

## SYNTHESIS OF THE 4A-TYPE ZEOLITE FROM PRETREATED RED OPALITE\*

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Synthetic 4A-type zeolite was obtained from a natural raw material of volcanic origin which was thermally and chemically pretreated. The procedures are described together with the characteristics of the zeolite. The 4A-type zeolite prepared in the described way exhibits about 70% of crystallinity when compared with the commercial products and a somewhat lower surface area.

The production of zeolites has been mainly based on pure starting materials. The price of zeolites can be reduced using suitable natural raw materials. The natural raw materials of volcanic origin including red opalite from Gorni Stubol in Macedonia are characterized by their high content of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ ; these materials are very useful for the synthesis of zeolites. However, they must be thermally and chemically pretreated prior to low-temperature synthesis which process is the subject of this contribution.

### EXPERIMENTAL

The red opalite from Gorni Stubol in Macedonia represents a rock of volcanic origin very intensively altered by hydrothermal processes; its composition is as follows: kaolinite, illite, cristoballite, tridymite, goethite and amorphous  $\text{SiO}_2$ . The rock is characterized by its red color due to the impurities of iron minerals<sup>1</sup>.

The red opalite samples were first crushed and then ground to grains of size lower than 0.063 mm which were used in further treatments: the chemical one, consisting of treatment with 10% HCl which was employed to decrease the Fe content and the thermal treatment at 973 K for 2 h.

Low-temperature synthesis was carried out by crystallization at 373 K for 6 h with additions of NaOH (R. G. quality) and sodium aluminate. The latter compound was characterized by the composition (in wt. %)  $\text{Al}_2\text{O}_3$  (20.5),  $\text{Na}_2\text{O}$  (20.1) and the density of  $1.478 \text{ g cm}^{-3}$ . The molar ratios of the oxides were selected according to the literature<sup>1</sup> and the composition of the starting mixtures was as follows:  $\text{Na}_2\text{O}/\text{SiO}_2 = 0.8, 0.9, 1$ ;  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 1.5, 1.72, 2$ ;  $\text{H}_2\text{O}/\text{Na}_2\text{O} = 34, 35, 36$ .

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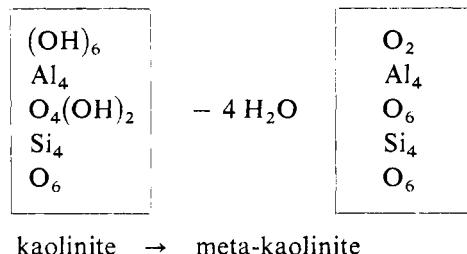
For the synthesis of the zeolites 3 mixtures with following calculated ratios were prepared: 1·2 Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-1·5 SiO<sub>2</sub>-41 H<sub>2</sub>O; 1·55 Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-1·72 SiO<sub>2</sub>-55 H<sub>2</sub>O; 2 Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-2 SiO<sub>2</sub>-72 H<sub>2</sub>O.

The products obtained by the synthesis (denoted as M01, M02, M03) were examined by means of XRD (HZG diffractometer Zeiss Jena, CuK $\alpha$ /Ni, 40 kV, 20 mA, 1° Zθ/min 1 700 V), IR spectroscopy (580 Perkin-Elmer infrared spectrophotometer) and DTA, TG (Nethen apparatus, 10 K/min,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>). The surface areas were determined from the Langmuir equation using water vapour adsorption at 293 K. The chemical analysis before and after the pretreatments as well as after the synthesis was carried out using gravimetric method.

## RESULTS AND DISCUSSION

The chemical composition of the red opalite before any treatment, after the chemical treatment with HCl and after the thermal treatment, is given in Table I. It is evident that the original red opalite contains iron minerals as impurities which are undesirable components in the further steps leading to the zeolite synthesis. The chemical treatment substantially reduces the Fe<sub>2</sub>O<sub>3</sub> content and the content of K and Na oxides. The thermal treatment increases somewhat the content of SiO<sub>2</sub>, while that of other components is almost unchanged.

After the thermal treatment, SiO<sub>4</sub> tetrahedra are still present in meta-kaolinite<sup>2,3</sup>, although the Al—O octahedron sheets (Al in 6-coordination) were transformed into the AlO<sub>4</sub> tetrahedra thanks to the water elimination from the Al—O octahedra coordination spheres. By the scheme presented elsewhere<sup>1</sup>, the above mechanism is described as follows:



The structure of the meta-kaolinite is highly strained as is indicated by diffuse X-ray reflexes because this mineral is not quite amorphous and consequently a certain degree of order in the structure is retained.

Employing the mixtures of oxides given in Experimental in the low-temperature synthesis, the 4A-type zeolite was obtained. By comparison with the characteristics of a commercial product (from Halle, Germany) it followed that the synthesized zeolite contained 71·26% of the crystalline phase (when the commercial zeolite contained 100%) and the specific surface area was 67·07 · 10<sup>3</sup> m<sup>2</sup> kg<sup>-1</sup> (the com-

TABLE I  
Chemical composition (in wt. %) of red opalite before and after chemical and thermal treatments

Oxide	Before treatments	After chemical treatment	After thermal treatment
SiO <sub>2</sub>	55.40	60.22	67.08
Al <sub>2</sub> O <sub>3</sub>	16.00	24.10	25.68
Fe <sub>2</sub> O <sub>3</sub>	12.80	2.04	2.24
MgO	0.16	—	—
CaO	0.34	0.72	0.79
K <sub>2</sub> O	0.40	0.15	0.17
Na <sub>2</sub> O	0.40	0.1	0.11
Weight loss	14.00	12.72	7.0

mercial zeolite:  $88.32 \cdot 10^3 \text{ m}^2 \text{ kg}^{-1}$ ) (refs<sup>4,5</sup>). The weight loss determined by TG-analysis was 15.84% compared to 18% for the commercial zeolite.

The DTA curves for the synthesized zeolites exhibited one endothermal and two exothermal peaks. These thermal effects are probably characteristic for the 4A-type zeolites.

## CONCLUSIONS

On the basis of the aforementioned investigations we can conclude that the red opalite from Macedonia can be used as a raw material for the synthesis of 4A-type zeolite. The preliminary chemical and thermal treatments are necessary, as well as the fulfilment of the optimal conditions of the synthesis.

The zeolite obtained exhibits somewhat lower crystallinity and surface area, compared to the commercial product. The chemical treatment of the red opalite with 10% HCl yields the solution enriched with Fe ions which can be employed in the production of Fe salts.

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