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Catalytic Performance of Gold Supported on Mn, Fe and Ni Doped Ceria in the Preferential Oxidation of CO in H₂-Rich Stream

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Abstract: Ceria supported metal catalysts often exhibit high activity in the preferential oxidation (PROX) of CO in H₂-rich stream and doping the ceria support with other metals proves to be rather effective in further enhancing their catalytic performance. Therefore, in this work, a series of ceria materials doped with Mn, Fe and Ni (CeM, where M = Mn, Fe and Ni; M/Ce = 1/8) were synthesized by a modified hydrothermal method; with the doped ceria materials (CeM) as the support, various supported gold catalysts (Au/CeM) were prepared by the colloidal deposition method. The influence of metal dopant on the performance of these ceria materials supported with gold catalysts in CO PROX was then investigated in detail with the help of various characterization measures such as N₂ sorption, XRD, TEM, Raman spectroscopy, H₂-TPR, XPS and XAS. The results indicate that the incorporation of Mn, Fe and Ni metal ions into ceria can remarkably increase the amount of oxygen vacancies in the doped ceria support, which is beneficial for enhancing the reducibility of ceria, the metal-support interaction and the dispersion of gold species. Although the gold catalysts supported on various doped ceria are similar in the size and state of Au nanoparticles, the CO conversions for CO PROX over Au/CeMn, Au/CeFe and Au/CeNi catalysts are 65.6%, 93.0% and 48.2%, respectively, much higher than the value of 33.6% over the undoped Au/CeO₂ catalyst at ambient temperature. For CO PROX over the Au/CeNi catalyst, the conversion of CO remains near 100% at 60–130 °C, with a PROX selectivity to CO_2 of higher than 50%. The excellent performance of Au/CeNi catalyst can be ascribed to its large amount of oxygen vacancies and high reducibility on account of Ni incorporation. The insight shown in this work helps to clarify the doping effect of other metals on the physicochemical properties of ceria, which is then beneficial to building a structure-performance relation for ceria supported gold catalyst as well as developing a better catalyst for removing trace CO in the hydrogen stream and producing high purity hydrogen.

Keywords: doping; ceria; supported gold catalyst; high purity hydrogen; oxygen vacancies; preferential oxidation of CO

1. Introduction

The catalytic oxidation of CO at lower temperatures is widely used in the removal of trace content of CO from various atmospheres; in particular, the preferential oxidation (PROX) of CO in H₂-rich



stream has received extensive attention, as it is rather effective in getting CO-free hydrogen sources (CO < 10 ppm) to feed the polymer electrolyte membrane fuel cell (PEMFC) [1–4]. An appropriate catalyst for CO PROX should be able to selectively oxidize CO with O₂ whereas have little impairment on the hydrogen stream such as catalyzing the oxidation of hydrogen to water; meanwhile, it should also have reasonable tolerance towards CO₂ (about 20–24%) and H₂O (about 2–10%) in the feed [5].

Various catalysts have been reported in CO PROX, including supported platinum group metals (Pt, Ru, and Rh) [6–9], gold [10–14] and copper [15–17]. The platinum group metal-based catalysts exhibited high activity, with a CO conversion of about 92–97% at 150–200 °C, but the PROX selectivity (about 40%) in the presence of CO₂ and H₂O was relatively low [18]. The Cu-based catalysts displayed high CO conversion (about 100%) and PROX stability (100%) at lower temperatures (about 90–170 $^{\circ}$ C); however, their performance decreased obviously at high space velocities and the resistance towards H₂O was also relatively poor [15]. In contrast, the gold-based catalysts were considered as a promising candidate for the selective removal of CO from reformate streams due to their high activity; over the gold-based catalysts, the conversion of CO reached almost 100% at low temperatures (<100 °C) [19,20]. It is generally accepted that the performance of a gold catalyst is mainly dependent on the gold particle size and oxidation state as well as the gold-support interface, which is closely related to the nature of the support material and the preparation method. Exceptionally high activities for CO oxidation have been reported for the highly dispersed gold catalysts supported on reducible metal oxides, such as TiO₂, Fe₂O₃, CeO₂, Co₃O₄, and so on; the reducible metal oxides may not only act as a support for the nanosized gold particles but also provide a large amount of highly mobile oxygen species for the activation of CO [21–23].

In particular, the CeO₂-based catalysts have demonstrated distinct advantages in the heterogeneous catalysis due to its remarkable redox properties (Ce^{4+}/Ce^{3+}) [24,25]. For the CO PROX, the ceria supported gold catalysts exhibited high activity and good preference for CO oxidation at 20–120 °C [26–28]. Moreover, it was also found that the doping of ceria support with other elements of different ionic radii and oxidation states can improve the oxygen migration ability and enhance the noble metal dispersion. For example, doping ceria with smaller isovalent non-reducible cations like Zr^{4+} and Hf^{4+} could obviously enhance its oxygen storage capacity (OSC) by creating more intrinsic oxygen vacancies [29]. Similarly, the incorporation of Ni²⁺ into ceria could also greatly increase the oxygen vacancies and improve the oxygen diffusion in ceria [30]. The performance of metal catalysts supported on doped ceria materials was then greatly enhanced. For CO PROX, Laguna and co-workers observed that the gold catalysts supported on Zr, Fe and Zn doped ceria were more active than undoped Au/CeO₂ at low temperatures, due to an enhancement in the reducibility and the oxygen exchange ability [11]. Tabakova and co-workers prepared a series of Ce-Fe mixed oxides by varying the Ce/(Ce + Fe) ratio; they found that the ability of the supports to activate oxygen and to disperse the gold particles played a crucial role in determining the catalytic performance of Au/CeO₂-Fe₂O₃ in CO PROX [5]. A series of rare earth metals (RE) (RE = La, Sm, Gd and Y) were used to dope ceria through co-precipitation (CP) and mechanochemical method (MA) by Ilieva and co-workers [13]; yttrium as a dopant gave a promising catalyst in CO PROX. Besides this, they also doped ceria with FeO_x , MnO_x and CoO_x and found that the gold catalysts supported on FeO_x and MnO_x doped ceria were also highly active in CO PROX [23]. Furthermore, the gold nanoparticles dispersed on other ceria supports with various dopants, such as CeO_{1-x}-ZrO_x [31], CeO₂-Al₂O₃ [32], CuO-CeO₂ [33] and CeO₂-Co₃O₄ [10], have also attracted great attention due to their high activity in various reactions. In our previous works, we also found that Pd and CuO supported on Ti doped ceria (CeO₂-TiO₂) exhibited excellent catalytic performance in CO oxidation and CO PROX, respectively [15,34]. In addition, CO PROX over Au supported on CeO_2 - Co_3O_4 mixed oxides has also been studied and a possible mechanism involving -OOH intermediate was proposed and used to explain the deactivation behavior in CO PROX [10,35].

To further enhance the performance of ceria supported gold catalyst in CO PROX and have a better understanding of the structure-performance relationship, in this work, a series of ceria materials doped with a second metal (CeM, M = Mn, Fe and Ni; M/Ce = 1/8) were synthesized by a modified hydrothermal method; with the doped ceria materials (CeM) as the support, various supported gold catalysts (Au/CeM) were prepared by the colloidal deposition method. The influence of metal dopant on the performance of these ceria materials supported gold catalysts in CO PROX was then investigated in detail with the help of various characterization measures. With the doped ceria materials having a defective fluorite structure as the support, the enhanced oxygen mobility, metal-support interaction, gold dispersion, and catalytic performance of Au/CeM in CO PROX were then demonstrated. This work should be helpful in clarifying the doping effect of other metals on the properties of ceria, which is then beneficial to building a structure-performance relation for ceria supported gold catalyst as well as for developing a better catalyst for CO oxidation.

2. Results and Discussion

2.1. Chemical Composition and Textural Properties

The chemical composition (M/Ce and Au loading) and textural properties (surface area, pore size and pore volume) of CeO₂, CeM mixed oxides, and corresponding supported Au/CeM catalysts (M = Mn, Fe, and Ni) are given in Table 1. Obviously, all the doped ceria materials have a Ce/M molar ratio close to the nominal value of 1/8, indicating that the hydrothermal method used here is an appropriate approach to get the doped ceria materials with well controlled stoichiometry. Meanwhile, the composition of CeM mixed oxides remains unchanged upon subsequent treatment such as impregnation with chloroauric acid and calcination, suggesting the stable and homogeneous properties of the doped ceria materials. The Au loadings of gold catalysts are in the range of 0.7–0.96 wt.%; although they are all close to the target value (1 wt.%), the relatively higher Au loadings for Au/CeM than that for Au/CeO₂ may suggest that the doped ceria materials as a catalyst support are more effective in dispersing and stabilizing the gold species.

Undoped CeO₂ exhibits the highest surface area (118 m² g⁻¹); the surface area decreases after the addition of the second metal, especially for CeNi. After loading gold, the surface area of gold catalysts remains almost unchanged in comparison with the corresponding supports, although a slight decrease in the average pore size and pore volume is observed for the supported gold catalysts, as given in Table 1.

Sample	M/Ce Ratio ^a	Dopant Content ^a (wt.%)	Au Loading ^a (wt.%)	Surface Area ^b (m ² g ⁻¹)	Pore Size ^b (nm)	Pore Volume ^b (cm ³ g ⁻¹)
CeO ₂	0			118	13.6	0.400
CeMn	0.125			108	11.5	0.306
CeFe	0.117			108	13.8	0.303
CeNi	0.118			74	16.7	0.306
Au/CeO ₂	0		0.70	119	9.8	0.292
Au/CeMn	0.125	3.4 (Mn)	0.96	109	11.4	0.304
Au/CeFe	0.118	3.4 (Fe)	0.80	109	9.6	0.260
Au/CeNi	0.119	3.6 (Ni)	0.80	71	13.0	0.232

Table 1. Chemical composition and textural properties of CeO_2 , CeM mixed oxides with different dopants and corresponding supported Au/CeM catalysts (M = Mn, Fe and Ni).

^a The M/Ce molar ratio, content of metal dopant and Au loading were measured by the ICP-OES analysis. ^b The textural properties including BET surface area, average pore size and pore volume were determined by nitrogen sorption.

2.2. XRD Results

The XRD patterns of CeO₂, CeM mixed oxides (M = Mn, Fe, and Ni), and corresponding supported Au/CeM catalysts are shown in Figure 1. All the CeM mixed oxides display only the diffraction peaks corresponding to the fluorite face-centered cubic (fcc) CeO₂ (JCPDS 34-0394); no diffraction lines for the dopant phases are observed, probably due to the relatively low content of dopants and the homogeneous incorporation of the metal dopants into the ceria lattice. As displayed in Figure 1, a slight shift of the diffraction lines to higher angles is observed for the doped CeM samples, in comparison

with that for undoped CeO₂, suggesting that the metal dopants have been incorporated into the CeO₂ lattice and a solid solution carrying the fluorite structure is formed, consistent with the previous observation [11,15,16].



Figure 1. XRD patterns of CeO₂, CeM mixed oxides with different dopants and corresponding supported Au/CeM catalysts: (**a**) CeO₂; (**b**) CeMn; (**c**) CeFe; (**d**) CeNi; (**e**) Au/CeO₂; (**f**) Au/CeMn; (**g**) Au/CeFe; (**h**) Au/CeNi.

Meanwhile, as given in Table 2, the calculated cell parameter of cubic CeO₂ in the CeM mixed oxides is somewhat smaller than that in pure CeO₂, further proving the formation of a solid solution, since the introduction of Mn, Fe and Ni components in the CeO₂ fluorite structure could lead to a contraction of the unit cell of CeM crystallites, due to the smaller ionic radii of the dopant elements than that of cerium [11,23,36–38]. In addition, the average crystallite sizes were also estimated by using the Scherrer equation, as provided in Table 2. The particle sizes of CeMn and CeFe composites are similar to that of CeO₂; however, the Ni doped CeNi shows a much larger crystallite size, consistent with its lower surface area (Table 1).

Table 2. XRD and XPS results of CeO_2 , CeM mixed oxides with different dopants and corresponding supported Au/CeM catalysts (M = Mn, Fe and Ni).

Sample	Cell Parameter ^a (Å)	Crystal Size ^a (Å)	O_v/F_{2g} b –	Au Content (at.%)		Au 4f _{7/2} BE	Ce ³⁺ Content ^c
				ICP	XPS	(eV)	(at.%)
CeO ₂	5.416	22.0	0.117				19.2
CeMn	5.400	21.3	0.210				22.6
CeFe	5.401	21.2	0.235				23.1
CeNi	5.406	26.0	0.290				24.9
Au/CeO ₂	5.416	22.3	0.082	0.19	0.58	83.7; 87.4	18.5
Au/CeMn	5.397	21.5	0.224	0.24	1.46	83.5; 87.2	22.9
Au/CeFe	5.398	21.6	0.239	0.19	1.40	83.6; 87.2	23.3
Au/CeNi	5.406	26.2	0.287	0.20	0.93	83.7; 87.2	24.8

^a The CeO₂ cell parameter was calculated by the MDI Jade5 software; the average CeO₂ crystallite sizes were estimated from the broadening of CeO₂ (111), (200), (220), and (311) diffraction peaks by the Scherrer formula from the XRD patterns. ^b The O_v / F_{2g} ratio is determined as the area ratio of the O_v band to the F_{2g} band in the Raman spectra. ^c The surface Ce³⁺ content was determined as $A_{Ce(III)} / (A_{Ce(III)} + A_{Ce(IV)})$, where $A_{Ce(III)}$ and $A_{Ce(IV)}$ were deconvoluted from the XPS spectra for the Ce(III) and Ce(IV) species, respectively.

After introducing the active gold component, the XRD patterns of gold catalysts remain almost unchanged in comparison with the corresponding supports and no distinct diffraction peaks for gold are detected, which is ascribed to the fact that the amount of gold is relatively small and/or the gold species is finely dispersed on the supports, with a particle size below 5 nm [39].

The TEM images of various Au catalysts shown in Figure 2 illustrate that all the Au/CeO_2 and Au/CeM catalysts take a well-defined rod-like morphology with the diameter of approximate 10 nm and length of 50 to 200 nm, although the as-obtained nanorods in Au/CeNi are relatively thicker and shorter [40].



Figure 2. TEM images of Au catalysts supported on CeO₂ and CeM mixed oxides with different dopants (Au/CeO₂; Au/CeMn; Au/CeFe; Au/CeNi).

The HRTEM images shown in Figure 3 indicate that gold nanoparticles are highly dispersed on the supports and all the gold catalysts display a similar particle size distribution (3–5 nm); the lattice spacing of Au nanoparticle is 0.23 nm, which is indexed as the {111} planes. Similar phenomena were also reported for the Au catalysts supported on TiO₂, ZnO, γ -Al₂O₃ and ZrO₂ prepared by the same method [41]; by using the colloidal deposition method, the gold metal particles were generated before they were deposited on the support, which is a rather effective way to control the size of gold particles in preparing the supported gold catalysts. As a result, when considering the influence of dopant on the performance of the supported gold catalysts in detail, the effect of gold size can then be excluded.



Figure 3. HRTEM images of Au catalysts supported on CeO₂ and CeM mixed oxides with different dopants (Au/CeO₂; Au/CeMn; Au/CeFe; Au/CeNi).

2.4. Raman Spectroscopy

Figure 4 shows the Raman spectra of CeO₂, CeM mixed oxides (M = Mn, Fe, and Ni), and corresponding supported Au catalysts. For pure CeO₂, two main bands are observed: The intense one at 460 cm⁻¹ is ascribed to the F_{2g} Raman active mode of CeO₂ fluorite structure, viewed as a symmetric breathing mode of the oxygen atoms around Ce⁴⁺ ions, whereas the weak one at ca. 600 cm⁻¹ is assigned to the oxygen vacancies (O_v) preferentially present on the surface of cubic CeO₂ [11,15,16,42,43]. The appearance of oxygen vacancies is evidence for the presence of Ce³⁺ ions.

In comparison with the undoped CeO₂, an evident change is observed for the doped CeM materials in the position and width of these two bands, confirming the tight interaction between the dopants and parent CeO₂, consistent with the XRD results. Meanwhile, the F_{2g} Raman band of CeO₂ is shifted to lower frequencies and becomes broader in the doped CeM materials, especially in the Mn-doped CeMn support [36,37]. The observed shifting and widening of the F_{2g} band for the doped CeM materials may be ascribed to the fact that the surroundings of Ce cations were modified by the

metal dopants added in CeO₂ [11,44], which should be also related to the formation of more oxygen vacancies upon the addition of the metal dopants [13].



Figure 4. Raman spectra of CeO₂, CeM mixed oxides with different dopants and corresponding supported Au/CeM catalysts: (**a**) CeO₂; (**b**) CeMn; (**c**) CeFe; (**d**) CeNi; (**e**) Au/CeO₂; (**f**) Au/CeMn; (**g**) Au/CeFe; (**h**) Au/CeNi.

After loading the gold component, the F_{2g} band of CeO₂ for the supported gold catalysts is even broader than that of the corresponding support (Figure 4), reflecting the enhanced gold-support interaction. The surroundings of surface species on the support may be modified by loading gold through an epitaxial contact between Au and the oxide support [11]. Besides, a decrease in the intensity of the weak Raman band (O_v) attributed to the oxygen vacancies is observed in Au/CeO₂ compared with that in CeO₂, implying that the Au species may consume certain oxygen vacancies on CeO₂. However, for the Au/CeM catalysts, the weak O_v band is still rather intense, suggesting that there are still abundant oxygen vacancies on the doped CeM surface, which is helpful to disperse and stabilize the Au species.

Quantitatively, the ratio of O_v band area to F_{2g} band area has been associated with the quantity of oxygen vacancies [44]; that is, the higher the O_v/F_{2g} ratio, the larger the amount of oxygen vacancies is in the doped CeM materials. As shown in Table 2, the doped CeM composite oxides exhibit much higher O_v/F_{2g} ratio than the undoped CeO₂ oxide, suggesting that the amount of oxygen vacancies can be enhanced greatly by doping ceria with the Mn, Fe and Ni species. The CeNi composite oxide doped with Ni shows the largest O_v/F_{2g} ratio, implying the formation of abundant oxygen vacancies. After loading Au, the O_v/F_{2g} ratio for Au/CeO₂ decreases markedly, compared with CeO₂; however, the O_v/F_{2g} ratios for the Au/CeM catalysts, especially for Au/CeNi, remain at a much higher level, in comparison with those for the undoped Au/CeO₂ catalyst. In addition, as given in Table 2, the O_v/F_{2g} ratios of three Au/CeM catalysts are similar to those of the corresponding CeM supports, which may be related to the enhanced reducibility of the supported Au catalysts, as discussed later in this article.

The oxygen vacancies on the CeO₂ surface help to disperse and stabilize the gold species and meanwhile are also of great importance in catalyzing CO oxidation [45]. As explained by the Mars-van Krevelen-type mechanism, CO oxidation involves the alternant reduction and oxidation of the oxide surface; the formation of surface oxygen vacancies and their replenishment by gas-phase oxygen are crucial for the catalytic reaction cycles of CO oxidation [45]. As a result, the abundant oxygen vacancies present on the doped ceria materials and corresponding supported gold catalysts may endow them with high activity in CO oxidation.

2.5. TPR Results

Figure 5 shows the H₂-TPR profiles of CeO₂, CeM mixed oxides (M = Mn, Fe, and Ni), and corresponding supported Au catalysts. For undoped CeO₂ (Figure 5a), two broad reduction peaks are observed; the low temperature one centered at 442 °C is attributed to the surface-capping oxygen of CeO₂, whereas the high temperature one around 740 °C is related to the reduction of bulk CeO₂ [15,46]. After doping with Mn, Fe and Ni, a significant decrease in the reduction temperature of the surface-capping oxygen in CeO₂ is observed, suggesting a great enhancement of the reducibility of CeO₂ by the dopants [11], which was related to the higher lattice oxygen mobility on account of the oxygen vacancies created by the dopants [13].



Figure 5. H₂-TPR profiles of CeO₂, CeM mixed oxides with different dopants and corresponding supported Au/CeM catalysts: (a) CeO₂; (b) CeMn; (c) CeFe; (d) CeNi; (e) Au/CeO₂; (f) Au/CeMn; (g) Au/CeFe; (h) Au/CeNi.

In particular, the CeMn mixed oxide display three distinct reduction peaks (Figure 5b): the broad one at about 200 °C represents the reduction of MnO₂ to Mn₂O₃ and the further reduction of Mn₂O₃ to Mn_3O_4 [47,48]; the peak around 330 °C corresponds to the combined reduction of Mn_3O_4 to MnOand surface Ce⁴⁺ to Ce³⁺ species, which is shifted to lower temperatures in comparison with that of undoped CeO₂ [16]; lastly, the peak at 745 $^{\circ}$ C is then associated with the reduction of bulk CeO₂. As for the CeFe composite (Figure 5c), the reduction of bulk CeO₂ appears around 754 $^{\circ}$ C; meanwhile, a small signal is detected around 533 °C and two overlapping reduction peaks centered at 334 and 402 °C are observed, with a broad shoulder at 228 °C. The reduction of Fe₂O₃ goes through two steps, viz., the transition of hematite to magnetite (Fe₂O₃ to Fe₃O₄) around 370 °C and magnetite to metallic iron (Fe₃O₄ to FeO to Fe) around 600 °C [23]; therefore, the reduction peak for CeFe at around 334 °C should be ascribed to the surface Fe^{3+} species [49]. However, an accurate differentiation of the specific reduction steps in the 400-600 °C region is especially difficult, because the reduction of surface Ce⁴⁺ occurs simultaneously with that of Fe₃O₄ to FeO. In contrast, the CeNi composite displays a similar TPR profile to CeFe (Figure 5d). As Ni^{2+} and Ce^{4+} cations are different in the size and valence state, the incorporation of Ni²⁺ ions into ceria lattice may form a Ni-O-Ce solid solution and generate abundant oxygen vacancies, bringing on large amount of adsorbed oxygen species that can be easily reduced by H₂ [50]. The reduction peak at 740 $^{\circ}$ C corresponds to bulk CeO₂, whereas the overlapped signals at 110–450 °C (with a broad shoulder at 170 °C) can be attributed to the reduction of adsorbed oxygen. In particular, the reduction peak at 235 °C may correspond to free NiO, whilst the peak at 318 °C is assigned to the reduction of strongly interactive NiO species with CeO₂ [48,50,51]. All of these prove that the introduction of metal dopants into CeO₂ is capable of facilitating the release of lattice oxygen and promoting the reduction of Ce⁴⁺ to Ce³⁺ [5,11,52]; the reducibility of four supports considered in this work follows the order of CeNi > CeFe > CeMn > CeO₂.

After loading the active gold component, the reduction of bulk CeO_2 in the supported gold catalysts occurs at ca. 720 °C (Figure 5e-h), approximately 20 °C below that of the corresponding supports, suggesting that the reducibility of bulk CeO₂ can be enhanced by the deposition of gold species. Besides, a broad feature corresponding to the reduction of surface-capping oxygen of CeO_2 or dopant oxides appears at lower temperatures (220–560 °C) [11]. In particular, an intense signal appears at very low temperatures (around 100 $^{\circ}$ C) in the H₂-TPR profiles of the supported gold catalysts, which is mainly attributed to the reduction of CeO₂ strongly bound with the gold species; in addition, these low temperature peaks would overlap with those for the reduction of cationic gold species, if their presence was assumed [11]. Moreover, it was reported that the easily reducible CeO_2 species, strongly bound with the gold species, are catalytically active for CO oxidation [53]. Current results illustrate that the reducibility of CeO_2 can be greatly enhanced by loading Au, especially on the doped CeM supports, which may be ascribed the occurrence of spillover phenomena, involving either hydrogen activated on the metal phase or lattice CeO₂ oxygen induced by intimate metal-support interactions [11,23,46]. Moreover, the enhanced reducibility of the supported Au/CeM catalysts may also contribute to their high content of oxygen vacancies expressed by the O_v/F_{2g} ratios determined from Raman spectra (Table 2).

2.6. XPS and XAS Results

Figure 6 shows the Ce 3*d* XPS spectra of CeO₂, CeM mixed oxides (M = Mn, Fe, and Ni), and corresponding supported Au catalysts. A deconvolution of these spectra suggests the presence of two types of cerium species, viz., Ce(III) and Ce(IV). The signals of U''' and V''' (916.5 and 898.4 eV), U'' and V'' (907.7 and 888.9 eV), and U and V peaks (901.3 and 882.7 eV) represent the Ce(IV) species, whereas the signals of U' and V' (903.5, 884.6 eV) and U⁰ and V⁰ (899.0, and 880.6 eV) correspond to the Ce(III) species [54]; as a result, the content of Ce(III) in the Ce-containing materials can be estimated by integrating these signals in the XPS spectra, as also shown in Table 2. The Ce(III) species is attributed to the interaction between ceria and the surrounding atoms and can be used as an indicator for the oxygen vacancies. Obviously, the contents of Ce(III) in the doped CeM supports and Au/CeM catalysts are much higher than those in the undoped CeO₂ support and Au/CeO₂ catalyst, consistent with the results of TPR and Raman spectroscopy.



Figure 6. Ce 3*d* XPS spectra of CeO₂, CeM mixed oxides with different dopants and corresponding supported Au/CeM catalysts: (**a**) CeO₂; (**b**) CeMn; (**c**) CeFe; (**d**) CeNi; (**e**) Au/CeO₂; (**f**) Au/CeMn; (**g**) Au/CeFe; (**h**) Au/CeNi.

oxides. Obviously, all the gold catalysts are similar in their Au 4*f* XPS spectra, with a pair of distinct peaks around 83.7 and 87.5 eV that were characteristic for metallic Au [55,56]. In contrast, the peaks located around 85.5 and 86.3 eV for the oxidized Au species cannot be detected [47], similar to that observed for the Au/TiO₂ catalyst prepared by the same method [41]. It can then be inferred that the gold species here is still mainly in the metallic state, in good agreement with the previous report [57]. It was known that the gold species in the catalyst prepared by deposition-precipitation and co-precipitation methods can be in the forms of metallic Au, Au₂O₃, Au (OH)₃, AuOOH·*n*H₂O, and so on; the performances of gold catalyst may be determined jointly by a mixture of these gold species with various nanostructures [58]. However, by using the colloidal deposition method in this work, the colloidal gold metal particles are generated before they are deposited on the support and the formation of the gold particles is then well controlled; as a result, the effect of Au species can be excluded when considering the influence of dopant in the doped support on the performance of supported gold catalysts [41]. In addition, the metallic gold species could activate hydrogen with subsequent spillover on the support and promote the reduction of ceria at lower temperature [56], as represented by the H₂-TPR results.



Figure 7. Au 4*f* XPS spectra of Au catalysts supported on CeO₂ and CeM mixed oxides with different dopants: (**a**) Au/CeO₂; (**b**) Au/CeMn; (**c**) Au/CeFe; (**d**) Au/CeNi.

Figure 8 shows the O 1*s* XPS spectra of CeO₂, CeM mixed oxides (M = Mn, Fe, and Ni), and corresponding supported Au catalysts. The main peak O' detected at about 529.1–529.3 eV is typical for the surface lattice oxygen of the metal oxides, whereas the peak O'' at 531.1 eV can be attributed to the loosely bonded surface absorbed oxygen species (hydroxide and adsorbed water) or the surface oxygen ions with low coordination numbers [57]. Mover, the main peak O' of the CeM mixed oxides (M = Mn, Fe, and Ni) and all the supported Au catalysts is shifted slightly to higher binding energy in comparison with that of pure CeO₂, which may indicate that the electron donating ability of oxygen species decreases somewhat after introducing Au and or dopant species. However, as the difference among all these samples in their O 1*s* XPS spectra is rather minor, the O 1*s* XPS spectra here disclose few messages concerning the redox and catalytic properties for the CeM mixed oxides and corresponding supported Au catalysts.

The contents of the bulk and surface gold component, determined by ICP-OES and XPS, respectively, are compared in Table 2. Obviously, the surface gold content is much higher than the bulk one for all the gold catalysts, meaning that the gold species is mainly located on the support surface. Moreover, it is noteworthy that the surface gold composition in the doped Au/CeM catalysts is higher than that in the undoped Au/CeO₂ catalyst. In comparison with undoped CeO₂, the CeM composites are provided with abundant oxygen vacancies and could be better supports for anchoring and dispersing the gold nanoparticles, which may in turn give the doped Au/CeM catalysts higher reducibility and activity of CO oxidation.

Figure 9 shows the Au L_{III} -edge X-ray absorption near-edge structure (XANES) spectra of the gold catalysts supported on CeO₂ and CeM mixed oxides, together with gold foil as a reference. Gold foil (Au⁰) shows a shoulder at 11,933 eV as well as two intense peaks at 11,947 and 11,970 eV; the peaks at 11,933 and 11,947 eV are characteristic for pure gold f.c.c. structure ordered up to the third shell [59]. Meanwhile, it was also reported that XAS was a very sensitive technique in detecting Au cations that gave a strong peak at 11,921.6 eV [60]. Clearly, Figure 9 illustrates that all the gold catalysts are identical to Au foil in their Au L_{III} -edge XANES spectra and almost no Au cations have been detected in the gold catalysts prepared by the colloidal deposition method in this work, in good agreement with the XPS results [57].



Figure 8. O 1*s* XPS spectra of Au catalysts supported on CeO₂ and CeM mixed oxides with different dopants: (a) CeO₂; (b) CeMn; (c) CeFe; (d) CeNi; (e) Au/CeO₂; (f) Au/CeMn; (g) Au/CeFe; (h) Au/CeNi.



Figure 9. Au L_{III}-edge XANES spectra of the Au catalysts supported on CeO₂ and CeM mixed oxides with different dopants: (**a**) Au foil; (**b**) Au/CeO₂; (**c**) Au/CeMn; (**d**) Au/CeFe; (**e**) Au/CeNi.

In summary, the doping of ceria with Mn, Fe and Ni (especially Ni) can distort the cubic ceria structure and promote the creation of abundant oxygen vacancies. The oxygen vacancies not only play a crucial role in the dispersion and stabilization of gold species, but also enhance the lattice oxygen mobility and reducibility of CeO_2 , which are of great benefit in improving the catalytic performance of the gold catalysts supported on doped ceria (CeM) in the CO oxidation.

2.7. Catalytic Performance of CeM and Au/CeM in CO PROX

The catalytic performance of CeO₂ and CeM mixed oxides with different dopants in the CO PROX is presented in Figure 10. Obviously, undoped CeO₂ exhibits rather poor catalytic activity in the CO PROX; the conversion of CO is only 5.7% at 200 °C. However, after doping with other metals, the catalytic activity of the CeM composite oxides in CO PROX is greatly enhanced. Especially, for CO PROX in the H₂-rich stream over CeNi, the conversion of CO reaches almost 100% at a temperature over 170 °C, with a PROX selectivity to CO₂ of higher than 50%. The catalytic activity of CeFe and CeMn composites is inferior to CeNi, but still much higher than that of undoped CeO₂, illustrating the crucial influence of the metal dopant on the catalytic performance of the doped ceria materials, which should be related to their abundant oxygen vacancies and enhanced reducibility. As reported by Luo and co-workers, the catalytic activity of the modified ceria-related materials was directly related to their reducibility; high reducibility favored the activation of CO molecules over the catalyst surface [52].



Figure 10. Light-off profiles (temperature-programmed reaction) of CO PROX in H₂-rich stream over CeO₂ and doped CeM mixed oxides with different dopants: (**a**) CeO₂; (**b**) CeMn; (**c**) CeFe; (**d**) CeNi.

A comparison of various Au catalysts supported on CeO₂ and CeM mixed oxides in their performance in CO PROX is shown in Figure 11. As expected, the gold catalysts are much more active than the corresponding supports. Moreover, a significant promoting effect of the metal dopant in the CeM supports on the activity of Au/CeM catalysts is also observed. At ambient temperature, the conversions of CO are 65.6%, 93.0% and 48.2% for CO PROX over Au/CeMn, Au/CeFe and Au/CeNi catalysts, respectively, much higher than the value of 33.6% over the undoped Au/CeO₂ catalyst. Although Au/CeMn and Au/CeFe are somewhat more active than Au/CeNi at low temperature (<50 °C), the Au/CeNi catalyst may perform better in the temperature range of 50 to 200 °C. For CO PROX over the Au/CeNi catalyst, the conversion of CO remains near 100% at 60–130 °C, with a PROX selectivity to CO₂ of higher than 50%. This may be ascribed to the fact that the Au/CeNi catalyst is provided with large amount of oxygen vacancies and high reducibility, in comparison with other doped Au/CeM catalysts.

Long-term tests were also performed for CO PROX over the Au/CeFe and Au/CeNi catalysts at 80 °C, as shown in Figure 12. Similarly, the Au/CeNi catalyst displays a CO conversion of ca. 92% and a PROX selectivity to CO₂ of ca. 50%, a little higher than those (88% and 48%) over the Au/CeFe catalyst. Meanwhile, both the CO conversion and PROX selectivity to CO₂ over two catalysts remain almost unchanged even after 260 h on stream, suggesting the high stability of the gold catalysts supported on the Ni and Fe doped ceria materials. Moreover, as shown in Figures S1 and S2 in the Supplementary Information, there are no structural changes for the doped Au/CeFe and Au/CeNi

catalysts after the long-term tests, in comparison with the fresh ones. As stated previously [57], the protective agent (PVA) used during the preparation of the gold catalysts cannot be completely removed through calcination at 250 °C and the residual protecting agent is capable of preventing the nano-particles of gold from sintering and aggregation during the thermal treatment and reaction at a relatively low temperature (<250 °C), which may contribute to the excellent stability of the Au/CeFe and Au/CeNi catalysts in CO PROX.



Figure 11. Light-off profiles (temperature-programmed reaction) of CO PROX in H₂-rich stream over CeO₂ and doped CeM supported gold catalysts: (a) Au/CeO₂; (b) Au/CeMn; (c) Au/CeFe; (d) Au/CeNi.



Figure 12. Long-term test of CO PROX over Au/CeFe (a1,a2) and Au/CeNi (b1,b2) catalysts at 80 °C.

The above results illustrate that the gold catalysts supported on the doped ceria (Au/CeM), especially Au/CeNi, exhibit much better performance in CO PROX than that supported on undoped ceria (Au/CeO₂). It was reported that the Au nanoparticles prepared by colloidal deposition method maintain in essence their metallic state and particle size distribution on different supports [41,57]. In this work, various characterization techniques including XPS, XAS and TEM prove that all the gold catalysts are alike in the size and state of Au nanoparticles, as the gold component were loaded by the colloidal deposition under the same conditions. As a result, the difference between the doped Au/CeM and undoped Au/CeO₂ catalysts in their catalytic performance should be derived from their difference in the nature of supports. As suggested by the Raman spectroscopy, XAS, XPS, and TPR results, the incorporation of metal dopants (especially Ni) into CeO₂ can remarkably increase the amount of oxygen vacancies in the doped CeM materials, which is beneficial to strengthening the metal-support interaction, dispersing and stabilizing the gold species, and enhancing the reducibility of doped CeM composites and supported gold catalysts. All these may contribute to the high performance

of the gold catalysts supported on the doped ceria (Au/CeM, especially Au/CeNi) in CO PROX. Actually, the catalytic performance of various gold catalysts follows the order of Au/CeNi > Au/CeFe > Au/CeMn > Au/CeO₂, the same as that for the amount of oxygen vacancies in these catalysts.

3. Materials and Methods

3.1. Catalyst Preparation

A series of CeM (M = Mn, Fe and Ni) mixed oxides, with an M/Ce molar ratio of 1/8, were synthesized by a modified hydrothermal method [41,57]. All chemical reagents were of analytical grade, purchased from Sinopharm Chemical Reagent Co., Ltd. (SCRC, Beijing, China) and used as received without further purification. Typically, Ce(NO₃)₃·6H₂O (4.0 mmol) and corresponding dopants (C₄H₆MnO₄·4H₂O, Fe(NO₃)₃·9H₂O or Ni(NO₃)₂·6H₂O, 0.5 mmol) were dissolved in aqueous KOH solution (90 mL, 6 mol L⁻¹) in a Teflon beaker, which was stirred continuously for 30 min at room temperature and then transferred into a Teflon-lined stainless steel autoclave, sealed and maintained at 110 °C for 24 h. After cooling down to room temperature, the obtained solid product was recovered by filtration and washed with deionized water. The final solid product was dried at 80 °C for 12 h and calcined at 400 °C in air for 4 h. For comparison, undoped CeO₂ was also prepared by the same procedure.

With the CeM composite oxides or CeO₂ as supports, gold catalysts (Au/CeM or Au/CeO₂) were then prepared through the colloidal deposition method, as described previously [41,57,58,61], with polyvinyl alcohol (PVA) as a protecting agent and NaBH₄ as a reducing agent.

3.2. Catalyst Characterization

The textural properties, elemental composition, crystal phase, morphology and surface properties of various components were characterized by nitrogen sorption (TriStar 3000 Gas Absorption Analyzer, Micromeritics Instrument Co., Norcross, CA, USA), inductively coupled plasma optical emission spectroscopy (ICP-OES, Thermo iCAP 6300, Thermo Scientific, Waltham, MA, USA), X-ray powder diffraction (XRD, Bruker AXS D8, Berlin, Germany), Transmission electron microscopy (TEM, JEM 2010 microscope (JEOL Ltd., Tokyo, Japan), high-resolution transmission electron microscopy (HRTEM, JEM 2010 microscope (JEOL Ltd., Tokyo, Japan) Raman spectroscopy (dispersive LabRam HR800 microscope, Horiba Jobin Yvon, Longjumeau, France), Temperature programmed reduction by hydrogen (H₂-TPR, Micromeritics AutoChem II 2920 Chemisorption Analyzer, Micromeritics Instrument Corp., Norcross, GA, USA), X-ray photoelectron spectroscopy (XPS, ULVAC PHI-5800 spectrometer, Chanhassen, MN, USA), and X-ray absorption spectroscopy (XAS, the beam line 1W1B of Beijing Synchrotron Radiation Facility (BSRF), Institute of High Energy Physics (IHEP), Chinese Academy of Sciences (CAS)), as described previously [46,57,62]. In addition, for the convenience of readers, detailed procedures for the catalyst preparation and characterization are also provided in the Supplementary Information.

3.3. Catalytic Tests and Analytical Procedure

The catalytic test for CO PROX in a H₂-rich stream was carried out in a quartz tubular flow microreactor with an internal diameter of 6.0 mm at atmospheric pressure, as described previously [15]. The catalyst was evaluated in the fresh state without any pretreatment. For each test, about 200 mg of catalyst sample (40–60 mesh) was used. The reaction stream consisted of 1.0% CO, 1.0% O₂, 50.0% H₂ (by volume), and balanced N₂, with a space velocity of 30,000 mL g⁻¹ h⁻¹. O₂, CO and CO₂ in the effluent gas were periodically analyzed online with a series of gas chromatographs. The CO and O₂ conversions (x_{CO} and x_{O2}) were determined with the CO and O₂ concentrations in the reactant

and effluent streams, while the selectivity of CO PROX or CO_2 selectivity (S_{CO2}) was defined as the fraction of O_2 consumption for the CO oxidation to CO_2 over the total O_2 consumption:

CO conversion $(x_{CO}) = [CO_2]_{out} / ([CO]_{out} + [CO_2]_{out}) \times 100\%$ O_2 conversion $(x_{O2}) = ([O_2]_{in} - [O_2]_{out}) / [O_2]_{in} \times 100\%$ CO_2 selectivity $(S_{CO2}) = x_{CO} / 2x_{O2}$.

4. Conclusions

A series of ceria materials doped with Mn, Fe and Ni were synthesized by a modified hydrothermal method; with the doped ceria materials (CeM, M = Mn, Fe, and Ni; M/Ce = 1/8) as the support, gold catalysts (Au/CeM) were prepared by the colloidal deposition method. The influence of metal dopant on the performance of these ceria materials supported gold catalysts (Au/CeM) in CO PROX was investigated in detail with the help of various characterization measures.

The results indicate that a defective fluorite structure for the doped CeM materials was obtained by incorporating Mn, Fe and Ni metal ions into ceria. Due to the strong doping effect, the amount of oxygen vacancies in the doped ceria support (especially in CeNi) is remarkably increased, which is beneficial to strengthening the metal-support interaction, dispersing and stabilizing the gold species, and enhancing the reducibility of doped CeM composites and supported gold catalysts.

The gold catalysts supported on the doped ceria (Au/CeM), especially Au/CeNi, exhibits much better performance in CO PROX than that supported on undoped ceria (Au/CeO₂). For CO PROX over the Au/CeNi catalyst, the conversion of CO remains near 100% at 60–130 °C, with a PROX selectivity higher than 50%. Moreover, the Au/CeNi catalyst also displays high stability in a long-term test at 80 °C; the CO conversion (ca. 92%) and PROX selectivity to CO₂ (ca. 50%) remain almost unchanged even after 260 h on stream.

As the gold catalysts supported on various doped ceria materials are alike in the size and state of Au nanoparticles, the difference between the doped Au/CeM and undoped Au/CeO₂ catalysts in their catalytic performance should be mainly derived from their difference in the nature of supports; that is, the excellent performance of the doped Au/CeM catalysts (especially Au/CeNi) can be ascribed to their large amount of oxygen vacancies and high reducibility on account of second metal incorporation. The insight shown in this work helps to clarify the doping effect of other metals on the properties of ceria, which is then beneficial to building a structure-performance relation for ceria supported gold catalyst as well as developing a better catalyst for removing trace CO in the hydrogen stream and producing high purity hydrogen.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/8/10/469/s1: Detailed procedures for the catalyst preparation, catalyst characterization and catalytic performance tests, Figure S1: XRD patterns of the Au/CeFe and Au/CeNi catalysts before and after the long-term test for CO PROX in H₂-rich stream, Figure S2: TEM images of the Au/CeFe and Au/CeNi catalysts after the long-term test for CO PROX in H₂-rich stream.

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