

Promotional role of ceria on cobaltic oxide catalyst for low-temperature CO oxidation

Jie Li,^a Guanzhong Lu,^{*ab} Guisheng Wu,^b Dongsen Mao,^b Yanqin Wang^a and Yun Guo^a

Received 27th February 2012, Accepted 24th April 2012

DOI: 10.1039/c2cy20118f

Ceria modified Co_3O_4 catalysts for low temperature CO oxidation were prepared by a precipitation–oxidation method, and characterized by low-temperature N_2 adsorption/desorption, TPR, O_2 -TPD, CO-TPD and transient–response reaction. The roles of ceria in CeO_2 - Co_3O_4 catalyst and the effect of pretreatment on the performance of CeO_2 - Co_3O_4 for CO oxidation were investigated in detail. The results show that the presence of CeO_2 can increase its surface area, reduce the crystal size of Co_3O_4 , and improve obviously the catalytic activity and stability of Co_3O_4 for CO oxidation, such as its T_{100} is only -60 °C. It was also found that the addition of CeO_2 can not only promote the adsorption of O_2 and the reaction of adsorbed CO with surface oxygen species to form CO_2 , but also increase the CO_2 desorption speed. The pretreatment method can affect the catalytic activity of CeO_2 - Co_3O_4 , the catalyst treated in N_2 exhibits higher catalytic activity for low-temperature CO oxidation due to formation of oxygen vacancy. The catalyst reduced in H_2 shows lower activity for CO oxidation although it has more surface oxygen vacancies, because of the difficult desorption of CO_2 on the reduced CeO_2 - Co_3O_4 catalyst.

1. Introduction

It is well known that cobalt oxide has high catalytic activity for CO oxidation at low temperature, which is important for the purification of exhausts from automobile and stationary sources in environment pollution control.^{1,2} Co_3O_4 has attracted considerable attention owing to their low cost, high activity, and low reaction temperature in comparison with other catalysts, such as noble metal catalysts (Pd, Pt, Rh and Au), CuO– CeO_2 , etc.^{3–5} Over the last decade, the catalytic performances of Co_3O_4 with different morphologies or structures, such as nanospheres, nanocubes, nanorods, and mesoporous structures have been investigated. The research results demonstrate that the properties of the synthesized Co_3O_4 materials strongly depend on their morphologies, crystal sizes, and exposed crystal facets.^{6–10} Furthermore, the different pretreatment methods of catalysts also impact on their catalytic performances. For example, the preoxidation treatment of $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$ leads to its high activity for low-temperature oxidation of CO,¹¹ and the pre-reduction treatment results in its light-off temperature increasing to 157 °C.¹² Recently, it was found that Co_3O_4 pretreated at 150–250 °C in the non-reducing dry gas shows

surprisingly high activity for CO oxidation at -80 °C.¹³ For the noble metal (Pt) supported on Co_3O_4 or $\text{Co}_3\text{O}_4/\text{CeO}_2$,¹⁴ the pre-reduction at certain temperature is necessary to induce their high catalytic activity at low temperature.

For the catalytic CO oxidation, the active sites of Co_3O_4 catalyst as well as the catalytic reaction mechanism have also been studied.^{15–18} It is the consensus that adsorbed CO reacts with the surface oxygen over catalysts to produce CO_2 , and then the depleted oxygen is replenished by gaseous O_2 . However, the active sites of Co_3O_4 catalyst are still debatable. For example, Xie *et al.*¹⁵ proposed that the perfect catalytic performance of Co_3O_4 nanorods should be attributed to more Co^{3+} species on its surface due to predominant exposition of its (110) facets. Pollard *et al.*¹⁶ believed that CO is adsorbed onto cobalt atoms with a low oxidation state (Co^{2+}) and the highest catalytic activity can be achieved when the ratio of $\text{Co(II)}/\text{Co(III)}$ is controlled to 1:4 on the surface and the particle size is smaller. Sadykov and co-workers^{17,18} proposed that the high catalytic activity of Co_3O_4 pretreated in He at 350 °C should be attributed to the formation of weakly bound oxygen species as well as surface reconstruction. Recently, Yu and co-workers¹³ found that the surface oxygen vacancies are formed over Co_3O_4 pretreated in non-reducing gases, which can accelerate the surface excess oxygen adsorption and then improve the catalytic activity. Based on the obtained results above, it is clear that both active sites of CO and O_2 should be taken into account simultaneously, since the adsorption and activation of these two reactants are equally important for CO oxidation.

^a Key Laboratory for Advanced Materials and Research Institute of Industrial Catalysis, East China University of Science and Technology, Shanghai 200237, P. R. China.
E-mail: gzhlu@ecust.edu.cn; Fax: +86-21-64253824

^b Research Institute of Applied Catalysis, Shanghai Institute of Technology, Shanghai 200235, P. R. China

CeO₂ and CeO₂-containing materials have recently attracted much attention as an efficient oxidation catalyst, because CeO₂ has a unique redox property and high oxygen storage capacity (OSC).^{19,20} They are cheap and environmentally friendly catalysts especially for the catalytic destruction of various volatile organic compounds (VOCs) and Cl-VOCs, such as methane, methanol, propane and trichloroethylene.²¹ In order to improve the CO or O₂ adsorption, accelerate the reaction of CO(ad) and O(ad), or make CO₂ desorb more quickly, we attempt to modify the active sites of Co₃O₄ by adding CeO₂, resulting in the improvement of the catalytic performance of Co₃O₄ for low-temperature CO oxidation.

Herein, the CeO₂-Co₃O₄ catalyst was developed and prepared by a precipitation-oxidation method. The performances of Co₃O₄ and CeO₂-Co₃O₄ for CO low-temperature oxidation and the effect of pretreatment on its properties were investigated. Temperature programmed desorption (TPD) of CO and CO₂ on the catalysts as well as the redox properties of catalysts were investigated. The promotional role of CeO₂ on the active site of Co₃O₄ for low temperature CO oxidation was elucidated.

2. Experimental

2.1. Catalysts preparation

The catalysts were prepared by a precipitation-oxidation method. 1 M NaOH aqueous solution was gradually added to 100 mL 0.62 M Co(NO₃)₂ aqueous solution or 100 mL mixed aqueous solution of Co(NO₃)₂ and Ce(NO₃)₃ (the total ionic concentration of Co²⁺ and Ce³⁺ is also 0.62 M) under stirring at 30 °C, and the pH of the synthesis solution was maintained to about 10. Then 30 mL 30% H₂O₂ solution was added dropwise under stirring, and this synthesis solution was aged for 2 h. The formed precipitation was filtered and washed with de-ionized water, and dried at 110 °C for 15 h. The dried samples were calcined at 350 °C in a muffle furnace for 3 h. In CeO₂-Co₃O₄, the molar ratio of Ce/Co is 2/8. A pure CeO₂ sample was prepared by a similar method.

2.2. Catalytic activity testing

The catalytic activities of catalysts for CO oxidation were tested in a continuous flow quartz tube microreactor (ϕ 8 mm \times 23 cm). 200 mg catalyst (40–60 mesh) and 600 mg silica sand were mixed up and filled into the reactor. The flow rate of feed gases consisted of 1% CO, 10% O₂ and 89% N₂ was 20 mL min⁻¹. Before activity testing, the catalysts were pretreated in N₂ flow at 500 °C for 30 min and then cooled down to room temperature.

2.3. Characterization of the catalysts

BET surface areas of the samples were measured by N₂ adsorption-desorption at -196 °C on a micromeritics ASAP-2020 instrument, and were calculated by the Brunauer-Emmett-Teller (BET) method. Powder X-ray diffraction (XRD) patterns were recorded on a PANalytical PW 3040/60 X'Pert Pro powder diffractometer using Cu-K α radiation, which was operated at 40 kV and 40 mA and a scanning speed was 0.5° min⁻¹.

H₂-Temperature programmed reduction (H₂-TPR) was performed in a quartz U-tube with 50 mg catalyst (40–60 mesh). After the catalyst was pretreated in N₂ at 500 °C for 30 min, it

was cooled down to room temperature, and then the mixture of 10 vol% H₂/N₂ (25 mL min⁻¹) was used instead of N₂. The heating rate was 10 °C min⁻¹. The uptake amounts of H₂ were measured by a thermal conductivity detector (TCD).

Temperature programmed desorption of O₂ (O₂-TPD) and CO (CO-TPD) was performed in a quartz tube reactor system equipped with a quadrupole mass spectrometer (MS, IPC 400, INFICON Co. Ltd.). 200 mg samples (40–60 mesh) were pretreated in N₂ at 500 °C for 30 min or reduced in H₂ (10%) at 300 °C for 30 min. After it was cooled down to room temperature, pure O₂ (30 ml min⁻¹) or pure CO (30 ml min⁻¹) was introduced through the catalyst bed for 60 min. Then He (30 mL min⁻¹) was switched and the temperature was raised to 750 °C at a heating rate of 10 °C min⁻¹. The mass signal of O₂ ($m/z = 32$), CO ($m/z = 28$), CO₂ ($m/z = 44$) was recorded.

The redox properties of catalysts were tested by the transient-response method which can be described as follows. The sample (200 mg, 40–60 mesh) filled in the reactor was pretreated in He (30 mL min⁻¹) at 500 °C for 30 min and then cooled down to room temperature in flowing He. Then 1.58 mL min⁻¹ CO (5% CO/He) was added in 30 mL min⁻¹ He carrier gas for 5 min; after He was kept to flow the sample for 5 min, 1.58 mL min⁻¹ O₂ (5% O₂/He) was added to the He carrier gas until the composition of tail gas out of the reactor was stable, and after O₂ gas was stopped the He carrier gas was flowed continually. Then the process above was repeatedly for a second time. The content of CO₂ ($m/z = 44$), CO ($m/z = 28$) and O₂ ($m/z = 32$) in the effluent gas was detected by a quadrupole mass spectrometer online.

3. Results and discussion

3.1. Physicochemical properties of catalysts

With the help of low-temperature N₂ adsorption, the BET surface areas (S_{BET}) of Co₃O₄, CeO₂-Co₃O₄ and CeO₂ were measured as 57, 123 and 76 m² g⁻¹, respectively, which illustrates that an introduction of CeO₂ in Co₃O₄ leads to an increase in its S_{BET} . The XRD results (Fig. 1) show that CeO₂-Co₃O₄ has weaker diffraction peaks of the Co₃O₄ phase than that of pure Co₃O₄, and CeO₂ peaks are much lower than that of pure CeO₂. These results indicate that CeO₂ is dispersed in Co₃O₄, resulting in smaller crystal sizes and a higher surface area of Co₃O₄. It can also be observed from Fig. 1 that the diffraction peaks of Co₃O₄ in CeO₂-Co₃O₄ catalyst shift a little to higher 2θ as compared to that of pure Co₃O₄, indicating that the presence of Ce makes the cell parameter of Co₃O₄ reduction, which can be attributed to the interaction between Co₃O₄ and CeO₂.

The results of H₂-TPR (Fig. 2) show that pure Co₃O₄ exhibits two reduction peaks. In general, the low temperature peak is attributed to the reduction of Co³⁺ to Co²⁺ and the high temperature peak to the reduction of Co²⁺ to Co⁰.^{22–24} In order to calculate the H₂ consumption amount of each step reduction, we did a blank test and built a relationship between the reduction peak area and the H₂ consumption amount for Co₃O₄. By calculation, the low temperature peak for the reduction of Co³⁺ to Co²⁺ has consumed 2.36×10^{-4} mol H₂, and is 6.52×10^{-4} mol H₂ for the high temperature peak.

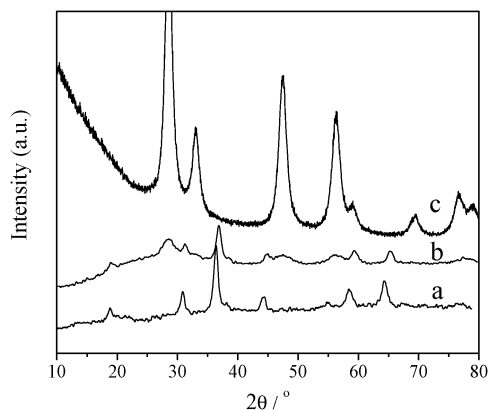


Fig. 1 X-Ray diffraction patterns of Co_3O_4 (a), $\text{CeO}_2\text{-Co}_3\text{O}_4$ (b), and CeO_2 (c).

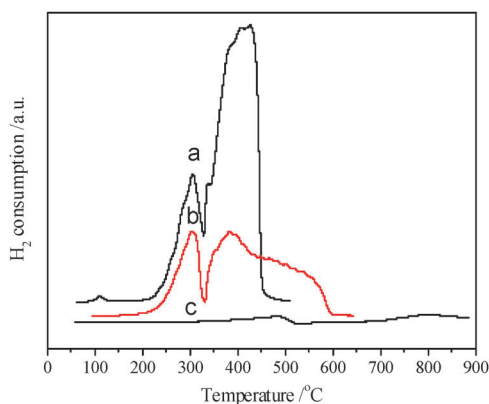


Fig. 2 H_2 -TPR profiles of Co_3O_4 (a), $\text{CeO}_2\text{-Co}_3\text{O}_4$ (b), and CeO_2 (c).

The ratio of the H_2 consumption amount in high temperature peak and that in low temperature peak is ~ 2.8 , which is close to 3, indicating that the reduction mechanism of Co_3O_4 is in agreement with the results reported,^{22–24} that is, Co_3O_4 was first reduced to CoO at ~ 300 °C, and then CoO was reduced to metallic cobalt at ~ 400 °C. Adding CeO_2 in Co_3O_4 hardly affects its reduction peak at low temperatures, but has a significant influence on the high temperature reduction peak, such as higher peak temperature, smaller peak area and broader shape. This is because CeO_2 is weakly reduced, and the presence of CeO_2 makes the reduction process of Co^{2+} difficult. To sum up, the reduction properties of Co_3O_4 and CeO_2 are changed markedly due to the interaction between two components.

3.2. Temperature-programmed desorption of O_2 and CO

The results of O_2 -TPD in Fig. 3 show that Co_3O_4 exhibits weak but complicated O_2 desorption peaks. CeO_2 displays two O_2 desorption peaks centred at ~ 160 and ~ 600 °C. $\text{CeO}_2\text{-Co}_3\text{O}_4$ exhibits a strong asymmetric desorption peak of O_2 centred at ~ 120 °C.

Generally, the adsorbed oxygen changes in the following procedures: $\text{O}_2(\text{ad}) \rightarrow \text{O}_2^-(\text{ad}) \rightarrow \text{O}^-(\text{ad}) \rightarrow \text{O}^{2-}(\text{lattice})$.^{25,26} The physically adsorbed oxygen relatively easily desorbs below 0 °C and the lattice O species desorbs with most difficulty. Therefore, the desorption peak at ~ 160 °C is ascribed to $\text{O}_2^-(\text{ad})$ species and one at ~ 600 °C to $\text{O}^{2-}(\text{lattice})$. The presence of CeO_2 can promote the formation of $\text{O}_2^-(\text{ad})$

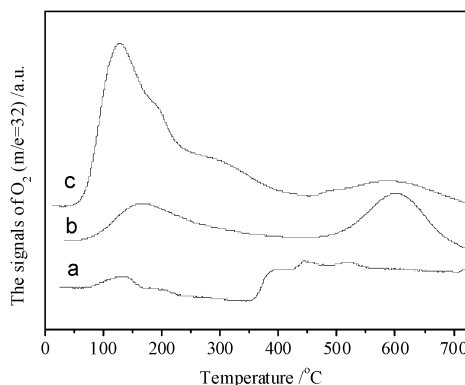


Fig. 3 O_2 -TPD profiles of Co_3O_4 (a), CeO_2 (b) and $\text{CeO}_2\text{-Co}_3\text{O}_4$ (c) pretreated in He atmosphere at 500 °C for 30 min.

species, which is crucial to the catalytic CO oxidation at low temperature.

The results of CO-TPD are shown in Fig. 4 and 5. By comparing the desorption profiles of CO and CO_2 , we can find that both profiles of CO and CO_2 are similar for $\text{CeO}_2\text{-Co}_3\text{O}_4$ (Fig. 4), except for the weaker intensity of CO desorption. The results of *in situ* FT-IR testing show that CO is generally adsorbed on the surface of Co_3O_4 to form the species of carbonate,¹⁶ which can decompose to form CO_2 and a small amount of CO.

The CO_2 desorption peaks over Co_3O_4 are wide and complicated, illustrating that CO is adsorbed strongly on multifold active sites. The more strongly CO adsorbs on a catalyst, the higher the desorption temperature of CO will be. With an introduction of CeO_2 , CO_2 desorption increases significantly, especially at ~ 140 °C, indicating that CeO_2 can accelerate the adsorption of CO, the reaction of adsorbed CO with surface oxygen and the desorption of CO_2 . It was reported that the CO oxidation on Co_3O_4 followed a redox cycle¹¹ and Co^{3+} was considered to be the active sites for CO adsorption.¹⁵ We consider that the CO species desorbed at low temperature is of high activity and played a crucial role in the low-temperature reaction of CO. Therefore we calculated the peak area (PA) centred at ~ 140 °C, and PA of Co_3O_4 is 2.58×10^{-6} (a.u.) and PA of $\text{CeO}_2\text{-Co}_3\text{O}_4$ is 4.02×10^{-6} (a.u.). The result above shows that adding CeO_2 in Co_3O_4 can obviously increase the number of active sites of the Co_3O_4 catalyst for CO adsorption.

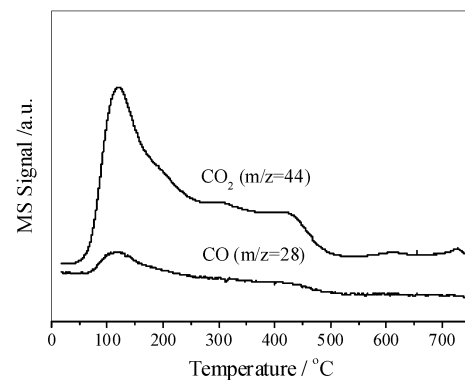


Fig. 4 Desorption profiles of CO_2 and CO during CO-TPD over $\text{CeO}_2\text{-Co}_3\text{O}_4$.

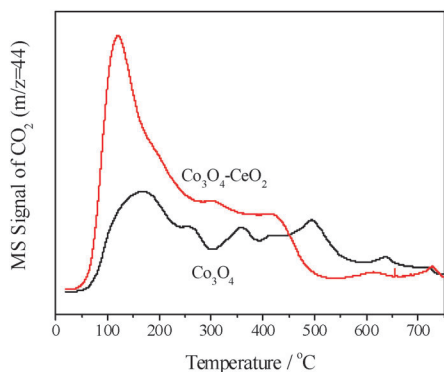


Fig. 5 Desorption profiles of CO₂ during CO-TPD over Co₃O₄ and CeO₂-Co₃O₄.

3.3. Transient-response reaction

In order to monitor the redox properties of the Co₃O₄ and CeO₂-Co₃O₄ catalysts and the surface reaction of adsorbed species over the surface of catalysts, transient-response reactions of CO and O₂ over catalysts were carried out, and the results are shown in Fig. 6 and 7. When CO was introduced through the Co₃O₄ catalyst (Fig. 6), some CO was adsorbed and a small amount of CO₂ was desorbed; when 5% O₂ was injected, CO₂ desorption was hardly observed; as CO was switched again, no evident CO₂ desorption or CO adsorption can be observed.

Being different from the Co₃O₄ catalyst, when CO was passed through CeO₂-Co₃O₄ (Fig. 7), more amount of CO was adsorbed, some CO₂ was desorbed and its desorption amount was more than the CO₂ amount desorbed on Co₃O₄ (Fig. 6). With switching O₂, however, much more CO₂ was desorbed quickly; after CO was switched a second time, some CO₂ was also produced in spite of the presence of CO adsorption. Switching O₂ again also led to producing a similar amount of CO₂ as that in the first injection. These results imply that CeO₂ can promote obviously the redox properties of Co₃O₄ and the reaction between O₂ and CO adsorbed species.

3.4. Catalytic activity testing

Fig. 8 shows the catalytic performances of Co₃O₄, CeO₂-Co₃O₄ and CeO₂ for CO oxidation. Among them,

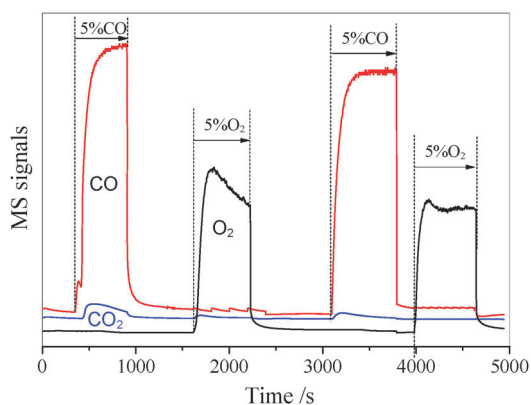


Fig. 6 Concentration changes of CO, O₂ and CO₂ on a transient-response reaction over Co₃O₄.

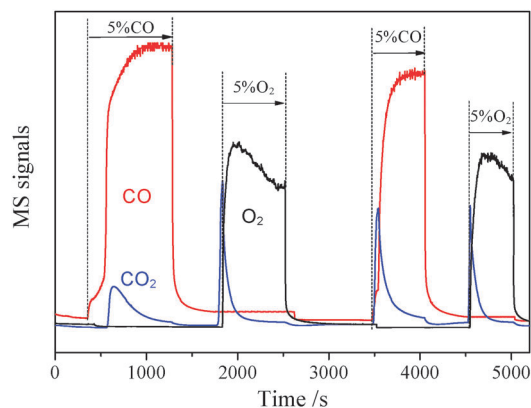


Fig. 7 Concentration changes of CO, O₂ and CO₂ on a transient-response reaction over CeO₂-Co₃O₄.

CeO₂ shows the lowest activity with T_{100} (the reaction temperatures for 100% CO conversion) as high as 323 °C. The catalytic activity of Co₃O₄ for the CO oxidation is obviously higher than that of CeO₂, and its T_{100} is 153 °C. The CeO₂-Co₃O₄ catalyst shows the highest activity and its T_{100} is only -60 °C.

It was reported that the high activity of Co₃O₄ for CO oxidation is likely to be due to the relatively low ΔH of O₂ vaporization from Co₃O₄,^{27,28} which means that the Co-O bond strength of Co₃O₄ is relatively weak, resulting in desorption of more lattice oxygen. Moreover, the pretreatment of the catalyst is also very important for improving its catalytic performance. Yu *et al.*¹³ found that the pretreatment of Co₃O₄ in dry air, CO in air, or N₂ at 150–250 °C can dramatically enhance its catalytic activity. Tang *et al.*²⁹ reported that 20% CeO₂/Co₃O₄ reduced at 200 °C exhibited a high surface area ($S_{\text{BET}} = 109 \text{ m}^2 \text{ g}^{-1}$) and high catalytic activity for CO oxidation. Therefore, the effect of the pretreatment conditions on the catalytic performance of CeO₂-Co₃O₄ has been investigated here.

The O₂-TPD-MS results in Fig. 9 show that the pretreatment conditions have an influence on the oxygen character of CeO₂-Co₃O₄. CeO₂-Co₃O₄ pre-oxidized at 500 °C shows the weakest oxygen desorption at ~192 °C. Pretreatment in N₂ can promote significantly the O₂ desorption on this catalyst, including more desorption amount and a lower desorption

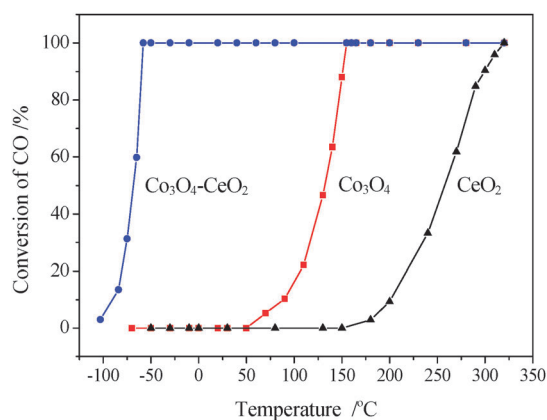


Fig. 8 The catalytic activities of CeO₂-Co₃O₄, Co₃O₄ and CeO₂ for CO oxidation. (1% CO, 10% O₂ and 89% N₂).

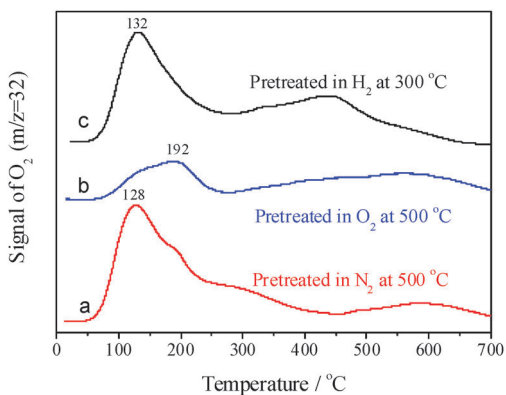


Fig. 9 O₂-TPD profiles of CeO₂-Co₃O₄ pretreated in N₂ at 500 °C (a), O₂ at 500 °C (b) and H₂ at 300 °C (c) for 30 min.

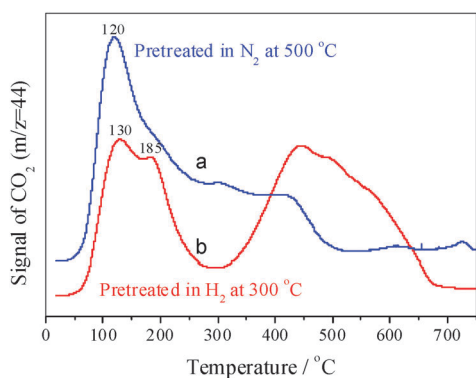


Fig. 10 CO-TPD profiles of CeO₂-Co₃O₄ pretreated in N₂ at 500 °C (a) and H₂ at 300 °C (b) for 30 min.

temperature (~ 128 °C). After CeO₂-Co₃O₄ is reduced in H₂ at 300 °C, its oxygen desorption peak at ~ 132 °C is decreased slightly, but there appears a new desorption peak at ~ 450 °C.

The CO-TPD-MS results show that CeO₂-Co₃O₄ pre-oxidized or pretreated in N₂ has a very similar desorption curve, so only the CO-TPD-MS curve of CeO₂-Co₃O₄ pretreated in N₂ is displayed in Fig. 10. The results show that CeO₂-Co₃O₄ pretreated in N₂ exhibits a main desorption peak of CO₂ at ~ 120 °C and two small peaks at 300 °C and 420 °C. For the catalyst reduced in H₂ at 300 °C, its desorption peak of CO₂ at ~ 120 °C became two overlapping peaks at 130 and 185 °C; furthermore, a strong and wide desorption peak at 350–650 °C appeared.

The effect of pre-treatment in different conditions on the catalytic activity of CeO₂-Co₃O₄ is presented in Fig. 11. The catalyst pretreated in He (or N₂) shows the highest catalytic activity with T_{100} of -60 °C, while the pre-oxidised one shows relatively lower catalytic activity with T_{100} of -40 °C. In contrast, the pre-reduced catalyst shows much lower catalytic activity, with T_{100} of 80 °C.

4. Discussions

The oxidation of CO over Co₃O₄ has been proposed to follow the redox cycle, where gas-phase CO adsorbs on a cobalt site, and adsorbed CO reacts with a lattice oxygen to form CO₂(g) and an oxygen vacancy. The oxygen vacancy is subsequently

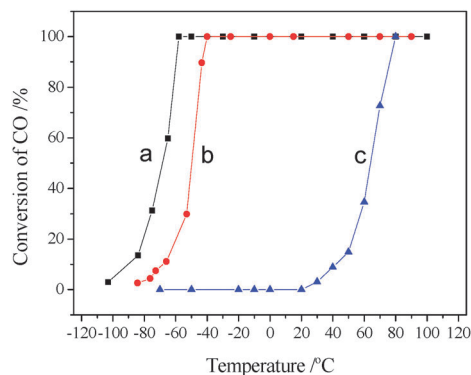


Fig. 11 Catalytic activities of CeO₂-Co₃O₄ pretreated in He at 500 °C (a), O₂ at 500 °C (b) and H₂ at 300 °C (c) for 30 min. (1% CO, 10% O₂ and 89% N₂).

replenished by oxygen from the gas phase.^{11,30} This proposal seems reasonable because both active sites of CO and O₂ have been taken into account. In the spinel structure of Co₃O₄ (Co²⁺(Co³⁺)₂O₄), Co²⁺ and Co³⁺ are located at the tetrahedral and octahedral sites, respectively, in which Co²⁺ can effectively adsorb O₂ to form superoxide (O₂⁻(ad)) and peroxide (2O⁻(ad)). The results of O₂-TPD over Co₃O₄ show that the desorption of oxygen species is ascribed to superoxide and peroxide species. Because of the lower Co²⁺ content relative to Co³⁺, the oxygen species formed over Co₃O₄ is less. However, Co³⁺ is generally regarded as the active site of CO adsorption according to experimental¹⁵ and theoretical research results.³¹ The results of CO-TPD show that CO₂ desorbs with difficulty on the surface of Co₃O₄. The results of the transient-response reaction also show that the adsorbed CO species on Co₃O₄, which is carbonate species from *in situ* diffuse reflectance infrared Fourier transform (DRIFT),³² is inert for reaction with O₂ to produce CO₂. In order to improve the catalytic activity of Co₃O₄, we should improve the CO or O₂ adsorption, accelerate the reaction of CO(ad) and O(ad), or make CO₂ desorb more quickly, by improving or modifying the property of active sites of Co₃O₄. Therefore, using foreign elements modification or an appropriate preparation method and pretreatment for Co₃O₄ catalyst are necessary to form optimum active sites on the surface, which can effectively adsorb CO and O₂ or make the surface reaction and desorption of CO₂ faster.

It is well known that ceria has a high oxygen storage/releasing capacity and redox properties by a couple of Ce⁴⁺/Ce³⁺, which makes more oxygen species available for the oxidation process.^{23,33–35} The O₂-TPD results indicate that CeO₂ alone displays a weak O₂ desorption peak, but can promote the formation of adsorbed oxygen species (mainly as superoxide) over CeO₂-Co₃O₄. As the superoxide holds a relatively weaker bond of O₂⁻ over the surface of the catalyst, Co²⁺ donates an electron to the π_{2p}^* antibonding orbital of O₂⁻, resulting in weakening of the O–O bond to facilitate O₂⁻ decomposing to O and O⁻. Consequently, the superoxide species seem more active than other oxygen species for CO oxidation. Transient-response results (Fig. 6 and 7) show that the adsorbed CO species over CeO₂-Co₃O₄ readily react with oxygen species to form CO₂, and the formed CO₂ can desorb more quickly. In addition, adding CeO₂ can also increase the

desorption of CO₂ or its amount formed at low temperature (shown in the CO-TPD spectra of Fig. 5), that is to say, the formed carbonate species are easy to decompose to CO₂ and H₂O, which should be attributed to the high activity of CeO₂-Co₃O₄. To sum up, CeO₂ plays a crucial role in improving the adsorption of O₂, the reaction of adsorbed CO with surface oxygen and the desorption of CO₂ on the catalyst surface, and the presence of CeO₂ can make the above-mentioned process take place more easily and quickly, resulting in the higher activity of CeO₂-Co₃O₄ for CO oxidation. In the three courses mentioned above which are promoted by CeO₂, we can find that adding CeO₂ improves the most effectively the reaction of adsorbed CO and activated O₂ on the surface of the catalyst (Fig. 6 and 7), comparing with other two courses. This means that the presence of CeO₂ makes the Co₃O₄ catalyst have much stronger ability to activate gas phase O₂ (Fig. 3) to react with adsorbed CO. Therefore, the course of adsorbed CO reacting with activated O₂ might be the rate-determining step for CO oxidation.

Besides, pretreatment is also necessary to activate catalysts,¹³ and Co₃O₄ based catalysts should be preoxidised at high temperature in order to form rich oxygen surface species that can effectively react with adsorbed CO. In the activity testing of CeO₂-Co₃O₄, we have found that its T₁₀₀ is only at -60 °C after the catalyst was pretreated in N₂ at 500 °C for 30 min, and using the catalyst peroxidised in O₂ its T₁₀₀ rises to -40 °C. These results are not consistent with the reported results of Co₃O₄, which may be attributed to the presence of ceria in Co₃O₄. It was reported that when the catalysts are located in vacuum or inert atmosphere, their surface is not only decontaminated, but also oxygen rich vacancies can be formed.³⁶ Moreover, at room temperature the single oxygen vacancy is highly mobile, and oxygen vacancy diffusion on the surface is fundamental in the oxidation process.^{37,38} Lately, we have put forward a two-step exchange mechanism for oxygen diffusion on the CeO₂ surface, in which the barrier of oxygen diffusion is only 0.61 eV.³⁹ After CeO₂-Co₃O₄ was pretreated in N₂, much more oxygen vacancies can be formed on the surface, leading to formation of more active sites; when the catalyst was heated in oxygen, the oxygen vacancies formed were filled by gaseous oxygen, and oxygen is hard to adsorb on the surface at low temperature. The O₂-TPD results in Fig. 9 demonstrate that pre-oxidized CeO₂-Co₃O₄ exhibits the lowest amount of oxygen desorption, while the one pretreated in N₂ displays the highest O₂ desorption. Therefore, CeO₂-Co₃O₄ pretreated in N₂ shows higher catalytic activity and stability for CO oxidation. If more oxygen vacancy formed on surface, will its catalytic activity be higher? We have pre-reduced the catalyst at 200 °C in H₂, as a result, the most oxygen vacancies formed. However, this pre-reduced CeO₂-Co₃O₄ showed the poorest catalytic activity (Fig. 11). The CO-TPD results in Fig. 10 also show that the desorption of CO₂ becomes difficult over pre-reduced CeO₂-Co₃O₄, and strong CO₂ desorption can be observed only at higher temperature, which shows that the carbonate species bond strongly on the surface of the catalyst, resulting in blocking the catalytically active sites and deactivation of the catalyst.

On the basis of the above results, we suggest that Co²⁺ is the active site of O₂ adsorption, and Co³⁺ is the active site of CO adsorption in the CeO₂-Co₃O₄ catalyst. Adding CeO₂ promotes the weak adsorption of CO, which readily reacts

with surface oxygen to form CO₂. The decomposition of surface carbonate species and desorption of CO₂ from the catalyst surface are also accelerated by CeO₂. Consequently, the CeO₂-Co₃O₄ catalyst shows excellent catalytic activity for low temperature CO oxidation.

5. Conclusions

In summary, the CeO₂-Co₃O₄ catalyst was prepared by a precipitation-oxidation method, and exhibits an excellent catalytic performance for low temperature CO oxidation. The results show that, (1) adding ceria in Co₃O₄ catalyst can increase its surface area and reduce the crystal size of Co₃O₄; (2) the presence of CeO₂ can improve the adsorption of O₂, the reaction of adsorbed CO with surface oxygen and the desorption of CO₂ on the catalyst surface; (3) pretreating CeO₂-Co₃O₄ in N₂ atmosphere can enhance its catalytic activity and stability for low temperature CO oxidation due to formation of oxygen vacancies. The catalyst pre-reduced in H₂ shows lower activity for CO oxidation although it has more oxygen vacancies on the surface, because of the difficult desorption of CO₂ on the reduced CeO₂-Co₃O₄ catalyst; (4) the presence of CeO₂ can make the above-mentioned process take place more easily and quickly, resulting in an obvious increase in the catalytic activity of CeO₂-Co₃O₄ for CO oxidation, for instance, T₁₀₀ is only -60 °C.

Acknowledgements

This project was financially supported by the National Basic Research Program of China (2010CB732300), the Fundamental Research Funds for the Central Universities, the "Shu Guang" Project (10GG23) and Leading Academic Discipline Project (J51503) of Shanghai Municipal Education Commission and Shanghai Education Development Foundation.

References

- 1 C. B. Wang, C. W. Tang, S. J. Gau and S. H. Chien, *Catal. Lett.*, 2005, **101**, 59.
- 2 H. K. Lin, H. C. Chiu, H. C. Tsai, S. H. Chien and C. B. Wang, *Catal. Lett.*, 2003, **88**, 169.
- 3 A. Holmgren, B. Andersson and D. Duprez, *Appl. Catal., B*, 1999, **22**, 215.
- 4 H. Q. Zhu, Z. F. Qin, W. J. Shan, W. J. Shen and J. G. Wang, *J. Catal.*, 2005, **233**, 41.
- 5 M. F. Luo, J. M. Ma, J. Q. Lu, Y. P. Song and Y. J. Wang, *J. Catal.*, 2007, **246**, 52.
- 6 L. Hu, Q. Peng and Y. Li, *J. Am. Chem. Soc.*, 2008, **130**, 16136.
- 7 T. He, D. R. Chen, X. L. Jiao, Y. Y. Xu and Y. X. Gu, *Langmuir*, 2004, **20**, 8404.
- 8 Y. Q. Wang, C. M. Yang, W. Schmidt, B. Spliethoff, E. Bill and F. Schuth, *Adv. Mater.*, 2005, **17**, 53.
- 9 B. B. Lakshmi, C. J. Patrissi and C. R. Martin, *Chem. Mater.*, 1997, **9**, 2544.
- 10 J. Feng and H. C. Zeng, *Chem. Mater.*, 2003, **15**, 2829.
- 11 J. Jansson, M. Skoglundh, E. Fridell and P. Thormahlen, *Top. Catal.*, 2001, **16/17**, 385.
- 12 P. Thormahlen, M. Skoglundh, E. Fridell and B. Andersson, *J. Catal.*, 1999, **188**, 300.
- 13 Y. B. Yu, T. Takei, H. Ohashi, H. He, X. L. Zhang and M. Haruta, *J. Catal.*, 2009, **267**, 121.
- 14 M. Kang, M. W. Song and C. H. Lee, *Appl. Catal., A*, 2003, **251**, 143.

-
- 15 X. W. Xie, Y. Li, Z. Q. Liu, M. Haruta and W. J. Shen, *Nature*, 2009, **458**, 746.
 - 16 M. J. Pollard, B. A. Weinstock, T. E. Bitterwolf, P. R. Griffiths, A. P. Newbery and J. B. Paine, *J. Catal.*, 2008, **254**, 218.
 - 17 V. A. Razonov, V. A. Sadykov, S. A. Veniaminov, N. N. Bulgakov, O. N. Kovalenko, Yu. D. Pankratiev, V. V. Popovskii, G. N. Kryukova and S. F. Tikhov, *React. Kinet. Catal. Lett.*, 1988, **37**, 109.
 - 18 V. A. Sadykov, S. F. Tikhov, S. V. Tsybulya, G. N. Kryukova, S. A. Veniaminov, V. N. Kolomiichuk, N. N. Bulgakov, E. A. Paukshtis, V. P. Ivanov, S. V. Koshcheev, V. I. Zaikovskii, L. A. Isupova and L. B. Burgina, *J. Mol. Catal. A: Chem.*, 2000, **158**, 361.
 - 19 H. Y. Li, H. F. Wang, X. Q. Gong, Y. L. Guo, Y. Guo, G. Z. Lu and P. Hu, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2009, **79**, 193401.
 - 20 H. F. Wang, Y. L. Guo, G. Z. Lu and P. Hu, *Angew. Chem., Int. Ed.*, 2009, **48**, 8289.
 - 21 H. F. Li, G. Z. Lu, Q. G. Dai, Y. Q. Wang, Y. Guo and Y. L. Guo, *Appl. Catal., B*, 2011, **102**, 475.
 - 22 L. Xue, C. B. Zhang, H. He and Y. Teraoka, *Appl. Catal., B*, 2007, **75**, 167.
 - 23 X. D. Hou, Y. Z. Wang and Y. X. Zhao, *Catal. Lett.*, 2008, **123**, 321.
 - 24 Y. Y. Liu, T. Hanaoka and T. Miyazawa, *Fuel Process. Technol.*, 2009, **90**, 901.
 - 25 C. Li, K. Domen, K. Maruya and T. Onishi, *J. Chem. Soc., Chem. Commun.*, 1988, 1541.
 - 26 Y. M. Choi, H. Abernathy, H. T. Chen, M. C. Lin and M. L. Liu, *ChemPhysChem*, 2006, **7**, 1957.
 - 27 B. A. Sazonov, V. V. Popovskii and G. K. Borekov, *Kinet. Catal.*, 1968, **9**, 255.
 - 28 M. Haneda, Y. Kintaichi, N. Bion and H. Hamada, *Appl. Catal., B*, 2003, **46**, 473.
 - 29 C. W. Tang, C. C. Kuo, M. C. Kuo, C. B. Wang and S. H. Chien, *Appl. Catal., A*, 2006, **309**, 37.
 - 30 J. Jansson, *J. Catal.*, 2000, **194**, 55.
 - 31 P. Broqvist, I. Panas and H. Persson, *J. Catal.*, 2002, **210**, 198.
 - 32 J. Fujita, A. E. Martell and K. Nakamoto, *J. Chem. Phys.*, 1962, **36**, 339.
 - 33 A. Martinez-Arias, M. Fernandez-Garcia, O. Galvez, J. M. Coronado, J. A. Anderson, J. C. Conesa, J. Soria and G. Munuera, *J. Catal.*, 2000, **195**, 207.
 - 34 Martinez-Arias, R. Cataluna, J. C. Conesa and J. Soria, *J. Phys. Chem. B*, 1998, **102**, 809.
 - 35 A. C. Serre, F. Garin, G. Belot and G. Maire, *J. Catal.*, 1993, **141**, 1; (b) 1993, **141**, 9.
 - 36 Y. Yu, T. Takei, H. Ohashi, H. He, X. Zhang and M. Haruta, *J. Catal.*, 2009, **267**, 121–128.
 - 37 Y. Namai, K. Fukui and Y. Iwasawa, *Catal. Today*, 2003, **85**, 79.
 - 38 Y. Namai, K. Fukui and Y. Iwasawa, *J. Phys. Chem. B*, 2003, **107**, 11666.
 - 39 H. Y. Li, H. F. Wang, Y. L. Guo and G. Z. Lu, *Chem. Commun.*, 2011, **47**, 6105.