

# **Transition-metal-containing LDH-derived mixed oxides as catalysts for methane combustion**

## **PhD Thesis**

**Author: Hussein Mahdi S. AL-AANI**

**Supervisor: Prof. dr. habil. Ioan-Cezar MARCU**

## **ABSTRACT**

In an attempt to converge the benefits of preparation of mixed oxides from layered double hydroxide (LDH) precursors with the high activity of Cu-based systems in methane combustion and taking simultaneously into consideration an expected Cu-Ce synergistic effect, the first part of this work is focused on new LDH-derived Cu-Ce-MgAlO mixed oxides catalysts. Thus, a series of five Cu(x)CeMgAlO mixed oxides with different copper contents (x) ranging from 6 to 18 at. % with respect to cations, but with fixed 10 at. % Ce and Mg/Al atomic ratio of 3, was prepared by thermal decomposition at 750 °C of precursors consisting of poorly crystallized LDH and boehmite (AlOOH) phases. Powder X-ray diffraction (XRD) was used to characterize the crystalline structure and scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX) was used to monitor the morphology and chemical composition of both as prepared and calcined materials. Additionally, the textural properties and the reducibility of the mixed oxide catalysts were studied by nitrogen adsorption/desorption and temperature programmed reduction with hydrogen (H<sub>2</sub>-TPR) techniques, respectively. X-ray photoelectron spectroscopy (XPS) was used to determine the chemical state of the elements on the catalyst surface and the diffuse reflectance UV-Vis spectroscopy (DR UV-Vis), to obtain information about the stereochemistry and aggregation of copper in the Cu-containing mixed oxides. It has been shown that the mixed oxide catalysts have slit-like bimodal mesopores and relatively high surface areas, which regularly decrease from 169 to 108 m<sup>2</sup> g<sup>-1</sup> with increasing the Cu content, and consist of periclase-like Mg(Al)O mixed oxide and CeO<sub>2</sub> fluorite phases, except for Cu(18)CeMgAlO, which also contains well developed CuO crystallites. At low Cu content, highly

dispersed Cu-doped ceria crystallites coexist with oligomeric  $(\text{Cu}^{2+}-\text{O}^{2-}-\text{Cu}^{2+})_n^{2+}$  species in the Mg(Al)O matrix, while at high Cu content larger ceria crystallites less exposed on the catalyst surface coexist with separate CuO particles enriching the surface. Their catalytic properties in the total oxidation of methane, used as a volatile organic compound (VOC) model molecule, were evaluated and compared with those of an industrial Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. Their catalytic behavior was explained in correlation with their physicochemical properties. The Cu(II)/Cu surface atomic ratio was shown to be a key factor controlling the catalytic activity of the Cu(x)CeMgAlO catalysts. Indeed, with the highest Cu(II)/Cu surface atomic ratio, the Cu(15)CeMgAlO mixed oxide was shown to be the most active catalyst in this series, with a T<sub>50</sub> (temperature corresponding to 50 % methane conversion) value of only ca. 45 °C higher than that of an industrial Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. Its enhanced catalytic activity was attributed to an excellent dispersion of CuO, oligomeric  $(\text{Cu}^{2+}-\text{O}^{2-}-\text{Cu}^{2+})_n^{2+}$  species coexisting with tiny not XRD-visible CuO crystallites strongly interacting with ceria, which leads to a strong synergy effect between Cu and Ce. The catalytic sites are located at the CuO-CeO<sub>2</sub> particles interface. Decreasing the calcination temperature of the Cu(15)CeMgAl precursor from 750 to 650 and 550 °C resulted in mixed oxides with higher surface areas and, hence, higher catalytic activities in terms of T<sub>50</sub>, which for the Cu(15)CeMgAlO-550 system is only ca. 25 °C higher than that of the industrial Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. However, in terms of intrinsic reaction rates the most active catalyst was that calcined at 750 °C accounting for a strengthened Cu-Ce interaction with increasing calcination temperature. The influences of the contact time and of the methane concentration in the feed gas on the catalytic performances of the Cu(15)CeMgAlO catalyst calcined at 750 °C have also been investigated and its good stability on stream was evidenced.

In the second part of this work, in order to improve the catalytic performance of the Cu(15)CeMgAlO mixed oxide catalyst calcined at 750 °C in the total oxidation of methane reaction, it was promoted with different transition-metal cations M (M = Mn, Fe, Co and Ni), an enhanced synergy effect between Cu and Ce in their presence being expected. Thus, two series of multicationic mixed oxides were prepared by the controlled thermal decomposition at 750 °C of their corresponding LDH precursors synthesized by coprecipitation at constant pH of 10 under ambient atmosphere. The first series of catalysts consisted of four M(3)CuCeMgAlO mixed oxides containing 3 at. % M (M = Mn, Fe, Co, Ni), 15 at. % Cu, 10 at. % Ce (at. % with respect to cations) and with Mg/Al atomic ratio fixed to 3. Taking into consideration that Co was found to be the best

promoter and that the content of the transition-metal promoter is known to strongly influence the trimetallic synergistic interaction and, hence, the catalytic performance of the mixed oxide, the second series consisted of four  $\text{Co}(x)\text{CuCeMgAlO}$  mixed oxides with  $x = 1, 3, 6$  and  $9$  at. % Co, while keeping constant the Cu and Ce contents and the Mg/Al atomic ratio. All the mixed oxides were characterized using a battery of techniques including XRD, transmission electron microscopy (TEM), SEM-EDX, XPS, nitrogen adsorption/desorption at  $-196$  °C,  $\text{H}_2$ -TPR, and DR UV-Vis, while thermogravimetric and differential thermal analyses together with XRD were used for the LDH precursors. The latter consisted of well-crystallized LDH phase together with poorly-crystallized boehmite ( $\text{AlOOH}$ ) side phase. All the mixed oxides calcined at  $750$  °C were mesoporous materials with surface areas lower than that of the parent  $\text{CuCeMgAlO}$  mixed oxide, in the range from  $66$  to  $78$   $\text{m}^2$   $\text{g}^{-1}$ , and consisted of periclase-like  $\text{Mg}(\text{Al})\text{O}$  mixed oxide,  $\text{CeO}_2$  fluorite, and  $\text{CuO}$  tenorite phases. The segregation of the  $\text{CuO}$  tenorite phase was shown to increase with the Co content in the  $\text{Co}(x)\text{CuCeMgAlO}$  series. The nature of the transition-metal M for the  $\text{M}(3)\text{CuCeMgAlO}$  catalysts series and the Co content for the  $\text{Co}(x)\text{CuCeMgAlO}$  series strongly influence, in a complex manner, their physicochemical characteristics and, hence, their catalytic performance in the complete oxidation of methane. No clear correlations could be observed between the catalytic performance and the physicochemical characteristics of the mixed oxide in the  $\text{M}(3)\text{CuCeMgAlO}$  series. However, their enhanced activity compared to the M-free  $\text{CuCeMgAlO}$  system was attributed to an enhanced synergistic interaction between Cu and Ce in the presence of transition-metal cations M. On the other hand, the catalytic activity in the  $\text{Co}(x)\text{CuCeMgAlO}$  series was shown to increase with increasing of both the  $\text{Co}^{3+}$ ,  $\text{Cu}^{2+}$  and  $\text{Ce}^{4+}$  surface concentrations and the catalyst reducibility, unambiguously demonstrating that the synergistic interaction between these species is a key factor controlling their catalytic behavior in the complete oxidation of methane. The Co-promoted  $\text{CuCeMgAlO}$  mixed oxide with  $3$  at. % Co was shown to be the most active catalyst in both series, with a  $T_{50}$  value of  $438$  °C, which is only  $19$  °C higher than that of a reference  $\text{Pd}/\text{Al}_2\text{O}_3$  catalyst. Notably, this  $T_{50}$  value is ca.  $25$  °C lower than that observed for the unpromoted  $\text{CuCeMgAlO}$  system, accounting for the improved performance of the Co-promoted catalyst. Its enhanced catalytic activity was attributed to an excellent Cu-Co-Ce synergistic interaction. A good stability on stream of the  $\text{Co}(3)\text{CuCeMgAlO}$  catalyst was also noticed.