Catalysis Letters 13 (1992) 395–405

^{13}C CP/MAS NMR study of isobutyl alcohol dehydration on H-ZSM-5 zeolite. Evidence for the formation of stable isobutyl silyl ether intermediate

Alexander G. Stepanov *, Vyacheslav N. Romannikov and Kirill I. Zamaraev *
Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences,
Novosibirsk 630090, Russia

Received 5 February 1992; accepted 5 March 1992

Dehydration of isobutyl alcohol selectively labelled with a ^{13}C nucleus in the CH_2 group (*i*-BuOH[1-^{13}C]) has been studied on H-ZSM-5 zeolite within the temperature range 296–448 K using ^{13}C CP/MAS NMR. The formation of the isobutyl silyl ether intermediate (IBSE) has been detected. It is stable below 398 K. Within the temperature range 398–423 K IBSE decomposes gradually to produce first a butene dimer, probably 2,5-dimethyl-1-hexene and then other butene dimers and oligomers. At $T > 423$ K scrambling of the selectively labelled carbon of the initial dimeric product over various positions in the carbon skeleton of the final dimers (oligomers) is observed. This is explained in terms of the formation of carbenium ion as the reaction intermediate.

Keywords: Isobutyl alcohol; dehydration; H-ZSM-5 zeolite; isobutyl silyl ether; di-isobutyl ether; carbenium ion; ^{13}C CP/MAS NMR

1. Introduction

Alkoxides, i.e. hydrocarbon fragments covalently bonded to zeolite framework are often assumed to be formed as reactive intermediates in the conversion of hydrocarbons [1–3] or alcohol dehydration [4,5] on zeolites. However, reliable spectroscopic evidence for the existence of alkoxides in zeolite catalysts is still rather limited [1,3].

This work is a part of our studies of the mechanism of dehydration of C_4 alcohols on H-ZSM-5 zeolite [6–10]. We report the results of the ^{13}C CP/MAS NMR study of dehydration of isobutyl alcohol on H-ZSM-5 zeolite into water and butene oligomers, which was carried out with the aim of detecting possible reaction intermediates. We expected that our previous GC and IR studies [7] of

---

* To whom correspondence should be addressed.

© J.C. Baltzer A.G. Scientific Publishing Company

the kinetics of *i*-BuOH dehydration at various temperatures on H-ZSM-5 would help to elucidate the signals from these intermediates in the ^{13}C CP/MAS NMR spectra. *i*-BuOH enriched selectively with ^{13}C nucleus in the carbon atom next to OH group has been used to monitor selectively the transformation of the CH_2 group of the initial *i*-BuOH to CH_3, CH_2 and CH groups of the reaction products. Besides, isobutyl alcohol, labelled with deuterium in CH_3 groups (*i*-BuOH[3-$^2H_6$] has been used to find out via ^2H NMR experiments, whether tert-butyl groups can be formed during the conversion of the initial *i*-BuOH to oligomeric products and water.

2. Experimental

2.1. MATERIALS

Two samples of zeolite H-ZSM-5 with Si/Al = 29 and 24 were prepared from Na-ZSM-5 via NH_4^+ ion exchange and subsequent calcination at 550°C as described in ref. [11]. According to the chemical analysis and ^{27}Al MAS NMR data the absolute concentration of the tetrahedral Al in the samples with Si/Al = 29 and 24 was, respectively, 458 and 527 μmol per 1 gram of the zeolite, that was kept in air. This corresponded to 94% and 93% of tetrahedral Al with respect to the overall amount of Al in these two samples, respectively. As shown by a special experiment, these zeolite samples contained 7.7 wt% of atmospheric moisture.

Isobutyl alcohol selectively enriched with 80.5% ^{13}C in the CH_2 group, i.e. 2-methyl-1-propanol[1-^{13}C], *i*-BuOH[1-^{13}C], contained less than 1% of admixtures. The ^{13}C chemical shift of the selectively labelled carbon atom coincided with that of the CH_2 group of *i*-BuOH with natural ^{13}C carbon abundance, where chemical shifts for CH_3, CH and CH_2 groups were, respectively, 19.22, 31.02 and 69.08 ppm with respect to the internal TMS reference. Isobutyl alcohol selectively enriched with 96.6% deuterium in the CH_3 groups, i.e. 2-methyl-1-propanol[3-$^2H_6$], *i*-BuOH[3-$^2H_6$], contained 1.55% admixture of diethyl ether. Di-isobutyl ether (*i*-Bu_2O) purchased from Aldrich, was distilled over metallic sodium just before its use.

2.2. SAMPLE PREPARATION

For ^{13}C CP/MAS NMR experiments ≈ 0.3 g of zeolite was loaded to a 5 mm glass tube. The sample was then heated at 450°C for 1.5 h in air and for 3–4 h under vacuum at 10^{-5} Torr. After cooling the sample back to room temperature (21–23°C), the zeolite was exposed to the vapour of the previously degassed alcohol (8 Torr) in the calibrated volume (138.5 ml). The procedure of adsorption was repeated for several times until the desired amount of alcohol (280–500 μmol per 1 g of zeolite, i.e. 2–5 wt%) was adsorbed. After the adsorption was over, the sample was immediately placed into liquid nitrogen and then was sealed off. Before recording ^{13}C NMR spectra the glass tube was opened and the sample was transferred into the rotor of the NMR spectrometer. We provided no special conditions to protect the sample from atmospheric moisture while recording ^{13}C CP/MAS spectra. The procedure of *i*-BuOH[3-$^{2}H_6$] adsorption for ^{2}H NMR experiments was the same as in ref. [10].

2.3. NMR MEASUREMENTS

Registration of ^{13}C NMR spectra at 100.613 MHz with cross-polarization and magic angle spinning was performed with a Bruker MSL-400 spectrometer in a 7 mm ZrO_2 rotor under the following conditions: proton high power decoupling field was 14 G (4.2 μs 90° ^{1}H pulse) at Hartmann–Hahn matching conditions $\gamma_C H_{1C}/2\pi = \gamma_H H_{1H}/2\pi = 60$ kHz, contact time 5 ms, delay time between scans (DO) 3 s, spinning rate ≈ 2.6 kHz, number of scans (NS) 600–20000. Temperature of spectra registration was 296 K.

Chemical shifts for carbon nuclei of adsorbed organic molecules were measured with respect to TMS as the external reference. The accuracy in the determination of the relative ^{13}C line positions was ≈ 0.1 ppm.

^{2}H NMR experiments were performed at 61.42 MHz using a high power probe with 10 mm horizontal solenoid coil following the same procedure as that described in ref. [10].

3. Results and discussion

3.1. ON THE FORMATION OF ISOBUTYL SILYL ETHER

It has been shown in ref. [7] that at $T = 296$ K *i*-BuOH dehydration on H-ZSM-5 does not occur to a notable degree, while at $T > 318$ K it proceeds with a noticeable rate. This means that above 318 K the conversion of the initial alcohol will be observed. Fig. 1 illustrates transformation of ^{13}C CP/MAS NMR spectra of *i*-BuOH[1-^{13}C] adsorbed on H-ZSM-5, upon the successive heating of the sample at various temperatures. The intensive line at 74.9 ppm in the initial alcohol belongs to the labelled CH_2 group and the weak line at 19.2 ppm is the signal of the CH_3 group with natural ^{13}C abundance (fig. 1A). Note that chemical shift for CH_3 of the adsorbed alcohol coincides with that for CH_3 in liquid alcohol, while the signal of the CH_2 group for adsorbed alcohol is shifted downfield by 5.8 ppm as compared to that for liquid alcohol.

Figs. 1B and 1C represent the spectra of the sample, that was subsequently heated first at 343 K for 70 min and then at 373 K for 30 min. According to ref. [7], at 343 K about 50% of the alcohol is dehydrated during 1 h and at 373 K more than 96% of the alcohol should be dehydrated for 30 min, provided that the activation energy for dehydration reaction is 19 kcal/mol. This means that the spectrum of fig. 1B represents a superposition of the spectrum of the initial

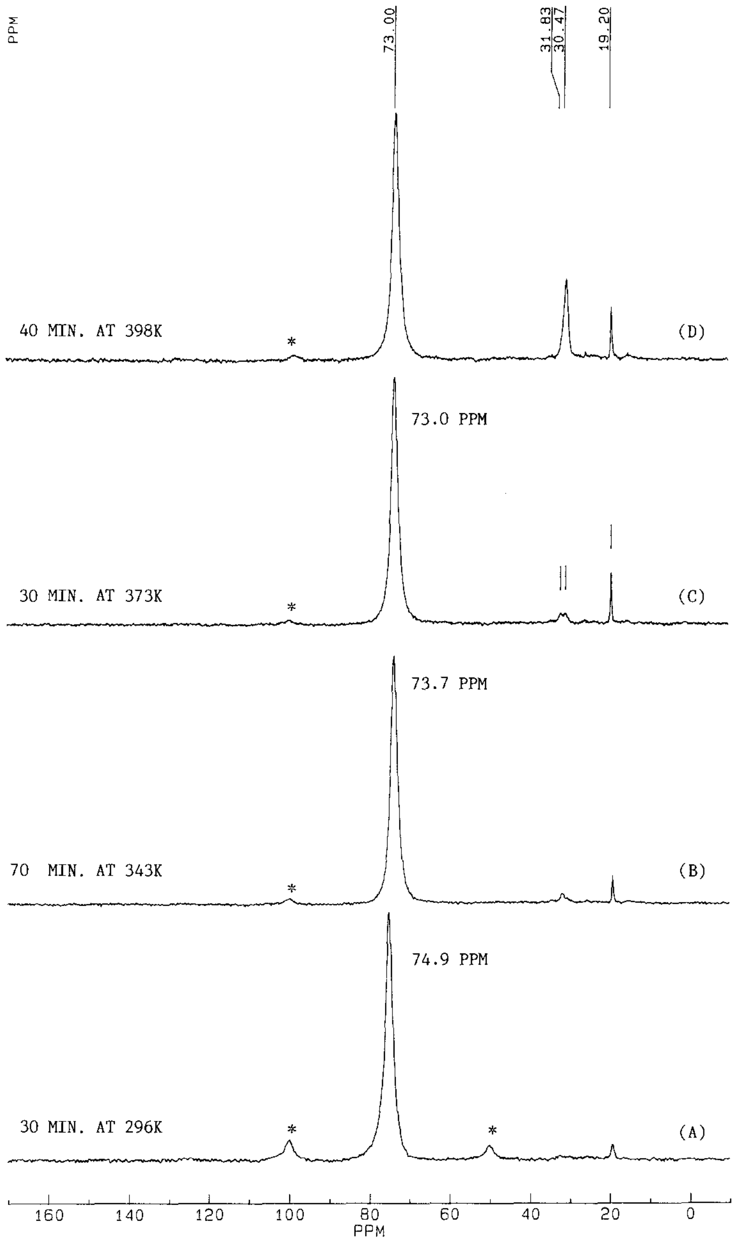


Fig. 1. The change of the ^{13}C CP/MAS NMR spectrum of *i*-BuOH[1-^{13}C], adsorbed on H-ZSM-5 (Si/Al = 24) at 296 K in the amount 283 μmol/g, upon successive heating for a certain period of time at various temperatures. For spectra A–D, NS = 600; for spectrum E NS = 1200; for spectrum F NS = 2200; for spectrum G NS = 1600. Temperature and time of the sample heating are given above each spectrum. * denote spinning sidebands.

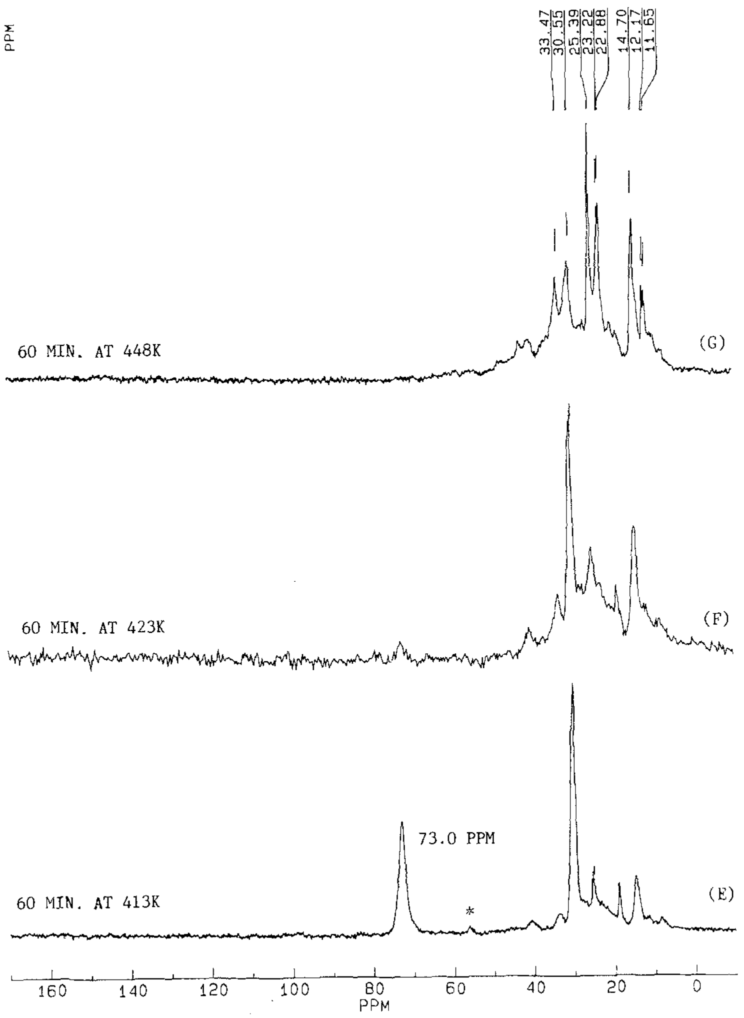


Fig. 1. (continued).

alcohol and the spectrum of some dehydration product, while the spectrum of fig. 1C belongs entirely to the dehydration product. The most intensive line of this product is located at 73.0 ppm. Subsequent increase of the temperature of the sample heating gives rise to the appearance of some new signals and decrease of the line intensity at 73.0 ppm (figs. 1D–1G).

FTIR spectroscopic studies [7] have shown that when dehydration of *i*-BuOH occurs on H-ZSM-5 in the temperature range 318–398 K, a stable intermediate is formed which retains the structure of the carbon skeleton of the initial *i*-BuOH. This intermediate was tentatively suggested to be di-isobutyl ether. If so, then the spectrum of the sample heated at 373 K for 30 min (fig. 1C) should be attributed to di-isobutyl ether (i-Bu_2O). Comparing the ^{13}C chemical shifts for liquid i-Bu_2O [19.61 (CH_3), 29.02 (CH), 78.2 ppm (CH_2)] with those for a

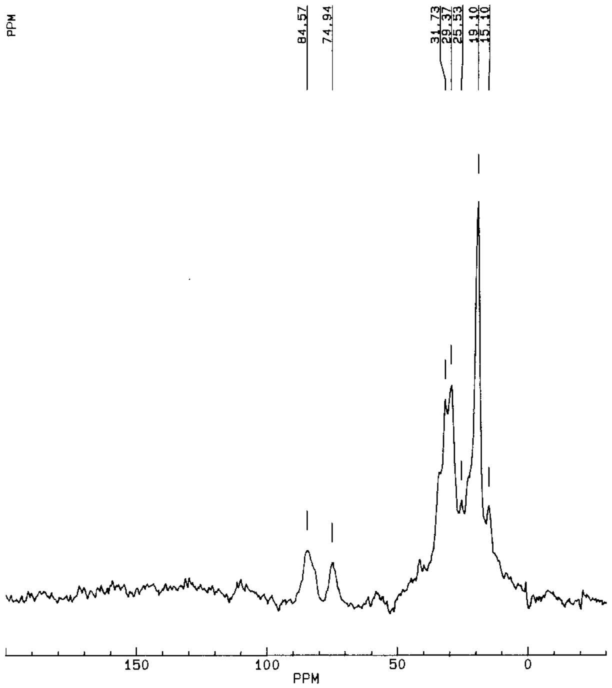
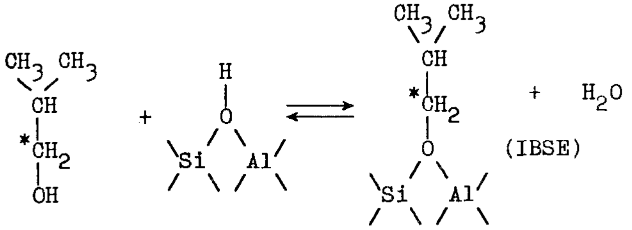


Fig. 2. ^{13}C CP/MAS NMR spectrum of di-isobutyl ether (natural abundance of ^{13}C), adsorbed on H-ZSM-5 (Si/Al = 24) in the amount of 281 μmol/g and retained at 343 K or 3 h, NS = 20000.

liquid *i*-BuOH, one can note that the CH_2 group in *i*-Bu_2O is shifted downfield by 9.13 ppm. Note that upon adsorption on H-form of zeolites a 2–4 ppm downfield shift is usually observed for ^{13}C atoms that are next to the oxygen atom [12]. Therefore, one should expect that the chemical shift for CH_2 group in adsorbed *i*-Bu_2O will exceed 80 ppm. This suggests that the intermediate with the line at 73.0 ppm is in fact different from di-isobutyl ether. The main argument in favour of the conclusion that this line does not belong to *i*-Bu_2O is provided by our direct ^{13}C CP/MAS NMR studies of *i*-Bu_2O adsorbed on H-ZSM-5. We freezed out the vapour of *i*-Bu_2O with the natural ^{13}C abundance in all carbon atoms, on our H-ZSM-5 zeolite at 296 K and then kept the sample for 3 h at 343 K for the *i*-Bu_2O diffusion inside H-ZSM-5 to occur. At 343 K *i*-Bu_2O undergoes the conversion to water and hydrocarbons in the same way as *i*-BuOH. The only difference is that the conversion degree is much less for *i*-Bu_2O [7]. Therefore, it is expected that after heating the sample with adsorbed *i*-Bu_2O for 3 h at 343 K, both the signals of the initial *i*-Bu_2O and those of the products of its conversion should be observed. Fig. 2 shows that there are two signals within the range 70–80 ppm in the spectrum of *i*-Bu_2O. In agreement with the data of fig. 1A, the signal at 74.9 ppm should be ascribed to *i*-BuOH. The second signal at 84.6 ppm can be attributed to the CH_2 group of the unreacted *i*-Bu_2O. The presence of the line at 84.6 ppm for *i*-Bu_2O and the lack

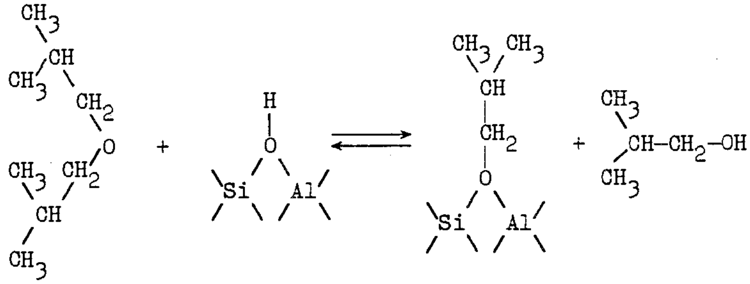


Scheme 1. (* denotes a ^{13}C selectively labelled carbon)

of this line in the ^{13}C NMR spectra of *i*-BuOH dehydration products at 343–448 K (see fig. 1) indicates that *i*-Bu_2O is not formed in a noticeable amount during the dehydration of *i*-BuOH. Thus, we conclude that di-isobutyl ether is not the main product of *i*-BuOH dehydration on H-ZSM-5 within the temperature range 343–373 K.

At the same time the observation of the line at 31.8 ppm for the CH group of the adsorbed *i*-BuOH along with the lines at 19.2 and 73.0 ppm for CH_3 and CH_2 groups in the case of both 50% (fig. 1B) and complete dehydration (fig. 1C), agrees with earlier conclusions [7], that the products of the alcohol dehydration at this temperature range retain the structure of the carbon skeleton of the initial *i*-BuOH. From its position the line at 73.0 ppm from the reaction intermediate can be attributed to a carbon atom that is bound directly to the oxygen atom [13]. This fact, when taken together with the facts that this intermediate retains the hydrocarbon skeleton of the initial alcohol and is formed after the evolution of water from *i*-BuOH is completely over [7], clearly indicates that the observed reaction intermediate is isobutyl fragment bound to the zeolite framework, i.e. the isobutyl silyl ether (IBSE). IBSE is the main product of the dehydration reaction at 343–373 K, and it decomposes at heating above 398 K. The formation of isobutyl silyl ether from *i*-BuOH at $T \leqslant 373$ K, probably, proceeds according to scheme 1.

Observation of the signal at 74.9 ppm from *i*-BuOH in addition to the signal at 84.6 ppm from *i*-Bu_2O after adsorption of *i*-Bu_2O on H-ZSM-5 points to the possible conversion of *i*-Bu_2O according to scheme 2. This scheme shows that the signal at 73.0 ppm from IBSE in addition to the signal from *i*-BuOH should



Scheme 2.

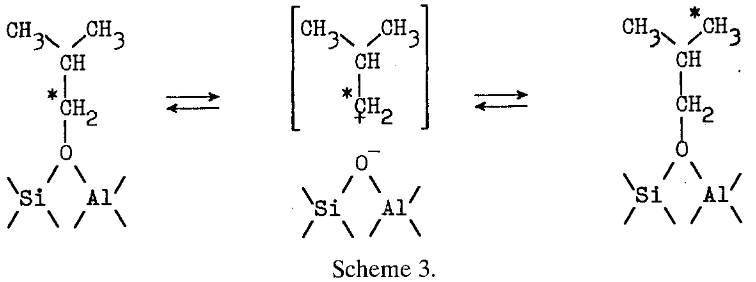
be observed. However, due to only a slight difference in the position of the CH_2 groups in both IBSE and *i*-BuOH and the low signal/noise ratio in the spectrum of fig. 2, one cannot measure the line position accurately enough. Therefore, the signal at 74.9 ppm observed after adsorption of *i*-Bu_2O on zeolite, may in fact belong to the superposition of the lines from CH_2 groups of both IBSE and *i*-BuOH.

3.2. REACTIVITY OF ISOBUTYL SILYL ETHER

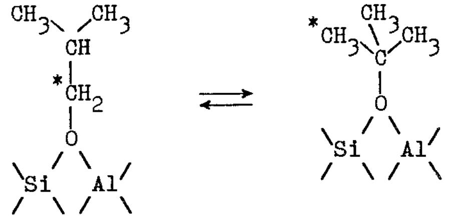
Fig. 1 shows that IBSE formed upon the dehydration of *i*-BuOH is a rather stable species at temperature below 398 K. Its notable conversion starts at 398 K and gives rise to the appearance of the line at 30.5 ppm. At temperature 413 K the intensity of the line of the CH_2 group of IBSE dramatically decreases, and at 423 K this line disappears almost completely. Attention should be paid to the growth of the relative intensity of the line at 19.2 ppm when the temperature increases from 343 to 373 K. Since initial *i*-BuOH is selectively labelled with ^{13}C in the CH_2 group, the increase of the signal at 19.2 ppm in the spectrum of IBSE (fig. 1C) compared to the same signal in the initial alcohol (fig. 1A), indicates that a part of the CH_2 groups in IBSE transforms to the CH_3. This transformation proceeds probably via the carbocationic state, as is indicated in scheme 3.

3.3. ON THE MECHANISM OF CONVERSION OF ISOBUTYL SILYL ETHER TO OLIGOMERIC (DIMERIC) SPECIES

At temperature 373 K and above, a new line at 30.5 ppm appears in the ^{13}C CP/MAS spectrum. At 373 K this line is scarcely visible. Its intensity is close to that of the weak 31.8 ppm signal from the CH group of IBSE. At 398 K the enhancement of the signal at 30.5 ppm is observed (fig. 1D). At 413 K the intensity of this line passes through the maximum (fig. 1E), and then decreases upon further increase of the temperature. Simultaneously with the increase of the line intensity at 30.5 ppm, the decrease of the line intensity at 73.0 ppm from IBSE is observed. This fact points to a rather selective conversion of IBSE to some other species with the line at 30.5 ppm. One of this possibilities can be



Scheme 3.



Scheme 4.

that alongside with the transformation of the CH_2 group in the IBSE into the CH_3 group of IBSE (scheme 3), the transformation of IBSE to the tert-butyl silyl ether (*t*-BuSE) takes place according to scheme 4.

The ^{13}C chemical shift of the CH_3 group of liquid *t*-BuOH is 31.35 ppm, i.e. close to the observed 30.5 ppm signal. Hence, the attribution of the line at 30.5 ppm to *t*-BuSE does not seem unrealistic. However, from the absolute intensity of the 30.5 ppm line it follows, that at 413 K a substantial amount of the IBSE would be transformed into *t*-BuSE (fig. 1E), provided that the equilibrium of scheme 4 does exist.

Our previous study of *t*-BuOH[2-$^2H_9$] dehydration on H-ZSM-5 with ^2H NMR has shown that CD_3 groups of tert-butyl fragments can be selectively distinguished from CH_3 of other fragments via the characteristic shoulders at ±5.8 kHz from the center of the ^2H NMR spectrum [10] (fig. 3A). To prove the presence or absence of tert-butyl groups in the products of *i*-BuOH dehydration we adsorbed *i*-BuOH[3-$^2H_6$] on H-ZSM-5 and performed the heating of the sample within the temperature range 296–413 K in the same manner as that used previously to achieve the maximum intensity of the signal 30.5 ppm in the ^{13}C CP/MAS spectrum of adsorbed *i*-BuOH[1 − ^{13}C]. The ^2H NMR spectrum

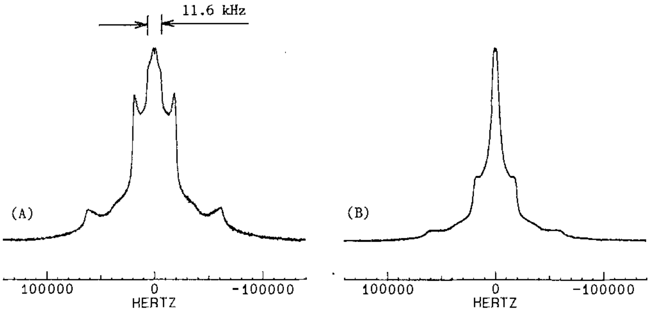


Fig. 3. (A) ^2H NMR line shape for the products of *t*-BuOH[2-$^2H_9$] dehydration on H-ZSM-5 (Si/Al = 29). Alcohol was adsorbed in the amount 565 μmol/g on zeolite, and, then the sample was heated for 1 h at 373 K, NS = 5700, DO = 0.2 s. (B) ^2H NMR line shape for the products of *i*-BuOH[3-$^2H_6$] dehydration on H-ZSM-5 (Si/Al = 24, 548 μmol/g). After adsorption of the alcohol the sample was heated within the temperature range 296–413 K in the same manner as that for the sample of figs. 1A–1E, NS = 5700, DO = 0.4 s. The temperature of the spectra registration for both samples is 173 K.

for *i*-BuOH[3-$^2H_6$] in such sample demonstrates a superposition of the following three solid-like line shape signals: (1) the line of CD_2 and CD groups with quadrupole splitting $(3/4)Q_0 = 123$ kHz, (2) the line of the rapidly rotating CD_3 groups with $(3/4)Q_1 = 37.6$ kHz and (3) the narrow line of D_2O (DHO) signal at the center of the spectrum (fig. 3B) [10]. The signal of tert-butyl groups with a solid-like line shape and $(3/4)Q_2 = 11.6$ kHz which appears in the spectrum of fig. 3A as shoulders at ± 5.8 kHz is not observed in the spectrum of fig. 3B. Thus, we conclude that the line at 30.5 ppm in ^{13}C CP/MAS spectra cannot be attributed to the tert-butyl groups, i.e transformation of IBSE to *t*-BuSE does not occur. Therefore, selective transformation of the line at 73.0 ppm to that at 30.5 ppm reflects subsequent transformation of IBSE to oligomeric species rather than its rearrangement into *t*-BuSE. The selective transfer of the intensity of the line at 73.0 ppm to that of the line at 30.5 ppm, points to the specific mechanism of IBSE conversion to oligomeric products.

One may suppose that the transformation of IBSE to oligomeric species occurs via its interaction with isobutene molecule, that can be formed from IBSE [9]. In general, various routes for the interaction between IBSE and isobutene molecule to produce dimeric species are possible. Of these routes, the one, that reasonably explains the observed selective transformation of the CH_2 group of IBSE, is the interaction of the CH_2 group of IBSE and $=CH_2$ group of isobutene to form 2,5-dimethyl-1-hexene, which is butene dimer. In this case the ^{13}C signal at 30.5 ppm can be assigned to the two labelled CH_2 groups, while the ^{13}C signal of the carbon–carbon double bond (110–140 ppm [13]) will not be observed.

At $T > 413$ K a decrease of the signal at 30.5 ppm from the dimer and appearance of the signals at 11–14 ppm from the terminal CH_3 groups together with the signals at 22–25, 33 ppm from various CH_2 groups of the CH_3–$(CH_2$–$CH_2)_n$– fragments [14], indicate further transformation of the primary dimer (figs. 1F, 1G). It is seen from figs. 1E–1G that the carbon atom of the selectively labelled $^*CH_2$ group of the dimer is distributed over various positions of the hydrocarbon skeleton of the secondary dimers and/or oligomers. Such scrambling of the ^{13}C carbon atom over various functional groups suggests the participation of carbenium ion intermediates or transition states in formation of the final reaction products.

The spectrum of oligomeric products that were formed after the heating of the sample at 448 K contains only ^{13}C signals of aliphatic carbon atoms. There are no signals in the region of the carbon–carbon double bond of the olefinic species at 110–140 ppm as well as ^{13}C signals at 60–90 ppm of the carbon atoms bound to the oxygen atom [13]. In principle, the lack of these signals in ^{13}C NMR spectra may be due to their large line width. However, the width of the line of CH_2 group in IBSE, i.e. of carbon atom bound to the oxygen atom of the zeolite framework, is only 240 Hz. Therefore, we assume that if final dimeric/oligomeric products were bound to the zeolite framework, then the signal at 60–80 ppm of the carbon atoms bound to the oxygen atoms of zeolite would be observed.

The width of ^{13}C signals at the double bond of the olefins sorbed by zeolites may exceed 1 kHz at ambient temperature [1]. Moreover, when scrambling of the ^{13}C label over various positions in the hydrocarbon skeleton of the oligomers occurs, the intensity of the signals from the double bonds may become rather small. Thus, we cannot exclude unambiguously that double bonds are present in oligomers, but their ^{13}C signals are unobservable because of their large line width and low intensity. Note however, that in the IR studies of *i*-BuOH and *t*-BuOH dehydration on H-ZSM-5 also no stretching bands near 1640 cm^{-1} and above 3000 cm^{-1} from the $\rangle C{=}CH_2$ and C–H fragments of olefins have been revealed for the final dehydration products [7,15]. These facts were tentatively explained in terms of formation of the species bound to zeolite framework [7], or by obscuring of these bands by broad vibrational bands of the zeolite [15]. One more alternative is that oligomeric species have the structure of cycloalkanes, which do not have olefinic double bonds. Thus, further studies are needed to clarify the nature of oligomeric species formed in H-ZSM-5 zeolite in reaction of the alcohol dehydration.

References

[1] J.F. Haw, B.R. Richardson, I.S. Oshiro, N.D. Lazo and J.A. Speed, J. Am. Chem. Soc. 111 (1989) 2052.

[2] V.B. Kazansky and I.N. Senchenya, J. Catal. 119 (1989) 108.

[3] N.D. Lazo, J.L. White, E.J. Munson, M. Lambregts and J.F. Haw, J. Am. Chem. Soc. 112 (1990) 4050.

[4] M.T. Aronson, R.J. Gorte, W.E. Farneth and D. White, J. Am. Chem. Soc. 111 (1989) 840.

[5] C. Pereira, G.T. Kokotailo, R.J. Gorte and W.E. Farneth, J. Phys. Chem. 94 (1990) 2063.

[6] C. Williams, M.A. Makarova, L.V. Malysheva, E.A. Paukshtis, E.P. Talsi, J.M. Thomas and K.I. Zamaraev, J. Catal. 127 (1991) 377.

[7] C. Williams, M.A. Makarova, L.V. Malysheva, E.A. Paukshtis, K.I. Zamaraev and J.M. Thomas, J. Chem. Soc. Faraday Trans. 86 (1990) 3473.

[8] M.A. Makarova, C. Williams, J.M. Thomas and K.I. Zamaraev, Catal. Lett. 4 (1990) 261.

[9] M.A. Makarova, C. Williams, V.N. Romannikov, K.I. Zamaraev and J.M. Thomas, J. Chem. Soc. Faraday Trans. 86 (1990) 581.

[10] A.G. Stepanov, A.G. Maryasov, V.N. Romannikov and K.I. Zamaraev, J. Chem. Soc. Faraday Trans., submitted.

[11] V.N. Romannikov, V.M. Mastikhin, S. Hočevar and B. Držaj, Zeolites 3 (1983) 311.

[12] C.E. Bronnimann and G.E. Maciel, J. Am. Chem. Soc. 108 (1986) 7154.

[13] A.J. Gordon and R.A. Ford, *The Chemist Companion* (Mir, Moscow, 1976) p. 309 (in Russian).

[14] J.P. van den Berg, J.P. Wolthuizen, A.D.H. Clague, G.R. Hays, R. Huis and J.H.C. van Hooff, J. Catal. 80 (1983) 13.

[15] M.T. Aronson, R.J. Gorte and W.E. Farneth, J. Catal. 105 (1987) 455.