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^{13}C solid state NMR evidence for the existence of isobutyl carbenium ion in the reaction of isobutyl alcohol dehydration in H-ZSM-5 zeolite

Alexander G. Stepanov [1] and Kirill I. Zamaraev [1]

Boreskov Institute of Catalysts, Siberian Branch of the Russian Academy of Sciences,
Pr. Akademika Lavrentieva 5, Novosibirsk 630090, Russia

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Using two-dimensional *J*-resolved and CP/MAS ^{13}C NMR, the pathway for the transfer of the ^{13}C label from the CH_2 group of isobutyl alcohol into the hydrocarbon skeleton of butene oligomers has been elucidated in the course of isobutyl alcohol dehydration inside H-ZSM-5 zeolite. First, the label is transferred selectively into the CH_2 group of the isobutyl silyl ether reaction intermediate (IBSE), and then into the CH and CH_3 groups of the isobutyl fragment ($-CH_2CH(CH_3)_2$) of IBSE and/or butene oligomers. Finally, it is scrambled over the carbon skeleton of the oligomers. The obtained data suggest that isobutyl carbenium ion is formed as a reaction intermediate or transition state during the transformation of isobutyl silyl ether into butene oligomers.

Keywords: Isobutyl carbenium ion; carbon scrambling; H-ZSM-5 zeolite; 2D *J*-resolved ^{13}C solid state NMR; dehydration of isobutyl alcohol

1. Introduction

The role of various intermediates in the conversion of olefins and dehydration of alcohols inside acidic zeolite catalysts is widely discussed [1–10]. NMR and IR evidences have been reported for the formation of both carbenium ions [5,8,9] and/or alkyl silyl ethers, i.e. hydrocarbon fragments covalently bonded to the zeolite framework [6,7,9–11], as reaction intermediates.

We have previously shown using ^{13}C CP/MAS NMR, that during dehydration of isobutyl alcohol (*i*-BuOH) on H-ZSM-5 zeolite isobutyl silyl ether intermediate (IBSE) is formed as the predominant organic species at 373 K [11]. Upon the increase of the reaction temperature up to 448 K IBSE transforms into the final reaction products, i.e. butene oligomers.

In this work we used ^{13}C CP/MAS NMR in combination with two-dimensional

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[1] To whom correspondence should be addressed.

(2D) *J*-resolved ^{13}C solid state MAS NMR to follow the pathways of the transfer of the ^{13}C atom from the CH_2 group of *i*-BuOH to various positions in IBSE intermediate and final oligomeric products.

2. Experimental

Procedures for H-ZSM-5 zeolite synthesis and treatment as well as *i*-BuOH adsorption were the same as in ref. [11].

^{13}C NMR spectra were recorded using cross-polarization and magic angle spinning (CP/MAS) at 100.613 MHz with a Bruker MSL-400 spectrometer at 296 K as described in ref. [11]. Heteronuclear two-dimensional *J*-resolved MAS spectra were recorded using the following pulse sequence: $90°C(^{13}C)–t_1–180°C(^{13}C)/180°C(^1H)–t_1$–acquisition [12,13]. Proton high power decoupling was used during the second half of the evolution period and acquisition time. Increment in t_1 between experiments was 0.5 ms. The increment in t_1 was synchronized with an integer number of rotor periods. Rate of the sample spinning was 2000 Hz. The length of both ^{13}C and ^1H 90° pulses was 4.9 μs. 32 experiments were recorded with a 4 s recycle delay. 960 transients were accumulated per experiment. Sweep width in F1 dimension was 500 Hz. FIDs in F1 dimension were zero-filled to 128 points to give digital resolution of 7.8 Hz per point. Gaussian apodization in the F1 and F2 dimensions and power calculation were used for the data processing, followed by a symmetrization.

3. Results and discussion

Fig. 1A represents ^{13}C CP/MAS NMR spectrum of the initial *i*-BuOH, selectively enriched with 80.5% ^{13}C in the CH_2 group (*i*-BuOH[1-^{13}C]). The intense signal at 74.9 ppm belongs to the labelled CH_2 group, while the weak signal at 19.2 ppm belongs to the CH_3 group with the natural ^{13}C abundance. According to ref. [11], heating of the zeolite sample with adsorbed *i*-BuOH[1-^{13}C] at 373 K results in the complete dehydration of the initial *i*-BuOH and formation of IBSE with the intense signal at 73.0 ppm from the labelled CH_2 group and the signals at 31.8 and 19.2 ppm from the initially unlabelled CH and CH_3, groups, respectively (fig. 1B). Figs. 1B and 1C show that the intensity of the signal of the CH_3 group of IBSE at 19.2 ppm increases with respect to the signals of the labelled CH_2 groups of the initial alcohol (fig. 1A) and IBSE (figs. 1B and 1C) as the temperature rises from 296 to 398 K. Furthermore, a new signal at 30.5 ppm appears at 373 K, and its intensity increases upon further heating up to 413 K (figs. 1B–1D). After heating above 413 K the intensity of the signal at 30.5 ppm decreases, while the signals from the final products, i.e. butene oligomers, increase (see figs. 1E and 1F).

Increase of the relative intensity of the signal at 19.2 ppm with respect to the signal at 73.0 ppm indicates that the ^{13}C label of IBSE is transferred from the CH_2

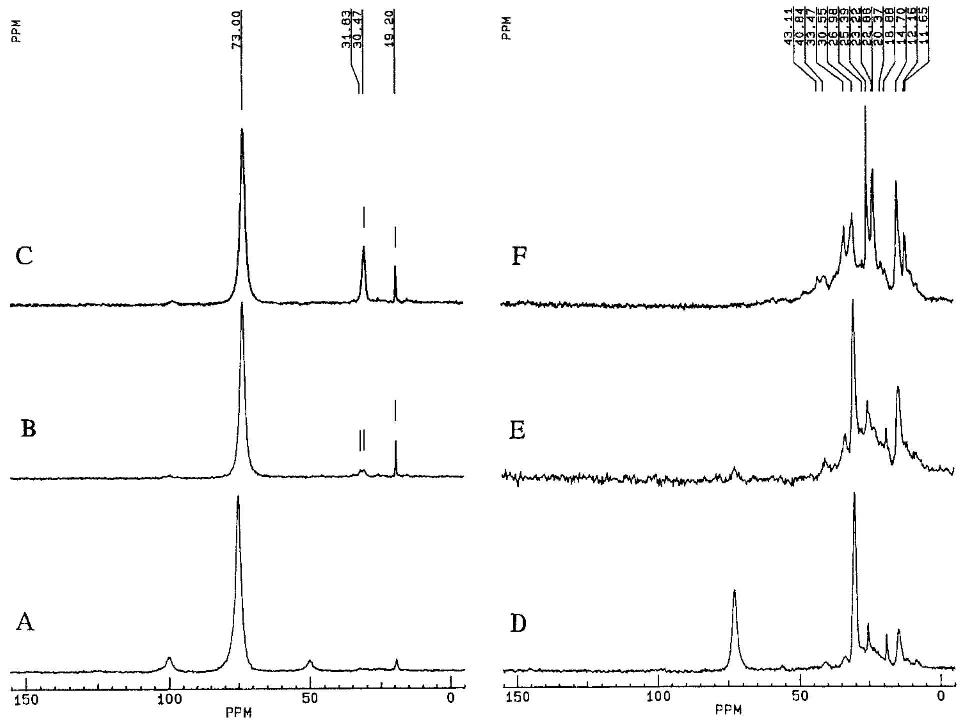


Fig. 1. The change of the ^{13}C CP/MAS NMR spectrum of *i*-BuOH[1-^{13}C], adsorbed on H-ZSM-5 zeolite (Si/Al = 24) at 296 K in the amount 283 μmol/g, upon successive heating of the sample for a certain period of time at various temperatures: (A) after adsorption on zeolite at 296 K; (B) 70 min at 343 K and 30 min at 373 K; (C) 40 min at 398 K; (D) 60 min at 413 K; (E) 60 min at 423 K; (F) 60 min at 448 K.

group into the CH_3 group. The growth of the signal at 30.5 ppm at the expense of the signal at 73.0 ppm indicates the transfer of the ^{13}C label carbon also into some other CH_n ($n = 0$–3) fragment which is different from the CH_2 and CH_3 groups of IBSE. This new signal at 30.5 ppm was preliminary ascribed by us to the CH_2 group of butene dimer – 2,5-dimethyl-1-hexene [11]. Note, however, that according solely to its position the signal at 30.5 ppm cannot be unambiguously ascribed to a CH_n fragment with the certain value of n [14].

To reliably assign the signal at 30.5 ppm to the definite CH_n group, two-dimensional (2D) *J*-resolved ^{13}C NMR [13] has been used. This technique allows for adsorbed species both to improve the resolution of the NMR signals in the F2 dimension, as compared to the one-dimensional ^{13}C CP/MAS NMR spectrum, and to observe in the F1 dimension the multiplicity of ^{13}C signals that arises from scalar ^{13}C–^{1}H nuclear spin–spin interaction with attached protons.

Fig. 2 represents a contour plot of the 2D *J*-resolved ^{13}C NMR spectrum in the vicinity of the signal at 30.5 ppm, that corresponds to the one-dimensional ^{13}C CP/MAS spectrum of fig. 1D. It is seen that the signal at 30.5 ppm in the

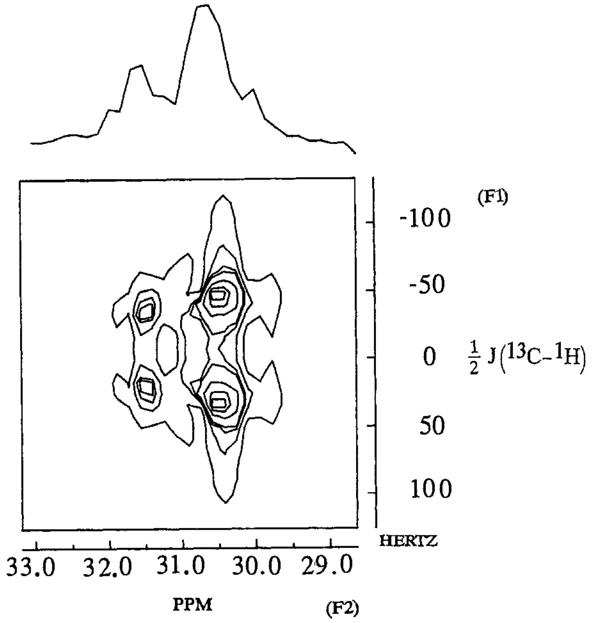


Fig. 2. Contour plot of the 2D *J*-resolved ^{13}C MAS NMR spectrum in the vicinity of the signal at 30.5 ppm. Projection along F2 dimension is given at the top of the contour plot. This spectrum corresponds to the spectrum depicted in fig. 1D. The observed value of scalar ^{13}C–^{1}H coupling ($J(^{13}C–^1H)$) is equal to a half of the real $J(^{13}C–^1H)$, because of using proton high power decoupling during the second half of the evolution time t_1 [13].

^{13}C CP/MAS spectrum of fig. 1D is in fact a superposition of two doublet signals at 30.5 and 31.5 ppm with scalar couplings $J(^{13}C–^1H) = 140 \pm 16$ and 120 ± 16 Hz, respectively. Note, that the observed values of $J(^{13}C–^1H)$ are in a reasonable agreement with $J(^{13}C–^1H)$ scalar couplings found earlier for organic solids with 2D solid state NMR [12,15,16].

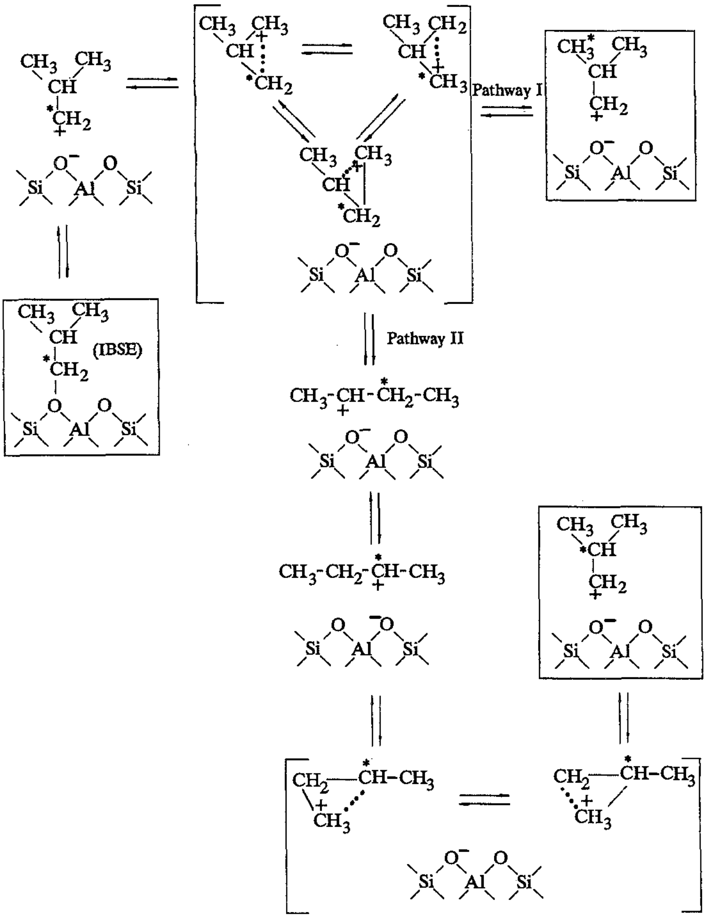
The doublet structure of the signals in fig. 2 shows [17] that the intense line at 30.5 ppm in the spectrum of fig. 1D arises from two CH groups. According to their chemical shifts both these CH signals may be ascribed to the $–CH_2CH(CH_3)_2$ fragments [14].

One of these two isobutyl fragments, namely that with the signal at 31.5 ppm, may be attributed, e.g. to the CH group of IBSE, because it is seen that the spectrum of IBSE (fig. 1B) indeed contains the signal at 31.8 ppm, i.e. in the nearest vicinity of 31.5 ppm. However, an alternative attribution of the signal at 31.5 ppm to the CH group of the $–CH_2CH(CH_3)_2$ fragment of some product of further transformation of IBSE at $T > 373$ K, is also possible.

The other CH signal, namely that at 30.5 ppm, should be ascribed to the CH group of the $–CH_2CH(CH_3)_2$ fragment in some product of further IBSE transformation (i.e. butene oligomer), rather than IBSE itself, since its intensity remains large when the signal of IBSE at 73.0 ppm vanishes (figs. 1E and 1F). Note, that in IBSE the $-CH_2CH(CH_3)_2$ fragment is bound to the oxygen atom of the zeolite framework, while in oligomers it should constitute a part of a longer hydrocarbon skeleton.

Thus, the ^{13}C label is selectively transferred from the CH_2 group of isobutyl fragment of IBSE into CH groups of two different isobutyl fragments and, to a smaller extent, into the CH_3 group of IBSE. One of these two $-CH_2CH(CH_3)_2$ fragments belongs to either IBSE or a butene oligomer, while the other to a butene oligomer, but certainly not to IBSE.

Such selective transfer of the ^{13}C label from the CH_2 group of isobutyl fragment into the CH_3 and CH groups of such fragment, suggests the formation of isobutyl carbenium ion as a reaction intermediate or transition state. Rearrangements of this cation, similar to those observed in solutions [18,19] or solid state [20], can indeed provide such transfer of the ^{13}C label. In scheme 1 possible pathways for the



Scheme 1.

observed selective scrambling of the ^{13}C label are presented. The process starts with the formation of isobutyl carbenium ion from IBSE. As it is seen from figs. 1C and 1D, pathway II for the transfer of the ^{13}C label into the CH group is preferential, as compared to the pathway I for the transfer of the label into the CH_3 group.

Various butenes (butene-1, butene-2, isobutene) can be formed from IBSE via various carbenium ions of scheme 1. The ^{13}C label in them can be located also at various positions, i.e. in CH_n groups with $n = 0, 1, 2$ or 3. Secondary reactions between various butenes and carbenium ions of scheme 1 should generate a family of butene oligomers, where the ^{13}C label is scrambled over the hydrocarbon skeleton. As a result, a variety of signals from aliphatic CH_n groups are observed in the ^{13}C CP/MAS NMR spectrum of the oligomers (see fig. 1F and ref. [11]).

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