Conversion of methanol to hydrocarbons on zeolite HZSM-5 investigated by *in situ* MAS NMR spectroscopy under flow conditions and on-line gas chromatography

Michael Seiler, Udo Schenk and Michael Hunger [*]

Institute of Chemical Technology I, University of Stuttgart, D-70550 Stuttgart, Germany
E-mail: michael hunger@po.uni-stuttgart.de

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In situ MAS NMR spectroscopy under flow conditions and on-line gas chromatography have been applied to study the onset of the conversion of methanol on zeolite HZSM-5 at temperatures between 373 and 573 K. In the steady states of methanol conversion at $T \geqslant 523$ K, by on-line gas chromatography mainly the formation of ethene and propene was observed. Simultaneously recorded *in situ* ^{13}C MAS NMR spectra show signals at 12–25 ppm and at ca. 125–131 ppm indicating the presence of adsorbed C_4–C_6 olefins. The observation of these adsorbates on a working catalyst supports the “hydrocarbon pool” mechanism previously proposed for the methanol-to-hydrocarbon conversion on acidic zeolites. Methanol conversion at 473 and 573 K and subsequent purging of the catalyst with dry nitrogen at 293 K led to a ^{13}C MAS NMR signal at 59 ppm due to methoxy groups. No hints to the presence of ethoxy, propoxy or butoxy groups and the formation of alkyl oxonium ions were found by *in situ* ^{13}C MAS NMR spectroscopy under flow conditions.

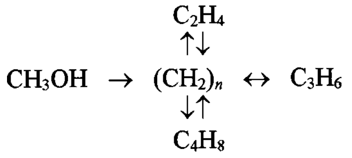
Keywords: heterogeneous catalysis, methanol-to-hydrocarbon conversion, MTG, zeolite HZSM-5, Brønsted acid sites, *in situ* MAS NMR spectroscopy, flow conditions

1. Introduction

Since the first reports on methanol-to-gasoline (MTG) conversion on zeolite HZSM-5 in 1976, this process is one of the mostly investigated reactions in heterogeneous catalysis [1–3]. Although a number of experimental and theoretical works have established various mechanisms for the conversion of methanol on zeolites (see [4–8], and references therein), the chemical reactions proceeding at the Brønsted acid sites of these catalysts are poorly understood. Generally, three reaction steps are distinguished: (i) the dehydration of methanol to dimethyl ether, (ii) the conversion of a mixture of methanol and dimethyl ether to olefins and (iii) a bond chain polymerization of olefins and isomerization [8]. Most of the recently published theoretical works investigate the mechanisms for the first C–C bond formation. As a reactive intermediate in steps (i) and (ii) methoxy groups bound to oxygen atoms in Si–O–Al bridges of the zeolite framework are proposed.

An often discussed way for the formation of the first C–C bond is the oxonium ylide mechanism [9,10]. According to this mechanism, trimethyl oxonium ions formed by a reaction of dimethyl ether molecules are deprotonated by a basic site and yield dimethyl oxonium methyl ylide. After an intramolecular Stevens rearrangement [9] or an intermolecular methylation [10], ethylmethyl oxonium or dimethylethyl oxonium ions are formed and split off the reaction product ethene (see also [11]).

Based on GC-MS experiments with ^{13}C- and ^{12}C-labelled reactants, Dahl and Kolboe (see [12,13]) explained the formation of olefins by a “hydrocarbon pool” mechanism which represents adsorbates such as



$$\begin{tikzcd} & C_2H_4 \arrow[d, shift left] & \\ CH_3OH \arrow[r] & (CH_2)_n \arrow[u, shift left] \arrow[r, leftrightarrow] \arrow[d, shift left] & C_3H_6 \\ & C_4H_8 \arrow[u, shift left] & \end{tikzcd}$$

According to this mechanism, “big” carbonaceous species exist inside the zeolite pores and add and split off reactants and products, respectively [12,13]. The “hydrocarbon pool” represents adsorbates with many characteristics of ordinary coke and would perhaps be better represented by $(CH_x)_n$ with $0 < x < 2$ [11].

Since 1989, with the first *in situ* MAS NMR study of methanol conversion on zeolite HZSM-5 carried out by Anderson and Klinowski [14–17], this spectroscopic method has been developed to a useful tool for the investigation of heterogeneously catalyzed reactions. In the last decade a growing number of groups performed *in situ* MAS NMR spectroscopic studies of the conversion of methanol on various aluminosilicate- and silicoaluminophosphate-type zeolites under batch conditions [18–25]. Applying a pulse-quench reactor, Goguen et al. [26] made methanol conversion experiments on zeolite HZSM-5 under semi-flow conditions. After giving a reactant pulse on the catalyst filled into an external reactor tube, the reaction was rapidly stopped by quenching with liquid nitrogen. Sub-

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[*] To whom correspondence should be addressed.

sequently, the catalyst loaded with reactants and reaction products was transferred into the precooled MAS NMR probe. Recently, Isbester et al. [27] introduced a MAS NMR probe with an isolated reactant flow. In a first application, this probe was used to observe the formation of dimethyl ether due to conversion of methanol on zeolite HZSM-5 without further gas chromatographic investigations of hydrocarbon formation. By our group, a technique for the continuous injection of reactant molecules into the spinning rotor of commercial variable temperature MAS NMR probes was introduced [28]. In a very recent work, this injection technique was coupled with on-line gas chromatography allowing simultaneous *in situ* MAS NMR studies of adsorbate complexes formed under flow conditions and gas chromatographical analysis of the reaction products [29]. In the present study, a high temperature MAS NMR probe was equipped with such an injection system allowing investigations of heterogeneously catalyzed reactions under flow conditions at temperatures up to 873 K. This equipment was applied to study the formation of hydrocarbons by conversion of methanol on zeolite HZSM-5. As done in previous works [16,17,24,25], especially the onset of this reaction at temperatures up to 573 K was studied.

2. Experimental

Zeolite NaZSM-5 with the chemical composition $Na_{4.2}Al_{4.2}Si_{91.8}O_{192}$ was synthesized as described elsewhere [30]. The ammonium form was prepared by fourfold ion exchange at 353 K in a 0.4 M aqueous solution of NH_4NO_3. After reaching an ion exchange degree of 98%, the zeolite powder was washed in demineralized water and dried at room temperature. The material was characterized by AES-ICP, XRD, ^{27}Al and ^{29}Si MAS NMR spectroscopy. No signal of extra-framework aluminum atoms was found in the ^{27}Al MAS NMR spectra of the hydrated samples.

The MAS NMR investigations were performed on a Bruker MSL 400 spectrometer at resonance frequencies of 400.1 MHz for ^{1}H, 100.6 MHz for ^{13}C nuclei and 83.5 MHz for ^{207}Pb and with sample spinning rates of 2.4 kHz for ^{1}H and 1.8 kHz for ^{13}C and ^{207}Pb MAS NMR spectroscopy. For bearing and driving the MAS NMR turbine, the same dry nitrogen gas (produced by a nitrogen evaporator) was used as for the carrier gas in the catalytic flow experiments (*vide infra*). The ^{13}C MAS NMR spectra were obtained after direct excitation and proton decoupling. For each ^{1}H MAS NMR spectrum, 100 free induction decays and for the ^{13}C and ^{207}Pb MAS NMR spectra from 100 to 2000 free induction decays were accumulated with a repetition time of 5 s. The ^{1}H and ^{13}C MAS NMR spectra were referred to TMS.

Prior to the NMR investigations, the ammonium form of zeolite was heated in vacuum with a rate of 20 K/h up to the final temperature of 723 K leading to zeolite HZSM-5. There, it was calcined at a pressure below 10^{-2} Pa for 12 h. On one sample of calcined zeolite HZSM-5, methyl iodide, C^*H_3I (Aldrich, 27.718-5, the asterisk indicates a ^{13}C-enrichment of the carbon atom) was adsorbed using a vacuum line and, subsequently, heated at 473 K for 1 h.

Before the *in situ* MAS NMR experiments under flow conditions, the calcined zeolite was filled into the MAS NMR rotor reactor under dry nitrogen in a glove box and pressed to a cylindrical catalyst bed (see [29]). After transferring the rotor into the MAS NMR probe, a second dehydration of the catalyst was performed at 673 K for 1 h under flowing nitrogen (30 ml/min). During the *in situ* MAS NMR experiments under continuous-flow conditions, nitrogen loaded with methanol (me), C^*H_3OH (Campro Scientific, 83-00005-9), or a mixture of C^*H_3OH and ethene ($C_2^=$), C_2H_4 (Fluka, 398815/1), were injected into a 7 mm MAS NMR rotor applying the equipment described elsewhere [29]. Via an exhaust tube on the top of the MAS NMR rotor reactor, the probe was connected with the sampling loop of a gas chromatograph (see [29]). The *in situ* MAS NMR flow probe is based on a modified DSI-740 7 mm STD MAS NB NMR probe delivered by Doty Scientific Instruments, Columbia, Texas, allowing measurements at temperatures up to 873 K with sample spinning rates up to 3.5 kHz. By ^{207}Pb MAS NMR spectroscopy of $Pb(NO_3)_2$, the temperature inside the MAS NMR rotor reactor and the temperature gradient over the whole sample volume of the modified *in situ* MAS NMR flow probe were investigated. According to Ferguson and Haw [31], the ^{207}Pb NMR shift of $Pb(NO_3)_2$ changes by 0.775 ppm/K with the temperature. The ^{207}Pb MAS NMR spectra of $Pb(NO_3)_2$ shown in figure 1 were recorded using the modified *in situ* MAS NMR flow probe during injection of nitrogen (15 ml/min) into the MAS NMR rotor spinning with

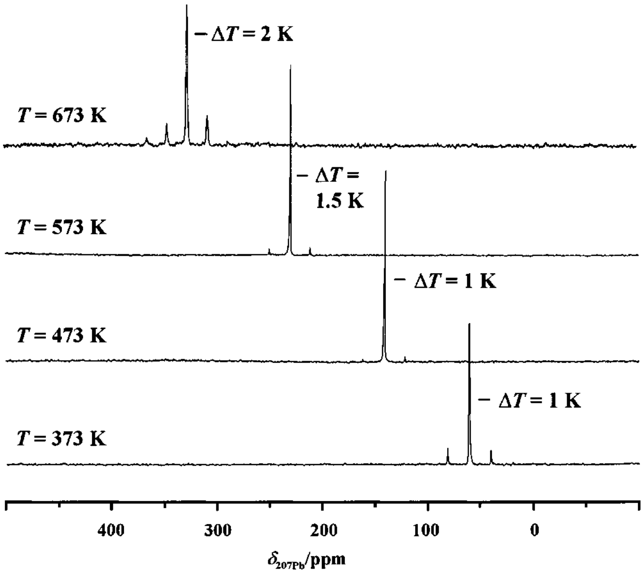

Figure 1. ^{207}Pb MAS NMR spectra of $Pb(NO_3)_2$ recorded using the modified *in situ* MAS NMR flow probe (see text) during injection of nitrogen (15 ml/min) into the MAS NMR rotor spinning with a rate of 1.8 kHz. The temperature gradients given in the figure were calculated by the residual linewidth of the ^{207}Pb MAS NMR signals obtained at the corresponding temperatures and the factor 0.775 ppm/K [28].

a rate of 1.8 kHz. At the maximum reaction temperature of 573 K applied in the present work a temperature gradient of $\Delta T = 1.5$ K was calculated via the residual linewidth of the ^{207}Pb MAS NMR signal determined at this temperature. The chemical shift was referred to 0 ppm for $Pb(NO_3)_2$ at 293 K.

The reaction products were analyzed using a gas chromatograph HP 5890 (Hewlett–Packard) equipped with a Coating Poraplot Q capillary column (Chrompack Plot fused silica, length 50 m, inner diameter 0.32 mm). The exhaust flow was sampled and analyzed in steps of 30 min. The reactant flow was adjusted by the carrier gas (dry nitrogen) flow rate and the temperature-dependent partial pressure of methanol in the saturator. In the *in situ* MAS NMR flow experiments, 100 mg of dry zeolite HZSM-5 and a modified residence time of $W/F_{\mathrm{me}} = 25$ g h/mol were used.

3. Results and discussion

3.1. Conversion of methanol on zeolite HZSM-5 at temperatures of 373–573 K

The first step of an *in situ* MAS NMR experiment under flow conditions was the dehydration of the zeolite filled into the MAS NMR rotor reactor. To prove the correct preparation of the zeolite, a ^{1}H MAS NMR spectrum was taken at 293 K after treating the catalyst at 673 K under *in situ* conditions. Because of the low sample spinning rate ($\nu_{\mathrm{rot}} = 2.4$ kHz), the central line of the ^{1}H MAS NMR spectrum shown in figure 2(a) is strongly broadened. Inspite of this broadening, it shows the characteristic ^{1}H MAS NMR signals of a dehydrated and intact zeolite HZSM-5: a weak shoulder at 1.8 ppm due to silanol groups (SiOH), a dominating large signal at 4.2 ppm caused by acidic bridging OH groups (SiOHAl) and a weak signal at 6.8 ppm which indicates a small amount of residual ammonium ions [32].

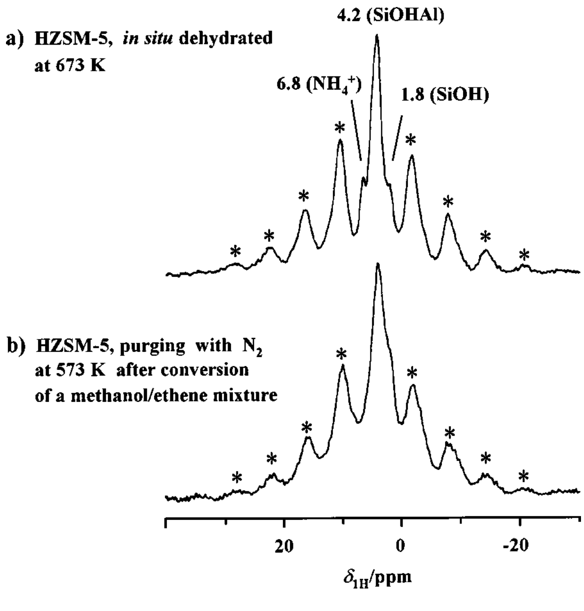

Figure 2. ^{1}H MAS NMR spectrum of zeolite HZSM-5 recorded after dehydration in the *in situ* MAS NMR probe at 673 K immediately before starting the methanol flow (a). Spectrum (b) was obtained at 293 K after conversion of methanol at 573 K and purging the catalyst with dry nitrogen gas (30 ml/min) at this temperature. Both spectra were recorded with a sample spinning rate of 2.4 kHz. Asterisks denote spinning sidebands.

The catalytic investigations were started at a temperature of 373 K (figure 3(a)). At this temperature no formation of dimethyl ether (dme) and hydrocarbons was found by GC (data on the left-hand side). The simultaneously recorded ^{13}C MAS NMR spectrum consists only of a single line at 50 ppm due to methanol [33]. The integral intensity of the methanol peak obtained by GC was used as an intensity standard for the further experiments. After raising the reaction temperature to 423 K, a yield of dimethyl ether (dme) of 10.7% was determined by GC and the ^{13}C MAS NMR spectrum shows an additional signal at 61 ppm due to dme [33] (figure 3(b)). At a reaction temperature of 473 K, a significant increase of the signal at 61 ppm as well as of the yield of dme occurred (figure 3(c)). The intensities of the ^{13}C MAS NMR signals of methanol and dme deviate from the amounts of reactant molecules determined by GC. This is due to differences in the residence times of these weakly adsorbed molecules inside the MAS NMR rotor reactor. A residence time shorter than the spin–lattice relaxation time T_1 causes a decrease or disappearance of the MAS NMR signals of the corresponding molecules and surface compounds.

Starting at the reaction temperature of 523 K, the formation of hydrocarbons was observed (figure 3 (d)–(f)). The yield of dimethyl ether (dme) as well as those of ethene ($C_2^=$), propene ($C_3^=$), propane (C_3), butenes ($C_4^=$) and butanes (C_4) increased (GC data on the left-hand side). In the ^{13}C MAS NMR spectra, the formation of hydrocarbons is accompanied with the appearance of signals at 12–25 ppm and ca. 125–131 ppm. Interestingly, no signal of ethene was found at 123 ppm [33] which indicates a short residence time of this molecule inside the MAS NMR rotor reactor. The increase of the hydrocarbon yields at the reaction temperatures of 548 and 573 K is accompanied by an increase of the ^{13}C MAS NMR signals at 15 and 18 ppm and of broad signals at ca. 125–131 ppm (figure 3 (e) and (f)). Although the latter signals lie in the aromatic region, neither benzene (128.5 ppm [33]) nor toluene (21.4, 125.7, 128.5, 129.3 and 137.8 ppm [33]), p-xylene (20.9, 129.1 and 134.5 ppm [33]) or naphthalene (125.6, 127.7 and 133.3 ppm [33]) can be assigned to these signals. All these molecules would cause additional signals out of the range of resonances observed in figure 3 (e) and (f) and/or they do not allow an explanation of the signals in the region between 12 and 25 ppm. Another situation occurs, considering *trans*-butene-2 (16.8 and 125.4 ppm [33]), *cis*-butene-2 (11.4 and 124.2 ppm [33]), n-pentene-2 (13.6, 17.3, 25.8, 123.8 and 133.2 ppm [33]), n-hexene-3 (14.1, 25.9 and 131.2 ppm [33]) and n-hexadiene-2,4 (17.5, 126.2 and 132.5 ppm [33]). A mixture of these C_4–C_6 olefins would lead to signals at 12–25 ppm as well as to broad res-

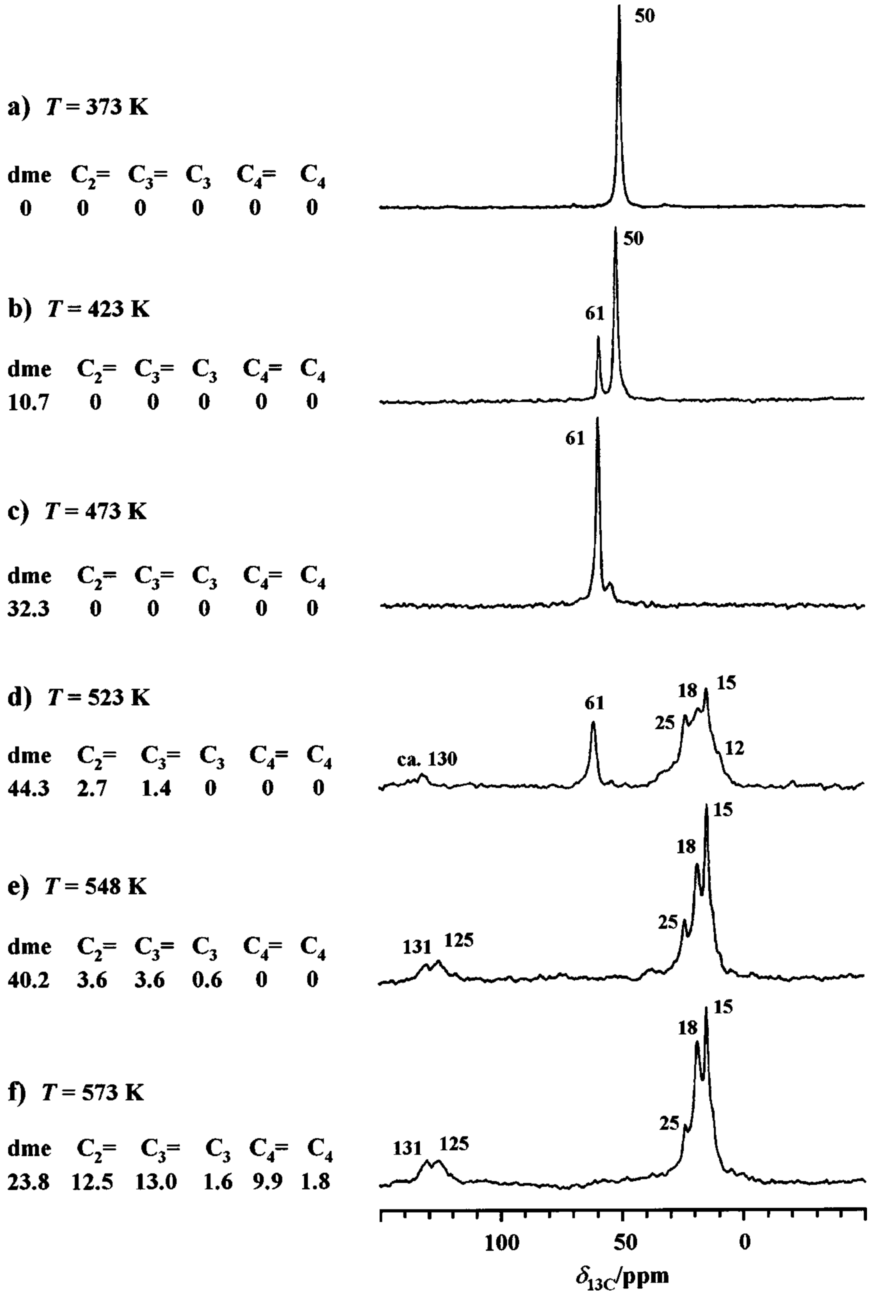

Figure 3. ^{13}C MAS NMR spectra of the conversion of $C^{*}H_3OH$ on zeolite HZSM-5 recorded under flow conditions with a modified residence time of $W/F_{\mathrm{me}} = 25$ g h/mol and at temperatures between 373 and 573 K. On the left-hand side the yields (in %) of dimethyl ether (dme), ethene ($C_2^{=}$), propene ($C_3^{=}$), propane (C_3), butenes ($C_4^{=}$) and butanes (C_4) determined by simultaneously performed on-line GC analysis are given.

onances at ca. 125–131 ppm. Hence, the ^{13}C MAS NMR spectra recorded at 523–573 K under flow conditions hint to the presence of a “hydrocarbon pool”, which indicates a formation of hydrocarbons according to the mechanism proposed by Dahl and Kolboe [12,13]. A formation of hydrocarbons according to the “rake mechanism” proposed by Cormerais et al. [34] cannot be supported. In this case, the “hydrocarbon pool” would consist of ethoxy (68 ppm [35]), propoxy (87 ppm [36]) and butoxy groups (77 ppm [37]) which were not observed in the present work. Furthermore, no indication for the formation of trimethyl oxonium ions (80 ppm [38,39]) was found.

3.2. Formation of methoxy groups

In most of the reaction mechanisms discussed for the MTG process, methoxy groups bound to oxygen atoms of Si–O–Al bridges in the zeolite lattice play a important role as methylating intermediates (see, e.g., [8]). In a previous work, Bosacek [40] prepared methoxy groups on zeolite HZSM-5 by loading methyl iodide and observed a narrow ^{13}C MAS NMR signal at the isotropic chemical shift of 59.4 ppm. Applying two-dimensional ^{13}C magic-angle-turning NMR spectroscopy (MAT NMR) on zeolite HZSM-5 after loading with methanol, heating at 473 K for

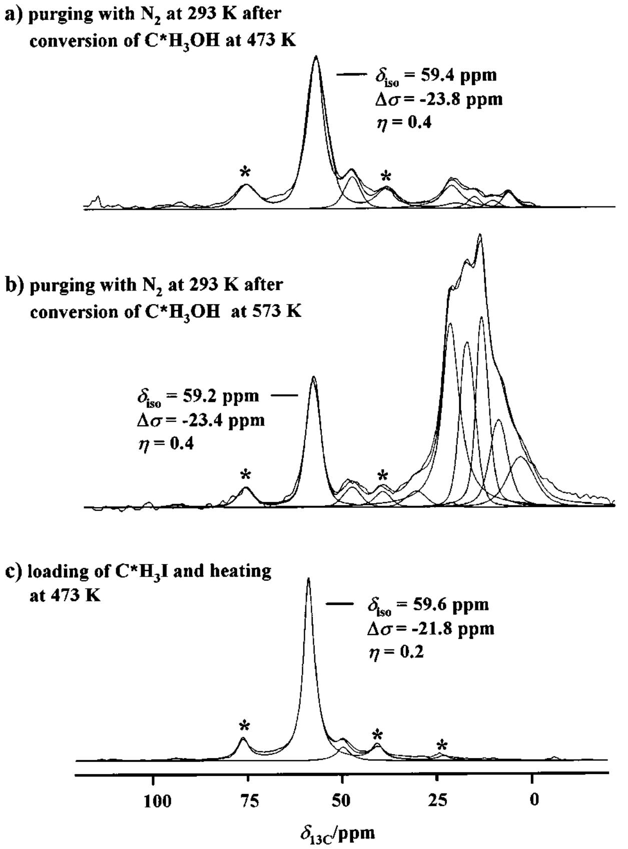

Figure 4. ^{13}C MAS NMR spectra recorded at 293 K after conversion of C*H$_3$OH on zeolite HZSM-5 at 473 (a) and 573 K (b) with $W/F_{\mathrm{me}} =$ 25 g h/mol and purging the catalyst with dry nitrogen gas (30 ml/min) at 293 K. The spectrum in (c) was obtained after loading the calcined zeolite HZSM-5 with C*H$_3$I and heating at 473 K. All spectra were recorded with a sample spinning rate of 1.8 kHz. Asterisks denote spinning sidebands. The decomposition and simulation of the spectra were performed with the Bruker software WINFIT.

15 min and subsequent evacuation, Philippou et al. [41] found a signal at 58.4 ppm which the authors assigned to methoxy groups formed on this zeolite. Considering the ^{13}C MAS NMR spectra shown in figure 3 (b)–(d), a signal of methoxy groups at ca. 59 ppm should be covered by the signal of dimethyl ether at 61 ppm. At higher reaction temperatures, the lifetime of the methoxy species could be too short for detection by ^{13}C MAS NMR spectroscopy. Therefore, after the conversion of methanol at a certain reaction temperature, the methanol flow was stopped and the catalyst was cooled down to 293 K and purged with dry nitrogen gas (30 ml/min). Subsequently, ^{13}C MAS NMR spectra were recorded of the purged samples. In figure 4 (a) and (b), the ^{13}C MAS NMR spectra obtained after conversion of methanol at 473 and 573 K, respectively, and purging are shown. The low-field range of both spectra consists of an MAS NMR sideband pattern with a central line at 59 ppm. The simulation of these sideband patterns yielded a chemical shift anisotropy of $\Delta\sigma = -23$ ppm and an asymmetry parameter, η, of 0.2–0.4. While the isotropic chemical shift of 59 ppm agrees well with that given in literature [40,41], the chemical shift anisotropy of $\Delta\sigma = -23$ ppm differs from the value obtained by Philippou et al. [41] applying 2D ^{13}C MAT NMR spectroscopy ($\Delta\sigma = -49$ ppm). Therefore, the zeolite HZSM-5 used in the present study was pretreated as described by Bosacek [40], i.e., the zeolite calcined at 673 K was loaded with methyl iodide (C*H$_3$I) and, subsequently, heated at 473 K for 1 h. The ^{13}C MAS NMR signal of the methoxy groups on the zeolite HZSM-5 prepared in this way (figure 4(c)) agrees very well with the low-field patterns of the spectra in figure 4 (a) and (b). This supports the assignment of the signal at 59 ppm in figure 4 (a) and (b) to methoxy groups formed at framework oxygen atoms. Hence, the conversion of methanol on zeolite HZSM-5 under flow conditions is accompanied by the formation of methoxy groups which are absent in the spectra recorded at 573 K (figure 3(f)) because of their short lifetime at high reaction temperatures. It is important to note that also in the spectra recorded at room temperature after conversion of methanol at 473 and 573 K, no signals due to ethoxy, propoxy or butoxy groups (77–87 ppm [35–37]) and trimethyl oxonium ions (80 ppm [38,39]) were observed.

3.3. Conversion of a methanol/ethene feed on zeolite HZSM-5

In a number of works [7,12,13], the role of ethene in the MTG process was investigated. Ethene has been discussed as a product of the first C–C bond formation. Dahl and Kolboe [13] studied the conversion of a feed of ^{13}C-methanol and ^{12}C-ethene on SAPO-34 by GC-MS and found that a large part of ethene leave the catalyst unreacted while methanol was almost completely converted to hydrocarbons. According to this finding, the authors suggested that higher hydrocarbons are not formed by a successive methylation of ethene.

In the present work, the co-reaction of ^{13}C-methanol and ethene (natural abundance of ^{13}C-isotopes) on zeolite HZSM-5 was studied applying *in situ* ^{13}C MAS NMR spectroscopy under flow conditions. These experiments were performed at reaction temperatures of 548 and 573 K with a molar feed ratio of $\dot{n}_{\mathrm{me}}/\dot{n}_{\mathrm{C}_2^=} = 2:1$ and a modified residence time of methanol of $W/F_{\mathrm{me}} = 25$ g h/mol (figure 5 (a) and (b)). Excepting two weak signals at 47 and 61 ppm, the spectrum shown in figure 5(a) agrees well with that obtained at 548 K for conversion of pure methanol on zeolite HZSM-5 (compare figure 3(e)). The product distribution determined by GC deviates only slightly from that found for the conversion of pure methanol. In contrast to this finding, the spectrum recorded at 573 K (figure 5(b)) shows differences in comparison with that obtained for conversion of pure methanol at the same temperature (compare figure 3(f)). The high-field region is dominated by the narrow signal at 18 ppm and the broad signals in the low-field region are increased. These effects can be explained by a higher content of n-hexadiene-2,4 (17.5, 126.2 and 132.5 ppm [33]) in the "hydrocarbon pool" formed in the zeolite pores. This variation in the composition of the "hy-

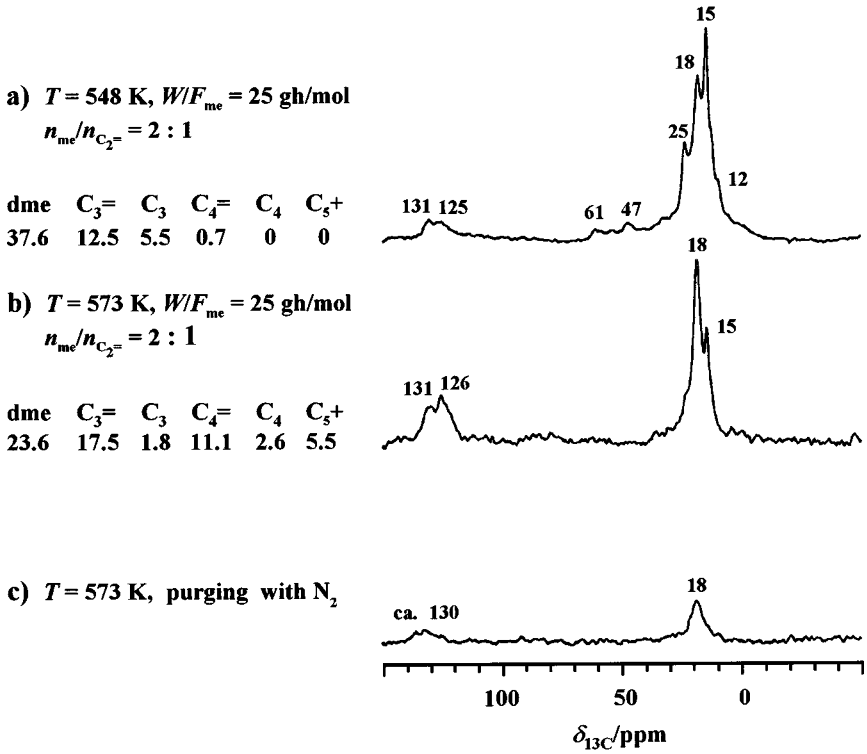

Figure 5. ^{13}C MAS NMR spectra of the conversion of a C^*H_3OH/ethene feed on zeolite HZSM-5 recorded under flow conditions with a modified residence time of $W/F_{\text{me}} = 25$ g h/mol, a molar methanol/ethene feed ratio of $\dot{n}_{\text{me}}/\dot{n}_{C_2^=} = 2:1$ and at temperatures of 548 (a) and 573 K (b). The spectrum shown in (c) was recorded after catalysis according to (b) and subsequent purging of the catalyst with dry nitrogen gas (30 ml/min) at 573 K. On the left-hand side the yields (in %) of dimethyl ether (dme), propene ($C_3^=$), propane (C_3), butenes ($C_4^=$), butanes (C_4) and higher hydrocarbons (C_{5+}) determined by simultaneously performed on-line GC analysis are given.

drocarbon pool" seems to be caused by the co-injection of ethene, but has no significant influence on the product distribution (GC data on the left-hand side). Purging the catalyst at 573 K with dry nitrogen after conversion of the methanol/ethene feed leads to a continuous decrease of the ^{13}C MAS NMR signals (figure 5(c)). After purging the catalyst at 573 K for 2 h, no ^{13}C MAS NMR signals could be observed, i.e., all hydrocarbons were removed from the catalyst. In agreement with this finding, the ^{1}H MAS NMR spectrum recorded at 293 K after the purging consists of a strong sideband pattern due to bridging OH groups without a hint to residual adsorbates (figure 2(b)). Interestingly, during the first 15 min of the catalyst purging at 573 K, ethene and propene were determined by GC as main desorptives. This shows that the higher olefins contributing to the previously existing "hydrocarbon pool" are split off into smaller compounds before the desorption from the surface of the zeolite HZSM-5 occurs.

4. Conclusions

In situ ^{13}C MAS NMR spectroscopy under flow conditions and on-line gas chromatography were successfully applied to study the conversion of methanol on zeolite HZSM-5. At reaction temperatures of $T \leqslant 523$ K methanol and dimethyl ether could be observed in the ^{13}C MAS NMR spectra at 50 and 61 ppm, respectively. At higher reaction temperatures, the residence time of these reactants on the catalysts surface becomes short in comparison to their residence time in the MAS NMR rotor reactor and their ^{13}C MAS NMR signals disappear. A similar behaviour was found for methoxy groups which are discussed in the literature as methylating intermediates. At reaction temperatures of $T \geqslant 423$ K their detection by ^{13}C MAS NMR spectroscopy is difficult. However, a signal observed at 59 ppm in the ^{13}C MAS NMR spectra recorded at 293 K, after methanol conversion at reaction temperatures of 473 or 573 K and purging with nitrogen, indicates that these species are present on the working catalyst. Starting at 523 K, hydrocarbons were determined by on-line GC, accompanied with the occurrence of ^{13}C MAS NMR signals at 12–25 ppm and ca. 125–131 ppm. Considering the resonance positions of aromatic and olefinic molecules, the above-mentioned signals are a hint to the formation of a pool of hydrocarbons probably consisting of a mixture of C_4–C_6 olefins. According to the "hydrocarbon pool" mechanism dicussed in the literature, these carbonaceous species exist inside the zeolite pores and add and split off reactants and product molecules. Co-injection of ethene led to a shift of the chemical equilibrium of the olefins contributing the "hydrocarbon pool" to higher olefins, probably to hexadiene. However, no significant variation of the product distribution was determined by simultaneously performed on-line GC analysis. Purging of the zeolite HZSM-5 after conversion of methanol at 573 K caused a disappearance of the ^{13}C MAS NMR signals at 12–25 ppm and ca. 125–131 ppm and a desorption of light olefins.

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