

Thermogravimetry of α,ω -diaminoalkanes used in synthesizing ZSM-5

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Thermogravimetry was determined on a series of α,ω -diaminoalkanes, in which the alkane chain contained from three to eight carbon atoms, that were located in zeolite ZSM-5 during synthesis. Of the series, 1,6-diaminohexane functions best as a template, and this was attributed to its having a size that most neatly fits into the zeolite structure; the other molecules were either too small or too large. It was found that the channels were not completely filled and, on average, there were 5.3 diaminoalkane molecules per unit cell of the zeolite. Further, the organic compound within the zeolite had undergone partial deamination during synthesis.

Keywords: Thermogravimetry; diaminoalkanes; templates; synthesis; ZSM-5

INTRODUCTION

The application of α,ω -diaminoalkanes instead of the conventional tetrapropylammonium cations as structure-directing agents in the synthesis of zeolite ZSM-5 and related materials has been shown to be practically feasible.¹⁻⁹ The propane and butane derivatives can lead to either ferrierite or ZSM-5. The pentane and hexane compounds can always produce ZSM-5, although caution must be taken with the latter as under certain conditions ZSM-48 often co-crystallizes.¹⁰ It has been shown that for producing ZSM-11, 1,8-diaminooctane is a highly satisfactory template.¹¹

Although these templates are now more regularly used, limited data have been accumulated for understanding how they function during the zeolitic synthesis. For example, Valyocsik and Rollmann³ found that when ZSM-5 was synthesized in the presence of diaminopentane and diaminohexane there were, respectively, 9.6 and 7.7 of these organic molecules per unit cell. Lowe and co-workers^{6,8} found the same value for the hexane derivative. As the ZSM-5 unit cell has four channel intersections, it was obviously concluded that eight of these linear molecules, with a terminal amine portion in an intersection, would neatly fill the entire zeolite. Gabelica et al.,⁴ however, found within the unit cell of ZSM-5 that with diaminopentane and diaminohexane there were only 5.6 and 5.4 molecules, respectively. Similarly, Jacobs and Martens¹² found that the pore filling was about

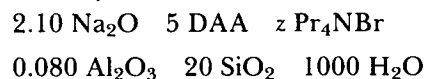
60% of the values determined by Valyocsik and Rollmann mentioned above.

Another question is the nature of the organic compound within the synthesized ZSM-5. MAS ¹³C n.m.r. spectra have indicated that the chemical composition of the diaminoalkanes remains unaltered when they are occluded in the ZSM-5 framework.^{4,13} However, direct analysis showed that the number of nitrogen atoms in the incorporated zeolite was always less than the two per molecule in the organic compound that was initially used.^{3,12} This means that there would not necessarily be an amine group at each end of the linear hydrocarbon portion of the molecule.

In another work, we prepared a number of ZSM-5 samples with the aid of various α,ω -diaminoalkanes.⁹ This paper covers the thermogravimetry coupled with the simultaneous analysis for nitrogen-bearing compounds, with the intention of supplying new information about the number and composition of the diaminoalkanes occluded in ZSM-5.

EXPERIMENTAL

All the samples were prepared from mixtures having the following basic formula:



where DAA is α,ω -diaminoalkane. The concentrations used for the different samples are given in *Table I*. In the first section of the preparations (samples 2 to 6), the composition was kept constant but the number of carbon atoms in the alkane portion of the diamine was varied. To all these mixtures, a small amount of

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Table 1 Variables used in the synthesis of the samples

Sample	DAA	z
2	Propane	0.084
3	Butane	0.084
4	Pentane	0.084
5	Hexane	0.084
6	Octane	0.084
14	Hexane	0.000
15	Hexane	0.042
5	Hexane	0.084
16	Hexane	0.420

DAA represents α,ω -diaminoalkane and the alkane molecule mentioned below this symbol is the linear hydrocarbon portion of the actual compound. The symbol z gives the amount of tetrapropylammonium cations used in the various preparation mixtures and was varied only with samples 14–16

tetrapropylammonium cations, which would act as the ideal seeding template for ZSM-5 crystallization,¹⁴ was added. Without the addition of the tetrapropylammonium cations, the above formulation could be inclined to lead to the formation of ZSM-48.¹⁰ It has been shown that the best results are obtained if the amount of these cations added was sufficient to fill 10% of the zeolite intersections.¹⁴

In the second part of the table, preparations were made to investigate certain effects of the small additions of tetrapropylammonium cations. Thus, with samples 14–16, while still using 1,6-diaminohexane as the main template, mixtures using more, less, and none of the tetrapropylammonium compound were made. Naturally, under these conditions, the drive to suppress the formation of ZSM-48 was ignored.

The silica used was a precipitated variety, Neosyl ET, obtained from Crosfield Chemicals. The remainder of the formula consisted of sodium hydroxide, aluminum sulfate, and the appropriate organic compounds, all of which were of analytical grade. The pH of the mixtures was around 12.4. The crystallizations were carried out in an autoclave in which the mixtures were continually stirred at 25 r.p.m. The reaction temperature was 170°C and duration of the crystallization was 36 h. The products were either ZSM-5 or ZSM-11; these details have been published earlier.⁹

Thermogravimetry was carried out on a DuPont 990/951 thermal analyzer. Coupled to this instrument was a method for measuring the amount of alkaline organic material released. In this technique,^{15,16} the samples were heated at 10°C/min and the released organic compound was carried to a titrator where the nitrogen-bearing or alkali portion was continuously neutralized with sulfamic acid. In the experiments, hydrogen was used as a carrier to prevent the oxidation of the nitrogen compound that was released.

Carbon and nitrogen contents were determined by a Carlo-Erba microanalyzer. MAS n.m.r. spectra were determined on a Bruker AM 300 instrument operating at a frequency of 75.5 MHz and spinning at 4 kHz.

RESULTS

Thermogravimetric analyses of preparations 2–6 are given in *Figure 1*. The top portion of the figure shows the rate at which alkalis were released, due to evolution of the nitrogen-bearing fragment of the organic compounds, from the zeolite. The rate is given in micromoles for an equivalent monovalent compound released, although in the original preparation mixture, the diamines are divalent. The quantity released from the sample formed with diaminopropane is low and is attributed to the ZSM-5 being not completely crystalline.⁹ Nevertheless, the rate of alkali release follows the same trend as that found with the two other preparations numbers 3 and 4.

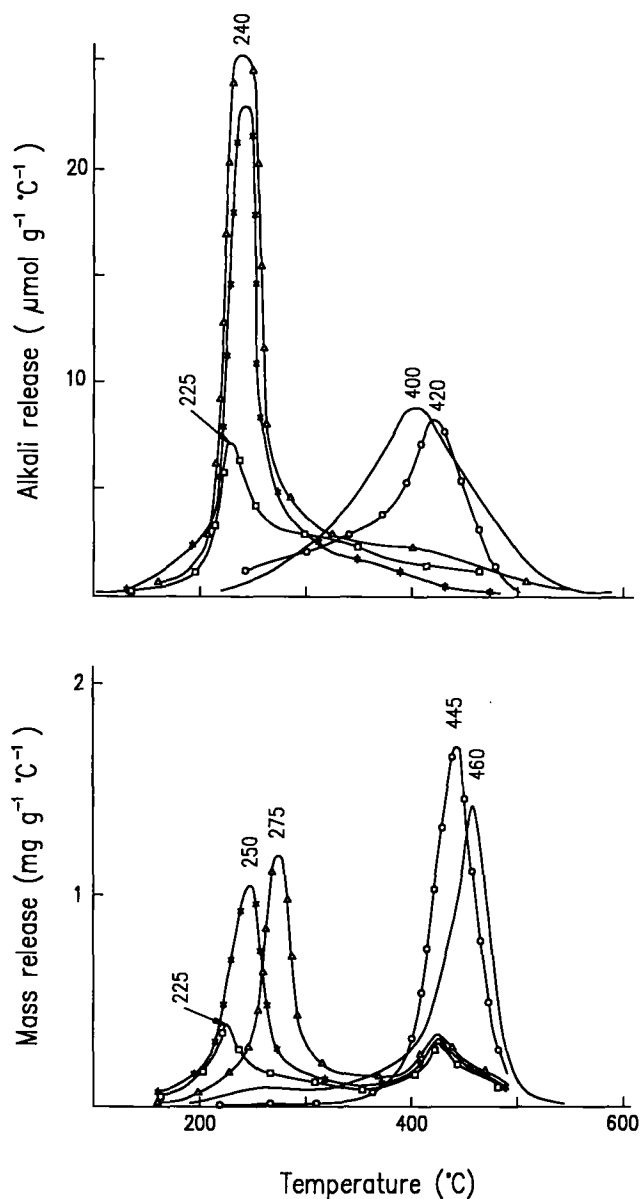


Figure 1 Thermogravimetry on preparations of ZSM-5/11, which were synthesized with different diaminoalkanes as the organic directing agent. Identification of the parent alkane is given by the symbols on each curve: (-□-□-) propane; (-*-*-*) butane; (-Δ-Δ-) pentane; (—) hexane; (-○-○-) octane.

Table 2 Data and calculations on the quantity and composition of organic compound from the thermogravimetry done on the ZSM-5/11 preparations using different diaminoalkanes as the template

Sample	DAA ^a	Alkali release (mmol/g)	Nitrogen atoms per u.c.	Mass loss > 160°C (%)	Alkane molecules per u.c.	Nitrogen atoms per alkane
2	Propane	0.82	5.4	5.2	4.5	1.1
3	Butane	1.35	8.7	8.6	6.3	1.3
4	Pentane	1.54	10.0	10.0	6.3	1.5
5	Hexane	1.32	8.6	10.0	5.4	1.5
6	Octane	0.92	6.0	9.9	4.2	1.3

^aThe alkane molecule mentioned below the symbol DAA is only the linear hydrocarbon portion of the actual diaminoalkane

Table 3 Data and calculations on the composition of the preparations of ZSM-5 using diaminohexane as main template but with different amounts of tetrapropylammonium cations as seeding compound

Sample	Max. filling by Pr ₄ N ⁺ cations (%)	Alkali release (mmol/g)	Nitrogen atoms per u.c.	Temp of alkali release (°C)	Mass loss > 160°C (%)	Temp of mass release (°C)
14	Nil	1.30	8.5	390	10.3	460
15	5	1.28	8.3	390	10.3	—
5	10	1.32	8.6	400	10.0	460
16	50	0.91	6.0	410	11.0	440
	100	±0.50	3.6	—	—	—

Calcination of the synthesized samples meant that both adsorbed water and organic template were driven from the zeolite structure. Below 160°C, most of the water was removed and the reduction in mass above this temperature should be attributed mostly to loss of the template. The lower portion of *Figure 1* shows the rate at which the total mass of the product was reduced.

From the total amounts of alkaline material released and the loss in mass between 160 and 600°C, some data on the diaminoalkanes within the zeolite structure were calculated; these results are given in *Table 2*. It is assumed that the tetrapropylammonium compound was preferentially incorporated into the zeolite structure and would account for 0.4 molecules per unit cell. The number of alkane molecules per unit cell was calculated from the total mass loss minus the amount resulting from the release of the tetrapropylammonium molecules.

To establish the effects of the presence of the small amounts of tetrapropylammonium compounds, thermogravimetric determinations similar to those mentioned above were carried out on preparations 14–16, and the results calculated from these experiments are

Table 4 The carbon-to-nitrogen mole ratios of the diaminoalkane occluded in zeolite

DAA	C/N ratio from t.g.	C/N ratio from chemical analysis	C/N ratio from Ref. 3
Propane	2.7	2.9	—
Butane	3.0	2.6	±3.0
Pentane	3.3	3.1	2.9
Hexane	3.9	4.2	4.5
Octane	6.1	6.2	8.3

Ratios were determined from thermogravimetry (*Table 2*) and direct chemical analysis and taken from results of Valyocsik and Rollmann³

given in *Table 3*. Also included is an estimate of a theoretical result in which only tetrapropylammonium cations and no diaminohexane would be used.^{16–19}

From the thermogravimetric data, the carbon-to-nitrogen mole ratios were determined and the results are given in *Table 4*. This ratio was also calculated from the chemical analysis for these elements, and the results are also included in *Table 4*. The MAS ¹³C n.m.r. for preparations 5 and 14, as well as that for pure 1,6-diaminohexane, are shown in *Figure 2*.

DISCUSSION

Thermal removal of templates

Samples 2, 3, and 4, synthesized with diamine compounds from propane, butane, and pentane, respectively, released nearly all their nitrogen portion at roughly the same temperature. This temperature is around 240°C and is higher than all the boiling points of these organic materials: 1,5-Diaminopentane boils at 179°C. Although it may appear that the product made from these diaminoalkanes can be driven from the zeolite without involving cracking reactions, this proved to be incorrect (see below).

From a comparison of the two curves in *Figure 1*, it is obvious that the thermal removal of the alkaline-containing portion takes place at a lower temperature than does the removal of the bulk of the template molecule. The difference between 240 and 275°C with sample 4 means that 1,5-diaminopentane must crack before leaving the zeolite. When diaminopropane and diaminobutane were used in the synthesis, the difference between the temperatures at which these two removals occurred was much smaller. Around 425°C, samples 2–4 release only small quantities of nitrogen- (alkali-)containing material. How-

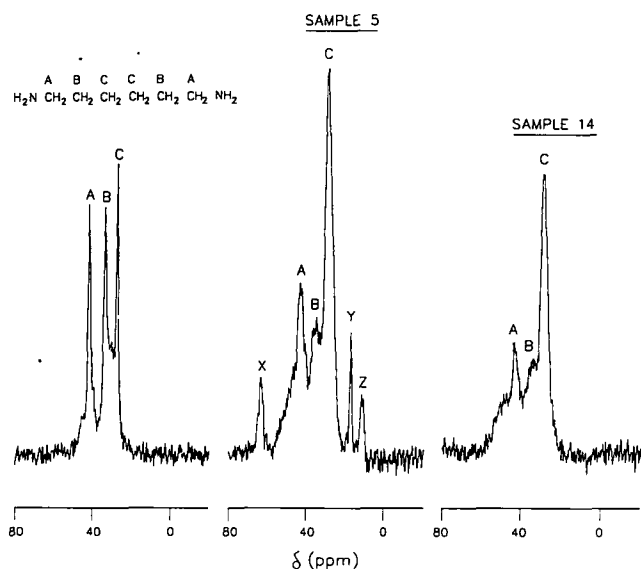


Figure 2 The MAS ^{13}C n.m.r. of pure 1,6-diaminohexane and samples 5 and 14. Sample 5 contains both diaminohexane and tetrapropylammonium cations as templates, whereas sample 14 contains only diaminohexane.

ever, the remaining bulk of the organic material, equivalent to 2.5% of the mass of the preparation, was freed at this temperature. The tetrapropylammonium molecules are also released at this temperature,¹⁶ but would account for a mass loss of only 1.1%. This means that some of this loss must be attributed to a hydrocarbon fraction originating from the diamine, which is strongly held and contains little (if any) nitrogen.

When diaminohexane and diaminoctane were used as the main template, the zeolites similarly released the nitrogen portion before the bulk of the organic molecule. However, the cracking and subsequent release of these compounds took place at significantly higher temperatures, which were above 400°C. Such high temperatures indicate that these organic compounds must be firmly incorporated into the zeolite structure. Since they form an intricate part of the zeolite structure, diaminohexane and diaminoctane function effectively as templates during the synthesis of ZSM-5 and ZSM-11, respectively.

Table 3 includes the peak temperatures at which the alkali portion and the total mass from the diaminoalkane are released. When comparing the results for preparation 14 with those for preparations 15 and 5, it can be seen that the addition of smaller amounts of tetrapropylammonium compound did not significantly shift the position of these peaks. It can therefore be concluded that the portion of the diaminoalkane containing the nitrogen atom is released around 390°C, whereas the much larger remainder of this organic compound is released only at a temperature that is 70°C higher. The hydrocarbon portion of the organic compound is more strongly attached within the zeolite structure and would play the major role in the direction of crystallization.

The above results show that the size of the organic

molecule plays an important role in zeolite synthesis. Diaminopropane, diaminobutane, and diamino-pentane are actually too small to control the direction of crystallization of ZSM-5 and would seem to act only as pore-filling material. Diaminohexane appears to be about the ideal size. Diaminoctane is too large and its longer size favors the formation of the straight channels in ZSM-11.

Quantity of template

The number of organic templates that were located in the ZSM-5 structure was far lower than that found by both Valyocsik and Rollmann³ and Lowe and co-workers.^{6,8} However, the results are similar to those of Gabelica et al.⁴ and Jacobs and Martens.¹² The latter investigators attributed the lower values to the use of a low concentration of the organic compound in the preparation mixture. However, in this work, a similar concentration to that of Valyocsik and Rollmann³ was used and a lower degree of filling was still found. These variations must be caused by differences in each individual's synthesis. Consequently, it can be concluded that during crystallization, although diaminoalkanes function as templates, some of the ZSM-5 zeolite can also form without the aid of these compounds.

The formulation of this work should give 0.76 aluminum atoms per unit cell. The lowest sodium analysis was found with the diaminoalkane preparation that had 0.51% Na_2O ,⁹ which is equivalent to about 1.1 Na cations per unit cell. Further, there are also 0.4 tetrapropylammonium cations as well as the 5–8 diaminoalkane molecules per unit cell of ZSM-5. The presence of each aluminum atom requires neutralizing, which would probably come from the sodium or propylammonium cations. Even if some of the diaminoalkane compounds were neutralizing cations, the major portion of them would be acting as structure-directing agents.

A question regarding this work is whether the presence of the small amounts of tetrapropylammonium compounds had any effect on the reduced degree of filling of the intersections and channels of the zeolites. The results in Table 3 show that preparations 15 and 5 contained no less diaminoalkane than did preparation 14, where no tetrapropylammonium cations were used in the synthesis mixture. This means that the addition of tetrapropylammonium cations to the reaction mixture of samples 2–6 did not significantly alter the degree to which the diaminoalkanes filled the zeolite channels.

It was only when significant amounts of tetrapropylammonium cations were used (enough to fill more than 10% of the channel intersections) that the thermogravimetry showed a decrease in the amount of alkali material being released. This means that there was also a reduction in the number of nitrogen atoms being incorporated into the zeolite structure. However, it must be remembered that when using tetrapropylammonium compounds as the template the maximum number of cations that can be found in the zeolite structure is 4 per unit cell. In

practice, this value is usually about 3.6 or less of these cations.¹⁶⁻¹⁹

Composition of template

As can be seen in *Table 2*, the number of nitrogen atoms in the alkane compound is less than the original two, with the average value being 1.4. These figures were converted to carbon-to-nitrogen mole ratios and the results are shown in *Table 4* and were confirmed by direct chemical analysis. Further, these figures were similar to those obtained by Valyocsik and Rollmann.³ Jacobs and Martens¹² also observed deamination down to a level of about one amino group per molecule. This observation implies that the diamine compound undergoes some deamination during synthesis.

However, it has previously been shown that the three chemical shifts at 43, 35, and 28 ppm from the MAS ¹³C n.m.r. spectra of 1,6-diaminohexane are also found when this compound is occluded in the ZSM-5 structure during synthesis.¹³ From this it was concluded that the organic molecule remains intact during synthesis^{4,13} and implies that no deamination had taken place. The n.m.r. spectrum of sample 5 (preparation using 1,6-diaminohexane) is given in *Figure 2* and show six peaks. Peaks marked X, Y, and Z at 63, 16, and 11 ppm are attributed to tetrapropylammonium cations,^{20,21} while the three remaining shifts, marked A, B, and C, are similarly located to those of pure 1,6-diaminohexane.

If during the synthesis the compound deaminated to the monoamine, shifts below 28 ppm should be evident. However, none were found. Although their absence is obscured by two of the tetrapropylammonium shifts, it is clear that there are no shifts in this region with sample 14, which contained none of the latter compound. Similar results were found with other samples using different diaminoalkanes.

Although the position of the n.m.r. shifts indicates no alteration in the diaminoalkanes, their magnitudes did show some changes. The magnitudes are proportional to the amount of carbon present. In pure 1,6-diaminohexane, peaks A and C ought to be, and are, the same size. After synthesis, peak A, which is attached to the amino group, is much smaller than the internal carbon atoms that are responsible for peak C. This does support the thermogravimetric data that some deamination takes place. However, this is no simple process like the formation of monoamines and there is still insufficient information to suggest a possible mechanism.

CONCLUSIONS

When α,ω -diaminoalkanes containing between three and five carbon atoms are used to synthesize zeolite ZSM-5, the organic material can be removed at a relatively low temperature of around 250°C. This indicates that these templates are not strongly held in the zeolite structure and that they are too small to function as the ideal structure-directing agents. However, as diaminohexane and diaminoctane re-

quire a much higher temperature of around 450°C for their removal, they can be regarded as superior templating agents. Whereas the longer 1,8-diaminoctane molecules are more suited to the straight channels of ZSM-11, 1,6-diaminohexane appears to have the most suitable size for the synthesis of ZSM-5. It was found that slightly more than half the channels were filled with these molecules.

During synthesis, a significant amount of deamination takes place, which means that the organic material within the zeolite is not a pure diamine compound. During calcination, the portion of the diaminoalkane containing the remaining nitrogen atoms was always driven from the zeolite structure at about 50–70°C before the remaining fragment of the organic material. This suggests that the amino group(s) does not feature as the main structure-directing agent.

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