



## Selective catalytic oxidation of ammonia to nitrogen over Mg–Al, Cu–Mg–Al and Fe–Mg–Al mixed metal oxides doped with noble metals

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### ABSTRACT

Mg–Al, Cu–Mg–Al and Fe–Mg–Al mixed oxides, were obtained by thermal decomposition of synthetic hydrotalcite-like materials and, in the next step, were modified with selected noble metals (Pt, Pd, Rh) by incipient wetness impregnation method. The process of thermal decomposition of hydrotalcite-like materials into metal oxide systems was studied by thermogravimetry method combined with the on-line analysis of gaseous products of the sample decomposition (TG–DTA–QMS). The obtained catalysts were studied with respect to chemical composition (EDS), structure (XRD, UV–vis–DRS), morphology (STEM), surface area (BET) and redox properties (H<sub>2</sub>–TPR). Metal oxide catalysts obtained from the hydrotalcite-like precursors were characterized by high dispersion of transition metals (Cu, Fe), which were present mainly in the form of monomeric or small aggregated species dispersed in the Mg–Al oxide matrix. Noble metals, as it was shown by STEM studies, were rather uniformly dispersed on the surface of the samples. The obtained samples were tested as catalysts of the selective catalytic oxidation (SCO) of ammonia to nitrogen. The Cu–Mg–Al oxide catalyst was active in the low-temperature SCO process, while the Fe-containing sample was found to operate in the high temperature range. Modification of these catalysts with noble metals significantly decreased temperature of the ammonia oxidation but also decreased the selectivity to nitrogen. The best catalytic properties were obtained for the Cu–Mg–Al oxide catalyst modified with small amount of platinum (0.2 wt%), which operated at relatively low temperature with high selectivity to nitrogen.

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### 1. Introduction

The increasing problem of atmospheric pollution by various N-containing compounds, such as NO, N<sub>2</sub>O, NO<sub>2</sub> and NH<sub>3</sub>, has resulted in stricter regulations on their emission. Many chemical processes use ammonia as a reactant or produce ammonia as a by-product (e.g. nitric acid and nitrogen fertilizer production, urea manufacturing, hydrodenitrification process, DeNO<sub>x</sub> process). The selective catalytic oxidation (SCO) of ammonia by oxygen to nitrogen and water vapour, according to the reaction given below (1), is one of the most promising methods for the removal of NH<sub>3</sub> from oxygen containing waste gases.



N<sub>2</sub>O and NO are the main by-products of this process. The effective SCO catalysts should operate in a relatively low temperature

range and additionally should selectively direct the reaction to the formation of nitrogen and water vapour.

Various transition metal oxides, including CuO, Fe<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>, MnO<sub>2</sub>, MoO<sub>3</sub>, V<sub>2</sub>O<sub>5</sub> [e.g. 1–6], were tested as catalysts for the SCO process. Among them the catalysts containing copper and iron were found to be one of the most interesting systems.

Our previous studies have shown that hydrotalcite-like materials are very promising precursors of the catalysts for various reactions: DeNO<sub>x</sub> [7,8], DeN<sub>2</sub>O [9], VOCs incineration [10] and SCO of ammonia [11,12]. Hydrotalcites, also called layered double hydroxides (LDHs), are characterized by the brucite-like structure [Mg(OH)<sub>2</sub>], where the octahedra of Mg<sup>2+</sup> (six-coordinated to OH<sup>−</sup>) form doubled layers. Part of Mg<sup>2+</sup> ions is replaced by trivalent cations (e.g. Al<sup>3+</sup>), what results in a positive charging of the brucite-like layers. This positive charge is compensated by anions (e.g. CO<sub>3</sub><sup>2−</sup>, NO<sub>3</sub><sup>−</sup>), which together with water molecules are located in the interlayer space of the material. Furthermore, some of the Mg<sup>2+</sup> as well as Al<sup>3+</sup> ions can be replaced by other di- (e.g. Cu<sup>2+</sup>) and trivalent- (e.g. Fe<sup>3+</sup>) cations, respectively. Calcination of the hydrotalcite precursors results in their decomposition and formation of thermally stable mixed metal oxides characterized by a

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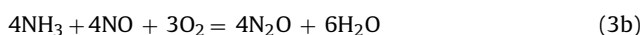
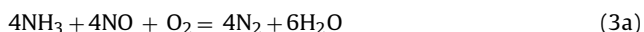
relatively high surface area and homogeneous distribution of metal cations. Taking into account these properties and additionally, a large number of various metals, which can be incorporated into the brucite-like layers, the hydrotalcite-like materials are very promising for the possible applications in catalysis.

Our previous studies [11] of the SCO reaction mechanism over the hydrotalcite originated metal oxide catalysts have shown that this process proceeds according to the *Internal Selective Catalytic Reduction* mechanism (i-SCR), which consists of the following steps:

- (i) part of ammonia is oxidized to NO:



- (ii) ammonia, unreacted in stage 2, reduces NO to N<sub>2</sub> (3a) or N<sub>2</sub>O (3b):



Taking into account both reaction steps it could be concluded that the effective catalysts of the SCO process should be active in ammonia oxidation to NO (2) as well as in selective reduction of NO with ammonia to nitrogen (3a). Distribution of the N-containing reaction products should be strongly dependent on the relative activities of the catalyst in reaction (2), (3a) and (3b).

The presented studies are focused on development of active and selective, bi-functional catalysts for the SCO process. Selected noble metals (Pt, Pd, Rh) play a role of the components active in the oxidation of ammonia into NO, while mixed metal oxides containing copper and iron are the components active in the selective reduction of NO with ammonia.

## 2. Experimental

### 2.1. Catalysts preparation

Mg-Al, Cu-Mg-Al and Fe-Mg-Al hydrotalcite-like materials with the intended atomic ratios of 71/29, 5/66/29 and 5/66/29, respectively, were synthesized by co-precipitation method using aqueous solutions of the following metal nitrates: Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Sigma), Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Fluka), Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (Merck), Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (POCh). A solution of NaOH (POCh) was used as a precipitating agent. The mixture of nitrates and NaOH were simultaneously added to a vessel containing aqueous solution of Na<sub>2</sub>CO<sub>3</sub> (POCh) at 60 °C. The pH of the mixture was maintained constant at 10.0 ± 0.2 by dropwise addition of NaOH solution. The obtained slurry was stirred at 60 °C for further 30 min, filtered, washed with distilled water and dried in air. The obtained samples were calcined at 600 °C for 12 h.

Calcined hydrotalcite-like materials were modified with selected noble metals (Pd, Pt, Rh) by incipient wetness impregnation method using methanol (Lach-ner) solutions of acetylacetonate complexes of these metals – Pd(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub>, Pt(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub>, Rh(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub> (all supplied by Accross). After impregnation, the samples were dried in air, crushed and calcined at 500 °C for 3 h. The obtained catalysts were kept in a desiccator in order to avoid the reconstruction of the hydroxide structure. The intended content of noble metals in the samples was 0.2 wt%, while the diameter of the catalyst grains was in the range of 160–315 μm.

### 2.2. Samples characterization

Thermal decomposition of the hydrotalcite samples was studied by thermogravimetric method combined with on-line analysis of gaseous products (TG-DTA-QMS). The measurements were carried out using a Mettler Toledo 851<sup>e</sup> thermobalance operated

under a flow of pure argon (80 cm<sup>3</sup>/min) in the temperature range of 25–1000 °C with a linear heating rate of 10 °C/min. The gases evolved during the thermal decomposition of the samples were continuously monitored with a quadruple mass spectrometer ThermoStar (Balzers) connected directly to the thermobalance.

The specific surface area of calcined hydrotalcites was determined by the BET method. The measurements were performed using Quantasorb Junior sorptometer (Ankersmit). Prior to the nitrogen adsorption at –196 °C the samples were outgassed in nitrogen atmosphere at 250 °C for 2 h.

The X-ray diffraction (XRD) patterns of the as-synthesised and calcined samples were recorded with a D2 Phaser diffractometer (Bruker) using Cu Kα radiation (λ = 1.54060 Å, 30 kV, 10 mA).

The chemical composition of the samples was determined by electron microprobe analysis using a HITACHI S-4700 instrument equipped with microanalysis system NORAN Vantage operated an accelerating voltage of 10 kV.

The STEM images were obtained with use of Tecnai Osiris 200 kV TEM/STEM system equipped with HAADF detector and Super-EDX windowless detector. STEM micrographs (512 × 512 points) were coupled with EDX data for presentation of distribution of the chosen element. Esprit software was used to control measurements and preparing the resulting images.

The redox properties of the catalysts were studied by temperature-programmed reduction method (H<sub>2</sub>-TPR). The experiments were carried out in a fixed-bed flow microreactor from room temperature (RT) to 1100 °C with a linear heating rate of 5 °C/min. The gas mixture containing of 5 vol.% of H<sub>2</sub> diluted in argon was supplied into microreactor with a flow rate of 6 cm<sup>3</sup>/min. Water vapour, which was a gas product of the metal oxides reduction, was removed from the effluent gas by means of a cold trap. Therefore, the signal of TCD detector (Valco) was associated only with consumption of hydrogen.

The species and aggregation state of the transition metals present in the samples was studied by UV-vis-DRS method. The UV-vis-DRS spectra were recorded using an Evolution 600 (Thermo) spectrophotometer. The measurements were performed in the range of 200–900 nm with a resolution of 1 nm.

### 2.3. Catalytic tests

The calcined hydrotalcites and their modifications with noble metals were tested in the role of catalysts for the selective catalytic oxidation of ammonia (SCO). The experiments were performed under atmospheric pressure in a fixed-bed flow reactor (i.d., 7 mm; l., 240 mm). The reactant concentrations were continuously monitored using a quadrupole mass spectrometer (PREVAC) connected to the reactor via a heated line. Prior to the reaction each sample of the catalyst (100 mg) was outgassed in a flow of pure helium at 600 °C for 1 h. The composition of the gas mixture at the reactor inlet was [NH<sub>3</sub>] = 0.5 vol.%, [O<sub>2</sub>] = 2.5 vol.% and [He] = 97 vol.%. Total flow rate of the reaction mixture was 40 cm<sup>3</sup>/min, while a space velocity was about 15,400 h<sup>-1</sup>. The reaction was studied at temperatures ranging from 50 to 500 °C. The intensities of the mass lines corresponding to all reactants and possible products were measured at a given temperature at least for 30 min after the reaction had reached a steady-state. The signal of the helium line served as an internal standard to compensate possible fluctuations of the operating pressure. The sensitivity factors of analyzed lines were calibrated using commercial mixtures of gases. The differences between the reactor inlet and outlet molar flows of the reactants were used to determine conversion of the reactants.

Additionally, the catalysts were tested in the process of selective catalytic reduction of NO with ammonia (NO-SCR, DeNOx). The catalytic experiments were performed in a fixed-bed flow

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