Journal of Catalysis **203,** 273–280 (2001)
doi:10.1006/jcat.2001.3318, available online at http://www.idealibrary.com on IDEAL®

n-Pentane Conversion on Sulfated Zirconia in the Absence and Presence of Carbon Monoxide

Evidence for Monomolecular Mechanism of Isomerization from the ^{13}C MAS NMR Study

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Received November 13, 2000; revised May 31, 2001; accepted June 14, 2001

In situ ^{13}C MAS NMR analysis of hydrocarbon products formed from the selectively ^{13}C-labeled *n*-pentane on sulfated zirconia in the absence and presence of carbon monoxide provide the evidence that *iso*-pentane forms by two parallel processes: isomerization and conjunct polymerization. Peculiarities of the ^{13}C label scrambling from *n*-pentane into *iso*-pentane provide unequivocal evidence for monomolecular mechanism of the alkane isomerization. Besides *iso*-pentane, conjunct polymerization affords also the products of *n*-pentane "disproportionation," butanes and hexanes and stable cyclopentenyl cations; the latter are in charge of the catalyst deactivation. Carbon monoxide suppresses completely the process of conjunct polymerization, whereas the process of intramolecular isomerization does not. In the presence of carbon monoxide carbonylation of *n*-pentane occurs in parallel with its isomerization, giving rise to a mixture of aldehydes, ketones, and carboxylic acids. Carbonylation of *n*-pentane with CO contributes to the earlier observed negative effect of CO on the alkane isomerization rate.

Key Words: ***n*-pentane; sulfated zirconia; isomerization; carbonylation; mechanism; NMR spectroscopy.**

1. INTRODUCTION

Sulfated zirconia (SZ) is among the most promising catalysts for *n*-alkane isomerization (1, 2) to produce the high-octane-number clean fuels. Unique ability of SZ to isomerize *n*-butane and *n*-pentane at low temperature (3, 4) stimulated the studies of the mechanism of *n*- to *iso*-alkane isomerization on this solid acid catalyst. Two pathways of *n*- to *iso*-alkane conversion are usually considered. The first one implies that the formation of *iso*- from *n*-alkane proceeds by monomolecular mechanism, i.e., isomerization of the intermediate carbenium ion (5, 6). The second pathway assumes the alkane conversion occurs by way of bimolecular mechanism (7, 8); i.e., the carbenium ion, initially formed from alkane presumably by hydride abstraction, interacts with alkene, which is in equilibrium with the carbenium ion, to produce dimeric cation. The isomerization and β-scission of the latter, followed by a hydride shift reaction lead to *iso*-alkane product. The base for the discrimination between two alternative mechanisms is indirect methods—tracer experiments (5, 8, 9), kinetics measurements (9–13), and observation of the disproportionation reaction products, i.e., lower and higher molecular weight alkanes, in parallel with isomerization products (as evidence for a bimolecular pathway) (9, 13, 14). To date the bimolecular mechanism has been accepted for *n*-butane isomerization and the monomolecular mechanism is assumed for *n*-pentane isomerization (9). However, conclusions on the mechanisms have been made without taking into account the processes of the formation of undesorbed deposits from the initial alkane which deactivate the catalyst (17). Lack of attention to this particular process may lead to a misunderstanding of the real mechanism of the isomerization. Therefore, clarification of the isomerization mechanism requires monitoring both the alkane transformation itself and parallel analysis of the nature of the deposits formed on the catalyst. So, further studies are needed to obtain more incontrovertible and unequivocal evidence for the mechanism of alkane isomerization on SZ.

The second point that should be addressed is how the observed process of disproportionation (besides isomerization) of the initial alkane to lower and higher molecular weight alkanes occurs. The suggested mechanism for disproportionation is similar to the bimolecular mechanism of alkane isomerization (9, 10, 14–16). It includes hydride abstraction/dimerization/β-scission/reverse hydride transfer steps. Again, it does not take into account parallel processes of the formation of undesorbed species, deactivating the catalyst.

In this paper unequivocal evidence for the monomolecular mechanism of *n*-pentane (**1**) isomerization on sulfated zirconia has been provided by monitoring with in situ ^{13}C,

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solid-state NMR spectroscopy of the scrambling of the selective ^{13}C label from [2-^{13}C]*n*-pentane into *iso*-pentane in the presence of coadsorbed carbon monoxide. Secondly, we demonstrate that in the absence of CO the conversion of **1** proceeds in full analogy with "conjunct polymerization" process of olefin conversion in liquid concentrated sulfuric acid to produce a mixture of alkanes and alkyl-substituted cyclopentenyl cations; the latter deactivates the catalyst in the isomerization process.

2. EXPERIMENTAL

2.1. Preparation of the Samples

A sample of sulfated zirconia of low temperature tetragonal phase with surface area of 60 m^2/g and 9.9% (wt) of SO_3 content was synthesized according to the procedure described earlier (14). The concentration of Brønsted acid sites was 50 μmol g^{-1} as estimated from ^{1}H, magic angle spinning, (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*-pentane or equal amounts of *n*-pentane and CO (and H_2O) (ca 300 μmol g^{-1} of each coadsorbate) on SZ under vacuum at the temperature of liquid nitrogen. After we sealed a glass tube with SZ sample off from the vacuum system, the sample was warmed to room temperature (~20°C) or heated at 50–150°C for 1 h.

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 magic angle spinning 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 Tesla) on a Bruker MSL-400 spectrometer at 23°C. 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 Hartmann–Hahn matching conditions of 50 kHz, and delay time between scans was 3 s. One pulse excitation ^{13}C MAS spectra was recorded with 45° flip angle ^{13}C pulses of 2.5 μs duration and 10–15-s recycle delay, which satisfied a $10T_1$ condition. Spinning rate was 2.7–14.5 kHz. A few thousand scans have been 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 ±0.5 ppm. Precision in the determination of the relative line position was 0.1–0.15 ppm. To facilitate NMR analysis *n*-pentane, labeled with ^{13}C isotope at the second carbon atom, which is next to the terminal methyl group, [2-^{13}C]*n*-pentane (82% ^{13}C isotope enrichment), or ^{13}CO (90% ^{13}C isotope enrichment) were used in NMR experiments. [2-^{13}C]*n*-pentane was prepared from [1-^{13}C]ethanol (82% ^{13}C) via a six-step synthesis.

3. RESULTS AND DISCUSSION

3.1. Conversion of *n*-Pentane in the Absence of Carbon Monoxide

n-Pentane is known to undergo both isomerization into *iso*-pentane and disproportionation into butanes and hexanes over sulfated zirconia at low temperature—two parallel mechanisms (intra- and inter-molecular or mono- and bimolecular) are supposed to contribute to the formation of the reaction products (9, 10, 14–16). Figure 1 displays the ^{13}C NMR spectra of the products formed from [2-^{13}C]*n*-pentane on SZ at 23°C. It should be emphasized that in this case only the ^{13}C-labeled CH_2 group of the initial *n*-pentane and the labeled carbons in the reaction products, where the label penetrates in the course of the reaction, could be observed in the spectra.

According to the ^{13}C MAS NMR spectrum recorded in first 20 min of the reaction, the main products formed from

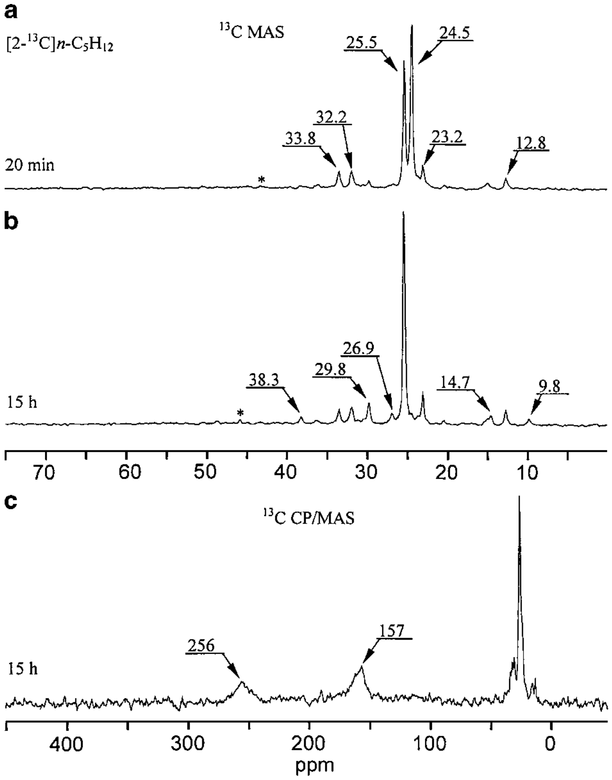
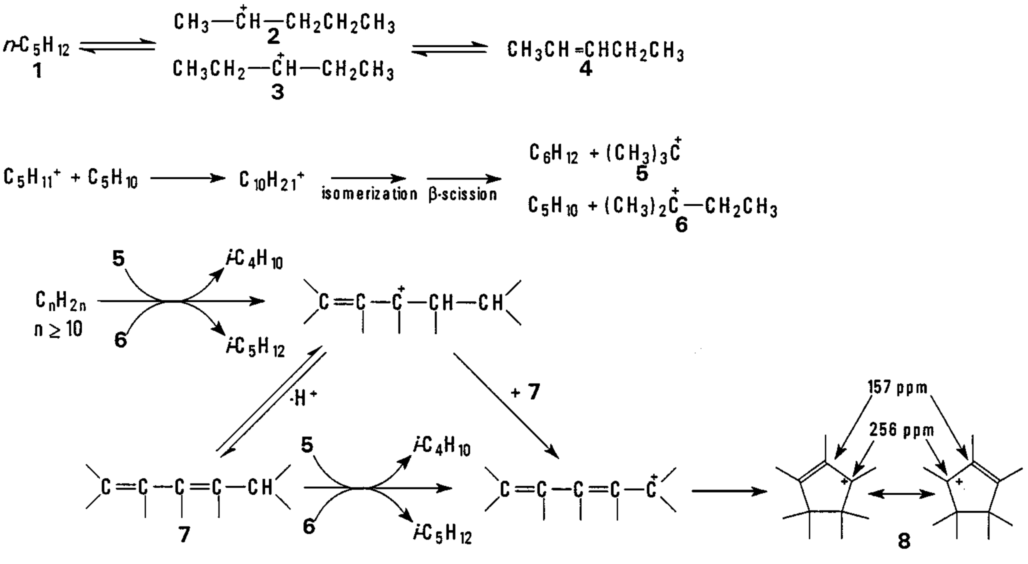


FIG. 1. ^{13}C NMR spectra of the products formed from [2-^{13}C]*n*-pentane on sulfated zirconia at 23°C: (a) ^{13}C MAS NMR spectrum recorded after 20 min of the reaction duration; (b) ^{13}C MAS NMR spectrum, and (c) ^{13}C CP/MAS NMR spectrum of the same sample recorded after 15 h of the reaction duration. Asterisks (∗) denote spinning side bands.

n-pentane are *iso*-butane and *iso*-pentane (Fig. 1a). Indeed, besides the signal from the ^{13}C-labeled CH_2 group of unreacted [2-^{13}C]*n*-pentane at 24.5 ppm (14, 20), the following new signals appeared in this spectrum. The more intense signal at 25.5 ppm arises from both the ^{13}C-labeled CH and CH_3 groups of *iso*-butane (20); the signals of less intensity are assigned to the ^{13}C-labeled groups of *iso*-pentane: at 33.8 [CH_2], 32.2 [CH], 23.2 [$(CH_3)_2$], and 12.8 ppm [CH_3] (14, 20). In the course of time the signal due to [2-^{13}C]*n*-pentane decreases in intensity, simultaneously the signal from *iso*-butane increases, and the intensity of the signals belonging to *iso*-pentane remains nearly constant. Finally, only the reaction products are identified in the spectrum (Fig. 1b): *iso*-butane, *iso*-pentane, and small fractions of 2,2-dimethylbutane (the signals are observed at 9.8 [CH_3], 29.8 [$(CH_3)_2$], 31.2 [C], and 38.3 ppm [CH_2]) and *n*-butane with the signals detected at 14.7 [CH_3] and 26.9 ppm [CH_2] (20). Penetration of the ^{13}C label from the CH_2 group of *n*-pentane in all carbon atoms of *iso*-pentane may in principle be explained by the label scrambling via protonated cyclopropane intermediates (or transition states) (22, 23) in *n*-pentyl cation formed from *n*-pentane by hydride abstraction and subsequent isomerization of *n*-pentyl cation into *iso*-pentyl cation. This would imply monomolecular mechanism of *n*-pentane isomerization. However, the observation of the signals from *iso*-butane and 2,2-dimethylbutane with the ^{13}C-labeled carbons, that is, the signals from the products of disproportionation, can be explained, at least, by the simple way of *n*-pentane dimerization as suggested earlier (14), scrambling of the selective label in the formed dimer with subsequent dimer isomerization, β-scission, and reversible hydride transfer steps. *Iso*-pentane can also be formed from the intermediate dimeric cation by a way similar to *iso*-butane and 2,2-dimethylbutane formation. Therefore based on these data an unequivocal conclusion about the mechanism of the isomerization cannot be made.

Noteworthy is the simultaneous growth of the new signals in the ^{13}C MAS NMR spectrum, different from the signals of alkanes (Fig. 1a and 1b). The new broad signals at 157 and 256 ppm appear in the spectrum recorded with cross-polarization; they are due to stable alkyl substituted cyclopentenyl cations (18–21) (Fig. 1c). Allylic and polyenilyc cations have been earlier identified by Spielbauer *et al.* with UV-VIS DR spectroscopy as the species that deactivates SZ in alkane isomerization (17). The characteristic chemical shifts at 157 and 256 ppm in our NMR spectrum indicate that polyenilyc cations identified in (17) are in fact of cyclic structure with five carbon atoms in the cycle (24). These cations are analogs to those identified earlier (25) in the reaction of "conjunct polymerization" of olefins in concentrated sulfuric acids (26–28); they were found to be formed from *iso*-butane in H_2SO_4 (29) and they were also identified on zeolites as the species deactivating zeolites at temperatures as low as 200°C in olefin (18, 19) and alcohol conversion (20).

Simultaneous observation of the formation of the products of *n*-pentane disproportionation, butanes and hexanes, and cyclopentenyl cations allow us to conclude that *n*-pentane conversion on SZ occurs in a similar way as the process of conjunct polymerization occurs in sulfuric acid (26) and on acidic zeolites (18). One can assume that *n*-pentyl cations **2**, **3** are initially generated from *n*-pentane (**1**) presumably via hydride abstraction by SZ (Scheme 1). Being in equilibrium with appropriate alkene **4**, pentyl cations can alkylate **4** to produce C_{10} carbenium ions. Isomerization and β-scission of the latter, followed by further



SCHEME. 1. The process of *n*-pentane conjunct polymerization on sulfated zirconia to produce a mixture of alkanes (butanes, pentanes, hexanes) and cyclopentenyl cations.

oligomerization of olefins and hydride transfer from generated oligomeric alkenes (C_nH_{2n}) ($n \geq 10$) to carbenium ions **5**, **6** formed lead to alkanes (preferentially *iso*-butane and *iso*-pentane) and allylic cations, from which dienes **7** are formed. Further, the formation of dienyl cations occurs either by oligomerization of dienes or via hydride abstraction from diene by carbenium ion. Finally, cyclization of the generated dienyl cations results in the formation of stable cyclopentenyl cations **8**. Cyclopentenyl cations are the reason for the catalyst deactivation. Their ability to be strongly bound to the catalyst Brønsted acid sites prevents access of *n*-pentane to the SZ active sites that results in slowing down *n*-pentane conversion. Scheme 1 reasonably rationalizes the observation of butanes, *iso*-pentane, hexane, and cyclopentenyl cations in ^{13}C MAS NMR spectra. The observation of *iso*-pentane (as well as the other alkanes) with the ^{13}C label distributed over the all carbon atoms can be the result of the ^{13}C label scrambling during the processes presented in Scheme 1.

Thus, it follows from NMR data the process of "*n*-pentane isomerization" may be a complex multistep process in which *iso*-pentane is formed as one of the reaction products, rather than the basic product. The formation of the products of *n*-pentane "disproportionation," butanes and hexanes, can also be reasonably explained in a frame of Scheme 1. In fact, conversion of *n*-pentane observed by NMR (Fig. 1 and Scheme 1) represents neither "isomerization" nor "disproportionation." This conversion is the analog of the "conjunct polymerization" process described earlier by Ipatieff and Pines for the reaction in sulfuric acid (26–28) and by Haw *et al.* on zeolite catalyst (18).

At the same time, as we mentioned above, our NMR data do not allow us to exclude the contribution of monomolecular isomerization of *n*-pentane to afford *iso*-pentane. So, new approaches are needed to discriminate between "monomolecular isomerization" (real isomerization) and "bimolecular isomerization;" the latter represents, in fact, a conjunct polymerization process.

3.2. Conversion of n-Pentane in the Presence of Carbon Monoxide

It has been recently found that carbenium ions (key intermediates of alkane isomerization (9)) generated on solid acid catalysts can be trapped with carbon monoxide to form carboxylic acids in the presence of water (30–32). The intriguing point of these results was that when alkenes and alcohols were used as carbenium ion precursors, carbon monoxide almost completely suppressed the oligomerization reaction with only carboxylic acids corresponding to the monomeric molecule of the initial reagent formed (30, 31). Therefore, we hoped the study of the conversion of alkane in the presence of CO could be helpful in the delimitation between mono- and bimolecular pathways of *n*-pentane isomerization by blocking bimolecular path with carbon monoxide.

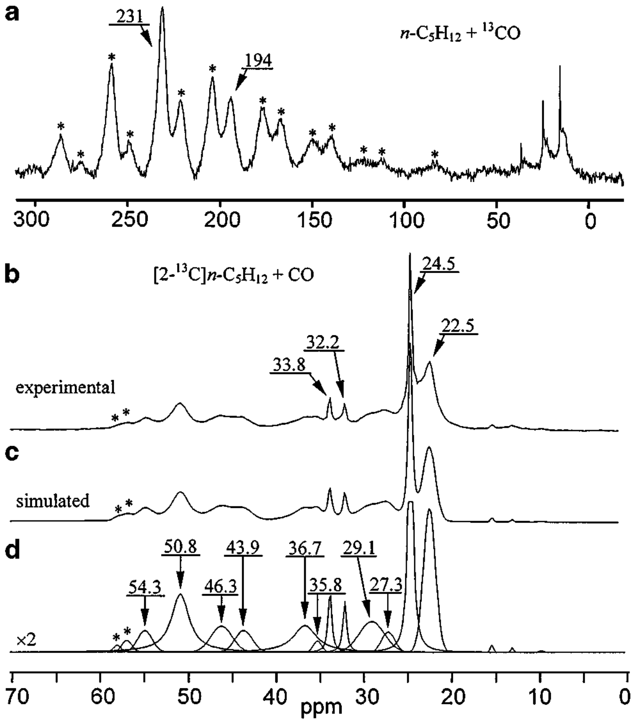
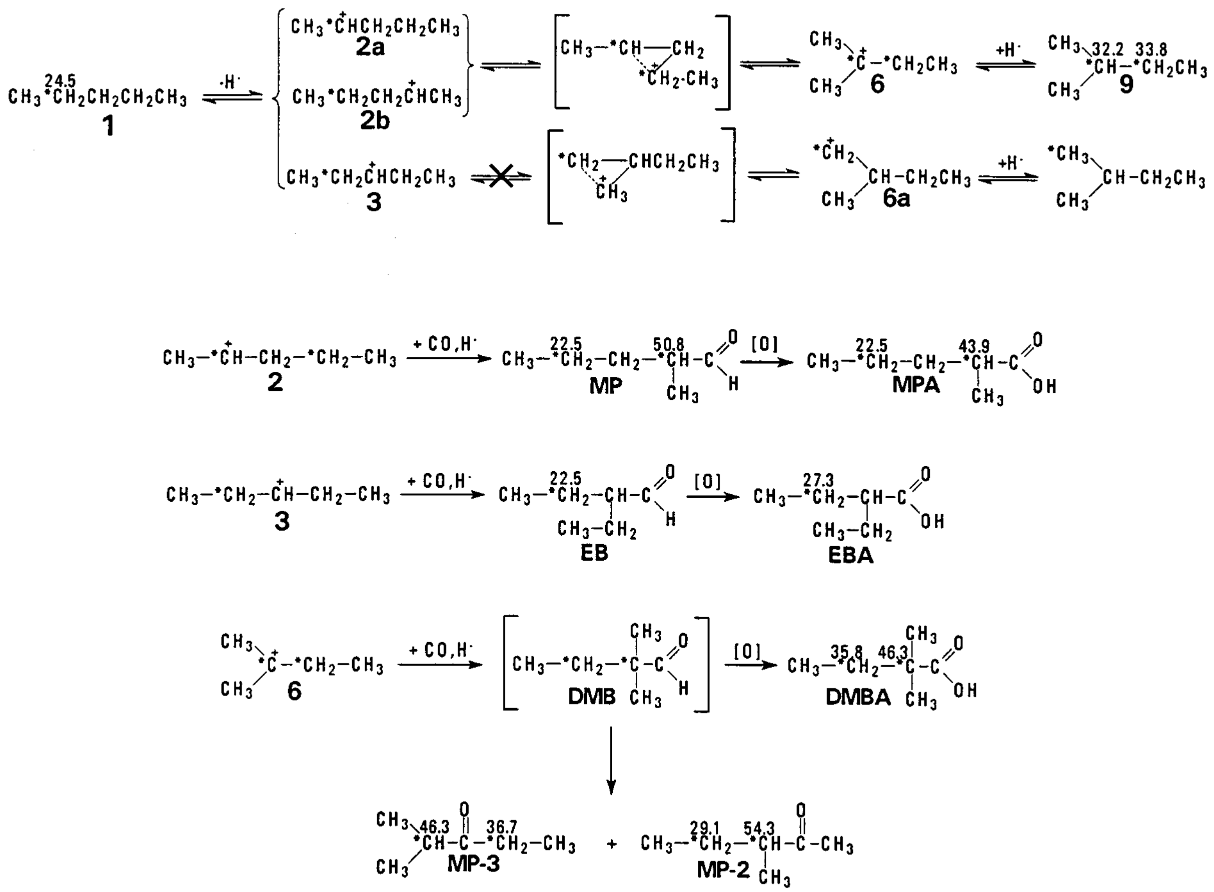


FIG. 2. ^{13}C CP/MAS NMR spectra of the products formed from *n*-pentane and CO on sulfated zirconia at 70°C: (a) coadsorption of the ^{13}CO and n-C_5H_{12}; (b) coadsorption of the [2-^{13}C]n-C_5H_{12} and CO; (c) and (d) simulation of experimental spectrum (b) to emphasize observation of nine signals from the carbonylation products. Asterisks (∗) denote spinning side bands.

Figure 2 shows the ^{13}C MAS NMR spectra obtained after coadsorption of *n*-pentane and CO on the sulfated zirconia and subsequent heating of the sample at 70°C for 1 h. Comparative analysis of these spectra allows us to make a conclusion about the formation of aldehydes, ketones, and carboxylic acids of C_6 family from *n*-pentane and CO. When ^{13}CO and unlabeled *n*-pentane were used for coadsorption, two signals became clearly visible in the region where the carbonyl group carbons from aldehydes, ketones, and carboxylic acids were usually observed (33) (Fig. 2a). The position of the most intense signal in this spectrum at 231 ppm indicates the formation of aldehydes and ketones (34, 35), whereas the signal at 194 ppm is indicative of carboxylic acid formation (30–32). To recognize the reaction products more accurately, we have used for coadsorption [2-^{13}C]*n*-pentane and unlabeled CO (Fig. 2b–2d). It follows from the spectrum in Fig. 2b isomerization of *n*-pentane is not completely suppressed in the presence of CO: two intense and narrow signals at 32.2 and 33.8 ppm are due to CH and CH_2 groups of *iso*-pentane (20). The penetration of the selective ^{13}C label from the CH_2 group of [2-^{13}C]*n*-pentane (the signal at 24.5 ppm) into both the CH and CH_2 groups of *iso*-pentane



SCHEME. 2. Mechanism of *n*-pentane carbonylation to a mixture of aldehydes, ketones, and carboxylic acids on sulfated zirconia. *C denote a ^{13}C-labeled carbon atom. Above each of the ^{13}C-labeled carbon atoms the corresponding ^{13}C NMR chemical shifts are given.

is unequivocal evidence for intramolecular isomerization of *n*-pentane through the intermediacy of the carbenium ions **2a** and **2b** as shown in Scheme 2. At the same time the absence of the signal from the methyl $[(CH_3)_2]$ group of *iso*-pentane at 23.2 ppm (Fig. 2b) indicates that carbenium ion **3** is not involved in intramolecular isomerization of *n*-pentane into *iso*-pentane. This is in good accordance with the extreme instability of the intermediate primary carbenium ion **6a** (compared to **6**) (36), that would provide formation of *iso*-pentane with the ^{13}C label in methyl $[(CH_3)_2]$ group from the cation **3**.

In addition to pentanes, nine signals are observed in this spectrum at 22.5–54.3 ppm (Fig. 2b–2d). They appear simultaneously with the signals from carbonyl groups (Fig. 2a) and belong to the aliphatic fragments of the carbonylation products. The formation of *iso*-pentane **9** with the ^{13}C labels in the CH and CH_2 groups implies the intermediateness of the cations **2** and **6**. Further evidence of the formation of the cations **2**, **6** as well as the cation **3** from *n*-pentane on SZ is provided by the analysis of distribution of the selective ^{13}C labels in the products of pentanes (**1** and **9**) carbonylation. The trapping of the cations **2**, **3**, **6** with carbon monoxide should result in aldehydes and/or carboxylic acids with the ^{13}C labels in certain carbon atoms of aliphatic fragments of aldehydes (acids) in accordance with Scheme 2. Indeed, the signals at 22.5 and 50.8 ppm arise from 2-methylpentanal (**MP**) (34) labeled with ^{13}C in the 4-C (CH_2) and 2-C (CH) positions, respectively, as should be expected, if cation **2** has been trapped with CO. Another product resulting from trapping the cation **3**, 2-ethylbutanal (**EB**) (34), appears in this spectrum as a signal at 22.5 ppm from the ^{13}C-labeled CH_2 group. Two signals observed at 36.7 and 46.3 ppm belong to 2-methylpentan-3-one (**MP-3**) (34) with the ^{13}C labels in the CH and CH_2 groups, respectively. The signals at 29.1 and 54.3 ppm are due to $^{13}CH_2$ and ^{13}CH carbons of 3-methylpentan-2-one (**MP-2**) (34). Both **MP-2** and **MP-3** are the result of the cation **6** trapping with CO. 2,2-Dimethylbutanal (**DMB**), whose formation from *iso*-pentenyl cation **6** could be expected, has not been observed. It is common knowledge that the aldehydes in which the carbonyl group is attached to the quaternary carbon atom, rapidly rearrange in liquid acids (37) and on solid $AlCl_3$ (40) by alkyl shift to form appropriate ketone. The situation proved to be the same in the case of carbonylation reaction on sulfated zirconia: two ketones are generated from intermediate **DMB** by methyl (**MP-2**) and ethyl (**MP-3**) shift reactions.

As mentioned above, the signal at 194 ppm in Fig. 2a clearly points to the formation of a small fraction of carboxylic acids in addition to aldehydes and ketones. The signals from ^{13}C-labeled aliphatic carbons of the acids become apparent in the spectrum of Fig. 2b–2d. The ^{13}C carbons of the 2-CH_2 and CH groups of 2-methylpentanoic acid (**MPA**) are observed at 22.5 and 43.9 ppm, respectively (41). The signal at 27.3 ppm belongs to the ^{13}C-labeled CH_2 carbon of 2-ethylbutanoic acid (**EBA**) (41). The remaining two signals at 35.8 and 46.3 ppm are due to $^{13}CH_2$ and ^{13}C groups of 2,2-dimethylbutanoic acid (**DMBA**) (41).

When the reaction was carried out in the presence of water, the same carboxylic acids with the same distribution of the selective ^{13}C label were formed as the only products of carbonylation. No signals from aldehydes and ketones were observed (Fig. 3). As in the case of the reaction under anhydrous conditions, the isomerization of *n*-pentane is not suppressed completely by CO, the ^{13}C label again penetrating selectively into the CH_2 (33.8 ppm) and CH (32.2 ppm) groups of *iso*-pentane formed in the presence of CO and H_2O (Fig. 2b–2d).

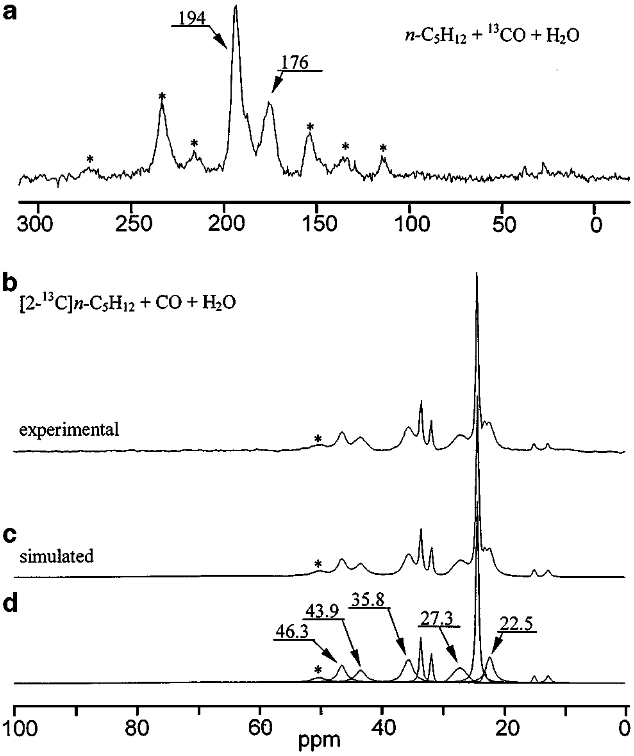


FIG. 3. ^{13}C CP/MAS NMR spectra of the products formed from *n*-pentane, CO, and water on sulfated zirconia at 150°C: (a) coadsorption of the ^{13}C-labeled CO, unlabeled n-C_5H_{12}, and water; (b) coadsorption of the [2-^{13}C]n-C_5H_{12}, unlabeled CO, and water; (c) and (d) simulation of the experimental spectrum (b) to emphasize that five signals arise from the carbonylation products. Asterisks (∗) denote spinning side bands.

We believe that the formation of carboxylic acids occurs by partial oxidation of aldehydes by SZ sulfate groups (42); in the presence of water the oxidation process seems to be completed faster (43), which provides observation of exclusively carboxylic acids. We reject an alternative path for carboxylic acid formation from pentanes in the presence of CO, which could involve quenching with water of the oxocarbenium ion formed from the cations **2**, **3**, **6** to produce acids and molecular hydrogen (H_2) (44, 45). We do not observe the formation of H_2 in any detectable amounts by ^{1}H MAS NMR as we observe H_2 formation as one of the reaction products in the carbonylation of *iso*-butane with CO on zeolite H-ZSM-5 (32). The lack of H_2 among the products formed on sulfated zirconia is in favor of the way of carboxylic acid formation by oxidation of aldehydes supposed in Scheme 2, rather than quenching of intermediate carboxonium ions with water.

Thus, comparison of the product distribution formed from *n*-pentane in the presence of carbon monoxide with that in its absence provides unambiguous confirmation for monomolecular mechanism of *n*-pentane isomerization. First, in the presence of carbon monoxide (both in the absence and in the presence of water) the bimolecular process of *n*-pentane conversion on SZ ("conjunct polymerization") is completely suppressed. We do not observe the formation of C_4, C_6 alkanes, and cyclopentenyl cations, which requires dimerization of pentyl cation with pentene molecule followed by isomerization and β-scission of C_{10}^+ carbenium ion, i.e., as the reaction in Scheme 1 proceeds. In the presence of carbon monoxide, only *iso*-pentane formation occurs, besides a parallel process of alkane carbonylation. This experimental finding clearly indicates that the interaction of the intermediate pentyl cation with CO proceeds considerably faster than the dimerization reaction. At the same time, the rate of carbonylation of pentyl cation is not sufficient for the intramolecular isomerization to be suppressed by CO. Secondly, the monomolecular mechanism of *n*-pentane isomerization is clearly proved by the distribution of the ^{13}C label during the reaction in the presence of CO and water. In the case of bimolecular mechanism random distribution of the ^{13}C label through the hydrocarbon skeleton of the products should be expected (see, e.g., (8)). However, this is not the case. In fact, we observe a very selective penetration of the ^{13}C label into *iso*-pentane, **MP-2**, **MP-3**, and **DMBA** molecules formed. This selective penetration of the ^{13}C label, located initially in the 2-CH_2 group of *n*-pentane, can be explained only by the formation of *n*-pentyl cation **2** from *n*-pentane on SZ and its subsequent isomerization, which proceeds monomolecularly via protonated cyclopropane intermediate (see Scheme 2). Monomolecular isomerization of *n*-pentyl cation **2** results in penetration of the ^{13}C label from the CH_2 and ^+CH groups of the cations **2a** and **2b** into the CH_2 and ^+C carbons of *iso*-pentyl cation **6**. Finally, the CH, CH_2 groups of *iso*-pentane, and the C, CH_2 carbons of **DMBA** proved to be labeled with ^{13}C, whereas intermediate **DMB,** ^{13}C-labeled in the C, and CH_2 carbons, are transformed into **MP-2** and **MP-3** with the ^{13}C labels in the CH and CH_2 groups.

Recall the disorderly distribution of the ^{13}C label over *iso*-pentane molecule observed at the end of the reaction in the absence of CO (see Fig. 1b). We suppose that in that case *iso*-pentane is generated initially via rapid intramolecular isomerization, causing the predominant formation of *iso*-pentane with the ^{13}C labels at the CH and CH_2 carbons (in accordance with Scheme 2). This is indeed observed at the early stages of the reaction: the signals from the CH (32.2 ppm) and CH_2 (33.8 ppm) prevail over those due to the CH_3 groups (Fig. 1a). Further, *iso*-pentane also forms by intermolecular pathway of a more slow, conjunct polymerization process, where the selective ^{13}C label becomes randomly redistributed over the reaction products, both alkanes and cyclopentenyl cations. This results in the formation of *iso*-pentane with the ^{13}C label evenly allocated over the hydrocarbon skeleton (see Fig. 1b).

Thus, we have obtained direct evidence that the formation of *iso*-pentane from *n*-pentane on SZ proceeds predominantly via an intramolecular pathway; i.e., the reaction really represents the isomerization process. Monomolecular isomerization is a considerably faster reaction when compared to the bimolecular pathway of conjunct polymerization. Isomerization is not completely suppressed by carbon monoxide, as compared to bimolecular pathway.

Note that the observation of the carbonylation reactions implies a new insight into inhibiting effect of carbon monoxide on the alkane isomerization on sulfated zirconia. According to our results, the suppression of the alkane isomerization by CO may result not only from blocking of Lewis acid sites with CO (46) or from the reversible formation of oxocarbenium ions, as it was supposed earlier (9). Carbon monoxide changes the reaction pathway from isomerization toward carbonylation, thus contributing to the inhibiting effect on the alkane isomerization rate.

It should be also noted that for ^{13}CO reacting with *n*-pentane in the presence of water, an additional signal has been observed from the carbonyl moiety at 176 ppm (Fig. 3a). Moreover, ^{13}C CP/MAS NMR spectra (not shown here) of the samples containing only ^{13}CO and water on SZ and heated under the same conditions revealed the same signal at 176 ppm, i.e., outside the region where the signals from carboxylic acids were observed (30–33). This signal belongs to formate species, which was reported earlier to be generated on acidic zeolites and other oxide catalysts (32, 47, 48). However, we do not have any experimental data which could help us elucidate whether the formate species is involved in the activation step of the alkane or if it only regenerates CO, which then participates in trapping the carbenium ions **2**, **3**, **6**.

4. CONCLUSIONS

Applying in situ ^{13}C MAS NMR spectroscopy to the analysis of the adsorbed hydrocarbon products formed on sulfated zirconia catalyst from *n*-pentane, selectively labeled with ^{13}C isotope in the second carbon atom of the alkane hydrocarbon skeleton, allowed us to draw the following conclusions about the processes of *n*-pentane conversion on SZ in the absence and presence of carbon monoxide:

(1) Conversion of *n*-pentane adsorbed on SZ occurs through two parallel processes: isomerization and conjunct polymerization. Both isomerization and conjunct polymerization provide the formation of *iso*-pentane. Formation of *iso*-pentane via isomerization proceeds faster compared to conjunct polymerization. Conjunct polymerization affords also the products of *n*-pentane “disproportionation,” butanes and hexanes and stable cyclopentenyl cations; the latter are in charge of deactivation of the catalyst.

(2) Isomerization of *n*-pentane proceeds via a monomolecular pathway as it follows from specific distribution of the selective ^{13}C label in *iso*-pentane.

(3) Carbon monoxide suppresses completely the process of conjunct polymerization, whereas the process of intramolecular *n*-pentane isomerization does not.

(4) In the presence of carbon monoxide, carbonylation of *n*-pentane occurs in parallel with its isomerization. Distribution of the ^{13}C labels in the hydrocarbon skeleton of the products of carbonylation, aldehydes, ketones, and carboxylic acids provides evidence for the formation of pentyl carbenium ions as intermediates from *n*-pentane, which are further trapped with carbon monoxide affording the products of *n*- and *iso*-pentane carbonylation.

(5) Carbonylation of *n*-pentane with CO may contribute to the negative effect of carbon monoxide on the isomerization which was earlier reported by Mastikhin *et al.* (14).

ACKNOWLEDGMENTS

This research was supported by Grant 99-03-32454 from the Russian Foundation for Basic Research. Authors are indebted to Mr. V. N. Zudin for the synthesis of the ^{13}C-labeled *n*-pentane.

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