

The fresh calcined SZ had a sulfur content of 1.7 wt% and a BET surface area of 137 m^2/g. XRD analysis showed only the tetragonal phase of ZrO_2.

3.2. Effect of nonspecific olefin addition on reaction rate

The effects of continuous addition of ethylene, propylene, 1-butene, isobutene, and 1-pentene on catalyst activity are shown in Fig. 1 at the optimum O/P ratio for maximum rate enhancement as determined previously [23]. The addition of any type of olefin increased the maximum rate of isobutane formation and shortened the induction period to varying degrees. The addition of optimum amounts of propylene, 1-butene, and 1-pentene enhanced catalyst activity equally, resulting in similar induction periods. However, catalyst activity was considerably increased to a maximum value of 0.27 $\mu mol/(g_{cat}\,s)$ in less than 2 min when ethylene was added at an even lower O/P ratio. A very fast induction period followed by a significant decrease in catalytic activity was observed with a maximum reaction rate 3 times higher than that observed for the reaction in the absence of added olefin (ca. 0.09 $\mu mol/(g_{cat}\,s)$). In contrast, catalyst activity was not significantly improved by the continuous addition of isobutene, with only a 30% rate increase with respect to the reaction with no olefin addition.

The deactivation rate constant for the reaction without olefin addition was 0.01 min^{-1}. The deactivation rate constant (k_d) is defined by $r_{iso}(t) = r_o \exp(-k_d t)$ after the induction period, where $r_{iso}(t)$ is the formation rate of isobutane and r_o is the maximum rate reached at the end of the induction period. The continuous addition of isobutene had only a moderate effect on catalyst deactivation, resulting in a k_d value of 0.024 min^{-1}. In contrast, continuous ethylene addition at an O/P ratio of 0.003 had a very high k_d value (0.096 min^{-1}). The k_d values for continuous addition of $C_3^=$, 1-$C_4^=$, and 1-$C_5^=$ were 0.045, 0.041, and 0.032 min^{-1}, respectively, at an O/P ratio of 0.009.

Fig. 2 shows a comparison in the rate of isobutane formation resulting when the catalyst was exposed to ethylene, propylene, 1-butene, and 1-pentene during only the initial 2 min of reaction. Iso-butene addition during the initial 2 min of the reaction was not done in this study due to its lesser effect in the continuous addition study. Similar to the continuous ethylene addition experiment, ethylene enhanced catalyst activity considerably, but with a lesser impact on catalyst deactivation, as was expected because it was added for only 2 min. The 2-min initial addition of propylene, 1-butene, and 1-pentene also resulted in higher activities and faster induction periods compared with no olefin addition, but slightly lower maximum activities. Similar deactivation profiles were obtained for the 2-min addition of these olefins as for the reaction without olefin addition.

3.3. The effect of nonspecific olefin addition on isobutane selectivity

Clearly, selectivity can provide insight into the reaction mechanism. The impact of ethylene, isobutene, propylene, 1-butene, and 1-pentene addition on isobutane selectivity is illustrated in Fig. 3. As shown in Fig. 3a, isobutane selectivity remained at approximately 97% for the 2-min ethylene addition experiment, comparable to that for the reactions without added olefin and with propylene, 1-butene, and 1-pentene addition for only the initial 2-min of reaction, as reported previ-

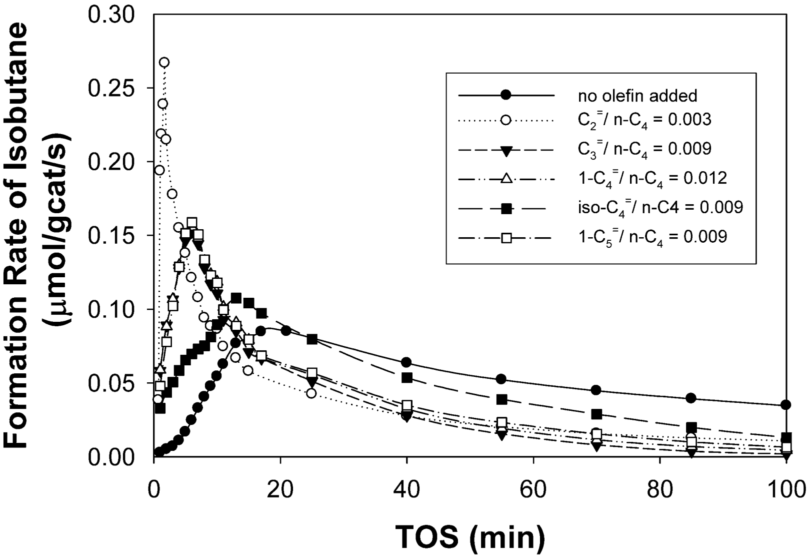


Fig. 1. The reaction rate at 100 °C when ethylene, propylene, 1-butene, isobutene or 1-pentene was added continuously.

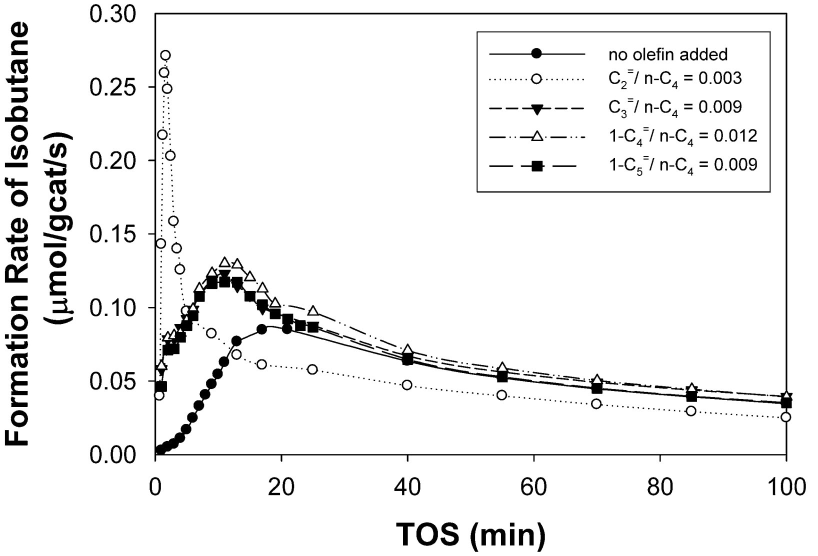


Fig. 2. The reaction rate at 100 °C when ethylene, propylene, 1-butene or 1-pentene was added during only the initial 2 min of reaction.

ously [23]. Iso-butane selectivity declined somewhat with TOS when ethylene was added continuously. This effect was also observed when the catalyst was continuously exposed to isobutene (Fig. 3b). Changes in isobutane selectivity at various O/P ratios of continuously added propylene, 1-butene, and 1-pentene are shown in Figs. 3c–e. Although the effect of olefin ($C_3^=$, 1-$C_4^=$ and 1-$C_5^=$) addition on isobutane selectivity has been addressed in previous work [23], we give additional results here to provide more details. In Fig. 3c, for propylene addition at low O/P ratios, the selectivity to isobutane did not change significantly with TOS (95–80%). Only when the O/P ratio was higher than the optimum value (0.009) did isobutane selectivity drop to 67% at 100 min TOS. However, the selectivity obtained at very low concentrations of 1-butene addition was higher than that observed with the addition of similar concentrations of propylene. This suggests that under very low partial pressures of added butene, the catalyst surface must remain essentially unchanged from that in the absence of added butene.

A decrease in selectivity was more evident for longer TOS, higher O/P ratios, and larger linear olefins (propylene, 1-butene, and 1-pentene, in that order). The decreased isobutane selectively was probably related to the formation and disproportionation of larger oligomers formed to a greater degree with TOS on the catalyst surface; however, branching changed the impact of olefin size on selectivity. The selectivity to isobutane was higher with isobutene addition (Fig. 3b) than with propylene addition (Fig. 3c). This may be due to a lower participation of isobutene in the formation of isobutane (with consequent lower rate enhancement). During the isobutene addition, the catalyst surface intermediates may have been more homogeneous, resulting in a lower probability that the reaction will produce undesirable byproducts.

3.4. The distribution of byproducts

Tables 1–3 present variations in the percent selectivity of all of the detectable reaction products at 100 °C with TOS at the maximum catalyst activity and at 85 min for the various olefins added. Table 1 shows the effect of continuous 1-butene addition on the percent selectivity of various products with variations in the O/P ratio. Continuous 1-butene addition had a negative impact on isobutane selectivity with increasing 1-butene concentration, causing formation of various byproducts. An unknown byproduct, C_{un}, was formed at long TOS during 1-butene addition at an O/P ratio $\geqslant 0.012$. Although absolute identification of this byproduct (C_{un}) was not possible, based on boiling point identification, it may have been cyclobutane. However, in any case, this compound did not appear to play any role in or to be a byproduct of the isomerization pathway. By the time that this byproduct was observed at long TOS, the catalyst had significantly deactivated, with an activity for isomerization of nearly zero. Other byproducts were C_3, iso-C_5, and traces of n-C_5 and iso-C_6.

The percent selectivities of all products were also affected by the type of olefin added continuously, as shown in Table 2. Ethylene and isobutene had the least impact on selectivity during continuous addition. Ethane was also found in very small concentrations when the SZ catalyst was exposed to ethylene, indicating that some hydride transfer took place between n-butane and the C_2^+ carbenium ion adsorbed on the surface. The formation of isohexane was observed only with continuous propylene, 1-butene, and 1-pentene addition. For continuous olefin addition, the selectivity toward isopentane increased and surpassed that of propane at long TOS. Table 2 also shows that a large amount of 2-pentene was detected during the continuous addition of 1-pentene. It is worthwhile to note that the amount of unidentified product C_{un} (possible cyclobutane) or 2-pentene formed was a function of the respective amount of 1-butene or 1-pentene consumed, and appeared to increase with TOS and O/P ratio (not shown). These byproducts became significant at long TOS, giving rise to low isobutane selectivity. The 2-pentene produced was likely formed via double-bond isomerization of 1-pentene, which readily occurs in the presence of even weak acid catalysts [28]. The greatest variety of

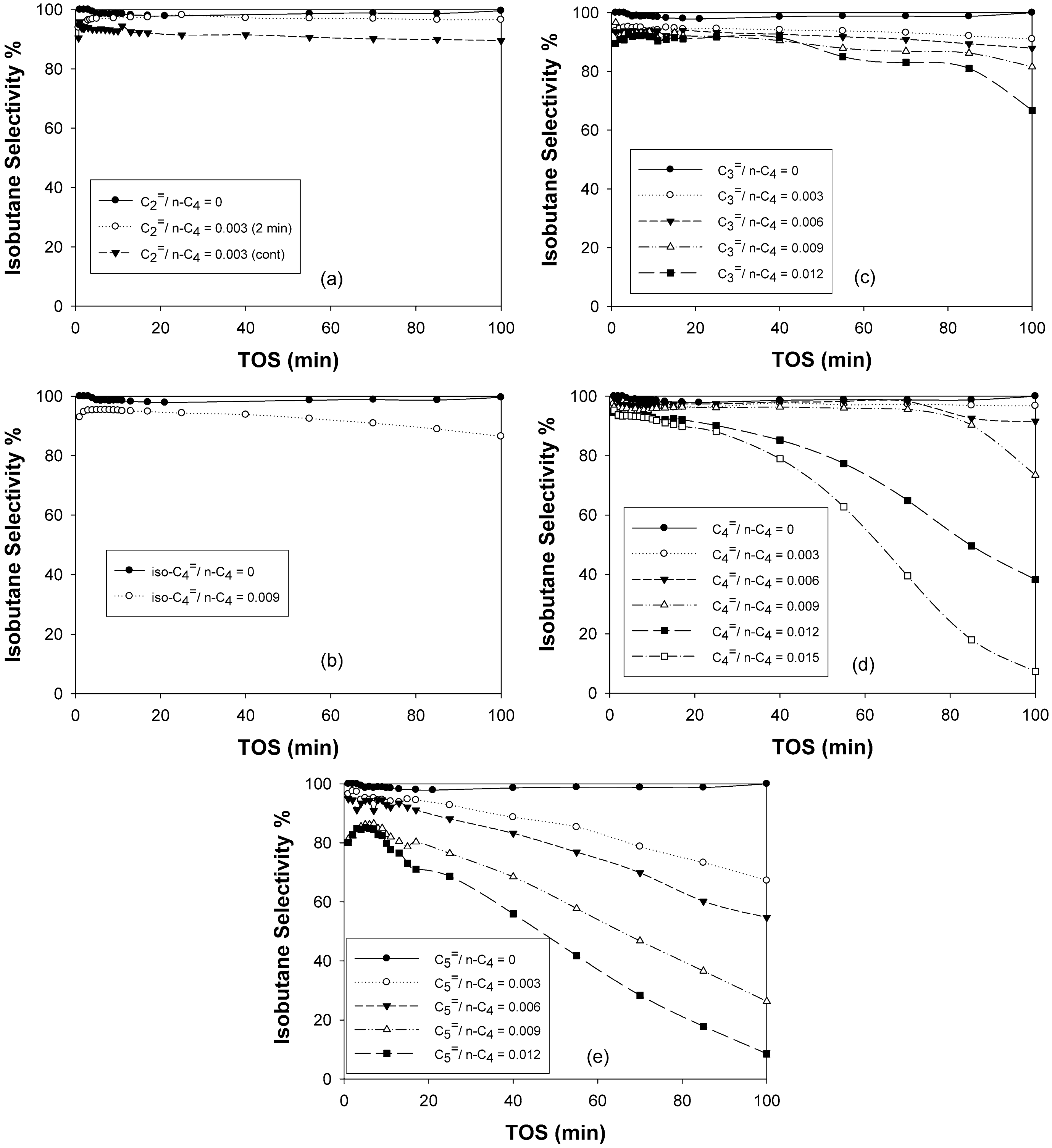


Fig. 3. The isobutane selectivity at 100 °C when (a) ethylene was added continuously and during only the initial 2 min of reaction at an O/P ratio 0.003, (b) isobutene was added continuously at an O/P ratio 0.009, (c) propylene, (d) 1-butene, and (e) 1-pentene were added continuously with varying O/P ratios.

byproducts was observed during continuous 1-pentene addition (Table 2), probably due to the formation of larger oligomeric species during the continuous addition of 1-pentene.

Table 3 shows that in the 2-min olefin addition experiments, more propane than pentane (iso-$C_5 + n$-C_5) was produced for all of the linear olefins, in agreement with other data in the literature for experiments with no olefin added [17,18]. The selectivities of byproducts without and with 2-min olefin addition were essentially the same except for ethylene addition, where the amount of pentane produced was relatively high for the initial 2-min addition of ethylene. Given that $t_{\max}$ for ethylene addition was less than 2 min, selectivity results at maximum

Table 1
Selectivities[a] (%) for isobutane and various byproducts for continuous 1-butene addition at various O/P ratios

Product	Ratio											
	0		0.003		0.006		0.009		0.012[b]		0.015	
	25 min[c]	85 min[d]	13 min[c]	85 min[d]	11 min[c]	85 min[d]	7 min[c]	85 min[d]	6 min[c]	85 min[d]	6 min[c]	85 min[d]
n-C_4 conversion (%)	1.77	0.79	2.22	0.59	2.43	0.16	2.94	0.14	3.28	0.27	3.32	0.24
iso-C_4	97.8	98.7	96.8	97.5	97.1	97.7	95.1	90.3	93.3	50	93.2	18
C_3	1.3	1	1.4	1.1	1.4	–	1.7	–	1.8	–	1.8	–
C_{un}[e]	–	–	–	–	–	–	–	–	1.2	46	1.2	77.2
iso-C_5	0.6	–	1.4	0.9	1	2.3	2	9.7	2.5	4.6	2.5	4.8
n-C_5	0.3	0.3	0.4	0.5	0.5	–	0.5	–	0.5	–	0.5	–
iso-C_6	–	–	–	–	–	–	0.7	–	0.7	–	0.8	–

[a] Max. error = ± 0.8%.
[b] The optimum O/P ratio for the maximum isobutane formation rate.
[c] Time at the maximum activity.
[d] Time at pseudo-steady state.
[e] Unknown product (based on relative boiling point, it may have been cyclobutane).

Table 2
Selectivities[a] (%) for isobutane and various byproducts for continuous addition of a variety of olefins

Product	Olefin											
	None		$C_2^=$		$C_3^=$		1-$C_4^=$		iso-$C_4^=$		1-$C_5^=$	
	25 min[c]	85 min[d]	O/P = 0.003		O/P = 0.009[b]		O/P = 0.012[b]		O/P = 0.009		O/P = 0.009[b]	
			1.75 min[c]	85 min[d]	6 min[c]	85 min[d]	6 min[c]	85 min[d]	13 min[c]	85 min[d]	6 min[c]	85 min[d]
n-C_4 conversion (%)	1.77	0.79	5.61	0.28	3.25	0.09	3.28	0.27	2.22	0.42	3.63	0.55
iso-C_4	97.8	98.7	94	90	92.7	85	93	49.7	95.3	88.9	86	36
C_2	–	–	0.2	0.4	–	–	–	–	–	–	–	–
C_3	1.3	1	2	1.6	3.3	–	1.9	–	1.4	1	1.8	0.6
C_{un}[e]	–	–	–	–	–	–	1.4	45.7	–	–	–	–
iso-C_5	0.6	–	3.3	8	2.7	15	2.5	4.6	2.8	10.1	2.6	2.7
n-C_5	0.3	0.3	0.5	–	0.6	–	0.5	–	0.5	–	–	–
2-$C_5^=$	–	–	–	–	–	–	–	–	–	–	8	58.7
iso-$C5^=$	–	–	–	–	–	–	–	–	–	–	0.7	2
1,3-$C_5^=$[f]	–	–	–	–	–	–	–	–	0.2	–	0.2	–
iso-C_6	–	–	0.7	–	0.7	–	–	–	0.7	–	0.7	–

[a] Max. error = ± 0.8%.
[b] The optimum O/P ratio for the maximum isobutane formation rate.
[c] Time at the maximum activity.
[d] Time at pseudo-steady state.
[e] Unknown product (based on relative boiling point, it may have been cyclobutane).
[f] 1,3-Pentadiene are designated as 1,3-$C_5^=$.

Table 3
Selectivities[a] (%) for isobutane and various byproducts for 2-min olefin additions and without olefin addition

Product	Olefin									
	None		$C_2^=$		$C_3^=$		1-$C_4^=$		1-$C_5^=$	
	25 min[c]	85 min[d]	O/P = 0.003		O/P = 0.009[b]		O/P = 0.012[b]		O/P = 0.009[b]	
			1.75 min[c]	85 min[d]	11 min[c]	85 min[d]	11 min[c]	85 min[d]	11 min[c]	85 min[d]
n-C_4 conversion (%)	1.77	0.79	2.98	0.6	2.48	0.87	2.66	0.89	2.39	0.79
iso-C_4	97.8	98.7	94.4	96.6	97.3	98.9	97.3	98.8	97.4	99.1
C_3	1.3	1	2.3	0.9	1.5	0.9	1.6	1	1.4	0.9
iso-C_5	0.6	–	2.6	0.9	0.9	–	0.8	–	0.8	–
n-C_5	0.3	0.3	0.7	1.6	0.3	0.2	0.3	0.2	0.4	–

[a] Max. error = ± 0.5%.
[b] The optimum O/P ratio for the maximum isobutane formation rate.
[c] Time at the maximum activity.
[d] Time at pseudo-steady state.

activity for both continuous (Table 2) and 2-min (Table 3) ethylene addition were identical within experimental error.

4. Discussion

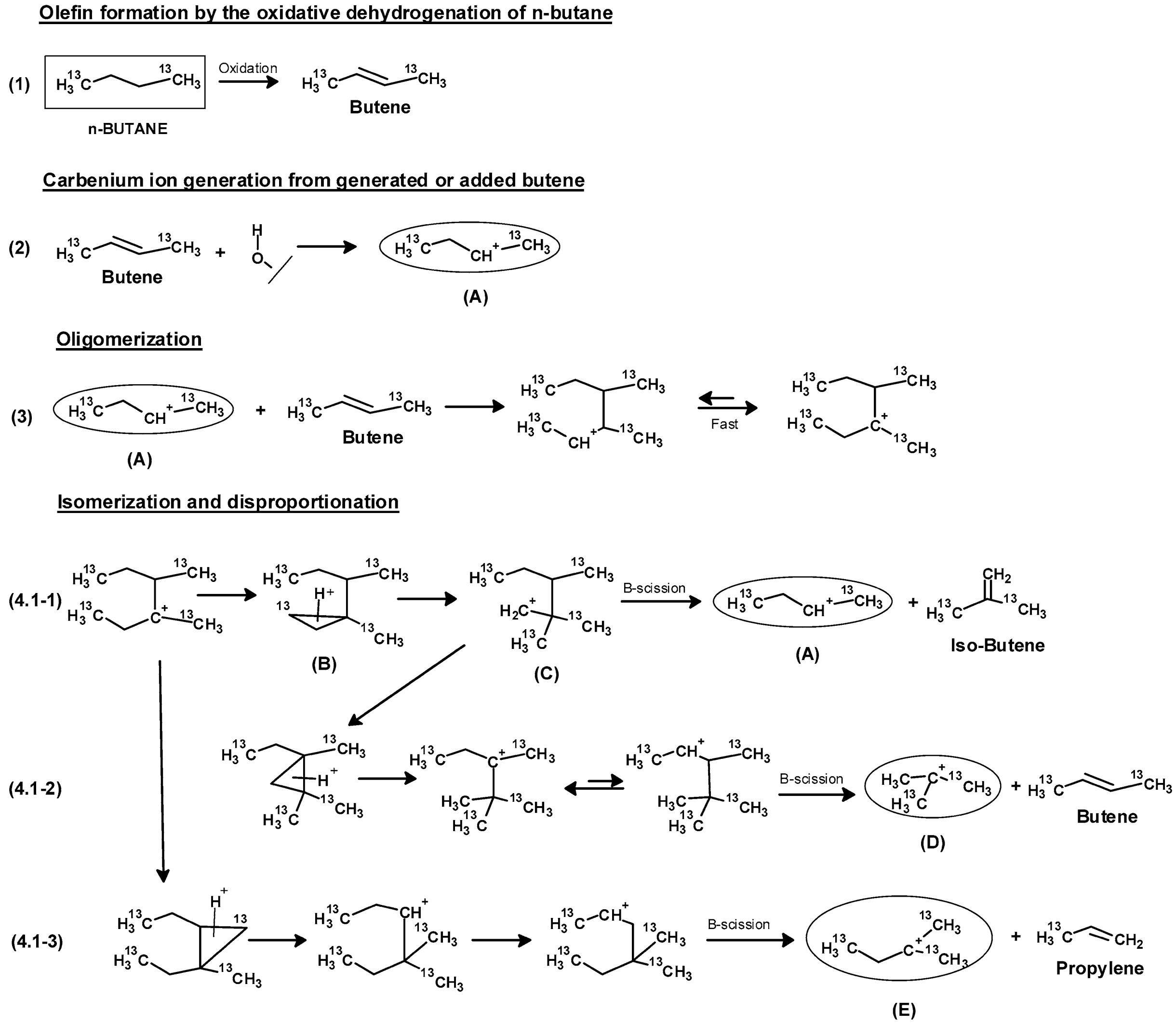
4.1. Proposed reaction mechanism

Most of our results with 1-butene addition for *n*-butane isomerization catalyzed by SZ, as well as experimental results reported by many others, can be explained using a bimolecular pathway [16–21,23,25,29]. However, such a pathway does not explain the high isobutane selectivity typically observed. Although a monomolecular pathway can easily account for the highly selective skeletal isomerization of *n*-butane [2,11–15], the monomolecular mechanism is inconsistent with the isobutane isotopic scrambling results for reactions carried out using 1,4 ^{13}C-labeled *n*-butane [20,24,30]. In addition, the additional amounts of isobutane produced in excess of the amounts of olefin molecules added in experiments using olefin addition cannot be justified by a simple monomolecular route [16,21]. We have concluded that any mechanistic model proposed for this reaction on SZ must have characteristics able to accommodate all of the factors mentioned above: high selectivity to isobutane, isotopic scrambling of the carbon atoms, and influence of olefins. Only in this way can we reconcile the dissimilar conclusions reached by many excellent research groups. Also, a mechanism able to account for the seemingly contradictory results would be logically more satisfying than just invoking a conclusion that sometimes one mechanism (a monomolecular pathway) is operable (short TOS, low conversion, high reaction temperature), whereas at other times the other mechanism (a bimolecular pathway) is in play (long TOS, high conversion, low reaction temperature).

As has been seen, all olefins, regardless of their particular characteristics, can influence (to varying degrees) the initial catalyst activity (induction period and maximum activity, Figs. 1 and 2), with only a small impact on isobutane selectivity for short TOS (Fig. 3). In addition, initial 2-min olefin addition experiments showed virtually no effect on isobutane selectivity for long TOS (Table 3). This suggests that no significant disruption of the chemical pathways occurs during isomerization by populating Brønsted acid sites primarily with olefins other than the hypothesized butene (in the bimolecular mechanism). As shown in Fig. 4, the effect of (added and/or formed) butene on the skeletal rearrangement reaction of *n*-butane is best explained by a bimolecular pathway with the underlying characteristics of a monomolecular mechanism using "olefin-modified sites" as centers of reaction. This proposed mechanism also explains the high isobutane selectivity observed with initial 2-min olefin addition. Note that the 1,4-^{13}C-labeled *n*-butane reactant is indicated in Figs. 4a and 5a and b; we later refer to these figures for the interpretation of isotopic scrambling data as reported in the literature.

Fig. 4a shows a proposed reaction mechanism with or without the addition of butene to *n*-butane isomerization. In step 1, butene is formed via the oxidative dehydrogenation of *n*-butane, as has been suggested previously [7,10,12]. This reaction probably occurs at sulfate [7] or pyrosulfate groups [10] on the catalyst surface. We suggest that step 1 occurs rapidly compared with other steps based on experiments carried out in our lab at 40 °C. Butene is usually not detected because it is so highly reactive. However, when reaction was carried out at 40 °C in the absence of butene addition, a small amount of butene (0.001 µmol/(g s)) was detected (as much as the isobutane product in the effluent) during the initial stages of a reaction. It is noteworthy that this butene could have been either 1-butene or isobutene, because these two isomers could not be separated by the gas chromatography method used. However, we believe that this unidentified butene should be 1-butene, because dehydrogenation of isobutane to isobutene is less thermodynamically favorable than the oxidative dehydrogenation of butane to 1-butene by sulfate groups [7,31]. To the best of our knowledge, butene has not been reported as a byproduct of *n*-butane isomerization on SZ at low temperatures. This is perhaps because those research groups who have studied *n*-butane isomerization at low temperatures (40–60 °C) carried out reactions using FMSZ (a more active catalyst than SZ) and did not report data collection at the very beginning of reaction (i.e., during the first 5 min of TOS) [1,18]. The reaction rate of olefins on the active sites in the catalyst should be greater at higher temperatures (above 40°) than at low temperatures. This offers a plausible explanation for why olefins have not been observed as byproducts at temperatures above 100 °C, at which most studies have been performed.

Step 2 shows the formation of olefin-modified sites (A) created by (formed or added) butene adsorbed on Brønsted acid sites that give rise to oligomer formation (step 3) when reacted with another butene molecule. Up to this point, this mechanistic approach follows the previously hypothesized bimolecular route, with the formation of a C_8^+ oligomer via olefin coupling [16,17,32]. One can expect that once the C_8^+ oligomer is formed, it should change into a more stable C_8^+ species with the positive charge on the tertiary cation (step 3). Then it can isomerize as shown in step 4.1-1 through a protonated cyclopropyl ion (B), giving rise to a C_8^+ carbocation with a positive charge on a primary carbon (C). Formation of a protonated cyclopropyl ion is similar to that hypothesized in the monomolecular mechanism. What makes our mechanistic approach unique is the isomerization of C_8^+ carbocation through a protonated cyclopropane ring, which probably exists as a very short-lived intermediate on the catalyst surface (transition state). After species (C) (C_8^+ primary carbocation) is formed, it should rapidly disproportionate through β-scission to yield the initial olefin-modified site (A) and isobutene (step 4.1-1). Alternatively, species (C) could possibly undergo a proton migration through another protonated cyclopropane ring state (step 4.1-2). This pathway would lead, after 1,3-hydride shift and β-scission disproportionation, to an isobutyl tertiary ion (D) and butene. The former would give rise to isobutane by hydride transfer reaction with *n*-butane, as seen in step 5. The latter (butene) could feed back into the catalytic cycle in step 2, forming another olefin-modified site (A) or reacting with such a site in step 3. Referring back to step 4.1-1, once isobutene is formed, it can readsorb on Brønsted acid sites, leading to



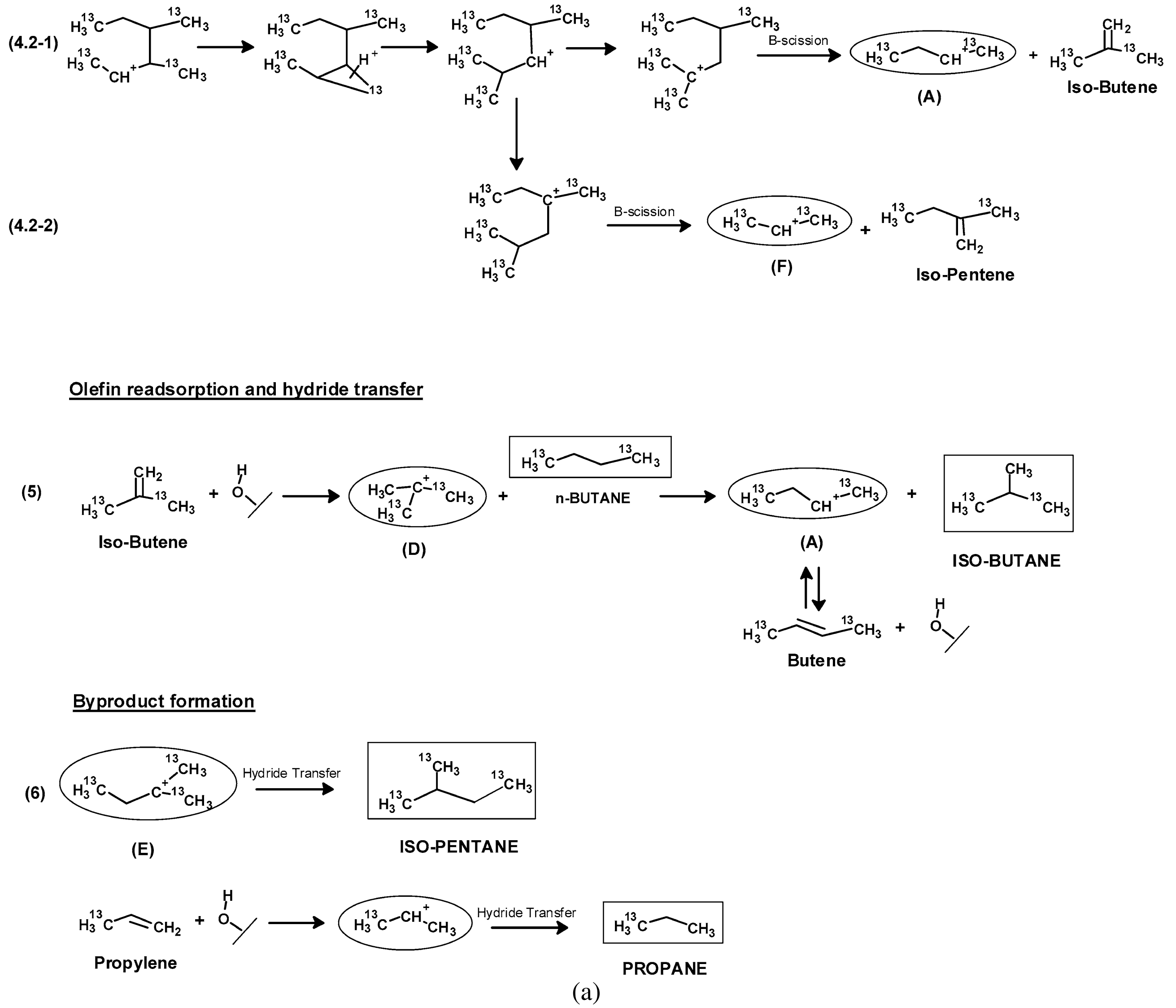
(a)

Fig. 4. The proposed reaction mechanism (a) with 1-butene and without olefin addition (normal reaction), (b) with ethylene addition, (c) with propylene addition, and (d) with 1-pentene addition. Boxed and oval compounds represent detected gas molecules and olefin-modified sites, respectively.

isobutyl ions [33], subsequently undergoing hydride transfer from *n*-butane and ultimately yielding the final isobutane product (step 5). C_4^+ carbenium ions formed during hydride transfer can remain adsorbed on the acid sites as "olefin-modified sites," integrating themselves into the catalytic cycle.

If one accepts that the monomolecular skeletal rearrangement of an adsorbed *sec*-butyl ion to a primary isobutyl ion is feasible [2,11,12], then the rearrangement of a "*sec*-butyl ion moiety" adsorbed on an olefin-modified acid site (a carbenium ion) also should be possible. As has been suggested by theoretical calculations and spectroscopic studies, carbenium ion intermediates are actually found in the form of alkoxides or ester species bound directly to an oxygen from the oxide framework through covalent C–O–M (M – metallic ion) bonds [34,35]. This surface oxygen provides nucleophilic assistance, resulting in a more stable primary carbenium ion than would exist as a free carbocation in a liquid system [35]. We speculate that these carbenium ions exist only as short-lived intermediates, so they are unlikely to be detectable. Thus, the larger C_8^+ oligomer as compared with a *sec*-butyl ion moiety (C_4^+) is likely to be more stable due to an increased inductive effect on the localized positive charge [35].

In the present study, the catalytic activity of SZ was enhanced not only by added butene, but also by added ethylene, propylene, and 1-pentene. This enhanced reaction activity observed for olefins other than butene suggests that skeletal isomerization of *n*-butane can occur via different oligomeric species. Thus, olefin-modified sites can be formed by added $C_2^=$, $C_3^=$, and 1-$C_5^=$ molecules as well. The addition of $C_2^=$, $C_3^=$, or 1-$C_5^=$ does not disturb the principle of this mechanistic pathway. Figs. 4b–d represent the mechanistic model when the reaction is exposed to the addition of ethylene, propylene, and 1-pentene, respectively. As can be seen, the reaction proceeds through the same mechanistic approach with or without added butene (Fig. 4a), but with the main difference that olefin-modified sites (A) are formed from added ethylene, propylene, and 1-pentene. Thus, the reaction between these olefin-modified sites and butene formed from the oxidative dehydrogenation of *n*-butane yields oligomeric intermediates C_6^+, C_7^+, and C_9^+ as shown in Figs. 4b–d, respectively.



(a)

Fig. 4. (*continued*)

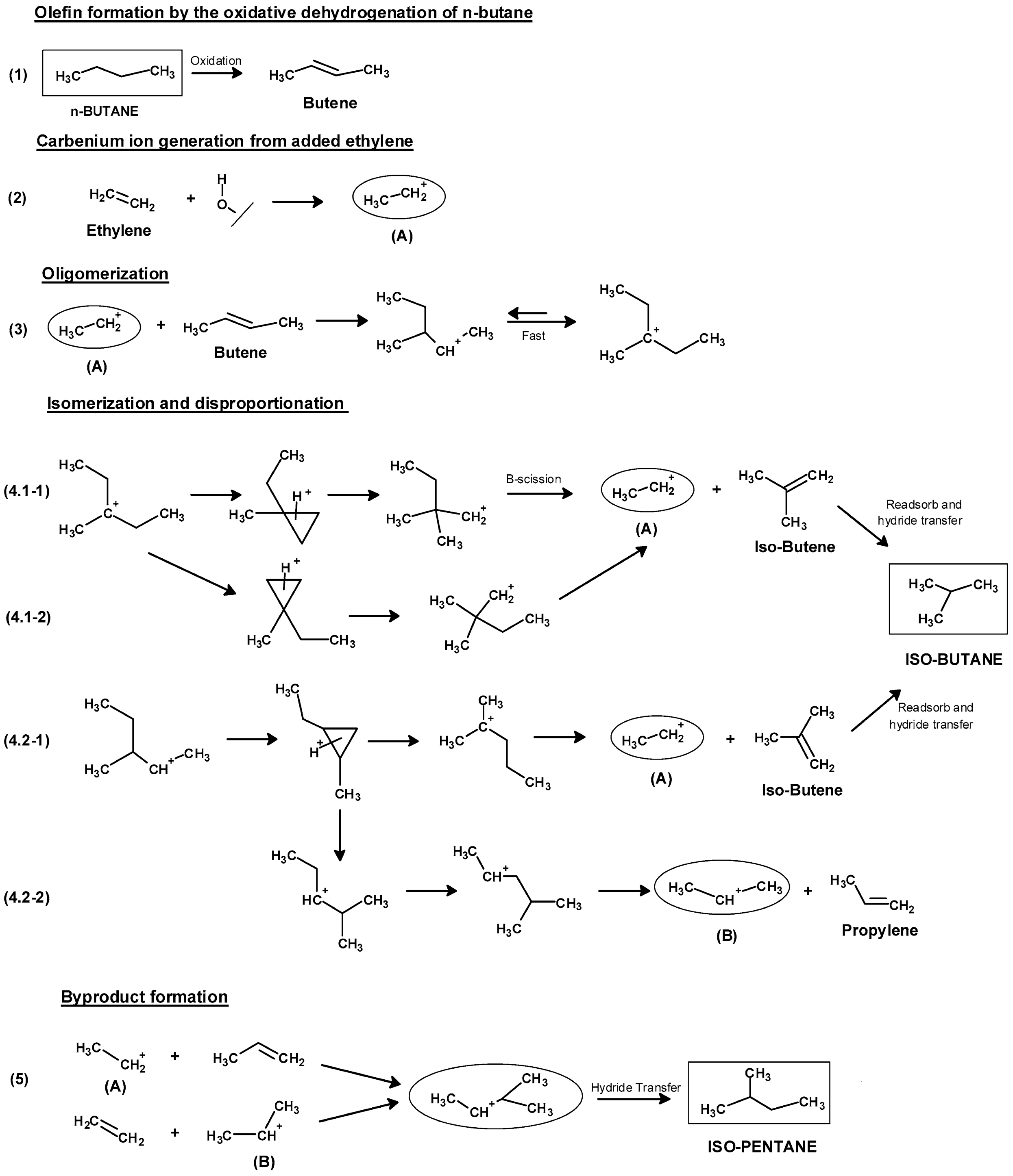
This mechanistic proposal can explain the formation of the observed byproducts. The fact that all reaction byproducts (mainly propane and isopentane) show observed parallel trends when 1-butene is added is in a good agreement with this proposed mechanism, as shown in steps 4.1-3, 4.2-2, and 6 in Fig. 4a. In other words, the fact that all observed reaction products reach the maximum production rate at the same time and show the same reaction profile during the induction period suggests that all products originate from a common reaction intermediate or intermediates of similar nature.

4.2. Mechanistic interpretation of major experimental observations

The proposed reaction mechanism cannot be described as a solely monomolecular or bimolecular pathway, but it can explain most experimental results reported to date in the literature. Here we summarize all major facts observed in the isomerization of n-butane on SZ and indicate how they fit into the proposed dual-nature mechanistic pathway.

4.2.1. Isotopic scrambling

One important aspect of the experimental evidence for a bimolecular pathway to n-butane isomerization is the isotopic scrambling observed for the isomerization of 1,4-^{13}C n-butane. Isotopic scrambling occurs for a wide range of reaction temperatures from 20 to 250 °C. For instance, it has been reported that the isomerization product (isobutane) contains ^{13}C closely following a binomial distribution [17,20,24,25]. This observation can be explained by two reaction pathways showing how isotopic scrambling may occur (Figs. 5a and b). Isotopic scrambling to single- and triple-labeled isobutane can be obtained by the same proposed mechanistic approach if the starting carbenium ion on the surface is di-labeled C_5^+ or C_3^+ (species A), as shown in Figs. 5a and b, respectively. Di-labeled C_5^+ can be produced from an adsorbed isopentene on a Brønsted acid site, whereas di-labeled C_3^+ is the same species as (F) in Fig. 4a, step 4.2-2. Clearly, scrambling should increase with an increasing population of C_3^+ and C_5^+ carbenium ions, and it is noteworthy that the two isotopic scrambling pathways pre-



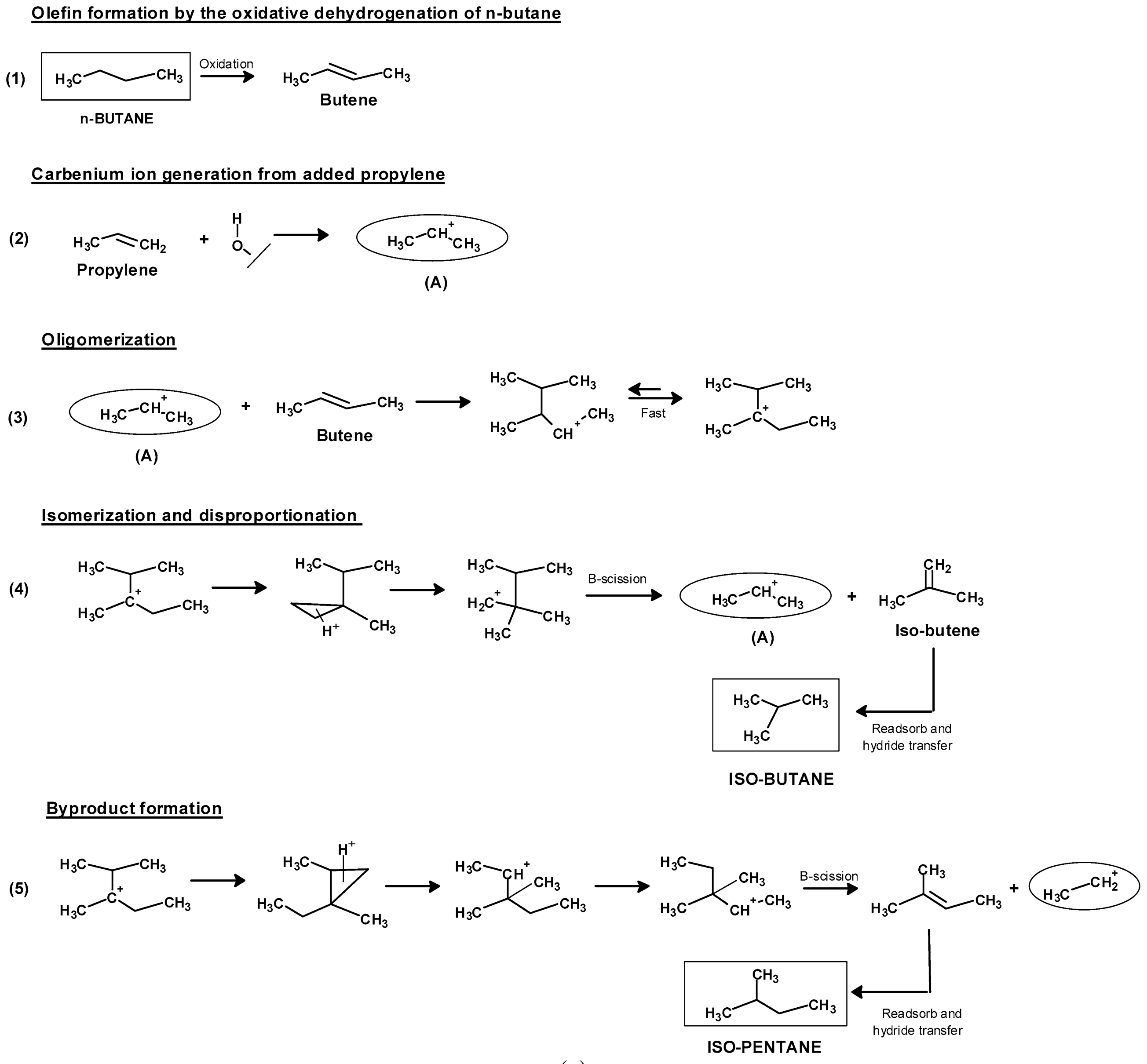
(b)

Fig. 4. (*continued*)

sented here should be considered only two possibilities among the many that may exist as the catalyst surface becomes rich with numerous carbenium species with varying isotopic compositions. In contrast, double-labeled isobutane is a major product of the reaction (as shown in Fig. 4a) due to the dominant isobutane formation compared with that of byproducts (C_3 and C_5), in agreement with findings from previous isotopic scrambling studies [17,25].

4.2.2. *Nonspecific olefin rate enhancement*

It has been long known that butene impurities present in the *n*-butane feed stream increase the formation rate of isobutane; thus, many investigators have suggested that butene plays a significant role in *n*-butane isomerization on SZ [16,17,21,22,26]. With the dual-nature mechanism, butene activates catalytic sites by forming adsorbed C_4^+ carbenium ions or the so-called "olefin-modified" sites [21].

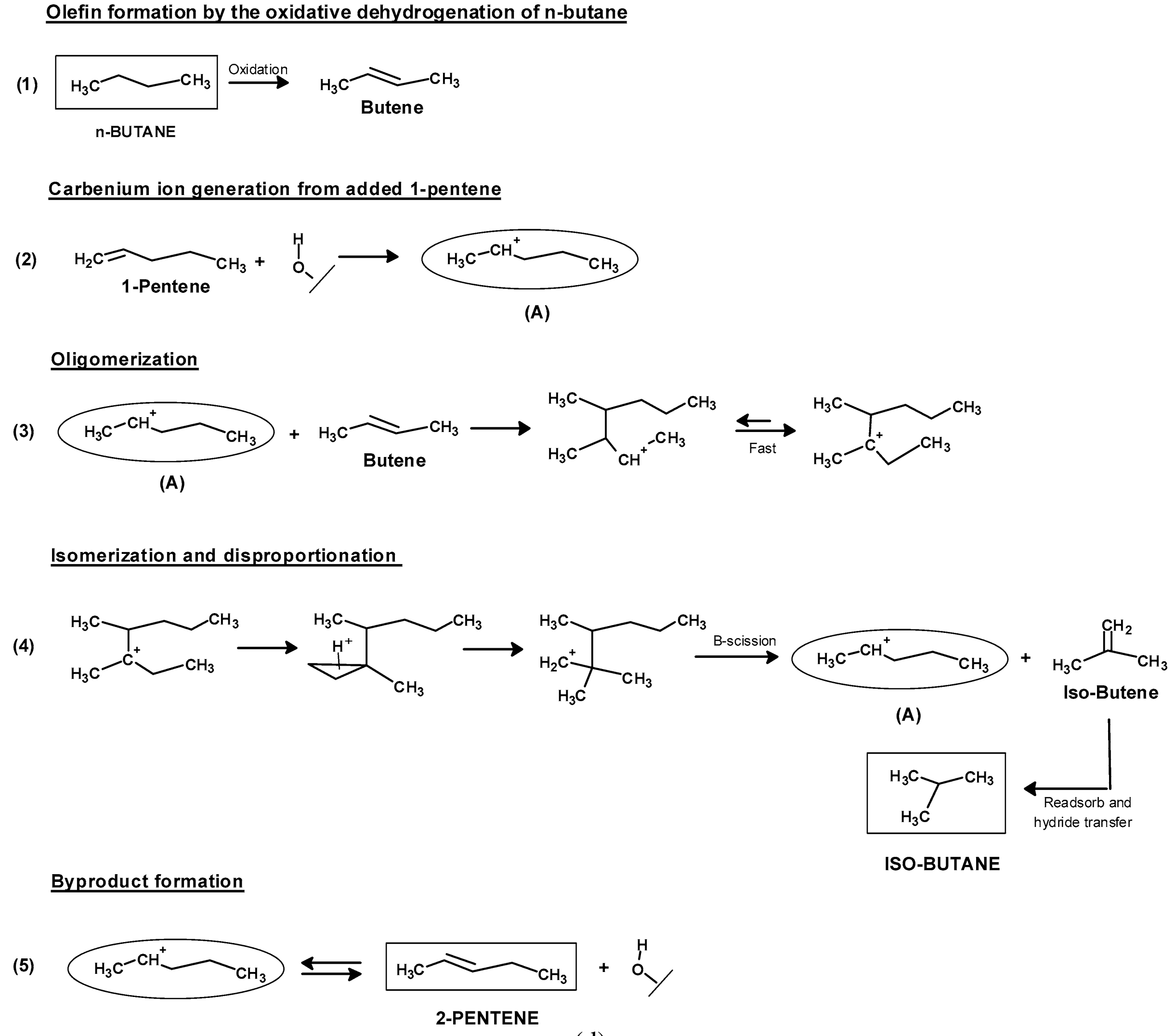


(c)

Fig. 4. (*continued*)

The faster induction period observed for ethylene addition may be the result of multiple dominant reaction pathways leading to the isobutane product. Fig. 4b shows how the isomerization of a C_6^+ carbocation followed by β-scission leads to isobutene and C_2^+ through multiple pathways. However, it is unlikely that isopentane, a major byproduct with the addition of ethylene, can be produced from β-scission and disproportionation of C_6^+ oligomer. Therefore, we suggest that in this case isopentane is formed by oligomerizing C_3 and C_2 species, as shown in step 5 in Fig. 4b. The higher reactivity associated with a primary carbenium ion formed from the adsorption of $C_2^=$ compared with the reactivity of any secondary or tertiary carbocations formed by the adsorption of $C_3^=$, $C_4^=$, $C_5^=$, or *iso*-$C_4^=$ olefins should also contribute to the increased activity observed for ethylene addition. However, it must be mentioned that a faster cracking of C_6^+ ions over C_7^+ and C_8^+ species is not consistent with the work of Buchanan et al. [36]. But their work was conducted on ZSM-5 at a much higher temperature (510 °C). Thus, to make a fair comparison, similar olefin cracking studies should be carried out on SZ at 100 °C.

Thus far, we can say that the addition of olefins provides an efficient way to rapidly form the olefin-modified sites hypothesized for the reaction to go forward. This is in agreement with two important observations made in our labs using olefin addition. First, olefin addition gives rise to the production of excess isobutane (amount of additional isobutane molecules per olefin molecule added), indicating that olefin-modified sites can withstand multiple reaction turnovers [21]. For instance, the excess ratio of isobutane formed per olefin added, as calculated from the 2-min olefin addition experiments, was 14 for propylene, 1-butene, and 1-pentene [23] and 16 for ethylene at 100 °C over 100 min of reaction. Second, produced butene was observed



(d)

Fig. 4. (*continued*)

only for the reaction carried out at low temperatures (40 °C) and during the initial reaction period. This implies that at lower temperatures, catalyst activation by olefins is limited by the amount of olefin adsorption, but at higher temperatures, the adsorption of olefins is rapid and the catalytic sites quickly initiate reaction.

The proposed dual-nature bimolecular route does not prevent the monomolecular route from occurring. However, skeletal isomerization should be energetically more favorable for larger oligomer carbenium ions ($C_6{}^+$, $C_7{}^+$, $C_8{}^+$, and $C_9{}^+$) than for $C_4{}^+$ carbenium ions. Indeed, olefin addition has been shown by SSITKA to increase the concentration of active surface intermediates leading to isobutane [21].

4.2.3. *Isobutane selectivity*

As mentioned earlier, the proposed mechanism can also explain the high isobutane selectivity observed in experiments without olefin addition or with any type of olefin initially added during the first 2 min of reaction (Table 3). This is a virtue of its monomolecular-like nature as a result of skeletal isomerization mainly on the alkyl moiety coming from the second adsorbed olefin on an olefin-modified site. The high selectivity to isobutane suggests that step 4.1-1 leading to isobutane formation is dominant over step 4.1-3, leading to byproducts (Fig. 4a). Note also that step 4.1-3 requires another 1,2-hydride shift before β-scission to form isopentane and propane. Similarly, step 4.2-2 should be less favorable than step 4.2-1 due to an expected lower equilibrium concentration of the secondary $C_8{}^+$ carbenium ion compared with that of the tertiary one.

Lower isobutane selectivities were observed for continuous addition of the larger olefins, however. The selectivity to isobutane decreased in the order propylene > 1-butene > 1-pentene. The isobutane selectivity appeared to correlate inversely with the hypothesized size of the oligomeric intermediates formed from ethylene, propylene, 1-butene, and 1-pentene addition ($C_6{}^+$, $C_7{}^+$, $C_8{}^+$, and $C_9{}^+$, respectively) even for short TOS. Clearly, the larger the intermediate, the higher the probability for other isomerization and disproportionation pathways to occur, lowering the selectivity (Table 2), as suggested by Buchanan et al. [36]. On the other hand, Sassi et al. [37] re-

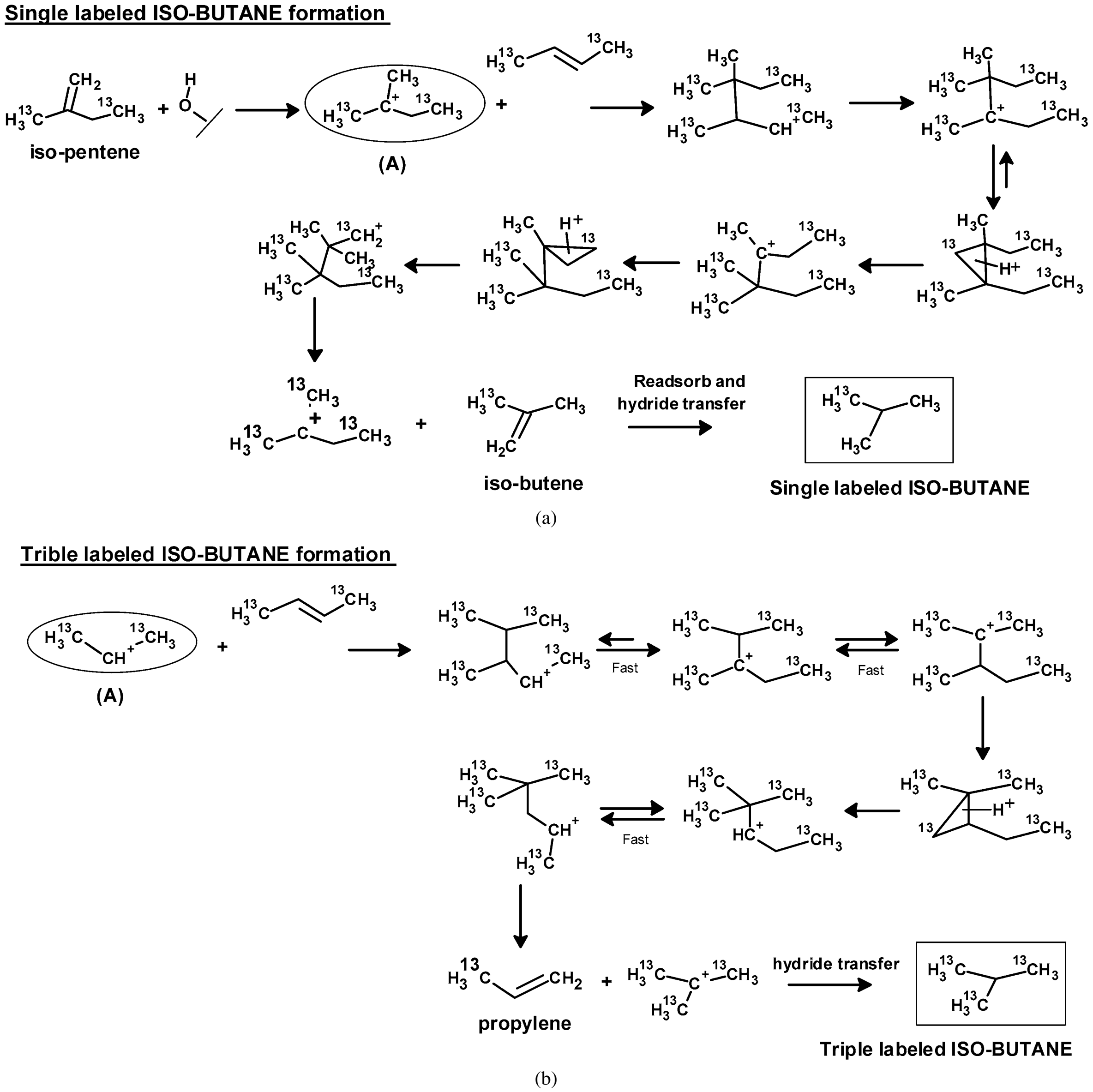


Fig. 5. The proposed reaction mechanism showing the formation of (a) single-labeled isobutane and (b) triple-labeled isobutane. Boxed and oval compounds represent detected gas molecules and olefin-modified site, respectively.

ported a low isobutane selectivity (only 80%) for the cracking of trimethylpentane at 100 °C on SZ, which would seem to contradict the assumption that the cracking of a C_8^+ oligomeric species can yield selectivities >90% for isobutane, as observed in *n*-butane isomerization. However, it should be noted that these authors carried out their reaction at relatively high conversions (>40%), at which the catalyst surface would certainly be more heterogeneous in terms of oligomer population and oligomer size distribution. In fact, considering that under these conditions C_{12}^+, C_{16}^+, and larger oligomers are possible, 80% selectivity for isobutane actually seems very good.

It was also observed that isobutane selectivity appeared to be more stable when no olefin was added or when olefin was added only during the initial 2 min of reaction, whereas it was significantly lower for continuous olefin addition at high O/P ratios for long TOS. With high olefin concentrations on the surface of the catalyst, multiple olefins could oligomerize with olefin-modified sites rather than butene from *n*-butane, leading to an improper configuration of the reaction intermediates. These inappropriate intermediates offer more opportunities for the reaction to follow undesirable pathways, resulting in a larger amount of byproducts, as can be produced in steps 4.1-3 and 4.2-2 in Fig. 4a. As reaction proceeds via these pathways, it creates intermediates that increase the probability for further reaction via nonselective pathways. Thus, selectivity to isobutane decreases with TOS.

4.2.4. Catalyst deactivation

Catalyst deactivation is another common feature of isomerization reactions catalyzed by SZ. As has been pointed out by many authors, deactivation of SZ under *n*-butane isomerization is due primarily to coke/oligomer formation. The polymerization, cyclization, and deprotonation of C_n^+ carbenium ions have been suggested to give rise to cycloalkenyl ions, which are precursors for aromatic species and ultimately coke [33,38,39]. As would be expected, catalyst deactivation increased under continuous olefin addition and increased olefin concentration. Olefins in the gas phase certainly can adsorb not only on free Brønsted acid sites, but also on available carbenium ions on the catalyst surface, giving rise to larger oligomers (C_{12}^+ or larger), which could undergo cyclization and dehydrogenation. This is consistent with the proposed mechanism in which the selectivity to isobutane should be hampered as larger or more complex oligomers can isomerize and disproportionate in different ways. Hence, those olefins promoting the catalytic cycle are also the same species that promote deactivation. Thus, unless a continuous system for addition/elimination of olefins that does not allow formation of large oligomeric species is established on the catalyst surface, catalyst deactivation is unavoidable.

5. Conclusion

A comprehensive reaction mechanism for *n*-butane isomerization on SZ has been proposed based on the results from the use of added nonspecific olefins as molecular probes. The addition of other olefins (ethylene, propylene, isobutene, and 1-pentene) besides the hypothesized intermediate butene promoted catalytic activity and modified induction periods. The proposed mechanism involves the concept of a bimolecular pathway with the underlying characteristics of a monomolecular mechanism (dual-nature mechanism). We also suggest that "olefin-modified" sites are the main centers of reaction. Such sites are formed from any type of olefin and are able to enhance the reaction rate by forming additional active sites.

The reaction mechanism proposed herein demonstrates how carbenium ions adsorbed on acid sites can give rise to oligomeric intermediates, C_n^+, ranging from $n = 6$ to 9 by oligomerizing butene, $C_4^=$ (from *n*-butane), with an olefin-modified site (C_2^+, C_3^+, C_4^+, or C_5^+ from added $C_2^=$, $C_3^=$, $C_4^=$, or $C_5^=$, respectively). Isomerization occurs by a skeletal rearrangement through protonated cyclopropane states. Isobutane is produced after β-scission, olefin readsorption, and hydride transfer with the *n*-butane reactant. The proposed mechanism can account for most of the major factors observed in *n*-butane isomerization (i.e., isotopic scrambling, nonspecific olefin rate enhancement, high isobutane selectivity, and catalyst deactivation), thereby helping explain the seemingly contradictory findings published by numerous credible research groups.

Acknowledgments

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