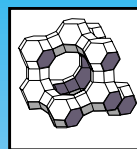


In situ stopped-flow (SF) MAS NMR investigation of the formation and decomposition of methylanilinium cations on acidic zeolite H-Y



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Summary

In situ ^{13}C MAS NMR spectroscopy under flow conditions was applied to investigate the mechanism of aniline methylation by methanol on zeolite H-Y. Via the new "stopped-flow" (SF) method, the formation and decomposition of N,N,N-trimethylanilinium cations were observed for the first time. The experimental results suggested that the chemical equilibrium between the anilinium cations carrying different numbers of methyl groups plays a key role for the products distribution in the gas phase.

Introduction

As an industrially important process for the manufacture of useful raw materials for organic syntheses and intermediates, aniline methylation has been studied on a number of catalysts [1]. The products were found to be N-methylaniline (NMA), N,N-dimethylaniline (NNDMA) and toluidines. Up till 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 has so far been achieved. Based on *in situ* continuous-flow (CF) MAS NMR spectroscopy, we introduced recently a new "stopped-flow" (SF) technique [2,3] 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, stopping the reactant flow and observing the further transformation of adsorbed compounds at reaction temperatures. In the present work, this method is utilized for the *in situ* investigation of aniline methylation on acidic zeolite H-Y and a new mechanism was thus proposed.

Experimental Section

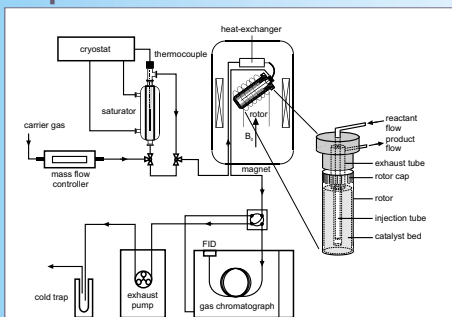


Fig. 1: Scheme of the equipment applied for simultaneous *in situ* MAS NMR spectroscopy and on-line gas chromatography and the design of the modified MAS NMR rotor with axially placed tubes for the injection of reactant molecules and the exhaust of reaction products.

The MAS NMR investigations were performed on a Bruker MSL 400 spectrometer at the resonance frequency of 100.6 MHz for ^{13}C nuclei. As shown in Fig. 1, *in situ* ^{13}C MAS NMR experiments under flow conditions [4] were performed with sample spinning rates of 1.5 to 2.8 kHz using a modified DSI-740 7 mm STD MAS NB NMR Doty probe. During the *in situ* MAS NMR experiments under flow conditions, dry nitrogen loaded with the gas phase mixture of $^{13}\text{CH}_3\text{OH}$ and aniline (modified residence time, W/F_{MeOH} , of 20 to 100 gh/mol, and molar $^{13}\text{CH}_3\text{OH}$ /aniline ratios of 1:1 to 4:1), was injected into the MAS rotor reactor. The protocol of the "stopped-flow" (SF) experiment is shown in Fig. 2.

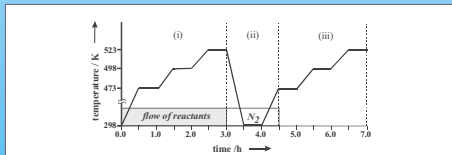


Fig. 2: The protocol of the "stopped-flow" (SF) experiment consists of: (i) recording of the *in situ* MAS NMR spectra at reaction temperature and under steady-state conditions during a continuous flow of the reactants into the MAS NMR rotor reactor, (ii) recording of spectra at room temperature after stopping the flow of reactants and purging the catalyst with dry nitrogen, and (iii) recording of spectra after raising the temperature to reaction conditions without starting the reactant flow.

Results and Discussion

In situ ^{13}C continuous-flow (CF) MAS NMR: Formation of anilinium cations

- The first reaction step is the dimethyl ether (DME) formation from methanol (Fig. 3a). The signal at 50 ppm is due to methanol adsorbed on zeolite H-Y, while the two signals at 63.5 and 60.5 ppm are attributed to side-on and end-on adsorbate conformations of DME.
- After a reaction time of 90 minutes at 473 K, ^{13}C NMR signals of N-methylanilinium, N,N-dimethylanilinium and N,N,N-trimethylanilinium cations appeared at 39, 48 and 58 ppm, respectively (Fig. 3b and 3c).
- Upon further raising the reaction temperature, the intensity of signal at 58 ppm increases, while the intensities of methanol and DME signals decrease and eventually disappear (Fig. 3c and 3d).
- At a reaction temperature of 523 K, signals of *ortho*- and *para*-toluidines appeared at 16 and 21 ppm (Fig. 3d).
- The chemical shift of N-methylanilinium and N,N-dimethylanilinium cations and toluidines were confirmed by loading authentic compounds on zeolite H-Y, while that of N,N,N-trimethylanilinium cations was supported by Ernst and Pfeifer [5] and Thursfield et al. [6].

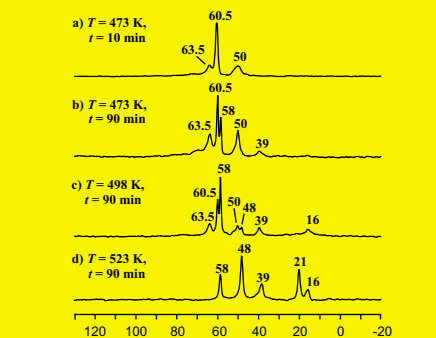


Fig. 3: *In situ* ^{13}C MAS NMR spectra recorded during aniline methylation on zeolite H-Y under CF conditions ($W/F = 40$ gh/mol, $^{13}\text{CH}_3\text{OH}$ /aniline = 2:1) at $T = 473$ K to $T = 523$ K.

Table 1. ^{13}C NMR chemical shifts (CS) and proton affinities (PA) of the species adsorbed on zeolite H-Y during aniline methylation.

	^{13}C CS (ppm)	PA ^b (kJ/mol)
Methanol	50	754.3
Dimethyl Ether (DME)	60.5, 63.5	792.0
Methoxy Group (CH_3OZ)	56.2	-
Aniline ^a	-	882.5
N-Methylanilinium Cations, $[\text{PhNH}_2\text{CH}_2]^+$	39	916.6 ^c
N,N-Dimethylanilinium Cations, $[\text{PhNH}(\text{CH}_2)_2]^+$	48	941.1 ^d
N,N,N-Trimethylanilinium Cations, $[\text{PhN}(\text{CH}_3)_3]^+$	58	-
<i>ortho</i> -Toluidine ^a	16	890.9
<i>para</i> -Toluidine ^a	21	896.7

^a probably also protonated on zeolite H-Y

^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)

In situ ^{13}C stopped-flow (SF) MAS NMR: Decomposition of anilinium cations

- N,N,N-trimethylanilinium cations were selectively retained after the flow of reactants was stopped and the catalyst was purged with dry nitrogen at room temperature (Fig. 4b).
- After raising the temperature again to 498 K without starting the flow of reactants, a strong intensity increase of the signal at 48 and 39 ppm was observed, accompanied by a decrease of the signal at 58 ppm (Fig. 4c), which indicates the 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 *ortho*- and *para*-toluidines (Fig. 4d). These C-alkylated products were formed by a further transformation or isomerization of N-alkylated anilines.

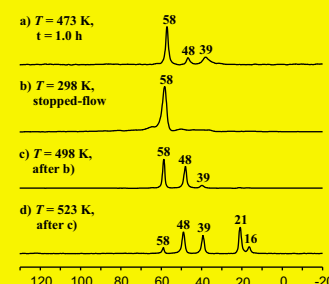
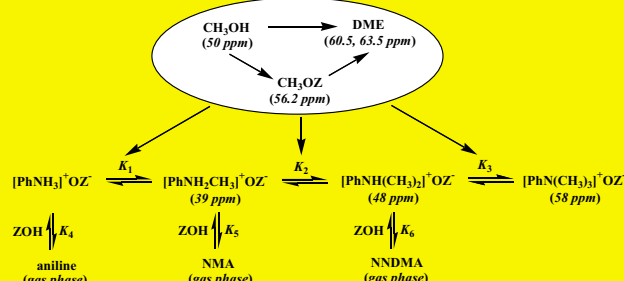


Fig. 4: *In situ* ^{13}C MAS NMR spectra recorded during aniline methylation on zeolite H-Y under CF conditions ($W/F = 75$ gh/mol, $^{13}\text{CH}_3\text{OH}$ /aniline = 4:1) at $T = 473$ K for 1.0 h (a), at $T = 298$ K after stopping the reactants flow and purging the catalyst with dry nitrogen (b), and, subsequently, at $T = 498$ K (c) and $T = 523$ K (d) without purging the catalyst.

Proposed mechanism of aniline methylation on acidic zeolite H-Y

- Based on *in situ* CF and SF MAS NMR experimental results, a new mechanism of aniline methylation on acidic catalysts was proposed. The ratio of equilibrium constants (K_1 : K_2 : K_3 : K_4 : K_5 : K_6) at different experimental conditions (temperature, methanol to aniline molar ratio) determines the final product distribution in the gas phase.



Acknowledgements

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Conclusions

- By application of the *in situ* "stopped-flow" (SF) MAS NMR technique, unequivocal experimental evidence for the decomposition of N,N,N-trimethylanilinium cations into N,N-dimethylanilinium and N-methylanilinium cations was obtained during aniline methylation by methanol on zeolite H-Y.
- 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.