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Synthesis of Methylamines Studied by *in Situ* Carbon-13 MAS NMR Spectroscopy

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Solid-state carbon-13 nuclear magnetic resonance (NMR) measurements under magic angle spinning conditions (MAS NMR) have been performed on alumina, NaZSM-5, and various catalysts of mordenite type loaded with ammonia and methanol. The samples were contained in sealed glass ampoules and spectra were measured at room temperature as a function of increasing pretreatment temperature. An analysis of the MAS NMR spectra provides not only information about the activity and deactivation of the catalysts but also quantitative results for the concentration of the reaction products (selectivity of the catalyst). In addition to the well-known fact that the values for the concentration of the reaction products c_e calculated under the assumption of thermodynamic equilibrium may be different from the values c_f measured under flowing gas conditions due to shape selectivity, it is shown in the present study that they are also different from the values c_s derived from MAS NMR measurements performed on sealed samples if adsorption complexes are formed by at least one of the reaction products. © 1992 Academic Press, Inc.

INTRODUCTION

The study of solid catalysts and of heterogeneous catalytic reactions by NMR spectroscopy has received much attention due to the unique possibilities of the various NMR methods which can be applied (*1*). Using the chemical shift of the various lines of an NMR spectrum as a fingerprint, the appearance of organic compounds can be observed quantitatively during a catalytic reaction by a cyclic heating of the sealed sample to increasing temperatures (pretreatment temperatures) while the NMR measurements are performed at lower temperatures (in most cases room temperature) at which the reaction is frozen. This possibility was demonstrated for the first time by Michel *et al.* (*2*) (see also Ref. (*3*), p. 451) in a study of the isomerization of but-1-ene adsorbed in zeolites NaCaY. This method has subsequently found widespread application (*3, 4*). By use of the MAS (magic angle spinning) technique introduced by Andrew *et al.* (*5*), a significant enhancement of the resolution and hence of the sensitivity toward ascertaining reaction products could be achieved. *In Situ* MAS NMR experiments of this kind were performed on sealed samples either by cyclic heating of the sample between ambient and higher temperatures (outside of the spectrometer) as described above (*6–8*) or by variable-temperature measurements (*9–11*).

In the following we present results of a study of the first type in order to derive quantitative information about catalytic properties and deactivation of various catalysts in the reaction of methanol (CH_3OH) and ammonia (NH_3) to monomethylamine (MMA), dimethylamine (DMA), and trimethylamine (TMA).

METHODS

Samples

The following catalysts have been studied: K1: sodium mordenite (Si/Al = 5); K2: sodium ZSM-5 zeolite (Si/Al = 15); K3: 20% proton-exchanged sodium mordenite K1; K4: amorphous alumina; K5: 65% K1 + 35% K4 as binder; K6: 65% K3 + 35% K4 as binder.

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All samples were prepared under the conditions of shallow-bed pretreatment: ca. 50 mg of a catalyst was pumped and heated at 10 K per h to the activation temperature of 400°C where the catalyst was kept under a pressure below 10^{-2} Pa for 24 h. Then the catalyst was cooled, loaded under vacuum at first with (70 ± 10) μmol methanol enriched to 99% in ^{13}C and after that with (50 ± 10) μmol ammonia and sealed. The concentration of ammonia corresponds to an NH_3/Al ratio of about 1/3, 1, 1, and 1/20 for K1, K2, K3, and K4, respectively.

NMR measurements

All ^{13}C MAS NMR measurements, combined in most cases with the cross-polarization (CP) technique to enhance the sensitivity (*12*), were performed on a commercial NMR spectrometer (Bruker MSL 300) at 74.5 MHz. Through the use of home-made plastic rotors a convenient and stable measurement of powdered samples contained in sealed glass tubes could be realized at a spinning rate of ca. 2 kHz.

RESULTS

Figure 1 shows the ^{13}C CP NMR spectra of an activated sodium mordenite loaded with methanol and ammonia pretreated at 275°C for 1 h: (A) under MAS conditions (f_{rot} = 2 kHz) and (B) for the static sample. Spectrum (A) demonstrates clearly the enhancement of resolution achieved by the use of the MAS technique. The assignment of the five significant lines is: MMA (26.2 ppm), DMA (34.2 ppm), TMA (44.8 ppm), $(CH_3)_4N^+$ (terамethylammonium ions, 55.8 ppm), and DME (dimethylether, 59.6 ppm) in the order of increasing values of the chemical shift. Between the signals of TMA and $(CH_3)_4N^+$ a small line due to residual methanol (49.7 ppm) can be seen. The assignment of the fourth line to $(CH_3)_4N^+$ follows not only from its position in the spectrum but also from the splitting of this line into a quartet if the proton decoupling is released (cf. Fig. 1C). In principle it is possible to derive the same information also from two-dimensional *J*-resolved MAS NMR spectra (*8*).

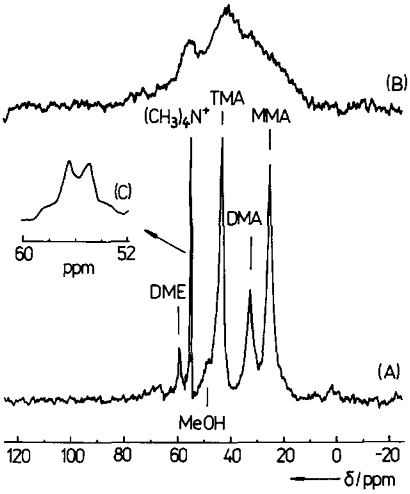

FIG. 1. ^{13}C CP NMR spectra of an activated sodium mordenite loaded with methanol and ammonia and pretreated at 275°C for 1 h: (A) under MAS conditions (f_{rot} = 2 kHz), (B) for the static sample, (C) the ^{13}C MAS NMR signal of the tetramethylammonium ions ($(CH_3)_4N^+$) without proton decoupling.

In Fig. 2, ^{13}C CP MAS NMR spectra are shown for the same system as a function of the pretreatment temperature at which the sample was kept for 30 min. From these spectra it is possible to derive the values for the relative concentrations of the methylamines (MMA, DMA, and TMA) in dependence on the pretreatment temperature, because the same relative intensities have been measured using spectra without cross-polarization enhancement (see Discussion).

Figure 3 shows ^{13}C CP MAS NMR spectra of the activated proton-exchanged sodium mordenite with 35% amorphous alumina as binder, loaded with methanol and ammonia, as a function of the pretreatment temperature and of the pretreatment time. At about 400°C the decomposition of the methylamines starts, giving rise to new lines in the aliphatic region of the ^{13}C NMR spectrum, and with increasing pretreatment time, also in the aromatic region due to coking of the catalyst (Fig. 4).

During the reaction of methanol with am-

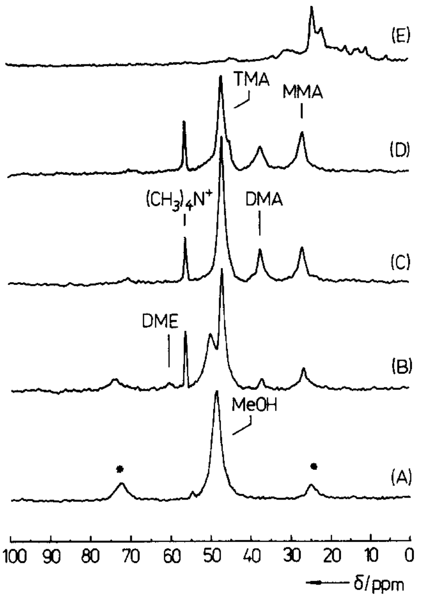

FIG. 2. ^{13}C CP MAS NMR spectra of an activated sodium mordenite loaded with methanol and ammonia, as a function of the pretreatment temperature at which the sample was kept for 30 min: (A) 275°C, (B) 300°C, (C) 350°C, (D) 400°C, (E) 450°C. The asterisks (*) denote spinning side bands.

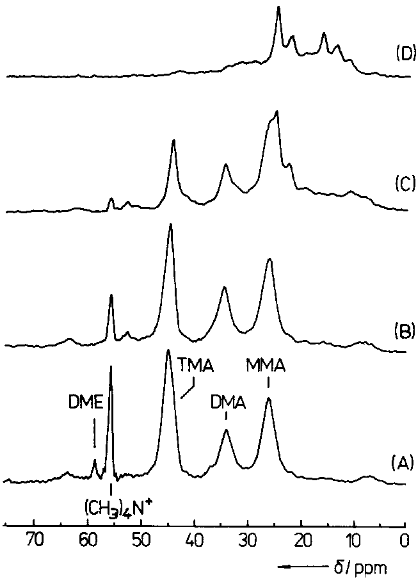

FIG. 3. ^{13}C CP MAS NMR spectra of the activated catalyst K6 (20% proton-exchanged sodium mordenite + 35% amorphous alumina as binder), loaded with methanol and ammonia, as a function of pretreatment temperature and pretreatment time: (A) 300°C and 0.5 h, (B) 300°C and 140 h, (C) 400°C and 0.5 h, (D) 400°C and 4 h.

monia, water is generated (cf. Discussion) so that at higher pretreatment temperatures conditions may prevail which are similar to a hydrothermal treatment of the catalyst. On the other hand, it is well known that such a treatment may lead to a dealumination of the catalyst framework (*13–16*), which should be visible (*3*) in the ^{29}Si MAS NMR spectra of the catalysts. An inspection of Fig. 5 shows, however, that a dealumination can be excluded.

DISCUSSION

From the NMR spectra information can be derived on (i) the activity of the catalyst, (ii) the concentration of the reaction products (selectivity), and (iii) the deactivation of the catalyst.

(*i*) *Activity of the catalyst.* The temperature of the onset of the catalytic reaction can be taken as a measure of the activity of the catalyst (*2*). For the system under study the

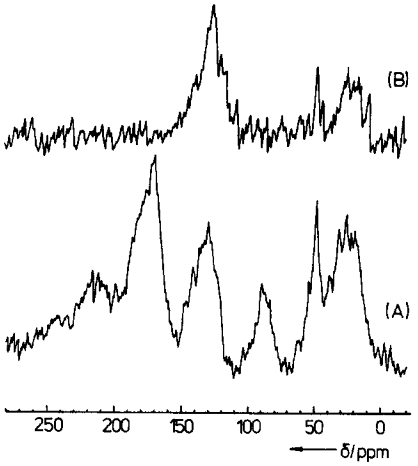

FIG. 4. ^{13}C NMR spectra of the activated catalyst K5 (sodium mordenite + 35% amorphous alumina as binder) loaded with methanol and ammonia and pretreated at 400°C for 4 h: (A) ^{13}C CP MAS NMR spectrum, 40.000 scans, (B) ^{13}C CP TOSS MAS NMR spectrum, 10.000 scans.

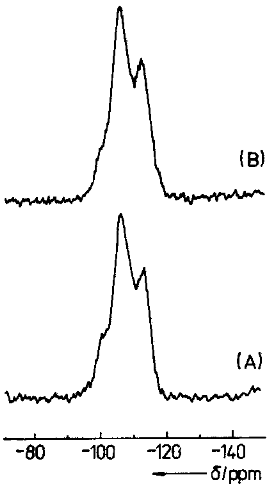

FIG. 5. ^{29}Si MAS NMR spectra of the catalyst K5 (sodium mordenite + 35% amorphous alumina as binder): (A) ^{29}Si MAS NMR spectrum of the fresh catalyst, (B) ^{29}Si MAS NMR spectrum of the activated catalyst loaded with methanol and ammonia and pretreated at 400°C for 4 h.

reaction starts in the case of the acidic catalyst K3, K4, K5, K6 at a temperature of about 250°C, and in the case of the nonacidic catalysts K1 and K2 at about 300°C. This difference can be explained by the existence of Brønsted acid sites in the proton-exchanged mordenites as well as in alumina, where these sites are formed by the interaction of water and Lewis-acid sites.

(*ii*) *Relative concentration of the reaction products.* From the intensities of the lines, values for the relative concentration of the corresponding reaction products can be derived. This, however, is only valid if the cross polarization technique does not mask the real relative intensities (*17*), which holds for methanol and the amines (MMA, DMA, and TMA) in all samples under study. Only for the tetramethylammonium ions has a significant deviation been observed which may be ascribed to the spherical shape of these ions allowing an isotropic reorientation. Values for the relative concentration of the amines (the ratio of the signal intensity for a given amine to the sum of MMA, DMA, and TMA) derived from the ^{13}C CP MAS NMR spectra for the nonacidic catalysts K1 and K2 at a pretreatment temperature of 400°C as well as those computed for the thermodynamic equilibrium (*20*) are given in Table 1. Within the limits of accuracy of the NMR measurements a reasonable agreement can be observed. In contrast, for the acidic catalysts K3, K4, K5, K6 pretreated at the same temperature, the relative concentration of MMA is strongly enhanced (cf. Table 2). This result can be explained by the formation of strong adsorption complexes between MMA and the Brønsted acid sites of the catalysts. The tripod structure of these complexes (*21*) is based on hydrogen bond formation between the Brønsted acid site and the lone electron pair of MMA as well as between the N–H's and suitably located nearby bridging oxygens of the catalyst framework. For DMA and TMA only bipod and monopod structures result, with a corresponding smaller stability.

Quantitatively the values collected in Table 2 can be explained as follows. At pretreatment temperatures above 300°C, the ^{13}C CP MAS NMR spectra reveal a total consumption of methanol for the acid catalysts. Assuming that this holds also for ammonia which is reasonable due to its preferential adsorption at the Brønsted acid sites (*22, 23*) the following equation must be ful-

TABLE 1

Values for the Relative Concentrations of Amines MMA, DMA, and TMA Derived from the ^{13}C CP MAS NMR Spectra for the Nonacidic Catalysts K1 and K2 at a Pretreatment Temperature of 400°C as well as those Computed for Thermodynamic Equilibrium (*13*)

Methylamine	Relative concentration (%)		
	From NMR Catalyst		For thermodynamic equilibrium (*13*)
	K1	K2	
MMA	40	25	22
DMA	20	23	32
TMA	36	49	45

TABLE 2

Values for the Relative Concentrations of Amines MMA, DMA, and TMA: (i) Derived from the ^{13}C CP MAS NMR Spectra for the Acidic Catalysts K3, K4, K5, K6 at a Pretreatment Temperature of 400°C, (ii) Computed for the Thermodynamic Equilibrium (*13*), and (iii) Computed for the Case of Total Consumption of CH_3OH

Methylamine	Relative concentration (%)					
	From NMR Catalyst				For thermodynamic equilibrium (*13*)	Value for total consumption of methanol
	K3	K4	K5	K6		
MMA	67	71	66	60	22	50 ... 75
DMA	18	17	20	23	32	50 ... 0
TMA	15	12	14	17	45	0 ... 25

filled for a C/N ratio of 1.5 (corresponding to the loading of the catalysts chosen in the present experiments):

$$1.5\ CH_3OH + NH_3 \rightarrow p_m CH_3NH_2 + p_d(CH_3)_2NH + p_t(CH_3)_3N + p_w H_2O. \quad (1)$$

In this equation, the existence of tetramethylammonium ions (see below) has been neglected due to their small concentration.

Considering the concentrations of the nuclei N, C, O, and H separately, from Eq. (1) it follows that

$$\begin{aligned} p_d &= 1.5 - 2p_m \\ p_t &= -0.5 + p_m. \end{aligned} \quad (2)$$

With the condition that the values of p_m, p_d, and p_t must be positive and not greater than 1, we find

$$\begin{aligned} 0.5 &\le p_m \le 0.75 \\ 0 &\le p_d \le 0.5 \\ 0 &\le p_t \le 0.25, \end{aligned} \quad (3)$$

which is in agreement with the experimental results presented in Table 2. *The essential point here is that due to the formation of adsorption complexes, the equilibrium of the methylamine synthesis (see Eq. (1)) is shifted to the right so that the values for the concentration of the reaction products measured with sealed samples (c_s) must be different from the values (c_e) calculated un-*

TABLE 3

Values for the ^{13}C Chemical Shifts of Amines MMA, DMA, and TMA Adsorbed on Acidic (K3, K4, K5, K6) and Nonacidic (K1, K2) Catalysts in ppm with Respect to TMS

Methylamine	^{13}C chemical shift (ppm)		
	Adsorbed on acidic catalysts K3, K4, K5, K6	Adsorbed on nonacidic catalysts K1, K2	In liquids
MMA	25.3–25.8	26.6–27.0	28.0
DMA	32.2–34.4	35.8–37.2	38.2
TMA	43.0–45.4	46.2–46.7	47.1

der the assumption of a thermodynamic equilibrium between methanol, ammonia and the reaction products in the gaseous state. As is well known, due to shape selectivity the latter values (c_e) will be also different in general from the values (c_f) measured under flowing gas conditions.

The existence of the amine-Brønsted-acid-site complexes in the case of the acidic catalysts (K3–K6) is also reflected by the differences of the chemical shifts of the amines MMA, DMA, and TMA with respect to the nonacidic catalysts (K1, K2). Values are collected in Table 3. To confirm this picture of adsorption complexes, proton MAS NMR studies are in progress.

It is interesting to note that the ^{13}C MAS NMR spectra of the sealed samples reveal the formation of tetramethylammonium ions during the catalytic reaction of methanol and ammonia. The relative concentration of these ions is in the range of 1 to 5% and correlates with the relative concentration of TMA so that the following equilibrium can be assumed:

$$(CH_3)_3N + CH_3OH \rightleftharpoons (CH_3)_4N^+OH^-. \quad (4)$$

(*iii*) *Amine decomposition and catalyst deactivation.* The onset of the amine decomposition and the nature of the decomposition products (carbonaceous deposits (*18, 19*)) characterize the deactivation of the catalyst. Figure 3 shows that the amine decomposition starts only at temperatures above 300°C, while the latter temperature is quite sufficient for the signal of methanol to vanish completely and of the signals of the amines MMA, DMA, and TMA to appear (Figs. 3A, 3B). At 400°C the amines start to be decomposed, as can be seen from the signals in the aliphatic region of the ^{13}C CP MAS NMR spectra (Figs. 3C, 3D). With increasing pretreatment time, additional signals appear in the aromatic region due to coking (deactivation) of the catalyst (Fig. 5A). The ^{13}C CP MAS NMR spectrum corresponding to Fig. 4A but with total sideband suppression (TOSS) is shown in Fig. 4B. This is a proof that the lines denoted by asterisks in Fig. 4A are spinning sidebands.

CONCLUSIONS

Carbon-13 MAS NMR spectroscopy performed on sealed samples has been proven to be a powerful method to characterize catalytic processes inside the pores of a zeolite catalyst. An analysis of the MAS NMR spectra provides not only information about the activity and deactivation of the catalyst but also quantitative results for the concentration of the reaction products, i.e., the selectivity of the catalyst. However, these concentrations can be significantly different from values calculated under the assumption of thermodynamic equilibrium if adsorption complexes are formed by at least one of the reaction products.

REFERENCES

1. Pfeifer, H., *Colloids Surf.* **45,** 1 (1990).
2. Michel, D., Meiler, W., and Pfeifer, H., *J. Mol. Catal.* **1,** 85 (1975/76).
3. Engelhardt, G., and Michel, D., "High-Resolution Solid-State NMR of Silicates and Zeolites." Wiley, New York, 1987.
4. Pfeifer, H., Meiler, W., and Deininger, D. *Ann. Rep. NMR Spectrosc.* **15,** 291 (1983).
5. Andrew, E. R., Bradbury, A., and Eades, R. G., *Nature* (*London*) **182,** 1659 (1958).
6. Anderson, M. W., and Klinowski, J., *Nature* (*London*) **339,** 200 (1989).
7. Anderson, M. W., and Klinowski, J., *J. Am. Chem. Soc.* **112,** 10 (1990).
8. Anderson, M. W., and Klinowski, J., *Chem. Phys. Lett.* **172,** 275 (1990).
9. Haw, J. F., and Speed, J. A., *J. Magn. Reson.* **78,** 344 (1988).
10. Haw, J. F., Richardson, B. R., Oshiro, J. S., Lazo, N. D., and Speed, J. A., *J. Am. Chem. Soc.* **111,** 2052 (1989).
11. White, J. L., Lazo, N. D., Richardson, B. R., and Haw, J. F., *J. Catal.* **125,** 260 (1990).
12. Mehring, M., "High Resolution NMR in Solids." Springer-Verlag, Berlin, 1983.
13. Scherzer, J., *Am. Chem. Soc. Symp. Ser.* **248,** 157 (1984).
14. Klinowski, J., *Progr. Nucl. Magn. Reson. Spectrosc.* **16,** 237 (1984).
15. Brunner, E., Ernst, H., Freude, D., Fröhlich, T., Hunger, M., and Pfeifer, H., *J. Catal.* **127,** 34 (1991).
16. Barrage, M. C., Bauer, F., Ernst, H., Fraissard,

J., Freude, D., and Pfeifer, H., *Catal. Lett.* **6,** 201 (1990).
17. Schulze, D., Ernst, H., Fenzke, D., Meiler, W., and Pfeifer, H., *J. Phys. Chem.* **94,** 3499 (1990).
18. Derouane, E. G., *in* "Catalysis by Acids and Bases" (B. Imelik *et al.*, Eds.). Elsevier, Amsterdam, 1985.
19. Guisnet, M., and Magnoux, P., *Appl. Catal.* **54,** 1 (1989).
20. Fetting F., and Dingerdissen, U., "Statusseminar im Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin-Dahlem, 1990," p. 61.
21. Kustanovich, I., Lutz, Z., Vega, S., and Vega, A. J., *J. Phys. Chem.* **94,** 3138 (1990).
22. Michel, D., Germanus, A., and Pfeifer, H., *J. Chem. Soc. Faraday Trans. 1* **78,** 237 (1982).
23. Earl, W. L., Fritz, P. O., Gibson, A. A. V., and Lunsford, J. H., *J. Phys. Chem.* **91,** 2091 (1987).