

Role of Surface Methoxy Species in the Conversion of Methanol to Dimethyl Ether on Acidic Zeolites Investigated by in Situ Stopped-Flow MAS NMR Spectroscopy

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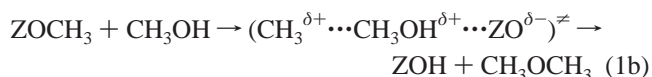
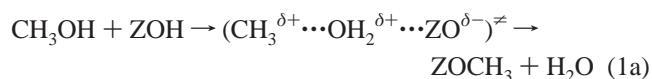
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In situ continuous-flow (CF) MAS NMR experiments indicated that the investigation of the role of surface methoxy species in the conversion of methanol to dimethyl ether requires the preparation of pure methoxy groups on the catalyst surface. Applying the novel in situ stopped-flow (SF) MAS NMR technique, methoxy species were selectively retained on zeolites H-Y ($n_{\text{Si}}/n_{\text{Al}} = 2.7$) and H-ZSM-5 ($n_{\text{Si}}/n_{\text{Al}} = 22.0$) and on the silicoaluminophosphate H-SAPO-34 [$n_{\text{Si}}/(n_{\text{Al}} + n_{\text{Si}} + n_{\text{P}}) = 0.088$]. These pure methoxy species were obtained after conversion of $^{13}\text{CH}_3\text{OH}$ under CF conditions at 423 K and purging the catalyst materials with dry nitrogen at 473 K. For H-Y, H-ZSM-5, and H-SAPO-34, the ^{13}C MAS NMR signals of selectively prepared methoxy species occurred at 56.2, 59.4, and 56.6 ppm, respectively. Application of cross polarization led to a strong enhancement of the above-mentioned signals accompanied by sideband patterns which indicates that these alkoxy species are rigidly bound on the catalyst surfaces. By conversion of methanol with ^{13}C -isotopes in natural abundance (denoted $^{12}\text{CH}_3\text{OH}$) on zeolite H-Y covered with ^{13}C -enriched methoxy species, the formation of partially ^{13}C -enriched dimethyl ether ($^{13}\text{CH}_3\text{O}^{12}\text{CH}_3$) was observed at 60.5 and 63.5 ppm. This finding gives experimental evidence for the formation of dimethyl ether on acidic zeolites by the reaction of methanol with surface methoxy species formed in a former reaction step.

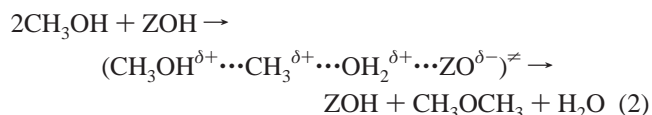
Introduction

The formation and reaction of alkoxy groups on the surface of solid catalysts have received considerable attention because of their importance in a number of heterogeneously catalyzed reactions, such as the conversion of methanol to olefins and gasoline (MTO, MTG), the alkylation of aromatic compounds and alkene transformations.^{1–3} Several groups have confirmed the formation of surface methoxy species on zeolite catalysts using ^{13}C MAS NMR spectroscopy under batch conditions with externally prepared samples.^{4–10} Bosacek proposed to rationalize the behavior of surface methoxy groups on zeolites using the equalized electronegativity concept of Sanderson.^{8–10} According to this concept, the ^{13}C resonance position and, therefore, the electronic shielding of methoxy groups formed at oxygen bridges between a tetrahedrally coordinated silicon and framework aluminum atoms depend on the mean electronegativity of the zeolite framework.

It is well accepted now that the first step of MTG/MTO process¹¹ is the dehydration of methanol to dimethyl ether (DME). However, the most important problem, whether surface methoxy species play a key role in the conversion of methanol to DME on acidic zeolites, remains a matter of debate. For this reaction, generally, two mechanisms have been proposed. In the indirect pathway (eqs 1a and 1b), methanol adsorbed on an acid site reacts first to methoxy species ZOCH_3 which subsequently converts with another methanol molecule to DME:^{12,13}



Here, Z stands for the zeolite framework. Alternatively, in the direct pathway (eq 2), two methanol molecules react with each other on an acid site of the zeolite, which acts merely as a solvent.¹⁴ This pathway involves the simultaneous adsorption and reaction of two methanol molecules, with the formation of a DME and a water molecule in one step:



To improve the understanding of adsorption and chemical conversion of methanol on acidic zeolites, a number of theoretical studies have been performed.^{15–20} Applying nonlocal periodic density functional calculations, Gale and co-worker¹⁶ suggested that both pathways 1 and 2 are reasonable energetic routes. On the contrary, by analyzing the calculated energy diagrams using a cluster model of the active site, Blaszkowski and van Santen^{18c} have calculated that the activation barriers for the DME formation via pathways 1 and 2 are +215 and +145 kJ/mol, respectively. They proposed that pathway 2 is preferred, due to the high-energy barrier of the formation of methoxy groups in pathway 1.

Until now, no direct experimental evidence could be obtained by NMR spectroscopy for the reaction pathway involved in the conversion of methanol to DME on acidic zeolites. Since 1995, we²¹ developed an in situ MAS NMR technique, which makes it possible to investigate directly the formation and reaction of surface compounds on working solid catalysts under steady-state conditions. In addition, this technique allows a simulta-

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neous gas chromatographic analysis of the reaction products.^{21c-e} Recently, we introduced a new in situ stopped-flow (SF) MAS NMR method which is suitable to monitor the consecutive conversion of adsorbates previously formed on the catalyst and to determine intermediates involved in heterogeneously catalyzed reactions.²² In this paper, we report on the application of this novel method to study the behavior of surface methoxy groups during conversion of methanol on acidic catalysts. With this method, the formation of surface methoxy groups under flow conditions and their further conversion to DME have been investigated.

Experimental Section

Materials. Zeolite ZSM-5 ($n_{\text{Si}}/n_{\text{Al}}$ ratio of 22.0) and the silicoaluminophosphate SAPO-34 [$n_{\text{Si}}/(n_{\text{Al}} + n_{\text{Si}} + n_{\text{P}})$ ratio of 0.088] were synthesized according to recipes given in refs 23 and 24, respectively. To remove the template, the as-synthesized 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. Zeolite Y ($n_{\text{Si}}/n_{\text{Al}}$ ratio of 2.7) is a commercial product and was purchased from Degussa AG, Germany (no. 48/550104). The ammonium form zeolites were obtained by a 4-fold ion exchange of the Na-form zeolites at 353 K in a 1.0 M aqueous solution of NH_4NO_3 .^{21e} After reaching an ion exchange degree of 99% for zeolite ZSM-5 and 92% for zeolite Y, the materials were washed in demineralized water and dried at room temperature. Subsequently, the ammonium form zeolites were heated in a vacuum with a rate of 20 K/h up to the final temperature of 673 K. There, the materials were calcined at a pressure below 10^{-2} Pa for 12 h leading to zeolites H-ZSM-5 and H-Y. All catalyst materials were characterized by AES-ICP, XRD, solid state ^1H , ^{27}Al , and ^{29}Si MAS NMR spectroscopy which indicated that the zeolite samples obtained after cation exchange and calcination were not damaged or dealuminated.

In Situ Continuous-Flow (CF) Experiments. Prior to the in situ CF MAS NMR experiments, 250 mg zeolite catalysts were filled into a 7 mm Doty MAS NMR rotor reactor under dry nitrogen in a glovebox and pressed to a cylindrical catalyst bed. After transferring the rotor into the Doty MAS NMR probe, a second in situ dehydration of this catalyst was performed at 673 K for 1 h under flowing nitrogen (30 mL/min). During the in situ MAS NMR experiments under CF conditions at temperatures between 298 and 573 K, carrier gas (dry nitrogen) loaded with $^{13}\text{CH}_3\text{OH}$ (modified residence times of $W/F = 40$ and 100 g h/mol) was injected into the MAS NMR rotor reactor applying the equipment described elsewhere.^{21c} Via an exhaust tube on the top of MAS NMR rotor reactor, the probe was connected with the sampling loop of an on-line gas chromatograph HP 5890 (Hewlett-Packard) equipped with a Coating Poraplot Q capillary column (Chrompack Plot fused silica, length 50 m, inner diameter 0.32 mm). The exhaust flow was sampled and analyzed in intervals of 20 min. For the in situ CF MAS NMR experiments, ^{13}C -enriched methanol ($^{13}\text{CH}_3\text{OH}$, 99%) purchased from Cambridge Isotopes was used.

In Situ SF Experiments. The SF experiment applied in the present work consists of the following steps (Figure 1): (i) recording of the in situ CF MAS NMR spectra at reaction temperature under steady-state conditions during a continuous injection of ^{13}C -enriched methanol into the MAS rotor reactor, (ii) recording of MAS NMR spectra after stopping the reactant flow and purging the catalyst with dry nitrogen after raising the temperature, and (iii) recording of MAS NMR spectra at

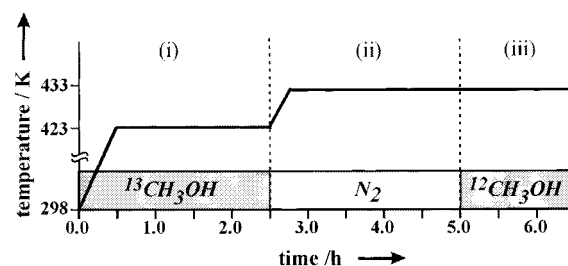


Figure 1. Protocol of the in situ SF MAS NMR experiment consisting of periods: (i) recording of spectra at reaction temperature during conversion of ^{13}C -enriched methanol, (ii) recording of spectra during purging the catalyst with dry carrier gas, and (iii) recording of spectra at reaction temperature during conversion of methanol molecules with a natural abundance of ^{13}C -isotopes. This method allows to study heterogeneously catalyzed reactions under steady-state conditions and the consecutive pathway of surface species previously formed during period i.

reaction temperature after starting the flow of methanol with ^{13}C -isotopes in natural abundance (denoted $^{12}\text{CH}_3\text{OH}$ in Figure 1). Since the in situ SF method allows a direct investigation of the further conversion of adsorbate compounds formed on the catalyst during period (i), this technique can provide detailed information on reaction mechanisms.

NMR Spectroscopy. ^{13}C NMR investigations were performed on a Bruker MSL 400 spectrometer at a resonance frequency of 100.6 MHz. The experiments under CF conditions were carried out with a sample spinning rate of ca. 2.0 kHz using a modified DSI-740 7 mm STD MAS NB NMR probe of Doty Scientific Instruments, Texas (see ref 21c). ^{13}C MAS NMR spectra were recorded using high-power decoupling exciting the spin system with $\pi/2$ pulses and using a repetition time of 5 s, while ^{13}C CP/MAS NMR experiments (CP = cross-polarization) were performed with a contact time of 2.5 ms and a repetition time of 4 s. The number of scans of 500–800 was optimized depending on the signal/noise ratio obtained at different temperatures. All spectra were referenced to tetramethylsilane (TMS).

Results and Discussion

1. Formation of Surface Methoxy Species on Zeolite H-Y by Conversion of Methanol under CF Conditions. Figure 2 shows the in situ ^{13}C CF MAS NMR spectra obtained during methanol ($^{13}\text{CH}_3\text{OH}$) conversion on zeolite H-Y under CF conditions at reaction temperatures of 298–473 K. These experiments were performed according to step i in Figure 1. The spectra recorded with CP/MAS NMR spectroscopy (Figure 2, right) were obtained directly after recording the corresponding spectra with MAS NMR technique at the same reaction temperatures (Figure 2, left).

The signal at 50 ppm which dominates the ^{13}C MAS NMR spectra at low reaction temperatures is due to methanol molecules adsorbed on the zeolite. Starting at a reaction temperature of 433 K, significant yields of DME (Y_{dme}) were determined by on-line gas chromatography (Figure 2, middle). According to Corma² and van Santen,^{18c} the signals at 60.5 and 63.5 ppm occurring at temperatures of 393 K and higher are caused by the reaction product DME, which has the two different adsorbate conformations shown in Scheme 1. The signal at 63.5 ppm is due to the side-on adsorbed DME which is more strongly adsorbed on the zeolite framework, while the signal at 60.5 ppm is due to the end-on conformation which is more mobile causing a more narrow line shape. A comparison of the MAS NMR and the CP/MAS NMR spectra recorded at 393–473 K shows

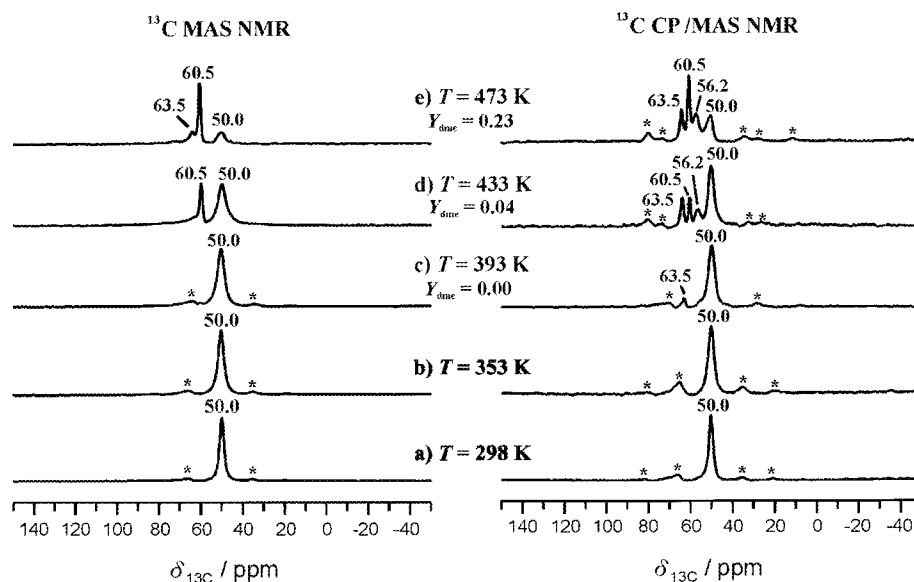
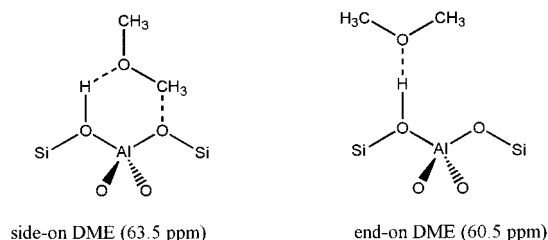


Figure 2. In situ ^{13}C MAS NMR spectra of zeolite H-Y recorded at temperatures between 298 (a) and 473 K (e) during a continuous injection of $^{13}\text{CH}_3\text{OH}$ ($W/F = 100$ g h/mol) into the MAS NMR rotor reactor. The spectra on the left-hand side were obtained with MAS NMR and proton decoupling while the spectra on the right-hand side were recorded applying the CP/MAS NMR (cross polarization) technique. Asterisks denote spinning sidebands.

SCHEME 1



that the DME species at 63.5 ppm are more rigidly adsorbed than the DME species at 60.5 ppm (Figure 2, spectra c–e) which agrees with the assignment in Scheme 1.

According to Bosacek,¹⁰ the ^{13}C MAS NMR signal of methoxy groups on zeolite H-Y with a $n_{\text{Si}}/n_{\text{Al}}$ ratio of 2.7 occurs at a chemical shift of ca. 56 ppm. While the MAS NMR spectra recorded under CF conditions at 298–473 K yield no hint at the formation of methoxy groups, in the CP/MAS NMR spectra a signal occurs at 56.2 ppm. This signal is assigned as methoxy groups, supported by its resonance position and sideband patterns.

The finding that methoxy groups cannot be observed in the MAS NMR spectra recorded under CF conditions (Figure 2, left) shows that these surface species have only a weak concentration in comparison with the other reactants. In addition, due to the broadening of the signal at 56.2 ppm, it is hidden in the neighboring signal of end-on adsorbed DME at 60.5 ppm. The CP/MAS NMR experiment^{5,25} which favors signals arising from rigidly adsorbed species which experience a static dipolar coupling, makes the ^{13}C MAS NMR signal of methoxy groups visible in our CF measurements.

Since the temperatures at which the formation of surface methoxy groups and of DME starts are very close, namely, at about 393–433 K, it is hard to determine whether the methoxy groups can further react with another methanol molecule to produce DME or the formation of DME occurs directly by a conversion of methanol. An experiment suitable to clarify this question should start with a catalyst which surface is covered by methoxy species only. Therefore, the formation of pure

surface methoxy species on acidic zeolites under in situ conditions was investigated more in detail.

2. Preparation of Surface Methoxy Species on Zeolites H-Y and H-ZSM-5 and on the Silicoaluminophosphate SAPO-34 by the SF Method. In most of the former studies,^{2,3,5,8–10,26} surface methoxy groups were prepared on acidic zeolites by a treatment with gaseous methyl iodide or methanol vapor under batch conditions using a vacuum line. In the present work, surface methoxy groups were prepared applying the in situ SF method which is very convenient for the study of their further conversion with reactant molecules.

Two different procedures have been applied under in situ conditions to obtain surface methoxy groups on acidic zeolites. The approach (I) consists of an injection of methanol into the MAS NMR rotor reactor at the temperature of 393 K for 10 min, followed by keeping the reaction temperature at 393 K for 2.0 h. The spectra of a zeolite H-Y treated in this way are shown in Figure 3. In this experiment, the reaction temperature was chosen as low as possible to form mainly surface methoxy species and only a small amount of DME. The signal at 56.2 ppm in the MAS NMR spectrum (Figure 3a) indicates the formation of a significant amount of surface methoxy species. The CP/MAS NMR spectra recorded at different sample spinning rates (Figure 3, panels b and c) show a second signal at ca. 51 ppm which is caused by strongly adsorbed methanol.^{2,5,10} As mentioned above, the weak signal at 63.5 ppm hints at the formation of DME adsorbed on zeolite H-Y in the side-on conformation. All signals occurring in the CP/MAS NMR spectra have sideband patterns which indicate the strong adsorption or bonding of the corresponding species at the zeolite framework. A simulation of the sideband pattern of methoxy groups at 56.2 ppm (Bruker software WINFIT) gives an anisotropy of chemical shift of $\Delta\sigma = -41.2$ ppm, which agrees very well with the data obtained for surface methoxy groups in previous studies.¹⁰

In approach (II), the methanol conversion is started at reaction temperature, i.e., a flow of methanol is injected into the MAS NMR rotor reactor at $T = 423$ K. Subsequently, the methanol flow is stopped and the catalyst is purged with dry nitrogen at $T = 473$ K. The spectra obtained were shown in Figure 4.

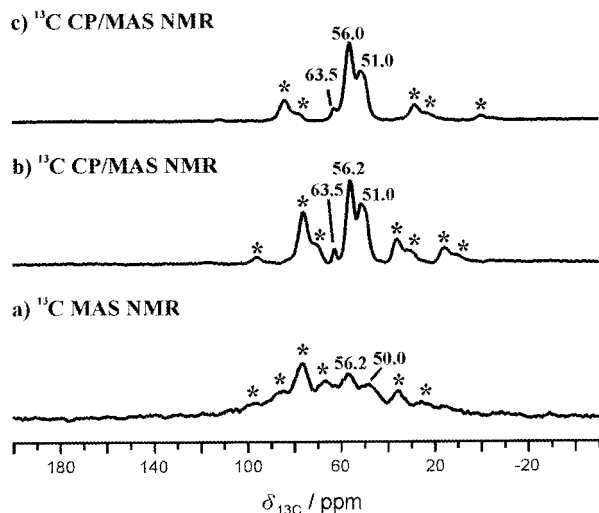


Figure 3. In situ ^{13}C MAS NMR spectra of zeolite H-Y recorded at $T = 298$ K after conversion of $^{13}\text{CH}_3\text{OH}$ under CF conditions ($W/F = 40$ g h/mol) at $T = 393$ K for 10 min and keeping the reaction temperature for 2.0 h. While the spectrum (a) was obtained with MAS NMR, the spectra b and c were recorded with CP/MAS NMR (cross polarization) using sample spinning rates of ca. 2.0 kHz (b) and 3.0 kHz (c). Asterisks denote spinning sidebands.

Similar to the results obtained in the CF experiments in Figure 2, the MAS NMR spectrum shown in Figure 4a consists of signals at 50.0, 60.5, and 63.5 ppm due to methanol and end-

on and side-on adsorbed DME species, respectively. However, after purging the catalyst with dry nitrogen at 473 K (Figure 4b), the signal at 60.5 ppm due to the weakly end-on adsorbed DME species decreases significantly, accompanied by a decrease of the signal at 50.0 ppm and a strong increase of the signal of surface methoxy groups at 56.2 ppm. According to the MAS NMR and CP/MAS NMR spectra obtained after purging the catalysts at 473 K, these surface methoxy groups are the major surface species.

Application of approach (II) for the formation of methoxy groups on zeolites H-ZSM-5 and H-SAPO-34 yielded the ^{13}C MAS NMR and ^{13}C CP/MAS NMR spectra shown in Figures 5 and 6. The signal at 59.4 ppm occurring in the spectra of zeolite H-ZSM-5 (Figure 5) agrees well with that of methoxy groups on H-ZSM-5 prepared by adsorption of methyl iodide (59.6 ppm).^{8a,21d} After conversion of $^{13}\text{CH}_3\text{OH}$ on H-SAPO-34 and purging the catalysts with dry nitrogen, a weak signal of methoxy groups occurred at 56.6 ppm which is overlapped by the signals of DME at 60.5 and methanol at 50.0 ppm (Figure 6). The chemical shift of 56.6 ppm observed for methoxy species on H-SAPO-34 is coincided with that reported by Anderson²⁷ and Haw.²⁸ The low intensity of the ^{13}C MAS NMR and ^{13}C CP/MAS NMR signal of methoxy groups at 56.6 ppm is a hint for a low chemical stability of these species on H-SAPO-34.

In comparison with the formation of surface methoxy groups by an external loading of reactants on solid catalysts, the above-mentioned approaches (I) and (II) for an in situ preparation of these species by the SF technique allow to selectively retain

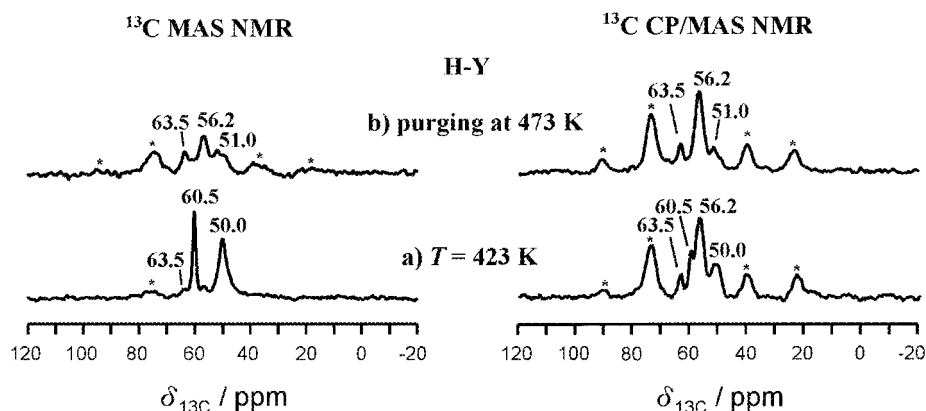


Figure 4. In situ ^{13}C MAS NMR spectra of zeolite H-Y recorded during conversion of $^{13}\text{CH}_3\text{OH}$ under CF conditions ($W/F = 40$ g h/mol) at $T = 423$ K (a) and after purging the catalyst with dry nitrogen at $T = 473$ K for 1.0 h (b). While the spectra on the left-hand side were obtained with MAS NMR, the spectra on the right-hand side were recorded with CP/MAS NMR (cross polarization) technique. Asterisks denote spinning sidebands.

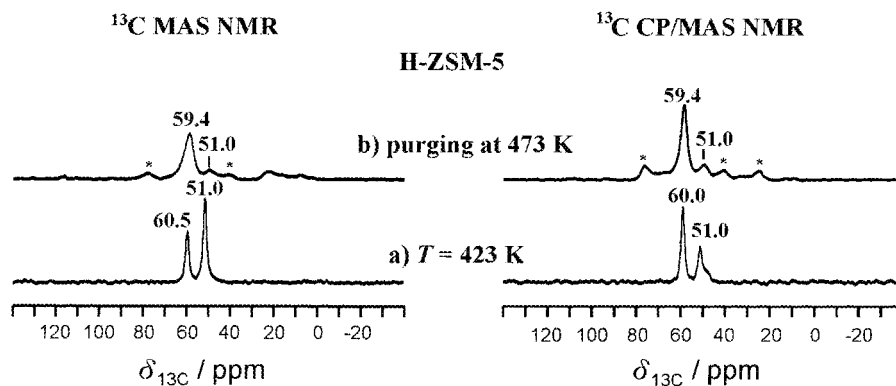


Figure 5. In situ ^{13}C MAS NMR spectra of zeolite H-ZSM-5 recorded during conversion of $^{13}\text{CH}_3\text{OH}$ under CF conditions ($W/F = 40$ g h/mol) at $T = 423$ K (a) and after purging the catalyst with dry nitrogen at $T = 473$ K for 1.0 h (b). While the spectra on the left-hand side were obtained with MAS NMR, the spectra on the right-hand side were recorded with CP/MAS NMR (cross polarization) technique. Asterisks denote spinning sidebands.

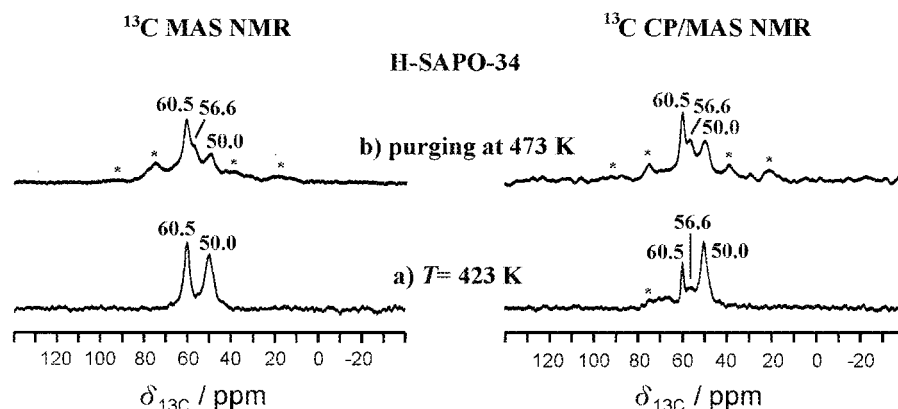


Figure 6. In situ ^{13}C MAS NMR spectra of the silicoaluminophosphate H-SAPO-34 recorded during conversion of $^{13}\text{CH}_3\text{OH}$ under CF conditions ($W/F = 40$ g h/mol) at $T = 423$ K (a) and after purging the catalyst with dry nitrogen at $T = 473$ K for 1.0 h (b). While the spectra on the left-hand side were obtained with MAS NMR, the spectra on the right-hand side were recorded with CP/MAS NMR (cross polarization) technique. Asterisks denote spinning sidebands.

the surface methoxy species and apply the methylated catalysts directly for studies of the further conversion of surface methoxy groups in heterogeneously catalyzed reactions.

3. Study on the Role of Methoxy Species during Methanol Conversion to DME by the in Situ SF Method. As described above, the ^{13}C MAS NMR signal of surface methoxy species on zeolite H-ZSM-5 is very close to the end-on adsorbed DME while on H-SAPO-34 only a small amount of these species could be prepared. Therefore, zeolite H-Y was selected as acidic catalyst to investigate the role of methoxy species in the conversion of methanol to DME. Due to the weak intensity of the surface methoxy groups in the MAS NMR spectra, the following experiments were performed applying the CP/MAS NMR technique.

By optimizing the reaction temperature, almost pure surface methoxy groups were obtained on zeolite H-Y applying the above-mentioned approach (II). First, $^{13}\text{CH}_3\text{OH}$ was converted on zeolite H-Y at a reaction temperature of 423 K. Subsequently, the flow was stopped and the catalyst was purged with dry nitrogen at $T = 433$ K for 2 h to remove almost all reactants excluding the methoxy species. The CP/MAS NMR spectrum obtained (Figure 7a) is dominated by a signal at 56.2 ppm due to methoxy groups accompanied by a strong sideband pattern. A weak shoulder at ca. 51.0 ppm indicates only a very small amount of strongly adsorbed methanol molecules. After preparing pure surface methoxy groups on zeolite H-Y, a flow of methanol with ^{13}C -isotopes in natural abundance ($^{12}\text{CH}_3\text{OH}$) was injected into the MAS NMR rotor reactor at the reaction temperature of 433 K for 10 min (Figure 7b) and 1.0 h (Figure 7c). After an injection of $^{12}\text{CH}_3\text{OH}$ for 10 min, weak signals occurred at 63.5 and 60.5 ppm due to the formation of DME accompanied by a decrease of the signal of surface methoxy groups at 56.2 ppm. This finding indicates a reaction of the ^{13}C -enriched surface methoxy groups with $^{12}\text{CH}_3\text{OH}$ leading to $^{13}\text{CH}_3\text{O}^{12}\text{CH}_3$ (Scheme 2). After an injection of $^{12}\text{CH}_3\text{OH}$ for 1.0 h, all signals disappeared excluding the ^{13}C CP/MAS NMR signal of partially ^{13}C -enriched DME ($^{13}\text{CH}_3\text{O}^{12}\text{CH}_3$) at 63.5 ppm. In a parallel experiment, performed with a zeolite H-Y methylated with $^{12}\text{CH}_3\text{OH}$, no signals of DME could be observed at 60.5 and 63.5 ppm under the same conditions. Hence, the ^{13}C -enriched surface methoxy groups prepared on zeolite H-Y by conversion of $^{13}\text{CH}_3\text{OH}$ are characterized by a high reactivity allowing their reaction with $^{12}\text{CH}_3\text{OH}$ to partially ^{13}C -enriched DME. This result gives evidence for the catalytic role of surface methoxy groups in the conversion of methanol to DME on acidic zeolites according to the indirect pathway

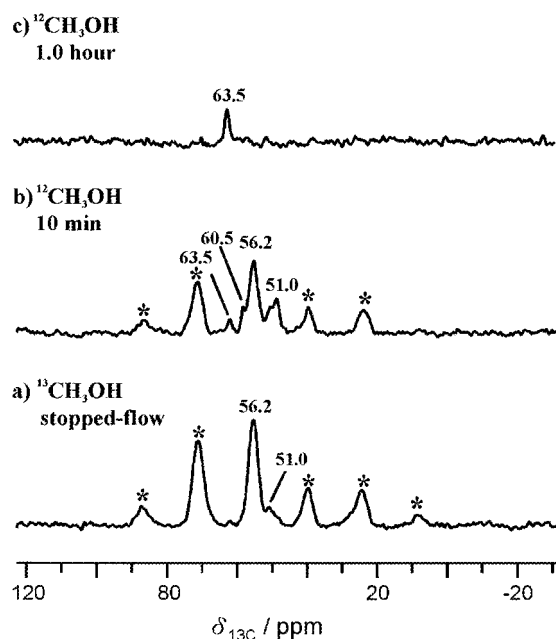
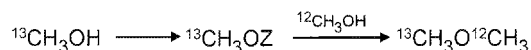


Figure 7. In situ ^{13}C CP MAS NMR spectra of zeolite H-Y recorded at $T = 433$ K after stopping the conversion of $^{13}\text{CH}_3\text{OH}$ at $T = 423$ K ($W/F = 40$ g h/mol) and purging the catalyst with dry nitrogen for 2.0 h (a), and after starting the flow of $^{12}\text{CH}_3\text{OH}$ ($W/F = 40$ g h/mol) at $T = 433$ K for 10 min (b) and 1.0 h (c). Asterisks denote spinning sidebands.

SCHEME 2



(eqs 1a and 1b). The experiments performed in this work, however, cannot exclude a contribution of the direct pathway (eq 2) in the formation of DME by conversion of methanol on acidic zeolites. Further efforts are necessary to develop suitable approaches allowing a determination of the rate constants of these two pathways.

Conclusions

The investigation of the role of methoxy groups formed by conversion of methanol on acidic zeolites requires a selective preparation of these species which can be reached applying the novel in situ SF MAS NMR technique. Testing two approaches for the formation of methoxy groups on zeolite H-Y— injection of a short $^{13}\text{CH}_3\text{OH}$ pulse at 393 K and keeping the reaction

temperature at 393 K (I) and conversion of $^{13}\text{CH}_3\text{OH}$ under CF conditions at 423 K and purging with dry nitrogen (II), the approach (II) was found to be the more successful method. By CP/MAS NMR experiments, it could be shown that the alkoxy species formed in this way are rigidly bound at the catalysts surface. The ^{13}C MAS NMR and ^{13}C CP/MAS NMR signals of the methoxy groups formed on zeolites H-Y and H-ZSM-5 occur at resonance positions of 56.2 and 59.4 ppm which agree well with those of methoxy groups formed by adsorption of methyl iodide. On the silicoaluminophosphate H-SAPO-34, only a small amount of methoxy species occurring at 56.6 ppm could be prepared.

To study the role of methoxy groups in the conversion of methanol to hydrocarbons on acidic zeolites, an in situ SF protocol was applied. Zeolite H-Y methylated by $^{13}\text{CH}_3\text{OH}$ at 423 K was used as catalyst for the conversion of methanol having ^{13}C -isotopes in natural abundance at 433 K. The occurrence of a ^{13}C MAS NMR signal of partially ^{13}C -enriched dimethyl ether at 60.5 and 63.5 ppm provides the experimental evidence for a catalytically active role of methoxy groups in the conversion of methanol to dimethyl ether.

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