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The Nature, Structure, and Composition of Adsorbed Hydrocarbon Products of Ambient Temperature Oligomerization of Ethylene on Acidic Zeolite H-ZSM-5

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The nature, structure, and composition of hydrocarbon products that form under oligomerization of ethylene on acidic zeolite H-ZSM-5 at room temperature (296 K) have been analyzed using a combination of *in situ* IR and ^{13}C NMR and *ex situ* ^{13}C NMR and GC-MS. It is shown that oligomers strongly retained by the zeolite framework represent a mixture of hydrocarbons which composition ranges from C_5 to ca C_{14+} carbon atoms. Adsorbed oligomers are bound to the oxygens of the zeolite framework to form alkoxy species. Alkoxy species represent main adsorption state of the oligomers, but they are in equilibrium with olefins and carbenium ions of the same composition, the concentration of both carbenium ions and olefins seems to be beyond the sensitivity of both NMR and IR. The reactivity of the adsorbed oligomers is defined by the reactivity of equilibrated carbenium ions which can easily interact with carbon monoxide and water to give a mixture of corresponding carboxylic acids. Oligomeric alkoxides with linear hydrocarbon fragments prevail in the mixture of the formed oligomers. The average length of the linear oligomer chain includes approximately seven carbon atoms. Prevalence of the linear hydrocarbon fragments over branched ones in adsorbed oligomers seems to be defined by both specific framework and dimensions of the channels of the zeolite H-ZSM-5. © 1998 Academic Press

1. INTRODUCTION

The nature of adsorbed hydrocarbon products formed under room temperature oligomerization of ethylene or other small olefins on acidic zeolites (e.g., on H-ZSM-5) is unclear so far and remains a subject for discussion (1–17). It is natural to suggest that oligomerization of a small olefin in the presence of acidic catalyst should give rise to the olefin too, but with long hydrocarbon skeleton. However, both *in situ* IR and ^{13}C NMR studies of the oligomeric products formed from the small olefins have not shown the presence of the characteristic signals from olefinic $>C{=}C<$ moiety in IR spectra (1–4, 6–8, 10, 12) at 1660–1670 cm^{-1} [$\nu(C{=}C)$] and 3020–3090 cm^{-1} [$\nu({=}C\text{-}H)$] (18) or in ^{13}C NMR spectra (4, 5, 9, 11, 13–17) at 110–140 ppm (19). Only the signals from paraffinic moiety were registered with both IR and ^{13}C NMR (1–17).

Usually, the lack of the signals from olefinic double bonds in adsorbed oligomers is being explained in terms of two alternative hypotheses. According to the one of the hypotheses adsorbed oligomers represent long chain aliphatic hydrocarbon fragments covalently bonded to the oxygens of the zeolite framework. Thus, a formation of alkyl silyl ethers (alkoxy species, alkoxides) which contain no olefinic double bonds was suggested (11–13, 17). The second hypothesis suggests that oligomers represent carbenium ions (6, 7, 16). They do not contain olefinic double bonds as well.

However, both hypotheses are not free from the contradictions. Indeed, if long chain oligomers are alkoxy species, then the signals from the C-O-Si fragments at 70–90 ppm should be observed in the ^{13}C NMR spectra (19, 20). But, the observation of these signals was never assigned to the long chain oligomeric products (4, 5, 9, 11, 13–17). Such signals were reliably detected (21–23) or reported (14, 17, 24–26) only for the small alkyl fragments bound for the framework oxygens of zeolites. Haw *et al.* observed the signal at 87 ppm from alkoxy species under propene oligomerization on HY zeolite (24). However, this signal was assigned to the long lived alkoxy intermediates in the oligomerization reaction, rather than final oligomeric products. Aronson *et al.* (25) reported the observation of the signal at 77 ppm from both tert-butoxy and oligomeric intermediates under tert-butyl alcohol dehydration and oligomerization on H-ZSM-5. However, further studies of the kinetics of tert-butyl alcohol dehydration on H-ZSM-5 by Williams *et al.* with IR (12) and Stepanov *et al.* with NMR (14) have indicated clearly that the signal at 77 ppm assigned in Ref. (25) to alkoxy species should be attributed to the initial unreacted alcohol, rather than tert-butoxy species or oligomeric alkoxides.

If stable long chain carbenium ions were formed under olefin oligomerization, these cations would exhibit the signals typical for alkyl carbenium ions earlier characterized

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in superacids: at 300–330 ppm in ^{13}C NMR (for C^+ center) (27, 28) or at 1260–1295 cm^{-1} for $\nu(^+C\text{-}C)$ stretch in IR spectra (29, 30). However, the signals from alkyl carbenium ions have never been detected in ^{13}C NMR or IR spectra for the oligomers occluded in acidic zeolites.

The studies of the adsorption on H-ZSM-5 of octene-1, which may be considered as one of the products of the oligomerization of small olefins, e.g., ethylene, have shown that adsorbed octene-1 exhibits the fluxionality typical for carbenium ions (16). Indeed, despite the fact that the signal from carbenium ion center was not detected in adsorbed octene-1, nevertheless a scrambling of the selective ^{13}C label, typical for carbenium ions (27), was observed for this adsorbed molecule at room temperature (16). It was suggested that inability to detect NMR signals from the carbenium ion center or from C-O-Si moiety of the alkoxy species may be related to the specific dynamic behavior of the oligomeric products that can obscure the signals at 70–90 or 300–330 ppm (16, 17). However, this suggestion requires further verification.

The structure and the composition of the adsorbed oligomers formed from ethylene on H-ZSM-5 at room temperature are also still unclear. It has been reported that according to ^{13}C CP/MAS NMR data linear oligomers (5, 9, 13) with ca 16 carbon atoms in the hydrocarbon chain (9) are formed. However, the position of the signals from methylene groups in linear fragments of oligomers and methyl groups in the branched fragments at 20–30 ppm are overlapping in ^{13}C NMR spectrum (19). Therefore, the conclusions on the structure and the length of hydrocarbon chain of oligomer could not be made, basing exclusively on the analysis of the position of the oligomer signals in ^{13}C NMR spectra.

In this paper we have carried out more attentive analysis of both IR and ^{13}C NMR spectra of the adsorbed oligomeric products formed from ethylene on H-ZSM-5. In our revision of IR and ^{13}C CP/MAS NMR spectra we have made an attempt to detect the characteristic signals identifying the nature of adsorbed oligomers. Two-dimensional *J*-resolved ^{13}C NMR was used to *in situ* clarify the structure of adsorbed oligomers. ^{13}C high resolution NMR and GC-MS analyses were applied to characterize the oligomers extracted from zeolite. A combination of all these techniques allows us to completely characterize the adsorbed hydrocarbon products of room temperature conversion of ethylene on zeolite H-ZSM-5.

2. EXPERIMENTAL

Sample Preparation

Zeolite H-ZSM-5 (Si/Al = 44, concentration of strongly acidic Al-OH-Si groups ca 350 μmol/g) was synthesized according to Ref. (31) and further characterized with X-ray powder diffraction and chemical analyses. For *in situ* ^{13}C NMR measurements approximately 0.1 g of the zeolite was placed into a 5-mm OD glass tube and further activated at 723 K for 1.5 h in air and 4 h under vacuum at 10^{-5} torr (1 Torr = 133.3 N m^{-2}). After cooling the zeolite sample to room temperature, ca 1 mmol/g of ethylene-1-^{13}C (40% of ^{13}C isotope enrichment) was adsorbed on zeolite at 296 K for a few hours. The zeolite sample with adsorbed ethylene was then sealed off from the vacuum system and retained at 296 K. For *in situ* NMR measurements the sealed glass tube was then tightly packed into the 7-mm zirconia NMR rotor (32). For conversion of the ethylene oligomers into the corresponding carboxylic acids (33) carbon monoxide and water (ca 350 μmol/g of each coadsorbate) were subsequently adsorbed on the zeolite sample, containing preliminary adsorbed ethylene (1 mmol/g).

For *ex situ* analysis of the hydrocarbon products similar procedure of the zeolite activation and ethylene adsorption was used, but the amount of the zeolite sample was 10 g. The sealed tube was then opened and zeolite sample with adsorbed oligomers was dissolved in 10% NaOH solution. The final solution that formed was neutralized with H_2SO_4, and organic products were extracted with Et_2O. After subsequent evaporation of Et_2O, a residue was dissolved in deuterobenzene and ^{13}C NMR analysis was made.

In case of the GC-MS analysis of the oligomers extracted from the zeolite in the form of carboxylic acids, the acids were preliminarily converted into the corresponding methyl esters by the treatment of a mixture of the acids with the solution of diazomethane in diethyl ether (33).

^{13}C Solid State and High Resolution NMR Measurements

^{13}C NMR spectra with magic angle spinning (MAS), cross-polarization (CP), and high power proton decoupling were recorded at 100.613 MHz (magnetic field of 9.4 Tesla) on a Bruker MSL-400 spectrometer at 296 K. The following conditions were used for recording MAS spectra with CP: proton high power decoupling field was 12 G (4.9 μs 90° ^{1}H pulse), contact time 5 ms at Hartmann–Hahn matching conditions 51 kHz, delay time between scans 3 s, spinning rate 2.4–3.3 kHz, number of scans 600–15000.

^{13}C high resolution NMR measurements were performed on the same NMR spectrometer at 100.613 MHz in deuterobenzene solution at 296 K. The 45° flip angle pulses of 6 μs duration and 10–15 s recycle delay, which justified a 10 T_1 condition were used for spectra acquisition. NMR measurements were carried out with and without broadband proton decoupling. The latter procedure was used to make an assignment of the observed NMR signals to certain CH_n ($n = 0$–3) groups. For quantitative estimation of the relative signal areas broadband proton decoupling was used only during acquisition time. This eliminates nuclear Overhauser enhancement of the signal areas and allows quantitative assessment of the signal areas (34).

^{13}C chemical shifts (δ) for carbon nuclei of adsorbed oligomeric species were measured with respect to TMS as the external reference with accuracy of ± 0.5 ppm. The precision in determination of the relative line position was 0.1–0.15 ppm.

The temperature of the samples was controlled with BVT-1000 variable-temperature unit.

In Situ 2D ^{13}C J-Resolved NMR Measurements

Heteronuclear two dimensional (2D) *J*-resolved ^{13}C MAS NMR spectra were recorded using the following pulse sequence: $90°(^{13}C)$-t_1-$180°(^{13}C)/180°(^{1}H)$-t_1-acquisition (15, 35, 36). Proton high power decoupling was used during the second half of the evolution period t_1 and acquisition time. The increment in t_1 between experiments was 0.5 ms. The rate of the sample spinning was 2000 Hz. The length of both ^{13}C and ^{1}H 90°-pulses was 4.9 μs; 32 experiments were recorded with a 4-s recycle delay; 1200 transients were accumulated per experiment. A sweep width in F1 dimension was 500 Hz. Free induction decays (FIDs) in F1 dimension were zero-filled to 128 points to give a digital resolution of 7.8 Hz per point. Gaussian apodization in the F1 and F2 dimensions and power calculation were used for data processing, followed by a symmetrization.

IR Measurements

IR measurements were carried out in a thermostatted *in situ* IR cell on a Bruker FTIR spectrometer (IFS-113V). The construction of the IR cell is described in more detail in Ref. (37). The zeolite samples were pressed into self-supporting discs (mass typically 25 mg, $\rho = 6$–12 mg/cm^2). The tablets were calcined for 1 h in air and 2 h under vacuum (10^{-4} Torr) at 450°C. The sample was then cooled to room temperature and the IR spectrum of the sample without adsorbed ethylene was recorded for reference purposes. The required amount of ethylene (or ethylene-d_4) (ca 1 mmol/g) was then injected into the cell. Consumption of ethylene by the zeolite sample was completed within 3 h. By plotting the difference between the spectrum with adsorbed ethylene and that of the pure zeolite sample, one can see the spectrum of the adsorbed oligomeric species. A typical number of scans was 200 with a resolution of 4 cm^{-1}.

GC-MS Analysis

For GC-MS analysis the fused silica capillary column of 35 m × 0.3 mm ID in a size with OV-101 as the active phase, forming a film of 0.3 μm thickness, was used in this study. The temperature was programmed from 50°C (2 min) to 280°C at 8°C/min rate. The detector was a mass-spectrometer (VG 70-70), which scanned from $m/e = 20$ to $m/e = 600$ at a cycle time of 4 s.

3. RESULTS AND DISCUSSION

3.1. Analysis of the Nature of the Adsorbed Oligomers

3.1.1. IR Spectra of the Oligomers Formed from Ethylene

Normal (Undeuterated) Ethylene. Our study of the nature of the adsorbed oligomeric products was started with the revision of the IR spectra observed earlier for the products of small olefin oligomerization on acidic zeolites (3, 4, 10, 12). Figure 1 shows IR spectrum of the oligomers formed from ethylene on H-ZSM-5. As it can be seen only the signals from the paraffinic moiety of oligomers can be reliably identified in this spectrum. Intense peaks at 2930 and 2862 cm^{-1} belong to asymmetric ν^{as}(C-H) and symmetric C-H stretch in the -CH_2-groups (18) of the oligomers. The vibration band at 2955 cm^{-1}, which is seen as a left shoulder to the band at 2930 cm^{-1} arises from asymmetric C-H stretch of the CH_3 group of the oligomers. The band at 2862 cm^{-1} may also contain a contribution from the symmetric CH_3 stretch, which is usually of essentially less intensity than the signal from ν^{as}(C-H) of the CH_3 group.

Two peaks at 1468 and 1375 cm^{-1} belong to the deformation vibrations of the -CH_2- and CH_3 groups in oligomeric products. The peaks for the stretching vibration of the acidic bridged Si-OH-Al groups in H-ZSM-5 (12) is observed as "negative" peak at 3615 cm^{-1}. The negative peak shows the decrease in the number of free OH groups in zeolite after ethylene adsorption and its oligomerization. A broad signal centered at 3450 cm^{-1} arises from the bridged OH groups of the zeolite interacting with the oligomer, presumably via a hydrogen bonding (10). The peaks for the olefinic double bond vibrations for ν(C=C) and ν(=C-H) at 1660–1670 and 3020–3090 cm^{-1} that would be evidence for the olefinic nature of the oligomeric products are not identified in the spectrum.

The characteristic signals from $\nu^{as}(C^+$-C) from carbenium ions should be disposed in the spectrum at 1260–1295 cm^{-1} (29, 30). However, this is a region of the IR spectrum with low transmittance frequency range, i.e. where zeolite framework vibrations (ν(Si-O) $\sim$ 1100 cm^{-1} (38)) start to absorb and, therefore, a comparatively weak signal from $\nu^{as}(C^+$-C) may not be reliably identified in the difference spectrum. Indeed, as seen from Fig. 1 there is no signal in the vicinity of 1260–1295 cm^{-1} that could be attributed to carbenium ions.

The $\nu^{as}(C^+$-C) stretch for deuterated analogue of the carbenium ion is shifted by 70–85 cm^{-1} to high frequencies (29, 30). Hence, we expect that the $\nu^{as}(C^+$-C) stretch at 1330–1380 cm^{-1} (29, 30) from the deuterated carbenium ions (if carbenium ions are formed) may be more reliably identified in the spectrum recorded after oligomerization of deuterated ethylene. The region 1330–1380 cm^{-1} is more transparent and less influenced by the strong signal from ν(Si-O) of the zeolite framework.

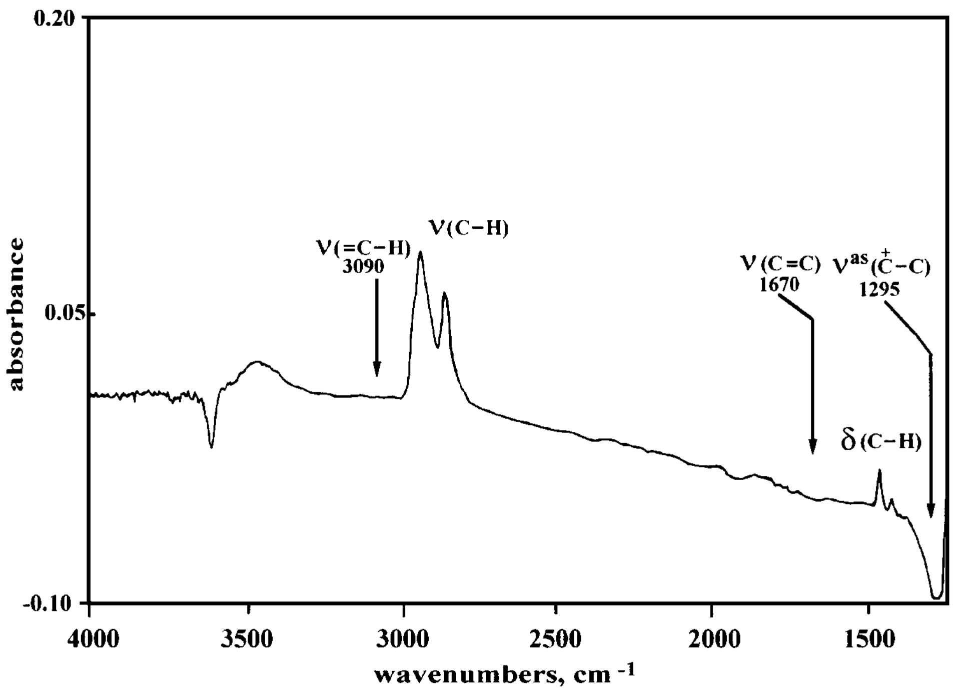


FIG. 1. IR difference spectrum (subtracting the spectrum for the pure dehydrated zeolite) of oligomers formed from ethylene on H-ZSM-5 zeolite at 296 K; 1 mmol/g of ethylene was adsorbed on the zeolite. Vertical arrows in the spectrum show the position of the expected peaks from ν(C=C) and ν(=C-H)) of the olefinic moiety or from ν^{as}(C^+-C) of the carbenium ion moiety of the adsorbed oligomers.

Deuterated ethylene. Figure 2 shows the IR spectrum of the oligomers formed from C_2D_4 on H-ZSM-5 at 296 K. Similar to the case with oligomers formed from C_2H_4, the most intense signals are observed in the region of the paraffinic fragments of the oligomers. The peaks at 2203 and 2088 cm^{-1} belong to the asymmetric and symmetric C-D stretch in the -CD_2- groups of the oligomer. The peaks of small intensity at 2750 and 2665 cm^{-1} belong to ν(O-D) in the terminal Si-OD and bridged Si-OD-Al groups resulted from the H/D exchange between initial C_2D_4 or oligomer

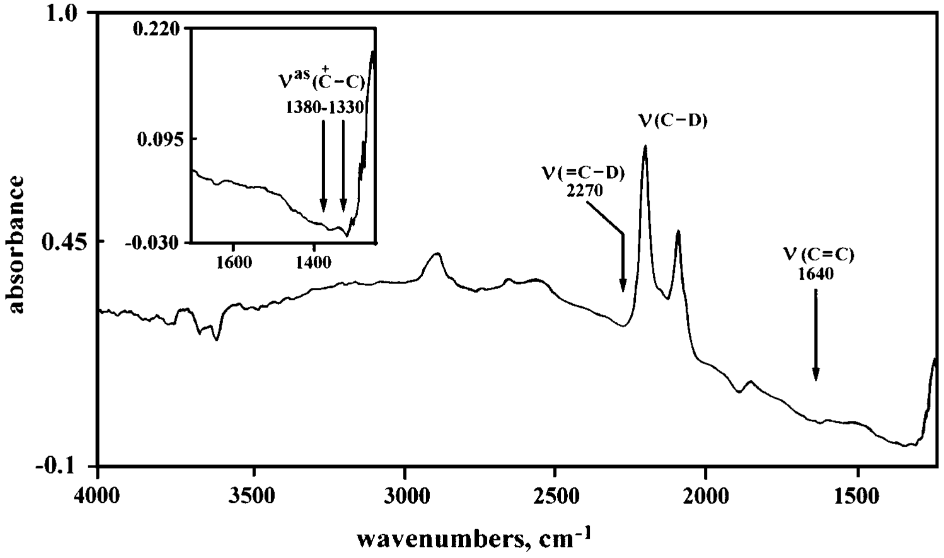


FIG. 2. IR difference spectrum (subtracting the spectrum for the pure dehydrated zeolite) of oligomers formed from deuterated ethylene on the H-ZSM-5 zeolite at 296 K; 1 mmol/g of ethylene-d_4 (99.6% ^{2}H isotope enrichment) was adsorbed on the zeolite. Vertical arrows in the spectrum show the position of the expected peaks from ν(C=C) and ν(=C-D)) of the olefinic moiety or from ν^{as}(C^+-C) of the carbenium ion moiety of the adsorbed oligomers.

and zeolite OH groups. A broad signal at 2560 cm^{-1} is analogous to the broad signal at 3450 cm^{-1} in the spectrum of Fig. 1. According to its position the vibration band at 2895 cm^{-1} is assigned to ν^{as}(C-H) in the methylene -CDH- group of oligomers. This group may form in the H/D exchange between the bridged OH group of the zeolite and the C_2D_4 molecule (1) and/or from penetrating the H atom from the oligomeric methyl CD_2H group, previously formed from the transfer of the zeolite acidic proton of OH group on a C_2D_4 molecule and subsequent scrambling of the H atom over the oligomer skeleton (16).

Similar to oligomers formed from undeuterated ethylene there are no signals at $\sim$2270 and $\sim$1640 cm^{-1} that could be attributed to ν(=C-D) and ν(C=C) (18) and thus shown for the olefinic nature of the oligomers.

As we have mentioned above, the band from the carbenium ion should be observed in this spectrum at 1330–1380 cm^{-1} (29, 30). However, as is seen from Fig. 2 there is no signal in this region (see inserted picture in Fig. 2) that could be reliably assigned to the ν^{as}(C^+-C) stretch of the carbenium ion.

Thus, analysis of the spectra in Figs. 1 and 2 shows that adsorbed oligomers exhibit no vibration bands from both olefinic double bonds and carbenium ion centers. This means that neither long chain olefins nor long chain carbenium ions represent the main adsorption state of the oligomers inside the acidic zeolite.

Further, after this conclusion has been made it is reasonable to assume that long-chain alkoxy species have to be the main adsorption state of the oligomers. This is in agreement with some of the earlier conclusions on the nature of the oligomeric species (see, e.g. Ref. (12)). Alkoxy species should be identified in the IR spectra on the basis of their characteristic ν(C-O) stretch at $\sim$1055–1175 cm^{-1} (39). However, unfortunately, the characteristic IR lines from oligomeric alkoxy species cannot be easily observed against the background of the essentially more intense band at $\sim$1100 cm^{-1} from ν(Si-O) of the zeolite framework (38). In this context, on one hand, our inability to observe with IR the band from ν(C-O) of oligomeric alkoxy species does not prove that these species are not present in the zeolite in a substantial amount. On the other hand, this shows that IR spectroscopy does not represent the method that can be used for reliable identification of the alkoxy species in the zeolites.

In contrast to IR, ^{13}C NMR spectra are not affected by the zeolite framework. Therefore, the C-O-Si groups of oligomeric alkoxy species should be identified with ^{13}C solid state NMR (19–24).

3.1.2. *^{13}C Solid State NMR Spectra of Adsorbed Oligomers*

Identification of the oligomeric alkoxy species. Figure 3 shows the ^{13}C CP/MAS NMR spectrum of the oligomeric products formed under ethylene adsorption on H-ZSM-5 at 296 K. In general, this spectrum is very similar to that obtained earlier for ethylene oligomers formed at room temperature (9): in Ref. (9) the signals at 14, 22, and 33 ppm were assigned to the terminal CH_3 group, -CH_2- group, which is next to the terminal CH_3-, and more distant -CH_2- groups of the oligomers, correspondingly. At first glance the signals that could clarify the nature of the oligomeric species are not identified in this spectrum. Indeed, there are no signals at 110–140 ppm (19) of some notable intensity that would show the olefinic nature of the oligomers. The signals from the carbenium ion center at 300–330 ppm (27, 28) are not identified either in Fig. 3. These experimental facts are in a good agreement with the IR data presented above. At the same time under 32-fold enhancement of the spectrum in Fig. 3 a weak and broad signal at 89 ppm becomes clearly visible. The position of this signal is in the region of the ^{13}C NMR spectrum typical for a carbon atom bound to an oxygen of the zeolite framework (C-O-Si fragment) (20–24) and, therefore, the signal at 89 ppm should be attributed to the alkoxy species. Thus, our experimental finding supports the conclusion based on IR data that inside H-ZSM-5 adsorbed oligomers represent alkoxy species.

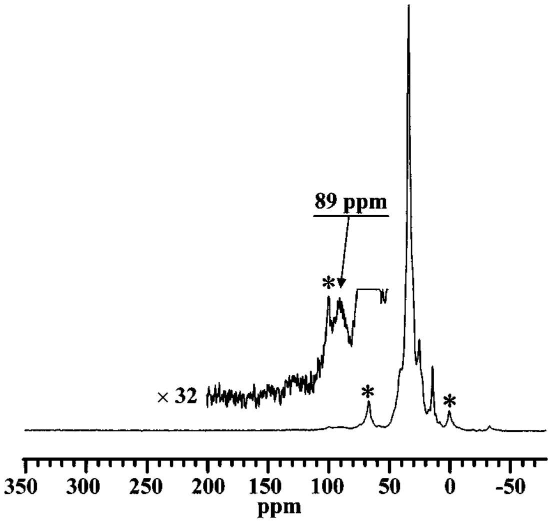


FIG. 3. ^{13}C CP/MAS NMR spectrum for the adsorbed hydrocarbon products of ethylene oligomerization on H-ZSM-5 at 296 K; ^{13}C labeled ethylene ($^{13}CH_2$=CH_2, 40% ^{13}C isotope enrichment) was used for adsorption; 1 mmol/g of ethylene was adsorbed on the zeolite. Asterisks (*) denote spinning side bands.

Carbenium ion properties of the adsorbed oligomers. It follows from the combined IR and ^{13}C NMR data that adsorbed oligomers represent alkoxy species. At the same time, our earlier studies of octene-1 adsorption (it may be formed as one of the products of the ethylene oligomerization) on H-ZSM-5 have shown that adsorbed octene-1 clearly exhibits the fluxionality (16) which is typical for carbenium ions in superacidic solutions (27, 28, 40). Figure 4 shows that upon octene-1[1-^{13}C] adsorption on a zeolite the

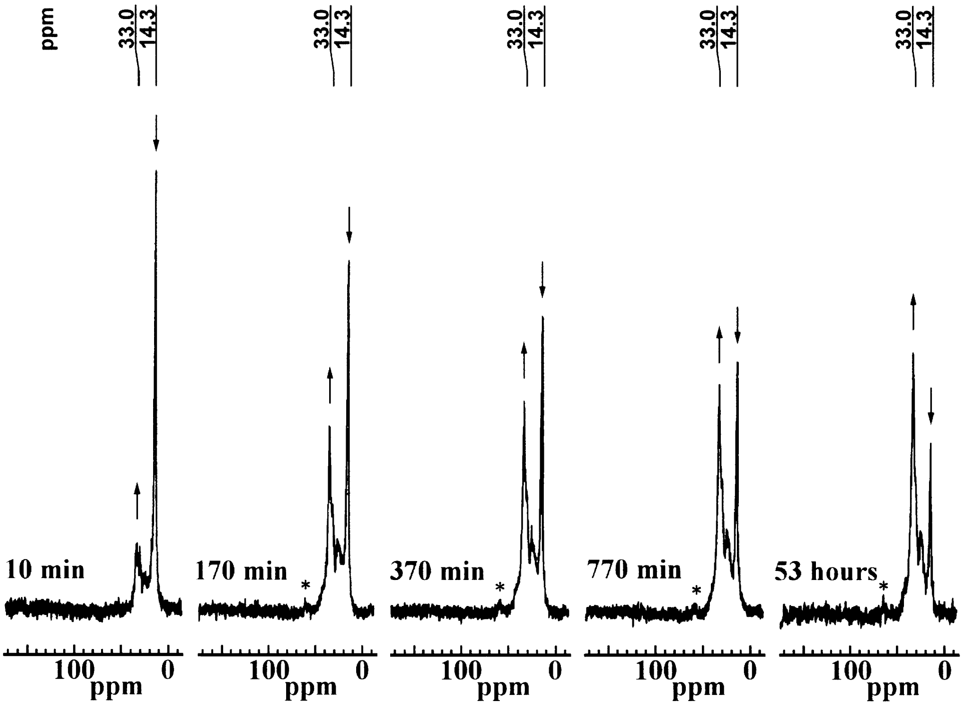
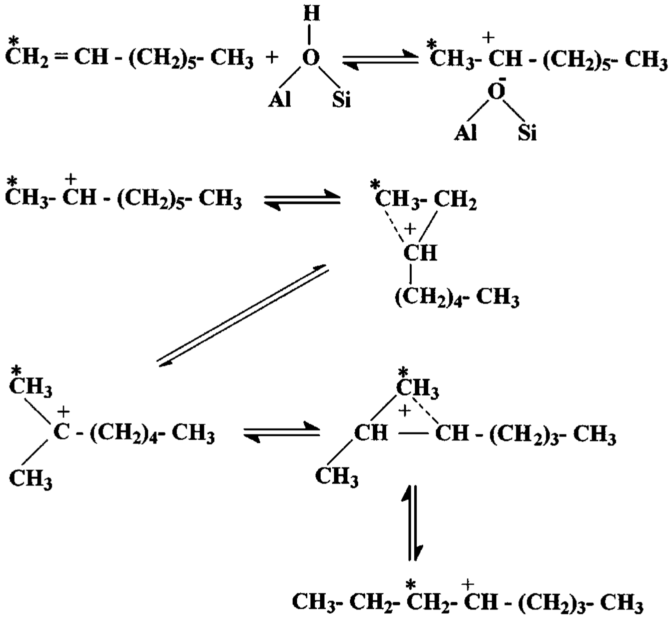


FIG. 4. The change with time of the ^{13}C CP/MAS NMR spectrum of octene-1[1-^{13}C] (labeled with ^{13}C in the terminal $=CH_2$ group) adsorbed on H-ZSM-5. All the spectra were recorded at 290 K after preliminary retaining of the zeolite sample with adsorbed octene-1 at this temperature for the period of time, which is indicated above each spectrum. Asterisks (*) denote spinning side bands. Reproduced from Ref. (16).

terminal ^{13}C-labeled olefinic $=CH_2$ group is transformed into the terminal ^{13}C-labeled paraffinic CH_3 group and, further, the selective ^{13}C-label penetrates into internal CH_2 groups of octene-1 hydrocarbon skeleton. A reasonable explanation of these experimental facts is in accordance with Scheme 1. First, a proton from the acidic OH group of the zeolite is transferred onto an octene-1 molecule, transforming the $=CH_2$ group into the CH_3 group to form a carbenium ion. The selective ^{13}C label is then scrambled over the hydrocarbon skeleton of the carbenium ion formed, as is observed for carbenium ions in superacidic solutions (27, 28, 40). This scrambling results in the growth with time of the intensity of the signals from internal CH_2 groups at 33 ppm and the diminishing of the intensity of the signal from CH_3 group at 14 ppm (Fig. 4).

Thus the scrambling of the selective ^{13}C-label in adsorbed octene-1 at room temperature shows the presence of the carbenium ions among the adsorbed oligomers. Taking into account that signals from carbenium ions at 300–330 ppm are not detected with both IR and ^{13}C NMR, we conclude that the concentration of carbenium ions in zeolite is too low or/and they represent transient species to be identified with IR or ^{13}C NMR.

It should be emphasized here that scrambling the ^{13}C selective labels was observed earlier for isobutylene adsorbed on H-ZSM-5 (41) and among oligomeric products of tert-butyl alcohol dehydration on H-ZSM-5 (14, 25). Those findings shown for carbenium ion formation and participation in olefin oligomerization process. The present finding of ^{13}C label scrambling in the adsorbed oligomeric product shows that carbenium ions are formed not only as an intermediate in the process of olefin oligomerization (14, 25), but a



SCHEME 1. Formation of carbenium ion from octene-1 upon its adsorption on H-ZSM-5 and scrambling of the selective ^{13}C label in the cation formed.

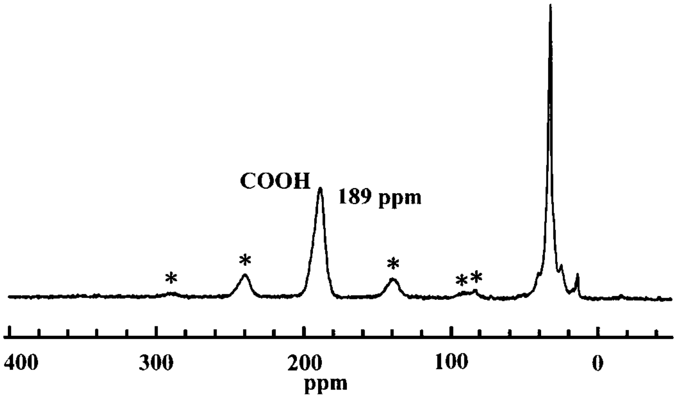


FIG. 5. Trapping of the oligomeric carbenium ions with carbon monoxide. ^{13}C CP/MAS NMR spectrum of adsorbed hydrocarbon products formed after coadsorption of CO and H_2O on zeolite sample with oligomerized ethylene. Unlabeled ethylene and ^{13}CO (90% ^{13}C isotope enrichment) were used for adsorption.

small concentration of carbenium ions always exists among adsorbed oligomeric products.

To substantiate our suggestion that a permanent concentration of carbenium ions exists among adsorbed products of olefin oligomerization we further used the property of carbenium ions (CI) to interact easily with carbon monoxide both in solutions of strong acids (42, 43) and in zeolites (33, 44), even if they form in the small concentration. Oxocarbenium ions that resulted from CI and CO can be quenched with water, carboxylic acids being the final products in this reaction. Hence, to further support that a small fraction of CI is in equilibrium with oligomeric alkoxide, we have made the following experiment. We adsorbed $CO + H_2O$ on the zeolite sample, containing preliminary adsorbed ethylene oligomers. Figure 5 shows the signal at 189 ppm, which points to the conversion of oligomeric alkoxides into the oligomeric carboxylic acids (33, 44), i.e. to a trapping of oligomeric carbenium ion with CO. This experimental fact, in addition to the ^{13}C label scrambling in adsorbed octene-1, clearly show the existence of adsorbed oligomeric carbenium ions which are certainly in equilibrium with oligomeric alkoxides. Note that the NMR spectrum in Fig. 5 exhibits no more weak signals from the oligomeric alkoxides. This indicates that the oligomeric alkoxides are transformed into oligomeric carboxylic acids via the interaction of the equilibrated carbenium ions with carbon monoxide and water (Scheme 2); i.e., the reactivity of the adsorbed oligomers is defined by the reactivity of the carbenium ions as equilibrated species.

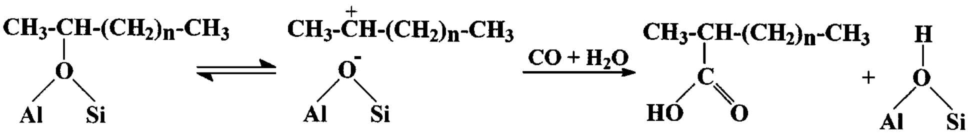
Furthermore, experiments on the conversion of small olefins (ethylene, propylene, butylene) on H-ZSM-5 at $T < 450$ K in the flow reactor indicated the formation of C_6-C_{18} olefins (45, 46). This means that oligomers may desorb as olefins from a zeolite and therefore oligomeric alkoxides are in equilibrium with oligomeric olefins; the concentration of the latter inside the zeolite seems to be beyond the sensitivity (similar to oligomeric carbenium ions) of both experimental methods IR and ^{13}C solid state NMR. Note that quantum-chemical calculations by Kazansky and Senchenya (47, 48) indicate that alkoxy species should be a notably more stable form of olefin adsorption on acidic zeolites than a carbenium ion or olefin. This is in good accordance with our observation of the NMR signals from oligomeric alkoxides and the lack of signals from carbenium ions and olefins in both NMR and IR spectra. At the same time recent theoretical findings by van Santen *et al.* (49) indicate that, although carbenium ions are much higher in energy and essentially less stable than alkoxides, for tertiary carbenium ions larger than C_4 local energy minima can be found, i.e., carbenium ions can indeed exist as metastable states.

Thus, we conclude that adsorbed oligomeric species exist inside an acidic zeolite in the form of three interconverting species (see Scheme 3), long chain alkoxide, carbenium ion, and olefin, alkoxy species being the main adsorption state.

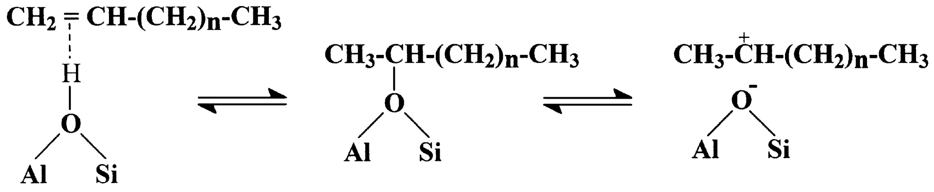
3.2. The Structure and the Composition of the Adsorbed Oligomers

Clarifying the structure of adsorbed oligomers with in situ 2D J-resolved ^{13}C NMR. As we have already mentioned above, the structure of adsorbed oligomers cannot be clarified by attributions of the singlet signals in Fig. 3 at 22–33 ppm to linear or branched fragments of the adsorbed oligomers as was made by van den Berg *et al.* (9), because of the possible overlapping signals from linear CH_2 and branched CH_3 groups (19).

For the assignment of the signals in Fig. 3 to certain CH_n groups ($n = 0$–3) we used two-dimensional (2D) *J*-resolved ^{13}C NMR (50). The advantage of 2D *J*-resolved NMR spectroscopy over usual one-dimensional ^{13}C MAS NMR spectroscopy is that the former allows to obtain information for the observed singlet lines on both chemical shifts



SCHEME 2. Transformation of the oligomeric alkoxides into oligomeric carboxylic acids via interaction of equilibrated oligomeric carbenium ions with CO and H_2O.



SCHEME 3. Interconversion of olefin oligomers adsorbed inside acidic zeolite.

(F2 dimension) and multiplicities ($J(^{13}C\text{-}^{1}H)$ couplings), arising from scalar interaction of carbon atoms with attached hydrogen atoms (F1 dimension) (35, 50). In 2D *J*-resolved ^{13}C NMR spectrum one can attribute singlet lines of carbon signals, which are in F2 dimension, to CH_n groups with the particular values of *n* by just counting the number of peaks of corresponding multiplet signal in F1 dimension (15, 34, 35, 50). Figure 6A represents a contour plot of the 2D *J*-resolved ^{13}C NMR spectrum for ethylene oligomers on H-ZSM-5. The corresponding one-dimensional NMR spectrum is given above the contour plot (Fig. 6B). It can be seen from Fig. 6A that the signals at 30 and 34 ppm represent triplets ($J(^{13}C\text{-}^{1}H) = 140 \pm 16$ Hz), and therefore, these signals should be attributed to the CH_2- groups of oligomers. The signal at 22 ppm is displayed as a singlet in F1 dimension. The position of this signal is in the region of chemical shifts typical for both terminal branched CH_3 group (it should be a quartet in F1 dimension (34)) of the paraffinic hydrocarbon chain and the CH_2 group (it should be displayed as a triplet (34)), which is next to the terminal CH_3 group in linear paraffinic hydrocarbons (19). The observed multiplicity of this signal (singlet) allow us to suggest that the signal at 22 ppm represents unresolved triplet, probably because of its low intensity (15, 36). Thus we conclude that the signal at 22 ppm belong the CH_2 group of the linear fragment oligomer.

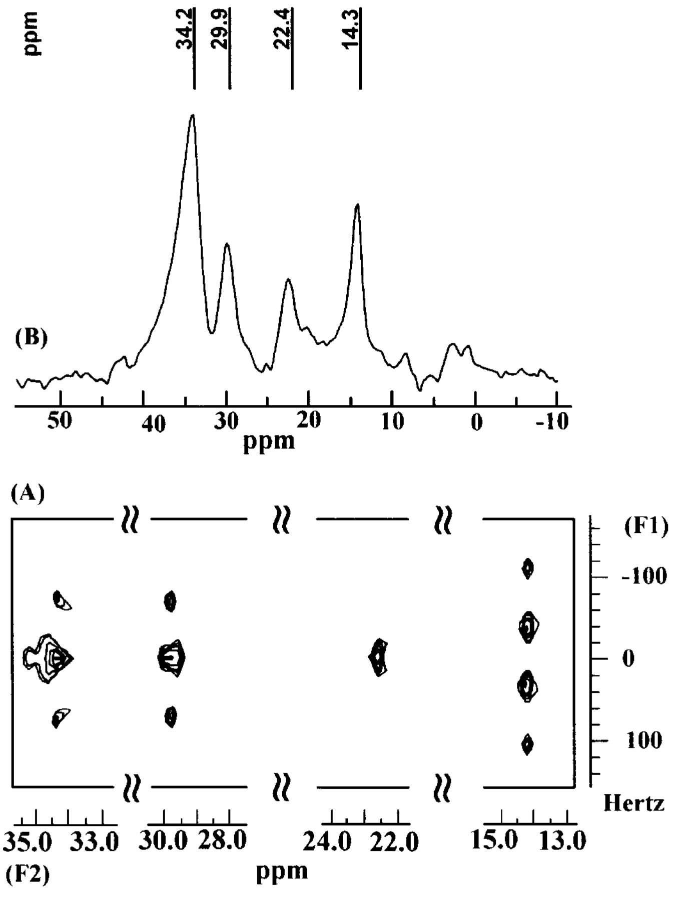


FIG. 6. **(A)** Contour plot of 2D *J*-resolved ^{13}C solid state MAS NMR spectrum for the products of ethylene ($CH_2{=}^{13}CH_2$, 40% ^{13}C isotope enrichment) oligomerization on zeolite H-ZSM-5 at room temperature. The observed value of scalar $J(^{13}C\text{-}^{1}H)$ coupling is equal to a half of the real $J(^{13}C\text{-}^{1}H)$, because of proton high power decoupling during the second half of the evolution time t_1(35). **(B)** Corresponding one-dimensional ^{13}C MAS spin echo NMR spectrum. Asterisk (*) denotes a spinning sideband.

Four peaks in the F1 direction for the signal at 14 ppm arise from the terminal CH_3 group of the oligomeric hydrocarbon chain. Thus, *in situ* NMR analysis of the multiplicity of signals from oligomer indicates that three signals between 22 and 34 ppm arise from CH_2 groups; i.e., they belong to linear chains of oligomers. The data obtained unambiguously indicate that adsorbed oligomers represent the species with linear hydrocarbons chains.

^{13}C high resolution NMR analysis of the hydrocarbons extracted from zeolite. To further substantiate the structure of the oligomers formed inside the zeolite, the zeolite framework, strongly retaining oligomers inside a zeolite framework was destroyed by dissolving the zeolite sample with adsorbed oligomers in 10% water solution of sodium hydroxide (33). The hydrocarbon products were then extracted with diethyl ether from the final residue solution and further ^{13}C high resolution NMR analysis of the hydrocarbons was carried out.

Figure 7 shows ^{13}C NMR spectrum of the hydrocarbons extracted from zeolite. At first glance this spectrum exhibits only a lot of signals at 14–40 ppm. There are no signals which would give us information on the nature of the extracted oligomers. Analysis of the multiplicities of the observed signals indicates that the most intense signals at 24 and at 30–33 ppm belong to CH_2 groups (triplets with $J(^{13}C\text{-}^{1}H) = 125$ Hz) and the signals near 10–14 ppm (quartets with $J(^{13}C\text{-}^{1}H) = 125$ Hz) arise from methyl groups. In common, if we compare the spectra in Figs. 3 and 7, then we

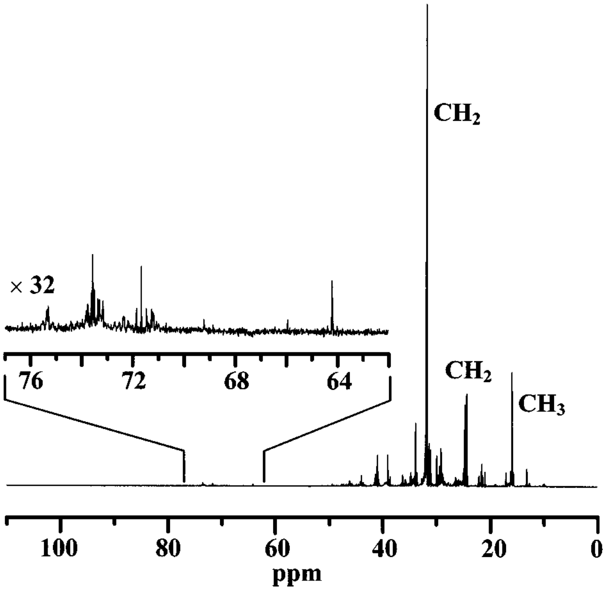
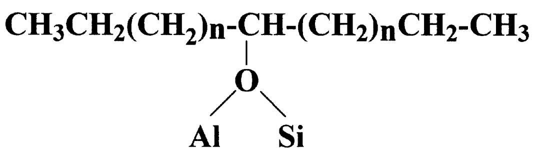


FIG. 7. High resolution ^{13}C NMR spectrum in benzene-d_6 of ethylene oligomers extracted from H-ZSM-5 after dissolution of the zeolite in NaOH solution.

see that the position of the signals in the spectra, the ratios among intensities of CH_2 and CH_3 groups and multiplicities (Fig. 6) of the signals are similar in adsorbed and extracted from zeolite hydrocarbon products. This fact allow us to conclude that dissolution of the zeolite in NaOH solution does not lead to the subsequent isomerization of oligomers upon their contact with NaOH solution and support our conclusion that adsorbed oligomers represent mainly linear species. As can be estimated from the ratios of the intensities of the signals at 14, 22, and 33 ppm in Fig. 7 the average length of linear oligomer chain includes ca seven carbon atoms in linear fragment $-(CH_2)_5CH_2CH_3$, bound to the oxygen of the zeolite framework, e.g. via a secondary carbon atom as depicted in Scheme 4, where $n \leq 5$.

It should be stressed here that not only oligomers with exclusively linear hydrocarbon fragments are formed. According to their chemical shifts the signals at 35–50 ppm (see Fig. 7) arise from the secondary and tertiary carbon atoms of branched hydrocarbon fragments (19, 51). Therefore our conclusion on the formation of the linear oligomers could be better formulated as a formation of the oligomers inside H-ZSM-5 not exclusively with linear fragments, but the formation of the oligomers in which *linear hydrocarbon fragments prevail*. Prevalence of the linear fragments in the oligomers seems to be defined by both specific framework and dimensions of the channels of the zeolite ZSM-5 (52).



$$CH_3CH_2(CH_2)n\text{-}\underset{\underset{Al\quad Si}{O}}{CH}\text{-}(CH_2)_nCH_2\text{-}CH_3$$

SCHEME 4. Tentative linkage of the linear fragment of ethylene oligomer to the framework of zeolite H-ZSM-5.

Thirty-two-fold enhancement of the signal intensities in the spectrum of Fig. 7 displays clearly a lot of weak signals at 60–80 ppm, besides intense signals at 10–50 ppm. The position of these signals is in the region of NMR spectrum, typical for carbon atoms attached to oxygens in alcohols (19). The observation of these signals allow us to conclude that oligomers are extracted from the zeolite in the form of aliphatic alcohols, which can be formed under interaction of oligomeric alkoxy species with water during zeolite dissolution. Observation of more than 20 signals at 60–80 ppm from alcohols indicates that mixture of more than 20 oligomeric alkoxides preferentially with linear hydrocarbon skeletons is formed upon ethylene adsorption on H-ZSM-5.

Note that a mixture of oligomers exhibits in ^{13}C CP/MAS NMR spectrum (Fig. 3) only one broad and small intensity signal at 89 ppm, indicative of the alkoxide nature of the formed oligomers. This signal has not been identified for a long time for adsorbed olefin oligomers (9, 11, 13, 41, 53). Sometimes the signals at 87–89 ppm observed for different olefins adsorbed on acidic zeolites under conditions of the their oligomerization were attributed to the short intermediate alkyl fragments (iso-propyl (24, 55), tert-butyl (14)). However, similarity of the chemical shift for alkoxides observed earlier under oligomerization of propylene on HY (24, 54) or H-ZSM-11 (55) and isobutylene (formed under dehydration of tert-butyl alcohol) on H-ZSM-5 (14) with that for alkoxides identified in this paper, allows us to conclude that signals from alkoxides at 87–89 ppm observed earlier in Refs. 14, 24, 54, 55 should be attributed to a mixture of oligomeric alkoxides, rather than to the short alkyl (iso-propyl (24, 55) or tert-butyl (14)) fragments.

At the same time it becomes evident from the comparison of Figs. 3 and 7 why the signals from oligomeric alkoxides have not been identified for ethylene oligomers for a long time (9, 53). The main reasons are that, (1) a mixture of more that 50 oligomeric alkoxides (*vide infra*, GC-MS data) are formed; (2) the signals of oligomeric alkoxides are broad and of small intensity; (3) these signals are spread over more than 15 ppm chemical shift range. It should be emphasized here that we could observe the characteristic NMR signals at 70–89 ppm, that would evidence for the formation of alkoxides only in case of using of 40–80% ^{13}C-enriched ethylene. In case of ethylene with natural abundance we could not identify the weak signal at 89 ppm for adsorbed ethylene oligomers (Fig. 3). Oligomers formed from unlabeled ethylene and extracted from the zeolite in the form of alcohols did not exhibit a lot of weak signals at 70–80 ppm like in Fig. 7, with only the signals at 10–50 ppm from paraffinic moiety of extracted alcohols being identified in ^{13}C high-resolution NMR spectra.

Our attempts to analyze the composition (length of hydrocarbon chain) of extracted alcohols with GC-MS was not successful. A mixture of aliphatic alcohols could not be separated in capillary column with nonpolar liquid phase OV-101 we used for GC separation of a mixture of extracted organics. Therefore, for further elucidation of the composition of adsorbed oligomers we have converted them into the adsorbed products, which could be, after extraction from the zeolite, easily analyzed by GC-MS with OV-101 (33, 44).

^{13}C NMR and GC-MS analysis of the oligomers extracted from zeolite in the form of carboxylic acids. For further elucidation of the composition of oligomers we have taken advantage of our conclusion (*vide supra*) (see also Refs. (17, 33)) that a small concentration of oligomeric carbenium ions always exists for adsorbed oligomers in zeolite. These carbenium ions are easily trapped with carbon monoxide and converts (inside the zeolite in the presence of water) oligomers into corresponding carboxylic acids (see Fig. 5).

As shown in Ref. (33) a mixture of carboxylic acids extracted from zeolite can easily be analyzed by GC-MS. Therefore, to elucidate the composition and the structure of the carboxylic acids, formed from ethylene oligomers, we followed a procedure already used for the analysis of the products formed from octene-1 (33). The zeolite sample with the formed carboxylic acids was dissolved in NaOH solution and after its neutralization with H_2SO_4, the organic products were extracted with Et_2O. Further, we analyzed these products with high resolution ^{13}C NMR and GC-MS.

^{13}C NMR spectrum of extracted organic products exhibits the signals at 178–186 ppm from carbonyl groups of the carboxylic acids (Fig. 8). The most intense signals at 20–33 ppm belong to CH_2 groups of the acids. The ratios among the CH_3 and CH_2 signals at 10–40 ppm from paraffinic moieties of the acids are similar to those in oligomers both adsorbed and extracted from zeolite in the form of alcohols (compare Figs. 3, 5, 7, 8). These facts indicate that linear structure of hydrocarbon chains is retained upon conversion of oligomeric alkoxides into corresponding carboxylic acids. This implies that inside zeolite H-ZSM-5 oligomeric carbenium ions retain linear structure of oligomeric alkoxides.

For GC-MS analysis of a mixture of the extracted carboxylic acids they were further converted with the aid of diazomethane (33) into more volatile methyl esters of these acids. This procedure facilitates both gas chromatographic separation of the acids and MS analysis of the products on the basis of their *m/e* ratio (56). As seen from Fig. 9, the GC-MS spectrogram of the extracted oligomeric products exhibits more than 50 peaks, which belong to methyl esters of carboxylic acids, different in their retention time and molecular weights. All peaks possess a characteristic value of $m/e = 74$, typical for methyl esters of fat carboxylic acids (56). Most of the peaks (except the smallest ones with retention time of more than 870 s) exhibit in their mass-spectra the signals from molecular ions characteristic of the methyl esters of the acids ranged from the $C_5H_{11}COOH$ family ($m/e = 130$) to $C_{14}H_{27}COOH$ family ($m/e = 256$). Thus, on the basis of GC-MS analysis of the extracted oligomers in the form of carboxylic acids one can conclude that a mixture of at least 50 different oligomers with the length of the hydrocarbon skeleton ranged from C_5 to C_{14} and even higher are formed upon ethylene oligomerization on H-ZSM-5 zeolite at room temperature. It should be noted, that as follows from GC-MS analysis, simultaneously with the process of subsequent oligomerization of ethylene to produce oligomers with *even number of carbon atoms* in a hydrocarbon chain, deoligomerization, as a reversible process, to produce oligomers with *odd number of carbon atoms*, also proceeds.

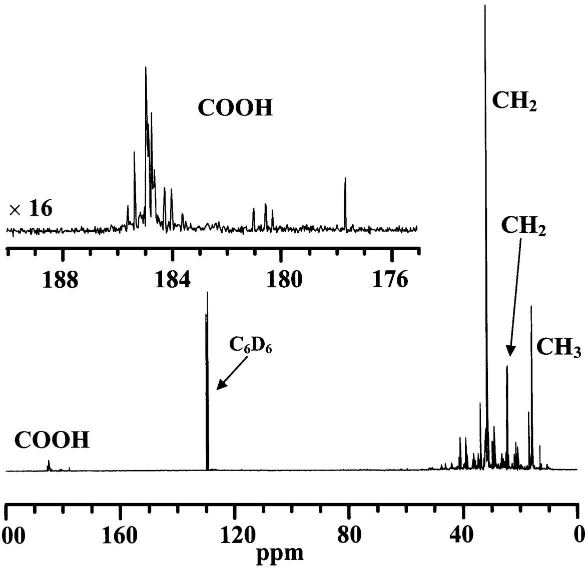


FIG. 8. High resolution ^{13}C NMR spectrum in benzene-d_6 of hydrocarbon products extracted from H-ZSM-5 after additional coadsorption of carbon monoxide and water on the zeolite, containing preliminary oligomerized ethylene.

4. CONCLUSIONS

Combined application of *in situ* IR and ^{13}C NMR and *ex situ* ^{13}C NMR and GC-MS to the analysis oligomers formed from ethylene on acidic zeolite H-ZSM-5 at room temperature and strongly retained by the framework of this zeolite, allow us to draw the following conclusions on the nature, structure and composition of the adsorbed oligomers:

1. Oligomers represent a mixture of more than 50 hydrocarbons, which composition ranges from five (C_5) to 14 and even higher (C_{14+}) carbon atoms in a molecule.
2. Adsorbed oligomers are bound to the oxygens of the zeolite framework to form alkoxy species.

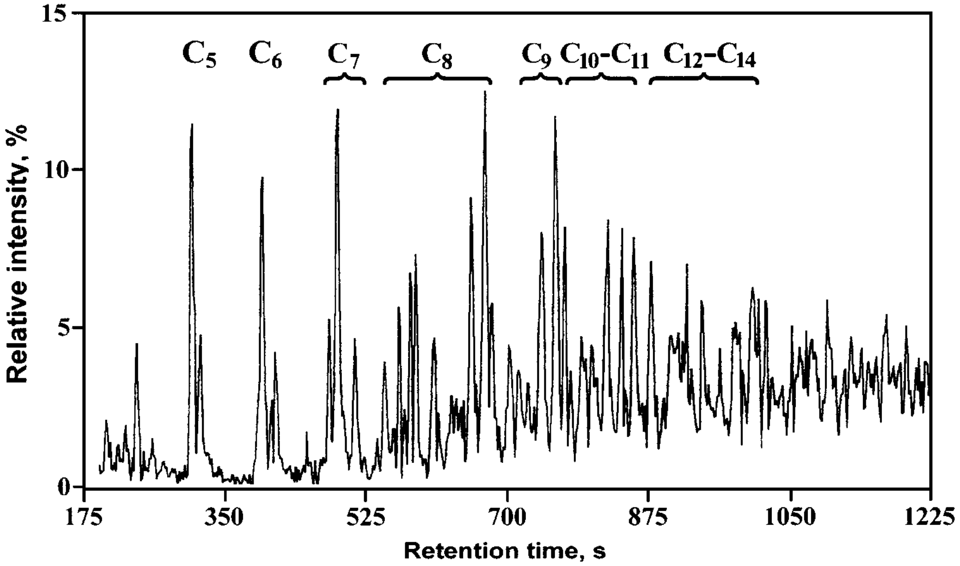


FIG. 9. GC-MS spectrogram of hydrocarbon products extracted from H-ZSM-5 after dissolving the zeolite sample in NaOH solution. Before zeolite dissolution $CO + H_2O$ (1 : 1) were coadsorbed on zeolite sample, containing preliminary adsorbed ethylene. To facilitate GC-MS analysis the extracted mixture of carboxylic acids was converted in their methyl esters with CH_2N_2.

3. Oligomeric alkoxy species represent main adsorption state of adsorbed oligomers, but they are in equilibrium with vanishing concentration of both oligomeric carbenium ions and olefins of the same composition. The reactivity of the adsorbed oligomers is defined by the reactivity of equilibrated carbenium ions.

4. Oligomeric alkoxy species with linear hydrocarbon fragments prevail in the mixture of the formed oligomers. The average length of the linear oligomer chain includes ca seven carbon atoms. Prevalence of the linear fragments in the oligomers seems to be defined by both specific structure and dimensions of the channels of the zeolite.

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