

SYNTHESIS OF FERRIERITE FROM GEORGIAN PERLITE

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Abstract. The synthesis of the FER type zeolite materials by hydrothermal transformation of natural Georgian volcanic glass perlite treated by HCl water solution and suspended in presence of the Li ions was investigated. Products are characterized by chemical composition, XRD, FTIR, SEM-EDS and thermal analyses, as well as water and n-hexane sorption at static conditions. Possibility to prepare the nearly pure Li-form of the ferrierite by autoclave synthesis at 160°C during 140 hours is shown.

Keywords: Georgian perlite, hydrothermal synthesis, ferrierite.

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1. Introduction

A silica-rich zeolite ferrierite first discovered in 1918 and having the crystal chemical formula $[\text{Mg}_2\text{Na}_2(\text{H}_2\text{O})_{18}][\text{Al}_6\text{Si}_{30}\text{O}_{72}]$ -FER (Baerlocher *et al.*, 2007), is listed among common zeolites in spite of its rarity in nature. More than 20 only the US patents according to the synthesis of ferrierite and its applications have been published in 1976-2015. Such attention is caused by ferrierite structure (Vaughan, 1966): it has two-dimensional channel system with the 10- and 8-rings (Fig. 1) that can include a spherical molecule with maximum diameter of 6.31 Å, and a molecule with diameter of 4.69 Å can diffuse along the *c* axis.

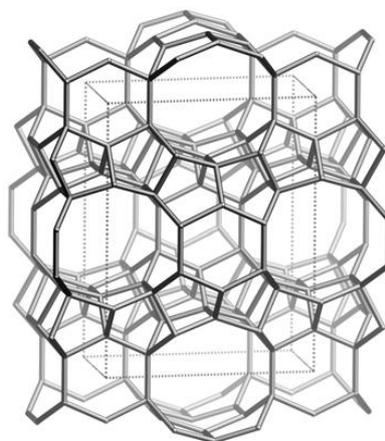


Figure 1. FER framework viewed along [001]

Hydrothermal synthesis of ferrierite without organic templates is based on results of investigation of strontium-containing gels published by R.M. Barrer and D.J. Marshall in 1964, the synthesis of ferrierite in the presence of potassium ions was examined by Toyo Soda (Inaoka *et al.*, 1990) and scaled up for commercial production. According to the US Patent 4,650,654¹, products have the Si/Al ratio in a range from 6 to 11.75, the negative charge of one aluminum atom is compensated by n_1 sodium ions and n_2 potassium ions, where n_1 varies from 0.193 to 0.824, n_2 from 0.366 to 0.905; the FER type structure is testified by X-ray diffraction patterns.

Ferrierite can be crystallized from an aqueous gel of composition $n_1\text{Na}_2\text{O} \cdot n_2\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O} \cdot z_1\text{CO}_2 \cdot z_2(\text{HCO}_2)_2$, where $n_1 \approx (1 - 10)n_2$, $n_1 + n_2 \approx 3.0$, x varies from 6 to 15, $y > 120$, $z_1 < 1$, $z_2 > 2$, at 250°C in reaction periods ranging from 40 to 95 hours, the crystallization time can be reduced with seeding (Çulfaz & Yilmaz, 1985). The hydrothermal transformation is rather careful procedure – in such system the ferrierite is a metastable phase and it is transformed into tridymite, high sanidine and orthoclase at longer reaction periods. At 200°C, chabazite was crystallized from the same batch composition at a very slow rate. At temperatures higher than 250 °C and in the absence of carbonates and bicarbonates in the batch mixture, tridymite, high sanidine and orthoclase crystallized directly without the formation of ferrierite.

Simple synthesis of the FER type zeolites with varying the Si/Al ratio is possible in the presence of a catalytic amount of pyrrolidine or ethylenediamine (Göğebakan, 2007). Application of surfactant moieties (sodium bis(2-ethylhexyl) sulfosuccinate) that direct pyrrolidine molecules in a particular fashion, results in a sixfold decrease in the required amount of template as compared to conventional procedure, for the FER type structure crystallization (Ahediet *et al.*, 2001). Recently ferrierite zeolite nanoneedles (Lee *et al.*, 2013) and hierarchical ferrierite (Chu *et al.*, 2017) with high catalytic stability and product selectivity in the 1-butene skeletal isomerization have been prepared.

Investigation of organotemplate-free synthesis of high-silica ferrierite (Zhang *et al.*, 2011) is still popular, so as to develop a simple and relatively cheap means of obtaining the FER type zeolites remains valid today.

The aim of our work was to study the synthesis of ferrierite in the presence of lithium ions and without application of organic templates.

2. Experimental

Preparation of synthetic zeolite material was carried out using Georgian natural perlite from the Paravani Lake (Southern Georgia) deposit having chemical composition



Processing of raw in target material includes following steps:

Preparation & acid treatment of raw material – perlite powder was treated at room temperature by the HCl water solutions under stirring, washed by water before the complete disappearance of Cl^- ions, and dried in the cabinet at 100-105°C; from the results of the X-ray powder diffractometry it was confirmed that obtained homogeneous compound was amorphous; changes of chemical composition (the Si/Al ratio and

¹T. JunjiArika, S. Hiroshi Miyazaki, S. Kuzushige Igawa, S. Keiji Itabashi. Process for Preparation of Ferrierite Type Zeolites. US Patent 4650654 (March 17, 1987), Toyo Soda Manufacturing

relative content of positively charged metal ions Me^+) at different acid concentration [HCl] are given in Fig. 2.

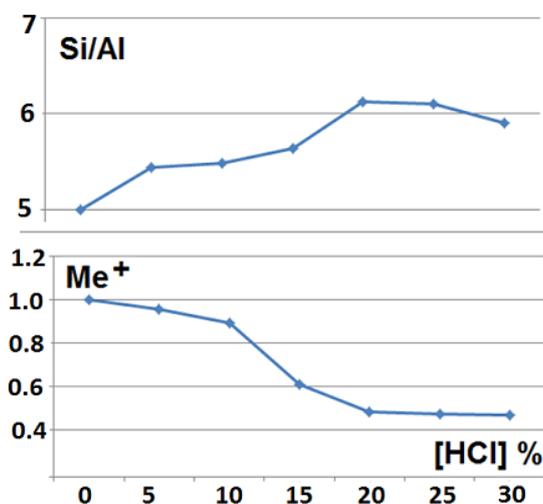


Figure 2. The Si/Al ratio and metal content in acid treated perlite

According to obtained data, highest Si/Al ratio is achieved after treatment in 20% HCl water solution, the metal content in such conditions is decreased twice, the potassium and sodium ions are removed mainly.

Preparation of suspension & treatment in basic solution – water suspension of the acid treated amorphous material was prepared with the solid to liquid ratio of 1 : 3; prepared suspension was treated at room temperature by 1% LiOH water solution, solid to liquid ratio of 1 : 6, gel homogenization takes from 30 minutes to 1 hour; water content generally is rather high to ensure viscosity suitable for crystallization process, but water molecules are compulsory units in assembling the zeolite structure and they play a significant role.

Crystallization – crystallization is effected by charging a starting gel (slurry) in an autoclave and heating the slurry at a temperature of 160°C, duration of the process – up to 140 hours; in order to uniformize the temperature in the autoclave during the crystallization, it is preferred that the crystallization be carried out with stirring.

Separation and cleaning – after completing the crystallization, separation of produced crystalline material from the mother liquor was carried out by filtration, solid material was cleaned by water until pH 8.0-8.5, and dried at 90-100°C.

Chemical composition of prepared samples was determined by elemental analyses carried out using a Spectromom 381L plasma spectrometer and a Perkin-Elmer 300 atomic absorption spectrometer, as well as by energy dispersive X-ray (EDS) analysis. X-ray powder diffraction patterns were obtained from a DRON-4 diffractometer, employing the Cu-K α line and scanning at 1° per minute, FTIR spectra in the wavenumber range 4000-400 cm⁻¹ were recorded on the Perkin-Elmer FTIR spectrometer (version 10.4.2) using the KBr pellet technique for sample preparation, SEM images were obtained by using Jeol JSM6510LV scanning electron microscope equipped with Oxford Instruments X-Max 20 analyzer for EDS. Sorption capacities are measured at room temperature under static conditions – water at $p/p_s=0.40$ and $p/p_s=1.0$, n-hexane at $p/p_s=1.0$.

3. Results and discussion

Chemical composition of prepared material, $(\text{Li}_{4.2}\text{Me}_{0.2})(\text{Al}_{4.4}\text{Si}_{31.65}\text{O}_{72}) \cdot 11.8\text{H}_2\text{O}$, is in a good accordance with the ideal chemical formula $\text{Li}_6(\text{Al}_6\text{Si}_{30}\text{O}_{72}) \cdot 18\text{H}_2\text{O}$ with the exception of some “lack” of the Al atoms and significant decrease of water molecules in the frame. Commercial samples of ferrierite used in many applications and studies generally are characterized by higher Si/Al ratio than the ideal formula predicts, prepared sample (Si/Al=7.2) can be compared with ferrierite characterized by empirical formula $\text{K}_{0.722}\text{Na}_{0.238}\text{AlSi}_{7.9}$ (example 2 of the US Patent 4,650,654) and prepared in autoclave at 170°C during 72 hours from slurry, containing metals in wt% ratio of NaOH:KOH = 0.50:2.21.

Prepared material is nearly pure (95.5%) Li-form, EDS spectra show irregular distribution of remaining Na, K, Mg, and Ca.

X-Ray powder diffraction patterns of obtained samples have been compared with experimental patterns from the US Patent 4,650,654 (see Fig. 3) and with calculated ones taken from the IZA database of zeolite structures². Experimental patterns of Li- and K, Na-forms are in a good accordance if one takes into account possible differences in the intensity of the peaks for low-angle ($2\theta < 15^\circ$) reflections resulting from different distribution of compensating ions.

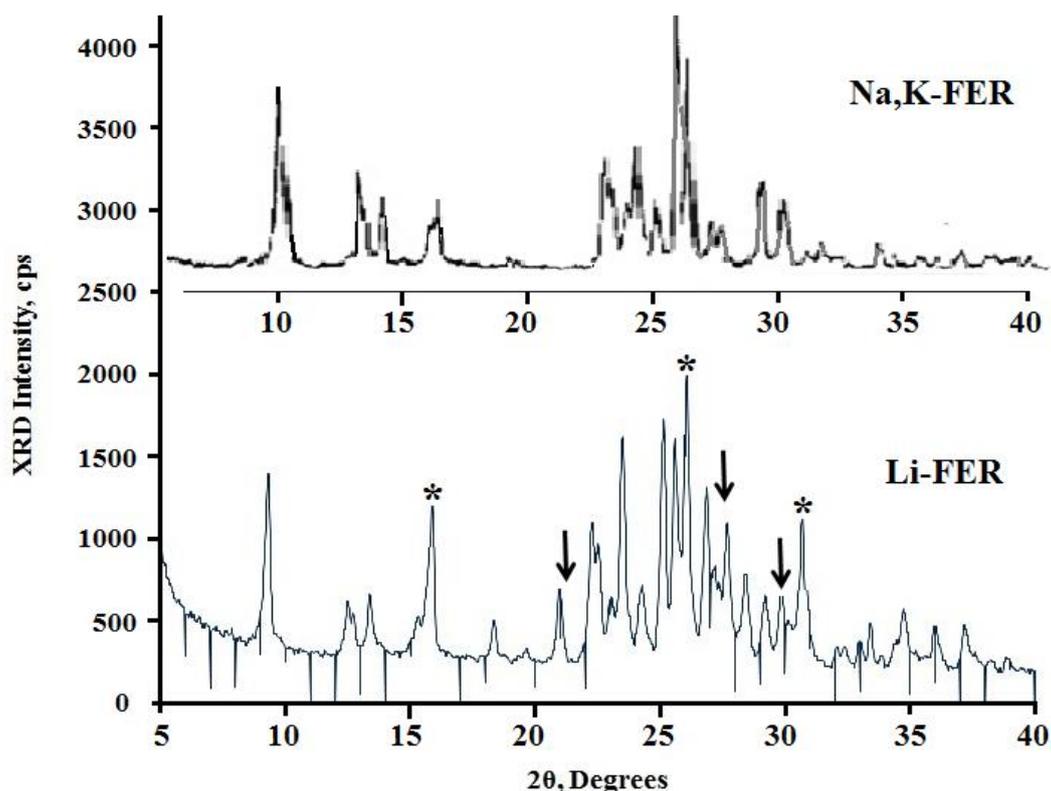


Figure 3. Comparison of XRD patterns for obtained Li-FER and reference K,Na-FER (Chu *et al.*, 2017) samples in a range of $5^\circ < 2\theta < 40^\circ$ (* – analcime peaks, ↓ – unidentified peaks)

²Database of Zeolite Structures of the International Zeolite Association <http://www.iza-structure.org/>

The (110) reflection at $2\Theta = 7.8^\circ$ is generally of much less intensity than expected from pattern simulation, as it was mentioned and discussed during first studies of ferrierite by X-ray diffraction (Fjellvåg *et al.*, 1989). Pattern calculated for siliceous ($\text{Si}/\text{Al} \rightarrow \infty$) FER structure gives possibility to assign comparatively high intensity peaks at following 2Θ angles: 9.2° ($hkl = 200$), 12.5° (020), 12.7° (101), 13.4° (011), 15.2° (310), 15.6° (220), 17.9° (121), 22.2° (321), 22.5° (420), 22.9° (411), 23.5° (330), 23.8° (002), 24.0° (510), 25.0° (112), 25.2° (040), 25.5° (202), 26.1° (501), 26.9° (022), 28.3° (141), 29.1° (521), 30.1° (530), 30.8° (132), 32.9° (422), 34.0° (512), 34.7° (350), 37.0° (602), 38.0° (730), and 38.9° (451).

Analcime (crystal chemical formula $[\text{Na}_{16}(\text{H}_2\text{O})_{16}][\text{Al}_{16}\text{Si}_{32}\text{O}_{96}]$ -ANA) is formed during the synthesis, its content varies from 8 to 20% depending on the temperature and duration of crystallization. Analcime has a cubic cell and gives strong peaks (Yokomori & Idaka, 1998) at $2\Theta = 15.7^\circ$ ($hkl = 211$, $d = 5.57\text{\AA}$), 26.1° (400, 3.42\AA), and 30.5° (332, 2.92\AA), overlapping with the (220), (501), and (620) reflections of ferrierite. Unidentified impurities give peaks at $2\Theta = 21^\circ$, 27.6° , and 29.8° .

Fourier transform infrared spectra of obtained Li-FER show following bands in mid infrared: broad band at 3400 cm^{-1} of asymmetric stretching of OH groups; peaks and shoulders in a range of $1510 - 1260\text{ cm}^{-1}$ due to bending vibrations of bridging –OH– groups; broad peak at 1000 cm^{-1} and a shoulder at 750 cm^{-1} of asymmetrical and symmetrical external stretch vibrations of the TO_4 tetrahedra; peak at 660 cm^{-1} and shoulders at 1190 and 700 cm^{-1} of internal stretch vibrations; peak at 550 cm^{-1} of double ring vibration, and peak at 460 cm^{-1} of T–O bend vibration.

Micropores & sorption. Both XRD and FTIR data show developed zeolitic crystal microporous structure in synthesized samples, and it has been confirmed also by comparatively high averaged value of water adsorption capacity under static conditions at the “plateau” pressure (see Table 1).

Table 1. Comparison of water and n-hexane sorption by Li-FER and reference K-FER, natural ferrierite from Santa Monika mountains, California, USA³

Zeolite	Sorption	H ₂ O		n-C ₆ H ₁₄
		p/p _s =0.4	p/p _s =1.0	p/p _s =1.0
Li-FER	mmole/g	4.42	5.0	0.136
	cm ³ /cm ³	0.164	1.917	0.289
Natural ferrierite from USA	mmole/g	3.63	3.95	0.102
	cm ³ /cm ³	0.138	1.151	0.217

The water and n-hexanesorption capacity of synthetic zeolite is 25-33% higher than that of natural zeolite, which can be explained by their different cation composition: natural ferrierite is “potassium-dominant”, while the pores of the synthetic zeolite contain comparatively small unhydrated lithium ions. The synthetic ferrierite behaves as a medium pore molecular sieve and sorbs small nonpolar organic molecules (benzene, toluene and cyclohexane (Çulfaz & Yilmaz, 1985), but the sorption capacity for “long” n-hexane molecules is comparatively low.

Thermal stability. According to studies of ferrierite structure (Çulfaz & Yilmaz, 1985; Fjellvåg *et al.*, 1989), thermally it is rather stable zeolite, the DTA curve show the endo-peak (120°C) of dehydration, a dehydroxylation and a sintering of the zeolite

³Ferrierite-K <https://www.mindat.org/min-6930.html>

convert the ferrierite at approx. 900°C into a glass-like species, unsuitable for adsorption (see Fig. 4)

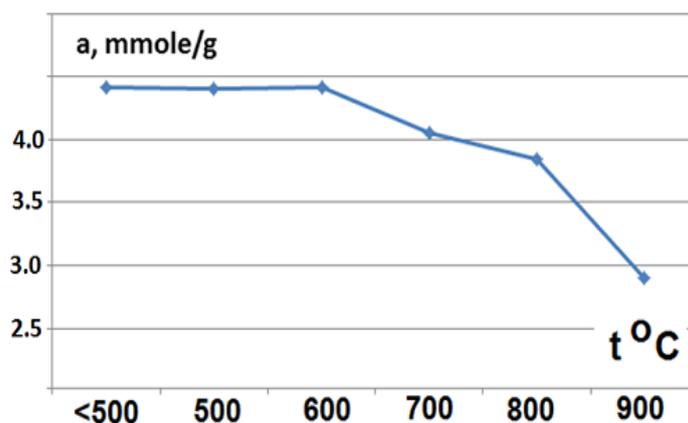


Figure 4. Water sorption on Li-FER after calcination at different temperatures

SEM images generally show micrometric crystallites (Fig. 5a), a smaller part of which (up to 15 wt%) are comparatively large (diameter from 3 to 12 μm), and a large part has a size from 0.5 to 1.2 μm (Fig. 5b). Formation of fibrous aggregates (Fig. 5c) with average diameter of 0.06 μm takes place locally at certain conditions. We hope that a careful selection of the conditions for crystallization will allow us to prepare “hierarchical ferrierite” for catalytic applications (Pérez-Ramírez *et al.*, 2008), but this, as well as study of Li-FER ion exchange properties, is the aim of our following studies.

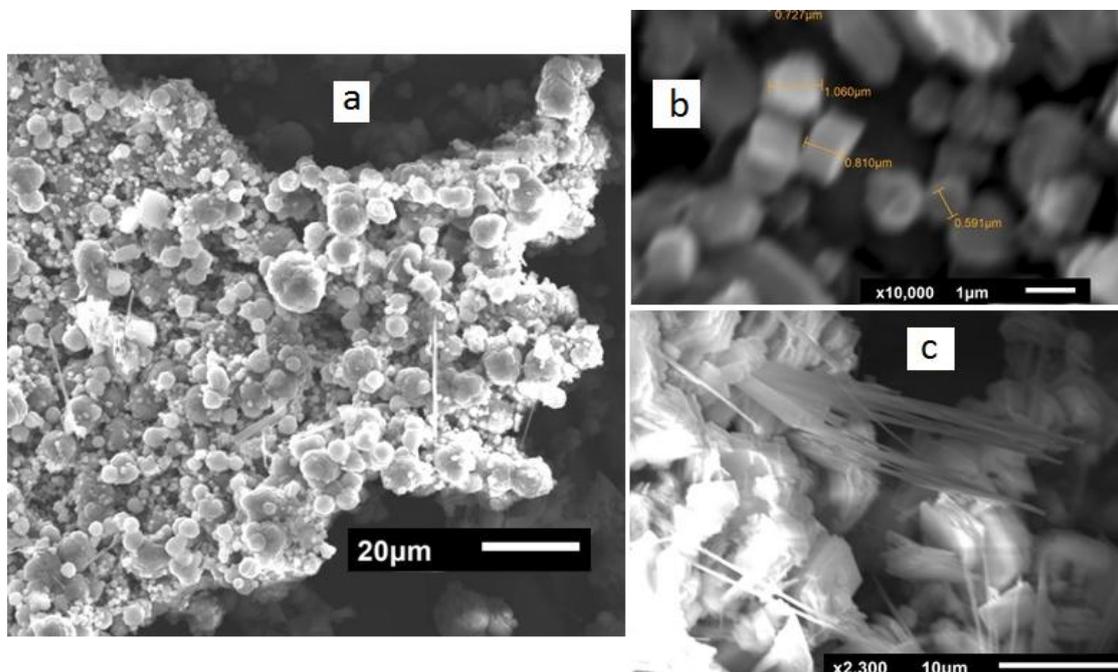


Figure 5. SEM images of Li-FER

4. Conclusion

The proposed method of Li-FER preparation is based on the use of natural silica-alumina raw material and inexpensive reagents (HCl, LiOH), and gives possibility to obtain monocationic ready-to-exchange Li-ferrierite without application of organic templates. Autoclave synthesis at 160°C during 140 hours gives possibility to prepare finely dispersed (0.5 – 1.2 µm) product suitable for catalytic and other applications.

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