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Synthesis of ferrierite-type zeolite by microwave method using ethylenediamine as an organic structure-directing agent

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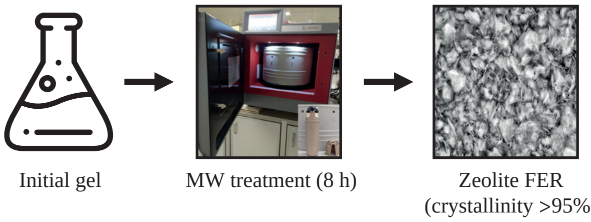
A new method for the synthesis of ferrierite-type zeolite has been developed using microwave irradiation in the presence of structure-directing agents (templates). The physicochemical characteristics of the synthesized zeolites were investigated by X-ray diffraction analysis, low-temperature nitrogen adsorption–desorption and SEM-EDX. When comparing the synthesis products, it was found that microwave irradiation significantly reduces the crystallization time of the synthesized zeolites compared to traditional hydrothermal treatment.



Keywords: ferrierite, FER, zeolites, microwave synthesis, organic structure-directing agents, ethylenediamine.

Ferrierite (FER) zeolite is of great interest as a catalyst due to its activity in acid-catalyzed reactions and the unique properties of the molecular sieve. The porous structure of FER is formed by a two-dimensional system of 10-membered (5.4 × 4.2 Å) and 8-membered (4.8 × 3.5 Å) ring channels.[1–4] FER found the most promising application in such processes as skeletal isomerization of linear olefins, synthesis of dimethyl ether, decomposition of N_2O, oligomerization of butene, isomerization of various substrates (including *m*-xylene and α-pinene), oxidative dehydrogenation of propane, epoxidation of styrene, oxidative dehydration of glycerol, pyrolysis of polyethylene and others.[5–14]

Despite the interesting catalytic properties of FER, the practical application of this zeolite is still limited due to the fact that its synthesis takes a long time. Traditionally, like most zeolites, FER is produced hydrothermally using various organic structure-directing agents (OSDAs) such as ethylenediamine (EDA), cyclohexylamine, piperidine, pyridine, pyrrolidine, *n*-butylamine and 1,8-diamino-octane.[15–23] The main disadvantage of this method is the long synthesis time; on average, the crystallization time is 2–3 days, but in some cases it can reach 10–14 days.[7,17,24] Another approach to producing FER is to use the seed-assisted method. This method also has limitations, since it is necessary to use extra pure FER crystals, free from foreign impurities, as a seed.[25,26] In recent years, works have appeared on the synthesis of crystalline aluminosilicates by the microwave (MW)-assisted method, which makes it possible to obtain zeolites with a uniform phase composition and a high degree of crystallinity in a short period of time.[27,28] In particular, a method for producing FER by MW treatment using seed crystals is described.[29] However, in this work, we obtained the FER zeolite by a new method without the use of seed crystals.

In this work, FER zeolites were obtained by MW method with different crystallization times of 6, 8 and 16 h in the presence of EDA as OSDA.[†] Also for comparison, FER was synthesized by the HT method for 72 h. The resulting zeolites were investigated by X-ray diffraction (XRD), low-temperature N_2 adsorption–desorption and SEM-EDX methods.[‡]

Figure 1 shows XRD patterns of the synthesized samples. Comparing the XRD patterns of these samples with the data for a typical FER structure (JCPDS-ICDD 82-1395),[20] it was found that the FER zeolite was obtained from all of the initial gels. The relative crystallinity (RC) of the zeolites was calculated from the sum of the intensities of the peaks at 2θ of 9.3°, 22.3°, 23.5°, 25.2° and 25.7°.[19] The maximum value of the sum was taken as 100%

[†] Zeolites were synthesized using the following reagents: sodium hydroxide (ChemMed), sodium aluminate (Sigma–Aldrich), tetraethyl orthosilicate (TEOS, Sigma–Aldrich), EDA (ECOS-1) and deionized water.

The synthesis of FER zeolites was carried out according to the following procedure. Sodium hydroxide was dissolved in deionized water for 5 min, then sodium aluminate was added and stirred for another 10 min. Next, TEOS was added dropwise to the solution with stirring for 30 min. At the last stage, EDA was injected dropwise into the resulting gel, and the mixture was stirred at maximum speed for 1 h. The prepared gel with the molar composition $1\,SiO_2-0.23\,NaAlO_2-0.08\,NaOH-1.4\,EDA-50\,H_2O$ was crystallized at 463 K for 6, 8 and 16 h with MW treatment or 72 h with hydrothermal (HT) treatment. MW-assisted synthesis was performed on an Anton Paar Multiwave PRO device. HT synthesis was carried out in a steel autoclave equipped with a Teflon lining. Finally, the resulting product was centrifuged, dried at 110 °C for 12 h and calcined in air at 550 °C (heating rate 5 °C min^{-1}) for 5 h. The samples obtained by the MW method were named FER-MW-6, FER-MW-8 and FER-MW-16, where 6, 8 and 16 are crystallization times (in hours), respectively. The sample obtained by the HT method was named FER-HT.

[‡] XRD analysis was performed on a Thermo Fisher Scientific ARL X'TRA diffractometer equipped with a Peltier energy-dispersive detector when scanning in the range of 2θ angles from 5 to 30°. N_2 adsorption–desorption isotherms at 77 K were measured using a Micromeritics Instrument

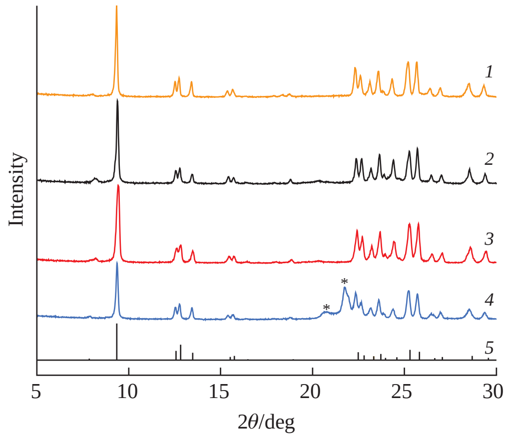


Figure 1 XRD patterns of the FER samples synthesized by MW and HT methods (asterisk indicates the presence of the Silicalite phase): (*1*) FER-MW-16 (RC = 100%), (*2*) FER-MW-8 (RC = 96%), (*3*) FER-MW-6 (RC = 94%), (*4*) FER-HT (RC = 65%) and (*5*) FER (JCPDS-ICDD 82-1395).

crystallinity. In this study, an RC value of 100% is demonstrated by the FER-MW-16 sample. The RC of FER zeolites obtained by MW synthesis is approximately the same (the difference in crystallinity is no more than 6%). These results indicate that a synthesis time of 6–8 h using MW treatment is sufficient to obtain FER with a high degree of crystallinity.

The FER-HT sample demonstrated the lowest crystallinity (RC = 65%) among the studied samples. However, increasing the synthesis time using the HT method will result in greater crystallinity.[17]

Also, the zeolite sample prepared by HT treatment contains impurity phases. The XRD pattern of the FER-HT zeolite shows peaks at 2θ of 20.9 and 21.8° corresponding to the Silicalite phase (JCPDS-ICDD 44-0696), indicating incomplete recrystallization of the original SiO_2 source into the FER structure. At the same time, FER-MW samples are homogeneous and do not contain any impurity phases.

Figure 2 presents N_2 adsorption–desorption isotherms of the prepared zeolites in the Na-form. Before measuring the isotherms, the samples were evacuated at 400 °C and 0.00133 Pa for 4 h. The isotherms of all synthesized samples correspond to type I isotherms characteristic of microporous materials.[30]

According to the results presented in Table 1, the FER-MW-8 sample has the best textural properties (highest $S_{\rm BET}$, total pore volume and micropore volume) of all obtained zeolites. Samples FER-MW-6 and FER-MW-16 have almost the same total pore volume (0.136 and 0.137 $cm^3\,g^{-1}$, respectively), while the FER-MW-16 zeolite has a larger micropore volume than the FER-MW-6 zeolite (0.111 and 0.097 $cm^3\,g^{-1}$, respectively). The FER-HT sample exhibits the smallest total pore volume and micropore volume (0.098 and 0.071 $cm^3\,g^{-1}$, respectively). The reason for this effect may be the lower crystallinity of the FER-HT sample compared to other obtained FER zeolites,[23] which is also confirmed by XRD results (see Figure 1).

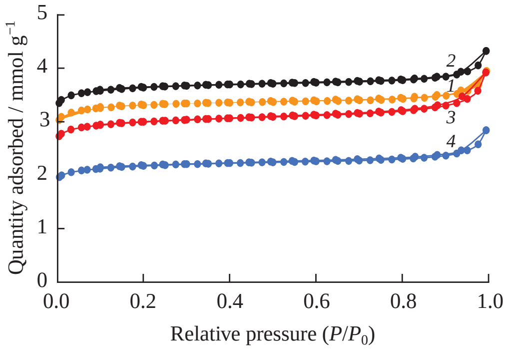


Figure 2 N_2 adsorption–desorption isotherms at 77 K for the resulting FER samples: (*1*) FER-MW-16, (*2*) FER-MW-8, (*3*) FER-MW-6 and (*4*) FER-HT.

Table 1 Properties of FER samples synthesized by MW and HT methods.

Zeolite	$S_{\rm BET}$[a]/ $m^2\,g^{-1}$	$V_{\rm total}$[b]/ $cm^3\,g^{-1}$	$V_{\rm micro}$[c]/ $cm^3\,g^{-1}$	$V_{\rm meso}$[d]/ $cm^3\,g^{-1}$	Si/Al ratio[e]
FER-MW-6	270	0.136	0.097	0.022	8.40
FER-MW-8	330	0.150	0.121	0.016	8.36
FER-MW-16	300	0.137	0.111	0.013	8.57
FER-HT	194	0.098	0.071	0.015	8.56

[a] BET surface area. [b] Total pore volume calculated from the adsorption value at $P/P_0 = 0.99$. [c] Micropore volume calculated using the '*t*-plot' method. [d] Mesopore volume calculated from the difference $V_{\rm total} - V_{\rm micro}$. [c] Molar ratio from EDX measurements.

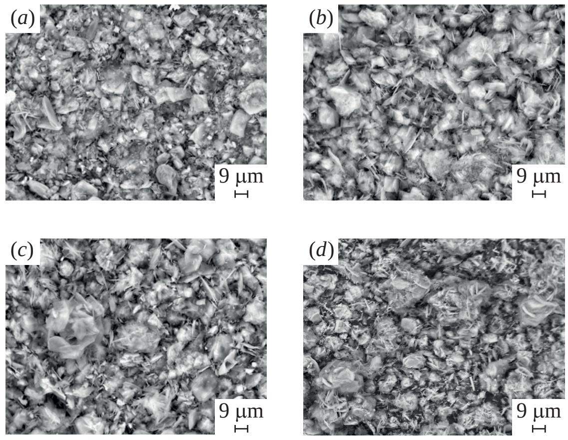


Figure 3 SEM images of the produced FER zeolites: (*a*) FER-MW-6, (*b*) FER-MW-8, (*c*) FER-MW-16 and (*d*) FER-HT.

The $S_{\rm BET}$ value for the FER samples obtained by MW synthesis exceeds that for FER-HT. At the same time, the FER-HT sample demonstrates the highest $S_{\rm BET}$ parameter among all the studied zeolites (see Table 1).

The morphology and elemental composition of the synthesized samples were studied by the SEM-EDX method. The values of the molar ratio of Si to Al are presented in Table 1. The results obtained for all samples are approximately the same. In Figure 3, we can see that the obtained FER samples are composed of the agglomerates of different sizes. Analysis of SEM images showed that the average crystallite size for samples FER-HT, FER-MW-6, FER-MW-8 and FER-MW-16 is 11 × 5.5, 12.5 × 6.5, 13 × 7 and 16 × 9 µm, respectively. Thus, FER crystallites formed under MW synthesis conditions are larger than those formed under HT synthesis conditions. Also, for the FER-MW samples, an increase in crystal size with increasing synthesis time is observed.

In conclusion, it was demonstrated that the FER zeolites synthesized by the MW-assisted method have better physicochemical properties compared to the FER sample obtained by the HT method. In addition, the preparation of FER zeolites by MW treatment makes it possible to significantly reduce their crystallization time (by 10–12 times). On the basis of the obtained results, we came to the conclusion that the optimal time for the synthesis of FER by the MW method is 8 h, since FER-MW-8 has a high crystallinity and the best textural characteristics of all the

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Corporation ASAP 2020 Plus system. The morphology and elemental composition of the obtained samples were examined using a Carl Zeiss EVO 50 XVP scanning electron microscope equipped with an Oxford Instruments INCA Energy 350 energy-dispersive spectrometer.

investigated FER samples. The described method can be employed to find optimal conditions for the synthesis of an almost important family of the FER-type zeolites, as well as other types of zeolites.

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