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# TETRAALKYLAMMONIUM SILICATES GELS AS PRECURSORS TO ZEOSILITES OF DIFFERENT STRUCTURES

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## ABSTRACT

The endotherms of the pure TAABr and dried TAAOH compounds as well as the endotherms of the $TAA^+$ ions occluded in the silicate gels in presence and in absence of sodium cations have been investigated by thermal analysis methods.

## INTRODUCTION

While the structure directing and the space filling effect of organic cations in the formation of various zeolites is rather well documented [1], few studies are devoted to the synthesis of very silica rich compounds of zeolitic structures (zeosilites) [2,3]. On the other hand, only few studies concern the state of tetraalkylammonium (TAA) cations in the various silic(oalumin)ic gels [4,5], while their various silicates present in the liquid phase are more documented [6]. It is now recognized, that the TAA-silicates or silicoaluminates are probable precursors for the zeolite nucleation [4-6]. It is then of paramount importance to investigate the various states of TAA cations in the gel and the final cristalline phases.

This paper is devoted to the study of tetramethyl (TMA)-, tetraethyl (TEA)-, tetrapropyl (TPA)- and tetrabutyl (TBA)-ammonium cations in a silica-rich gel in presence and in absence of $Na^+$ cations.

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## EXPERIMENTAL

Two different types of gels were prepared from precipitated $SiO_2$ (BDH, containing 0.6 wt% Na), TAABr, TAAOH, 30% NaOH solution (reagent grade, Carlo Erba) and distilled water: $8TAABr-4Na_2O-100SiO_2-1000H_2O$ and $4(TAA)_2O-100SiO_2-1000H_2O$. The following TAA compounds were used: TMABr, TEABr, TPABr and TBABr (all Fluka purum); TMAOH (25% aq. sol.), TEAOH (20% aq. sol.), TPAOH (20% aq.sol.) and TBAOH (40% aq. sol.),all Fluka products. The highly viscous gels were further dried at ca. 100 °C during 16 h.

The syntheses of various zeosilites were carried out in static conditions at 170 °C under autogeneous pressure, using sealed teflon containers. The chemical composition of the samples were determined by atomic absorption ($Si/Al \geq 2000$).
The nature and crystallinity of the solid phases were determined using X-ray powder diffraction patterns, recorded on a Philips PW 1349/30 diffractometer controlled by Olivetti M24 computer using CuK$\alpha$ radiation, and 0.5 2 tetha per minute, 10% $Pb(NO_3)_2$ was used as internal standard.

Thermal analyses DTA-TGA-DTGA were recorded on a Netzsch STA 429 Thermal analyzer controlled by H.P. 86 computer (Nitrogen flow: 15ml/min; heating rate 10 °C/min).

## RESULTS AND DISCUSSION

The Fig. 1 illustrates the endotherms of the pure TAABr and dried TAAOH compounds (1 and 2) as well as the endotherms of the $TAA^+$ ions occluded in the silicate gels in presence (4) and in absence (5) of sodium cations. The difference between the two gels is striking: while the endotherms of $TAA^+$ ions in presence of $Na^+$ ions are different for each TAABr (4), the endotherms of $TAA^+$ without $Na^+$ ions (5)are all very similar. This latter could be explained by the presence of hydrated $TAA^+$ ions neutralizing the silicate anions of the gel.
Indeed, it was shown previously by combined thermal analysis and $^{13}C$-N.M.R. spectroscopy [4, 5], that these hydrated species exist essentially, when the amount of the available alkali cations is less, than the corresponding negative charges in the gel. The hydrated nature of these species is also suggested by the quasi

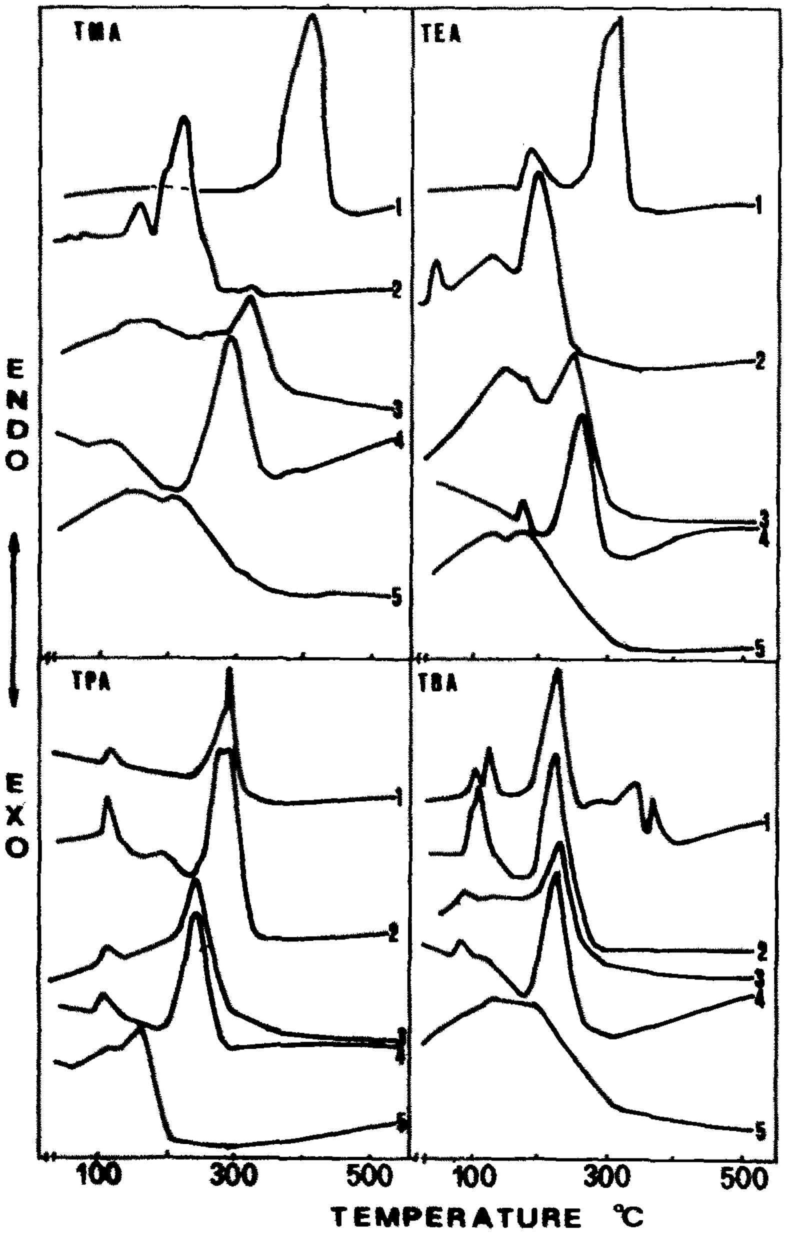

Fig. 1. DTA endotherms of pure TAABr(1), pure dried TAAOH (2), TAABr-$SiO_2$ mixture(3), TAA ions occluded in dried $8TAABr-4Na_2O-100SiO_2-1000H_2O$ hydrogels (4) and in dried $4TAA_2O-100SiO_2-1000H_2O$ hydrogels(5).

TABLE 1

Various Zeosilites formed in autogeneous conditions at 170 °C in presence of TAA ions

| Gel system | Time (days) | Crystalline phases |
|---|---|---|
| TMABr | 20 | ZSM-48 (ZSM-39) |
| TMAOH | 20 | ZSM-48 (ZSM-39) |
| TEABr | 10 | ZSM-48 (ZSM-39) (ZSM-5) (Cristobalite) (Quartz) |
| TEAOH | 20 | ZSM-48 (ZSM-39) (Cristobalite) (Quartz) |
| TPABr | 1 | ZSM-5 |
| TPAOH | 1 | ZSM-5 |
| TBABr | 2 | ZSM-11 |
| TBAOH | 3 | ZSM-11 |

In parenthesis: minor components

fusion of the large endotherms at ca. 160-210 °C with that of water at ca. 100-150 °C (5).

It has to be emphasized, that the endotherms for $TPA^+$ and $TBA^+$ ions are quite different from the corresponding endotherms of pure dried TPAOH and TBAOH phases (2). The DTA of pure TPAOH includes a phase transition at ca. 113 °C, a small endotherm at 190 °C which is accompanied by a weight loss (14%) and finally an endotherm at 276 °C (shoulder) and 291 °C (4). The DTA of pure TBAOH also shows a phase transition at 111 °C and the main endotherm at 222 °C. The endotherms of pure TMAOH and TEAOH do occur in the same temperature ranges as the endotherms of TAA occluded in the gel. Nevertheless, they still can be distinguished from the endotherms of TMA and TEA associated with the gel, as the main endotherms at 224 °C (pure TMAOH), and at 203 °C (pure TEAOH) are absent in the gel-TMA and gel-TEA systems.

On the other hand, the TAA endotherms in presence of $Na^+$ ions, are quasi similar to those encountered in a $TAABr-SiO_2$ mixture (3). It follows, that the TAABr in presence of $Na^+$ ions is not well dispersed and the species detected by thermal analysis stem essentially from the solution after evaporation of the solvent.

These results emphasize the fact, that $Na^+$ is the preferential countercation to gel negative charges ( $\geqq SiO^-$ ) [5].

When these gels are put in hydrothermal conditions at 170 °C, various zeosilites ($SiO_2$ with zeolitic structures) can be crystallized, the nature of which is reported in the Table 1. With TMABr and TMAOH, essentially high silica ZSM-48 is formed (Si/Al$\geq$ 2000), with some ZSM-39. In presence of TEABr or TEAOH the crystallinity is very low. Only small amounts of ZSM-48, ZSM-39 are detected, with traces of ZSM-5 for the TEABr system.

## CONCLUSIONS

Finally, the TPA- and TBA- gels lead to the well known and highly crystalline zeosilites of ZSM-5 and ZSM-11 structures respectively. The only difference, for example, between the beviour of TPABr- gel and TPAOH-gel is shown in the higher crystallization rate for the latter (7).

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