Promotion Of Copper On The Reduction Of Cobalt Ions In Perovskite-Type Oxides

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Abstract

Ground LaCo_{1-x}Cu_xO_3 and mixed oxide CuO+LaCoO_3 were characterized by several physical means as X-ray diffraction, BET, SEM, and H_2-TPR. LaCo_{1-x}Cu_xO_{3-δ} samples show a well crystallized rhombohedral structure and uniform nanocrystallites. The substitution cobalt by copper in perovskite lattice has no significant changes in the structure, but remarkably affects the reducibility of perovskite up to x =0.3. Under hydrogen treatment, the reduction temperature of cobalt ions in LaCo_{1-x}Cu_xO_3 varies with the intra-lattice copper. A lower cobalt reduction temperature observed for LaCo_{1-x}Cu_xO_{3-δ} in comparison to LaCoO_3 produces a finely dispersed bimetal on the La_2O_3 matrix. A close distance between cobalt and copper sites in the perovskite framework facilitates the reducibility of cobalt ions and improves the metallic dispersion of metals in the reduced form.

Keywords: Nanoperovskite, promotion, intra-lattice, copper, cobaltite, LaCoCuO_3, reducibility.

1. Introduction

Perovskite-type mixed oxides have the cubic structure with the general formula of ABO_3 and the space-group Pm3m-Oh [1]. In the cubic structure, cation A is at the body center while the transition-metal cations (B) occupy at the cube corners. All oxygen anions stay at the midpoint of the cube edges. Thus, both A and B positions can be partially replaced by a di- or trivalent element to produce some more complicated perovskites [1,2]. For example, La can be replaced by either Sr or Th to produce a series of La_{1-x}Sr_x(Th)_3O_3 perovskites which played as active catalysts for carbon dioxide hydrogenation [3] and methane oxidation [4]. Nevertheless, the replacement of the cation at A-position is much less attractive than that at B-site because the nature of cation A is usually less attractive because of inactive nature of cations A [5]. In other context, the substitution of cation B by another transition element could produce various active catalysts for many potential reaction applications [1,2,6] and/or numerous supported bimetallic catalysts after tailored reductions [1,2,7-9]. For instance, Bedel et al. [5] prepared a Fe-Co alloy after reduction of LaFe_{0.75}Co_{0.25}O_3 orthorhombic perovskite at 600°C. Lima and Assaf [9] found that the partial substitution of Ni by Fe in the perovskite lattice leads to a decreased reduction temperature of Fe^{3+} ions and the formation of Ni-Fe alloy. In the latter cases, the intercalation of another transition metal (Fe^{3+}, Ni^{3+}…) into the perovskite lattice always leads to modify the catalyst morphology and the catalytic behavior [1,7-10]. In addition, this modification also causes dilution of the transition metal sites and also may affect the reducibility of the parent perovskite.

This article is to report the role of intra-lattice copper in the reduction of cobalt ions in the perovskite lattice. The result may also suggest a simple way to prepare a well-homogenized supported bimetal catalyst system.

2. Experimental Section

2.1 Perovskite preparation

Three nominal formulae of LaCo_{1-x}Cu_xO_3 perovskite-type mixed oxides were synthesized by the reactive grinding method [10,11]. In brief, the stoichiometric proportions of commercial lanthanum, copper, and cobalt oxides (99%) were mixed together with three hardened steel balls in a hardened steel crucible (50 mL). Then, the resulting powder was mixed to 50% sodium chloride and further milled for 12 hours before washing the additives with distilled water. The slurry was dried in oven at 60-80°C before calcination at 250°C for 150 min.

A reference sample, LaCoO_3 + CuO, was prepared by milling a mixture of the ground perovskite LaCoO_3 having a specific surface area of 43 m^2/g with cupric...
oxide (CuO/LaCoO$_3$ = 1.5 molar ratio) at ambient temperature before drying at 120°C overnight in oven.

2.2. Characterization

The specific surface area of all obtained samples was measured from nitrogen adsorption equilibrium isotherms at -196 °C measured using an automated gas sorption system (NOVA 2000; Quantachrome). Phase analysis and particle size determination were performed by powder X-ray diffraction (XRD) using a SIEMENS D5000 diffractometer with CuKα radiation (λ = 1.54059 nm). Temperature programmed characterization (TPR) was examined using a multifunctional catalyst testing (R XM-100 from Advanced Scientific Designs, Inc.). Prior to each test analysis, a 50 mg sample was calcined at 500 °C for 90 min under flowing 20% O$_2$/He (20 mL/min, ramp 5 °C/min). The sample was then cooled down to room temperature under flowing pure He (20 mL/min). TPR of the catalyst was then carried out by ramping under 5 vol% of H$_2$/Ar (20 mL/min) from room temperature up to 800°C (5 °C/min). The effluent gas was passed through a cold trap (dry ice/ethanol) in order to remove water prior to a thermal conductivity detector (TCD).

3. Results and Discussion

3.1 Physical characteristics

A major drawback of grinding method is usually to produce a low chemical homogeneity and yields a small amount of impurities of unreacted constituent oxides in the final product mixture [2,10]. To investigate the formation of perovskite phase, all perovskite-type mixed oxides are recorded X-ray diffraction. Figure 1 presents XRD patterns for all prepared samples.

**Figure 1.** XRD patterns for all ground samples

XRD diffractograms of three perovskites and a mixture of LaCoO$_3$ and CuO are displayed in Figure 1. In general, it is observed that the ground LaCoO$_3$ appears a set of sharp reflection peaks at 23.1, 33.2, 40.6, 47.3, 52.8 and 58.6° representing for the typically crystalline rhombohedral perovskite, in accordance with the JSCDS card Nos. 48-0123, 46-0059, 51-1511) [10, 12,13]. The substitution of Co$^{3+}$ by Cu$^{2+}$ in LaCo$_{0.7}$Cu$_{0.3}$O$_3$ perovskite mixed oxides is possible up to x = 0.3, and the perovskite is still preserved without changing the crystal symmetry [9,12], substantiated by no observable change in XRD diffractograms between LaCoO$_3$ and LaCoCuO$_x$ patterns. No appearance of other peaks indicates that copper ions are fully incorporated into the perovskite lattice [6,8,9,14]. For the physical mixture, XRD pattern shows the presence of CuO reflected by the appearance of 2-theta values of 35.4 and 38.6° in addition to the LaCoO$_3$ perovskite phase (Fig. 1). In all cases, the reflection lines are rather broadening, implying the formation of nanocrystalsites of perovskite [12,13]. The crystal domains of LaCoO$_3$, LaCo$_{0.7}$Cu$_{0.3}$O$_3$ and LaCo$_{0.9}$Cu$_{0.1}$O$_3$, estimated from the Full Width at Half Maximum (FWHM) of the (102) diffraction peak (2θ = 33.2°) using Scherrer’s equation are around 10 nm, in good agreement with SEM observation [6,11,14].

3.2 Morphology and Surface area

Morphological perovskite was examined by SEM technique. Microphotographs of two representative samples are depicted in Figure 2. It is observed a similar surface morphology of SEM micrographs between two selected ground perovskite samples, indicating a high productivity of the grinding synthesis [6,10,11,14]. Moreover, the perovskite powder is constituted by the aggregation of various spherical particles with the average particle size in the range of numerous nanometers, in coincident with the results estimated from Scherrer’s equation.

The arrangement of such spherical particles yields many slit-shaped spaces between nanometric particles and thus external surface area increases [11,12,14]. Indeed, the specific surface area of the ground perovskites is in the range of 25 - 56 m$^2$/g as reported in Table 1 using the BET (Brunauer-Emmett-Teller) equation. The nitrogen adsorption/desorption isotherms are displayed in Figure 3. Adsorption curves of all examined samples are classified into type of II isotherm which is characteristic of a nonporous or possibly micro- and macro-porous material having a high energy of adsorption [15]. However, the isothermal curves are not parallel to the horizontal axis and appears a hysteresis loop at high relative pressure in the narrow range of 0.8-
1.0. This observation may suggest the existence of micropores and some slit-like mesopores in the ground perovskite samples. Indeed, the ground perovskite is consisted of uniform spherical particles [10,14]. There are considerable spaces between the nanometric perovskite grains. As indicated by SEM images, the particles are perfect spheres, the “pore space” or porosity is rather high and the pore sizes are more uniform. The porous structure of the ground perovskite would facilitate the reducibility of transition metal ions in perovskite lattice [12,13].

![Figure 2. SEM photographs of LaCoO\(_3\) (A) and LaCo\(_{0.9}\)Cu\(_{0.1}\)O\(_3\) (B)](image)

<table>
<thead>
<tr>
<th>Nominal composition</th>
<th>BET surface area (m(^2)/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaCoO(_3)</td>
<td>56</td>
</tr>
<tr>
<td>LaCo(<em>{0.9})Cu(</em>{0.1})O(_3)</td>
<td>24</td>
</tr>
<tr>
<td>LaCo(<em>{0.7})Cu(</em>{0.3})O(_3)</td>
<td>25</td>
</tr>
<tr>
<td>LaCoO(_3) + CuO</td>
<td>21</td>
</tr>
</tbody>
</table>

**Table 1. Specific surface area of samples**

![Figure 3. Nitrogen adsorption/desorption isotherms of ground perovskites and reference sample](image)

### 3.3 Reducibility

The reducibility of the ground perovskites is investigated by the temperature programmed reduction of hydrogen (H\(_2\)-TPR). All experiments are carried out from room temperature to 800 °C under H\(_2\)/Ar flowrate [12,14,16,17]. Figure 4 represents the variation of TCD signal of hydrogen consumed with reduction temperature.

![Figure 4. H\(_2\)-TPR profiles of ground samples](image)

The reduction of cobaltite perovskites takes place in two consecutive steps as described in Figure 4. H\(_2\)-TPR profiles of cobaltite perovskite (LaCoO\(_3\)) shows two broad bands at 411 and 713 °C. The first peak is attributed to the reduction of Co\(^{3+}\) to Co\(^{2+}\) in the perovskite lattice [1,2,11,17]. At this step, the perovskite
structure is still remains, evidenced by the XRD patterns collected at different reduction temperatures. As seen in Figure 5, no significant changes in X-ray diffractograms of LaCoO₂ are observed in the reduction temperature range of 300-450 °C. In the temperature window of 450-500 °C, the corresponding XRR patterns of LaCoO₃ are essentially unchanged, but the noise to signal ratio dramatically increases, indicating the slightly modification of the perovskite structure at high reduction temperature [16]. This is in good agreement with H₂-TPR result displayed in Figure 4. Furthermore, H₂-TPR signal for the ground LaCoO₃ perovskite sample does not reach the baseline after the first reduction step, implying the commencement of second reduction step at 460 °C (Fig. 4). Thus, it is suggested that the second step starts at 460 °C and lasts through a maximum at 730 °C [17,18]. In practice, the XRD pattern of LaCoO₃ significantly changes and some new peaks are observed at 550 °C, demonstrating the gradual modification in the perovskite structure [2,17,18]. Therefore, this step describes the complete reduction of Co³⁺ to Co⁰ accompanied by the gradual destruction of the perovskite structure.

![Figure 5. XRD patterns for LaCoO₃ reduced at different temperatures in H₂/Ar flowrate](image)

H₂-TPR profiles of LaCo₁₋ₓCuₓO₃ perovskites show a slight change in shape as compared with that of cobaltite perovskite. Indeed, H₂-TPR curve of LaCo₀.₇Cu₀.₃O₃ sample displays a broad peak at lower temperatures along with a visible shoulder at 370°C. These peaks are ascribed to the reduction of Co³⁺ and Cu²⁺ to lower oxidation states [8,11-13,18]. These signal peaks in LaCo₀.₇Cu₀.₃O₃ combine into a single peak as increased copper content to x = 0.3 (sample LaCo₀.₇Cu₀.₃O₃ in Fig. 4). Meanwhile the broad peak at high temperature in the latter sample LaCo₀.₇Cu₀.₃O₃ becomes more broadening and reaches nearly flat in the range of 400- 650 °C. Therefore, it is suggested that the reduction temperatures of both Co³⁺/Co²⁺ and Co³⁺/Cu⁰ in LaCoCuO₃ are much lower than those in LaCoO₃ (Fig. 1). To demonstrate this hypothesis, we have collected some XRD patterns of a representative sample LaCo₀.₇Cu₀.₃O₃ reduced at different temperatures [17]. In line with H₂-TPR interpretation, the first reduction step almost terminates at 350 °C [19,20] and thus the reduction of LaCo₀.₇Cu₀.₃O₃ at 450 °C leads to the deformation of perovskite structure (Fig. 6). This is different from the copper-free perovskite sample (LaCoO₃) (Fig. 5) [10,14,15,17]. Moreover, the appearance of week diffraction peaks at 43.6 and 50.6° is characteristics of metallic copper (JCPDS card No. 04-0836) [11] in addition to the reflection signals of La₂O₃ (JCPDS card No. 74-2430) and Co (JCPDS card 15-0806) and intermediate perovskite phases. These diffraction line intensities increase as increasing reduction temperature to 550°C [2,9].

![Figure 6. XRD patterns for LaCo₀.₇Cu₀.₃O₃ reduced at different temperatures in H₂/Ar flowrate](image)

Thus, the presence of copper in the perovskite lattice has strongly promoted the reducibility of cobalt ions in the framework while extra-lattice copper does not significantly affect the reduction ability of cobaltite as analyzed by H₂-TPR traces of CuO/LaCoO₃ mixture. The reduction temperatures of Co³⁺ and Cu²⁺ in the blend are almost on par with those in LaCoO₃ and single CuO oxide (Fig. 4). The facilitation of intra-lattice copper on the reducibility of cobalt ions in the perovskite lattice is...
interpreted by the corresponding extraction of Cu$^0$ at low
temperatures which may act as an active site for
dissociation of hydrogen [9,14,18-20]. Therefore,
hydrogen molecules chemisorbed on Cu$^0$ sites who are
proximate to cobalt ions. Accordingly, these cobalt ions
should be attacked by atomic hydrogen and easily
convert to metallic clusters at significantly lower
temperatures [9,11,19]. As a consequence, the reduction
of LaCoCuO$_3$ leads to the formation of high dispersion
of bimetallic copper-cobalt at lower temperatures.

4. Conclusions

Three ground LaCo$_{1-x}$Cu$_x$O$_3$ ($x = 0 - 0.3$) oxides and
a blend of LaCoO$_3$ with CuO are prepared by milling
method. All LaCo$_{1-x}$Cu$_x$O$_3$ samples show well
rhombohedral perovskite structure. The perovskite
structure is preserved up to $x = 0.3$. The ground solids
are composed of nanometric particles with the average
diameter around 10 nm. They possess a moderate surface
area and consist of slit-like micro and mesopores. The
presence of intra-copper lattice has strongly promoted
the reducibility of cobalt in the perovskite framework
while extra-lattice copper has negligibly impacted on the
thermal stability of LaCoO$_3$ perovskite. All Cu-
containing perovskite are reduced at lower temperature
as compared with the copper-free perovskite sample and a
blend of CuO-LaCoO$_3$.

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