^{13}C CP/MAS and ^{2}H NMR study of tert-butyl alcohol dehydration on H-ZSM-5 zeolite. Evidence for the formation of tert-butyl cation and tert-butyl silyl ether intermediates

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The dehydration reaction of tert-butyl alcohol, selectively labelled with ^{13}C in CH_3 or C–O groups (*t*-BuOH[2-$^{13}C_1$] and *t*-BuOH[1-^{13}C]), as well as selectively deuterated in methyl groups (*t*-BuOH[2-$^{2}H_9$]), was studied on H-ZSM-5 zeolite simultaneously with ^{13}C CP/MAS and ^{2}H solid state NMR. When adsorbed and dehydrated on zeolite at 296 K, *t*-BuOH[2-$^{13}C_1$] and *t*-BuOH[1-^{13}C] give rise to identical ^{13}C CP/MAS NMR spectra of oligomeric aliphatic products. This is explained in terms of the fast isomerization of the tert-butyl hydrocarbon skeleton via the formation of tert-butyl cation as the key reaction intermediate. An alkoxide species, most probably tert-butyl silyl ether (*t*-BuSE), was also detected as the "side" reaction intermediate. This intermediate was stable within the temperature range 296–373 K and decomposed at 448 K to produce additional amounts of final reaction products, i.e. butene oligomers. NMR data point to the existence of equilibria between the initial tert-butyl alcohol, tert-butyl cation and butene that is formed from the intermediate carbocation.

Keywords: tert-butyl alcohol, dehydration, H-ZSM-5 zeolite, tert-butyl cation, tert-butyl silyl ether, mechanism of reaction

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1. Introduction

Mechanisms of the reaction of tert-butyl alcohol dehydration on H-ZSM-5 zeolite have been intensively studied using IR, kinetic GC [1,2] and ^{13}C NMR [3]. However, the conclusions of earlier works remain rather controversial. On the one hand, observation of the IR and ^{13}C spectra of the intermediate carbenium ions or alkoxy species was reported [1,3]. On the other hand, it was reported that IR spectra of these intermediates could not be observed, because of the fast isomerization and oligomerization of the primary hydrocarbon product, i.e. butene [2].

In this work, which is a part of our systematic kinetic and spectroscopic studies of dehydration of C_4 alcohols on H-ZSM-5 [2,4–6], we report the results of our study of the mechanism of tert-butyl alcohol dehydration simultaneously with ^{13}C CP/MAS and ^{2}H solid state NMR. Two different tert-butyl alcohols, selectively labelled with ^{13}C in CH_3 or C–O groups were used in ^{13}C CP/MAS NMR experiments to follow selectively the transfer of the primary and quaternary carbon atoms of tert-butyl alcohol to the final reaction products, i.e. butene oligomers. Furthermore, *t*-BuOH selectively deuterated in methyl groups was used in ^{2}H NMR experiments to follow selectively the transfer of the deuterium atoms of the tert-butyl group $(CD_3)_3C$ to butene oligomers and water. We expect that the results of our previous kinetic study of *t*-BuOH dehydration in H-ZSM-5 zeolite with GC and IR methods [2] will help us to assign the signals in the ^{13}C CP/MAS and ^{2}H NMR spectra more reliably and to identify the signals from reaction intermediates.

2. Experimental

Two H-ZSM-5 zeolite samples with Si/Al = 29 and 24 were used in this work. They were obtained and characterized following the procedures described in ref. [4]. Concentration of the tetrahedral Al in the samples with Si/Al = 29 and 24 was, respectively, 458 and 527 μmol per 1 g [4]. 82% ^{13}C enriched in the C–O group tert-butyl alcohol, *t*-BuOH[1-^{13}C], b.p. 83°C, contained 3 mol% pentane admixture. 67% ^{13}C selectively enriched in the CH_3 group tert-butyl alcohol, *t*-BuOH[2-$^{13}C_1$], contained less than 2 mol% admixtures. *t*-BuOH labelled with deuterium in methyl groups, *t*-BuOH[2-$^{2}H_9$], contained 99% of the main substance with deuterium enrichment 99.5% and water content less than 0.2%.

Procedures of sample preparation and their subsequent treatments before recording NMR spectra were the same as those described in refs. [4,5]. ^{13}C CP/MAS and ^{2}H NMR spectra were recorded with a Bruker MSL-400 spectrometer under the same experimental conditions as those in refs. [4,5], respectively.

3. Results

3.1. ^{13}C CP/MAS NMR STUDY OF THE DEHYDRATION OF *t*-BuOH[1-^{13}C]

Figs. 1 and 2 show ^{13}C CP/MAS NMR spectra of *t*-BuOH, selectively labelled with ^{13}C in the C–O group, against time after the exposure of the alcohol to the zeolite. Two groups of signals are clearly distinguished: the signal at 81.7 ppm, which is in the region typical for carbon atoms bonded to the oxygen atom [7], and the signals in the region of 14–40 ppm that are typical for carbon atoms in saturated aliphatic hydrocarbons [8]. With increasing time interval after the alcohol adsorption there is a diminution in the intensity of the signal at 81.7 ppm. Figs. 1 and 2 show that the line at 81.7 ppm disappears completely only after the zeolite sample has been kept at 296 K for 15.5 h (figs. 1E and 2E). As the intensity of the line at 81.7 ppm decreases, a weak and broad line (line width ≈ 1 kHz) at 86 ppm can be clearly observed (fig. 2). Subsequent heating of the sample at 373 K for 1 h (figs. 1E and 2E) results neither in the disappearance of the signal at 86 ppm nor in any changes of the signals in the region 14–40 ppm (figs. 1F and 2F). The signal at 86 ppm disappears only after heating the sample at 448 K for 1 h (fig. 2G).

3.2. ^{13}C CP/MAS NMR STUDY OF THE DEHYDRATION OF *t*-BuOH[2-$^{13}C_1$]

Figs. 3 and 4 show the spectra of *t*-BuOH, selectively labelled with ^{13}C in the CH_3 group, against time after the exposure of the alcohol to the zeolite. Two groups of signals are clearly distinguished: the intense line at 29.7 ppm, which is in the vicinity of the line from the CH_3 group of the liquid alcohol (31.71 ppm), and the signals at 14–40 ppm from aliphatic fragments. In addition, a broad signal of weak intensity at ≈ 86 ppm is observed (figs. 3 and 4), which is quite similar to that observed for the case of *t*-BuOH[1-^{13}C] (vide supra).

The ^{13}C CP/MAS NMR spectrum of adsorbed *t*-BuOH[2-$^{13}C_1$] after it has been kept for 15 h at 296 K (figs. 3 and 4) coincides with that of *t*-BuOH[1-^{13}C], recorded under similar conditions (figs. 1 and 2). It can also be seen that the spectra of the sample with BuOH[2-^{13}C] that was heated at 373 and 448 K, are similar to those of the *t*-BuOH[1-^{13}C] sample that was kept in the same experimental conditions (compare figs. 3 and 4 with figs. 1 and 2). In particular, the following characteristic changes in the spectra of the *t*-BuOH[1-^{13}C] and *t*-BuOH[2-$^{13}C_1$] samples that were heated at 448 K, compared to those of the samples that were kept at 296 K, should be mentioned: disappearance of the signal at 86 ppm and changes in the relative intensities of the signals in the region of the aliphatic carbon atoms (14–40 ppm). Note that we observed no signals in the region of the carbon–carbon double bonds (110–140 ppm [7]) both when keeping the samples of both labelled alcohols at 296 K and after heating them at 373 and 448 K.

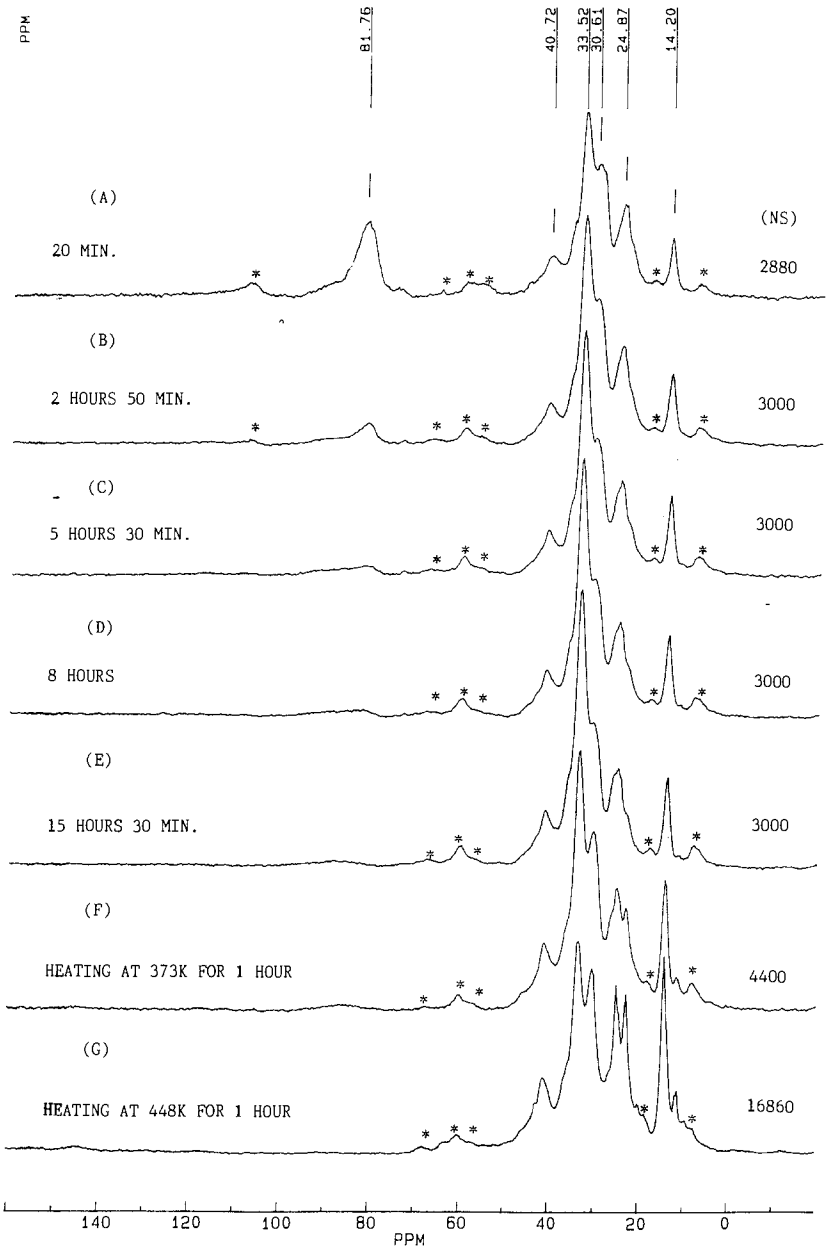


Fig. 1. Variation of the ^{13}C CP/MAS NMR spectra at 296 K of t-BuOH[1-^{13}C] adsorbed on H-ZSM-5 with Si/Al = 24 in amount $C_a = 262$ μmol/g, against time after the exposure of the alcohol vapour to the zeolite: (A)–(E) The sample was kept at 296 K for various times. The time given above spectra (A)–(E) corresponds to the start of signal accumulation. (F) Sample (E) was subsequently kept at 373 K for 1 h. (G) Sample (F) was subsequently kept at 448 K for 1 h. The number of scans (NS) is given above each spectrum. The delay time between scans DO = 3 s. (*) denote spinning sidebands.

3.3. ^{2}H NMR STUDY OF THE DEHYDRATION OF t-BuOH[2-$^2H_9$]

The line shape of the ^{2}H NMR spectrum of the zeolite sample with adsorbed t-BuOH[2-$^2H_9$] that was kept at 296 K for 20 min, represents a superposition of three signals: the weak line of the CD_2 and/or CD groups with the quadrupole splitting $(3/4)Q_0 = 123$ kHz, the weak line of the rapidly rotating (around the C–C bonds) CD_3 groups with the splitting $(3/4)Q_1 = 37.6$ kHz and the most intense line with the splitting $(3/4)Q_2 = 11.6$ kHz, which belongs to the $(CD_3)_3C$

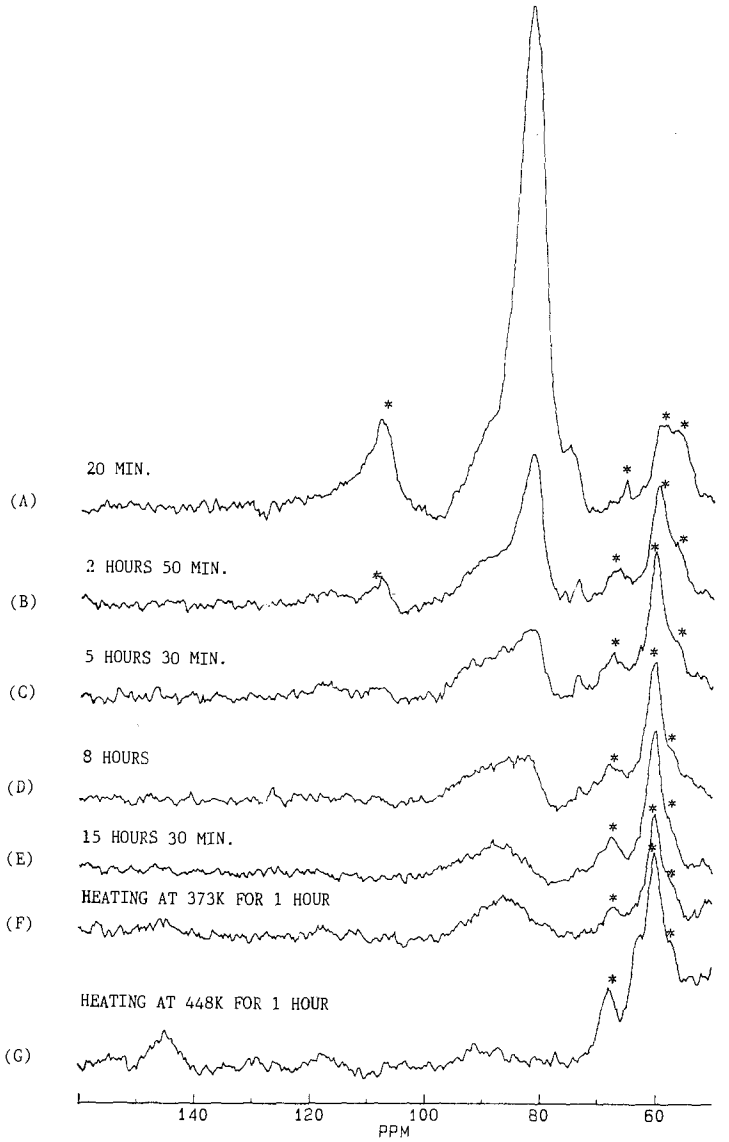


Fig. 2. Eight-fold extension of the region 50–150 ppm for ^{13}C CP/MAS NMR spectra of t-BuOH[1-^{13}C] adsorbed on H-ZSM-5. Spectra (A)–(G) correspond to those in fig. 1.

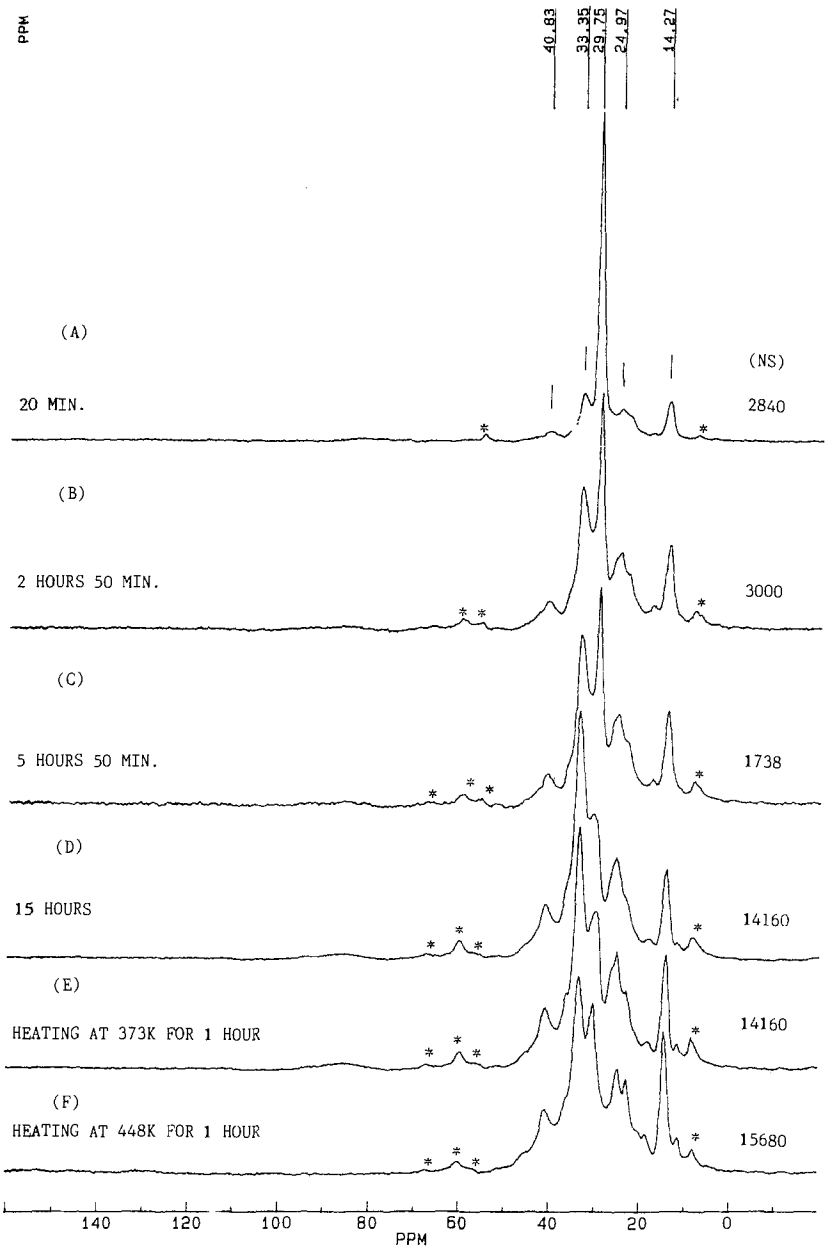


Fig. 3. Variations of the ^{13}C CP/MAS NMR spectra at 296 K of t-BuOH[2-$^{13}C_1$] adsorbed on H-ZSM-5 with Si/Al = 24 in amount $C_a = 282$ μmol/g, against time after the exposure of the alcohol vapour to the zeolite: (A)–(D) The sample was kept at 296 K for various times. The time given above spectra (A)–(D) corresponds to the start of signal accumulation. (E) Sample (D) was subsequequently kept at 373 K for 1 h. (F) Sample (E) was subsequently kept at 448 K for 1 h. The number of scans (NS) is given above each spectrum. The delay time between scans DO = 3 s. (*) denote spinning sidebands.

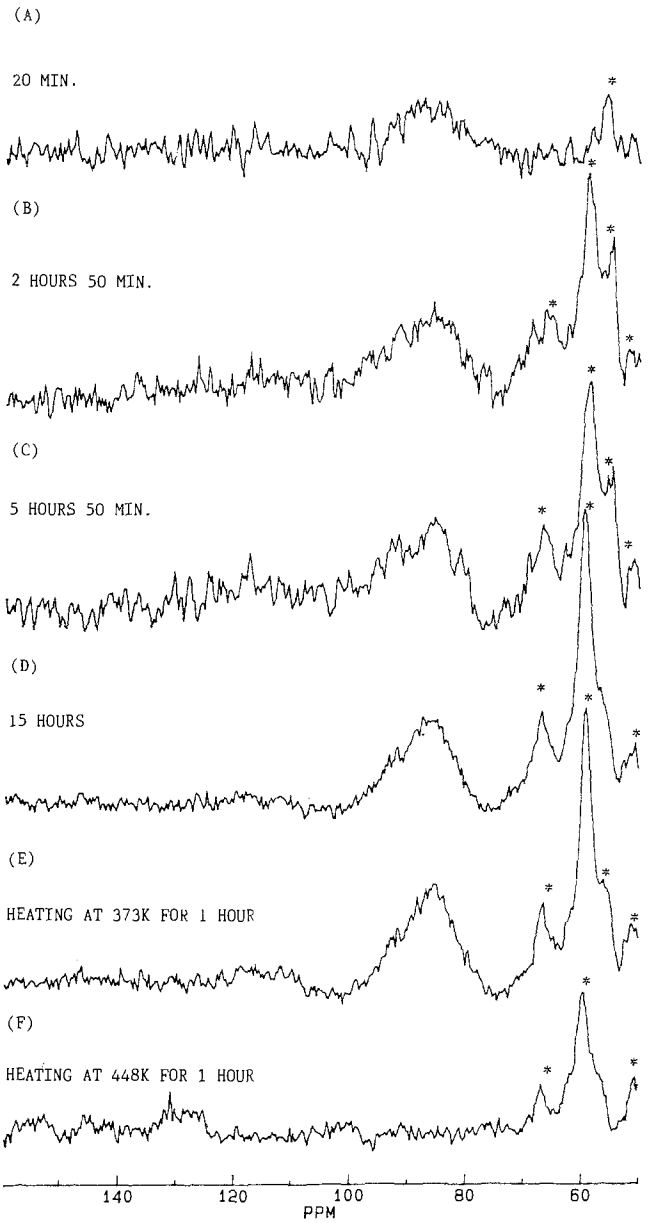


Fig. 4. Eight-fold extension of the region 50–150 ppm for ^{13}C CP/MAS NMR spectra of t-BuOH[2-$^{13}C_1$] adsorbed on H-ZSM-5. Spectra (A)–(F) correspond to those in fig. 3.

group of tert-butyl alcohol [5] (fig. 5A). The spectrum recorded after the zeolite sample with adsorbed t-BuOH[2-$^2H_9$] had been kept at 373 K for 1 h (fig. 5B) should be assigned to the final oligomeric species and water [2,5]. This spectrum represents a superposition of several lines; only two of them with quadrupole

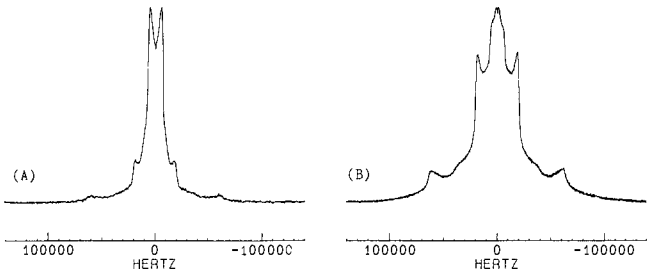


Fig. 5. ^2H NMR line shapes for t-BuOH[2-$^2H_9$], adsorbed at 296 K on H-ZSM-5: (A) After adsorption the sample was kept at 296 K for 20 min (Si/Al = 24, C_a = 260 μmol/g), NS = 1100, delay time between scans DO = 0.4 s; (B) After adsorption the sample was kept at 373 K for 1 h (Si/Al = 29, C_a = 214 μmol/g), NS = 5700, DO = 0.2 s. The temperature of spectra recording is 173 K.

splittings 37.6 and 123 kHz can be reliably attributed to CD_3 and $CD_2(CD)$ groups of oligomeric species.

In order to assign the rest of the signals observed in the ^2H NMR spectrum, we carried out ^2H NMR inversion-recovery experiments that are ordinarily used to measure spin–lattice relaxation times [9]. The following four lines are clearly distinguished in the inversion-recovery spectra (fig. 6): (1) The line with the quadrupole splitting $(3/4)Q_2 = 11.6$ kHz. The time τ_0, when the intensity of this NMR line turns from the inverted negative position to the normal positive one, i.e. passes through zero, is approximately 10 ms. This line is observed most clearly in the spectrum with the delay time $t_v = 55$ ms. (2) The line with $(3/4)Q_1 = 37.6$ kHz and $\tau_0 \approx 15$ ms. (3) The line with $(3/4)Q_0 = 123$ kHz and $\tau_0 < 10$ ms. (4) The line with $(3/4)Q_3 = 1.9 \pm 0.1$ kHz. For this line $\tau_0 \approx 55$ ms.

Thus, inversion-recovery experiments for dehydration products allow us clearly to reveal two additional lines with quadrupole splittings $(3/4)Q_2$ and $(3/4)Q_3$. The first of them has the same quadrupole splitting $(3/4)Q_2$ as that for the $(CD_3)_3C$ group in t-BuOH[2-$^2H_9$], and thus should be attributed to tert-butyl groups in the reaction products. It cannot belong to the initial t-BuOH[2-$^2H_9$], since from the data of figs. 1–4, as well as from our previous kinetic studies of t-BuOH dehydration [2] we know that t-BuOH molecules do not survive heating at 373 K for 1 h. The signal with $(3/4)Q_3$ belongs to D_2O (or DHO) [5], that can be formed as a result of H/D isotope exchange between CD_3 groups and H_2O [1]. Subsequent heating of the zeolite sample at 448 K leads to the disappearance of the signal with $(3/4)Q_2 = 11.6$ kHz from the $(CD_3)_3C$ groups in the dehydration products (fig. 7). In this case, ^2H NMR inversion-recovery spectra show only the signals of $CD_2(CD)$ groups and CD_3 groups of different mobilities [5] and the signal of water molecules with $(3/4)Q_3 = 1.9$ kHz.

4. Discussion

4.1. IDENTIFICATION OF ^{13}C NMR SIGNALS FROM UNREACTED ALCOHOL AND ALIPHATIC FRAGMENTS OF BUTENE OLIGOMERS

Aronson et al. [3] were the first to observe the signal of labelled ^{13}C carbon of the C–O group in adsorbed *t*-BuOH[1-^{13}C] near 80 ppm. The large value of the additional downfield chemical shift for the carbon atom adjacent to the OH

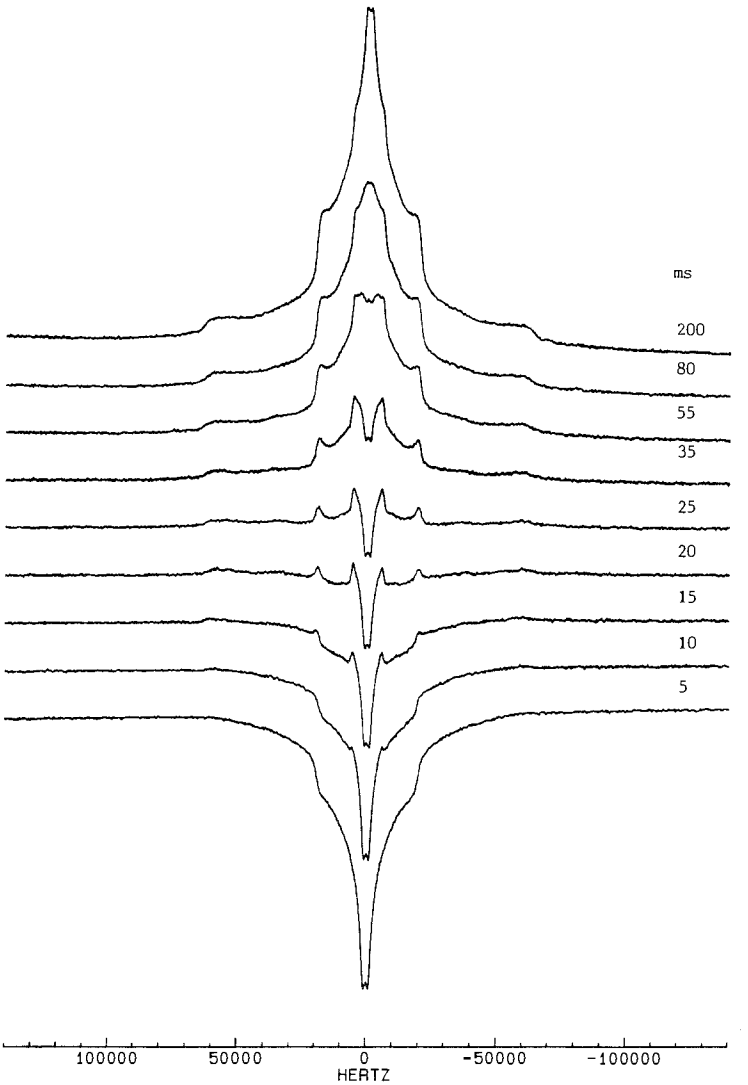


Fig. 6. ^{2}H NMR inversion-recovery spectra recorded at 243 K for dehydration products of *t*-BuOH[2-$^{2}H_9$] on H-ZSM-5 (Si/Al = 29, C_a = 214 μmol/g). After alcohol absorption the sample was heated at 373 K for 1 h. Delay time t_v between inverting 180° and probing 90° pulses is given above each spectrum. For all spectra NS = 1500, DO = 0.4 s.

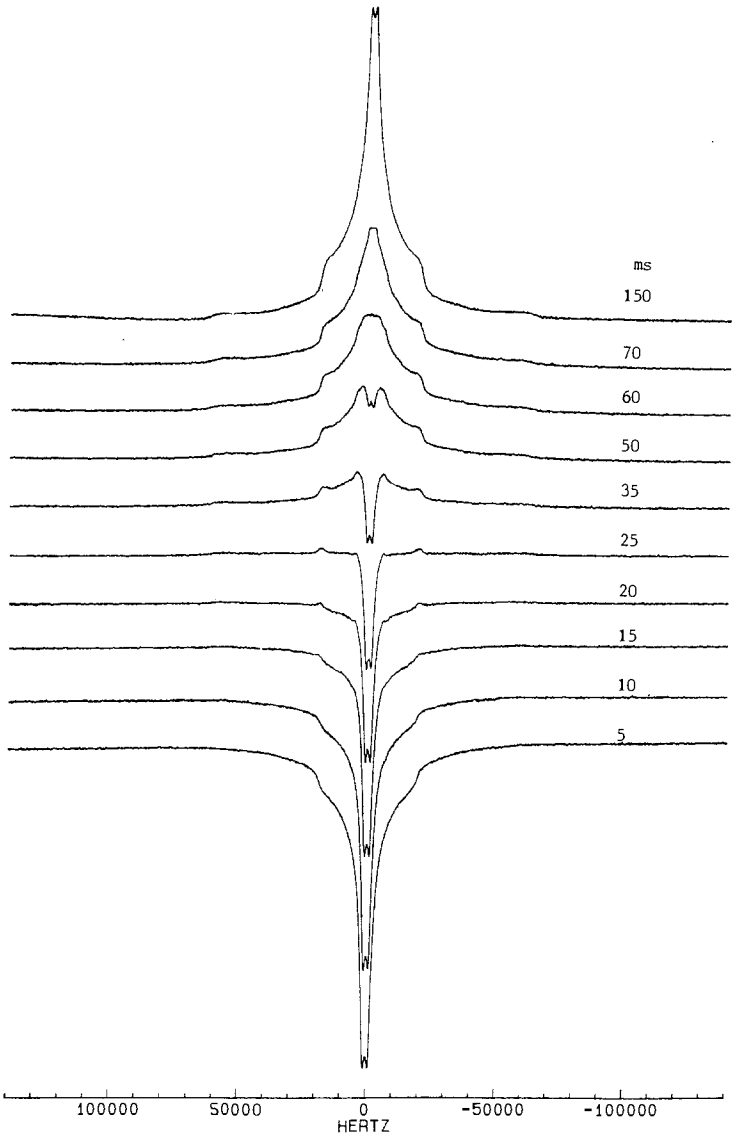


Fig. 7. ^2H NMR inversion-recovery spectra recorded at 243 K for dehydration products of t-BuOH[2-$^2H_9$] on H-ZSM-5 (Si/Al = 29, C_a = 214 μmol/g). After the alcohol had been absorbed on the zeolite, the sample was heated at 373 K for 1 h and then at 448 K for 1 h. t_v is given above each spectrum. For all spectra NS = 1500, DO = 0.4 s.

group in adsorbed alcohol (77 ppm in Aronson's experiment and 81.7 ppm in our experiment) with respect to that in liquid alcohol (68.97 ppm) was probably the main argument in favour of attributing this signal to the intermediate alkoxy species. Aronson's suggestion would be correct, if water abstraction from the alcohol occurred at 298 K very rapidly and were completed within the first 20

min following alcohol adsorption. However, at 298 K, dehydration proceeds slowly and the rates of oligomerization and isomerization of butene released from the alcohol essentially exceed the rate of water abstraction [2]. Moreover, only 30% of the alcohol is dehydrated into oligomeric species within the first 20 min after its exposure to the zeolite, and dehydration of the remaining alcohol occurs slowly for more than 5 h [10]. It means that 20 min after adsorption the spectra of reaction intermediates can be observed only against the background of more intense lines from the unreacted alcohol and from the oligomeric species. Therefore it is reasonable to assign the slowly decreasing signals at 29.7 and 81.7 ppm in the spectra of our samples with adsorbed *t*-BuOH[2-$^{13}C_1$] and *t*-BuOH[1-^{13}C] that were kept at 296 K, respectively, to the primary and quaternary carbon atoms of the unreacted alcohol, and increasing signals at 14–40 ppm to aliphatic fragments of butene oligomers (figs. 1–3).

The reason for the additional 12.7 ppm shift of the ^{13}C signal of the C–O group in adsorbed alcohol with respect to that in liquid alcohol can be explained by perturbating action of the zeolite on both bond angles and bond lengths in the alcohol molecule [5,11].

As it can be seen from figs. 1–4, *t*-BuOH molecules selectively labelled with ^{13}C in the C–O or CH_3 groups, give rise to identical signals from the reaction products in the region of 14–40 ppm with nearly the same ratios between the line intensities. Besides, both types of labelled alcohols give the same broad signal at 86 ppm, which appears at 296 K within 20 min after adsorption. Similarity of the ^{13}C CP/MAS NMR spectra of the final reaction products, formed upon the dehydration of the alcohols labelled in the different positions, clearly points to the complete scrambling of the primary and quaternary carbon atoms of *t*-BuOH during the dehydration. As a result of this scrambling, the distribution of the ^{13}C label over butene oligomers is the same for the differently labelled alcohols. Such scrambling unambiguously points to the existence of carbocations as reaction intermediates or transition state [12]. Perhaps, tert-butyl cation (*t*-BuC)* is formed initially at 296 K as a reaction intermediate, and then it participates in various rearrangements, similar to carbocations in solution and in the solid state [13,14]. These rearrangements result in the scrambling of the ^{13}C label over the C_4 skeleton. Further interaction of *t*-BuC with isobutene, which is probably in a dynamic equilibrium with *t*-BuC, may result in a variety of linear and branched oligomeric (presumably C_8) species where ^{13}C is again scrambled over the hydrocarbon skeleton.

We did not observe in our ^{13}C spectra the signals from tert-butyl cation. "Static" *t*-BuC is known to exhibit the signals at 48 and 330 ppm [15]. In the case of rapid scrambling of the ^{13}C label over all the carbon atoms, a single line

* Arguments in favour of the formation of tert-butyl cation rather than other cations are given below.

at (3/4)48 + (1/4)330 = 118.5 ppm should be observed. However, we have not detected the characteristic signals from *t*-BuC at either 330 or 118.5 ppm. This phenomenon can be explained by a rather small stationary concentration of the *t*-BuC intermediate.

4.2. ASSIGNMENT OF THE ^{13}C SIGNAL AT 86 ppm

Based on its position, the ^{13}C signal at 86 ppm should be assigned to a carbon atom bound to the oxygen atom. This signal appears simultaneously with the signals of aliphatic carbon atoms and has a peak intensity of only $\approx 3\%$ with respect to the most intensive signal in the region 14–40 ppm.

The line at 86 ppm belongs to a reaction intermediate, which is stable up to 373 K and is destroyed following heating at 448 K. Two alternative assignments may be proposed for the signal at 86 ppm: (1) tert-butyl silyl ether Si–(*t*-BuO)–Al, that can be formed directly upon the interaction of *t*-BuOH with the Si–OH–Al group of the zeolite or in the secondary reaction between the Si–OH–Al group and isobutene formed upon the dehydration of *t*-BuOH, or (2) oligomers in the form of alkyl silyl ethers Si–OR–Al, where $R = C_nH_{2n+1}$, $n \geqslant 8$. It is difficult to choose unambiguously between these two possibilities. However, possibility (1) looks to us preferential on the ground of the following arguments. Upon heating the sample at 448 K, the following three important changes occur simultaneously in the ^{13}C CP/MAS and ^{2}H NMR spectra: (1) the ^{13}C signal at 86 ppm disappears; (2) the ^{13}C signal intensity at 33.5 ppm slightly decreases, while the rest ^{13}C signals between 14–40 ppm slightly increase; (3) the line shape typical for tert-butyl group disappears from the ^{2}H NMR spectra of the final reaction products (fig. 7). Such simultaneous changes in ^{13}C and ^{2}H NMR spectra of the samples heated at 448 K allow us to suggest that we observe disappearance of the tert-butyl group, which has the quaternary carbon atom attached to an oxygen atom of the zeolite framework. In other words, we conclude that the signal at 86 ppm and likely part of the signal at 33.5 ppm belong to tert-butyl silyl ether (*t*-BuSE). Note, that *t*-BuSE cannot be the key intermediate of *t*-BuOH dehydration into oligomers since it survives heating at 373 K for the period of 1 h during which *t*-BuOH has completely disappeared and most of oligomeric species have already been formed. *t*-BuSE is formed from the alcohol as a side product of the reaction in a small amount while the main stream of *t*-BuOH conversion to butene oligomers proceeds via the carbocation as the key intermediate. At 448 K *t*-BuSE is destroyed to form an additional amount of oligomeric species. Note that we did not observe in the ^{13}C NMR spectra of figs. 1–4 the characteristic signals at 110–140 ppm from carbon–carbon double bonds. This means either that these signals are too broad to be observed [16,17], or that oligomers formed upon dehydration of *t*-BuOH are cycloalkanes rather than higher olefins.

4.3. SCRAMBLING OF DEUTERIUM ATOMS OVER TERT-BUTYL ALCOHOL, BUTENE OLIGOMERS AND WATER

Following exposure of D_2O to the zeolite with preliminary adsorbed *t*-BuOH, incorporation of deuterium into the C–H bonds has been observed [1]. This fact was explained by the formation of a carbocation as an intermediate favouring H/D exchange. We agree with this explanation. However, from the data reported in ref. [1], it was not possible to specify the structure of the carbocation intermediate. We have taken advantage of the ^2H NMR to clarify the structure of the carbocation intermediate by following the migration of the deuterium label from D_2O to the reaction products in the course of the dehydration of $(CH_3)_3OH$. Undeuterated *t*-BuOH was adsorbed on H-ZSM-5 and then kept at 296 K for 1 h 40 min. During this time *t*-BuOH was partly dehydrated to produce water and oligomeric species. Then we adsorbed D_2O on this zeolite sample in an amount equal to that of preliminary adsorbed *t*-BuOH. Fig. 8 shows that after the sample prepared in this way was kept for 5 min at 296 K, only the line of adsorbed D_2O with the width of ≈ 10 kHz is observed, i.e. no H/D exchange reaction is observed between the adsorbed *t*-BuOH and the products of its dehydration on the one hand and D_2O on the other hand. Subsequent keeping of the sample at 296 K for 1 h resulted in the appearance of the ^2H NMR line shape with quadrupole splitting $(3/4)Q_2 = 11.6$ kHz, that is

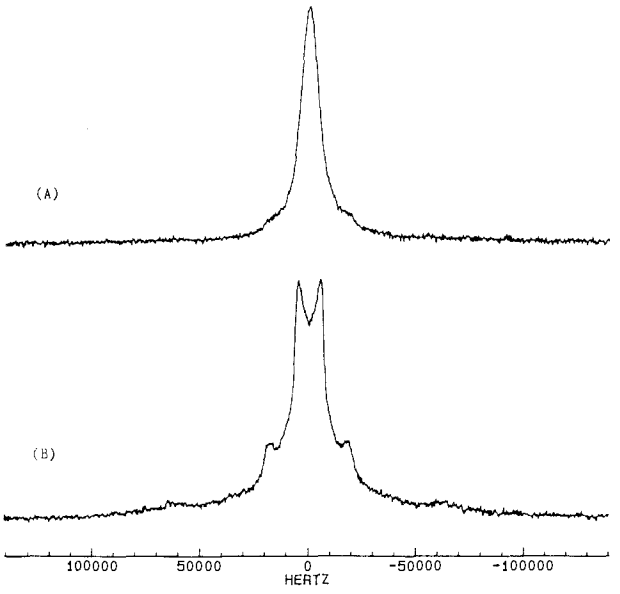
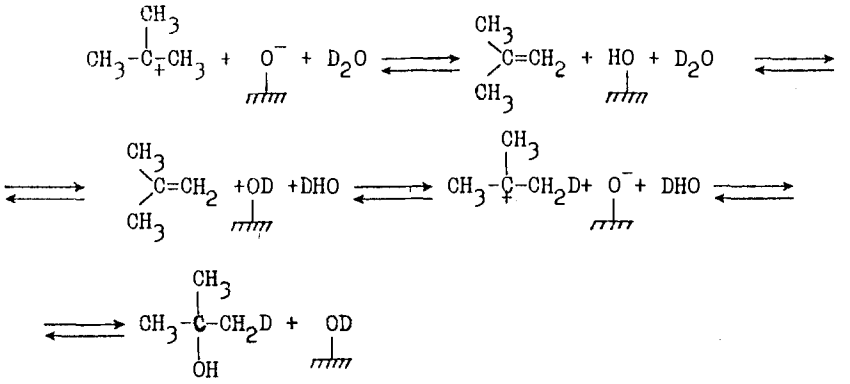


Fig. 8. ^2H NMR spectrum of D_2O, adsorbed on H-ZSM-5 (Si/Al = 24, $C_a = 311$ μmol/g) containing preliminary adsorbed *t*-BuOH ($C_a = 301$ μmol/g), against time after the exposure of the sample to D_2O. (A) The sample was kept at 296 K for 5 min, NS = 2630, DO = 0.4 s. (B) the sample was kept at 296 K for 1 h, NS = 4200, DO = 0.4 s. In both cases the sample with previously adsorbed *t*-BuOH was kept at 296 K for 1 h 40 min. The spectra were recorded at 173 K.



Scheme 1.

typical for the tert-butyl group [5]. Besides the signals of CD_3 and $CD_2(CD)$ groups of butene oligomers with the splittings $(3/4)Q_1 = 38$ kHz and $(3/4)Q_0 = 123$ kHz are also noticeable (compare figs. 8 and 5). Two important conclusions follow from these experiments. (1) Deuterium from D_2O is incorporated both into the tert-butyl groups of the initial alcohol and into the products of its dehydration. (2) The intermediate carbocation that provides such H/D exchange should have the structure of the tert-butyl cation. Otherwise deuterium from D_2O could not be incorporated into the initial *t*-BuOH. (We have checked that no such H/D exchange with D_2O occurred for isobutyl alcohol at 296 K.) Moreover, if the tert-butyl cation were not formed, we would not observe the signal of the C–O group in *t*-BuSE when the initial alcohol was selectively labelled in the CH_3 group. Selectively labelled carbon-13 could hardly penetrate from the CH_3 group into the C–O group of *t*-BuSE without formation of *t*-BuC and its fast rearrangements.

A way of deuterium transfer from D_2O into *t*-BuOH via *t*-BuC as the key intermediate is shown in scheme 1. This scheme includes the stage of H/D exchange between the water molecule and the proton of the zeolite Brønsted acid center, i.e. Si–OH–Al group. To prove the existence of such H/D exchange process at 296 K, we adsorbed H_2O on preliminary deuterated D-ZSM-5 zeolite, prepared as described in ref. [1]. The ^2H NMR spectrum of this system was then recorded. Fig. 9 shows that 15 min after H_2O was adsorbed on D-ZSM-5, the ^2H NMR spectrum that is typical for D_2O on H-ZSM-5 [5] appears. This proves that H/D exchange between H_2O and the Brønsted acid center of the zeolite indeed easily occurs at 296 K.

Thus, experimental data obtained in the present work allow us to suggest the following scheme for the transformation of *t*-BuOH into butene oligomers and water (scheme 2). In the first stage of the reaction, *t*-BuOH is slowly dehydrated to produce tert-butyl cation. tert-butyl cation is a rather labile species, which can participate in rapid skeletal rearrangements, probably via cyclopropane interme-

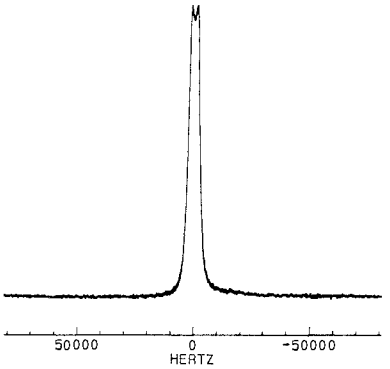
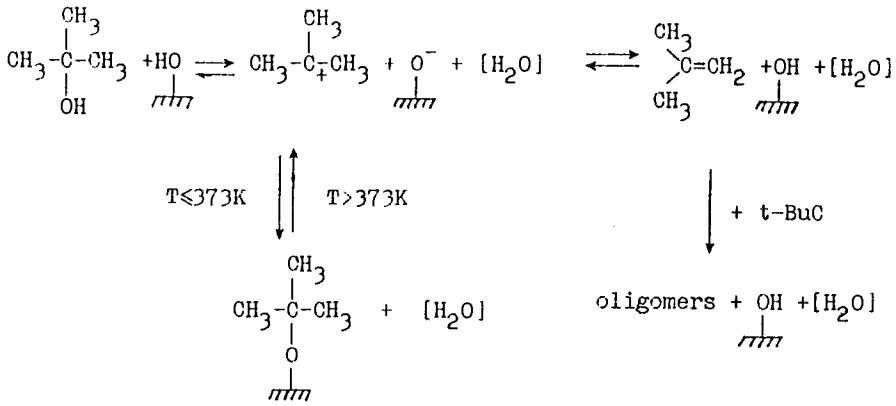


Fig. 9. ^{2}H NMR spectrum of H_2O adsorbed on D-ZSM-5 (Si/Al = 29, C_a = 323 μmol/g, NS = 7650, DO = 0.4 s. We start accumulation of the spectrum 15 min after the exposure of H_2O to the zeolite. The spectrum was recorded at 296 K.

diates [13,14]. This leads to the scrambling of the ^{13}C label over all four carbon atoms of the C_4 skeleton. Moreover, labile *t*-BuC may transform into various other carbocations.

Scheme 2 explains the formation of a small amount of tert-butyl silyl ether as a side reaction intermediate. Scrambling of carbon atoms in its precursor, *t*-BuC, accounts for the transfer of the ^{13}C label from the CH_3 group of the *t*-BuOH[2-$^{13}C_1$] into the C–O group of *t*-BuSe. *t*-BuSE is stable at least up to 373 K. At 448 K it decomposes to produce an additional amount of final reaction products, i.e. butene oligomers.

According to scheme 2, *t*-BuC formed from *t*-BuOH is in dynamic equilibria with both *t*-BuOH and butene. Due to these equilibria, incorporation of deuterium from D_2O into *t*-BuOH takes place. Finally, fast reaction between butene and carbocation gives rise to the oligomeric species. Possible equilibria between carbocations of different structures may lead to a number of oligomeric species with different structures that result in a variety of carbon signals in the



Scheme 2.

region 14–40 ppm. Further studies are needed to characterize these oligomeric species more accurately.

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