Active yet extremely durable Co3O4 spheroids of different texture without/with Au deposition for CO oxidation

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Introduction

Low-temperature CO oxidation, perhaps the most extensively studied reaction in the history of heterogeneous catalysis, is becoming increasingly important in the context of cleaning air and lowering automotive emissions, as well as an important model catalysis reaction \(^{(1,2)}\). The noble metals of Pt and Rh were firstly found to be active for CO oxidation, however, these metals are very costly and their resources are also quite limited. According to the early observations reported by Hutchings et al. \(^{(3)}\) and Haruta et al. \(^{(2,4-6)}\), gold (Au) can exhibit high activity when deposited in nano-sized form on certain transition-metal oxides.

These findings motivated follow-up studies on different supported Au catalysts \(^{(7-8)}\). Many efforts have been devoted to explore other effective catalysts for CO oxidation. Among them, transition metal oxides have attracted great interest for the target reaction \(^{(9)}\). For instance, Wei et al. studied low temperature CO oxidation on the IB group metals and metal oxides \(^{(10)}\). Recently, Qian et al. studied the catalytically active structures of SiO\(_2\)-supported Au nanoparticles (NPs) for low-temperature CO oxidation. It was emphasized that not only the particle size but also the electronic property of Au NPs determined the CO oxidation activity \(^{(11)}\). Besides CO oxidation, the Au NPs highly dispersed on metal oxides were also found to be active for the reactions such as ozone decomposition, hydrogen oxidation, and CO + NO reaction \(^{(12-15)}\). It is generally recognized that preparation chemistry plays an important role in determining the Au-based catalysts \(^{(16-18)}\). On the other hand, the development of active yet stable catalysts without noble metals for CO oxidation under mild conditions still remains a challenge \(^{(2)}\). Among various metal oxides, cobalt oxide was reported to be active for CO as well as hydrocarbons oxidation \(^{(19-23)}\). It is known that the properties of materials with the same composition but different structure or morphologies can vary substantially \(^{(15,24,25)}\). Therefore, various morphologies of Co\(_3\)O\(_4\) structures, such as Co\(_3\)O\(_4\) nanobelts \(^{(26)}\), nanosheets \(^{(27)}\), nanowires \(^{(28)}\), nanorods \(^{(3)}\), and nanocubes \(^{(29)}\), showed distinct morphological effect in CO oxidation. Co\(_3\)O\(_4\) also showed morphology-dependent catalysis in certain reactions \(^{(2,26-29,30)}\). For instance, the Co\(_3\)O\(_4\) entities of different morphology showed the following activity order for CH\(_4\) combustion: nanosheets >
nanobelts > nanocubes. The specifically exposed facets of a certain morphological nano-crystallite comprise the unique arrangement of surface cations and anions, which in turn build up active sites of different reactivity. Featuring the hollow interior surfaces and high surface/volume ratio, the CoO₄ nanotubes were synthesized by Bae et al. The synthesis of CoO₄ nanotubes through Kirkendall effect has been recently reported by us, and the obtained material showed excellent activity and good stability toward the catalytic combustion of CH₄. The CoO₄-based materials exhibited a reaction-induced activity enhancement for CO oxidation even if the Au NPs are absent. This observation is remarkably different from that on the hollow structured Au/FeOₓ nanostructures recently reported by us.

In recent years, the core-shell type materials have been widely studied for their unique chemical and physical properties and potential applications in different areas. High activity and/or unique selectivity of core-shell nanostructures can be obtained by fine-tuning the size and shape of cores as well as the composition and thickness of shells. The protective shells can effectively avoid the small-sized core particles from sintering especially when the reactions were operated at high temperatures. Compared to the microporous silica shells, the mesoporous silica shells encapsulated the Fe, Ni, and Ru cores showing superior activities for ammonia decomposition, methane partial oxidation to syngas, and CO oxidation. Deng et al. employed a surfactant-templating approach to fabricating the magnetite core and the ordered mesoporous silica shell with perpendicularly oriented channels. For the yolk-shell type catalyst, the structural configuration can provide a unique reaction environment, which can function as a micro capsular-like reactor in some circumstances.

In the present study we synthesized the CoO₄ based catalysts (with/without Au deposition) for CO oxidation. The major concern is catalyst durability. We fabricated the CoO₄ bases of spherical morphology through an easy solvothermal treatment of Co(NO₃)₂. Upon different thermal treatment (drying/calcination), we were able to modify the texture/porosity of CoO₄ base, and further the Au-CoO₄ interaction, which would in turn dramatically influence catalyst stability for the target reaction. We also fabricated the CoO₄ based catalysts by isolating the CoO₄ particles with SiO₂ layer and further tuned the CoO₄ particle size by acid etching of the derived core-shell type catalysts. The employed preparation strategies enable us to have developed the CoO₄ based catalysts (with/without Au deposition) showing significantly different catalyst stability and activity. We also learned the originality of catalyst behaviors from the detailed characterizations, which was proved not to be limited to the Co⁷⁺ content in the samples.

Experimental

Preparation of catalysts

Spherical CoO₄ particles: Co(NO₃)₂-6H₂O (1.4 g) was dissolved in n-octanol (100 ml) to make a solution, then the temperature was increased to 180 °C and kept at this temperature for 4 h. After that the material was collected by centrifugation, washed three times with distilled water, and dried under an IR-lamp. The dried sample was denoted as d-CoO₄. If the dried sample was further calcined in air at 500 °C for 3 h, the calcined sample was denoted as c-CoO₄.

Au/CoO₄: the deposition-precipitation method was employed to prepare the Au/CoO₄ samples. In the case of Au/d-CoO₄, certain amount of d-CoO₄ was dispersed in a mixture of distilled water and ethanol (10:1, v/v), and the use of ethanol is helpful to achieve uniform dispersion of d-CoO₄ in the suspension. The HAuCl₄-3H₂O solution (0.01 M) was then added, giving the nominal Au loading is 3% by weight. In the case of Au/c-CoO₄, certain amount of c-CoO₄ was dispersed in distilled water (30 ml). The ammonium solution (0.07 mol/L) was added to the preparation media until the pH value of 9 was reached for preparing both Au/d-CoO₄ and Au/c-CoO₄. After that, the slurry was put into a water bath (at 50 °C) and magnetically stirred for 2 h. The solids were collected by repeated centrifugation and washing with distilled water (twice) and ethanol (one time). They were dried at room temperature (RT) overnight. The Au content of Au/d-CoO₄ and Au/c-CoO₄ is 1.9 wt% and 2.1 wt% respectively according to the ICP-AES measurement.

CoO₄@SiO₂: certain amount of CoO₄ particles (d- and c-CoO₄) was first dispersed in a mixture of distilled water (30 ml) and ethanol (10 ml), after that ammonium hydroxide (2 ml) was added under sonication in an ultrasound cleaner (KQ-100DE, 40 kHz, 100 W). Then TEOS (the Si/Co atomic ratio =1/2) was injected into the suspension by a microsyringe under sonication. One hour later, the materials were collected by centrifugation, washed three times by distilled water and dried at 100°C.

Acid-etched CoO₄@SiO₂: The CoO₄@SiO₂ particles (1 g) was put into a mixture containing HNO₃ (20 ml, 5 mol/L) and distilled water (10 ml) and magnetically stirred for 30 min. The slurry was put into a water bath (at 50 °C) and the suspension was continuously stirred for 5 h. The solids were collected by centrifugation, washed with distilled water, and dried at 80 °C overnight.

Materials characterization

X-ray diffraction (XRD) measurement was conducted on a Philips X’Pert MPD Pro X-ray diffractometer with Cu Kα radiation (λ = 0.1541 nm). The TEM images were taken over a JEOL JEM-1010 microscope operated at 100 kV. The HRTEM images were taken on a JEOL JEM-2010 microscope operated at 200 kV. N₂ sorption measurement was performed on a NOVA-2020 Material Physical Structure Determinator. Before measurement, sample was degassed at 300 °C for 3 h. BET surface areas were calculated based on a multipoint BET analysis of the nitrogen adsorption isotherms. Oxygen temperature-programmed desorption (O₂-TPD) was carried out...
using a U-shaped quartz reactor. The catalyst (100 mg) was first pretreated in a He stream at 120 °C for 1 h, and then oxygen adsorption proceeded by exposure to pure O2 at RT for 0.5 h. The sample was purged in a He flow (60 ml min\(^{-1}\)) for 1 h and then heated to 600 °C at a rate of 10 °C min\(^{-1}\) in a He flow (60 ml min\(^{-1}\)), and the effluent gas was analyzed using a thermal conductivity detector (TCD). Hydrogen temperature-programmed reduction (H\(_2\)-TPR) was performed using the same system as in O\(_2\)-TPD. The sample (100 mg) was purged in a He flow (50 ml min\(^{-1}\)) for 1 h and then heated to 700 °C at a rate of 10 °C min\(^{-1}\) in a 5%H\(_2\)-Ar flow (50 ml min\(^{-1}\)), and the effluent gas was analyzed using a TCD. X-ray photoelectron spectroscopy (XPS) analysis was performed on a PHI 5000 Versaprobe system, using monochromatic Al K\(\alpha\) radiation (1486.6 eV) operating at 25 W. The sample was outgassed overnight at RT in a UHV chamber (< 5×10\(^{-7}\) Pa). All binding energies (BEs) were referenced to the C1s peak at 284.6 eV. TG analysis was operated on NETZSCH STA 449C (Germany). The sample of ca. 100 mg was first purged in an Ar flow (50 ml min\(^{-1}\)) at 100°C for 1 h and then cooled down to RT. After that, the sample was heated to 450 °C at a rate of 5 °C min\(^{-1}\) in a 5%H\(_2\)-Ar flow (50 ml min\(^{-1}\)) meanwhile the weight loss was recorded.

**Catalyst activity**

Catalyst of 50 mg was placed into a quartz tube reactor and evaluated in CO oxidation operated at atmospheric pressure. The feed gas (1.6% CO, 21.0% O\(_2\), and balanced N\(_2\)) was passed through the catalyst bed at a total flow rate of 25 ml min\(^{-1}\), giving a corresponding gas hourly space velocity (GHSV) of 30,000 ml g\(_{\text{cat}}^{-1}\) h\(^{-1}\). In some cases, the catalysts were first pretreated in a flow of reaction feed at 180 °C for 120 min. Inlet and outlet gas compositions were analyzed online using a gas chromatograph (GC-122). The TORs were calculated on the basis of unit surface area of samples. Both the Co\(_3\)O\(_4\) substrates and the Au species were found to be comparably active for the reaction, the TORs were thus estimated based on the total surface area of supports rather than that of Co\(_3\)O\(_4\) or Au individual, which were determined by physisorption of N\(_2\) at low temperature (BET).

**Results and discussion**

**TEM/XRD**

The mono-dispersed and spherically shaped Co\(_3\)O\(_4\) particles with diameters of ca. 170-200 nm can be obtained by employing Co(NO\(_3\))\(_2\)-6H\(_2\)O and n-octanol as the raw materials upon solvothermal treatment without PVP addition. For the d-Co\(_3\)O\(_4\) particles without calcination, it is clearly evident that there are rich of fine pores inside the bulk phase, yielding a highly loose sample texture (Fig. 1a). Upon 500 °C-calcination of d-Co\(_3\)O\(_4\) spheroids, some hollow structures are evidently developed inside the spheroids meanwhile the sample texture became highly condensed (Fig. 1b), resulting from the shrinkage of structurally loose d-Co\(_3\)O\(_4\) spheroids upon high temperature calcination, which was further confirmed by the following N\(_2\) sorption measurement.

In case PVP was employed, the morphological and textural properties of the resulting Co\(_3\)O\(_4\) particles could be notably modified. Xie et al.\(^2\) reported that the adsorption of PVP onto the Co\(_3\)O\(_4\) particle surface via the hydrogen bonding stabilized the Co\(_3\)O\(_4\) entities and prevent them from agglomeration under the employed solvothermal conditions. In case the d-Co\(_3\)O\(_4\) spheroids were used as support, extremely fine Au NPs (< 2 nm) could be confined in the micropores of d-Co\(_3\)O\(_4\) (Fig. 1a), while if the c-Co\(_3\)O\(_4\) spheroids were applied, the Au NPs were found to be uniformly distributed on the condensed surfaces of the Co\(_3\)O\(_4\) spheroids. Note also that the Au NPs deposited on the surfaces of c-Co\(_3\)O\(_4\) spheroids showed rather flat particle morphology (Fig. 1b), with the mean particle size of 3.0 ± 0.6 nm (Fig. 2a). HRTEM analysis was conducted on Au/c-Co\(_3\)O\(_4\) (used) to take a close view of Au-Co\(_3\)O\(_4\) interface. The trapezoidal Au entity with a ratio of height to basement width being about 2 and the hemispheric Au entity with the largest basement area can be figured out from the HRTEM images (Fig. S1). In both cases, large Au-Co\(_3\)O\(_4\) interfaces were developed, and in the case of trapezoidal Au entity, change in Au atoms arrangement (from oblique rows to nearly vertical ones with respect to substrate) at the Au-Co\(_3\)O\(_4\) boundary can also be figured out. Such structural variation is thought to be the result of the most favourable and intensive Au-Co\(_3\)O\(_4\) interaction.
It is commonly recognized that Au NPs easily suffer from a significant activity drop upon high-temperature calcination and/or reaction 8. This situation may adversely influence the application of Au NPs when the operation and regeneration of catalysts at elevated temperature are needed 41. In the present case, the mean particle size of the Au NPs on the c-Co$_3$O$_4$ spheroids only slightly changed (4.2 ± 0.8 nm, Fig. 2b) even subjected to a reaction period > 70 h. It is deduced that there is strong interaction between the Au NPs and the condensed surfaces of the calcined Co$_3$O$_4$ spheroids, which in turn effectively stabilized the small-sized Au NPs during the reaction. In this study, the core-shell structured Au/Co$_3$O$_4$@SiO$_2$ was also fabricated by coating a silica layer of approximately 10 nm in thickness onto the Au/Co$_3$O$_4$ system (Fig. 1d).

In addition, the core-shell structures of Co$_3$O$_4$@SiO$_2$ (without Au deposition) with tunable size of Co$_3$O$_4$ cores were fabricated by the controlled acid-etching process (Fig. 3). Employing different acid-etching temperature and period, the size of Co$_3$O$_4$ cores can be systematically tuned; generating the internal cavities of different sizes in the resulting core-shell structures. These are the first examples of the Co$_3$O$_4$-based catalysts with the unique core-shell structural features for CO oxidation.

According to the XRD patterns of various samples shown in Fig. 4, only the Co$_3$O$_4$ phase structure can be identified even for the d-Co$_3$O$_4$ (JCPDS 42-1467) 42. The d-Co$_3$O$_4$ based samples, whether containing Au NPs or not, showed relatively low peak intensities, indicating comparably lower sample crystallinities. This is consistent with the TEM observations. There is no signal attributable to the Au component, suggesting high dispersion of very fine Au entities on the substrates of both d-Co$_3$O$_4$ and c-Co$_3$O$_4$, as previously revealed by the TEM images (Figs. 1a-c).

**Fig. 1** TEM images of (a) Au/d-Co$_3$O$_4$, (b) Au/c-Co$_3$O$_4$, (c) used Au/c-Co$_3$O$_4$.

**Fig. 2** Au particle size distribution in (a) Au/c-Co$_3$O$_4$ and (b) used Au/c-Co$_3$O$_4$ (> 70 h reaction).

**Fig. 3** TEM images: (a) non-acid-etched Co$_3$O$_4$@SiO$_2$, (b) slightly acid-etched Co$_3$O$_4$@SiO$_2$, (c) moderately acid-etched Co$_3$O$_4$@SiO$_2$, and (d) heavily acid-etched Co$_3$O$_4$@SiO$_2$.

**Fig. 4** XRD patterns of various Co$_3$O$_4$-based catalysts.
Based on the N₂ sorption measurements of the d-Co₃O₄, c-Co₃O₄, Au/d-Co₃O₄, and Au/c-Co₃O₄, the BET surface areas of samples and the adsorption-desorption isotherms are presented in Table 1 and Fig. 5, respectively. The BET surface area of d-Co₃O₄ and Au/d-Co₃O₄ is 215.6 and 127.1 m²/g respectively. Note that the value of c-Co₃O₄ and Au/c-Co₃O₄ was 8.5 and 12.3 m²/g respectively. Not only surface areas but also pore volumes dramatically decreased on the c-Co₃O₄ and Au/c-Co₃O₄ samples. Upon thermal treatment, the structurally loose d-Co₃O₄ substrate (also in Au/d-Co₃O₄) would transformed into more structurally dense c-Co₃O₄, accompanying structure shrinkage, loss of abundant micro-porosity, and creation of inaccessible internal hollows. These dramatic structural variations upon calcination significantly reduced the surface area of d-Co₃O₄ and Au/d-Co₃O₄ and eliminated most of the pore volume mainly existing in d-Co₃O₄ substrate (Table 1). Au presence in the micropores of d-Co₃O₄ substrate likely blocked some fine pores, leading to decrease in pore volume and also apparent shift of pore size. The surface area of c-Co₃O₄ was increased from 8.5 to 12.3 m²/g after Au addition, mainly attributable to the presence of Au entities. Note that pore volume of c-Co₃O₄ changed insignificantly (from 0.02 to 0.03 cm³/g), and this minor increment in pore volume could be due to the result of slight dissolution of c-Co₃O₄ in the acidic HAuCl₄ medium. The results of N₂ sorption measurements are coincident well with the TEM observations (Fig. 1).

**Fig. 5** (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution of d-Co₃O₄ and Au/d-Co₃O₄.

There are type II and V isotherms with inconspicuous hysteresis loops for d-Co₃O₄ and Au/d-Co₃O₄ (Fig. 5a), suggesting the presence of nonlinear mesopores in the samples. The pore size distributions (Fig. 5b) calculated by the Barrett-Joyner-Halenda (BJH) method based on the desorption branches of the isotherms demonstrated that the average pore diameter of the corresponding samples are in the range of 2.5-3 nm.

**Table 1** BET surface areas and pore volumes of d-Co₃O₄, c-Co₃O₄, Au/d-Co₃O₄, Au/c-Co₃O₄, and CoO₄@SiO₂ (calcined)

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<th>Catalyst</th>
<th>BET surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
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<tr>
<td>d-Co₃O₄</td>
<td>215.6</td>
<td>0.18</td>
</tr>
<tr>
<td>c-Co₃O₄</td>
<td>8.5</td>
<td>0.02</td>
</tr>
<tr>
<td>Au/d-Co₃O₄</td>
<td>127.1</td>
<td>0.09</td>
</tr>
<tr>
<td>Au/c-Co₃O₄</td>
<td>12.3</td>
<td>0.03</td>
</tr>
<tr>
<td>CoO₄@SiO₂ (calcined)</td>
<td>276.3</td>
<td>0.16</td>
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**O₂-TPD/H₂-TPR/TGA**

In order to better understand the nature of the Co₃O₄ substrates (with and without calcination) as well as the Au-containing catalysts in CO oxidation, the O₂-TPD technique was employed to investigate the oxygen adsorption/desorption behaviors over these catalysts, and the results are shown in Fig. 6. The desorption peak below 350 °C can be ascribed to the desorption of weakly adsorbed oxygen species such as O₂⁻ and O^−, while the one above 400 °C can be attributed to the desorption of the lattice oxygen species. The molecularly adsorbed oxygen O₂ (ad) and the O₂⁻ (ad) and O^− (ad) ones are weakly bonded to substrate surface, while the O₂⁻(lattice) species is usually thought to be a kind of surface lattice oxygen, and is difficult to remove. In general, the greater amount of surface oxygen species exists (corresponding to the desorption peaks in the 150-350 °C range).
range), the higher the catalytic ability for oxidation reaction will be\textsuperscript{12}. According to Fig. 6, the type and amount of oxygen adspecies change with sample constitution and preparation history. There was higher concentration of surface oxygen adspecies on the d-Co\textsubscript{3}O\textsubscript{4} substrate as compared to the c-Co\textsubscript{3}O\textsubscript{4} counterpart, due to the fact that the former had much greater specific surface area than the latter. When Au NPs were deposited onto the Co\textsubscript{3}O\textsubscript{4} substrate, the density of surface oxygen adspecies apparently decreased. Similar observation was made on the hollow structured Au/FeO\textsubscript{3} \textsuperscript{34} and further demonstrated by XPS investigation (see below). With silica encapsulation of Co\textsubscript{3}O\textsubscript{4}, the amount of surface oxygen adspecies also decreased (in the 150-350 °C range), suggesting there should be strong interaction between the Co\textsubscript{3}O\textsubscript{4} cores and the SiO\textsubscript{2} shells. Such core-shell interaction could restrain oxygen adsorption on the core surfaces, which in turn affected the catalytic behavior of the core-shell type catalyst. Note that there were additional desorption peaks in the 400-500 °C range over the core-shell catalyst, probably attributable to the presence of SiO\textsubscript{2} shells. In view of the higher desorption temperatures, the associated species would be less reactive for CO oxidation.

H\textsubscript{2}-TPR and TG analysis under reducing atmosphere were conducted over d-Co\textsubscript{3}O\textsubscript{4}, c-Co\textsubscript{3}O\textsubscript{4}, Au/d-Co\textsubscript{3}O\textsubscript{4}, and Au/c-Co\textsubscript{3}O\textsubscript{4}. The temperature range for removal of adsorbed oxygen species and lattice oxygen species associated with Co\textsuperscript{3+} and Co\textsuperscript{2+} can be figured out in terms of H\textsubscript{2}-TPR measurements (not shown). Based on such information, the weight loss below 225°C can be ascribed to the removal of adsorbed oxygen species while that beyond 225°C to the removal of lattice oxygen species associated with Co\textsuperscript{3+} as well as Co\textsuperscript{2+} cations (Fig. S2). Therefore, the amount of adsorbed oxygen species can be quantitatively estimated: d-Co\textsubscript{3}O\textsubscript{4} (1.16 mmol g\textsubscript{cat}\textsuperscript{-1} or 5.4 \(\mu\)mol m\textsuperscript{-2}), c-Co\textsubscript{3}O\textsubscript{4} (0.06 mmol g\textsubscript{cat}\textsuperscript{-1} or 7.1 \(\mu\)mol m\textsuperscript{-2}), Au/d-Co\textsubscript{3}O\textsubscript{4} (0.81 mmol g\textsubscript{cat}\textsuperscript{-1} or 6.4 \(\mu\)mol m\textsuperscript{-2}), and Au/c-Co\textsubscript{3}O\textsubscript{4} (0.31 mmol g\textsubscript{cat}\textsuperscript{-1} or 25.2 \(\mu\)mol m\textsuperscript{-2}). On the basis of unit mass of catalyst, the values obtained on d-Co\textsubscript{3}O\textsubscript{4} and Au/d-Co\textsubscript{3}O\textsubscript{4} are considerably higher than that on c-Co\textsubscript{3}O\textsubscript{4} and Au/c-Co\textsubscript{3}O\textsubscript{4}; while on the basis of unit surface area of catalyst, the values showed an opposite trend. Clearly, the estimated amount of adsorbed oxygen species can in part account for the catalytic behaviours of different samples, but it is not the sole factor that determined the catalytic activities in either conversion rates or TORs (Table 3).

XPS

The results of XPS investigation on the treated and untreated samples are shown in Fig. 7. For the untreated Au/d-Co\textsubscript{3}O\textsubscript{4}, the BE of Au 4f\textsubscript{5/2} as well as Au 4f\textsubscript{7/2} is 83.9 eV and 87.6 eV, respectively; while for the treated one, the BE is 84.0 eV and 87.7 eV, respectively (Fig. 7a). Although the Au NPs are largely in metallic state according to the corresponding BE values \textsuperscript{4}, there seemed AuO\textsubscript{2} species existing in the untreated Au/d-Co\textsubscript{3}O\textsubscript{4} and they were essentially changed into Au\textsuperscript{8} entities after pretreatment. Note also that there is little change in the BE of Au\textsuperscript{8} entities after in situ pretreatment, and this is different from our previous observation made on the hollow structured Au/FeO\textsubscript{3} system where the Au NPs became electronically deficient upon pretreatment \textsuperscript{33}. This may explain the reason why comparably small enhancement in CO oxidation activity over the treated Au/d-Co\textsubscript{3}O\textsubscript{4} with respect to the treated d-Co\textsubscript{3}O\textsubscript{4}. The results of O1s signals of the treated and untreated d-Co\textsubscript{3}O\textsubscript{4} and Au/d-Co\textsubscript{3}O\textsubscript{4} with deconvolution (Fig. 7b) clearly illustrated that after in situ pretreatment, there appears less amount of oxygen adspecies but increased amount of surface lattice oxygen species on the treated d-Co\textsubscript{3}O\textsubscript{4} substrate as well as Au/Co\textsubscript{3}O\textsubscript{4} \textsuperscript{44,45}, coincident with the fact that there are higher fractions of Co\textsuperscript{3+} in the treated samples and the shift in BEs of surface lattice oxygen to lower end.

![Fig. 7](image_url) (a) Au 4f, and (b) O 1s XPS spectra of the treated and untreated d-Co\textsubscript{3}O\textsubscript{4} and Au/d-Co\textsubscript{3}O\textsubscript{4} nanostructures.

Concerning the oxidation state of the Co cations, one can see that the adopted pretreatment notably increased the Co\textsuperscript{3+} fraction in the treated d-Co\textsubscript{3}O\textsubscript{4} (Co\textsuperscript{3+}/Co\textsuperscript{2+} = 5.4 vs. 2.5) while it caused slight change in the Co\textsuperscript{3+} fraction of the treated Au/d-Co\textsubscript{3}O\textsubscript{4} (Co\textsuperscript{3+}/Co\textsuperscript{2+} = 4.2 vs. 4.0) (Fig. 8). Clearly, the presence
of Au NPs had an impact on the surface state of Co₃O₄ substrate.

**Fig. 8** Deconvolution analysis of the Co 2p XPS peaks of the untreated and treated d-Co₃O₄ and Au/d-Co₃O₄.

Previous studies revealed that the Co³⁺ species are the active sites for CO oxidation. The results of the current work are also coincident well with the early observations: the in-situ pretreated catalysts containing high fraction of surface Co³⁺ showed enhanced activity (see below); and XPS analysis of c-Co₃O₄ which had experienced calcination indicated the surface Co cations were essentially Co³⁺ (not shown), accounting for its reserved activity even if the catalyst had rather small surface area.

Applying the technique of temporal analysis of products (TAP), Widmann et al. demonstrated that the calcined Au/CoO₂ was only slightly active for CO oxidation, and small amount of surface oxygen should be removed before the catalyst reached its more active steady-state surface composition. The activity was notably increased on a catalyst surface with relatively lower surface oxygen concentration, while the over-reduction of surface oxygen coverage would cause lower initial activity. In the present case, although there was small effect on the original Au⁰ entities upon in situ pretreatment; the accompanying transformation of AuOₓ to Au⁰ may enhance competitive CO adsorption on the generated Au⁰ entities.

Both O₂-TPD and XPS results of the present study (Figs. 6 and 7) indeed demonstrated that there was relatively low surface concentration of oxygen adspecies on the treated d-Co₃O₄ and Au/d-Co₃O₄. Bear in mind that, the spillover of oxygen adspecies from Au NPs onto the Au-Co₃O₄ boundary region could not only reduce surface oxygen coverage on the Au NPs, but also add extra oxygen anions around the Au-Co₃O₄ boundary where the coming oxygen species would react with the neighboring adsorbed CO to CO₂.

**Catalytic activity**

There were investigations demonstrating single and mixed transition metal oxides potential for CO oxidation. Co₃O₄ was found to be one of the most active oxides toward this reaction. However, the activity and stability was found to be highly dependent on sample morphology, and the deposition of Au NPs on the unique Co₃O₄ spheroids for CO oxidation has not been explored yet. Fig. 9 illustrates the CO conversions at elevated temperatures on various catalysts. In view of Fig. 9a, CO oxidation performance was enhanced only when the Au NPs were deposited on the d-Co₃O₄ spheroids. Interestingly, the pretreatment of the catalysts at 180 °C for 2 h in the reaction stream [CO/O₂/N₂ = 1.6/21/77.4 (v/v/v)] would significantly enhance catalyst activity (Fig. 9b). According to the values of T₁₀₀ (the temperature at which 100% CO conversion is achieved), both Au/c-Co₃O₄ and Au/d-Co₃O₄ became more active in CO oxidation after in-situ pretreatment, and the T₁₀₀ of the treated Au/d-Co₃O₄ is only 80 °C. It is worth noting that the Co₃O₄ substrates, whether calcined or not, also encountered the in-situ pretreatment effect on CO oxidation, particularly the d-
Co$_3$O$_4$ (Fig. 9c). Table 2 summarized the activities of all treated catalysts on the basis of per unit mass of catalyst, and the following activity sequence was obtained based on the $T_{100}$ values: treated Au/d-Co$_3$O$_4$ ($T_{100} = 80 \degree C$) > treated d-Co$_3$O$_4$ ($T_{100} = 90 \degree C$) > treated Au/c-Co$_3$O$_4$ ($T_{100} = 110 \degree C$) > treated c-Co$_3$O$_4$ ($T_{100} = 120 \degree C$) > untreated d-Co$_3$O$_4$ ($T_{100} = 130 \degree C$). Note that the d-Co$_3$O$_4$ associated catalysts generally outperformed the c-Co$_3$O$_4$ based counterparts. On the other hand, when the catalyst activities were compared on the basis of per unit surface area of catalyst (TORs), the opposite tendency was observed (Table 3). This implies that although the surface areas of the c-Co$_3$O$_4$ based catalysts are rather small, the density of active sites is still sufficiently high for CO oxidation over the c-Co$_3$O$_4$ based catalysts.

**Table 2** Temperatures at CO complete conversion over various Co$_3$O$_4$-based catalysts subjected to in situ pretreatment

<table>
<thead>
<tr>
<th>Catalysts-calcined</th>
<th>c-Co$_3$O$_4$</th>
<th>Au/c-Co$_3$O$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{100}$/$\degree C$</td>
<td>130</td>
<td>110</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Catalysts-dried</th>
<th>d-Co$_3$O$_4$</th>
<th>Au/d-Co$_3$O$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{100}$/$\degree C$</td>
<td>90</td>
<td>80</td>
</tr>
</tbody>
</table>

In the case of Au/d-Co$_3$O$_4$, the Au particle size is comparably small (ca. 2 nm), and with decreasing Au particle size, the electronic property of Au NPs deviate somewhat from bulk Au. However, the Co$_3$O$_4$ substrate is non-inert and can modify the electronic state of Au NPs especially when a strong Au-Co$_3$O$_4$ interaction exists. That should be true for both Au/d-Co$_3$O$_4$ and Au/c-Co$_3$O$_4$, since in the former the very fine Au NPs can be confined in the fine pores of d-Co$_3$O$_4$ while in the latter the flat Au entities can tightly contact with the condensed surfaces of c-Co$_3$O$_4$. Note also that it is hard to say the metallic Au is always more active than AuO$_x$ species, since the activity of the latter species is rather dependent upon the oxygen stoichiometry in AuO$_x$. In the current study, there seems AuO$_x$ species with high oxygen content (i.e. high oxidation state of Au$^{n+}$) in the untreated Au/d-Co$_3$O$_4$, accounting for its comparatively poor activity.

**Table 3** CO conversion rates and TOPs over various treated catalysts at 80$\degree C$

<table>
<thead>
<tr>
<th>Sample</th>
<th>CO conversion rate/ µmol g$^{-1}$ min$^{-1}$</th>
<th>TOR/ µmol m$^{-2}$ min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>treated c-Co$_3$O$_4$</td>
<td>31.4</td>
<td>3.7</td>
</tr>
<tr>
<td>treated d-Co$_3$O$_4$</td>
<td>191.4</td>
<td>0.9</td>
</tr>
<tr>
<td>treated Au/c-Co$_3$O$_4$</td>
<td>23.2</td>
<td>1.9</td>
</tr>
<tr>
<td>treated Au/d-Co$_3$O$_4$</td>
<td>222.8</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Liu et al. synthesized the ordered mesoporous Co$_3$O$_4$ supported Au nanocatalysts for CO and VOCs combustion. According to the $T_{100}$ values, the d-Co$_3$O$_4$ of this study was nearly as active as the ordered mesoporous Co$_3$O$_4$ substrate under the comparable conditions. The mesoporous Co$_3$O$_4$ supported Au NPs seemed remarkably active for CO oxidation, although the Au particle size distribution in Au/mesoporous Co$_3$O$_4$ looked similar to that of Au/d-Co$_3$O$_4$. The method used for Au introduction, however, was different in the two studies. In the present case, the Au introduction was achieved via the DP process, while in the case of Au/mesoporous Co$_3$O$_4$, the Au introduction was established via chemical reduction of HAuCl$_4$ with NaBH$_4$ and adsorption of Au colloid particles. Therefore, the nature of Co$_3$O$_4$ substrate (even in the same chemical constitution) as well as the Au NPs and the involved Au-Co$_3$O$_4$ interaction, which are greatly influenced by preparation history, should account for the difference in activity of these Au/Co$_3$O$_4$ systems. Li et al. reported CO oxidation over the iodine-ion-induced size-tunable Co$_3$O$_4$ nanowires. This catalyst system was highly efficient by employing extraordinarily high value of GHSV, but it became almost inactive below 100 $\degree$C and deactivated over time below 120$\degree$C. In addition, the very reactive Au-containing catalysts generally suffer poor durability of catalyst.
In the current study, when Au/c-Co₃O₄ and Au/d-Co₃O₄ first experienced CO oxidation at 350 °C for 5 h, and then were operated at temperatures of 50-90 °C, the former can obviously outperform the latter (Fig. 10a), although the corresponding substrates still showed a reverse order (Fig. 10b). This indicated that Au/c-Co₃O₄ is more competent to a high-temperature environment, and the stability tests over Au/c-Co₃O₄ and Au/d-Co₃O₄ within a period of 350-650 min further confirmed this point (Fig. S4). Clearly, Au aggregation is more evident in Au/d-Co₃O₄ (Fig. 1a vs. Fig. S3a) than Au/c-Co₃O₄ (Fig. 1b vs. Fig. S3b). In addition, the former is notably less durable than the latter after pre-reaction at 350 °C for 5 h (Fig. S4). We also tested several yolk-shell type Co₃O₄@SiO₂ catalysts by controllable acid-etching of Co₃O₄ cores, in contrast to those prepared by employing the acid-etching of auxiliary shells. The measured Tₚ₁₀ values obtained on the catalysts of non-acid-etched Co₃O₄@SiO₂, slightly acid-etched Co₃O₄@SiO₂, and moderately acid-etched Co₃O₄@SiO₂ are 157 °C, 100 °C, and 130 °C respectively. The acid-treatment did dissolve portion of the cobalt oxide, especially at the SiO₂-Co₃O₄ boundary, releasing some free surfaces of Co₃O₄, meanwhile modifying the surface morphology of Co₃O₄ cores. By changing the condition of acid-treatment, the degree of acid-etching of the core-shell catalyst can be controlled, resulting in different sized Co₃O₄ cores and certain Co₃O₄@SiO₂ contact. As indicated, only the slightly acid-etched catalyst showed favourable Co₃O₄ core size and optimal Co₃O₄@SiO₂ contact for the reaction. Even when operated at a rather high temperature, these Co₃O₄-based core-shell catalysts showed their superb stability because of the protective SiO₂ shells. Note that there is micro-/meso-porosity in SiO₂ shells reflected by big differences in the BET surface area and pore volume between Co₃O₄ and Co₃O₄@SiO₂ (Table 1), which allows effective acid-etching of Co₃O₄ cores through the pores of SiO₂ layers. Moreover, our previous studies have indicated that there is no mass transportation limitation for catalytic NH₃ decomposition, CH₄ partial oxidation, and CO oxidation on a variety of core-shell structured M@SiO₂ (M = Fe, Co, Ni, and Ru) where the SiO₂ encapsulation was achieved by employing the essentially identical synthetic approach as in the current study.

For CO oxidation over the Co₃O₄ nanostructures of different morphologies, the specifically prepared Co₃O₄ nanorods were found to be exceptionally active. Nie et al. recently reported that oxygen pretreatment of Au(3d)₃(SR)₁₈ nanoclusters supported on CeO₂, TiO₂, and Fe₂O₃ oxides at 150 °C resulted in a notable enhancement in the CO oxidation activities. The same phenomenon was also reported by us on the hollow structured Au/FeOₓ, the specifically prepared Co₃O₄@SiO₂ (Table 1), which allows effective acid-etching of Co₃O₄ cores through the pores of SiO₂ layers. Moreover, our previous studies have indicated that there is no mass transportation limitation for catalytic NH₃ decomposition, CH₄ partial oxidation, and CO oxidation on a variety of core-shell structured M@SiO₂ (M = Fe, Co, Ni, and Ru) where the SiO₂ encapsulation was achieved by employing the essentially identical synthetic approach as in the current study.

In the current study, we made the comparative study on the Co₃O₄ substrates with/without Au deposition. It was found that the effect of Au deposition was determined by not only type of oxide substrate but also preparation history and characteristics of Co₃O₄ substrate itself. The presence of Au did modify the physic-chemical properties of the Co₃O₄ substrates (for instance the surface oxidation state, the adsorption/desorption as well as reduction behaviours of oxygen species etc., as revealed by the investigations of XPS, O₂-TPD, and H₂-TPR). The nature of Co₃O₄ substrate in turn strongly influenced the Au-dispersion and Au-Co₃O₄ interaction. The effectiveness in activity and particularly durability of Au species on the target Co₃O₄ substrate has been revealed, which is meaningful for developing highly durable Au-containing catalysts for different applications.
Conclusions

Spherically shaped CoO₂₃ particles were synthesized by one-pot solvothermal process free of structure directing agent or pore former. The dried CoO₂₃ spheroids processed rich of fine pores in which very small sized Au NPs (ca. 2 nm) were confined in the micropores of dried CoO₂₃ active (Tₐ₂ₐ₉ = 80-90 °C) and very stable (TOS > 70 h) for CO oxidation. Upon calcination, there were condensed CoO₂₃ spheroids formed on which small sized flat Au entities (3.0 ± 0.6 nm) with remarkably large Au/CoO₂₃ interfaces were uniformly dispersed, outperforming Au/d-CoO₂₃ in both activity and stability even after experienced a pre-reaction at 350°C for 5 h. As for the yolk-shell type CoO₄@SiO₂ catalysts synthesized by controllable acid-etching of CoO₂₃ cores, there were an optimal CoO₂₃ core-SiO₂ shell interaction and also appropriate CoO₂₃ core particle size for CO oxidation. The Au/c-CoO₂₃ and Au/c-CoO₂₃@SiO₂ catalysts were substantially durable even at temperatures ≥ 350 °C, due to the intensive Au-CoO₂₃ interaction in Au/c-CoO₂₃ or the effective protection of SiO₂ shells in Au/c-CoO₂₃@SiO₂. The CoO₂₃ spheroids as well as their supported Au NPs encountered the in-situ pretreatment enhanced CO oxidation, as previously observed on the hollow structured Au/FeOₓ by us. The pretreatment resulted in: (i) transformation of AuOₓ to Au⁴⁺, (ii) higher fraction of surface Co⁴⁺, and (iii) suitably lower concentration of surface oxygen adspecies, accounting for the enhanced activities of CO oxidation.

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Notes and references

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† Electronic supplementary information (ESI) available: HRTEM images of Au/e/c-CoO₂₃ (used); TGA profiles of d-CoO₂₃, c-CoO₂₃, Au/d-CoO₂₃, and Au/c-CoO₂₃ in reducing atmosphere (5%H₂-Ar); TEM images of Au/e-CoO₂₃ and Au/d-CoO₂₃ after pre-reaction at 350 °C for 5 h; and stability tests over Au/e-CoO₂₃ and Au/d-CoO₂₃ after pre-reaction at 350 °C for 5 h.

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