Comparison of the nickel addition patterns on the catalytic performances of LaCoO₃ for low-temperature CO oxidation

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Abstract

Effect of nickel on the catalytic performances of LaCoO_3 for CO oxidation is investigated, by partial substitution of Co with Ni atoms in the framework or by deposition of NiO on the surface of LaCoO_3 . Results show that the activity decreases in order of $10\%\text{Ni}/\text{LaCoO}_3 > \text{LaCoO}_3 > \text{LaCo}_{0.8}\text{Ni}_{0.2}\text{O}_3$, with the CO ignition temperature of 60, 110 and 140 °C, respectively (reaction conditions: 0.5% CO/Ar and 7.5 % O_2 /Ar, balanced with Ar; space velocity of 30000 $\text{mL g}^{-1} \text{h}^{-1}$). Based on the characterizations such as XPS, H_2 -TPR, O_2 -TPD and CV measurements, we inferred that the high activity of $10\%\text{Ni}/\text{LaCoO}_3$ is attributed to a synergistic effect induced by NiO and LaCoO_3 , and the low activity of $\text{LaCo}_{0.8}\text{Ni}_{0.2}\text{O}_3$ is to the enrichment of La atoms on the surface, caused by the Ni incorporation. Long-time stability test indicates that $10\%\text{Ni}/\text{LaCoO}_3$ is stable in the reaction, with no appreciable loss of activity within 32 h. The highly active and stable activity of $10\%\text{Ni}/\text{LaCoO}_3$ suggests that impregnation of metal oxides on the surface of perovskite can be a feasible strategy for the preparation of industrial catalyst for CO oxidation.

Keywords: LaCoO_3 ; Nickel; Impregnation; Synergistic effect; CO oxidation

1. Introduction

Catalytic CO oxidation is an attractive reaction from both fundamental study and practical application, as it is not only a widely used model reaction for evaluating catalytic performances of solid catalysts, but also an effective technology for removing CO pollutant from various devices[1]. However, although this technology has been widely applied in practice for long time, the gradually increased CO concentration in air atmosphere year by year suggests that there is still an urgent demand for the improvement of this technology in order to meet the strict regulation issued on CO emission. From the viewpoint of catalysis, the core problem is to search for catalysts that are efficient for the reaction.

Noble metals, e.g. Ru[2], Pt[3], and Au[4], are active for CO oxidation at low temperature, but are rare and expensive, and there has a trend to avoid using these metals at today in order to save these rare sources. Transition metal oxides[5] also are active for the reaction, and it was reported that 100% CO conversion can be obtained at temperature below zero if the catalyst is fabricated with specific surface morphology[6]. However, they are easily deactivated due to the repair of oxygen vacancy by the molecular oxygen and possibly the transformation of surface morphology during the reaction. Perovskite oxides with ABO_3 structure are potential alternatives of noble metals and metal oxides in various applications including CO oxidation, due to their high thermal and structural stability, which enables a stable activity [7, 8]. Indeed, many works reported that perovskite oxides are good catalysts for oxidation reactions, including the catalytic oxidation of toluene[9], nitric oxide[10], benzene[11], methane[12], and ethyl acetate[13]. Nevertheless, they need to be performed at higher temperature in order to achieve desired activity.

Several strategies have been reported to improve the catalytic performances or lower the

reaction temperature of perovskite oxides for CO oxidation, including the use of new synthesis method[14], the deposition on a high-surface-area support [8], and the doping of other transition metals on the surface or in the framework[15]. The principle of the former two is by altering the textural structure of catalyst, while that of the third is by changing the chemical compositions of catalyst, which seems more interesting as it has the potential to tune the natural properties (e.g., redox ability) of the catalyst, and has the possibility of inducing synergistic effect between the different metal oxides. For example, Vaz et al.[16] reported that the substitution of Co for Ni in $\text{LaNi}_{1-x}\text{Co}_x\text{O}_3$ system and, Seyfi et al.[17] reported that the substitution of Cu for Co in $\text{LaCo}_{1-x}\text{Cu}_x\text{O}_3$ system, both are efficient for improving the CO oxidation activity, due to a collaborating effect induced between the metals.

In this work, we investigated the effect of Ni addition on the catalytic performances of LaCoO_3 for CO oxidation, by depositing NiO on the surface or by partial substitution of Ni for Co in the LaCoO_3 framework. LaCoO_3 is a promising perovskite catalyst for CO oxidation [18], and Ni is reported to be a suitably substituted metal to enhance the catalytic performance of LaCoO_3 for the reaction[19, 20]. Meanwhile, NiO is also an active phase for CO oxidation when deposited on specific supports (e.g., Al_2O_3 , ZrO)[21, 22].

Characterizations from XRD, FT-IR and TEM measurements indicate that desired catalysts, namely, LaCoO_3 , $\text{LaCo}_{0.8}\text{Ni}_{0.2}\text{O}_3$ and 10%Ni/ LaCoO_3 (for convenience, we defined the catalyst with Ni loading, instead of NiO loading), are well prepared using the citric-complexing method[23, 24]. Catalytic tests show that their activity for CO oxidation is in order of 10%Ni/ LaCoO_3 > LaCoO_3 > $\text{LaCo}_{0.8}\text{Ni}_{0.2}\text{O}_3$, indicating that the impregnation of NiO on the surface of LaCoO_3 improves, while the substitution of Ni for Co atoms in the framework decreases the activity of

LaCoO₃. This is explained by the reasons that a synergistic effect between NiO and LaCoO₃ is induced for 10%Ni/LaCoO₃, while for LaCo_{0.8}Ni_{0.2}O₃, the exposure of active sites is less due to the enrichment of La atoms on the surface, as verified by XPS analysis. Further studies show that 10% is the optimum Ni loading, and the 10%Ni/LaCoO₃ shows stable activity for the reaction, with no appreciable loss of activity within 32 h. The good and stable activity of 10%Ni/LaCoO₃ for CO oxidation suggests that the impregnation of metal oxides on the surface of perovskite oxides is a feasible strategy to design industrial catalyst for low-temperature CO oxidation, avoiding the use of noble metals.

2. Experimental

2.1 Catalysts preparation

The materials were metal nitrates with A.R. grade and all were purchased from Sinopharm Chemical Reagent Co., Ltd. China. The catalysts were prepared by citric-complexing method according to a previous report[23]. For LaCo_{1-x}Ni_xO₃ ($x = 0, 0.2$), 5 mmol La(NO₃)₃, 5 mmol Co(NO₃)₃ and Ni(NO₃)₂ (the ratio of them depends on the x value), and 12 mmol citric acid were dispersed in a solution containing 20 mL H₂O and 12 mmol glycol. The resulting mixture was then stirred at 80 °C until became gel status. The gel was dried at 120 °C overnight, calcined at 500 °C for 4 h and 700 °C for another 4 h, with a heating rate of 2 °C/min.

For 10%Ni/LaCoO₃, the above obtained LaCoO₃ (1 g) was wet incipient impregnated with an aqueous solution of Ni(NO₃)₂ (4.5 mol/L), then dried at 100 °C overnight and calcined at 700 °C for 4h. The Ni loading was set at 10 wt.% so that it has the same amount as that of LaCo_{0.8}Ni_{0.2}O₃. For comparison, a silica supported NiO catalyst, defined as 10% Ni/SiO₂, was prepared with the same procedure as that of 10% Ni/LaCoO₃.

2.2 Catalyst characterization

Powder X-Ray diffraction (XRD) were performed on a Bruker D8 Advance X-ray diffractometer with Cu K α ($\lambda = 1.5406 \text{ \AA}$, scanning step = 0.02°) irradiation. The 2θ angle ranges from 10 to 80° at a scanning rate of $10^\circ \text{ min}^{-1}$. Fourier-transform infrared (FT-IR) spectra were obtained using a NEXUS-470 infrared spectrophotometer with KBr pellets in the $400\text{-}4000 \text{ cm}^{-1}$ range. The specific surface areas were calculated based on the Brunauer–Emmett–Teller (BET) method in the relative pressure range of $0.05\text{-}0.3$, determined from the adsorption branch of N_2 physisorption isotherms at -196°C . The surface morphology was observed by transmission electron microscopy (TEM) on a Tecnai G² 20 S-Twin apparatus with the gun voltage of 200 kV , and an SU8000 field-emission scanning electron microscope (FESEM, Hitachi, Japan) connected with Energy dispersive spectrum analysis (EDS) system.

The surface composition of catalysts were analyzed by an X-ray photoelectron spectroscopy (XPS) using a Thermo Electron Corporation VG Multilab 2000 apparatus with a monochromatic Al K α X-ray source (300 W) and analyzer pass energy of 25 eV . All binding energies were corrected referencing to the binding energy of C1s at 284.6 eV . Temperature programmed desorption of oxygen ($\text{O}_2\text{-TPD}$) measurement was preformed on a FINESORB-3010 apparatus (Zhejiang Fantai instrument company, china) equipped with a thermal conductivity detector (TCD). The sample (0.1 g) was pretreated in O_2 (30 mL/min) at 500°C for 1 h and then cooled to 50°C . Subsequently, pure He was switched and after reaching a stable baseline, the temperature was raised from 50 to 900°C at a rate of 10°C/min to record the oxygen desorption profile. Temperature programmed reduction of hydrogen ($\text{H}_2\text{-TPR}$) measurements were carried out on the same setup as $\text{O}_2\text{-TPD}$. Prior to the reduction experiment, the catalysts (0.05 g) were first flushed

with pure Ar (30 mL/min) at 500 °C for 1 h, and then cooled to 50 °C. Thereafter, a 10 vol.% H₂/Ar mixture was passed with a flow rate of 30 mL/min, and after a stable baseline was obtained, the temperature was raised from 50 to 800 °C, with a heating rate of 10 °C/min, to record the hydrogen consumption profile.

Cyclic voltammetry (CV) experiments were performed on a CR2025 cion-type cell in an automatic battery test system (Neware, China). The working electrode is composed of a mixture of 60 wt.% catalysts, 30 wt.% acetylene black and 10 wt.% poly vinylidene fluoride binder. Lithium foil was used as the counter electrode and ethylene carbonate, dimethyl carbonate (1:1, v/v) and 1 M LiPF₆ mixture were used as electrolyte. The mass of electrode is 6 mg and the voltage ranges from 1.0 to 4.0 V.

2.3 Catalytic activity

The CO oxidation reaction was conducted on a fixed-bed quartz reactor (i.d. = 8 mm) and operated at atmospheric pressure. The feed gas (0.5 vol.% CO/Ar + 7.5 vol.% O₂/Ar, balanced with Ar) was passed through 100 mg of catalyst at a total flow rate of 50 mL/min [space velocity (SV) = 30000 mL g⁻¹ h⁻¹]. The inlet and outlet gas compositions were analyzed by a gas chromatograph (Agilent 7890), equipped with Porapak Q and 5A molecular sieve columns and thermal conductivity detector (TCD). The CO conversion was evaluated based on the equations: $CO\ conversion\ (\%) = ([CO]_{in} - [CO]_{out}) / [CO]_{in} \times 100$, where [CO]_{in} and [CO]_{out} refer to CO concentrations in the feed and effluent stream, respectively.

3. Results and discussion

Figure 1. Wide-angle XRD patterns for LaCoO₃, LaCo_{0.8}Ni_{0.2}O₃ and 10% Ni/LaCoO₃ and NiO.

Figure 1A shows that LaCoO₃ and LaCo_{0.8}Ni_{0.2}O₃ with pure perovskite structure are formed (JCPDS 48-0123) and no impurity forms, suggesting that Ni atoms are incorporated into the framework of LaCoO₃, in accordance to results of previous work[25]. For 10% Ni/LaCoO₃, besides these of LaCoO₃, diffraction peaks at 2θ of 37.4°, 43.5°, and 63.2°, attributed to the (111), (200), (220) face of NiO (JCPDS 00-001-1239) [26, 27], also appear (Figure 1B), indicating that NiO is formed on the surface of LaCoO₃. The weak peak intensity suggests that the NiO is highly dispersed on the surface of LaCoO₃. FT-IR spectra confirm the formation of perovskite structure, as verified by the absorption band at ca. 410 and 603 cm⁻¹, which are attributed to the stretching vibration and bending vibration of Co-O (or Ni-O) bond, respectively (Figure S1) [28].

Table 1. Physicochemical properties of the investigated catalysts.

Catalyst	D (nm) ^a	SAs (m ² g ⁻¹) ^b
10% Ni/LaCoO ₃ -Fresh	24.9	7.7
10% Ni/LaCoO ₃ -Used	26.3	4.6
LaCo _{0.8} Ni _{0.2} O ₃	24.6	20.5
LaCoO ₃	23.3	6.2
NiO/SiO ₂	—	31.6
NiO	34.5	11.8

^aCrystalline sizes determined from XRD patterns; ^b BET surface area of the samples

The crystalline size of the perovskites, calculated by the Scherrer equation at $2\theta = 27^\circ$, is similar for the three catalysts, ranging from 23.3 to 24.9 nm, Table 1. This could be that they are prepared with the same procedure. The crystallite size of supported NiO is not calculated since the peak intensity is weak and thus, big errors would be produced when calculated by the Scherrer equation. However, from the peak intensity observed in Figure 1B, it can be inferred that the crystalline size should be far smaller than that of the bulk NiO (34.5 nm), due to the supporting effect. On the other hand, the BET surface areas (SAs) determined from the N₂ physisorption measurements is 6.2 m²/g for LaCoO₃, which increases abruptly to 20.5 m²/g for LaCo_{0.8}Ni_{0.2}O₃, indicating that the addition of Ni atoms to the catalyst facilitates the improvement of surface area. Even for the supported 10%NiO/LaCoO₃ sample, its surface area (7.7 m²/g) is higher relative to that of LaCoO₃ (6.2 m²/g), due to the Ni addition.

Figure 2. TEM images of LaCoO₃ (A, C), and 10% Ni/LaCoO₃ (B, D)

Figure 2 shows the TEM images of LaCoO₃ and 10%Ni/LaCoO₃. The former exhibits a homogeneous microstructure with grain size ranging from 10 to 30 nm, which is in agreement

with result obtained from the XRD patterns. For the latter, it is interesting to find that the NiO particles are well dispersed on the surface of LaCoO_3 , as seen from the HRTEM image in Figure 2D, a layer of white film is covered on the surface.

Figure 3. EDS mapping of La, O, Co and Ni atoms for 10% Ni/ LaCoO_3 , obtained from SEM measurement.

To verify that NiO is highly dispersed on the surface of LaCoO_3 , EDS mapping photograph of the sample is taken on an SEM apparatus. Figure 3 shows that the Ni atoms, as well as that of La, Co and O atoms, are homogeneously dispersed, confirming the above conclusions (SEM image can be found in Figure S2). As expected, the dispersion of Ni atoms is sparser than that of the La, Co and O atoms, due to its smaller mass percentage.

Figure 4. CO conversion obtained from the series catalysts as a function of temperature.

Figure 4 displays the CO oxidation activity obtained from the samples, showing that CO conversion increases with increasing the reaction temperatures, and the activity is in order of $\text{NiO} < \text{LaCo}_{0.8}\text{Ni}_{0.2}\text{O}_3 < \text{LaCoO}_3 < 10\% \text{Ni/LaCoO}_3$. NiO itself has low activity to the reaction, but it

can significantly improve the activity of LaCoO_3 when deposited on the surface, indicating that the presence of NiO alters the surface properties of LaCoO_3 and promotes its ability for CO oxidation. To exclude that the high activity of 10%Ni/ LaCoO_3 is not due to the high dispersion of NiO particles, a comparative catalyst, 10%Ni/ SiO_2 , is prepared, which shows less than 30% CO conversion even at 250 °C. This suggests that the high activity obtained from 10%Ni/ LaCoO_3 is not due to the highly dispersed NiO particles, but to a synergistic effect induced between LaCoO_3 and NiO. The synergistic effect between perovskite and metal oxides for CO oxidation has also been found for LaCoO_3 - Co_3O_4 system in a previous work of our group[29].

On the other hand, it is found that the activity of $\text{LaCo}_{0.8}\text{Ni}_{0.2}\text{O}_3$ is lower than that of LaCoO_3 , indicating that the incorporation of Ni to the framework of LaCoO_3 deteriorates the reaction. In order to explore the reasons, we analyzed the surface chemistries and redox properties of the catalysts by XPS, H_2 -TPR, O_2 -TPD and CV measurements, as below.

Figure 5. XPS spectra surveyed from (A) Co 2p_{3/2} and (B) O 1s of the investigated catalysts.

Figure 5 shows the XPS spectra of Co 2p and O 1s of the catalysts. According to literature, the Co 2p_{3/2} spectrum can be fitted to two peaks[30], as high-valence Co^{3+} centered at 779.3 eV and low-valence Co^{2+} at 782.2 eV. While for the O 1s spectrum, it can be fitted with three peaks, corresponding to the adsorbed water molecules (or hydroxyl group) at 533.0 eV, the oxygen

chemically adsorbed on oxygen vacancy at 530.8 eV and the surface lattice oxygen at 528.6 eV[31, 32]. On this basis, the surface composition of each atom was calculated and listed in Table 2, showing that the ratio of $\text{Co}^{3+}/\text{Co}^{2+}$ and that of the $\text{O}_{\text{latt}}/\text{O}_{\text{ads}}$ increase in order of $\text{LaCo}_{0.8}\text{Ni}_{0.2}\text{O}_3 < \text{LaCoO}_3 < 10\%\text{NiO}/\text{LaCoO}_3$, with the same order as that of the activity. This demonstrates that the activity depends intimately on the surface percentage of Co^{3+} and the oxygen vacancy.

Table 2. Surface compositions of the catalysts, measured from XPS spectra

Catalyst	La/(Co+Ni)	$\text{Co}^{3+}/\text{Co}^{2+}$	$\text{O}_{\text{latt}}/\text{O}_{\text{ads}}$
10% Ni/LaCoO ₃	1.16	4.1	0.67
LaCoO ₃	2.99	3.6	0.55
LaCo _{0.8} Ni _{0.2} O ₃	3.58	3.3	0.47

On the other hand, it is found that the atomic ratio of La/(Co+Ni) for all the samples is above unity and increases in order of $10\%\text{Ni}/\text{LaCoO}_3 < \text{LaCoO}_3 < \text{LaCo}_{0.8}\text{Ni}_{0.2}\text{O}_3$, suggesting that La atoms are enriched on the surface, and the substitution of Ni for Co in the framework intensifies the enrichment progress. That is, the exposure of Co and/or Ni atoms on the surface of LaCo_{0.8}Ni_{0.2}O₃, which are the part of active site[33], lowered after the incorporation of Ni atoms, explaining why decreased activity is observed for LaCo_{0.8}Ni_{0.2}O₃, relative to that of LaCoO₃.

Figure 6. (A) H₂-TPR and (B) O₂-TPD profiles of LaCoO₃, LaCo_{0.8}Ni_{0.2}O₃ and 10%Ni/LaCoO₃, together with that of NiO (for H₂-TPR).

To study further the surface chemistries and oxygen properties of the catalysts, H₂-TPR and O₂-TPD measurements were conducted and the results are displayed in Figure 6. Figure 6A shows that three reduction peaks appear in the H₂-TPR profile. According to literature, the first two peaks were attributed to the removal of oxygen species adsorbed on oxygen vacancies and the reduction of Co³⁺ to Co²⁺ (or Ni³⁺ to Ni²⁺), respectively, and the third peak is to the reduction of Co²⁺ to Co⁰, (or Ni²⁺ to Ni⁰)[34]. For comparison, the reduction profile of pure NiO was also conducted, showing a big peak at 300-400 °C, due to the reduction of NiO to Ni, as observed elsewhere[35].

The addition of Ni atoms, either supported on the surface or incorporated into the framework of LaCoO₃, leads to decreased reduction temperature, due to its stronger reducibility. However, together with the activity shown in Figure 4, we inferred that reduction temperature should not be the crucial factor determining the activity, as LaCo_{0.8}Ni_{0.2}O₃ with lower reduction temperature shows lower CO oxidation activity, relative to that of LaCoO₃.

O₂-TPD profiles of the samples show essentially two desorption peaks. The first appeared at T < 700 °C is attributed to oxygen species adsorbed on oxygen vacancy (denoted α-oxygen), and the second one at T > 700 °C is to oxygen in the lattice (denoted β-oxygen)[36]. Similar as that observed in the H₂-TPR profile, the addition of Ni leads to lower oxygen desorption temperature, confirming that the Ni addition, either supported on the surface or incorporated to the framework, can improve the oxidation ability of LaCoO₃.

It is generally believed that the surface α-oxygen play an important role in CO oxidation via a suprafacial catalytic process[37]. Whereas, together with the activity profiles it is found that LaCo_{0.8}Ni_{0.2}O₃ with the lowest desorption temperature and considerable desorption peak shows the worst activity, while 10%NiO/LaCoO₃ with the smallest peak area shows the best activity for

CO oxidation, this suggests that there must be other crucial factors, other than oxygen vacancy, influence the reaction. For example, the enrichment of La atoms (or less exposure of active sites) on the catalyst surface for $\text{LaCo}_{0.8}\text{Ni}_{0.2}\text{O}_3$, the synergistic effect induced for CO oxidation between NiO and LaCoO_3 , and probably a more suitable redox properties for 10%Ni/ LaCoO_3 .

Figure 7. CV curves of 10% Ni/ LaCoO_3 , $\text{LaCo}_{0.8}\text{Ni}_{0.2}\text{O}_3$ and LaCoO_3

In previous works[38, 39] it is suggested that cyclic voltammetry (CV) is a useful means to evaluate redox potentials of perovskite oxides in heterogeneous catalysis, and for suprafacial CO oxidation reaction, its activity depends intimately on the redox peak area of the catalyst. For this reason, the CV curve of the catalysts were conducted. As expected, the redox peak area increases in order of $\text{LaCo}_{0.8}\text{Ni}_{0.2}\text{O}_3 < \text{LaCoO}_3 < 10\% \text{ Ni/LaCoO}_3$, with the same trend as that of the activity, Figure 7, demonstrating that the activity is indeed intimate to the redox peak area of the catalyst.

To justify further the catalytic performances of catalysts, the reaction rate and the apparent activation energy (E_a) of CO oxidation over the catalysts were calculated, with the assumption that the reaction obeys first-order toward CO and zero toward O_2 [40]. Figure 8 and Table 3 display the reaction rate obtained at 150 °C and the E_a value calculated at CO conversion below 10% (see Figure S3), together with the CO ignition temperature (T_{ig}), the temperature for 100% CO

conversion (T_{100}), and the TOF value obtained from Figure 5. Results show that 10%Ni/LaCoO₃ has the lowest E_a value (24.9 kJ mol⁻¹), verifying why it exhibits the best catalytic performances for CO oxidation, with the lowest T_{ig} and T_{100} , and the highest TOF and reaction rate.

Figure 8. The Arrhenius plots for CO oxidation conducted over the catalysts

Table 3. Activity, reaction rate and activation energy of CO oxidation over the catalysts

Catalyst	T_{ig}^a (°C)	T_{100}^b (°C)	TOF ^c ($\times 10^{-3} \text{ s}^{-1}$)	Rate (150 °C) ($\times 10^{-4} \text{ mol g}^{-1} \text{ s}^{-1}$)	E_a^d (CO) (kJ mol ⁻¹)
10% Ni/LaCoO ₃	60	200	14.1	25	24.9
LaCoO ₃	110	225	3.1	6.2	82.3
LaCo _{0.8} Ni _{0.2} O ₃	140	300	2.4	5.5	96.4

^a The ignition temperature for CO oxidation; ^b The temperature for full CO conversion; ^c The TOF values obtained at 150 °C; ^d Activation energy of CO oxidation over the catalysts.

Effect of NiO loading on the activity of LaCoO₃ are conducted to optimize the loading and the results are shown in Figure 9A. A significant increase in the activity can be observed even 2%Ni is added, demonstrating that the presence of NiO is crucial to the reaction. The activity increases slightly up to 10%Ni, and then decreases with further increase of Ni loading. This can be explained by the reason that the increase of NiO at the beginning increases the synergistic effect

by improving the contact area with LaCoO_3 , but the excess presence of NiO on the one hand leads to large particle size, and on the other hand decreases the exposure of LaCoO_3 . As a compromise, the optimum NiO loading reaches at 10% Ni loading.

Figure 9. CO oxidation obtained from (A) Ni/LaCoO_3 with different Ni loading and (B) 10% Ni/LaCoO_3 and mechanically mixed NiO+LaCoO_3 sample; (C) Influence of space velocity on the catalytic activity of 10% Ni/LaCoO_3 ; (D) The long-time stability of 10% Ni/LaCoO_3 at reaction temperature of 170 °C.

The synergistic effect between NiO and LaCoO_3 are confirmed further by comparing the activity of 10% Ni/LaCoO_3 with that of mechanically mixed NiO and LaCoO_3 (10% NiO+LaCoO_3) for CO oxidation. Figure 9B shows obviously that the former has better activity than the latter, indicating that the higher activity of 10% Ni/LaCoO_3 is not due to a simple addition, but to a synergistic effect induced between LaCoO_3 and NiO .

To check the application possibility, effects of space velocity (SV) and the long-time stability of 10% Ni/LaCoO_3 for CO oxidation are also investigated and the results are presented in Figure 9C and 9D, respectively. As expected, the activity decreases with the increase of SV (from 30000

to 60000 mL g⁻¹ h⁻¹), while 100% CO conversion can still be obtained at 225 °C. Long-time stability test shows that no appreciable loss of activity is observed within 32 h, demonstrating that the catalyst is highly stable in the reaction and has the potential for practical application. XRD patterns on the fresh and used 10%NiO/LaCoO₃ catalysts shows no essential difference in the diffraction peaks (Figure S4), and only a slight increase in the crystalline size, from 24.9 to 26.3 nm for LaCoO₃ is observed, see Table 1.

4. Conclusions

Effect of NiO on the catalytic performances of LaCoO₃ for CO oxidation was investigated, with different trends obtained by impregnation and substitution strategies. The impregnation of NiO on the surface leads to improved activity due to a synergistic effect induced between LaCoO₃ and NiO, while the incorporation of Ni to the framework leads to decreased activity due to the enrichment of La atoms on the surface, covering the active sites. The synergistic effect is verified, directly or indirectly, by the XPS, H₂-TPR, O₂-TPD and CV measurements, and that of a comparative catalyst NiO/SiO₂, which shows less than 30% CO conversion even at 250 °C. Activation energy verifies that the 10%Ni/LaCoO₃ is the best catalyst for CO oxidation because of its lowest value (24.9 kJ mol⁻¹). Further experiments indicate that the optimum Ni loading is 10 wt.%, and the 10%Ni/LaCoO₃ catalyst has the potential for practical application due to its high activity at high space velocity and the long-time stability.

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References

- [1] S. Li, H. Zhu, Z. Qin, G. Wang, Y. Zhang, Z. Wu, Z. Li, G. Chen, W. Dong, Z. Wu, *Appl. Catal. B: Environ.* 144 (2014) 498-506.
- [2] H. Öström, H. Öberg, H. Xin, J. LaRue, M. Beye, M. Dell'Angela, J. Gladh, M.L. Ng, J.A. Sellberg, S. Kaya, *Science* 347 (2015) 978-982.
- [3] F. Pilger, A. Testino, M.A. Lucchini, A. Kambolis, M. Tarik, M.E. Kazzi, Y. Arroyo, M.D. Rossell, C. Ludwig, *J. Nanosci. Nanotechnol.* 15 (2015) 3530-3539
- [4] J.A. Rodriguez, R. Si, J. Evans, W. Xu, J.C. Hanson, J. Tao, Y. Zhu, *Catal. Today* 240 (2015) 229-235.
- [5] J. Li, G. Lu, G. Wu, D. Mao, Y. Guo, Y. Wang, Y. Guo, *Catal. Sci. Technol.* 4 (2014) 1268-1275.
- [6] X. Xie, Y. Li, Z.-Q. Liu, M. Haruta, W. Shen, *Nature* 458 (2009) 746-749.
- [7] R.J.H. Voorhoeve, D.W. Johnson, J.P. Remeika, P.K. Gallagher, *Science* 195 (1977) 827-833.
- [8] P. Xiao, J. Zhu, H. Li, W. Jiang, T. Wang, Y. Zhu, Y. Zhao, J. Li, *ChemCatChem* 6 (2014) 1774-1781.
- [9] X. Li, H. Dai, J. Deng, Y. Liu, S. Xie, Z. Zhao, Y. Wang, G. Guo, H. Arandiyán, *Chem. Eng. J.* 228 (2013) 965-975.
- [10] C. Zhou, X. Liu, C. Wu, Y. Wen, Y. Xue, R. Chen, Z. Zhang, B. Shan, H. Yin, W.G. Wang, *Phys. Chem. Chem. Phys.* 16 (2014) 5106-5112.
- [11] W.Y. Jung, Y.I. Song, K.T. Lim, G.D. Lee, M.S. Lee, S.S. Hong, *J. Nanosci. Nanotechnol.* 15 (2015) 652-655.
- [12] I. Popescu, Y. Wu, P. Granger, I.-C. Marcu, *Appl. Catal. A: Gen.* 485 (2014) 20-27.
- [13] X. Chen, S.A.C. Carabineiro, P.B. Tavares, J.J.M. Órfão, M.F.R. Pereira, J.L. Figueiredo, *J. Environ. Chem. Eng.* 2 (2014) 344-355.
- [14] H. Taguchi, S. Yamasaki, A. Itadani, M. Yosinaga, K. Hirota, *Catal. Commun.* 9 (2008) 1913-1915.
- [15] T.H. Luu, X.D. Nguyen, T.M.H. Phan, S. Schulze, M. Hietschold, *Adv. Nat. Sci.:*

Nanosci. Nanotechnol. 6 (2015) 025016.

- [16] T. Vaz, A.V. Salker, Mater. Sci. Eng.: B, 143 (2007) 81-84.
- [17] B. Seyfi, M. Baghalha, H. Kazemian, Chem. Eng. J. 148 (2009) 306-311.
- [18] H. Einaga, Y. Nasu, M. Oda, H. Saito, Chem. Eng. J. 283 (2016) 97-104.
- [19] J.J. Zhu, D.H. Xiao, J. Li, X.G. Yang, Catal. Lett. 129 (2009) 240-246.
- [20] Y. Teraoka, T. Harada, S. Kagawa, J. Chem. Soc. Farad. Trans. 94 (1998) 1887-1891.
- [21] S.W. Han, D.H. Kim, M.-G. Jeong, K.J. Park, Y.D. Kim, Chem. Eng. J. 283 (2015) 992-998.
- [22] Z. Chen, Y.L. Xie, J.X. Qiu, Z.H. Chen, Characterization and Catalytic Activity of CuO and NiO Supported on ZrO₂ for CO Low Temperature Oxidation, in, Trans. Tech. Publ., 2014, pp. 237-241.
- [23] Y. Fang, Y. Liu, W. Deng, J. Liu, J. Energ. Chem. 23 (2014) 527-534.
- [24] S.Q. Chen, Y. Liu, Int. J. Hydrogen Energ. 34 (2009) 4735-4746.
- [25] F. Liu, Y. Qu, Y. Yue, G. Liu, Y. Liu, RSC Adv. 5 (2015) 16837-16846.
- [26] C. Jia, J. Gao, J. Li, F. Gu, G. Xu, Z. Zhong, F. Su, Catal. Sci. Technol. 3 (2013) 490-499.
- [27] K.Y. Koo, H.-S. Roh, Y.T. Seo, D.J. Seo, W.L. Yoon, S.B. Park, Int. J. Hydrogen Energ. 33 (2008) 2036-2043.
- [28] H. Liang, Y. Hong, C. Zhu, S. Li, Y. Chen, Z. Liu, D. Ye, Catal. Today 201 (2013) 98-102.
- [29] L. Zhong, F. Hai, P. Xiao, J. Hong, J. Zhu, RSC Adv. 4 (2014) 61476-61481.
- [30] J. Deng, L. Zhang, H. Dai, H. He, C.T. Au, Ind. Eng. Chem. Res. 47 (2008) 8175-8183.
- [31] A. Machocki, T. Ioannides, B. Stasinska, W. Gac, G. Avgouropoulos, D. Delimaris, W. Grzegorzczuk, S. Pasieczna, J. Catal. 227 (2004) 282-296.
- [32] Y. Wu, T. Yu, B.-S. Dou, C.-X. Wang, X.F. Xie, Z.L. Yu, S.R. Fan, Z.R. Fan, L.C. Wang, J. Catal. 120 (1989) 88-107.
- [33] J.J. Zhu, X.G. Yang, X.L. Xu, K.M. Wei, J. Phys. Chem. C 111 (2007) 1487-1490.

- [34] S. Zhong, Y. Sun, H. Xin, C. Yang, L. Chen, X. Li, *Chem. Eng. J.* 275 (2015) 351-356.
- [35] K. Takehira, *Catal.Surv. Asia* 6 (2002) 19-32.
- [36] S. Kaliaguine, A. Van Neste, V. Szabo, J.E. Gallot, M. Bassir, R. Muzychuk, *Appl. Catal. A: Gen.* 209 (2001) 345-358.
- [37] R. Zhang, N. Luo, B. Chen, S. Kaliaguine, *Energ. Fuel* 24 (2010) 3719-3726.
- [38] J. Zhu, X. Yang, X. Xu, K. Wei, *Chinese Sci. Bull.* 51 (2006) 374-376.
- [39] J. Zhu, Z. Zhao, D. Xiao, J. Li, X. Yang, Y. Wu, *Electrochem. Commun.* 7 (2005) 58-61.
- [40] A.P. Jia, G.S. Hu, L. Meng, Y.L. Xie, J.Q. Lu, M.F. Luo, *J. Catal.* 289 (2012) 199-209.

Graphical Abstract