The structure directing effect of cations in aqueous silicate solutions - a Si-29-NMR study

Citation for published version (APA):

Wijnen, P. W. J. G., Beelen, T. P. M., Haan, de, J. W., Ven, van de, L. J. M., & Santen, van, R. A. (1990). The structure directing effect of cations in aqueous silicate solutions - a Si-29-NMR study. *Colloids and Surfaces*, 45, 255-268. <https://doi.org/10.1016/0166-6622%2890%2980029-4>, [https://doi.org/10.1016/0166-6622\(90\)80029-4](https://doi.org/10.1016/0166-6622(90)80029-4)

DOI:

[10.1016/0166-6622%2890%2980029-4](https://doi.org/10.1016/0166-6622%2890%2980029-4)

[10.1016/0166-6622\(90\)80029-4](https://doi.org/10.1016/0166-6622(90)80029-4)

Document status and date:

Published: 01/01/1990

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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The Structure Directing Effect of Cations in Aqueous Silicate Solutions. A ^{29}Si -NMR Study

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(Received 7 August 1989; accepted 18 September 1989)

ABSTRACT

Studies of the dissolution of amorphous silica gel in aqueous hydroxides by ^{29}Si -MAS-NMR, give information on the oligomerisation of dissolved monomeric silicic acid and on the interaction between cations and the silica gel surface. The dissolution rate increases in the order $(\text{LiOH} \approx \text{CsOH}) < (\text{RbOH} \approx \text{NaOH}) < \text{KOH}$, indicating different promoting effects of the corresponding cations in the dissolution reaction. We attribute these differences to hydration properties of adsorbed alkali metal cations. Formation of silicate oligomers at high pH-values proceeds via cyclic trimeric silicate anions which, at high pH-values are more stabilised than the linear silicate anions. Further, the structure of highly polymerised silicate species depends on the alkali metal cation. Here we show for the first time that tetramethylammonium (TMA) hydroxide initially inhibits the dissolution of amorphous silica gel, which is caused by strong adsorption of rather hydrophobic TMA-cations on the silica gel surface. The effect of sodium/TMA-ratios on the dissolution rate was studied, showing that in the case where sodium is present, the rate of silica gel dissolution substantially increases. Studies on the reaction mechanism for the formation of cubic octameric silicate anions stabilised by TMA-cations are also reported.

INTRODUCTION

The diversity and success in applications of silica gels and powders have contributed to the fact that the structure and formation of silica systems have been studied rather extensively. An outstanding review on the chemistry and physics of silica was given by Iler in 1979 [1]. Significant advances, however, have been made since this review, mainly due to developments of new spectroscopic techniques such as FT-high frequency NMR [2-9], FT-IR [10], Raman spectroscopy [11] and small angle X-ray scattering [12,13]. Thus the rather phenomenological studies as reviewed by Iler are strengthened by the molecular studies performed in the last decade.

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In heterogeneous catalysis silica gels are commonly used as a support material of the catalytic active phase. Since catalytic reactions may take place at elevated temperatures and pressures it is very important to retain structure stability and surface inertness of the support material. Moreover, since catalytic systems are prepared in bulk, the structures of the supports should be well-defined and should not suffer from batch to batch variations. Composition of precursors and especially concentration and type of cations present in precursor material may be seen as the main source of variations in the structure of silica gels. Knowledge of the physical chemistry of precursor solutions for silica gels and powders may thus lead to new insights in polymerisation pathways of silica gels. Especially in the field of zeolite synthesis it has been noted that only small amounts of cationic impurities may impose different structures on the as-synthesised zeolites. Moreover, there has been considerable speculation on the role of organic molecules or ions in the synthesis of zeolitic aluminosilicates [14]. For instance, in the synthesis of ZSM-5 zeolites, the tetrapropyl ammonium cation is seen as a template molecule for the formation of intermediates: cage structures consisting of double five ring silicate anions. Using silicon-29 high frequency NMR on silicate solutions, enriched to 95.3 wt% silicon-29, Knight identified as many as 22 silicate anions [7]. Studies with respect to the composition of aqueous silicate solutions and exchange reactions between various silicate anions have been published. From tetraalkyl ammonium silicate solutions it was concluded that organic cations direct the structure of silicate anions [4]. Further, exchange reactions between anions in tetraalkyl ammonium silicate solutions are slow compared to alkali metal silicate solutions [15], whereas the approach towards thermodynamic equilibrium is reported to be slow as well [16].

The above mentioned results were obtained with silicate solutions being in thermodynamic equilibrium. In this paper we present studies on the dissolution of amorphous silica gel. Dissolving silica gel in aqueous alkaline solutions yields a gradual increase in the concentration of monomeric silicate anions. After reaching the thermodynamic equilibrium concentration of monomeric silicate anions, as governed by the pH of the solution (i.e. silica to base ratio), prolonged dissolution of silica leads to oligomerisation of the monomeric silicate anions. In this way, we were able to investigate the polymerisation process of monomeric silicate anions in highly alkaline, aqueous silicate solutions. A reaction pathway for the formation of cubic octameric silicate anions is also given.

EXPERIMENTAL

Aqueous silicate suspensions were prepared by adding appropriate amounts of alkali metal hydroxide and tetramethyl ammonium (TMAOH) hydroxide to amorphous silica gel (Aerosil 380 from Degussa). Teflon containers were

used to minimise the effect of contamination of the solutions by cations leached out of the container wall. Alkali metal hydroxides were obtained from Merck (pro analysi NaOH, KOH) and from Janssen Chimica (pro analysi LiOH, crystalline TMAOH, and 50 wt% solutions of CsOH and RbOH in water). The silica to base ratio in the suspensions as initially mixed were $\text{SiO}_2:\text{M}_2\text{O}=3, 1$ and 0.5 ; M_2O denotes the base used. Doubly distilled and demineralised water was added to yield a 2.6 mol.% solution of silica in water. The freshly prepared suspensions were, as quickly as possible, introduced into a double air bearing magic angle spinning (DB-MAS) rotor obtained from Bruker Spectrospin. A typical time from initial mixing to the first acquisition was 5 min. Alumina or zirconia rotors were sealed with Teflon tape to ensure no liquid leakage in the probehead. MAS was applied to average any chemical shift anisotropies arising from highly viscous fluids [17,18] and to average any ^{29}Si and ^1H dipolar coupling, which are probably small anyway. The spinning frequency of the spinners was 1500 ± 100 Hz. Spectra were recorded on a Bruker CXP300 FT-NMR spectrometer operating at 7.05 T or on a AM500 FT-NMR spectrometer at the Dutch National High Frequency NMR facility at Nijmegen, The Netherlands. On both spectrometers, the same single pulse excitation program was applied: 3 μs pulse duration and 4 to 10 s pulse delay. In order to be able to follow the dissolution of silica gel in time, we applied a 45° flip angle. The effect on peak intensity was minimal.

RESULTS AND DISCUSSION

1. Rate dependence of silica gel dissolution on cation hydroxides

Dissolution of amorphous silica gels is achieved by increasing the pH of the suspension. Slowly saturating and subsequently super-saturating the solution in monomeric silicate anions leads to oligomerisation of the monomeric silicate anions. Dissolving amorphous silica gel in aqueous alkaline solutions thus results in a gradual increase in monomer concentration, which subsequently leads to oligomerisation in larger silicate anions. In this way, oligomerisation of monomeric silicate anions can be studied in situ using ^{29}Si -MAS-NMR.

Figure 1 presents a series of natural abundance ^{29}Si -NMR spectra taken at intervals of 100 min in the dissolution reaction of amorphous silica gel in cesium hydroxide at a molar ratio $\text{SiO}_2:\text{Cs}_2\text{O}=3.0$. Throughout this paper we will use the Q_n^i notation as introduced by Engelhardt [2] to specify a certain NMR-line: the superscript i denotes the number of siloxane (Si-O-Si) bridges observed at the silicon-29 atom, whereas the subscript n denotes the number of equivalent Q^i groups within the same molecule. In case no strict assignments can be made, the subscript n (giving the number of Q^i sites within a molecule) will not be referred to since the (broad) NMR line originates from several different silicate anions.

Fig. 1. Natural abundance ^{29}Si -MAS-NMR spectra of aqueous cesium silicate solutions ($\text{Cs}_2\text{O} \cdot 3\text{SiO}_2 \cdot 108\text{H}_2\text{O}$) as a function of reaction time at 296 K. (a) 100, (b) 200, (c) 300, (d) 400, (e) 500, (f) 1000 min. 1500 scans with 4 s pulse delay at 7.05 T.

A relative number for the total amount of dissolved silica gel can be obtained from the total area of the resonance lines. Thus, it is possible to quantify the dissolution rate of amorphous silica gel in alkaline solutions. The maximum concentration of monomeric silicate anions is already reached within 100 min of reaction. This suggests that formation of monomeric silica by dissolution of the gel surface is considerably faster than oligomerisation of the latter to dimer, etc.

In Fig. 2 the relative dissolution rates as derived from NMR line areas are given as a function of the intrinsic radii of alkali metal cations. Normalization was achieved by using the first spectrum of potassium silicate suspensions as an external standard. Undoubtedly, a profound effect of the alkali metal cation on the silica gel dissolution rate is encountered. Also large differences in viscosities of the silica gel suspensions are noticed: potassium hydroxide suspensions are less viscous than suspensions containing lithium or cesium cations. This is somewhat contrary to expectations based on the sheer size of the cations.

Fig. 2. Normalised rate of dissolution (a.u.) obtained from ^{29}Si -NMR spectra as a function of intrinsic cation radii of the alkali metal cations.

The differences in silica gel dissolution rate observed in alkaline solutions cannot simply be attributed to differences in degree of alkali metal adsorption on the silica gel surface: adsorption on silica surfaces decreases uniformly ($\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$) with increasing cation radii [19]. However, in the silica gel dissolution rate an optimum is found for potassium cations. Apparently, in studying the dissolution of silica gel no reference should be made to the intrinsic cation radii but hydration shells must be considered as well. The amount of water molecules forming the hydration shell decreases in the order $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$, where lithium and sodium show the strongest interactions with the water molecules. For this reason, lithium and sodium cations are known as water structure formers whereas potassium, rubidium and cesium are referred to as water structure breakers [20]. The mechanism of silica gel dissolution can be visualised as in Scheme 1.

Negatively charged surface silanol groups (Si-O^-), neutralised by hydrated cations M^+ , are attacked by hydroxyl anions (OH^-) by which the coordination number of the silicon atom is increased to more than four. As a result, the underlying silicon bonds are weakened and monomeric silicate anions are released from the amorphous silica gel phase.

Here we propose that hydration shells of alkali metal cations adsorbed on the negatively charged silicate gel surface, play an important role in the transport of hydroxyl anions towards the surface. Since lithium and to a lesser extent sodium cations interact strongly with the water molecules within their hydration shell, no fast transport of hydroxyl anions towards the surface can occur. Further, rubidium and cesium have loosely bound water molecules and are weakly bound to the silica gel surface. Therefore, in the latter case transport of hydroxyl anions will be slow. In this way, potassium cations combine the relatively small and loose hydration sphere with relatively strong bonds to the silica gel surface and therefore optimally transport the hydroxyl anions towards the silica gel surface. This transport effect is well in line with the observed dependence of silica gel dissolution in suspensions containing different alkali metal cations.

Investigating silica gel dissolution in aqueous tetramethyl ammonium hydroxides (TMAOH) underlines the above mentioned observations. Although tetramethyl ammonium cations are strongly adsorbed on silica surfaces [21] the absence of hydration shells should result in a large inhibition effect in the dissolution of silica gel. This inhibition effect caused by diffusion of hydroxyl anions must become more pronounced in the case where the effective cation radius is increased or in the case where the hydrophilicity of the cations is decreased. Indeed, when amorphous silica gel is dissolved in aqueous TMAOH solutions the dissolution rate decreases drastically as can be concluded from Fig. 3. After 12 h of dissolution only a small part of the amorphous silica gel

Fig. 3. Total amounts of dissolved silicate anions in solutions of cesium silicate (dashed line) and tetramethyl ammonium silicate as a function of reaction time (296 K).

phase has dissolved and resides in monomeric or small oligomeric forms. Since TMA-cations are hydrophobic compared to the alkali metal cations no, or just a very weakly bonded hydration shell around the TMA-cations, is expected. This contributes to the fact that transport of hydroxyl anions towards the fully TMA-covered silica gel surface is very slow and thus silica gel dissolution is very slow. In the case where sodium hydroxide is added to the TMA-silicate suspension, an increase in dissolution rate is observed which is attributed to the fact that besides adsorption of TMA cations on the silica gel surface, adsorption of sodium cations takes place as well.

2. Oligomerisation of monomeric silicate anions at high pH-values

In Fig. 4 ^{29}Si -NMR spectra are presented for silica gel suspensions (Aerosil 380) as a function of dissolution time in cesium hydroxide. The reaction temperature was chosen as 276 K to slow down dissolution and retain high spectral resolution. The total molar composition of the suspension was $\text{Cs}_2\text{O}:\text{SiO}_2:\text{H}_2\text{O}=1:1:36$. Due to the relatively low viscosities of the suspensions and the relatively high concentrations of silicate anions in solution, a

Fig. 4. Natural abundance ^{29}Si -MAS-NMR spectra of aqueous cesium silicate solutions ($\text{Cs}_2\text{O}:\text{SiO}_2:36\text{H}_2\text{O}$) at different times from initial mixing. (a) 15, (b) 45, (c) 60, (d) 120, (e) 205 min. At 276 K and a field strength of 11.75 T. 200 45° pulses at 5 s pulse delay.

marked increase in spectral resolution and signal-to-noise ratios were obtained compared with spectra of higher silica to base ratios as shown in Fig. 1.

During dissolution of silica gel initially monomeric silicate anions are released from the silica gel surface as is deduced from the Q^0 resonance line arising in Fig. 4a at -71.52 ppm relative to TMS. pH-Values, alkali metal cation and silica to base ratio were chosen such that the amorphous silica gel phase steadily dissolves. From the time the solution was saturated in monomeric silicate anions, these oligomerised to form dimeric silicate anions as is deduced from Fig. 4b. Dimeric anions react in turn with monomeric anions forming a trimeric silicate anion. From the position of the resonance line in the NMR-spectrum (Fig. 4c) it was concluded that at these experimental conditions (silica to base ratio) the cyclic structure of the trimeric silicate anion (Q_3^2) is formed first. At a later moment in the dissolution reaction the linear trimeric silicate anion ($Q_2^1Q_1^2$) emerges (Fig. 4d).

Increasing the silica to base ratio leads to significant broadening of the NMR lines. Further, the distinction in the formation of cyclic and linear trimeric silicate anions is less pronounced. The latter implies that in oligomerisation reactions of aqueous silicate anions, the pH-value of the solution is a critical parameter concerning the formation of ring structures (probably expandable to cage structures). At the high pH-values used in our experiments (silica to base ratio = 1.0 or 0.5) cyclisation of silicate anions is preferred rather than formation of linear oligomers. The tendency of silanol groups of a silicate molecule to ionise increases in the order $Q^0 > Q^1 > Q^2 > Q^3$ [1]. Linear trimeric anions contain Q^1 as well as Q^2 silanol groups whereas cyclic trimeric silicate anions only contain Q^2 silanol groups. Since Q^1 -silanol groups are easier to ionise than Q^2 silanols, the ionic charge of the linear silicate anions will be more negative than the ionic charge of the cyclic silicate anions at the same experimental conditions. Further, symmetry considerations concerning the position of negative charges lead to the fact that in the case where the linear structures are ionised, the charges will be divided less evenly over the silicate anion, whereas in cyclic trimeric silicate anions all silanol groups are equivalent and the charge distribution is more symmetrical and thus energetically more favorable. Lowering the pH-value of the solution (increasing the silica to base ratio) causes the structures to be less ionised resulting in an increased stability of the linear structures. Ab-initio calculations on cyclic silicate molecules show that cyclic trimeric silica is energetically less favourable than the cyclic tetrameric (Q_4^2) or larger cyclic silicate molecules [22]. However in these studies no charge effects were considered. In a following publication we will demonstrate the effect of ionic charge on the stability of cyclic and linear silicate structures, using ab-initio calculations.

The final composition of aqueous silicate solutions depends on the type of cation present in solution. Highly polymerised silicate anions are favored to a larger extent by potassium cations. Moreover, lithium silicate solutions con-

Fig. 5. ^{29}Si -NMR spectra of silicate solutions containing different alkali metal cations. (a) Li, (b) Na, (c) K, (d) Rb, (e) Cs. 1500 45° pulses with 4s pulse delay at 296 K and a field strength of 7.05 T.

tain silicate anions of the Q^3 resonance group resonating at the high field edge of the band (δ more negative) whereas cesium silicate solutions contain anions resonating at the low field edge (Fig. 5).

3. Oligomerisation in the presence of organic hydroxides

In Fig. 6a-e natural abundance NMR spectra of tetramethylammonium silicate solutions are shown as a function of time from initial mixing. In contrast to spectra of alkali metal silicate suspensions (Fig. 1) we observed rather sharp resonance lines indicating a narrow distribution of silicate anions. Moreover, the initial rate of silica gel dissolution was very slow compared to rates observed in aqueous alkali metal suspensions (Fig. 3). Monomeric silicate anions oligomerised very slowly to form dimeric silicate anions (Fig. 6b) which in turn gradually evolved into a Q^2 -silicate structure. Besides a very sharp resonance line, several diffuse lines at slightly lower field were observed. After a considerable time delay (833 min from mixing) a resonance line denoting Q^3 -structures emerged. From the moment these structures are formed, the rate of silica

Fig. 6. Dissolution of amorphous silica gel in aqueous tetramethyl ammonium hydroxide ($\text{TMA}_2\text{O} \cdot 3\text{SiO}_2 \cdot 108\text{H}_2\text{O}$) after; (a) 83, (b) 250, (c) 833, (d) 1083, (e) 1250, (f) 1500, (g) 1666, (h) 1833, (i) 2083, (j) 2500 min. 500 45° pulse with 10 s pulse delay, a field strength of 7.05 T and 296 K.

gel dissolution increases sharply as is concluded from the total amount of dissolved silicate anions (Fig. 3). The molar composition of the final solutions resembled compositions used by Hoebbel et al. [24] and Knight and Oldfield [15]. From these studies we learned that in aqueous silicate TMA-silicate solutions, cubic octameric silicate anions Q_8^3 were preferentially present. Moreover, since the chemical shift values in our spectra are in agreement with values given in literature, the main component in the final solution was assigned as the cubic octameric silicate anion. Table 1 lists chemical shifts as given in the literature [7] and found in this study. A reaction pathway for the formation of cubic octameric silicate anions in aqueous solutions can be proposed using the spectra given in Fig. 6. Observing the line intensities of the resonance at

TABLE 1

Chemical shift values for silicate anions in aqueous silicate solutions (relative to δ_{TMS})

Solution	Q^0	Q_2^1	Q_3^2	Q_4^3	Q_6^3	Q_8^3
K-SiO ₂ 2 ^a	-72.42	-81.01	-82.59	-88.51	-89.64	-99.3
TMA-SiO ₂	-71.91	-80.59	-82.10	-88.26	-89.17	-99.11
TEA-SiO ₂	-71.53	-79.98	-81.82	-88.35	-89.20	-

^aValues taken from Ref. [7].

Fig. 7. Dissolution of amorphous silica gel in aqueous tetramethyl ammonium hydroxide (TMA₂O:SiO₂:35H₂O) after; (a) 133, (b) 400, (c) 1067, (d) 1600, (e) 2000, (f) 2800, (g) 3333, (h) 4000 min. 400 45° pulse with 20 s pulse delay, a field strength of 7.05 T and 296 K.

$\delta = -89.17$ ppm, an optimum in intensity was seen indicating that the structure causing this resonance must be an intermediate in the reaction towards the formation of the cubic octameric silicate anion. Consulting the chemical shift values given by Harris and Knight [6] several structurally different silicate anions can be assigned to the resonance line emerging in Fig. 6c. Since there was no strong other line evolving in the spectrum we assumed that the corresponding silicate anion consisted of silicon nuclei with equal chemical

Fig. 8. Comparison between aqueous tetramethyl ammonium silicate (TMA) and tetraethyl ammonium (TEA) silicate solutions.

shifts. Possible candidates for the -89.17 ppm ^{29}Si -NMR line were the prismatic hexameric anion Q_6^3 (having a chemical shift in the Q^2 -resonance area) and the cyclic tetrameric silicate anion. Since our chemical shift values for the 'unknown' resonance line were in between the chemical shift values for the Q_6^3 and Q_4^2 structures taken from Refs [5,6] (Table 1), it was not possible to assign the line to one of these structures directly.

Figure 7 shows the process of silica gel dissolution in excess tetramethylammonium hydroxide ($\text{TMA}_2\text{O}:\text{SiO}_2=1$). As in the case of alkali metal hydroxides, at high pH small oligomers are favoured rather than large oligomeric silicate anions. This resulted in a higher concentration for the intermediate silicate anions as clarified by the spectra in Fig. 7. However, still no decision can be made for the assignment of the resonance line at $\delta = -89.17$ ppm. Further, silylation and subsequent analyzation of the trimethyl silylated silicate anions by GLC [23], did not exclude one of the possible intermediate anions: in trimethyl silylated silicate solutions the amounts of Q_4^2 and Q_6^3 were comparable.

Tetraethyl ammonium cations are known to stabilise prismatic hexameric silicate anions [24]. Figure 8 shows silicon-29 NMR spectra of tetraethyl ammonium silicate solutions and tetramethyl ammonium silicate solutions. Comparing these spectra might give a decision for the silicate anion acting as the intermediate in the formation of cubic octameric silicate anions. The prismatic hexameric silicate anion was seen as the main intermediate structure in the

formation of cubic octameric silicate anions at high pH. However, at the moment we still cannot exclude Q_4^2 being the intermediate, since fast reaction between two Q_4^2 -anions might yield Q_8^3 as well.

Further, the strong inhibition effect of TMA-cations on the dissolution of amorphous silica gel encountered in Fig. 4, is explained by the fact that strong adsorption of apolar TMA-cations on the silica gel surface causes screening of the surface. Only few hydroxyl anions are able to reach the silanol surface groups. From the moment cubic octameric silicate anions are present in solution, the dissolution rate increases substantially. This we attribute to the fact that cubic octameric silicate anions are in the vicinity of TMA-cations adsorbed on the silica gel surface, resulting in a more hydrophilic silica gel surface. Transport of hydroxyl anions can now take place via (hydrated) cubic octameric silicate anions.

This effect of TMA-cations on the dissolution of amorphous silica gel has not been noticed in previous studies to the best of our knowledge. The induction period observed in zeolite synthesis might result from the inhibition effect encountered in this study.

CONCLUSIONS

An optimum in the dissolution rate of amorphous silica gel in aqueous alkali metal cation solutions was encountered with potassium hydroxide as the counter-ion. Lithium and cesium hydroxide solutions show the lowest dissolution rates. Differences in dissolution rates are ascribed to transport (diffusion) effects through the cation layer surrounding the silica gel surface: hydroxyl anion transport takes place via the hydration shell of the cations. Compared to potassium cations, lithium cations barely exchange their water molecules whereas cesium cations only have few directly bonded water molecules.

Oligomerisation of aqueous monomeric silicate anions takes place via dimeric anions towards cyclic trimeric anions. The amounts of cyclic trimeric silicate anions relative to linear trimeric silicate anions decrease in the case where the pH value of the solution is lowered, i.e. when the silica to base ratio is raised.

Dissolution of amorphous silica gel in aqueous tetramethyl ammonium hydroxide initially takes place at a very slow rate. Since TMA-cations strongly adsorb on the silica gel surface, screening of the surface by these apolar cations prevents dissolution. From the moment cubic octameric silicate anions are present in solution, the dissolution rate increases markedly caused by a change in hydrophilicity of the silica gel surface: strong interactions between (hydrated) cubic octameric silicate anions and TMA-cations adsorbed on the silica gel surface, renders the surface more hydrophilic. As in other studies, prismatic hexameric silicate anions can be identified as intermediates in the oligomerisation of monomeric silicate to cubic octameric silicate anions.

ACKNOWLEDGEMENTS

This study was financed as an IOP-Catalysis by the Dutch Department of Economic Affairs, The Hague, The Netherlands. We appreciate the assistance of Mr Van der Donck (TUE) in performing silylation experiments and Mrs G. Nachtegaal of the SON-NWO HF-NMR facility at Nijmegen, The Netherlands.

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