

Zeolite Rho Loaded with Methylamines. II. Dimethylamine Loadings

CLAUDIA WEIDENTHALER,^a REINHARD X. FISCHER^{a*} AND LLOYD ABRAMS^b

^aFachbereich Geowissenschaften der Universität, † Klagenfurter Strasse, D-28359 Bremen, Germany, and ^bCentral Research and Development Department, ‡ E.I. du Pont de Nemours & Co., Experimental Station, Wilmington, DE 19880, USA. E-mail: rfischer@min.uni-bremen.de

(Received 3 May 1996; accepted 7 October 1996)

Abstract

Samples of two differently prepared zeolite rho loaded with different amounts of dimethylamine (DMA) were studied in their hydrated forms by X-ray diffraction. Both zeolites are partially dealuminated, as indicated by nonframework Al which is assumed to be Al₂O₃ or AlOOH. Series I was prepared from dry-calcined NH₄-rho at 873 K, series II from steam-calcined NH₄-rho at 773 K. The samples were loaded with different amounts of DMA. Rietveld refinements yielded the following results for series I: (1) H_{3.8}(H-DMA)₅Cs_{0.2}Al₉Si₃₉O₉₆.Al₂O₃.21H₂O, X-ray data collection at room temperature, *Im* $\bar{3}$ *m*, *a* = 15.0590 (2) Å, *R*_{wp} = 0.089; (2) (H-DMA)_{8.8}Cs_{0.2}Al₉Si₃₉O₉₆.Al₂O₃.18H₂O, X-ray data collection at room temperature, *Im* $\bar{3}$ *m*, *a* = 15.0680 (2) Å, *R*_{wp} = 0.091. Series II: (3) H_{0.3}(H-DMA)₅Cs_{0.7}Al₆Si₄₂O₉₆.2.5Al₂O₃.24H₂O, X-ray data collection at room temperature, *Im* $\bar{3}$ *m*, *a* = 15.0596 (2) Å, *R*_{wp} = 0.120. DMA resides on the center axis through the α -cage with the N atoms pointing to the single eight-ring and the two methyl groups oriented towards the center of the α -cage.

1. Introduction

This is the second part of our investigation of methylamine-loaded zeolite rho. The first part (Weidenthaler, Fischer, Abrams & Hewat, 1997) dealt with monomethylamine (MMA)-loaded zeolites studied by thermal analyses and neutron and X-ray diffraction experiments. Here we describe the zeolite rho modifications loaded with dimethylamine (DMA), which is the preferred product in the commercial production of methylamines by size-selective catalysis.

2. Experimental

2.1. Sample preparation

All samples were prepared as described in Weidenthaler *et al.* (1997). The hydrogen forms of the

zeolites were prepared from NH₄-rho by deammoniation under shallow bed conditions in dry nitrogen at 873 K (Series I) and under steam at 773 K (Series II), as described previously. The samples dehydrated at 633 K were exposed to different amounts of DMA, as given in Table 1. The methylamines are expected to be associated with the H atoms of the hydrogen zeolite to form ionic groups of H-DMA⁺. Thermal analyses, X-ray diffraction experiments and Rietveld analyses were performed with the equipment and programs described in Weidenthaler *et al.* (1997).

3. Results

The reactions and weight losses for the differently loaded samples are shown in Fig. 1, the corresponding data are given in Table 1. The thermal reactions proceed similarly as in the case of the MMA zeolites (see also discussion of deviations between the amount of sorbed molecules and the amount of thermally analysed molecules in Weidenthaler *et al.*, 1997).

For the Rietveld analyses, intramolecular distances and angles in DMA were restrained by prescribed distances (mean value for C—N = 1.4735 Å, C—N—C = 113.0°) taken from Thomas & Pramatus (1975). All structure analyses were performed with combined Rietveld and distance least-squares (DLS) runs. Crystal data are listed in Table 2.†

3.1. Rho-I-5DMA

Fourier calculations following refinements of the zeolite framework yielded electron density maxima at 0, 0, 0.35 and 0, 0.05, 0.23, which were assigned to N atoms and to the C atoms of the methyl groups, respectively (Fig. 2). Incorporation of the N position improved the *R*_B value by 0.081 and the C atom position lowered the residual by another 0.115. Additional electron density was assigned to water positions. Final atomic parameters are listed in Table 3, observed and calculated diffraction patterns are shown in Fig. 3(a).

† The numbered intensity of each measured point on the profile has been deposited with the IUCr (Reference: SE0200). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† Part of this work was carried at the Institut für Geowissenschaften der Universität Mainz, Germany.

‡ Contribution No. 7368.

Table 1. DMA loadings in the zeolite rho samples

Water content determined by TG analysis in the temperature range between room temperature and 673 K (samples Rho-I-9DMA between room temperature and 623 K), methyl amine content between 673 and 973 K; series II: shallow bed calcined under steam at 773 K, water determined between room temperature and 573 K, methyl amine content between 573 and 1073 K. See Weidenthaler *et al.* (1997) for definitions.

Sample series	Initial loading (no. per unit cell)	Weight loss of H ₂ O (mg)	No. of H ₂ O per unit cell	Weight loss of DMA (mg)	No. of DMA per unit cell	Desorption temperature (K)
Rho-I	5 DMA	6.5	20.5	5.3	6.5	733
Rho-I	9 DMA	3.1	17.8	3.9	8.7	703
Rho-II	5 DMA	5.1	23.5	3.7	6.7	653

3.2. Rho-I-9DMA

Although the DMA loadings are higher in this sample, Fourier maps did not reveal the molecule positions as clearly as in sample Rho-I-5DMA with a lower

Table 2. Crystal data [space group, lattice constant *a*, volume *V*, framework density *FD* (no. of *T* atoms per 1000 Å³), channel aperture *A*] and residuals; for definitions see Weidenthaler *et al.* (1997), Table 3

	Rho-I		Rho-II
	5 DMA	9 DMA	5 DMA
Space group	<i>Im</i> $\bar{3}m$	<i>Im</i> $\bar{3}m$	<i>Im</i> $\bar{3}m$
<i>a</i> (Å)	15.0590 (2)	15.0680 (2)	15.0596 (2)
<i>V</i> (Å ³)	3415.0	3421.1	3415.4
<i>FD</i> (10 ⁻³ Å ⁻³)	14.06	14.03	14.05
<i>A</i> (Å)	3.90	3.78	3.81
<i>R</i> _{wp}	0.089	0.091	0.120
<i>R</i> _B	0.047	0.064	0.049

Apertures represent the smallest diameters of the channels as defined by Baur & Fischer (1997). Based on ionic oxygen (*r* = 1.35 Å).

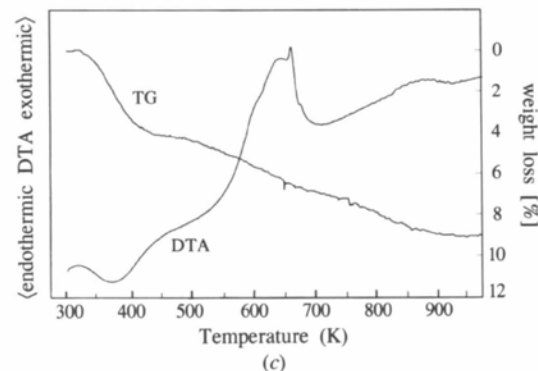
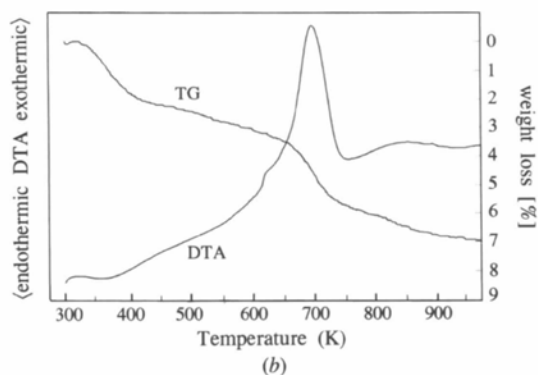
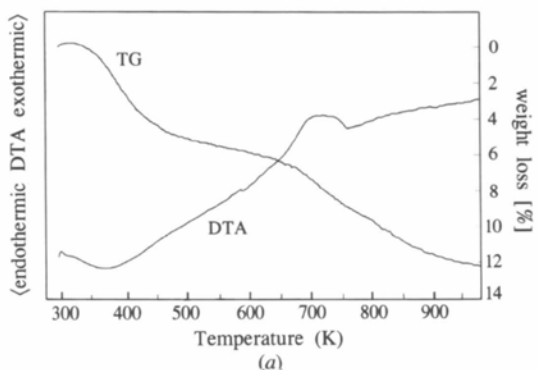


Fig. 1. Thermal reactions recorded by differential thermal analyses (DTA) and weight loss determined by thermogravimetry (TG): (a) Rho-I-5DMA; (b) Rho-I-9DMA; (c) Rho-II-5DMA.

loading. Just the N atom and the W1 positions could be directly inferred from the Fourier analyses. Successive refinements and electron density maps finally gave the results listed in Table 3. The sum of the occupancies of N, Cs and W1 was constrained to 12 atoms per unit cell to account for the close contacts between these atoms. The occupancies of W1 and Cs, however, were allowed to yield a sum of 12 atoms, together with the nine DMA molecules. Final atomic parameters are listed in Table 3, observed and calculated diffraction patterns are shown in Fig. 3(b).

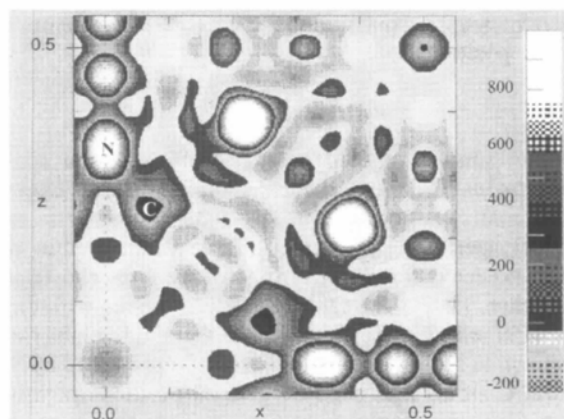


Fig. 2. Fourier map of the sample Rho-I-5DMA in the layer *z* = 0 with *F*_{obs} values from X-ray diffraction data and *F*_{calc} values from the corresponding refinements of the framework atoms. The highest maximum is scaled to 999. The positions of the molecules are indicated by the labels for the N and C atoms.

Table 3. Atom positions in fractional coordinates

Isotropic displacement factors (\AA^2) and occupancies given in number of atoms per unit cell.

Sample	Atom	x	y	z	B	Atoms per unit cell	Wyckoff position
Rho-I-5 DMA	Si/Al	1/4	0.1024 (1)	$\frac{1}{2} - y$	1.15 (4)	39/9	(48i)
Rho-I-9DMA	Si/Al	1/4	0.1025 (1)	$\frac{1}{2} - y$	1.45 (4)	39/9	(48i)
Rho-II-5 DMA	Si/Al	1/4	0.1027 (1)	$\frac{1}{2} - y$	1.73 (5)	42/6	(48i)
Rho-I-5 DMA	O1	0	0.2191 (3)	0.3781 (2)	4.7 (1)	48	(48j)
Rho-I-9DMA	O1	0	0.2150 (3)	0.3790 (2)	3.5 (1)	48	(48i)
Rho-II-5 DMA	O1	0	0.2162 (3)	0.3810 (3)	2.6 (2)	48	(48j)
Rho-I-5 DMA	O2	0.1665 (2)	x	0.3780 (3)	B(O1)	48	(48k)
Rho-I-9DMA	O2	0.1654 (2)	x	0.3751 (3)	B(O1)	48	(48k)
Rho-II-5 DMA	O2	0.1653 (2)	x	0.3751 (4)	4.5 (2)	48	(48k)
Rho-I-5 DMA	Cs	0	0	0.4149 (6)	5	0.6 (1)*	(12e)
Rho-I-9DMA	Cs	0	0	0.4259 (6)	5	1.4 (1)*	(12e)
Rho-II-5 DMA	Cs	0	0	0.435 (1)	5	1.0 (1)*	(12e)
Rho-I-5 DMA	W1	0	0	0.4149 (6)	5	6.4 (1)*	(12e)
Rho-I-9DMA	W1	0	0	0.323 (5)	5	1.6 (1)*	(12e)
Rho-II-5 DMA	W1	0	0	0.325 (1)	5	6.6 (1)*	(12e)
Rho-I-5 DMA	W2	0.0300 (7)	x	0.2683 (7)	5	13.0 (1)	(48k)
Rho-I-5 DMA	W3	0.1549 (7)	x	0.139 (1)	5	14.4 (1)	(48k)
Rho-I-9DMA	W3	0.1629 (7)	x	0.138 (1)	5	12.3 (1)	(48k)
Rho-II-5 DMA	W3	0.132 (1)	x	0.188 (2)	5	11.4 (2)	(48k)
Rho-I-5 DMA	W4	0.0570 (9)	x	0.103 (1)	5	6.8 (1)	(48k)
Rho-I-9DMA	W4	0.0456 (7)	x	0.1427 (7)	5	11.1 (1)	(48k)
Rho-II-5 DMA	W4	0.0460 (9)	x	0.1675 (9)	5	11.2 (2)	(48k)
Rho-I-5 DMA	N	0	0	0.3174 (7)	5	5	(12e)
Rho-I-9DMA	N	0	0	0.3053 (6)	5	9	(12e)
Rho-II-5 DMA	N	0	0	0.2974 (12)	5	5	(12e)
Rho-I-5 DMA	C	0.0539 (8)	0.0616 (8)	0.2629 (7)	5	10	(96f)
Rho-I-9DMA	C	0.0406 (8)	0.0707 (6)	0.2534 (6)	5	18	(96f)
Rho-II-5 DMA	C	0.0253 (8)	0.0893 (6)	0.2673 (11)	5	10	(96f)

* Occupancies constrained to give a total of 12 atoms in the sum of W1, Cs and DMA with a fixed number of 5, respectively, with nine DMA molecules.

3.3. Rho-II-5DMA

Analysis steps similar to Rho-I-5DMA and Rho-I-9DMA led to the results listed in Table 3 and shown in Fig. 3(c). The chabazite impurity was treated as a second phase in the refinements with lattice constants $a = 13.67 (1)$ and $c = 14.72 (3) \text{\AA}$. All positions determined in the Fourier analyses remain relatively stable in the refinements, confirming the correct assignments of atomic positions.

4. Discussion

All the samples studied here crystallize in the space group $Im\bar{3}m$. Therefore, the framework structures exhibit only small variations in their lattice constants and channel apertures. All values (Table 2) lie within the range expected for centrosymmetric zeolites rho (Baur & Fischer, 1997). The DMA molecules reside with their central N atoms on 0, 0, z close to the single eight-ring, as shown in Fig. 4. The methyl groups represented by the central C atoms are found on general positions pointing away from the single eight-ring towards the center of the α -cage. The molecule is oriented in such a way that the C atoms point away from the framework O1 and O2 atoms, as shown in Fig. 4(b). However, small rotations about 0, 0, z alternately yield closer contacts with the

O1 or O2 atoms. In Rho-I-5DMA the closest contact of the methyl group to framework O atoms is 2.89\AA to O2. In Rho-I-9DMA and Rho-II-5DMA the molecule is slightly rotated about 0, 0, z , approaching O1 with C—O distances of 2.95 and 2.59\AA , respectively.

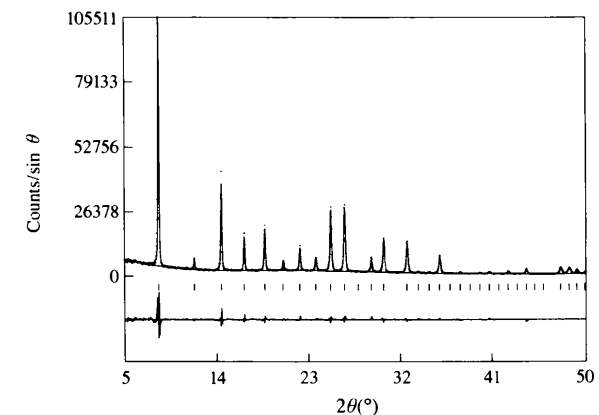
Sorption of DMA causes a reduction of the water content, compared with samples containing the smaller MMA molecules. Especially the W1 and W2 sites are reduced in their water content. The W3 site does not seem to be affected by the size and amount of molecules. However, changes of a few molecules are not significant considering the statistical distribution of molecules on the partially occupied sites. As discussed in the previous paper on the MMA zeolites (Weidenthaler *et al.*, 1997), some water molecules could statistically occupy the same positions as nonframework aluminum species (n.f.a.), which form condensed complexes of Al_2O_3 or AlOOH . The n.f.a. atoms are expected to be randomly distributed in the zeolite cavities and therefore will not be determined unambiguously in the crystal structure determinations. Selected interatomic distances are listed in Table 4.

This work was supported by the Deutsche Forschungsgemeinschaft under grant Fi442/2. A Heisenberg fellowship to RXF is gratefully acknowledged.

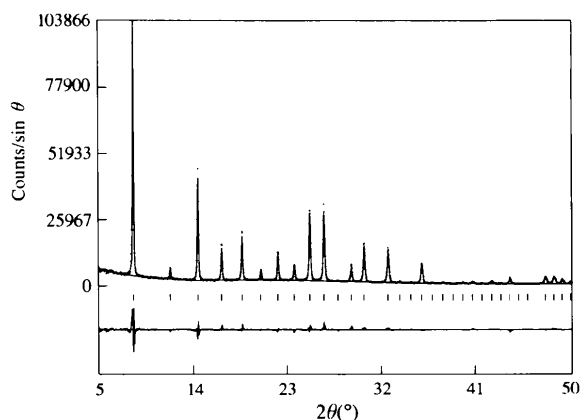
Computing time was provided by the Zentrum für Datenverarbeitung, University of Mainz. We thank U. Ciesla and W. Schmidt (University of Frankfurt) for the thermal analyses, N. Groschopf (University of Mainz) for support with the chemical analyses and W. H. Baur (University of Frankfurt) for his careful reading and numerous comments on the manuscript.

Table 4. Selected interatomic distances (\AA) and angles ($^\circ$)

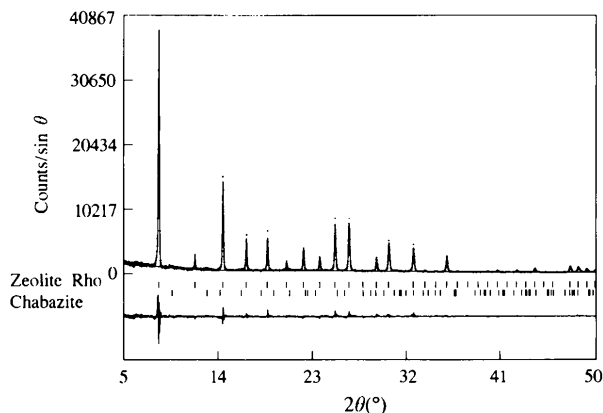
	Rho-I		Rho-II
	5 DMA X-ray	9 DMA X-ray	5 DMA X-ray
T—O1	1.638 (4) 2 \times	1.656 (4)	1.647 (5) 2 \times
T—O2	1.612 (3) 2 \times	1.624 (3)	1.621 (4) 2 \times
mean	1.625 (4)	1.640 (4)	1.634 (5)
O1—T—O1	114.7 (2)	114.6 (2)	112.0 (3)
O1—T—O2	106.6 (2) 2 \times	105.0 (2) 2 \times	105.8 (2) 2 \times
O1—T—O2	108.0 (2) 2 \times	110.2 (2) 2 \times	110.5 (2) 2 \times
O2—T—O2	113.0 (2)	111.9 (2)	112.4 (2)
mean	109.5 (2)	109.5 (2)	109.5 (2)
N—O1	3.424 (4) 4 \times	3.425 (5) 4 \times	3.490 (7) 4 \times
N—O2	3.661 (4) 4 \times	3.679 (4) 4 \times	3.709 (6) 4 \times
C—O1		2.95(1)	2.59(1)
C—O2	2.89(1)		



(a)

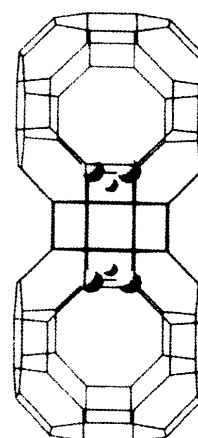


(b)

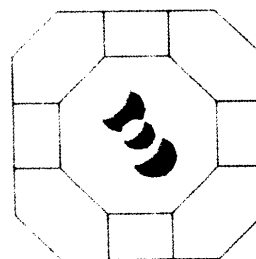


(c)

Fig. 3. Observed (dots) and calculated (solid line) intensity profiles with difference plot underneath. Theoretical peak positions are indicated by tick marks below the bottom line of the profiles: (a) Rho-I-5DMA; (b) Rho-I-9DMA; (c) Rho-II-5DMA.



(a)



(b)

Fig. 4. Projection of the framework structure of Rho-I-5DMA as a skeleton model with the DMA molecule close to the single eight-ring. The small circles represent the N atoms, the larger circles C atoms (methyl groups): (a) side view; (b) top view.

References

- Baur, W. H. & Fischer, R. X. (1997). *Numerical Data and Functional Relationships in Science and Technology*. Landolt-Börnstein Series III, edited by W. H. Baur & R. X. Fischer, in preparation.
- Thomas, J. O. & Pramatus, S. (1975). *Acta Cryst.* **B31**, 2159–2163.
- Weidenthaler, C., Fischer, R. X., Abrams, L. & Hewat, A. (1997). *Acta Cryst.* **B53**, [SE0199].