Methyl ethyl ketone combustion over La-transition metal (Cr, Co, Ni, Mn) perovskites

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ABSTRACT

A series of $LaBO_3$ (B = Cr, Co, Ni, Mn) and $La_{0.9}K_{0.1}MnO_{3+\delta}$ perovskites have been prepared and tested as catalysts in the combustion of methyl ethyl ketone (MEK) at two concentration levels in air. Complete MEK conversion can be achieved for the most concentrated stream (1250 ppmv, WHSV = 425 h^{-1}) at temperatures between 270 °C (manganite) and 345 °C (chromite). Activity is governed by the nature of the cation in position B and related to reducibility, being comparable for manganite activity with that of the much more expensive Pt-supported catalysts. Doping with K of lanthanum manganite produces an increase in surface area, as well as the formation of non-stoichiometric oxygen and a greater proportion of Mn^{4+} on the surface. All these factors may have a role in increasing its activity for catalytic combustion. Catalytic results suggest a marked influence of MEK concentration on the combustion rate. MEK oxidation to CO_2 goes through acetaldehyde as intermediate product; methyl vinyl ketone and diacetyl (2,3-butanedione) were also formed, albeit in very low amounts. Nevertheless, acetaldehyde yield is zero at complete conversion, so the combustion of MEK can be carried out over these perovskite systems with 100% selectivity for CO_2.

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1. Introduction

Methyl ethyl ketone (MEK) is a commonly used solvent in chemical industries that is a hazard to human health and the environment, with control required of its emission into the atmosphere by total oxidation. Supported noble metals [1–3], manganese oxide [4], both supported manganese and palladium oxide [5] and perovskite-type oxides [6] have been investigated for the catalytic combustion of MEK. Perovskite-type oxides have long been used as catalysts also for the combustion of methane and for the complete oxidation of other volatile organic compounds (VOCs) [7]. These systems are mixed oxides represented by the general formula ABO_3 where A is usually a lanthanide and B a transition metal. Interest in them lies mainly in their good thermal stability in the high temperature (700–1100 °C) range of operation and in their lower cost than supported noble metals. In some cases, the activity of perovskites in combustion reactions can be comparable to that of noble metal-based catalysts [8]. A wide range of chemical elements can occupy positions A and B in the perovskite structure, and partial substitutions of these cations give rise to multi-component oxides ($A_{1-x}A'_xB_{1-y}B'_yO_3$), in which the mixed or unusual oxidation states of some elements can be stabilized [7]. A relevant feature of perovskites is non-stoichiometry resulting from structural and electronic defects, being better represented by $ABO_{3\pm\delta}$. In this context, the activity of perovskites as oxidation catalysts has been ascribed to several aspects of their surface composition, as well as to their defective nature in relation to the mobility and reactivity of lattice and surface oxygen species [9,10]. Since the synthesis of these bulk materials requires a high temperature that gives low surface area, the main challenge in the development of these systems is to obtain the perovskite structure with high surface area and, hence, improve their catalytic performance [11]. The application of this type of catalysts in reactions that take place at temperatures that are not very high, such as the combustion of VOCs, can be appropriate as it avoids the sintering of the material during reaction.

High activities have been reported in literature with lanthanide perovskites for the combustion of VOCs, such as $La_{0.8}Sr_{0.2}CoO_3$ for the deep oxidation of toluene [12], $LaMnO_3$ for the combustion of acetone, butyl acetate and isopropanol [13] and $LaCoO_3$, $LaMnO_3$,

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$La_{0.8}Sr_{0.2}CoO_3$ and $La_{0.8}Sr_{0.2}MnO_3$ for the combustion of toluene and MEK [6]. In this last contribution, Co-containing perovskites were considerably more active than their Mn counterparts.

By partially substituting the A ion with another of lower oxidation state, electroneutrality can be achieved through the formation of oxygen vacancies or the shifting of the B metal toward higher valences. The presence of B^{4+} can increase the activity toward combustion, since the perovskite can act as an oxygen pump toward the molecule that is going to be oxidized, when B^{4+} shifts to B^{3+} [14]. Moreover the partial substitution of A by an ion of lower oxidation state could result in an increase in surface area, as reported in the literature in the case of lanthanum manganite, in which potassium incorporation produces an increase in surface area [15].

In this work, $LaBO_3$ (B = Cr, Co, Ni, Mn) and $La_{0.9}K_{0.1}MnO_{3+\delta}$ perovskites have been prepared and used as catalysts for the oxidation in air of methyl ethyl ketone, a common ambient air pollutant, at two different levels of ketone concentration. Interest has focused on the formation of partially oxidized compounds during the reaction, an aspect that has received little attention [16] in spite of the abundant literature available on VOC combustion. This issue, however, is of great concern since some intermediates are much more harmful than the original pollutant. In the case of lanthanum manganite, potassium incorporation has been considered with the aim of enhancing the catalytic performance of this perovskite system.

2. Experimental

2.1. Catalyst preparation

$LaBO_3$ (B = Cr, Co, Ni, Mn) and $La_{0.9}K_{0.1}MnO_{3+\delta}$ perovskite samples were prepared by amorphous citrate decomposition. A concentrated solution of citric acid was added to a solution of the metal nitrates of appropriate concentration, whereby the ratio of equivalent grams of metal to equivalent grams of citric acid would be unity. The resulting solution was evaporated to dryness at 100 °C. The precursor obtained was then decomposed at 350 °C for 2 h, and finally calcined in air at 700 °C for 4 h. An aliquot of K-substituted sample was also calcined at 900 °C.

2.2. Catalyst characterization

The calcined materials were characterized with Brunauer–Emmett–Teller (BET) specific surface area measurements using nitrogen adsorption at −196 °C, taking a value of 0.162 nm² for the cross-section of N_2 molecule adsorbed at this temperature. These measurements were performed with a Micromeritics ASAP 2100 apparatus on samples previously degassed at 150 °C for 12 h.

The oxide catalysts were characterized by powder X-ray diffractometry according to the step-scanning procedure (step size 0.02°; 0.5 s) with a computerized Seifert 3000 diffractometer, using Ni-filtered Cu Kα (λ = 0.15406 nm) radiation and a PW 2200 Bragg–Brentano θ/2θ goniometer equipped with a bent graphite monochromator and an automatic slit. The assignment of the various crystalline phases was based on JCPDS powder diffraction file cards. The mean particle size of perovskites was estimated from X-ray line broadening using Scherrer's equation. The lattice parameters and the space group of the samples have been estimated using FullProf Software© (2005 version 2.0) [17].

TPR experiments were conducted on a Micromeritics 2900 device. Prior to reduction, the catalysts (ca. 50 mg) were heated at a rate of 20 °C/min to a final temperature of 300 °C, and kept for 0.5 h at that temperature under a flow of He to remove water and other contaminants. The catalysts were cooled to ambient temperature in the same He flow; then reduced in flowing gas containing 10 vol.% vol. H_2 in Ar at a total flow rate of 50 mL/min, and finally heated at a rate of 15 °C/min to a final temperature of 1000 °C.

Photoelectron spectra (XPS) of the fresh and used catalysts were acquired with a VG Escalab 200R spectrometer equipped with a hemispherical electron analyzer and an Al Kα ($h\nu$ = 1486.6 eV, 1 eV = 1.6302×10^{-19} J) 120 W X-ray source. The powder samples were placed in a pretreatment chamber and degassed at 300 °C. All binding energies (BE) were referred to C 1s line at 284.9 eV.

Elemental chemical analysis was performed to determine the carbon content in the used catalysts. This was accomplished using a Leco CHNS-932 device with an AD-4 PerkinElmer microbalance (resolution 0.1 μg).

2.3. Catalytic performance

The MEK combustion reaction was carried out in a tubular (8 mm i.d.) fixed-bed Pyrex glass reactor at atmospheric pressure. The catalyst (0.1 g), with a particle size in the range of 100–200 μm, was diluted with 0.2 g of inert solids (Pyrex glass beads) with similar particle size, forming a bed of about 20 mm in length. An air stream saturated with MEK (Panreac, PA) was created using a saturator equipped with temperature and pressure control, and then diluted with synthetic air (99.999%), resulting in MEK partial pressures in the reactor feed of 126 or 32 Pa, 1250 or 320 ppmv of MEK, respectively. Prior to each experiment, the catalyst was treated with 100 cm³ min⁻¹ (STP) of synthetic air for 1 h at 400 °C. In order to evaluate the light-off performance, once the pretreatment of the catalyst is completed, the MEK-air mixture is fed into the reactor while keeping the temperature at 400 °C. The catalytic bed is allowed to stabilize for about 1 h and then the temperature is decreased in order to measure the ignition curves. All the experiments were performed with a total feed flow rate of 550 cm³ min⁻¹ (STP) and WHSV (feed mass flow rate divided by catalyst weight excluding the inert solids) of 425 h⁻¹. On-line analysis of the product stream was performed on a Hewlett Packard 6890 gas chromatograph, equipped with a HayeSep Q column connected to a TCD for CO_2 determination, and a HP-INNOWax column connected to an FID for MEK and partial oxidation products analysis.

3. Results and discussion

3.1. Characterization results

3.1.1. Textural characterization

Table 1 shows the specific surface area (S_{BET}) data of the prepared samples. As expected for bulk materials, without internal porosity, all the samples have a relatively low S_{BET} (in the range 4.4–14.4 m² g⁻¹). The $LaCrO_3$ material records the lowest S_{BET} among all the perovskites studied, and the largest S_{BET} corresponds to the LaKMn-700 sample. While this latter sample records the highest value of BET area (14.4 m² g⁻¹), this decreases markedly in its counterpart calcined at 900 °C (9.3 m² g⁻¹) due, as will be commented below, to an increase in the average crystallite size. Although parameters such as calcination and type of precursor, among others, determine to a large extent the textural properties of the final material, it can be assumed that obtained surface area values are in the average of those reported in literature for similar perovskites prepared by the citrate method [18–23]. The observed increase in surface area of $LaMnO_3$ with the addition of potassium could be attributed to a decrease in grain size caused by the separation of crystal domains [24], although it cannot be excluded the contribution of segregated species of potassium oxide over the perovskite particles to the observed surface area increase in LaKMn-700 sample.