PILLARED MONTMORILLONITES MODIFIED WITH SILVER
Temperature programmed desorption studies

Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Cracow, Poland

Abstract
Alumina, zirconia and titania pillared montmorillonites additionally modified with silver were tested as catalysts of NO reduction with NH₃ or C₂H₄. Ammonia was much more effective reducer of NO than ethylene. The silver containing TiO₂-pillared clay has been found to be the most active catalyst for NO reduction both with NH₃ or C₂H₄. Oxidation of the reducing agents by oxygen limited the NO conversion in the high temperature region. The ammonia and nitric oxide adsorption sites were studied by the temperature programmed desorption methods (TPD).

Keywords: ammonia, DeNOx, ethylene, pillared montmorillonites, TPD

Introduction
Montmorillonite is a natural clay characterized by a laminar structure in which the negative charge of layers is compensated by interlayer cations (e.g. Na⁺, Ca²⁺) [1, 2]. Pillared clays are obtained by replacement of these common cations by large polynuclear cationic species, which during thermal treatment are transformed into metal oxide pillars. Such modification of montmorillonite increases its microporosity and surface area. The texture parameters can be controlled by the choice of a suitable pillaring agent. The density and strength of acidic surface centers might be increased by the acid-pretreatment of the clay materials, while the redox centers can be generated through the introduction of transition metals into the montmorillonite structure. The pillared clays are thermally stable up to about 400–500°C. Due to such properties, montmorillonites intercalated with metal oxides were found to be very interesting materials for catalytic applications [3–6].

Pillared clays modified with different transition metals were recognized as very promising catalysts for NO reduction due to their high activity and stability in the presence of typical components of flue gases (e.g. SO₂, water vapor) [7, 8]. This paper is concerned with the study of the alumina, zirconia and titania pillared montmorillonites additionally modified with silver as catalysts of NO reduction by ammonia or ethylene.

* Author for correspondence: E-mail: chmielar@chemia.uj.edu.pl
Experimental

The montmorillonite used in this study was the sodium-exchanged Wyoming bentonite (A-15). The cation exchange capacity of this clay is 83 meq per 100 g (the total charge of interlayer cations which compensates negative charge of the montmorillonite layers related to 100 grams of a dry clay material).

Alumina pillars were introduced to the montmorillonite by the ion-exchange method using an aluminium hydroxy-oligomeric solution. The pillaring solution was obtained by adding 0.1 mol NaOH into an AlCl₃ solution until the molar ratio of OH/Al=2.5 was reached. The modified montmorillonite was separated, washed with distilled water to remove chloride ions and then dried (120°C/12 h).

The solution of the titania oligocations was prepared by adding TiCl₄ into HCl until the final concentrations of Ti⁴⁺ and HCl equal to 0.82 and 0.11 mol, respectively were reached. The pillaring agent was then added to the montmorillonite suspension until the Ti/clay ratio reached a value of 10 mmol g⁻¹. The final product was separated, washed and dried at 120°C for 12 h.

The montmorillonite was pillared with zirconia using an aqueous solution of zirconyl chloride (10 mmol Zr/1 g of clay). The modified clay was separated, washed with distilled water to remove Cl⁻ ions and then dried (120°C/12 h). A more detailed description of the preparation procedure of the pillared montmorillonites was presented in a previous paper [9].

Silver was introduced into the pillared clays by the ion exchange method. One gram of the pillared montmorillonite was added to 100 mL of the 0.02 mol silver nitrate solution. The vigorously stirred suspension of the pillared clays was left in contact with the solution of transition metal nitrate at 60°C for 12 h. The silver modified clays were separated, washed and dried at 120°C for 12 h and then calcined at 400°C for 12 h.

The chemical composition of the samples was determined by X-ray fluorescence (XRF) using an Oxford 2000 instrument. The analytic response was calibrated using standard materials. The X-ray diffraction studies of the calcined montmorillonites were performed with a PW3710 Philips X’pert diffractometer using CuKα radiation (λ=0.154178 nm). The BET measurements were performed using an ASAP 2010 instrument (Micromeritics). Prior to N₂ adsorption at liquid nitrogen temperature (~196°C), the samples of calcined clay were outgassed at 350°C under vacuum for 12 h.

The temperature-programmed desorptions of NH₃ (NH₃-TPD) or NO (NO-TPD) were carried out in the temperature range of 70–600°C in a fixed bed continuous flow microreactor. The desorption temperature was measured with a K-type thermocouple located in a quartz capillary immersed in the catalyst bed. The molecules desorbing from the samples were monitored on-line by a quadrupole mass spectrometer (VG Quartz) connected to the reactor outlet via a heated line. Prior to TPD experiments, the clay sample (50 mg) was outgassed at 400°C for 1 h in a flow of helium (20 ml min⁻¹). Subsequently, the sample was cooled down to 70°C and saturated for about 30 min in a flow of 1% NH₃/He or 1% NO/He (20 ml min⁻¹). Then the catalyst was purged in a helium stream until a constant baseline was attained. Desorption was carried out with a linear...