# Influence of Mn content on the catalytic properties of Cu-(Mn)-Zn-Mg-Al mixed oxides derived from LDH precursors in the total oxidation of methane

Monica Răciulete [a,b], Géraldine Layrac [c], Florica Papa [b], Cătălin Negrilă [d], Didier Tichit [c], Ioan-Cezar Marcu [a,e,*]

[a] Research Center for Catalysts and Catalytic Processes, Faculty of Chemistry, University of Bucharest, 4-12 Blv Regina Elisabeta, 030018, Bucharest, Romania
[b] "Ilie Murgulescu" Institute of Physical Chemistry of the Romanian Academy, 202 Spl. Independentei 060021 Bucharest, Romania
[c] Institut Charles Gerhardt, UMR 5253 CNRS/ENSC/UM2/UM1, équipe Matériaux Avancés pour la Catalyse et la Santé, ENSCM, 8 rue de l'Ecole Normale, 34296, Montpellier Cedex 5, France
[d] National Institute of Material Physics, P. O. Box MG 7, Magurele, Romania
[e] Laboratory of Chemical Technology and Catalysis, Department of Organic Chemistry, Biochemistry and Catalysis, Faculty of Chemistry, University of Bucharest, 4-12 Blv Regina Elisabeta, 030018, Bucharest, Romania

### ABSTRACT

Cu-(Mn)-Zn-Mg-Al mixed oxides with Cu/Zn atomic ratio of 1 and different Mn contents were synthesized by thermal decomposition of layered double hydroxides (LDHs) precursors. They were characterized using X-ray diffraction, textural measurements, EDX, TEM, $H_2$-TPR and XPS techniques, and their catalytic properties in the total oxidation of methane were evaluated. The precursors consisted in nitrate-interlayered multicationic LDH phase with additional $Mn_3O_4$ side phase for Mn-containing systems. Their thermal decomposition resulted in complex mixed oxides containing periclase-like, CuO and different spinel ($Cu_{1.5}Mn_{1.5}O_4$, $CuMn_2O_4$, and $MnAl_2O_4$) phases. XPS analysis confirmed the existence of copper and manganese with different valence states in the Cu,Mn-containing mixed oxides. The catalytic activity expressed as the intrinsic rate of $CH_4$ conversion increased by adding Mn to the CuZnMgAl mixed oxide calcined at 650 °C and by increasing its content. The intrinsic activity also strongly increased when the calcination temperature increased from 650 to 800 °C. The increased activity was correlated to enhanced catalyst reducibility due to the favorable Cu-Mn interaction. Among the different catalytic active phases, i.e. CuO, $Cu_{1.5}Mn_{1.5}O_4$ and $CuMn_2O_4$, the $Cu_{1.5}Mn_{1.5}O_4$ spinel seems to be the most active one.

© 2017 Elsevier B.V. All rights reserved.

## 1. Introduction

Control of volatile organic compounds (VOCs) emission has become a major concern of the chemical and petrochemical industries commitment towards the environment. In this context, it is necessary to develop new eco-friendly techniques to limit and control vapor emission which can affect the climate change, the growth of plants and the health of human beings. Catalytic total oxidation is a suitable alternative to conventional incineration due to its practical applications both for pollution abatement and power generation. Precious metals have been widely reported in the literature as very active catalysts for the complete oxidation of short-chain hydrocarbons [1–4]. However, they are expensive, easily sintered and volatile at moderate temperatures [5]. Many efforts have been devoted to the replacement of noble metals by transition metals to obtain highly active metal oxide catalysts for methane combustion [6–9]. Mn-, Co- or Cu oxides and their mixtures prepared by different methods, proved to be very promising catalysts in the combustion of VOCs as cheap and environmental friendly systems [10,11].

Layered double hydroxides (LDHs) are a class of lamellar compounds which attracted an increasing interest as precursors of mixed oxides particularly efficient in many catalytic processes including among others, $DeNO_x$ [12], $NH_3$ oxidation [13] and $N_2O$ decomposition [14]. Their general formula is $[M^{2+}_{1-x}M^{3+}_x(OH)_2]A^{n-}_{x/n} \cdot mH_2O$ where $M^{2+}$ and $M^{3+}$ are di- and trivalent metal ions, $A^{n-}$ is

* Corresponding author at: Research Center for Catalysts and Catalytic Processes, Faculty of Chemistry, University of Bucharest, 4-12 Blv Regina Elisabeta, 030018, Bucharest, Romania.

E-mail addresses: ioancezar.marcu@chimie.unibuc.ro, ioancezar_marcu@yahoo.com (I.-C. Marcu).

an interlayer anion and $m$ is the number of water molecules. The large variety of $M^{2+}$ and $M^{3+}$ metal cations able to belong to the brucite-like layers coupled with the wide choice of anionic compensating moieties lead to the synthesis of a large range of LDHs and then of mixed oxide catalysts obtained by thermal decomposition. They exhibit unique properties like large surface areas, high metal dispersion, tunable redox and acid-base character and good thermal stability [15,16], which make them remarkable oxidation catalysts [17].

The recent studies by Tanasoi et al. [18] over a series of M-MgAlO mixed oxides catalysts (M = Mn, Fe, Co, Ni, Cu, Zn, Ag and Pd) obtained from LDH precursors showed that among the non noble metal-containing mixed oxides, Cu-MgAlO was the most active and stable in the complete oxidation of methane, while Co- and Mn-MgAlO led to the highest propene yield in the oxidative dehydrogenation of propane. Cu-Mg-Al mixed oxides derived from LDH precursors showed excellent activity in the toluene combustion [19]. The activity increased with the Cu content and it was suggested that the highly reducible copper species were the catalytically active species. Chmielarz et al. [20] reported a study over a series of LDH-derived Cu-Mg-Al, Co-Mg-Al and Cu-Co-Mg-Al mixed oxides catalysts for the complete oxidation of mono-carbon VOCs (methane, methanol and formic acid). The calcination temperature of the LDH precursors and the addition of potassium promoter strongly influenced the catalytic performances. On the other hand, Hutchings et al. [21] found that Mn-Cu catalysts containing a mixture of $Cu_{1.4}Mn_{1.6}O_4$ spinel and $Mn_2O_3$ phases were more active in the oxidation of CO at room temperature than the catalysts containing the same spinel and CuO phases. A similar effect was recently observed by different authors [22,23]. Manganese form oxides with a wide range of oxidation states ($MnO_2$, $Mn_2O_3$, $Mn_3O_4$ or MnO). Lahousse and Baldi [10,24] have found that $MnO_2$ and $Mn_3O_4$ were highly active and stable catalysts for the combustion of organic compounds. Obalova et al. [25] studied the $N_2O$ decomposition over Co-Mn-Al mixed oxides catalysts derived from LDH precursors and found that $Mn^{3+}$ were much more active than $Mn^{4+}$ cations. $Mn_2O_3$ was shown to be more active than MnO, $Mn_3O_4$ and $MnO_2$ [26]. Palacio et al. [27] used mixed oxides obtained from trimetallic LDH Zn-Cu-Al and Mn-Cu-Al precursors in toluene combustion and found that Mn-containing LDH exhibited the best catalytic performance.

Based on the above-mentioned results showing the good performances in the total oxidation of VOCs of the Mn- and Cu-containing mixed oxides obtained from LDH precursors obviously due to the good cooperation between the elements favoring the redox cycles, we extended the coprecipitation method to MnCu-based multicationic LDH phases in order to obtain precursors of mixed oxide catalysts for the total oxidation of methane. Thus, we prepared Cu-(Mn)-Zn-Mg-Al LDH-type phases with a constant Cu content but with different Mn/Cu ratios ranging from 0.5 to 2. These compositions were chosen based, on one hand, on our previous studies [28,29] showing that Cu-Zn-Al and Cu-Mg-Al mixed oxides catalysts containing 10 at.% Cu were the most active for the combustion of methane. On the other hand, the presence of Mg and Zn would allow controlling the acid-base equilibrium. The aim of this work was to study the influence of the Mn content on the properties of the catalyst and on the catalytic activity in the total oxidation of methane.

## 2. Experimental section

### 2.1. Catalysts preparation

Four multicationic Cu(Mn)ZnMgAl-LDH precursors with atomic ratios M/Al = 3 (M = Cu + Mn + Zn + Mg), Cu/Zn = 1 and Mn/Cu = 0,

0.5, 1 and 2, respectively, were synthesized by coprecipitation at room temperature and constant pH. Typically, a mixed nitrate salts solution (200 mL) containing the required amounts of $Cu(NO_3)_2 \cdot 3H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ and a NaOH solution (2 M) were simultaneously added dropwise into a beaker containing 100 mL of deionized water under vigorous stirring. The pH during precipitation was kept at a constant value of 9. The obtained precipitates were aged in their mother liquor for 24 h at 80 °C and then filtered, thoroughly washed with deionized water until pH 7 and finally dried overnight at 80 °C. They were labeled as MnXCu-LDH where $X$ represents the Mn/Cu atomic ratio. The obtained LDH precursors were calcined in air at 650 °C for 8 h at a heating-up rate of 2 °C min$^{-1}$ to obtain their corresponding mixed oxide catalysts. In order to investigate the influence of the calcination temperature on the catalytic properties of the mixed oxides, the MnCu1-LDH precursor was calcined in air for 8 h at three different temperatures: 550, 650 and 800 °C, respectively. All the mixed oxide catalysts are denoted as MnXCu-T where $X$ represents the Mn/Cu atomic ratio and $T$ is the calcination temperature.

### 2.2. Catalysts characterization

Powder X-ray diffraction (XRD) patterns of the samples were recorded using a Siemens D5000 Diffractometer and the monochromatic Cu-Kα radiation (λ = 1.5418 Å). They were recorded with 0.02° ($2\theta$) steps over the 3–70° $2\theta$ angular range with 1 s counting time per step. Crystalline phases were identified using standard JCPDS files. The chemical composition of the solids was estimated by EDX microprobe on a Cambridge Stereoscan 260 apparatus. The textural measurements used the adsorption-desorption isotherms collected with $N_2$ at −196 °C on a Micromeritics ASAP 2010 sorption analyzer. Prior to nitrogen adsorption, the catalysts were outgassed at 200 °C for 12 h. Specific surface areas have been obtained using the BET method and pores distribution, using the BJH equation. Transmission electron microscopy (TEM) was carried out on a JEOL JEM-2000EX-II device with an accelerating voltage of 100 keV. Samples for microscopy were dispersed in alcohol in an ultrasonic bath and a drop of supernatant suspension was poured onto a holey carbon-coated grid and dried completely before the measurements. The $H_2$-TPR measurements were performed using a CHEMBET Quantachrome apparatus equipped with thermal conductivity detector (TCD). Fresh calcined samples (60 mg) were heated up to 850 °C at the constant rate of 10 °C min$^{-1}$ in the stream of the 5 vol.% $H_2$/Ar reduction gas and a flow rate of 70 mL min$^{-1}$. A silica gel water trap was interposed between the analyzed sample and the TCD detector in order to ensure a good stability and sensitivity of the detection system. The hydrogen consumption was estimated from the area of the recorded peaks. The calibration of the TCD signal was performed by injecting a known quantity of hydrogen (typically 50 µL) in the carrier gas (Ar). The experimentally obtained peak surface (mV s) was thus converted in micromoles of hydrogen. X-ray photoelectron spectroscopy (XPS) was used to determine the chemical state of the elements on the catalyst surface with a SPECS spectrometer using a monochromatic Al Kα radiation source (1486.61 eV). The acquisition was operated at a pass energy of 20 eV for the individual spectral lines and 50 eV for the extended spectra.

### 2.3. Catalytic test

The catalytic activity tests of methane were performed in a fixed bed quartz tube down-flow reactor operated at atmospheric pressure. A mixture of $CH_4$/air (1/99 v/v) and a total flow rate of 333.33 mL min$^{-1}$ was passed through the catalyst bed. The gas hourly space velocity (GHSV) was kept at 20000 h$^{-1}$. Before each