Evidence for an Initiation of the Methanol-to-Olefin Process by Reactive Surface Methoxy Groups on Acidic Zeolite Catalysts

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Abstract: Recent progress reveals that, in the methanol-to-olefin (MTO) process on acidic zeolites, the conversion of an equilibrium mixture of methanol and DME is dominated by a "hydrocarbon pool" mechanism. However, the initial C−C bond formation, that is, the chemistry during the kinetic "induction period" leading to the reactive hydrocarbon pool, still remains unclear. With the application of a stopped-flow protocol, in the present work, pure surface methoxy groups [SiO(CH$_3$)Al] were prepared on various acidic zeolite catalysts (H−Y, H−ZSM-5, H−SAPO-34) at temperatures lower than 473 K, and the further reaction of these methoxy species was investigated by in situ ^{13}C MAS NMR spectroscopy. By using toluene and cyclohexane as probe molecules which are possibly involved in the MTO process, we show the high reactivity of surface methoxy species. Most importantly, the formation of hydrocarbons from pure methoxy species alone is demonstrated for the first time. It was found that (i) surface methoxy species react at room temperature with water to methanol, indicating the occurrence of a chemical equilibrium between these species at low temperatures. In the presence of aromatics and alkanes, (ii) the reactivity of surface methoxy groups allows a methylation of these organic compounds at reaction temperatures of ca. 433 and 493 K, respectively. In the absence of water and other organic species, that is, under flow conditions and on partially methylated catalysts, (iii) a conversion of pure methoxy groups alone to hydrocarbons was observed at temperatures of $T \geq 523$ K. This finding indicates a possible formation of the first hydrocarbons during the kinetic induction period of the MTO process via the conversion of pure surface methoxy species (case iii). After the first hydrocarbons are formed, or in the presence of a small amount of organic impurities, surface methoxy groups contribute to a further methylation of these organic compounds (case ii), leading to the formation of a reactive hydrocarbon pool which eventually plays an active role in the steady state of the MTO process at reaction temperatures of $T \geq 573$ K.

Introduction

Because of the increasing demands for light olefins, the catalytic conversion of methanol to hydrocarbons (MTG, methanol-to-gasoline; MTO, methanol-to-olefin) on solid acid catalysts continues to be an industrially interesting process in heterogeneous catalysis.[1] It has been well established that the first step of the MTG/MTO process is the dehydration of methanol to dimethyl ether (DME). Applying the stopped-flow MAS NMR spectroscopy, we have shown the role of surface methoxy groups [SiO(CH$_3$)Al] in the formation of DME on zeolite H−Y.[2] Recent progress reveals that, in the MTO process, the further conversion of the equilibrium mixture of methanol and DME is dominated by a "hydrocarbon pool" route[3−5] in which methanol is directly added onto reactive organic com-

pounds, such as methylbenzenes, cyclic carbenium ions, and probably methylbenzenium cations, while light olefins are formed via an elimination from these compounds. However, the initial C−C bond formation, that is, the chemistry during the kinetic "induction period" leading to the formation of the first organic compounds and, subsequently, to the reactive hydrocarbon pool, still remains unclear. On the basis of gas chromatographic investigations, Haw and co-workers[4b] claimed very recently that methanol and DME are not reactive on either zeolite H−ZSM-5 or H−SAPO-34 in the absence of an initial hydrocarbon pool. They explained that an initiation of the MTO

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reaction is typically caused by organic impurities instead of any direct route from pure methanol or DME.

More than 20 mechanistic proposals exist for the first C−C bond formation in the MTO process.[1a] However, the existence and possible intermediary role of surface-bound species have received significant support from both experimental studies[6−13] and theoretical calculations.[14−20] In particular, in situ spectroscopic methods[21] that have been developed in recent years have shown their great potentials for this issue. For example, using an in situ infrared cell which functions as a pulsed microreactor, Howe and co-workers[6] have been able to study the MTG/MTO process on zeolite H−ZSM-5 at reaction temperatures of 473−623 K. After the injection of methanol into the reactor filled with the fresh catalyst at temperatures of $T > 473$ K, these authors observed FTIR bands at ca. 2980, 2868, and 1460 cm^{-1} and assigned them to methoxy species. Moreover, the first appearance of hydrocarbon products was found to correlate with the formation of these methoxy species.[6] Surface methoxy species were also successfully detected in situ and ex situ by solid-state ^{13}C MAS NMR spectroscopy during the methanol conversion on various solid acid catalysts. ^{13}C MAS NMR signals at chemical shifts of ca. 56 ppm for zeolite H−Y,[2,22−24]

59 ppm for zeolite H−ZSM-5,[2,5a,12,23] and 56 ppm for the silicoaluminophosphate H−SAPO-34[2,10,25] were observed. However, the further investigation of their catalytic reactivity was hindered to a large extent by a superposition of the signals of surface methoxy groups with those of other reactants and by the system complexity. For unambiguous elucidation of their nature and reactivity during the MTO process, therefore, the preparation of pure methoxy species on acidic zeolite catalysts is an important prerequisite.

On the basis of in situ MAS NMR spectroscopy under continuous-flow (CF) conditions applying the MAS NMR rotor as a microreactor,[5,21c,26] very recently new stopped-flow (SF) protocols were introduced, which prove to be suitable for determining intermediates and elucidating the mechanisms for heterogeneously catalyzed reactions.[2,27−29] In one of our previous papers,[2] this new approach was applied toward the simultaneous preparation and detection of pure methoxy species on solid acid catalysts. Upon a continuous injection of ^{13}C-enriched methanol into the MAS NMR rotor reactor filled with acidic zeolites and at temperatures between 393 and 473 K, the formation of methoxy species was detected by ^{13}C CP MAS NMR spectroscopy. After the ^{13}CH$_3$OH flow was stopped and pure carrier gas (dry nitrogen) was flowed into the MAS NMR rotor reactor for purging of methanol, DME, and water, methoxy species were selectively retained. Moreover, after the further reaction of these ^{13}C-enriched surface methoxy groups with methanol having ^{13}C-isotopes in natural abundance, their important role in the formation of DME was shown. This finding has promoted further investigations of the reactivity of surface methoxy species during the induction period of the MTO process.

In this contribution, we first studied the reactivity of surface methoxy species by different probe molecules which are possibly involved in the MTO process, for example, water, toluene (aromatics), and cyclohexane (saturated hydrocarbons). Moreover, we report the first experimental evidence for the formation of hydrocarbons via a reaction of surface methoxy species alone on zeolites H−Y, H−ZSM-5, and H−SAPO-34. Applying a stopped-flow protocol, pure methoxy groups were prepared on the above-mentioned catalysts at temperatures lower than 473 K, allowing the further investigation of the reactivity of these methoxy species by in situ ^{13}C MAS NMR spectroscopy.

Experimental Section

Materials. Zeolite Na−Y ($n_{Si}/n_{Al} = 2.7$) was purchased from Degussa AG, Hanau, Germany. Template-free zeolite Na−ZSM-5 (n_{Si}/n_{Al} ratio of 22.0) was synthesized according to the recipe given in ref 30. The NH$_4$-form zeolite was prepared by a 4-fold ion exchange of the corresponding Na-form at 353 K in a 1.0 M aqueous solution of NH$_4$NO$_3$. After an ion-exchange degree of 90% for zeolite Y or 99% for zeolite ZSM-5 was reached, the material was washed in deminer-

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Scheme 1

56.2 - 59.2 ppm

$^{13}CH_3$

~ 50.0 ppm

$SiO(^{13}CH_3)Al$ + H_2O ⇌ $SiO(H)Al$ + $^{13}CH_3OH$
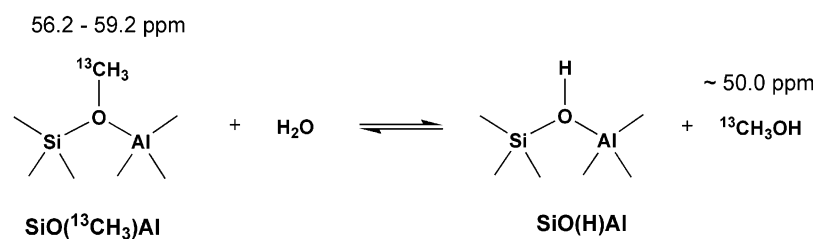
alized water and dried at room temperature. Subsequently, the NH_4-form zeolite was heated in a vacuum with a rate of 20 K/h up to the final temperature of 723 K. There, the material was calcined at a pressure below 10^{-2} Pa for 12 h, leading to zeolites H−Y and H−ZSM-5. The silicoaluminophosphate H−SAPO-34 with an $n_{Si}/(n_{Al} + n_{Si} + n_P)$ ratio of 0.11 was prepared according to the recipe in ref 31 for the synthesis of Ni−SAPO-34, but omitting the nickel salt. To remove the template, the as-synthesized material was heated with a rate of 1 K/min to 873 K in dry nitrogen and calcined at this temperature for 6 h in synthetic air (20 vol % oxygen, 60 L/h). Subsequently, the sample was subjected to an additional calcination in a vacuum with a heating rate of 20 K/h up to the final temperature of 673 K. At this temperature, the material was calcined at a pressure below 10^{-2} Pa for 12 h, leading to H−SAPO-34. These dehydrated samples were sealed in glass tubes until their further use. All catalysts were characterized by AES-ICP, XRD, and solid-state ^1H, ^{27}Al, and ^{29}Si MAS NMR spectroscopy, indicating that the material obtained after cation exchange and calcination was neither damaged nor dealuminated.

In Situ NMR Experiments. The experimental setup used for the in situ investigations under flow conditions was described elsewhere.[26] Prior to the in situ MAS NMR experiments, ca. 200 mg of dehydrated solid catalysts was filled into a 7 mm MAS NMR rotor under dry nitrogen in a glovebox and pressed to a cylindrical catalyst bed. After the rotor was transferred into the high-temperature Doty MAS NMR probe, a second in situ dehydration was performed at 673 K for 1 h under flowing nitrogen (30 mL/min). Subsequently, ^{13}C MAS NMR spectroscopy was applied to monitor the in situ formation of methoxy species during the stopped-flow experiments, which consisted of a continuous injection of $^{13}CH_3OH$ (^{13}C-enrichment of 99%, Cambridge Isotopes) into the MAS NMR rotor reactor at room temperature for 20 min (modified residence time of W/F = 40 g·h/mol) in the first step. In the second step, a purging with dry nitrogen (200 mL/min) was performed at temperatures of 298−473 K, leading to a conversion of methanol to methoxy groups and a desorption of all compounds except surface methoxy groups. The detailed description of the preparation of methoxy species can be found elsewhere.[2,29] In some experiments, water was injected into the MAS NMR rotor reactor after the formation of pure surface methoxy groups.

After the in situ preparation of pure surface methoxy groups using the high-temperature Doty probe, the methylated catalyst was transferred into an MAS NMR insert (Wilmad, 5.6 mm o.d. with constrictions) inside a glovebox and, subsequently, sealed. In some experiments, the MAS NMR insert containing the methylated catalyst was sealed after the adsorption of cyclohexane (>99%, Acros Organics) or toluene (>99%, Acros Organics) molecules having ^{13}C-isotopes in natural abundance. As a control experiment, a dehydrated H−Y sample was loaded with cyclohexane and then sealed in an MAS NMR insert. Prior to the ^{13}C MAS NMR measurements performed at room temperature, the sealed glass inserts were heated to the reaction temperature for a given time.

Solid-State NMR Spectroscopy. All ^{13}C MAS NMR investigations were performed on a Bruker MSL-400 spectrometer at a resonance frequency of 100.6 MHz. The in situ ^{13}C stopped-flow MAS NMR experiments were carried out at reaction temperature with a sample

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spinning rate of ca. 2.0 kHz inside a modified DSI-740 7 mm STD MAS NB NMR probe of Doty Scientific Instruments, Texas (see ref 26b). The spectra were recorded with high-power proton decoupling after an excitation with a $\pi/2$ pulse and with a repetition time of 5 s. ^{13}C MAS NMR investigations of the sealed glass inserts were performed with a sample spinning rate of ca. 3.0 kHz by using a 7 mm Bruker MAS NMR probe at ambient temperature. An excitation with a $\pi/2$ pulse, high-power proton decoupling, and a repetition time of 5 s were used. Applying an external intensity standard (194 mg of dehydrated zeolite H−Y loaded with $^{13}CH_3OH$, $p_{CH3OH} = 37$ mbar), we performed a ^{13}C spin-counting with a repetition time of 30 s. All ^{13}C MAS NMR spectra were referenced to tetramethylsilane (TMS). The deconvolution of the NMR spectra was performed using the Bruker software WINFIT.

Results and Discussion

Reaction of Surface Methoxy Species and Water. The existence of surface methoxy species during methanol conversion on solid acid catalysts, for example, on zeolites H−Y, H−ZSM-5, and H−SAPO-34, has been confirmed by in situ MAS NMR spectroscopy under flow conditions.[2] Moreover, an in situ stopped-flow protocol[2,29] made it possible to prepare pure surface methoxy species on these solid acid catalysts. Therefore, the reactivity of surface methoxy species can be further studied by using different probe molecules.

After surface methoxy species were prepared in situ, water was injected into the MAS NMR rotor reactor filled with the methylated catalysts, and the further reaction was investigated by ^{13}C MAS NMR spectroscopy. It was found that surface methoxy species react with water at room temperature, leading to the formation of methanol (see Scheme 1).

Figure 1a shows the ^{13}C MAS NMR spectrum recorded at room temperature after the in situ preparation of surface methoxy species on zeolite H−Y. The spectrum is dominated by a signal at 56.2 ppm[2,22−24] due to surface methoxy species. The signal at 63.5 ppm is caused by side-on adsorbed DME, and the signal at 50.2 ppm is originated by terminal methoxy species ($SiOCH_3$) or strongly bonded methanol.[2,29] Figure 1b shows the in situ ^{13}C MAS NMR spectrum obtained after water was injected into the MAS NMR rotor reactor filled with the methylated zeolite catalyst, $CH_3−Y$. It can be seen that the surface methoxy species (56.2 ppm) react with water to produce methanol (50.2 ppm) on zeolite Y at room temperature. Similar results were obtained on both methylated silicoaluminophosphate SAPO-34 and zeolite ZSM-5. Figure 1c shows the ^{13}C MAS NMR spectrum recorded after the in situ preparation of surface methoxy species on the silicoaluminophosphate H−SAPO-34. The spectrum is dominated by the signal at 56.6 ppm[2,10,25] of surface methoxy species. After water was injected into the MAS NMR rotor reactor at room temperature, the formation of methanol (50.0 ppm) is evident (Figure 1d). Figure 1e shows the ^{13}C MAS NMR spectrum recorded after the in situ preparation of surface methoxy species on zeolite H−ZSM-5. The spectrum is
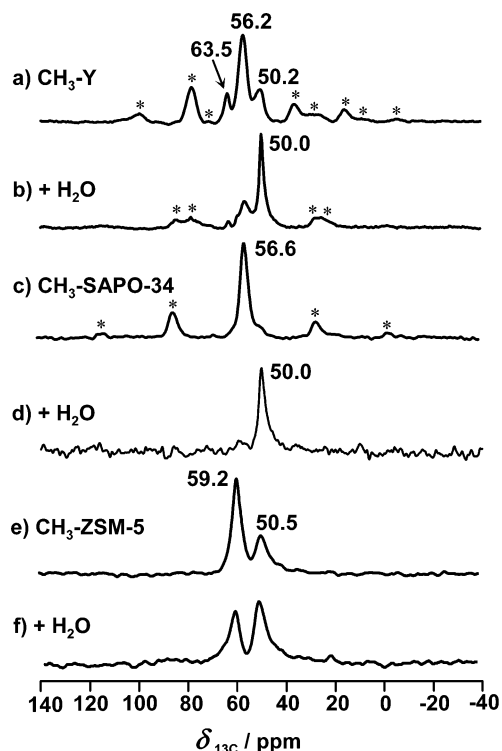
Figure 1. ^{13}C MAS NMR spectra of methylated zeolites Y (a, b), SAPO-34 (c, d), and ZSM-5 (e, f) recorded before (a, c, e) and after (b, d, f) reaction with water. After preparation of surface methoxy groups at 298–493 K under flow conditions, water was injected into the MAS NMR rotor reactor at room temperature. Asterisks denote spinning sidebands.

dominated by a signal at 59.2 ppm[2,5a,12,23] caused by surface methoxy species, while the signal at 50.5 ppm indicates the presence of a small number of terminal methoxy species (SiOCH$_3$) or strongly bonded methanol.[2,29] Figure 1f shows the ^{13}C MAS NMR spectrum recorded after water was injected into the MAS NMR rotor reactor. The change of signal intensities indicates a reaction of methoxy species and water to methanol on zeolite H−ZSM-5.

The above-mentioned results indicate that the conversion of methanol to methoxy species on acidic zeolite catalysts is a reversible process involving a chemical equilibrium. 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, however, methoxy species are readily hydrolyzed back to methanol. This finding explains why surface methoxy species cannot be easily observed during the methanol conversion (or other methylation processes by methanol) under batch conditions, for example, during the experiments performed either in fused glass ampules or without evacuation in a vacuum at high temperatures.

Reaction of Surface Methoxy Species and Toluene. Figure 2 shows the reaction of surface methoxy species with toluene (natural abundance of ^{13}C-isotopes) on zeolite CH$_3$−Y at elevated temperatures. After surface methoxy species were prepared in situ, the methylated catalyst was loaded with toluene via a vacuum line and sealed in a glass insert. Figure 2a shows the ^{13}C MAS NMR spectrum directly recorded after adsorption of toluene at room temperature. The spectrum is dominated by methoxy species at 56.2 ppm with spinning sidebands, while the weak signals at 140.2, 129.6, 125.6, and 19.2 ppm are due
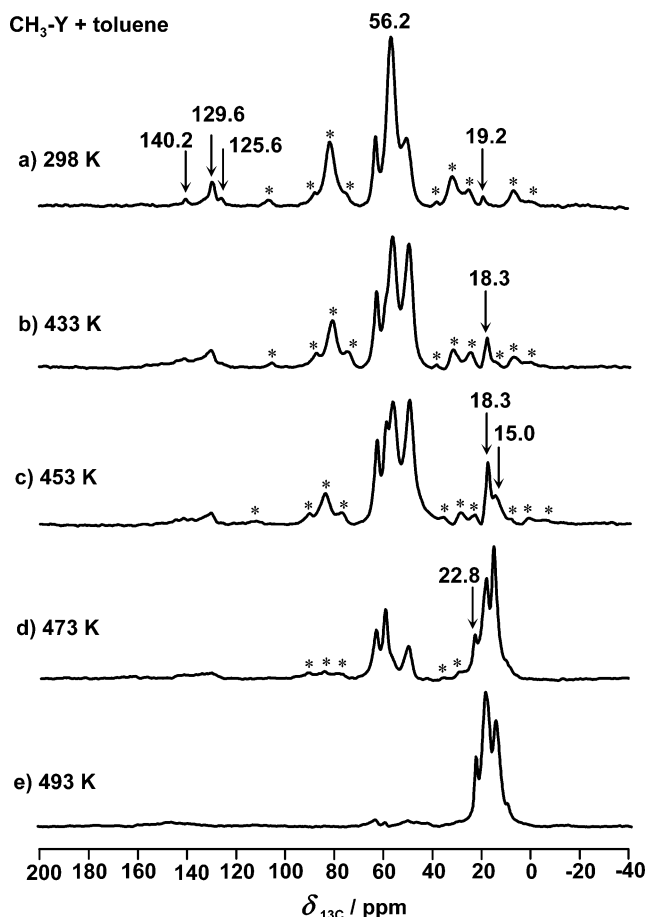

Figure 2. ^{13}C MAS NMR spectra of methylated zeolite Y (CH$_3$−Y) recorded after loading with toluene (natural abundance of ^{13}C-isotopes) and thermal treatments from 298 (a) to 493 K (e). Asterisks denote spinning sidebands.

to toluene. As indicated in Figure 2b by the decrease of the intensity of surface methoxy species and the occurrence of the signal at 18.3 ppm due to o-xylene, toluene methylation[32] on zeolite CH$_3$−Y by surface methoxy species starts at ca. 433 K (see Scheme 2).

At a reaction temperature of 453 K, ethylbenzene (C$_6$H$_5$-CH$_2$^{13}CH$_3$) occurred at 15.0 ppm (Figure 2c). Upon further heating at 473 K, a new signal appeared at 22.8 ppm due to p- or m-xylenes. After the reaction temperature was increased to 493 K, all of the surface methoxy species and the residual DME and methanol molecules were consumed by the reaction with toluene, and the resulting spectrum is dominated by the signals of ethylbenzene, xylenes, and polymethylbenzenes (Figure 2e). However, a formation of saturated hydrocarbons from secondary reactions, such as cracking and oligomerization of olefins, cannot be absolutely ruled out.

The above-mentioned results indicate that methoxy species are highly reactive for methylating toluene on zeolite H−Y at temperatures of $T \geq 433$ K. At reaction temperatures lower than those in the steady state of the MTO process ($T \geq 573$ K), methoxy species can readily react with aromatic compounds such as toluene, leading to ring and side-chain methylations.

Reaction of Surface Methoxy Species and Cyclohexane. The ^{13}C MAS NMR spectra shown in Figure 3 are experimental evidence for the reaction of surface methoxy species with

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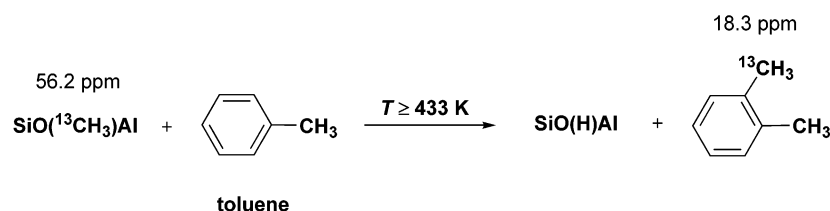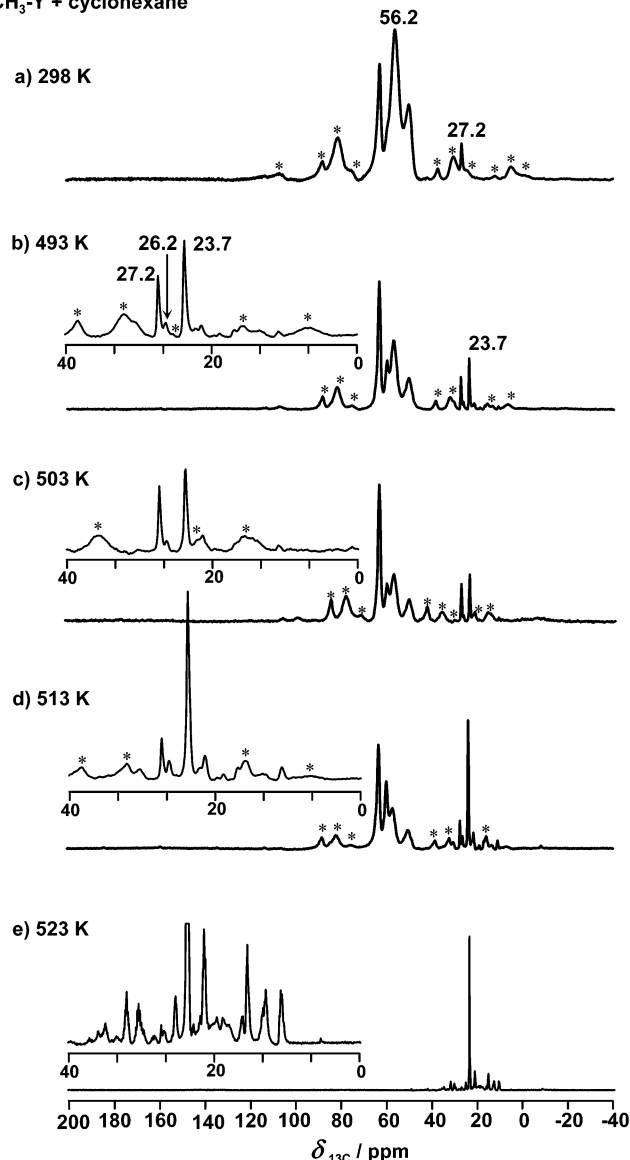
Scheme 2

toluene

CH₃-Y + cyclohexane

Figure 3. ¹³C MAS NMR spectra of methylated zeolite Y (CH₃−Y) recorded after loading with cyclohexane (natural abundance of ¹³C-isotopes) and thermal treatments from 298 (a) to 523 K (e). The signals that appeared at 0−40 ppm are highlighted in the insets. Asterisks denote spinning sidebands.

cyclohexane (natural abundance of ¹³C-isotopes) on zeolite CH₃−Y at elevated temperatures. After surface methoxy species were prepared in situ, the methylated catalyst was loaded with cyclohexane via a vacuum line and sealed in a glass insert. Figure 3a shows the ¹³C MAS NMR spectrum directly recorded after adsorption of cyclohexane at room temperature. The spectrum is dominated by the methoxy species at 56.2 ppm with spinning sidebands and a weak signal at 27.2 ppm due to cyclohexane. As shown in Figure 3b, the reaction starts at 493

K, which is indicated by the decrease of the intensity of methoxy species and the occurrence of a signal at 23.7 ppm due to the ¹³C-enriched methyl groups of methylcyclohexane (see Scheme 3). The assignment of the signal at 23.7 ppm to the methyl groups of methylcyclohexane is supported by the occurrence of weak signals at 26.2 ppm due to the C3/C4/C5 carbon atoms of this molecule. The signals in the aliphatic range (10−40 ppm) are highlighted in Figure 3b, inset. Up to a reaction temperature of 523 K, almost all surface methoxy groups and cyclohexane were consumed, and the spectrum is dominated by a signal at 23.7 ppm (Figure 3e). A variety of hydrocarbons are formed, the signals of which are highlighted in Figure 3e, inset.

As a control experiment, the possible cracking of cyclohexane alone on zeolite H−Y was further investigated, which did not start until 623 K (not shown). Therefore, the methylation of cyclohexane on methylated zeolite Y occurs only by the reaction of cyclohexane with surface methoxy species. At reaction temperatures of $T \geq 493$ K, these surface methoxy species most probably act as precursors of carbene or ylide intermediates.[33]

Formation of Hydrocarbons from Surface Methoxy Species at High Temperatures. Previous investigations indicated that, at temperatures lower than 473 K, surface methoxy species act as reactive methylating agents. For example, they react with water to methanol, with methanol[2] to DME, with toluene to xylenes, and with aniline[24,28] to *N*-methylaniline. In the temperature range of 298−473 K and in the absence of other reactants, on the other hand, isolated surface methoxy species themselves show a high thermal stability. For example, surface methoxy species can be selectively retained on zeolite Y at 473 K after the purge of dry nitrogen.[2,29] Because the MTO process starts at temperatures higher than 473 K, the behavior of surface methoxy species at reaction temperatures of $T > 473$ K was further investigated by in situ ¹³C MAS NMR spectroscopy under batch conditions. It was found that surface methoxy species decompose already at 523 K on acidic zeolite catalysts, leading to the formation of hydrocarbons (see Scheme 4).

Figure 4 shows ¹³C MAS NMR spectra of methylated zeolite Y (CH₃−Y) recorded after thermal treatments at 473−673 K. After the zeolite CH₃−Y was heated at 473 K for 20 min, the ¹³C MAS NMR spectrum shown in Figure 4a is dominated by the surface methoxy species at 56.2 ppm with a relative intensity of ca. 89%. As determined by ¹³C spin-counting, the concentration of surface methoxy species in this sample was determined to 1.76 mmol per gram, which corresponds to ca. 0.45 methoxy species per bridging OH group. Upon further heating at 523 K for 20 min, a reaction of methoxy species occurred as indicated by the ¹³C MAS NMR spectrum in Figure 4b. The dominating signal at 23.5 ppm is due to isobutane, which was observed as a volatile product in the early stage of the MTO process.[1]

(33) Carbene can undergo the sp³ insertion into the C−H single bonds. For a detailed discussion of the carbene mechanism for the MTO process, see for example ref 1a and references therein.

Scheme 3
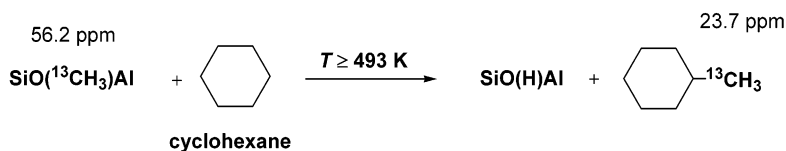
Scheme 4
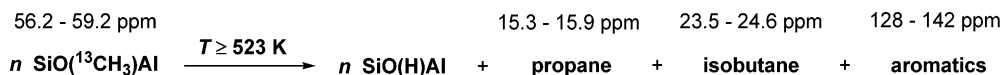
Meanwhile, weak signals in the aliphatic shift range of 10−35 ppm occurred, and trace signals of olefins and aromatics occurred at 128−142 ppm. Upon further heating of the methylated zeolite Y, secondary reactions, for example, cracking reactions, happened as indicated in Figure 4c−e by the occurrence of ^{13}C MAS NMR signals due to smaller aliphatic compounds. At a reaction temperature of 673 K (Figure 4e), 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).

A reaction of surface methoxy species was also observed on the methylated silicoaluminophosphate SAPO-34 (CH$_3$−SAPO-34), as indicated in Figure 5. Figure 5a shows the ^{13}C MAS NMR spectrum recorded at room temperature after heating of

CH$_3$−SAPO-34 at 473 K for 20 min. The spectrum is dominated by surface methoxy species occurring at 56.6 ppm accompanied by a shoulder at 50.7 ppm due to terminal methoxy species (SiOCH$_3$) or strongly adsorbed methanol.[2,29] A relative intensity of the surface methoxy species of 94% was determined. Upon further heating at 523 K for 20 min, a reaction of methoxy species is evident in Figure 5b. The ^{13}C MAS NMR signals of methyl-substituted benzenes (ca. 120−145 ppm and ca. 20 ppm) can be observed in a significant amount. Similar to the reaction of methoxy groups on zeolite CH$_3$−Y, alkanes, such as isobutane, propane, ethane, and methane, occurred due to secondary reactions.

Evidence for a reaction of surface methoxy species was also obtained for the methylated zeolite ZSM-5 (CH$_3$−ZSM-5), which is indicated by the ^{13}C MAS NMR spectra in Figure 6. The dominating signal at 15.9 ppm is due to propane, while the weak signals in the shift range of 128−142 are caused by
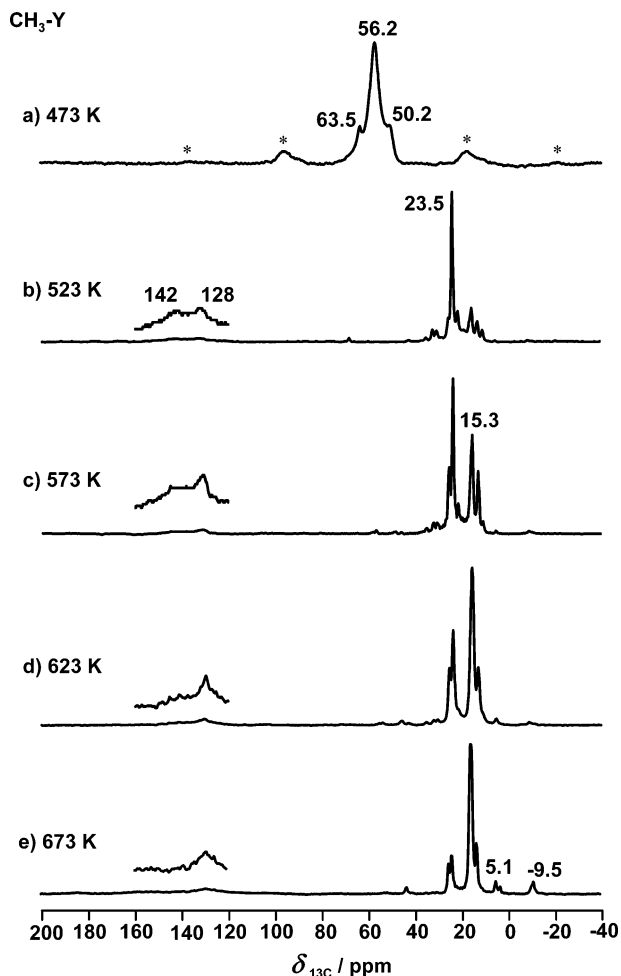

Figure 4. ^{13}C MAS NMR spectra of methylated zeolite Y (CH$_3$−Y) recorded after thermal treatments from 473 (a) to 673 K (e). Asterisks denote spinning sidebands.
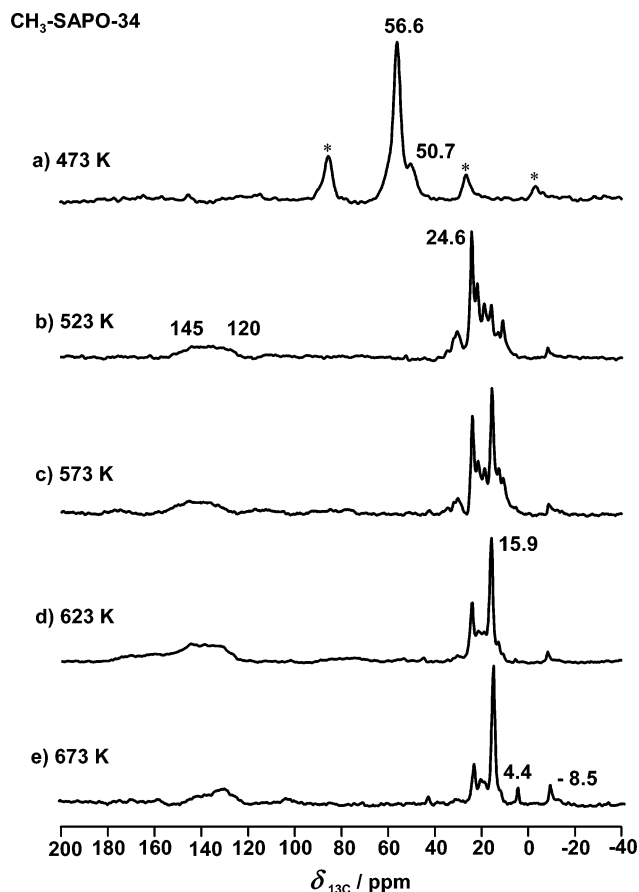

Figure 5. ^{13}C MAS NMR spectra of methylated silicoaluminophosphate SAPO-34 (CH$_3$−SAPO-34) recorded after thermal treatments from 473 (a) to 673 K (e). Asterisks denote spinning sidebands.
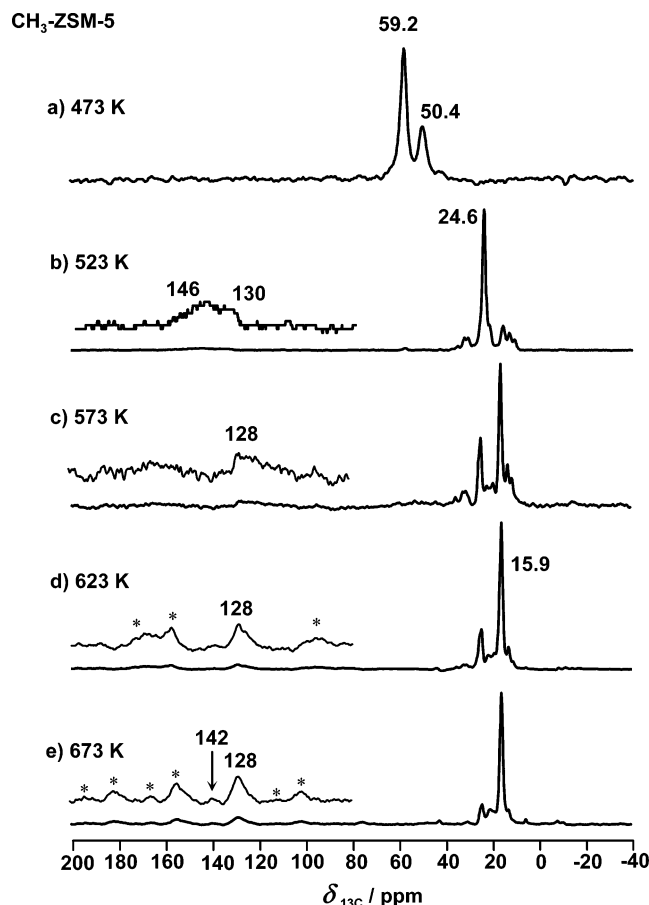
Figure 6. ^{13}C MAS NMR spectra of methylated zeolite ZSM-5 (CH₃−ZSM-5) recorded after thermal treatments from 473 (a) to 673 K (e). Asterisks denote spinning sidebands.

polymethyl aromatics. No apparent indication for the formation of cyclopentenyl cations[4a,34] could be observed.

Initial C−C Bond Formation in the Methanol to Hydrocarbon Catalysis. NMR investigations of the formation and catalytic role of surface methoxy species have been somewhat controversial. Most of the NMR investigations were performed under batch conditions in which water could not leave the working catalyst. As shown above, the presence of water will quench off surface methoxy species to react back to methanol. Under continuous-flow conditions, the water formed via the reaction of methanol can be purged out, and the methoxy groups can occur on the solid acid catalyst. The in situ stopped-flow MAS NMR technique makes it possible to ambiguously elucidate the reactivity of surface methoxy species on acidic zeolite catalysts. Previous work[2,24,28] and the present study have evidenced that surface methoxy species readily react with water, methanol, aniline, toluene, and cyclohexane at temperatures lower than 493 K. Therefore, it is very likely that methoxy species, acting as reactive intermediates, are widely involved in the reaction of methanol with different reactants on acidic zeolite catalysts.

In particular, for the first C−C bond formation in the MTO/MTG process, surface methoxy species, which can act as precursors of carbene or ylide intermediates, have long been

proposed as a possible key intermediate.[1a] IR investigations[6,8,9,11] have provided much evidence for the presence and a catalytic role of surface methoxy species. In agreement with FTIR studies, our NMR investigations indicate that surface methoxy species themselves react at temperatures higher than 473 K and, therefore, can act as the source of primary hydrocarbons during the induction period of the methanol conversion on solid acid catalysts. Furthermore, our studies have shown that, in the presence of alkanes and aromatics, surface methoxy species can contribute to the methylation of these compounds, leading to the formation of a hydrocarbon pool starting the MTO/MTG process.

In a recent communication, Haw and co-workers[4b] claimed that the initiation of the MTO process, that is, the formation of the primary hydrocarbons, is typically caused by organic impurities instead of any direct route from pure methanol and DME. On the other hand, they also observed the formation of surface methoxy species on the silicoaluminophosphate H−SAPO-34 during the MTO process.[25a] The concentration of these methoxy species decreased as the reaction went on, implying their possible role as a reactive intermediate.[25a] The reaction of surface methoxy species with cyclohexane and toluene evidenced in the present work indicates that, if there are "reactive impurities" on a solid acid catalysts, these organic compounds would also react with surface methoxy species at temperatures lower than the starting temperature of the MTO process. The ^{13}C MAS NMR spectra of methylated zeolites, obtained in the present study after heating at 473 K, show that there is no reaction of the methoxy species with other organic compounds (Figures 4a, 5a, and 6a). Therefore, organic impurities are not responsible for the formation of the primary hydrocarbons observed by ^{13}C MAS NMR spectroscopy of methylated zeolite catalysts in the present study (Figures 4−6).

Conclusions

In the present work, the reaction of surface methoxy groups on the acidic zeolite catalysts Y, SAPO-34, and ZSM-5 with compounds of different reactivity such as water, toluene, cyclohexane, and with themselves was investigated by ^{13}C MAS NMR spectroscopy. Our results indicate that surface methoxy species are very likely involved as key reactive intermediates, in the methanol conversion and other methylation processes by methanol on acidic zeolite catalysts. Under flow conditions, which are characteristic for the industrial MTO process, the formation of surface methoxy species via the conversion of methanol on acidic zeolite catalysts is greatly favored by the continuous removal of water at temperatures of 393−473 K. In the presence of water, however, surface methoxy species readily react with water back to methanol. At temperatures of $T \geq 433$ K and in the presence of aromatic compounds, such as toluene, surface methoxy species work as reactive methylating agents. Most importantly, at reaction temperatures of $T \geq 493$ K, the C−H bonds in the surface methoxy groups are weakened, and hydrogen can be readily abstracted by the basic oxygen atoms of the framework. As a result of the decomposition of the surface methoxy species, intermediates with ylide or carbene nature are very likely formed, which are further responsible for the methylation of aliphatic compounds ($T \geq 493$ K) and for the first C−C bond formation ($T \geq 523$ K) and, thereafter, for the formation of hydrocarbons as evidenced by the present [13]C

(34) (a) Oliver, F. G.; Munson, E. J.; Haw, J. F. *J. Phys. Chem.* **1992**, *96*, 8106−8111. (b) Haw, J. F.; Nicholas, J. B.; Song, W.; Deng, F.; Wang, Z.; Xu, T.; Heneghan, C. S. *J. Am. Chem. Soc.* **2000**, *122*, 4763−4775.

MAS NMR investigations. The hydrocarbons formed in this way are aliphatics, such as propane and isobutane, and aromatics, such as polymethylbenzenes. Because the latter compounds are characteristic for the hydrocarbon pool playing an active role in the steady state of the MTO process, surface methoxy species are important for the initial C−C bond formation in the kinetic induction period of this process.

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