

EXPERIMENTAL STUDY OF THE INCORPORATION OF AMMONIA, METHANE AND PROPANE IN NATROLITE AND SCOLECITE STRUCTURES

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With the purpose of the experimental definition of direct incorporation possibility (without a cation exchange) of the C-H-N fluids' molecular forms in structural cavities of porous zeolites experiments were carried out at $T=200\text{ }^{\circ}\text{C}$, $P=20\text{ MPa}$ within 168 hours. Two monomineral fractions of natrolite' and scolecite' crystals with the dimensions 0.25-0.4 and less 0.25 mm were used as initial material (tabl. 1). The lack of inclusions in minerals was confirmed by the optical observations of colourless prismatic soldered popouts in the initial zeolites. The natrolite's [1] crystal formula is $\text{Na}_{1.85}\text{Mg}_{0.05}\text{Ca}_{0.03}[\text{Al}_{2.06}\text{Si}_{2.95}\text{O}_{10}]\cdot 2.05\text{H}_2\text{O}$ (The Khibiny massif, Kola Peninsula, Russia) According to the differential thermogravimetric analysis (DTGA) the water content in it is 9.6-9.9 mass %. The scolecite (Berufjord, Iceland) $\text{Ca}_{0.97}\text{Na}_{0.02}[\text{Al}_{1.96}\text{Fe}_{0.02}\text{Si}_{3.02}\text{O}_{10}]\cdot 3.04\text{H}_2\text{O}$ composition contained 13.75 mass % of water. The preparing of the zeolite samples for experiments consists in their preliminary dehydration in a vertical pipe furnace with time lag of 15 days. Heating was carried out in steps: 7 day at temperature $280\text{ }^{\circ}\text{C}$, 5 day at $300\text{ }^{\circ}\text{C}$, 3 day at $330\text{ }^{\circ}\text{C}$. Heating time is selected with the taking into account of data [2, 3] on kinetics of dehydration. The sterility of initial matrix on light constituents at a level of sensitivity of analytical methods is confirmed by IR-spectroscopic and gas-chromatographic analyses. Filling up by gas of annealed gold ampoules with beforehand loaded powder of a mineral and their capsulation were carried out in the device, permitting to weld up ampoules at refrigerating by liquid nitrogen. The technique is circumscribed in works [4, 5]. A source of methane, propane and ammonia were the national standards built in an IC SB RAS.

Table 1. Parameters of natrolite's and scolecite's unit cells before and after their treatment by ammonia and alkanes during experiences. (The dispersion is indicated in brackets)

Mineral, sp.gr.- fraction / structure of fluid above the mineral in experiment	Parameters of a unit cell				
	$a, \text{\AA}$	$b, \text{\AA}$	$c, \text{\AA}$	$\beta, ^{\circ}$	\AA^3
Initial natrolite, <i>Fdd2</i>	18.2941(12)	18.6505(12)	6.5879(4)		2247.77(18)
Natrolite, fr. 0.25-0.4 mm / NH_3	18.314(7)	18.624(6)	6.584(3)		2245(1)
Natrolite, fr. 0.25-0.4 mm / CH_4	18.34(4)	18.56(2)	6.54(4)		2228(11)
Natrolite, fr. 0.25-0.4 mm / C_3H_8	18.32(2)	18.62(2)	6.56(1)		2239(5)
Initial scolecite, <i>F1d1</i>	18.5054(9)	18.9776(11)	6.5276(4)	90.588(5)	2292.30(16)
Scolecite, fr. 0.25-0.4 mm / NH_3	18.58(5)	18.96(4)	6.52(3)	90.5(3)	2301(9)
Scolecite, fr. ≤ 0.25 mm / NH_3	18.38(1)	18.82(1)	6.544(9)	90.58(8)	2264(3)
Scolecite, fr. ≤ 0.25 mm / CH_4	18.32(4)	18.57(4)	6.55(3)	90.5(6)	2232(9)

Results of gas-chromatographic analysis of the fluid's structure above the crystalline matrix after experiments confirm almost the complete invariance of gas structure in comparison with the initial, the difference consists in the presence of an insignificant impurity of hydrogen. The lack of air admixings testifies the tightness of ampoules during experiment.

In spite of common similarity of structures of natrolite and scolecite they react differently to an introduction of the identical fluid "fillers". On X-ray structural analysis data (tabl. 1) the greatest strains of frame and changes of parameters of the natrolite and scolecite unit cells are characteristic for samples, which treated by methane. In general, the incorporation of methane, propane and ammonia in natrolite results in increasing of parameter a and reduction of parameters b and c of natrolite's structure. As for scolecite, modified by methane or ammonia, on the contrary, we can observe reduction of parameters a and b with the increasing of the parameter c . It was established the complete failure of scolecite structure under influence of propane in the indicated conditions of experiment.

In IR spectra of zeolites (fig. 1), saturated by methane, there are fixed not only strips of methane and water, but also CO strips in the frame that is connected, apparently, with the reaction of the Fisher – Troppsh: $\text{CH}_4 + \text{H}_2\text{O} \Rightarrow \text{CO} + 2\text{H}_2$ that occurs at heating. Usually such reaction proceeds at tempera-

tures of nearly 800 °C and in the presence of the catalyst. In this case the crystalline structure of zeolite is catalyst itself, the factors, defining passing of this reaction - duration of experiments and high pressure. The presence of wide strips at 3225 cm^{-1} and two narrow peaks at frequencies of 3078 and 3230 cm^{-1} in Raman-spectra of zeolites from a series with ammonia specify the presence of ammonia molecules both in scolecite, and in natrolite. In IR spectra of a diffuse reflection of natrolite, which was saturated by propane, there are fixed weak wide adsorbing bands close to 2959 and 2869 cm^{-1} , and also to 2924 and 2851 cm^{-1} which were assigned by us to valent C-H-vibrations in CH_3 - and CH_2 -groups of propane accordingly.

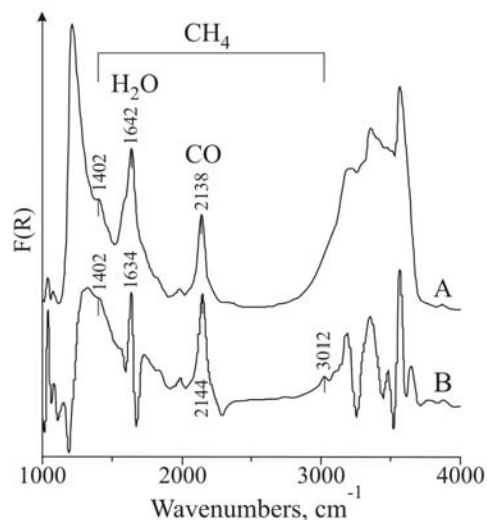


Fig. 1. IR-spectra diffuse reflectance of powders natural natrolite (A) and scolecite (B), processed by "dry" methane at 200 °C and 20 MPa within 168 hours.

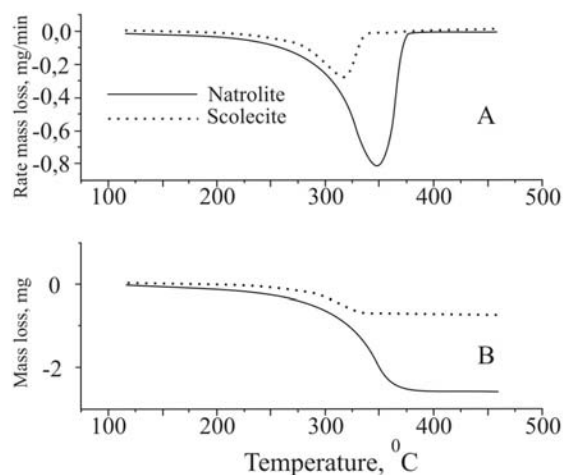


Fig. 2. DTG (A) and TG (B) curves powders CH_4 -natrolite and scolecite after experiments on their processing by "dry" methane. Speed of heating of samples of 20°/min.

During preparation of the samples to DTGA it was not possible to protect zeolites from sorption of an atmospheric water. It seems, that the polar molecule of ammonia attracts the molecule of water from an atmosphere around of zeolite that results in reaction: $\text{NH}_3 + \text{H}_2\text{O} = \text{NH}_4\text{OH}$. At heating up oxyhydroxide of ammonia is decomposed and ammonia leave structure channels together with the water. In this connection it is important that the dehydration of the NH_3 -modified zeolites (fig. 2) does not differ from natural [2]. The degassing singularity of the scolecite treated by ammonia, is observed in DTG- and TG- profiles, where on the first inflection of a differential curve "break" is seen, that is not characteristic for water scolecites [2]. The single-pass loss of 9.7 mass % at temperature ~ 350 °C occurs while heating NH_3 -natrolite. The NH_3 -scolecite is degassing in steps: 4.5 mass % at 300 °C, 5.4 mass % at 480 °C and in the interval from 500 °C up to 850 °C descends 3.6 mass %. Thus, gas saturation of zeolites makes up: for natrolite 9.7 mass %; for scolecite 14.4 mass % (a fraction of 0.25-0.4 mm) and 13.6 mass % for fraction less than 0.25 mm. It is not detected the essential differences of losing weight speed between natural natrolite and CH_4 - or NH_3 -natrolite. For CH_4 -scolecite is typical the single-stage degassing at temperature of 350°C. The lose of weight for sample began on 50-60 °C above, than in a case with NH_3 -scolecite.

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