

Quantitative determination of ammonium salts in organo-zeolites by infrared spectroscopy

Barbara Szala, Tomasz Bajda, Jakub Matusik

AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection;
al. Mickiewicza 30, 30-059 Krakow, Poland; e-mail: basia.szala@gmail.com

© 2014 Authors. This is an open access publication, which can be used, distributed and reproduced in any medium according to the Creative Commons CC-BY 4.0 License requiring that the original work has been properly cited.

In recent years, the feasibility of using fly ash from the combustion of coal for the synthesis of zeolites has been studied (Belviso et al. 2010, Derkowski et al. 2010). One of the many uses of zeolites is to leverage their properties to act as organic sorbents (Bowman 2003). Unfortunately, the sorption process of organic substances on zeolites is hampered by the negatively-charged surface of the crystallites (Jashua & Bowman 2009). In order to increase the chemical affinity of the zeolite's surface to the organic molecules, its modification by organic surfactants is necessary. This leads to the formation of an organo-mineral complex with improved sorption properties. It has been found that organo-zeolites may be used to remove volatile compounds in a pure form, and those which occur in nature as impurities of air, water and soil (Damjanović et al. 2010, Vidal et al. 2012). Therefore, it seems reasonable to search for an organo-zeolite sorbent which is cheap, efficient and environmentally-friendly (Apreutesei et al. 2008).

The zeolites modification takes place only on the outer surface of the crystallites as the ammonium salts' molecules are too large to enter the zeolite's channels. Therefore, external cation exchange capacity (ECEC) is an important property in the synthesis of organo-zeolites. The type of surfactant introduced and its amount, often given by ECEC values, is crucial-subsequently leading to the formation of materials differing in

sorption properties. Thus, it is essential to determine the effectiveness of modification by examining the amount of surfactant adsorbed on zeolites' surface. In the experiments, a Na-P1 zeolite synthesized from fly ash remaining after coal combustion and a natural Ukrainian zeolite were transformed into organo-zeolites. This involved the replacement of original exchangeable cations (K^+ , Na^+ , Ca^{2+} , Mg^{2+}) by organic cations from the following salts: hexadecyltrimethylammonium bromide (HDTMA) and octadecyltrimethylammonium bromide (ODTMA) in amounts equal to 0.25, 0.50, 0.75 and 1.00 of ECEC. ECEC for synthetic zeolite Na-P1 was determined, and it was 24.4 meq/100 g, which corresponds to a single layer (1.0). The aim of this study was to use the infrared spectroscopy (FTIR) to determine the quantity of the surfactant adsorbed on the crystallites surface. The FTIR spectra were collected by a Thermo Scientific Nicolet 7600 spectrometer using the DRIFT technique. The CHN analysis was used to investigate the modification efficiency through quantification of the attached surfactant. The normalized intensity of selected bands attributed to C-H stretching vibrations in the $3,000-2,800\text{ cm}^{-1}$ region was compared with CHN results. The results revealed a high correlation ($R^2 > 0.99$) between spectroscopic and chemical analyses. The band intensities compared with the efficiency of modification enabled to obtain appropriate calibration

curves. This proved that FTIR could be used for a fast determination of the surfactants amount in the obtained organo-zeolites.

We gratefully acknowledge the support of NCBiR having provided grant PBS1/A2/7/2012.

REFERENCES

- Apreutesei R.E., Catrinescu C. & Teodosiu C., 2008. Surfactant-modified natural zeolites for environmental applications in water purification. *Environmental Engineering and Management Journal*, 7, 149–161.
- Belviso C., Cavalcante F. & Fiore S., 2010. Synthesis of Zeolite from Italian coal fly ash: Differences in crystallization temperature using sea water instead of distilled water. *Waste Management*, 30, 839–847.
- Bowman R.S., 2003. Applications of surfactant-modified zeolites to environmental remediation. *Microporous and Mesoporous Materials*, 61, 43–56.
- Damjanović L., Rakić V., Rac V., Stošić D., Auroux A., 2010. The investigation of phenol removal from aqueous solutions by zeolites as solid adsorbents. *Journal of Hazardous Materials*, 184, 477–484.
- Derkowski A., Franus W., Beran E. & Czimerová A., 2006. Properties and potential applications of zeolitic materials produced from fly ash using simple method of synthesis. *Powder Technology*, 166, 47–54.
- Joshua A.S. & Bowman R.S., 2009. Nonequilibrium sorption and transport of volatile petroleum hydrocarbons in surfactant-modified zeolite. *Journal of Contaminant Hydrology*, 108, 1–11.
- Vidal C.B., Raulino G.S.C., Barros A.L., Lima A.C.A., Ribeiro J.P., Pires M.J.R. & Nascimento R.F., 2012. BTEX removal from aqueous solution by HDTMA-modified Y Zeolite. *Journal of Environmental Management*, 112, 178–185.