

Short communication

Preferential oxidation of CO on a La-Co-Ru perovskite-type oxide catalyst



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ABSTRACT

A Ru-containing perovskite-type oxide La(Co,Ru)O₃ of nominal composition LaCo_{0.8}Ru_{0.2}O₃ was prepared by ultrasonic spray combustion and tested for the preferential oxidation of CO (PROX). EXAFS indicated that Ru adopted the coordination environment of Co in LaCoO₃ while Co was present as LaCoO₃ and Co₃O₄. PROX activity was replaced by CO hydrogenation activity above 250 °C. Short oxidation at 500 °C between temperature programmed reaction ramps did not restore the initial La(Co,Ru)O₃ structure but generated a catalyst with improved PROX activity compared to the initial La(Co,Ru)O₃. Under reductive PROX conditions the material experienced structural changes that improved its overall catalytic activity only if the catalyst was oxidized after each temperature programmed ramp.

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1. Introduction

Perovskite-type oxides (ABO₃) are acknowledged as efficient catalysts for oxidation reactions [1–5]. It was recognized early that when doped with transition and precious metals this class of mixed oxides exerts a stabilizing function towards the dopant to avoid formation of volatile oxides and catalyst degradation. To this end, ruthenium was the major focus of studies already in the early 70's as it became a potential candidate for the removal of NO_x from treatment of exhaust gases of vehicles [6–8]. Moreover, the possibility to produce perovskite-type oxides with catalytically relevant B-site doping elements was shown to protect the metals from particle growth in automotive catalysis as a consequence of reversible segregation-incorporation within the perovskite-type structure [9]. Recently, the interest for Ru-doped perovskite-type oxides has been placed rather on high temperature applications such as fuel reforming [10–18] because of the thermal stability of perovskite-type oxides and the intrinsic activity of ruthenium. Fierro and co-workers [11–15] have shown that addition of Ru to LaCoO₃ improves especially the stability of the catalyst to high temperature reaction conditions. Because of the reducing environment of these reactions, the reducible LaCoO₃ can be used as an ideal catalyst precursor. During reaction or pretreatment, La₂O₃ or La₂O₂CO₃ supported Co and Ru particles are generated and constitute the final catalyst. The improved catalytic activity of Ru was attributed to the enhanced reducibility of LaCoO₃ by Ru and to the consequent improved formation of Co, Ru

and possible Co-Ru metallic phases. This strategy could be exploited to generate suitable materials for catalytic processes operating at low and moderate temperatures. Therefore, in this work we use Ru-doped LaCoO₃ prepared by ultrasonic spray combustion [19,20] as a possible catalyst for preferential oxidation of CO in excess hydrogen (PROX) in a broad temperature range. Ru is an active metal for this reaction [21] but it also catalyzes CO hydrogenation to CH₄ occurring at higher temperature than PROX [22]. Besides exploiting the reducibility of LaCoO₃ enabling the segregation of Ru, we show preliminary data on the structural regeneration of the catalyst, under sequential temperature programmed reaction and oxidation steps.

2. Experimental

An aqueous solution of La(NO₃)₃·6H₂O (Fluka, >99%), Co(NO₃)₂·6H₂O (Sigma-Aldrich, >98%), RuCl₃·xH₂O (Aldrich >99%) and citric acid (Riedel-de Haën, >99.5%) in the necessary molar ratio to obtain LaCoO_{3-δ} and LaCo_{0.8}Ru_{0.2}O_{3-δ} (La(Co,Ru)O₃) was atomized in an ultrasonic nebulizer and transported by air flow through a vertical quartz reactor heated to 600 °C [23]. The ratio between the amount of citric acid and the total amount of metal ions was 1. The resulting oxide powders were collected on a heated membrane filter (150 °C) and calcined at 600 °C for 4 h.

X-ray diffractograms (XRD) were recorded with a Philips X'pert Pro MPD diffractometer using Ni-filtered Cu Kα radiation (λ = 1.5418 Å). In situ XRD data during temperature programmed reduction (H₂-TPR) were collected at steady state in 5 vol% H₂/Ar up to 700 °C (10 °C/min) and 70 vol% H₂/N₂ up to 500 °C (5 °C/min) at temperature

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increments of 25 °C (2θ range, 24–56°; step size, 0.05°). The BET specific surface area was measured from N₂ adsorption–desorption isotherms at –196 °C using a Micromeritics ASAP 2020 instrument. Temperature programmed reduction (H₂-TPR) was performed in a setup equipped with a thermal conductivity detector (TCD) to quantify the H₂ concentration and an online mass spectrometer (MS) to monitor products formation [24]. CuO was used for quantification of the H₂ consumption. After heating in 5 vol% H₂/Ar to 700 °C (10 °C/min), cooling to room temperature and purging with He, the sample was heated in 3 vol% O₂/He to 700 °C (10 °C/min). This procedure was repeated three times and the reduction profiles were labelled as TPR-1, TPR-2 and TPR-3. Transmission extended X-ray absorption fine structure (EXAFS) spectra were collected at the Co (7709 eV) and Ru (22,117 eV) K-edges (BM01B beamline, ESRF, Grenoble) using Co and Ru foils for energy calibration.

The preferential oxidation of CO (PROX) was carried out by heating the catalyst (50 mg) in a quartz tubular reactor to 500 °C (1 °C/min) in 1 vol% O₂, 1 vol% CO and 70 vol% H₂, 100 mL/min (He balance). After cooling to room temperature, the catalyst was heated to 500 °C in 20 vol% O₂/He followed by 5 min dwell at 500 °C and cooling to room temperature. Five activity–oxidation cycles were performed that were followed by five activity cycles without intermediate oxidation (Fig. S1). The effluent gas was analyzed by gas chromatography (Varian GC-3800; TCD; Molecular Sieve 5 Å and Porapak®-N columns). CO and O₂ conversion, CO₂ and CH₄ yield were determined as follows:

$$X(\text{CO}) (\%) = 100 \times (n\text{CO}_{\text{in}} - n\text{CO}_{\text{out}}) / n\text{CO}_{\text{in}}$$

$$X(\text{O}_2) (\%) = 100 \times (n\text{O}_{2\text{in}} - n\text{O}_{2\text{out}}) / n\text{O}_{2\text{in}}$$

$$Y(\text{CO}_2) (\%) = 100 \times n\text{CO}_{2\text{out}} / n\text{CO}_{\text{in}}$$

$$Y(\text{CH}_4) (\%) = 100 \times n\text{CH}_{4\text{out}} / n\text{CO}_{\text{in}}$$

where *n_i* is the amount of every component (*i*) in moles.

3. Results and discussion

The XRD pattern of La(Co,Ru)O₃ (30.2 m²/g) calcined at 600 °C exhibited only the reflections of the rhombohedral structure of LaCoO₃ (ICDD, 01-084-0847, R-3c; Fig. 1). The missing doublets characteristic

of the rhombohedral structure reflected the low degree of crystallinity as a result of the low synthesis and calcination temperatures. The significant shift to lower 2θ values of the reflections compared to LaCoO₃ suggests that Ru was inserted at the B-site [12]. The edge energy (7723 eV) of the Co K-edge XANES spectrum of La(Co,Ru)O₃ (Fig. 2) was intermediate between that of LaCoO₃ (Co³⁺, 7724 eV) and Co₃O₄ (Co^{2+/3+}, 7717 eV). The white line presented a second peak attributable to Co₃O₄. Beside the Co–O coordination shell at 1.5 Å, which did not match that of Co₃O₄ (1.7 Å), the peak at ca. 3.2 Å that is due to multiple contributions of Co–La, Co–Co, and Co–O–Co bonds was weaker than in LaCoO₃ in the FT-EXAFS spectrum (Fig. 2) suggesting a large degree of disorder induced by Co substitution [25]. The contribution at 2.5 Å resembled the coordination environment of cobalt in Co₃O₄. These observations suggest the presence of a mixed local environment of Co and the coexistence of LaCoO₃ and Co₃O₄ phases in La(Co,Ru)O₃. Its dispersion and amorphous character, reflecting the structural disorder observed in the FT-EXAFS of La(Co,Ru)O₃ explain the absence of Co₃O₄ in the XRD (Fig. 1).

The Ru K-edge XANES spectrum of La(Co,Ru)O₃ (Fig. 2) did not match the spectra of reference materials with nominal Ru oxidation state +3 (RuCl₃) and +4 (RuO₂). It was composed of two major peaks due to 1s → 5p_x and 1s → 5p_{y(z)} transitions in distorted RuO₆ octahedra in perovskites [26], implying that Ru adopted the oxidation and coordination states of the B-site. By comparison of the position of the maximum of the first derivative of La(Co,Ru)O₃ with that of compounds with oxidation state +3 (RuCl₃), +4 (RuO₂), +4.5 (Pb₂Ru₂O_{6.5}) and +5 (Ca₂YRuO₆) (Fig. 2) [27], we assign Ru an oxidation state close to +5 and octahedral coordination. This oxidation state could be justified by the similar ionic radius of Ru⁵⁺ (0.705 Å) in octahedral coordination and Co³⁺ (0.685 Å) compared to lower oxidation states of Ru (Ru⁴⁺: 0.76 Å or Ru³⁺: 0.82 Å) [28]. The slightly larger radius of Ru⁵⁺ induced the shift to lower diffraction angles in the XRD. Because no Ru K-edge spectrum was reported, we could not compare our spectra with those measured by Mota et al. [13], who proposed Ru⁴⁺ in LaCo_{0.8}Ru_{0.2}O₃. The high oxidation state of Ru is consistent with the large degree of disorder evident from the FT spectrum of the Co K-edge and the partial reduction of Co³⁺ to Co²⁺ related to the presence of Co₃O₄. Charge compensation/redistribution and the unit cell distortion can suggest the Co segregation if all Ru adopted the coordination state of Co and was all integrated in the perovskite lattice. Assuming that Co was

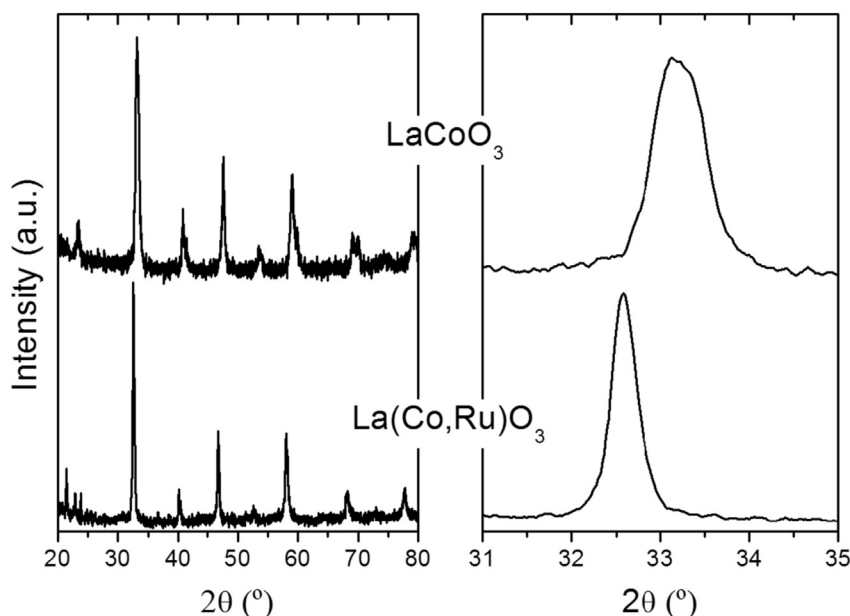


Fig. 1. X-ray diffraction patterns of LaCoO₃ and La(Co,Ru)O₃. The right panel details the major reflection line.

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