ELSEVIER

Catalysis Today 41 (1998) 37–40

CATALYSIS TODAY

Zeolites as tailor-made catalysts: Control of the crystal size

Francesco Di Renzo*

Laboratoire de Matériaux Catalytiques et Catalyse en Chimie Organique, UMR 5618 CNRS, ENSCM, 8 rue de l'Ecole Normale, 34296 Montpellier, France

Abstract

The size of zeolite crystals – a property which influences the efficiency of catalysts and the selectivity for several reactions – can be controlled by a proper choice of crystallization conditions. A review of the influence of chemical and physical parameters on zeolite crystal size is given. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Zeolites; Crystallization; Synthesis; Crystal size

1. Scope of zeolite crystal-size control

The sensitivity of zeolite catalysts to crystal-size effects derives from the same properties that account for their selectivity. Slow configurational diffusion in molecular-size micropores justifies the preferential adsorption of small reagents and the selective desorption of small products, but this property can also severely impair the effectiveness of the catalyst. Shape-selective catalytic reactions on zeolites [1–3] and diffusion in zeolites [4,5] have been the object of recent reviews. In any case, shape selectivity is higher for larger crystals. The optimum crystal size for shape-selective catalysis is the result of a compromise between selectivity and effectiveness.

Several parameters influence the choice of the optimum size of zeolite crystals: (a) shape-selective catalysis requires larger crystals; (b) catalyst effectiveness is larger for smaller crystals; (c) in bifunctional catalysts, crystal size can influence the average distance between acidic and metallic sites, and modify the product distribution; (d) coke deactivation can be more severe for larger crystals; (e) diffusion of matrix components is easier in the case of smaller crystals; (f) template extraction, cation exchange, even distribution of metal functions are more easily performed for smaller crystals; (g) diffusion of water and extra-framework species as a function of crystal size affect the hydrothermal stability in activation conditions; (h) regeneration of used catalysts can be more difficult for larger crystals; (i) filtration and recovery of very small crystals is a technological challenge.

Crystal size is ultimately imposed by the catalytic reaction: TS-1 crystals larger than a fraction of μm are considered unfitted as phenol hydroxylation catalysts, due to the slow diffusion at the low temperature of reaction [6,7]. In other cases, the optimum crystal size should take into account both reactivity and zeolite activation, as in the case of zeolite beta as cracking catalyst [8].

---

*Corresponding author. Tel: +33 467 144392; fax: +33 467 144349; e-mail: direnzo@cit.enscm.fr

PII S0920-5861(98)00036-4

2. Parameters affecting zeolite crystal size

How to control the size of zeolite crystals? Zeolites follow the usual laws of crystal growth, available in recently re-edited textbooks [9,10]. In batch crystallization, crystal size is a function of the ratio between rate of nucleation and rate of growth. Both rates increase with supersaturation, but the exponential law of the nucleation rate rises more sharply than the low-order power law of the growth rate. As a consequence, smaller crystals and rapid syntheses are observed at high supersaturation. Unfortunately, supersaturation can hardly be considered as an independent variable in zeolite synthesis, concentrations being often controlled by the solubility of ill-characterized amorphous precursors [11]. Several parameters (alkalinity, ionic strength, dilution, and temperature) influence silicate solubility and modify the concentration levels in the synthesis system. The presence of an amorphous ''gel'' also affects diffusion processes in the mother solution, and stirring effectively modifies crystallization kinetics. Nucleation can be affected by other procedures, like aging of the synthesis medium, seeding, and selective crystallization poisoning. The application of classical laws of crystal growth to zeolite synthesis has been thoroughly checked by modelling of zeolite crystallization with population balance models [12–17].

The formation of unwanted competing phases is especially easy in zeolite crystallization. The preparation of each phase has to be independently optimized, and classical reviews are available on zeolite synthesis [18–21]. Notwithstanding the differences among procedures for the formation of diverse phases, several parameters affect in a similar way all zeolite crystallizations. We can classify these parameters as:

- crystallization conditions: temperature, stirring, seeding, gel aging;
- composition-dependent parameters: alkalinity, dilution, ratio between Si and other tetrahedron-forming elements, template concentration, ionic strength, presence of crystallization poisons.

3. Influence of crystallization conditions

Higher growth rates and larger crystals have been observed at higher temperature for zeolites as different as Na–X [11] and silicalite [22,23]. This effect implies that temperature raises growth rate more than nucleation rate. Temperature affects not only the size, but also the morphology of crystals: aspect ratio (length/width) of silicalite crystals increases with temperature [22,23]. This corresponds to different activation energies for the growth of each crystal face, as measured in the case of silicalite [22,23] or mazzite [24].

A correlated phenomenon is the aging of the synthesis mixture at room temperature, which significantly increases the nucleation rate. The influence of aging, observed since early studies on crystallization of zeolites A and X [11,25], has been described in the case of zeolite A [26,27] by assuming that nucleation rate is significant at room temperature, but growth rate is negligible, and nuclei lie dormant until the temperature is raised. This phenomenon is not limited to aluminium-rich zeolites and has been observed, for instance, in the case of TS-1 [28].

Stirring rate significantly affects crystal size. Smaller crystals are obtained from stirred than from static batches for both zeolite beta [29] and TS-1 [28,30]. The effect corresponds to the formation of large zeolite crystals in viscous systems, where convective motion is hindered and mass transfer is diffusion-controlled. Zeolite A, X and gismondine (zeolite P) crystals up to 150 μ have been obtained by counter-diffusion of silicate and aluminate solutions in Carbopol gel [31] or by synthesis in triethanolamine solution [32]. It can be observed that stirring often modifies the selectivity of zeolite crystallization. For instance, zeolite A is preferred to zeolite X in stirred systems, and MFI is formed instead of TON from several unstirred synthesis systems [33].

In the seeding method, a small amount of zeolite is introduced in the synthesis system, usually just before the hydrothermal treatment, in order to direct crystallization towards a given zeolite and control the size of the final crystals. In slightly supersaturated systems, primary nucleation does not take place, and seeds provide the whole growth surface. In this case, seeding produces a faster crystallization and smaller final crystals, as shown in the case of zeolite Y [34,35] and silicalite [36,37]. In more supersaturated systems, the surface of seeds can compete for supersaturation with primary nuclei. In this case, as modelled in the case of zeolite A [38], primary nucleation can be suppressed and seeding results in the formation of larger final crystals.

4. Composition effects

The concentration of OH^- ions, usually referred to as alkalinity of the synthesis system, strongly increases the solubility of silicate species [39]. The formation of smaller crystals at higher alkalinity has been observed for zeolites as different as MFI [40–42] and zeolite X [43]. The morphology of the zeolite formed is affected by alkalinity, in a similar way than by temperature. Higher aspect ratio (length/width) is observed for MFI crystallized at lower alkalinity, suggesting that the aspect ratio of MFI increases at lower supersaturation. Larger crystals at higher alkalinity have been observed in the case of TS-1, but high alkalinity can result in enhanced Hoffmann degradation of the alkylammonium template used, and interfere in the formation of the zeolite [30], as observed at very high alkalinity in the case of the synthesis of ZSM-5 [40].

Not surprisingly, an overall dilution of the synthesis system cause larger crystals to form, for instance in the case of TS-1 [30] or TON [33]. At lower supersaturation growth is favoured at the expense of nucleation. In a similar way, very large zeolite crystals are obtained at low supersaturation when F^- is used as mineralizer instead of OH^- ions [44].

The solubility of the source of silica has been recognized as a relevant parameter since early synthesis of zeolite X [25,45]. Smaller crystals are formed from monomeric silicate solutions than by dissolution of colloidal silica. The same effect has been confirmed in the case of ZSM-5 [40]. Smaller crystals of TS-1 are formed by the hydrolysis of tetraethylorthosilicate than by the dissolution of Ludox colloidal silica [30]. A fair correlation has been obtained between formation of smaller crystals of mordenite and solubility of the silicic acid used as a silica source [46]. In a similar way, when aluminate instead of silica is the limiting nutrient, as in the case of the crystallization of mazzite [24], larger crystals with flat faces are formed from less soluble sources of aluminate [47].

The electrolyte concentration of the synthesis solution influences ion activities. Typically the addition of salts to the synthesis system decreases supersaturation, and larger crystals are obtained, as in the case of ZSM-5 [40] or TON [33] syntheses.

Specific cations can act as poisons for the synthesis of given zeolites. Potassium is well known to act as a crystallization poison for zeolite A [48] and zeolite beta [49]. It can be observed that K hinders the formation of zeolite A more than the formation of faujasite, and this property is exploited in the synthesis of low-silica zeolite X (LSX) [50]. The presence of organics not implied in the formation of the zeolite, but adsorbed on the growth surface, also results in larger crystals, as in another interpretation of the effect of triethanolamine in the formation of large crystals of zeolite A or X [32]. More surprisingly, the effects of the concentration of organics intervening in the crystallization as templates are not straightforward. Larger crystals of MFI have been observed at higher tetrapropylammonium concentration [51], notwithstanding a faster crystallization process [51,52]. Also in the case of zeolite beta, tetraethylammonium (TEA) accelerates the crystallization, but crystal size features a maximum as a function of the amount of TEA [29].

The partial isomorphous substitution of silicon by other tetrahedron-forming elements can influence crystal size. The presence of aluminium often implies the formation of smaller crystals, as observed in the case of MFI [51] and zeolite beta [29]. A similar effect has been observed in the case of gallium incorporation in the same structures, MFI [53] and zeolite beta [54]. On the contrary, the presence of boron brings to the formation of larger crystals of zeolite beta [55].

References

[1] S. Bhatia, Zeolite Catalysis: Principles and Applications, CRC Press, Boca Raton, 1990.
[2] R.A. Rajadhyaksha, M.G. Palekar, in: B. Viswanathan, C.N. Pillai (Eds.), Recent Developments in Catalysis, Technip, Paris, 1992, p. 13.
[3] P.B. Venuto, Microporous Mater. 2 (1994) 297.
[4] J. Kärger, D.M. Ruthven, Diffusion in Zeolites, Wiley, New York, 1992.
[5] N.Y. Chen, T.F. Degnan Jr., C.M. Smith, Molecular Transport and Reaction in Zeolites, VCH, New York, 1994.
[6] B. Notari, Stud. Surf. Sci. Catal. 67 (1991) 243.
[7] A.J.H.P. Van der Pol, A.J. Verduyn, J.H.C. Van Hoof, Appl. Catal. A 92 (1992) 112.
[8] L. Bonetto, M.A. Camblor, A. Corma, J. Pérez-Pariente, Appl. Catal. 82 (1992) 37.

[9] J.W. Mullin, Crystallization, 3rd ed., Butterworth-Heinemann, Oxford, 1993.

[10] O. Söhnel, J. Garside, Precipitation, Butterworth-Heinemann, Oxford, 1992.

[11] S.P. Zhdanov, N.N. Samulevich, in: L.V.C. Rees (Ed.), Proceedings of the Fifth International Conference on Zeolites, Heyden, London, 1980, p. 75.

[12] R.W. Thompson, T.C. Ying, Zeolites 4 (1984) 353.

[13] R.W. Thompson, A. Dyer, Zeolites 5 (1985) 202.

[14] R.W. Thompson, A. Dyer, Zeolites 5 (1985) 292.

[15] R.W. Thompson, in: C.R.A. Catlow (Ed.), Modelling of Structure and Reactivity in Zeolites, Academic Press, London, 1992, p. 231.

[16] C.S. Cundy, M.S. Henty, R.J. Plaisted, Zeolites 15 (1995) 353.

[17] C.S. Cundy, M.S. Henty, R.J. Plaisted, Zeolites 15 (1995) 400.

[18] R.M. Barrer, Hydrothermal Chemistry of Zeolites, Academic Press, London, 1982.

[19] J.L. Guth, P.J. Caullet, Chim. Phys. 83 (1986) 155.

[20] P.A. Jacobs, J.A. Martens, Synthesis of High-Silica Aluminosilicate Zeolites, Elsevier, Amsterdam, 1987.

[21] R. Szostak, Molecular Sieves: Principles of Synthesis and Identification, Van Nostrand Reinhold, New York, 1989.

[22] N.N. Feoktistova, S.P. Zhdanov, W. Lutz, M. Bülow, Zeolites 9 (1989) 136.

[23] C.S. Cundy, B.M. Lowe, D.M.J. Sinclair, Chem. Faraday Discuss. 95 (1993) 235.

[24] F. Fajula, S. Nicolas, F. Di Renzo, C. Gueguen, F. Figueras, in: M.L. Occelli, H.E. Robson (Eds.), Zeolite Synthesis, American Chemical Society Symposium Series, vol. 398, 1989, p. 493.

[25] E.F. Freund, J. Crystal Growth 34 (1976) 11.

[26] J.D. Cook, R.W. Thompson, Zeolites 8 (1988) 322.

[27] B. Subotic, J. Bronic, Poster Abstracts of the Seventh International Zeolite Conference, Japan Association of Zeolite, Tokyo 1986, p. 45.

[28] S. Gontier, A. Tuel, Zeolites 16 (1996) 184.

[29] M.A. Camblor, A. Mifsud, J. Pérez-Pariente, Zeolites 11 (1991) 792.

[30] A.J.H.P. Van der Pol, J.H.C. Van Hoof, Appl. Catal. A 92 (1992) 93.

[31] J. Ciric, Science 155 (1967) 689.

[32] J.F.J. Charnell, Crystal Growth 8 (1971) 291.

[33] F. Di Renzo, F. Remoué, P. Massiani, F. Fajula, F. Figueras, T. Des Courières, Zeolites 11 (1991) 539.

[34] H. Kacirek, H. Lechert, J. Phys. Chem. 79 (1975) 1589.

[35] V. Valtchev, S. Mintova, V. Dimov, A. Toneva, D. Radev, Zeolites 15 (1995) 193.

[36] L.Y. Hou, R.W. Thompson, Zeolites 9 (1989) 526.

[37] E.A. Tsokanis, R.W. Thompson, Zeolites 12 (1992) 369.

[38] A.G. Dixon, R.W. Thompson, Zeolites 6 (1986) 154.

[39] R.K. Iler, The Chemistry of Silica, Wiley, New York, 1979.

[40] R. Mostowicz, J.M. Berak, Stud. Surf. Sci. Catal. 24 (1985) 65.

[41] S.G. Fegan, B.M. Lowe, J. Chem. Soc., Faraday Trans. I 82 (1986) 785.

[42] D.T. Hayhurst, A. Nastro, A. Aiello, F. Crea, G. Giordano, Zeolites 8 (1988) 416.

[43] H. Lechert, H. Kacirek, Zeolites 13 (1993) 192.

[44] J.L. Guth, H. Kessler, J.M. Higel, J.M. Lamblin, J. Patarin, A. Seive, J.M. Chezeau, R. Wey, in: M.L. Occelli, H.E. Robson (Eds.), Zeolite Synthesis, American Chemical Society Symposium Series, vol. 398, 1989, p. 176.

[45] K.E. Hamilton, E.N. Coker, A. Sacco Jr., A.G. Dixon, R.W. Thompson, Zeolites 13 (1993) 645.

[46] J. Warzywoda, A.G. Dixon, R.W. Thompson, A. Sacco Jr., S.L. Suib, Zeolites 16 (1996) 125.

[47] F. Di Renzo, F. Fajula, F. Figueras, S. Nicolas, T. Des Courières, Stud. Surf. Sci. Catal. 49 (1989) 119.

[48] J. Warzywoda, R.W. Thompson, Zeolites 11 (1991) 577.

[49] M.A. Camblor, J. Pérez-Pariente, Zeolites 11 (1991) 202.

[50] G.H. Kühl, Zeolites 7 (1987) 451.

[51] V.N. Romannikov, V.M. Mastikhin, S. Hocevar, B. Drzaj, Zeolites 3 (1983) 311.

[52] C.S. Cundy, B.M. Lowe, D.M. Sinclair, J. Crystal Growth 100 (1990) 189.

[53] M.A. Camblor, J. Pérez-Pariente, V. Fornés, Zeolites 12 (1992) 280–286.

[54] G. Giannetto, R. Monque, J. Perez, J. Papa, L. Garcia, Zeolites 13 (1993) 557.

[55] M. Derewinski, F. Di Renzo, P. Espiau, F. Fajula, M.A. Nicolle, Stud. Surf. Sci. Catal. 69 (1991).