Physico-chemical aspects of zeolite-A synthesis and application for environmental safe detergents

Abstract Synthesis of zeolites is characterized by a long lag crystallization period. However, this period is not dead; many precrystallization processes are active, leading to nucleation, followed by rapid crystallization. The most lag-active species are complexes of aluminum and, to a lesser extent, silicium and sodium. If these complexes are exposed to non-equilibrium conditions or outside stress, modified zeolite-A can be obtained. This zeolite has a few properties important for surfactants: significantly higher rate of Ca\(^{2+}\) exchange, lattice windows large enough for Mg\(^{2+}\) binding (21 mg Mg\(^{2+}\) per g zeolite) and increased sorption capacity for nonionics and co-polymers. In connection with trends (compact detergents) the outside zeolite surface area plays an important role. Only under non-equilibrium conditions can zeolite synthesis lead from low (1.3--2.6 m\(^2/g\)) to high surface area (9--12 m\(^2/g\)). Modification can also be made, respective catalytic or inhibitory properties for bleaching substances like perborate or peracids. Appearance of huge quantities of zeolite in the environment (precostal and sludge fertilized field) might have negative side-effects. However, results with six microorganisms (Staphylococcus aureus — gram positive, Escherichia coli — gram negative, Bacillus subtilis, Trichophyton mentagrophytes, Candida albicans and Aspergillus fumigatus) show significant bactericidal effects. The effect is highest for the dangerous Trichophyton mentagrophytes fungi; already 0.1% of zeolite suspension at 20°C is sufficient. In this respect, and due to high affinity for heavy metals, zeolite suspension at 20°C is sufficient. In this respect, and due to the high affinity for heavy metals, zeolite behaves as an environmental cleaner. Results with different algal species are not conclusive within the limited laboratory period of examination that has been conducted.

Key words zeolite-A — synthesis — impure raw material — particle size — ion exchange capacity

Introduction

Although less than 20 years have passed since the first patents [1, 2] of zeolite-A as inorganic builders, its usage in laundry detergents reached 1.1 million tons in 1993, and is still growing [3]. Zeolite-A synthesis in the laboratory was known long before its usage in detergents [4]. Being in crystal form, it seems that physical properties should be stable and unchangeable. Based on that, in the beginning, involvement of zeolite as insoluble material in washing powder demanded significant changes of detergent formulations. As formulations became more sophisticated and new trends appeared (compact detergent) new
physico-chemical characteristics of zeolite itself were needed. Fortunately, zeolite-A properties can be varied to some degree, not only during synthesis, but also in the processing (filtration and drying), so these requirements have been achieved. This is especially valid for two important factors: rate of exchange and crystal-surface.

Many papers and an extensive review [5] of zeolite cleaning action and zeolite-based detergents have been published. Surprisingly, in spite of millions of tons of production, except for craftsmen’s patents, very few papers and no review of synthesis from this point of view have been published so far.

There are two, basically different, syntheses: solute-hydrothermal and precrystallization of solid kaolin (or other natural aluminosilicates). The latter, due to difficulties in obtaining high quality, has not been used in Europe (and only partially in the USA) and is not discussed in this paper. Readers are referred to papers [6—10].

Mechanisms and kinetics of hydrothermal zeolite-A crystallization

From the chemical point of view the reaction is very simple; mixing silicate- and aluminate-solution in excess of water leads to small zeolite crystals of fixed stoichiometry. If the silicate-solution is water glass with a ratio SiO$_2$/Na$_2$O of 2 (very common in detergent zeolite production) and aluminate-solution obtained from Al(OH)$_3$ dissolution in NaOH (also usual) with a ratio Na$_2$O/AI$_2$O$_3$ of 2, the chemical reaction can be presented in a simple way:

\[
\begin{align*}
\text{Na}_2\text{O} \cdot 2\text{SiO}_2 \text{(aq.)} + \text{Al}_2\text{O}_3 \cdot 2\text{Na}_2\text{O} \text{(aq.)} & \rightarrow \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \text{(cryst.)} + 2\text{Na}_2\text{O} \text{(aq.)} \\
\end{align*}
\]  

Equation (1) is very useful for many purposes:

a) analytical determination of all reactants is presented in oxide form;

b) stability of aluminate solutions depends on Na$_2$O/Al$_2$O$_3$ ratio;

c) crystallization field is determined within the Na$_2$O/Al$_2$O$_3$/SiO$_2$/H$_2$O ratio;

d) some properties such as crystal size, exchange rate, and induction period are sensitive to some ratio.

Factors a, b, and c are important for production, and for the application properties. Species from Eq. (1), of course, do not exist in solution. The crystallization mechanism, reaction with real species should be presented. In an ideal case, when waterglass consists of monomeric species only, the reaction is given by:

\[
\begin{align*}
\text{NaH}_3\text{SiO}_4 \text{(aq.)} + [\text{Al(OH)}_3^-\text{Na}^+] \text{(aq.)} & \rightarrow \text{Na}[\text{AlO}_2^- \cdot \text{SiO}_2^-] \cdot 3\text{H}_2\text{O}_{\text{(cryst.)}} + \text{Na}^+ + \text{OH}^- . \\
\end{align*}
\]  

Although the chemical reaction given by Eq. (2) seems quite simple, the underlying mechanism is very complex. Immediately after mixing tetrahedral silicate monomers:

\[
\begin{align*}
\text{OH} & \\
\text{NaO}--\text{Si}--\text{OH} \quad \text{and tetrahedral aluminate:} \\
\text{OH} & \\
\text{OH} & \\
\text{OH} & \\
\text{HO}--\text{Al}--\text{OH} \quad \text{Na}^+ , \\
\text{OH} &
\end{align*}
\]  

an aluminosilicate gel is precipitated. Crystallization begins after a long “induction time,” from 1 to 20 h, depending on the experimental conditions (temperature, Al$_2$O$_3$, H$_2$O and SiO$_2$ concentrations).

There are two basic hypotheses about a possible mechanism:

Gel hypothesis

First proposed by Barrer [15] and Kerr [16, 17], and later by many others [18], nucleation is the result of polymerization of aluminate-silicate-tetrahedral and possibly more complex ions in the liquid phase. When the “current” of nuclei exceeds a critical size, fast crystal growth starts, supplied continuously with silicate and aluminate units from gel dissolution. Aluminosilicate species found in solution by Raman and $^{29}$Si-NMR spectroscopy [19—21] and the possibility of obtaining zeolite directly from liquid phase, omitting gel stage [22], favor this concept.

At present, there is an inclination towards liquid phase crystallization, although, no doubt, both mechanisms appear simultaneously or consecutively, or one of them dominates depending on crystallization conditions.

Industrial processes always occur with overlapping mechanisms and a significant role of gel/liquid interface. The typical example is an early production process. Waterglass and aluminate-solution are simultaneously mixed at 90°C with ratios of:

\[
(2.8—3.1)\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:2\text{SiO}_2 \cdot (70—100)\text{H}_2\text{O} . 
\]

Under these conditions the following results were obtained:

a) Amorphous gel is surprisingly stoichiometric: SiO$_2$/Al$_2$O$_3$ = 2.3 which corresponds to the fusion of 7 silicate with 3 aluminate tetrahedra. Na$_2$O/Al$_2$O$_3$ ratio
