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Mechanistic investigations of the methanol-to-olefin (MTO) process on acidic zeolite catalysts by in situ solid-state NMR spectroscopy

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Abstract

This paper reviews mechanistic investigations of the methanol-to-olefin (MTO) process by in situ solid-state NMR spectroscopy, mainly performed under continuous-flow and stopped-flow conditions. During methanol conversion on the silicoaluminophosphate H-SAPO-34 under continuous-flow conditions, a hydrocarbon-pool consisting of a mixture of C_6–C_{12} olefins and aromatics was found. The hydrocarbon-pool mechanism was verified as the dominating route in the MTO process under steady-state conditions. By in situ MAS NMR experiments under continuous-flow conditions it could be demonstrated that methanol molecules are added to the hydrocarbon-pool and light olefins are split off as reaction products. The reactivity of surface methoxy groups in the MTO process were evidenced by the reaction with different probe molecules. By the new developed in situ MAS NMR-UV/vis technique, the initial formation of the hydrocarbon-pool during the induction period was investigated.

Keywords: Heterogeneous catalysis; MTO (methanol-to-olefin) process; Acidic zeolites; Hydrocarbon-pool; Methoxy groups; In situ NMR spectroscopy

1. Introduction

Since its discovery by Chang and Silvestri at Mobil Oil in 1977, the conversion of methanol to hydrocarbons (MTHC) on acidic zeolite catalysts has attracted significant research attention [1–3]. The MTHC technology, mainly the methanol-to-gasoline (MTG) and methanol-to-olefin (MTO) reactions, was regarded as a new route to convert coal or natural gas into high-octane gasoline and chemicals in general [1]. In 1986, the MTG process was commercialized in New Zealand, producing ca. 600,000 tonnes gasoline per year via this route [4]. Unfortunately, this attempt has not led to a world-wide industry as expected and the MTG production part of the factory was later closed down, due to the more benefit from methanol than gasoline. However, the extensive interest in the reaction mechanism has still been rising from both industrial and academic researchers. Due to increasing demands for light olefins in the past decade, research in the field of heterogeneous catalysis focused on the mechanisms of the MTO process.

The main reaction route of the MTO process can be described in the following [1]: the first step is the formation of dimethyl ether (DME) by the dehydration of methanol on acidic zeolite catalysts. The equilibrium mixture of methanol, DME and water is converted to light olefins, which further form higher olefins, paraffins, aromatics and naphthenes via hydrogen transfer, alkylation, isomerization, polycondensation and other secondary reactions. The detailed mechanism involved in the MTO process has been, however, a matter of discussions till now. Two issues are mainly argued: (i) dehydration of methanol to DME in the low-temperature range of $T \leq 523$ K. It has been a matter of research, whether or not the surface methoxy groups, which can be formed from methanol at bridging OH groups of acidic zeolites, act as active intermediates during the conversion of methanol to DME. (ii) The initial C–C bond formation from the C_1 reactants in the high-temperature range of $T \geq 523$ K. More than 20 mechanistic proposals were suggested for the first C–C bond formation in the MTO process, some of which are based on surface-bound alkoxy species, oxonium ylides, carbenes, carbocations or free radicals as key intermediates [1]. The various mechanistic

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proposals concerning the first C–C bond formation were summarized recently in the review paper of Stoecker [1].

In situ spectroscopic methods [5–8] toward getting snapshots of a working catalyst are superior approaches to investigate the mechanisms involved in heterogeneous catalysis. Solid-state Magic-Angle Spinning (MAS) NMR spectroscopy [9–13], which can provide both structural and dynamic information about the heterogeneous catalytic system, is certainly considered as one of the most suitable approaches for these in situ studies. In the last two decades, various MAS NMR spectroscopic techniques [5–8,14–22] have been developed for in situ investigations on heterogeneous catalysis. Among the in situ NMR techniques successfully applied to study the conversion of methanol on acidic zeolites in the low-temperature ($T \leq 523$ K, formation of DME) and/or high-temperature range ($T \geq 523$ K, formation of olefins and gasoline), are the stop-and-go method under batch conditions [23,24], the pulse-quench method [25,26] and various flow techniques [27–34]. This paper summarizes mechanistic studies of the MTO process by in situ MAS NMR spectroscopy mainly performed under continuous-flow and stopped-flow conditions.

2. Investigation of the MTO process under steady-state conditions: hydrocarbon-pool mechanism

Haag [35], Hoelderich et al. [36], Dessau [37] and Kolboe and Dahl [38–41] suggested a hydrocarbon-pool mechanism to explain the formation of light olefins. According to this proposal, large carbonaceous species are initially formed during the induction period of the reaction, which can further add reactants and split off products in the steady-state of the reaction. The hydrocarbon-pool species were proposed to possess many characteristics for ordinary coke, which may be described by $(CH_x)_n$ with $0 < x < 2$ [1]. Recent studies [17,25,26,29,30,34,42–46] have verified that the MTO process under steady-state conditions is dominated by this hydrocarbon-pool route. Methanol is added onto the reactive organic species, such as polymethylbenzenes, large olefins, cyclic carbenium ions and probably methylbenzenium cations, while light olefins are formed via the elimination of alkyl chains from these organic centers. In situ MAS NMR spectroscopy under flow conditions has been applied to shed more light on this hydrocarbon-pool route involved in the MTO process under steady-state conditions on zeolites H-ZSM-5, H-SAPO-34 and H-SAPO-18 as catalysts [29,30,34].

2.1. Characterization of the hydrocarbon-pool

The various NMR techniques, developed for in situ investigations of heterogeneously catalyzed reactions, have been reviewed elsewhere [5,18,20–22]. In 1995, the first in situ MAS NMR technique under continuous-flow (CF) conditions was introduced [47,48]. This technique utilizes an MAS NMR rotor inside a variable-temperature probe as a microreactor for heterogeneous catalysis. This technique successfully realizes the continuous feeding of the volatile reactants (vapor) by carrier gas (dry nitrogen) into the spinning MAS NMR rotor [47,48]. By a special tool, the activated catalyst in the MAS NMR rotor is pressed to a hollow cylinder. An injection tube is inserted into the sample volume via an axially placed hole in the MAS NMR rotor cap. The reactant feed is injected into the inner space of the hollow cylinder and flows from the bottom to the top of the MAS NMR rotor reactor [47,48]. The volatile products leave the sample volume continuously via an annular gap in the rotor cap, and can be further introduced into the sampling loop of an on-line gas chromatograph [49]. Using a DSI-740 7 mm STD MAS NMR probe (Doty Scientific Instruments, Columbia, TX, USA) modified with a home-built injection system, in situ NMR investigations of heterogeneously catalyzed reactions can be performed under flow conditions at atmospheric pressure, at temperatures up to 723 K, and with sample spinning rates of 2–3 kHz [29,50].

With this technique, a direct NMR investigation of the formation and transformation of surface species and a simultaneous gas chromatographic analysis of the reaction products under steady-state conditions is possible. The MTO process was, therefore, investigated by this in situ CF MAS NMR technique. To ensure that meaningful catalytic investigations are performed in the spinning MAS NMR rotor reactor, the catalytic experiments were reproduced in a conventional fixed-bed reactor under the identical operating conditions. Methane was deliberately added as an internal gas standard to the methanol flow and analyses of the reaction products were undertaken via on-line gas chromatography [30]. In Fig. 1, the conversion of methanol, X_{me}, and the yields, Y_i, of main reaction products obtained on H-SAPO-34 in the reaction temperature range of 373–648 K are plotted. The modified residence time of methanol was $W/F = 25$ g h/mol in both reactors [30]. The results obtained for the studies performed with the fixed-bed reactor (Fig. 1a) agree well with those obtained with the spinning MAS NMR rotor reactor (Fig. 1b). Methanol conversion takes place in the same temperature range, and the same qualitative shapes of the conversion and yield curves were obtained both using the fixed-bed reactor and the spinning MAS NMR rotor reactor [30]. Slight quantitative deviations in the yield curves are explained by the different shapes of the catalyst beds inside the two reactors. In conclusion, the in situ CF MAS NMR technique is reliable to characterize methanol conversion on acidic zeolite catalysts under steady-state conditions.

To investigate the methanol conversion under steady-state conditions by in situ CF MAS NMR spectroscopy, a flow of ^{13}C-enriched methanol ($W/F = 25$ g h/mol) was injected into a spinning 7 mm MAS NMR rotor reactor filled with ca. 100 mg of the calcined zeolites H-ZSM-5, H-SAPO-18 or H-SAPO-34 [29,30]. Fig. 2 shows the in situ ^{13}C CF MAS NMR spectra obtained during the conversion of $^{13}CH_3OH$ on H-SAPO-34 ($n_{Si}/(n_{Al} + n_{Si} + n_P) = 0.088$) at reaction temperatures of 373–673 K. In the low-temperature range of $T \leq 523$ K (Fig. 2a–d), the conversion of methanol to DME takes place, indicated by the ^{13}C MAS NMR signals at 50 (methanol) and 61 (DME) ppm. This finding agrees with the high yield of DME ($Y_{dme} = 58\%$) at 523 K obtained by the on-line gas chromatography (Fig. 2d). After the reaction temperature was increased to 548 K or higher, ^{13}C MAS

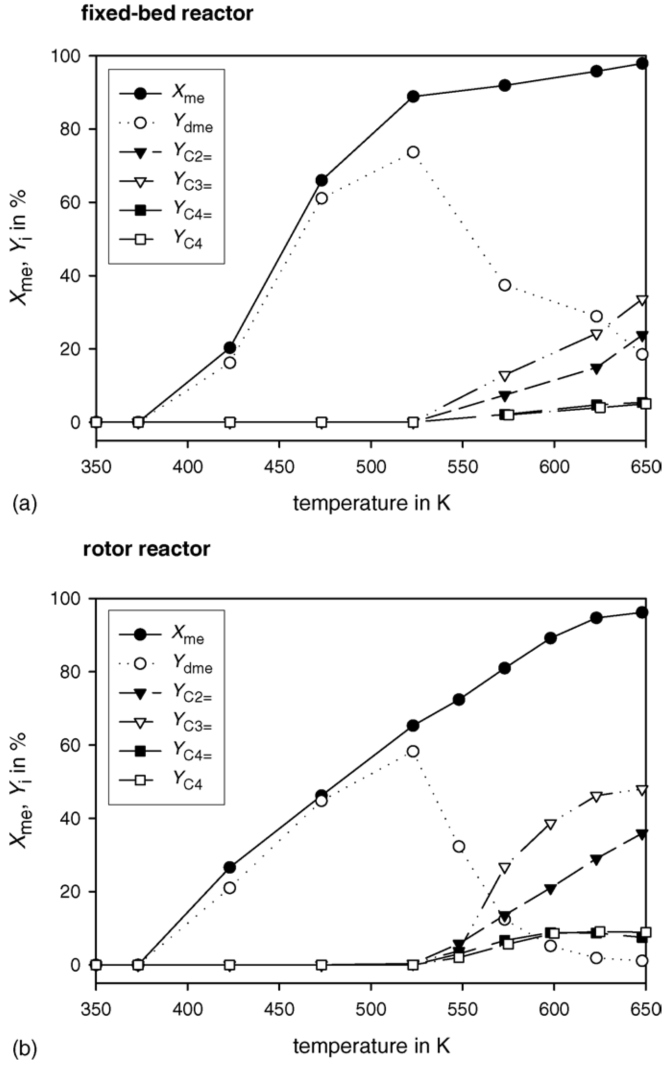


Fig. 1. Conversion of methanol, X_{me}, and yields, Y_i, of dimethyl ether (dme), ethylene ($C_{2=}$), propylene ($C_{3=}$), butenes ($C_{4=}$) and butanes (C_4) on the silicoaluminophosphate H-SAPO-34 at reaction temperatures of 350–650 K, obtained with a modified residence time of $W/F = 25$ g h/mol in a fixed-bed reactor (a) and in an MAS NMR rotor reactor spinning with ca. 2 kHz (b) [30].

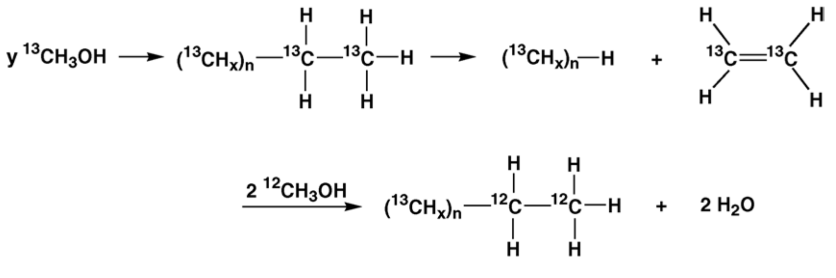
NMR signals appeared in the alkyl region of 10–35 ppm accompanied by broad signals in the olefinic and aromatic region of 129–134 ppm (Fig. 2e–h), indicating the formation of the hydrocarbon-pool. Simultaneously, strong increases in the yields of light olefins were observed by the on-line gas chromatography. To study the hydrocarbon-pool species, which are chemically stable and occluded in H-SAPO-34 after methanol conversion at 673 K, the working catalyst was further purged with dry carrier gas (30 ml/min) at the same temperature. The spectrum obtained after purging consists of signals at 22 and 129 ppm (Fig. 2i).

For a detailed analysis of the hydrocarbon-pool species formed under steady-state conditions, a line separation of the ^{13}C MAS NMR spectra was performed using the BRUKER software WINFIT [30]. The ^{13}C CF MAS NMR signals observed during methanol conversion on H-SAPO-34 at reaction temperatures of 548–673 K were attributed to a mixture of C_6–C_{12} aromatics and olefins, such as polymethylbenzenes (134, 129 and 21 ppm), 3-hexene (131–133, ca. 21 and 15 ppm), 2,5-dimethyl-3-hexene (134–136, ca. 32 and 22 ppm), 2,3-hexadiene (132–134, 126–128 ppm and ca. 18 ppm), alkylated octadienes (133–135, ca. 25, 23 and 15 ppm), cyclopentene (131–133, ca. 33 and 23 ppm) and diethylcyclopentene (133–135 and various signals at 14–33 ppm) [30]. The signals at ca. 22 and 129 ppm (Fig. 2i), observed after purging the working catalyst at 673 K with dry carrier gas, indicate the presence of aromatic compounds such as *para*-xylene (134, 129 and 21 ppm) occluded in the pores of H-SAPO-34 [30]. These findings are in agreement with the work of Kolboe's group [42–44] and Haw's group [26,46]. The repeated methylations of arenes lead to the formation of pentamethylbenene and hexamethylbenzene, which are unstable and can split off ethane or propene under the reaction conditions. Subsequently, these alkylbenzenes are methylated again and involved in the catalytic cycles.

2.2. *Catalytic role of the hydrocarbon-pool in the MTO process under steady-state conditions*

In order to identify the catalytic role of the hydrocarbon-pool, the MTO process was further studied by in situ ^{13}C CF MAS NMR spectroscopy with an altering flow of $^{13}CH_3OH$ and $^{12}CH_3OH$ [34]. After the conversion of $^{13}CH_3OH$ under steady-state conditions, the reactant flow was switched to $^{12}CH_3OH$ with identical reaction parameters. If the alkyl groups of the hydrocarbon-pool were involved in the conversion of methanol, e.g. by adding methanol and splitting off products, such as ethene, the ^{13}C-isotope abundance of these groups would strongly decrease after switching from $^{13}CH_3OH$ to $^{12}CH_3OH$ (Scheme 1).

To quantify the ^{13}C-isotope abundance of the alkyl groups contributing to the hydrocarbon-pool, the ^{13}C MAS NMR spectral region of 0–40 ppm was integrated in the absolute intensity mode [34]. These integrals were set to 100% in the



Scheme 1.

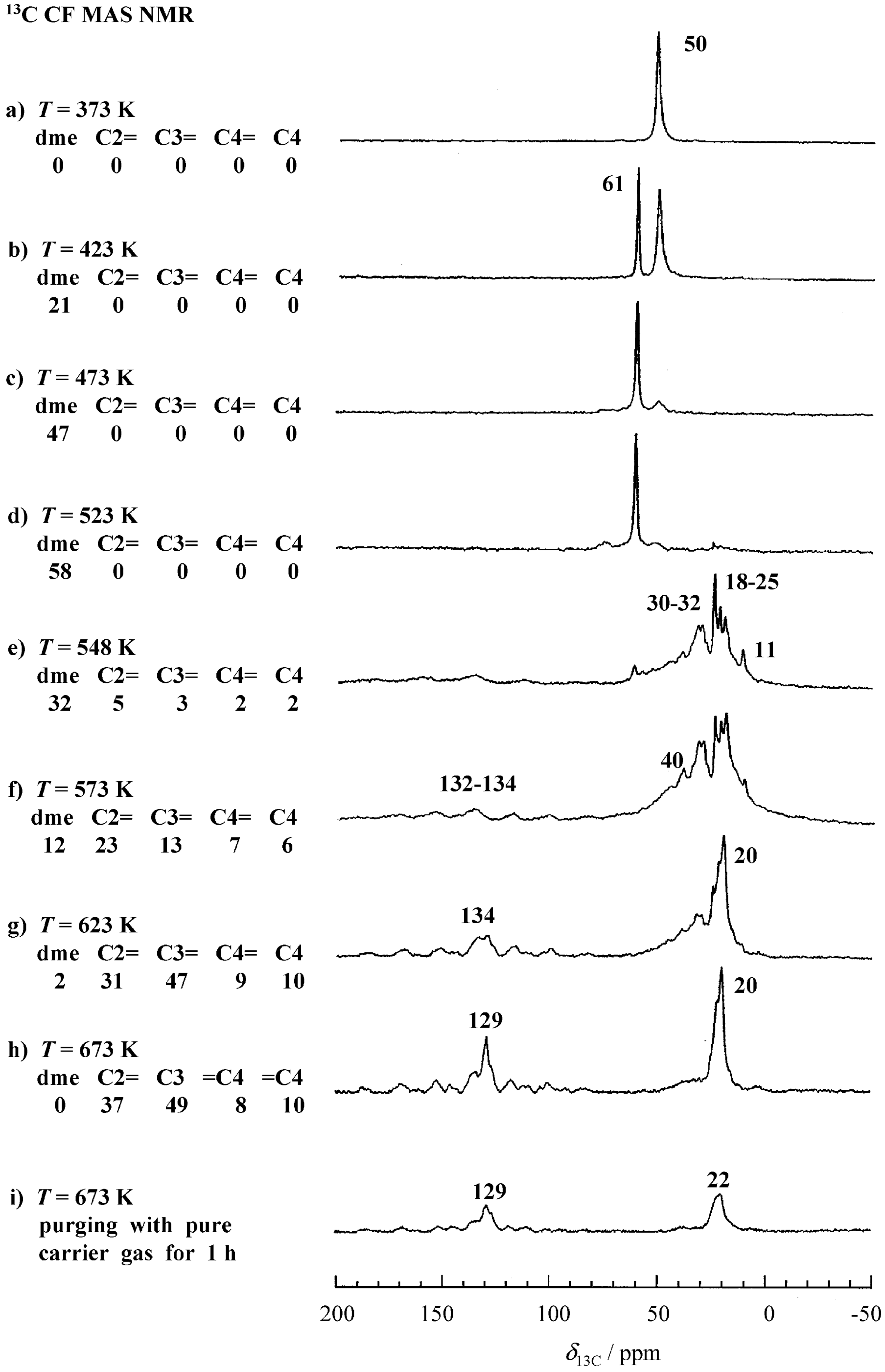


Fig. 2. ^{13}C CF MAS NMR spectra of calcined H-SAPO-34 recorded during the conversion of ^{13}C-enriched methanol (*W*/*F* = 25 g h/mol) at reaction temperatures of 373 (a) to 673 K (h). Spectrum (i) corresponds to spectrum (h) but was recorded after the purge of the working catalyst with dry nitrogen 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 [30].

spectra recorded during the conversion of ^{13}C-enriched methanol under steady-state conditions at 548 and 573 K [34]. After the reactant flow was switched from $^{13}CH_3OH$ to $^{12}CH_3OH$ for 1 h, the ^{13}C-isotope abundance of the corresponding alkyl groups was decreased by ca. 40%. The ^{1}H CF MAS NMR spectra, on the other hand, showed no change of the total hydrogen atoms contributing to the hydrocarbon-pool. This finding provides direct experimental evidence that the olefinic and aromatic species of the hydrocarbon-pool play an active role in the MTO process under steady-state conditions.

2.3. Study of the hydrocarbon-pool on acidic zeolite catalysts by in situ MAS NMR-UV/vis spectroscopy

A very recent development in our group is the direct coupling of in situ UV/vis and in situ CF MAS NMR

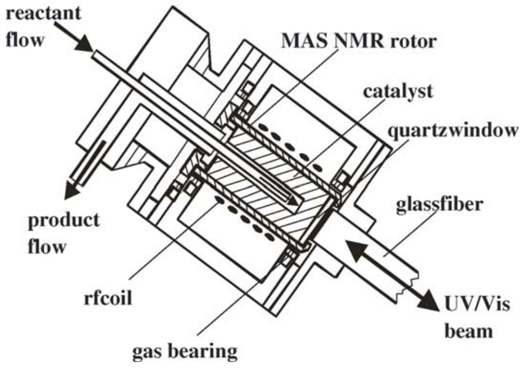


Fig. 3. Scheme of the CF MAS NMR probe coupled with a glass-fiber optics for UV/vis spectroscopy [51].

spectroscopy under flow conditions [51]. The CF MAS NMR-UV/vis probe is still based on the injection technique depicted in Refs. [47] and [48]. Inside the 7 mm CF MAS NMR-UV/vis probe shown in Fig. 3, a glass fiber was fixed to the bottom of the stator. The MAS NMR rotor was modified at the bottom with a quartz window. Via the quartz window and the glass fiber, working catalysts in the rotor reactor can be investigated by a fiber-optic UV/vis spectrometer and an NMR spectrometer simultaneously. This new technique was applied to study the formation of hydrocarbons during the conversion of methanol on a weakly dealuminated zeolite H-ZSM-5 ($n_{Si}/n_{Al} = 22.0$) [51].

The ^{13}C CF MAS NMR spectrum recorded at 413 K during the conversion of ^{13}C-enriched methanol (Fig. 4a, left) consists of signals at 51 and 61 ppm due to methanol and DME, respectively. A very weak signal appeared at ca. 23 ppm, probably due to alkanes or alkylated cyclic compounds [51]. The occurrence of the signals at 23 and 61 ppm indicates that the conversion of methanol on weakly dealuminated zeolite H-ZSM-5 starts already at 413 K. The simultaneously recorded UV/vis spectrum (Fig. 4a, right) consists of bands at 275, 315 and 375 nm. The band at 275 nm indicates the formation of neutral aromatic compounds [52,53], while those at 315 and 375 nm may be due to mono- and dienylic carbenium ions [52,53], respectively. The UV/vis spectrum of the non-dealuminated zeolite H-ZSM-5 (i.e. the parent sample of zeolite H-ZSM-5), recorded under the same reaction conditions, consists only of a very weak band at ca. 300 nm. Therefore, the formation of first hydrocarbons and carbenium ions on the weakly dealuminated zeolite H-ZSM-5, already at 413 K, may be caused by Lewis acid sites at extra-framework aluminum species [51].

The conversion of ethene (^{13}C-isotopes in natural abundance) was further studied on the weakly dealuminated zeolite H-ZSM-5 after methanol conversion (Fig. 4b). ^{13}C MAS NMR signals at 14, 23 and 32 ppm (Fig. 4b, left), occurring after the conversion of ethene at 413 K for 1 h, are due to alkyl groups of alkylated cyclic compounds. The simultaneously recorded UV/vis spectrum (Fig. 4b, right) shows bands at 300 and 375 nm, which hint to the formation of neutral cyclic compounds and dienylic carbenium ions, respectively [52]. For a comparison, the spectra recorded after the conversion of ethene on a fresh dealuminated zeolite H-ZSM-5 are shown in Fig. 4c. The ^{13}C MAS NMR spectrum consists of signals at 14, 24 and 34 ppm (Fig. 4c, left). In addition, a broad signal in the chemical shift range of olefinic and aromatic compounds occurred at ca. 120 ppm. The UV/vis spectrum consists of bands similar to those

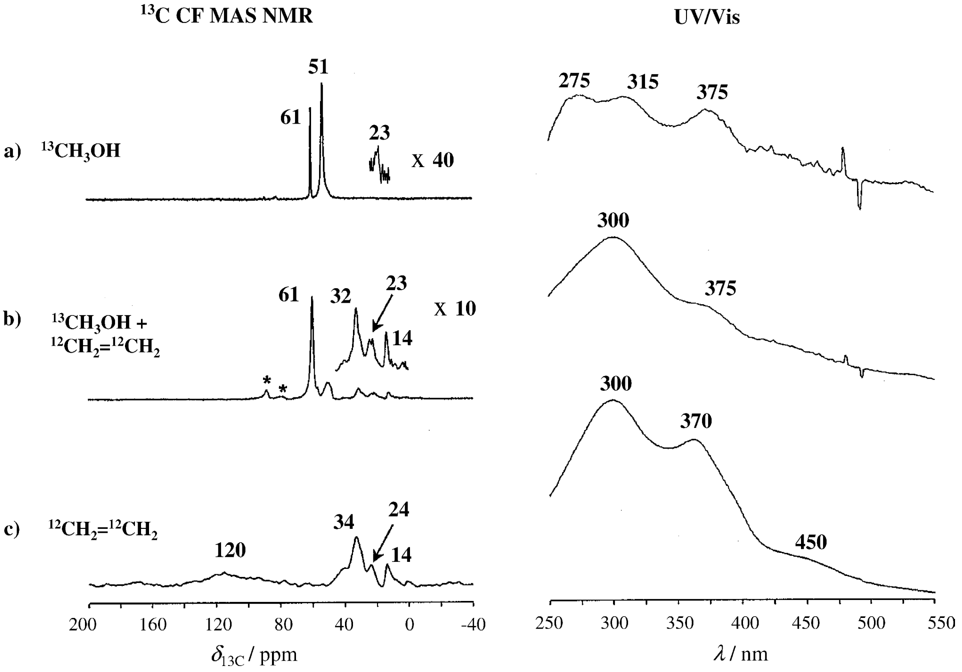


Fig. 4. In situ ^{13}C CF MAS NMR (left) and UV/vis (right) spectra of dealuminated zeolite H-ZSM-5 recorded during conversion of $^{13}CH_3OH$ under continuous-flow conditions (W/F = 25 g h/mol) at 413 K for 2 h (a), during a subsequent conversion of $^{12}CH_2{=}^{12}CH_2$ (W/F = 10 g h/mol) at 413 K for 1 h (b) and during conversion of $^{12}CH_2{=}^{12}CH_2$ (W/F = 10 g h/mol) at 413 K on a fresh catalyst for 2 h (c) [51]. Asterisks denote spinning sidebands. The narrow peaks at ca. 500 nm in UV spectra are due to the equipment.

in Fig. 4b and an additional weak band at ca. 450 nm. The latter may be attributed to condensed aromatics or trienylic carbenium ions [52]. The weak shoulder at ca. 400 nm could be an indication for the formation of hexamethylbenzenium ions [53].

The simultaneous investigation of methanol conversion on weakly dealuminated zeolite H-ZSM-5 by in situ ^{13}C CF MAS NMR and UV/vis spectroscopy has shown that first cyclic compounds and carbenium ions are formed already at 413 K. This result is in agreement with UV/vis studies of the methanol conversion on dealuminated zoelite H-ZSM-5 performed by Karge et al. [54]. Extra-framework aluminum species acting as Lewis acid sites are probably responsible for accelerating the formation of hydrocarbons and carbenium ions at low reaction temperatures. While NMR spectroscopy allows the identification of alkyl signals in more detail, UV/vis spectroscopy gives hints to the formation of low amounts of aromatic compounds and carbenium ions [51].

3. Reactivity of surface methoxy groups

As described in Section 2, recent investigations evidence that the MTO process under steady-state conditions is dominated by the hydrocarbon-pool mechanism. However, the initial C–C bond formation, i.e. the chemistry during the ‘‘induction period’’ leading to the formation of the first organic compounds and, subsequently, to the reactive hydrocarbon-pool remains unclear. Among the mechanistic proposals for the first C–C bond formation in the MTO process [1], the existence and possible intermediary role of surface-bound species have received significant support from both experimental studies [55–68] and theoretical calculations [69–81]. For example, surface methoxy groups have been successfully detected in situ or ex situ by ^{13}C MAS NMR spectroscopy during the methanol conversion on various zeolite catalysts. ^{13}C MAS NMR signals at chemical shifts of ca. 56 ppm for zeolite H-Y [31–33,82–87], 59 ppm for zeolite H-ZSM-5 [29,31,33,67,83–86] and 56 ppm for the silicoaluminophosphate H-SAPO-34 [26,31,33,64,65,88] were consistently observed. However, the further investigation of their catalytic role was hindered by the system complexity, for example, by the superposition of the signals of surface methoxy groups and other species. By the in situ stopped-flow MAS NMR technique, we have been able to prepare zeolite catalysts covered by surface methoxy groups only [31–33]. The high reactivity of surface methoxy groups was further investigated using different probe molecules, which are possibly involved in the MTO process, for example, water, methanol, toluene (aromatics) and cyclohexane (saturated hydrocarbons) [31,33]. Moreover, the experiments indicated that the decomposition of surface methoxy groups may contribute to the formation of the first hydrocarbons on zeolites H-Y, H-ZSM-5 and H-SAPO-34 [33].

3.1. Study of surface methoxy groups during the conversion of methanol to DME on acidic zeolites under continuous-flow (CF) conditions

At reaction temperatures of $T \leq 523$ K, the conversion of methanol on acidic zeolites is dominated by the dehydration of methanol to dimethyl ether (DME) [1]. The mechanism involved in the formation of DME has been a matter of discussions. Two arguments were generally proposed. In the indirect route (Eqs. (1a) and (1b)), methanol molecules adsorbed on bridging OH groups are converted first to methoxy groups (ZOCH$_3$), which subsequently react with another methanol molecule to form DME [56,66]. Here Z stands for the zeolite framework.

$$\mathrm{CH_3OH + ZOH} \rightarrow (\mathrm{CH_3}^{\delta+}\cdots\mathrm{OH_2}^{\delta+}\cdots\mathrm{ZO}^{\delta-})^{\neq} \rightarrow \mathrm{ZOCH_3 + H_2O} \quad (1a)$$

$$\mathrm{ZOCH_3 + CH_3OH} \rightarrow (\mathrm{CH_3}^{\delta+}\cdots\mathrm{CH_3OH}^{\delta+}\cdots\mathrm{ZO}^{\delta-})^{\neq} \rightarrow \mathrm{ZOH + CH_3OCH_3} \quad (1b)$$

In the direct route (Eq. (2)), however, two methanol molecules react with each other on one Brønsted acid site [89]. This pathway involves the simultaneous adsorption and reaction of two methanol molecules, with the formation of one DME and one water molecule in a single step.

$$\mathrm{2CH_3OH + ZOH} \rightarrow (\mathrm{CH_3OH}^{\delta+}\cdots\mathrm{CH_3}^{\delta+}\cdots\mathrm{OH_2}^{\delta+}\cdots\mathrm{ZO}^{\delta-})^{\neq} \rightarrow \mathrm{ZOH + CH_3OCH_3 + H_2O} \quad (2)$$

To clarify the mechanism of the formation of DME by conversion of methanol on acidic zeolites, in situ ^{13}C CF MAS and ^{13}C CF CP/MAS NMR spectroscopy was applied [31]. After loading of ^{13}C-enriched methanol on zeolite H-Y ($n_{\mathrm{Si}}/n_{\mathrm{Al}} = 2.7$) at 393 K, the ^{13}C CF MAS NMR spectrum consisted of a single signal at 50 ppm due to methanol. In the spectrum recorded with cross polarization (CP) technique, an additional signal occurred at 63.5 ppm [31] due to DME strongly adsorbed with a side-on conformation [78,90]. After the reaction temperature was increased to 433 K, conversion of methanol to DME was detected via on-line gas chromatography ($Y_{\mathrm{dme}} = 0.04$). At this reaction temperature, the ^{13}C MAS NMR spectrum showed a decrease of the signal of adsorbed methanol molecules (50 ppm), and the presence of DME adsorbed with an end-on conformation (60.5 ppm). A new signal occurring at 56.2 ppm indicated the formation of surface methoxy groups [31]. Simultaneously with an increase of the DME yield at 473 K ($Y_{\mathrm{dme}} = 0.23$), an increase of the signal of surface methoxy groups (56.2 ppm) was observed by ^{13}C CF CP/MAS NMR spectroscopy [31].

This experiment indicates that methoxy groups are formed during the conversion of methanol to DME under continuous-flow conditions. However, the temperatures for the formation of surface methoxy groups and DME are very close. Under these conditions it is difficult to determine unambiguously whether the methoxy groups are the intermediates responsible for DME formation or only spectator species. Therefore, a meaningful experiment clarifying the catalytic role of methoxy groups has to start with catalysts exclusively covered by these surface species.

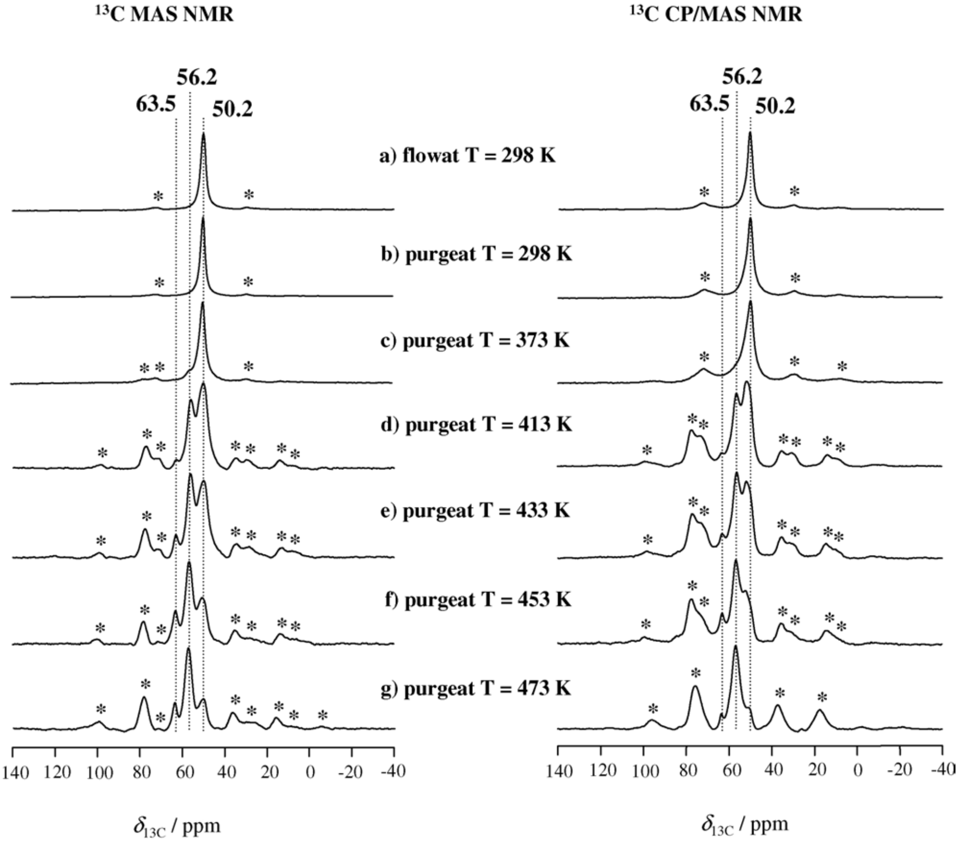


Fig. 5. In situ ^{13}C MAS NMR (left) and CP/MAS NMR (right) spectra of zeolite H-Y ($n_{Si}/n_{Al} = 2.7$) recorded during the formation of methoxy groups (56.6 ppm) at different temperatures. The spectra were obtained after a continuous injection of $^{13}CH_3OH$ into the MAS NMR rotor reactor at room temperature for 20 min (a) and upon a subsequent purging with dry nitrogen (200 ml/min) at room temperature (b), 373 K (c), 413 K (d), 433 K (e), 453 K (f) and 473 K (g). The temperature treatments were performed for 2 h at each temperature [32]. Asterisks denote spinning sidebands.

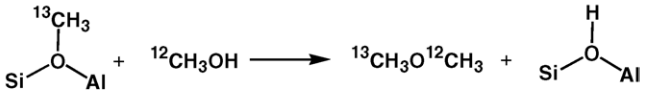
3.2. *In situ preparation of methoxy groups on acidic zeolite catalysts by the stopped-flow technique*

To unambiguously elucidate the nature and reactivity of surface methoxy groups, the preparation of a high concentration of methoxy groups on the zeolite catalysts is an important prerequisite. This issue has been successfully achieved by a stopped-flow protocol. This protocol starts with a flow of ^{13}C-enriched methanol into the reactor filled with acidic zeolites followed by purging of the catalyst with dry nitrogen both at room temperature and, subsequently, by purging at elevated temperatures [31,32]. The latter step removes progressively the surplus of methanol and DME, together with water produced during the conversion of methanol.

Fig. 5 shows in situ ^{13}C MAS NMR (left) and ^{13}C CP/MAS NMR spectra (right), which were recorded to monitor the formation of methoxy groups on zeolite H-Y ($n_{Si}/n_{Al} = 2.7$) [32]. After adsorption of $^{13}CH_3OH$ on zeolite H-Y at room temperature and purging at $T \leq 373$ K, the signal at 50.2 ppm due to methanol molecules dominates the ^{13}C MAS NMR spectra (Fig. 5a–c). The signal of surface methoxy groups at 56.6 ppm occurs after purging at 413 K (Fig. 5d), and finally it dominates the ^{13}C MAS NMR spectra after purging at 473 K (Fig. 5e–g). The weak signal at 63.5 ppm is caused by side-on adsorbed DME [32]. In contrast to the spectra obtained under continuous-flow conditions [31], the signal of weakly bound DME at 60.5 ppm is absent due to the rapid purging by nitrogen. With similar stopped-flow protocols, surface methoxy groups were successfully prepared on zeolites H-ZSM-5 ($n_{Si}/n_{Al} = 22.0$) and H-SAPO-34 ($n_{Si}/(n_{Al} + n_{Si} + n_P) = 0.088$) [31].

3.3. *Role of surface methoxy groups in the formation of DME*

The preparation of zeolite catalysts exclusively covered by methoxy groups allowed one to study the role of these surface species during the conversion of methanol to DME. These investigations were performed by in situ stopped-flow MAS NMR spectroscopy [31]. After surface methoxy groups were prepared by conversion of ^{13}C-enriched methanol on zeolite H-Y ($n_{Si}/n_{Al} = 2.7$), a flow of methanol with a natural abundance of ^{13}C-isotopes ($^{12}CH_3OH$) was injected at 433 K for 10 min into the spinning MAS NMR rotor reactor [31]. In the ^{13}C CP/MAS NMR spectrum recorded, the appearance of weak signals



Scheme 2.

at 60.5 and 63.5 ppm due to DME was accompanied by a decrease of the signal of surface methoxy groups at 56.2 ppm. This finding indicates the reaction of ^{13}C-enriched surface methoxy groups with $^{12}CH_3OH$ leading to $^{13}CH_3O^{12}CH_3$ as described in Scheme 2. After the injection of a flow of $^{12}CH_3OH$ at 433 K for 1.0 h, all signals disappeared except the signal of DME at 63.5 ppm [31]. This result demonstrated that surface methoxy groups are reactive and contribute to the formation of DME via the mechanism described in Eq. (1a) and (1b). However, the experiment cannot exclude a contribution of the direct pathway (Eq. (2)) in the formation of DME.

Applying the non-local periodic density functional calculations, Gale and co-workers [72–74] suggested that both pathways, described in Eqs. (1a), (1b) and (2), are energetically reasonable routes. By contrast, Blaszkowski and van Santen [75–78] found that the pathway described in Eq. (1a) and (1b) is less preferred, due to the high-energy barrier for the formation of methoxy groups. Therefore, suitable experimental approaches have to be further developed to determine the rate constants of these two pathways.

3.4. Reaction of surface methoxy groups with water

The occurrence of surface methoxy groups on zeolite catalysts was observed by in situ MAS NMR spectroscopy under flow conditions [31–33] as well as by the pulse-quench technique [26,88]. However, these surface species are not easily to detect during the methanol conversion under batch conditions, e.g. in fused glass ampoules (or gas-tight rotors), where the water formed cannot leave the working catalyst. The reaction of surface methoxy groups with water molecules was investigated by the in situ stopped-flow MAS NMR spectroscopy [33].

Fig. 6a shows the ^{13}C MAS NMR spectrum recorded at room temperature after the in situ preparation of surface methoxy groups on zeolite H-Y [33]. After water was injected into the MAS NMR rotor reactor, filled with the methylated zeolite CH_3-Y, the in situ ^{13}C MAS NMR spectrum shown in Fig. 6b was recorded. The surface methoxy groups (56.2 ppm) are found to react with water to produce methanol (50.2 ppm) at room temperature. Similar results were obtained on both the methylated silicoaluminophosphate CH_3-SAPO-34 and the methylated zeolite CH_3-ZSM-5 (Fig. 6c–f).

The above-mentioned results indicate that the conversion of methanol to methoxy groups on acidic zeolite catalysts is a reversible process (Scheme 3). Under flow conditions and at elevated temperatures, such as in the industrial MTO process, the water formed via the conversion of methanol is purged out and the acidic catalysts are covered by methoxy groups. In the presence of water, such as under batch conditions, methoxy groups are readily hydrolyzed back to methanol, which hinders their observation by spectroscopic methods.

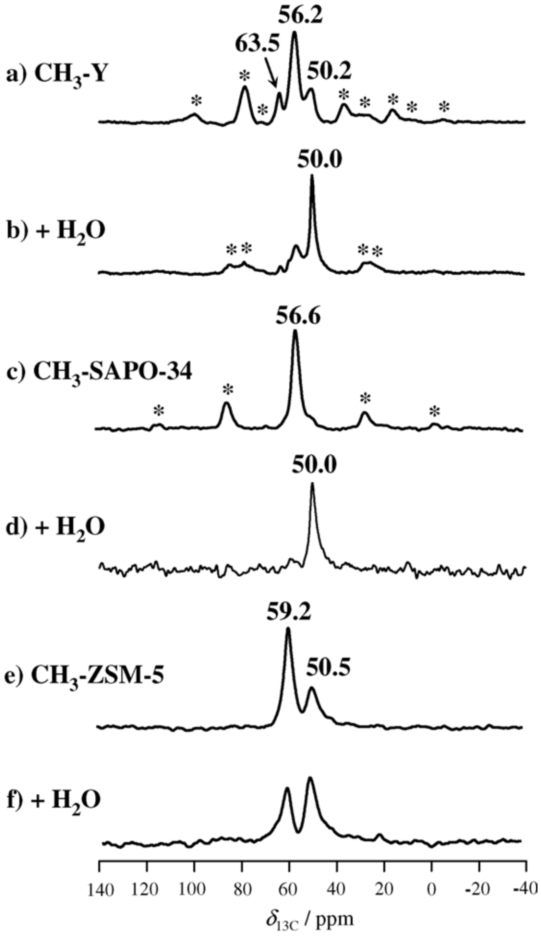
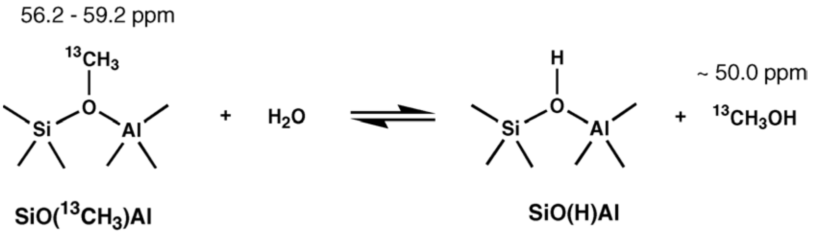


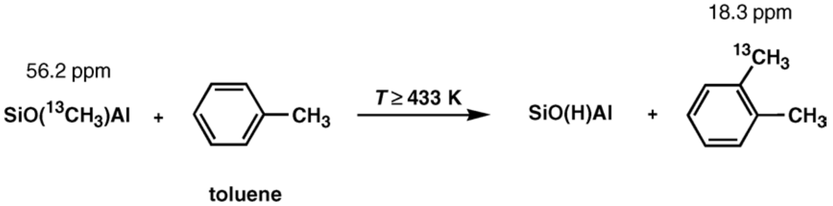
Fig. 6. ^{13}C MAS NMR spectra of methylated zeolites CH_3-Y (a and b), CH_3-SAPO-34 (c and d) and CH_3-ZSM-5 (e and f) recorded before (a, c and e) and after (b, d and f) reaction with water. After preparation of surface methoxy groups at 298–493 K under flow conditions, water was injected into the MAS NMR rotor reactor at room temperature [33]. Asterisks denote spinning sidebands.

3.5. Reaction of surface methoxy groups with aromatics

The reaction of surface methoxy groups with toluene on methylated zeolite CH_3-Y was investigated by ^{13}C MAS NMR spectroscopy at elevated temperatures [33]. After surface methoxy groups were prepared under stopped-flow conditions, the methylated catalyst was loaded with toluene (natural



Scheme 3.



Scheme 4.

abundance of ^{13}C-isotopes) and sealed in a glass insert. Fig. 7a shows the ^{13}C MAS NMR spectrum of the methylated catalyst recorded after adsorption of toluene at room temperature. The spectrum is dominated by the signal of methoxy groups at 56.2 ppm with a characteristic spinning sideband pattern. The weak signals at 140.2, 129.6, 125.6 and 19.2 ppm are due to toluene (natural abundance of ^{13}C-isotopes). The toluene methylation, indicated by the decrease of the signal due to surface methoxy groups at 56.2 ppm and the occurrence of the signal of *o*-xylene at 18.3 ppm (Scheme 4) starts at 433 K (Fig. 7b) [91]. At the reaction temperature of 453 K, ethylbenzene ($C_6H_5CH_2{}^{13}CH_3$) occurred at 15.0 ppm (Fig. 7c). Upon further heating at 473 K, a new signal appeared at 22.8 ppm, probably due to *p*- and/or *m*-xylenes. Upon increasing the temperature to 493 K, all surface methoxy groups and the residual DME and methanol molecules were consumed and the spectrum is dominated by the signals of ethylbenzene, xylenes and/or polymethylbenzenes (Fig. 7e) [33]. These results indicate that methoxy groups are highly reactive for methylating aromatic compounds such as toluene on acidic zeolites at temperatures (starts from 433 K) much lower than those for the MTO process under steady-state conditions ($T \geq 523$ K).

3.6. Reaction of surface methoxy groups with aliphatic compounds

Fig. 8a shows the ^{13}C MAS NMR spectrum of methylated zeolite CH_3-Y recorded after adsorption of cyclohexane

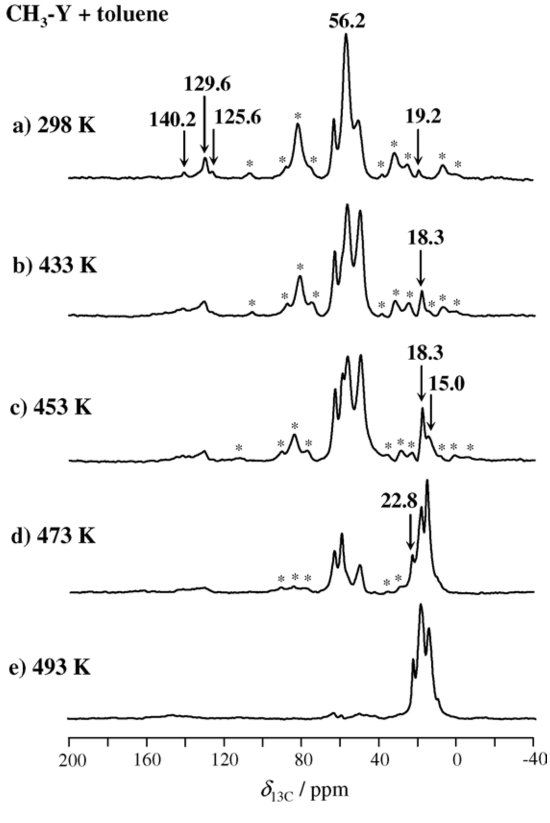


Fig. 7. ^{13}C MAS NMR spectra of methylated zeolite CH_3-Y recorded after loading with toluene (natural abundance of ^{13}C-isotopes) and upon thermal treatments at 298 (a) to 493 K (e) [33]. Asterisks denote spinning sidebands.

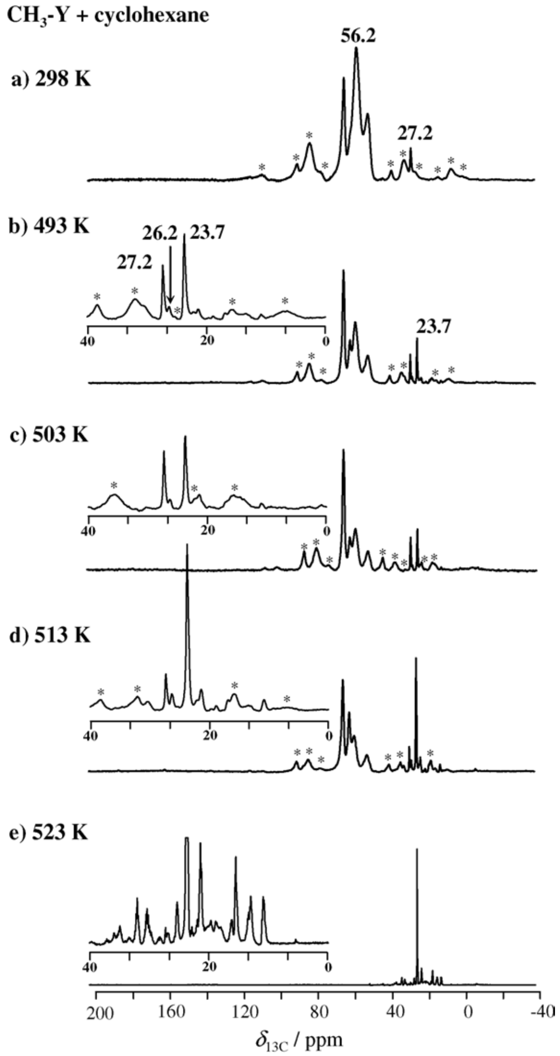
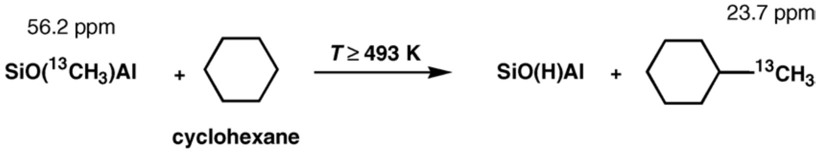


Fig. 8. ^{13}C MAS NMR spectra of methylated zeolite CH_3-Y recorded after loading with cyclohexane (natural abundance of ^{13}C-isotopes) and upon thermal treatments at 298 (a) to 523 K (e). The signals appeared at 0–40 ppm are highlighted in the insets [33]. Asterisks denote spinning sidebands.



Scheme 5.

(natural abundance of ^{13}C-isotopes) at room temperature. This spectrum consists of the signal of methoxy groups at 56.2 ppm with a characteristic spinning sideband pattern and a weak signal at 27.2 ppm due to cyclohexane (natural abundance of ^{13}C-isotopes). As indicated by the decrease of surface methoxy groups and the occurrence of a signal at 23.7 ppm due to the ^{13}C-enrich methyl groups of methylcyclohexane in Fig. 8b, the reaction starts at 493 K (Scheme 5) [33]. Up to the reaction temperature of 523 K, almost all surface methoxy groups and cyclohexane were consumed and the spectrum is dominated by the signal of methylcyclohexane at 23.7 ppm (Fig. 8e). A variety of hydrocarbons are formed, the signals of which are highlighted in Fig. 8, insets.

The cracking of cyclohexane alone on zeolite H-Y did not start up to 623 K [33]. Therefore, the methylation of cyclohexane on methylated zeolite Y occurs exclusively by the reaction of cyclohexane with surface methoxy groups. At reaction temperatures of $T \geq 493$ K, these surface methoxy groups most probably act as precursors of carbene, which can undergo the sp^3 insertion into the C–H single bonds [1].

3.7. Formation of initial hydrocarbons by surface methoxy groups

As indicated by the experiments described in Sections 3.3–3.6, surface methoxy groups act as reactive methylating agents at temperatures lower than 473 K. They react with water to methanol [33], with methanol to DME [31], with toluene to xylenes [33] and with aniline [87] to *N*-methylaniline. In the temperature range of 298–473 K and in the absence of other reactants, on the other hand, surface methoxy groups show a high thermal stability. For example, surface methoxy groups can be retained on zeolite Y at 473 K after purging with dry nitrogen [31–33]. When the reaction temperature is increased to 523 K or higher, however, decomposition of surface methoxy groups takes place leading to the formation of hydrocarbons (Scheme 6) [33].

The decomposition of surface methoxy groups was investigated by ^{13}C MAS NMR spectroscopy using samples sealed in glass ampoules [33]. Upon heating of the methylated zeolite CH_3-Y at 473 K for 20 min, no change of the signal of surface methoxy groups occurred, which indicates their high stability [33]. In the presence of other reactants, such as aromatics, the reaction of methoxy groups would already start at this temperature. After heating at 523 K for 20 min, however, the decomposition of methoxy groups occurred as indicated by the ^{13}C MAS NMR spectrum, which is dominated by the signal of isobutane at 23.5 ppm. In addition, signals in the aliphatic range of 10–35 ppm could be observed and weak signals of olefins and aromatics occurred at 128–142 ppm. Upon further heating of the methylated zeolite CH_3-Y, secondary reactions happen as indicated by the occurrence of signals due to smaller aliphatic compounds [33]. At the reaction temperature of 673 K, the products consisted mainly of methane (−9.5 ppm), ethane (5.1 ppm), propane (15.3 ppm), isobutane (23.5 ppm) and methyl-substituted benzenes (128–142 ppm) [33]. Decomposition of surface methoxy groups was also observed on the silicoaluminophosphate H-SAPO-34 and on zeolite H-ZSM-5 [33].

The above-mentioned findings indicate a possible contribution of surface methoxy groups to the formation of the first hydrocarbons during the induction period of the MTO process. As a result of the decomposition of surface methoxy groups, intermediates with ylide or carbene nature are very likely formed, which are further responsible for the first C–C bond formation and, thereafter, for the formation of hydrocarbons. The hydrocarbons formed are aliphatics, such as propane and isobutane, and aromatics, such as polymethylbenzenes, which are characteristic for the hydrocarbon-pool playing an active role in the steady-state of the MTO process.

3.8. Initiation of the MTO process: surface methoxy groups versus impurities

For the first C–C bond formation in the MTO process, surface methoxy groups, which can act as precursors of carbene or ylide intermediates, has long been proposed as a possible key intermediate [1]. IR investigations [55,56,59–63,66] have provided evidence for the presence and catalytic role of surface methoxy groups during the MTO process. In agreement with FTIR studies, our NMR investigations indicate that decomposition of surface methoxy groups takes place at temperatures higher than 473 K. Therefore, these surface species may act as a source of primary hydrocarbons during the induction period of the methanol conversion on acidic zeolite catalysts [33]. Furthermore, surface methoxy groups may further contribute to the methylation of alkanes and aromatics, leading to the formation of a reactive hydrocarbon-pool starting the MTO process [33].

$$n\ \mathrm{SiO(^{13}CH_3)Al} \xrightarrow{T \geq 523\ \mathrm{K}} n\ \mathrm{SiO(H)Al} + \text{propane} + \text{isobutane} + \text{aromatics}$$

56.2 - 59.2 ppm; 15.3 - 15.9 ppm; 23.5 - 24.6 ppm; 128 - 142 ppm

Scheme 6.

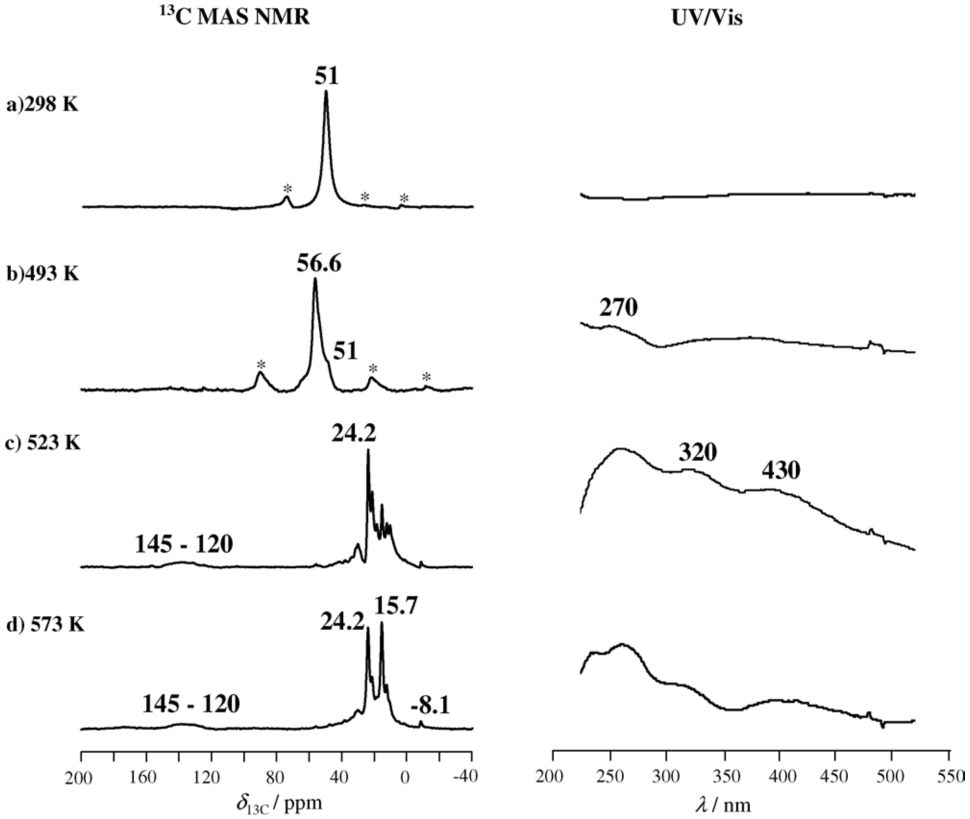


Fig. 9. ^{13}C MAS NMR (left) and UV/vis (right) spectra of silicoaluminophosphate H-SAPO-34 loaded with methanol at 298 K (a) and methylated silicoaluminophosphate CH_3-SAPO-34 recorded after thermal treatments at 493 (b), 523 (c) and 573 K (d). Asterisks denote spinning sidebands.

Recently, Haw and co-workers [17,45] claimed that the initiation of the MTO process is typically caused by organic impurities instead of any direct route from pure methanol and DME. A few ppm of organic impurities are sufficient for the creation of an initial hydrocarbon-pool [17,45]. Moreover, the rate of formation of the initial reaction centers and, therefore, the duration of the kinetic induction period are governed by impurities. On the other hand, also Haw and co-workers [26] observed the formation of surface methoxy groups on the silicoaluminophosphate H-SAPO-34 at 673 K applying the pulse-quench technique. The concentration of the methoxy groups decreased when the methanol conversion was quenched after longer reaction times [26], which implies the possible role of these surface species as reactive intermediates.

While the reactivity of surface methoxy groups is evident during the MTO process, the initial formation of hydrocarbons is not so conclusive from impurities or surface methoxy groups only. The in situ MAS NMR-UV/vis technique [51] was, therefore, applied to address this issue [92]. Similar to the previous procedure [33], methylated CH_3-SAPO-34 was in situ prepared and sealed in a glass ampoule. After heating CH_3-SAPO-34 at 493 K for 20 min, the ^{13}C MAS NMR spectrum consists exclusively of the signal of surface methoxy groups at 56.6 ppm with a characteristic spinning sideband pattern (Fig. 9b, left). The simultaneously recorded UV/vis spectrum (Fig. 9b, right) consists of a weak band at 270 nm, which indicates the formation of neutral aromatic compounds [52]. It is important to note that neither the UV/Vis spectra of the calcined (673 K) H-SAPO-34 nor of H-SAPO-34 loaded with methanol at room temperature (Fig. 9a) or of CH_3-SAPO-34 methylated at 453 K show a UV/vis band. Therefore, the UV band at 270 nm observed for CH_3-SAPO-34 at 493 K is due to neutral aromatics formed by the decomposition of methoxy groups rather than caused by reactive impurities on the working catalyst. At this temperature, however, the decomposition of methoxy groups cannot be detected by NMR spectroscopy due to the low sensitivity of this spectroscopic method. Upon further heating of CH_3-SAPO-34 at 523 K for 20 min, the decomposition of methoxy groups occurred evidently, as indicated by the ^{13}C MAS NMR spectrum shown in Fig. 9c, left, which is almost identical to the result obtained before [33]. The UV/vis spectrum obtained contains an additional band at 320 nm (Fig. 9c, right), which indicates the formation of monoenylic carbenium ions [52]. Upon further heating at 573 K (Fig. 9d, right), a new band at 430 nm is evident, which is due to trienylic carbenium or hexamethyl-benzenium cations [52–54]. These results obtained by in situ MAS NMR-UV/vis spectroscopy provide additional evidence that surface methoxy groups are able to contribute to the initiation of the MTO process on acidic zeolite catalysts (see also Ref. [92]).

4. Conclusion

The mechanism of the MTO process is still a matter of investigations and discussions. In situ MAS NMR spectroscopy under flow conditions and the new developed in situ MAS

NMR-UV/vis technique are suitable tools to study the key issues of this heterogeneously catalyzed process.

In agreement with other analytical methods, in situ NMR spectroscopy could evidence that the steady-state of the MTO process is dominated by the hydrocarbon-pool route. During methanol conversion on the silicoaluminophosphate H-SAPO-34 at reaction temperatures of 548–673 K under continuous-flow conditions, a hydrocarbon-pool consisting of a mixture of C_6–C_{12} olefins and aromatics, such as polymethylhexenes, alkylated octadienes and polymethylbenzenes, was found by in situ CF MAS NMR spectroscopy. By switching the reactant flow from $^{13}CH_3OH$ to $^{12}CH_3OH$ under steady-state conditions, the catalytic role of the alkyl groups contributing to this hydrocarbon-pool was studied. The decrease of the ^{13}C-isotope abundance of the corresponding alkyl groups provided direct experimental evidence that methanol molecules are added to the hydrocarbon-pool and light olefins are further split off as reaction products.

Methoxy groups were found to act as reactive surface species. In particular, they can form DME in the low temperature range of $T \leq 523$ K and may contribute to the formation of initial hydrocarbons in the high temperature range of $T \geq 523$ K. The high reactivity of surface methoxy groups has been demonstrated by their reactions with different probe molecules, such as water, methanol, aniline, aromatics and saturated hydrocarbons. During the induction period of the MTO process, the high reactivity of surface methoxy groups may be responsible for the first C–C bond formations. Hence, these methoxy groups may contribute to the formation of hydrocarbon-pool species, which play an active role in the steady-state of the MTO process.

Note added in proof

Recent review papers concerning the mechanistic investigations of the MTO process were published by Olsbye et al. [93] and Haw and Marcus [94].

Acknowledgments

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