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Synthesis of ferrierite coatings on the FeCrAl substrate

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Abstract

Zeolite coatings on metal substrates are highly desirable materials that can be used as efficient catalysts. In this paper we report on preparation of ferrierite type zeolite coatings on a pre-oxidized metal substrate. Ferrierite was chosen due to its unique catalytic properties, including potential application in nitrogen oxides removal. FeCrAl ferritic steel was used as a substrate.

The FeCrAl foil was oxidized in air at 800 °C. The in situ synthesis of ferrierite on the FeCrAl substrate and in bulk were studied using XRD, laser diffraction (LD) and scanning electron microscopy (SEM). Various conditions were applied for coatings preparation, including static and dynamic syntheses, variable nucleation time and type of a gel used. The kinetics of ferrierite crystallization is also reported.

Keywords: Zeolite coatings; Ferrierite crystallization; FeCrAl substrate; Laser diffraction

1. Introduction

Monolithic reactors are becoming more frequently used, especially in environmental applications. First ceramic, then metal monoliths were introduced. Monoliths exhibit low pressure drop, enhanced diffusion properties and excellent heat transfer characteristics. Moreover, high gas flow rates may be applied and the in-flowing stream can even contain solid particles, which do not need to be removed before the catalytic reactor [1].

The catalytically active phase may be deposited in form of a thin layer on a pre-shaped monolith (e.g. honeycomb). Such a phase may be a zeolite. Crystalline aluminosilicates and related solids are microporous and mesoporous materials exhibiting high activity in a number of catalytic processes [2,3]. Scarce information is available on preparation of zeolites on metal substrates [4–6]. Contrary to ceramic honeycombs, it is much more difficult to prepare structural catalyst packings (sheets, nets, monoliths) with desired mechanical properties, i.e. a zeolite coating deposited on the metal surface. A number of metal and metal alloys has been proposed for manufacturing of monoliths, and frequently used is Fecralloy (22% Cr, 5.3% Al, addition of Y). In this contribution we have explored the properties of FeCrAl ferritic steel used in a form of flat and pleated foils 50 μm thick, produced by cold rolling of commercial FeCrAl steel labelled 0H18J5 (76.65% Fe, 18.5% Cr, 4.6 % Al, 0.05% C, 0.001% S, 0.2% other).

A medium-pore zeolite ferrierite (FER), with slightly smaller pore openings than present in ZSM-5 (MFI), was chosen for several reasons. Ferrierite was classified in the group no. 6 by Breck [7]. Its structure was solved by Vaughan [8] and Kerr [9]. The unit cell of ferrierite is composed of 36T atoms (where T = Si, Al], and Si/Al ratios are generally in the range 3.2–6.2, corresponding to 5–8.6 Al per unit cell [10]. It is quite distinct from most known zeolites as the four-membered rings are not present in its structure, and its topological density N_1–N_{10} is high (1021), as compared to faujasite (579), mordenite (938) or MFI (960). Ferrierite is noticeable as having a very stable structure against thermal/hydrothermal and chemical treatments.

Isomorphous substitution on the zeolite T-site is possible. Thus a gallosilicate with the ferrierite structure was obtained [11], as well as a purely siliceous analogue [12]. The catalytic reactions proceeding on this zeolite comprise: isomerization of 1-butene, *n*-octane cracking, NO_x removal and oxidative dehydrogenation of propane [13–18]. Ferrierite is produced commercially and applied in isomerization of butenes on the industrial scale. Catalytic transformations of alkylaromatic hydrocarbons on ferrierite-based solids were also studied [19,20].

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The objective of this work was to study crystallization of ferrierite type zeolite on the pre-oxidized FeCrAl steel as a metallic support. The FeCrAl foil applied exhibits good mechanical resistance properties coupled with relatively low cost. The FeCrAl monoliths might be used for preparation of catalysts required for protection of environment. The hydrothermal crystallization was studied under static and dynamic conditions.

2. Experimental

2.1. Substrate material

A FeCrAl steel was used as a metallic substrate for zeolite crystallization. The steel used in this study was in a form of flat and pleated foil 50 μm thick. The ferritic FeCrAl foil was manufactured by cold rolling of commercial FeCrAl-type steel denoted 0H18J5 with the composition: 76.65% Fe, 18.50% Cr, 4.60% Al, 0.05% C, 0.001% S, 0.20% others (Si, P, Ca, Cu). No Y, Hf, Zr and Ti were present in the steel. After rolling, the steel foil was tempered at 800 °C and degreased in an ultrasonic-aided cleaning system using organic solvents and alkaline detergents. Before using for zeolite crystallization the steel foil was first degreased and then oxidized in air at 800 °C for 5 h. During oxidation a thin film of Al_2O_3 was formed on the surface of the foil (Fig. 1b). The alumina film exhibited a very good adhesion to the substrate. The outer surface of the film was well developed, with some nodules and whiskers present.

2.2. Ferrierite crystallization

Hydrothermal crystallization of ferrierite was carried out at 160 °C using a standard gel composition (cf. Section 2.3), without any metal substrate present in autoclaves.

2.3. Synthesis of zeolite coating on FeCrAl foil

Heat-resistant steel OH18J5 (labelled FeCrAl) was used as a metallic substrate for synthesis of zeolite coatings. Hydrothermal synthesis of ferrierite coatings on the metal substrates was performed using the synthesis gel of following standard composition: 25 SiO_2:1 Al_2O_3:5.6 piperidine:625 H_2O (pH ≅ 12). The silica source was a water glass R. 132 of Vitrosilicon S.A., containing 25.62% SiO_2 and 7.65% Na_2O. The gel was aged at room temperature for 24 h. The oxidized foil was placed in the Teflon-lined autoclaves in horizontal position. After synthesis carried out at 160 °C for 144 h without stirring, the autoclaves were cooled down to ambient temperature. For some experiments another gel was used: 66.5 SiO_2:1 Al_2O_3:37 pyrrolidine:20 Na_2O:6.3 H_3PO_4:1460 H_2O. The gel was aged at room temperature for 2 h, and the synthesis was performed at 160 °C for 40 h. The substrates covered with zeolite coatings were washed with demineralized water, dried at 120 °C for 24 h and, after mechanical removal of loose crystals, calcined at 550 °C for 6 h (to remove the organic template from the zeolite crystals). Calcination of ferrierite-coated substrates in air did not affect the quality of the coatings.

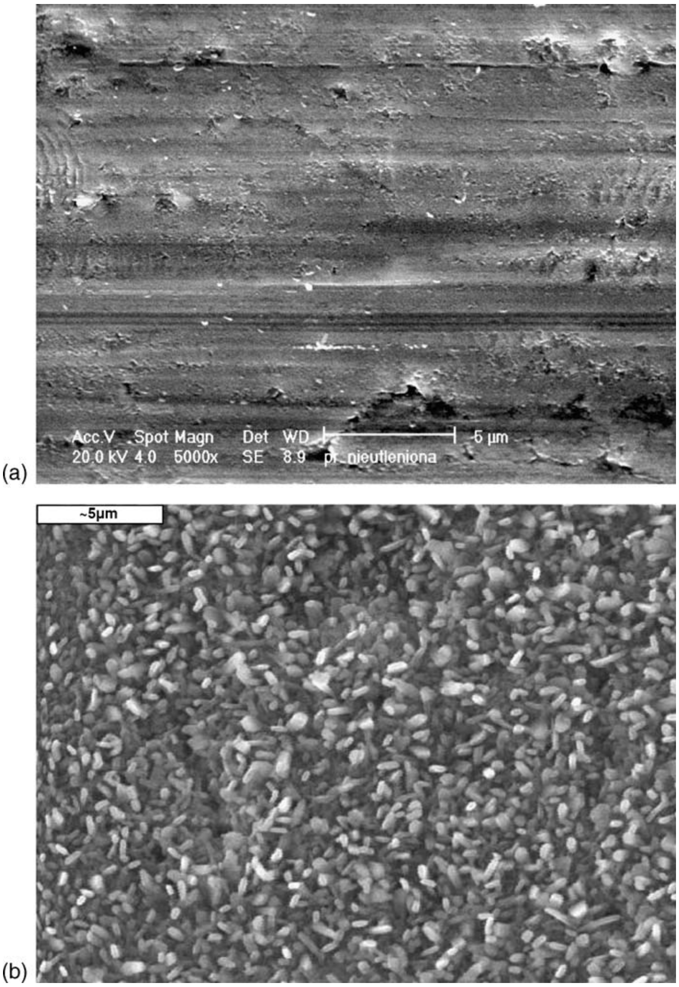

Fig. 1. Scanning electron microscopy (SEM) microphotographs of the FeCrAl foil before (a) and after (b) oxidation in air at 800 °C for 5 h.

2.4. Samples characterization

X-ray diffraction (XRD) patterns from 5° to 50° 2θ of both ferrierite coatings and bulk phase formed were obtained on a Siemens D5005 automatic diffractometer with Cu Kα radiation. Crystallinity was evaluated taking into account the XRD signals from 21° to 26° 2θ.

Particle size distribution of the bulk phase crystals formed was determined by Laser Diffraction (LD) using a LS 13 320 Particle Size Analyzer (Beckman–Coulter). The technique is based on multi angle detection of light scattered from the sample. The apparatus is equipped with a laser of 4 mW power, giving the light of 750 nm wavelength. The range of size measured is between 0.04 and 2000 μm. For particles studied here the refractive index equal to 1.50 was taken for size calculations.

The surface of the substrate before and after oxidation and morphology of zeolite coatings were studied by scanning electron microscopy (SEM) using a Philips Electron Optics XL30 or a Joel JSM 5400 instruments.

3. Results and discussion

3.1. Standard ferrierite synthesis

The microphotograph of the raw FeCrAl foil is shown in Fig. 1a. The substrate is flat with some features typical for the rolled material. Before using for synthesis of coatings, the FeCrAl foil was oxidized in air at 800 °C. As seen in Fig. 1b, after oxidation the surface was covered uniformly with characteristic nodular crystals resembling small whiskers. Analysis of whiskers revealed predominately the presence of the α-Al_2O_3 phase, with minor amounts of θ-Al_2O_3. The length of whiskers was different and changed from 0.5 to 2 μm (Fig. 1 b). No cracks, fissures and other defects were found in the thin film of alumina.

Ferrierite can be crystallized from inorganic gels at higher temperatures (250 °C), or with organic templates like pirydine, piperidine or pyrrolidine below 200 °C [6,22]. Following our earlier studies [17,21], standard ferrierite synthesis has been performed at 160 °C, both without and then with a metal substrate fixed in the autoclaves. XRD diffraction patterns (not shown) revealed a pure ferrierite phase, and SEM microphotographs confirmed formation of the elongated crystals. The graph showing distribution of crystals size of the bulk phase formed in autoclaves is shown in Fig. 2. The mean size of aggregates was 21.7 μm, while the average crystal size estimated by SEM was in the range of 8.3–13.5 μm. This was very close to the average crystals size formed in bulk without metallic foil present (8.3–11.6 μm). The predominating size of zeolite crystals was very close, i.e. 11.6 μm obtained without the foil and 11.2 μm for the coating on the foil.

3.2. Kinetics of ferrierite crystallization

Following these preliminary approaches, the kinetics of ferrierite crystallization was studied in more detail. First, zeolite formation using a standard gel composition was followed at 160 °C without the FeCrAl foil. Crystallinity of the samples taken at different time was estimated using XRD and the results are shown in Fig. 3. As seen, after the induction period of about 24 h a fast formation of ferrierite is observed; the process is already finished at about 72 h and then the curve levels out, showing even a slight decrease with prolonged crystallization time. In our previous studies aimed at regular synthesis of ferrierite, the more concentrated gel was used, thus crystallization was faster and a pure ferrierite phase was obtained after 43 h only [17,21]. We also note that crystal-

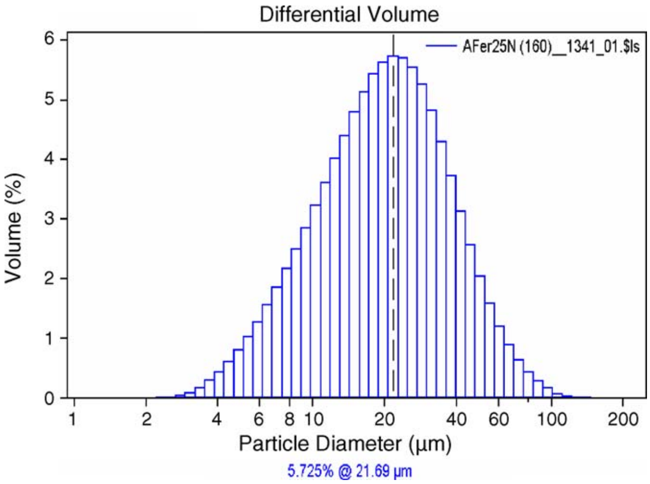

Fig. 2. Distribution of ferrierite crystal aggregates formed in bulk using standard gel for crystallization (160 °C, 144 h).

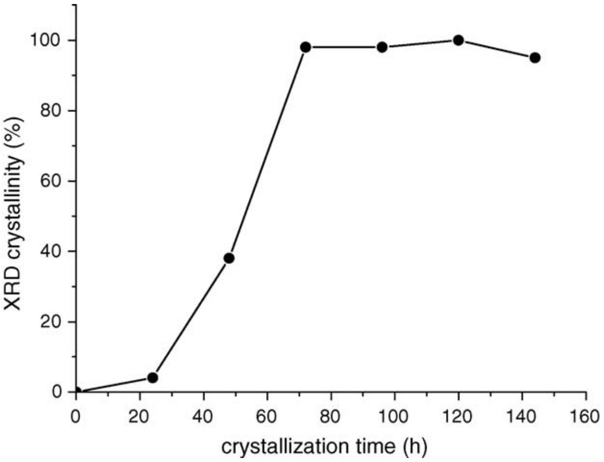

Fig. 3. The kinetics curve of the ferrierite type zeolite crystallization carried out using the standard gel composition at 160 °C without metal substrate.

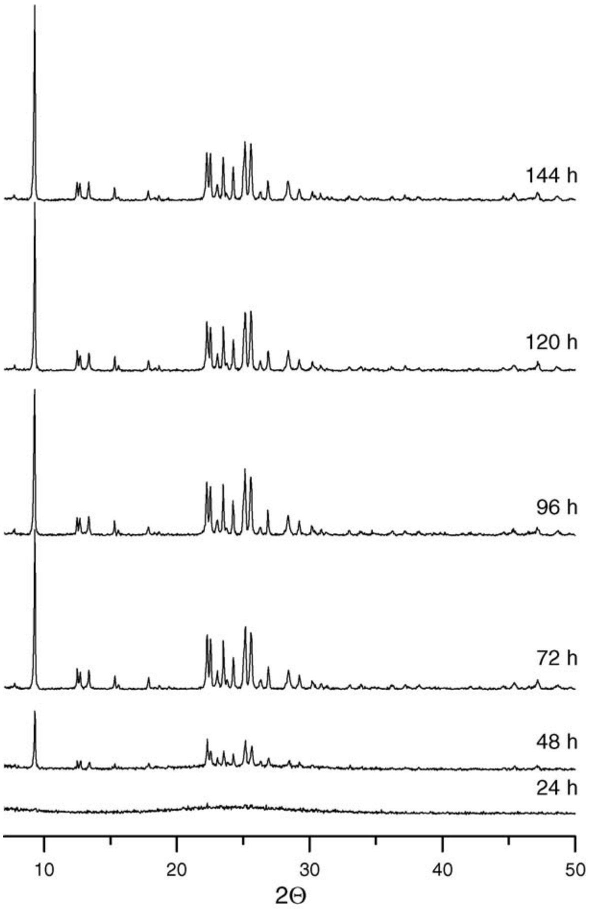

Fig. 4. XRD patterns of the samples taken at 24–144 h of crystallization time using the standard gel at 160 °C.

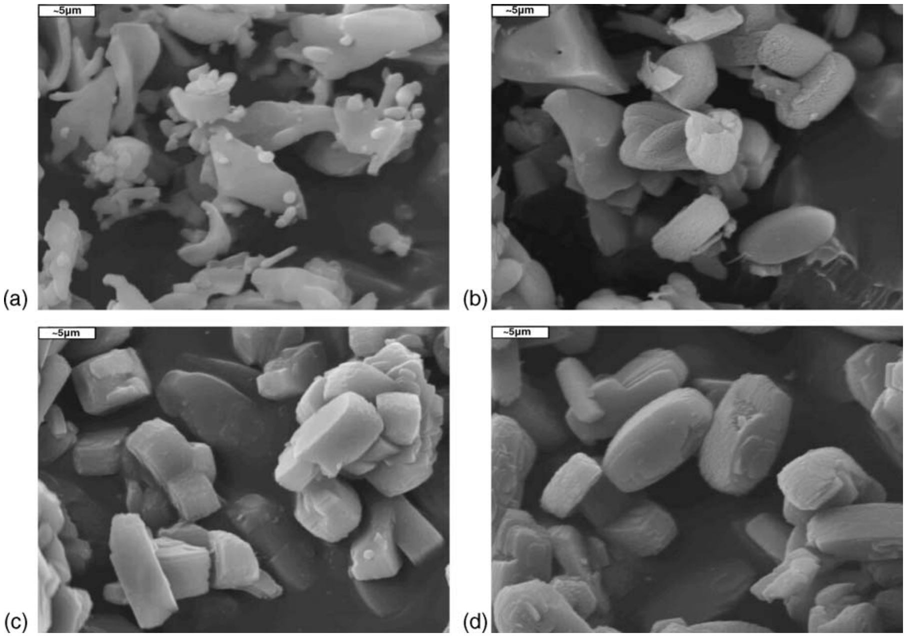

Fig. 5. Scanning electron microscopy (SEM) microphotographs of the samples recovered from the autoclaves after: (a) 24 h; (b) 48 h; (c) 72 h; and (d) 120 h of crystallization at 160 °C.

lization of ferrierite without organic templates at 250 °C was similar, and after induction period of 18–40 h the crystal growth was accomplished after ~40–50 h [22].

SEM microphotographs show well-developed elongated crystals, while the inspection of XRD patterns revealed pure ferrierite phase formation (Fig. 4). The distribution curve of crystal size was symmetrical, and the average crystal size was in the range 8.3–11.6 µm (crystal modal size 11.6 µm). SEM microphotographs (Fig. 5) visualize evolution of zeolite crystals formed in bulk during 1–5 days. Already after 3 days the crystal facets were well developed. In the XRD patterns no difference between the crystal morphology was found after 3 and 4 days of synthesis. Taking into account the results of this experiment, and the crystallinity drop after 5 days (Fig. 3), the time and temperature of ferrierite crystallization for further experiments were set at 96 h and 160 °C, respectively.

Using the conditions chosen as above (160 °C, 96 h), the synthesis was performed in the presence of the oxidized metal foil. XRD confirmed the structure of ferrierite. The average crystal size on the substrate was 5.0–7.9 µm, with average size of crystal aggregates of 14.9 µm, but the coverage was relatively low (4 g/m^2).

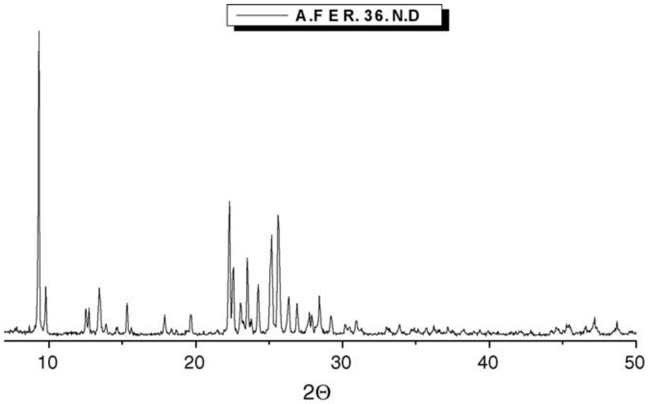

Fig. 6. The typical XRD pattern of crystals formed in bulk at 160 °C for 144 h using stirring conditions.

3.3. Synthesis under dynamic conditions

The adhesion between the metal foil and the zeolite coating is a major problem affecting the mechanical stability of the latter. The surface roughness and the interaction forces between the ferrierite crystals and metal substrates oxidized in air and SO$_2$ were studied recently using atomic force microscopy [23].

Taking into account the presence of alumina whiskers on the foil and their size, we made an attempt to prepare coatings consisting of smaller crystals, thus enabling a better contact between the two phases. Thus synthesis with rotating of

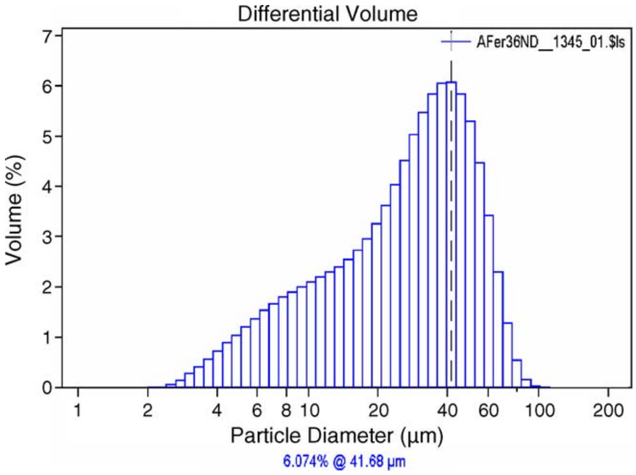

Fig. 7. Distribution of crystal aggregates size formed in bulk using a standard gel under stirring at 160 °C for 144 h.

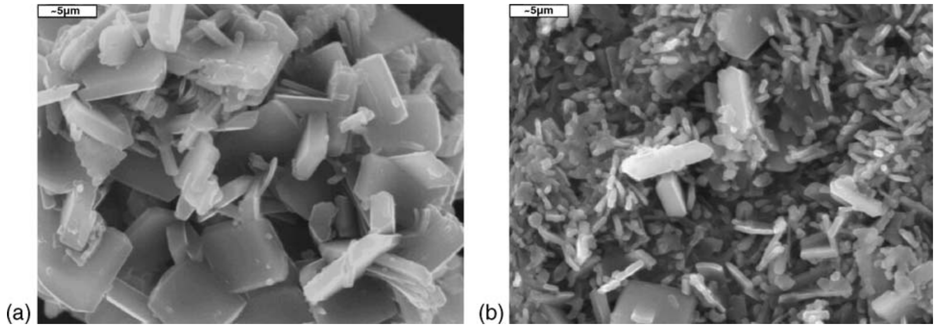

Fig. 8. SEM microphotographs of the samples obtained under stirring at 160 °C for 144 h: (a) in bulk; (b) on the FeCrAl foil.

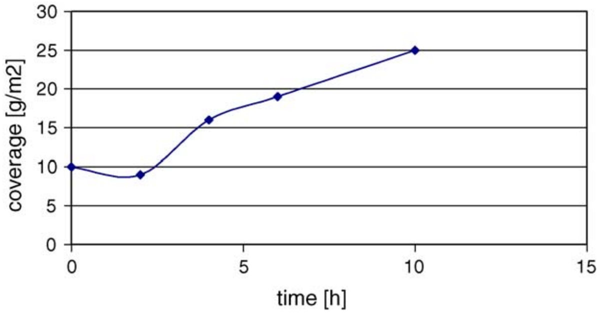

Fig. 9. The coverage of the foil with coating as a function of nucleation time. Synthesis conditions: standard gel, 160 °C, 144 h.

autoclaves was carried out to check how the dynamic conditions affect the crystals size and coverage of the foil.

The sample formed under stirring conditions without the substrate was highly crystalline (Fig. 6) and composed of aggregates of smaller rectangular crystals (Fig. 8a) with distribution vs. volume as shown in Fig. 7. The modal size of crystals was 6.2 μm.

Preparation of zeolite coating yielded much smaller crystals covering uniformly (10 g/m^2) the foil (Fig. 8b). However, in this case the morphology was changed, giving elongated crystals protruding randomly from the foil surface (Fig. 8b). The mean crystal size obtained under stirring conditions was as expected lower, and equal to 5.4–8.3 μm without the foil and 2.0–3.7 μm on the foil. In the latter case some rectangular crystals were occasionally present (ca. 6 μm). The modal size of crystals prepared on the foil was lower (3.5 μm), thus enabling better adhesion to the metal substrate.

Crystallization of the coatings using another gel, that is in the presence of phosphoric acid, was also studied. The average size of rectangular crystals obtained at 160 °C for 40 h was similar (3.3–5.8 μm), and the coating coverage was 3 g/m^2.

3.4. Synthesis of coating with different nucleation time

Another approach to the preparation of zeolite coatings was made, by changing the nucleation time. Thus the temperature of synthesis was increased continuously from 60 to 160 °C for 2–

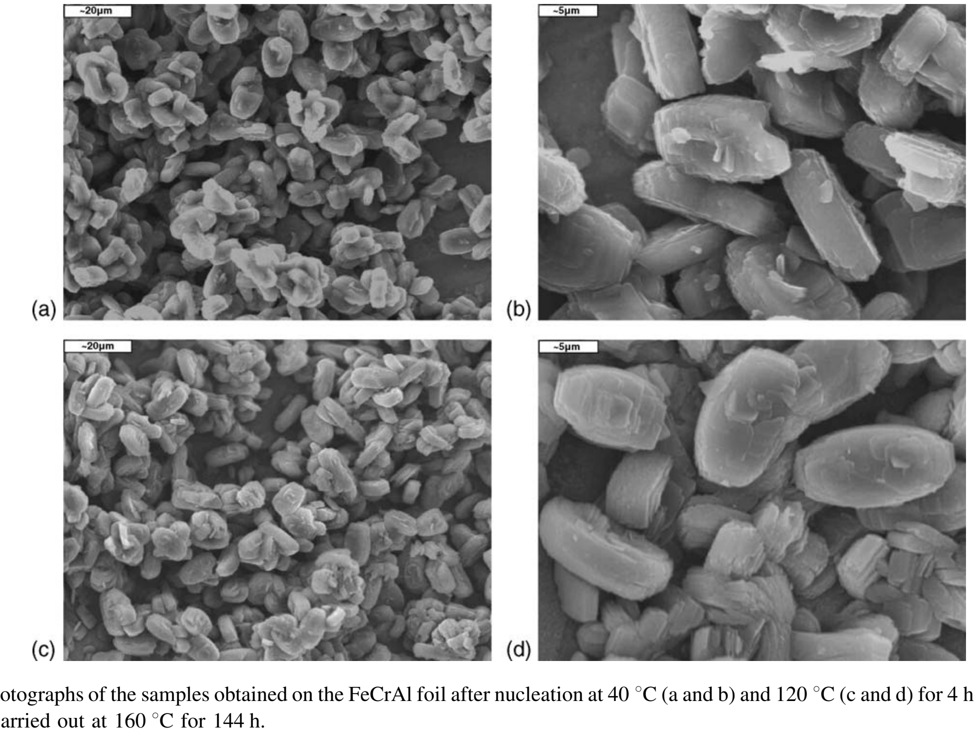

Fig. 10. SEM microphotographs of the samples obtained on the FeCrAl foil after nucleation at 40 °C (a and b) and 120 °C (c and d) for 4 h. The crystallization using the standard gel was carried out at 160 °C for 144 h.

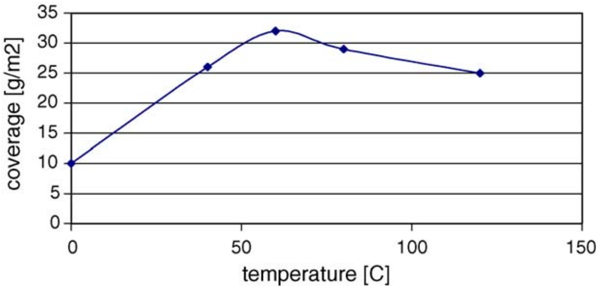

Fig. 11. A relationship between the constant temperature of nucleation for 4 h and the substrate coverage with ferrierite. The crystallization using the standard gel was carried out at 160 °C for 144 h.

10 h. The highly crystalline coatings were obtained, consisting of elongated, twinned and intergrown crystals (SEM not shown). The modal crystal size was decreased from 12.5 μm (2 h) to 10 μm (10 h). The coverage was increased with the time, as shown in Fig. 9, approaching 25 g/m^2 for 10 h.

Finally, instead of continuous increase of temperature, the autoclaves were kept at desired and constant temperature (40–120 °C) for 4 h, before the final crystallization performed at 160 °C for 144 h. Also in these experiments the pure ferrierite phase was obtained.

The morphology of crystals obtained is visualized in Fig. 10. The crystals revealed similar shape and size, and covered the substrate uniformly. As seen, the coverage depends on the nucleation temperature, reaching maximum 32 g/m^2 for 60 °C (Fig. 11). The modal size of the crystals was 11.2–12.5 μm.

4. Conclusions

Ferrierite coatings were successfully prepared, using the FeCrAl foil as a metal substrate. Before using for zeolite crystallization the steel foil was oxidized in air at 800 °C. During oxidation a thin regular film of Al_2O_3 was formed on the surface of the foil. The alumina film exhibited a very good adhesion to the substrate. The outer surface of the film was well developed. No cracks, fissures and other defects were found in the alumina film. The ferrierite crystal size and the coverage of the foil depended on the conditions applied. By limiting the time of synthesis, applying another gel containing phosphoric acid or performing synthesis under stirring it was possible to decrease the mean size of ferrierite crystals.

Finally, by applying either continuous or ramped increase of temperature of nucleation, it was possible to control the coverage of substrate with zeolite (up to 32 g/m^2). The optimum nucleation time found was around 60 °C for 4 h.

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References

[1] P. Avila, M. Montes, E.E. Miró, Chem. Eng. J. 109 (2005) 11.
[2] B. Sulikowski, Heterogeneous Chem. Rev. 3 (1996) 203.
[3] W.F. Höldereich, D. Heinz, Catalysis 14 (1999) 148.
[4] Y. Wang, Y. Ting, X. Wang, W. Shei, C. Ke, Z. Gao, J. Hu, W. Yang, J. Mater. Sci. Lett. 20 (2001) 2091.
[5] S. Mintova, V. Valtchev, V. Engström, B.J. Schoeman, J. Sterte, Microporous Mater. 11 (1997) 149.
[6] G.B.F. Seijger, S.G. Palmaro, K. Krishna, H. van Bekkum, C.M. van den Bleek, H.P.A. Calis, Microporous Mesoporous Mater. 56 (2002) 33.
[7] D.W. Breck, Zeolite Molecular Sieves, Wiley, New York, 1974.
[8] P.A. Vaughan, Acta Crystallogr. 21 (1966) 983.
[9] I.S. Kerr, Nature 210 (1966) 294.
[10] W.S. Wise, R.W. Tschernich, Am. Miner. 61 (1976) 60.
[11] B. Sulikowski, J. Klinowski, J. Chem. Soc., Chem. Commun. (1989) 1289.
[12] H. Gies, R.P. Gunawardane, Zeolites 7 (1987) 442.
[13] B.S. Kwak, J. Sung, Catal. Lett. 53 (1998) 125.
[14] S.-H. Lee, D.-K. Lee, C.-H. Shin, W.C. Paik, W.M. Lee, S.B. Hong, J. Catal. 196 (2000) 158.
[15] B. Sulikowski, J. Janas, J. Haber, A. Kubacka, Z. Olejniczak, E. Wloch, Chem. Commun. (1998) 2755.
[16] B. Gil, J. Datka, A. Kubacka, J. Janas, B. Sulikowski, Stud. Surf. Sci. Catal. 158 B (2005) 1137.
[17] A. Kubacka, J. Janas, E. Wloch, B. Sulikowski, Catal. Today 101 (2005) 139.
[18] V. Cortés Corberán, R.X. Valenzuela, B. Sulikowski, M. Derewinski, Z. Olejniczak, J. Krysciak, Catal. Today 32 (1996) 193.
[19] D. Seddon, J. Catal. 98 (1986) 1.
[20] R. Rachwalik, Z. Olejniczak, B. Sulikowski, Catal. Today 101 (2005) 147.
[21] J. Haber, Z. Olejniczak, B. Sulikowski, M. Derewiński, A. Kubacka, in: Proceedings of 29th Polish Symposium on NMR Spectroscopy and its Application, Kraków, 2–3 December, Institute of Nuclear Physics, Kraków, 1997, pp. 247–250.
[22] A. Culfaz, A.K. Yilmaz, Cryst. Res. Technol. 20 (1985) 11.
[23] B. Sulikowski, E. Wloch, Z. Zurek, A. Gil, M. Lekka, B. Zmudzinska-Zurek, in: J.M. Howe, D.E. Laughlin, J.K. Lee, U. Dahmen, W.A. Soffa (Eds.), Proceedings of International Conference on Solid-Solid Phase Transformations in Inorganic Materials 2005, vol. 2, Phoenix, USA, 29 May–3 June 2005, The Minerals, Metals and Materials Society (TMS), 2005, pp. 1049–1054.