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Aerobic selective oxidation of alcohols using $La_{1-x}Ce_xCoO_3$ perovskite catalysts

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ABSTRACT

The synthesis of porous perovskites with high and stable activity for alcohols oxidation using molecular oxygen as oxidant is reported. $La_{1-x}Ce_xCoO_3$ catalysts are prepared by a sol–gel method using methanol and ethylene glycol as complexing agents. Calcination at 600 °C allows the formation of macro- and mesopores, in contrast to similar materials that often show a bulk structure. Catalytic tests show that $La_{0.9}Ce_{0.1}CoO_3$ is highly active for benzyl alcohol oxidation with molecular oxygen, with both conversion and selectivity above 95% (60 min, 88 °C, 1 atm). Further tests show that 94% of the original activity can be obtained after surface regeneration of the used catalyst. The good catalytic performance is explained by the presence of cerium, which is able to attract and release adsorbed oxygen on the oxygen vacancies. The electrons donated by alcohols improve the ability of oxygen vacancies to activate molecular oxygen into oxygen anions, which react with the alcohol and increase the reaction rate. A mechanism is proposed.

1. Introduction

The green synthesis of chemical intermediates is an increasingly important subject since regulations on environmental protection have become more restricted in recent years. For chemicals synthesized by oxidation, the use of oxygen as oxidant is preferred, instead of the traditional metal oxides, such as chromate and permanganate [1], since oxygen is a cheap, abundant nonpolluting natural gas, whose only by-product is water [2].

Noble metal [3–6] and metal oxide [7–10] catalysts are two types of materials widely used for alcohol oxidation reactions, but show drawbacks when used in practical applications. Noble metals are expensive and need to be prepared at the nanoscale to achieve the desired catalytic performance. This, however, would lead to catalyst problems, e.g., the leaching or aggregation/sintering of small nanoparticles. In addition, a basic medium is needed to initiate the reaction, which can decrease the product selectivity [11,12]. Metal oxides (such as Co_3O_4) are cheap and show good initial activity for oxidation, but they are prone to deactivation, as the oxygen defects acting as active sites would be repaired by O_2 during the reaction [13].

Perovskite oxides with ABO_3 structure are promising materials in heterogeneous catalysis and are potential substitutes for noble metals and simple metal oxides in many catalytic applications [14–17]. Compared with noble metals and metal oxides, perovskites are low-cost materials with a stable structure, and thus more practical for industrial applications [18]. Very often they are used for reactions carried out at high temperatures, such as purification of exhaust gases [19,20]. Recent reports show that perovskites are also active in reactions carried out at mild temperatures, such as the room-temperature oxidation of organic dyes by H_2O_2, although they are less active for H_2O_2 decomposition [21]. This shows that the ability of perovskites to activate H_2O_2 can be improved in the presence of an organic substrate, which can coordinate with the transition metals of the perovskite and influence the electronic structure of the metal–oxygen bond, improving H_2O_2 activation.

In view of the above, and given our past experience with perovskites [17,21–25], we attempted to investigate if these oxides would also have the ability to activate molecular oxygen and subsequently catalyze the oxidation of organic substrates into desired

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fine chemicals at mild temperatures. Given the strong affinity of Ce^{4+} to oxygen [22], $La_{1-x}Ce_xCoO_3$ ($0 \leqslant x \leqslant 1.5$) catalysts were prepared by a sol–gel method using methanol and ethylene glycol as complexing agents, with calcination at 600 °C for 5 h. The $LaCoO_3$ activity and the efficiency for aerobic oxidation of alcohols at mild temperatures (e.g., 88 °C) were compared with those of materials with cerium incorporated into the framework. The catalysts' performance was also compared with those of other materials, including noble metals and metal oxides, in the liquid-phase selective oxidation of benzyl alcohol to benzaldehyde with molecular oxygen conducted under the same conditions.

2. Experimental

2.1. Catalyst preparation

Samples were prepared by a sol–gel method using ethylene glycol and methanol as complexing agents. Briefly, 5 mmol of La$(NO_3)_3$ and/or $Ce(NO_3)_3$ and 5 mmol of $Co(NO_3)_3$ were dissolved in a mixed solution containing 3 mL ethylene glycol and 2 mL methanol and stirred for 6 h. The resulting solution was aged overnight at 95 °C, yielding a gel-like product, which was calcined in a static air oven at 600 °C for 5 h (with a heating rate of 1 °C min^{-1}). Depending on the amount of $Ce(NO_3)_3$ added, the samples were denoted as $La_{1-x}Ce_xCoO_3$ ($x = 0, 0.05, 0.10, 0.15$).

The synthesis of other materials used for comparison (namely Au/AC, Co_3O_4/AC, and K-OMS-2) was described in the Supporting Information (SI).

2.2. Catalyst characterizations

X-ray diffraction (XRD) patterns were collected using a Bruker D8 Advance X-ray diffractometer with CuKα irradiation ($\lambda = 1.5406$ Å). Transmission electron microscopy (TEM) images were obtained on a Tecnai G^2 20 S-Twin apparatus with high-resolution transmission electron microscope (200 kV). The samples were dispersed in ethanol by an ultrasonic method before being deposited on the copper mesh. N_2 physisorption isotherms were measured on a TriStar II 3020 measurement at liquid nitrogen temperature (−196 °C) and the surface areas were calculated using the Brunauer–Emmett–Teller (BET) method. Before measurements, samples were treated in vacuum for 5 h at 200 °C. X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Thermo Electron Corporation VG Multilab 2000 apparatus using a monochromatic AlKα X-ray source (300 W) and an analyzer pass energy of 25 eV. Binding energies were obtained by referencing to the C (1*s*) binding energy of carbon (peak at 284.6 eV).

Temperature-programmed reduction using H_2 (H_2 TPR) was performed on a FINESORB-3010 apparatus (Fantai Technology Company, China) equipped with TCD detector. The sample (0.10 g) was first treated under Ar at 500 °C for 1 h and then cooled to room temperature. Then 10 vol.% H_2/Ar mixture was switched with a flow rate of 25 mL min^{-1}. After a stabilized baseline was reached, the sample was heated from room temperature to 800 °C, at a rate of 10 °C min^{-1}.

2.3. Catalytic tests

Experiments were conducted at atmospheric pressure, in a 50 mL three-necked batch reactor fitted with a reflux condenser, oil bath, thermocouple, and magnetic stirrer. Typical reaction conditions were 20 mL toluene, 20 μL benzyl alcohol, 10 μL dodecane (used as internal standard), 50 mg catalysts (the molar ratio of substrate/catalyst was 0.95), oxygen (99.99%) flow rate 50 mL/min, reaction temperature 88 °C. The products were analyzed by GC (Agilent 7890) with a flame ionization detector, using an HP-5 column and N_2 as carrier gas. The catalytic activities (conversion and selectivity) were calculated as indicated in a previous work [26].

3. Results and discussion

3.1. Phase and textural structure of catalysts

Fig. 1A depicts the XRD patterns of $La_{1-x}Ce_xCoO_3$ ($0 \leqslant x \leqslant 1.5$) materials, showing that the perovskite structure is formed for samples with $x \leqslant 0.05$. A small peak at $2\theta \approx 28°$, assignable to CeO_2, is observed for $x \geqslant 0.1$. This indicates that $LaCoO_3$ can accommodate at least 5 mol.% Ce in its framework. In contrast, when formic acid is used instead of methanol, or Sr^{2+} is used instead of Ce^{4+}, pure perovskite structure is not formed and impurities are detected (see XRD pattern in Fig. S1A of the SI), showing that the use of suitable complexing agents and metal ions is important for the formation of perovskite-type oxides. The effects of complexing agents and metal ions on the formation of perovskites have been widely reported in literature [23,27]. However, to the best of our knowledge, the calcination temperature of 600 °C used in this work is the lowest ever reported for the preparation of perovskites by a sol–gel method. Low temperature can reduce the degree of aggregation and retain a high surface area. That is a very important issue, as the catalytic activity of a catalyst is often intimately related to its surface area.

N_2 physisorption measurements (see Fig. 1B) show that the BET surface area of $La_{0.95}Ce_{0.05}CoO_3$ is 23 m^2/g, which is higher than is generally reported in the literature (below 10 m^2/g) for this type of materials [28]. Although Ce doping does not much affect the surface area and pore size, it greatly influences the pore volume, the highest value being found for $x = 0.05$ and the lowest for $x = 0.15$, as shown in Table S1 of the SI. The variations in pore volume can be related to the segregation of CeO_2, as identified from the XRD patterns. Although the pore volume can be enlarged using a low Ce content ($0 \leqslant x \leqslant 0.5$), it decreases for larger Ce amounts ($x \geqslant 1.0$). This could be that some CeO_2 are formed and fill in the pores of the perovskite, as shown below by transmission electron microscopy (TEM) images.

3.2. Surface morphology of catalysts

TEM images show that a randomly macroporous structure is formed for $La_{1-x}Ce_xCoO_3$ samples, regardless of the Ce content, as depicted in Fig. 2. This explains why improved surface areas are observed for our samples, in comparison with the previously reported bulk perovskites [28]. It should be noted that nanoparticles are formed instead of a porous structure if methanol is replaced with formic acid (see Fig. S1B of the SI). This demonstrates that the complexing agents used in this work have the ability to create pores. Moreover, the process reported is smoother and safer, compared with the solution combustion synthesis (SCS) method, which also has the ability to create pores in perovskites but involves a fast and explosive reaction [29,30].

Furthermore, it can be seen that a large number of small white spots are visible on the walls of the materials (Fig. 2A–D), showing that both meso- and macropores are created. The formation of hierarchical pores in the structure is possible, as these pores are generated by the combustion of organic complexes with release of CO_2/H_2O and/or by the decomposition of nitrate ions with release of NO/NO_2, leading to varied pore sizes. To prove this, a TEM image with high magnification is shown in Fig. S2 of the SI (for sample $x = 0.05$), where mesopores are observed. The porosity can increase the contact area between the catalyst and the sub-