Time-resolved observation of the decomposition process of N,N,N-
Trimethylanilinium cations on zeolite H-Y by in situ stopped-flow
$^{13}$C MAS NMR spectroscopy

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Abstract

N,N,N-Trimethylanilinium cations were synthesized on acidic zeolite H-Y by direct reaction of N,N-dimethylaniline and methanol. Time-resolved observation of the detailed decomposition process of N,N,N-trimethylanilinium cations was achieved by in situ $^{13}$C stopped-flow (SF) MAS NMR spectroscopy at reaction temperatures of 498 K to 573 K. © 2003 Elsevier Science Inc. All rights reserved.

Keywords: Time-resolved in situ NMR spectroscopy; Stopped-flow; Heterogeneous catalysis; Zeolites; Methylammonium cations

1. Introduction

The great importance of probing events taking place in heterogeneous catalysis under reaction conditions has been prompting ingenious designs of various in situ spectroscopic methods toward getting “snapshots” of a working solid catalyst [1]. MAS NMR spectroscopy, which could provide both structural and dynamic information about the heterogeneous catalytic systems, is certainly considered as one of the most suitable methods for these in situ studies. Since 1995 [2], we have been developing an in situ MAS NMR technique for the study of heterogeneously catalyzed reactions toward real industrial conditions, i.e., under continuous-flow (CF) conditions. With this technique, a direct NMR investigation of the formation and transformation of surface compounds under steady-state conditions and a simultaneous gas chromatographic analysis of the reaction products can be achieved.

Based on the in situ CF MAS NMR technique, we introduced very recently a novel stopped-flow (SF) protocol [3-5], which possesses a high potential for determining intermediates and elucidating the mechanisms of a broad variety of heterogeneously catalyzed reactions. By use of this stopped-flow MAS NMR technique, for example, the mechanism of aniline methylation by methanol on acidic zeolite H-Y was revealed [5]. It was found that, at reaction temperatures as low as 473 K, the successive methylation of aniline produces N-methyleneiminium, N,N-dimethylammonium, and eventually, N,N,N-trimethylanilinium cations as the main species on the working catalyst. At reaction temperatures higher than 473 K, however, the decomposition of N,N,N-trimethylanilinium cations to N,N-dimethylammonium and N-methylanilinium cations occurred, and the chemical equilibrium between those anilinium cations carrying different numbers of methyl groups was suggested be crucial for the product distribution in the gas phase [5].

Kühl and co-workers [6] revealed recently that, even at a temperature as low as 523 K, ammonia in zeolite LTA could react with tetramethylammonium cations (TMA$^+$) acting as template molecules which generates mono- and dimethylamine. As a result, the presence of ammonia makes the decomposition of the template TMA$^+$ easier. In contrast, in the absence of ammonia, the decomposition of template molecules needs temperatures higher than 773 K. In our previous study [5], however, it was not possible to distinguish whether the decomposition was achieved by N,N,N-trimethylanilinium cations alone or helped by aniline, in that we could not rule out the presence of adsorbed aniline. In this contribution, we focus on the decomposition process of N,N,N-trimethylanilinium cations more in detail. We produced N,N,N-trimethylanilinium cations directly on acidic zeolite H-Y by reaction of N,N-dimethylaniline (NNDMA) and methanol so as to simplify the catalytic system of aniline methylation. Subsequently, in situ $^{13}$C SF...
MAS NMR spectroscopy was applied to perform a time-resolved observation of the decomposition process of N,N,N-trimethylanilinium cations at reaction temperatures of 498 K to 573 K (Fig. 1). It was found that N,N,N-trimethylanilinium cations alone do decompose at temperature as low as 498 K on acidic zeolite H-Y generating gradually N,N-dimethylanilinium, N-methylanilinium and toluidinium cations which agrees very well with our previous study of aniline methylation.

2. Experimental section

Zeolite Na-Y \( (n_{Si}/n_{Al} = 2.7) \) was purchased from Degussa AG, Hanau, Germany. The ammonium form \( (\text{NH}_4-Y) \) was prepared by a fourfold ion exchange of Na-Y at 353 K in a 1.0 M aqueous solution of \( \text{NH}_4\text{NO}_3 \) [7]. After reaching a cation exchange degree of 90%, the material was washed in deionized water and dried at room temperature. Subsequently, zeolite \( \text{NH}_4-Y \) was heated in 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 \( 10^{-2} \text{ Pa} \) for 12 h leading to zeolite H-Y. Zeolite H-Y was characterized by AES-ICP, XRD and solid-state \(^1\text{H}, ^{27}\text{Al} \) and \(^{29}\text{Si} \) MAS NMR spectroscopy which indicated that the material obtained after cation exchange and calcination was neither damaged nor dealuminated. Methanol,\(^{13}\text{C} \) (\(^{13}\text{C}-\text{enrichment 99\%}) \) was obtained from Cambridge Isotopes. N,N-dimethylaniline (NNDMA, > 99\%) was purchased from Aldrich.

Prior to the in situ MAS SF NMR experiments, 250 mg of calcined zeolite H-Y was filled into a 7 mm MAS NMR rotor reactor under dry nitrogen in a glove box and pressed to a cylindrical catalyst bed. After transferring the rotor into the high-temperature Doty MAS NMR probe, a second in situ dehydration was performed at 673 K for 1 h under flowing nitrogen (30 mL/min). To synthesize N,N,N-trimethylanilinium cations in situ at 473 K, carrier gas (dry nitrogen) loaded with \(^{13}\text{CH}_3\text{OH} \) and N,N-dimethylaniline was injected into the MAS NMR rotor reactor for 30 min applying the equipment described elsewhere [2b]. A modified reaction time of \(^{13}\text{CH}_3\text{OH}, W/\text{F}_{\text{CH}_3\text{OH}} \) was 20 g h/mol, and the molar \(^{13}\text{CH}_3\text{OH} \) to N,N-dimethylaniline ratio was optimized as 1.2: 1.

\(^{13}\text{C} \) MAS NMR investigations were performed on a Bruker MSL 400 spectrometer at a resonance frequency of 100.6 MHz 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, Texas, USA [2c]. Time-resolved in situ MAS NMR spectra (in steps of 18 min per spectrum) were recorded at reaction temperatures after a \( \pi/2 \) pulse excitation with high-power proton decoupling, a repetition time of 5 s and 200 scans. All spectra were referenced to tetramethyl silane (TMS).

3. Results and discussion

**Formation of N,N,N-trimethylanilinium cations in situ by direct reaction of N,N-dimethylaniline and methanol.** Aniline methylation on acidic zeolite H-Y at 473 K is a step-wise reaction which produces N-methylanilinium, N,N-dimethylanilinium, and N,N,N-trimethylanilinium cations successively [5]. For a better investigation of its further decomposition mechanism, therefore, the formation of pure N,N,N-trimethylanilinium cations is an important prerequisite. Quaternary ammonium cations, which are commonly used as templates during zeolite crystallization, can be conveniently reintroduced inside calcined acidic zeolites by a reaction of tertiary amine and alcohol [8]. Following this approach, we synthesized N,N,N-trimethylanilinium cations on zeolite H-Y by a direct reaction of N,N-dimethylaniline (NNDMA) and methanol (\(^{13}\text{C}-\text{enrichment}) at 473 K according to Scheme 1.

![Scheme 1](image)

Fig. 2a shows the \(^{13}\text{C} \) MAS NMR spectrum recorded at 473 K during the reaction of NNDMA and methanol (period i in Fig. 1). The spectrum is dominated by the signal of N,N,N-trimethylanilinium cations at 58 ppm. The scarcely visible signals at 63.5 and 50 ppm are due to a trace amount of unreacted dimethyl ether (DME) and methanol, both of which are strongly bonded on the catalyst [5]. In contrast to the working catalysts occurring during aniline methylation [5], the working catalyst in the present study is free of
anilinium, N-methylanilinium (39 ppm) and N,N-dimethylanilinium (48 ppm) cations, favoring the further investigation on the decomposition of N,N,N-trimethylanilinium cations alone.

Time-resolved observation of the decomposition process of N,N,N-trimethylanilinium cations by in situ $^{13}$C CF MAS NMR spectroscopy. After the N,N,N-trimethylanilinium cations were prepared on zeolite H-Y, the reactant flow was stopped and time-resolved NMR observation of the decomposition process was achieved (period ii, iii and iv in Fig. 1). We recorded the in situ $^{13}$C MAS NMR spectra (high-power proton decoupling) of the working catalyst at reaction temperatures of 498 to 573 K. Figs. 2b to 2j show representative time-resolved $^{13}$C MAS NMR spectra in absolute intensity mode. At 498 K, the N,N,N-trimethylanilinium cations at 58 ppm decomposed gradually to N,N-dimethylanilinium cations at 48 ppm immediately after stopping the reactant flow (Fig. 2b). Successive decomposition to N-methylanilinium cations at 39 ppm started after ca. 72 min (Fig. 2c), and a trace amount of toluidinium (para-toluidinium at 21 ppm and ortho-toluidinium at 16 ppm) cations were formed as well. While reaction temperatures were increased to 553 K and 573 K, the N,N,N-trimethylanilinium cations continued to decompose (Figs. 2e to 2g) and completely vanished at 573 K after ca. 36 min (Figs. 2i). The signal of the N,N-dimethylanilinium cations at 48 ppm dominated the spectra recorded at 553 K (Figs. 2e to 2g) and decreased gradually at 573 K (Figs. 2h to 2j) which indicates their further transformation and desorption. C-alkylated products, such as para-toluidinium at 21 ppm and ortho-toluidinium at 16 ppm, occurred mainly at temperatures higher than 553 K (Figs. 2e to 2j). At this stage, we cannot figure out exactly how the transformation reactions for toluidinium cations [9] took place due to the system complexity. A deliberate production of N-methylanilinium or N,N-dimethylanilinium cations only and a separate investigation of their further decomposition and transformation are currently going on to understand this issue.

The present work indicates clearly that N,N,N-trimethylanilinium cations alone do decompose at temperatures as low as 498 K. Further work should be done to compare the decomposition rates of N,N,N-trimethylanilinium cations in the presence and absence of aniline to figure out whether the decomposition process can be accelerated by aniline.

4. Conclusion

Aniline methylation by methanol on acidic zeolites involves chemical equilibria among different N-methyl-substituted anilinium cations and adsorption/desorption equilibria as well [5]. The detailed mechanism is possible to be tackled by approaches in which each step can be investigated separately. Therefore, we synthesized the N,N,N-trimethylanilinium cations by a direct reaction of N,N-dimethylaniline and methanol on zeolite H-Y, followed by a time-resolved NMR observation of its decomposition. This attempt identifies that N,N,N-trimethylanilinium cations alone do decompose at temperatures as low as 498 K and provides a detailed view of its successive decomposition process in the temperature range of 498 K to 573 K.

Fig. 2. a) $^{13}$C MAS NMR spectrum recorded at 473 K showing the formation of N, N, N-trimethylanilinium cations via the reaction of N, N-dimethylaniline and methanol on zeolite H-Y. b) to j): representative time-resolved spectra (in absolute intensity mode) obtained at temperatures of 498 K to 573 K during the successive decomposition of N, N, N-trimethylanilinium cations.
Acknowledgments

Financial support by the Deutsche Forschungsgemeinschaft, Volkswagen-Stiftung, Max-Buchner-Forschungsstiftung and Fonds der Chemischen Industrie is gratefully acknowledged.

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