Catalytic conversion of large organic molecules on modified silicates

Karolina Grzybowska¹, Agnieszka Węgrzyn¹, Artur Błachowski², Kamila Komędra², Wacław Makowski¹

¹ Jagiellonian University Department of Chemistry, Gronostajowa 2, 30-387 Cracow, Poland
² Mössbauer Spectroscopy Laboratory, Pedagogical University, Podchorążych 2, 30-084 Cracow, Poland

Introduction

In this work we used an innovative methodology to obtain mesoporous materials from vermiculite. Unlike other works which were using saponite or kaolinite (also natural clay minerals), application of vermiculite as a source of building elements of mesoporous silica are not very common. Vermiculite is a natural clay mineral. Its essential properties such as resistance to high temperatures, ability to maintain humidity, water absorption and high cation exchange capacity allows to apply vermiculite not only in building industry, agriculture or cosmetics industry, it is also promising material for catalysis and adsorption.

Experimental

In order to obtain a composite of MCM-41-vermiculite a natural vermiculite from Uganda (GUe) was mechanically and chemically modified. Combined acid-base treatment was used to generate mesoporosity. Subsequently, ion exchange process was carried out to introduce aluminum ions from the methanol solution. In the second path, MCM-41-vermiculite composite was first calcinated, then aluminum was introduced using hydrothermal method.

The structure of the obtained materials was characterized by X-ray diffraction (XRD), FT-IR spectroscopy and Mössbauer spectroscopy. The porosity was examined by Quasi-Equilibrated Temperature Programmed Desorption and adsorption (QE-TPDA). QE-TPDA is an experimental technique for testing the sorption properties of solids and has been successfully used in the study of zeolites and mesoporous silicas. It relies on cyclic measurements of hydrocarbons desorption and adsorption profiles. Outgassed sample, being in continuous contact with the adsorbate at a stable partial pressure, is consecutively heated and cooled down. By means of QE-TPDA it is possible to obtain in a very quick and reproducible manner results of total pore volume and pore size distribution.

Calcined vermiculite-derived mesoporous catalysts, before and after Al-doping, were used in α-pinene isomerisation.

Results

In obtained materials a typical broad peaks of MCM-41 structure were observed in XRD patterns. Infrared spectra confirmed removal of octahedrally coordinated metals from vermiculite and transformation of tetrahedral silica layer into amorphous material. Mössbauer spectroscopy confirmed changes in iron species distribution. Evolution of porosity measured by QE-TPDA confirmed increase of total pore volume from 0.05 cm³ g⁻¹ to 0.18 cm³ g⁻¹ in the case of composite MCM-41-vermiculite material.

Conversion of α-pinene increased from 5% to 98% for raw vermiculite and MCM-41-vermiculite composite materials, respectively.

Keywords: clay minerals; vermiculite; MCM-41; QE-TPDA.

Reference