



Influence of the synthesis method on structural properties and catalytic activity for oxidation of CO and C₃H₆ of pirochromite MgCr₂O₄

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ABSTRACT

The work examines comparatively MgCr₂O₄ oxide samples prepared by three methods (solid state reaction, sol–gel and co-precipitation within reverse microemulsion) with respect to their structural/morphological characteristics and catalytic properties for complete combustion of carbon monoxide and propene. For this purpose, the samples are examined by XRD, S_{BET}, SEM, XPS and TPR techniques. The results reveal achievement of optimum catalytic properties for the sample prepared by microemulsion, a method which apparently allows achievement of high surface area nanocrystals in this type of material.

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1. Introduction

The spinel structure includes a large family of compounds exhibiting a wide variety of physicochemical properties with important practical interest. Thus, spinel oxide (AB₂O₄) as the pirochromite (MgCr₂O₄) and other related binary oxides have important technological applications, including their use as magnetic materials [1], high-temperature ceramics [2], strengthening agents [3], sensor elements [4–10], interconnect materials for solid oxide fuel cells [11], combustion catalysts [12–15] or catalytic supports [16]. For many of these applications, achievement of high surface area materials is greatly desired.

The spinel MgCr₂O₄ displays a cubic structure belonging to the space group Fd3m, in which Mg and Cr ions occupy the tetrahedral and octahedral sites, respectively [16]. In turn, MgCr₂O₄ has been taken as a model of transition metal-oxide combustion catalysts within chromite-related materials [13]. The catalytic activity of this material in the oxidation of propane and propene has been also investigated, confirming that MgCr₂O₄ is an efficient complete combustion catalyst [17].

Traditionally, these oxides are prepared by solid state reaction (RS), which requires employment of extremely high temperatures (typically above 1200 °C) [12,18,19], leading to low specific surface and low catalytic activity. To overcome this limitation, several synthesis techniques have been developed, including the sol–gel method (SG), co-precipitation or solution combustion, which provide surface areas higher than that achieved upon use of the solid state reaction method [16,20,21]. Thus, the activity of samples prepared by SG is generally high, in principle because of the possibility of achieving relatively large specific surface for the catalysts [13]. Nevertheless, pure thermally stable materials are typically obtained by SG only after relatively high temperatures are achieved (around 850–900 °C); however, the specific surface sharply drops above 700–800 °C [13,21]. Among possible alternative synthesis methods, co-precipitation within reverse microemulsion (ME) has lately shown to be a very promising technique for the preparation of ultrafine particles for mixed oxides, allowing controlled size and morphology with generally good compositional homogeneity [6,22,23]. In this sense, to the best of our knowledge, a comprehensive study on the preparation of spinel MgCr₂O₄ by this method and its catalytic properties is not available yet.

Within this context, the objective of this study is to compare morphological and structural properties of pirochromite MgCr₂O₄ obtained by different synthesis methods, and evaluate their respective properties for catalytic oxidation of CO and C₃H₆. The choice of these two reactions was made because they could be in

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principle supposed to have two different mechanisms of oxidation, designated as suprafacial (CO) and intrafacial (C_3H_6) [24]. For the mentioned purpose, the catalytic properties of samples prepared by the three mentioned methods (RS, SG and ME), were analyzed on the basis of characterization results achieved by X-ray diffraction (XRD), analysis of specific surface (S_{BET}), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and temperature programmed reduction (TPR). The results show the achievement of high surface area nanoparticles with consequently enhanced catalytic activity for the sample prepared by the microemulsion method.

2. Experimental

2.1. Preparation

Solid state reaction (RS): The proportions of stoichiometric MgO and Cr_2O_3 were ground in an agate mortar until homogeneity in the mixture was attained. Then, the mixture was treated in a furnace under air at a temperature of 1200 °C for 24 h with a heating ramp of 30 °C min^{-1} .

Sol-gel (SG): $Mg(NO_3)_2 \cdot 6H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$ and citric acid were used as raw materials. Citric acid was added as a complexing agent to the aqueous solution containing the two mentioned nitrates. The amount of citric acid employed was such that the molar ratio between total cations and citric acid was 1:1. The excess water was then evaporated at 80 °C under slow agitation. The thus obtained solid precursor was then crushed and burned under air for 10 h at 850 °C (note this calcination temperature lies within the range typically applied for samples of mixed oxides prepared by this type of method [13,21,25]) with a heating ramp of 10 °C min^{-1} .

Co-precipitation in reverse microemulsion (ME): For this synthesis, two reverse microemulsions, of similar characteristics concerning the volumes employed of organic (n-heptane) and aqueous phases as well as of surfactant (Triton X-100) and co-surfactant (1-hexanol), were prepared; details of the method can be found elsewhere [22]. The first one contained in its aqueous phase the dissolved (nitrate) salts of Mg and Cr while the second one contained in its aqueous phase a dissolved base (tetramethyl ammonium hydroxide or TMAH) which is employed as precipitating agent. Mixing both microemulsions produces the precipitation of the cations and after separation of the solid by centrifugation and decanting, the resulting solid is rinsed with methanol and dried for 24 h at 100 °C. The resulting material is then calcined under air at 600 °C during 5 h employing relatively slow heating ramp of 2 °C min^{-1} .

2.2. Characterization

The crystal structure of the samples prepared by the three methods was analyzed on a powder diffractometer Bruker D8-Advance using Ni-filtered $Cu K\alpha$ radiation. The diffractograms were taken with a step of 0.02° using 2 s counting time and a measuring range between 10° and 80° (in 2θ). The position and fitting of the peaks were analyzed with the program Winplotr while refinement of cell parameters was achieved by using software CELREF.

The specific surface of the oxides (S_{BET}) was determined by the BET method applied to nitrogen adsorption isotherms taken at -196 °C, recorded with an apparatus Micromeritics model ASAP-2000. Before adsorption, the samples were degassed for 2 h at a temperature of 180 °C.

The size of crystallites or particles (D) in the samples was calculated by two methods: from the full width at half maximum of the most intense diffraction using the Scherrer equation; and

from S_{BET} measurements, using the equation $D_{BET} = 6/(S_{BET}\rho)$ (considering a spherical particle model) where the density of the pirochromite is considered as $\rho = 4.2 \text{ g cm}^{-3}$ [16]. The general morphology of the samples preformed as pellets was analyzed by SEM using Philips XL 30 equipment.

The characteristics of the samples surface were examined by X-ray photoelectron spectroscopy (XPS), performed with the spectrometer VG Escalab 200R using Al $K\alpha$ X-ray source (1486.6 eV). The sample was placed first in the pre-treatment chamber at room temperature for 1 h before being transferred to the test chamber. The XPS data were signal averaged for a number of scans enough to get a good signal/noise ratio, at increments of 0.1 eV and fixed pass energy of 50 eV. The binding energies (BE) were calibrated relative to the C1s peak from residual carbonaceous species at 284.6 eV, used as internal standard to take into account charge effects. The areas of the peaks were calculated from fitting of the experimental spectra using Gaussian/Lorentzian combined shapes, after the elimination of background noise upon use of Shirley-type curves. The surface atomic contents of the different components were calculated from such fittings, taking into account corresponding atomic sensitivity factors [26].

Gravimetric temperature programmed reduction (TPR) was carried out on a Mettler Toledo TGA/SDTA851e instrument, using 200 $cm^3 \text{ min}^{-1}$ of N_2 as carrier gas, 20 $cm^3 \text{ min}^{-1}$ of hydrogen as reactive gas, and a heating rate of 10 °C min^{-1} . Before the TPR analysis, the samples were pre-treated by heating them, at 10 °C min^{-1} , from room temperature up to 600 °C for ME, 850 °C for SG, and 1100 °C for RS catalysts. After this pre-treatment, the sample was cooled down in the O_2/N_2 mixture, and the TPR was carried out.

2.3. Catalytic activity

The spinel type $MgCr_2O_4$ samples prepared by the three methods were tested for propene (C_3H_6) and carbon monoxide (CO) oxidation reactions at atmospheric pressure. Powder catalyst particles (obtained by sieving to 0.125–0.250 mm; 500 mg being employed in every test) were mixed homogeneously with SiC to obtain a total volume of 2 ml. The mixture was then loaded in a cylindrical Pyrex reactor tube (5 mm i.d.; ca. 10 mm catalyst bed height). The total flow employed in any case was of 250 $ml \text{ min}^{-1}$, corresponding to WHSV (weight hourly space velocity) of 30,000 $ml \text{ h}^{-1} \text{ g}^{-1}$, and feed compositions of 0.3% C_3H_6 and 5.4% O_2 for the oxidation of propene and 1% CO and 2% O_2 for the oxidation of CO (volume percentages balanced with N_2 employed as carrier gas) were employed (mass flow controllers being used for this purpose). The products of the reaction were analyzed by infrared spectroscopy using a PerkinElmer 1725X FTIR spectrometer fitted with a multiple reflection transmission cell for gas analysis (Infrared Analysis). Propene bands appearing in the 3200–2700 cm^{-1} range and carbon dioxide bands in the 2400–2200 or 750–600 cm^{-1} range (depending on the degree of saturation of the most intense former ones) and the bands of CO(g) in the range of 2000–2260 cm^{-1} were employed to determine conversion levels using adequate calibration curves. In all cases, the samples were pre-treated under O_2 diluted in inert gas at 500 °C and then taken to the measurement temperature under the reaction atmosphere with a ramp of 5 °C min^{-1} and stabilized for 45 min prior to analysis, in order to ensure stationary conditions.

3. Results and discussion

3.1. XRD structural analysis

The X-ray diffractograms of the samples prepared by the three methods are shown in Fig. 1, while Table 1 collects some structural parameters derived from these results. All the diffractograms

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