ON THE STRUCTURE AND CATALYTIC PROPERTIES OF SILICA-ALUMINA

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ABSTRACT

From basic, neutral and even weakly acidic solution, amorphous
sodium aluminosilicates are obtained. During the thermal treatment of
the corresponding ammonium form, obtained by ion exchange from the
sodium form, most of the aluminium is removed from the tetrahedral
positions, accompanied by a strong increase of the condensation
degree of the silica fragments in the solid. Structure and catalytic
properties of such silica rich silica-alumina closely resemble those
of hydrothermally treated zeolites possessing a large amount of extra
lattice aluminium.
Silica-alumina samples of equal composition but precipitated at
different pH values may widely differ in their properties. Under
certain preparation conditions an alumina rich sample may even reach
an acidity and catalytic activity as high as that of a silica rich
sample.

INTRODUCTION

Silica-alumina still continues to be of interest as catalyst
component for the processing of high-boiling petroleum fractions.
Fripiat et al. concluded /1/ that at low alumina contents (30 wt %)
silica-alumina consists of a zeolite-type network structure. The
nature of the Brönsted sites at the silica-alumina surface according-
ly should correspond to that of the acidic OH groups in H-zeolites.
This conception of the silica-alumina structure, however, turned out
to be incompatible with results obtained by other authors /2-4/.
Pott /2/ concluded from X-ray phosphorescence studies that the

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H-form of amorphous aluminosilicates is unstable and that tetra-
hedrally coordinated Al is probably absent in silica-alumina; his
experimental evidences, however, did not remain uncontradicted.
Independently of the sample preparation, a maximum of the catalytic
activity as a function of sample composition was found /5-7/ at
about 15-40 wt % Al_2O_3. Existence and position of this maximum is
explained /6/ by the isomorphous incorporation of Al into the silica
matrix up to 30 wt % Al_2O_3. At higher alumina content, part of the
Al is present in separate alumina phases, or bound in mullite-type
structures /6/.
The present work is directed on the existence and stability of the
H-form of X-ray amorphous aluminosilicates. The impact of sample
preparation and composition on the catalytic properties of silica-
alumina is emphasized.

EXPERIMENTAL

Sample preparation. SiO_2-Al_2O_3 samples were prepared by
continuous precipitation from a sodium aluminate solution (4 wt %
Al_2O_3) and water glass (4 wt % SiO_2). The pH value of the precipi-
tation suspension was adjusted by adding sulphuric acid. The gels
were filtered, washed and dried at 390 K. By subsequent ion exchange
with 1 m aqueous solution of ammonium sulphate the residual sodium
content was decreased to 0.02 wt %.
Sample series A, B. Samples of different composition were obtained
by varying the flow rate of the partial streams (aluminate, water
glass, sulphuric acid), the pH value was adjusted to 9 in the series
A and to 6 in the series B. Thermal activation of the NH_4^+ ex-
changed samples was carried out prior to catalytic investigation in
a stream of oxygen at 780 K.
Samples I-IV. Sample NaI (atomic ratio Si/Al = 1.1) was precipitated
from a solution of the composition 2.3 $SiO_2 \cdot 1.0$ $Al_2O_3 \cdot 3.4$ $Na_2O \cdot 170$
H_2O; the gel was aged under the mother liquor for 6 hrs at 355 K.
Samples NaII (Si/Al = 2.8), NaIII (Si/Al = 4) and NaIV (Si/Al = 4.2)
were precipitated from a solution of 9 $SiO_2 \cdot 1.0$ $Al_2O_3 \cdot 3.7$ $Na_2O \cdot 120$
H_2O, with a pH value of 12 (NaII), 10 (NaIII) and 6 (NaIV) being
adjusted by sulphuric acid. The gels were filtered after 5 min
stirring. The corresponding H-forms HI-HIV were obtained by ammonium
ion exchange and subsequent thermal deammonization.
Characterization methods used in this work (cumene cracking,

IR, DTA, NMR and the molybdate reaction) have been described in detail in references /8-10/.

RESULTS AND DISCUSSION

Formation and stability of the H-form of X-ray amorphous aluminosilicates

The X-ray amorphous precipitates NaI - NaIV are true amorphous aluminosilicates: the Na/Al atomic ratio is 1, the Na$^+$ ions are susceptible to nearly complete and stoichiometric cation exchange, and no structure sensitive bands characteristic of zeolites appear in the IR spectra.

The amount of tetrahedrally coordinated Al (Al^{IV}) strongly affects the asymmetrical T-O valence vibration band ($\tilde{\nu}_{asym}$; T = Si, Al) in the IR-spectra. As is evident from Figure 1, nature and magnitude of this functional relationship between the position of the $\tilde{\nu}_{asym}$ band and the amount of Al^{IV} correspond to the relationship known from zeolites /11/. Hence, the amount of Al^{IV} can be determined from the position of this band for silica-alumina just as in the case of partially dealuminated zeolites.
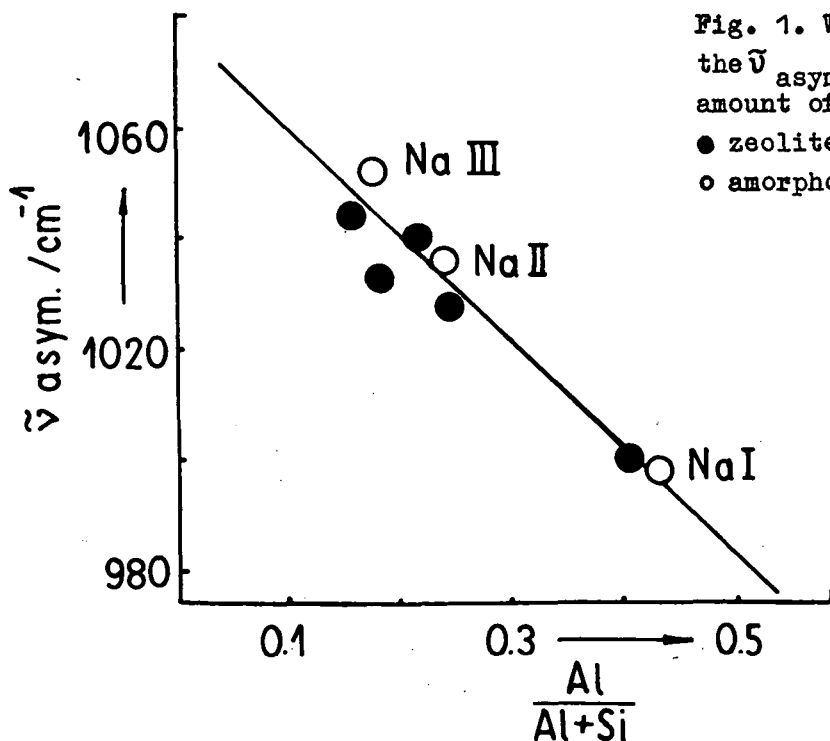

Fig. 1. Wave number of the $\tilde{\nu}_{asym}$ IR band and amount of Al^{IV}.
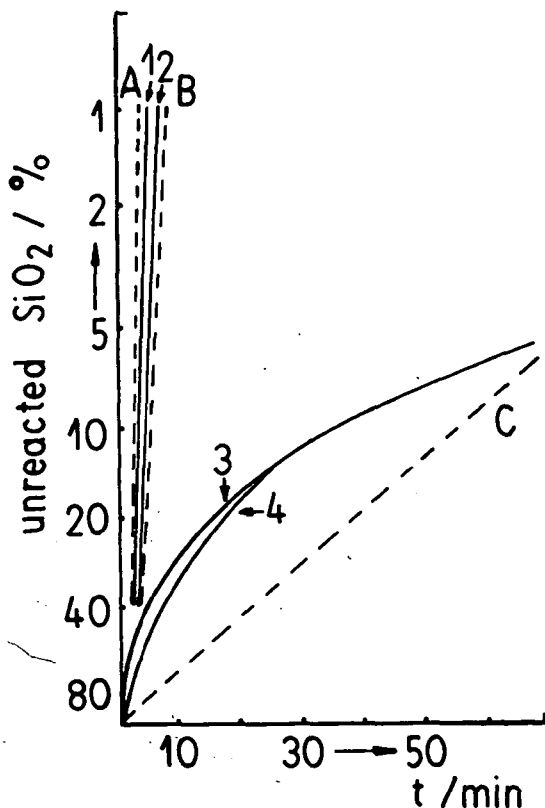● zeolites Y /11/,
o amorphous samples.

Fig. 2. Molybdate reac-
tion curves.
A-monosilicic acid,
B-disilicic acid,
C-polysilicic acid,
1-NaI. 2-NaI, tempered
at 775 K, 3-NaII,
4-NaII, tempered at
775 K.

The isomorphous incorporation of Al into a silica matrix
decreases the number of directly interconnected $SiO_{4/2}$ tetraedra
that is the condensation degree of the silicate fragments present in
the solid. As a consequence the reaction rate of the solid with
molybdate yielding β-dodecamolybdato silicic acid increases.
Figure 2 presents the reaction curves obtained by the molybdate
method for samples NaI and NaII. The reaction curves of the mono-
and disilicic acid as well as of a polysilicic acid are added for
comparison. The slopes of the curves represent the first order re-
action rate constants of the formation of the coloured silico-
molybdato complex. The comparison reveals that sample NaI mainly
contains monosilicate fragments, whereas in sample NaII (Si/Al = 2.8)
also fragments of a higher condensation degree exist. A thermal
treatment at 390 and 780 K scarcely affects the condensation degree
in the case of the Na-samples; the slight increase (which is
paralleled by a decrease of the 920 cm^{-1} band in the IR spectra) is
caused by condensation of terminal silanol groups.

By contrast with the Na samples, thermal treatment of NH_4^+
exchanged samples results in a marked increase of the silicate

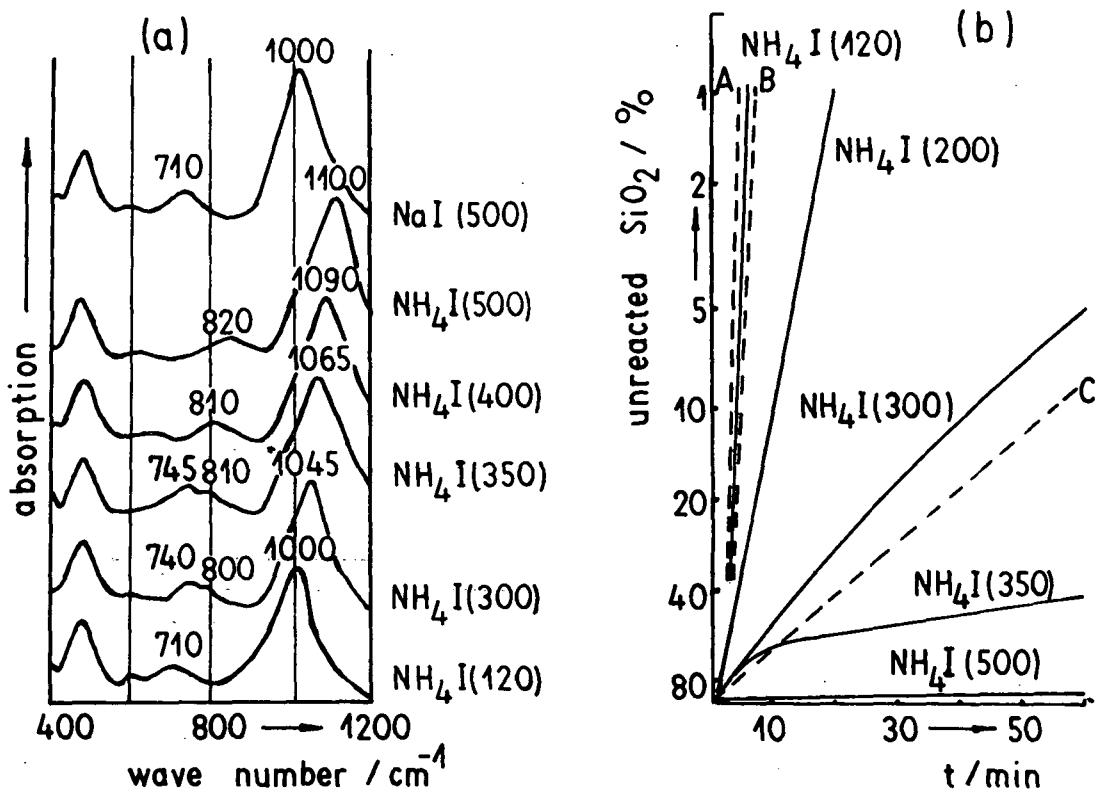condensation degree (cf. Fig. 3b).

Fig. 3. IR spectra (a) and molybdate reaction curves (b) of samples NaI and NH$_4$I after thermal pretreatment at the indicated temperatures.

After a pretreatment at 770 K the condensation degree is so high that the reaction rate with molybdate is scarcely perceptible. New Si-O-Si bonds are formed along with changes in the IR spectra (Fig. 3a), which are in agreement with a removal of Al from 4-fold coordinated sites: shift of the $\widetilde{\jmath}_{asym}$ band to higher wave numbers, development of the $\widetilde{\jmath}_{sym}$ band at 820 cm^{-1} at the expense of the 740 cm^{-1} band.

The information obtained by various methods about the structure of sample NaI and the corresponding acidic form are summarized in Figure 4. In the Na form (as well as in the uncalcined NH$_4$ form) all Al is present in tetrahedral sites. In the ^{27}Al MAS NMR spectrum a single signal appears with a chemical shift of 52 ppm due to Al in AlO$_{4/2}$ tetrahedra (AlCl$_3$ in aqueous solution as external standard) /10/ /12/. Because there are no direct Si-O-Si bonds as derived from

the molybdate reaction, and taking into account the sample
composition (Si/Al~1), the validity of the Loewenstein rule can be
assumed for this sample. This is in accordance with the appearance
of only one signal in the ^{29}Si NMR spectrum /13/. The pure H form
is not obtained. In accordance with the results of the molybdate
method and IR spectroscopy, ^{29}Si NMR proves the formation of new
Si-O-Si bonds. In the ^{27}Al NMR spectrum, the intensity of the
52 ppm line is drastically reduced. The amount of Al remaining in
tetrehedral sites is small, but still sufficient to account for
the Brönsted acid sites. The signal at 0 ppm is due to unstrained
AlO-octahedra. The structure-less broad background signal indicates
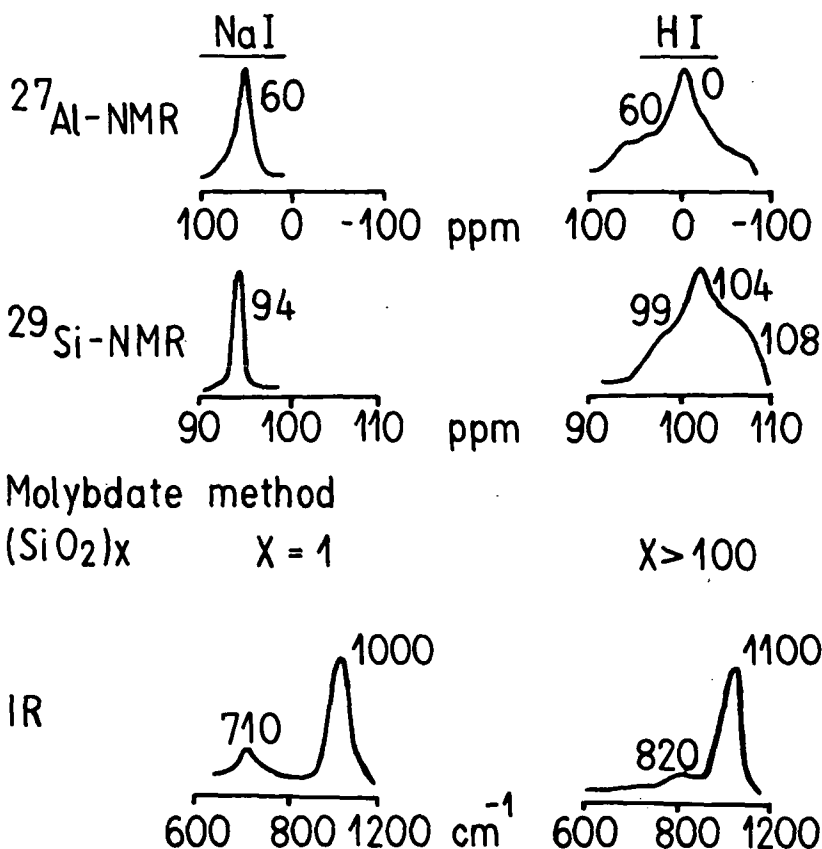that part of the Al is present in strained Al-O-polyhedra.

Fig. 4. Results obtained by different methods on the structure of
samples NaI and HI.

Silica-alumina and zeolites

SiO_2-rich silica-alumina can be regarded as true aluminosilicates possessing a highly dealuminated lattice and a large amount of extra lattice Al. In this respect, it is comparable to hydrothermally ultrastabilized zeolites. This is emphasized by the resemblance between the ^{27}Al NMR spectra of sample HIV and of a zeolite US (w), given in Figure 5a. The US (w), prepared from an NH_4Y zeolite by a 3 hrs vapor treatment at 1090 K /14/, contains 90% of the Al in extra lattice positions. Strength ($H_R \approx -16$) and concentration ($\approx 10^{-5}$ mequ./m^2) of acid sites in both samples are of comparible magnitude. Structural acidic OH groups in silica-alumina resembling those in silica-rich zeolites have been proved by IR /15/.
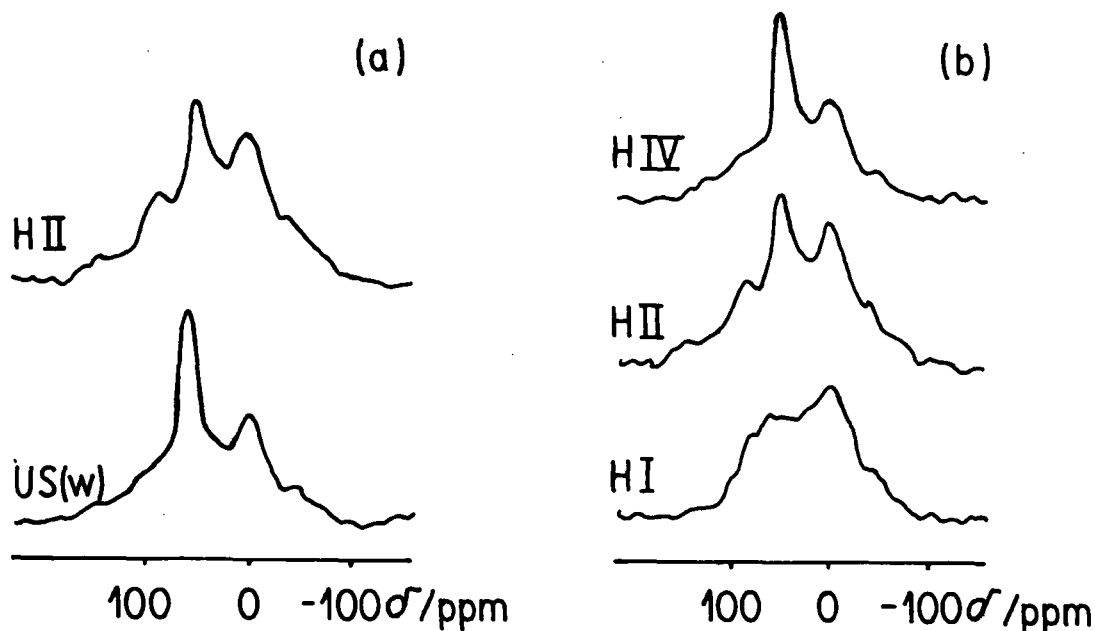

Fig. 5. ^{27}Al MAS NMR spectra of a) samples HI and US (w) and b) samples HI (Si/Al = 1.1), HII (Si/Al = 2.8) and HIV (Si/Al = 4.2).

Such OH groups can be formed by dissociative adsorption of water on extra lattice Al /16/, as it is known for zeolites loaded with polyvalent cations. This may explain the reversible transformation of Lewis into Brönsted sites in silica-alumina upon addition of water /17/. The higher Lewis site concentration explains the stronger tendency of silica-alumina for coking in hydrocarbon conversions.

The selectivity in some complex reactions, e. g. toluene methylation, may be considered as typical for highly dealuminated aluminosilicates /18/.

Effects of composition and preparation

Comparison of the ^{27}Al NMR spectra of samples HI, HII and HIV in Figure 5b suggests that the distribution of the Al over different coordination sites is affected by the Si/Al ratio: In samples HIV (Si/Al = 4.2) and HII (Si/Al = 2.8), which are richer in Si, the intensity of the 52 ppm line (Al^{IV}) is more strongly marked than is sample HI (Si/Al = 1.1) containing less Si.

The simultaneous effect of composition and preparation on the catalytic activity is demonstrated in Figure 6 with the samples of series A and B in the cumene cracking.
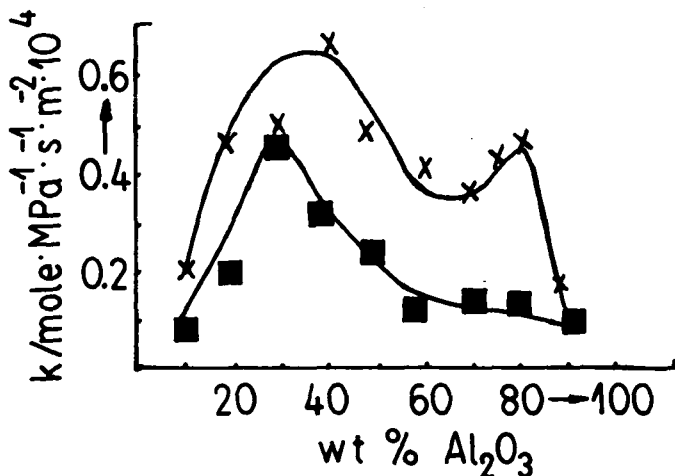

Fig. 6. First order rate constant k of cumene cracking at 675 K on silica-alumina of series A (■) and B (✗).

At a given composition, samples B exhibit a higher activity than samples A. Apart from the maximum at 40 wt %, a marked local maximum appears at 80 wt % Al$_2$O$_3$ in series B. The sequence of activity of

the various samples correspond to their sequence of acid site
concentration, only samples of series B with about 80 wt % Al_2O_3
are characterized by a particularly high concentration of weakly
acidic sites /8/.
Obviously, the interaction between the both components alumina and
silica is stronger in samples B than in samples A. These differences
cannot be levelled by subsequent tempering, as is evident from
different tendencies for mullite formation, considerably more pro-
nounced in samples B /8/. The nature of the amorphous alumina phase
in the alumina-rich samples of series B appears to be related to
that of the amorphous oxide phase formed by the extra lattice Al
on the crystallite surface of zeolites at prolonged hydrothermal
treatment /14/. This phase is very reactive, and is rapidly attacked
by diluted acids, moreover, it appears to play a special role as
adsorption sites in catalytic hydrocarbon reactions /19/.

CONCLUSION

Structure and properties of silica-alumina can be compared to
those of highly dealuminated zeolites containing a large amount of
extra lattice aluminium.

REFERENCES

 1. Fripiat, J.J., Léonard, A., Uytterhoeven, J.B., J. Phys. Chem.
    69, 3274 (1965).
 2. Pott, G.T., Proc. 6th Intern. Congr. Catal., London 1970, Vol.1,
    p. 195.
 3. Peri, J.B., J. Catal. 41, 227 (1976).
 4. Miesserov, K.G., J. Catal. 13, 169 (1969).
 5. Sato, M., Aonuma, T., Shiba, T., Proc. 3rd Intern. Congr.
    Catal., Amsterdam 1964, p. 396.
 6. Léonard, A., Suzuki, S., Fripiat, J.J., De Kimpe, C., J. Phys.

$\underline{68}$, 2608 (1964).

7. Damon, J.P., Delmon, B., Bonnier, J.M., J. Chem. Soc., Faraday Trans. I $\underline{73}$, 372 (1977).

8. Bremer, H., Jank, M., Weber, M., Wendlandt, K.-P., Z. anorg. allg. Chem. $\underline{505}$, 79 (1983).

9. Bremer, H., Jank, M., Fahlke, B., Starke, P., Wendlandt, K.-P., Z. anorg. allg. Chemie $\underline{500}$, 51 (1983).

10. Müller, D., Starke, P., Jank, M., Scheler, G., Bremer, H., Wendlandt, K.-P., Z. anorg. allg. Chem. $\underline{517}$, 167 (1984).

11. Lohse, U., Alsdorf, E., Stach, H., Z. anorg. allg. Chem. $\underline{482}$, 49 (1981).

12. Müller, D., Hoebbel, D., Gessner, W., Chem. Phys. Lett. $\underline{84}$, 25 (1981).

13. Heidemann, D.,
Z. anorg. allg. Chem. in press.

14. Lohse, U., Dissertation B, Berlin 1981.

15. Kazansky, V.B., Kustov, L.M., Borovkov, V.Yu., Zeolites $\underline{3}$, 77 (1983).

16. Hunger, M., Dissertation, Leipzig 1984.

17. Basila, M.R., Kantner, T.R., Rhee, K.H., J. phys. Chem. $\underline{68}$, 3197 (1964).

18. Wendlandt, K.-P., Bremer, H., Proc. 8th Intern. Congr. Catal., Berlin (West) 1984, Vol. IV, p. 507.

19. Bremer, H., Weber, M., Vogt, F., Wendlandt, K.-P., this book.