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Formation of methylamines by the reaction of ammonia with surface methoxy species on zeolite H-Y and the silicoaluminophosphate H-SAPO-34

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ABSTRACT

In the present work, the amination of surface methoxy species formed by methanol on acidic zeolite H-Y and the silicoaluminophosphate H-SAPO-34 was studied and it was found that these methoxy groups are reactive compounds in amination reactions already at room temperature. The above-mentioned reaction was investigated for different molar ammonia to methoxy ratios (N/C) and at various reaction temperatures by ^{13}C MAS NMR spectroscopy. By a subsequent thermal treatment, it was evidenced that the selectivities towards monomethylamine, dimethylamine, and trimethylamine strongly depend on the reaction temperature. Moreover, due to the different pore architectures of the catalysts under study, H-SAPO-34 has the higher selectivity towards mono- and dimethylamine in comparison with zeolite H-Y. This finding may be an indication that the silicoaluminophosphate H-SAPO-34 is a selective amination catalyst with the additional ability to change the contents of monomethylamine, dimethylamine, and trimethylamine by varying the reaction temperature.

1. INTRODUCTION

Methylamines are important compounds, which can be utilized in a variety of applications including agricultural chemicals, paint industries, water treatment chemicals, as well as, pharmaceuticals, corrosion inhibitors, etc. [1]. The commercial production of methylamines is the amination of methanol *via* a heterogeneously catalyzed process in the vapour phase and in the presence of solid catalysts. The products of this reaction are monomethylamine (MMA), dimethylamine (DMA), and trimethylamine (TMA). Among them, DMA is highly demanded, but the above-mentioned reaction has the lowest selectivity to this product and is relatively invariant in the process conditions. In the thermodynamic equilibrium, TMA is the main product [1]. Therefore, most of the efforts were made to produce preferentially MMA and DMA. Recently, intensive investigations have been performed in an attempt to improve the understanding of the reaction mechanism of the synthesis of methylamines on solid catalysts [1]. It has been suggested that ammonia and methylamines are preferentially adsorbed on Brønsted acid sites due to their higher proton affinities in the gas phase in comparison with methanol. Therefore, most of the proposed mechanisms assume that the contribution of surface methoxy species in the amination reaction is negligible [2]. However, the existence of surface methoxy species has been experimentally observed by *in situ* IR spectroscopy during the reaction of ammonia and methanol on acidic zeolite H-ZSM-5 [3]. In addition, the

formation of surface methoxy species during the methylation of aniline on acidic zeolite H-Y has been evidenced by *in situ* MAS NMR spectroscopy [4].

A number of groups has investigated the heterogeneously catalyzed amination of methanol on faujasite zeolites, e.g., on H-Y, Na-Y, Na-X, and Ca-X [8-10]. Using ^{13}C MAS NMR spectroscopy, Ernst and Pfeifer [11] observed the products of the synthesis of methylamines on H-mordenite, H-ZSM-5, and amorphous alumina at 548 K. In our recent work [5], the reaction of ammonia with surface methoxy species on acidic zeolite H-Y was studied by ^{13}C MAS NMR spectroscopy. It was found that ammonia react with surface methoxy species readily at room temperature leading to the formation of methylamines and methylammonium cations. In the present contribution, the effect of the molar ratio of ammonia molecules to methoxy groups (N/C), the reaction temperature, and the pore size of acidic zeolites on the methylamine formation was studied. Furthermore, the product selectivities of zeolite H-Y and the silicoaluminophosphate H-SAPO-34 for the reaction of ammonia with surface methoxy species under different conditions are compared by ^{13}C MAS NMR spectroscopy. The application of this spectroscopic method allows the observation of reactants adsorbed and formed on the zeolite catalysts and, therefore, provides insight into the mechanism of this heterogeneously catalyzed reaction.

2. EXPERIMENTAL PART

2.1 Materials

Zeolite Na-Y (n_{Si}/n_{Al} = 2.7) was purchased from Degussa AG, Hanau, Germany. Zeolite NH_4-Y was prepared by a fourfold ion exchange of zeolite Na-Y at 353 K in a 1.0 M aqueous solution of NH_4NO_3. After the ion-exchange degree of 90 % was reached, the material was washed in demineralized water and dried at room temperature. Subsequently, the zeolite NH_4-Y was heated in vacuum with a rate of 20 K/h up to the final temperature of 723 K. There, the material was calcined at a pressure below 10^{-2} mbar for 12 h leading to zeolite H-Y. The silicoaluminophosphate H-SAPO-34 with an $n_{Si}/(n_{Al}+n_{Si}+n_P)$ ratio of 0.11 was prepared according to the recipe described in the literature [6] for the synthesis of Ni-SAPO-34, but omitting the nickel salt. To remove the template, the as-synthesized material was heated with a rate of 60 K/h to 873 K in dry nitrogen and calcined at this temperature for 6 h in synthetic air (20 vol. % oxygen, 60 l/h). Subsequently, the sample was subjected to an additional calcination in vacuum with a heating rate of 20 K/h up to the final temperature of 673 K. At this temperature, the material was calcined at a pressure below 10^{-2} mbar for 12 h leading to the silicoaluminophosphate H-SAPO-34. The dehydrated catalysts were sealed in glass tubes until their further use. All catalysts were characterized by AES-ICP, XRD, and solid-state ^{1}H, ^{27}Al, and ^{29}Si MAS NMR spectroscopy. The results indicated that the materials obtained after cation exchange and calcination were highly crystalline and intact. ^{13}C-enriched methanol (^{13}C-enrichment of 99%) was purchased from Cambridge Isotopes.

2.2. Sample preparation

The *in situ* preparation of surface methoxy species was performed by adsorption of ^{13}C-enriched methanol (7.5 mbar) on the calcined zeolites at 393 K, evacuation for 6 h at 393 K, and subsequent heating for 6 h at 473 K [7]. By ^{13}C spinning-counting experiments, the coverage of the catalysts with methoxy species was determined to *ca.* 0.6 surface species per acid site for zeolite H-Y and *ca.* 0.4 surface species per acid site for the silicoaluminophosphate H-SAPO-34. The methylated catalysts (*ca.* 300 mg) were loaded with dried (zeolite Na-A) ammonia using a vacuum line and, subsequently fused in glass tubes for

further thermal treatments. After heating for 30 min, the glass tubes were opened in a glove box and the catalysts were transferred into a 7 mm MAS NMR rotor for solid-state MAS NMR measurements.

2.3. ^{13}C MAS NMR experiments

^{13}C MAS NMR investigations were performed with a 7 mm Bruker MAS NMR probe on a Bruker MSL-400 spectrometer at the resonance frequency of 100.6 MHz. High power proton decoupling (HPDEC) MAS NMR spectra were recorded after an excitation with of the ^{13}C nuclei with a $\pi/2$ pulse of 4 µs and using a repetition time of 5 s. The ^{13}C spin-counting MAS NMR experiments were performed with a repetition time of 30 s and an external intensity standard (dehydrated zeolite H-Y loaded with $^{13}CH_3OH$). Sample spinning rates of *ca.* 3-4 kHz were applied. All ^{13}C MAS NMR spectra are referenced to tetramethylsilane (TMS).

3. RESULTS AND DISCUSSION

3.1. Amination of surface methoxy species on zeolite H-Y

Fig. 1a shows the ^{13}C HPDEC MAS NMR spectrum recorded directly after the *in situ* preparation of surface methoxy species ($^{13}CH_3$-Y) on zeolite H-Y by conversion of pure ^{13}C-enriched methanol. The dominating signal at 56 ppm with spinning sidebands is due to surface methoxy species. The weak shoulder at ca. 63 ppm originates from side-on adsorbed dimethylether (DME), while the shoulder at 50 ppm is caused by terminal methoxy species ($SiOCH_3$) [7]. In Figs. 1b-1e, the ^{13}C HPDEC MAS NMR spectra of methylated zeolite Y (denoted as $^{13}CH_3$-Y) recorded after loading with ammonia are given. Upon loading of *ca.* 1 molecule ammonia per 2 surface methoxy species on zeolite CH_3-Y (corresponding to N/C = 1 : 2) at room temperature (Fig. 1b), the samples were heated at 353 to 473 K for 30 min (Figs. 1c - 1e). All spectra are dominated by the signal of surface methoxy species at 56 ppm, which indicates that the ammonia molecules do not react with the surface methoxy species on acidic zeolite H-Y at this ammonia coverage.

Figs. 1f-1d show the ^{13}C HPDEC MAS NMR spectra of zeolite $^{13}CH_3$-Y obtained after adsorption of ammonia with the molar ammonia to methoxy ratio of N/C = 3 : 1 and upon heating at 353 to 473 K. Already at room temperature (Fig. 1f), new signals appeared at 26 and 24 ppm, which are assigned to monomethylamine, CH_3NH_2, and protonated monomethylamine, $CH_3NH_3^+$, respectively [11, 12]. The additional signal at 34 ppm is due to protonated dimethylamine, $(CH_3)_2NH_2^+$ [11, 12]. The slightly larger signal at 50 ppm is due to terminal methoxy species ($SiOCH_3$). Upon heating of the ammonia-loaded zeolite $^{13}CH_3$-Y at 353 K (Fig. 1g), the signal at 50 ppm obtained a weak high-field shoulder at *ca.* 48 ppm, which strongly increased upon heating at 413 and 473 K (Figs. 1h and 1i). According to former studies [11, 12], the signal at 48 ppm is assigned to trimethylamine, $(CH_3)_3N$. Upon thermal treatment, the terminal methoxy species at 50 ppm were completely consumed, which indicates that also these methoxy species react with ammonia at the loading of N/C = 3 : 1. In addition, the selectivity of zeolite H-Y to trimethylamine was extremely enhanced by increasing of reaction temperature.

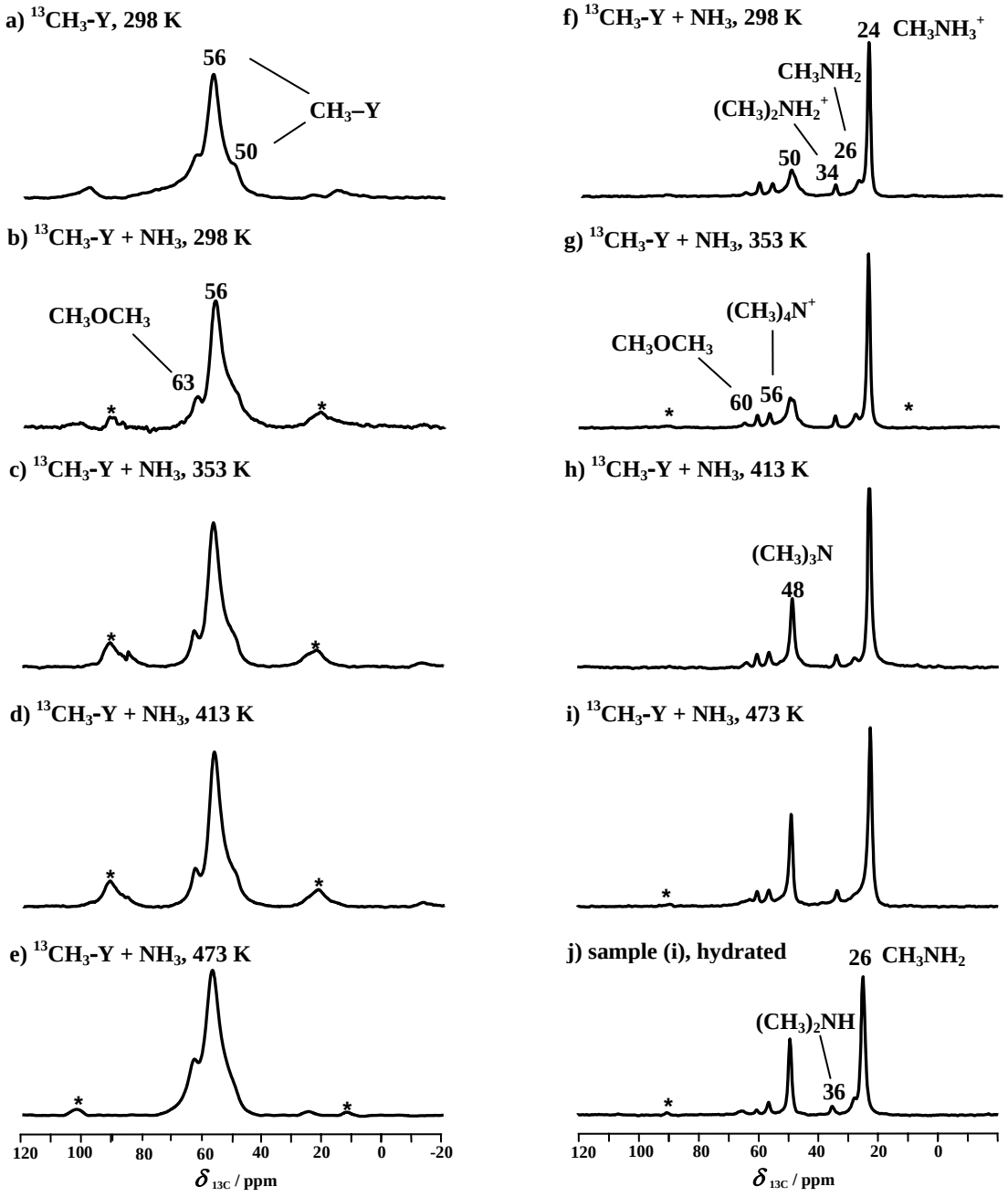

Fig. 1. ^{13}C HPDEC MAS NMR spectra of the methylated zeolite H-Y (a) recorded after loading of ammonia with different molar ammonia to methoxy ratios ((b)-(e): N/C = 1 : 2; (d)-(i): N/C = 3 : 1) at 298 K (b, f), 353 K (c, g), 413 K (d, h) and 473 K (e, i). The ^{13}C HPDEC MAS NMR spectrum in (j) was recorded after full hydration of the catalyst sample used for (i). Asterisks denote spinning sidebands.

Interestingly, there is only a negligible effect of the thermal treatment on the weak signals at *ca.* 56 and 60 ppm (Figs. 1f - 1i). The latter signal, which has a weak low-field hump at *ca.* 63 ppm, is caused by DME adsorbed in different states [7]. The signal at 56 ppm is much narrower in comparison with the signals of methoxy groups occurring at the same chemical shift (see Figs. 1a - 1 e). In addition, the narrow signal at 56 ppm survived upon

hydration (Fig. 1j), which is not typical for surface methoxy groups [7]. Therefore, the narrow signal at 56 ppm may be caused by tetramethylammonium cations, $(CH_3)_4N^+$ [11-13]. Upon hydration of the ammonia-loaded zeolite $^{13}CH_3$-Y, a low-field shift of the signals at 24 and 34 ppm by *ca.* 2 ppm occurred. This low-field shift indicates that the hydration of the catalyst converts mono- and dimethylammonium cations into non-protonated mono- and dimethylamines. The assignments of the ^{13}C MAS NMR signals of methylamines and methylammonium cations on acidic zeolites used in the present study are collected in Table 1.

Table 1 Assignments of ^{13}C MAS NMR signals of methylamines and methylammonium cations adsorbed on acidic zeolites [11, 12]

	^{13}C NMR shift / ppm	
	non-protonated	protonated
monomethylamine	26-27	24-25
dimethylamine	36-37	34-35
trimethylamine	46-48	43-45
tetramethylammonium		56-57

3.2. Amination of surface methoxy species on the silicoaluminophosphate H-SAPO-34

The silicoaluminophosphate H-SAPO-34 is characterized by a lower number of bridging OH groups with a lower acid strength in comparison with zeolite H-Y. Nevertheless, H-SAPO-34 is an interesting catalyst for the methylamine synthesis [14-16]. While Olson *et al.* [15] found that the H-SAPO-34 is less active in the methylamine synthesis than aluminosilicate-type catalysts, other authors observed a high selectivity towards smaller methylamines. In 1998, Thursfield *et al.* [12] performed first ^{13}C and ^{15}N MAS NMR studies of the conversion of ammonia and methanol on H-SAPO-34. The present ^{13}C MAS NMR investigation focuses on the amination of surface methoxy species on H-SAPO-34.

Fig. 2 shows the ^{13}C HPDEC MAS NMR spectra of methylated silicoaluminophosphate H-SAPO-34 (Fig. 2a), loaded with ammonia according to N/C = 3 : 1 (Fig. 2b), and heated at 353 to 473 K (Figs. 2c - 2e). In Fig. 2f, the ^{13}C HPDEC MAS NMR spectrum of ammonia-loaded CH_3-SAPO-34 recorded upon heating at 473 K and hydration is given.

The spectrum of $^{13}CH_3$-SAPO-34 recorded before loading with ammonia is dominated by the signal of surface methoxy species at *ca.* 56 ppm. Immediately after adsorption of *ca.* 3 ammonia molecules per surface methoxy species, signals at 24 and 34 ppm due to protonated monomethylamine, $CH_3NH_3^+$, and protonated dimethylamine, $(CH_3)_2NH_2^+$, respectively, occurred. In addition, a weak signal of protonated trimethylamine appeared at *ca.* 44 ppm. Upon heating of the ammonia-loaded $^{13}CH_3$-SAPO-34 at temperatures between 353 and 473 K, further formation of protonated trimethylamine, $(CH_3)_3NH^+$, trimethylamine, $(CH_3)_3N$, and tetramethylammonium cations, $(CH_3)_4N^+$, was evidenced by the increase of the signals at 44, 48, and 56 ppm, respectively.

Finally, upon hydration of the ammonia-loaded $^{13}CH_3$-SAPO-34, heated at 473 K, the protonated monomethylamine and protonated dimethylamine are converted into their non-protonated state. As found for zeolite H-Y, this was accompanied by a low-field shift of the signals at 24 and 34 ppm to 26 and 36 ppm, respectively.

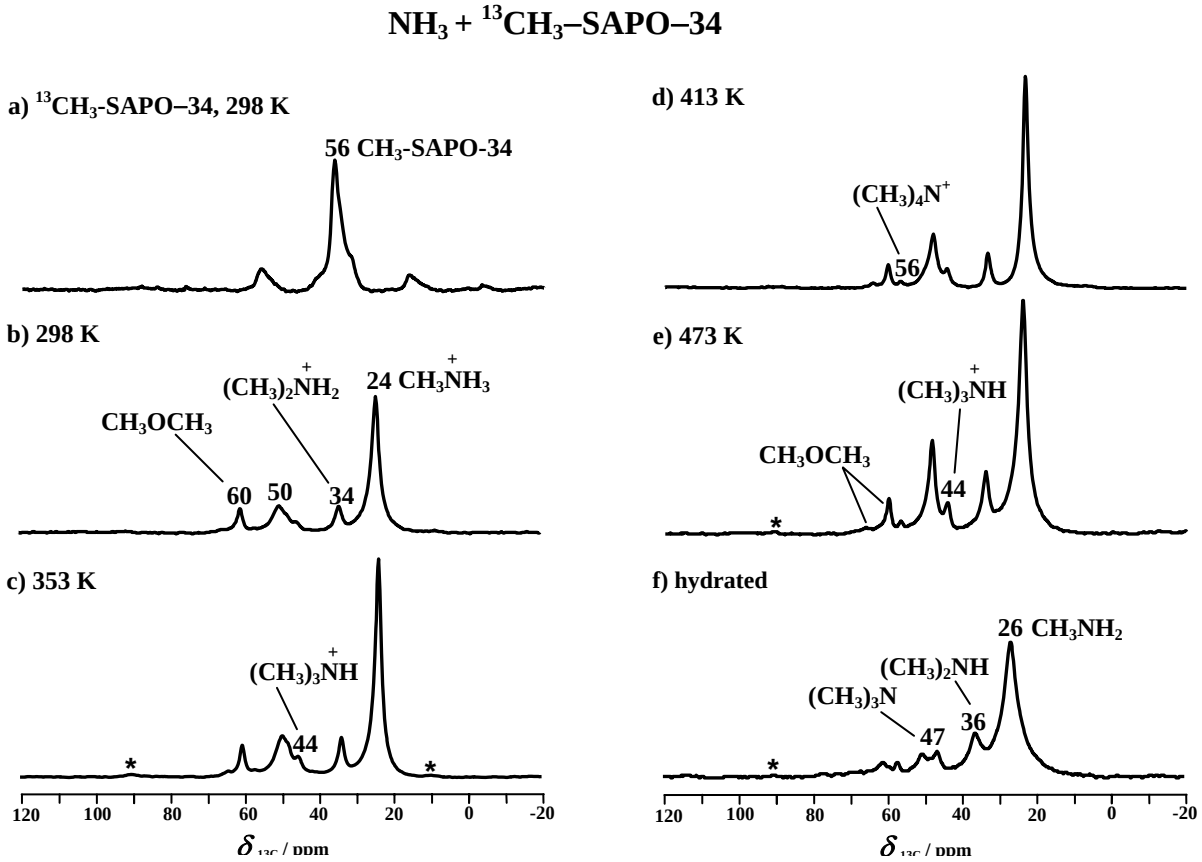

Fig. 2. ^{13}C HPDEC MAS NMR spectra of the methylated silicoaluminophosphate H-SAPO-34 (a) recorded after loading of ammonia with the molar ammonia to methoxy ratio of N/C = 3 : 1 at 298 K (b), 353 K (c), 413 K (d), and 473 K (e). The ^{13}C HPDEC MAS NMR spectrum in (f) was recorded after full hydration of the catalyst sample used for (e). Asterisks denote spinning sidebands.

Generally, it is important to note that the signals of highly methylated amines at 44 to 56 ppm are weaker in the spectra of the silicoaluminophosphate H-SAPO-34 in comparison with those obtained for zeolite H-Y under same reaction conditions. This finding could be explained by the lower pore and cage size SAPO-34 in comparison with zeolite H-Y. The silicoaluminophosphate SAPO-34 is characterized by the chabasite (CHA) structure with cages of *ca.* 1 nm diameter that are interconnected *via* 8-ring windows with a diameter of 0.38 nm [17]. Some fairly large molecules, such as TMA (0.39 nm × 0.54 nm × 0.61 nm) [1, 18], can fit in the cages of H-SAPO-34, but they cannot migrate from cage to cage. Therefore, the distribution of the reaction products tends towards the smaller MMA (0.39 nm × 0.39 nm × 0.44 nm) and DMA (0.39 nm × 0.47 nm × 0.60 nm) [1, 18]. Hence, H-SAPO-34 is more selective for the synthesis MMA and DMA in comparison with zeolite H-Y characterized by the faujasite (FAU) structure with 12-ring windows (diameter ca. 0.74 nm) [1, 18]. In addition, the present ^{13}C MAS NMR investigation indicates that the methylation level of the amines is a function of the reaction temperature. These findings indicate that the silicoaluminophosphate H-SAPO-34 is an amination catalyst with the flexibility of varying the ratio of the different methylamines by changing the reaction temperature.

4. CONCLUSIONS

In this contribution, ^{13}C MAS NMR spectroscopy is utilized to study the amination of surface methoxy species on zeolite H-Y and the silicoaluminophosphate H-SAPO-34 under comparable reaction conditions. It was found that, at a molar ammonia to methoxy ratio of N/C = 1 : 2, surface methoxy species on zeolite H-Y do not react with ammonia even up to reaction temperatures of 473 K. At N/C = 3 : 1, however, surface methoxy species formed on zeolite H-Y and the silicoaluminophosphate H-SAPO-34 react readily with ammonia at room temperature leading to the formation of methylamines and methylammonium cations. By subsequent thermal treatment up to 473 K, it was evidenced that the selectivities towards monomethylamine, dimethylamine, and trimethylamine were varying, which strongly depended on the amination temperature. Moreover, due to the smaller pore and cage sizes of the silicoaluminophosphate H-SAPO-34 in comparison with zeolite H-Y, the former catalyst shows a lower selectivity towards trimethylamine. These findings indicate that H-SAPO-34 is selective for the synthesis of mono- and dimethylamine with the additional advantage of changing the ratio of different methylamines by varying the reaction temperature.

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