Aerobic selective oxidation of alcohols using $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ perovskite catalysts

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Abstract

The synthesis of stable, highly active, porous perovskites is reported. $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ catalysts were prepared by a sol-gel method using methanol and ethylene glycol as complexing agents. Calcination at 600 °C allows the formation of macro and meso- pores, in contrast to similar materials that often show a bulk structure. Catalytic tests show that $\text{La}_{0.9}\text{Ce}_{0.1}\text{CoO}_3$ 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 performances are 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.

Keywords: $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$; Porous structure; Selective oxidation; Benzyl alcohol; Molecular oxygen

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, non-pollutant natural abundant 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 these reactions, but show drawbacks when used in practical applications. Noble metals are expensive and need to be prepared in nanoscale, in order to achieve 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 (*like* Co_3O_4) are cheap and show good initial activities for oxidation, but they are prone to deactivation, as the oxygen defects acting as active sites will 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 to noble metals and metal oxides, perovskites are low-cost materials with a stable structure, 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 can also be 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 H₂O₂ activation.

In view of the above, and given our past experience with perovskites [17, 21-25], we decided to investigate if these oxides would also have the ability to activate molecular oxygen and subsequently catalyse the oxidation of organic substrates into desired fine chemicals at mild temperatures. Given the strong affinity of Ce⁴⁺ to oxygen [22], La_{1-x}Ce_xCoO₃ ($0 \leq x \leq 1.5$) catalysts were prepared by a sol-gel method using, for the first time, methanol and ethylene glycol as complexing agents, with calcination at 600 °C for 5 h. The LaCoO₃ activity and the efficiency for aerobic oxidation of alcohols at mild temperature (e.g., 88 °C) were compared to that of materials with cerium incorporated into the framework. The catalysts performance was also compared to that of other materials, including noble metal 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, for the first time, ethylene glycol and methanol as complexing agents. Briefly, 5 mmol of La(NO₃)₃ and/or Ce(NO₃)₃ and 5 mmol of Co(NO₃)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 at 95 °C, overnight, 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(NO₃)₃ added, the samples were denoted as La_{1-x}Ce_xCoO₃ ($x = 0, 0.05, 0.10, 0.15$).

The synthesis of other materials used for comparison (namely Au/AC, Co₃O₄/AC, and K-OMS-2) is described in Supporting Information (SI).

2.2 Catalyst Characterizations

X-Ray diffraction (XRD) patterns were collected using a Bruker D8 Advance X-ray diffractometer with Cu K α ($\lambda = 1.5406 \text{ \AA}$) irradiation. Transmission electron microscopy (TEM) images were obtained on a Tecnai G² 20 S-Twin apparatus with high-resolution transmission electron microscope (200 kV). The samples were dispersed in ethanol by ultrasonic method before being deposited on the copper mesh. N₂ 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 at 200 °C for 5 h. X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Thermo Electron Corporation VG Multilab 2000 apparatus using a monochromatic Al K α X-ray source (300 W) and analyser pass energy of 25 eV. Binding energies were obtained by referencing to the C (1s) binding energy of carbon (peak at 284.6 eV).

Temperature-programmed reduction using H₂ (H₂-TPR) was performed on a FINESORB-3010 apparatus (Fantai technology company, China) equipped with TCD detector. The sample (0.10 g) was first treated in Ar atmosphere at 500 °C for 1 h and then cooled to room temperature. Then 10 vol.% H₂/Ar mixture was switched with a flow rate of 25 cm³ 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 μ L benzyl alcohol, 10 μ L 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 analysed by GC (Aglient 7890) with a flame ionization detector, using a HP-5 column and N₂ 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

Figure 1A depicts the XRD patterns of $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ ($0 \leq x \leq 1.5$) materials, showing that the perovskite structure is formed for samples with $x \leq 0.05$. A small peak at $2\theta \approx 28^\circ$, assignable to CeO_2 , is observed for $x \geq 0.1$. 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+} , a pure perovskite structure is not formed and impurities are detected (see XRD pattern in Figure S1A of SI), showing that the use of suitable complexing agents and metal ions are important for the formation of perovskite-type oxides. The effects of complexing agents and metal ions on the formation process of perovskites have been widely reported in literature [23, 27]. However, to the best of our knowledge, the temperature of 600 °C, used in this work, is the lowest calcination temperature ever reported for the preparation of perovskites by a sol-gel method. Low temperature can reduce the degree of aggregation and remain 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.

Figure 1. (A) XRD and (B) N_2 physisorption isotherms of the $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ ($0 \leq x \leq 1.5$) catalysts.

N_2 physisorption measurements (see Figure 1B) show that the surface area of $\text{La}_{0.95}\text{Ce}_{0.05}\text{CoO}_3$ is $23 \text{ m}^2/\text{g}$, which is higher than what is generally reported in literature (below $10 \text{ m}^2/\text{g}$) for this type of materials [28]. Although Ce doping does not affect much the surface area and pore size, it greatly influences the pore volume, being the largest value found for $x = 0.05$ and

the lowest for $x = 0.15$, as shown in [Table S1](#) of 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 ($0 \leq x \leq 0.5$), it decreases for higher Ce amounts ($x \geq 1.0$). This could be that some CeO_2 are formed and fill in the pores of the perovskite, as shown below by the transmission electron microscopy (TEM) images.

3.2. Surface morphology of catalysts

TEM images show that a randomly macroporous structure is formed for $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ samples, regardless of the Ce content, as depicted in [Figure 2](#). This explains why improved surface areas are observed for our samples, in comparison to the previously reported bulk perovskites [28]. It should be noted that nanoparticles are formed instead of a porous structure if methanol is replaced by formic acid (see [Figure S1B](#) of SI). This demonstrates that the complexing agents used in this work have the ability to create pores. Moreover, the process herein reported is smoother and safer, compared to the solution combustion synthesis (SCS) method, which also has the ability to create pores in perovskites but undergoes a fast and explosive reaction [29, 30].

Furthermore, it can be seen that a large amount of small white spots are visible on the walls of the materials ([Figures 2A-2D](#)), showing that both meso- and macro- pores are created. The formation of hierarchical pores in the structure is possible, as these pores are generated by the combustion of organic complexes with releasing of $\text{CO}_2/\text{H}_2\text{O}$ and/or by the decomposition of nitrate ions with releasing of NO/NO_2 , leading to varied pore sizes. To prove this, a TEM image with large magnification is shown in [Figure S2](#) of SI (for sample $x = 0.05$), where mesopores are clearly observed. The porosity can increase the contact area between the catalyst and the substrate, and subsequently the selectivity to special products, improving the reaction efficiency [31, 32].

Figure 2. TEM images of the $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ catalysts, $x = 0$ (A); 0.05 (B); 0.10 (C); 0.15 (D). HRTEM images for $x = 0.05$ (E) and 0.15 (F).

In order to confirm that CeO_2 is segregated for $x \geq 0.1$ (as found by the XRD results), high resolution TEM (HRTEM) images were obtained for $\text{La}_{0.95}\text{Ce}_{0.05}\text{CoO}_3$ and $\text{La}_{0.85}\text{Ce}_{0.15}\text{CoO}_3$ (Figures 2E and 2F). It is known from the standard XRD database that the lattice distance of the (110) crystal face of $\text{La}(\text{Ce})\text{CoO}_3$, corresponding to the characteristic diffraction peak at $2\theta \approx 33^\circ$, is 0.2711 nm, and the lattice distance of the (111) crystal face of CeO_2 , corresponding to the characteristic diffraction peak at $2\theta \approx 28^\circ$, is 0.3127 nm. Measurements performed on the obtained images show that the (111) crystal face of CeO_2 (see also Figure S3 of SI) is indeed observed on the edge of $\text{La}_{0.85}\text{Ce}_{0.15}\text{CoO}_3$, but not on $\text{La}_{0.95}\text{Ce}_{0.05}\text{CoO}_3$, confirming the XRD results.

3.3. Redox ability of catalysts

In order to determine the effect of Ce addition on the redox ability of LaCoO_3 , H_2 -TPR experiments were performed. Two reduction regions, located between 250 – 400 °C and 450 –

650 °C, are observed for all the samples, Figure 3, which can be ascribed to the reduction of Co^{3+} to Co^{2+} and Co^{2+} to Co^0 , respectively [24, 33, 34]. At lower temperatures, a main peak at 312 °C and a shoulder at 352 °C appear. Those temperatures increase as the Ce content increases. According to literature [24], the main peak can be assigned to the reduction of surface Co^{3+} to Co^{2+} and to the removal of adsorbed oxygen species, while the shoulder peak is due to the reduction of bulk Co^{3+} to Co^{2+} , accompanying with the formation of $\text{LaCoO}_{2.5}$ with a brownmillerite structure [35]. The temperature of the first reduction peak is almost the same for LaCoO_3 and $\text{La}_{0.95}\text{Ce}_{0.05}\text{CoO}_3$, both being perovskite structures. The value increases for $x > 0.5$, especially for the shoulder peak, which can be due to 1) the reduction of Co^{3+} species is delayed because of the presence of Ce^{4+} , which also consumes hydrogen ($2\text{Ce}^{4+} + \text{H}_2 \rightarrow 2\text{Ce}^{3+} + 2\text{H}^+$), and 2) the segregation of CeO_2 on the surface takes place, which suppresses the reduction process.

Figure 3. H_2 -TPR profiles of the $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ ($0 \leq x \leq 1.5$) catalysts.

At higher temperature, one peak is seen for $x = 0$ and 0.5, while two peaks are observed for $x = 1.0$ and 1.5, indicating that more species are being reduced in the latter two samples. By correlation with the XRD results, it can be inferred that the first peak is due to the reduction of

cobalt species, while the additional (shoulder) peak, observed for $x = 1.0$ and 1.5 , refers to the reduction of CeO_2 . Regarding the reduction of cobalt, the temperature of the peak maxima increases with the Ce content, from 543 to 557 and 576 °C, for samples with $x = 0, 0.05$ and 0.1 , respectively, and remains the same for $x = 0.15$. This suggests that the increase in temperature is due to the presence of Ce in the framework, which provides electrons to hydrogen and delays the reduction of cobalt species, as mentioned above. The larger the amount of Ce incorporated, the more the reduction is delayed. The unchanged temperature at $x \geq 0.1$ can mean that the Ce content in the framework reaches a saturation point. The increasing intensity of the shoulder peak, from $x = 1.0$ to 1.5 , confirms that this feature is indeed due to the reduction of segregated CeO_2 .

It is worthy to note that the reduction temperature observed in our work (400 °C) is significantly lower than that of $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ found in literature (635 °C) [36]. That is most likely due to the porous structure of our material, which allows more Co species to be exposed on the catalyst surface and be thus reduced.

3.4. Catalytic performances of catalysts for aerobic oxidation of alcohols

Figure 4A presents the activity of the $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ materials in the aerobic oxidation of benzyl alcohol to benzaldehyde, showing that LaCoO_3 ($x = 0$) is already active for the reaction, and that the Ce addition improves the activity, up to $x = 0.1$. Taking into account the results obtained by XRD, it can be inferred that the increase of activity for samples $0 \leq x \leq 1.0$ is due to the increased Ce content in the framework, which has the ability to attract electrons and improve the oxygen mobility (e.g., $\text{Ce}^{4+} + \text{O}^- = \text{Ce}^{3+} + \text{O}$) [22], as illustrated below (Figure 5). The decreased activity of sample $x = 0.15$ is ascribed to the segregation of CeO_2 , which exists on the catalyst surface and prevents the progress of the reaction. Indeed, additional experiments

demonstrated that CeO_2 alone is inactive for this reaction (not shown here). Thus, the higher activity observed for $\text{La}_{0.9}\text{Ce}_{0.1}\text{CoO}_3$ is likely due to the fact that this material has the majority of Ce ions in its framework, although traces are also found on the surface.

It is worthy to note that the selectivity in all the tests is above 95%, suggesting that benzyl alcohol is mostly converted to benzaldehyde. It is possible that some by-products, like benzoic acid, benzyl benzoate and even toluene (produced by disproportionation of benzyl alcohol [6, 37]) were formed in the reaction, but their amounts were too low to be detected. Therefore, we will discuss the main (highly selective) reaction, disregarding the formation of by-products.

Figure 4. (A) Conversion of benzyl alcohol obtained with the $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ catalyst ($t = 90$ min); (B) Dependence of benzyl alcohol conversion on the reaction time over $\text{La}_{0.9}\text{Ce}_{0.1}\text{CoO}_3$, with and without filtration of the catalyst; (C) Benzyl alcohol conversion ($t = 60$ min) obtained with different catalysts (* - for K-OMS-2 catalyst, the reaction conditions are 110 °C, 4 h, 1 mmol benzyl alcohol, 50 mg catalysts, air flow rate: 200 mL/min); (D) Benzyl alcohol conversion obtained with the fresh, dried and calcined $\text{La}_{0.9}\text{Ce}_{0.1}\text{CoO}_3$ catalyst. (Note: The selectivity to benzaldehyde in all the tests is above 95%, not shown in figures for simplicity).

The evolution of the activity with reaction time is presented in [Figure 4B](#), showing that $\text{La}_{0.9}\text{Ce}_{0.1}\text{CoO}_3$ is active for the reaction, with 25% conversion at 10 min and ~100% conversion at 90 min. Compared to Au/AC [26], $\text{Co}_3\text{O}_4/\text{AC}$ [8, 38] and K-OMS-2 [7, 39] catalysts (see synthesis details in the Experimental section of SI), we find that $\text{La}_{0.9}\text{Ce}_{0.1}\text{CoO}_3$ shows a conversion value 24% higher than the other materials, at 60 min reaction time, as shown in [Figure 4C](#), suggesting that $\text{La}_{0.9}\text{Ce}_{0.1}\text{CoO}_3$ is a very promising catalyst for this reaction. Moreover, unlike what might happen with noble metal supported catalysts, perovskites are homogeneous materials, thus no attention needs to be paid on the leaching of active sites. Indeed, we found that the activity keeps unchanged when the catalyst is filtered at 40 min and the reaction continues for another 50 min, as seen in [Figure 4B](#). This shows that the leaching of metal is negligible and the reaction is conducted by heterogeneous catalysis.

The effects of reaction temperature and concentration of substrate were also studied, showing that the increase of temperature improves the activity, while the increase of substrate has the opposite effect, as seen in [Figure S4](#) of SI. This is understandable, as the former can supply much energy to the system, facilitating the oxygen activation; while the latter can reduce the capacity of active sites and prevent the access of oxygen to the catalyst surface, restraining the reaction.

Reusability tests were conducted to confirm the possibility of the material to be used in industry. [Figure 4D](#) shows that the activity of $\text{La}_{0.9}\text{Ce}_{0.1}\text{CoO}_3$ is largely decreased if the catalyst is reused after being dried in an oven at 110 °C for 2 h, but can be significantly recovered when it is calcined in an air oven at 500 °C for 2 h (see the “Dried” and “Calcined” curves, respectively, in the Figure). This shows that the active site is not destroyed during the reaction, and the decreased activity observed for the “Dried” catalyst is most likely due to active sites being covered by the

substrate or product after the reaction. The adsorbed compounds cannot be removed by drying at 110 °C (since they have a high boiling point), but can be combusted into CO₂ if the material is calcined in air at 500 °C, regenerating the active sites. The calcined catalyst shows a slightly lower activity than the fresh sample, implying that the catalyst surface changes, and these changes are detrimental to the reaction. To confirm this, we used X-ray photoelectron spectroscopy (XPS), a powerful surface sensitive technique, to study the fresh, dried and calcined La_{0.9}Ce_{0.1}CoO₃.

3.5. Surface analysis on the chemical composition of catalysts

Table 1 shows the XPS data obtained from the fresh, dried and calcined samples. The respective XPS spectra of Co 2p, Ce 3d and O 1s of the samples are shown in Figure S5 of SI. The atomic percentage of oxygen (O 1s) increases from the fresh to the dried sample, and decreases again for the calcined material, suggesting that the oxygen vacancies of catalyst are repaired (by oxygen) after the reaction, but can be regenerated if the catalyst undergoes a calcination treatment. This explains why the activity decreases and then is recovered for the dried and calcined samples, respectively. The atomic percentage of La and Co changes with an opposite trend, but the atomic percentage of Ce increases all along the process, suggesting that Ce reacts with oxygen and forms CeO₂ on the surface, due to the strong affinity of cerium to oxygen, as illustrated below.

Table 1. Data obtained from the XPS spectra of the fresh, dried and calcined La_{0.9}Ce_{0.1}CoO₃

Sample	At.% ^a				(La+Ce)/Co	Ce ⁴⁺ /Ce ³⁺	Co ³⁺ /Co ²⁺	O _A /O _L
	O 1s	La 3d	Ce 3d	Co 2p				
Fresh	69.42	17.74	2.83	10.01	2.06	2.57	2.01	0.95
Dried	72.52	16.21	2.91	8.36	2.29	2.24	1.85	1.31
Calcined	68.92	18.60	3.07	9.41	2.30	2.03	1.86	0.82

^a Surface atomic percentages

Enrichment of lanthanum is also observed for the calcined sample, which shows a La surface percentage of 18.60%, compared to 17.74% for the fresh sample. The enrichment of La and Ce is also confirmed by the molar ratio of (La+Ce)/Co, which increases from 2.06, for the fresh sample, to 2.30, for the calcined material. The enrichment of rare-earth atoms on the surface of perovskite catalysts, after reaction, has been observed by many authors [40, 41], confirming our findings. The molar ratio of (La+Ce)/Co for the dried and calcined samples are similar, indicating that the enrichment of La and Ce occurs not in the calcination step, but in the reaction process.

The molar ratio of $\text{Ce}^{4+}/\text{Ce}^{3+}$ and $\text{Co}^{3+}/\text{Co}^{2+}$, obtained from the deconvoluted XPS spectra (see [Figure S5](#) of SI) decreases after the reaction. This is probably due to the reduction of surface Ce^{4+} or Co^{3+} in the reaction, as alcohol or aldehyde can act as reducing agents, to some extent [42, 43]. As a consequence, the surface oxygen is more abundant and a shift in the O 1s peak to higher binding energies is observed. The change in the ratio of $\text{O}_\text{A}/\text{O}_\text{L}$ (O_A is adsorbed oxygen and O_L is lattice oxygen) can be explained as follows. The increase from 0.95 to 1.31 is due to the reason that oxygen is adsorbed on the catalyst after reaction, contributing to the O_A part of the O 1s spectra. The decrease from 1.31 to 0.82 can be ascribed to two reasons: one is that the adsorbed oxygen is removed, and the other is due to the enrichment of La and Ce or to the formation of La_2O_3 and CeO_2 , which contributes to the O_L part of the O 1s spectra.

In summary, the XPS results indicate that the oxygen vacancies (active sites) can be regenerated after a calcination treatment, but the slight enrichment of La and Ce on the surface blocks the active sites, resulting in an incomplete recovery of activity. La and Ce species are hard to detect by XRD measurements, due to their trace amounts. In fact, the XRD patterns of samples, before and after the reaction, are very similar (not shown).

3.6. Proposed reaction mechanism

Based on the above discussions, a reaction mechanism for aerobic oxidation of benzyl alcohol to benzaldehyde over perovskite oxides is proposed and shown in Figure 5. The molecular oxygen is adsorbed and activated on the oxygen vacancy, and the benzyl alcohol is on the B-site cation (cobalt site). The coordination between benzyl alcohol and cobalt allows the electrons of the former to be transferred to the latter, and subsequently to the oxygen vacancy, accompanying the formation of positively charged benzyl alcohol. Meanwhile, the oxygen adsorbed on the oxygen vacancy will capture the transferred electrons and be activated, forming a negatively charged oxygen anion. The negatively charged oxygen and the positively charged benzyl alcohol react to yield benzaldehyde and water. The detailed reaction process can be found in Figure 5 (right side), where the activated oxygen attacks the carbocation of benzyl alcohol to form a C-O bond, accompanying the rupture of the C-H bond. The broken H atom will then be transferred into the oxygen site, forming an O-H bond (that is, a C-OH group). However, the presence of two -OH groups at one carbocation is not stable; they will distort and react with each other to release a water molecule, resulting in the formation of benzaldehyde.

Figure 5. Proposed reaction mechanism for aerobic oxidation of benzyl alcohol to benzaldehyde over perovskite $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ catalysts.

We propose that the role of cerium in the reaction is to enhance the mobility of surface oxygen that participates in the reaction, as described in Figure 5 (right side). The Ce^{4+} at the A-site tends to be reduced to Ce^{3+} by attracting one electron from the O^- anion. Because of the loss of electron, the oxygen atom is liberated from the oxygen vacancy and can move freely to attack the benzyl alcohol, accelerating the reaction rate. The electron will move back after the formation of the C-O bond, and Ce^{3+} will be reverted to Ce^{4+} in order to keep electro-neutrality (see step 3). When compared to lanthanum, which has a stable oxidation state, cerium has a changeable oxidation state, having the ability to attract electrons from the O^- anion and be reduced ($\text{Ce}^{4+} + \text{O}^- \rightarrow \text{Ce}^{3+} + \text{O}$), allowing the surface oxygen atoms to move freely and thus improve the activity.

Figure 6. Benzyl alcohol conversion obtained with Ce, K, and Sr substituted LaCoO_3 catalysts

In order to elucidate the importance of cerium and oxygen vacancies in the reaction, we prepared three additional samples: $\text{La}_{0.9}\text{K}_{0.1}\text{CoO}_3$, $\text{La}_{0.9}\text{Sr}_{0.1}\text{CoO}_3$ and $\text{La}_{0.9}\text{Sr}_{0.3}\text{CoO}_3$ for further investigation. From the principle of electro-neutrality, it is known that the substitution of Sr^{2+} for La^{3+} can lead to the generation of oxygen vacancies, and further Sr^{2+} substitution generates more oxygen vacancies [44]. Thus, $\text{La}_{0.9}\text{Sr}_{0.3}\text{CoO}_3$ exhibits better activity than $\text{La}_{0.9}\text{Sr}_{0.1}\text{CoO}_3$, as shown in Figure 6, due to the larger amount of oxygen vacancies generated. Similarly, $\text{La}_{0.9}\text{K}_{0.1}\text{CoO}_3$ shows better activity than $\text{La}_{0.9}\text{Sr}_{0.1}\text{CoO}_3$, due to the lower oxidation state of K^+ (vs. Sr^{2+}).

However, we found that the Ce^{4+} doped $\text{La}_{0.9}\text{Ce}_{0.1}\text{CoO}_3$ shows the highest activity among the catalysts studied, although it has higher oxidation state than K^+ and Sr^{2+} (thus fewer oxygen vacancies). This indicates that oxygen vacancies are not the only determining factor, and that the presence of Ce^{4+} ions in the framework has a positive effect, by attracting electrons from the O^- anions, as discussed above.

3.7. Applicability of catalysts to various solvents and substrates

The applicability of $\text{La}_{0.9}\text{Ce}_{0.1}\text{CoO}_3$ for alcohol oxidation reactions, using various solvents and different substrates, was also investigated. Results are listed in [Table 2](#), showing that both solvent and substrate can influence the activity. Regarding the solvents, their influence decreases with the decrease of nucleophilic ability, in the order of 1,4-dioxane > cyclohexane > toluene. The reason can be that there is a competitive coordination to the cobalt ions between the solvent and the substrate (benzyl alcohol). Thus, the chance of benzyl alcohol to be coordinated and activated on the cobalt ions decreases with the increase of the nucleophilic ability of the solvent. In the case of substrates (when toluene is used as solvent), the activity decreases in order: Benzyl alcohol > 4-Methoxybenzyl alcohol > 1-Phenylethanol > Cyclohexanol > Diphenylmethanol $\approx$ 1-Octanol, which can be explained by the competitive adsorption of functional groups, electron-donating ability and the steric hindrance of the substrates. For example, the methoxy function of the 4-methoxybenzyl alcohol is an electron donating group that can compete with the methylol moiety for coordination with the Co^{3+} ions of the catalyst, thus decreasing the activity.

Regarding 1-Phenylethanol, although the methyl group also has the ability to donate an electron, its presence will block the contact of the methylol group with the active site, due to its larger size (compared to that of the hydrogen atom), causing a stereo-hindrance effect and thus

decreasing the activity. This effect is especially crucial for diphenylmethanol, which shows negligible conversion in the studied reaction, since phenyl has an even larger size than methyl. For cyclohexanol and 1-Octanol, which have poor ability for electron donation, the low activity can thus be ascribed to their weak coordination ability with the active sites.

Table 2. Catalytic activity of the $\text{La}_{0.9}\text{Ce}_{0.1}\text{CoO}_3$ material for aerobic oxidation of alcohols using various solvents (with benzyl alcohol as substrate) and substrates (with toluene as solvent).

Entry	Solvent	Substrate	Conversion (%)
1	Toluene		95
2	cyclohexane		20
3	1,4-dioxane		8
4	Toluene	$\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{OH}$	<5
5	Toluene		30
6	Toluene		38
7	Toluene		91
8	Toluene		<5

4. Conclusions

In summary, this work reports that $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ are promising catalysts for aerobic alcohol oxidation reactions, conducted in liquid-phase, at atmospheric pressure, without the need of a promoter. In particular, $\text{La}_{0.9}\text{Ce}_{0.1}\text{CoO}_3$ shows better activity than noble metal and simple metal oxide catalysts. This material has several advantages, including 1) a suitable preparation method, which has the ability to create pores in the structure and remains a high surface area of the sample; 2) the presence of Ce^{4+} in the framework facilitates the surface oxygen to react with the substrate, by attracting one electron to form a transitional Ce^{3+} ; and 3) stable oxygen vacancies (component of the active sites), which can easily be regenerated and reused for the reaction. The excellent catalytic performances, the low cost compared to noble metals, as well as the recyclability, show that perovskites are potential materials for aerobic oxidation of alcohols in the liquid phase and atmospheric pressure, opening a new direction in the quest of materials for “greener” syntheses of organic intermediates for industrial use in the future.

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Graphical abstract