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Short Communication

Nucleation promotion of zeolite crystals by in situ formation of silver-based heterogeneous nuclei

F. Hamidi [a,b], F. Boukli-Hacène [a,b], T. Cacciaguerra [c], A. Bengueddach [b], F. Di Renzo [c,*]

[a] *Département de Chimie, Faculté des Sciences, USTO-MB, B.P. 1505 El-Menaouer, 31000 Oran, Algeria*
[b] *Laboratoire de Chimie des Matériaux, Université d'Oran, B.P. 1524 El-Menaouer, 31000 Oran, Algeria*
[c] *Institut Charles Gerhardt, UMR 5253 CNRS-UM2-ENSCM-UM1, Matériaux Avancés pour la Catalyse et la Santé, ENSCM, 8 rue Ecole Normale, 34296 Montpellier Cedex 5, France*

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ABSTRACT

The size of zeolite crystals can be controlled by modifying the nucleation frequency by the addition of silver-based promoters. Nanoparticles of silver oxide can be formed in the alkaline solutions used in zeolite synthesis and can act as effective heterogeneous nuclei for the crystallization of zeolites in a wide range of topology and composition (zeolites LSX, X, Y, A, L, and beta). The presence of silver oxide does not affect the normal nucleation mechanism of zeolites from gels and provides a number of additional seeds proportional to the amount of silver oxide precursors introduced in the synthesis systems. The yield of zeolite crystallization is not significantly affected by the presence of the nucleation promoters. The volume of the crystals formed can be decreased by a factor 20 in the appropriate conditions. The effectiveness of the nucleation promotion is not affected by the presence of organic cations but is largely reduced in extremely alkaline media, in which silver oxides are significantly soluble.

1. Introduction

Most of the applications of zeolites in adsorption and catalysis are related to the small size of their micropores, which implies a relatively slow intracrystalline diffusion and the need to control the size of the crystals to achieve the desired shape selectivity with the shortest effective diffusion path [1–4]. The classical methods to control the crystal size by mastering the residence time in continuous crystallizers [5] are virtually unknown in zeolite synthesis and tuning of zeolite crystal size is usually attained in batch crystallization processes by modifying parameters as temperature, alkalinity and concentration [6–11]. The formation of unwanted phases often limits the field of variation of such parameters and nucleation on heterogeneous seeds appears as an interesting alternative method to control the size of zeolite crystals [12–14]. Albeit several examples of heterogeneous nucleation of zeolites by breeding crystalline zeolite germs [15–22] have been reported, the effectiveness of breeding zeolite nucleation by other kinds of heterogeneous particles is under debate and has been considered a secondary effect by comparison with the formation of zeolite germs by gel ripening or templating [23]. In a typical instance of nucleation promotion by inorganic ions, a substantial reduction of the crystal size of zeolite L, obtained by introducing in the synthesis media barium cations at a concentration exceeding the solubility of barium hydroxide [24], has not been attributed to heterogeneous nucleation but to the property of barium cations to template the structure of zeolite L [25–27]. However, the case for heterogeneous nucleation effects has been strengthened by the observation of a decrease of the size of crystals of zeolite L with the addition of traces of several other sparingly soluble cations, which are not indicated as possible templates of zeolite L [28]. Similar attempts to modify the nucleation rate of mordenite by addition of inorganic cations were unsuccessful [29] and led open to questioning the validity of general mechanisms of nucleation promotion in zeolite synthesis. In this communication, we propose the in situ generation of particles of silver oxide in zeolite synthesis batches as a test to verify the effectiveness of heterogeneous nucleation as a tool to control the size of zeolite crystals.

2. Experimental

The reagents used in the syntheses were Aerosil 200 from Fluka (for syntheses of zeolites LSX and X), precipitated silica Zeosil 75MP from Rhône-Poulenc (for synthesis of zeolites Y), Ludox HS40 from Dupont (for synthesis of zeolite L), sodium hydroxide, potassium hydroxide and sodium aluminate from Carlo Erba, aluminium hydroxide from Merck (for synthesis of zeolite L), tetraethyl ammonium (TEA) hydroxide 40% solution from Sigma–Aldrich, deionized water (1.3 μS cm^{-1}). The molar composition of the different batches of synthesis are given in Table 1. The nominal alkalinity of the synthesis batches was conventionally calculated as the molar ratio $OH^-/Si = (Na + K + TEA - Al)/Si$.

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[*] Corresponding author. Tel.: +33 607508148.
E-mail address: direnzo@enscm.fr (F. Di Renzo).

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Table 1
Molar composition and alkalinity of the synthesis batches.

Zeolite	Na/Si	K/Si	TEA/Si	Al/Si	H_2O/Si	OH^-/Si	OH^- (mol L^{-1})
LSX	5.75	1.2		0.77	71	6.2	4.86
X	2.8			0.67	53	2.1	2.25
A	3.15			1.057	120	2.1	1.67
Y	0.8			0.2	16	0.6	2.14
Beta	0.014		0.41	0.012	11.4	0.41	1.99
L		0.34		0.26	12	0.09	0.40

Zeolite syntheses were carried out in gas-tight stainless steel vessels. In most syntheses, the aluminate was dissolved in the alkaline or template aqueous solution before the addition of silica under stirring. In the synthesis of zeolite Y, the primary gel was aged 24 h at room temperature before heating 72 h at 90 °C. In the synthesis of low-silica X, the primary gel was heated for 8 h at 95 °C. In the synthesis of zeolite beta, the primary gel was heated for 48 h at 150 °C. In the synthesis of zeolite L, Ludox silica suspension was added to the solution obtained by dissolving $Al(OH)_3$ at reflux temperature in the solution of KOH and one third total water [30]. Hydrothermal synthesis was carried out 96 h at 150 °C. In the synthesis of zeolite X, silica was added to a solution obtained by dissolving 70% of total NaOH in 30% of total water. The gel was stirred 5 h before addition of a solution obtained by dissolving sodium aluminate in the remaining NaOH and water. Hydrothermal synthesis was carried out 40 h at 80 °C.

At the end of the preparation of the primary gels, the synthesis batches were stirred 15 min before addition of the amount of 0.01 M solution of silver nitrate from Sigma–Aldrich needed to achieve a 0.6 mM concentration in the synthesis batch (1.1 mM for the synthesis of zeolites Y and beta). After the addition of silver nitrate, the gels were further stirred 30 min before the hydrothermal treatment.

At the end of the hydrothermal treatments, the solid phases were filtered, water-washed and dried at 80 °C. The phases present were determined by powder X-ray diffraction (Bruker D8 diffractometer, Cu Kα radiation, Ni filter) and the crystal size distributions were determined by image analysis on scanning electron micrographs (Hitachi S4500 apparatus). Grain size was measured by light scattering on a Malvern Mastersizer 2000 in water dispersant.

Some amorphous precursors of zeolites were studied by carrying out hydrothermal treatments for a time shorter than the time needed for crystallization of the zeolite. Synthesis times were 1 h for the precursor of zeolites LSX and A and 4 h for the precursors of zeolites Y, L, and beta. At the end of the hydrothermal treatments, the solid phases were filtered, water-washed, progressively dehydrated by immersion in ethanol solutions of increasing concentration (10%, 30%, 50%, 70%, 90%, 100%) and dried by supercritical CO_2 in a Polaron 3100 apparatus. Hydrothermal precursors as well crystallized zeolites were characterized by powder X-ray diffraction and N_2 adsorption at 77 K in a Micromeritics ASAP 2010 apparatus.

3. Results and discussion

SEM images of zeolites LSX, X, Y, L, A, and beta formed in the presence of nucleation promoters are presented in Fig. 1. Zeolites formed were pure phases, with the exception of zeolites A and L, which contained small amounts of, respectively, sodalite and merlinoite impurities.

The mass of zeolite formed in each experiment, reported in Table 2, was not significantly affected by the addition of silver nitrate. The average particle sizes of the zeolites formed in the presence and in the absence of silver nucleation promoter are also reported in Table 2 and the corresponding particle size distributions from scanning electron micrographs are reported in Fig. 2.

The particle size data reported in Table 2 and Fig. 2 indicate that the addition of silver nitrate solution systematically brings about a decrease of the average size of the zeolite grains. The mass of crystals formed being virtually unaffected by the addition of the silver promoter, the observed decrease corresponds to an increase of the number of zeolite grains formed, as reported in Table 2. It can be easily observed that the variation of grain number induced by the promoter largely varies from one preparation to another, spanning from a less than twofold increase, in the case of zeolites LSX, A, and beta, to a more than 15-fold increase in the case of zeolite X.

Grain size data from light scattering are also reported in Table 2 and the corresponding size distributions for zeolites A and X are reported in Fig. 3. Sizes measured by light scattering are usually larger than sizes from SEM image analysis, due to the higher impact of crystal aggregation on the measurement. This effect was especially evident in some distributions, like in the case of the zeolite X of Fig. 2b, which presents a secondary peak beyond 10 μm corresponding to large crystals aggregates. Such large-size aggregation peaks were not taken into account in the grain size determinations reported in Table 2. Grain size measured by light scattering confirmed the decrease of size with the addition of silver nitrate for all samples, with the only exception of zeolite LSX, for which the prevention of aggregates heavily reduces the reliability of crystal size determination also in the case of SEM image treatment.

The correlation between the conditions of synthesis and the effectiveness of the promotion of nucleation by silver can be better apprehended through the simplifying hypothesis of addictivity between nucleation in absence of promoter and formation of additional critical germs due to the addition of silver solution. Under this hypothesis, the number of zeolite germs formed by silver addition can be evaluated for each synthesis condition as the difference between grains formed in the presence and in the absence of promoter. The concentration of silver-generated germs is reported in Fig. 4 as a function of the nominal alkalinity of the synthesis batches.

For synthesis conditions with alkalinity lower than 2.5 mol L^{-1}, the number of germs induced by the addition of silver is virtually constant and corresponds to about one zeolite germ generated per four millions silver ions. This indicates that, in this range of alkalinity, the effectiveness of the nucleation promoter does not depend on the different compositions of the synthesis batches. The apparent variations of effectiveness suggested by the data of Table 2 and Fig. 2 are indeed variations of the relative effectiveness between the silver-promoted nucleation and the spontaneous nucleation by gel evolution. The multiplying ratio of the number of crystals formed is lower when the constant number of silver-generated germs is added to a higher number of spontaneously generated crystals (like in the case of zeolite A or beta) than when it is added to a lower number of spontaneously generated crystals, like in the case of zeolite Y.

For synthesis at higher alkalinity, like in the case of zeolite LSX, the effectiveness of silver promotion as measured from SEM grain size variation drops by orders of magnitude and the light scattering data suggest that possibly no nucleation promotion takes place. The variations in effectiveness of silver promotion with alkalinity can be related to the solubilities of silver compounds in the synthesis system. Silver nitrate is very soluble (more than 2 kg L^{-1} at room temperature) but this is not the case for several silver compounds which can be formed in the synthesis conditions. The solubility products of silver chloride is 1.6×10^{-10} and the use of low-grade deionized water provided about 6 μM Cl^- anions in solution, able to precipitate about 1% of the silver present as AgCl. More significantly, AgOH has a solubility product 8.3×10^{-9} and the synthesis solution is alkaline enough to precipitate virtually all silver cations present as silver hydroxide, which spontaneously dehydrates to silver oxide. AgO has an amphoteric character and its