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ZSM-5 zeolite films on cordierite modules. Effect of dilution on the synthesis medium

E.I. Basaldella*, A. Kikot, J.F. Bengoa, J.C. Tara

Centro de Investigación y Desarrollo en Procesos Catalíticos (CINDECA), Facultad de Ciencias Exactas, Universidad Nacional de La Plata calle 47 No. 257-CP1900 La Plata, Argentina

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Abstract

Continuous, multilayered ZSM-5 zeolite films have been grown by direct synthesis on cordierite modules. The influence of the H_2O/SiO_2 ratio used in the synthesis mixture on the film properties was studied by inspecting the film formed in the external module surface at several water contents. It is shown that dilution prevents the film to become dense, modifies zeolite crystal morphology and reduces markedly the crystallization of zeolite into a non-adhered powder form.

Keywords: ZSM-5; Synthesis; Films; Cordierite; Zeolite

1. Introduction

The molecular sieve properties of zeolites make them attractive to use as thin films, either as membranes or surface coating. Many works have been reported on the preparation of these films [1–5].

In some applications, this zeolitic coating is used in reactor design with the aim of reducing pressure drop through the catalytic bed. In these cases, zeolite films are deposited or allowed to grow on monolithic ceramic structures, so as to obtain a "composite" that may work either as zeolitic catalyst or otherwise as support of metals, e.g. Cu to be used in the NO_x reduction reaction [6].

One of the methods used to prepare continuous films on a porous substrate is the synthesis method "in situ", by which a zeolite can be deposited by direct crystallization on different supports. In this procedure, the supports used are immersed in a synthesis gel whose composition is like that of the gels used to homogeneously crystallize the required zeolite. Owing to this feature, composition conditions must be varied to avoid the formation of crystals that, while crystallizing in parallel to film formation, do not adhere to substrate. These particles, sized about 1–10 μm, deposit as powder at the bottom of the reactor; they are undesirable since they only consume a considerable amount of reactants that are not used to generate the film. However, changing the conditions may affect film properties which play an important role in the diffusion process of molecules for catalytic reactions, particularly thickness, porosity and adhesivity.

* Corresponding author. Tel.: +54-221-421-0711; fax: +54-221-425-4277.

E-mail address: eib@dalton.quimica.unlp.edu.ar (E.I. Basaldella).

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On these grounds, films of ZSM-5 zeolite were deposited on cordierite modules to assess the effect of diluting the reaction medium on film characteristics.

2. Experimental

The cordierite modules used as supports are small, square section monoliths, with nine channels per section, and 1 cm in length. The density was 62 channels/cm^2. To obtain the zeolite film on this support, the synthesis conditions were: temperature, 150 ± 5 °C and autogenous pressure. These were selected based on Ref. [7]. To obtain the synthesis mixtures, a solution of Mejorsil commercial waterglass (SiO_2, 26.8% w/w; Na_2O, 9.2% w/w; H_2O, 64% w/w) was added with a stirred solution of tetrapropylammonium bromide (TPA, Fluka, pure) and sodium hydroxide solution (99%, Carlo Erba); the pH was adjusted with H_2SO_4 (Merck, 96% w/w). The compositions of the hydrogels obtained are listed in Table 1, which differ only in the contents of water used. The hydrogels were then transferred to stainless steel autoclaves of 50-ml capacity each, along with cordierite module. The autoclaves were set to the reaction temperature and kept under stirring. Samples were taken at the following reaction times: 24, 72, 144 and 240 h. The loose solids obtained as well as the coated monoliths were washed and dried at 110 °C. Products were identified by X-ray diffraction (XRD). The zeolite types obtained were established by comparing the XRD spectra with those reported in the literature [8]. The diffractograms were obtained in a Philips 1732/10 diffractometer, fitted with CuKα. radiation.

Table 1
Composition of the reaction mixtures used

Test no.	Na_2O/SiO_2	TPA/SiO_2	H_2SO_4/SiO_2	H_2O/SiO_2
935	0.31	0.1	0.16	76
936	0.31	0.1	0.16	106
937	0.31	0.1	0.16	142
938	0.31	0.1	0.16	171
939	0.31	0.1	0.16	240

To evaluate size and morphology of the film crystals, as well as film thickness and porosity, the coated monoliths were split into two pieces. Cross-sections and external surfaces were observed by scanning electron microscopy (SEM) in a Philips 505 microscope. The samples used were coated by a thin Au film. The semiquantitative chemical analysis performed to estimate the Si/Al ratio was carried out by X ray dispersion (EDAX), using a DXPRIME 10 fitted to the scanning electron microscope. The EDAX analysis was done in the conditions stipulated in Ref. [9].

3. Results and discussion

3.1. General characteristics of the films obtained

In all the experiments conducted by using the various initial compositions listed in Table 1, we obtain complete coating of cordierite surface, as well as loose crystals produced by crystallization in the bulk of the synthesis medium. The nature of the obtained zeolite was independent of dilution since the diffractograms of the cordierite–zeolite composite, prepared here at different reaction times, were similar. For example, the diffractogram of the test no. 935 (72 h of reaction) is plotted in Fig. 1, the diffraction peaks correspond to the cordierite–ZSM-5 zeolite mixture, without showing reflections of any crystalline impurity.

Likewise, the chemical composition analysis carried out with the EDAX electronic microprobe indicates that support composition maintains its initial value, i.e., that presented by cordierite before entering the synthesis reactor. With regard to the zeolite generated, the EDAX analyses of different zones of the film give a SiO_2/Al_2O_3 ratio of ≈ 40, which is also maintained constant in all tests. Concerning the XRD and EDAX studies of the powder zeolite that was generated in parallel, they show a material whose characteristics are like that of the film.

The SEM analysis also shows in all cases a continuous, multilayered coating composed of crystals whose morphologies were similar to those described for ZSM-5. The film was found to be composed always of, generally, similar thickness on all walls of a given monolith. Thicknesses varied from

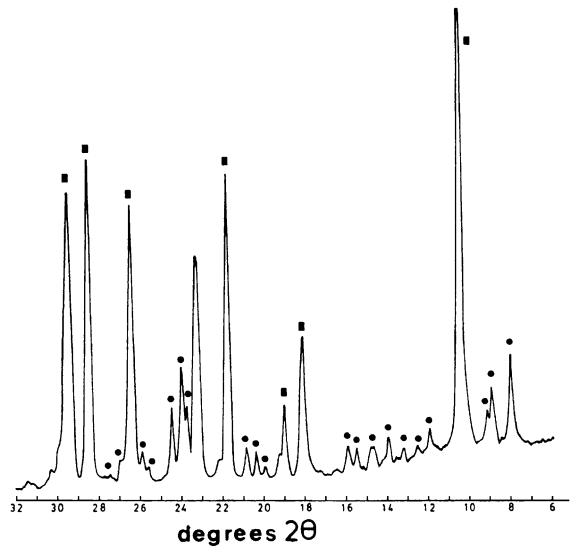

Fig. 1. XRD diagram of zeolite-cordierite composite: (■) cordierite + (●) zeolite.

70 to 100 μm in the different samples, around 10 times the particle size. In samples of the same composition taken at different reaction times, the thicknesses found were also of the same order, so it is considered that the film is already formed before 24 h of reaction.

The SEM analysis detected, in some samples, an evolution of film porosity with the reaction time. At short times, a porous film is observed, formed by superposition of individual crystals, showing that the nucleation sites were distributed homogeneously in the deposited film. For longer times, a variable-density coating appears, composed of a denser zone close to cordierite surface, which is a product of cyrstalline intergrowth, and an outer individual crystal layer, similar to that formed at short times. The formation of the denser, compact layer would seem to modify film adhesivity to the support. In this regard, for cases where the film is less dense, many experiments show crystal detachments. Monoliths presenting the denser zone can survive manipulation and calcination at 540 °C.

3.2. Effect of dilution

The target of obtaining less crystallization by homogeneous nucleation is achieved by dilution, as indicated by the results of Table 2. For various dilutions, the table shows the way the loose solid production varies with reaction time (loose solids expressed as % solids weight/(initial mixture volume), column 4). The growth of the compact film with time (expressed as thickness of compact film/thickness of total film, column 3) is also included.

Dilution causes an important decrease in the loose crystal production. This was evident in the test 935, where an non-adhered solid amount was obtained, which was six times as high as that of test 939. This scarce loose solid formation obtained in the test at higher dilution occurs simultaneously to the crystallization of a continuous film of zeolite crystal multilayers on the cordierite. This composition allows us to observe the effect of cordierite as promoter of a preferential nucleation process at the cordierite–hydrogel interface. If nucleation is considered to occur whenever the concentration of reactant in the reaction medium allows a given supersaturation level to be reached, this level results evidently lower for

Table 2
Effect of dilution on thickness evolution in the dense zone of the film and on loose solids production

Test no.	Reaction time [h]	Dense thickness/ total thickness	Solid weight/ initial mixture volume [g×10^2/ml]
935	24	0	2.4
	72	0.5	2.1
	144	0.6	2.6
	240	0.6	2.5
936	24	0	2.1
	72	0.4	2.1
	144	0.4	1.8
	240	0.5	1.9
937	24	0	1.5
	72	0.3	1.4
	144	0.3	1.2
	240	0.4	1.3
938	24	0	0.6
	72	0	0.7
	144	0.2	0.7
	240	0.2	0.8
939	24	0	0.2
	72	0	0.4
	144	0	0.4
	240	0	0.5

heterogeneous nucleation. The decrease of the homogeneous crystallization process is accompanied by a decrease of thickness of the compact zone, whose formation is noticeably retarded when a less concentrated synthesis medium is used. The film formation and stability are believed to be due to a partial dissolution of the cordierite substrate, which promotes surface nucleation and produces a strong interaction between the first zeolite nuclei layer and the support. These results show the tendency to obtain more stable films deposited on substrates reacting with the zeolite precursor solution, as described by Mintova et al. [10].

If the formation of an amorphous layer of aluminosiliceous gel on the support surface precedes zeolite crystallization, as stated in some film growth models [5], the thickness of this gel should be affected by a considerable dilution in the reaction medium, i.e., by the H_2O/SiO_2 ratio.

Therefore, thicker films would be found at greater dilution. The results of our experiments indicate that the dilutions carried out do not affect the total thickness obtained in any considerable way, though they modify film density. The size of the particles that make up the film do not seem to increase with dilution either, since the characteristics of the particles obtained are very similar, varying only from 7 to 10 μm in the composition range studies. Considering these small differences in particle size, it could be inferred that nucleation process is not altered.

The SEM micrographs of the crystalline coating obtained in tests 935–939, all at a crystallization time of 72 h, are shown in Figs. 2 and 3. Dilution alters the morphology of crystals present in the film, which is the same as that of the loose material taken from the bottom of the reactor. Dilution does not affect the growth rate of the different zeolite crystalline planes to the same extent. The more concentrated reaction mixtures lead to rounded morphology (Fig. 2a), those of intermediate concentration produce intercrystalline growth of cubic crystals (Fig. 2b and c), whereas highly diluted mixtures give raise to cubic crystals without intergrowth (Fig. 3a and b). On the other hand, at intermediate dilutions, the micrographs allow us to see the dense and the porous zones (Fig. 2b and c), while in more diluted mixtures, only a porous layer is formed on cordierite surface (Fig. 3a). Dense zone formation seems to be

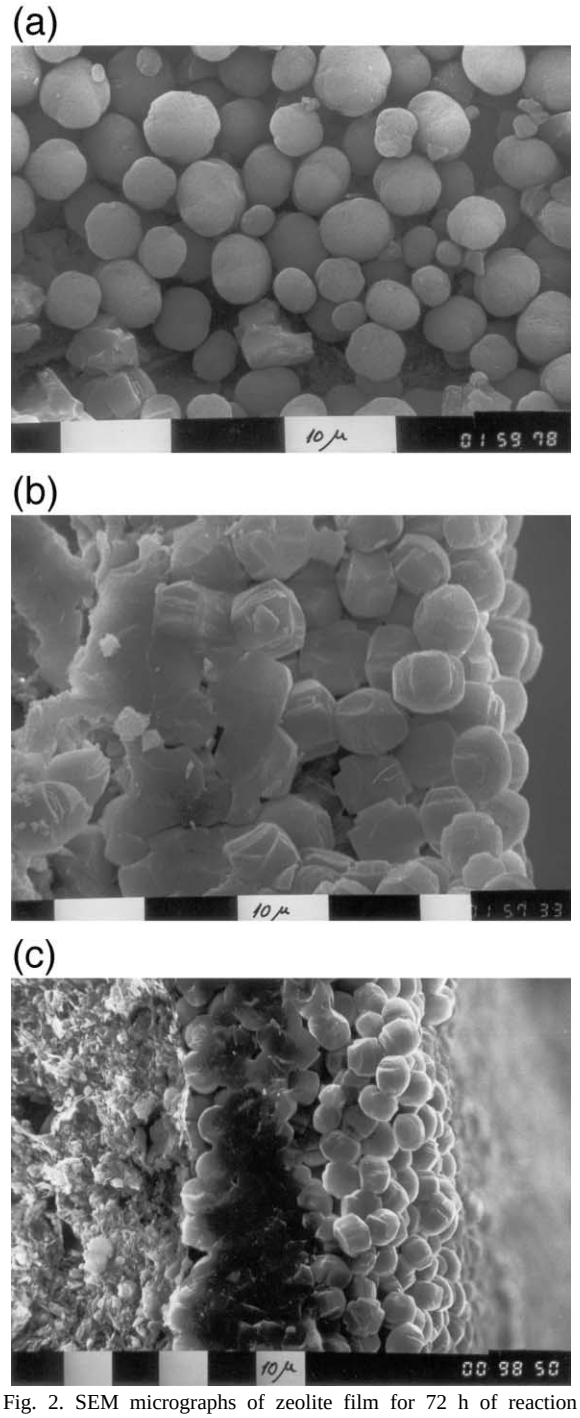

Fig. 2. SEM micrographs of zeolite film for 72 h of reaction (datum 10 μm): (a) Test 935, front view; (b) Test 936, cross-section; (c) Test 937, cross-section.

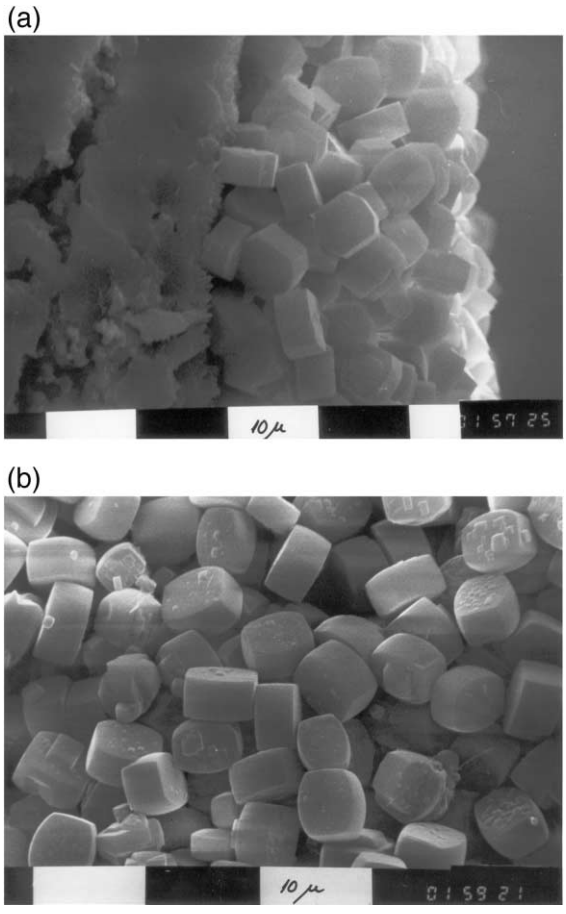

Fig. 3. SEM micrographs of zeolite film for 72 h of reaction (datum 10 μm): (a) Test 938, cross-section; (b) Test 939, front view.

retarded by higher dilution, since a longer reaction time is needed to obtain it (Table 2). It could be stated that the density of nucleation sites on the cordierite surface diminishes with dilution, and although a growth process is taking place, the inter-nuclei spacing becomes so large that the dense film zone is not obtained for the more diluted compositions.

4. Conclusions

The direct, hydrogels-based, synthesis of ZMS-5 zeolite films on cordierite monoliths has shown that the homogeneous nucleation phenomenon can be considerably diminished by increased dilution of the reaction medium.

This increase also produces a decrease of density in the nucleation centers present in cordierite surface. This effect modifies zeolite morphology and slows down the increase in film density with crystallization time.

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References

[1] D.L. Wernick, E.J. Osterhuber, J. Membr. Sci. 22 (1985) 137.
[2] A. Ishikawa, T.H. Chiang, F. Toda, J. Chem. Soc., Chem. Commun. (1989) 764.
[3] E.R. Geus, J.C. Jansen, J. Schoonman, H. van Bekkum, in: G. Shlmann, H. Pfeifer, R. Fricke (Eds.), Studies in Surface Science and Catalysis, vol. 65, Elsevier, Amsterdam, 1991, p. 457.
[4] T. Sano, Y. Kiyozumi, K. Maeda, M. Toba, S. Niwa, F. Mizukami, in: R. Von Ballmoos, J.B. Higgins, M.M.J. Treacy (Eds.), Proceedings of the 9th International Zeolite Conference, Montreal, 1992, Butterworth-Heinemann, Stoneham, 1993, p. 239.
[5] J.H. Koegler, H. van Bekkum, J.C. Jansen, Zeolites 19 (1997) 262.
[6] J.E. Antia, R. Govind, Appl. Catal. A 131 (1995) 107.
[7] E.I. Basaldella, A. Kikot, J.F. Bengoa, M. Sánchez, J.C. Tara, Actas XVI Simposio Iberoamericano de Catálisis, 1998, p. 2213.
[8] D.W. Breck, Zeolite Molecular Sieves, Wiley, New York, 1974, p. 373.
[9] E.I. Basaldella, R. Bonetto, J.C. Tara, Ind. Eng. Chem. Res. 32 (1993) 751.
[10] S. Mintova, V. Valtchev, L. Konstantinov, Zeolites 17 (1996) 655.