New route to CeO₂/LaCoO₃ with high oxygen mobility for total benzene oxidation

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Abstract: Electrospun LaCoO₃ and Ce(NO₃)₃·6H₂O were used as precursors to synthesize CeO₂/LaCoO₃ (SSI-LaCoCe) with high oxygen mobility by solid state impregnation. Besides, electrospinning and ball milling technologies were also adopted to prepare the other two La-Co-Ce oxides, which are denoted as ES-LaCoCe and BM-LaCoCe, respectively. The catalysts were evaluated for total benzene oxidation in comparison with bare electrospun LaCoO₃ and CeO₂, and characterized by means of O₂-TPSR, XRD, BET, TEM, H₂-TPR, O₂-TPD, and XPS. Relative to LaCoO₃, an enhanced catalytic performance can be obtained for La-Co-Ce oxides. Importantly, the concentration of surface adsorbed oxygen species from the highest to the lowest is SSI-LaCoCe > BM-LaCoCe > ES-LaCoCe, which is in good agreement with the order of catalytic activity in terms of T₅₀. The high oxygen mobility in SSI-LaCoCe can be connected with sufficient interaction between active LaCoO₃ and CeO₂. On the other hand, O₂-TPSR analysis match well with the catalytic behaviors of La-Co-Ce oxides. Moreover, the catalyst with the best performance, SSI-LaCoCe, also represents good thermal stability during the long-term continuous test.

Keywords: CeO₂/LaCoO₃; Solid state impregnation; Total benzene oxidation; O₂-TPSR; Surface

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oxygen species.

1. Introduction

Volatile organic compounds (VOCs) produced by painting, printing, petroleum refiners, fuel storage, loading operations and motor vehicles present widespread environmental implications, such as photochemical smog and ozone depletion [1, 2]. Moreover, some of these compounds are toxic and/or carcinogenic [3]. Thus, VOCs are regulated in many sectors of industry and traffic. Among VOCs removal methods, environment-friendly catalytic oxidation has been considered as one of the best options to treat VOCs emissions due to the fact it operates at lower temperature causing less NO_x formation than conventional thermal combustion which requires higher temperature (650-1100 °C) and additional fuel [4, 5].

The design of highly efficient catalysts has been the key point for catalytic oxidation. In general, supported noble metals and metal oxides can be used as efficient catalysts for total VOCs oxidation. Although the former materials are highly active at low temperature, the use of metal oxides offers considerable economic advantages in terms of operating costs [6, 7]. Among metal oxides, the perovskite oxide containing La at the A-site and Co at the B-site showed promising performance for total VOCs oxidation [8-11]. However, one major limitation of this material as efficient heterogeneous catalyst is its low surface area, providing small contact area between the catalyst and VOCs.

To tackle the aforementioned challenge, the LaCoO₃ perovskite can be modified by A/B sites substitution or supported on a high surface area of metal oxide (MO_x). In

our former work, a series of electrospun $\text{La}_{1-x}\text{Ce}_x\text{CoO}_\delta$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$) oxides were investigated for total benzene oxidation, and the increased activity over perovskite phase dominated oxides is ascribed to a larger surface area [12]. Alifanti et al. reported that an enhanced total VOCs oxidation can be obtained on ceria supported LaCoO_3 compared to bulk LaCoO_3 for an improved surface area and higher oxygen mobility [13, 14]. Another solution is to load MO_x on ABO_3 , in which ABO_3 plays roles of both support and active compose. Dai et al. prepared highly active $\text{MnO}_x/\text{LaCoO}_3$ for toluene and methanol oxidation as a result of high concentration of oxygen species adsorbed on the surface, good low-temperature reducibility and strong interaction between MnO_x and LaMnO_3 [15].

Apart from the improvement of catalyst configurations, the dispersion of active LaCoO_3 should be taken into account. Common complex route can not ensure the high dispersion of active LaCoO_3 on MO_x . What is more, LaCoO_3 and MO_x should be synthesized beforehand. Tang et al. fabricated $\text{CuO-CeO}_2/\text{SBA-15}$ catalysts by the solid state impregnation, which showed an enhanced CO-PROX activity benefitted from the reduced nanoparticle size and increased interfacial entities [16].

All the above discussions suggest that combining active electrospun LaCoO_3 with CeO_2 *via* solid state impregnation may create a promising material with excellent oxygen mobility for VOCs oxidation. Herein, we loaded CeO_2 using $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ as precursors on as-prepared electrospun LaCoO_3 by solid state impregnation. During the process, the formed CeO_2 acts as good sintering barrier and ensure sufficient contacting with LaCoO_3 nanoparticles, promoting oxygen mobility and thus good

oxidation ability. For comparison, electrospinning and ball milling techniques were also adopted to synthesize La-Co-Ce mixed oxides, in which the molar ratio of La: Co: Ce was fixed at 1: 1: 1. The actual weigh ratios of elements in La-Co-Ce mixed oxides were analyzed by Inductively Coupled Plasma (ICP) performed on a JY Ultima2 spectrometer and listed in Table 1. Meanwhile, benzene (a typical carcinogenic VOC) was selected as a probe molecule to determine the catalytic performances of as-prepared oxides. The work aims to explore the differences in the structure of obtained catalysts and correlate them with the activity of total benzene oxidation.

2. Experimental

2.1 Catalyst preparation

Bare LaCoO_3 was synthesized using an electrospinning method. Specially, 0.3690 g $\text{La}(\text{NO}_3)_3$, 0.3215 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and 2.0000 g PVP ($M_w = 1, 300, 000$) were dissolved in 20 mL of N,N-dimethylformamide (DMF) under stirring to form a homogeneous solution. The solution was subsequently transferred into a plastic syringe for electrospinning with an applied electric voltage of 23 kV, and the jet flow rate was 1.0 mL h^{-1} . The distance between the stainless steel needle and collector was fixed at 15 cm. The as-electrospun materials were calcined in air at 500°C for 4 h with a heating rate of 5°C/min to yield LaCoO_3 . Bare CeO_2 was obtained by the same procedure as described for LaCoO_3 except that the raw salt material consisted only of 0.7000 g of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$.

2.1.1 Preparation of La-Co-Ce oxides by electrospinning

The electrospinning La-Co-Ce oxides (denoted as ES-LaCoCe) was synthesized using 0.2166 g of $\text{La}(\text{NO}_3)_3$, 0.1940 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and 0.2894 g of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ as raw salt materials while the other parameters are the same to those in electrospun LaCoO_3 or CeO_2 .

2.1.2 Preparation of La-Co-Ce oxides by ball milling

The synthesis of La-Co-Ce oxides by ball milling (denoted as BM-LaCoCe) was as follows: 0.5714 g of electrospun LaCoO_3 and 0.4000 g of electrospun CeO_2 were subjected to milling in the presence of suitable water for 2 h at a speed of 1200 rpm and constant oscillation frequency of 20 cycles/s. The ball-to-powder weight ratio was 3:1. After ball milling, the powders were collected and dried in an oven for 12 h.

2.1.3 Preparation of La-Co-Ce oxides by solid state impregnation

The La-Co-Ce oxides from solid state impregnation (denoted as SSI-LaCoCe) follow a similar process reported by Tang [16]. Typically, 0.3364 g of LaCoO_3 and 0.5942 g of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were subjected to milling without medium for 0.5 h at a speed of 1200 rpm and constant oscillation frequency of 20 cycles/s. The ball-to-powder weight ratio was 3:1. Then the mixed powder was transferred into a crucible, which was placed in an oven at 80 °C for 12 h and finally in a muffle furnace. The thermal treatment in air started at room temperature to 500 °C with a heating ramp of 1 °C min⁻¹, and maintained at that temperature for 4 h.

2.2. Catalytic tests

The activity measurement of the catalysts for total benzene oxidation was carried out in a continuous-flow quartz fixed-bed reactor (i.d. = 10 mm) at atmospheric

pressure. 0.05 g of the catalysts with 40-80 mesh was used in each test. A thermocouple was inserted inside the catalytic bed to measure the reaction temperature. The reaction feed (flow rate = 80 mL/min) was composed of 500 ppm benzene and air, corresponding to the weight space velocity (WHSV) of 96,000 mL g⁻¹ h⁻¹. The measurement of catalytic performance was made after 30 min at each testing temperature. The benzene conversion was measured by determining the outlet concentration of benzene using an on-line GC equipped with a flame ionization detector (FID).

2.3. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Bruker AXS D8 Avance X-ray diffractometer with Cu-K_α radiation at 40 kV and 40 mA. The diffraction patterns were recorded in angles 2θ ranging from 10–80° with a step size of 0.02° and a counting time of 2 s per step. The textural properties were determined by N₂ adsorption/desorption at 77 K using BELSORP-mini II apparatus. Prior to the measurement, the catalysts were degassed at 250 °C for 6 h under vacuum. Transmission electron microscope (TEM) images were obtained using a JEM-2010 microscope operating at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on Physical Electronics Quantum 2000, equipped with a monochromatic Al-K_α source (K_α = 1,486.6 eV) and a charge neutralizer. Binding energy was calibrated with C 1s = 284.8 eV.

H₂ temperature-programmed reduction (H₂-TPR) was carried out on an AutoChem 2920 instrument equipped with a thermal conductivity detector (TCD). Before

H₂-TPR measurement, 0.05 g of the sample was pretreated with He (30 ml/min) at 300 °C for 0.5 h, and then cooled down to room temperature. Subsequently, the sample was exposed to 10 vol% H₂/Ar stream (30 mL/min) and ramped from 40 to 900 °C at a constant rate of 10 °C /min. O₂ temperature-programmed desorption (O₂-TPD) was performed by using the same apparatus. The sample (0.05 g) was first treated under 3 vol% O₂/He at 300 °C for 0.5 h. After the temperature was slowly cooled down to room temperature, followed by a He purge (40 mL/min) for 20 min, the sample was heated from 40 to 900 °C. The signal of desorbed oxygen was monitored by a quadrupolar mass spectrometer (Hiden Analytical Ltd, UK).

Temperature-programmed surface reaction (TPSR) experiments were performed on the same apparatus as for H₂-TPR. Before the experiment, the sample was pretreated in He at 300 °C for 0.5 h. After the sample was cooled to 50 °C, the He flow was switched to a pulse injection of 10 vol% benzene/He until complete adsorption of benzene, followed by a purging in He for 10 min. Finally, the TPSR run was started under a flow of 40 ml/min of 3 vol% O₂/He ramping at 5 °C /min to 500 °C. A mass spectrometer (Cirrus) was used for on-line monitoring of effluent gases. The signals at mass-to-charge (m/z) ratios of 28 (CO), 44 (CO₂) and 78 (C₆H₆) were monitored, and the profile of CO had been deducted from the contribution of m/z =28 fragment of CO₂.

3. Results and discussion

3.1. Benzene oxidation and O₂-TPSR analysis

The catalytic activities of La-Co-Ce oxides, bare electrospun LaCoO₃ and CeO₂ for

total benzene oxidation as a function of the reaction temperature are shown in Fig. 1a. The temperature at which the benzene conversion reached 50% (T_{50}) and 90% (T_{90}) is taken as an evaluation of the catalytic activity. Bare CeO_2 shows a peculiar activity with reaction temperature, which is similarly reported by Lai [17]. The benzene conversion is increased until 270 °C, then dropped up to 400 °C and again increased with increasing temperature. As for bare LaCoO_3 , if comparing T_{50} , it exhibits an inferior performance than La-Co-Ce oxides. This result indicates that compositing CeO_2 is conducive to promote benzene oxidation. Regarding La-Co-Ce oxides, a lowest T_{50} value of 288 °C for benzene oxidation is achieved over SSI-LaCoCe, whereas that is 295 and 311 °C for BM-LaCoCe and ES-LaCoCe, respectively. Compared to previous studies [14, 18], SSI-LaCoCe is a good candidate to benzene oxidation. Meanwhile, SSI-LaCoCe shows a lowest T_{90} value, which is raised by 88 and 57 °C for BM-LaCoCe and ES-LaCoCe, respectively. However, the catalytic oxidation is triggered faster for BM-LaCoCe when compared to the other two La-Co-Ce oxides below 280 °C. The reason will be explored by analyzing the active oxygen species accumulated on the catalysts using O_2 -TPD technique. Fig. 1b shows the on-stream reaction experiment of the best-performanced catalyst SSI-LaCoCe at 500 °C. No significant drop in catalytic activity with 48 h on-stream reaction can be seen, indicating that SSI-LaCoCe possesses high thermal stability in catalytic oxidation.

Additional O_2 -TPSR experiments were carried out to gain information about the final product and the reactivity of preadsorbed benzene over ES-LaCoCe,

BM-LaCoCe and SSI-LaCoCe, the results of which are depicted in Fig. 2. No CO and benzene are observed in the entire process whereas only CO₂ is detected in all cases, demonstrating three catalysts all show excellent deep oxidation activity. From Fig. 2a, it is observed that the onset temperature of CO₂ desorption is increased as follows: BM-LaCoCe (143 °C) < SSI-LaCoCe (164 °C) < ES-LaCoCe (180 °C) . It implies that BM-LaCoCe could exhibit the best oxidation performance at low temperature, which is in line with the results of catalytic activities tested below 280 °C. Nevertheless, the amount of produced CO₂ is considerably larger on SSI-LaCoCe with respect to the other two catalysts, going well with its most powerful oxidation ability at high temperature. For example, a benzene conversion of 90% can be achieved at 405 °C over SSI-LaCoCe, but only 79% and 81% can be obtained over BM-LaCoCe and ES-LaCoCe under the same tested temperature, respectively.

3.2. Structure, texture and morphologies of catalysts

Fig.3 shows the XRD patterns of the as-prepared samples. It is revealed that the prepared CeO₂ is indexed to a pure fluorite cubic structure (JCPDS 03-065-5923), while electrospun LaCoO₃ corresponds to the Rhombohedral structure of cobalt lanthanum oxide (JCPDS 00-048-0123). For BM-LaCoCe and SSI-LaCoCe, a mixture phase containing cubic CeO₂ and LaCoO₃ perovskite is found. Moreover, the crystallinity degree is lower for SSI-LaCoCe, indicating the “barrier effect” (hindering the grown-up of nanoparticles mutually) is more significant when using a solid state impregnation. Differently, XRD pattern of ES-LaCoCe shows the main crystalline phase of cubic Ce₄O₇ as well as some segregated Co₃O₄. Ce₄O₇ can be considered as a

mixture oxide of Ce_2O_3 and CeO_2 , and this finding is assumed for the direct calcination of as-electrospun Ce^{3+} -containing salt rather than hydroxide whose Ce^{3+} is easily oxidized to Ce^{4+} [19]. Besides, No reflections assigned to La_2O_3 but the presence of small Co_3O_4 points to the possible existence of LaCoO_3 , which can not be detected possibly due to a dilution effect [13]. The dominated Ce_4O_7 phase in ES-LaCoCe leads to its weaker oxidation ability with respect to the other two La-Co-Ce oxides. Additionally, the crystallite sizes of LaCoO_3 in La-Co-Ce oxides were calculated from the line broadening of (1 0 4) reflection of LaCoO_3 by using the Debye-Scherrer formular (Table 1). The LaCoO_3 crystallize size decreases from 21.5 nm in the pure LaCoO_3 to 13.4, 11.0, <11.0 nm in samples BM-LaCoCe, SSI-LaCoCe, ES-LaCoCe, respectively.

Textural properties of the catalysts were characterized by nitrogen physisorption, and the isotherms are plotted in Fig. 4. All the N_2 physisorption isotherms are Type IV indicative of mesoporous materials, but their hysteresis loops associated with capillary condensation vary with different samples. While for LaCoO_3 and BM-LaCoCe the hysteresis loops occur at relatively higher pressure, implying larger pore radii than those of the other investigated samples. BET surface area and pore volume are shown in Table 1. The electrospun CeO_2 and LaCoO_3 exhibit a surface area of 109 and 18 m^2/g , respectively. Because the surface area of La-Co-Ce oxides is mainly contributed to the higher surface area of CeO_2 , a notable drop in the specific surface area is observed when compared with CeO_2 . Among La-Co-Ce oxides, ES-LaCoCe shows the highest surface area (60 m^2/g) probably related to its

dominated phase of Ce_4O_7 and the largest pore volume, $0.176 \text{ cm}^3/\text{g}$. However, combined with the results of catalytic activity tests, it is concluded that textural property is a minor factor for affecting the total benzene oxidation in these catalysts.

The morphology of ES-LaCoCe, BM-LaCoCe and SSI-LaCoCe was investigated using TEM technology, as shown in Fig. 5. The TEM images (Fig. 5a-c) show that all La-Co-Ce oxides feature an irregular morphology of aggregated nanoparticles, and the average grain size is smaller in ES-LaCoCe. The typical HRTEM image of ES-LaCoCe (Fig. 5d) shows the Ce_3O_4 grains with fringe spacing of 0.3185 and 0.1958 nm corresponding to (111) and (220) planes, respectively, and LaCoO_3 grain with a fringe spacing of 0.2720 nm corresponding to (110) plane. The result is in good accordance with the XRD analysis of ES-LaCoCe. In the case of BM-LaCoCe and SSI-LaCoCe, sufficient interfacial entities between active LaCoO_3 and CeO_2 nanoparticles are found, which strongly improves the reactivity for benzene oxidation. LaCoO_3 grains reveal fringe spacing of 0.2718-0.2719 and 0.2684-0.2816 nm corresponding to (110) and (104) planes respectively, and CeO_2 grains reveal fringe spacing of 0.3112-0.3117 nm corresponding to (111) plane.

3.3. Redox and surface properties

H_2 -TPR offers an effective way to study the catalysts redox properties, the results of which are illustrated in Fig. 6. There are two main reduction peaks at about 510 and 812 °C for bare CeO_2 , which is ascribed to the reduction of the surface oxygen and bulk oxygen, respectively [20]. Remarkably, a reduction peak at low temperature (375 °C) could be related with small ceria crystallites [21] via electrospinning process. In

the case of LaCoO_3 , two main successive reduction steps are observed. The signal in the temperature range of 200-450 °C is ascribed to the reduction of surface/lattice Co^{3+} to Co^{2+} and the removal of adsorbed oxygen species, while the second signal at high temperature is caused by the reduction of Co^{2+} to Co^0 [22, 23]. Considering La-Co-Ce oxides, the ascription of H_2 reduction peaks is difficult because of interaction between Co_3O_4 , CeO_2 and LaCoO_3 according to the shift of first main reduction peak position compared to bare LaCoO_3 and CeO_2 , as well as some adsorbed oxygen species like $\text{Co}^{3+}\text{O}^{2-}\text{Co}^{3+}\text{O}_2(\text{g})$. Moreover, it is found that H_2 consumption occurs immediately at 50 °C for La-Co-Ce catalysts, indicating enhanced low-temperature reducibility. Since the catalytic activity is evaluated below 500 °C, we compare the H_2 consumption amount of three La-Co-Ce oxides in that temperature range. Obviously, ES-LaCoCe exhibits smaller H_2 consumption than BM-LaCoCe and SSI-LaCoCe, indicating less easily reducible species in ES-LaCoCe, which correlates with its worst catalytic activity.

To study the relationship between the catalytic performance and the oxygen species absorbed on the surface of the catalysts, O_2 -TPD were conducted within the temperature range of 40-900 °C for three La-Co-Ce oxides. The O_2 -TPD plots for LaCoO_3 perovskite consist of the three oxygen desorption regions as depicted in Fig. 7. The α desorption peak is ascribed to superoxide ion O_2^- , the β desorption peak is related to peroxide ion $\text{O}_2^{2-}/\text{O}^-$, and the γ desorption peak can be assigned to lattice oxygen ion O^{2-} [24].

From Fig. 7, it can be seen the maximum of α desorption peak follows the order of

BM-LaCoCe < SSI-LaCoCe < ES-LaCoCe, which can well elucidate the highest activity of BM-LaCoCe catalyst below 280 °C. Regarding β desorption peak, SSI-LaCoCe sample reveals the distinct desorption peak centered at 441 °C. It is in accordance with its highest catalytic performance above 280 °C. It should be pointed out that the global amount of surface active oxygen species, in terms of the sum of α and β desorption area, is in the sequence of ES-LaCoCe < BM-LaCoCe < SSI-LaCoCe. Thus SSI-LaCoCe should exhibit the highest oxidation activity since electrophilic O_{ads} (O_2^- , O_2^{2-} , O^-) plays a critical role in the total oxidation of organics [25].

To get the information about the elements on the surface of the catalysts, XPS spectra of the Ce 3d, Co 2p and O 1s are analyzed, as shown in Fig. 8 and Table 2. The complex spectra of Ce 3d are deconvoluted into eight peaks corresponding to four pairs of spin-orbit doublets. The four main $3d_{5/2}$ features at 882.5, 884.6, 888.9 and 898.3 eV are assigned to v, v', v'' and v''' components, while the $3d_{3/2}$ features at 901.0, 904.1, 907.4 and 916.5 eV are assigned to u, u', u'' and u''' components, respectively [26]. The amount of Ce^{3+} is estimated by calculating the relative integrated areas of u' and v' to the total bands [27], and a slightly higher Ce^{3+} concentration (Table 2) is found in ES-LaCoCe probably due to the appearance of Ce_4O_7 phase in the catalyst.

The Co $2p_{3/2}$ signal at binding energy (BE) = 779.8 eV is indicative of surface Co^{3+} , whereas the one at BE = 781.6 eV together with the shake-up satellite at BE = 786.7 eV demonstrates the presence of surface Co^{2+} [28]. The surface Co^{2+}/Co^{3+} molar ratios

of the samples are listed in Table 2. In comparison with ES-LaCoCe, the surface $\text{Co}^{2+}/\text{Co}^{3+}$ molar ratio increases to 1.10 and 1.33 for BM-LaCoCe and SSI-LaCoCe, respectively. It implies SSI-LaCoCe possesses the highest concentration of surface oxygen vacancies [29], which could favor oxygen mobility and accelerate total benzene oxidation.

As for the O 1s spectra, three kinds of oxygen species are distinguished. The oxygen species at BE = 529.3, 531.5 and 532.4 eV could be assigned to surface lattice oxygen (O_{latt}), the electrophilic O_{ads} (eg., O_2^- , O_2^{2-} , O^-) and physically adsorbed oxygen species (eg., H_2O , O_2), respectively [30]. Generally, the higher value of $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$, the better performance of total organics oxidation obeying with a suprafacial mechanism [31]. From table 2, it is found the value of $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$ is the highest for SSI-LaCoCe, which is in a great agreement with the results of O_2 -TPD, further verifying the important role of electrophilic O_{ads} in total benzene oxidation.

4. Conclusions

$\text{CeO}_2/\text{LaCoO}_3$ with sufficient interfacial entities was synthesized using electrospun LaCoO_3 and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ as precursors *via* solid state impregnation. It was evaluated in total benzene oxidation in comparison with electrospinning and ball milling prepared catalysts. The results of catalytic performances match well with O_2 -TPSR analysis. A mixture phase of cubic CeO_2 and LaCoO_3 perovskite is detected in the procedure of ball milling or solid state impregnation, while electrospinning method gives rise to a dominant phase of Ce_4O_7 and weak reducibility, leading to poor oxidation ability. O_2 -TPD and XPS results demonstrate that SSI-LaCoCe possesses

the largest amounts of electrophilic oxygen species, which are helpful for total benzene oxidation obeying with a suprafacial mechanism. Thus good reducibility and high concentration of surface oxygen adspecies are responsible for the superior catalytic performance of SSI-LaCoCe. Additionally, the best catalyst SSI-LaCoCe shows high thermal stability at 500 °C with a durable time of 48 h.

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Figure Captions:

Fig. 1. (a) Benzene conversion as a function of reaction temperature of La-Co-Ce oxides, LaCoO_3 and CeO_2 , (b) Catalytic activity versus on-stream reaction time over the best-performanced catalyst SSI-LaCoCe for the oxidation of benzene at 500 °C.

Fig. 2. O_2 -TPSR profiles of (a) CO_2 , (b) C_6H_6 and (c) CO after adsorption of C_6H_6 at 50 °C.

Fig. 3. XRD patterns of (1) CeO_2 , (2) LaCoO_3 , (3) ES-LaCoCe, (4) BM-LaCoCe and (5) SSI-LaCoCe.

Fig. 4. Nitrogen physisorption isotherms of catalysts.

Fig. 5. (HR) TEM images of ES-LaCoCe (a, d), BM-LaCoCe (b, e), and SSI-LaCoCe (c, f).

Fig. 6. H_2 -TPR profiles of catalysts.

Fig. 7. O_2 -TPD profiles of samples: (1) ES-LaCoCe, (2) BM-LaCoCe, and (3) SSI-LaCoCe.

Fig. 8. Ce 3d, Co 2p and O 1s XPS spectra of (1) ES-LaCoCe, (2) BM-LaCoCe, and (3) SSI-LaCoCe.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

Table 1

Textural and structural properties as well as element weight ratios of samples.

Sample	BET surface area (m ² /g) ^a	Average pore diameter (nm) ^b	Pore volume (cm ³ /g) ^c	Crystallite size (nm) ^d	elemental weight ratio (wt%) ^e		
					La	Co	Ce
CeO ₂	109	3.9	0.140	-	-	-	-
LaCoO ₃	18	16.4	0.129	21.5	-	-	-
ES-LaCoCe	60	5.0	0.176	< 11.0	25.0	13.4	33.5
BM-LaCoCe	45	21.8	0.123	13.4	27.3	14.2	30.3
SSI-LaCoCe	44	3.9	0.078	11.0	22.6	12.7	32.0

^a Calculated by BET method.^b Determined by BJH method using the desorption branch.^c Determined from amount adsorbed at P/P₀ = 0.99.^d Calculated by applying the Debye-Scherrer formula on the LaCoO₃ (1 0 4) diffraction peaks at 33.2 °.^e Measured by ICP.

Table 2

XPS-derived characteristics for the La-Co-Ce mixed oxides.

Sample	$\text{Ce}^{3+}/(\text{Ce}^{3+}+\text{Ce}^{4+})$	$\text{Co}^{2+}/\text{Co}^{3+}$	$\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$
ES-LaCoCe	0.18	1.06	0.59
BM-LaCoCe	0.15	1.10	0.63
SSI-LaCoCe	0.15	1.33	0.77