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Influence of metal core of mixed-metal carboxylates in preparation of spinel: $ZnFe_2O(O_2CCF_3)_6$ as a single-source precursor for preparation of $ZnFe_2O_4$

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The mixed-metal and mixed-valance carboxylates of $MFe_2O(O_2CCF_3)_6(C_4H_8O)_2(H_2O)$ (M = Zn, Mn, Cu) and $MFe_2O(O_2CCCl_3)_6(C_4H_8O)_2(H_2O)$ (M = Zn, Fe) were utilized as potential precursors for the preparation of spinel. In the pyrolysis of $ZnFe_2O(O_2CCF_3)_6(C_4H_8O)_2(H_2O)$ in air at 400 °C pure $ZnFe_2O_4$ is formed, in contrast to pyrolysis of the trichloro derivative, which resulted in the formation of ZnO and Fe_2O_3. In the pyrolysis of $MnFe_2O(O_2CCF_3)_6(C_4H_8O)_2(H_2O)$ in nitrogen, $MnFe_2O_4$ was the main phase and single oxides were the minor phases. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: spinel; $ZnFe_2O_4$; mixed-valent; carboxylate; pyrolysis

INTRODUCTION

Complex metal oxides with spinel structure, represented by the general formula MM'_2O_4,[1,2] have been the subject of extensive investigation due to their potential applications as oxidation catalysts, semiconductors, gas sensors, magnetic devices, ceramic pigments and high-density data storage.[3–8] Several techniques have been employed previously for the preparation of various spinels. For instance zinc ferrite (franklinite), which has normal spinel structure, was prepared by combustion synthesis,[9] coprecipitation,[10] high-energy ball-milling,[11] thermal plasma synthesis,[12] hydrothermal method,[13] rapid quenching,[14] thermal decomposition of zinc–iron citrates[15] and spray pyrolysis of metal nitrate solutions.[16] The sol–gel approach, which is an established technique for the preparation of high-purity binary oxides in the form of bulk and thin film, have been used extensively for the preparation of $MgAl_2O_4$ and $ZnAl_2O_4$, $CoAl_2O_4$ and $NiAl_2O_4$ spinel, but the preparation of spinel where M′ is a transition metal by the sol–gel method from metal alkoxides is very limited due to difficulty in the synthesis and handling of transition metal alkoxides. In the normal spinel structure of $ZnFe_2O_4$ the tetrahedral and octahedral sites are occupied by Zn(II) and Fe(IIII) ions, respectively. There are claims that partial inversions in spinel structure can occur, depending on the preparation conditions.[17] This becomes especially important in the preparation of valuable magnetic materials such as ferrites (MFe_2O_4), whose magnetic properties are sensitive to cation distribution, purity and stoichiometry.[17] Furthermore, processing temperatures in the majority of techniques are high and often lead to the formation of more than one phase. Binary metal oxides also are important in advance technology, and alternatives routes for the preparation of spinels continue to thrive.

Single-source precursors have attracted a considerable amount of interest for the preparation of various materials due to the precise control achievable over the stoichiometry of the materials. An extensive effort has been made to design molecules that lead us to well-defined materials. This approach has been applied successfully for the preparation of GaAs and Fe_4N.[18,19]

The present study shows the possible application of mixed-metal and mixed-valance carboxylates as a single-source precursor in the preparation of spinel by pyrolysis. The molecular structures of homo- and heteronuclear mixed-valance carboxylates represented by the formula $M^{II}M^{III}{}_2O(O_2CR)_6L_3$, where L is a donor ligand, belong to a large family of oxo-centred trinuclear acetates.[20] The range of metal ions, carboxylate anions and donor ligands is enormous but more than 250 such complexes have been characterized crystallographically[20] that have the correct metal ratio in their core for the production of spinel.

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EXPERIMENTAL

Materials and methods

All chemicals were purchased from Merck and used without further purification Both $ZnFe_2O(O_2CCF_3)_6(THF)_2(H_2O)$ (**1**) and $CuFe_2O(O_2CCF_3)_6(THF)_2(H_2O)$ (**2**) mixed-metal mixed-valance carboxylates were prepared according to the literature procedure and purified by crystallization from hexane–THF.[21,22] Infrared spectra were recorded on a Shimadzo 470 instrument at 4 cm^{-1} resolution using KBr pellets. The ^{19}F NMR spectrum was obtained in CD_3OD (vs. Me_4Si in ppm) using a Brucker DRX-500 spectrometer. X-ray diffractograms of powders were collected on a Phillips PW-1730 diffractometer with Cu Kα radiation. Scanning electron microscopy (SEM) was performed on a Phillips XL-30 scanning electron microscope. For observation of morphology by SEM, the powder was coated with gold–palladium.

Synthesis of $MnFe_2O(O_2CCF_3)_6(THF)_2(H_2O)$ (3)

To a solution (45 ml) of sodium bicarbonate (4.12 g, 49 mmol) was added trifluoroacetic acid (5.5 g, 48 mmol) followed by an aqueous (15 ml) solution of ferric nitrate nonahydrate (6.46 g, 16 mmol) and an aqueous (5 ml) solution of manganese nitrate hexahydrate (2.36 g, 8 mmol). The mixture was stirred for 24 h and then water was removed under reduced pressure and the residue dissolved in a THF–hexane mixture. After the solvent was removed, the oily residue obtained was washed with hexane to remove oil. The solid that remained was recrystallized from hexane, to which a few drops of THF were added. By slow evaporation brown crystals were formed; yield 38%, m.p. 147–149 °C. Anal. (calc.) for $C_{20}H_{18}F_{18}Fe_2MnO_{16}$: C, 23.46; H, 1.76. Found: C, 2283; H, 1.70. IR (KBr pellet, cm^{-1}): 2980, 1704, 1614, 1464, 1015, 917, 866, 796, 740, 691, 554, 533, 473. ^{19}F NMR (500 MHz, methanol-d_4) δ 77.4.

Synthesis of $CuFe_2O(O_2CCCl_3)_6(THF)_2(H_2O)$ (4)

To a solution (45 ml) of sodium bicarbonate (4.12 g, 49 mmol) was added trichloroacetic acid (7.84 g, 48 mmol) followed by an aqueous (25 ml) solution of ferric nitrate nonahydrate (6.46 g, 16 mmol) and copper nitrate hexahydrate (1.93 g, 8 mmol). The mixture was stirred for 3 h at room temperature and then at 70 °C for another 3 h. Solvent was removed under reduce pressure and then the residue was dissolved in THF, filtered and evaporated to dryness. The solid that remained was crystallized from hexane at room temperature; yield 32%, m.p. 238–239 °C. Anal. (calc.) for $C_{20}H_{18}Cl_{18}CuFe_2O_{16}$: C, 18.04; H, 1.35. Found: C, 18.71; H, 1.46. IR (KBr pellet, cm^{-1}): 2980, 1696, 1653, 1371, 1334, 1022, 962, 918, 854, 742, 686, 560, 520, 475.

Synthesis and characterization of $ZnFe_2O(O_2CCCl_3)_6(THF)_2(H_2O)$ (5)

Compound **5** was obtained by reaction of sodium bicarbonate, trichloroacetic acid, ferric nonahydrate and copper nitrate hexahydrate in a similar procedure to that described for compound **4**; yield 36%, m.p. 215–216 °C. Anal. (calc.) for $C_{20}H_{18}Cl_{18}Fe_2ZnO_{16}$: C, 18.06; H, 1.35. Found: C, 18.25; H, 1.29. IR (KBr pellet, cm^{-1}): 2970, 1612, 1471, 1429, 1360, 1195, 1153, 1038, 1013, 916, 852, 794, 729, 660, 568, 526, 462.

Pyrolysis of mixed-metal carboxylates

In a typical reaction, 100 mg of precursor was ground with a pestle and mortar, pyrolized at 400 °C for 3 h in air or nitrogen in a tube furnace and then cooled to room temperature in a flow of the same gas.

RESULTS AND DISCUSSION

Three new mixed-metal and mixed-valance carboxylates—$MnFe_2O(O_2CCF_3)_6(THF)_2(H_2O)$ (**3**), $CuFe_2O(O_2CCCl_3)_6(THF)_2(H_2O)$ (**4**) and $ZnFe_2O(O_2CCCl_3)_6(THF)_2(H_2O)$ (**5**)–were characterized by infrared and elemental analysis. The identical infrared spectral patterns of carboxylates **3, 4** and **5** compared with carboxylates **1** and **2** confirmed the formation of oxo-centred trinuclear acetate.

The prepared compounds were used as potential precursors for the preparation of spinel by pyrolysis. Figure 1 shows the X-ray diffraction pattern of the compound obtained from pyrolysis of carboxylate **1**. The X-ray diffraction (XRD) pattern with *d* values of 4.87, 2.98, 2.54, 2.44, 2.11, 1.72 and 1.62 matches very well that of the $ZnFe_2O_4$ reference (franklinite, JCPDS 22-1012) and no detectable amount of zinc or iron oxide is visible in the pattern. Interestingly, pyrolysis of the trichloro derivative of **4** in exactly similar conditions did not result in the formation of a spinel phase. Apparently, the nature of the precursor plays a significant role in the formation of spinel. The reason for this interesting phenomenon is not clear at this time but, by taking into consideration the very strong electron-withdrawing nature of the trifluoro group, it may be that the trifluoro group is facilitating cleavage of the C–O bond and formation of the spinel phase. Ironically, the behaviour of precursor **3** in pyrolysis is different from that of precursor **1**. The XRD pattern showed the formation

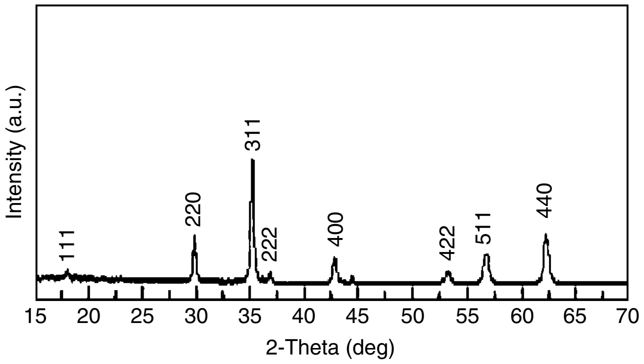

Figure 1. X-ray diffractogram of the pyrolysis product of $ZnFe_2O(O_2CCF_3)_6(THF)_2(H_2O)$ in air.

Table 1. Pyrolysis products of mixed-metal carboxylates at 400 °C

Precursor	Pyrolysis gas	Product
$ZnFe_2O(O_2CCF_3)_6(THF)_2(H_2O)$	Air	$ZnFe_2O_4$
$ZnFe_2O(O_2CCl_3)_6(THF)_2(H_2O)$	Air	$Fe_2O_3 + ZnO$
$ZnFe_2O(O_2CCl_3)_6(THF)_2(H_2O)$	Nitrogen	$Fe_2O_3 + ZnO$
$MnFe_2O(O_2CCF_3)_6(THF)_2(H_2O)$	Air	$MnO + Fe_2O_3$ $MnFe_2O_4$
$MnFe_2O(O_2CCF_3)_6(THF)_2(H_2O)$	Nitrogen	$MnFe_2O_4$ $MnO + Fe_2O_3$
$CuFe_2O(O_2CCF_3)_6(THF)_2(H_2O)$	Air	$CuO + CuFeO_2$
$CuFe_2O(O_2CCCl_3)_6(THF)_2(H_2O)$	Air	$CuO + Fe_2O_3$

of spinel phase $MnFe_2O_4$ (jacobsite, JCPDS 10-0319) as the minor phase, along with Mn_2O_3 (bixbyite, JCPDS 41-1442) and Fe_2O_3 (*hematite*, JCPDS 33-0664) as the major phases upon heat treatment in air for 3 h, but, when heat treatment proceeded in nitrogen, spinel formed as the main phase and oxides as the minor phases (Table 1). The different behaviour of precursor **3** to precursor **1** can be attributed to the nature of manganese, which has a high tendency for oxidation, as evidenced by its change of oxidation state and also by the formation of spinel as the major phase in a flow of nitrogen. Pyrolysis of precursor **2** in air neither resulted in the formation of spinel nor single oxides; $CuFe_2O$ (delafossite, JCPDS 39-0246) has been characterized as the major phase and Fe_2O_3 (iron oxide, 390 238) as the minor phase (Table 1). Interestingly, pyrolysis of the trichloro derivative of **4** resulted in the formation of Fe_2O_3 (JCPDS 33-0664) and CuO (tenorite, JCPDS 45-0937).

The morphology of $ZnFe_2O_4$ spinel was observed by SEM and the micrographs are shown in Fig. 2. It can be seen that the well-faceted crystals for spinel and fine grains are visible to some extent. The morphology of the spinel obtained in the present study differs slightly from that prepared by the ceramic route[23] and even more so from that prepared by decomposition of oxalate salts.[24]

In conclusion, it seems that the type of metal core, the substituent on the carboxylate group and the pyrolysis conditions are very crucial for the production of spinel from mixed-metal carboxylates of general formula $M^{II}M^{III}_2O(O_2CR)_6L_3$. Apparently, the metal that has a lower oxidation state in the metal core of the precursor has the most dominant role in the development of spinel. Formation of the spinel phase from some mixed-metal carboxylates at a low temperature of 400 °C (cf. 600 °C by the citrate route[23] and 1200 °C by the ceramic route[17]) is the main advantage of this method.

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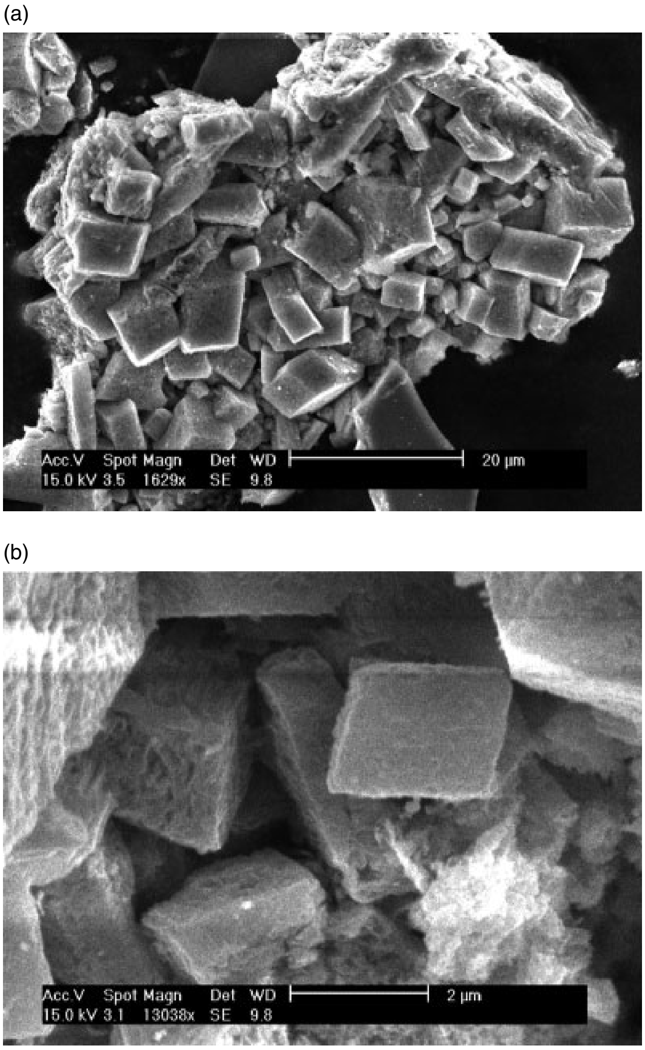

Figure 2. Scanning electron micrographs of the pyrolysis product of $ZnFe_2O(O_2CCF_3)_6(THF)_2(H_2O)$.

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