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Effects of iron and cerium in $La_{1-y}Ce_yCo_{1-x}Fe_xO_3$ perovskites as catalysts for VOC oxidation

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ABSTRACT

Perovskite-type mixed oxides $La_{1-y}Ce_yCo_{1-x}Fe_xO_3$ with high specific surface area were prepared by reactive grinding. These catalysts were characterized by N_2 adsorption, X-ray diffraction, oxygen storage capacity (OSC), H_2-temperature-programmed reduction (TPR-H_2), O_2-, and CH_3OH-temperature-programmed desorption (TPD). The catalytic performance of the samples for volatile organic compounds (VOC), CH_3OH, CO and CH_4 oxidation was evaluated. Cerium allows an enhancement of the reducibility of the B-site cations in perovskite structure during OSC and TPR-H_2 and an increase in the amount of β-O_2 desorbed during TPD-O_2. As opposed to cerium, the addition of iron in the perovskite structure causes a drop in B-site cations reducibility and a decrease of the oxygen mobility in the bulk. As a consequence, the catalytic activity in VOC oxidation is enhanced by introduction of cerium and weakened by iron in the lattice.

1. Introduction

Perovskite-type mixed oxides have been widely studied for the last four decades. These materials present an ABO_3 formula, with the tolerance factor defined by Goldschmidt [1] as: $t = (r_A + r_O)/\sqrt{2}(r_B + r_O)$, where r_A, r_B and r_O are the ionic radii for the ions A, B and O. Perovskite structures are obtained at $0.8 < t < 1$. Their high catalytic activity was reported for a wide set of reactions and particularly for oxidation reactions of hydrocarbons and volatile organic compounds. Cobalt- and manganese-based perovskites were usually reported as the two most efficient structures in oxidation reactions and they were even proposed as an alternative to noble metal supported catalysts since they present similar activities in oxidation and a lower synthesis cost [2–7]. However the low specific surface area generally displayed by these solids is still the major impediment to their use. In spite of the numerous synthesis procedures developed including: coprecipitation [8], citrate complexation [9], spray drying [4], freeze drying [10] and flame hydrolysis [11] the specific surface area observed rarely exceeds 25 m^2/g. The calcination required for crystallization has been usually pointed out as responsible for this situation since the decrease in specific surface area occurs according to a sintering process. Reactive grinding allows the synthesis of mixed oxides including perovskites at rather low temperature owing to the replacement of the thermal treatment by a mechanical treatment [12]. The nanometric structure and the high specific surface area (over 100 m^2/g) displayed by these oxides when prepared by reactive grinding have been reported [13]. The Québec firm Nanox Inc. has installed a demonstration unit of reactive grinding for the production of perovskites with capacity of 15 t/y.

As a result of our previous studies, the iron contamination induced by the use of stainless steel balls during the grinding process has been underlined [14]. Royer et al. [14] indeed indicated that some iron traces in the perovskite structure lead to a decrease of its intrinsic activity in methane oxidation. They also evaluated the impact of this iron content in isotopic exchange experiments and they were able to relate the presence of iron in perovskite and the low mobility of oxygen in the bulk of the structure [15]. This indicates that the reoxidation of the active sites during the methane oxidation may be limited by oxygen mobility in the perovskite lattice since this oxidation reaction occurs according to a Mars–Van-Krevelen mechanism.

Cerium is usually reported as a good promoter in perovskite lattice. According to several studies, partial substitution of 10% of La by Ce in cobalt or manganese-based perovskites leads to an increase in catalytic oxidation activity including propane [16], CO [17], CH_4 [18] and ethanol [19]. Reducibility and oxygen desorption, were also found to be enhanced when cerium was added in the perovskite lattice [16,20]. However, over 10% cerium in the structure causes some segregation: phases of CeO_2 appear which provokes a decrease in catalytic activity.

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This paper deals with the effect of partial substitution of cerium and iron on the catalytic activity in VOC oxidation. In this study, five cobalt-based perovskite-type oxides were prepared with different cerium and iron contents. These solids were characterized by X-ray diffraction, temperature-programmed reduction by hydrogen (TPR-H_2) and temperature-programmed desorption of oxygen (TPD-O_2) and methanol (TPD-CH_3OH). Their activity was also evaluated in three different oxidation reactions (CH_3OH, CO and CH_4). The aim of this work is to understand the promotor effect usually associated to the cerium in literature and the inhibitory effect induced by the presence of iron in the perovskite structure.

2. Experimental

2.1. Catalysts preparation

Five samples of perovskites-type materials were prepared, by reactive grinding ($LaCoO_3$, $LaCo_{0.8}Fe_{0.2}O_3$, $LaCo_{0.6}Fe_{0.4}O_3$, $LaFeO_3$ and $La_{0.9}Ce_{0.1}CoO_3$). They were synthesised by grinding the single oxides. The precursors were first calcined at 600 °C and then introduced in a SPEX laboratory grinder for a first grinding during 4 h under O_2. After this step the perovskite phase was obtained but a second grinding was performed in order to increase the specific surface area [13]. NaCl or ZnO was then introduced as an additive in a weight ratio perovskite/additive = 1. Then the obtained powder was repeatedly washed with diluted NH_4NO_3 (if the additive was ZnO) or with water (if the additive was NaCl) in both cases in order to leach the additive from the sample. Finally the perovskite was calcined under air at 550 °C for 6 h.

2.2. Catalysts characterization

Surface specific areas were obtained from adsorption/desorption isotherms of N_2 at -196 °C determined using an OMNISORB apparatus. Before adsorption the samples were first evacuated for 6 h at 200 °C to remove moisture. The specific surface area was then determined from the linear part of the BET curve. The crystalline phases identification was done by X-ray diffraction using a SIEMENS D5000 diffractometer and Cu Kα radiation (λ = 1.5406 Å). Diffractograms were recorded with a step of 0.05° for 2θ between 15° and 75°. Phase recognition was made by comparison with JCPDS files. Particle sizes (D) were evaluated by means of the Scherrer equation $D = K\lambda/(\beta\cos\theta)$ after Warren's correction for instrumental broadening. K is a constant equal to 0.86 and λ is the wavelength of the X-ray used. β is the effective linewidth of the X-ray reflexion, calculated by the formula $\beta^2 = B^2 - b^2$, where B is the FWHM and b is the instrumental broadening determined by the FWHM of the X-ray reflection of SiO_2, having particles larger than 150 nm, at $2\theta \approx 27°$. Sample compositions were determined by ICP using a P40 atomic adsorption spectrometer from PerkinElmer after dissolution of the catalyst in diluted HCl at 60 °C.

2.3. TPD–TPR characterization

A RXM-100 multi catalyst testing and characterization system (Advanced Scientific Design Inc.) was used to perform oxygen thermodesorption (TPD-O_2) and temperature-programmed reduction (TPR). For TPR experiments, 100 mg of catalysts were placed in a quartz reactor, pretreated under a flow of 20 mL/min (20% O_2 in He) at 550 °C for 2 h and cooled down to room temperature under same composition flow. The TPR-H_2 was carried out under a 10 mL/min flow of 5% H_2 in Ar. The temperature was risen from 25 to 900 °C with a ramp of 5 °C/min. The consumption of hydrogen was monitored and quantified using a TCD. For TPD-O_2 the same pretreatment was performed as for the TPR experiments. The catalysts (100 mg) were submitted to the following conditions: 10 mL/min He, temperature from 25 to 900 °C with a ramp of 5 °C/min. To obtain a complete desorption the catalysts were maintained at 900 °C for 15 min. A TCD was used for the quantification of the oxygen and a mass spectrometer to detect any other desorbing compounds desorption or possible leaks. The amount of oxygen was determined by deconvolution and integration of the desorption profile. To perform a TPD-CH_3OH or TPD-CO_2, two steps were required. During the first step the catalysts (100 mg) were calcined in the same conditions as for TPR experiments. Then the catalysts were treated under 15% CH_3OH in He or under CO_2 at room temperature for 1 h. Thereafter the methanol thermodesorption was carried out under 10 mL/min flow of He from 25 to 900 °C with a ramp of 5 °C/min followed by an isotherm at 900 °C for 15 min. Like TPD-O_2, TCD and mass spectrometer were used to quantify and identify the desorbed species.

2.4. Oxygen storage capacity (OSC) measurements

Oxygen storage capacity (OSC) measurements were performed on the same system as for TPD-O_2 and TPR-H_2 experiments. The catalyst (30 mg) was placed in a U-shaped microreactor, reactant and products were separated on a Porapak Q type column (i.d. = 1 mm, L = 1 m) and analyzed with a TCD. The temperature is set to 500 °C for the four successive steps required for the OSC measurements [20,21]:

(1) a series of O_2 pulses to reach the saturation of the catalyst,
(2) a series of CO pulses until zero conversion of CO or constant CO uptake,
(3) a series of O_2 pulses until complete reoxidation of the solid,
(4) alternated CO–O_2–CO–O_2–CO–O_2 pulses.

The measure of the oxygen storage capacity (OSC value in Table 3) is determined based on the CO uptake during the first CO pulse from the alternated series (step 4). This value corresponds to the amount of highly reactive oxygen which is immediately available for the reaction. The oxygen storage complete capacity (OSCC) is another meaningful measure which represents the total amount of reactive oxygen available for oxidation reactions. This value is determined from the total amount of CO consumed until the end of the CO pulses series (step 2). Since the zero conversion of CO is often not reached at 500 °C, a OSCC-30 value (Table 3) was defined in order to compare the five catalysts under study. Thus this value corresponds to the total amount of CO consumed during the first 30 CO pulses. Finally to evaluate the amount of oxygen in the perovskite lattice ABO_ξ the ξ value is calculated based on the total CO uptake.

2.5. Oxidation reactions

Methanol, methane and carbon monoxide oxidations were performed in a U-shaped quartz reactor (i.d. = 5 mm). The catalytic bed was set up with 100 mg of catalyst inserted between two quartz wool plugs for the three reactions under study. The temperature was controlled using a K-type thermocouple placed in the reactor. In order to purge the catalytic system the catalysts were flushed with a 20 mL/min flow of He for 1 h at room temperature. The feed of methanol oxidation (composed of 0.5% CH_3OH, 20% O_2 in He), methane oxidation (composed of 0.25% CH_4, 20% O_2 in He) and carbon monoxide oxidation (composed of 5% CO, 20% O_2 in He) was passed through the reactor and the temperature was risen. The flow rate was adjusted for each oxidation reactions to 30 mL/min which corresponds to a VHSV of 22500 h^{-1}. Gas samples were collected in the steady state regime at various