# Co–Mn–Al mixed oxides on anodized aluminum supports and their use as catalysts in the total oxidation of ethanol

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**ABSTRACT**

The Co–Mn–Al mixed oxide catalysts over $Al_2O_3$/Al supports were obtained by calcination of layered double hydroxide (LDH) precursors formed on anodized aluminum foils during hydrothermal reaction in aqueous solutions containing Co and Mn nitrates. The precursors crystallized as thin curved platelets with nearly perpendicular orientation to the support; the morphology of the deposited LDH films remained preserved after heating at 500 °C, when spinel-like mixed oxides were formed. The Mn/Co molar ratio in the range from about 4 to 8 in the nitrate solution was found to be favorable for obtaining catalysts with demanded contents of active components. The supported Co–Mn–Al mixed oxide catalysts were tested in the total oxidation of ethanol and compared with the grained sample obtained from the coprecipitated LDH precursor. The specific activity of the catalysts increased with increasing Mn/Co molar ratio in the solid up to value of about 0.4. Compared to the grained catalyst, the layers of Co–Mn–Al mixed oxides formed over anodized aluminum foils showed slightly higher specific activity in the total oxidation of ethanol (calculated per a weight of the active components Co and Mn). Formation of main reaction intermediate, acetaldehyde did not change practically with increasing Mn/Co molar ratio.

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## 1. Introduction

Emissions of volatile organic compounds (VOC) in industrial gases represent a serious environmental problem. Some of them exhibit toxic, narcotic, or carcinogenic properties, and they can react with nitrogen oxides and oxygen to form harmful ozone. Therefore, the abatement of VOC emissions is very desirable. Concentration of these pollutants in air can be reduced applying the catalytic total oxidation to carbon dioxide and water as the final products; this process is markedly energy saving compared to the elimination of VOC by thermal combustion. Catalysts containing noble metals are currently used; they are highly active and stable but expensive [1–3]. A cheaper alternative to the noble metal catalysts are oxides of transition metals (in particular Cu, Mn, Cr, Co, and Ni); they are highly active but more sensitive to deactivation [4].

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 $M^{II}_{1-x}M^{III}_x(OH)_2 A^{n-}_{x/n} \cdot yH_2O$ where $M^{II}$ and $M^{III}$ are divalent and trivalent metal cations, $A^{n-}$ is an $n$-valent anion, and $x$ usually has

values between 0.20 and 0.33. Heating of LDHs gives finely dispersed mixed oxides of $M^{II}$ and $M^{III}$ metals with large surface area and good thermal stability. Various LDH-related mixed oxides were studied as catalysts for the VOC total oxidation, with often using toluene or ethanol as representative compounds [5–13]. The Co- and Mn-containing mixed oxides showed high catalytic oxidation activity. Recently we have reported the active Co–Mn–Al mixed oxide with Co:Mn:Al molar ratio of 4:1:1; its catalytic performance in ethanol total oxidation was even improved by modification with potassium [14]. Mixed oxide catalysts obtained from LDH precursors containing transition metal cations have also been studied in the total oxidation of methane as a model VOC because of its chemical inertness [15–19].

The coprecipitated LDH precursors are usually obtained as a fine powder, which has to be formed into pellets and calcined before using in an industrial reactor. The content of rather expensive active components in the formed catalysts is high and a considerable part of the pellet volume is not fully utilized because of internal diffusion in the fast oxidation reaction. Therefore, distribution of the active components in the grains is desirable to be optimized and 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 ($Ni^{2+}$, $Co^{2+}$, or $Zn^{2+}$) at ambient temperature and near neutral pH [20]. The impregnation procedure was carried out in the presence of diluted ammonia and thermally stable systems were obtained upon calcination due to a strong ion-support interaction.

A reaction mechanism was proposed, consisting of alumina dissolution and precipitation of $Al^{3+}$ cations, released from the support, with divalent metal cations in the solution. In this process alumina is not only the supporting material but also the source of $Al^{3+}$. A controlled growth of LDH crystals has been applied for obtaining oriented LDH films on porous anodic alumina [21]. Thin films growing directly from a substrate can have better adhesion and mechanical stability in comparison with films obtained by colloidal-deposition techniques (e.g., spin coating or dip coating). A monolayer of LDH microcrystals consisting of thin curved platelets with perpendicular orientation to the substrate was observed. The microstructure of LDH films was affected by temperature and time of crystallization and also by the type of metal cations [21,22]. The mixed oxides prepared by thermal decomposition of deposited LDHs have been shown to maintain the original morphology of the precursor films [23]. In the review published by Guo et al. [24] more detailed information about preparation and applications of oriented LDH films can be found.

Recently we studied the formation of LDH phases on the surface of $Al_2O_3$/Al support (anodized aluminum foil) in aqueous solutions containing various divalent metal nitrates under hydrothermal conditions [25,26]. The LDH growth was facilitated by increasing the reaction temperature and time; the surface hydration of the aluminum oxide and the subsequent formation of a boehmite-like phase took place before crystallization of the LDH [25]. The $M^{II}$–(Mn)–Al LDHs ($M^{II}$ = Ni, Co, Ni–Co, Ni–Cu, and Co–Cu) deposited on $Al_2O_3$/Al substrate were obtained but only slight Mn contents in the deposited products were found. Supported mixed oxides were obtained after heating; they exhibited worse reducibility and lower catalytic activity in the total oxidation of ethanol in comparison with mixed oxides prepared from the coprecipitated LDH precursors [26]. Higher reduction temperatures (>400 °C) of Ni- and Co-containing species can be explained by formation of spinel-like phases during precursors heating and high structural ordering of the calcination products. When the grained aluminum hydroxide or alumina heated at moderate temperatures (550 °C) were used as supports for LDH deposition, the supported mixed oxide catalysts with similar catalytic activity were obtained [27]. Therefore, the anodized aluminum foil can be used as suitable model support for studying the deposition of LDH precursors on alumina-based materials and preparation of structured mixed oxide catalysts.

The present work deals with preparation and characterization of Co–Mn–Al mixed oxides deposited on $Al_2O_3$/Al foils and their activity in the total oxidation of ethanol, which was chosen as a model volatile organic compound. Ethanol is often used as a fuel for buses and cars, e.g., in Scandinavian countries and especially in South America; therefore, the total oxidation of ethanol and its reaction intermediates is interesting and worth studying. The results of previous experiments showed a beneficial effect of increased pH in the nitrate solutions used for deposition but the Mn content in the obtained products was very low [26]. For that reason, the relation between Mn/Co molar ratio in the solutions and active components incorporated in the product formed on the support surface was studied in detail. The effect of Mn and Co contents in the supported mixed oxides on their physical chemical properties and catalytic activity and selectivity in the total oxidation of ethanol was examined as well.

## 2. Experimental

### 2.1. Preparation of samples

The $Al_2O_3$/Al support was prepared by anodic oxidation of the aluminum foil (purity >99.9%, thickness 0.1 mm) in $H_2SO_4$ aqueous solution (2.8 mol l$^{-1}$) for 60 min at room temperature and current density of 20 mA cm$^{-2}$. The anodized foil was thoroughly washed in distilled water, diluted aqueous ammonia (5 wt%), and again in distilled water, and then it was dried at 60 °C.

The method reported by Chen et al. [21] was adopted for LDH deposition. The $Al_2O_3$/Al support (4 cm × 12 cm) was placed into aqueous solutions (75 ml) containing ammonium nitrate (0.6 mol l$^{-1}$) and Co and Mn nitrates in various molar ratios (Mn/Co from 0.5 to 10, total metal ion concentration of 0.1 mol l$^{-1}$); pH of 8.5 was adjusted by adding aqueous ammonia solution. The deposition was carried out under hydrothermal conditions at 140 °C for 65 h using sealed 100 ml Teflon lined stainless steel bombs. The precursors of supported catalysts were taken out, rinsed with distilled water and dried at 60 °C. The supported mixed oxide catalysts were obtained by heating the washed and dried samples at 500 °C for 4 h in air. The catalysts were denoted by acronyms with Mn/Co molar ratios in the nitrates solution used during precursors preparation, e.g., Mn/Co = 4. The hydrothermal deposition of LDH precursors in the nitrate solutions with Mn/Co molar ratio ranging from 4 to 8 was carried out repeatedly; the additional samples were denoted as "a" (e.g., Mn/Co = 4a) and included into the set of examined mixed oxide catalysts. The samples deposited in nitrate solutions containing only $Co^{2+}$ or $Mn^{2+}$ cations were also prepared; they were denoted as Co and Mn, respectively.

For comparison, the grained catalyst was prepared by calcination of coprecipitated Co–Mn–Al LDH precursor. An aqueous solution (450 ml) of appropriate nitrates, i.e., $Co(NO_3)_2 \cdot 6H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$, and $Al(NO_3)_3 \cdot 9H_2O$, with Co:Mn:Al molar ratio of 4:1:1 and total metal ion concentration of 1.0 mol l$^{-1}$ was added with flow rate of 7.5 ml min$^{-1}$ into 1000 ml batch reactor containing 200 ml of distilled water. The flow rate of simultaneously added alkaline solution of $Na_2CO_3$ (0.5 mol l$^{-1}$) and NaOH (3.0 mol l$^{-1}$) was controlled to maintain the reaction pH = 10.0 ± 0.1. The coprecipitation was carried out under vigorous stirring at 25 °C and the resulting suspension was further stirred for 1 h at 25 °C. The product was then filtered off, washed thoroughly with distilled water and dried overnight at 60 °C in air. The dried and powdered product was formed into pellets and calcined at 500 °C for 4 h in air. After cooling to room temperature, the calcined pellets were crushed and sieved to obtain the fraction of particle size 0.160–0.315 mm, which was used in further experiments. The catalyst was denoted as Mn/Co = 0.25cp.

### 2.2. Characterization of the precursors and catalysts

The content of Co and Mn in the deposited products was determined by atomic absorption spectroscopy (AAS). A sample (about 0.12 g) of the $Al_2O_3$/Al support after deposition was dissolved in 1.5 ml of hot hydrochloric acid (35 wt%) and the obtained solution was diluted with distilled water to 25 ml. The concentrations of Co and Mn were determined using a SpectrAA880 instrument (Varian). The content of metals was related to the weight increase of the dried support after deposition (considered as the approximate weight of the deposited product). The chemical composition of the coprecipitated sample was also determined by AAS after dissolution of the sample in hydrochloric acid.

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

Scanning electron micrographs (SEM) of the samples were taken with a Hitachi S-4700 or TESCAN VEGA 3 SEM scanning electron