Some nanograined ferrites and perovskites for catalytic combustion of acetone at low temperature

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Abstract

Two types of nanograined oxide compounds, $CuFe_2O_4$, $MgFe_2O_4$, $Ni_{0.5}Co_{0.5}Fe_2O_4$, with spinel-type structure, and $SrMnO_3$, $FeMnO_3$, $La_{0.6}Pb_{0.2}Ca_{0.2}MnO_3$ with perovskite-type structure, were prepared by sol–gel self-combustion method and tested for the catalytic combustion of dilute acetone in air. Their structure and surface properties were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), BET surface area measurements and energy-dispersive X-ray spectroscopy (EDX). We chose acetone as a VOC model because, among all VOCs, it is a common organic solvent extensively used in the manufacture of plastics, fibers, drugs and other chemicals. The catalytic activity studies revealed that between these two types of catalysts, the perovskite catalysts exhibited the best activity in the catalytic combustion of acetone. The acetone conversion degree over perovskite catalysts can exceed 95% at 300 °C, while over ferrospinel catalysts it is of about 70%. Our experimental results indicate that the $SrMnO_3$ and $La_{0.6}Pb_{0.2}Ca_{0.2}MnO_3$ perovskites are the preferred catalysts in the catalytic combustion of acetone at low temperatures. The time stability of $La_{0.6}Pb_{0.2}Ca_{0.2}MnO_3$ catalyst for acetone combustion was also investigated and no deactivation was observed for 36 h at 250 °C.

1. Introduction

The removal of volatile organic compounds (VOCs) from air is important for environmental and human health [1,2]. Several technologies have been used to remove VOCs emissions [3,4]. The conventional thermal incineration requires high operating temperature (> 750 °C) and significant energy amount. Catalytic combustion is the most promising method for release of VOCs [5–9] which operates at low temperature (< 500 °C) and its efficiency is determined by the activity and stability of the catalyst used. Various kinds of catalysts, such as supported noble metals [10–12], metal oxides [13–15] or mixed metal oxides [16–20] can be employed. Transition metal oxides, although generally less active than noble metal, are cheaper and more resistant to deactivation by poisoning than other materials [11,13,21,22].

In the last years much attention has been paid to the perovskite-type ceramic oxides, ABO_3 (A is usually rare earth and B is transition metal [23–27]), and to the spinel ferrite-type oxides, MFe_2O_4 (M is divalent metal ion) [28–31] as promising combustion catalysts mainly due to their excellent thermal stability properties, low cost and easy processing. Moreover, the structural stability of the perovskites allows for the partial substitution of A and/or B by other metal that can improve their catalyst properties.

The catalytic properties of the spinel ferrites are influenced by the cation distribution among the tetrahedral and octahedral sites in the spinel structure [31]. Jacobs et al. [32] suggested that in the spinel structure, the octahedral sites are almost exclusively exposed at the surface of the spinel crystallite and that the catalytic activity is mainly due to octahedral cations.

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For catalytic purposes, the production of catalyst materials with nanosized particles is a priority. Nanograined ceramic materials present new opportunities for enhancing the performance of solid catalysts because of the much higher surface to bulk ratio compared to the coarse micrograined materials. Various methods have been proposed [33–37] to obtain catalyst materials with superior microstructure. In the present work we applied a nonconventional procedure, sol–gel coupled with self-combustion described in our previous papers [38,39]. This procedure offers a number of advantages including homogenous mixing on the atomic scale, high purity, simple equipment and control of the grain size by subsequent heat treatments.

Below we present a comparative study on the catalytic performances of the two nanocrystalline material types prepared by sol–gel self-combustion: $CuFe_2O_4$, $MgFe_2O_4$, $NiCoFe_2O_4$ ferrites with spinel-type structure and $SrMnO_3$, $FeMnO_3$, LaPb-CaMnO$_3$ manganites with perovskite-type structure. The samples were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), BET surface area measurements, and energy-dispersive X-ray spectroscopy (EDX). We analyzed the catalytic properties of the six samples, which have different compositions and structures, in the catalytic flameless combustion of dilute acetone. We have chosen acetone as a VOC model because, among all the VOCs, it is a common organic solvent extensively used in the manufacture of plastics, fibers, drugs and other chemicals.

2. Experimental

2.1. Sample preparation

Three nano-grained perovskite powders of nominal compositions: $SrMnO_3$, $FeMnO_3$, $La_{0.6}Pb_{0.2}Ca_{0.2}MnO_3$ and three nano-grained ferrospinel powders of nominal compositions: $CuFe_2O_4$, $MgFe_2O_4$, $Ni_{0.5}Co_{0.5}Fe_2O_4$ were prepared by sol–gel self-combustion procedure followed by heat treatment in the 900–1000 °C range (depending on the crystalline phase of materials). We used metal nitrates, ammonium hydroxide and polyvinyl alcohol (PVA) as starting materials. A solution containing metal nitrates was mixed with an aqueous solution (10% concentration) of polyvinyl alcohol. A small amount of NH$_4$OH solution (10% concentration) was dropped to adjust the pH value to about 8. This produced a sol of metal hydroxides and ammonium nitrate. By drying at 100 °C for 12 h, the sol was turned into a dried gel. The dried gel was ignited in a corner and a combustion reaction spontaneously propagated through the whole gel. The obtained powders were calcined at 500 °C to eliminate the residual organic compounds. Finally, the calcined powders were annealed in air at 900 °C for 20 min (ferrite powders) and at 1000 °C for 320 min (perovskite powders). More details on the preparing procedure are given in [40].

2.2. Characterization techniques

The crystal structure and phase composition of the samples were analyzed by XRD. X-ray diffraction measurements of the powders were performed at room temperature using PANALYTICAL X' PERT PRO MPD powder diffractometer and Cu$K\alpha$ radiation. The spectra were scanned between 20 and 80° (2θ) at a rate of 2°/min. The average crystallite size was evaluated based on XRD peak broadening using the Scherrer equation $D = 0.9\lambda/\beta\cos\theta$, where λ is radiation wavelength (0.15405 nm) of Cu$K\alpha$, β is the half width of the peak, and θ is the Bragg diffraction peak angle. A scanning electron microscope (JEOL-200 CX) was used to visualize the surface morphology. NOVA 2200 apparatus was used to obtain N$_2$ adsorption/desorption isotherms at 77 K. The BET specific surface area (S_{BET}) was determined from nitrogen sorption data using the Brunauer–Emmett–Teller (BET) equation [41]. The elemental composition of the surface particles was examined with Energy Dispersive X-ray Spectrometer (Genesis, EDX) using a voltage of 20 kV.

2.3. Catalytic testing

Catalyst activity tests were conducted in a laboratory scale with a flow type set-up (flow rate of 100 cm^3/min, acetone concentration in air of 1–2‰ and the gas hourly space velocity, GHSV, of 5100 h^{-1}), previously described by us in [39,42]. The catalyst powder (0.3–0.5 g) was sandwiched between two layers of quartz wool in a quartz tubular micro-reactor (ϕ=7 mm) placed in an electrical furnace. The increase of the temperature was made in steps of 50 °C, from 50 °C to 550 °C. At every predetermined temperature, as a result of catalytic combustion, the gas concentration at the exit of reactor will be smaller than the inlet gas concentration. The catalytic activity of the heat treated materials under study was evaluated in terms of the conversion degree of the acetone over these materials as:

$$\text{Conv} = \frac{c_{in} - c_{out}}{c_{in}} \times 100\%,$$

where c_{in} and c_{out} are the inlet and outlet gas concentration, respectively, measured by a photo-ionization detector (PID-TECH) for VOCs. Data were collected when the flameless catalytic combustion had reached a steady state, after about 20 min at each temperature. These experiments were repeated decreasing the temperature and similar results were obtained, suggesting the stability of the ferrites and perovskites.

3. Results and discussion

3.1. Characterization of materials

XRD patterns of the six oxide compounds prepared by sol–gel self-combustion and heat treated are shown in Fig. 1. Diffractograms show well-defined peaks indicating a good crystalline quality of the powders. The broadening of the peaks indicates the generation of crystallites in the nano-size range. Phase identification was performed using PDF standard cards: for $MgFe_2O_4$ (PDF # 17-464), for $CuFe_2O_4$ (PDF # 34-425), for $NiCoFe_2O_4$ (PDF # 44-1485 and # 22-1086), for LaPb-CaMnO$_3$ (PDF # 75-440), for $SrMnO_3$ (PDF # 72-197) and for $FeMnO_3$ (PDF # 75-1573). Results revealed that all samples