Highly Dispersed Pt Species with Excellent Stability and Catalytic Performance by Reducing a Perovskite-Type Oxide Precursor for CO Oxidation

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Abstract

A new scheme for the preparation of highly dispersed precious metal catalysts is proposed in this work. Samples of $\text{LaCo}_{1-x}\text{Pt}_x\text{O}_3/\text{SiO}_2$ ($x = 0.03, 0.05, 0.07, 0.09$, and 0.10) were prepared through a simple method of citrate acid complexation combined with impregnation. In a nanocrystallite of $\text{LaCo}_{1-x}\text{Pt}_x\text{O}_3$, ions of lanthanum, cobalt, and platinum are evenly mixed at the atomic level and confined within the nanocrystallite. In the reduction process, platinum ions were reduced and migrated onto the surface of the nanocrystallite, and the platinum should be highly dispersed owing to the even mixing of the platinum ions in the precursor. When $x = 0.05$ or lower, the highest dispersion of Pt could be achieved. The highly dispersed Pt is stable, because of the strong interaction between Pt atoms and the support. The catalysts were characterized by BET surface area, temperature-programmed reduction, X-ray diffraction, transmission electron microscopy, CO temperature-programmed desorption, and turnover frequency. Compared with general precious metal Pt catalysts, the $\text{LaCo}_{0.95}\text{Pt}_{0.05}\text{O}_3/\text{SiO}_2$ catalyst exhibited better activity for CO oxidation, and it maintained stability at a high temperature of 400°C for 250 h with complete CO conversion.

Keywords High dispersion · Perovskite-type oxide · Platinum · Carbon monoxide · Catalytic oxidation

Introduction

Supported precious metal catalysts are widely used in the industry for their very good catalytic performance. The size of metal nanoparticles (NPs) is a key element in terms of the catalytic activity. For general metal catalysts, only part of the metal atoms or ions serves as the active sites to play the catalytic role during the reaction. To improve the utilization of noble metals, higher distributions of the metal active sites are expected [1, 2]. Recently, theoretical and experimental results have proved that highly dispersed catalysts have better catalytic activity and selectivity than common metal particles [3]. Particularly for precious metal catalysts, the

highly dispersed catalysts can improve the atom catalytic efficiency substantially, thus reducing the cost. At the same time, the highly dispersed metallic atoms make it possible to study the mechanism of heterogeneous catalysis at the molecular level [4, 5].

As mentioned above, highly dispersed catalysts have many advantages, but their preparation is a challenge. The key problem is the high surface free energy of atoms, which promotes aggregation to form small clusters [6]. The reported preparation methods for highly dispersed catalysts include the following: Ramos-Fernandez et al. [7] used the metal organic framework to prepare PTA-MOF catalysts for CO oxidation and the hydrogenation of toluene. Watanabe et al. [8] prepared highly dispersed Pt + Ru alloy clusters through the co-deposition of platinum and ruthenium oxides at the atomic level for the electro-oxidation of methanol. In 2011, Qiao et al. [9] prepared a catalyst of single atom Pt/ FeO_x by a co-precipitation method for CO oxidation. A photochemical method was used to synthesize Pd/ TiO_2 monatomic catalysts for styrene hydrogenation [10]. High-temperature heat transfer atom trapping on polyhedral ceria and nanorods was adopted to synthesize thermally stable

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single-atom platinum-on-ceria catalysts for CO oxidation [11]. The methods above can only be applied to a narrow range, as they are expensive and of low-yield. Therefore, simple and feasible methods for the preparation are needed.

Perovskite-type oxides (PTOs) are mixed oxides with a cubic lattice structure of general formula ABO_3 , where rare earth elements are usually at the A-site positions and the smaller transition metals are located at the B-sites. The large range of tolerance factors ($0.75 \leq t \leq 1.0$) makes it possible to tolerate significant partial substitution. At the same time, oxygen vacancies caused by doping of perovskites with different species are helpful to the activity of many oxidation reactions. PTOs also have other advantages, such as lower cost and higher thermal stability than noble metals. Furthermore, they exhibit excellent partial substitution tolerance for precious metals (Pd, Rh, and Pt) and are capable of recycling the noble metal atoms in and out of the perovskite lattice in oxidizing and reducing conditions, which can prevent the aggregation of the metal atoms [12–14]. The specific surface area of a PTO is low, generally below $10 \text{ m}^2/\text{g}$ [15]. Loading a PTO on a support with high specific surface area is one strategy to overcome this problem.

In this article, a new scheme for preparing highly dispersed catalyst was proposed, as shown in Scheme 1. Taking advantage of the strong interaction between a PTO and precious metals (Pt, here), by supporting a PTO with high specific surface area on silica, it is possible to overcome their disadvantage of low specific surface area. A PTO of $\text{LaCo}_{0.95}\text{Pt}_{0.05}\text{O}_3$ was highly dispersed on SiO_2 , where the

Scheme 1 A schematic illustration for preparing the highly dispersed catalyst of $\text{Pt}/\text{LaCoO}_3/\text{SiO}_2$

ions of Pt should be uniformly dispersed in the PTO lattice. In the reduction process, ions of Pt should be reduced and migrate onto the surface of the PTO to achieve high

dispersions. The as-prepared catalyst showed high activity and very good stability to CO oxidation.

Experimental

Catalyst Preparation

Materials

The catalysts were prepared by a citric acid complexation, combined with an incipient wetness impregnation method. The chemicals involved in the preparation of the catalysts were as follows: $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and citric acid ($\text{C}_6\text{H}_8\text{O}_7$) supplied by Aladdin Industrial Corporation, China; $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ procured from Tianjin Delan Fine Chemical Plant; $\text{C}_2\text{H}_6\text{O}_2$ purchased from Tianjin Guangfu Fine Chemical Research Institute; and silica (SiO_2) commercially available from Qingdao Bangkai Separation Material Co., Ltd.

Preparation of $\text{LaCo}_{1-x}\text{Pt}_x\text{O}_3/\text{SiO}_2$

$\text{LaCo}_{0.95}\text{Pt}_{0.05}\text{O}_3/\text{SiO}_2$ is given as the example to illustrate the preparation of $\text{LaCo}_{1-x}\text{Pt}_x\text{O}_3/\text{SiO}_2$. Typically, 2 g of $\text{LaCo}_{0.95}\text{Pt}_{0.05}\text{O}_3/\text{SiO}_2$ was prepared according to the following method. The support, 1.74 g of SiO_2 , was calcined at 700°C for 6 h to break down impurities and then dried at 120°C for 12 h to remove absorbed air and water. The SiO_2 support was incipient-wetness-impregnated with an aqueous solution of lanthanum nitrate (1.03 mmol), cobalt nitrate (0.98 mmol), and chloroplatinic acid (0.05 mmol) at a La/Co/Pt molar ratio of 1:0.95:0.05, while citric acid in 120 mol% of the total cations (2.47 mmol) and ethylene glycol in 20 mol% of the citric acid (0.49 mmol) were added. The mixture was left for 24 h to disperse evenly. After complexing for 6 h at 80°C , the sample was dried for 12 h at 120°C . Then, the sample was calcined at 350°C for 2 h with a heating rate of $2^\circ\text{C}/\text{min}$ to decompose citric acid and subsequently was washed to remove chloride with deionized water. After drying at 120°C for 12 h, the sample was calcined at 700°C for 6 h with a heating rate of $2^\circ\text{C}/\text{min}$. The mass fractions of Pt in the calcined catalysts of $\text{LaCo}_{0.97}\text{Pt}_{0.03}\text{O}_3/\text{SiO}_2$, $\text{LaCo}_{0.95}\text{Pt}_{0.05}\text{O}_3/\text{SiO}_2$, $\text{LaCo}_{0.93}\text{Pt}_{0.07}\text{O}_3/\text{SiO}_2$, $\text{LaCo}_{0.91}\text{Pt}_{0.09}\text{O}_3/\text{SiO}_2$, and $\text{LaCo}_{0.90}\text{Pt}_{0.10}\text{O}_3/\text{SiO}_2$ are 0.3, 0.5, 0.7, 0.88, and 1%, respectively, and the mass fraction of $\text{LaCo}_{1-x}\text{Pt}_x\text{O}_3$ in all of the catalysts is 13%.

Similarly, Pt/SiO_2 and $\text{LaCoPtO}_3/\text{SiO}_2$ were prepared by the same method with a mass fraction of 0.5% for Pt, except that no citric acid or ethylene glycol was added during the preparation process. $\text{LaCoO}_3/\text{SiO}_2$ was also prepared by the same method with a mass fraction of 13% for the perovskite.

For comparison, unsupported PTOs of $\text{LaCo}_{1-x}\text{Pt}_x\text{O}_3$ were prepared similarly as for $\text{LaCo}_{1-x}\text{Pt}_x\text{O}_3/\text{SiO}_2$, except that no SiO_2 support was added for impregnation.

Catalyst Characterization

Specific surface areas and hole structures were calculated by the BET method and the BJH model. The data came from a Micromeritics apparatus, model ASAP-2020, and were collected at -196°C . Before the measurements, 200 mg of samples were pretreated for 2 h at 300°C to remove absorbed air and moisture.

H_2 -temperature-programmed reduction (H_2 -TPR) experiments were performed on a Thermo-Finnigan TP-5079 which was equipped with a thermal conductivity detector. Samples of 150 mg were heated from 30 to 900°C at a heating rate of $10^\circ\text{C}/\text{min}$ under a reduction gas mixture of 5 vol% H_2/Ar with a flow rate of $25\text{ cm}^3/\text{min}$. It should be noted that 19.5 mg of LaCoO_3 and 130.5 mg of quartz sand were mixed for the TPR tests.

X-ray diffraction (XRD) experiments were conducted on a Bruker D8-Focus X-ray diffractometer with nickel-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406\text{ \AA}$). The data range was from 15 to 85° (2θ range), with a scanning speed of $8^\circ/\text{min}$.

Transmission electron microscopy (TEM) measurements were performed on a Technai G² F20 transmission electron microscope. The Pt-containing samples were pretreated at 220°C in hydrogen for 2 h, followed by grinding and dispersing in ethanol. The samples were loaded onto Cu grid for testing.

During CO temperature-programmed desorption (CO-TPD) measurements, the $\text{LaCo}_{1-x}\text{Pt}_x\text{O}_3/\text{SiO}_2$ catalysts were first reduced in H_2 at 220°C for 2 h. The chemisorption of CO onto the catalysts was performed in a reactor at atmospheric pressure and 25°C . The catalyst was outgassed and purged with helium of ultrahigh purity grade (99.9999%, $30\text{ cm}^3/\text{min}$) at 400°C for 0.5 h. The sample was purged at 50°C for 3 h and allowed to adsorb CO under CO atmosphere for 2 h. Then, TPD measurements were completed at a constant heating rate ($5^\circ\text{C}/\text{min}$) from 50 to 500°C under helium flow ($30\text{ cm}^3/\text{min}$) by an SRS RGA300 quadrupole mass spectrometer. The Pt dispersion (D) was calculated based on the following equation [16]:

$$D(\%) = \frac{M_{\text{CO}} \times \text{SF} \times \text{FW}_{\text{m}}}{\text{WF}_{\text{m}} \times m_{\text{cat}}} \times 100 \quad (1)$$

where M_{CO} is the amount of CO adsorption in μmol ; SF is the stoichiometric factor, i.e., the Pt/CO ratio in chemisorption, which is 1 in this study [17]; FW_{m} is the formula weight of the metal Pt; WF_{m} is the weight fraction of the metal Pt in the catalyst; and m_{cat} is the mass of the catalyst.

Based on the Pt dispersion in the catalyst, the turnover frequency (TOF) value at 145°C was calculated according to the following equation [18]:

$$\text{TOF (s}^{-1}\text{)} = X_{\text{CO}} F_{\text{CO}} \frac{M_{\text{Pt}}}{m_{\text{cat}} X_{\text{Pt}} D_{\text{Pt}}} \quad (2)$$

where X_{CO} is the CO conversion at 145°C ; F_{CO} is the flow rate of CO in mol/s ; m_{cat} is the mass of catalyst; X_{Pt} is the Pt loading in the catalyst; D_{Pt} is the dispersion of Pt which was calculated based on the CO-TPD results; and M_{Pt} is the molar weight of Pt (195.1 g/mol).

Catalytic Performance Test for CO Oxidation

The catalytic activity measurements were performed on a fixed bed micro-reactor at atmospheric pressure. Firstly, a 100 mg sample was reduced at 220°C for 2 h in H_2 atmosphere with a heating rate of $5^\circ\text{C}/\text{min}$. The feed gases contained 1% CO, 1% O_2 , and 98 vol% N_2 and reached the flow rate of $40\text{ mL}/\text{min}$ in total. The catalyst sample was well distributed from 40 to 60 mesh. A thermocouple was inserted into the catalyst bed and used to measure the reaction temperature. The reaction exhaust was analyzed by an online gas chromatograph, SP-3420, which was equipped with a TCD and a 5 A molecular sieve column. The performance of samples was determined by CO conversion, which was defined as follows [19]:

$$\text{Conversion of CO(\%)} : X_{\text{CO}} = \frac{[\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}}{[\text{CO}]_{\text{in}}} \times 100 \quad (3)$$

where $[\text{CO}]_{\text{in}}$ is the concentration of CO in the feed gases and $[\text{CO}]_{\text{out}}$ is the concentration of CO in the effluent stream.

Results and Discussion

Catalyst Characterizations

N_2 Adsorption and Desorption Isotherms

Nitrogen adsorption–desorption isotherms and the BJH pore size distribution of SiO_2 and $\text{LaCo}_{0.95}\text{Pt}_{0.05}\text{O}_3/\text{SiO}_2$ are shown in Fig. 1. The isotherms belong to Type IV under IUPAC classifications [20], which closely relates to the properties of a mesoporous structure. As shown in Fig. 1, the most probable size and the specific surface area declined slightly from 9.45 nm and $369.8\text{ m}^2/\text{g}$ for the SiO_2 support to 8.76 nm and $326.6\text{ m}^2/\text{g}$ for $\text{LaCo}_{0.95}\text{Pt}_{0.05}\text{O}_3/\text{SiO}_2$, respectively, which is likely caused by the blockage of some mesopores by the NPs of the PTO. The average pore size (12 nm) is larger than the size of the PTO (below 9 nm),

which can be seen in Fig. 4a–c, meaning that the NPs of the PTO can enter the mesopores. The specific surface area of the SiO_2 support is large enough to highly disperse the PTO of $\text{LaCo}_{0.95}\text{Pt}_{0.05}\text{O}_3$ when the amount of the PTO loaded is 13 wt%.

Temperature-Programmed Reduction (TPR)

The TPR profiles are shown in Fig. 2. The reduction curves of LaCoO_3 have been well studied, where the peak at the low temperature of approximately 400 °C is attributed to the reduction of Co^{3+} to Co^{2+} , and the peak at high temperature of approximately 570 °C is attributed to the reduction of Co^{2+} to metallic Co^0 [21, 22]. Compared with LaCoO_3 , for $\text{LaCoO}_3/\text{SiO}_2$, the peak at around 570 °C moved toward a higher temperature, which is due to the effect of the carrier. Compared with $\text{LaCoO}_3/\text{SiO}_2$, the TPR peaks for $\text{LaCo}_{1-x}\text{Pt}_x\text{O}_3/\text{SiO}_2$ shifted back to lower temperatures, and the magnitude of the shift increased with the increase in Pt content in the catalyst, which agrees with the shift due to the hydrogen spillover from the sites of Pt as pointed out in previous works [23, 24]. The most important information is that the outlines of the TPR profiles of $\text{LaCo}_{1-x}\text{Pt}_x\text{O}_3/\text{SiO}_2$ are similar to that of the PTO of LaCoO_3 , indicating that PTO was formed as $\text{LaCo}_{1-x}\text{Pt}_x\text{O}_3/\text{SiO}_2$.

Ions of Pt in the PTO lattice of $\text{LaCo}_{1-x}\text{Pt}_x\text{O}_3/\text{SiO}_2$ can easily be reduced at a reduction temperature generally lower than 300 °C [3, 17, 19]. Additionally, the content of Pt in $\text{LaCo}_{1-x}\text{Pt}_x\text{O}_3/\text{SiO}_2$ is small; therefore, no reduction peaks corresponding to the ions of Pt were detected. The TPR results indicate that after reduction, $\text{LaCo}_{1-x}\text{Pt}_x\text{O}_3/\text{SiO}_2$ was converted to $\text{Pt}/\text{LaCoO}_3/\text{SiO}_2$, which is further confirmed by the following XRD and TEM results.

Fig. 1 Nitrogen adsorption–desorption isotherms and BJH pore diameter distributions, (square) SiO_2 calcined at 700 °C, (circle) $\text{LaCo}_{0.95}\text{Pt}_{0.05}\text{O}_3/\text{SiO}_2$ calcined at 700 °C

Fig. 2 TPR profiles of a LaCoO_3 , b $\text{LaCoO}_3/\text{SiO}_2$, c $\text{LaCo}_{0.97}\text{Pt}_{0.03}\text{O}_3/\text{SiO}_2$, d $\text{LaCo}_{0.95}\text{Pt}_{0.05}\text{O}_3/\text{SiO}_2$, e $\text{LaCo}_{0.93}\text{Pt}_{0.07}\text{O}_3/\text{SiO}_2$, f $\text{LaCo}_{0.91}\text{Pt}_{0.09}\text{O}_3/\text{SiO}_2$, g $\text{LaCo}_{0.90}\text{Pt}_{0.10}\text{O}_3/\text{SiO}_2$

XRD Results

Figure 3A shows XRD patterns of the unsupported PTOs of $\text{LaCo}_{1-x}\text{Pt}_x\text{O}_3$. The characteristic diffraction peaks of the perovskite phase at $2\theta = 32.9, 33.3, 47.5$, and 59.0° are clearly seen, and no peaks corresponding to other impurity phases could be observed, suggesting that the PTOs were synthesized well. From the enlarged pattern of $\text{LaCo}_{1-x}\text{Pt}_x\text{O}_3$ in Fig. 3B, it is seen that the diffraction peaks of the perovskite phase shifted to smaller values of 2θ , which means that the crystal lattice spacing of the perovskite phase increased. The shift increased with the increase in the Pt content in the PTOs. This should be indicative of the imbedding of Pt ions into the lattice of PTO. The size of the Pt ion is larger than the size of the Co ion, leading to the increase in the lattice spacing. Since no diffraction peak corresponding to platinum or platinum oxide was detected, entering of Pt ions into the lattice of PTO is supported.

The XRD patterns of the supported catalysts of $\text{LaCo}_{0.95}\text{Pt}_{0.05}\text{O}_3/\text{SiO}_2$ and SiO_2 are shown in Fig. 3C. Besides the broad diffraction peaks corresponding to SiO_2 , weak diffraction peaks corresponding to the perovskite phase could be detected, indicating that the PTOs were successfully supported on silica. The peak intensity of PTO increased with the increase in PTO loading amount, and when the loading amount of PTOs is 13 wt%, diffraction peaks of perovskite could hardly be detected, suggesting that the PTOs were highly dispersed, which is consistent with the TEM results in Fig. 4.

TEM Images

Figure 4a, b shows representative TEM images of the calcined $\text{LaCo}_{0.95}\text{Pt}_{0.05}\text{O}_3/\text{SiO}_2$. From the images of $\text{LaCo}_{0.95}\text{Pt}_{0.05}\text{O}_3/\text{SiO}_2$, many of PTO NPs with sizes below

Fig. 3 XRD patterns of **A**: a LaCoO_3 , b $\text{LaCo}_{0.95}\text{Pt}_{0.05}\text{O}_3$, c $\text{LaCo}_{0.93}\text{Pt}_{0.07}\text{O}_3$, d $\text{LaCo}_{0.91}\text{Pt}_{0.09}\text{O}_3$, and e $\text{LaCo}_{0.89}\text{Pt}_{0.11}\text{O}_3$; **B**: the partially enlarged drawing of **A**; **C**: a SiO_2 , b 13% $\text{LaCo}_{0.95}\text{Pt}_{0.05}\text{O}_3/\text{SiO}_2$, c 25% $\text{LaCo}_{0.95}\text{Pt}_{0.05}\text{O}_3/\text{SiO}_2$, d 30% $\text{LaCo}_{0.95}\text{Pt}_{0.05}\text{O}_3/\text{SiO}_2$, e 40% $\text{LaCo}_{0.95}\text{Pt}_{0.05}\text{O}_3/\text{SiO}_2$, f 50% $\text{LaCo}_{0.95}\text{Pt}_{0.05}\text{O}_3/\text{SiO}_2$

9 nm can be found on the surface of SiO_2 . Figure 4b shows a representative crystallite of the PTO, with a crystal spacing of 2.74 Å, corresponding to the crystalline plane [110] of $\text{LaCo}_{0.95}\text{Pt}_{0.05}\text{O}_3$.

After reduction at 220 °C, the NPs with an interplanar crystal spacing of 2.72 Å, consistent with crystal spacing of plane [110] for LaCoO_3 , can be found in Fig. 4d. The slight

Fig. 4 TEM images of **a** fresh $\text{LaCo}_{0.95}\text{Pt}_{0.05}\text{O}_3/\text{SiO}_2$; **b** the enlarged view of **a** in the red circle; **c** $\text{LaCo}_{0.95}\text{Pt}_{0.05}\text{O}_3/\text{SiO}_2$ reduced at 220 °C; **d** the enlarged view of **c** in the red circle; **e** $\text{LaCo}_{0.90}\text{Pt}_{0.10}\text{O}_3/\text{SiO}_2$ reduced at 220 °C; **f** the enlarged view of **e** in the red circle

decrease in the lattice spacing from 2.74 Å in Fig. 4b to 2.72 Å here would be attributed to platinum ions' escaping from the perovskite lattice. At the same time, no platinum lattices can be detected for $\text{LaCo}_{0.95}\text{Pt}_{0.05}\text{O}_3/\text{SiO}_2$, indicating that platinum is highly dispersed on the support. It agrees well with XRD results and our assumption in Scheme 1.

The representative images of $\text{LaCo}_{0.90}\text{Pt}_{0.10}\text{O}_3/\text{SiO}_2$ (Pt loading is 1 wt%) reduced at 220 °C are shown in Fig. 4e, f; the crystallites of LaCoO_3 can be seen. The image in Fig. 4f shows a typical metallic Pt NP. The crystal lattice spacing is 2.27 Å, which is in accordance with the crystalline plane [111] of platinum metal. The result indicates that too much Pt added resulted in the comparatively poor dispersion of Pt atoms.

Fig. 5 Variation of CO conversion with reaction temperature for **a** supported catalysts with the same platinum content of 0.5 wt% or the same PTO content of 13 wt%, **b** the catalysts of PTO supported on SiO_2 with different platinum contents of 0.3, 0.5, 0.7, 0.88%, and 1 wt%. Reaction conditions: 1% CO , 1% O_2 , 98 vol% N_2 balance, space velocity = 24,000 $\text{mL}/(\text{g}_{\text{cat}}\text{h})$

Catalytic Performance

To study the catalytic performance of the supported Pt catalysts, CO oxidation was chosen as the probe reaction, which is an extensively used probe and a very important reaction in environmental protection [25]. CO conversions over the catalysts with the same platinum content of 0.5 wt% are shown in Fig. 5a. The complete CO oxidation temperatures are 240, 260, and 320 °C for $\text{LaCo}_{0.95}\text{Pt}_{0.05}\text{O}_3/\text{SiO}_2$, $\text{LaCoPtO}_x/\text{SiO}_2$, and Pt/SiO_2 , respectively. Meanwhile, the

highest CO conversion is about 90% for $\text{LaCoO}_3/\text{SiO}_2$ at a temperature of 480 °C. It indicates that the catalyst prepared according to Scheme 1 is highly active.

Considering the similar synthesis process and perovskite content between $\text{LaCo}_{0.95}\text{Pt}_{0.05}\text{O}_3/\text{SiO}_2$ and $\text{LaCoO}_3/\text{SiO}_2$, the huge difference in activity comes from the small amount of metallic platinum. Reducing $\text{LaCo}_{1-x}\text{Pt}_x\text{O}_3/\text{SiO}_2$ resulted in $\text{Pt}/\text{LaCoO}_3/\text{SiO}_2$, as stated in the discussion about TPR results, over which CO is adsorbed on the highly dispersed platinum and would react with the oxygen species adsorbed in the perovskite vacancies [26]. The mechanism on $\text{LaCoO}_3/\text{SiO}_2$ is generally proposed that oxygen species, adsorbed at the oxygen vacancies on LaCoO_3 , react with CO adsorbed on Co^{3+} adjacent to the oxygen vacancies to generate CO_2 [26]. Platinum atoms are much more active than Co^{3+} , therefore leading to the much better activity of $\text{LaCo}_{1-x}\text{Pt}_x\text{O}_3/\text{SiO}_2$. For Pt/SiO_2 , CO adsorbed on Pt atoms reacts with oxygen activated on the Pt surface [27], and the platinum species loaded with the regular impregnation method at a calcination temperature of 700 °C is not highly dispersed, thus showing obviously inferior activity. As for $\text{LaCoPtO}_x/\text{SiO}_2$, a PTO was not formed, which means that Pt is not in close contact with the oxide of cobalt, and the dispersion of Pt atoms would not be very high;

Fig. 6 Stability of $\text{LaCo}_{0.95}\text{Pt}_{0.05}\text{O}_3/\text{SiO}_2$ reduced at 220 °C. Reaction conditions: 1% CO , 1% O_2 , 98 vol% N_2 balance at 400 °C and a space velocity of 24,000 $\text{mL}/(\text{g}_{\text{cat}}\text{h})$

Table 1 Some tested results of the catalysts

	$\text{LaCo}_{0.97}\text{Pt}_{0.03}\text{O}_3/\text{SiO}_2$	$\text{LaCo}_{0.95}\text{Pt}_{0.05}\text{O}_3/\text{SiO}_2$ (after stability test)	$\text{LaCo}_{0.93}\text{Pt}_{0.07}\text{O}_3/\text{SiO}_2$	$\text{LaCo}_{0.91}\text{Pt}_{0.09}\text{O}_3/\text{SiO}_2$	$\text{LaCo}_{0.90}\text{Pt}_{0.10}\text{O}_3/\text{SiO}_2$
Amount of adsorbed CO from CO-TPD (μmol)	1.00	1.58 (1.53)	1.96	2.35	2.48
Pt dispersion (%)	92.5	88.3 (85.1)	78.2	74.4	69.1
CO conversion (%) [*]	6.45	9.82	11.69	13.84	14.42
TOF ($\times 10^{-2} \text{ s}^{-1}$) [*]	1.35	1.29	1.24	1.23	1.21

^{*}Reaction conditions: at 145 °C; in 1% CO , 1% O_2 , 98 vol% N_2 balance, space velocity = 24,000 $\text{mL}/(\text{g}_{\text{cat}}\text{h})$, atmospheric pressure

Table 2 Catalysts with good performance in recent years and compared with the catalyst in this work for CO oxidation at atmospheric pressure

Catalyst (wt%)	Stability performance			Refs.
	WHSV (mL/g h)	T (°C)	Time (h)	
1% Pt–ZrO ₂	30,000	90	40	[28]
5.0% Pt/γ–Al ₂ O ₃	25,000	160	112	[29]
1% Pt/Fe ₂ O ₃	96,000	25	2.2	[30]
3.32% Co/1.44% Pt/TiO ₂	22,000	45	2	[31]
1% Pt/Ce _{0.8} Zr _{0.2} O ₂	16,800	60	50 ^a	[32]
Leached 4% Pt–0.3% Fe/CB	30,000	25	11	[33]
0.5% Pt/LaCoO ₃ /SiO ₂ ^b	24,000	400	250	This work

^aThe CO conversion is maintained at 80%^bThe catalyst was derived from reducing LaCo_{0.95}Pt_{0.05}O₃/SiO₂ at 220 °C

thus, CO oxidation proceeds via a similar mechanism to LaCo_{0.95}Pt_{0.05}O₃/SiO₂. Therefore, LaCoPtO_x/SiO₂ showed inferior activity compared to LaCo_{0.95}Pt_{0.05}O₃/SiO₂.

Figure 5b shows the variations of CO conversion over the series of catalysts of LaCo_{1-x}Pt_xO₃/SiO₂ with the reaction temperature. The complete CO conversion temperatures are 280, 240, 230, 215, and 205 °C over the catalysts, when *x* is 0.03, 0.05, 0.07, 0.09, and 0.10, respectively, which increases with the increase in the amount of platinum present. This is in the expectation, as a higher content of platinum would provide more active sites. The TOFs, CO converted on per atom of platinum per second, decreased slightly with the increase in platinum content as listed in Table 1, suggesting that elevating the dispersion could improve the utilization efficiency of the noble metal platinum.

As shown in Fig. 6, LaCo_{0.95}Pt_{0.05}O₃/SiO₂ shows excellent stability at the high temperature of 400 °C during 240 h testing, as complete CO conversion was maintained from the start to the finish. At the same time, the dispersion of Pt atoms slightly decreased from 88.3 to 85.1% after the stability test, and no Pt NPs could be observed from TEM images.

It has been reported that under oxidation conditions, Pt, Pd, or Rh atoms on the surface of a PTO could enter into the lattice of the PTO support, thus acting as the lattice ions of the PTO. Under reduction conditions, the Pt/Pd/Rh ions in a PTO would be reduced to metal atoms and migrate out onto the surface of the PTO. The “entering into” and “migrating out” may cycle under certain atmospheres, meaning that Pt/Pd/Rh species may be cycling between the surface and lattice of a PTO [13, 14, 34, 35]. This cycling might function for LaCo_{0.95}Pt_{0.05}O₃/SiO₂ in the CO oxidation reaction process, considering that the reaction gas mixture contains CO/O₂ at a ratio of 1:1. Therefore, the highly dispersed platinum atoms showed excellent sintering resistance ability. At least, the Pt species could interact with the support of LaCoO₃, and the interaction would prevent the Pt atoms from moving, therefore showing excellent sintering resistance ability.

Table 2 summarizes representative excellent Pt-based catalysts developed in recent years and compares them with the LaCo_{0.95}Pt_{0.05}O₃/SiO₂ of this work. It can be seen that

LaCo_{0.95}Pt_{0.05}O₃/SiO₂ exhibited excellent stability, which was tested at an obviously higher temperature and maintained for a much longer time compared to other reactions in the table.

To combine the above results, the process shown in Scheme 1 is analyzed as follows. A PTO of LaCo_{1-x}Pt_xO₃ was highly dispersed on SiO₂ with a high surface area, and the platinum ions should be uniformly dispersed in the PTO lattice. In the reduction process, platinum ions should be reduced and migrate out from the lattice onto the surface of LaCoO₃. In the lattice of LaCo_{1-x}Pt_xO₃, platinum ions were uniformly dispersed; therefore, in the reduction process, platinum ions should migrate out evenly and highly disperse on the surface of LaCoO₃. When the content of platinum in LaCo_{1-x}Pt_xO₃ is low, the platinum atoms (migrated from the lattice of LaCo_{1-x}Pt_xO₃) would be highly dispersed. When *x* in LaCo_{0.95}Pt_{0.05}O₃/SiO₂ is 0.05 or below, the characterization results suggest that the content of platinum is low enough, as when *x*=0.03 and 0.05, the dispersions of Pt are 92.5 and 88.3%, respectively, and no Pt NPs could be found by using high-resolution TEM. It is accepted that Pt atoms can activate CO and the oxygen vacancies can activate oxygen, and the two activated species therefore bond to generate CO₂, leading to the high activity for CO oxidation.

Conclusions

Highly dispersed Pt catalysts can be prepared by using PTOs as the precursor via a simple method of citrate acid complexation combined with impregnation. Specifically, in LaCo_{0.95}Pt_{0.05}O₃/SiO₂, the PTO of LaCo_{0.95}Pt_{0.05}O₃ could be highly dispersed on SiO₂ supports, and after reduction, Pt/LaCoO₃/SiO₂ was generated, where the platinum was highly dispersed, since the platinum ions were uniformly dispersed in the precursor of LaCo_{0.95}Pt_{0.05}O₃. It is interesting to note that the highly dispersed Pt exhibited excellent resistance to sintering, being attributed to the confinement of Pt atoms by LaCoO₃ on SiO₂. Thus, the prepared catalyst showed high activity and excellent stability for CO oxidation.

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