Olefin as an intermediate in *n*-butane isomerization on sulfated zirconia. An *in situ* ^{13}C MAS NMR study of *n*-octene-1 conversion

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By using *in situ* ^{13}C MAS NMR and *ex situ* GC-MS, the analysis of hydrocarbon products formed from *n*-octene-1 adsorbed on sulfated zirconia catalyst (SZ) has been performed. It is shown that a mixture of alkanes and stable alkyl substituted cyclopentenyl cations (CPC) is formed as the basic reaction products. Formation of both alkanes and CPC from *n*-octene-1, a precursor of C_8^+ cation, the key intermediate in *n*-butane isomerization *via* a "bimolecular pathway", implies that formation of the isomerized alkane occurs by a complex process of "conjunct polymerization", rather than isomerization itself. CPC deposited on the SZ surface can be in charge of the catalyst deactivation.

KEY WORDS: *n*-octene-1; sulfated zirconia; isomerization; ^{13}C MAS NMR; alkanes; cyclopentenyl cations

1. Introduction

The ability of sulfated zirconia (SZ) to isomerize *n*-butane at low temperature opened up a pathway towards a production of high quality and environmentally friendly motor fuels with the aid of heterogeneous catalysts [1,2]. It also stimulated the studies of the mechanism of *n*- to isobutane isomerization with the aim of clarifying how the activation of the alkane and isomerization itself occur on this solid acid catalyst [3–7]. To date the hypothesis of so-called "bimolecular" mechanism is prevailing in the literature as it is assumed to be substantiated experimentally and theoretically [7]. Although, the experimental data by Sommer *et al.* [6] and Matsuhashi *et al.* [8] could not allow one to discard the possibility of monomolecular isomerization of *n*-butane on SZ. Bimolecular isomerization is assumed to occur in the following way: C_4-carbenium ion, initially formed from *n*-butane presumably by hydride abstraction, interacts with alkene, which is in equilibrium with the carbenium ion, to produce a dimeric C_8^+ cation. The isomerization and β-scission of the latter, followed by hydride shift reaction, lead to isoalkane product.

The bimolecular mechanism can be further verified by monitoring the conversion of octyl (C_8^+) cation if formed by some manner on SZ. This can be done by adsorption of C_8 olefin on SZ, a proton of the Brønsted acid site being transferred to the olefin affording the expected cation.

In this paper we have monitored with ^{13}C MAS NMR the transformation of C_8 olefin as the possible precursor to generate C_8^+ cation, the expected intermediate in *n*-butane isomerization to verify a bimolecular pathway for *n*-butane isomerization.

2. Experimental

A sample of sulfated zirconia of the low-temperature tetragonal phase with surface area of 60 $m^2\,g^{-1}$ and 9.9 wt% of SO_3 content was prepared by a procedure described earlier [9]. The sample of SZ was calcined at 600 °C in air for 1 h and at 400 °C in vacuum (10^{-3} Pa) for 2 h. 300 μmol g^{-1} of [1-^{13}C]-*n*-octene-1 (82% ^{13}C isotope enrichment) [10] was frozen out on SZ under vacuum at liquid-nitrogen temperature. After sealing a glass tube of 0.2 cm^3 volume with the SZ sample, it was heated at 296–448 K for 1 h. Reaction products were analyzed *in situ* with ^{13}C MAS NMR in the sealed glass tubes.

^{13}C NMR spectra with cross-polarization (CP) and magic angle spinning (MAS) (^{13}C CP/MAS NMR) were recorded on a Bruker MSL-400 NMR spectrometer at room temperature (~296 K). The detailed conditions used for NMR measurements were similar to those described earlier in [11,12].

Thermodesorption experiments with subsequent GC-MS analysis of the reaction products desorbed from the SZ sample were performed with a VG 70-70 mass spectrometer, as described in [12].

3. Results and discussion

In order to get an idea about the conversion of octene-1 adsorbed on SZ, two analytical methods were used. The volatile products that could be desorbed from the SZ sample

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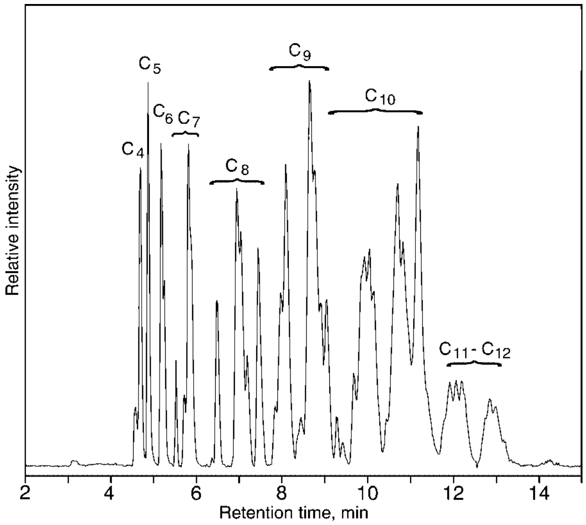


Figure 1. GC-MS spectrogram of the hydrocarbon products desorbed at 373 K from SZ sample after *n*-octene-1 adsorption at 296 K. A mixture of C_4–C_{12} alkanes is evolved. A similar spectrogram is observed for the thermodesorption experiment at 296 K.

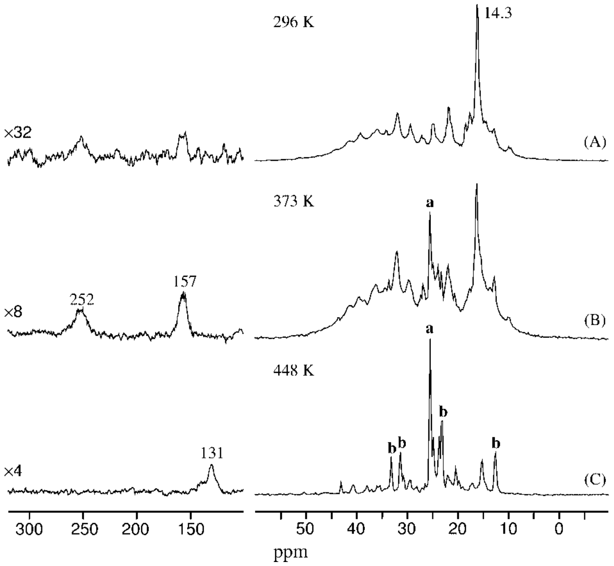
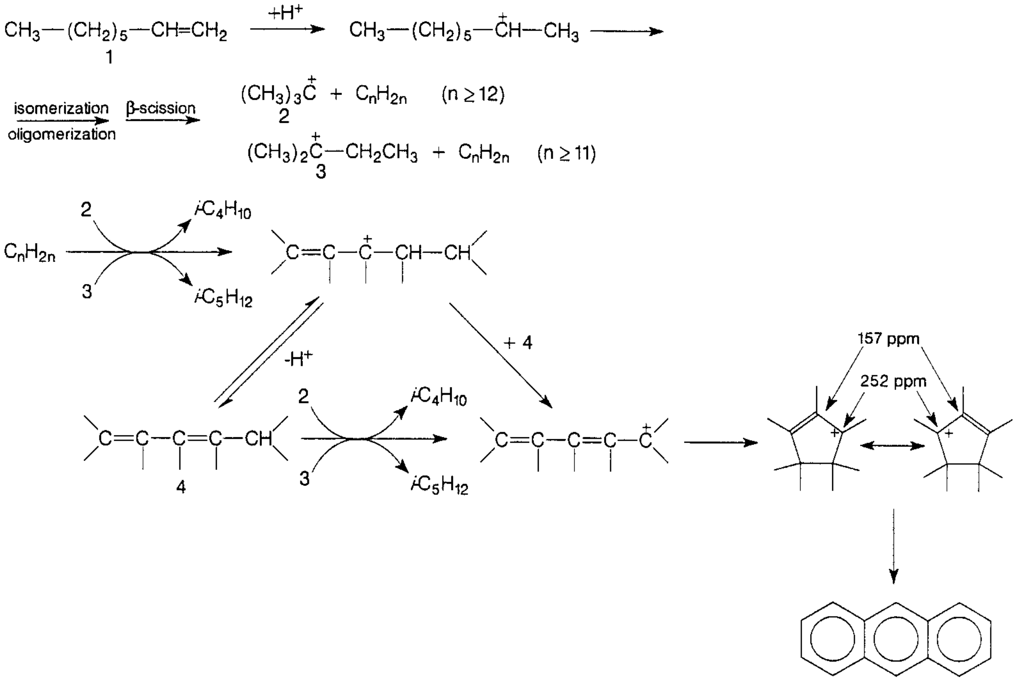


Figure 2. ^{13}C MAS NMR spectra for [1-^{13}C]-*n*-octene-1 adsorbed on SZ sample. Spectra (A) and (B) were recorded with cross-polarization (CP), spectrum (C) – without CP. Before the spectrum registration the sample was kept for 1 h at 296 K (A), 373 K (B), 448 K (C). The signal a at 25.5 ppm belongs to both CH and CH_3 groups of isobutane; four signals b arise from isopentane: 12.7 (CH_3), 23.2 (iso-CH_3), 31.4 (CH), 33.2 ppm (CH_2).

were analyzed *ex situ* with GC-MS, whereas the undesorbed products were identified *in situ* with ^{13}C MAS NMR.

Olefins usually oligomerize in the presence of acidic catalysts. Therefore, *a priori* the conversion of *n*-octene-1 on SZ as acidic catalyst implies an oligomerization process. The GC-MS spectrogram of the hydrocarbon products desorbed from SZ sample at 293–448 K shows a mixture of C_4–C_{12} alkanes evolved from the catalyst (figure 1). None of the expected oligomers of *n*-octene-1 evolved were identified. The GC-MS detection of the alkanes evolution from the SZ sample (figure 1) means that the ^{13}C MAS NMR spectrum in figure 2(A) should be attributed at least to a mixture of *n*-octene-1 oligomers and alkanes. By using for adsorption of *n*-octene-1 with the selective ^{13}C label at double bond, [1-^{13}C]-*n*-octene-1 (**1**), we hoped we would follow the transformation of the terminal $=CH_2$ group upon the olefin adsorption on SZ. The ^{13}C NMR signal for this group should be expected at 114 ppm [10]. However, the spectrum of the adsorbed **1** exhibits no signals from the olefinic double bond, only the signals at 10–45 ppm from paraffinic CH_n ($n = 1$–3) groups being observed in the spectrum (figure 2(A)). As far as the labelling with ^{13}C isotope implies that the signals at 10–45 ppm from the ^{13}C-label carbon atoms would be mainly observed in the spectrum, we assume that the signals belong to the ^{13}C-labelled CH_n groups in the reaction products in both oligomers and alkanes. The most intense signal at 14 ppm is certainly from the methyl group of the initial *n*-octene-1 or its linear oligomer or some linear alkane formed from the olefin. The transformation of the ^{13}C-labelled olefinic $=CH_2$ group of **1** into the terminal CH_3 group of either **1** or some oligomeric product can easily be explained by acidic proton transfer from SZ catalysts to the olefinic double bond [10], affording carbenium ion species, stabilized on SZ presumably in the form of alkylsulfate ester, $–CH_2–O–SO_3Zr–$. The signal of the carbon attached to the oxygen is not visible in the spectrum. It is very difficult to observe this broad signal, similarly to the case with zeolites [13]. It should be noted we did not observe any change of the intensity of the signal from the ^{13}C-labelled CH_3 group at 14 ppm with time, where the labelled $=CH_2$ was transformed as was in the case with the adsorption of **1** on H-ZSM-5 zeolite [10]. This seems to indicate that oligomerization is a fast process compared to a possible ^{13}C-label scrambling, which should result in a decrease of the signal from the CH_3 group at 14 ppm and an increase of the signals from aliphatic CH_2 groups at 20–45 ppm. This can be accounted for by either the essentially lower quantity of the equilibrated with alkyl-sulfate ester carbenium ions or their lesser stability on SZ compared to that on H-ZSM-5 to provide the scrambling of the selective ^{13}C-label from the CH_3 group over the rest of the hydrocarbon skeleton of **1** or oligomeric species at room temperature.

Formation of alkanes from the expected olefinic products of *n*-octene-1 oligomerization implies cracking, intermolecular hydrogen transfer reaction and the formation of hydrogen deficient products besides alkanes. Therefore, hydrogen deficient diens, triens, *etc.* or aromatics should be formed as well. These products may be strongly bound to SZ catalyst surface and are not desorbed in our thermodesorption experiment to be observed with GC-MS. The signals from the expected polyenylic species are really observed (figure 2(B)). Two signals at 157 and 252 ppm are the ^{13}C NMR “fingerprints” for the stable alkyl-substituted cyclic pentenyl cations [14], which seem to be a form of existence of polyenylic species in strong acidic media [15] and on strong acidic surfaces [12,16]. The signal at 252 ppm is a characteristic of C atom in the carbenium ion center and the signal at 157 ppm is due to C atoms adjacent to the carbenium ion center of



Scheme 1.

cycloalkenyl cations with five-membered ring [14]. These cations are analogs to those identified earlier by NMR in the reaction of olefins in concentrated sulfuric acid [15] and in the conversion of alcohols and olefins on acidic zeolites at temperatures as low as 200 °C [12,16].

At temperature as high as 448 K the pattern of the signals at 10–45 ppm becomes typical for a mixture of C_3–C_7 alkanes with isobutane and isopentane as prevailing species [12], the signals from condensed aromatics being simultaneously observed at 131 ppm [12] (figure 2(C)).

Simultaneous formation of a mixture of alkanes (with isobutane and isopentane prevailing at 448 K) and cyclopentenyl cations allows us to conclude that the conversion of *n*-octene-1 on SZ occurs in accordance with scheme 1. First, a transfer of acidic proton from SZ to **1** occurs affording C_8^+ carbenium ion, which further oligomerizes, isomerizes and undergoes β-scission. Further intermolecular hydrogen transfer provides for the formation of the alkanes and polyenylic species, the latter being protonated and cyclized to give the stable cyclopentenyl cations. This conversion of *n*-octene-1 observed on SZ is similar to the well-known process of “conjunct polymerization”, described earlier by Ipatieff and Pines, producing a mixture of alkanes and cyclic dienes from isobutene in 96% H_2SO_4 [17], and observed by Haw *et al.* producing a mixture of alkanes and cyclopentenyl cations from propene on acidic zeolites [16]. At 448 K the condensed aromatics are produced from the cyclopentenyl cations [12].

The bimolecular mechanism of *n*-butane isomerization implies the formation of the cationic C_8^+ species which further isomerizes and undergoes β-scission, then intermolecular hydrogen transfer affords isomeric butane. Our data indicates that C_8^+ species formed undergoes further a complex process of conjunct polymerization that can afford isomeric alkane with simultaneous formation of cyclopentenyl cations. In this respect isomerization of linear alkane *via* a bimolecular pathway cannot be considered as isomerization itself. It is in fact a conjunct polymerization process, where isomeric alkane forms only as one of the reaction products. The other reaction products, cyclopentenyl cations, earlier characterized by Knözinger as allylic and polyenylic cations [18], strongly interacting with SZ Brønsted acid sites, are the reason for catalyst deactivation.

Usually, when a bimolecular mechanism of *n*-alkane isomerization is considered it does not take into account the process of the catalysts deactivation during the isomerization process at all or it is considered as the result of side reactions of C_8^+ intermediate [19]. The observed process of conjunct polymerization for *n*-octene-1 as precursor of C_8^+ intermediate, suggested in bimolecular isomerization of *n*-butane, accounts for the formation of both isomerized alkane and the deposited product which deactivates the catalyst.

4. Conclusions

Conversion of *n*-octene-1, as a possible precursor of C_8^+ carbenium ion, suggested as a key intermediate in *n*-butane isomerization *via* a “bimolecular” mechanism on sulfated zirconia catalyst, proceeds similar to conjunct polymerization of olefins in 96% H_2SO_4 and on acidic zeolite to produce a mixture of alkanes and alkyl-substituted cyclopentenyl cations. In this respect in the “bimolecular” mechanism isomeric alkane forms in the complex processes of conjunct polymerization, affording also alkyl substituted cyclopentenyl cation, rather than in a more simple process of C_4^+ formation from n-butane, its dimerization, isomerization and β-scission processes.

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