In situ MAS NMR spectroscopic investigation of the conversion of methanol to olefins on silicoaluminophosphates SAPO-34 and SAPO-18 under continuous flow conditions

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Applying *in situ* ^{13}C MAS NMR spectroscopy under continuous flow (CF) conditions and on-line gas chromatography, the conversion of methanol on silicoaluminophosphates SAPO-34 and SAPO-18 was studied. At reaction temperatures of 573 to 673 K, a strong increase of the yield of propylene and ethylene was observed by on-line gas chromatography. Simultaneously with the occurrence of *in situ* ^{13}C CF MAS NMR signals at 126–135 ppm indicates the formation of a mixture of aliphatic and/or cyclic olefins and alkylated aromatics with carbon numbers of C_6–C_{12}. All these support the "hydrocarbon pool" mechanism for the formation of light olefins on the SAPO-34 and SAPO-18.

KEY WORDS: methanol-to-olefin conversion; reaction mechanism; SAPO-34; SAPO-18; *in situ* MAS NMR spectroscopy; flow conditions

1. Introduction

The methanol to hydrocarbon (MTG: *methanol-to-gasoline*; MTO: *methanol-to-olefin*) conversion on acidic zeolites is, since its first application in 1976, one of the mostly investigated reactions in heterogeneous catalysis [1]. During the last decades, MTG and MTO have been studied extensively using theoretical [2–7], IR spectroscopic [8,9] and NMR spectroscopic [10–20] methods. In these works various mechanisms for the conversion of methanol on the Brønsted sites in zeolites (see [5], and references therein) have been established. However, until now the chemical reactions occurring on the internal surface of these catalysts are poorly understood. Since 1989, with the first *in situ* MAS NMR study of methanol conversion on zeolite HZSM-5 carried out by Anderson and Klinowski [21], this spectroscopic method has been developed to a useful tool for the investigation of heterogeneous reaction systems under batch conditions. Most of the experimental investigations were performed under batch conditions. Recently, first *in situ* MAS NMR spectroscopic studies of methanol conversion on zeolite H-ZSM-5 under continuous flow conditions (CF) coupled with a simultaneous analysis of the reaction products by on-line gas chromatography were performed [18]. This new technique allows the investigation of intermediates occurring on the catalyst surface in the steady state of a reaction. By on-line gas chromatography, a preferential formation of ethylene and propylene was observed at reaction temperatures of $T \geqslant 523$ K. Simultaneously recorded *in situ* ^{13}C MAS NMR spectra showed signals at 12–25 ppm and at *ca.* 125–131 ppm indicating the presence of adsorbed C_4–C_6 olefins. No hint for the presence of ethoxy, propoxy or butoxy groups and the formation of alkyl oxonium ions were found [18]. Haw *et al.* [16,19,20] studied the formation of intermediates formed by conversion of methanol, dimethyl ether and ethylene on zeolites H-ZSM-5 and silicoaluminophosphate SAPO-34 applying an external reactor allowing the rapid quenching of the reaction after injecting pulses of reactants onto the catalyst and transferring, subsequently, the catalyst into the MAS rotor and the NMR spectrometer. On silicoaluminophosphate SAPO-34, these authors observed a broad signal at 129 ppm with a shoulder at 134 ppm which they assigned the methylbenzenes [20]. On zeolite H-ZSM-5, Haw *et al.* [19] found the formation of 1,3-dimethylcyclopentenyl carbenium ions causing ^{13}C MAS NMR signals at 24, 48, 148 and 250 ppm. In addition, they determined a half-life of the above-mentioned carbenium ions of 10 min at 548 K and 6 s at 723 K [19]. Quantum-chemical calculations [19] yielded an electronic energy of the 1,3-dimethylcyclopentenyl carbenium ions which is only 2.2 kcal/mol lower than that of the corresponding neutral π complexes. Interestingly, the barriers to a methylation of the above-mentioned carbenium ions are significantly higher than those for the methylation of the neutral π complexes. Hence, the methylation reaction, being an important step in the mechanism of the MTO process, is promoted by the presence of neutral π complexes of the olefinic species.

In the present work, the continuous flow MAS NMR technique has been applied to study the conversion of methanol on 8-ring silicoaluminophosphates SAPO-34 (CHA) and SAPO-18 (AEI) at reaction temperatures between 373 and

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673 K. As known from catalytic investigations, methanol conversion on these materials leads to a preferential formation of light olefin making them interesting for MTO.

2. Experimental

Silicoaluminophosphates SAPO-34 and SAPO-18 were synthesized according to recipes given in [22,23], respectively. To remove the template, the powder samples were heated with 1 K/min to 393 K and dehydrated at this temperature for 2 h. Subsequently, they were heated with 1 K/min to 823 K and calcined under flowing nitrogen for 1 h with 5 vol% and for 3 h with 20 vol% oxygen. The calcined and rehydrated catalysts were characterized by AES-ICP, XRD, REM, ^{27}Al, ^{29}Si, ^{31}P and ^{1}H MAS NMR spectroscopy.

The characterization of the silicoaluminophosphates SAPO-34 and SAPO-18 by ^{27}Al, ^{29}Si, ^{31}P and ^{1}H MAS NMR spectroscopy was performed on a Bruker MSL 400 spectrometer at resonance frequencies of 104.3, 79.5, 161.9 and 400.1 MHz, respectively, using 7 mm (^{29}Si) and 4 mm (all other resonances) Bruker DB MAS NMR probes. The *in situ* ^{1}H and ^{13}C CF MAS NMR investigations were carried out at the same spectrometer at resonance frequencies of 400.1 and 100.6 MHz, respectively, applying a high-temperature 7 mm Doty MAS NMR probe (DSI-740) modified as described in [24]. ^{13}C CF MAS NMR spectra were recorded after direct excitation and proton decoupling. For each ^{1}H and ^{13}C CF MAS NMR spectrum, 100 and from 500 to 700, respectively, free induction decays were accumulated with a repetition time of 5 s. The ^{1}H, ^{13}C and ^{29}Si MAS NMR signals were referred to TMS and for ^{27}Al and ^{31}P MAS NMR spectroscopy, 0.1 M solution of $Al(NO_3)_3$ and H_3PO_4 (85%), respectively, were used as external chemical shift standards.

Via a glass tube, axially inserted into the MAS NMR rotor of the modified high-temperature 7 mm Doty MAS NMR probe, carrier gas loaded with reactant molecules could be injected into the sample volume of the MAS NMR rotor spinning with a rate of up to 3.5 kHz at temperatures up to 873 K. *Via* an exhaust tube at the rotor cap, the probe was connected with the sampling loop of an on-line gas chromatograph HP 5890 equipped with a Coating Poraplot Q capillary column (see [24]). To improve the quantitative evaluation of the chromatograms, an internal gas standard (methane) was added to the carrier gas. Before the *in situ* CF MAS NMR experiments, all samples were heated with 20 K/h up to the final temperature of 673 K and evacuated at this temperature at a pressure below 10^{-2} Pa for 12 h. The dehydrated catalysts were filled into the MAS NMR rotor reactor under dry nitrogen in a glove box and pressed to a cylindrical catalyst bed (see [24]). After transferring the rotor into the MAS NMR probe, a second dehydration of the catalyst was performed for 1 h at 673 K under flowing nitrogen (30 ml/min). The *in situ* CF MAS NMR experiments were carried out with 100 mg of dry catalyst during the injection of deuterated (Fluka, 34,385-4) or ^{13}C-enriched (Campro, Scientific, 83-00005-9) methanol according to a modified residence time of $W_{cat}/F_{CH_3OH} = 25$ g h/mol.

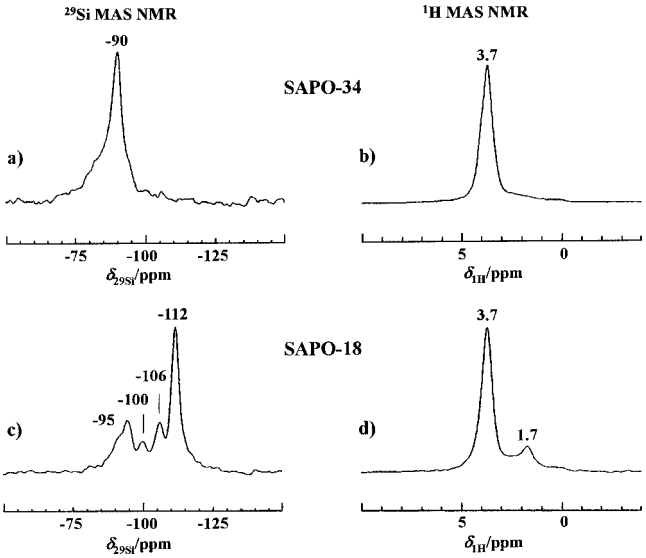


Figure 1. ^{29}Si and ^{1}H MAS NMR spectra of the silicoaluminophosphates SAPO-34 (a, b) and SAPO-18 (c, d), recorded after calcination and rehydration (a, c) and in the dehydrated state (b, d).

3. Results and discussion

3.1. Characterization of the calcined SAPO-34 and SAPO-18

The X-ray diffraction patterns of the calcined and rehydrated SAPO-34 and SAPO-18 agree well with the pattern given in [25]. As shown by REM, the silicoaluminophosphates SAPO-34 and SAPO-18 have crystals with mean diameters of 0.5–1.0 μm. The ^{31}P MAS NMR spectra of both samples consist of a single line at *ca.* -30 ppm due to framework phosphorus atoms bound *via* oxygen bridges with four framework aluminium atoms. In the ^{27}Al MAS NMR spectra of the hydrated samples, signals of tetrahedrally coordinated framework aluminium at 39–41 ppm, of octahedrally coordinated aluminium at -12 to -14 ppm and a weak signal of fivefold coordinated *ca.* 13 ppm occurred. The ^{29}Si MAS NMR spectra shown in figure 1 indicate that in the SAPO-34 with an $n_{Si}/(n_{Al} + n_{Si} + n_P)$ ratio of 0.088 (ICP-AES) nearly all silicon atoms are located at framework Si(4Al) sites leading to the signal at -90 ppm. In contrast to this finding, the ^{29}Si MAS NMR spectrum of the SAPO-18 with an $n_{Si}/(n_{Al} + n_{Si} + n_P)$ ratio of 0.115 (ICP-AES) consists of signals at -94.5, -99.8, 105.8 and 111.5 ppm due to silicon atoms located at Si(3Al,1Si), Si(2Al,2Si), Si(1Al,3Si) and Si(4Si) sites, respectively [26,27]. The signal at -111.5 ppm hints at the formation of silicon islands. In agreement with these results, the ^{1}H MAS NMR spectrum of SAPO-34 shows a single line of bridging OH groups at 3.7 ppm while in the spectrum of SAPO-18 an additional line of SiOH groups occurs at 1.7 ppm, probably caused by silicon islands [28].

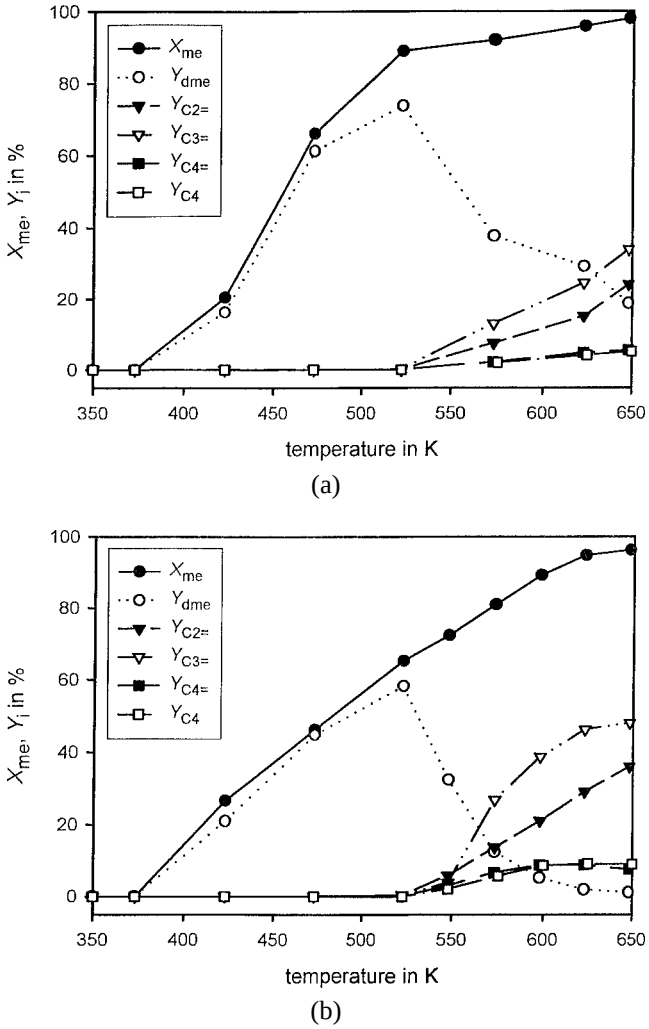


Figure 2. Conversion of methanol, X_{me}, and yields, Y_i, of dimethyl ether (dme), ethylene ($C_{2=}$), propylene ($C_{3=}$), butenes ($C_{4=}$) and butanes (C_4) obtained on the silicoaluminophosphate SAPO-34 at reaction temperatures between 350 and 650 K and with a modified residence time of $W_{cat}/F_{me} = 25$ g h/mol in a fixed-bed reactor (a) and in an MAS NMR rotor reactor (b) spinning with 1.7–2 kHz.

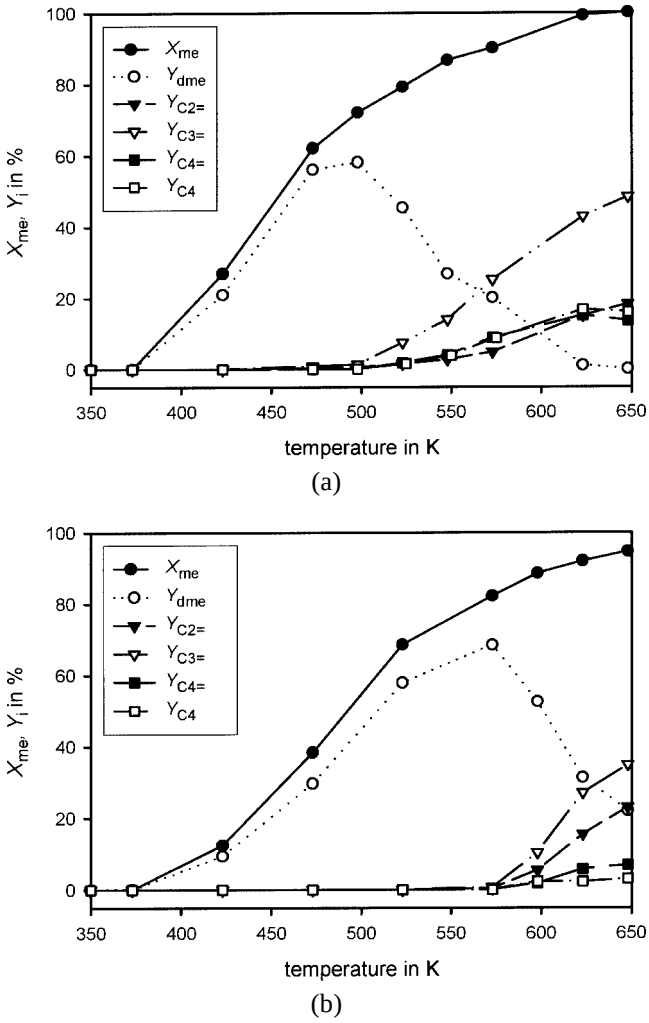


Figure 3. Conversion of methanol, X_{me}, and yields, Y_i, of dimethyl ether (dme), ethylene ($C_{2=}$), propylene ($C_{3=}$), butenes ($C_{4=}$) and butanes (C_4) obtained on the silicoaluminophosphate SAPO-18 at reaction temperatures between 350 and 650 K and with a modified residence time of $W_{cat}/F_{me} = 25$ g h/mol in a fixed-bed reactor (a) and in an MAS NMR rotor reactor (b) spinning with 1.7–2 kHz.

3.2. Comparative catalytic investigation of methanol conversion on SAPO-34 and SAPO-18 in a fixed-bed and a spinning MAS NMR rotor reactor

To clarify the significance of *in situ* MAS NMR investigations under continuous flow (CF) conditions for the study of the mechanism of methanol conversion on SAPO-34 and SAPO-18, the catalytic investigations were performed under equal conditions in a fixed-bed reactor and a spinning MAS NMR rotor reactor. The fixed-bed reactor with an inner diameter of 8 mm was filled with 100 mg of dry catalysts. During the catalytic measurements, a flow of methanol according to a modified residence time of $W_{cat}/F_{CH_3OH} = 25$ g h/mol was introduced. In figures 2(a) and 3(a) the conversions of methanol (X_{me}) on SAPO-34 and SAPO-18 and the yields of hydrocarbons (Y_i) obtained at reaction temperatures between 373 and 648 K are summarized. The conversions of methanol (X_{me}) on the SAPO-34 and SAPO-18 and the yields of hydrocarbons (Y_i) determined under the same conditions with catalysts in a spinning MAS NMR rotor reactor are given in figures 2(b) and 3(b). In the latter case, 100 mg of dry catalyst was pressed to a hollow cylinder in a 7 mm Doty MAS NMR rotor. After transferring the rotor into the MAS NMR turbine, a glass tube was inserted to the centre of the hollow cylinder and dry carrier gas (nitrogen) loaded with methanol was injected into the sample volume of the MAS NMR rotor reactor.

Comparing the reaction of methanol on SAPO-34 and SAPO-18 in the fixed-bed and the spinning MAS NMR rotor reactor, on both catalysts a lower conversion of methanol, X_{me}, was obtained for the rotor reactor. This may be due to the fact that in the rotor reactor the reactants flow along the surface of the catalyst bed and not through the catalyst bed as in the fixed-bed reactor. However, these differences in the methanol conversion are only significant at low reaction temperatures (423–573 K). Differences were observed also for

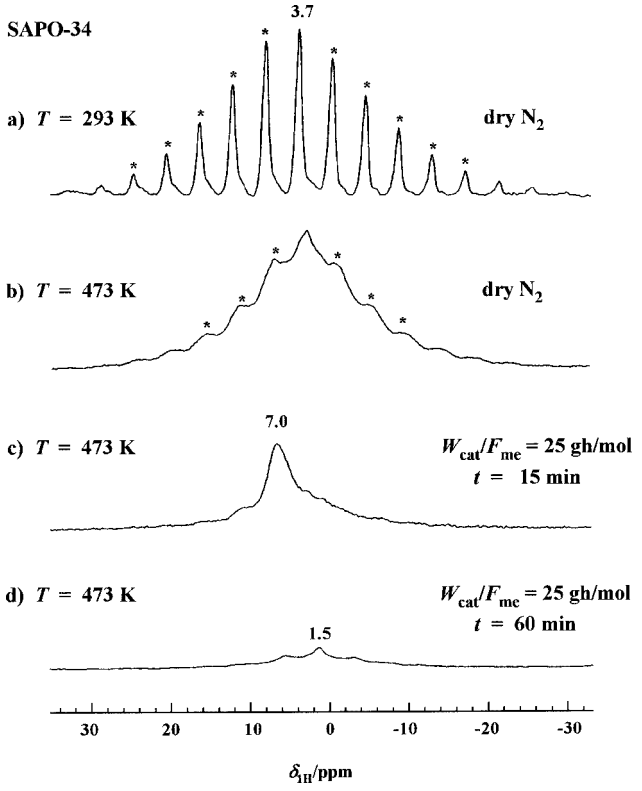


Figure 4. ^{1}H CF MAS NMR spectra of the silicoaluminophosphate SAPO-34, recorded at room temperature (a) and 473 K (b) under purging with dry carrier gas (nitrogen) and at 473 K during the conversion of deuterated methanol (W_{cat}/F_{me} = 25 g h/mol) for 15 (c) and 60 min (d). Asterisks denote spinning sidebands.

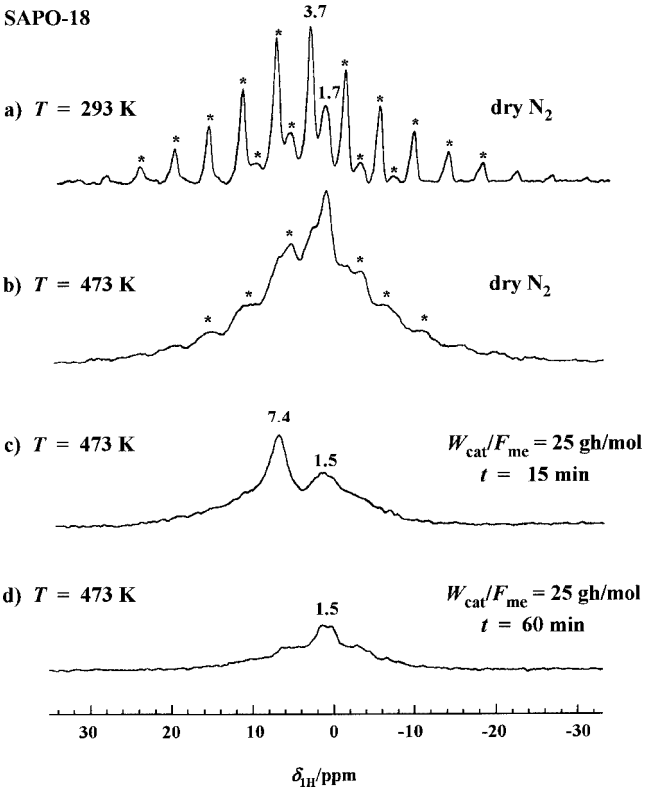


Figure 5. ^{1}H CF MAS NMR spectra of the silicoaluminophosphate SAPO-18, recorded at room temperature (a) and 473 K (b) under purging with dry carrier gas (nitrogen) and at 473 K during the conversion of deuterated methanol (W_{cat}/F_{me} = 25 g h/mol) for 15 (c) and 60 min (d). Asterisks denote spinning sidebands.

the yields of hydrocarbons on SAPO-34 and SAPO-18 in the two reactor types. However, on both the catalysts and with the two reactor types the same characteristic behavior of the yields of hydrocarbons was found: a preferential formation of dimethyl ether at temperatures from 423 to 548 K and a preferential formation of propylene and ethylene at temperatures higher than 573 K. Interestingly, for SAPO-34 higher yields of propylene ($Y_{C_{3=}}$) and ethylene ($Y_{C_{2=}}$) and lower yields of dimethyl ether (Y_{dme}) were obtained in the spinning MAS NMR rotor reactor. The catalytic experiments clearly demonstrate the qualitative agreement of the conversion of methanol on SAPO-34 and SAPO-18 in the fixed-bed reactor and the rotor reactor. Hence, *in situ* experiments performed with the *in situ* CF MAS NMR technique described in [24] can be used to model the conversion of methanol on acidic catalysts in fixed-bed reactors. In addition, catalytic studies over a time on stream of 8 h (not shown) showed that there is no deactivation of the catalysts up to a time on stream of 6 h. These results ensure constant reaction conditions over the accumulation time from 42 to 58 min used in the *in situ* ^{13}C CF MAS NMR experiments.

3.3. ^{1}H CF MAS NMR investigations of the conversion of deuterated methanol on SAPO-34 and SAPO-18

The application of deuterated methanol allows one to study the fate of the catalytically active Brønsted sites after starting the reaction under continuous flow conditions. For a catalytic cycle consisting of a proton transfer to the reactant molecules, the conversion of deuterated methanol molecules on acidic OH groups results in an H/D exchange and leads to a decrease of the ^{1}H MAS NMR signals caused by Brønsted sites. Before the *in situ* ^{1}H CF MAS NMR investigations of the conversion of deuterated methanol on SAPO-34 and SAPO-18, the dehydrated catalysts were studied in a flow of dry carrier gas (nitrogen) yielding the spectra shown in figures 4 (a) and (b), 5 (a) and (b). Due to the low sample spinning rate of 2 kHz, the spectra recorded at room temperature consist of broad sideband patterns with central lines of silanol and bridging OH groups at 1.7 and 3.7 ppm, respectively. In agreement with earlier investigations [29–31], raising of the temperature to 473 K leads to a broadening of the central lines and the sidebands indicating an increase in the mobility of the corresponding hydroxyl protons.

The ^{1}H MAS NMR spectra shown in figures 4 (c) and (d), 5 (c) and (d) were recorded under a continuous flow of deuterated methanol (W_{cat}/F_{me} = 25 g h/mol) at 473 K. After a conversion of CD_3OD on SAPO-34 over a time of 15 min, a decrease of the ^{1}H MAS NMR intensity of Brønsted sites by 82% was found (figure 4(c)). According to figure 2(b), a preferential formation of dimethyl ether occurs at this reaction temperature. The residual ^{1}H MAS NMR signal of non-deuterated bridging OH groups is shifted from

a resonance position of 3.7–7.0 ppm. This low field shift indicates an interaction of the non-deuterated bridging OH groups with reactant molecules. After a time on stream of 60 min (figure 4(d)), only a weak signal of silanol groups occurs at 1.5 ppm, which indicates that all bridging OH groups were deuterated. Conversion of CD_3OD on SAPO-18 leads to similar results (figure 5 (c) and (d)). After a time on stream of 15 min, the ^{1}H MAS NMR intensity was decreased by 76%. The corresponding ^{1}H MAS NMR spectrum consists of signals at 1.5 ppm due to silanol groups and at 7.4 ppm caused by bridging OH groups interacting with the reactants. Again, after a time on stream of 60 min the spectrum shows only a single signal at 1.5 ppm due to silanol groups which are not involved in the deuteration. The complete disappearance of the signal of bridging OH groups indicates that all these hydroxyl groups were deuterated and, therefore, involved in the conversion of methanol. According to this finding the conversion of methanol carried out in a spinning MAS NMR rotor reactor occurs in the whole catalyst bed and not only in a surface-near layer.

Quantum-chemical investigations of adsorbate complexes formed by methanol molecules and bridging OH groups yielded that twofold H-bonded complexes are the most stable adsorption structures [2]. In this adsorption structure, both the hydroxyl proton of the bridging OH group and that of the methanol molecule are involved in H-bondings. Using an MP2-optimized structure, Haase and Sauer [2] obtained a mean ^{1}H NMR shift for the twofold H-bonded complex amounting to 10.8 ppm. The ion-pair structure consisting of the deprotonated framework cluster and a methoxonium ion was found to be a transition state and yielded a ^{1}H NMR shift of 17.4 ppm [2]. A comparison of these theoretical shift values with the ^{1}H MAS NMR shifts of the hydroxyl signals in figures 4(c) and 5(c) indicates the formation of adsorbate structures consisting of twofold H-bonded complexes. The smaller values of the experimentally observed shifts of 7.0–7.4 ppm in comparison with the theoretical value of 10.8 ppm may be due to the low acid strength of bridging OH groups in silicoaluminophosphates.

3.4. ^{13}C CF MAS NMR investigations of the conversion of ^{13}C-enriched methanol on SAPO-34 and SAPO-18

The *in situ* ^{13}C CF MAS NMR spectra shown in figures 6 and 7 were recorded during the conversion of ^{13}C-enriched methanol on SAPO-34 and SAPO-18 under reaction conditions identical to those applied for the catalytic investigations summarized in figures 2(b) and 3(b). The yields of dimethyl ether and C_2–C_4 hydrocarbons given on the left-hand side of figures 6 and 7 were simultaneously determined by on-line gas chromatography.

The ^{13}C CF MAS NMR spectra recorded during the conversion of methanol at reaction temperatures between 373 and 473 K (figures 6 (a)–(c) and 7 (a)–(c)) consist of signals at 50 and 61 ppm due to methanol and dimethyl ether (dme), respectively. The increase of the line at 61 ppm with raising the reaction temperature to 523 K is coupled with an increase of the yield of dme to 58%. In a recently published work of methanol conversion on zeolite H-ZSM-5 [18], a signal of methoxy groups was observed at *ca.* 59 ppm after the conversion of methanol and purging the catalyst with dry carrier gas (nitrogen) at 473 K. In contrast to this finding, no signal of methoxy groups occurred after methanol conversion on SAPO-34 and SAPO-18 at 473 K and purging with dry carrier gas. This finding indicates that methoxy groups on the silicoaluminophosphates SAPO-34 and SAPO-18, if they were formed, have a lower chemical stability than on the stronger acidic zeolite H-ZSM-5. After the further increase of the reaction temperature to 523 and 548 K, additional ^{13}C MAS NMR signals occurred at *ca.* 11–40 ppm due to CH_2 and CH_3 groups of saturated hydrocarbons (figures 6 (e) and (f), 7 (e) and (f)). Starting at the reaction temperature of 573 K, significant amounts of light olefins were determined by on-line gas chromatography. Simultaneously, signals of olefinic compounds occurred in the low-field range of the ^{13}C MAS NMR spectra at 129 ppm and 132–135 ppm (figures 6 (g) and (h), 7 (g) and (h)). With the increase of the formation of propylene and ethylene, the high-field range of the spectra is dominated by signals at 20–22 ppm while most of the other signal of CH_2 and CH_3 groups disappear. It is important to note that no signal of ethoxy, propoxy or butoxy groups (77–87 ppm [32–34]), trimethyl oxonium (80 ppm [13,35]) and 1,3-dimethylcyclopentenyl carbenium ions (24, 48, 148 and 250 ppm [19]) was observed. After purging the working catalysts at 673 K with dry carrier gas, a significant amount of the hydrocarbons responsible for the ^{13}C MAS NMR signals at resonance positions from 20 to 22 ppm and from 132 to 135 ppm were removed. This indicates that most of the above-mentioned signals are not due to coke deposits.

A more detailed evaluation of the low-field range of the ^{13}C CF MAS NMR spectra recorded at 573 and 623 K is given in figure 8. A suitable simulation of the low-field range was achieved using sideband patterns with central lines at resonance positions of 129 ppm and from 132 to 135 ppm. The spectrum recorded during conversion of methanol on SAPO-34 at 573 K (figure 8(a)) can be described by two signals at 132 and 134 ppm with an anisotropy of the chemical shift, $\Delta\sigma$, of 0 and -70 ppm, respectively, and an asymmetry parameter of $\eta = 0.8$. The increase of the reaction temperature to 623 K (figure 8(b)) led to a further increase of the above-mentioned sideband patterns and the occurrence of weak signals at 126 and 130 ppm with $\Delta\sigma$ values of -40 and -25 ppm, respectively, and $\eta = 0.8$. The simulation of the spectrum recorded during conversion of methanol on SAPO-18 at 573 K (figure 8(c)) was performed using two sideband patterns at 135 ppm with $\Delta\sigma$ values of 0 and -70 ppm and $\eta = 0.8$ and of weak signals at 127, 132 and 142 ppm. The increase of the reaction temperature to 623 K (figure 8(d)) led to a further increase of all signals, especially of the signals at resonance positions from 127 to 132 ppm. The occurrence of sideband patterns indicates the formation of organic compounds, olefinic or aromatic species with a low mobility in the 8-ring pore system of SAPO-34 and SAPO-18.

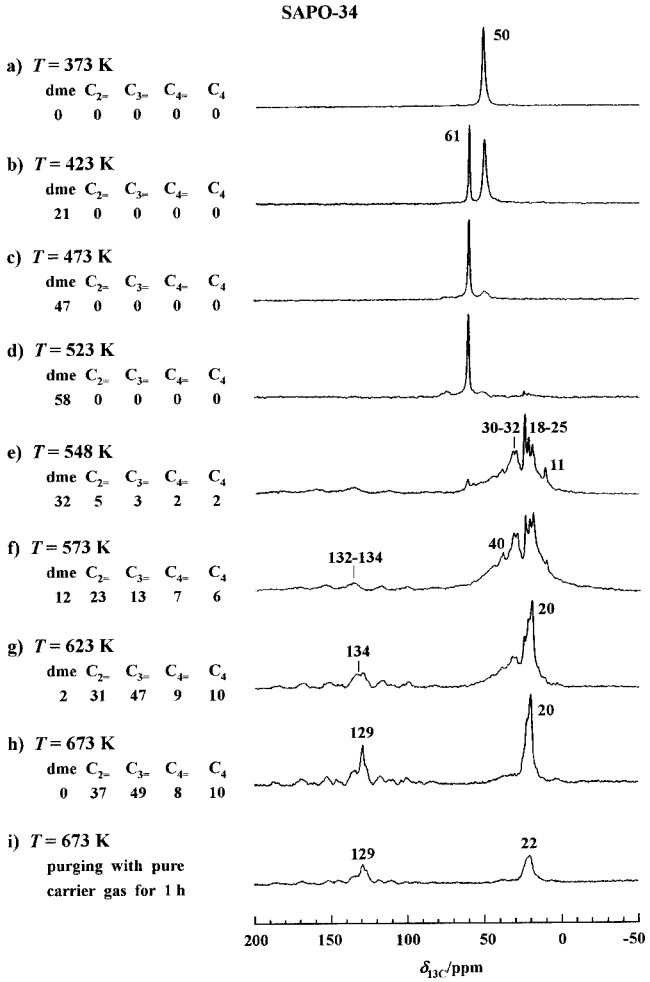


Figure 6. ^{13}C CF MAS NMR spectra recorded during the conversion of ^{13}C-enriched methanol (W_{cat}/F_{me} = 25 g h/mol) on the silicoaluminophosphate SAPO-34 at reaction temperatures between 373 and 673 K (a)–(h). The spectrum (i) was obtained after purging the catalysts with dry carrier gas at 673 K after methanol conversion at 673 K. On the left hand side, the yields of dimethyl ether (dme), ethylene ($C_{2=}$), propylene ($C_{3=}$), butenes ($C_{4=}$) and butanes (C_4) simultaneously determined by on-line gas chromatography are given.

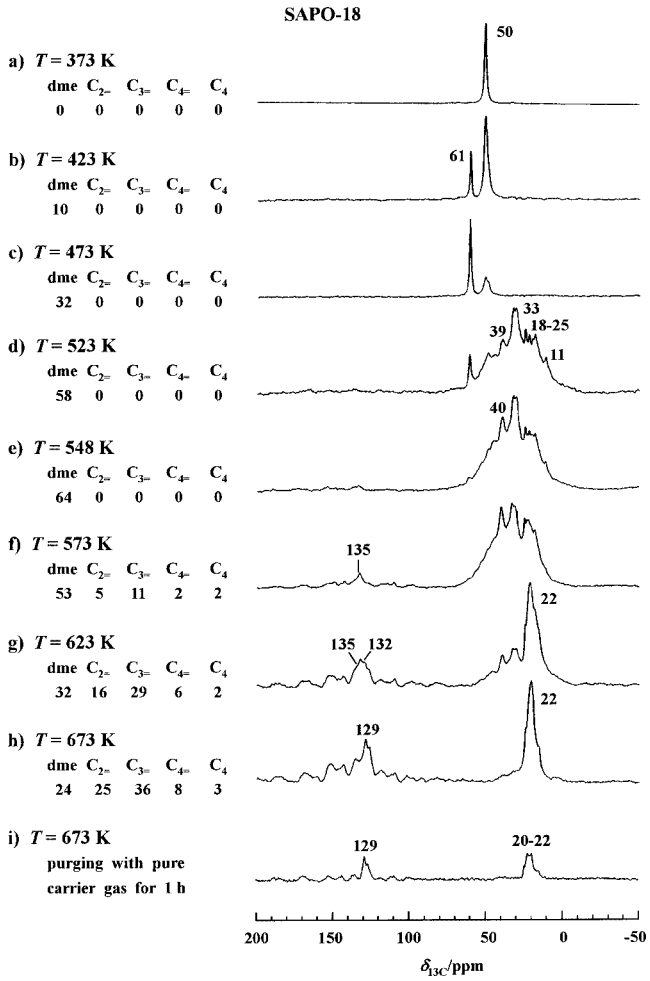


Figure 7. ^{13}C CF MAS NMR spectra recorded during the conversion of ^{13}C-enriched methanol (W_{cat}/F_{me} = 25 g h/mol) on the silicoaluminophosphate SAPO-18 at reaction temperatures between 373 and 673 K (a)–(h). The spectrum (i) was obtained after purging the catalysts with dry carrier gas at 673 K after methanol conversion at 673 K. On the left hand side, the yields of dimethyl ether (dme), ethylene ($C_{2=}$), propylene ($C_{3=}$), butenes ($C_{4=}$) and butanes (C_4) simultaneously determined by on-line gas chromatography are given.

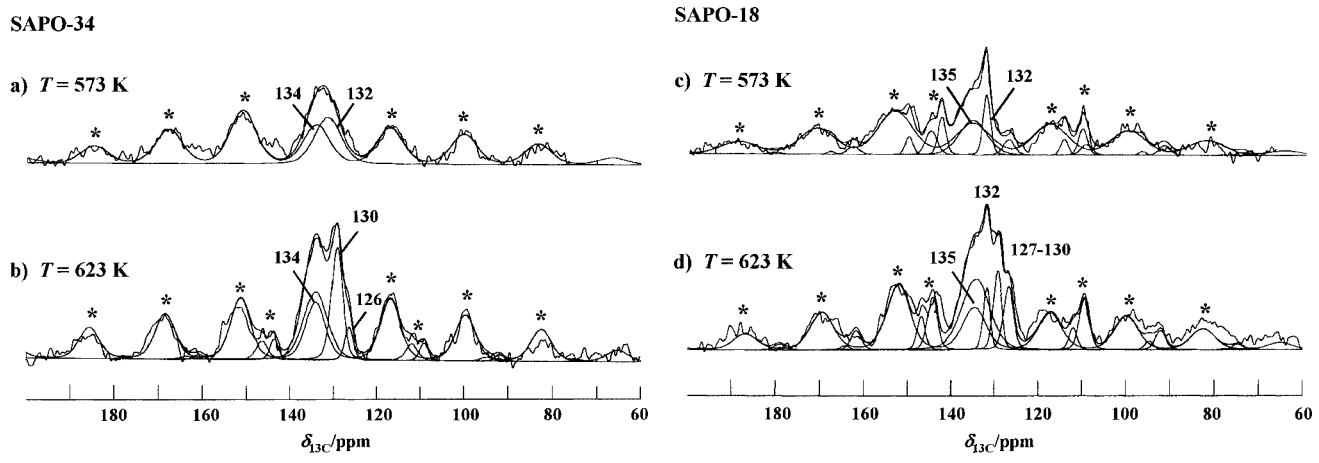


Figure 8. Simulation of the aromatic and olefinic region of the ^{13}C CF MAS NMR spectra recorded during conversion of methanol on silicoaluminophosphates SAPO-34 (a, b) and SAPO-18 (c, d) at reaction temperatures of 573 and 623 K (compare figures 6 (f) and (g) and 7 (f) and (g)) with a sample spinning frequency of 1.7 kHz. Asterisks denote spinning sidebands. The simulations were performed with the Bruker software WINFIT.

A suitable way for the assignment of the above-mentioned ^{13}C CF MAS NMR signals is the adsorption of all molecules which could be formed by conversion of methanol on acidic solids. However, in the present case this method is problematic since large molecules such as arenes could be formed in the cages of the CHA and AEI framework, but cannot be adsorbed due to the limitations of the 8-ring pore systems. The adsorption of reactive olefins requires the application of low temperature NMR spectroscopy yielding signals which are not characteristic for the *in situ* ^{13}C CF MAS NMR experiments in the present work. Studying chemically stable alkanes adsorbed on acidic zeolites at temperatures up to 673 K, a low-field shift of there resonance positions of maximum 2 ppm in comparison with those obtained in inert solutions was found. Therefore, the assignment of the signals in the aromatic and olefinic shift range in figure 8 was performed using data given in [36–38]. Based on these data, the signal occurring at *ca.* 129 ppm in the spectra recorded at 673 K (figures 6(h) and 7(h)) indicate the formation of aromatic compounds. Since these signals remain in the spectra after purging with dry carrier gas (figures 6(i) and 7(i)), the aromatic compounds are occluded in the cages of SAPO-34 and SAPO-18. The best assignment for the ^{13}C MAS NMR signals observed at reaction temperatures of 573 and 623 K (figure 8) is a mixture of 3-hexene (131–133, *ca.* 21 and *ca.* 15 ppm), 2,5-dimethyl-3-hexene (134–136, *ca.* 32 and *ca.* 22 ppm), 2,3-hexadiene (132–134, 126–128 and *ca.* 18 ppm) and alkylated octadienes (133–135, *ca.* 25, *ca.* 23 and *ca.* 15 ppm). But the formation of cyclic olefins such as cyclopentene (131–133, *ca.* 33 and *ca.* 23 ppm) and cyclopentadiene (133–135 and *ca.* 42 ppm) and alkylated cyclopentenes such as diethylcyclopentene (133–135 ppm and various signals at *ca.* 14–33 ppm) and *para*-xylene (129, 134 and 21 ppm) cannot be excluded. The occurrence of a large number of different peaks and the broadening of the low-field signals, which indicates a distribution of chemical shifts, hint to the formation of a mixture of aliphatic and cyclic olefins and alkylated aromatics with carbon numbers of C_6–C_{12}. Species similar to the latter compounds were proposed by Haw *et al.* [19]as neutral π complexes of alkylated cyclopentenyl carbenium ions observed during the induction period of the conversion of methanol on zeolite H-ZSM-5. However, there are no indications for the presence of carbenium cations such as 1,3-dimethylcyclopentenyl carbenium ions (250, 148, 48 and 24 ppm) as described by Haw *et al.* [19]. The half-life of this carbenium ion of 6 s at 723 K [19] is long enough for its detection under the conditions of the *in situ* ^{13}C CF MAS NMR experiments in the present work. A possible explanation for the absence of 1,3-dimethylcyclopentenyl carbenium ions may be the low energy barrier of only 2.2 kcal/mol [19] for their transformation into the corresponding neutral π complexes.

The presence of C_6–C_{12} olefins and aromatics on working SAPO-34 and SAPO-18 catalysts during conversion of methanol supports the "hydrocarbon pool" mechanism proposed by Hoelderich *et al.* [39], Kolboe [40] and Dessau [41]. According to this mechanism, "big" carbonaceous species such as C_6–C_{12} olefins exist inside the zeolite pores and add reactants by methylation and split off product molecules.

4. Conclusions

Catalytic investigations of the conversion of methanol on silicoaluminophosphates SAPO-34 and SAPO-18 performed under continuous flow conditions in the fixed-bed reactor and in the spinning MAS NMR rotor reactor yielded a good qualitative agreement in the reaction products analysed by on-line gas chromatography. Hence, the results obtained by *in situ* ^{13}C MAS NMR spectroscopy under continuous flow conditions (CF) are significant for the study of the mechanisms of methanol conversion on solid catalysts in fixed-bed reactors.

Via the conversion of deuterated methanol on SAPO-34 and SAPO-18 at 473 K, the fate of the bridging OH groups acting as catalytically active Brønsted sites was studied by ^{1}H CF MAS NMR spectroscopy. The low field shift of the ^{1}H MAS NMR signal of bridging OH groups to resonance positions of 7.0–7.4 ppm during the first 15 min of time on stream indicates the formation of twofold H-bonded adsorbate complexes as a first step of the methanol conversion at 473 K. The complete disappearance of the ^{1}H MAS NMR signal of bridging OH groups after a time of stream of 60 min shows that all bridging OH groups were deuterated, *i.e.*, they were all involved in the conversion of CD_3OD.

In situ ^{13}C CF MAS NMR and on-line gas chromatographic investigations of the conversion of ^{13}C-enriched methanol on SAPO-34 and SAPO-18 at reaction temperatures of 373 to 473 K yielded the formation of dimethyl ether. In contrast to a recently published *in situ* ^{13}C CF MAS NMR study of methanol conversion on zeolite H-ZSM-5 [18], no signal of methoxy groups was observed after purging the working catalysts at 473 K with dry carrier gas. This finding indicates a lower chemical stability of methoxy groups on silicoaluminophosphates than in the stronger acidic zeolite H-ZSM-5.

As analysed by on-line gas chromatography, the increase of the reaction temperature to 673 K results in a preferential formation of propylene and ethylene. Simultaneously with the increase in the formation of light olefins, the *in situ* ^{13}C CF MAS NMR spectra indicate the formation of a mixture of aliphatic and cyclic olefins and alkylated aromatics with carbon numbers of C_6–C_{12} on SAPO-34 and SAPO-18 catalysts. In contrast, in the steady state of methanol conversion on zeolite H-ZSM-5, the formation of C_4–C_6 olefins was observed [18]. The presence of a mixture of aliphatic and cyclic olefins and alkylated aromatics with carbon numbers of C_6–C_{12} on working SAPO-34 and SAPO-18 catalysts support the "hydrocarbon pool" mechanism proposed for the formation of light olefins by conversion of methanol on acidic zeolites. Most of the above-mentioned compounds can be removed from the catalyst by purging with dry carrier gas at reaction temperature. The residual signals observed after the purging are due to a small amount of aromatic compounds which agrees with the finding of Song *et al.* [20]

by converting methanol on SAPO-34. The absence of additional signals due to aliphatic and cyclic olefins in [20] may be caused by differences in the reaction conditions such as the modified residence time of the reactant methanol and the requirements of the technique applied such as the transfer of the catalyst material loaded with reactants into the MAS rotor and the NMR spectrometer after stopping the reaction performed in an external reactor.

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