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n-Butane conversion on sulfated zirconia: the mechanism of isomerization and ^{13}C-label scrambling as studied by in situ ^{13}C MAS NMR and ex situ GC-MS

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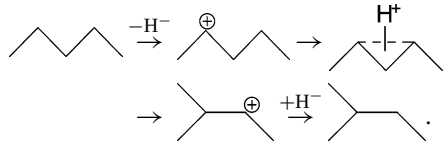
Abstract

Using ^{13}C MAS NMR, conversion of selectively ^{13}C-labeled *n*-butane on sulfated zirconia catalyst has been demonstrated to proceed initially via two parallel routes: scrambling of the selective ^{13}C label in the *n*-butane molecule and selective formation of isobutane. The combination of the results obtained by both in situ ^{13}C MAS NMR and ex situ GC-MS analysis provides evidence for the monomolecular mechanism of the ^{13}C-label scrambling, whereas isomerization into isobutane proceeds through a pure bimolecular mechanism. Further, the intermolecular mechanism of *n*-butane isomerization is complicated and turns into conjunct polymerization. Besides isobutane, conjunct polymerization gives also the products of butane disproportionation, propane and pentanes, as well as the stable cyclopentenyl cations; the latter may be in charge of catalyst deactivation.

Keywords: *n*-Butane; Sulfated zirconia; Isomerization; ^{13}C-Label scrambling; Mechanism; NMR spectroscopy; GC-MS analysis

1. Introduction

The skeletal isomerization of alkanes catalyzed by solid acids plays an important role in industrial petrochemical processes. Among the solid acids, those based on sulfated zirconia (SZ) possess the highest acid strength and represent the perspective catalysts for short-chain alkane isomerization [1,2] for improving the octane number of the gasoline cut. The ability of SZ to isomerize *n*-butane and *n*-pentane at low temperatures [3,4] has spurred numerous studies of the isomerization mechanism. Two different reaction pathways have been proposed for the conversion of linear alkanes on sulfated zirconia. The monomolecular (or intramolecular) mechanism, implying the isomerization of the intermediate carbenium ion through a protonated cyclopropane intermediate or transition state, has been supposed to dominate *n*-pentane conversion on SZ [5]:



In addition to indirect confirmation of this mechanism based predominantly on kinetic measurements [5], we have obtained recently the first unequivocal evidence for monomolecular pathway by observing with ^{13}C MAS (magic-angle spinning) NMR a very selective distribution of ^{13}C label in the products formed from *n*-[2-^{13}C]pentane in the presence of CO [6].

In contrast, the monomolecular mechanism of isomerization is unfavorable in the case of *n*-butane. Indeed, a consequence of this mechanism is that the opening of the protonated cyclopropane ring to a secondary carbenium ion is only possible for hydrocarbons with at least five carbon atoms, but in the case of *n*-butane the monomolecular route would lead to a primary carbenium ion, which has a much higher energy compared to secondary ions [7]. Thus, the

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monomolecular mechanism of *n*-butane isomerization on solid acids was virtually excluded. The kinetic data [5,8–11] and tracer experiments [5,12], as well as observation of the disproportionation of *n*-butane in addition to its isomerization, provided experimental evidence for a bimolecular mechanism of *n*-butane isomerization on SZ. According to this mechanism, the formation of isomerized alkane proceeds via consecutive stages of the formation of C_8^+ cations by dimerization of C_4^+ carbenium ions with equilibrated alkene and the isomerization and β-scission of C_8^+ followed by reversible hydride transfer to produce isobutane, as well as the products of *n*-butane disproportionation, propane and pentanes. However, it has been shown recently that for the conversion of *n*-butane on SZ the change in apparent activation energy and the product selectivity occurs with time of reaction [13]. The exceptional selectivity in isobutane and higher activation energy observed during the initial period of reaction have been attributed to a monomolecular pathway of isomerization; then with the accumulation of surface alkenes it is substituted for a bimolecular mechanism characterized by a lower activation barrier and additional formation of propane and pentanes [13]. Therefore, controversy over the mechanism of *n*-butane isomerization [8,9,12,13] requires its further study by using a novel not yet applied technique.

The second point, which requires supplementary consideration, is the actual mechanism of intermolecular transformations of alkanes on SZ. In fact, a simple bimolecular model is usually assumed to rationalize the formation of isomerized alkanes as well as lower and higher molecular weight alkanes. This model (vide supra) includes hydride abstraction, dimerization, isomerization of dimeric cation, β-scission, and reversible hydride transfer steps; it does not take into account the possible stages of the formation of undesorbed carbonaceous species (coke). A similar distribution of the desorbed products (alkanes) is possible as a result of a more complex process known as conjunct polymerization [14,15]. It has been demonstrated recently that, in addition to monomolecular isomerization to isopentane, the conversion of *n*-pentane into the mixture of alkanes (isopentane, butanes, hexanes) and stable cyclopentenyl cations takes place via conjunct polymerization [6]. In the case of *n*-butane, further investigations are required to elucidate which mechanism (simple bimolecular or conjunct polymerization) is in fact responsible for the intermolecular conversion of *n*-butane.

In this paper we provide evidence that the conversion of the selectively ^{13}C-labeled *n*-butane proceeds via two parallel routes: the scrambling of ^{13}C label in *n*-butane and its isomerization into isobutane; the latter is the single reaction product observed at the initial period of the reaction. Combined application of both in situ ^{13}C MAS NMR and ex situ GC-MS analysis allowed us to conclude that the scrambling is realized via a monomolecular pathway, whereas the skeletal isomerization proceeds through an actual bimolecular mechanism with the selective formation of isobutane. Eventually, the bimolecular mechanism is complicated and leads to conjunct polymerization, producing a mixture of alkanes and stable cyclopentenyl cations; the latter can be the reason for catalyst deactivation.

2. Experimental

2.1. Preparation of samples

A sample of low-temperature tetragonal-phase sulfated zirconia with a surface area of 60 $m^2\,g^{-1}$ and 9.9% (wt) of SO_3 content was synthesized according to the procedure described earlier [16]. The concentration of Brønsted acid sites was 50 $\mu mol\,g^{-1}$ as estimated from ^{1}H MAS NMR by comparison of the intensity of the signal at 6.2 ppm from the acidic sites with that from adsorbed propane as internal standard. The sample of SZ was calcined at 600 °C in air and at 400 °C under vacuum (10^{-3} Pa) for 2 h. We then adsorbed *n*-butane (ca. 300 $\mu mol\,g^{-1}$) on SZ under vacuum at the temperature of liquid nitrogen. After a glass tube with SZ sample was sealed off from the vacuum system, the sample was warmed to room temperature ($\sim$ 293 K) and the registration of ^{13}C MAS NMR spectrum was started.

2.2. NMR analysis

The reaction products were analyzed in situ with ^{13}C MAS NMR in the sealed glass tubes. ^{13}C NMR spectra with high-power proton decoupling and MAS and with or without cross-polarization (CP) (denoted below as ^{13}C CP/MAS NMR and ^{13}C MAS NMR) were recorded at 100.613 MHz (magnetic field of 9 T) on a Bruker MSL-400 spectrometer at 293 K. The following conditions were used for recording spectra with CP: proton high-power decoupling field was 11.7 G (5.0 µs length of 90° ^{1}H pulse), contact time was 5 ms at a Hartmann–Hahn matching condition of 50 kHz, and delay time between scans was 3 s. One pulse excitation ^{13}C MAS spectra were recorded with 45° flip angle ^{13}C pulses of 2.5 µs duration and 4 s recycle delay, which satisfied a $10T_1$ condition. Spinning rate was 2.5–14.5 kHz, and 100–20,000 scans were collected for each spectrum. ^{13}C chemical shifts for carbon nuclei of adsorbed organic species were measured with respect to TMS as the external reference with accuracy $\pm$0.5 ppm. Precision in the determination of the relative line position was 0.1–0.15 ppm. To facilitate NMR analysis *n*-butane, labeled with ^{13}C isotope at the methyl group, *n*-[1-^{13}C]butane (99% ^{13}C isotope enrichment) was used. *n*-[1-^{13}C]Butane was prepared from [1-^{13}C]ethanol (99% ^{13}C) via a six-step synthesis.

2.3. GS-MS analysis

The products formed from *n*-[1-^{13}C]butane and extracted from the SZ sample with Et_2O were also analyzed using a Varian CP-3800 gas chromatograph equipped with a PLOT

fused-silica capillary column of 30 m × 0.32 mm i.d. in a size with CP-PoraPLOT Q-HT as the stationary phase, forming a film of 10-μm thickness. Temperature was programmed from 35 °C with 8 °C/min rate. The detector was a Varian Saturn-2000 mass spectrometer, which scanned from $m/e = 10$ to 650 at a cycle time of 0.5 s.

3. Results and discussion

3.1. Conversion of n-butane as studied by in situ ^{13}C MAS NMR

n-Butane readily isomerizes on sulfated zirconia to give isobutane, with propane and pentanes also produced as the other reaction products [5,7–11]. The bimolecular (intermolecular) mechanism was concluded to dominate in this reaction [5,7–11]. However, the recent results by Matsuhashi et al. [13] did not exclude the possibility of a monomolecular pathway.

Fig. 1 shows the ^{13}C MAS NMR spectra of the products formed from *n*-[1-^{13}C]butane[1] adsorbed on SZ at 293 K. According to the spectra recorded in the first 10 h of the reaction (initial period of the reaction), two parallel processes proceed with *n*-butane on SZ (Fig. 1, spectra a and b): (1) scrambling of the ^{13}C label in *n*-butane molecules and (2) skeletal isomerization into isobutane. Indeed, two signals are readily identified in the spectrum recorded in the first 30 min of the reaction besides the signal from the ^{13}C-labeled CH_3 group of the initial *n*-butane at 14.7 ppm (Fig. 1a). The first signal at 27.1 ppm is indicative of the formation of *n*-[2-^{13}C]butane; i.e., the migration of the ^{13}C label from the methyl group of *n*-butane into its methylene group takes place. The second signal at 25.5 ppm, which is initially less intense, belongs to ^{13}C-labeled isobutane; both CH_3 and CH groups could be responsible for the appearance of this signal [6,17]. The intensity of these two signals increases with time (Fig. 1, spectra a and b), isobutane being the sole product of the reaction in the first 10 h.

The transfer of the selective ^{13}C label from the CH_3 into the CH_2 group of *n*-butane as well as selective formation of isobutane may be rationalized in terms of the rearrangement of *sec*-butyl carbenium ions via a protonated cyclopropane intermediate (or transition state) [18,19]. Either *n*-[2-^{13}C]butane or [1-^{13}C]isobutane could finally be formed from *n*-[1-^{13}C]butane dependent on whether the particular C–C bond in the cyclopropane ring is broken (see Scheme 2). In principle, the selective formation of isobutane at the initial stage of reaction is in favor of a monomolecular mechanism of *n*-butane isomerization, since the complete absence of the disproportionation products, propane and

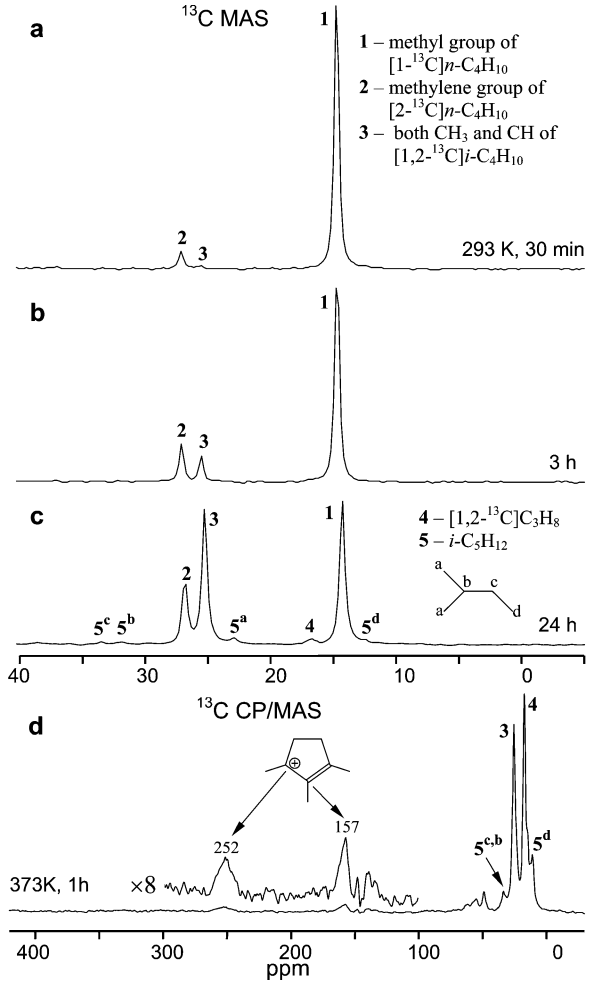
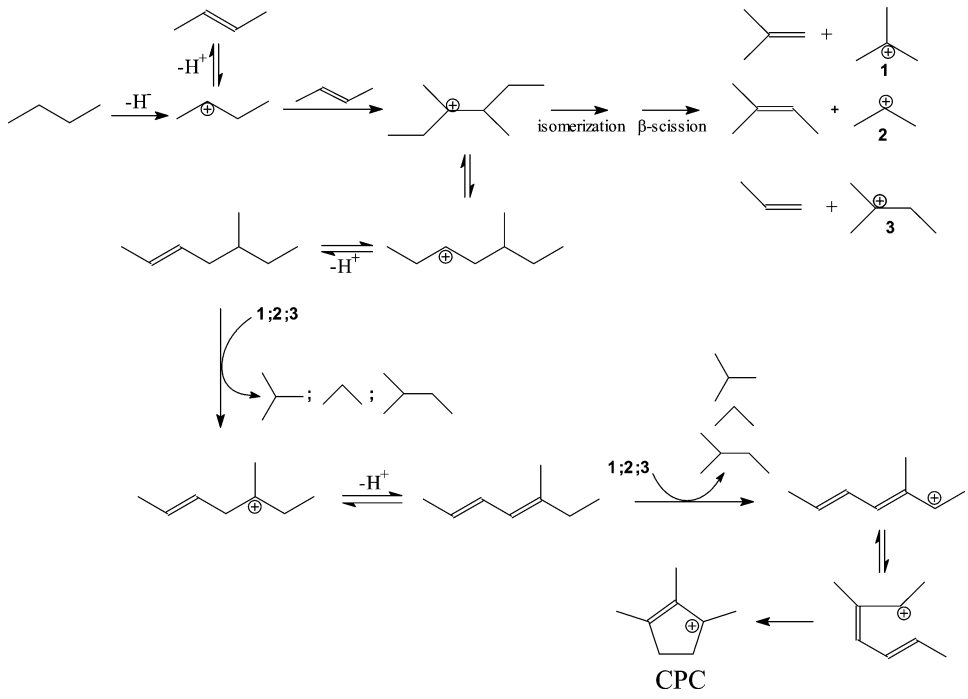


Fig. 1. ^{13}C MAS NMR spectra of the products formed from *n*-[1-^{13}C]C_4H_{10} on sulfated zirconia at 293 (a–c) and 373 K (d): (a) ^{13}C MAS NMR spectrum recorded after 30 min of the reaction duration; (b) spectrum after 3 h; (c) spectrum after 24 h; (d) ^{13}C CP/MAS NMR spectrum recorded after 1 h of the reaction at 373 K.

pentanes, could serve as an argument against a bimolecular pathway. This experimental fact was indeed considered in Ref. [13] as key evidence of the realization of a monomolecular isomerization of *n*-butane. However, one cannot exclude the possibility that intermolecular transformation of *n*-butane via dimerization, isomerization, and β-scission of C_8^+ carbenium ions and reverse hydride transfer steps may also result in the selective isobutane formation. Therefore, we cannot make a definitive conclusion on the reaction mechanism based only on these results.

After a rather long initial period of the reaction ($\sim$ 10 h) the signals from other reaction products become visible in the ^{13}C MAS NMR spectrum (Fig. 1, spectrum c). Four signals belong to the ^{13}C-labeled groups of isopentane at 33.8 (CH_2), 32.2 (CH), 23.2 ((CH_3)$_2$), and 12.8 ppm (CH_3) [6,17]. The other signal at 18.0 ppm is due to CH_3 and CH_2 groups of propane [6,17]. Simultaneously with the formation of propane and isopentane, the new broad signals at 157 and 252 ppm appear in the spectrum recorded

[1] It should be emphasized that in this case only the labeled $^{13}CH_3$ group of the initial *n*-butane as well as the labeled carbons in the reaction products, where the ^{13}C label migrates in the course of the reaction, could be observed in the spectra.



Scheme 1. Conjunct polymerization of *n*-butane on sulfated zirconia.

with cross-polarization, which emphasizes the resonances from less mobile species, strongly interacting with the surface of the catalyst. These signals are rather weak at 293 K, but become intense at 373 K (Fig. 1, spectrum d); simultaneously the signals from propane and pentanes increase notably. The signals at 157 and 252 ppm are characteristic of alkyl-substituted cycloalkenyl cations with five carbon atoms in a ring [20]. The simultaneous formation of propane, pentane, and cyclopentenyl cations (CPC) can easily be explained in terms of conjunct polymerization of *n*-butane as depicted in Scheme 1. This process represents a complex number of steps, including oligomerization of carbenium ions with equilibrated alkenes, isomerization, β-scission, hydride transfer from oligomeric olefins (and, afterward, from dienes) to carbenium ions, cyclization, producing in the long run a mixture of alkanes, and stable CPC.

Thus, the product distribution revealed by ^{13}C NMR for *n*-butane conversion on SZ is similar to that typical for conjunct polymerization observed earlier for olefins and alkanes in concentrated sulfuric acid [14,21,22] and for olefins and alcohols on acidic zeolites [17,23,24], as well as for *n*-pentane conversion on sulfated zirconia [6]. Formation of cyclopentenyl cations can be the reason for the catalysts deactivation. In earlier studies the deactivation of sulfated zirconia in alkane isomerization has been rationalized by the formation of allylic and polyenylic cations identified with UV-VIS DR spectroscopy [25] or hydrocarbonaceous deposits detected by means of XPS [26]. However, the experimental techniques used in [25] did not allow to make more precise conclusions about the nature of these surface species. The characteristic chemical shifts at 157 and 252 ppm in our NMR spectrum indicate that these deactivating species are in fact of a cycloalkenylic structure, with five carbon atoms in the ring [20]. The ability of cyclopentenyl cations to be strongly bound to the SZ Brønsted acid sites prevents access of *n*-butane to the SZ active sites that results in slowing down *n*-butane isomerization.

It should be noted that simultaneous formation of propane, isopentane, and cylopentenyl cations implies that these alkanes are unlikely to be produced via a simple bimolecular pathway. Thus, one can distinguish two stages in *n*-butane conversion on SZ. The initial period of reaction ($\sim$ 10 h) is characterized by simultaneous processes of ^{13}C label scrambling in *n*-butane molecules and selective formation of isobutane. In the course of the reaction, these processes are replaced by conjunct polymerization. Our NMR data do not allow unambiguous elucidation of which alternative mechanism, mono- or bimolecular, is responsible for the selective generation of isobutane in the initial period. So, another approach is needed to clarify this point.

3.2. Ex situ GC-MS analysis

To distinguish between two alternative pathways, which may lead selectively to isobutane, we have analyzed by GS-MS the products extracted from the sulfated zirconia with Et_2O. We again used *n*-[1-^{13}C]butane for the reaction. The distribution of ^{13}C isotope in the reaction products detected by mass spectrometry would be expected to elucidate the mechanism of isomerization.

Adeeva et al. [12] already used mass spectrometry to explore the mechanism of *n*-butane isomerization on SZ. The ^{13}C-label distribution observed for isobutane formed from a double ^{13}C-labeled *n*-butane was in favor of an intermole-

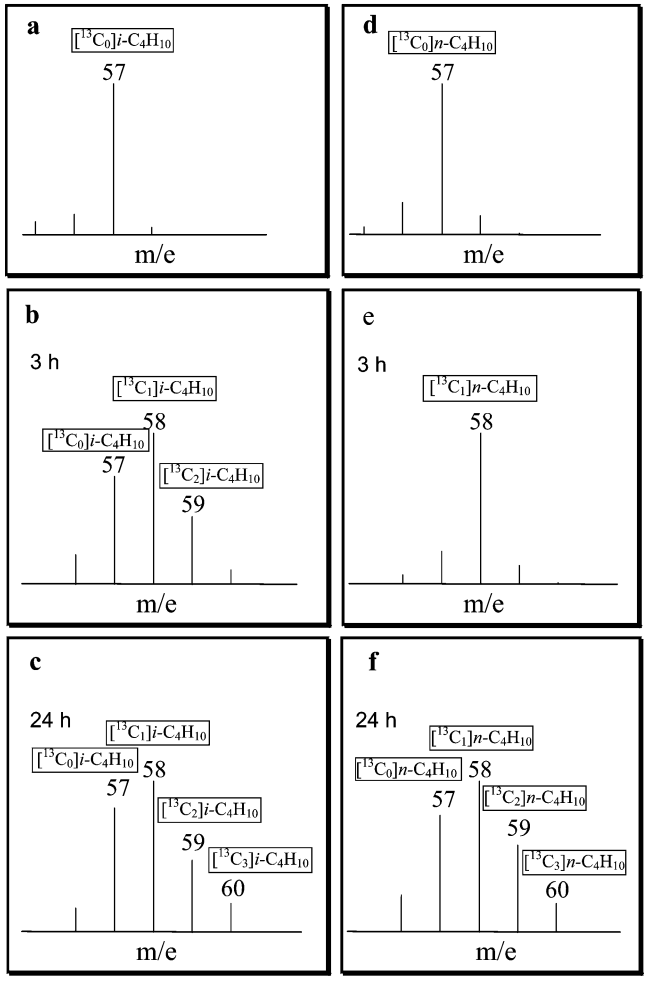
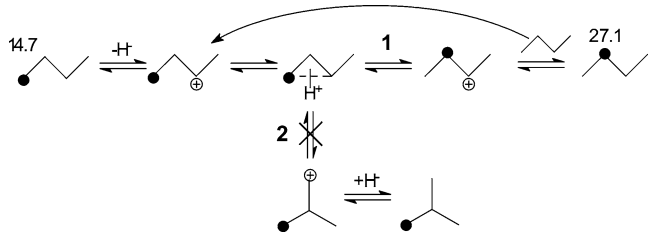


Fig. 2. Mass spectra of isobutane (a–c) and *n*-butane (d–f) formed on sulfated zirconia from *n*-[1-$^{13}C_1$]C_4H_{10} and extracted from the catalyst with Et_2O: (a) the reference *i*-C_4H_{10}; (b) isobutane extracted after 3 h of the reaction at 293 K; (c) isobutane extracted after 24 h of the reaction at 293 K; (d) the reference *n*-C_4H_{10}; (e) *n*-butane extracted after 3 h of the reaction at 293 K; (f) *n*-butane extracted after 24 h of the reaction at 293 K.

cular mechanism [12]. However, one cannot exclude the possibility that the distribution of the ^{13}C labels, observed in Ref. [12], resulted from the complex processes of conjunct polymerization realized in a later stage of reaction. Indeed, GC-MS analysis in Ref. [12] revealed the formation of propane and pentanes as the other reaction products.

Our GC analysis of the mixture released from SZ after 3 h of the reaction, i.e., the one corresponding to the ^{13}C MAS NMR spectrum in Fig. 1b, where isobutane was identified as the only product, confirmed the complete absence of the other reaction products. Fig. 2 shows the mass spectra of isobutane and *n*-butane extracted from SZ after 3 h of reaction in comparison with mass spectra of unlabeled alkanes. The comparison of the mass spectrum of isobutane formed from *n*-[1-^{13}C]butane (Fig. 2b) with that of unlabeled isobutane (Fig. 2a) leads to a conclusion that, in addition to single-labeled isobutane ([$^{13}C_1$]*i*-C_4H_{10}), both unlabeled ([$^{13}C_0$]*i*-C_4H_{10}) and double-labeled ([$^{13}C_2$]*i*-C_4H_{10}) molecules are



Scheme 2. The monomolecular mechanism of ^{13}C label scrambling in *n*-butane on SZ. (●) Denotes the ^{13}C-labeled carbon atom with chemical shifts indicated nearby.

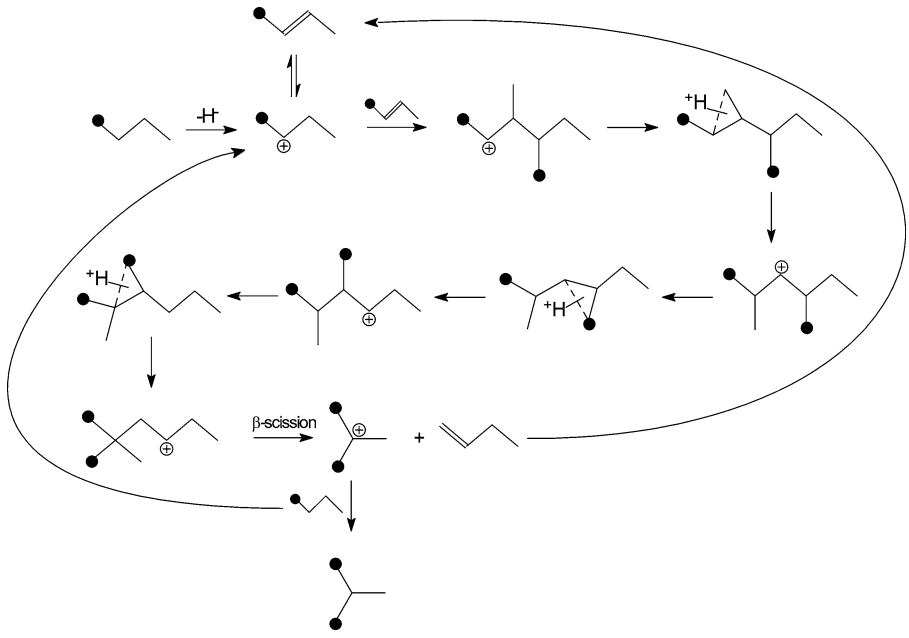
generated. Indeed, according to their m/e ratio, the lines with $m/e = 57$, 58, and 59 correspond to the ions $C_4H_9^+$ formed from [$^{13}C_0$]*i*-C_4H_{10}, [$^{13}C_1$]*i*-C_4H_{10}, and [$^{13}C_2$]*i*-C_4H_{10}, respectively.

At the same time, *n*-butane released from the catalyst contains only the single-labeled molecules, the ions with $m/e = 58$, i.e., generated from [$^{13}C_1$]*n*-C_4H_{10}, being the only species observed in mass spectrum (see Fig. 2, spectrum e). One should take into account that due to ^{13}C label scrambling observed by ^{13}C NMR, the *n*-butane molecules analyzed after 3 h of reactions hold the ^{13}C labels at either CH_3 or CH_2 positions. This means that the scrambling of the ^{13}C label in *n*-butane on SZ proceeds without changing the number of ^{13}C labels per molecule. It is possible only if a monomolecular mechanism of the ^{13}C label scrambling is realized (see Scheme 2).

According to the Scheme 2, *sec*-butyl carbenium ions, formed from *n*-butane by hydride abstraction, isomerize through a protonated cyclopropane intermediate or transition state. The reversible opening of a cyclopropane ring toward more stable *sec*-butyl cations (pathway **1** in Scheme 2) results in a selective transfer of the ^{13}C label from the CH_3 to the CH_2 group of the cation, from which *n*-[2-^{13}C]butane forms.

By analogy with the label scrambling, the monomolecular isomerization of *n*-[1-^{13}C]butane would lead to the formation exclusively of a single-labeled isobutane (Scheme 2, pathway **2**). However, in contrast to the ^{13}C-label scrambling in *n*-butane, the conversion of the single-labeled *n*-butane molecules into unlabeled and double-labeled isobutane clearly points to the bimolecular mechanism of isomerization according to Scheme 3. This is in a good accordance with the concept, explaining the very low possibility of the formation of isobutane through a monomolecular mechanism. According to this concept, a monomolecular mechanism requires the formation of highly energetic (compared to the secondary cation) primary cation [12], which should be a precursor of isobutane via pathway **2** in Scheme 2. Alternatively, the isomerization of dimeric cation via successive stages of hydrogen and methyl shift reactions toward C_8^+ carbenium ions with *tert*-butyl fragment allows the intermediacy of primary cations (Scheme 3) to be avoided.

In fact, the intermolecular mechanism of *n*-butane conversion can provide a situation when two ^{13}C labels in C_8^+



Scheme 3. The bimolecular mechanism of the skeletal isomerization of *n*-butane on SZ. The scheme rationalizes the formation of double-labeled isobutane from single-labeled *n*-butane. (●) Denotes the ^{13}C-labeled carbon.

carbenium ions find each other simultaneously in a common *tert*-butyl fragment of dimeric cation (see Scheme 3). β-Scission of such isomeric dimer results in a double-labeled *tert*-butyl cation, from which $[^{13}C_2]i$-C_4H_{10} is produced (a similar scheme can also rationalize the formation of unlabeled isobutane).

The same distribution of ^{13}C label in isobutane molecules formed would be possible as a result of more complex processes of conjunct polymerization. Conjunct polymerization should have inevitably resulted also in the formation of the products of *n*-butane disproportionation, as well as in the formation of multilabeled *n*-butane; however, this is not the case. Thus, the selective formation of isobutane at the initial stage of the conversion of *n*-butane on SZ occurs by a purely bimolecular mechanism.

As was noted above, the initial period is followed by a more complex process of conjunct polymerization. GC analysis revealed the formation of propane and isopentane in addition to isobutane. Moreover, the mass spectra of both isobutane and *n*-butane evolved from the catalysts provide evidence for ^{13}C-label redistribution, both alkanes containing unlabeled, single-labeled, double-labeled, and triple-labeled molecules (Figs. 2c and f). This experimental finding implies the formation of isobutane and *n*-butane as the products of conjunct polymerization, the intermolecular nature of this process being responsible for the ^{13}C-label redistribution.

The substitution of a simple bimolecular process by conjunct polymerization can be easily rationalized as follows. In the course of the reaction, the accumulation of olefinic species and the consumption of *n*-butane occur. So, the alkenes rather than alkanes, giving rise to more stable allylic cations compared to carbenium ions, become a more probable source of hydrogen for hydride transfer steps depicted in Scheme 3. Being formed from alkenes, allylic cations stimulate all the steps of conjunct polymerization which results finally in a mixture of alkanes and cyclopentenyl cations (Scheme 1).

Thus, the change in the reaction mechanism with time observed in Ref. [13] and attributed to the replacement of a monomolecular route by a bimolecular one represents, in reality, the change from a simple bimolecular pathway to conjunct polymerization.

4. Conclusions

Using both in situ ^{13}C MAS NMR and ex situ GC-MS analysis, we drew the following conclusions about the conversion of *n*-butane, selectively labeled with ^{13}C in the CH_3 group, on sulfated zirconia at 293 K.

During the initial period of the reaction ($t \leqslant 3$ h) two parallel processes proceed: the ^{13}C-label scrambling in *n*-butane, resulting in migration of the selected ^{13}C label from the methyl into its methylene groups, and the selective formation of isobutane.

The distribution of ^{13}C label monitored in mass spectra provides evidence that the scrambling of the ^{13}C label in *n*-butane represents a monomolecular reaction, whereas skeletal isomerization into isobutane proceeds via a purely bimolecular mechanism.

The simple bimolecular route of isomerization is complicated with time to turn into conjunct polymerization. Besides isobutane, conjunct polymerization gives rise to propane and pentanes, the stable cyclopentenyl cations being simultane-

ously formed. The latter can be in charge of reducing the catalytic activity of SZ in isomerization reactions.

Acknowledgments

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