Formation of Methylamines by Reaction of Ammonia with Surface Methoxy Species on Acidic Zeolites

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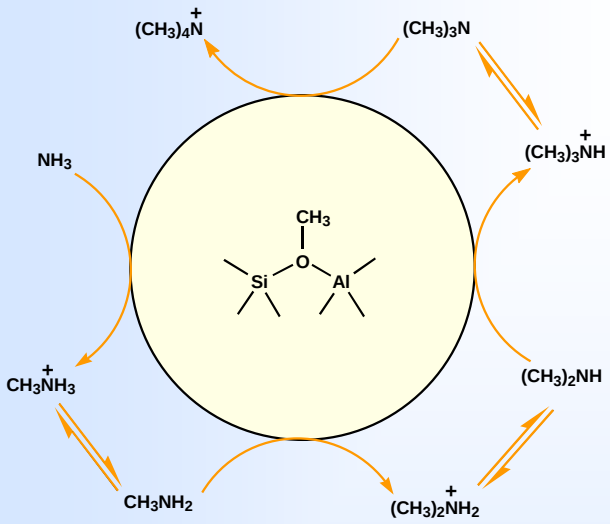
Introduction

The methylation of ammonia by methanol on acidic zeolites has attracted significant interest in recent years [1]. It has been suggested that ammonia and methylamines are preferentially adsorbed on Broensted acid sites due to their higher proton affinities in the gas phase than that of methanol. Therefore, most of the proposed mechanisms assume that the reaction does not involve surface methoxy species [2]. However, the formation of surface methoxy species during aniline methylation on acidic zeolite H-Y has been shown with the application of *in situ* MAS NMR spectroscopy [3]. In this study, the reaction of surface methoxy species and ammonia was studied by ^{13}C MAS NMR spectroscopy [4].

Results and Discussion

As shown in Fig. 1b, upon loading of 200 mbar of NH_3 on methylated zeolite Y (^{13}CH-Y) at room temperature (RT), new signals appear at 26 (CH_3NH_2) and 24 ppm (protonated $CH_3NH_3^+$). After adsorption of 500 mbar of NH_3 on $^{13}CH_3$-Y at RT, additional signals at 34 (protonated $(CH_3)_2NH_2^+$) and 56 ppm ($(CH_3)_4N^+$) become evident. As indicated in Fig. 1d, the signal of $(CH_3)_4N^+$ at 56 ppm survived from hydration, upon which surface methoxy species would not. As shown in Fig. 1d, the broad signal at 50 ppm (Fig. 1c) becomes narrowed after hydration, which indicates the reaction of terminal methoxy species (50 ppm) with water to methanol. The assignments of ^{13}C MAS NMR signals of methylamines are summarized in Tab. 1. The reaction pathways of surface methoxy species and NH_3 on H-Y are depicted in Scheme 2. It is important to note that methylamines and methylammonium cations have previously been observed only after the reaction of CH_3OH and NH_3 on acidic zeolites at temperatures higher than 513 K. According to Figs 1b and 1c, however, the same products are readily formed *via* the reaction of surface methoxy species and NH_3 on H-Y at RT.



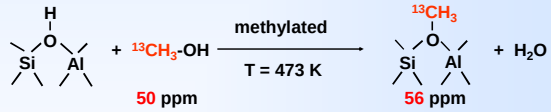
Scheme 2 The reaction pathways of surface methoxy species and NH_3 on H-Y.

Tab.1 Assignments of ^{13}C MAS NMR signals of methylamines and methylammonium cations adsorbed on acidic zeolites.

Chemical Compounds	^{13}C NMR Shift / ppm	
	non-protonated	protonated
monomethylamine, CH_3NH_2	26-27	24-25
dimethylamine, $(CH_3)_2NH$	36-37	34-35
trimethylamine, $(CH_3)_3N$	46-48	43-45
tetramethylammonium, $(CH_3)_4N^+$	-	56-57

Experimental Section

The preparation of surface methoxy species on the acidic zeolite H-Y was performed *via* a vacuum line. The calcined and dehydrated zeolites (300 mg) filled in a glass tube were subjected to methanol at a pressure of 7.5 mbar and at a temperature of 393 K. Thereafter, an evacuation for 6 h at 393 K and additional evacuation for 6 h at 473 K were performed. Subsequently, the methylated catalysts were loaded with NH_3 on a vacuum line and fused in a glass tube for the further use. Before the ^{13}C MAS NMR measurements, the glass tube was opened in a glove box and the catalyst was transferred into a 7 mm MAS NMR rotor. Scheme 1 shows the formation of surface methoxy species (see also Fig. 1a).



Scheme 1 Formation of surface methoxy species.

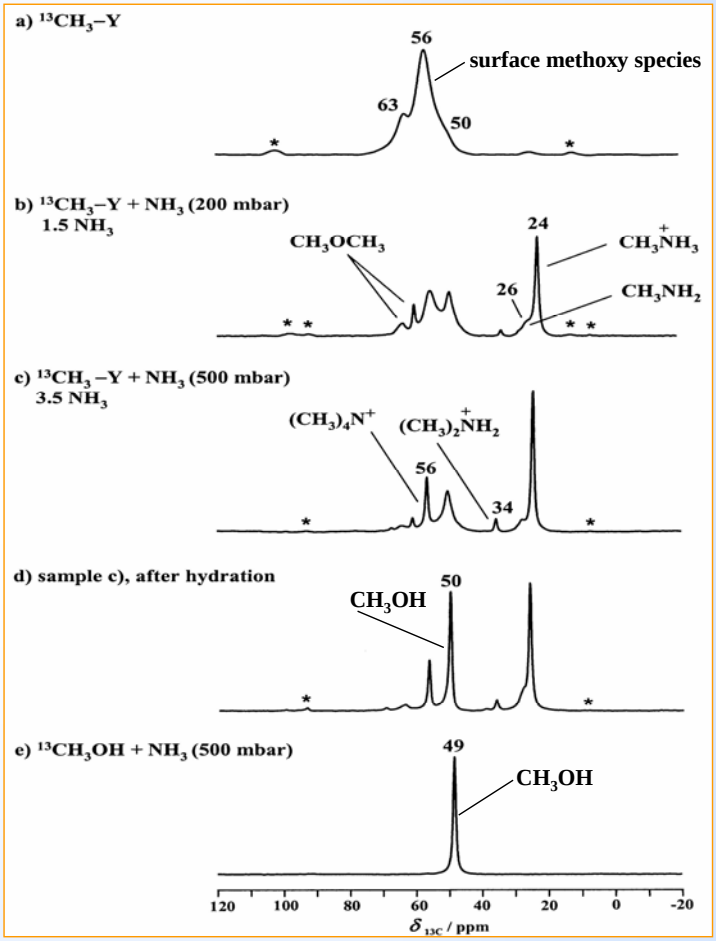


Fig. 1 ^{13}C HPDEC MAS NMR spectra of $^{13}CH_3$-Y (a), after loading of 200 mbar of NH_3 at RT (b), after loading of 500 mbar of NH_3 at RT (c). (d) was recorded after the catalyst sample (c) was fully hydrated at RT. (e) shows the spectrum of H-Y after loading of CH_3OH and NH_3 at RT. Asterisks denote spinning sidebands.

Conclusion

Surface methoxy species react with NH_3 on acidic zeolite H-Y at RT, by which methylamines and methylammonium cations are formed. On the contrary, methanol and NH_3 do not react under the same conditions. The significant difference in reactivity between surface methoxy species and methanol indicates that surface methoxy species are very reactive in methylating amines on acidic zeolites and, if involved, their formation is the rate-determining step during the methylation of amines by methanol on acidic zeolites.

Acknowledgements

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References

1. D.R. Corbin, S. Schwarz, G.C. Sonnichsen, *Catal. Today 37* (1997) 71.
2. V.A. Veefkind, J.A. Lercher, *Appl. Catal. A: General* 181(1999) 245.
3. W. Wang, M. Seiler, I.I. Ivanva, U. Sternberg, J. Weitkamp, M. Hunger, *J. Am. Chem. Soc*. 124 (2002) 7548.
4. Y. Jiang, M. Hunger, W. Wang, *J. Am. Chem. Soc.*,128 (2006) 11679.