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In situ MAS NMR spectroscopy of surface compounds formed from methanol and from a toluene/methanol mixture on basic zeolite X

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Abstract

The conversion of methanol and a toluene/methanol mixture on a basic form of zeolite X has been investigated by in situ MAS NMR spectroscopy, both under batch and flow conditions at temperatures between 573 K and 723 K. The zeolite CsNaX/24CsOH used as basic catalyst was prepared by cesium ion exchange and subsequent impregnation with cesium hydroxide followed by calcination. By ^{13}C MAS NMR spectroscopy, the formation of surface compounds that caused signals at 166 and 171 ppm was observed. The compound that gave rise to the signal at 166 ppm was formed by conversion of methanol on zeolite CsNaX/24CsOH at 573 K. Upon purging the catalyst with dry nitrogen at temperatures from 623 K to 723 K, the compound, at 166 ppm, was transformed into the compound at 171 ppm. This process could be reversed by addition of methanol at 573 K. Based on a comparison between the MAS and CP/MAS spectra of the compounds at 166 and 171 ppm, and on literature data, the compound at 166 ppm was assigned to formate species. These formate species are formed by dehydrogenation of methanol to formaldehyde and subsequent reaction with the zeolite framework. The main content of the compound at 171 ppm, occurring as MAS spinning sideband pattern with a chemical shift anisotropy of $\Delta\sigma = -40 \pm 2$ ppm and an asymmetry parameter of $\eta = 0.8 \pm 0.1$, is due to carbonate species. In situ ^{13}C MAS NMR studies of the conversion of toluene/methanol mixtures on zeolite CsNaX/24CsOH indicated that the above-mentioned formate species could play an active role as alkylating agent in the side-chain alkylation of toluene. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Side-chain alkylation of toluene; Formate species; Basic zeolites; In situ MAS NMR spectroscopy; Flow conditions

1. Introduction

The side-chain alkylation of toluene with methanol is a reaction which offers potential advantage of lower raw material cost compared with industrially applied Friedel–Crafts alkylation of benzene with ethene. Therefore, a detailed study of the side-chain alkylation continues to be of interest for the industrial production of ethylbenzene and styrene [1]. Basic zeolites have been shown as suitable catalysts for the side-chain alkylation of toluene with methanol [2–13].

There are various strategies to prepare basic zeolites. The most widely applied method is the exchange of sodium cations by the more elec-

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tropositive cesium or rubidium cations [14]. This treatment results in a decrease of the mean electronnegativity of the zeolite framework that corresponds to a higher basicity [15]. A similar effect is reached by the isomorphous incorporation of germanium atoms into the zeolite framework [16,17]. Martens et al. [18,19] prepared strongly basic alkali metal clusters in zeolite cavities by chemical vapor deposition. Still another route is the impregnation of zeolites X or Y by alkali metal hydroxides or acetates [20–24] followed by a calcination which brings about the formation of basic guest-compounds consisting of alkali metal oxide clusters in the zeolite cavities.

According to a generally accepted mechanism of the side-chain alkylation of toluene with methanol (see, e.g., Refs. [3,8]), toluene is alkylated by formaldehyde which, in turn, is produced by dehydrogenation of methanol on the basic catalyst. The hydrogen formed by the methanol decomposition is in part consumed for hydrogenating styrene to ethylbenzene. A zeolite catalyst with a high selectivity to styrene and ethylbenzene must exhibit basic sites and cations within the zeolite cavities or pores which strongly adsorb toluene [2,3]. In addition, the existence of spatial constraints was envisaged to inhibit the rotation of toluene in the zeolite cavities [11].

Various spectroscopic techniques have previously been applied to study the side-chain alkylation with methanol under in situ conditions [5,6,9–13]. By IR spectroscopy, the decomposition of methanol and the formation of formate species on zeolites CsX, KX and RbX were investigated [5,6]. These studies indicated that formate species may act as intermediates for the side-chain alkylation of toluene. Palomares et al. [9,10] investigated the side-chain alkylation of toluene on MgO, hydrotalcites and alkali metal exchanged zeolites X and Y. In an earlier ^{13}C NMR work, Sefcik [11] found a restricted mobility of toluene adsorbed on zeolite CsX. The first in situ ^{13}C MAS NMR study of the side-chain alkylation of toluene on alkaline

metal exchanged zeolite X was performed by Philippou and Anderson [12]. These authors confirmed the formation of formate species and denoted them as 'spectators in the reaction'. Recently, we published multi-nuclear investigations of zeolite CsNaY impregnated with CsOH [13,25]. By [133]Cs MAS NMR spectroscopy, a strong adsorption of toluene on cesium cations was found [13]. In contrast to zeolite CsNaY, on zeolite CsNaY impregnated with CsOH, no signals of by-products formed via acid-catalyzed reactions were observed by in situ ^{13}C MAS NMR spectroscopy of the side-chain alkylation of toluene with methanol under batch conditions [13]. A signal at ca. 168 ppm indicated the presence of formate species and its preferential formation on impregnated zeolite CsNaY. Signals of ethylbenzene occurred in the ^{13}C MAS NMR spectrum were recorded after heating the sample at 723 K.

In the present work, zeolite CsNaX impregnated with cesium hydroxide was applied as catalyst for the side-chain alkylation of toluene. For the first time, this reaction was investigated by in situ ^{13}C MAS NMR spectroscopy under flow conditions [26,27]. This new technique allows to observe the formation and transformation of surface compounds under steady state conditions with different reactant flow rates. It will be demonstrated as a major result that formate species are by no means the dead-end of methanol conversion on basic zeolites.

2. Experimental

The parent zeolite NaX (Union Carbide, Tarrytown, NY, USA, $n_{Si}/n_{Al} = 1.3$) was fivefold ion exchanged in a 0.4 M aqueous solution of CsCl (CsCl: Aldrich, 19,831-5) at 353 K leading to an ion exchange degree of 55% (zeolite CsNaX). Subsequently, this material was suspended in a 0.2 M aqueous solution of CsOH (CsOH: Aldrich, 19,833-1). The absolute amount of CsOH dissolved equaled the one desired in the final material. The suspension

was stirred overnight to dryness at 353 K. The impregnated material is denoted as CsNaX/ 24CsOH which indicates that zeolite CsNaX was loaded with 24 CsOH per unit cell (u.c.). Finally, the sample was calcined in a stream of nitrogen gas at 773 K for 4 h. The sample was characterized by X-ray diffraction, atomic absorption spectroscopy (AAS), and atomic emission spectroscopy with an inductively coupled plasma (ICP-AES). By ^{29}Si and ^{27}Al MAS NMR spectroscopy, it was ensured that neither ion exchange nor impregnation were accompanied by a dealumination of the zeolite framework. Likewise, by ^{1}H MAS NMR spectroscopy of the dehydrated sample, any formation of acidic OH groups during the above-described preparation steps could be excluded.

Prior to the NMR investigations, the powdered materials were heated in vacuum with a rate of 20 K/h up to the final temperature of 673 K. At this temperature the samples were calcined for 12 h at a pressure below 10^{-2} Pa. The adsorption of methanol (me), C^*H_3OH (Campro Scientific, 83-00005-9, the asterisk denotes a ^{13}C-enrichment of the carbon atom), or a mixture of methanol and toluene (tol), $C_6H_5C^*H_3$ (Campro Scientific, 83-84003-3), was performed on the calcined sample using a vacuum line. The samples applied for in situ ^{13}C MAS NMR investigations under batch conditions were sealed in 3.0 mm glass ampoules.

The NMR investigations were carried out on a Bruker MSL 400 spectrometer with a resonance frequency of 100.5 MHz for ^{13}C NMR spectroscopy. The spectra were recorded after single pulse excitation or, if indicated, with cross polarization (CP) applying contact pulses between 1 and 5 ms. The chemical shifts were referenced to tetramethylsilane (TMS). The sample spinning rate, ν_{rot}, amounted to 8 kHz in the measurements under batch conditions with a 4 mm MAS NMR probe, and to 1.8 kHz for the experiments under flow conditions performed with a 7 mm MAS NMR probe.

Prior to the in situ ^{13}C NMR investigations under batch conditions, the samples were heated

to the reaction temperature (rate 5 K/min, 1 h at the final temperature) in an external furnace, and the NMR spectra were then taken at room temperature. Before the in situ MAS NMR experiments under flow conditions, the calcined zeolite was filled into the MAS NMR rotor reactor under dry nitrogen in a glove box and pressed to a cylindrical catalyst bed (for more details see Refs. [26,27]). After transferring the rotor into the MAS NMR probe, a second dehydration of the catalyst was performed at 673 K for 1 h in flowing nitrogen (30 cm^3/min). During the in situ MAS NMR experiments under continuous-flow conditions, nitrogen loaded with methanol or with a mixture of methanol and toluene was injected into the 7 mm MAS NMR rotor reactor applying the equipment described earlier [26,27]. The in situ MAS NMR flow probe is based on a modified DSI-740 7 mm STD MAS NB NMR probe delivered by Doty Scientific Instruments, Columbia, TX, allowing measurements at temperatures up to 873 K with sample spinning rates up to 3.5 kHz. By ^{207}Pb MAS NMR spectroscopy of Pb(NO$_3$)$_2$ [28], the temperature gradient over the whole sample volume of the modified in situ MAS NMR flow probe was determined. It amounted to 2.5 K at 723 K during injection of nitrogen gas (15 cm^3/min) into the MAS NMR rotor reactor spinning with a rate of 1.8 kHz.

3. Results and discussion

3.1. Conversion of pure methanol and of a toluene / methanol mixture on zeolite CsNaX / 24CsOH under batch conditions

The zeolite samples used for in situ ^{13}C MAS NMR investigations under batch conditions were sealed in glass ampoules, heated in an external furnace and measured at room temperature. Fig. 1 shows ^{13}C MAS NMR spectra recorded in this way after conversion of methanol (left-hand side) and side-chain alkylation of toluene with methanol (right-hand side) on zeolite CsNaX/
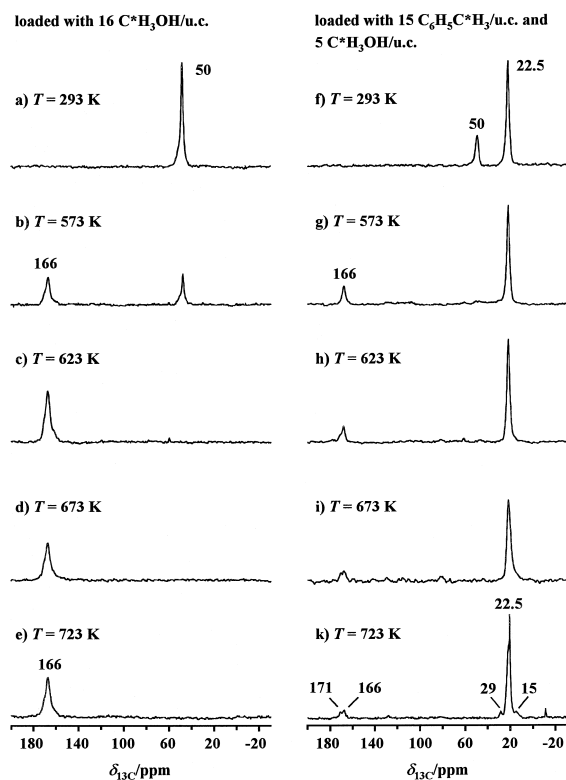
loaded with 16 C*H₃OH/u.c.

loaded with 15 C₆H₅C*H₃/u.c. and 5 C*H₃OH/u.c.

Fig. 1. ^{13}C MAS NMR spectra of zeolite CsNaX/24CsOH recorded after loading 16 C*H$_3$OH/u.c. (left-hand side) or a mixture of 15 C$_6$H$_5$C*H$_3$/u.c. and 5 C*H$_3$OH/u.c. (right-hand side) and heating the samples under batch conditions (fused glass ampoules) in an external furnace at the given temperatures for 1 h.

24CsOH at temperatures between 293 K and 723 K. Considering the conversion of methanol, the spectrum of the non-heated sample (Fig. 1a) consists of a single line at 50 ppm due to methanol which decreases and eventually disappears, as the pretreatment temperature is raised (Fig. 1b,c). This is accompanied by the appearance of a new signal at ca. 166 ppm due to a surface compound. No signals of formaldehyde could by found at 197 ppm [29]. Interestingly, methanol conversion on zeolite CsNaY/16CsOH, studied in our previous work [13], led to the formation of dimethyl ether (60.5 ppm) and CO (184 ppm). On zeolite CsNaX/24CsOH, neither by-products of acid catalyzed side reactions (e.g., dimethyl ether) nor the products of the decomposition of

formaldehyde (CO, CO_2) could be observed. Hence, it is reasonable to assume that all methanol molecules were converted into surface compounds.

A similar behavior of the conversion of methanol was found for zeolite CsNaX/24CsOH loaded with a mixture of toluene and methanol (right-hand side). The two signals in the ^{13}C MAS NMR spectrum of the non-heated sample (Fig. 1f) are caused by the methyl group of toluene (22.5 ppm) and methanol (50 ppm). Again, upon raising the pretreatment temperature, the signal of methanol disappears (Fig. 1g) and the line at 166 ppm indicates the formation of surface compounds. Starting at 673 K, this signal is split into two weak lines with resonances at 166 and 171 ppm. It is important to note that the formation of ethylbenzene starts at 673 K that can be observed by broad feet at the flanks of the signal at 22.5 ppm. In the spectrum recorded after heating at 723 K, these broad feet occur as weak lines at 15 and 29 ppm due to the ethyl group of the reaction product ethylbenzene.

Considering the spectra shown in Fig. 1g,h, all methanol molecules were converted into surface compounds before ethylbenzene is formed. This suggests that at least one of the surface compounds causing the signals at 166 and 171 ppm acts as alkylating agent in the side-chain alkylation of toluene.

3.2. Conversion of pure methanol and of a toluene/methanol feed on zeolite CsNaX/24CsOH under flow conditions

Application of in situ MAS NMR spectroscopy under flow conditions allows to follow the fate of surface compounds both in a steady state and after changing the reaction conditions. The objective of the ^{13}C MAS experiments leading to the spectra in Figs. 2 and 3 was to answer the question whether the surface compounds responsible for the ^{13}C MAS NMR signals at 166 and 171 ppm are dead-ends of the formaldehyde decomposition or reactive species. Sig-
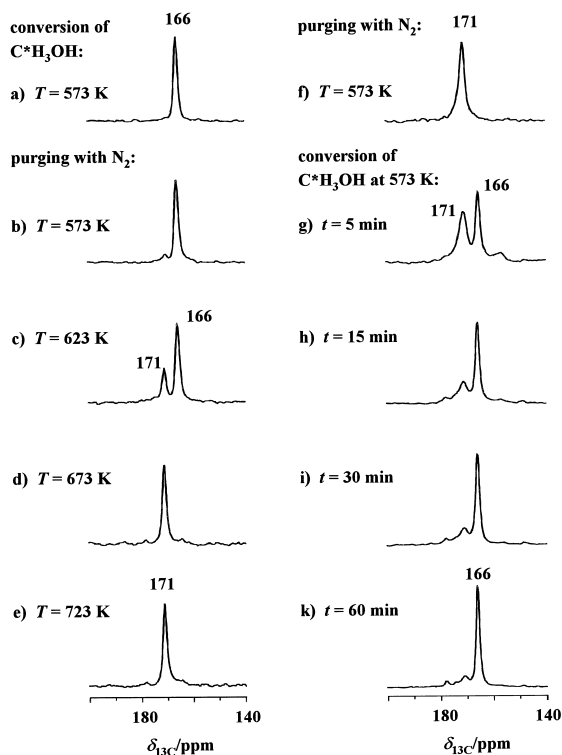
Fig. 2. ^{13}C MAS NMR spectra recorded during (a,g–k) and after (b–e,f) conversion of methanol on zeolite CsNaX/24CsOH under flow conditions ($W/F_{me} = 60$ gh/mol). The spectra on the left-hand side were obtained after giving a methanol pulse on the catalyst and purging with nitrogen (30 ml/min) at temperatures between 573 K and 723 K. On the right-hand side the formation of surface compounds as a function of time after starting the methanol flow at $t = 0$ min and 573 K is shown.

nals in this chemical shift range can be due to formate species (see Scheme 1) [11–13] and/or carbonates [30]. The ^{13}C MAS NMR spectrum recorded during the conversion of methanol on zeolite CsNaX/24CsOH with a modified residence time of $W/F_{me} = 60$ gh/mol at a reaction temperature of 573 K consists of a strong signal at 166 ppm (Fig. 2a) similar to the one found under batch conditions (Fig. 1b). To check whether this compound is chemically stable on the catalyst surface, the reactant flow was stopped after conversion of methanol at 573 K and the reaction system was purged with dry nitrogen at temperatures between 573 K and 723 K. As shown in Fig. 2b–e, this treatment leads to a strong decrease of the compound at

166 ppm and the formation of the compound at 171 ppm. Interestingly, this transformation can be reversed. After purging at 723 K (Fig. 2e) and decreasing the temperature to 573 K (Fig. 2f), the methanol flow was started again. As shown in Fig. 2g, this leads to an involution of the compound at 171 ppm and the reappearance of the signal at 166 ppm. After injecting methanol at 573 K for 60 min (Fig. 2k), nearly all compounds causing the signal at 171 ppm were removed.

The experimentally observed chemical transformation of the surface compounds at 166 and 171 ppm can be explained in two ways. In an earlier ^{13}C NMR investigation of formate species on zeolite Y, Duncan and Vaughan [30] found signals at 165 and 172 ppm which they attributed to unidentate and bidentate formate species, respectively (see Scheme 1). This assignment was based on a comparison of chemical shift anisotropies of the above-mentioned signals and the C–O bond lengths of crystallographically distinct formate species. According to these data [30], the reaction of formaldehyde with the basic zeolite framework could lead to formate species existing as unidentate formate (166 ppm). After raising the temperature, these species would be transformed into a bidentate formate (171 ppm). Another possibility is the dehydrogenation of unidentate formates and the formation of carbonates (171 ppm) by raising the reaction temperature (Fig. 2b–e). After starting the methanol flow for a second time (Fig. 2g), the formation of formaldehyde leads to a production of hydrogen that hydrogenates the carbonates and decreases the signal at 171 ppm.
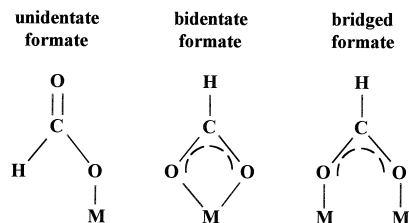
Scheme 1.

In addition, the conversion of methanol to formaldehyde would result in the formation of new formate species at 166 ppm. It is recognized in both mechanisms that the signal at 166 ppm is due to formates. The intention of the subsequent experiments was to investigate whether or not the formate species at 166 ppm is a reactive compound and to find a definite assigment of the signal at 171 ppm.

The ^{13}C MAS NMR experiments leading to the spectra on the left-hand side of Fig. 3 were performed to study the formate species at 166 ppm under steady state conditions during the conversion of pure methanol. In contrast to the spectra in Fig. 2b–e, the formate species continue to be present up to 723 K (Fig. 3a–d). At
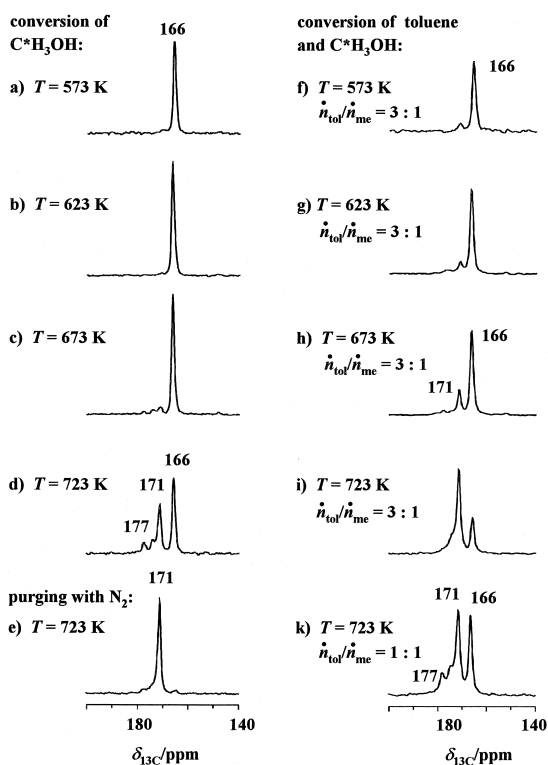
this temperature, additional compounds are formed causing signals at 171 and 177 ppm. Purging the reaction system after methanol conversion at 723 K results in a ^{13}C MAS NMR spectrum with a single line at 171 ppm (Fig. 3e) and virtually identical to that in Fig. 2e.

The ^{13}C MAS NMR spectra on the right-hand side of Fig. 3 were recorded during conversion of a toluene/methanol mixture. In these experiments, the same reaction temperatures as for the conversion of pure methanol (left-hand side) and molar toluene/methanol feed ratios of $\dot{n}_{tol}/\dot{n}_{me} = 3:1$ and $\dot{n}_{tol}/\dot{n}_{me} = 1:1$ were chosen. Considering the spectra in Fig. 3d and Fig. 3h recorded at 723 K, the main difference consists in the intensity ratio of the signals at 166 and 171 ppm. As found by the experiments performed under batch conditions (Fig. 1k), side-chain alkylation of toluene occurs at this temperature. Hence, the low intensity of the formate species at 166 ppm in the spectrum recorded at 723 K under flow conditions (Fig. 3i) indicates that these species contribute to the side-chain alkylation of toluene. This assumption is supported by the spectrum shown in Fig. 3k: if the toluene content in the feed is lowered ($\dot{n}_{tol}/\dot{n}_{me} = 1:1$), then the signal of formate species at 166 ppm increases.

3.3. Assignment of the ^{13}C MAS NMR signals at 166 and 171 ppm

The assignment of the surface compounds causing the ^{13}C MAS NMR signals at 166 and 171 ppm is supported by previous investigations of formate and carbonate species on zeolites and amorphous catalysts like Cu/Al_2O_3, Zn/Al_2O_3, and $Cu/ZnO/Al_2O_3$ [30,31]. In these studies, the ^{13}C chemical shift tensors of the surface compounds were determined by analysis of the statically recorded spectra or by sideband analysis of the MAS NMR spectra according to the method introduced by Herzfeld and Berger [32]. For carbonate species, isotropic chemical shifts (δ_{iso}) of 162 to 170 ppm, chemical shift

Fig. 3. ^{13}C MAS NMR spectra recorded during conversion of pure methanol ($W/F_{me} = 60$ gh/mol, left-hand side) and of a mixture of toluene and methanol (right-hand side) on zeolite CsNaX/24CsOH at temperatures between 573 K and 723 K. For the conversion of the reactant mixture, a modified residence time of $W/F_{me} = 60$ gh/mol and molar toluene/methanol feed ratios of $\dot{n}_{tol}/\dot{n}_{me} = 3:1$ (f–i) and $\dot{n}_{tol}/\dot{n}_{me} = 1:1$ (k) were used.
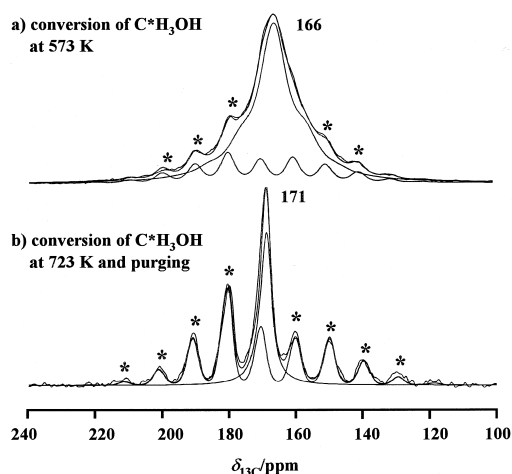
Fig. 4. ^{13}C MAS NMR spectra recorded at 293 K after conversion of methanol on zeolite CsNaX/24CsOH at 573 K under flow conditions with a modified residence time of $W/F_{me} = 60$ gh/mol (a) and after conversion of methanol under flow conditions at 723 K and subsequent purging with 30 ml/min nitrogen (b). The spectra were obtained with a sample spinning rate of $\nu_{rot} = 1$ kHz. Asterisks denote spinning sidebands.

anisotropies ($\Delta\sigma = \sigma_{33} - \sigma_{iso}$) of -48 to -69 ppm, and asymmetry parameters (η) of 0.6 to 0.9 were obtained [31]. For unidentate formate species, $\delta_{iso} = 165$ ppm, $\Delta\sigma = -88$ ppm, and $\eta = 0.2$ were determined while for bidentate formate species, $\delta_{iso} = 172$ ppm, $\Delta\sigma = -63$ ppm, and $\eta = 0.65$ [30].

To evaluate the chemical shift tensor of the surface compounds observed in the present study, the ^{13}C MAS NMR spectra of zeolite CsNaX/24CsOH were recorded at 293 K with a sample spinning rate of 1 kHz after conversion of methanol at 573 K (compare Fig. 3a) and after conversion of methanol at 723 K and purging with nitrogen gas (compare Fig. 3e). The spectra of these samples and their simulation using the Bruker software WINFIT are shown in Fig. 4a,b, respectively. Both spectra consist of a superposition of two signals. One of these signals is MAS sideband pattern with an isotropic chemical shift of 171 ppm, a chemical shift anisotropy of $\Delta\sigma = -40 \pm 2$ ppm, and an asymmetry parameter of $\eta = 0.8 \pm 0.1$. In addition to this pattern, the spectrum in Fig. 4a consists of a signal at the isotropic chemical

shift of 166 ppm, with a weak chemical shift anisotropy (ca. 15 ppm) and an intensity contribution of 80% which was previously assigned to formate species [30] (vide supra). The significant broadening of this signal indicates a mobility of the formate species according to a correlation time, τ_c, in the order of the sample spinning period, τ_{rot} ($\tau_c \approx \tau_{rot} = 1/\nu_{rot}$). In the spectrum shown in Fig. 4b, in addition to the MAS sideband pattern, a weak isotropic line occurs at ca. 171 ppm with an intensity contribution of 28%. This signal indicates the presence of a further surface compound with a high mobility (no MAS sidebands).

Considering these results, the formate species at 166 ppm are weakly bound on the zeolite surface under the condition of flowing nitrogen. The signal at 171 ppm can be caused by two different compounds, a weakly bound compound occurring as an isotropic line and a strongly bound one leading to an MAS sideband pattern. From a comparison between ^{13}C MAS NMR and ^{13}C CP/MAS NMR spectrum of zeolite CsNaX/24CsOH after methanol conversion at 573 K (Fig. 5a,b, respectively), one is led to conclude that the compound causing the
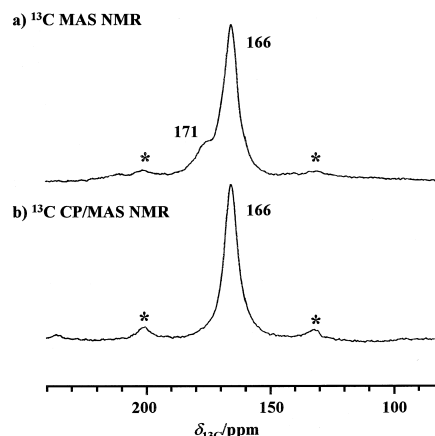

Fig. 5. ^{13}C MAS NMR (a) and ^{13}C CP/MAS NMR spectra (b) recorded at 293 K after conversion of methanol on zeolite CsNaX/24CsOH under flow conditions with a modified residence time of $W/F_{me} = 60$ gh/mol at 573 K. The spectra were obtained with a contact pulse of 1 ms and a sample spinning rate of $\nu_{rot} = 3.5$ kHz. Asterisks denote spinning sidebands.

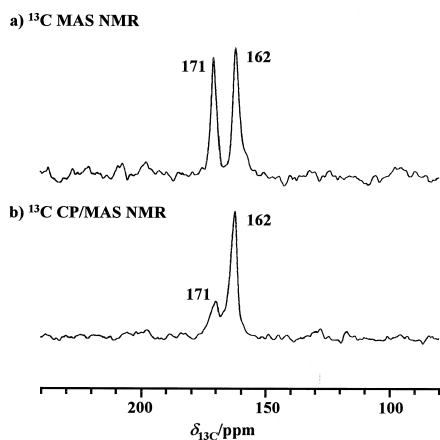Fig. 6. ^{13}C MAS NMR (a) and ^{13}C CP/MAS NMR spectra (b) of zeolite CsNaX/24CsOH impregnated with cesium carbonate and dehydrated at 393 K. The spectra were recorded with a contact pulse of 5 ms and a sample spinning rate of $\nu_{rot} = 3.5$ kHz.

pattern at 171 ppm is not accompanied with hydrogen atoms as it is expected for carbonate species (e.g., Cs_2CO_3 [33]). In contrast, the signal at 166 ppm was excited by CP that agrees with the behavior of formate species where the carbon atom is bound to at least one hydrogen atom (see Scheme 1).

The above-mentioned assignment of the signal at 171 ppm is supported by a ^{13}C MAS NMR experiment on zeolite CsNaX/24CsOH impregnated with cesium carbonate. After impregnation with a 1 M solution of Cs_2CO_3, the zeolite material was dehydrated at 393 K for 12 h. The ^{13}C MAS NMR spectrum of this material (Fig. 6a) consists of two signals at 162 and 171 ppm. As expected for surface carbonate species, application of CP leads to a strong decrease of the signal at 171 ppm (Fig. 6b). The signal at 162 ppm occurring in the spectra recorded with the MAS and CP/MAS technique is caused by a hydrogen carbonate (e.g., $CsHCO_3$ [33]). The weak isotropic signal at 171 ppm, which is superimposed by the MAS sideband pattern in Fig. 4b, can be explained by a small amount of a second type of formate species (see Scheme 1). According to Duncan and Vaughan [30], the isotropic chemical shift of 171 ppm is a hint to formate species of the bidentate type.

4. Conclusions

Applying in situ MAS NMR spectroscopy under batch and flow conditions, the conversion of methanol and of toluene/methanol mixture on a basic zeolite CsNaX/24CsOH and the formation of surface compounds were investigated. Depending on the reaction conditions during the flow experiments, the low-field range of the ^{13}C MAS NMR spectrum is dominated by a signal at 166 or 171 ppm. The signal at 166 ppm occurs in the steady state conversion of methanol, while the signal at 171 ppm is formed after subsequent purging with nitrogen gas. CP/MAS experiments unequivocally indicated that the main content of the signal at 171 ppm is due to a surface compound that is free from hydrogen atoms. This is expected for carbonate species. Based on chemical shift data given in the literature and the MAS and CP/MAS experiments performed in the present work, the signal at 166 ppm was assigned to formate species.

Investigating the conversion of a toluene/methanol mixture on zeolite CsNaX/24CsOH by in situ ^{13}C MAS NMR spectroscopy under batch conditions, the formation of ethylbenzene was observed after a complete conversion of methanol into the formate species at 166 ppm. In the in situ ^{13}C MAS NMR spectra recorded under flow conditions, the signal of formate species occurring at 166 ppm is small for toluene/methanol feeds with a high toluene content ($\dot{n}_{tol}/\dot{n}_{me} = 3:1$) and becomes large for toluene/methanol feeds with a low toluene content ($\dot{n}_{tol}/\dot{n}_{me} = 1:1$). Both observations indicate that the formate species formed by conversion of methanol on basic zeolite CsNaX/24CsOH are reactive and contribute as alkylating agent to the side-chain alkylation of toluene.

Acknowledgements

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