

Mechanistic studies of the side-chain alkylation of toluene with methanol on basic zeolites Y by multi-nuclear NMR spectroscopy¹

Michael Hunger^{*}, Udo Schenk, Jens Weitkamp

Institute of Chemical Technology I, University of Stuttgart, D-70550 Stuttgart, Germany

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Abstract

The side-chain alkylation of toluene with methanol on cesium-exchanged zeolites Y, with and without subsequent impregnation with cesium hydroxide, was investigated by ¹³³Cs and ¹³C MAS NMR spectroscopy. In the first step, the catalysts under study were characterized by different spectroscopic techniques showing a high dispersion of the oxidic guest compound on the zeolitic host and an influence of the guest compound on the intrinsic base strength of the host framework. Adsorption of toluene led to ¹³³Cs MAS NMR signals pointing to a strong interaction of the toluene molecules with the cesium cations. ¹³C MAS NMR experiments on the zeolites Y loaded with pure methanol and toluene/methanol mixtures revealed a rapid decomposition of formaldehyde formed by dehydrogenation of methanol. Interestingly, on the impregnated zeolite Y, formaldehyde decomposition was inhibited by toluene. Parallel to the conversion of methanol to formaldehyde, surface-bound formate species were formed. Since these species were stable at high reaction temperatures, as well, they may be responsible for catalyst deactivation. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Side-chain alkylation of toluene; Basic zeolites; Cesium cations; Solid-state NMR spectroscopy

1. Introduction

Up to now, scarce attention has been given to the application of basic zeolites in heterogeneous catalysis. On the contrary, there is a high potential of such materials for a number of industrially important reactions, such as the dehydrogenation of alcohols, the isomerization of

olefins, the side-chain alkylation of toluene or the synthesis of 4-methylthiazol [1]. The chemical properties of basic zeolites are determined by the alkali metal cations which act as weak Lewis acid sites, and by the basic framework oxygen atoms. Exchanging the sodium cations in as-synthesized zeolites by rubidium or cesium cations leads to a decrease in the mean electronegativity of the zeolite framework, whereby the base strength of the oxygen atoms increases [2]. Strong base sites can be created by incorporating alkali metal compounds into

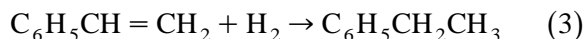
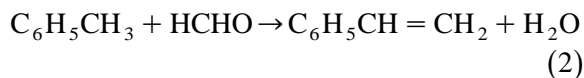
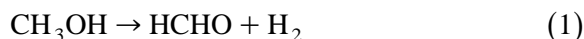
^{*} Corresponding author.

¹ Dedicated to Professor Herman van Bekkum on the occasion of his 65th birthday.

the zeolite pores [3,4] (Fig. 1). Inside the zeolite host, such guests occur with a high dispersion. Kim et al. [5] observes a high 1-butene isomerization rate on zeolites X and Y impregnated with cesium acetate. While at the same reaction conditions, the non-impregnated samples are inactive.

Compared to acid-catalyzed reactions, the mechanisms on basic zeolites are less understood. Using basic catalysts, the alkylation of toluene with methanol selectively leads to an alkylation of the side-chain. Therefore, this reaction could open an alternative route for the synthesis of styrene and ethylbenzene which are currently synthesized via ethylation of benzene with various acid catalysts, including aluminum chloride, alkaline-earth metal phosphates or zeolite HZSM-5 [6].

The side-chain alkylation of toluene with methanol on basic catalysts requires the complete absence of Bronsted acid sites, since these would catalyze ring alkylation at a much higher rate [1]. For the base-catalyzed reaction, Itoh et al. [7] discuss a mechanism consisting of three steps:



In this mechanism, the role of the catalyst is twofold. First, it promotes the dehydrogenation of methanol to formaldehyde (step (1)). Subse-

quently, in step (2), styrene is formed from toluene and formaldehyde. This reaction may be enhanced through polarization of the methyl group of toluene by the catalyst which leads to a carbanion structure [1]. Finally, in step (3), styrene is hydrogenated to ethylbenzene with H_2 generated in step (1).

Quantum-chemical calculations indicate that specific configurations of acid and base sites with steric restrictions are necessary for the side-chain alkylation of toluene [7]. While an acid site (e.g., an alkali metal cation as a Lewis acid site) interacts with the benzene ring of toluene, the methyl group interacts with a base site (e.g., framework oxygen). The presence of such steric conditions in alkali-metal-exchanged zeolites X and Y was one argument for the high activity of these materials in the side-chain alkylation of toluene [7].

During the past decade, in situ MAS NMR spectroscopy has been developed as a useful tool which allows the investigation of mechanisms of heterogeneously catalyzed reactions (for a review, see Ref. [8]). Applying this technique, Philippou and Anderson [9] studied the side-chain alkylation of toluene on zeolites NaX, KX and CsX. Since all the zeolite catalysts studied by these authors contained hydroxyl groups (e.g., 24 equiv.-% for zeolite CsX), the ^{13}C MAS NMR spectra consisted of signals stemming from products of both base and acid-catalyzed reactions. This made their interpretation of the results difficult and somewhat ambiguous.

In the present study, multinuclear NMR spectroscopy is employed to investigate the side-chain alkylation of toluene on Y-type zeolites prepared by exchange with cesium cations, with or without subsequent impregnation with cesium hydroxide followed by calcination. The ^{13}C MAS NMR spectra of both the pure reactant molecules and the reaction mixtures are recorded. The application of ^{133}Cs MAS NMR spectroscopy furnish information on the behavior of the oxidic guest components and reactant/cation interactions. In the first part, the

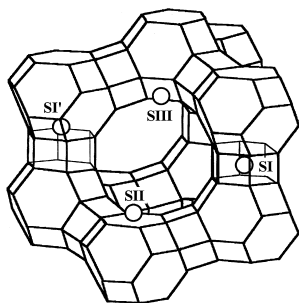


Fig. 1. Structure of a zeolite Y with the cation positions SI, SI', SII and SIII.

host–guest interactions in the impregnated zeolites will be addressed. The techniques applied on this study have recently been described for the first time [10].

2. Experimental

The parent zeolite NaY (Union Carbide, Tarrytown, NY, USA, $n_{\text{Si}}/n_{\text{Al}} = 2.6$) was ion-exchanged fivefold in a 0.4 M aqueous solution of CsCl (CsCl: Aldrich, 19,831-5) at 353 K, which led to a 70% degree of sodium exchange (zeolite CsNaY-70). Subsequently, part of this material was suspended in a 0.2 M solution of CsOH (CsOH: Aldrich, 19,833-1). The absolute amount of CsOH dissolved corresponded to the one desired in the final material. The suspension was stirred to dryness overnight at 353 K. For impregnated materials, codes such as CsNaY-70/16CsOH will be used to indicate that a zeolite was loaded with, e.g., 16 CsOH per unit cell (u.c.). Finally, the samples were calcined in nitrogen gas for 12 h at 673 K. The chemical compositions of the samples were analyzed by atomic absorption spectroscopy (AAS) and atomic emission spectroscopy with an inductively coupled plasma (ICP-AES).

Prior to the NMR investigations, 50 mg of the powder materials were heated in a 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 probe molecules ($\text{C}^* \text{H}_3\text{I}$, Aldrich, 27,718-5; the asterisk indicates a ^{13}C -enrichment of carbon atoms) and reactants (CH_3OH : Fluka, 655541; $\text{C}^* \text{H}_3\text{OH}$: Campro Scientific, 83-00005-9; $\text{C}_6\text{H}_5\text{CH}_3$: Janssen, 26,837,65; $\text{C}_6\text{H}_5\text{C}^* \text{H}_3$: Campro Scientific, 83-84003-3) on the calcined samples was carried out in a vacuum line. All samples applied for ^{13}C and ^{133}Cs MAS NMR spectroscopy were sealed in 3.0 mm glass ampules.

The NMR investigations were carried out on a Bruker MSL 400 spectrometer with resonance frequencies of 100.5 MHz for ^{13}C , 104.2 MHz

for ^{27}Al , 79.5 MHz for ^{29}Si , and 52.5 MHz for ^{133}Cs NMR spectroscopy. All spectra were recorded after single pulse excitation, excluding the investigations of methyl iodide on zeolites which were carried out with cross polarization (CP). The chemical shifts were referenced to TMS for ^{13}C and ^{29}Si , to 0.1 M aqueous solution of $\text{Al}(\text{NO}_3)_3$ for ^{27}Al and to 1.0 M aqueous solution of CsCl for ^{133}Cs MAS NMR spectroscopy. The sample spinning rates were adjusted to ca. 4 kHz for ^{29}Si MAS NMR spectroscopy and to ca. 10 kHz for all other resonances. ^{13}C NMR investigations were carried out using zeolite samples fused in glass ampules. These samples were heated at the reaction temperature (rate 5 K/min, 1 h at the final temperature) in an external furnace, and the NMR spectra were taken at room temperature.

3. Results and discussion

3.1. Characterization of the zeolite samples

The X-ray patterns of zeolites Y recorded after cesium exchange, impregnation with CsOH and calcination at 673 K show strong changes in the positions and intensities of the reflections (see Fig. 2). These changes are caused by the different scattering coefficients of sodium and cesium cations and the additional reflections of the guest compound which render characterization of the zeolite framework difficult. Therefore, application of ^{27}Al and ^{29}S MAS NMR spectroscopy is a suitable way to prove the quality and integrity of the framework of the cation-exchanged and impregnated zeolites. The spectra of the parent zeolite NaY, of zeolite CsNaY-70 and of CsNaY-70/16CsOH (Fig. 3), recorded after calcination at 673 K and rehydration, neither show a variation in the intensities of the ^{29}Si MAS NMR signals due to Si(nAl) atoms (left), nor can ^{27}Al MAS NMR signals of extra-framework aluminum at 0 ppm be observed (right). It can be concluded that the zeolitic host framework remained intact, both

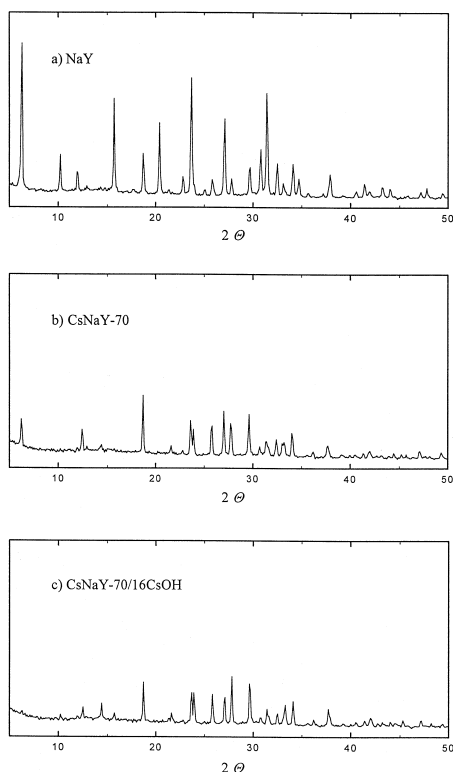


Fig. 2. XRD patterns of zeolites NaY (a), CsNaY-70 (b) and CsNaY-70/16CsOH (c), recorded after calcination at 673 K and rehydration.

during the cesium exchange and the impregnation with CsOH and the subsequent calcination.

In our previous work [10], the coverage of the zeolite framework with hydroxyl groups was investigated by ^1H MAS NMR spectroscopy. Interestingly, cesium exchange of the parent zeolite NaY, impregnation with CsOH and calcination did not bring about a formation of OH groups. On the contrary, a strong decrease of silanol groups, from 1.4 SiOH/u.c. for the calcined zeolite NaY to 0.4 SiOH/u.c. for the calcined zeolite CsNaY-70/16CsOH, was found. This is best interpreted in terms of a chemical bonding of the oxidic guest components at initial framework defect sites.

Various approaches were made to study the influence of guest components on the zeolite framework [10]. As shown in Fig. 3, neither ^{29}Si nor ^{27}Al MAS NMR spectroscopy indicated any

variation in the local structure of the TO_4 tetrahedra ($\text{T} = \text{Si}$ or Al) in the hydrated zeolites NaY, CsNaY-70 and CsNaY-70/16CsOH. However, the quadrupole coupling constant of framework aluminum atoms in the dehydrated zeolites was sensitive enough to reveal a change in the local structure of framework AlO_4 tetrahedra as a result of cesium exchange and impregnation with CsOH. A simulation of the ^{27}Al spin-echo NMR spectra gave quadrupole coupling constants of 5.9 MHz, 4.0 MHz and 3.4 MHz for zeolites NaY, CsNaY-70 and CsNaY-70/16CsOH, respectively [10].

Another method allowing the investigation of host-guest interactions in zeolites was proposed by Bosacek [11,12]. With this method, the mean electronegativity and basicity of the zeolite framework can be characterized. After loading a large number of different zeolites with methyl iodide, Bosacek found a correlation between the isotropic ^{13}C NMR shift of methoxy groups formed upon decomposition of methyl iodide and the mean Sanderson electronegativity S^m [13] of the zeolite framework. A decrease in S^m

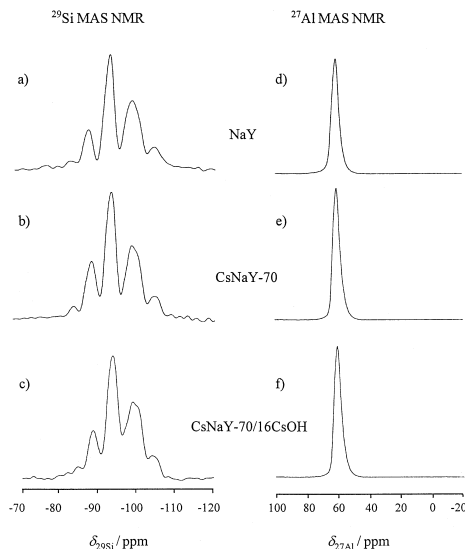


Fig. 3. ^{29}Si (left-hand side) and ^{27}Al MAS NMR spectra (right-hand side) of zeolites NaY (a,d), CsNaY-70 (b,e) and CsNaY-70/16CsOH (c,f), recorded after calcination at 673 K and rehydration.

from 3.04 for zeolite HZSM-5 ($n_{\text{Si}}/n_{\text{Al}} = 21.8$) to 2.26 for zeolite CsNaX-49 ($n_{\text{Si}}/n_{\text{Al}} = 1.2$) was accompanied by a resonance shift for the methoxy groups from $\delta_{13\text{C}} = 59.4$ ppm to $\delta_{13\text{C}} = 54.1$ ppm (slope $\Delta\delta_{13\text{C}}/\Delta S^{\text{m}} \approx 6.8$ ppm) [12]. Fig. 4 shows the ^{13}C CP/MAS NMR spectra of the dehydrated zeolites NaY (a), CsNaY-70 (b), CsNaY-70/4CsOH (c), CsNaY-70/8CsOH (d) and CsNaY-70/16CsOH (e) after adsorption of 16 $\text{C}^*\text{H}_3\text{I}$ molecules per unit cell. The signals at -20 ± 0.5 ppm are due to physisorbed $\text{C}^*\text{H}_3\text{I}$ [12]. The chemical shifts of the methoxy groups in zeolites NaY (56.7 ppm, Fig. 4a) and CsNaY-70 (56.1 ppm, Fig. 4b) correlate well with their

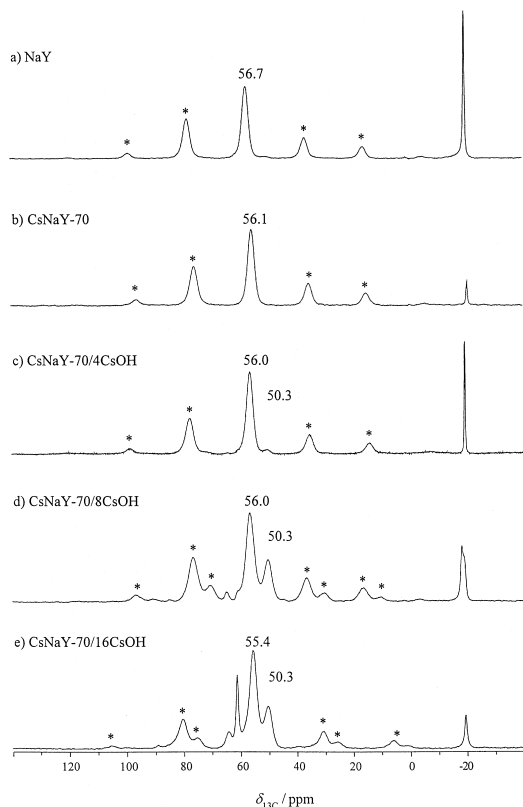


Fig. 4. ^{13}C CP/MAS NMR spectra of calcined (673 K) zeolites NaY (a), CsNaY-70 (b), CsNaY-70/4CsOH (c), CsNaY-70/8CsOH (d) and CsNaY-70/16CsOH (e), loaded with 16 $\text{CH}_3\text{I}/\text{u.c.}$ and recorded with a sample spinning rate of 2.0 kHz. The intensities of the spinning sidebands were used to determine the anisotropy of chemical shifts of the signals observed (see text).

mean Sanderson electronegativities (2.60 and 2.46, respectively). The spectra of the impregnated zeolites (Fig. 4c to e) consist of signals at 55.4 ppm to 56.0 ppm, at 50.3 ppm and of a narrow signal at 61.0 ppm. This latter signal, with an intensity contribution of up to 10%, is caused by dimethyl ether [12]. Since there is no signal at 56.1 ppm (methoxy groups in zeolite CsNaY-70), the whole framework of zeolite CsNaY-70/16CsOH must have been affected uniformly by the CsOH impregnation. The ^{13}C resonance shift, from 56.1 ppm for methoxy groups in zeolite CsNaY-70 to 55.4 ppm for methoxy groups in zeolite CsNaY-70/16CsOH, corresponds to an increased framework basicity of the latter material.

The signals marked by asterisks are due to spinning sidebands and indicate that the species causing the sideband pattern are rigidly bound to the zeolite framework, as expected for methoxy groups. The quantitative analysis of the MAS sideband intensities, according to the method introduced by Herzfeld and Berger [14], allows a determination of the anisotropy $\Delta\sigma$ of the chemical shift, a characteristic parameter for rigid species. The simulation of the MAS sideband patterns (Bruker software WINFIT), which are due to the ^{13}C MAS NMR central lines at 54 ppm to 56 ppm, leads to a chemical shift anisotropy of $\Delta\sigma = -41.4$ ppm. This value is in good agreement with the chemical shift anisotropy of methoxy groups in zeolite NaX found by Bosacek [12] ($\Delta\sigma = -42.7$ ppm). Interestingly, the simulation of the MAS sideband patterns of the signal at 50.3 ppm, observed with increasing intensities in the ^{13}C MAS NMR spectra of zeolites Y after impregnation with CsOH and calcination (Fig. 4c to e), yields a chemical shift anisotropy of ca. -42 ppm as well. Obviously, methoxy groups are responsible for these signals. Furthermore, they are bound at the oxidic guest compound introduced by impregnation. The high intensity of the 50.3 ppm signal observed for zeolite CsNaY-70/16CsOH ($32 \pm 5\%$ of the total intensity) points to a large surface and, hence, to a high

dispersion of the oxidic guest compound in this sample.

We can state the ^{13}C MAS NMR shift of methoxy groups bound to the zeolite framework, and not only the behavior of the quadrupole coupling constants of framework aluminum atoms in the dehydrated zeolites, indicates that the cesium exchange and the impregnation with CsOH influence the host framework and increase its own base strength. However, the strongest base sites are generated by the oxidic guest compound which is highly dispersed in the host framework.

3.2. ^{133}Cs MAS NMR investigations of cesium cations and the guest compound in basic zeolites Y

In a number of studies, ^{133}Cs MAS NMR spectroscopy was successfully applied to study

the distribution and migration of cesium cations in zeolites [5,15–20]. Fig. 5 and Fig. 6 show the ^{133}Cs MAS NMR spectra of calcined zeolites CsNaY-70 and CsNaY-70/16CsOH before (a) and after (b to e) loading with adsorbate molecules. The application of a sample spinning rate of more than 10 kHz was an important prerequisite to achieve a separation of MAS central lines and spinning sidebands which partially overlapped in the spectra published in previous papers. The ^{133}Cs MAS NMR spectrum of the calcined and unloaded zeolite CsNaY-70 (Fig. 5a) consists of signals at -74 ppm, -91 ppm, -109 ppm and -156 ppm. Koller et al. [18] compared the intensities of the ^{133}Cs MAS NMR signals of a zeolite Y (with a cesium exchange degree of 72%) with the cation populations derived by X-ray diffraction and Rietveld refinement, then, assigned the above-mentioned lines to cesium cations on SII, SI',

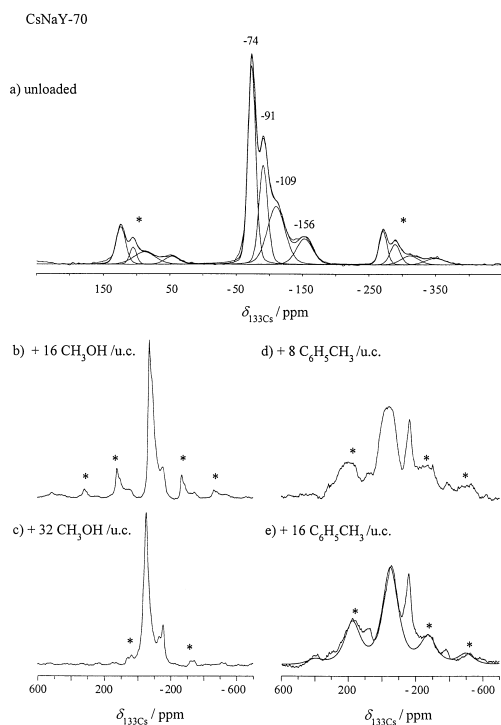


Fig. 5. ^{133}Cs MAS NMR spectra of calcined zeolite CsNaY-70, recorded before (a) and after the loading of 16 (b) and 32 (c) CH_3OH molecules per unit cell and of 8 (d) and 16 (e) molecules $\text{C}_6\text{H}_5\text{CH}_3$ per unit cell. The asterisks denote spinning sidebands.

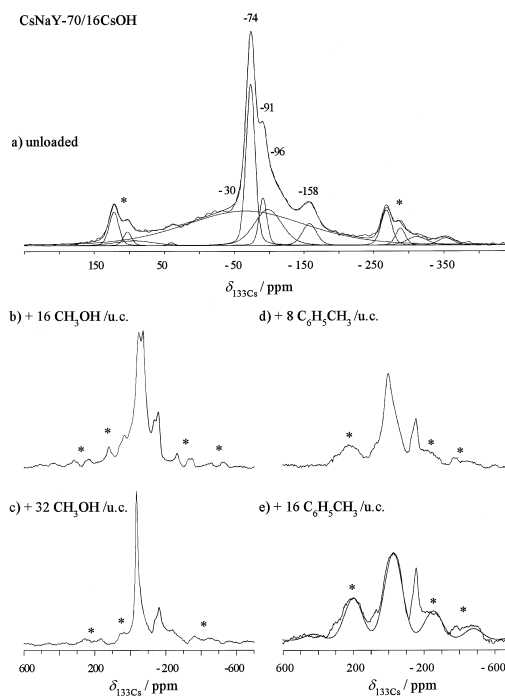


Fig. 6. ^{133}Cs MAS NMR spectra of calcined zeolite CsNaY-70/16CsOH, recorded before (a) and after the loading of 16 (b) and 32 (c) CH_3OH molecules per unit cell and of 8 (d) and 16 (e) $\text{C}_6\text{H}_5\text{CH}_3$ molecules per unit cell. The asterisks denote spinning sidebands.

SIII and SI positions, respectively. In a more recent work, Malek et al. [19] studied the accessibility of cesium cations in cesium-exchanged and calcined zeolites Y by the adsorption of tungsten hexacarbonyl molecules, $W(CO)_6$. The authors proposed an assignment of the ^{133}Cs MAS NMR lines, in order of increasing field strength, to cesium cations at SII, SIII, SI' and SI. Both papers agree in the assignment of the strong signal at -74 ppm to cesium cations located at position SII in the supercages of zeolite Y. With the number of cesium cations in zeolite CsNaY-70 determined by AAS and the relative ^{133}Cs MAS NMR intensity of the signal at -74 ppm (Fig. 5a), obtained by a decomposition of the spectrum, a population of cesium cations at position SII of $18 Cs^+/u.c.$ was calculated. Considering the interaction of cesium cations in zeolites Y with molecules like methanol and toluene, these cesium cations at SII should be the most favored interaction partners.

A comparison between the ^{133}Cs MAS NMR spectra of zeolites CsNaY-70 and CsNaY-70/16CsOH in Fig. 5a and Fig. 6a shows that the impregnation with CsOH and subsequent calcination at 673 K produce a guest compound, causing a ^{133}Cs MAS NMR signal at a resonance position of ca. -30 ppm with a linewidth of $\Delta\nu_{1/2} = 10 \pm 1$ kHz. Its intensity contribution of $30 \pm 5\%$ agrees well with the amount of cesium atoms introduced by impregnation. Investigating bulk Cs_2O mixed with amorphous anhydrous silica, Kim et al. [5] found a broad sideband pattern with a ^{133}Cs MAS NMR central line at 225 ppm. The impregnation of amorphous silica with CsOH, according to the method applied for the preparation of zeolite CsNaY-70/16CsOH and subsequent calcination at 673 K, leads to a broad sideband pattern with a ^{133}Cs MAS NMR central line at 236 ppm (not shown). Hence, bulk Cs_2O , as well as dehydrated CsOH on an inert support, yield a ^{133}Cs MAS NMR signal located by about 260 ppm downfield of the signal of the oxidic guest compound of zeolite CsNaY-70/16CsOH (vide

supra). This significant difference in the chemical shift of the bulk phase compounds (Cs_2O , dehydrated CsOH) and the oxidic guest compound in zeolite CsNaY-70/16CsOH indicates that the latter species do not exist in the form of large clusters and hint to a high dispersion of the oxidic guest compound at the zeolitic host.

3.3. ^{133}Cs MAS NMR investigations of the chemical interaction of adsorbate molecules with cesium cations and the guest compound in basic zeolites Y

Initial ^{133}Cs MAS NMR studies concerning the interaction of adsorbate molecules with cesium cations in dehydrated zeolites were carried out by Murray et al. [17] and Malek et al. [19]. The present investigation aims at clarifying the chemical interaction of the reactant molecules, methanol and toluene, with cesium cations in dehydrated zeolites Y. In Fig. 5 and Fig. 6, the ^{133}Cs MAS NMR spectra of calcined zeolites CsNaY-70 and CsNaY-70/16CsOH, loaded with the reactant molecules, i.e., methanol (b,c) or toluene (d,e), are given. The spectra, recorded after adsorption of 16 and 32 methanol molecules per unit cell (Fig. 5b,c and Fig. 6b,c) show an adsorbate-induced low-field shift of the signals of cesium cations located originally at chemical shifts between -74 ppm and -91 ppm (compare Fig. 5a and Fig. 6a). Loading of 32 methanol molecules per unit cell onto zeolites CsNaY-70 and CsNaY-70/16CsOH leads to narrow low-field signals at -52 ppm and -33 ppm, respectively. The weak lines appearing at -130 ppm and -156 ppm are due to cesium cations which are not affected by the adsorbate molecules. According to the assignment proposed by Malek et al. [19], these signals may be caused by cations located at positions SI' and SI. An additional effect of the methanol adsorption is the absence of ^{133}Cs MAS NMR sideband patterns (Fig. 5a and Fig. 6a) which is characteristic for mobile spins with correlation times smaller than the reciprocal MAS frequency [21]. Hence, the methanol

molecules are not rigidly bound to cesium cations responsible for the low-field signals at -52 ppm and -32 ppm.

By contrast, adsorption of toluene on zeolites CsNaY-70 and CsNaY-70/16CsOH causes low-field ^{13}C MAS NMR signals with very broad sideband patterns indicating the formation of rigidly bound adsorbate complexes (Fig. 5d,e and Fig. 6d,e). After the loading of $16 \text{ C}_6\text{H}_5\text{CH}_3/\text{u.c.}$, the low-field lines appearing in the spectra of zeolites CsNaY-70 and CsNaY-70/16CsOH had resonance positions of ca. -40 ppm and -20 ppm, respectively. Hence, as found after adsorption of methanol, the adsorption of toluene on the non-impregnated and the impregnated zeolites Y leads to low-field signals differing in their resonance positions by about 20 ppm. This behavior may be caused by the different base strengths of the host frameworks. Looking at the signals which were not affected by toluene adsorption, the line of cesium cations located at position SI can be observed at -156 ppm. The weak low-field shoulder of this line agrees with the resonance position of the signal at -130 ppm, found after adsorption of methanol (Fig. 5b,c and Fig. 6b,c), and indicates a second type of inaccessible cesium cations, possibly of cesium cations, at position SI'.

By field dependence studies of the ^{13}C MAS NMR signals of cesium cations in dehydrated zeolites Y, Malek et al. [19] found that the observed spinning sidebands originate from chemical shift anisotropy rather than from satellite transitions effects. Hence, the method proposed by Herzfeld and Berger [14] can be applied to the simulation of the ^{13}C MAS NMR sideband patterns due to the low-field lines at -40 ppm and -20 ppm. A corresponding simulation, which is demonstrated in Fig. 5e and Fig. 6e, yields a chemical shift anisotropy of $\Delta\sigma = -450 \pm 20$ ppm and an asymmetry parameter of $\eta = 0.5 \pm 0.1$. The large chemical shift anisotropy indicates an anisotropic charge distribution in the electron cloud, shielding the nuclei of cesium cations contributing to adsor-

bate complexes. This effect is a hint to a strong interaction of the toluene molecules with the cesium cations possibly via a one-side docking.

3.4. ^{13}C MAS NMR investigations of methanol conversion on zeolites CsNaY-70 and CsNaY-70/16CsOH

As a first step, zeolites CsNaY-70 and CsNaY-70/16CsOH, each loaded with $16 \text{ C}^*\text{H}_3\text{OH}/\text{u.c.}$ and heated to reaction temperatures between 573 K and 723 K, were studied. The ^{13}C MAS NMR spectra recorded before thermal treatment (Fig. 7a and f) consist of a single line at 49.5 ppm due to the ^{13}C -enriched methyl groups of methanol [8,9,22]. The most

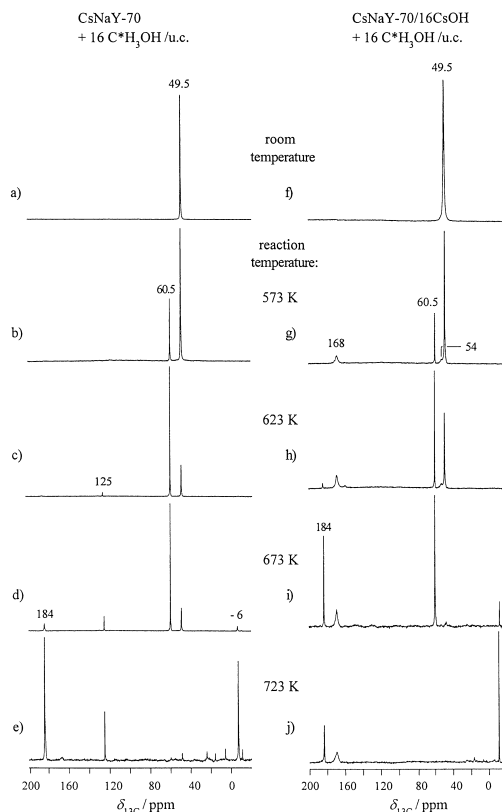
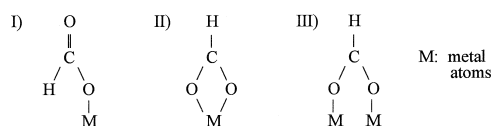


Fig. 7. ^{13}C MAS NMR spectra of calcined zeolites CsNaY-70 (left-hand side) and CsNaY-70/16CsOH (right-hand side), recorded after the loading of $16 \text{ C}^*\text{H}_3\text{OH}$ molecules per unit cell (^{13}C -enriched methyl groups) before (a,f) and after heating of the samples in an external furnace at temperatures between 573 K and 723 K (b to e and g to j).

significant change observed after heating the zeolite samples at 573 K is the formation of dimethyl ether indicated by the signal at 60.5 ppm [8,9,22]. The different catalytic behavior of the two zeolites is revealed by the appearance of two weak lines at 54 ppm and 168 ppm after the methanol conversion on zeolite CsNaY-70/16CsOH (Fig. 7g). None of these two lines is observed on zeolite CsNaY-70 (Fig. 7b). The two weak signals were previously found by Lazo et al. [23] who studied the conversion of methanol on Cu/ZnO/Al₂O₃ catalysts by means of ¹³C MAS NMR spectroscopy. They attributed the weak shoulder at 54 ppm to a small amount of surface-bound methoxy groups characterized by a chemical shift anisotropy $\Delta\sigma$ equal to the above-mentioned value of methoxy groups formed from adsorbed methyl iodide (vide supra). The second signal, i.e., the weak line at 168 ppm, was explained by the formation of formate species [23]. Formate species can exist in three different surface-bound modes, viz. a monodentate (I), bidentate (II) or bridging mode (III):



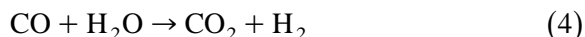
Analyzing the ¹³C NMR chemical shift tensors of surface complexes formed by adsorption of molecules like CO₂, mono- and bicarbonates, ammonium formate, *para*-formaldehyde and formic acid, Lazo et al. [23] found a good agreement between the tensor components of the 168 ppm signal with those of directly adsorbed formic acid. As known for formic acid, the authors proposed a formation of formate species which are bound to the surface in the bidentate mode (II) [23].

Considering the mechanism of the side-chain alkylation of toluene as discussed by Itoh et al. [7] (reactions (1) to (3)), the conversion of methanol to formaldehyde plays a key role. The

presence of gaseous formaldehyde would cause a ¹³C MAS NMR signal at 197 ppm [22].

However, as known from the literature [24], HCHO decomposes into CO and H₂ when interacting with base sites. In addition, the rate of decomposition of formaldehyde increases with the strength of the base sites [24]. Hence, if formaldehyde is formed as an intermediate on zeolites CsNaY-70 and CsNaY-70/16CsOH, it is likely that this can only be proved in an indirect manner, viz. through the occurrence of its decomposition products. Upon heating the zeolites CsNaY-70 and CsNaY-70/16CsOH loaded with C^{*}H₃OH to 673 K (Fig. 7d) and 623 K (Fig. 7h), respectively, one of these decomposition products, viz. carbon monoxide, is indeed detected through the NMR line at 184 ppm [22]. Interestingly, the formation of carbon monoxide and formate does not start at the same temperature. Formate species are first formed, e.g., on zeolite CsNaY-70/16CsOH already at 573 K. This could indicate the existence of different pathways for the formation of formate and formaldehyde.

The appearance of signals at -6 ppm and 125 ppm, after treating the samples at 673 K and 723 K, is a hint for two further reactions. One of these is the water-gas shift reaction causing the signal of CO₂ at 125 ppm [22]:



The second reaction is the methanization of carbon monoxide:



which is responsible for the formation of methane as evidenced by the signal at -6 ppm [6,22]. From the fact that the signal at 125 ppm is completely lacking in the ¹³C MAS NMR spectra of CsNaY-70/16CsOH (Fig. 7, right-hand spectra), one has to conclude that the water-gas shift reaction (4) is strongly inhibited on this zeolite.

A survey of the conversion of methanol on zeolites CsNaY-70 and CsNaY-70/16CsOH, as a function of the reaction temperature, is given

in Fig. 8. The relative ^{13}C MAS NMR intensities of methanol (at 49.5 ppm), formate species (at 168 ppm) and carbon monoxide (at 184 ppm) were derived from a decomposition of the spectra recorded in the absolute intensity mode. Fig. 8 shows that the formation of formate species and of the product of formaldehyde decomposition (CO) starts on zeolite CsNaY-70/16CsOH at temperatures which are about 100 K lower than those necessary for the same reactions on zeolite CsNaY-70. A negative feature of the impregnated zeolite CsNaY-70/16CsOH is the high level of formate formation which could result in a rapid deactivation of the catalyst. A more detailed evaluation of this effect requires further NMR investigations,

desirably under flow conditions. Such experiments are currently being planned in our group.

3.5. ^{13}C MAS NMR investigations of toluene adsorbed on zeolites CsNaY-70 and CsNa-70/16CsOH

Itoh et al. [7] discussed a promotion of reaction (2) by a polarization of the methyl group of toluene leading, in the limiting case, to a carbanion. In previous studies, Paterman et al. [25] and Beno et al. [26] investigated benzyl carbanion complexes with organometallics containing lithium atoms as metallic component. Because of its strong electric field effect and its small ionic radius, lithium is favored as a counterion or electron-withdrawing group (EWG) for the formation of benzyl carbanions [27]. Most of the complexes formed by benzyl carbanions like $\text{C}_6\text{H}_5\text{CH}_2^-$ and organometallics-containing lithium have an η^1 -structure [27]. In this structure-type, the lithium atoms are directly arranged at the carbon atoms of the methyl groups. The effect of the electron withdrawing group of $\text{C}_6\text{H}_5\text{CH}_2^-$ -EWG complexes in tetrahydrofuran and dimethyl sulfoxide on the ^{13}C NMR shift of carbon atoms at the *para*- (C_p) and α -positions (C_α) were investigated by Bradamante and Paganì [28], and Bottin-Strzalko and Seyden-Penne [29]. In general, the EWG causes a low-field shift of the ^{13}C NMR signal of C_α -atoms by a maximum of 40 ppm and a high-field shift of the ^{13}C NMR signal of C_p -atoms by a maximum of 20 ppm [27–29].

In the present work, toluene was adsorbed on dehydrated zeolites CsNaY-70 and CsNaY-70/16CsOH. The use of toluene, with a ^{13}C -enriched methyl group, enabled the study of the chemical shift of the C_α -atoms. The above-mentioned ^{133}Cs MAS NMR investigations suggested a one-side docking of toluene on cesium cations in dehydrated zeolites Y. In contrast to the counterions applied by Bradamante and Paganì [28], and Bottin-Strzalko and Seyden-Penne [29], cesium cations in zeolites Y had only a weak electric field effect due to their large ionic

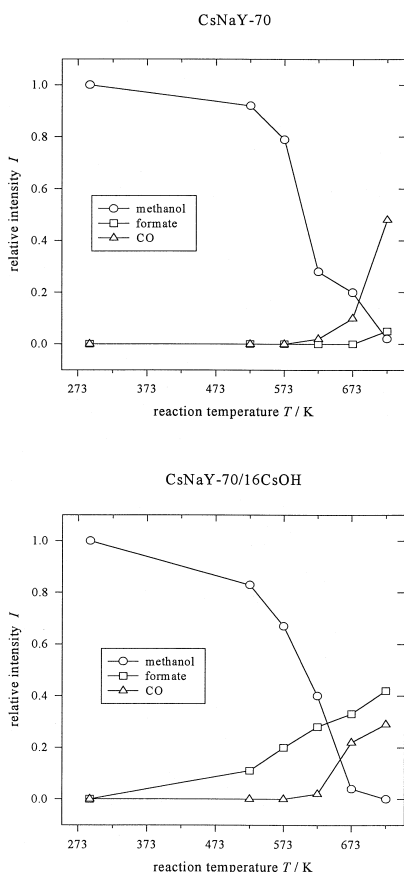


Fig. 8. Relative ^{13}C MAS NMR intensities of the reactant molecules plotted as a function of the reaction temperature, derived by an evaluation of the spectra shown in Fig. 7.

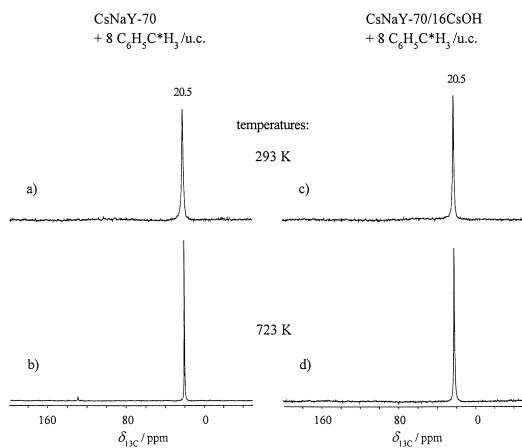


Fig. 9. ^{13}C MAS NMR spectra of calcined zeolites CsNaY-70 (left-hand side) and CsNaY-70/16CsOH (right-hand side), recorded after the loading of 16 $\text{C}_6\text{H}_5\text{C}^*\text{H}_3$ molecules per unit cell (^{13}C -enriched methyl groups) before (a,c) and after heating of the samples in an external furnace at a temperature of 723 K (b,d).

radius. Fig. 9 shows the ^{13}C MAS NMR spectra of $\text{C}_6\text{H}_5\text{C}^*\text{H}_3$ adsorbed on the dehydrated zeolites CsNaY-70 and CsNaY-70/16CsOH, recorded before (a,c) and after (b,d) thermal treatment at 723 K. All spectra consisted of a signal at 20.5 ppm, independent of the zeolite sample and its pretreatment. Weak lines at ca. 130 ppm were due to the non-enriched carbon atoms of the benzyl ring. According to literature [22], the chemical shift of the C_α -atoms of toluene molecules in the gas phase amounts to 21.4 ppm, which agrees well with the value found after adsorption of toluene on zeolites CsNaY-70 and CsNaY-70/16CsOH. Hence, a polarization of the methyl group of toluene adsorbed on cesium-exchanged zeolites is not supported by the results of this work.

3.6. ^{13}C MAS NMR investigations of the conversion of toluene/methanol mixtures on zeolites CsNaY-70 and CsNa-70/16CsOH

In previous studies dealing with side-chain alkylation of toluene on basic zeolites [7,24,30], as toluene/methanol molar feed ratios between 3 and 6 were applied. The zeolite samples used in the present ^{13}C MAS NMR experiments were,

therefore, loaded with a mixture of 15 $\text{C}_6\text{H}_5\text{C}^*\text{H}_3$ and 5 $\text{C}^*\text{H}_3\text{OH}$ molecules per unit cell corresponding to a molar feed ratio of three. The thermal treatment of these samples and the regime of ^{13}C MAS NMR measurements were the same as applied for the study of methanol conversion (vide supra). Fig. 10 shows the ^{13}C MAS NMR spectra of zeolites CsNaY-70 (left) and CsNaY-70/16CsOH (right) loaded with the above-mentioned reaction mixture and recorded before (a,f) and after heating the samples at temperatures between 573 K and 723 K (b to e and g to j). Nearly all signals appearing in these spectra were also observed in the spectra of the

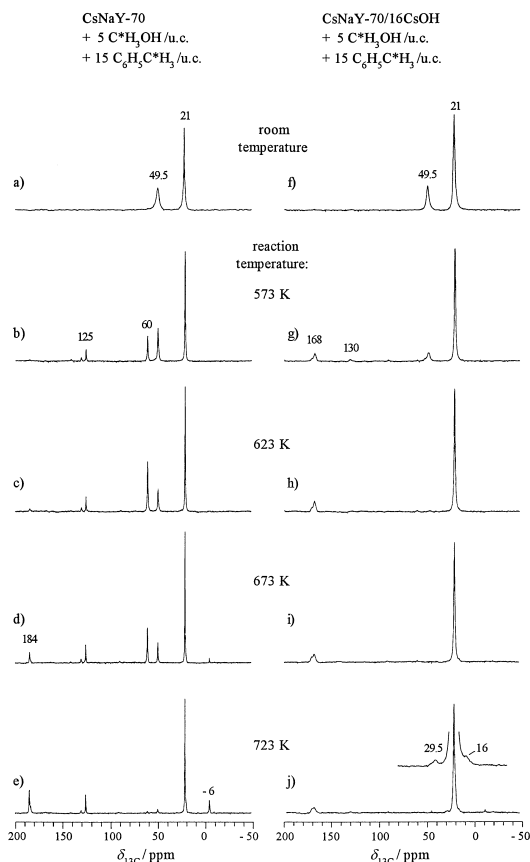


Fig. 10. ^{13}C MAS NMR spectra of calcined zeolites CsNaY-70 (left-hand side) and CsNaY-70/16CsOH (right-hand side), recorded after the loading of 5 $\text{C}^*\text{H}_3\text{OH}$ molecules and 15 $\text{C}_6\text{H}_5\text{C}^*\text{H}_3$ molecules per unit cell (^{13}C -enriched methyl groups) before (a,f) and after heating of the samples in an external furnace at temperatures between 573 K and 723 K (b to e and g to j).

zeolites loaded with pure methanol (the signals of reaction products appear in the order as discussed above). At first, dimethyl ether was formed, causing the signal at 60.5 ppm. Next, the signal of CO₂, formed by the water–gas shift reaction (4), can be observed at 125 ppm. The lines of CO at 184 ppm and of CH₄ at –6 ppm indicated the decomposition of formaldehyde and the methanization of CO (reaction (5)) after treatment at 673 K and 723 K. Although the reactant toluene was present, methanol reacted on zeolite CsNaY-70 in the same way as if toluene were absent.

Another situation is encountered on the impregnated zeolite CsNaY-70/16CsOH, as revealed by the spectra shown in Fig. 10f to j. Interestingly, neither the signal of dimethyl ether at 60.5 ppm, nor the one of carbon monoxide at 184 ppm, can be found. The conversion of methanol, which is directly observed via the decrease of the methanol line at 49.5 ppm, starts at 573 K (Fig. 10g). The signal at 168 ppm, appearing at the same reaction temperature, indicates the formation of formate species. The splitting of this signal (Fig. 10g to j) suggests that the formate species exist in more than one surface-bound mode. In addition to these signals, a weak line of the ring carbons appears at ca. 130 ppm. After treating the sample at 623 K (Fig. 10h), methanol is completely converted (no signals left at 49.5 ppm). An increase of the reaction temperature to 723 K does not result in a further variation of the ¹³C MAS NMR spectra (compare Fig. 10h, i and j).

According to the literature [22], the final products of the side-chain alkylation of toluene cause signals of the ¹³C-enriched side-chains at 137.0 ppm and 113.2 ppm for styrene, and at 29.1 ppm and 16.0 ppm for ethylbenzene. Styrene seems to be unstable in the time scale of the NMR experiments and, therefore, could not be observed. The formation of ethylbenzene is confirmed by the signals at 29.5 ppm and 16 ppm which are enlarged in Fig. 10j.

The comparison of the conversion of pure methanol and toluene/methanol mixtures on ze-

olite CsNaY-70/16CsOH clearly indicates that, in spite of the presence of strong base sites, toluene prevents the decomposition of formaldehyde to CO and H₂. Hence, the presence of this reactant molecule enables another reaction path, viz. the conversion of formaldehyde with toluene to styrene and ethylbenzene.

4. Conclusions

In the present work, basic zeolites Y, prepared by cesium exchange and impregnation with cesium hydroxide and subsequent calcination, were investigated. By the application of ¹³³Cs MAS NMR spectroscopy of the impregnated and calcined zeolite, and by using ¹³C MAS NMR spectroscopy of methoxy groups bound to the oxidic guest compound, a high dispersion of the guest compound was found. Another interesting result of the ¹³C MAS NMR investigations of methoxy groups is an increase in the intrinsic base strength of the zeolitic host framework upon impregnation with CsOH. Hence, there is a synergism between the host and the guest [10]: the zeolitic host causes a high dispersion of the oxidic guest compound, and the guest compound influences the intrinsic chemical properties of the host framework.

¹³³Cs MAS NMR studies of cesium-exchanged zeolites Y, before and after impregnation with CsOH and loaded with toluene, indicated the formation of complexes formed by an adsorption of toluene at cesium cations. The chemical shift anisotropy of about –450 ppm, determined by the simulation of the ¹³³Cs MAS NMR sideband patterns of cesium cations contributing to these adsorbate complexes, indicates a strong interaction between the adsorbate molecules and the cesium cations possibly via a one-side docking.

In the ¹³C MAS NMR spectra of the basic zeolites Y, the dehydrogenation of methanol to formaldehyde was indirectly revealed to occur since the signals of its decomposition products were observed. Furthermore, it was found that

this key reaction of the side-chain alkylation of toluene proceeds both on non-impregnated and on impregnated CsNaY zeolites, the reaction temperatures required being lower by about 100 K on the impregnated catalyst.

A reaction paralleling the conversion of methanol to formaldehyde leads to the formation of surface-bound formate species which are stable even at high reaction temperatures. These surface species, which are probably bound in a bidentate mode, may be responsible for catalyst deactivation.

^{13}C MAS NMR studies of the conversion of toluene/methanol mixtures on the cesium-exchanged zeolite Y show the same reaction sequence as the conversion of pure methanol, i.e., decomposition of formaldehyde to CO and H_2 and the water–gas shift reaction leading to the formation of CO_2 . By contrast, the reaction of toluene/methanol mixtures on cesium-exchanged and impregnated zeolite Y leads to a direct conversion of formaldehyde and toluene to styrene and ethylbenzene. In spite of the presence of strong base sites in this catalyst, toluene seems to prevent the decomposition of the intermediate formaldehyde to CO and H_2 .

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