



Co–Mn-oxide spinel catalysts for CO and propane oxidation at mild temperature



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ABSTRACT

$\text{Co}_x\text{Mn}_{3-x}\text{O}_4$ oxides ($0 \leq x \leq 3$) were prepared by controlled decomposition of mixed oxalates near 200°C , followed by a calcination at 300°C . These oxides are amorphous for $x < 0.9$. For higher cobalt fraction they have a cubic spinel structure and their crystallite size grows with the cobalt fraction. These materials have a large surface area; the highest values, exceeding $250\text{ m}^2/\text{g}$, were obtained for $x \approx 2$. The spinel oxides exhibit an outstanding catalytic activity for propane oxidation at mild temperature ($20\text{--}200^\circ\text{C}$). They are also active for CO oxidation at ambient temperature. This high activity was correlated both with the surface area and the cobalt concentration. The most efficient material is $\text{Co}_{2.3}\text{Mn}_{0.7}\text{O}_4$, which has a better activity than cobalt oxide catalysts reported in the literature.

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1. Introduction

Catalytic oxidation is a very effective method for the abatement of low concentrations of Volatile Organic Compounds (VOCs). Currently, the most active catalysts are supported noble metals [1–3]. However these catalysts are very expensive and their activity can be strongly inhibited by CO [4], water or chloride [5]. For low temperature applications, like VOCs removal in indoor air, precious metals can be replaced by transition metal oxides [6]. Especially spinel cobalt oxide (Co_3O_4) was reported to be the best catalyst for the total oxidation of CO [7] and hydrocarbons [6,8]. Spinel oxides, with the general formula AB_2O_4 , contain cation sites of different coordination (tetrahedral and octahedral) with the oxide anions arranged in a cubic close-packed lattice. Partial substitution of cobalt by manganese gives mixed Co–Mn spinel oxides, which can be better catalysts than Co_3O_4 for the oxidation of VOCs [9–11].

Most often the catalysts reported in the literature are synthesized at high temperature ($>500^\circ\text{C}$). This requirement, unavoidable for automotive catalytic converters, becomes useless for VOCs abatement at mild temperature ($<300^\circ\text{C}$). Actually it is expected that metastable nanocrystalline oxides, with very large porosity and surface area, will be highly active catalysts. This kind of materials can be easily obtained by thermal decomposition of metal oxalates. Indeed a close control of the decomposition allows prepar-

ing mixed oxides with very high surface area ($300\text{--}500\text{ m}^2/\text{g}$) [12,13]. Moreover this easy and inexpensive method is also very convenient to obtain mixed oxides [14].

The goal of this study was the synthesis of large surface area $\text{Co}_x\text{Mn}_{3-x}\text{O}_4$ oxides ($0 \leq x \leq 3$) by controlled decomposition of mixed oxalates and the evaluation of the catalytic performance of these metastable materials for the total oxidation of carbon monoxide and propane at mild temperature ($20\text{--}200^\circ\text{C}$). Carbon monoxide is produced in large amount by transportation, industrial and domestic activities. It is extremely toxic and catalytic oxidation into CO_2 constitutes the best solution for CO removal from indoor air [7]. Thus low cost, precious metal free catalysts, working at room temperature are highly demanded. Propane is largely used as domestic and industrial fuel. Besides it is also the third most common motor vehicle fuel in the world behind gasoline and Diesel fuel. On the other hand it is generally admitted that alkanes are the least reactive among VOCs and a catalyst able to remove propane at mild temperatures is expected to be active for other VOCs as well.

2. Experimental

2.1. Synthesis of oxides

2.1.1. Preparation of mixed oxalates

Mixed oxalates $\text{Co}_{x/3}\text{Mn}_{(3-x)/3}\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ were precipitated at room temperature by quick introduction of an aqueous solution of cobalt and manganese nitrates (200 mL; 0.2 M) into an aqueous solution of ammonium oxalate (200 mL; 0.22 M) under vigor-

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ous stirring. After 30 min, the precipitate was filtered, thoroughly washed with deionized water and dried in air at 70 °C.

2.1.2. Thermal decomposition of oxalates

The thermal decomposition of oxalates was carried out in a vertical tubular fixed-bed flow reactor under atmospheric pressure. The internal diameter of reactor was 1 cm. The flow rate of the inlet gas (4% O₂ in Ar) was 100 cm³/min. The outlet gas composition was followed using a mass spectrometer (HPR20-QIC from Hiden Analytical). The temperature of the reacting solid was recorded by a K thermocouple positioned inside the powdered sample. This setup allowed controlling both the temperature of the reacting material and the composition of the atmosphere. The temperature was increased at 2.5 °C/min until CO₂ emission was detected; from then the decomposition was done in isothermal conditions. For example, in the case of manganese oxalate this temperature was about 210 °C. When CO₂ emission was over, to ensure a total decomposition, even in the core of particles, the partial pressure of O₂ was augmented gradually to 20%; then the temperature was increased at 5 °C/min up to 300 °C and maintained to this value for 1 h.

2.2. Thermal analysis (TGA-DSC)

The thermal decomposition of oxalates was studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), using a constant heating rate (5 °C/min), on a TGA-DSC-1 Mettler-Toledo device in the temperature range 30–600 °C. The flowing gas was a mixture 20% O₂ in Ar. About 5 mg of oxalate powder were placed in a 40 mL aluminium pan and the reference was an empty aluminium pan.

2.3. Powder X-ray diffraction (PXRD)

The crystal structure was investigated via powder X-ray diffraction. Data was collected, at room temperature, with a Bruker AXS D4 θ -2 θ diffractometer, in the Bragg-Brentano geometry, using filtered Cu K α radiation and a graphite secondary-beam monochromator. Diffraction intensities were measured by scanning from 20 to 80° (2 θ) with a step size of 0.02° (2 θ).

A quantitative estimation of the lattice parameters and peak broadening was accomplished by profile fitting of the whole XRD patterns using the Fullprof software [15]. The peak profiles were modeled by Thompson-Cox-Hastings [16] pseudo-Voigt functions. The parameters refined were zero shift (2 θ), background, cell parameters and peak shape. The size and strain contribution to the integral breadth of each reflection were calculated by the software. The instrumental broadening contribution was evaluated by using an α -alumina sample (NIST Standard Reference Material 1976b).

The structural changes versus temperature were followed by High Temperature X-ray Diffraction (HTXRD) with a Bruker AXS D8 diffractometer (using Ni-filtered Cu K α radiation) equipped with a high temperature chamber Anton Paar HTK1200N. Diffraction intensities were recorded in synthetic air flow (20% O₂ in N₂), at fixed temperature, every 10 °C, in the range 100–500 °C. The heating rate between each step was 10 °C/min. The time needed to record each pattern was about 15 min.

2.4. Specific surface area, pore size distribution

Specific surface area and pore size distribution were calculated from nitrogen adsorption-desorption isotherms collected at 77 K, using an adsorption analyzer (Micromeritics Tristar II 3020). The specific surface areas were computed from adsorption isotherms, using the Brunauer-Emmett-Teller (BET) method [17]. The pore size distributions (PSD) were computed from desorption isotherms

by the NLDFT method [18] (with Quantachrome Autosorb-1 software using silica equilibrium transition kernel at 77K, based on a cylindrical pore model).

Pore volume (V_{pore}) was calculated from the adsorbed volume at a relative pressure of 0.995 (V_{sat}) by:

$$V_{\text{pore}} = \frac{N_2 \text{ gas density}}{N_2 \text{ liq. density}} V_{\text{sat}} = 0.00155 V_{\text{sat}}$$

Prior to analysis, to remove the species adsorbed on the surface, the oxalate samples (about 0.5 g) were degassed for 16 h at 70 °C whereas the oxide samples (about 0.1 g) were degassed for 16 h at 90 °C (final pressure <10⁻³ Pa).

2.5. Electron microscopy

Transmission electron microscopy analyses were performed with a Jeol JEM-1400 operating at 80 kV. Samples were prepared by putting a drop of an ethanol suspension of particles on a carbon-coated copper grid.

Scanning electron microscopy analyses were performed with a SEM FEG FEI Quanta-250 at 20 kV. The samples were prepared by putting a drop of an ethanol suspension of particles on an aluminum sample holder. Before analysis, the samples were covered with a thin layer (5 nm) of Pt by sputter coating.

2.6. Chemical analysis by X-ray fluorescence

The elemental composition was determined on powder samples by X-ray fluorescence with a Bruker S2 Ranger working with a maximum voltage of 50 kV and a current of 2 mA.

2.7. Catalytic tests

The activities of catalysts were tested for CO and C₃H₈ total oxidation. These tests were performed, at ambient pressure, in a tubular fixed bed flow glass reactor (internal diameter = 6 mm). The catalyst mass was always close to 0.05 g. The catalyst powder was packed in the tube giving a 2–3 mm bed length. The volumetric flow rate was 1.63 mL s⁻¹ giving a contact time of 0.03 s. The size of catalyst particles was about 10 μ m. The reactor operates at differential conditions only for propane oxidation, at mild temperatures (conversion <10%). The reactants were dosed by mass flow controllers (Brooks 5850). The catalyst temperature was controlled by a K-type thermocouple positioned inside the catalyst bed. For CO oxidation the temperature range was 30–200 °C and the inlet gas composition was 0.8% CO + 20% O₂ in Ar. For C₃H₈ oxidation the temperature range was 30–300 °C and the inlet gas composition was 0.4% C₃H₈ + 20% O₂ in Ar. The catalyst temperature was increased at a heating rate of 200 °C/h. The gas phase composition during the tests was monitored by mass spectrometry (HPR20-QIC from Hiden Analytical). Before the CO oxidation test, the catalysts were first pretreated with 20% O₂ in Ar for 60 min at 200 °C. The C₃H₈ oxidation test was done after CO test without any pretreatment.

3. Results and discussion

3.1. Characterization of oxalate precursors

3.1.1. XRD

The XRD pattern (Fig. 1) of manganese oxalate corresponds to the monoclinic structure with the space group C2/c (PDF # 00-025-0544) whereas cobalt oxalate has the orthorhombic structure with the space group Cccm (PDF # 00-025-0250). The structure of mixed Co-Mn oxalates depends on their manganese content. For oxalates containing more Mn than Co, pattern matching with the monoclinic

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