



# Supported mixed oxide catalysts for the total oxidation of volatile organic compounds

František Kovanda<sup>a,\*</sup>, Květa Jiráťová<sup>b</sup>

<sup>a</sup> Department of Solid State Chemistry, Institute of Chemical Technology, Prague, Technická 5, 166 28 Prague, Czech Republic

<sup>b</sup> Institute of Chemical Process Fundamentals of the AS CR, v.v.i., Rozvojová 135, 165 02 Prague, Czech Republic

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## ABSTRACT

Supported mixed oxide catalysts of various cation composition were obtained by heating (500 °C) of layered double hydroxide (LDH) precursors deposited on Al<sub>2</sub>O<sub>3</sub>/Al support (anodized aluminum foil) or grained alumina calcined at various temperatures during hydrothermal reaction in aqueous solutions of Co, Cu, Ni, and Mn nitrates. The M<sup>II</sup>–(Mn)–Al LDHs (M<sup>II</sup> = Co, Ni–Co, Ni–Cu, and Co–Cu) with only low Mn content were obtained. NiO-like and spinel-like mixed oxides but no distinct Cu-containing phases were detected in the supported catalysts. A low-temperature peak ascribed to reduction of an amorphous copper oxide was detected in TPR patterns of the supported mixed oxides containing Cu. TPR results indicated reduction of Ni- and Co-containing species at temperatures higher than 400 °C; it can be explained by formation of spinel-like phases and high structural ordering of the calcination products. Heating of grained alumina support at high temperatures (>550 °C) resulted in substantial decrease in surface area and, consequently, the amount of deposited active species. Among the examined catalysts, the Ni–Cu–(Mn)–Al mixed oxide showed the highest catalytic activity. Slight acetaldehyde formation during ethanol deep oxidation over the supported mixed oxides was observed.

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## 1. Introduction

Volatile organic compounds (VOCs) in industrial gases are dangerous pollutants and represent a serious environmental problem. Concentration of VOCs in air can be reduced applying the catalytic total oxidation to carbon dioxide and water as the final products. Catalysts containing noble metals or transition metal oxides are currently used; the latter are cheaper and less sensitive to deactivation [1]. Efficient mixed oxide catalysts can be easily prepared by a controlled thermal decomposition of layered double hydroxide (LDH) precursors. Layered double hydroxides, known also as hydrotalcite-like compounds or anionic clays represent a class of synthetic layered materials with general chemical composition of M<sup>II</sup><sub>1-x</sub>M<sup>III</sup><sub>x</sub>(OH)<sub>2</sub>A<sup>n-</sup><sub>x/n</sub>·yH<sub>2</sub>O where M<sup>II</sup> and M<sup>III</sup> are divalent and trivalent metal cations and A<sup>n-</sup> is an n-valent anion. Heating of LDHs gives finely dispersed mixed oxides of M<sup>II</sup> and M<sup>III</sup> with large surface area and good thermal stability. Various LDH-related mixed oxides were studied as catalysts for total oxidation of VOCs, with most using toluene or ethanol as representative compounds [2–8]. The coprecipitated LDH precursors are usually obtained as a fine

powder, which has to be formed into pellets and calcined. In such catalysts, a considerable part of the grain volume is often not fully utilized because of internal and external diffusion in case the reaction is very fast. Therefore, deposition of thin active layer on a supporting material is advantageous.

The formation of LDH phases was observed during impregnation of γ-alumina with aqueous solutions containing divalent metal cations at ambient temperature and near neutral pH [9]. A controlled growth of LDH crystals has been applied for obtaining oriented LDH films on porous anodic alumina [10] and the mixed oxides prepared by thermal decomposition of deposited LDHs maintained the original morphology of the precursor film [11]. In our recent work [12] we have studied the formation of LDH phase on porous anodic alumina in diluted aqueous solutions of Co and Mn nitrates under hydrothermal conditions. The surface hydration of aluminum oxide and subsequent formation of boehmite-like phase took place before LDH crystallization. The present work focused on preparation of LDH-related mixed oxide catalysts deposited on Al<sub>2</sub>O<sub>3</sub>/Al support (anodized aluminum foil) and grained alumina calcined at various temperatures. The deposition of LDH precursors was carried out in aqueous solutions containing various transition metal nitrates (Co, Cu, Ni, Mn) under hydrothermal conditions. The physical chemical properties of the deposited mixed oxides and their catalytic activity in ethanol total oxidation were studied.

\* Corresponding author. Tel.: +420 220444087; fax: +420 224311082.  
E-mail address: [Frantisek.Kovanda@vscht.cz](mailto:Frantisek.Kovanda@vscht.cz) (F. Kovanda).

## 2. Materials and methods

### 2.1. Preparation of samples

The  $\text{Al}_2\text{O}_3/\text{Al}$  support was obtained by anodic oxidation of the aluminum foil (purity >99.9%, thickness 0.1 mm) in 2.8 M  $\text{H}_2\text{SO}_4$  for 60 min at room temperature and current density of  $30 \text{ mA cm}^{-2}$ . The anodized foil was thoroughly washed and then dried at  $60^\circ\text{C}$ . A set of grained alumina supports differing in surface area was also prepared. The sample of commercial alumina (Cherox 33-00, Czech Republic) was sieved to obtain grains with particle size of 0.160–0.315 mm. This sample (calcined originally at  $550^\circ\text{C}$ ) was additionally heated in a laboratory microwave oven at various temperatures ranging from  $750$  to  $1050^\circ\text{C}$ . The non-calcined aluminum hydroxide used for alumina preparation was added to the set of the supports (grained sample with particle size of 0.160–0.315 mm dried at  $130^\circ\text{C}$ ).

The method reported by Chen et al. [10] was adopted for LDH deposition. The  $\text{Al}_2\text{O}_3/\text{Al}$  support ( $4 \text{ cm} \times 12 \text{ cm}$ ) was vertically placed into aqueous solutions (75 ml) containing various divalent metal nitrates (total metal ion concentration of  $0.1 \text{ mol l}^{-1}$ ) and ammonium nitrate ( $0.6 \text{ mol l}^{-1}$ ); pH = 6.8 was adjusted by adding diluted aqueous ammonia solution. The deposition was carried out under hydrothermal conditions in 100 ml Teflon lined stainless steel bombs at  $140^\circ\text{C}$  for 65 h. The composition and molar ratios of metal cations in used solutions were adjusted as follows: Co–Mn (2:1), Ni–Co–Mn, Ni–Cu–Mn, and Co–Cu–Mn (all 1:1:1). Then the precursors of supported catalysts were taken out, rinsed with distilled water and dried at  $60^\circ\text{C}$ . The supported mixed oxide catalysts were obtained by calcination of washed and dried samples at  $500^\circ\text{C}$  for 4 h in air.

The mixed oxide catalysts deposited on alumina grains were prepared by analogous way. The grained support (4 g) was placed into aqueous solution (600 ml) of Ni, Cu, and Mn nitrates (Ni:Cu:Mn molar ratio of 1:1:1, pH = 6.8) and stirred in 1000 ml stainless steel autoclave for 70 h at  $140^\circ\text{C}$ . Then the grained samples were filtered off, washed thoroughly with distilled water, dried at  $60^\circ\text{C}$  in air and calcined at  $500^\circ\text{C}$  for 4 h in air.

### 2.2. Characterization of the samples

The content of transition metals (Co, Cu, Mn, and Ni) in the deposited products was determined by AAS method using a Spectr AA880 instrument (Varian) after dissolving the samples (0.10–0.15 g of the supports after deposition) in hydrochloric acid.

Powder X-ray diffraction (XRD) patterns were recorded using a Seifert XRD 3000P instrument with  $\text{Co K}\alpha$  radiation ( $\lambda = 0.179 \text{ nm}$ , graphite monochromator, goniometer with the Bragg–Brentano geometry) in  $2\theta$  range  $10$ – $80^\circ$ , step size  $0.05^\circ$ . The qualitative analysis was performed with a HighScore software package (PANalytical, The Netherlands, version 1.0d).

Scanning electron micrographs (SEM) of the samples were taken with a Hitachi S-4700 scanning electron microscope. No conductive layer was applied for observing the samples in order to maintain all surface details at high resolution. A low accelerating voltage of about 2 kV was applied to avoid the surface charging.

Surface area of the calcined samples was determined by adsorption/desorption of nitrogen at  $-196^\circ\text{C}$  using Micromeritics ASAP 2010 instrument. The BET method was applied for data evaluation.

Temperature programmed reduction (TPR) measurements of the calcined samples (0.2 g) were performed with a  $\text{H}_2/\text{N}_2$  mixture (10 mol%  $\text{H}_2$ ), flow rate  $50 \text{ ml min}^{-1}$  and linear temperature increase  $20^\circ\text{C min}^{-1}$  up to  $1000^\circ\text{C}$ . A change in  $\text{H}_2$  concentration was detected with a mass spectrometer Omnistar 300 (Pfeiffer Vakuum). Reduction of the grained  $\text{CuO}$  (0.160–0.315 mm) was

repeatedly performed to calculate absolute values of the hydrogen consumed during reduction of the calcined samples.

### 2.3. Catalytic measurements

The catalytic measurements were carried out in a fixed-bed glass reactor (5 mm i.d.) under unsteady-state reaction temperature with heating rate of  $2.0^\circ\text{C min}^{-1}$  in the range from  $100$  to  $400^\circ\text{C}$ . The catalysts deposited on  $\text{Al}_2\text{O}_3/\text{Al}$  support were cut to small pieces (approximately  $2 \text{ mm} \times 2 \text{ mm}$ ) and the weight of 0.4 g was placed into the reactor; the catalysts deposited on the grained aluminas were used as prepared. The catalysts were examined at  $20 \text{ m}^3 \text{ kg}^{-1} \text{ h}^{-1}$  space velocity; GHSV calculated for the conditions in the reactor by using the apparent density of the catalysts in the bed (approximately  $0.40 \text{ g cm}^{-3}$  for the catalysts deposited on  $\text{Al}_2\text{O}_3/\text{Al}$  support and  $0.89 \text{ g cm}^{-3}$  for the catalysts deposited on grained aluminas) was around  $8000 \text{ h}^{-1}$  and  $18,000 \text{ h}^{-1}$ , respectively. The inlet concentration of ethanol in the air was  $1 \text{ g m}^{-3}$ . Reaction products were analysed using a Hewlett-Packard 6890 gas chromatograph equipped with a FID detector and a capillary column (HP-5 19091 J-413,  $30 \text{ m} \times 0.32 \text{ mm} \times 0.25 \text{ mm}$  with 5% phenylmethyl silicone). Temperatures  $T_{50}$  and  $T_{90}$  (the temperatures, at which 50 and 90% conversion of ethanol were observed) were chosen as a measure of the catalysts activity. Selectivity in ethanol conversion was evaluated as the GC peak area of byproducts analysed at 95% conversion of ethanol. The accuracy of the conversion and selectivity determination was  $\pm 3\%$ .

## 3. Results and discussion

### 3.1. Formation of LDH precursors and mixed oxides on supporting materials

Well-crystallized hydroxalite-like phases were found in powder XRD patterns of the  $\text{Al}_2\text{O}_3/\text{Al}$  support after hydrothermal deposition, together with two sharp diffraction lines, corresponding to aluminum in the support (Fig. 1). Boehmite ( $\text{AlOOH}$ ) was also formed during hydrothermal treatment of the  $\text{Al}_2\text{O}_3/\text{Al}$  support as a result of surface aluminum oxide hydration [12]. Chemical analysis of the dried samples indicated only low incorporation of Mn into the deposited solid (Table 1); preferred formation of  $\text{M}^{\text{II}}\text{-Al}$  LDHs was expected. Therefore, the samples deposited on  $\text{Al}_2\text{O}_3/\text{Al}$  support were denoted as  $\text{M}^{\text{II}}\text{-(Mn)-Al}$  ( $\text{M}^{\text{II}} = \text{Co}, \text{Ni-Co}, \text{Ni-Cu}, \text{and Co-Cu}$ ). The difference in molar ratios of metal cations determined in the solutions and deposited LDHs can be explained by various values of pH, at which the metal cations in solutions used for hydrothermal deposition are precipitated; the following pH values have been reported for precipitation of divalent metal hydroxides in 0.01 M solutions: Cu 5, Ni 7, Co 7.5, and Mn 8.5 [13].

Relatively homogeneous layers consisting of thin curved LDH platelets with nearly perpendicular orientation to the  $\text{Al}_2\text{O}_3/\text{Al}$  support were observed in SEM images (Fig. 2a). The same morphology of the deposited products was also found in the calcined samples (Fig. 2b). Heating of LDHs deposited on  $\text{Al}_2\text{O}_3/\text{Al}$  support led to a formation of  $\text{M}^{\text{II}}\text{-(Mn)-Al}$  mixed oxides with only slight Mn content (Table 2). NiO-like and spinel-like mixed oxides were found in powder XRD patterns of the Ni- and Co-containing samples (Fig. 1). No distinct oxide phases containing Cu were detected in the Ni–Cu–(Mn)–Al and Co–Cu–(Mn)–Al samples despite the relatively high amount of Cu determined by chemical analysis.

Total amounts of hydrogen consumed during reduction ( $25$ – $1000^\circ\text{C}$ ) of the  $\text{M}^{\text{II}}\text{-(Mn)-Al}$  mixed oxides deposited on both  $\text{Al}_2\text{O}_3/\text{Al}$  and grained  $\text{Al}_2\text{O}_3$  supports are summarized in Table 3; the portions corresponding to the components reducible in the low temperature range ( $25$ – $400^\circ\text{C}$ ), potentially having relation

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