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Formation and Decomposition of *N*,*N*,*N*-Trimethylanilinium Cations on Zeolite H−Y Investigated by in Situ Stopped-Flow MAS NMR Spectroscopy

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Abstract: Methylation of aniline by methanol on zeolite H−Y has been investigated by in situ ^{13}C MAS NMR spectroscopy under flow conditions. The in situ ^{13}C continuous-flow (CF) MAS NMR experiments were performed at reaction temperatures between 473 and 523 K, molar methanol-to-aniline ratios of 1:1 to 4:1, and modified residence times of $^{13}CH_3OH$ between 20 and 100 (g·h)/mol. The methylation reaction was shown to start at 473 K. *N*,*N*,*N*-Trimethylanilinium cations causing a ^{13}C NMR signal at 58 ppm constitute the major product on the catalyst surface. Small amounts of protonated *N*-methylaniline ($[PhNH_2CH_3]^+$) and *N*,*N*-dimethylaniline ($[PhNH(CH_3)_2]^+$) were also observed at ca. 39 and 48 ppm, respectively. After increase of the temperature to 523 K, the contents of *N*,*N*-dimethylanilinium cations and ring-alkylated reaction products strongly increased, accompanied by a decrease of the amount of *N*,*N*,*N*-trimethylanilinium cations. With application of the in situ stopped-flow (SF) MAS NMR technique, the decomposition of *N*,*N*,*N*-trimethylanilinium cations on zeolite H−Y to *N*,*N*-dimethylanilinium and *N*-methylanilinium cations was investigated to gain a deeper insight into the reaction mechanism. The results obtained allow the proposal of a mechanism consisting of three steps: (i) the conversion of methanol to surface methoxy groups and dimethyl ether (DME); (ii) the alkylation of aniline with methanol, methoxy groups, or DME leading to an equilibrium mixture of *N*,*N*,*N*-trimethylanilinium, *N*,*N*-dimethylanilinium, and *N*-methylanilinium cations attached to the zeolite surface; (iii) the deprotonation of *N*,*N*-dimethylanilinium and *N*-methylanilinium cations causing the formation of *N*,*N*-dimethylaniline (NNDMA) and *N*-methylaniline (NMA) in the gas phase, respectively. The chemical equilibrium between the anilinium cations carrying different numbers of methyl groups is suggested to play a key role for the products distribution in the gas phase.

Introduction

Since 1995, a number of new in situ MAS NMR techniques under continuous-flow (CF) conditions have been developed for the study of heterogeneously catalyzed reactions under industrial conditions.[1−6] With these techniques, a direct NMR investigation of the formation and transformation of surface compounds under steady-state conditions and, in some cases, a simultaneous gas chromatographic analysis of the reaction products are possible.[1] Using an isolated flow variable-temperature (VT) MAS NMR probe, Munson and co-workers have been able to study the conversion of methanol to dimethyl ether on zeolite HZSM-5 in situ and found that there is no equilibrium between methanol and dimethyl ether in the catalyst at high temperatures under flow conditions.[2] Inspired by the spectroscopic study of enzyme catalytic reactions, Haw and co-workers[3] have exploited an external microreactor to freeze the reaction system by a rapid quench technique and obtained the snapshot of the working catalysts after transferring them into the MAS

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rotor and NMR spectrometer. Recently, continuous-flow MAS NMR techniques have been also successfully combined with an optical pumping process to deliver laser-polarized xenon allowing a selective coherence transfer to nuclei located at the surface of solid materials and a sophisticated characterization of microporous solids by ^{129}Xe NMR spectroscopy.[7−10]

On the basis of in situ CF MAS NMR spectroscopy, we introduced very recently a new stopped-flow (SF) technique,[11,12] which possesses a high potential for determining intermediates and elucidating the mechanisms of a broad variety of heterogeneously catalyzed reactions. The main feature of this method is a consecutive in situ MAS NMR investigation of the working catalyst under flow conditions by *stopping the reactant flow and observing the further transformation of adsorbed compounds at reaction temperatures*. By comparing the in situ MAS NMR spectra obtained under CF and SF conditions, it is possible to unambiguously distinguish intermediates from reaction products, thus allowing a safer identification of the reaction mechanisms involved. Following this approach, *N*-methyleneaniline was identified for the first time as an intermediate in the methylation of aniline on a basic zeolite CsOH/Cs,Na−Y.[11] Furthermore, a variant of the new in situ stopped-flow MAS NMR technique was introduced, the salient feature of which is the application of a purging period.[12] During the purging period, surface compounds such as methoxy groups formed on the catalyst were *selectively retained*, and the role of methoxy groups in the catalytic formation of dimethyl ether (DME) has been shown.[12]

Although stopped-flow spectroscopic techniques are well established in many fields of chemistry, such as for NMR investigations of the real-time refolding of proteins,[13] the application of the in situ SF MAS NMR technique in heterogeneous catalysis is entirely new. In this work, this technique is utilized for an investigation of aniline methylation on acidic zeolite H−Y. As an industrially important process for the manufacture of raw materials for organic syntheses and intermediates, aniline methylation by methanol has been performed on a number of different catalysts.[14−16] The products were found to be *N*-methylaniline (NMA), *N*,*N*-dimethylaniline (NNDMA), and toluidines. The product distribution is influenced by the reaction temperature, the modified residence time, and the molar methanol-to-aniline ratio as well as by the nature of the catalyst. Up until now, however, the reaction was studied almost exclusively by analyzing the product distribution in the gas phase using gas chromatography. No direct observation of the working catalyst, which is desirable for the formulation of more reliable and more sophisticated reaction mechanisms, has so far been achieved. Recently, in situ ^{13}C MAS NMR investigations of aniline methylation on zeolite H−Y under batch conditions using samples sealed in glass ampules were performed for the first time.[17] With a molar methanol-to-aniline ratio of 1:3 at reaction temperatures between 373 and 523 K, the primary alkylation product was *N*-methylaniline (NMA), and the formation of surface methoxy groups was found to be the rate-limiting step of the overall reaction.

In this work, we report on in situ ^{13}C MAS NMR investigations of the methylation of aniline by methanol on acidic zeolite H−Y under flow conditions. With application of the in situ stopped-flow (SF) MAS NMR technique, the formation and decomposition of *N*,*N*,*N*-trimethylanilinium cations on zeolite H−Y were studied, and unequivocal experimental evidence for the decomposition of *N*,*N*,*N*-trimethylanilinium cations into *N*,*N*-dimethylanilinium and *N*-methylanilinium cations was obtained. Moreover, a mechanism of catalytic aniline methylation, in which the equilibrium between *N*,*N*,*N*-trimethylanilinium, *N*,*N*-dimethylanilinium, and *N*-methylanilinium cations on the catalyst surface plays an important role, is proposed and discussed.

Experimental Section

Materials. Zeolite Na−Y (n_{Si}/n_{Al} = 2.7) was purchased from Degussa AG, Hanau, Germany. The ammonium form (NH_4−Y) was prepared by a 4-fold ion exchange of Na−Y at 353 K in a 1.0 M aqueous solution of NH_4NO_3.[18] When an ion exchange degree of 92% was reached, the material was washed in deionized water and dried at room temperature. Subsequently, NH_4−Y was heated in a vacuum with a rate of 20 K/h up to the final temperature of 673 K. There, the material was calcined at a pressure below 10^{-2} Pa for 12 h leading to zeolite H−Y. Zeolite H−Y was characterized by AES−ICP, XRD, and solid-state ^{1}H, ^{27}Al, and ^{29}Si MAS NMR spectroscopy which indicated that the material obtained after cation exchange and calcination was neither damaged nor dealuminated.

Methanol-^{13}C (^{13}C-enrichment 99%) and methyl-^{13}C iodide (^{13}C-enrichment 99%) were obtained from Cambridge Isotopes. Aniline (>99.5%) was purchased from Fluka. Dimethyl ether (DME, >99%), *N*-methylaniline (NMA, >99.5%), *N*,*N*-dimethylanline (NNDMA, >99%), and *ortho*- (>99.5%) and *para*-toluidines (> 99.5%), all with a natural abundance of ^{13}C isotopes, were obtained from Aldrich.

In Situ Continuous-Flow (CF) MAS NMR Experiments. Prior to the in situ CF MAS NMR experiments, 250 mg of calcined zeolite H−Y was filled into a 7 mm MAS NMR rotor reactor under dry nitrogen in a glovebox and pressed to a cylindrical catalyst bed. After transfer of the rotor into the high-temperature Doty MAS NMR probe, a second in situ dehydration of the catalyst material was performed at 673 K for 1 h under flowing nitrogen (30 mL/min). During the in situ MAS NMR experiments under continuous-flow conditions at temperatures between 298 and 523 K, carrier gas (dry nitrogen) loaded with $^{13}CH_3OH$ and aniline was injected into the MAS NMR rotor reactor by applying the equipment described elsewhere.[1b] In different experiments, a modified residence time, *W*/*F*, of $^{13}CH_3OH$ between 20 and

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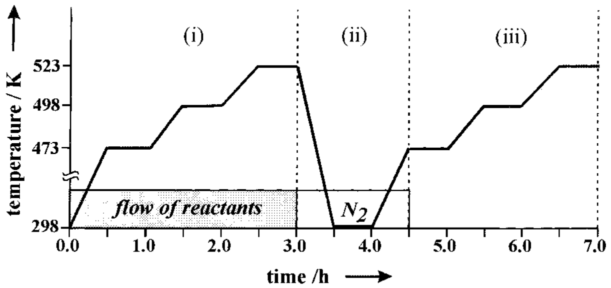

Figure 1. Protocol of the in situ stopped-flow (SF) MAS NMR experiment consisting of periods i−iii specified in the text, allowing the study of heterogeneously catalyzed reactions under steady-state conditions and of the progressive reaction of adsorbates previously formed during period i.

100 (g·h)/mol was used, and the molar $^{13}CH_3OH$ to aniline ratio was varied from 1:1 to 4:1.

In Situ Stopped-Flow (SF) MAS NMR Experiments. The stopped-flow experiment applied in this work consists of the following steps (Figure 1): (i) recording of the in situ MAS NMR spectra at reaction temperatures and under steady-state conditions during a continuous flow of the reactants into the MAS NMR rotor reactor; (ii) recording of MAS spectra at room temperature after stopping the flow of reactants and purging the catalyst with dry nitrogen, which is different from the protocol used in ref 11 and, in some cases,[12] has the advantage of selectively removing reactants from the catalyst prior to the subsequent investigation of intermediates; (iii) recording of MAS NMR spectra after raising the temperature to reaction conditions without starting the reactant flow. By comparison of the NMR spectra recorded before and after stopping the reactant flow, detailed information on the progressive reaction of adsorbates formed in period i can be collected.[11,12]

Experiments with Externally Loaded Samples. Experiments with externally loaded samples were mainly performed to confirm the assignments of the ^{13}C NMR signals of reaction products observed by in situ MAS NMR under flow conditions. Different chemical species, such as *N*-methylaniline (NMA), *N*,*N*-dimethylaniline (NNDMA), *ortho*-toluidine, *para*-toluidine, and mixtures of DME and aniline, were adsorbed at different partial pressures on calcined zeolite H−Y which had been filled into an MAS NMR rotor in advance. Prior to the loading, several "freeze−pump cycles" were carried out to purify the adsorptives. During the external loading, the rotor was connected to a vacuum line. Subsequently, the MAS NMR rotor was sealed off and the MAS NMR spectra were recorded at ambient temperature. To prepare a sample loaded with a mixture of DME and aniline, the zeolite was filled into a glass tube and calcined as mentioned above. The adsorption of the reactants was performed in the vacuum line by cooling the glass tube with liquid nitrogen. Subsequently, the glass tube was rapidly fused under liquid nitrogen and carefully heated to a desired reaction temperature. Prior to the NMR measurements, the samples were filled into a gastight MAS NMR rotor under dry nitrogen.

NMR Spectroscopy. ^{13}C MAS NMR investigations were performed on a Bruker MSL 400 spectrometer at a resonance frequency of 100.6 MHz. CF and SF MAS NMR experiments were carried out with a sample spinning rate of ca. 2.0 kHz using a modified DSI-740 7 mm STD MAS NB NMR probe of Doty Scientific Instruments, TX (see ref 1c). ^{13}C MAS NMR investigations under batch conditions with externally loaded samples were performed with a sample spinning rate of ca. 3.5 kHz using a 7 mm Bruker MAS NMR probe at ambient temperature. In situ ^{13}C CF MAS NMR and SF MAS NMR spectra were recorded at reaction temperature with high-power proton decoupling after an excitation with $\pi/2$ pulses and a repetition time of 5 s. ^{13}C CP/MAS NMR experiments (CP: cross-polarization) were carried out at reaction temperature with a contact time of 2.5 ms and a repetition time of 4 s. The number of scans of 200−500 was optimized depending on the signal/noise ratio obtained at different temperatures. To record ^{13}C MAS NMR spectra of externally loaded samples (natural abundance of ^{13}C isotopes), excitations with $\pi/2$ pulses, high-power proton decoupling, and a repetition time of 5 s were used. The typical number of scans was between 16 000 and 20 000. All spectra were referenced to tetramethylsilane (TMS).

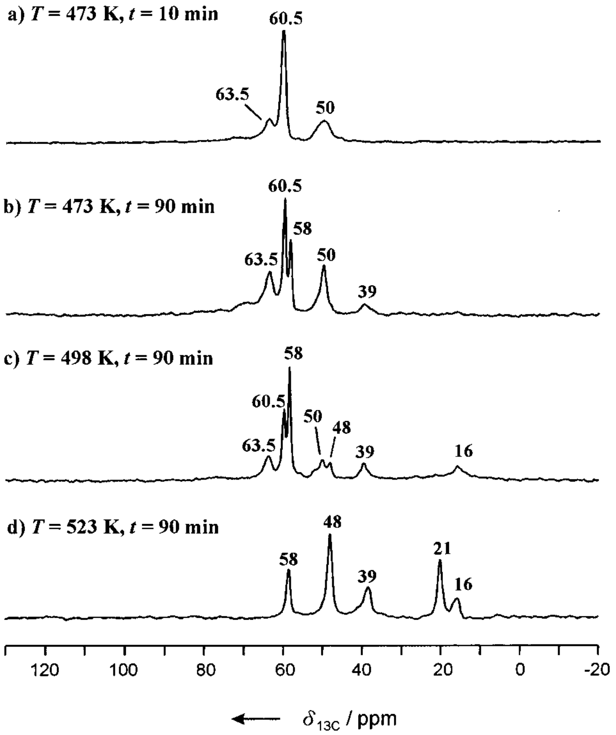

Figure 2. In situ ^{13}C MAS NMR spectra recorded during aniline methylation on zeolite H−Y under continuous-flow conditions ($W/F = 40$ (g·h)/mol, $^{13}CH_3OH$/aniline = 2:1) at reaction temperatures of 473 K for 10 min (a), 473 K for 90 min (b), 498 K for 90 min (c), and 523 K for 90 min (d).

Results and Discussion

Formation of *N,N,N*-Trimethylanilinium Cations. Figure 2 shows the in situ ^{13}C CF MAS NMR spectra recorded during methylation of aniline by methanol at reaction temperatures of 473−523 K. During these experiments, a mixture of $^{13}CH_3OH$ ($W/F = 40$ (g·h)/mol) and aniline in a molar ratio of 2:1 was continuously injected into the MAS NMR rotor reactor. The signal occurring at 50 ppm in the spectrum recorded at 473 K (Figure 2a) is caused by methanol adsorbed on zeolite H−Y. The signals occurring at 63.5 and 60.5 ppm are due to dimethyl ether (DME) formed from methanol. According to Ivanova and Corma[19] and Blaszkowski and van Santen,[20] these two signals are attributed to side-on and end-on adsorbate conformations of dimethyl ether, respectively, in agreement with the stronger adsorption of the species occurring at 63.5 ppm.[12]

After a reaction time of 90 min at 473 K, a signal of *N*-methylanilinium cations ($[PhNH_2CH_3]^+$) appears at 39 ppm (Figure 2b), which were formed on the Brønsted acid sites of zeolite H−Y. The chemical shift of the *N*-methylanilinium cations was confirmed by loading pure NMA on zeolite H−Y indicating a strong low-field shift of the methyl signal of NMA due to a protonation by strong Brønsted acid sites (vide infra). In addition, another signal occurs at 58 ppm (Figure 2b). Upon further increase of the reaction temperature, the intensity of this

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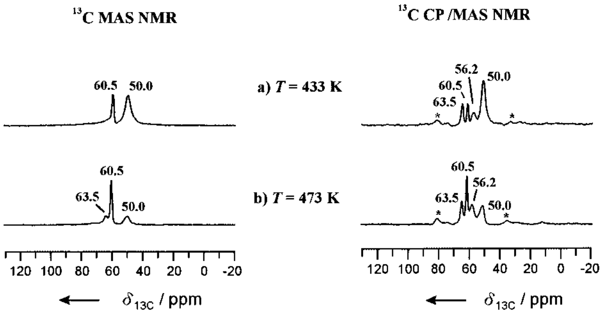

Figure 3. In situ ^{13}C MAS NMR spectra of zeolite H−Y recorded at temperatures of 433 K (a) and 473 K (b) during a continuous injection of $^{13}CH_3OH$ (W/F = 40 (g·h)/mol) into the MAS NMR rotor reactor. The spectra on the left-hand side were obtained by MAS NMR and proton decoupling, while the spectra on the right-hand side were recorded applying CP/MAS NMR (cross polarization). Asterisks denote spinning sidebands.

signal increases, while the intensities of the methanol signal at 50 ppm and of the DME signals at 60.5 and 63.5 ppm decrease and eventually disappear (Figure 2c,d). During aniline methylation at reaction temperatures of 498−523 K, additional signals appear at 48, 21, and 16 ppm (Figure 2c,d). The signal at 48 ppm, dominating in Figure 2d, is due to *N*,*N*-dimethylanilinium cations ($[PhNH(CH_3)_2]^+$), while the signals at 16 and 21 ppm originate from ring-alkylated reaction products, i.e., by anilines (*ortho*- and *para*-toluidine) or anilinium cations with methyl groups in *ortho* and *para* positions. These assignments have been confirmed by an external loading of the individual compounds onto zeolite H−Y.

Since the resonance position at 58 ppm may be indicative of carbon atoms bound to oxygen, the formation of surface methoxy groups (CH_3OZ, Z denotes the zeolite framework)[17,21] was considered in more detail. However, an assignment of the signal at 58 ppm to surface methoxy groups could be ruled out for the following reasons: (i) The conversion of *pure* methanol on zeolite H−Y under the same continuous-flow conditions gave no ^{13}C MAS NMR signal at 58 ppm (Figure 3, left). A simultaneous CP/MAS NMR experiment which favors signals arising from rigidly bound species led to a signal with a resonance position of 56.2 ppm which is characteristic for methoxy groups formed on zeolite H−Y (Figure 3, right). (ii) In situ ^{13}C CP/MAS NMR spectra recorded during the conversion of *mixtures* of $^{13}CH_3OH$ and aniline consist of two separate signals, a narrow line at 58 ppm and a broad signal at 56.2 ppm with spinning sidebands corresponding to surface methoxy groups (Figure 4).

The ^{13}C MAS NMR signal at 58 ppm was, therefore, attributed to *N*,*N*,*N*-trimethylanilinium cations ($[PhN(CH_3)_3]^+$) formed on zeolite H−Y, on the basis of the result of the conversion of methanol and aniline. This assignment is strongly supported by the resonance position of 57 ppm for the signal of tetramethylammonium cations, $(CH_3)_4N^+$, observed by Thursfield et al.[22] investigating the reaction of methanol and ammonia on acidic zeolites H−Rho and H−SAPO-34 by ^{13}C MAS NMR spectroscopy under batch conditions. Studying the same reaction, Ernst and Pfeifer[23] clearly assigned a narrow ^{13}C NMR signal at ca. 56 ppm to tetramethylammonium cations by the observation of a quartet which splits up after releasing the proton decoupling. An origination of the signal at 58 ppm from hydrogen-bonded adsorbate complexes, such as methanol or dimethyl ether interacting with aniline, could be clearly excluded by molecular dynamic calculations.[24] The assignments of all ^{13}C NMR signals in this work are listed in Table 1.

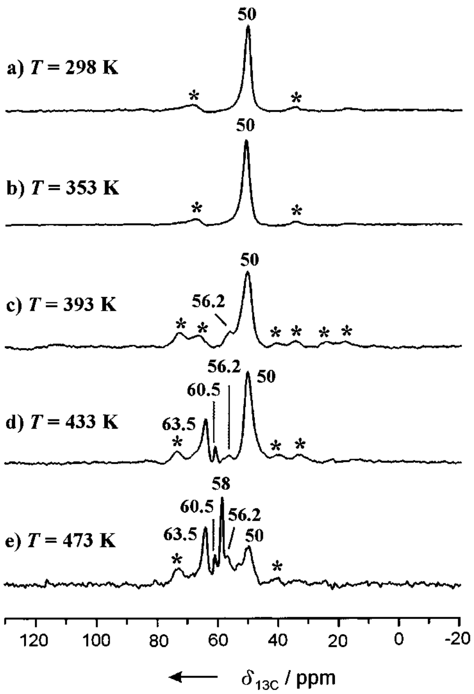

Figure 4. ^{13}C CP/MAS NMR spectra (CP: cross polarization) recorded during aniline methylation on zeolite H−Y under continuous-flow conditions (W/F = 40 (g·h)/mol, $^{13}CH_3OH$/aniline = 2:1) at temperatures between 298 and 473 K. Asterisks denote spinning sidebands.

Table 1. ^{13}C Chemical Shift and Proton Affinity (PA) of the Species Absorbed on Zeolite H−Y during Aniline Methylation by Methanol

	^{13}C chem shift (ppm)	proton affinity[b] (kJ/mol)
methanol	50	754.3
dimethyl ether (DME)	60.5, 63.5	792.0
methoxy groups (CH_3OZ)	56.2	
aniline[a]		882.5
N-methylanilinium cations, $[PhNH_2CH_3]^+$	39	916.6[c]
N,*N*-dimethylanilinium cations, $[PhNH(CH_3)_2]^+$	48	941.1[d]
N,*N*,*N*-trimethylanilinium cations, $[PhN(CH_3)_3]^+$	58	
ortho-toluidine[a]	16	890.9
para-toluidine[a]	21	896.7

[a] Probably also protonated on zeolite H−Y; see the text. [b] Data obtained from NIST Chemistry WebBook (http://webbook.nist.gov/chemistry). [c] PA value of the parent compound, *N*-methylaniline (NMA). [d] PA value of the parent compound, *N*,*N*-dimethylaniline (NNDMA).

The ^{13}C CF MAS NMR spectra in Figure 2 indicate that, at temperatures between 473 and 498 K, *N*,*N*,*N*-trimethylanilinium cations are formed as the major reaction product on the catalyst surface, accompanied by a decrease of the signals of methanol and DME. At 523 K, however, the intensities of the ^{13}C NMR signals of *N*,*N*-dimethylanilinium (48 ppm) and *N*-methylanilinium cations (39 ppm) and of *para*- (21 ppm) and *ortho*-methylated products (16 ppm) increase, while the intensity of the signal of *N*,*N*,*N*-trimethylanilinium cations (58 ppm) de-

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creases. Various in situ ^{13}C CF MAS NMR experiments were performed with different modified residence times of $^{13}CH_3OH$ ($W/F = 20$, 40, 75, and 100 (g•h)/mol) and molar $^{13}CH_3OH$ to aniline ratios (1:1, 2:1, and 4:1). In some experiments, the in situ ^{13}C CF MAS NMR spectra were recorded after raising the reaction temperature directly to the desired temperature of 473, 498, 523, or 573 K rather than by increasing it in steps of 25 K. In each case, the same result was obtained: at low reaction temperatures, *N*,*N*,*N*-trimethylanilinium cations were formed as the predominant product, while *N*,*N*-dimethylanilinium and *N*-methylanilinium cations and *para*- and *ortho*-methylated compounds were observed as main reaction products after the reaction temperature was increased.

From the in situ MAS NMR results obtained under continuous-flow conditions, however, it is difficult to determine the role of *N*,*N*,*N*-trimethylanilinium cations in the overall reaction leading to the formation of NMA, NNDMA, and ring-alkylated products on zeolite H−Y. Therefore, the in situ stopped-flow (SF) technique was applied, allowing a detailed investigation of the reaction pathway. After *N*,*N*,*N*-trimethylanilinium cations were formed on zeolite H−Y under continuous-flow conditions, the reactant flow was stopped and an in situ MAS NMR investigation of the progressive reaction of these surface compounds was performed at different reaction temperatures.

Decomposition of *N*,*N*,*N*-Trimethylanilinium Cations. As mentioned above, the stopped-flow experiment could be achieved by either directly observing[11] the further transformation of adsorbed compounds at reaction temperatures or adding a purging period[12] before that. Since it has the advantage of selectively retaining the *N*,*N*,*N*-trimethylanilinium cations after the purging period, we prefer the latter protocol—although the results are of no difference by use of these two protocols in this study. Details of the in situ SF MAS NMR experiment are displayed in Figure 1. After the continuous injection of the reactants at 473 K for 1 h with a molar $^{13}CH_3OH$ to aniline ratio of 4:1 and a modified residence time of $^{13}CH_3OH$ of $W/F = 75$ (g•h)/mol (Figure 5a), the flow was stopped and the catalyst was purged with dry nitrogen at ambient temperature for 1 h. In the spectrum recorded subsequently at ambient temperature, only the signal of *N*,*N*,*N*-trimethylanilinium cations occurred at 58 ppm (Figure 5b). After increase of the temperature to 498 K without starting the flow of reactants again, a strong intensity increase of the signals at 48 and 39 ppm was observed, accompanied by a decrease of the signal at 58 ppm (Figure 5c), which indicates a decomposition of *N*,*N*,*N*-trimethylanilinium cations to *N*,*N*-dimethylanilinium and *N*-methylanilinium cations. At 523 K, additional signals at 16 and 21 ppm appeared due to ring-alkylated reaction products with methyl groups in *para* and *ortho* positions, respectively (Figure 5d). The ^{13}C-labeled methyl groups which are abstracted during these decomposition processes may react with adsorbed aniline molecules giving NMA and NNDMA and/or contribute to the ring-alkylation leading to reaction products with methyl groups in *para* and *ortho* positions.

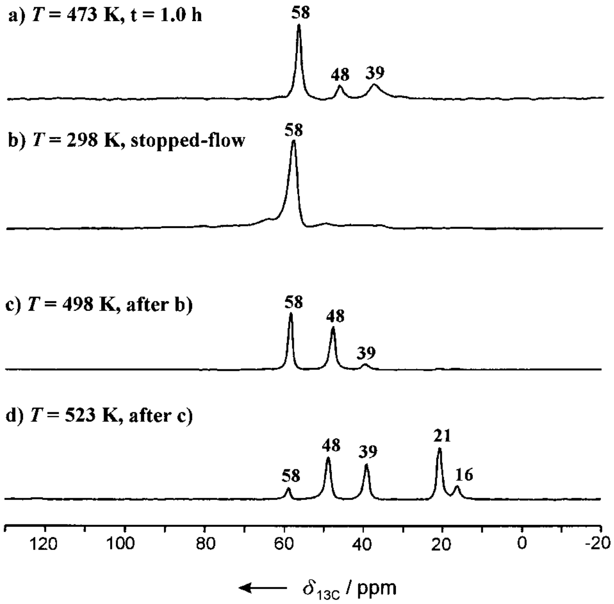

Figure 5. In situ ^{13}C MAS NMR spectra recorded during aniline methylation on zeolite H−Y under continuous-flow conditions ($W/F = 75$ (g•h)/mol, $^{13}CH_3OH$/aniline = 4:1) at a reaction temperature of 473 K for 1.0 h (a), at 298 K after stopping the flow of reactants and purging the catalyst with dry nitrogen (b), and, subsequently, at reaction temperatures of 498 K (c) and 523 K (d) without purging the catalyst.

It is well established that the alkylation of ammonia with methanol proceeds in a stepwise manner, the products being methylamine, dimethylamine, trimethylamine, and the tetramethylammonium cation.[25] On the other hand, hints for the decomposition of tetramethylammonium cations at elevated temperatures were obtained by ^{13}C MAS NMR studies of ammonia methylation on solid catalysts under batch conditions.[22,23] From an analysis of ^{13}C MAS NMR data collected during the hydrothermal synthesis of the $AlPO_4$ material UiO-12, Kongshaug et al. were led to propose that the tetramethylammonium cations used as a structure-directing agent may decompose into dimethylammonium and small amounts of methylammonium.[26] To the best of our knowledge, however, the decomposition behavior of quaternary anilinium cations in acidic zeolites was never studied before under in situ conditions.

Mechanism of Aniline Methylation. Although the methylation of aniline on acidic catalysts has been investigated in a number of previous studies, the reaction mechanism continues to be a matter of discussion.[14−16] In situ MAS NMR spectroscopy performed under batch[17] and continuous-flow conditions now furnish direct insight into the intermediates on the surface of the working catalyst during the methylation of aniline on acidic zeolites. Especially, the chemical equilibria of the anilinium cations presented in Scheme 1 deserve particular attention.

Experimental studies established that the fastest step of the methanol-to-olefin process (MTO) on acidic zeolites is the conversion of methanol to DME.[27] Generally, the starting temperature of DME formation on acidic zeolites is as low as ca. 423 K. Under continuous-flow conditions and at reaction temperatures higher than 473 K, the equilibrium between methanol and DME is greatly shifted to DME.[2,12] The present in situ CF MAS NMR results indicate that this conversion also happens during aniline methylation on zeolite H−Y (Figure 2b). Furthermore, the formation of *N*,*N*,*N*-trimethylanilinium cations and other products is accompanied by a decrease of the surface

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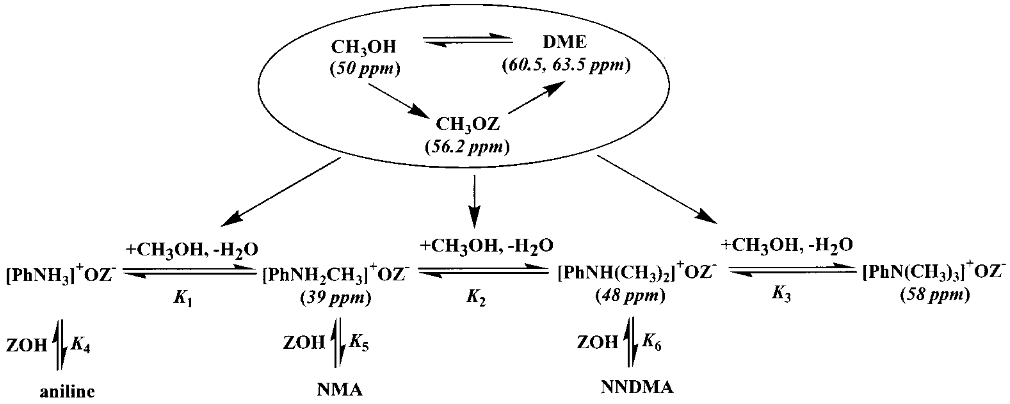
Scheme 1



concentration of DME (Figure 2c). The ^{13}C MAS NMR results obtained from methylation of aniline[17] and ammonia[22,23] by methanol under batch conditions also showed that DME occurs at low reaction temperatures and decreases or disappears at high reaction temperatures. It is necessary to clarify whether DME is involved in the methylation of aniline. Thus, the reaction of DME itself with aniline on zeolite H−Y was studied by in situ MAS NMR spectroscopy under batch conditions. The ^{13}C MAS NMR spectra obtained are shown in Figure 6. After heating of zeolite H−Y externally loaded with DME and aniline at 453 K, the signal of *N*,*N*,*N*-trimethylanilinium cations occurred at 58 ppm along with the signal of *N*-methylanilinium cations at 39 ppm. Thus, it is very likely that DME can react with aniline, although the reaction could have occurred via the conversion of dimethyl ether to methanol through trace quantities of water present in the catalyst. On the other hand, methoxy groups prepared by adsorption and conversion of $^{13}CH_3I$ and $^{13}CH_3OH$ under batch conditions can also react with aniline to NMA.[17] In addition, in situ SF MAS NMR investigations[12] of the conversion of methanol to DME showed that methoxy species (CH_3OZ) formed from methanol can react with other methanol molecules to yield DME. From these we conclude that methanol, methoxy species, and DME are all possible alkylating agents involved in the methylation of aniline under continuous-flow conditions (Scheme 1, top).

Compared with the ^{13}C NMR shift data of NMA and NNDMA in an inert solution (30.2 and 40.3 ppm, respectively)[28] and of NMA on a basic zeolite CsOH/Cs,Na−Y (29 ppm),[11] a significant low-field shift of the methyl groups of NMA (39 ppm) and NNDMA (48 ppm) adsorbed on acidic zeolite H−Y occurs. According to theoretical calculations performed by Nicholas and Haw,[29] the formation of a persistent cation on a zeolite in its H^+ form requires that the adsorptive has a proton affinity of at least 875 kJ/mol. Thus, the above-mentioned low-field shifts are most probably caused by a protonation of NMA and NNDMA (proton affinity[30] of 916.6 and 941.1 kJ/mol, respectively) on the Brønsted acid sites of zeolite H−Y leading to *N*-methylanilinium and *N*,*N*-dimethylanilinium cations. Observing the low-field ^{13}C NMR shifts of aniline (proton affinity[30] of 882.5 kJ/mol) adsorbed on zeolite H−Y, Ivanova et al.[17] also suggested a protonation of these molecules. Furthermore, although there are still longstanding arguments on the preferred protonation site of aniline and substituted anilines in the gas phase,[31] we believe that, according to their basic behavior in solution, the protonation of aniline or substituted anilines on zeolite H−Y occurs preferentially at the nitrogen atom rather than at carbon atoms of the aromatic ring. In the methylation of aniline, therefore, the N-alkylation preferentially occurs instead of the C-alkylation[32] because the N atom is more nucleophilic. Protonation of *ortho*- or *para*-toluidines at the nitrogen atom (proton affinities[30] of 890.9 and 896.7 kJ/mol, respectively) shows no influence on the ^{13}C NMR shift of the *ortho*- and *para*-methyl groups (21 and 16 ppm, respectively), although it may cause similar low-field shifts of aromatic carbon atoms as in the case of aniline.

The conversion of reactant mixtures with a molar methanol-to-aniline ratio of 1:3 on zeolite H−Y under batch conditions led to protonated NMA.[17] On the contrary, with a molar methanol-to-aniline ratio of more than 1:1 under flow conditions, aniline methylation does not stop after the formation of *N*-methylanilinium cations. Instead, *N*,*N*,*N*-trimethylanilinium cations are formed at low reaction temperatures, together with small amounts of *N*-methylanilinium and *N*,*N*-dimethylanilinium cations. It should be noted that the weak ^{13}C NMR signal of *N*,*N*-dimethylanilinium cations overlaps with the signal of adsorbed methanol molecules at 50 ppm (Figure 2b). However, at reaction temperatures of 523 K and higher, *N*,*N*-dimethylanilinium cations together with *N*-methylanilinium cations and ring-methylated compounds occurred as the main products on the working catalyst accompanied by a decrease of the *N*,*N*,*N*-trimethylanilinium cations (Figure 2d). The in situ SF MAS NMR results clearly indicate that at these reaction temperatures *N*,*N*,*N*-trimethylanilinium cations decompose to *N*,*N*-dimethylanilinium cations (Figure 5). All these observations can be rationalized by invoking that the equilibrium between *N*-methyl-*N*,*N*-dimethyl- and *N*,*N*,*N*-trimethylanilinium cations is established, as shown in Scheme 1. At high methanol-to-aniline ratios and low temperatures, the equilibrium shifts to *N*,*N*,*N*-trimethylanilinium cations, while at low methanol-to-aniline ratios and

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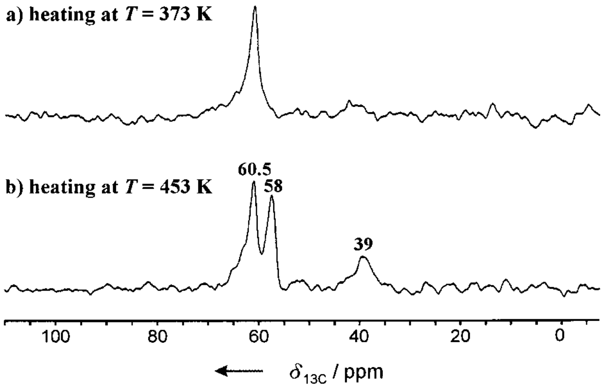

Figure 6. ^{13}C MAS NMR spectra of zeolite H−Y recorded at 298 K after heating at 373 K for 2.0 h (a) and at 453 K for 2.0 h (b). Zeolite H−Y was externally loaded with a mixture of dimethyl ether and aniline in a molar ratio of 2:1.

high temperatures *N*-methylanilinium and *N*,*N*-dimethylanilinium cations are preferentially formed. The content of gaseous products at the outlet of the flow reactor will further depend not only on the equilibrium constants of formation and decomposition of *N*,*N*,*N*-trimethylanilinium, *N*,*N*-dimethylanilinium, and *N*-methylanilinium cations on the surface of the catalyst (K_1-K_3) but also on the equilibrium constants of deprotonation and desorption of *N*-methylanilinium and *N*,*N*-dimethylanilinium cations (K_5, K_6). Hence, the ratio of these constants (K_1:K_2:K_3:K_5:K_6) at different experimental conditions (temperature, methanol to aniline molar ratio) determines the final product distribution in the gas phase.

It should be mentioned that the reaction pathway including the formation of quaternary cations and their subsequent decomposition suggested in this work may, in some cases, explain the appearance of unexpected products observed during amine alkylation on acidic catalysts. For example, Pouilloux et al. synthesized dimethylethylamine from ethylamine and methanol on an acidic catalyst.[33] At the reaction temperature of 503 K, an unexpected product, trimethylamine, was determined in high yield by gas chromatographic analysis. This can be easily explained by the formation and decomposition of trimethylethylammonium cations, $(CH_3)_3N^+CH_2CH_3$, during the reaction. Additionally, investigations of template decomposition upon calcination of as-synthesized zeolites has recently received much research interest.[26,34,35] However, the decomposition mechanisms of quaternary ammonium salts being commonly used as template molecules are poorly understood. Thus, it can be expected that in situ NMR studies of the decomposition of quaternary ammonium cations in zeolites bear the potential of significantly improving our understanding of these processes.

Conclusions

On the basis of the results of in situ ^{13}C NMR investigations performed in the present work, a mechanism of aniline methylation on acidic zeolite H−Y is proposed: In the first step of the reaction, methanol is converted to DME and surface methoxy groups, which are further involved in the methylation as alkylating agents along with methanol. Alkylation starts at 473 K and leads to a consecutive and reversible formation of *N*-methylanilinium, *N*,*N*-dimethylanilinium, and *N*,*N*,*N*-trimethylanilinium cations attached to the zeolite surface. The products of the N-alkylation of aniline, *N*-methylaniline and *N*,*N*-dimethylaniline, are further formed via deprotonation of the corresponding *N*-methylanilinium and *N*,*N*-dimethylanilinium cations. We propose that the product distribution in the gas phase is determined to a large extent by the chemical equilibrium between the different methylanilinium cations, which is in turn affected by the reaction conditions (temperature, molar methanol-to-aniline ratio). C-alkylated products are formed via transformation of methylanilinium cations at temperatures higher than 523 K.

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