Selective catalytic oxidation of ammonia to nitrogen over bi-functional hydrotalcite originated mixed metal oxides doped with noble metals

Lucjan Chmielarz^{*}, Magdalena Jabłońska, Agnieszka Węgrzyn, Zofia Piwowarska ¹Jagiellonian University, Faculty of Chemistry, Ingardena 3, 30-060 Kraków, Poland *corresponding author: Lucjan.Chmielarz@uj.edu.pl

Introduction

The increasing problem of atmospheric pollution by various N-containing compounds, such as NO, N_2O , NO_2 and NH_3 , has resulted in stricter regulations on their emissions. Many chemical processes use ammonia as a reactant or produce ammonia as a by-product (e.g. nitrogen fertilizer production, urea manufacturing, HDN, DeNOx process). The selective catalytic oxidation (SCO) of ammonia to nitrogen, according to the reaction given below, is one of the most promising methods for the removal of NH_3 from oxygen containing waste gases.

$4 \text{ NH}_3 + 3 \text{ O}_2 = 2 \text{ N}_2 + 6 \text{ H}_2\text{O}$

N₂O and NO are the main by-products of this process. Therefore, the effective SCO catalysts should operate at a relatively low temperature range and additionally should selectively direct the reaction to formation of nitrogen.

Our previous studies have shown that hydrotalcite-like materials are very interesting precursors of catalysts for various reactions, including also the SCO process [1, 2]. These studies [1] have shown that the SCO 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: $4 \text{ NH}_3 + 5 \text{ O}_2 = 4 \text{ NO} + 6 \text{ H}_2\text{O}$

(ii) unreacted NH_3 reduces NO formed in stage (i): **4** NH₃ +**4** NO + O₂ = **4** N₂ + **6** H₂O Taking into account both reaction steps it could be concluded that effective catalysts of the SCO process should be active in ammonia oxidation (i) as well as in selective reduction of NO with ammonia (ii). The distribution of N-containing reaction products should be strongly dependent on the relative activities of the catalyst in both reactions (i and ii).

The 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 components active in the oxidation of ammonia into NO, while mixed metal oxides containing cooper and iron were used as components active in the reduction of NO with ammonia.

Materials and Methods

Mg/Al, Cu/Mg/Al, Fe/Mg/Al hydrotalcites were synthesized by co-precipitation method using solutions of suitable metal nitrates and a solution of NaOH as a precipitating agent. The obtained slurry was filtered, washed with distillated water, dried and finally calcined (600°C/12 h). The calcined samples were doped with selected noble metals (Pd, Pt, Rh) by incipient wetness impregnation method using methanol solutions of acetylacetonates complexes of these metals. Finally, the catalysts were dried and calcined (600°C/3 h). The obtained catalysts were characterized with respect to: chemical composition (XRF), structure (XRD, FT-IR, UV-vis-DRS), textural parameters (BET), morphology (SEM), thermal stability (TG-QMS) and redox properties (H₂-TPR).

Catalytic tests in the SCO process were performed in a flow microractor system equipped with QMS detector connected directly to the reactor outlet. Moreover, the reaction mechanism was studied by temperature programmed methods (TPD, TPSR) as well as catalytic tests performed with various space velocity.

Results and Discussion

Calcined hydrotalcites containing Cu or Fe were found to be active and selective catalysts of the SCO process. Examples of the catalytic results are presented in **Figure 1**. The catalyst containing copper (Cu-Mg-Al) was active in the low-temperature range, while calcined hydrotalcite containing iron (Fe-Mg-Al) effectively operated at higher temperatures. For both the catalysts high selectivity to nitrogen was obtained. Doping of calcined hydrotalcites with small amount of noble metals, as it was shown for the samples modified with platinum, significantly activated them in the low-temperature range and decreased their selectivity to N₂. Moreover, it was shown that the SCO process proceeds according to the i-SCR mechanism



Figure 1. Results of catalytic studies in the process of selective ammonia oxidation (SCO)

Significance

Hydrotalcite based catalysts, containing Cu or Fe, are active and selective in the SCO process. Noble metals increase their catalytic activity but decrease selectivity to N₂.

References

- Chmielarz, L., Węgrzyn, A., Wojciechowska, M., Witkowski, S, Michalik, M., Catalysis Letters 2011, 141, 1345.
- Chmielarz, L., Kuśtrowski, P., Rafalska-Łasocha, A., Dziembaj, R., Applied. Catalysis. B 2005, 58, 235.