

Effect of organic impurities on the hydrocarbon formation via the decomposition of surface methoxy groups on acidic zeolite catalysts

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Abstract

The possible effects of traces of organic impurities in methanol on the formation of hydrocarbons by surface methoxy groups on acidic microporous catalysts were studied under batch conditions. For this purpose, surface methoxy groups were prepared on zeolite H-Y and silicoaluminophosphate H-SAPO-34 from ¹³C-enriched methanol (¹³C-enrichment of 99%, chemical purity of 98+%, with total organic impurities of ca. 1000 ppm) and highly purified nonenriched methanol (organic impurities <30 ppm), respectively. The conversion of these surface methoxy groups on thermal treatments at 473–673 K was investigated by the combined ¹³C MAS NMR-UV/vis spectroscopy. It was found that the formation of primary aromatics and carbenium ions on the methylated zeolite catalysts occurs at identical reaction temperatures from the conversion of both ¹³C-enriched and nonenriched surface methoxy groups. ¹³C MAS NMR-UV/vis studies of H-SAPO-34 catalyst loaded with ethanol and acetone show that a coverage of at least 0.1 molecule per bridging OH group is essential to obtain aromatics and carbenium ions in a similar fashion as those formed by the conversion of surface methoxy groups; however, this coverage is at least two orders of magnitude higher than the ethanol and acetone content present as trace organic impurities in the aforementioned methanol feeds. These findings indicate that traces of organic impurities present in the methanol do not govern the formation of primary hydrocarbons from surface methoxy groups.

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1. Introduction

The conversion of methanol and low molecular weight alcohols on acidic zeolite catalysts has attracted much attention in recent years [1]. At higher temperatures, generally methanol is converted to light olefins, whereas at lower temperatures, more aromatics and other hydrocarbons are produced. Moreover, the course of the methanol conversion on acidic zeolites depends strongly on the particular catalyst structure. Currently it is well accepted that the steady state of the methanol-to-olefin (MTO) process [1] is dominated by the “hydrocarbon pool” route [2–5]. In this case, methanol is added onto reactive or-

ganic species, such as large olefins, methylbenzenes, and cyclic carbenium ions, while light olefins are formed via elimination from these species. But the initial C–C bond formation during the kinetic induction period and the chemistry leading to the reactive hydrocarbon-pool remains a matter of debate. Theoretical calculations have recently been performed in an attempt to improve the understanding of the reaction mechanisms in the MTO process [6–8]. In agreement with earlier catalytic and spectroscopic studies [1a,1f,9–11], recent solid-state ¹³C MAS NMR investigations [12] indicated that the decomposition of surface methoxy groups results in the formation of primary hydrocarbons on acidic zeolite catalysts. Furthermore, it was demonstrated that surface methoxy groups can contribute to the methylation of aromatics, acting as compounds of the reactive hydrocarbon pool in the MTO process [12].

In contrast, it has been suggested that initiation of methanol conversion toward hydrocarbons on acidic zeolite catalysts

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might be affected by cofeeding of impurities in the methanol feed [13]. On the basis of GC experiments, Haw et al. [14] lent further support to this suggestion by claiming that the initiation of the MTO process is typically caused by organic impurities instead of any direct route from pure methanol and dimethyl ether (DME).

Traces of organic impurities are generally present in commercial methanol [15]. To clarify whether traces of organic impurities also govern the conversion of surface methoxy groups, the present work compares the formation of primary hydrocarbons on the methylated zeolite catalysts prepared from the ^{13}C -enriched methanol (^{13}C -enrichment of 99%, chemical purity of 98+%, with total organic impurities of ca. 1000 ppm) and from the highly purified nonenriched methanol (organic impurities < 30 ppm) on zeolite H-Y and silicoaluminophosphate H-SAPO-34, respectively.

In recent years, a number of combined spectroscopic methods have been developed to investigate heterogeneously catalyzed reaction systems simultaneously with different techniques [16–20]. In the present work, the recently introduced MAS NMR-UV/vis spectroscopy [20] is used to study the initiation stage of methanol conversion on acidic zeolite catalysts via the methoxy route. ^{13}C MAS NMR spectroscopy is a suitable tool for observing the formation of surface methoxy groups and their conversion in a general manner, although with limited sensitivity for some of the reaction products, whereas UV/vis spectroscopy detects the formation of primary aromatics and unsaturated carbenium ions with high sensitivity. This advantage of the combined MAS NMR-UV/vis spectroscopy is used to clarify whether traces of organic impurities present in the ^{13}C -enriched methanol govern the formation of primary hydrocarbons by conversion of surface methoxy groups on zeolite catalysts.

2. Experimental

2.1. Materials

Zeolite Na-Y ($n_{\text{Si}}/n_{\text{Al}} = 2.7$) was purchased from Degussa AG (Hanau, Germany). The zeolite $\text{NH}_4\text{Na-Y}$ was prepared by a fourfold ion exchange of zeolite Na-Y at 353 K in a 1.0 M aqueous solution of NH_4NO_3 leading to an ion-exchange degree of 90%. Subsequently, the material was washed with demineralized water and dried at room temperature. The zeolite $\text{NH}_4\text{Na-Y}$ was heated in vacuum at a rate of 20 K/h up to the final temperature of 723 K. At this temperature, the material was calcined at a pressure < 10^{-2} Pa for 12 h, giving the zeolite H-Y. The silicoaluminophosphate H-SAPO-34 with an $n_{\text{Si}}/(n_{\text{Al}} + n_{\text{Si}} + n_{\text{P}})$ ratio of 0.11 was prepared as described previously [21] for the synthesis of Ni-SAPO-34, but omitting the nickel salt. To remove the template, the as-synthesized material was heated at a rate of 60 K/h 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 vacuum at 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 < 10^{-2} Pa for 12 h, leading to

H-SAPO-34. The calcined material was sealed and kept in glass tubes for further use. All of the zeolite 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.

The preparation of ^{13}C -enriched methoxy species was performed by adsorption of the ^{13}C -enriched methanol (^{13}C -enrichment of 99%, chemical purity of 98+% [22], purchased from Cambridge Isotope Laboratories). In addition, methanol with a natural abundance of ^{13}C -isotopes (chemical purity \geq 99.9%, purchased from Sigma–Aldrich), further purified by fractional distillation, was used (denoted as $^{12}\text{CH}_3\text{OH}$). GC and GC/MS analysis showed that ^{13}C -enriched methanol contains 1000 ± 5 ppm of organic impurities (925 ppm of ^{13}C -enriched ethanol). The highly purified $^{12}\text{CH}_3\text{OH}$ contains <30 ppm of organic impurities (ca. 21 ppm of acetone and ca. 7 ppm of ethanol). ^{13}C -1-ethanol (^{13}C -1-enrichment of 99%, purchased from ISOTEC) and ^{13}C -2-acetone (^{13}C -2-enrichment of 99%, purchased from Cambridge Isotope Laboratories) were used as model compounds of typical impurities.

2.2. MAS NMR-UV/vis experiments

To ensure identical preparation procedures for ^{13}C -enriched and highly purified nonenriched surface methoxy groups, the preparation of methoxy species on the acidic catalysts H-Y and H-SAPO-34 was performed via a vacuum line. The calcined and dehydrated catalysts (300 mg) filled in a glass tube (ca. 6 mm o.d., ca. 180 mm long) were subjected to methanol at a pressure of 7.5 mbar and at a temperature of 393 K. Thereafter, an evacuation for 6 h at 393 K and additional evacuation for 6 h at 473 K were performed. Subsequently, the methylated catalysts were fused for further thermal treatments at 473–673 K for 20 min.

In some experiments, 300 mg of dehydrated H-SAPO-34 were loaded with ^{13}C -1-ethanol or ^{13}C -2-acetone and fused in a glass tube. After heating at a given temperature (473–673 K) for 20 min, the glass tube was opened in a glove box, and the catalyst was transferred to a 7-mm MAS NMR-UV/vis rotor [20].

The ^{13}C MAS NMR investigations were performed with a modified 7-mm Bruker MAS NMR probe on a Bruker MSL-400 spectrometer at a resonance frequency of 100.6 MHz. High-power proton decoupling (HPDEC) MAS NMR spectra were recorded after an excitation with a $\pi/2$ pulse and with a repetition time of 5 s. Cross-polarization (CP) MAS NMR spectra were performed with a contact time of 5 ms and a repetition time of 2 s. A sample spinning rate of ca. 3.5 kHz was applied. Applying an external intensity standard (dehydrated zeolite H-Y loaded with $^{13}\text{CH}_3\text{OH}$), ^{13}C spin counting, with a repetition time of 30 s, was performed. The ^1H MAS NMR investigations were performed with a 4-mm Bruker MAS NMR probe on a Bruker MSL-400 spectrometer at a resonance frequency of 400.1 MHz. The sample spinning rate of ca. 10.0 kHz was applied. The ^1H spin counting was carried out with a repetition time of 10 s, applying dehydrated zeolite H,Na-Y with an exchange degree of 35% as an external intensity standard. All of

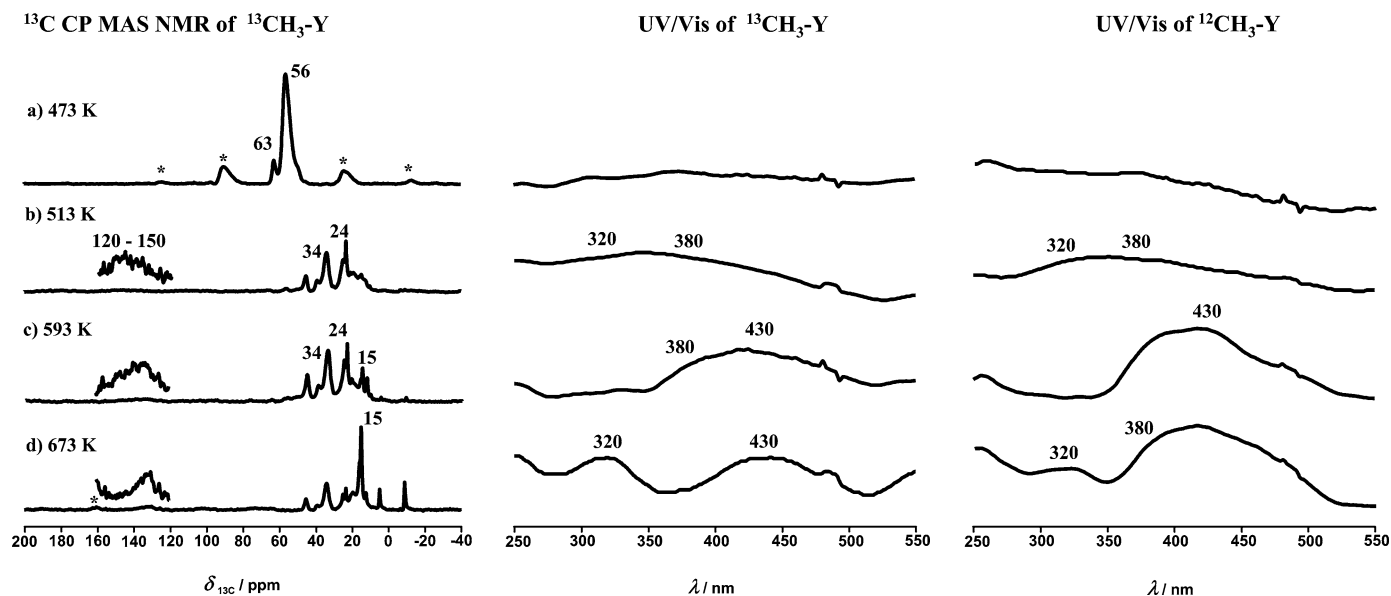


Fig. 1. ^{13}C CP MAS NMR (left) and UV/vis spectra (middle and right) of zeolite H-Y methylated by $^{13}\text{CH}_3\text{OH}$ ($^{13}\text{CH}_3\text{-Y}$, middle) and highly purified $^{12}\text{CH}_3\text{OH}$ ($^{12}\text{CH}_3\text{-Y}$, right) after thermal treatments at 473 (a) to 673 K (d) for 20 min. Asterisks in the NMR spectra denote spinning sidebands. The narrow UV peaks at ca. 460–500 nm are caused by the equipment.

the ^1H and ^{13}C MAS NMR spectra were referenced to tetramethylsilane (TMS). The decomposition and simulation of NMR spectra were performed using the Bruker WINNMR and WINFIT software.

UV/vis spectra were recorded with an AvaSpec-2048 fiber-optic spectrometer, an AvaLight-DH-S deuterium light source, and a glass fiber reflection probe (FCR-7UV20-3-SR-S1) by Avantes [20]. The dehydrated and unloaded zeolite H-Y and the silicoaluminophosphate H-SAPO-34 were used as reference standards for the UV/vis measurements.

3. Results and discussion

3.1. MAS NMR-UV/vis investigation of the conversion of surface methoxy groups on methylated zeolite Y ($\text{CH}_3\text{-Y}$)

Fig. 1a shows the ^{13}C CP MAS NMR spectrum of methylated zeolite Y prepared from ^{13}C -enriched methanol. This spectrum is dominated by the signal of ^{13}C -enriched surface methoxy groups at 56.2 ppm with spinning sidebands, which is characteristic for a methylated zeolite Y ($^{13}\text{CH}_3\text{-Y}$) [12]. The weak signal at 63.5 ppm is caused by a small amount (relative intensity of ca. 2%) of side-on adsorbed dimethyl ether (DME) [12]. The UV/vis spectrum of zeolite $^{13}\text{CH}_3\text{-Y}$ (Fig. 1a) shows no UV/vis bands. This finding indicates that the formation of surface methoxy groups on zeolite H-Y at temperatures of up to 473 K is not accompanied by the formation of primary aromatics and unsaturated carbenium ions.

On heating of zeolite $^{13}\text{CH}_3\text{-Y}$ at 513 K, the conversion of surface methoxy groups to hydrocarbons occurred, as indicated by the disappearance of the ^{13}C CP MAS NMR signal at 56.2 ppm and the appearance of new signals in the aliphatic range of ca. 10–45 ppm (Fig. 1b). Only weak signals of a small amount of aromatic compounds can be observed at ca. 120–

150 ppm (see inset). The UV/vis spectrum of this sample contains broad bands at ca. 320–380 nm (Fig. 1b) indicating the formation of polyalkylaromatics, monoenylic, and dienylic carbenium cations [23–25]. On thermal treatments at 593 and 673 K (Figs. 1c and 1d), new UV bands occur at 380 and 430 nm due to the formation of dienylic and trienylic carbenium ions or hexamethyl-benzenium cations [23–25]. The ^{13}C CP MAS NMR spectra of these two samples (Figs. 1c and 1d) show an increase of the signals of aromatic compounds at ca. 120–150 ppm. The corresponding ^{13}C HPDEC MAS NMR spectra (not shown) on thermal treatments at given temperatures are essentially identical to those published before (Fig. 4 in Ref. [12]).

The preparation of nonenriched surface methoxy groups on zeolite H-Y from highly purified nonenriched methanol ($^{12}\text{CH}_3\text{OH}$, total organic impurities <30 ppm) was performed under identical conditions as the preparation of ^{13}C -enriched methoxy groups. Due to the low natural abundance of ^{13}C -isotopes in the nonenriched material, no ^{13}C CP MAS NMR investigations of zeolite $^{12}\text{CH}_3\text{-Y}$ could be performed. The identical formation of surface methoxy groups from ^{13}C -enriched and highly purified nonenriched methanol was clarified by ^1H MAS NMR measurements. The results are shown and discussed in the supporting materials.

Fig. 1 shows the UV/vis spectra obtained for the material after thermal treatments at temperatures of 473–673 K. The comparison of the UV/vis spectra recorded for zeolites $^{13}\text{CH}_3\text{-Y}$ and $^{12}\text{CH}_3\text{-Y}$ indicates the formation of same organic compounds (aromatics and unsaturated carbenium ions) on identical thermal treatments for both catalysts. This finding indicates that traces of organic impurities present in the ^{13}C -enriched methanol (ca. 1000 ppm) have no influence on the formation of primary hydrocarbons on zeolite Y.

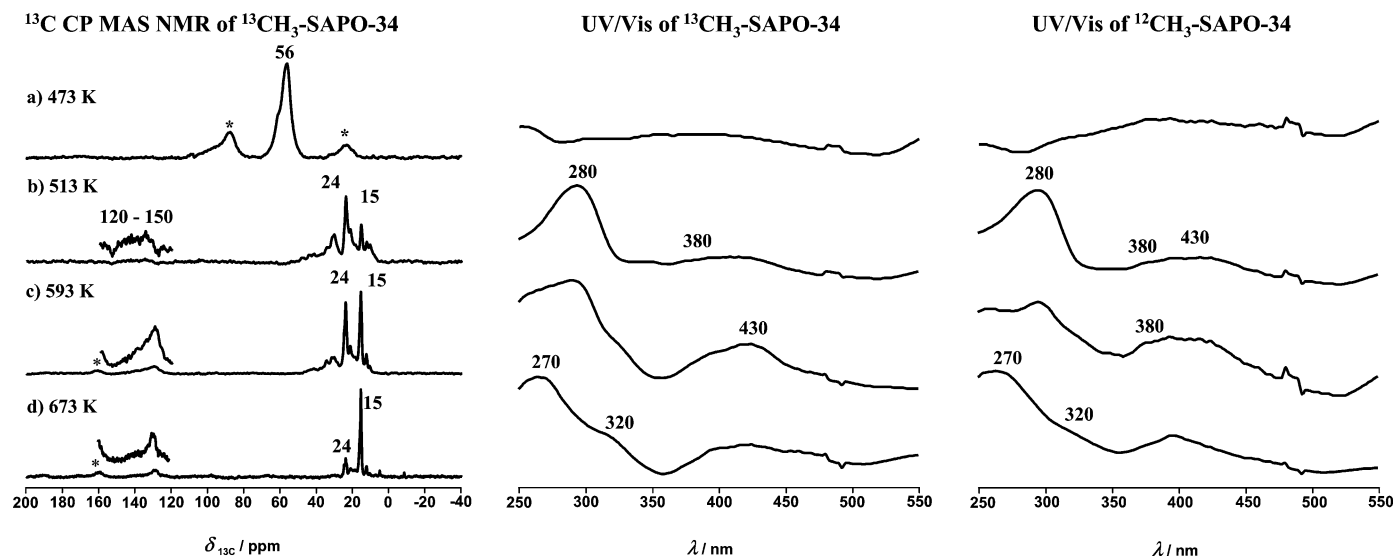


Fig. 2. ^{13}C CP MAS NMR (left) and UV/vis spectra (middle and right) of the silicoaluminophosphate H-SAPO-34 methylated by $^{13}\text{CH}_3\text{OH}$ ($^{13}\text{CH}_3\text{-SAPO-34}$, middle) and highly purified $^{12}\text{CH}_3\text{OH}$ ($^{12}\text{CH}_3\text{-SAPO-34}$, right) after thermal treatments at 473 (a) to 673 K (d) for 20 min. Asterisks in the NMR spectra denote spinning sidebands. The narrow UV/vis peaks at ca. 460–500 nm are caused by the equipment.

3.2. MAS NMR-UV/vis investigation of the conversion of surface methoxy groups on the methylated silicoaluminophosphate SAPO-34 ($\text{CH}_3\text{-SAPO-34}$)

The silicoaluminophosphate H-SAPO-34 is characterized by a lower number of bridging OH groups with lower acid strength in comparison with zeolite H-Y, but it gives high yields of light olefins in the MTO process [1]. Therefore, it is also interesting to study the conversion of surface methoxy groups on this catalyst. The procedure of the investigation is the same as that for the study of the conversion of surface methoxy groups on zeolite Y.

The ^{13}C CP MAS NMR-UV/vis spectra of the methylated silicoaluminophosphate $^{13}\text{CH}_3\text{-SAPO-34}$ recorded on thermal treatments at 473–673 K are shown in Fig. 2. The ^{13}C CP MAS NMR spectrum of $^{13}\text{CH}_3\text{-SAPO-34}$ recorded on thermal treatment at 473 K is dominated by the signal of surface methoxy groups at 56.6 ppm (Fig. 2a). The comparison of the intensity of the signal at 56.6 ppm with the external intensity standard gives a concentration of ca. 0.6 methoxy groups per bridging OH group (SiOHAl). Again, no UV/vis bands occur for this sample, indicating that the formation of methoxy groups on H-SAPO-34 at 473 K is not accompanied by the formation of aromatics and unsaturated carbenium ions.

First, on thermal treatment at 513 K, the UV/vis spectrum of $^{13}\text{CH}_3\text{-SAPO-34}$ shows a band at ca. 280 nm due to neutral aromatics (Fig. 2b). Simultaneously, the ^{13}C CP MAS NMR signal of the surface methoxy groups disappears and the formation of aliphatic and aromatic compounds can be observed at ca. 14–45 ppm and 120–150 ppm, respectively (Fig. 2b). Further thermal treatments up to 673 K led to the formation of monoenylic, dienylic, and trienylic carbenium ions, which are responsible for the broad UV/vis bands at ca. 320, 380, and 430 nm (Figs. 2c and 2d). In contrast to zeolite $^{13}\text{CH}_3\text{-Y}$, however, the UV/vis spectra of the silicoaluminophosphate $^{13}\text{CH}_3\text{-SAPO-34}$ recorded on thermal treatments at 593

and 673 K show significantly larger bands in the region of neutral aromatics. This finding closely agrees with the formation of methylbenzenes occluded in the chabazite cages of SAPO-34. These methylbenzenes are assumed to be the most reactive hydrocarbon pool compounds in the MTO process [1e].

The preparation of nonenriched surface methoxy groups on the silicoaluminophosphate H-SAPO-34 by conversion of a highly purified nonenriched methanol ($^{12}\text{CH}_3\text{OH}$, total organic impurities <30 ppm) and the subsequent thermal treatments led to samples giving the UV/vis spectra shown in Fig. 2. The UV/vis spectra recorded for the silicoaluminophosphates $^{13}\text{CH}_3\text{-SAPO-34}$ and $^{12}\text{CH}_3\text{-SAPO-34}$ indicate the formation of same neutral aromatics and carbenium ions on identical thermal treatments. Hence, like in the case of zeolite Y, the traces of organic impurities occurring in the ^{13}C -enriched methanol (ca. 1000 ppm) have no influence on the formation of primary hydrocarbons on H-SAPO-34 as detected by UV/vis spectroscopy.

3.3. Effect of ethanol and acetone on the formation of primary hydrocarbons on silicoaluminophosphate H-SAPO-34

In addition to water, typical impurities in commercial methanol are ethanol and acetone [15]. Our GC/MS investigations indicate that the most important impurity in ^{13}C -enriched methanol (^{13}C -enrichment of 99%, chemical purity of 98+% [22], derived from Cambridge Isotope Laboratories) is ethanol. To study the influence of ethanol in methanol on the decomposition of surface methoxy groups, the conversion of ethanol on silicoaluminophosphate H-SAPO-34 was investigated by ^{13}C MAS NMR-UV/vis spectroscopy. For this purpose, the ^{13}C -1-enriched ethanol was loaded with coverage of 0.02–0.25 molecule per bridging OH group (SiOHAl) on the dehydrated H-SAPO-34. After thermal treatments of the ethanol-loaded H-SAPO-34 samples at 673 K for 20 min, the ^{13}C MAS NMR and UV/vis spectra were recorded (Fig. 3). Starting with a loading of 0.05 ethanol molecule per SiOHAl group,

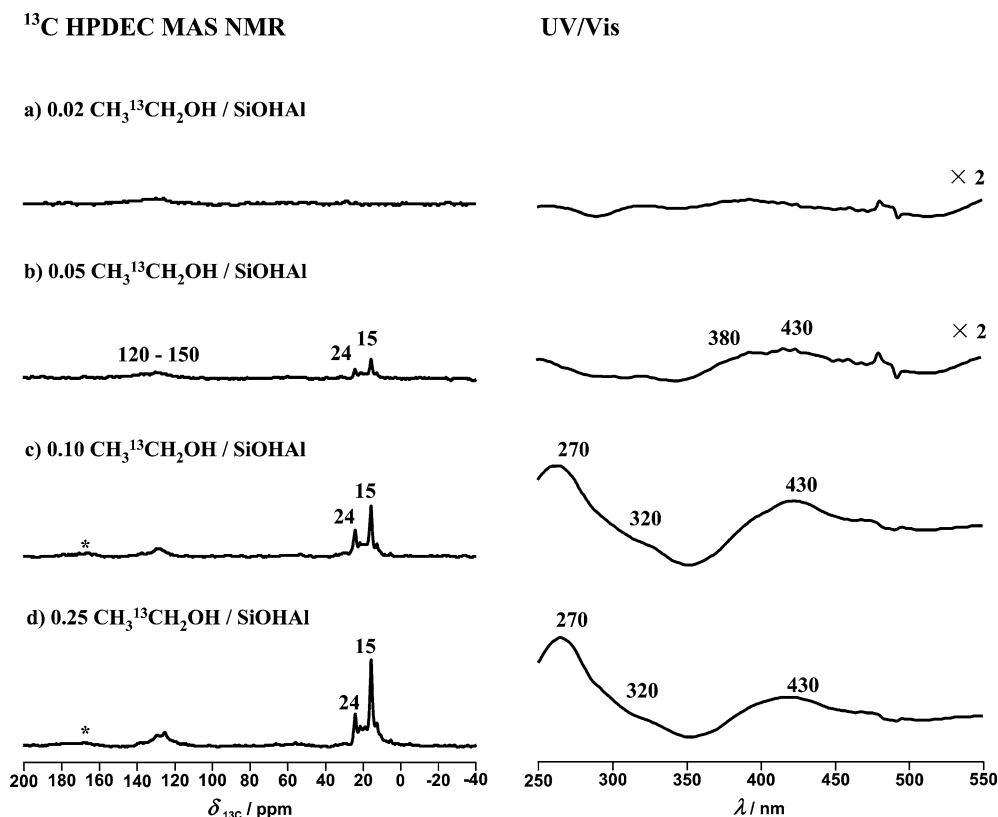


Fig. 3. ^{13}C HPDEC MAS NMR (left) and UV/vis spectra (right) recorded after thermal treatment (673 K) of silicoaluminophosphate H-SAPO-34 loaded with 0.02 (a)–0.25 molecules (d) ^{13}C -1-ethanol per bridging OH group (SiOHAl). Asterisks in NMR spectra denote spinning sidebands. The narrow peaks at ca. 460–500 nm in UV/vis spectra are caused by the equipment.

weak signals and bands due to the formation of hydrocarbons from ethanol on H-SAPO-34 catalyst are evident (Fig. 3b). The UV/vis bands comparable with those observed on thermal conversion of the methoxy groups on H-SAPO-34 (cf. Fig. 2d) occur for the sample loaded with at least 0.10 ethanol molecule per SiOHAl group (Fig. 3c). Also in the case of the conversion of ethanol on H-SAPO-34, a strong UV/vis band of neutral aromatics occurs at 270 nm, accompanied by a broad ^{13}C MAS NMR signal at ca. 120–150 ppm. A similar result was obtained after thermal treatment of the ethanol-loaded H-SAPO-34 catalysts at 593 K (not shown).

It is important to note that there are no UV/vis bands of aromatics and carbenium ions up to a loading of H-SAPO-34 with 0.05 ethanol molecule per SiOHAl group. First significant NMR signals and UV/vis bands were observed on a loading of H-SAPO-34 with 0.10 ethanol molecule per bridging OH group (Fig. 3c), the intensities of which are comparable with those obtained for the conversion of ^{13}C -enriched methanol on H-SAPO-34 (Fig. 2d). When preparing 0.6 methoxy group per bridging OH group on H-SAPO-34 from ^{13}C -enriched methanol (cf. Fig. 2), the maximum ethanol coverage is 0.6×1000 ppm, that is, 6×10^{-4} per bridging OH group (assuming that the organic impurities are all due to ethanol). This ethanol coverage, however, is ca. two orders of magnitude lower ($6 \times 10^{-4}/0.1 = 6 \times 10^{-3}$) than the loading of 0.10 ethanol molecule per bridging OH group, which is required to give UV/vis bands with similar intensities as in Fig. 2c. Therefore, traces of ethanol in the ^{13}C -enriched methanol cannot be re-

sponsible for the NMR signals and UV bands shown in Fig. 2. In the case of preparation of 0.6 methoxy group per bridging OH group on H-SAPO-34 via highly purified nonenriched methanol ($^{12}\text{CH}_3\text{OH}$, total organic impurities <30 ppm), the ethanol coverage (0.6×30 ppm = 1.8×10^{-5}) is even ca. four orders magnitude lower ($1.8 \times 10^{-5}/0.1 = 1.8 \times 10^{-4}$) than that required to give the UV/vis bands of significant and observable intensities.

A similar result was also obtained after thermal treatment of acetone-loaded H-SAPO-34 on thermal treatment at 673 K (Fig. 4). To reach comparable intensities of bands in the UV/vis spectra as in Figs. 2d and 3c, the acetone coverage has to be at least 0.05 molecule per bridging OH group (see, e.g., Fig. 4b). This acetone coverage is much higher than the coverage, which can be reached by traces of acetone in ^{13}C -enriched methanol.

Commercial methanol consists of, in general, several hundred ppm of different organic impurities [15], the concentrations of which are between those of impurities in the highly purified nonenriched methanol (<30 ppm) and the ^{13}C -enriched methanol (ca. 1000 ppm) used in the present study. For the aforementioned concentrations of impurities, no effect on the formation of primary hydrocarbons during the conversion of the surface methoxy groups on zeolite catalysts could be observed by MAS NMR-UV/vis spectroscopy. Therefore, traces of organic impurities in the methanol should not govern the initiation of the methanol conversion on these catalysts via the methoxy route.

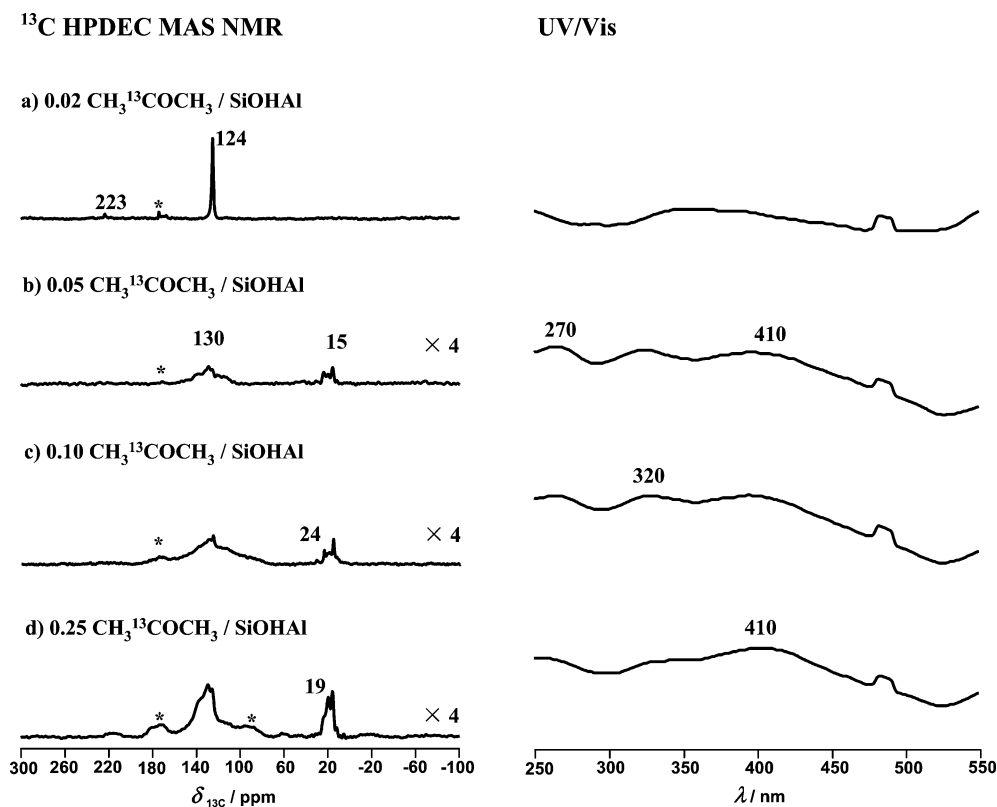


Fig. 4. ^{13}C HPDEC MAS NMR (left) and UV/vis spectra (right) recorded after thermal treatment (673 K) of silicoaluminophosphate H-SAPO-34 loaded with 0.02 (a)–0.25 molecules (d) ^{13}C -2-acetone per bridging OH group (SiOHAl). Asterisks in NMR spectra denote spinning sidebands. The narrow peaks at ca. 460–500 nm in UV/vis spectra are caused by the equipment.

4. Conclusion

The aim of this work was to clarify whether traces of organic impurities govern the formation of first hydrocarbons on acidic zeolite type catalysts from the conversion of the surface methoxy groups. For this purpose, samples of zeolite H-Y and silicoaluminophosphate H-SAPO-34 were methylated by adsorption of ^{13}C -enriched methanol (^{13}C -enrichment of 99%, chemical purity of 98+%, with total organic impurities of ca. 1000 ppm) and highly purified nonenriched methanol (organic impurities <30 ppm). The conversion of the surface methoxy groups on the two above-mentioned catalysts on thermal treatments at 473–673 K was investigated by ^{13}C MAS NMR and UV/vis spectroscopy. Because the formation of first aromatics and carbenium ions was observed at same reaction temperatures for both ^{13}C -enriched and nonenriched surface methoxy groups, the influence of traces of organic impurities present in the ^{13}C -enriched methanol on the formation of primary hydrocarbons on the methylated zeolite catalysts can be excluded.

Ethanol and acetone are the most important organic impurities in commercial methanol. Therefore, the formation of primary hydrocarbons by the conversion of ethanol and acetone on H-SAPO-34 was investigated by combined ^{13}C MAS NMR-UV/vis spectroscopy. These experiments demonstrate that coverage of at least 0.1 ethanol and acetone molecule per bridging OH group is necessary to obtain neutral aromatics and carbenium ions similar to those formed by the conversion of the

methylated catalyst at the same reaction temperature. Considering the number of 0.6 methoxy groups per bridging OH group prepared on H-SAPO-34, the ethanol and acetone coverage mentioned above is more than two orders of magnitude higher than the ethanol and acetone coverage attainable by impurities in methanol. Therefore, studies of the ethanol- and acetone-loaded H-SAPO-34 sample give additional evidence that the ^{13}C MAS NMR-UV/vis spectra of the methylated SAPO-34 on thermal treatment are not governed by ethanol and acetone occurring as traces of organic impurities.

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Supporting material

The online version of this article contains additional supporting material.

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