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1. Introduction

It is well known that ceria (CeO$_2$) is a key component in the formulation of catalysts owing to its excellent redox property and high oxygen storage capacity, thus, has attracted tremendous interest in fundamental studies and practical applications. Over the last decade, the synthesis of CeO$_2$-based bimetal oxide catalysts and the optimization of their size, morphology, and composition were extensively studied because some bimetal oxides exhibit remarkable properties distinctly different from their monometallic counterparts, known as the synergistic effect in catalysis due to the interaction between two oxides. During the catalytic reactions, the interfacial contact between CeO$_2$ and secondary metal oxide is proposed to be active site, which is of great importance in determining their catalytic performance. Therefore, from a structural viewpoint, a considerable contact within components is highly expected in a good catalyst, which can enable an efficient diffusion of reactants into the active sites. Until now, co-precipitation, impregnation and sol-gel approaches are widely used to prepare CeO$_2$-based bimetal oxides. Although the components mix well even at the atomic level, the exposure of the active sites to reactants is suppressed for the catalysts prepared using the former two routes, except in the case of the utilization of specific templates (e.g. mesoporous templates). Since the hydrolysis and condensation rates of the precursors differ considerably, phase separation is ineluctable during the sol-gel process, thus leading to the decrease in contact within components.

To address the issues above, the fabrication of bimetal oxides with core-shell structures by depositing the secondary shell onto the pre-synthesized core surface seems feasible, because the sufficient contact between core and shell is guaranteed in this kind of structure. However, the conventional layer-by-layer technique is a multistep process that requires precise control in surface modification and shell deposition. Specifically, to avoid homogeneous nucleation of the shell component, it is necessary to perform a surface modification to the core with the assistance of organic species (e.g. polymers or surfactants). Because the heterogeneous catalytic reaction occurs on the catalyst surface, these organic species need to be removed so as to fully expose the surface active sites. Unfortunately, a complete removal of these organic species is still challenging, and hence resulting in the deactivation of the catalyst. Moreover, the organic compounds and precipitation agents for the shell deposition always need to be carefully chosen. Obviously, this method is not economically feasible for a mass production of catalysts and is not preferred in industrial fields. Therefore, it is of highly interest to develop a surface modification-free, and easily scale-up approach to synthesize bimetal oxide catalysts with core-shell structure.

Solid-liquid interfacial reaction, proceeded by a sacrificial solid template reacting with one designated solution, has been identified as an effective method to synthesize core-shell structured materials. In this method, the surface modification-free manipulation can be realized as the formation of new shells is merely driven by the chemical reactions between templates and ions in solution. For example, a simple redox reaction in Ce$^{4+}$ ion solution with the presence of Cu$_2$O as the sacrificial template leads to the formation of Cu$_2$O-CeO$_2$ core-shell bimetal oxides. Recently, we also prepared Ce$_2$O$_3$-MnO$_2$ bimetal oxides by treating Ce(OH)CO$_3$ templates with KMnO$_4$ aqueous solution, where MnO$_4^-$ is reduced to MnO$_2$ and the Ce$^{4+}$ in Ce(OH)CO$_3$ is simultaneously oxidized to form CeO$_2$. In addition to the redox interfacial reaction, ion exchange is a well-

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It is still an important issue of developing a facile, environmental way to synthesize bimetal oxide materials. In this paper, Co$_9$O$_9$-CeO$_2$ core-shell catalysts were prepared by an interfacial reaction, where Co(CO)$_{1.8}$Cl$_{0.2}$OH$_{1.1}$ nanorods were dispersed in Ce$^{3+}$ aqueous solution for 2 days, followed by a calcination step. The samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). Based on the characterization and comparative experimental results, we proposed that the OFF ions slowly dissociated from Co(CO)$_{1.8}$Cl$_{0.2}$OH$_{1.1}$ precursor combine with Ce$^{3+}$ to develop into Ce(OH)$_3$ nanoparticles because of its smaller solubility product constant than that of Co precursor or Co(OH)$_2$. Neither additional precipitation agent nor stabilizing molecules were employed during the whole preparation. Raman spectroscopy and H$_2$-Temperature program reduction (H$_2$-TPR) analysis revealed that there is a synergistic effect between Co$_9$O$_9$ and CeO$_2$ in the as-prepared Co$_9$O$_9$-CeO$_2$ core-shell catalysts, which is responsible for their enhanced catalytic activity toward CO oxidation in comparison to pure Co$_9$O$_9$ and CeO$_2$...
known way to synthesize core-shell nanomaterials. For example, 
CuO-Cu2S core-shell structure can be achieved upon the addition of 
CuO templates into Na2S solution due to the small solubility 
product constant of Cu2S ($K_{sp}$ = 10^{-48}). So far, the ion exchange 
procedure is restricted to chalcogenide based core-shell 
nanomaterials, in contrast, the synthesis of bimetal oxide with 
core-shell structures via an ion exchange method has not been 
estensively studied yet.

In this paper, we choose CoO$_2$-CeO$_2$ nanostructure as an example to 
demonstrate the interfacial process capable of generating core-
shell bimetal oxides. CoO$_2$-CeO$_2$ bimetal oxide is an interesting 
catalyst that was studied in CO, hydrocarbon and diesel oxidation 
reactions. Herein, CoO$_2$-CeO$_2$ core-shell structured nanorods were 
successfully fabricated by easily reacting the Co(CO)$_6$CeCl$_2$2(OH)$_1$1 nanorods with Ce$^{3+}$ aqueous solution, 
followed by calcination. Compared to the traditional synthetic 
process, neither additional precipitation agent nor stabilizing 
molecules are involved during the whole preparation. The solubility 
product difference between Ce(OH)$_3$ and the employed Co precursor 
plays the key role for the formation of the CeO$_2$ shell.

2. Experimental

2.1 Materials

CoCl$_2$·6H$_2$O was purchased from Aladdin Industrial Corporation, urea (H$_2$NCONH$_2$), cerium(III) nitrate hexahydrate (Ce(NO$_3$)$_3$·6H$_2$O), ammonium cerium(IV) nitrate (NH$_4$)$_2$Ce(NO$_3$)$_6$) and ethanol were purchased from Sinopharm Chemical Reagent Co. Ltd. They were of analytical grade and were 
used without further purification.

2.2 Synthesis of the Co(CO)$_6$CeCl$_2$2(OH)$_1$1 precursor 

Co(CO)$_6$CeCl$_2$2(OH)$_1$1 can be easily prepared by mixing CoCl$_2$ and urea. In a typical synthesis, 1.1897 g (5 mmol) of CoCl$_2$·6H$_2$O was first dissolved in 40 mL of deionized water under vigorous magnetic stirring and 300.3 mg (5 mmol) of urea was then added into the water solution. The obtained claret-red solution was transferred into a Teflon-lined steel autoclave and heated at 100 °C for 12 h in an electric oven. After the autoclave was cooled to room temperature, pink products were collected and washed with deionized water and ethanol three times and dried overnight at 80 °C.

2.3 Synthesis of the CoO$_2$-CeO$_2$, pure CoO$_2$ and CeO$_2$

Different amounts of Ce(NO$_3$)$_3$ were dissolved in 30 mL of 
deionized water under stirring. Then the as-prepared 
Co(CO)$_6$CeCl$_2$2(OH)$_1$1 was added into the above clear solutions and 
kept still for 2 days. Finally, the samples were thoroughly washed 
with ultrapure water, dried, followed by a calcination at 550 °C for 4 h. 

Pure CoO$_2$ was synthesized from direct thermal decomposition of 
Co(CO)$_6$CeCl$_2$2(OH)$_1$1 at 550 °C for 4 h. In the case of pure CeO$_2$, it was prepared by mixing Ce(NO$_3$)$_3$ and NaOH solution. Then the product was washed with deionized water, dried and calcined at 550 °C for 4 h.

2.4 Characterization 

The phases and purity of the prepared samples were examined by 
X-ray powder diffraction (XRD) performed on a Rigaku D/Max-$\gamma$A 
rotating anode X-ray diffractometer with Cu Kα radiation ($\lambda$ = 
1.54178 Å). N$_2$ adsorption–desorption isotherms were measured at 
77 K on a Micromeritics TriStar II 3020 surface area & pore size 
analyzer. Before measurement, the samples were outgassed in a 
vacuum at 300 °C for 4 h. The Brunauer-Emmett-Teller (BET) 
method was used to calculate the surface areas of the samples. The 
morphology and structure of samples were observed by transmission 
electron microscopy (TEM, JEM 2100) equipped with an energy 
dispersive X-ray spectrometer (EDS). X-ray photoelectron spectrometer (XPS) spectra were recorded by a PHI 5300 X-ray photoelectron spectrometer with Al Kα radiation. Micro-Raman 
measurement was conducted with an LabRAM HR Evolution High 
Resolution Raman Spectrometer. H$_2$-Temperature-programmed 
reduction (H$_2$-TPR) experiment was performed with a thermal 
conductivity detector on 50 mg sample using a gas mixture 
composed of 95% (molar) argon and 5% (molar) hydrogen at a flow 
rate of 30 mL min$^{-1}$. The temperature ramping rate was set to be 10 
K min$^{-1}$. The CeO$_2$ contents in CoO$_2$-CeO$_2$ samples were 
determined using inductively coupled plasma mass spectrometer 
(ICP-MS, Thermo Scientific XSeries-2).

2.5 Catalyst Test 

Catalytic activity was tested using a continuous flow fixed-bed 
micro-reactor at atmospheric pressure. In a typical experiment, the 
system was first purged with high purity N$_2$ gas and then a gas 
mixture (1% CO, 10% O$_2$, 89% N$_2$) passed through the reactor at a 
flow rate of 50 mL/min, corresponding to a space velocity of 60 000 
hr$^{-1}$g$^{-1}$ of catalyst. Composition of the gas exiting from the 
reactor was analyzed with an online infrared gas analyzer 
(Gasboard-3100, China Wuhan Cubic Co.), which can 
simultaneously detect CO, CO$_2$ and O$_2$.

3. Results and discussion

Fig. 1 XRD patterns of pure CeO$_2$ (i), CoO$_2$ (ii), and CoO$_2$-CeO$_2$ bimetal oxide catalysts with different CeO$_2$ compositions: 18.5 wt% (iii), 41.7 wt% (iv) and 63.4 wt% (v).

After interfacial reaction and heat-treatment at 550 °C, there are 
two sets of diffraction peaks, one set is corresponding to fluorite-
phase CeO$_2$ (JCPDS no.34-0394), and the other one is indexed to 
spinel-phase CoO$_4$ (JCPDS no.43-1003) (Fig. 1), suggesting that 
CoO$_2$-CeO$_2$ composite can be successfully synthesized through 
an interfacial reaction of Co(CO)$_6$CeCl$_2$2(OH)$_1$1 precursor and Ce$^{3+}$ 
followed by a thermal-treatment. Moreover, the relative intensity of 
CeO$_2$ diffractions is gradually enhanced as the increase of the Ce/Co
mole ratio, suggesting that the CeO₂ content is tunable by simply varying the Ce³⁺ concentration during the interfacial reaction.

Fig. 2 TEM images of the Co(CO₃)₀.₃₅Cl₀.₂(OH)₁.₁ precursor (a, b), the sample obtained by reacting Co precursor with Ce³⁺ ions before (c, d) and after calcination (e-g), and SAED pattern (h) of the Co₃O₄-CeO₂-18.5 wt% bimetal oxide catalyst. Inset in (f) is the EDS result detected from the rod in (f).

The morphologies of the Co(CO₃)₀.₃₅Cl₀.₂(OH)₁.₁ precursor and the Co₃O₄-CeO₂ bimetal oxide are characterized by TEM. As shown in Fig. 2a, the Co precursor is characteristic of one-dimensional (1D) rod(or needle) structure. The rod with a smooth surface is of several micrometers in length and average 80 nm in width (Fig. 2b). After dispersing Co precursor into the Ce(NO₃)₃ solution, there are some dispersed nanoparticles (NPs) depositing on the Co precursor surface, as shown in Fig. 2c,d. Upon calcination, the one-dimensional structure is still maintained although the length of the rods becomes short. Higher magnification TEM image of the rod demonstrates that unlike the structure prior to the interfacial reaction, at this stage the rod turns less compact and is constructed by interconnected NPs surrounded by a NP-string-like thin shell (Fig. 2e,f). The co-existence of Ce and Co in the as-prepared sample is also supported by Energy Dispersive Spectroscopy (EDS) measurement (inset of Fig.2f). Fig. 2g shows the HR-TEM image of the interface of the core-shell structure, constituted with interfused NPs. The lattice spacings of 0.312 nm and 0.285 nm correspond well to the (111) crystal plane of the fluorite-structured CeO₂, and the (220) plane of the spinel-phase of Co₃O₄, respectively. These results regarding crystalline structure are consistent with that obtained from selected area electron diffraction (SAED) pattern shown in Fig. 2h, where two sets of diffraction rings belonging to the fluorite-phase CeO₂, and spinel-phase Co₃O₄ can be recognized.

The chemical bonding states of the core-shell structure are further investigated by XPS analysis. Fig. 3 shows the XPS spectra of the typical Co₃O₄-CeO₂ sample with CeO₂ content of ~18.5 %. The coexistence of Co and Ce can be clearly observed from the wide spectrum (Fig. 3a). Fig 3b presents the high resolution XPS spectrum of Ce 3d, where the peaks can be assigned to four pairs of spin-orbit doublets: the doublets (v ~882.05 eV, u ~900.45 eV), (u' ~906.97 eV, v' ~888.26 eV), and (u'' ~916.34 eV, v'' ~897.94 eV) are characteristic of Ce⁴⁺ state, whereas the doublet (u ~902.19 eV and v ~884.34 eV) is indicative of Ce³⁺ state, indicating the existence of Ce³⁺ species in the as-prepared Co₃O₄-CeO₂ sample. In the case of O 1s XPS spectrum (Fig. 3c), two identical peaks are clearly displayed, indicating the presence of multi oxygen species. The peak at the lower binding energy side (O₆: 529-530 eV) is ascribed to lattice oxygen and the shoulder peak at higher banding energy side (O₇: 531-532.8 eV) can be assigned to defective or adsorptive oxygen species. The Co 2p XPS spectrum in Fig. 3d

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shows two major peaks at 795.5 and 780.4 eV which are corresponding to Co 2p\(_{3/2}\) and Co 2p\(_{1/2}\) spin-orbit signals, respectively. These results demonstrate that the surface of the Co\(_{2}O_{4}\)-CeO\(_{2}\) core-shell sample is not fully covered with CeO\(_{2}\) within the detection range of XPS.

*Fig. 4* TEM images of the pure Co\(_{2}O_{4}\) (a, b) derived from the thermal decomposition of Co(CO\(_{3}\))\(_{0.35}\)Cl\(_{0.2}\)(OH)\(_{1.1}\) precursor, Co\(_{2}O_{4}\)-CeO\(_{2}\)-41.7 wt\% (c, d) and Co\(_{2}O_{4}\)-CeO\(_{2}\)-63.4 wt\% (e, f).

By simply changing the Ce\(^{3+}\) concentration, a series of Co\(_{2}O_{4}\)-CeO\(_{2}\) bimetal oxides with different surface coverage of CeO\(_{2}\) are obtained. Fig. 4a, b shows the pure Co\(_{2}O_{4}\) nanorods derived from the thermal decomposition of Co(CO\(_{3}\))\(_{0.35}\)Cl\(_{0.2}\)(OH)\(_{1.1}\), which leads to the volume shrinkage and generates subsequent porosity structure throughout the rod (Fig. 4b). After interfacial reaction and heat-treatment, compared with that shown in Fig. 2f, more dense CeO\(_{2}\) NPs are formed around the rod surface as the concentration of Ce(NO\(_{3}\))\(_{3}\) increases (Fig. 4c-f). Specifically, a considerable surface coverage is reached for the sample with CeO\(_{2}\) content of ~63.4 wt\% (Co\(_{2}O_{4}\)-CeO\(_{2}\)-63.4 wt\%) as shown in Fig. 4e and f. In the Co\(_{2}O_{4}\)-CeO\(_{2}\)-18.5 wt\% and 41.7 wt\% samples, the surface coverage by CeO\(_{2}\) is less pronounced, where the shell is constructed by discontinuous CeO\(_{2}\) NPs. In principle, this kind of structure enables more interfaces between Co\(_{2}O_{4}\) and CeO\(_{2}\) to expose.

When the Co(CO\(_{3}\))\(_{0.35}\)Cl\(_{0.2}\)(OH)\(_{1.1}\) precursor is added into Ce(NO\(_{3}\))\(_{3}\) aqueous solution, Co\(^{2+}\), Co\(^{3+}\), Cl\(^{-}\) and OH\(^{-}\) ions are slowly dissociated simultaneously, and the released OH\(^{-}\) ions prefer to combine with Ce\(^{3+}\) to form Ce(OH)\(_{3}\) due to the smaller solubility product constant of Ce(OH)\(_{3}\) (K\(_{sp}\)=1.6×10\(^{-38}\)). The newly produced Ce(OH)\(_{3}\) nucleates in situ and grows on the surface of the Co(CO\(_{3}\))\(_{0.35}\)Cl\(_{0.2}\)(OH)\(_{1.1}\) rods. Upon calcination, Ce(OH)\(_{3}\) easily transferred into CeO\(_{2}\). Meanwhile, the residual Co(CO\(_{3}\))\(_{0.35}\)Cl\(_{0.2}\)(OH)\(_{1.1}\) precursor is converted into Co\(_{2}O_{4}\) eventually to form Co\(_{2}O_{4}\)-CeO\(_{2}\) bimetal oxide.

*Fig. 5* Photographs of the supernatant obtained from Co\(_{2}O_{4}\) rods (a) and Co precursor (b) dispersing into Ce\(^{3+}\) aqueous solution; TEM images of Co precursor (c) and pure Co\(_{2}O_{4}\) (d) dispersed in Ce\(^{4+}\) aqueous solution, and TEM images of Ce(OH)CO\(_{3}\) precursor dispersed in Ce\(^{3+}\) (e) and Ce\(^{4+}\) (f) aqueous solution.

To further understand the transformation mechanism during the interfacial reaction, Co\(_{2}O_{4}\) rods derived from Co(CO\(_{3}\))\(_{0.35}\)Cl\(_{0.2}\)(OH)\(_{1.1}\) are used as a Co precursor. Obviously, the supernatant still keeps colorless when Co\(_{2}O_{4}\) rods are dispersed in Ce\(^{3+}\) aqueous solution even for more than 2 days (Fig. 5a). By stark contrast, light pink, characteristic color of Co\(^{3+}\) ions, appears when Co(CO\(_{3}\))\(_{0.35}\)Cl\(_{0.2}\)(OH)\(_{1.1}\) is dispersed in Ce\(^{4+}\) aqueous solution for 2 days, as illustrated in Fig. 5b. In another case, (NH\(_{4}\))\(_{2}\)Ce(NO\(_{3}\))\(_{6}\) instead of Ce(NO\(_{3}\))\(_{3}\) aqueous solution is mixed with Co(CO\(_{3}\))\(_{0.35}\)Cl\(_{0.2}\)(OH)\(_{1.1}\) precursor, TEM result verifies that in addition to NPs depositing on the rod surface, a lot of “free” particles are individually dispersed in solution (Fig. 5c), possibly due to the smaller solubility product constant of Ce(OH)\(_{3}\) (K\(_{sp}\)=2×10\(^{-26}\)) than that of Ce(OH)\(_{2}\) (K\(_{sp}\)=1.6×10\(^{-38}\)). A crossover experiment was performed by dispersing Co\(_{2}O_{4}\) rods in (NH\(_{4}\))\(_{2}\)Ce(NO\(_{3}\))\(_{6}\) aqueous solution for 2 days, TEM analysis confirms that no small particles formed on the Co\(_{2}O_{4}\) rod surface (Fig. 5d). According to above phenomena, one can rule out the possibility that the formation of CeO\(_{2}\) is due to the hydrolysis of Ce\(^{3+}\). Similarly, when Ce(OH)CO\(_{3}\) nanorods instead of Co(CO\(_{3}\))\(_{0.35}\)Cl\(_{0.2}\)(OH)\(_{1.1}\) is mixed with Ce\(^{3+}\) and Ce\(^{4+}\) aqueous solution, respectively, the Ce(OH)CO\(_{3}\) nanorod surface is clean in the former case (Fig. 5e) while plenty of “free” NPs are observed in the latter case (Fig. 5f), because the solubility product constant of Ce(OH)\(_{2}\) is far smaller than that of Ce(OH)\(_{3}\).
Herein, CO catalytic oxidation, being a model reaction, was carried out to evaluate the catalytic performance of the obtained CoO$_2$-CeO$_2$ core-shell materials. As for comparison, the catalytic activities of pure CoO$_2$ rods derived from the thermal decomposition of Co(CO)$_{3}$Cl$_2$(OH)$_{1}$ precursor, and pure CeO$_2$ prepared by precipitation method were also examined. Their light-off curves (CO conversion rate vs. temperature) for CO oxidation are presented. The temperature for 50% of CO conversion ($T_{50}$) is an important parameter to assess the activity of the catalyst. As shown in Fig. 6a, pure CoO$_2$ shows the $T_{50}$ at ~180 °C, while for the CoO$_2$-CeO$_2$ core-shell samples with different Co/Ce ratios, they exhibit higher catalytic activity than that of either pure CoO$_2$ or pure CeO$_2$. Specifically, the one with the lowest content of CeO$_2$, CoO$_2$-CeO$_2$:18.5 wt %, exhibits the superior catalytic activity with $T_{50}$ at ~139 °C among all samples compared. Instead, the enrichment of CeO$_2$ induces the decrease of the catalytic activity, reflected as the increase of $T_{50}$ for samples of CoO$_2$-CeO$_2$:41.7 wt% ($T_{50}$ = 146 °C) and CoO$_2$:CeO$_2$:63.4 wt% ($T_{50}$ = 157 °C). The pure CeO$_2$ sample does not show observable activity even at 200 °C. To evaluate the durability of the as-prepared CoO$_2$-CeO$_2$ catalyst, the CoO$_2$-CeO$_2$:18.5 wt% sample was selected as a typical example for successive CO oxidation test under the same experimental conditions. As shown in the inset of Fig. 6a, after five cycles up to 150 °C, the as-prepared CoO$_2$-CeO$_2$ catalyst still maintained almost 100% conversion rate of CO. Generally, the catalytic performance is closely related to the surface area of the catalysts. However, BET surface area analysis testified that no clear correlation between surface area and catalytic activity in our case, as shown in Fig. 6b. The pure CeO$_2$ possesses the largest surface area while displays the lowest catalytic activity. Even for the CoO$_2$:CeO$_2$ samples prepared from same procedure, the catalytic activity is independent on the surface area. These observations strongly suggest that the formation of the CoO$_2$:CeO$_2$ bimetal oxide structure catalyst introduces distinctly different and significant synergistic effect in the catalytic CO oxidation.

![Fig. 6](image)

**Fig. 6** (a) CO conversion as a function of temperature for CoO$_2$:CeO$_2$ bimetal oxide catalysts with different CeO$_2$ compositions: 18.5 wt% (i), 41.7 wt% (ii), 63.4 wt% (iii), and pure CoO$_2$ (iv), CeO$_2$ (v). (b) The comparisons in catalytic activity and BET surface area for the tested samples in (a). Inset in (a) shows the stability of CoO$_2$-CeO$_2$:18.5 wt% sample for catalytic oxidation under the conditions of (a).

It is widely recognized that the interaction between CoO$_2$ and CeO$_2$ is responsible for enhanced catalytic activity toward CO oxidation. To investigate the surface chemistry feature of all samples, Raman spectroscopy characterization was performed. As illustrated in Fig. 7a of the Raman spectra, the band at ~466 cm$^{-1}$ is related to the triply degenerated F$_{2g}$ mode of fluorite CeO$_2$, and the bands at ~192, ~475, ~515, ~614 and ~682 cm$^{-1}$ can be assigned to the vibrations of spinel CoO$_2$. Interestingly, the peak intensity is strong at ~466 cm$^{-1}$ for pure CeO$_2$, while nearly no obvious active Raman band can be detected at this position for all CoO$_2$:CeO$_2$ catalysts, indicating that the CoO$_2$ highly likely enables the closely contacted CeO$_2$ NPs to be structurally deformed. H$_2$-TPR analysis was also conducted to study the interaction between CoO$_2$, CeO$_2$, and Co$_3$O$_4$. As shown in Fig. 7b, pure CeO$_2$ exhibits two reduction peaks (indexed as α, β), corresponding to the reductions of CoO$_2$ to CoO and CeO to metallic Co, respectively. In the case of CoO$_2$:CeO$_2$ catalysts, their reduction peaks (α) slightly shift to lower temperature in comparison to the pure CoO$_2$, further demonstrating a synergistic effect between CoO$_2$ and CeO$_2$.

During CO catalytic oxidation, it is consensus that the whole process mainly involves the adsorption and desorption of gas molecules on the surface/or at the interface of the catalyst. In the case of CoO$_2$:CeO$_2$ structures, the synergistic interaction between CoO$_2$ and CeO$_2$ could modify Ce$^{3+}$/Ce$^{4+}$ and Co$^{3+}$/Co$^{2+}$ redox cycles and increases oxygen mobility. In addition, the oxygen vacancies, widely existed in CeO$_2$, could increase the adsorption amount and capacity of CoO$_2$:CeO$_2$ for oxygen molecules, and promote the dissociation of O$_2$ into O$_{ad}$, thus facilitating the CO oxidation. However, when the CeO$_2$ species increases to certain extent, e.g. CoO$_2$:CeO$_2$:63.4 wt% catalyst, it may significantly cover the CoO$_2$ surface, thus blocking the pore channel and causing the decrease of catalytic activity.

![Fig. 7](image)

**Fig. 7** Raman spectra (a) and H$_2$-TPR profiles (b) of pure CoO$_2$ (i), CoO$_2$:CeO$_2$:63.4 wt% (ii), CoO$_2$:CeO$_2$:41.7 wt% (iii), CoO$_2$:CeO$_2$:18.5 wt% (iv), and pure CeO$_2$ (v).
4. Conclusions

In summary, Co$_2$O$_3$–CeO$_2$ core–shell catalysts were successfully synthesized by a facilely interfacial reaction between Co(CO)$_{2}$H$_3$Cl$_3$·3H$_2$O and Ce$^{3+}$ aqueous solution, followed by a calcination step. The OH$^-$ ions dissociated from Co(CO)$_{2}$H$_3$Cl$_3$·3H$_2$O combine with Ce$^{3+}$ to form Ce(OH)$_3$, which can easily convert into CeO$_2$ upon a calcination process. The small solubility product constant of Ce(OH)$_3$ is responsible for the heterogeneous nucleation of CeO$_2$ NPs onto the Co precursor surface, even in the absence of any surfactants or polymers. Moreover, the coverage degree of CeO$_2$ onto the Co$_2$O$_3$ rod surface can be tuned by changing the concentration of Ce$^{3+}$ aqueous solution. The as-prepared Co$_2$O$_3$–CeO$_2$ core–shell catalysts display higher catalytic activity toward CO oxidation in comparison to either pure CeO$_2$ or Co$_2$O$_3$, indicating a strong synergistic effect between the two components. This work also demonstrates the feasibility of designing core-shell structure by virtue of the utilization of solubility product constant difference, and also expands the strategies of preparing binary oxide catalysts by means of interfacial reactions.

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Notes and references

Graphical Abstract

Ion exchange procedure, one kind of solid-liquid interfacial reactions, is so far restricted to chalcogenide based core-shell nanomaterials, in contrast, the bimetal oxide with core-shell structures by means of ion exchange has not extensively studied yet. Herein, Co₃O₄-CeO₂ core-shell catalysts are successfully fabricated by an ion exchange procedure between Co(CO₃)₀.₃₅Cl₀₂(OH)₁₁ nanorods and Ce³⁺ aqueous solution, followed by a calcination step.