

## ORIGINAL PAPER

# Montmorillonite intercalated with SiO<sub>2</sub>, SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub>–TiO<sub>2</sub> pillars by surfactant-directed method as catalytic supports for DeNO<sub>x</sub> process

<sup>a</sup>Lucjan Chmielarz\*, <sup>a</sup>Andrzej Kowalczyk, <sup>a</sup>Magdalena Wojciechowska,  
<sup>a</sup>Paweł Boroń, <sup>a</sup>Barbara Dudek, <sup>b</sup>Marek Michalik

<sup>a</sup>Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Krakow, Poland

<sup>b</sup>Institute of Geological Sciences, Jagiellonian University, Oleandry 2a, 30-063 Krakow, Poland

Received 21 March 2013; Revised 5 June 2013; Accepted 13 June 2013

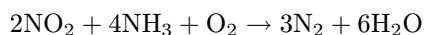
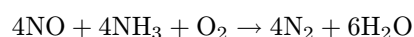
The intercalation of natural montmorillonite with SiO<sub>2</sub>, SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub>–TiO<sub>2</sub> pillars by the surfactant-directed method resulted in the formation of high surface area porous materials; these were tested as catalytic supports for the process of selective catalytic reduction of NO (DeNO<sub>x</sub>). The incorporation of titanium or aluminium into the structure of the silica pillars significantly increased the surface acidity of the clay samples. Iron and copper were deposited onto the surface of the pillared clays mainly in the form of monomeric isolated cations and oligomeric metal oxide species. The contribution of the latter species was higher in the clay intercalated with SiO<sub>2</sub>–TiO<sub>2</sub> pillars than in the samples modified with SiO<sub>2</sub> and SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> pillars. The pillared clay-based catalysts were active in the DeNO<sub>x</sub> process but, in this group, the best results were obtained for the clay intercalated with SiO<sub>2</sub>–TiO<sub>2</sub> pillars and doped with iron and copper. The catalytic performance of the samples is discussed in respect of their surface acidity and active forms of transition metal species deposited.

© 2013 Institute of Chemistry, Slovak Academy of Sciences

**Keywords:** montmorillonite, intercalation, surfactant-directed method, porous clay heterostructures (PCHs), selective catalytic reduction (DeNO<sub>x</sub>), nitric oxide

## Introduction

Emissions of nitrogen oxides (NO<sub>x</sub>, i.e. NO, NO<sub>2</sub>) from static (e.g. power plants) and mobile (e.g. cars, aircraft) sources is a major environmental problem. The most important method used for the elimination of NO<sub>x</sub> from stationary sources is its catalytic reduction by ammonia (NO<sub>x</sub>-SCR, DeNO<sub>x</sub>), e.g. Busca et al. (1998).



In commercial installations, this process is carried

out in the presence of monolithic catalysts based on the vanadia–titania systems at temperatures of 300–400 °C, e.g. Busca et al. (1998). The disadvantages of such commercial catalytic systems are the relatively high volatility of toxic vanadium, the narrow range of effective operation and their relatively high cost. Recently, a modified version of the DeNO<sub>x</sub> process, in which urea solution is used as a source of ammonia, was applied to the elimination of NO<sub>x</sub> emitted by diesel car engines, e.g. Steinbach et al. (2007). For this process, known as AdBlue, effective catalysts operating in a much broader temperature range are required. Hence, studies on the development of new catalytic systems for the DeNO<sub>x</sub> process, with the ability to operate in a much broader temperature range and

\*Corresponding author, e-mail: chmielar@chemia.uj.edu.pl