

Role of Selected Synthesis Variables in Nucleation and Growth of Zeolite ZSM-5

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Important reaction variables which affect the hydrothermal synthesis of ZSM-5 zeolites are reviewed. Nucleation and growth mechanisms of these materials are strongly dependent on the nature and concentration of the Al- and Si-bearing reactants, pH, and the type of autoclave used. The resulting ZSM-5 particles exhibit specific sizes and morphologies desired for various catalytic applications: large single crystals having a Si-rich core and an Al-enriched outer surface or polycrystalline aggregates composed of small and homogeneous particles. A close control of these variables enables the formation of a submicrocrystalline material, possibly ZSM-5-like, embedded in an Al-rich aluminosilicate gel phase. The major role of OH⁻ species in controlling the formation of stable nuclei is emphasized. The competitive interaction between various alkali and organic cations with (alumino)silicate anionic species in the initial hydrogel affects the kinetics of crystallization, the product morphology, the particle size, and the Al radial distribution. In addition to zoning, for a given synthesis, the Si/Al ratio of different crystallites increases with their particle size. © 1986 Academic Press, Inc.

Introduction

Since the publication of the first patents describing the synthesis of the high silica zeolite ZSM-5 (1, 2), a large number of patents have reported improved and elaborated recipes yielding this material. In recent years, many efforts and increasing attention have been devoted to gain understanding of the mechanisms which govern the different synthesis procedures. Most of these investigations are summarized and/or discussed in some recent review articles (3-12).

The crystallization of ZSM-5 from hydrogels soon appeared to be strongly dependent on a large number of physical and

chemical variables that affect, jointly or independently, the successive nucleation and growth steps.

In a series of papers, we have described and studied in detail two different synthesis procedures for preparation of ZSM-5 from the Na₂O-(Pr₄N)₂O-Al₂O₃-SiO₂-H₂O system (12-15). For the first time, we obtained evidence that ZSM-5 could be grown from media involving the two extreme synthesis mechanisms that have been already recognized for the formation of Al-rich zeolites. One mechanism (A) implies the growth of ZSM-5 by a liquid phase transportation process and yields large crystals with an inhomogeneous Al distribution. The other mechanism (B) involves a solid gel reconstruction (or surface nucleation) and gives polycrystalline ZSM-5 aggregates

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composed of very small crystallites with rather uniform Al radial distribution. The occurrence of these two types of mechanisms in ZSM-5 synthesis was recently confirmed for the $[\text{NH}_4^+ - \text{Pr}_4\text{N}^+]$ system (16).

In our initial approach (13), most of the classical synthesis variables, such as the chemical nature of the ingredients and their relative molar ratios, the type of autoclave, and the temperature, were optimized. In the next series of investigations, specific attention was focused on other critical factors that may play a prominent role in the synthesis of Si-rich zeolites, i.e., the nature of alkali (12, 15) and organic (14, 17) cations. In addition, the systematic investigation of the role of other parameters (pH, viscosity, stirring time) allowed us to improve the synthesis conditions for procedure B (12).

The aim of the present paper is to emphasize and discuss the most important factors that affect the growth of ZSM-5 in each system, in order to prepare crystalline materials with properties optimized for various catalytic applications.

Description of the Synthesis Procedures A, B, and B'

Procedure A

This procedure involves the addition at room temperature of a sodium aluminate solution to silica dissolved at 80°C in a solution of Pr_4NOH . The pH of the obtained gel is about 11.5–12. The gel is vigorously stirred for about 2 hr at room temperature prior to crystallization.

Procedure B

In procedure B, an acidic (H_2SO_4) solution containing Al^{3+} (from Al sulfate) and Pr_4N^+ (from Pr_4N bromide) is added to an aqueous solution of sodium silicate. The resulting acidic mixture is stirred for about 3 hr before adjusting its pH (around 2) to about 11 by further addition of concen-

trated NaOH. The final gel is aged at room temperature for several hours before heating.

Procedure B'

An improvement of this synthesis (procedure B') consists in simultaneously adding to an aqueous NaCl solution the $\text{Al}^{3+} - \text{Pr}_4\text{N}^+ - \text{H}_2\text{SO}_4$ solution and the amount of Na silicate required to adjust the pH of the gel to about 3–3.5. After about 3 hr stirring, the pH is raised to 9–9.5 by addition of the remaining Na silicate solution. The final gel is stirred for 3–4 hr before hydrothermal treatment.

In the latter procedure, NaCl and the Pr_4N^+ ions can be replaced by other alkali or ammonium chlorides and organic bases or cations, respectively. On the other hand, the final pH of the aged gel can be varied by subsequent addition of concentrated H_2SO_4 or NaOH.

Details on molar compositions and operating conditions are given and discussed elsewhere (12–15). Table I compares the three synthesis procedures. Figure 1 shows the pH variations occurring during the preparation and aging of the gels.

Effect of pH on Nucleation

Procedure A

It has been already demonstrated (13–15) that in procedure A the rate-limiting step for the formation of ZSM-5 nuclei is the slow depolymerization of silica dissolved in Pr_4NOH . A small number of probably single (18) or double (19) five-membered Si–O cyclic species may be formed at these pH values (20). The solution of silica in Pr_4NOH is readily supersaturated (21) and Pr_4N^+ –silica-condensed species appear (22). According to a recent study by Scholle (23), who reinvestigated the synthesis of type A, these Pr_4N^+ –silica entities can be considered as simple associations,

TABLE I
SYNTHESIS PARAMETERS AND OPERATING
CONDITIONS FOR PROCEDURES A, B, AND B'

	Procedure		
	A	B	B'
Source of Al (soln. I)	Na aluminate	Al sulfate (in H ₂ SO ₄ + Pr ₄ NBr)	
Source of Si (soln. II)	SiO ₂ in Pr ₄ NOH	Na silicate (28.5 wt% SiO ₂ , 8.8 wt% Na ₂ O)	
Other ingredients (soln. III)	—	NaOH	NaCl
Mixing	(I) in (II)	(I) in (II), then (III)	(I) + (II) in III, then III
	Final gel composition (molar ratios)		
Si/Al	12.20	44.60	48.30
Al/Na	0.97	0.03	0.02
OH ⁻ /SiO ₂	0.68	0.20	0.10
Pr ₄ N ⁺ /SiO ₂	0.60	0.10	0.09
H ₂ O/SiO ₂	17.00	45.10	25.30
	Hydrothermal, PYREX autoclaves		
Temperature (°C)	120	120	130
Time (hr)	320	48	110
required to obtain 100% crystallinity			

precursors to the stable ZSM-5 nuclei. They further arrange into chains and layers of five-membered rings as found in the ZSM-5 crystalline structure, in which the Pr₄N⁺ ions are stabilized only after 2 days heating.

When aluminate ions are introduced in the system, they essentially condense with the silicate anions and form aluminosilicate complexes which are less soluble in basic media (20). They precipitate as a gel. In procedure A, ZSM-5 nuclei were shown to grow by transportation of soluble species in equilibrium with the gel (13, 24). As supersaturation for aluminate or Al-rich aluminosilicate species is achieved later than for the remaining silicate anions, the Si-rich nuclei initially formed continue to grow by incorporation of the Si-richer species (25). Consequently, growth is favored over nucleation. The number of crystallites stays constant during the crystallization step and the crystals grow, eventually at the expense

of the remaining aluminosilicate gel. The latter progressively releases the Al-enriched soluble species which will ultimately be incorporated in the outer layer of the crystallites.

It is concluded that such a liquid phase ion transportation process will always yield large ZSM-5 crystals showing Al zoning. The presence of an Al-enriched outer rim was indeed confirmed in the present case by combining surface and bulk analytical methods (12, 13, 15) or by analyzing the intermediate phases by high resolution solid state ²⁷Al and ²⁹Si NMR (27). This phenomenon was also observed in other syntheses involving an A-type mechanism (23, 24, 28–30).

Note also that a rapid growth of Si-rich ZSM-5 crystals in the presence of an Al-rich amorphous gel phase sometimes yields well-outlined single crystals which contain, either admixed (23, 31) or occluded (32), an Al-rich amorphous phase as impurity. In the present case, such a phase was indeed detected by combined analytical methods (12) within the crystalline material prepared by our type A procedure.

Procedures B and B'

The main step in procedures B and B' consists in admixing the ingredients at

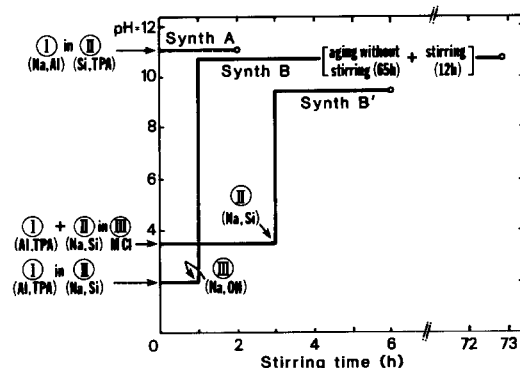


FIG. 1. pH variations occurring during the preparation and aging of the gels in procedures A, B, and B'.

acidic pH. Upon rapid acidification of Na silicates having a $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio between 2 and 4, the oligomeric silicate anions readily depolymerize, yielding quasi-monomeric H_4SiO_4 or HSiO_4^{3+} species at pH 1.5–3.0 (33–36). At higher pH values, they begin to aggregate and gelation is rapidly achieved at pH 5–6 (36).

In the presence of Al^{3+} ions, the hydrogel which is immediately formed is also supposed to involve nearly monomeric aluminosilicate species. It actually has nearly the composition expected from the ingredient ratios because the supply of silicate ions is no longer limited by depolymerization. Thus, nucleation can start during the early stages in acidic medium, directly within the gel in which numerous Pr_4N^+ structure-directing cations are well dispersed. Such a gel is ready to undergo direct recrystallization by surface nucleation. Higher pH values drastically reduce the induction period and favor rapid growth (4, 26, 37). During heating, rapid nucleation yields a large number of small crystallites that eventually form larger aggregates. Their Al distribution is expected to be homogeneous, which is confirmed experimentally (12, 13).

Obviously, deviations from the above-described ideal conditions can occur easily. Al gradients (surface Al enrichment) are sometimes observed in ZSM-5 individual crystallites obtained by procedure B or B' (38). It implies ion transportation processes that can always occur at the end of the synthesis, especially when the gel is not perfectly homogeneous.

On the other hand, above pH 8, the Si/Al ratio is not always constant for the different aluminosilicate polyanions that are rapidly formed through the quasi-instantaneous rise in pH. These inhomogeneous domains may reorganize independently and finally yield ZSM-5 nuclei which will grow at a rate somewhat inversely proportional to their Al content. The size of the corresponding crystals will obviously depend on

Si/Al, e.g., the lower the Al content, the larger the size, as confirmed experimentally (12, 13).

A new advantage brought by synthesis B' (with respect to B) is the presence of NaCl in the initial mixture. The primary role of NaCl is to shorten considerably the aging time needed for nucleation by increasing the supersaturation of the gel. It also provides an easy way to introduce in the synthesis mixture other alkali cations that are otherwise less readily available as silicates or hydroxides.

Effect of pH on Crystallization

While the nucleation and growth rates normally increase with increasing pH, at very high OH^- concentrations (e.g., pH values above 11–12), the OH^- species attached to aluminosilicate groups undergo ionization and can prevent further polymerization. Nucleation starts to compete with growth and can even become predominant (36). The formation of very small zeolitic particles is then observed, mainly due to a secondary nucleation of the ingredients released from the dissolution of larger units. Actually, it is the OH^-/SiO_2 ratio that most strongly influences the composition and the degree of polymerization of an aluminosilicate unit, and thus the final size of the zeolite crystallites (26).

In contrast, at lower pH values (e.g., below 9), the dissolution process is essentially absent and well-defined large crystals are formed (39). At pH 8.2 their size can reach about $100 \mu\text{m}$ (40) or more at even lower pH values (41).

Three gel portions withdrawn from the same batch prepared according to procedure B' were heated at 130°C at three different pH values. The characteristics of the final phases are shown in Table II.

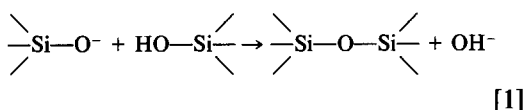
Low pH values result in long crystallization times. For sample 1, the gel transfor-

TABLE II
 VARIATION OF SOME SYNTHESIS PARAMETERS FOR ZSM-5 SYNTHESIZED ACCORDING TO PROCEDURE B'
 AS A FUNCTION OF GEL pH

Expt	pH		Crystallization time (hr)	Crystals		
	Before heating	After heating		Size (μm)	Morphology	Zeolite yield (wt%)
1	6.9	8.4	64	5×10	Single twinned crystals	30
2	9.0	10.0	44	1-5 15-20	Polycrystalline aggregates	3 97
3	11.05	10.9	15	2	Polycrystalline aggregates	100

mation is still incomplete after 3 days. However, the presence of large single crystals is observed. From this observation, it can be anticipated that large ZSM-5 particles could be prepared in neutral and possibly slightly acidic medium more rapidly and in higher yield, by the optimization and control of other parameters of synthesis B'.

The pH increase during heating in Experiments 1 and 2 (Table II) illustrates either the progressive polymerization of the aluminosilicate species or the building of the zeolitic framework at their expense:



At higher pH the depolymerization of the aluminosilicate entities or the redissolution of the zeolite crystals will compensate the release of OH^- species following Eq. [1] so that the final pH value will remain nearly unchanged (41) (Experiment 3).

It is concluded that careful buffering of the synthesis medium should result in an accurate control of the crystal size and in a substantial increase of the zeolite yield (42).

Synthesis of ZSM-5 at low pH values has promising potential applications, e.g., the

preparation of metallosilicates (Fe, Cr, Ti) isotypes. The addition of soluble metal-bearing compounds to a gel prepared at neutral or acidic pH should favor the incorporation of soluble metal entities into the zeolitic lattice.

Finally, high pH is also responsible for the chemical attack of the walls of autoclaves made of borosilicate glass. The Pyrex autoclaves used in our case had the following composition (wt%): SiO_2 , 80.8; Al_2O_3 , 2.2; B_2O_3 , 12.5; Na_2O , 4.2. During heating, boron, among other elements, is transferred into the gel phase and ultimately incorporated into the framework of the growing zeolitic particles. Indeed, the presence of framework tetrahedral BO_4 units in intermediate phases isolated during the crystallization processes A and B' was detected and quantitatively measured by ^{11}B NMR spectroscopy (43, 44). Boron species stemming from Pyrex, mostly present as soluble $\text{B}(\text{OH})_4^-$ anions in the pH range 10-12 (45), are very easily incorporated in the growing zeolite crystallites. The presence of Al, however, retards and/or inhibits the incorporation of B (55).

Such uncontrolled contamination by the guest anions solubilized at high pH can occur very easily. They would be prevented to a large extent by achieving crystallization at lower pH values.

Effect of the Organic Cation on Nucleation

The ability of organics to alter the course of a zeolite crystallization process is a well-recognized phenomenon (3). The clathrating and templating effects of Pr_4N^+ ions in directing the structure of ZSM-5 were recognized early (46) and thoroughly reviewed and discussed in the recent literature (4, 7, 10, 11, 14, 17).

Pr_4N^+ cations form complexes with silicate (22) and aluminosilicate (47) species at the early stages of the nucleation process. It is generally believed that ZSM-5 cannot be formed in the absence of Pr_4N^+ ions or (Pr_4N^+) -ZSM-5 seeds. However, a recent investigation (48) gives a solid indication that ZSM-5 can grow very slowly in the absence of (poly)alkylammonium or NH_4^+ cations if Na^+ ions are present. Addition of slight traces of Pr_4N^+ ions markedly accelerates the formation of ZSM-5. It was concluded that Na^+ cations induce the formation in solution of building blocks which are precursors to the ZSM-5 framework.

Several other studies have indicated that traces of Pr_4N^+ ions are needed to link together the primary (alumino)silicate ring structures to form the first nuclei (14, 22, 23, 47).

We have shown that a submicrocrystalline material exhibiting several properties analogous to ZSM-5 can be prepared and stabilized during the early steps of the crystallization of a gel prepared following procedure B or B'. Such phases may consist of an admixture of microdomains of Pr_4N^+ -ZSM-5-type associations dispersed within the nonzeolitic remaining amorphous aluminosilicate (12, 13, 27, 49).

While such entities are too small to be detected by techniques probing long-range ordering (X-ray diffraction, XRD) (12, 13), we were able to find evidence of some short-range properties that characterize (Pr_4N^+) -ZSM-5-type associations similar to

those encountered in a macrocrystalline (TPA)-ZSM-5 framework. For that purpose, a series of physicochemical techniques was used. Some of them, e.g., DTA (12, 13, 50) or ^{13}C NMR (49), probe exclusively the behavior of the organic molecule whereas others characterize the structure of the aluminosilicate entity that interacts with Pr_4N^+ : infrared (51), Raman (52), or combined ^{29}Si and ^{27}Al NMR (27) spectroscopy. Several of these techniques were also used recently by Scholle *et al.*, to characterize XRD invisible (Pr_4N^+) -ZSM-5 phases prepared according to procedure A (23).

Whatever the real structure of these ZSM-5 precursors is, we would agree with others (19, 23) by stating that traces of Pr_4N^+ ions are needed for these entities to be formed and stabilized. This also substantiates one of our previous findings showing that a ZSM-5-type structure is not readily induced using procedure B or B' unless small traces of Pr_4N^+ ions initiate its nucleation (14).

Such materials were shown to exhibit catalytic properties characteristic of an intermediate pore-size zeolite (51). Their full catalytic potential still needs to be determined.

Finally, once the appropriate (Pr_4N^+) -ZSM-5 nuclei are formed, they grow by incorporating the remaining Pr_4N^+ ions which are regularly positioned into their framework as crystallization proceeds (53).

The Role of Alkali Cations

Cations present in a reaction mixture are often the dominant factor which not only determines the zeolite structure obtained from a given synthesis medium (3) but also affects several of the properties of a given zeolite.

In the case of ZSM-5, alkali ions undoubtedly influence the nucleation and growth rates. The role of the whole series

of alkali cations introduced as chlorides in procedure B' was investigated and thoroughly discussed in the light of their intrinsic structure-ordering properties in aqueous solution (12, 15). In particular, they were shown to modify the Pr_4N^+ -(alumino)silicate gel interactions during the aging period, enough as to affect drastically the morphology, size, chemical composition, and homogeneity of the resulting crystallites (12, 15).

The particular role of Na^+ , the most widely structure-forming cation used in zeolite synthesis (3), was specifically investigated. These ions interact quite readily with the complex aluminosilicate species by ordering the water molecules. Another way to visualize their role is to envisage that the result of such an interaction is the induction of specific building blocks which can interact with Pr_4N^+ and form the first nuclei (48).

In any case, the consequence is that the hydrogel will nucleate rapidly. This was clearly illustrated for the nucleation of ZSM-5 in the presence of Pr_4N^+ and one single cation, Li, Na, K, Rb, or Cs, respectively. Continuous variation was found between the induction period and the cation ionic radius. The curve showed a minimum for Na^+ , in agreement with the optimal structure-directing behavior of this ion.

The predominant role of Na^+ in both nucleation and growth processes is emphasized by the following experimental observations.

Five (M , Pr_4N)-ZSM-5 samples were synthesized from gels using Na silicate and Li, Na, K, Rb, and Cs cations added as chlorides (procedure B'). Each system was bicationic (an exception was made for Na^+ only).

When M (from $M\text{Cl}$, M other than Na^+) is present in the gel, few Na^+ ions (stemming from Na silicate) are incorporated in the corresponding final zeolite (Table III). On the other hand, in procedure B, where only Na silicate is involved in the absence

TABLE III
CHEMICAL COMPOSITION OF THE VARIOUS
 M -ZSM-5 SAMPLES SYNTHESIZED IN THE PRESENCE
OF $M\text{Cl}$ ACCORDING TO PROCEDURE B'

Zeolite	Molar ratios		Unit cell content			
	Al/Na	Al/M	Na	M	Na + M	Al
(Li)-ZSM-5	14.2	3.5	0.19	0.81	0.88	2.70
(Na)-ZSM-5	3.2	2.4	0.80	—	0.80	2.56
(K)-ZSM-5	13.9	2.2	0.17	1.10	1.27	2.36
(Rb)-ZSM-5	9.1	1.8	0.22	1.10	1.32	2.0
(Cs)-ZSM-5	10.0	1.1	0.21	2.00	2.21	2.15

of $M\text{Cl}$, about the same Al/Na ratio (~ 2) and the same Na content per unit cell (~ 1) were found (13). This indicates that Na^+ ions readily interact with the aluminosilicate gel to induce its nucleation in the presence of Pr_4N^+ . Na^+ ions are incorporated along with the organic entities as charge-compensating cations (the Al/Na and Al/M ratios are always higher than unity, Table III). We also demonstrated that their incorporation in the growing crystallite is preferred to that of the other alkali cations (15). This was also confirmed recently by Nastro *et al.* (54). Consequently, the so-formed ZSM-5 should principally contain Na^+ counterions and only a few other M^+ cations. The low Na^+ content and the high M^+ concentration per unit cell (Table III) do not appear in agreement with these observations. We therefore suggest that when the zeolite is grown in the presence of both Na^+ and M^+ ($M^+ = \text{Li, K, Rb, Cs}$), Na^+ ions induce nucleation and are preferentially incorporated during growth, whereas the other alkali ions act as exchange cations toward Na^+ , either during or at the end of the growth process, following the affinity series predicted by the ion exchange diagrams of Chu and Dwyer (56).

Conclusion

We have enlightened and emphasized the roles of selected reaction variables that affect the formation of ZSM-5 nuclei and

their growth in classical hydrogel systems. pH and its variation through the aging and heating steps as well as the competitive interaction between the various organic and alkali cationic species toward the aluminosilicate anions are among the major factors that affect the final properties of the crystalline zeolitic materials. Severe and simultaneous control of these variables is essential to obtain ZSM-5 crystallites with the desired size, morphology, and composition. Procedures allowing the preparation of stable, very small ZSM-5 like submicrocrystallites or large and well-defined macrocrystals, are proposed and optimized. The crystallization of ZSM-5 in neutral or acidic medium has also been evidenced. This observation has potential applications for the preparation of metallosilicates with zeolitic structures.

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