



Redox-performance correlations in Ag–Cu–Mg–Al, Ce–Cu–Mg–Al, and Ga–Cu–Mg–Al hydrotalcite derived mixed metal oxides



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ABSTRACT

Ag-, Ce- and Ga-promoted Cu–Mg–Al hydrotalcite derived mixed metal oxides were obtained by standard coprecipitation, followed by calcination. The obtained Ag(Ce, Ga)–Cu–Mg–Al–O_x mixed metal oxides were characterized with respect to their crystalline structure (XRD, TEM), texture (BET), surface acidity (NH₃-TPD), redox properties (H₂-TPR), chemical surface composition (XPS), and tested in the selective catalytic oxidation of ammonia into nitrogen and water vapour (NH₃-SCO). The loading of Ag_y-, Ce_y-, or Ga_y-Cu₅-Mg_{6-y}-Al₂₉ (y = 0–1) had a clear effect on the catalytic performances. For materials with low metal loadings (y ≤ 0.25), the redox properties determined the catalytic performances in NH₃-SCO. The formation of easily reducible CuO_x played a crucial role for enhanced catalytic activity at lower temperatures, with a drop in the selectivity to N₂ at higher temperatures. Higher metal loading (y ≥ 0.5) led to the formation of surface and bulk copper oxide species, and other aggregated metal oxide phases, which enhanced the catalytic activity for Ag–Cu–Mg–Al–O_x, and diminished activity for Ce(Ga)–Cu–Mg–Al–O_x.

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1. Introduction

Hydrotalcite-like compounds can be represented by the general formula M²⁺_{1-y}M³⁺_y(OH)₂(Aⁿ⁻)_{y/n}·mH₂O, where M²⁺ and M³⁺ are bi- and trivalent metal cations, respectively. Aⁿ⁻ presents an interlayer anion, and y – M³⁺/(M³⁺ + M²⁺) exhibits a value between 0.17 and 0.50 [1,2]. Thus, a great variety of possible metal combinations – including monovalent M⁺ (e.g. Ag⁺ or Li⁺ [e.g. [3,4]]) or even tetravalent M⁴⁺ (e.g. Zr⁴⁺ or Sn⁴⁺ [e.g. [5,6]]) – led to a large number of possible materials. Hydrotalcite-like compounds serve mostly as precursors for mixed metal oxides with a high specific surface area, homogenous dispersion of metals within the oxide matrix, high thermal stability, etc. [7,8]. Among them, copper-containing hydrotalcite derived mixed metal oxides (Cu–Mg–Al–O_x, 5.0–8.0:66.0–63.0:29.0, mol.%) present the most active, selective to N₂ and stable catalysts among copper modified clays for the selective ammonia oxidation into nitrogen and water vapour (NH₃-SCO) [9,10]. On the other side, bi- or trimetallic (transition metal-copper) hydrotalcite derived mixed metal oxide systems, such as Pt(Pd,Rh)–Cu [11,12], Zn–Cu, Fe–Zn–Cu

or Fe–Cu [7,13] were scarcely investigated in NH₃-SCO. However, the available studies revealed a correlation between the reduction temperature of CuO_x and the catalytic performance in ammonia oxidation. The proximity of other transition metals in Cu-based catalysts significantly influenced the reducibility of copper oxide species. Catalysts containing easily reducible CuO_x revealed enhanced activity together with a drop in N₂ selectivity at higher temperatures.

According to the literature [e.g. [9,11,14]], a cooperative effect of copper with other metals (e.g. noble metal, rare earth metal, etc.) clearly influences the reduction temperature of copper oxide species. Ag-, Ce-, or Ga-promoters should influence the reducibility of CuO_x over a broad range, and thus the catalytic performance in NH₃-SCO. However, a limited number of reports refer to bimetallic: Ag–Cu, Ce–Cu or Ga–Cu hydrotalcite derived mixed metal oxides. Recently, Xu et al. [15] reported Ag–Cu supported on Mg–Al–O_x for the dehydrogenative cross-coupling of primary and secondary benzylic alcohols. These catalysts were obtained through calcination and subsequent reduction in H₂; thus, both metals existed in the metallic form (based on XPS studies). For Ag–Cu deposited on inorganic supports (e.g. BaCO₃ [16], SiO₂ [17], or Al₂O₃ [18,19]), an enhanced CuO_x reducibility correlated with a distinct interaction between Ag and Cu species. One of the possible explanations refers to electronic interactions – copper reduction–silver oxida-

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tion – in bimetallic Ag–Cu systems, together with an improved dispersion of CuO_x [e.g. [17,18]]. Analogously, cerium promoted the reduction of copper oxide species. Wang et al. [20] and Wen et al. [21] investigated Ce–Cu–Mg–Al– O_x for soot oxidation and NO reduction with CO, respectively. The presence of cerium enhanced the reduction of copper oxide species (based on H_2 -TPR studies) [14], possibly due to the generation of a large quantity of easily reducible Cu^+ (based on XPS analysis) [21]. Although, Cu–Mg–Al hydrotalcite derived mixed oxides obtained through calcination in air only revealed the presence of Cu^{2+} species [e.g. [22,23]]. $\text{Cu}^{2+}/\text{Cu}^+$ coexisted also in CuO – CeO_2 mixed oxides prepared by a surfactant-templated method [24]. Gallium has mostly been studied in Mg–(Al)–Ga hydrotalcite derived systems [e.g. [25–28]], while only few reports refer to Cu–Ga catalysts [e.g. [29,30]]. For example, Venugopal et al. [29] investigated Ga–Cu–Zn–Al– O_x among (Y, Zr, La, Ga)–Cu–Zn–Al hydrotalcite derived mixed metal oxides for dimethyl ether synthesis. Gallium-containing samples reached the highest reduction temperature, indicating the presence of bulk CuO_x (based on H_2 -TPR and SEM analysis). Moreover, the presence of gallium retarded the reduction of CuO_x in other Ga–Cu catalytic systems (e.g. $\text{CuO}/\text{Ga}_2\text{O}_3$ – ZnO [31], $\text{CuO}/\text{Ga}_2\text{O}_3$ or $\text{CuO}/\text{Ga}_2\text{O}_3$ – ZrO_2 [32], etc.). Thus, the presence of gallium led to the formation of bulk copper oxides species in the form of CuO_x and/or a CuGa_2O_4 spinel phase [32,33].

In the present work, we prepared hydrotalcite-like precursors of different composition by coprecipitation covering Ag_y -, Ce_y -, or Ga_y – Cu_5 – Mg_{66-y} – Al_{29} ($y=0$ – 1). We characterized the as-synthesized materials and/or their derived forms using XRD, TG–DTG, BET, NH_3 -TPD, TEM, XPS and H_2 -TPR, and tested them as catalysts in the selective ammonia oxidation. To the best of our knowledge, this study presents for the first time the redox-performance correlation of Ag–Cu, Ce–Cu, and Ga–Cu hydrotalcite derived mixed metal oxides for NH_3 -SCO. Our aim was to gain a comprehensive understanding of the influence of different dopants (Ag, Ce or Ga) on CuO_x reducibility, and consequently on catalytic activity and selectivity in ammonia oxidation.

2. Experimental

2.1. Catalysts preparation

A series of hydrotalcite-like compounds with an intended composition of Y–Cu–Mg–Al (Y = Ag, Ga, Ce; $y:5:66-y:29$ ($y=0, 0.1, 0.25, 0.5, 0.75, 1$)) were prepared by coprecipitation using 1 M aqueous solutions of the following metal nitrates: $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Sigma), $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sigma), AgNO_3 (Sigma), $\text{Ga}(\text{NO}_3)_3$ (Chempur), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Sigma). A solution of 1 M sodium hydroxide (Chemsolute) was used as precipitating agent. The solution of metal salts was dropped simultaneously with NaOH to a vigorously stirred aqueous solution at 60°C containing a slightly over-stoichiometric excess of Na_2CO_3 (Sigma). The pH of the reaction mixture was maintained constant at 10.0 ± 0.2 throughout the whole synthesis. The obtained suspension was aged at 60°C for another 0.5 h after complete coprecipitation. The solid was filtered, washed carefully with distilled water and dried at room temperature. Afterwards, all samples were crushed and calcined at 600°C for 6 h with a heating ramp of 10 K/min, and in static air. The mixed metal oxides obtained from hydrotalcite-like compounds were kept in a desiccator in order to avoid the reconstruction of the hydroxide-like structure. For catalytic experiments, a fraction of particle size in the range of 0.250–0.500 mm was used.

2.2. Catalysts characterization

The X-ray diffraction analysis (XRD) of the as-synthesized hydrotalcite-like compounds and their calcined forms was performed applying a Siemens D5000 XRD diffractometer using Cu– $\text{K}\alpha$

radiation ($\lambda = 1.54056 \text{ \AA}$, 45 kV, 40 mA). The cell parameters were calculated using a position of (1 1 0) reflection: $a = 2(d_{110})$ and positions of basal reflections: $c = [3(d_{003}) + 6(d_{006})]/2$. The crystal sizes were calculated from the Scherrer equation $D = 0.89 \cdot \lambda / \beta \cdot \cos \theta$, where D is the crystallite size, λ is the X-ray wavelength, β is the line broadening and θ is the Bragg angle.

The thermogravimetric analysis (TG) of the hydrotalcite-like compounds (~ 20 mg) was carried out using a Netzsch STA 409C/CD operated under a flow of air ($10 \text{ cm}^3/\text{min}$) in the temperature range of 30 – 1000°C with a linear heating rate of 5 K/min.

The chemical composition of the samples was determined by ICP-MS using an Agilent Technologies 8800 Triple Quad spectrometer.

The specific surface area (S_{BET}) of the mixed metal oxides was determined by low-temperature (-196°C) N_2 sorption using a Quantachrome Quadrasorb SI. Prior to nitrogen adsorption the samples were outgassed at 250°C for 12 h using a Quantachrome Flocav degasser. The specific surface area (S_{BET}) was calculated using the Brunauer–Emmett–Teller (BET) multiple point method in the p/p_0 range from 0.05 to 0.3. Pore size distributions were obtained from analysis of the desorption branches of the nitrogen isotherms using the Barrett–Joyner–Halenda method.

The surface acidity of the mixed metal oxides was determined by temperature-programmed desorption of ammonia (NH_3 -TPD) in a fixed-bed flow microreactor system equipped with a QMS MKS, Cirrus 2 detector. Prior to the analysis, the sample (100 mg) was outgassed in a flow of pure argon at 500°C for 1 h, and afterwards cooled down to 70°C . Subsequently, the sample was saturated with ammonia in a flow of 1.0 vol.% NH_3/Ar ($20 \text{ cm}^3/\text{min}$) for about 2 h. Afterwards, the sample was purged with pure argon (about 2 h) in order to remove physisorbed ammonia. Finally, the desorption of ammonia was measured in the temperature range of 70 – 500°C with a linear heating rate of 5 K/min in a flow of pure argon ($20 \text{ cm}^3/\text{min}$).

The micrographs of selected mixed metal oxides were obtained using a transmission electron microscope JEOL 2100F working at 200 KV, with Field Emission Gun (FEG), EDX analysis and STEM detectors for bright and dark mode.

The redox properties of the mixed metal oxides were studied by temperature-programmed reduction (H_2 -TPR) using the Quantachrome ChemBET Pulsar TPR/TPD. H_2 -TPR runs for the samples (30 mg) were carried out starting from room temperature to 1000°C , with a linear heating rate of 10 K/min and in a flow ($25 \text{ cm}^3/\text{min}$) of 5.0 vol.% H_2/Ar . Water vapour was removed from effluent gas by means of a cold trap placed in an ice-water bath. The H_2 consumption was detected and recorded by a TCD detector.

The X-ray photoelectron spectra (XPS) of selected mixed metal oxides were measured on a VSW spectrometer equipped with a hemispherical analyzer. The photoelectron spectra were measured using a magnesium $\text{Mg K}\alpha$ source ($E = 1253.6 \text{ eV}$). The base pressure in the analysis chamber during the measurements was $3 \times 10^{-6} \text{ Pa}$ and the spectra were calibrated on a main carbon C 1s peak at 284.6 eV. The composition and chemical surrounding of the sample surface were investigated based on the areas and binding energies of Ag 3d, Ce 3d, Ga 3d, Cu 2p, Mg 2p, Al 2p, C 1s and O 1s photoelectron peaks. Mathematical analyses of the XPS spectra were carried out using the XPSpeak 4.1 computer software (RWM, Kwok, The Chinese University of Hong Kong).

2.3. Catalytic studies

The catalytic performances of the mixed metal oxides were evaluated in the selective oxidation of ammonia into nitrogen and water vapour (NH_3 -SCO). The catalytic experiments were carried out under atmospheric pressure in a fixed-bed flow microreactor

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