EXPERIMENTAL SYNTHESIS OF AMMONIA - AND METHANE BEARING NATROLITE ZEOLITES

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Key words: zeolites, ammonia, methane, fluid

Ionic exchange and molecular sieving are most notable properties of zeolites. Natrolite and scolecite were chosen, because their crystal structure is a relatively simple and these minerals were well-studied. Fluid which is present in natural mineral-forming processes has a complex composition. In addition to main fluid components (water, carbon dioxide) [1, 2, 5] it contains noticeable amounts of methane and ammonia. Estimation of selectivity of zeolites with respect to methane and ammonia components of fluid and determination of difference in outgassing of natural and modified zeolites have been carried out.

Natrolite from Hibiny, Russia; $Na_{1.80}Mg_{0.05}Ca_{0.03}[Al_{2.07}Fe_{0.01}Si_{2.95}O_{10}]\cdot 2.05H_2O$, Z=8, contains 9,6-9,9% of water. Scolecite from Berufjord, Iceland; $Ca_{0.97}Na_{0.02}[Al_{1.96}Fe_{0.02}Si_{3.02}O_{10}]\cdot 3.04H_2O$, Z=8, contains 13.75% of water. Experimental samples were prepared by preliminary dehydrotation in alundum crucibles placed in a furnace which was gradually heated to 300°C within 360 hours.

The experiments were carried out with UVD-1000 apparatus, in the Tuttle reactor with the cooled gate. Annealed gold ampoules were used as containers for minerals. To avoid mixing methane and ammonia with atmosphere gases the unit for the charging of ampoules was connected to the vacuum pump. The construction of the unit allowed simultaneous cooling by liquid nitrogen during welding. Experiment parameters were chosen as 200°C and 20Mpa to avoid amorphization of zeolites on the one hand and to provide sufficient saturation kinetics – on the other. The lengths of tests were 168 hours for methane and 144 hours for ammonia.

Impermeability of ampoules had been controlled by checking constancy of their weights before experiments and after them. Gas chromatography of the fluid above crystals confirmed invariability of gas composition after tests in comparison with its initial state. However, some amount of hydrogen was found. Differential thermogravimetry (DTG) data showed that curve of outgassing had no significant changes from that of natural zeolites. Scolecite treated by methane showed one-stage outgassing, while the natural scolecite had three-stage outgassing. Total gas saturation of zeolites was 9.7% wt. for natrolite and 14.4% wt. for scolecite. Outgassing temperature was 350°C for natrolite; first stage temperature for scolecite was 300°C that of the second stage was 480°C, third stage temperature ranged from 500 to 850°C. The temperature stage of scolecite treated by methane was 380°C.

The presence of ammonia and methane molecules in zeolites was confirmed by spectroscopic investigation (FTIR and Raman). In Raman spectra a band (3225cm^{-1}) referable at N-H groups of vibrations was found. This band differs from the frequency of gaseous ammonia (3444cm^{-1}) [3]. In FTIR spectra a band (1402 cm$^{-1)}$ was found, which is referable at deformation vibration C-H group (1402 cm^{-1}) and this band does not agree with a frequency of gaseous methane (1490cm^{-1})[3]. Those guest molecules such as methane and ammonia seem to be bound with zeolitic framework by hydrogen bond, which cab be indirectly supported by the reducing molecular frequency. Besides, in FTIR spectra there were found the bands of carbon monoxide. The interaction of methane and water yielding hydrogen and carbon monoxide seems to take place in this case.

Conclusions:

1. In the process of outgassing ammonia and methane leave zeolitic framework at the temperature between 340 and 350 °C. Total gas content in natrolite is 9,7% wt, in scolecite – 13,6 -14,4% wt.
2. Detecting bands of methane and carbon monoxide in natrolite and scolecite spectra is a sign of Fisher-Tropsh reaction in this framework.

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Electronic Scientific Information Journal "Herald of the Department of Earth Sciences RAS" № 1(22)'2004
Informational Bulletin of the Annual Seminar of Experimental Mineralogy, Petrology and Geochemistry – 2004
URL: http://www.scgis.ru/russian/cp1251/h_dgggms/1-2004/informbul-1_2004/mineral-26e.pdf
Published on July, 1, 2004