



Surface characterization of ZnO/ZnMn₂O₄ and Cu/Mn₃O₄ powders obtained by thermal degradation of heterobimetallic complexes

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ABSTRACT

From the selective transformation of the heterometallic (Zn–Mn or Cu–Mn) carboxylate complexes with 2,2′-bipyridyl by thermal degradation at relatively low (350 °C) temperature, it was possible to get either well defined spinel ZnMn₂O₄ over zinc oxide or well dispersed copper particles surrounded by a manganese oxide (Mn₃O₄) in a core–shell like structure. Morphology of the powder surface was examined by scanning electron microscopy with energy dispersive X-ray microanalysis (SEM/EDX). Surface composition was determined by X-ray photoelectron spectroscopy (XPS). Specific surface of the powders by nitrogen adsorption was found to be 33 ± 0.2 and 9 ± 0.06 m² g^{−1} for Zn–Mn and Cu–Mn samples, respectively, which is comparable to those of commercial products.

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1. Introduction

Application of heterometallic carboxylate complexes as precursors of fine-dispersed mixed-metal oxides and metal/oxide systems has recently been demonstrated [1–4] to have some advantages over conventional methods based on co-precipitation of monometallic salts [5–7], mainly due to precise control over stoichiometry and potential ability to obtain the most homogeneous metals distribution, caused by initial presence of M¹–O–M² covalent bridge in the coordination compound.

Traditional methods implying mixture of precursor salts usually require fine control of initial metals ratio and relatively high temperatures of degradation [8]. Application of heterometallic complexes with easily decomposing ligands allows to decrease the temperatures of nanodispersed oxide phase formation down to ~210 °C but synthetic route to such compounds is often complicated [9]. As it has been demonstrated recently, heterometallic Zn/Mn and Cu/Mn complexes can be obtained via simple one pot synthetic procedure (so-called direct synthesis [10]) starting from cheap and common reagents with good reproducibility and high yield, so use of such complexes as precursors for solid-state catalysts

if affordable. As shown previously [11], fine ZnO/ZnMn₂O₄ and Cu/Mn₃O₄ powders can be obtained in a facile synthetic manner by thermal degradation of [Zn₂Mn(OAc)₆(bpy)₂] and [Cu₂Mn(OAc)₆(bpy)₂] (bpy – 2,2′-bipyridyl), respectively, at 350 °C. Significant content of spinel-type ZnMn₂O₄ and Mn₃O₄ phases allows one to anticipate catalytic efficiency in reactions of oxidation of small molecules (e.g., CO, CH₄, etc.) [12], while presence of submicro-sized copper particles in combination with Mn₃O₄ may indicate a perspective precursor for the materials with catalytic activity in alcohols reforming process [13,14]. However, morphology of the reported samples still has to be examined before studying catalytic properties. Also, micro-structure of Cu/Mn₃O₄ system is a point of interest, since it reveals the mechanism of the precursor complex thermal degradation. Therefore, the study of surface area by N₂ adsorption, X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy with energy dispersive X-ray microanalysis (SEM/EDX) examination of ZnO/ZnMn₂O₄ and Cu/Mn₃O₄ powders are reported in this communication.

2. Experimental section

2.1. Thermal degradation

ZnO/ZnMn₂O₄ and Cu/Mn₃O₄ powders were prepared by thermal degradation of complexes [Zn₂Mn(OAc)₆(bpy)₂] and [Cu₂Mn(OAc)₆(bpy)₂], respectively, analogously to the procedure

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described in [11]. The process was carried out in air, using a glass closed-bottom cylindrical reactor (diameter 30 mm) stationed at 45° position to the vertical line with the perpendicular extension oriented downwards for the sublimating bpy collecting, in a self-constructed thermostated tube furnace. The temperature of the sample, crucible and inside isothermal cell was monitored using Pt/Pt–Rh thermopiles. Overall 6 h stepwise heating procedure was applied with maximum heating temperature of 350 °C. The powders obtained after cooling in air were finally washed with 2-propanol in order to remove the residual soluble admixtures and then dried at 100 °C for 30 min.

2.2. Nitrogen adsorption studies

The specific surface areas of all samples are obtained from the nitrogen adsorption at –196 °C using a micromeritics tristar surface analyzer. Before plotting the isotherms, the samples are treated under vacuum (10^{-3} Pa) at 200 °C for 2 h. Using a software programme provided with the apparatus, the total surface area is calculated, according to the BET model, from the linear part of the BET plot at relative pressures $0.01 < P/P_0 < 0.30$.

2.3. Scanning electron microscopy

Scanning electron microscopy is performed with a JEOL/5600LV microscope for conventional observation. The microscope is equipped with a full X-ray microanalysis (EDX detector) giving

Table 1
Specific surface area from BET analysis (N_2 adsorption–desorption).

Sample	BET area, $m^2 g^{-1}$
ZnO/ZnMn ₂ O ₄	33 ± 0.2
Cu/Mn ₃ O ₄	9 ± 0.06

Table 2
EDX analysis of ZnO/ZnMn₂O₄ and Cu/Mn₃O₄: subsurface layer composition obtained from the micrographs presented in Figs. 1 and 2).

Sample	Mn (%)	Zn (%)	Cu (%)
ZnO/ZnMn ₂ O ₄	67	33	–
Cu/Mn ₃ O ₄	90	–	10

access to the chemical composition of the sample since the measurements were conducted with the accurate Mn, Cu or Zn standards.

2.4. X-ray photoelectron spectroscopy

XPS analysis was done with a PHI 5000 Versaprobe spectrometer (the X-ray source is Al K_{α} radiation, 1486.7 eV). Analysis was performed using mg quantities of each sample placed in ultra high vacuum ($5 \cdot 10^{-8}$ Pa).

3. Results and discussion

3.1. Adsorption

Results obtained from the N_2 adsorption–desorption (Tables 1 and 2) indicate a moderate specific surface area of ZnO/ZnMn₂O₄ sample. Nevertheless such areas are comparable to these of commercial products for which a value between 5 and $50 m^2 g^{-1}$ is commonly mentioned [15]. Now with respect to the Cu/Mn₃O₄ powder a rather low specific surface area of about $10 m^2 g^{-1}$ is obtained. From previous works mentioned in the literature and from some researches done in our laboratory [15,16] it appears that despite it is rather easy to get highly dispersed manganese oxide (MnO) with a surface area between 50 and $100 m^2 g^{-1}$, other oxides such as Mn₃O₄ or mixed oxides have a lower surface especially when activated at high temperature.

Finally, if we compared these oxides to commercial materials used for example in various oxidation reactions, solids prepared *via* the thermal degradation of well chosen complexes precursors have a specific surface area of the same order of magnitude [17,18].

3.2. Electron microscopy and XPS

SEM images (Fig. 1) demonstrate that the surface of ZnO/ZnMn₂O₄ sample comprises aggregates consisting of submicro-sized pseudo-spherical particles (1–5 μm). Intergranular pores of irregular shape can be also observed, providing some access to the internal porosity of the particles. EDX analysis demonstrate that the Mn:Zn ratio is close to 2:1, which is consistent with the ZnMn₂O₄ stoichiometry. This result suggests that ZnO particles, representing ~67% of the initial sample (according to XRD data [11]), are covered with a zinc-manganese spinel. The conclusion was supported by XPS data showing the superficial atomic ratio Mn/Zn to be close to two. Thus ZnMn₂O₄ oxide can be considered as a rather well dispersion of

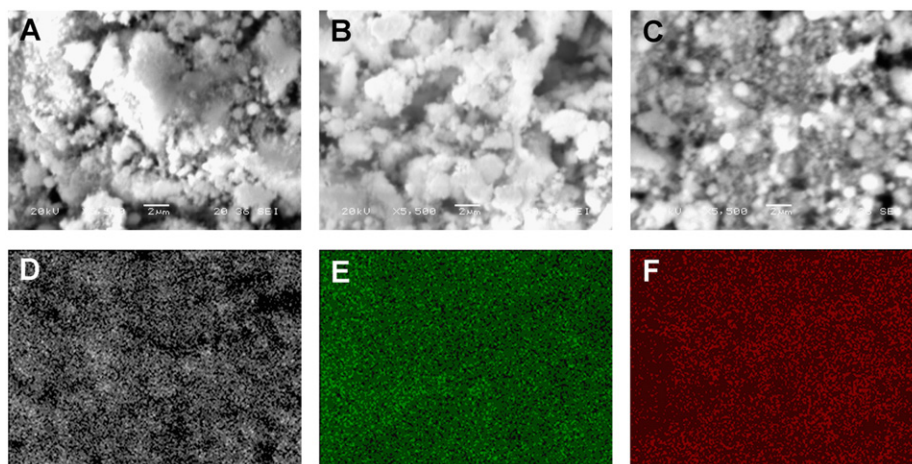


Fig. 1. Characterization of ZnO/ZnMn₂O₄. SEM micrographs (A)–(C) and SEM–EDX cartography for the localization of O (D), Zn (E) and Mn (F). (Zoom × 5.500).

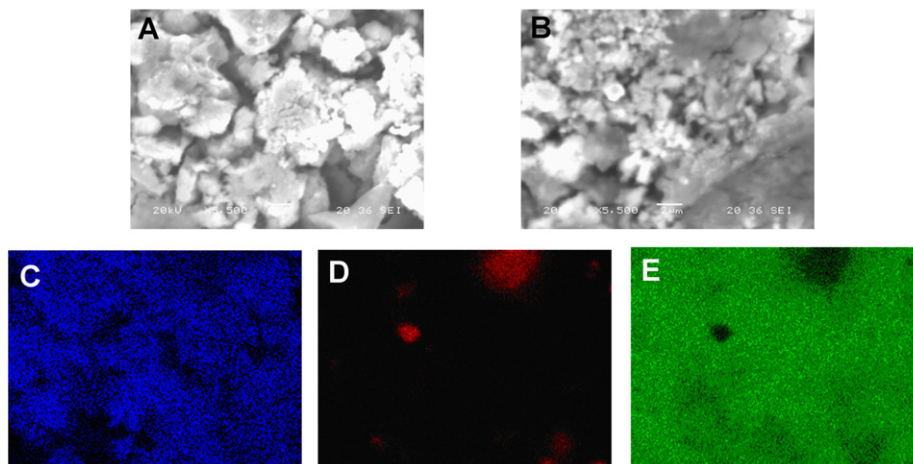


Fig. 2. Characterization of Cu/Mn₃O₄. SEM micrographs (A), (B) and SEM–EDX cartography for the localization of O (C), Cu (D) or Mn (E) of Cu/Mn₃O₄. (Zoom × 5.500).

a superficial phase which corresponds both to the objective of the preparation and the catalytic applications. SEM/EDX cartography (Fig. 1) of the ZnO/ZnMn₂O₄ sample shows a very homogeneous distribution of Zn and Mn at the surface of the material which strongly supports the idea of the use of complexes as precursors for the preparation of dispersed mixed oxides.

In contrast to the ZnO/ZnMn₂O₄ sample, aggregates formed from the Cu/Mn₃O₄ powder have a larger size (5–10 μm) and the particles in the aggregates are more densely packed (Fig. 2), which is in agreement with the data presented before for the specific surface area. Moreover, metallic copper particles of pseudospherical shape are observed. But the superficial composition of these materials is quite different of the bulk one. According to EDX analysis the superficial Cu content is rather low, ca. 10% which is quite lower than those corresponding to the bulk value (67%). This result is consistent with XPS data, showing that the superficial atomic ratio Mn/Cu is between 5 and 7, i.e., a strong manganese enrichment is observed if one compares it to that in the precursor. That could mean that (i) big copper particles are partly covered with Mn₃O₄ species or (ii) small copper particles are well dispersed over manganese oxide due to surface manganese enrichment. Such modifications were previously observed when non-noble metals are dispersed over rare earth oxides or formed from perovskite precursors [19].

As has been proposed in [11], the complexes melt in the temperature range 220–270 °C, retaining their molecular structure, whilst further partial decomposition of acetates is also observed, conjugated with organic ligand sublimation. Depending on the nature of metal (zinc or copper) degradation of acetates leads to ZnO and metallic Cu, respectively.

In the case of Zn/Mn complex decomposition, the MnO sub-micro-sized particles, formed upon the first stage of manganese acetate heating, are partially oxidized by atmospheric oxygen and then react with the neighboring ZnO particles to produce ZnMn₂O₄ phase. Since Zn:Mn ratio in the precursor is 2:1, the ZnO in excess remains as the separate phase, covered by a zinc-manganese spinel.

One may suppose that upon thermal degradation of the precursor complex the metal copper particles of a sub-micron size are formed simultaneously with MnO_x particles, aggregating around and further oxidizing to Mn₃O₄ with oxygen (air) (a preorganization of MnO_x particles around a metallic copper "core" and probable surface reactions between MnO_x particles with CuO_x nanoparticles could occur during the preparation-activation). The resulting Cu/Mn₃O₄ aggregates have a core-shell structure

roughly analogous to that obtained in [14], with Mn₃O₄ spinel phase more sintered than the ZnMn₂O₄ phase in the previous case.

4. Conclusions

Concluding, one can emphasize that ZnO/ZnMn₂O₄ dispersed system with dominating ZnMn₂O₄ spinel surface layer can be obtained in a cheap and facile manner at relatively low (350 °C) temperature. On the other hand, Cu/Mn₃O₄ particles have a core-shell structure with manganese spinel mainly defining the surface properties of the powders.

It follows that both materials might be exploited for dedicated catalytic applications [20,21]. Indeed in the first case from the control of the nature and the dispersion of the active phase, it should be possible to get catalytic materials with well defined acid–base pairs for application in bio-fuels production [22] or for fine chemicals reactions [23–25]. From the second series a modulated oxygen mobility could be obtained for selective oxidation in mild conditions [17,18] or for the preparation of multifunctional catalysts having both redox and acid–base properties as evidenced in recent papers about the selective conversion of cellulosic compounds [23,26].

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