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Article

CO oxidation over Au/ZrLa-doped CeO₂ catalysts: Synergistic effect of zirconium and lanthanum

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ABSTRACT

The physicochemical properties of nanosized Au catalysts supported on doped CeO₂ and their catalytic performance for the CO oxidation reaction were investigated. The Au/Zr-doped CeO₂ catalyst is much more active than undoped Au/CeO₂, while Au/ZrLa-doped CeO₂ shows the highest activity. Characterization of the catalysts by X-ray diffraction, transmission electron microscopy (TEM), high-resolution TEM, and the X-ray absorption fine structure technique shows high homogeneity of the oxide supports and well-dispersed nanosized Au nanoparticles. Raman spectroscopy, X-ray photoelectron spectroscopy, and H₂-temperature-programmed reduction show that the surface oxygen species are the main factor for the catalytic activity in the CO oxidation reaction, while the supported Au species can improve the redox properties and create oxygen vacancy sites on the support. The oxidation state of Au is not the main factor governing the activity of Au/doped-CeO₂ catalysts. Additionally, the synergistic effect of Zr and La is discussed.

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1. Introduction

Well-dispersed Au on metal oxide supports is one of the most widely studied catalysts for low-temperature CO oxidation [1–3]. These catalysts show potential for many important applications, including purification of hydrogen for automotive fuel cells [4–6]. However, numerous contradictory suggestions have been made concerning the nature of the active sites on supported gold catalysts for this simple reaction. Because various factors can influence the catalytic performance, including the gold particle size [7,8], valence state of gold species (Au⁰, Au⁺, and Au³⁺) [9–11], role of the support [12,13], oxygen supply [14–16], and metal-support interaction [17], the interrelationship between the different factors is very difficult to determine. Consequently, there has been growing interest in the

catalytic activity of metal-oxide-supported gold catalysts in the last 25 years.

CeO₂ is widely used in various fields because of its oxygen storage capability and the low redox potential between Ce³⁺ and Ce⁴⁺ [18,19]. For these reasons, CeO₂ is a good candidate for preparing active gold catalysts for CO oxidation at low temperature. However, it has been reported that the catalytic activity of gold deposited on CeO₂ catalysts can drastically change when CeO₂ is prepared by different methods [20]. Corma et al. [20,21] suggested that the characteristics of the CeO₂ surface were extremely important in determining whether a CeO₂-supported gold catalyst is active or not for CO oxidation. For Au/CeO₂, investigation of the catalytic mechanism shows that the nature of surface oxygen vacancy sites plays an important role in the catalytic process. It is known that doping

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facilitates reduction of ceria by weakening Ce–O bonds around the dopant [14]. Therefore, doping metals with different chemical natures into CeO₂, especially when generating the solid solution, is considered to be an effective strategy to improve the oxygen mobility properties. For example, doping ceria with lower valence ions such as La³⁺ can create extrinsic oxygen vacancies [22], while smaller ions such as Zr⁴⁺ lead to a highly defective structure with lattice strain [23], which decreases the activation energy for Ce⁴⁺/Ce³⁺ reduction. It is reasonable to presume that greater efficiency may be obtained by combining the above two strategies. Therefore, doping ceria with Zr and La would be a good way of testing whether the catalytic activity of gold can be improved by improving its oxygen mobility properties.

In this study, we investigate the support effect of Au/doped-CeO₂ catalysts for CO oxidation using deposition-precipitation (DP) to anchor gold to CeO₂, CeZrO_x, and CeZrLaO_x supports. Furthermore, the synergistic effect of Zr and La doping on the reactivity is discussed. The aim of the present study is to obtain a defective fluorite structure with increased oxygen mobility that could result in enhanced activity.

2. Experimental

2.1. Catalyst preparation

Au/ZrLa-doped CeO₂ was synthesized in a two-step process. CeO₂, Ce_{0.5}Zr_{0.5}O_x, and Ce_{0.5}Zr_{0.42}La_{0.08}O_x were prepared by a previously reported controlled hydrolysis method [22], where (NH₄)₂Ce(NO₃)₆, ZrO(NO₃)₂, and La(NO₃)₃·6H₂O were used as the precursors and urea (2 mol/L) was used as the base with a fixed metal concentration of 0.1 mol/L in a Teflon bottle (inner volume 100 mL). The Teflon bottle was held in a stainless steel autoclave and then hydrothermal treatment was performed. After cooling, the precipitates were collected, washed, dried at 110 °C overnight, and finally calcined in air at 400 °C for 4 h. Gold (1 at%) was then introduced by the DP method at 60 °C and pH = 8–9 (HAuCl₄·4H₂O was used as the precursor and (NH₄)₂CO₃ as the base) [24]. The resulting precipitate was washed with deionized water until total chloride removal, followed by drying at 60 °C in vacuum for 24 h and calcining at 400 °C for 4 h. The obtained catalysts are designated Au/CeO₂, Au/CeZrO_x, and Au/CeZrLaO_x.

2.2. Characterization

X-ray diffraction (XRD) analysis was performed on a Rigaku D/MAX 2550/PC diffractometer with Ni filtered Cu K_α radiation operated at 40 kV and 40 mA. The catalysts were scanned from 10° to 75° at a scan rate of 4°/min.

Raman spectra were collected on a Horiba Jobin Yvon LabRam-HR 800 laser micro-Raman spectrometer with excitation light of 514 nm. The scanning range was 100–1000 cm⁻¹.

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were performed on a Philips Tecnai F20 microscope operating at 200 kV. Before TEM examination, the samples were supported on copper grids coated with holey

carbon membranes by dropping an ethanol suspension containing uniformly dispersed catalysts.

X-ray photoelectron spectroscopy (XPS) measurements were carried out on an Axis Ultra XPS spectrometer (Kratos, UK) with 225 W Al K_α radiation, and the C 1s peak at 284.8 eV was used as an internal standard.

Temperature-programmed reduction with H₂ (H₂-TPR) was performed with a Builder PCSA-1000 instrument (Beijing, China) equipped with a thermal conductivity detector to determine H₂ consumption. The fresh catalysts (30 mg, 20–40 mesh) were pretreated at 350 °C in ambient air for 0.5 h and then cooled to room temperature. The samples were finally heated from room temperature to 300 °C at a heating rate of 5 °C/min in a 10% H₂/Ar gas mixture (20 mL/min).

Surface area and pore volume measurements of the catalysts were performed on an ASAP 2010 unit (Micromeritics) at –196 °C using liquid N₂. The samples were evacuated at 200 °C for 4 h under a vacuum of 1.33 × 10⁻³ Pa prior to adsorption.

X-ray absorption fine structure (XAFS) spectra at the Au L-III edge (*E*₀ = 11919 eV) were collected at BL14W1 beamline of the Shanghai Synchrotron Radiation Facility with the storage ring operated at 3.5 GeV and 240 mA (top-up mode). The XAFS data was collected in fluorescence mode with a 32 element Ge solid-state detector. The energy was calibrated according to the absorption edge of pure Au foil. The X-ray absorption near edge spectroscopy (XANES) and extended XAFS (EXAFS) data were analyzed using the Athena and Artemis programs.

2.3. Catalytic performance

Catalytic activity evaluation was performed in a plug-flow reactor using 50 mg of sieved (20–40 mesh) catalyst in a gas mixture of 1 vol% CO, 20 vol% O₂, and 79 vol% N₂ at a flow rate of 67 mL/min, corresponding to a space velocity of 80 000 mL h⁻¹ g_{cat}⁻¹. Before the measurements, the catalysts were pretreated in a stream of O₂ at 300 °C for 30 min for activation, and then cooled to room temperature under a flow of N₂. The catalytic tests were carried out with a heating rate of 3 °C/min. The outlet gas compositions of CO and CO₂ were monitored online by nondispersive infrared (IR) spectroscopy (ABB EL 3020). CO conversion was calculated by CO conversion = CO_{reaction}/CO_{input} = CO₂ output/(CO₂ output + CO_{output}). A typical “steady-state” experiment (90 °C) was performed in the same gas mixture at 90 °C for 10 h.

3. Results and discussion

3.1. Structural properties of the catalysts

The XRD patterns of the three catalysts are shown in Fig. 1(a). The sample containing gold and ceria has the face-centered cubic structure (fluorite-type), which is commonly found for pure CeO₂. No obvious phase related to Au was found, suggesting that Au is well dispersed on the surface of the CeO₂ support [12]. For the Au/CeZrO_x and Au/CeZrLaO_x samples, the gold, zirconium, and lanthanum phases were hardly found, suggesting a well-dispersed gold phase and formation of

Fig. 1. XRD patterns (a) and Raman spectra (b) of the Au/CeO₂, Au/CeZrO_x, and Au/CeZrLaO_x catalysts.

CeZrO_x and CeZrLaO_x solid solutions. The barely detectable XRD peaks of Au(111) indicates that the Au particles formed on the three supports are < 5 nm in size [12,23]. However, the reflections in the diffractograms of Au/CeZrO_x and Au/CeZrLaO_x are significantly broader than that of Au/CeO₂, indicating their nanocrystalline nature, which makes it difficult to investigate the crystal structures of the present samples. CeO₂–ZrO₂ mixed oxides have a complex phase diagram containing three stable phases (monoclinic, tetragonal (t), and cubic) and two metastable phases (t' and t'') [25]. The Ce/Zr molar ratio of the prepared solids is the threshold value (Ce/Zr = 1) for transition of tetragonal-cubic cerium and zirconium oxides [26]. Therefore, Raman spectroscopy is an effective tool to detect the crystal structure of fine particles, and it was used to determine the exact phases of the prepared samples. Fig. 1(b) shows the Raman spectra of the three catalysts. The Au/CeO₂ catalyst shows one strong peak at 460 cm⁻¹, corresponding to the triply degenerate F_{2g} mode of cubic CeO₂ [27], which is consistent with the XRD results. For the Au/CeZrO_x catalyst, there are four peaks at 250, 308, 471, and 622 cm⁻¹, indicating the metastable phase (t'') of cerium and zirconium oxide [28]. The peak at 622 cm⁻¹ is caused by oxygen vacancies associated with the defective pseudocubic t'' structure in CeO₂–ZrO₂ materials, suggesting that formation of the solid solution is beneficial for formation of oxygen vacancies [28]. Similar to Au/CeZrO_x, the Au/CeZrLaO_x catalyst also shows the metastable phase (t''). Previous research has shown that doping La³⁺ into CeZrO_x oxide stabilizes of the pseudocubic t'' structure because the relatively large radius of La³⁺ ($r_{\text{La}^{4+}} = 1.16 \text{ \AA}$ compared with $r_{\text{Ce}^{4+}} = 0.97 \text{ \AA}$ and $r_{\text{Zr}^{4+}} = 0.84 \text{ \AA}$) can relax lattice compression [22].

The physical properties of the three catalysts were calculated from the XRD patterns and N₂ sorption (Table 1). The average crystallite sizes were estimated using the Scherrer equation based on the (111) reflection of CeO₂. The results show that doping Zr or Zr and La into CeO₂ decreases the average crystal size. This can be explained by the greater thermal stability because of formation of a solid solution [29]. The specific surface areas of the three catalysts increase in the following order: Au/CeO₂ < Au/CeZrO_x < Au/CeZrLaO_x. Because the pore volumes of the three catalysts hardly changes, this effect

can be mainly ascribed to the smaller average crystallite sizes of the oxide supports. Generally, a large surface area is believed to be beneficial for various catalytic reactions because it can make the active sites more accessible to reactants [30]. The lattice constants (*a*) of CeO₂, CeZrO_x, and CeZrLaO_x were calculated to be 5.4025, 5.3178, and 5.3535 Å, respectively. Because the Zr⁴⁺ cation (0.84 Å) is smaller than the Ce⁴⁺ cation (0.97 Å), Zr⁴⁺ cations occupying Ce⁴⁺ sites cause lattice shrinkage. However, the La³⁺ cation (1.16 Å) is larger than the Ce⁴⁺ cation, so the lattice constant of CeZrLaO_x is larger than that of CeZrO_x. These results confirm the conclusion that ceria, zirconium, and lanthana form CeZrO_x and CeZrLaO_x solid solutions under the experimental conditions. The homogeneous chemical composition of the oxide support is important to determine the structure–function correlation and understand the underlying principles behind the improved catalytic efficiencies of the nanocatalysts.

3.2. Catalytic properties

Fig. 2 shows CO oxidation over the Au/CeO₂, Au/CeZrO_x, and Au/CeZrLaO_x catalysts. The 100% conversion temperatures (°C) of CO for the Au/CeO₂, Au/CeZrO_x, and Au/CeZrLaO_x catalysts are 200, 175, and 140 °C, respectively. A rough comparison of the catalytic activity with other CeO₂-based Au catalysts reveals that the present catalysts are quite active (Table 2). Additionally, compared with pure CeO₂-supported Au catalysts, the Au/CeZrO_x catalyst is more active. The Au/CeZrLaO_x cata-

Table 1
Structural parameters of the three catalysts.

Catalyst	Phase	Space group	<i>d</i> ^a (nm)	<i>a</i> ^b (Å)	<i>A</i> _{BET} ^c (m ² /g)	Pore volume (cm ³ /g)
Au/CeO ₂	cubic	<i>Fm</i> 3 <i>m</i>	9.8	5.4025	84	0.24
Au/CeZrO _x	t''	<i>P</i> 4 ₂ / <i>nmc</i>	4.4	5.3178	135	0.23
Au/CeZrLaO _x	t''	<i>P</i> 4 ₂ / <i>nmc</i>	3.8	5.3535	156	0.17

^a Average crystallite size of CeO₂(111) according to the Scherrer equation.

^b 2θ correction and the cell dimension calculation were performed using the LAPOD code with least squares refinement.

^c Brunauer-Emmett-Teller (BET) surface area.

Fig. 2. Temperature dependence of the catalytic activity in the CO oxidation reaction over Au/CeO₂ (1), Au/CeZrO_x (2), and Au/CeZrLaO_x (3) catalysts.

lyst shows the highest activity, which may be related to the synergistic effect of Zr and La on the reactivity. In addition to transient mode, we also ran long-term stability tests of the Au/CeZrO_x and Au/CeZrLaO_x catalysts (Fig. 3) in an oven at 90 °C for 10 h. Because Au/CeO₂ showed almost no catalytic activity at 90 °C, the stability test is not shown here. For Au/CeZrLaO_x, CO conversion slightly decreases from 81% to 74% during the reaction time of 10 h. For Au/CeZrO_x, CO conversion slightly increases from 55% to 60% in the initial 2 h, and then reaches a steady stage with constant CO conversion of 60%. Because of the presence of a structure-activity relation in heterogeneous catalysis, these increases in the catalytic reactivity should be correlated with improvement of the structural properties by incorporation of the dopant.

3.3. Active species for the CO oxidation reaction

TEM analysis was performed to determine the details of the Au species (Fig. 4(a)–(c)). Different areas were chosen to analyze Au particles. EDX was used to obtain concentration information about gold to ensure that these areas are representative of the material. However, both Au particles and atomic Au were not detected in these areas, which may be because of the low gold content and well dispersed Au species. HRTEM was performed to identify the gold particles in the three catalysts (Fig. 4(d)–(f)). The well-crystallized particles identified by fast Fourier transform (FFT) are cerium oxide, mainly the (111), (200),

Fig. 3. Conversion of CO on stream over Au/CeZrO_x and Au/CeZrLaO_x catalysts.

(220) planes with *d*-spacings of 0.32, 0.27, and 0.19 nm, respectively. No Au(111) plane (*d*-spacing 0.24 nm) was detected, indicating that the gold particles on the three supports are too small to be detected under the operational conditions, especially because of the low contrast between Au and Ce. These gold particles/clusters are not crystalline. Therefore, the XAFS technique was used to determine structural information about the gold species.

In Fig. 5, the white line intensity XANES of the catalysts indicates the density of *d*-holes in Au, which is consistent with its O-rich environment [35]. Analysis of the Au L_{III} edge data corroborates the finding that only the Au/CeO₂ catalyst contains a small amount of the stable cationic state of gold, whereas the Au/CeZrO_x and Au/CeZrLaO_x catalysts do not. The XANES of the Au/CeZrO_x and Au/CeZrLaO_x catalysts essentially match that of metallic gold. This observation is consistent with the *R*-space EXAFS data in Fig. 6 and Table 3. For Au/CeO₂, the coordination number (CN) of the Au–O bond with an interatomic distance of 1.91 Å is 0.6 ± 0.2 , and that of the Au–Au bond with an interatomic distance of 2.85 Å is 10.0 ± 2.0 , indicating that the Au–Au contribution is dominant. For Au/CeZrO_x and Au/CeZrLaO_x, the EXAFS result only shows Au–Au bonds with CNs of 8.9 ± 1.4 and 10.8 ± 0.7 , respectively, suggesting that the gold species on these two supports are in the metallic form. Typically, for about 2–4 nm gold particles/clusters, the Au–Au CNs are 8–10 [1,36]. Therefore, the average particle diameters of gold on the three supports are almost at the same level according to the EXAFS results. Despite the size of gold particles being an important

Table 2

Complete (100%) conversion temperature (°C) of CO over the three catalysts compared with other ceria-based gold catalysts.

Catalyst	Preparation method	CO (%) : O ₂ (%)	GHSV (mL h ⁻¹ g _{cat} ⁻¹)	Temperature (°C)	Reference
1 at% Au/CeO ₂	DP	1:20	80000	200	This study
1 at% Au/CeZrO _x	DP	1:20	80000	175	This study
1 at% Au/CeZrLaO _x	DP	1:20	80000	140	This study
1 at% Au/CeO ₂	Combustion	Unknown	Unknown	350	[31]
1 wt% Au/CeO ₂	DP	1:20	11000	70	[32]
10 wt% Au/CeO ₂	CP	1:1	60000	200	[33]
3 wt% Au/CeO ₂	SMAD	1:1	60000	150	[33]
55 wt% Au/CeO ₂	Arc-melting	2:2	300000	110	[34]
55 wt% Au/Ce _{0.5} Zr _{0.5} O ₂	Arc-melting	2:2	300000	120	[34]

Fig. 4. TEM ((a)–(c)) and HRTEM ((d)–(f)) images and EDS spectra ((g)–(i)) of Au/CeO₂ (a, d, g), Au/CeZrO_x (b, e, h), and Au/CeZrLaO_x (c, f, i) catalysts.

factor in the catalytic activity in the CO oxidation reaction, in this study, the well-dispersed Au species with nearly the same size distribution allow us to conclude that the different catalytic activities of the three catalysts are not mainly caused by the

gold particle size.

The three catalysts were also examined by XPS. Fig. 7 shows the Au 4f, O 1s, and Ce 3d regions of the XPS spectra of the catalysts, and Table 4 shows the atomic concentrations and rela-

Fig. 5. XANFS spectra of the Au/CeO₂, Au/CeZrO_x, Au/CeZrLaO_x catalysts, and Au foil.

Fig. 6. EXAFS R space spectra of the Au/CeO₂, Au/CeZrO_x, and Au/CeZrLaO_x catalysts.

Table 3
EXAFS fitting results of the three catalysts.

Catalyst	Au–O		Au–Au	
	R^a (Å)	CN ^b	R^a (Å)	CN ^b
Au foil	—	—	2.86 ± 0.00	12
Au/CeO ₂	1.91 ± 0.03	0.6 ± 0.2	2.85 ± 0.01	10.0 ± 2.0
Au/CeZrO _x	—	—	2.83 ± 0.01	8.9 ± 1.4
Au/CeZrLaO _x	—	—	2.85 ± 0.01	10.8 ± 0.7

^a Interatomic distance.

^b Coordination number.

tive concentrations after deconvolution. For the three catalysts, the measured surface atomic concentrations of Ce, Zr, and La are in good agreement with the bulk values, indicating that the synthesized solid solutions have good stoichiometric and structural homogeneity. However, the surface Au concentrations of Au/CeO₂, Au/CeZrO_x, and Au/CeZrLaO_x obtained by XPS are 1.0, 0.5, and 0.5 at%, respectively. Considering that the Au species are well dispersed suggested by XRD, the different atomic concentrations of Au on the three supports might be because of the lower effectiveness of Au deposition for the CeZrO_x and CeZrLaO_x supports.

The high-resolution XPS spectra (Fig. 7) show a distinct binding energy shift of the Au 4f peaks for the Au/CeO₂, Au/CeZrO_x, and Au/CeZrLaO_x samples. For quantitative evaluation, the XPS spectra of the Au 4f signals were fitted by three different states with binding energies of 83.5, 84.5, and 86.1 eV corresponding to Au⁰, Au⁺, and Au³⁺ species, respectively [37]. Au⁺ species are caused by the weak interaction between Au and the CeO₂ surface that involves charge transfer from Au to CeO₂

[38]. From Table 4, in the Au/CeO₂ catalyst, Au exists in mixed oxidation states of Au⁰, Au⁺, and Au³⁺, and the atomic ratios of Au⁰, Au⁺, and Au³⁺ to the total surface Au species are 45%, 48%, and 7%, respectively. For the Zr⁴⁺-doped catalyst, the Au³⁺ oxidation state is not present, and metallic gold (Au⁰) is the dominant species with an atomic ratio of 84%. However, after adding a small amount of La³⁺ to CeZr oxide, the atomic ratio of the Au⁰ decreases to 65%, and that of Au⁺ increases to 35%. The XPS results suggest that zirconium weakens the interaction between gold and cerium oxide while lanthanum enhances the interaction. Additionally, although the oxidation state of Au has been reported to be an important factor for CO oxidation, there is no direct correlation between the concentrations of Au⁰, Au⁺, and Au³⁺ species and the catalytic activities in experiments. This shows that the oxidation state of Au is not the dominant factor governing the activity of these catalysts.

Further information can be obtained from the O 1s spectrum. The two types of oxygen species can be distinguished by deconvolution of the O 1s spectrum. The lower binding energy (BE) peak (529.0–529.2 eV) is related to lattice oxygen (O_{lat}), whereas the higher BE peak at 531.3 eV is attributed to loosely bound surface oxygen species (O_{ads}) [39]. The lower energy peak of Au/CeO₂ (529.0 eV) shifted to higher BE after Zr and Zr/La doping (529.2 and 529.1 eV, respectively), indicating that lattice oxygen can be more easily transferred to the catalyst surface after modification [40]. The peak deconvolution results (Table 4) show that the atomic ratios of O_{ads} are 28%, 37%, and 45% for Au/CeO₂, Au/CeZrO_x, and Au/CeZrLaO_x, respectively. On the one hand, this suggests that doped CeO₂ can increase

Fig. 7. XPS spectra of Au 4f, O 1s, and Ce 3d of Au/CeO₂ (1), Au/CeZrO_x (2), and Au/CeZrLaO_x (3) catalysts.

Table 4
Summary of the XPS results of the three catalysts.

Catalyst	Concentration (at%)				Proportion (at%)				
	Au	Ce	Zr	La	Au ⁰ /Au ^a	Au ⁺ /Au ^a	Au ³⁺ /Au ^a	O _{ads} /O ^b	Ce ³⁺ /Ce ^c
Au/CeO ₂	1.0	98.9	—	—	45	48	7	28	17
Au/CeZrO _x	0.5	46.7	52.8	—	84	16	—	37	29
Au/CeZrLaO _x	0.5	45.6	46.1	7.8	65	35	—	45	23

^a Au = Au⁰ + Au⁺ + Au³⁺. ^b O = O_{lat} + O_{ads}. ^c Ce = Ce³⁺ + Ce⁴⁺.

Fig. 8. H₂-TPR profiles of Au/CeO₂, Au/CeZrO_x, and Au/CeZrLaO_x catalysts. The inset shows the H₂-TPR profiles of the corresponding initial supports.

surface oxygen species by causing a highly defective structure and/or creating extrinsic oxygen vacancies, which is confirmed by the Raman spectra. On the other hand, although Au/CeZrLaO_x has a slightly larger surface area than Au/CeZrO_x, it has a higher O_{ads} atomic ratio than Au/CeZrO_x, which can be attributed to the stronger interaction between Au and CeZrLaO_x than between Au and CeZrO_x owing to the conclusion that lanthanum can enhance the interaction. Furthermore, this result clearly shows a direct correlation between the surface oxygen species and the catalytic activity, indicating that the performance of these catalysts sensitively depends on the oxygen content of the near-surface regions of the catalyst. In other words, surface oxygen is an essential factor for CO oxidation. The existence of surface oxygen species is related to the Ce³⁺ species, as evidenced by the Ce 3d XPS results. Because of the presence of Ce³⁺ in the CeO₂ lattice, oxygen vacancies are formed. O₂ can adsorb on the vacancies, which reduces the surface Gibbs energy, balances the surface charge, and forms surface active oxygen species [38].

Because the metal–support interaction is an important factor in the CO oxidation reaction, H₂-TPR was performed to investigate the interaction between the metal (Au) and the CeO₂, CeZrO_x, and CeZrLaO_x supports (Fig. 8). The results show the nonreducible nature of the three initial supports in the temperature range 30–300 °C. However, the Au-containing catalysts show different reduction behavior. This significant change in the reduction behavior indicates that the presence of gold weakens the surface oxygen and improves the redox properties of the supports. The degree of weakening of oxygen strongly depends on the components of the support. Because of the complicate chemical environment of surface oxygen species in mixed oxides, we did not deconvolute the H₂-TPR spectra. The hydrogen consumption amounts in H₂-TPR increase in the following order: Au/CeO₂ (234 μmol/g_{cat}) < Au/CeZrLaO_x (398 μmol/g_{cat}) < Au/CeZrO_x (584 μmol/g_{cat}), which is deduced from the XPS O 1s results that the binding energy peak of lattice oxygen shifts to higher BE after modification, especially for

Zr-doped CeO₂. It can be deduced that the most easily transferred lattice oxygen leads to the largest amount of reducible oxygen species of Au/CeZrO_x catalysts, which might be the reason for the high stability of Au/CeZrO_x in the CO oxidation process. Our results suggest that Au species stabilized on supports can improve the redox properties and create oxygen vacancy sites, which are critical for the activity of the catalyst.

4. Conclusions

To clarify the support effect of Au/doped-CeO₂ catalysts in CO oxidation reaction, Au/CeO₂, Au/CeZrO_x, and Au/CeZrLaO_x catalysts with well-dispersed gold species and similar gold particle sizes were synthesized by the DP method. The results show that the oxidation state of Au is not the dominant factor determining the catalyst activity. But the concentration of surface oxygen species is the main factor. The interaction between gold and the support can improve the redox properties and create oxygen vacancy sites on the support, which results in a high catalytic activity. Owing to the synergistic effect of Zr and La dopants, the Au/CeZrLaO_x catalyst has the most surface oxygen species and shows the highest activity among the three catalysts.

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Graphical Abstract

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CO oxidation over Au/ZrLa-doped CeO₂ catalysts: Synergistic effect of zirconium and lanthanum

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The Au/CeZrLaO_x catalyst has the most surface oxygen species because of the synergistic effect of Zr and La dopants, and shows the highest activity for the CO oxidation reaction.

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Au/ZrLa 掺杂 CeO₂ 催化剂在 CO 氧化反应中优异的催化活性：锆镧协同作用

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摘要: 在过去的25年, 纳米金催化剂上 CO 氧化反应得到广泛研究, 但始终没有一致的结论. 这是因为影响纳米金催化活性的因素很多, 包括金的价态、载体的性质、氧空位、金属与载体之间的相互作用等, 尤其是各影响因素之间相互牵制, 增加了催化反应机理的研究难度. 氧化铈载体表面氧缺陷的浓度较高, 有利于活性金属组分在其表面的稳定和分散, 因此氧化铈纳米晶负载的 Au 催化剂受到广泛关注. 此外, 当 CeO₂ 晶格中部分 Ce 被化学性质不同的其它元素取代后, 可以促进 CeO₂ 晶格氧的活化, 提高氧的储放能力, 从而有利于催化反应进行. 因此, 本文采用水热法合成了组成均匀的 CeO₂, CeZrO_x 和 CeZrLaO_x 三个载体, 并通过沉淀-沉积法负载金. 利用 X 射线衍射 (XRD)、拉曼光谱 (Raman)、X 射线光电子能谱 (XPS)、高分辨透射电镜 (HRTEM)、X 射线吸收精细结构 (XAFS) 和氢气程序升温还原 (H₂-TPR) 等技术分析了催化剂的物相结构、表面性质、形貌以及金纳米颗粒的大小和价态等性质, 并结合其在 CO 氧化反应中催化性能的差异, 探讨影响金催化剂活性的关键因素.

XRD, TEM, HRTEM 和 XAFS 结果表明, 三个载体上所得金纳米颗粒的平均尺寸都在 2–4 nm, 且分散较好; XPS 结果表明, 影响催化剂活性的关键因素不是金的价态, 而是载体表面的活性氧物种. 从 Raman 结果可知, 掺杂后的氧化铈载体上氧空位浓度明显增加, 因而催化剂活性都有所提高. H_2 -TPR 进一步探讨了三个载体以及负载金后其氧化还原能力的变化, 结果表明, 金和载体之间的相互作用可以增强载体的氧化还原性能以及表面氧空位浓度, 进一步提高了催化剂活性, 而负载金催化剂氧化还原性能的变化与载体的组成密切相关. 由于锆的掺杂可使金与载体之间相互作用减弱, 而镧则增强了二者间相互作用, 因此 Au/CeZrLaO_x 催化剂上锆和镧的协同掺杂作用使其表面活性氧物种浓度最高, 低温时表现出最高的催化活性.

关键词: 金催化剂; 二氧化铈掺杂; 氧空位; 一氧化碳氧化; 金属-载体相互作用

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