CEC AND EGME RETENTION *VS.* TEXTURAL PROPERTIES OF Na-X (FAU) ZEOLITE

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The retention of ethylene glycol monoethyl ether (EGME) is a useful technique for determination of the total surface area (TSA) of expandable clay minerals (CARTER *et al.*, 1965). Diameter of zeolite X micropores is probably wide enough for access of EGME molecules, thus EGME should fill pores in a capillary way and cover as monolayer the external surface of grains in the produced material (DERKOWSKI *et al.*, submitted). Cobalt (III) hexamine chloride (ORSINI & REMY, 1976) is commonly used for the determination of CEC of clay minerals, beside the conventional methodology.

The study focuses on EGME and cation exchange capacity of zeolitic materials containing various percent of Na-X zeolite (FAU structure), versus their textural characterization. Zeolite X was synthesized at room temperature directly from raw fly ash, without prior treatment.

Increase of the BET surface area clearly depends on the development of microporous texture (S_{BET} *vs.* V_{mic} and S_{mic}, $R^2 = 0.99$). Micropore volume and area strictly follow the Na-X content but mesopore volume and surface area calculated from the BJH adsorption algorithm are independent on the zeolite content.

The CEC values measured with $[Co(NH_3)_6]Cl_3$ increase with the perfect linearity according to the development of micropore texture (CEC *vs.* V_{mic} and S_{mic}, $R^2 = 0.99$). Due to the great share of S_{mic} in the total surface area, the linearity for CEC *vs.* S_{BET}, may seem to be derivative of CEC *vs.* S_{mic}. But $R^2 = 0.99$ for CEC *vs.* S_{BET} exists even for samples with distinctive S_{ext} values. Thus, it is clear that CEC depends on the total surface area, including external one. Total CEC value (including sodalite cages) of materials rich in Na-X zeolite, measured using Ba^{2+} and Mg^{2+} cations is ca. twice higher than CEC measured by $[Co(NH_3)_6]^{3+}$ cation. Exchange positions available for $[Co(NH_3)_6]^{3+}$ cation occur only inside 12-ring space and loops of FAU framework.

The temperature of pre-heating is a crucial factor for the amount of retained EGME. Insufficient dehydration at 250 ºC (as in conventional procedure for clays) does not allow EGME molecules to enter all micropores. Pre-heating at 400 ºC causes EGME adsorption on all available surfaces. Mass of retained EGME linearly correlates with micropore volume and surface area ($R^2 = 0.96$), as well as S_{BET} ($R^2 = 0.97$). The retention of EGME does not correlate with micropore volume, however the incomplete dehydration (preheating at 250 ºC) allows for the partial EGME-water substitution in micropores and depends more on available mesopore surface area. Potential dimension of cylindrical micropores of the Na-X phase is ca. 43 $Å^2$, thus EGME retention inside the structure may be considered as a capillary infilling as well as surface adsorption (QUIRK & MURRAY, 1999). EGME molecule occupation area is ca. 41 $Å^2$, using BET algorithm and ca. 52 $Å^2$ for Langmuir equation, or package ratio 16 $Å^3$/1 EGME molecule if calculating adsorption as mechanism of micropores infilling.

Simple procedure of EGME retention can be successfully used to determine microporous texture of X zeolite available to organic molecules. The adsorption of EGME probably does not depend on charge density inside 12-ring space of FAU framework.

References

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