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Article

Effect of Ni doping on the catalytic properties of nanostructured peony-like CeO₂

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ABSTRACT

Nanostructured ceria materials have attracted wide attention as catalysts, and the doping of these materials with rare earth elements to modify their catalytic activity has been comprehensively investigated. A novel type of Ni-doped hierarchical nanostructured peony-like ceria (PCO) has been prepared and its catalytic activity is investigated and compared with that of Ni-loaded samples. The prepared Ni-doped ceria have nanoscale grain sizes and open mesopores. This unique morphology endows it with superior catalytic activity for the oxidation of CO and the partial oxidation of methane. It is found that extra oxygen vacancies are generated in the ceria, and the reducibility of the ceria is highly enhanced after Ni-doping. The catalytic activity for CO oxidation is improved after Ni-doping, compared with that of pure ceria and Ni-loaded ceria. In the reaction for the partial oxidation of methane, the 3.8 atm% Ni-loaded PCO sample realizes a higher CH₄ conversion than the Ni-doped ceria. However, it is found that the onset temperature for CH₄ conversion decreases from 400 °C for the pure PCO and 3.8 atm% Ni-loaded PCO sample, to 340 °C for the 5.7 atm% Ni-doped PCO sample.

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1. Introduction

CeO₂-based materials have attracted much attention in recent years, due to their high catalytic activity for CO oxidation [1–3], water-gas shift reactions [4–6], reformation of hydrocarbons [7,8], and three-way catalysis for the elimination of toxic auto-exhaust [6,9]. The excellent catalytic activity of CeO₂-based materials is related to the redox reaction of Ce^{III}/Ce^{IV} and the presence of intrinsic oxygen vacancies [10,11]. The catalytic activity can be significantly enhanced by changing the morphology of the catalysts [12,13]. Recently, hierarchical nanostructured ceria materials have been prepared using a hydrothermal method in our group [14,15]. They have a similar morphology to the Chinese peony, so we named

these materials as peony-like CeO₂ (PCO). The PCO-based materials have an open mesoporous microstructure. The thickness of the petals is in the range of 20–50 nm, and the grain size is approximately 6–8 nm. Their surface area is above 100 m²/g. Compared with commercial ceria, they show higher thermal stability [16] and much higher activity for CO oxidation [14,15], ethanol reformation [17], and as active supporters in the anode active layer and cathode layer in solid oxide fuel cells (SOFCs) [18,19].

The catalytic activity of CeO₂ can also be modified significantly by metal loading. It has been found that CeO₂ interacts with the loaded metal, and the interfacial interaction gives the composite oxide unusual features compared with pure ceria [20]. One of the most studied catalysts is Ni supported by

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CeO₂-based materials; this catalyst is effective in exploiting the synergetic effects of Ni and CeO₂. Nickel shows high activity for the reformation of hydrocarbons, similar to precious metals, but with a much lower cost [21,22]. Nickel is also used as a catalyst for carbon nanotube growth because of its high catalytic activity for the cleavage of the C–C bond in hydrocarbons [23–25]. This also gives rise to the deactivation of the Ni-based catalyst in the reformation of the hydrocarbons, due to the formation of carbon. Fortunately, the coking problem can be alleviated by modifying the properties of the support [24,26–28]. As an oxygen ion conductor, CeO₂ has been demonstrated to be effective in impeding the formation of carbon; it achieves this by transporting oxygen vacancies from the bulk to the surface, to promote the oxidation of carbon species [10,11]. Accordingly, Ni-loaded CeO₂ catalysts are widely used in water-gas shift reactions [4,29], the partial oxidation of methane (POM) [30–32], and the reformation of ethanol [17,33]. The most important component in this composite catalyst is believed to be the metallic Ni, while the ceria support also plays a noticeable role. It has been confirmed that catalysts with CeO₂ support have higher activity and lower deactivation rates than those with inert supports, such as Al₂O₃ or SiO₂ [34–36]. The former benefits from the superior oxygen storage capacity and transport activity in the ceria.

The catalytic activity of ceria can be also modified by doping with Ga, La, Zr, Sn, Pr, or Cu [10,12,37]. The Cu-doped ceria material shows unusual structural and chemical properties that favor the formation of oxygen vacancies, and can be reversibly reduced [37]. Taking this approach further, we expect that Ni-doped ceria materials would show some novel properties. However, it is difficult to dope Ni into the CeO₂ lattice with a large molar ratio, due to the large discrepancy in ionic radius between Ce and Ni. This could be one of the reasons for the relative lack of reports in the literature on Ni-doped ceria. Thurber et al. [38] studied the ferromagnetism of Ni doped into CeO₂. It was claimed that the CeO₂ retained its cubic fluorite structure even when the Ni doping concentration reached as high as 10 atm% of the nominal composition, and that the doping could decrease the grain size and generate additional strain in the lattice. Jalowiecki-Duhamel et al. [39] found that CeNi_xO_y mixed oxides are large catalytic hydrogen reservoirs with marked diffusion properties for hydrogen species. Yisup et al. [40] reported that Ce–Ni–O mixed oxides were highly active for the catalytic oxidation of methane. Kaneko et al. [41] claimed that the reactivity in a two-step water-splitting reaction for solar H₂ production was improved by Ni-doping in ceria. However, none of these studies clarified this basic fact for Ni-doped ceria; did the nickel really enter the lattice of the ceria?

The activities of Ni-loaded and Ni-doped ceria catalysts have been extensively studied [17,21,22,39–41], but the difference in the catalytic activity between them is rarely reported. In this work, Ni-doped peony-like ceria catalysts were successfully prepared, and the effects of Ni doping on the structure and catalytic activity of CeO₂ were studied. For comparison, Ni-loaded PCO samples were also prepared at the same time. The catalytic activities for CO oxidation and POM reactions were also investigated.

2. Experimental

2.1. Catalyst preparation

2.1.1. Synthesis of Ni-doped peony-like ceria

All of the doped peony-like ceria materials were synthesized using the hydrothermal method described in our previous report [14]. In brief, hydrate cerium (III) nitrate (AR, 99%), hydrate nickel nitrate (AR, ≥ 98%), glucose, acrylamide, and ammonia aqueous solutions were purchased from Beijing Chemical Reagents Company. The hexahydrated nickel nitrate was dissolved in de-ionized water to obtain a solution with a Ni²⁺ concentration of 0.2 mol/L. Then, hydrate cerium nitrate, the Ni²⁺ solution (the total cation concentration was 0.005 mol, with molar ratios of dopant cation Ni²⁺ to Ce³⁺ of 0.05:0.95, 0.1:0.9, 0.15:0.85, and 0.2:0.8), 0.01 mol glucose, 0.015 mol acrylamide, and 80 ml of de-ionized water were mixed in a Teflon autoclave with a capacity of 100 ml. The pH value of the solution was then adjusted to approximately 10 via dropwise addition of an aqueous ammonia solution. After continuous stirring at room temperature for 3 h, the autoclave was sealed and kept in an oven at 180 °C for 24 h. The precipitate was collected from the autoclave after the suspension was cooled to room temperature. After being washed with de-ionized water and alcohol and dried at 80 °C, the Ni-doped peony-like ceria materials were obtained via calcining, using a previously reported two-step procedure [14].

2.1.2. Synthesis of Ni-loaded peony-like ceria

The peony-like CeO₂ materials were synthesized using the same process as that described in a previous paper [14]. The Ni-loading was achieved using the nitrate impregnation method. Peony-like CeO₂ (0.5 g) was added to 40 ml of de-ionized water, and after stirring at room temperature for 3 h, 855 μl (5.7 atm% Ni content) of a 0.2 mol/L Ni²⁺ solution was added; 8 h of additional, vigorous stirring was performed, and the sample was dried at 80 °C. The Ni-loaded material was obtained after the sample was dried at 110 °C for 2 h and calcined at 450 °C for 4 h in air.

2.2. Characterization

X-ray diffraction (XRD) measurements were carried out using a Holland X'Pert Pro MPD X-ray diffractometer equipped with a monochromatized Cu K_α radiation source (λ = 0.15405 nm) operated at 40 kV and 40 mA using a step rate of 0.017°. The morphology of the samples was observed using a scanning electron microscope (SEM, XL30s-FEG, 10 kV). To determine the true amount of Ni doped into the CeO₂, induced coupled plasma (ICP, Thermo Electron Corporation) analysis was used to test the chemical composition. The Raman spectra of the Ni-containing materials were recorded on a JY HR800 spectrometer at ambient temperature using a laser source of 514 nm and resolution of 1 cm^{−1}. The X-ray photoelectron spectroscopy (XPS) analysis was performed on a PHI Quantera SXM instrument, using an Al X-ray source, and the binding energies were calibrated using the binding energy of the C 1s (284.8 eV).

peak as a reference. Temperature-programmed reduction (TPR) was performed to determine the reduction behavior of the 5.7 atm% Ni-doped and 3.8 atm% Ni-loaded catalysts, using 10% H₂-90% Ar as the reducing gas on a Micromeritics Chem 2920 instrument equipped with a thermal conductivity detector. The samples were heated from room temperature to 900 °C at a rate of 10 °C/min, and the gas flow rate was 50 ml/min. Typically, 20 mg of fresh catalyst was used in each experiment. A sample pretreatment was performed by flowing Ar over the sample at 300 °C for 0.5 h, to remove the adsorbed species on the surface. The H₂ consumption was determined from the integrated peak area of the reduction profiles.

2.3. Catalytic testing

All of the Ni-doped and Ni-loaded samples were examined in the catalysis tests. Activity tests were performed under atmospheric pressure, in a continuous down-flow quartz fixed-bed reactor. The catalyst (50 mg) was loaded in the reactor, using quartz wool. A feed with a constant CO:O₂:N₂ volume ratio of 2:3:95 (for CO oxidation), and CH₄:O₂:N₂ volume ratio of

2:1:4 (for POM) was used. The total gas flow rate was 50 ml/min for CO oxidation, and 49 ml/min for POM. The effluent gas was analyzed using an online gas chromatograph (Agilent 7890a) equipped with Porapak Q, ShinCarbon ST, and a thermal conductivity detector (TCD). The conversions of CO and CH₄ were calculated as:

$$X_{\text{CO}} = \frac{\text{mol CO}_{2\text{out}}}{(\text{mol CO}_{\text{out}} + \text{mol CO}_{2\text{out}})} \times 100\%$$

$$X_{\text{CH}_4} = (1 - \text{mol CH}_{4\text{out}}/\text{mol CH}_{4\text{in}}) \times 100\%$$

3. Results and discussion

3.1. Characterization results of the catalysts

All of the Ni-doped ceria catalysts present a peony-like nanostructure morphology, as shown in Fig. 1. Some small particles can be clearly observed on the surface of the Ni-loaded ceria sample. These are suggested to be residual Ni salt. As listed in Table 1, the actual Ni contents in the samples with nominal compositions of 5, 10, 15, and 20 atm% Ni doping were determined as 1.1, 3.2, 5.7, and 10.7 atm%, respectively, using ICP analysis. Some of the Ni was lost during the washing

Fig. 1. SEM images of the Ni-doped peony-like CeO₂ (PCO) and 3.8 atm% Ni-loaded PCO catalysts. (a) 1.1 atm% Ni doping; (b) 3.2 atm% Ni doping; (c) 5.7 atm% Ni doping; (d) 3.8 atm% Ni loading.

Table 1

Characterization results for the Ni-doped/loaded peony-like ceria catalysts.

Ni content (atm%)		NiO phase ^b	Lattice parameter ^c (nm)	CeO ₂ grain size ^d (nm)	Surface element ^e (atm%)		Surface Ce/O ratio (%)	ΔH ₂		
Expected ^a	ICP result				O	Ni		P1	P2	P3
0	—	no	0.54156	6.2	77.27	—	29.41	0	0.329	0.606
5 ^D	1.1	no	0.54169	6.6	79.18	0	26.30	—	—	—
10 ^D	3.2	no	0.54171	6.8	79.18	0	26.30	—	—	—
15 ^D	5.7	no	0.54172	6.3	71.13	5.40	38.40	0.00387	0.471	0.585
20 ^D	10.7	yes	0.54157	6.5	—	—	—	—	—	—
5.7 ^L	3.8	no	0.54122	10.9	75.89	13.99	31.77	0.116	0.0678	0.571

^a The superscript D refers to doping, and L refers to loading. ^b From Fig. 2. ^c Calculated from the XRD data shown in Fig. 2 using the Jade program.

^d Calculated from the (111) XRD data for the ceria, as shown in Fig. 2. ^e From XPS.

Fig. 2. XRD patterns of different catalyst samples. (1) Pure PCO; (2) 1.1 atm% Ni-doped PCO; (3) 3.2 atm% Ni-doped PCO; (4) 5.7 atm% Ni-doped PCO; (5) 10.7 atm% Ni-doped PCO; (6) 3.8 atm% Ni-loaded PCO.

with water and alcohol. Figure 1(d) shows the Ni-loaded PCO catalyst with a nominal composition of 5.7 atm%. The actual Ni content was 3.8 atm%.

The XRD patterns of the samples are shown in Fig. 2. The NiO phase is not found in the 3.8 atm% Ni-loaded PCO catalyst, which could be due to the detection limit of the XRD measurements. It is not clear from these results whether some of the Ni was doped into the CeO₂ lattice, or if it was all dispersed on the surface. This will be clarified in a later section. All of the doped catalysts show a cubic fluorite structure. The NiO phase presents only in the XRD pattern of the 10.7 atm% Ni-doped PCO. The lattice parameters of CeO₂ increase with increasing of Ni-doping amounts, as listed in Table 1. The Ni^{II} radius (0.069 nm) is much smaller than that of Ce^{IV} (0.092 nm), and the lattice should shrink when Ni enters the CeO₂ lattice. In fact, the conversion of Ce^{IV} (0.092 nm) to Ce^{III} (0.103 nm) will happen after the Ni-doping. The increase in the amount of Ce^{III} will expand the CeO₂ lattice [38], which will counteract the shrinking effects caused by the Ni-doping. The more Ni doping that occurs, the more Ce^{III} is generated. Therefore, the CeO₂ lattice expands until the shrinking lattice effects of the Ni^{II} doping begin to dominate. As shown in Table 1, the lattice parameters of CeO₂ decrease to 0.54157 nm under 10.7 atm% of Ni doping. These values are much smaller than those of the other Ni-doped samples. Although it is difficult to determine the real Ni-doping content (due to the appearance of NiO impurities), it seems that the shrinking effects of the Ni-doping overcome the expanding effects of the increasing Ce^{III} amounts after 10.7 atm% of Ni-doping. It should be noted that the lattice parameters for the 3.8 atm% Ni-loaded PCO is much smaller than those of pure PCO, as listed in Table 1. After the impregnation process, the 3.8 atm% Ni-loaded PCO sample was calcined at 450 °C in air for 4 h, to make the nickel nitrate decompose. Due to extra sintering procedure in air, the amount of Ce^{III} in the bulk material of ceria decreases compared to pure ceria and hence the lattice parameter of ceria decreases in this case [42].

The grain sizes in the prepared catalysts are calculated using the Scherrer equation. The grain size is approximately 6 nm

Fig. 3. Raman spectra of different catalyst samples. (1) Pure PCO; (2) 3.8 atm%Ni-loaded PCO; (3) 1.1 atm% Ni-doped PCO; (4) 3.2 atm%Ni-doped PCO; (5) 5.7 atm%Ni-doped PCO. The small graph inset shows an enlargement of the peak at 450 cm⁻¹.

in all of the Ni-doped samples, but is 10.9 nm in the 3.8 atm% Ni loaded PCO, as shown in Table 1. After the impregnation process, the 3.8 atm% Ni-loaded PCO sample was calcined at 450 °C for 4 h in air to make the nickel nitrate decompose. This extra sintering also made the PCO grains grow bigger compared with those in the doped samples, which did not occur extra sintering.

The Raman spectra are shown in Fig. 3. The peak at 462.0 cm⁻¹, the typical F_{2g} Raman active modes of a fluorite structured ceria [43], shift to 455.2, 455.0, and 459.8 cm⁻¹ for the 1.1, 3.2, and 5.7 atm% Ni-doped samples, respectively. It does not shift for the Ni-loaded sample. For clarity, an enlargement of the spectra is shown in the inset. The red-shift suggests a significant modification of the M–O bonding symmetry, which probably results from the presence of Ni in the fluorite lattice [40,44]. As mentioned above, the doping of Ni into the ceria lattice results in extra strain and increases the concentration of Ce^{III} in the bulk [38], which also influences the Raman bands. The shoulder peaks around 230 and 590 cm⁻¹ are related to the addition of Ni. The relative intensity of the band from 540 to 636 cm⁻¹ increases with increases in the Ni-doping amount. This is ascribed to the formation of oxygen vacancies in the Ni-doped ceria [45].

The XPS spectra for the binding energies of Ce 3d and Ni 2p core levels are given in Fig. 4. The signals from Ce^{IV} are marked as u, u', and u'' for 3d_{3/2}, while those for 3d_{5/2} are marked as v, v', and v''. The four peaks labeled as u⁰, u', v⁰, and v' were assigned to Ce^{III}, as reported in the literature [46]. Although the absolute binding energies are referenced against the C 1s photoelectron peak at 284.8 eV, some scattering of the binding energies in the Ce 3d and Ni 2p regions could occur. This is due to the low conductivity of the catalysts, which caused charging effects. Therefore, the positions of the peaks may not have reflected the exact binding energies. However, it is clear from Fig. 4(a) that the relative intensities of the v⁰/v, v', u⁰/u, and u' peaks increase with increasing amounts of doped Ni. This behavior was not observed in the Ni-loaded catalyst. The u⁰/u and v⁰/v peaks are too close to be distinguished, but from the in-

Fig. 4. Ce 3d (a), Ni 2p (b), and O 1s (c) XPS spectra of the samples. (1) Pure PCO; (2) 1.1 atm% Ni-doped PCO; (3) 3.2 atm% Ni-doped PCO; (4) 5.7 atm% Ni-doped PCO; (5) 3.8 atm% Ni-loaded PCO. Ce^{IV} peaks are marked as u, u', and u'' for 3d_{3/2} and v, v', and v'' for 3d_{5/2}. The four peaks labeled as u⁰, u', v⁰, and v' were assigned to Ce^{III}.

crease of the relative intensity of the v' and u'' peaks, it is clear that the Ce^{III} concentration increases with increasing Ni-doping amounts. A similar phenomenon has been reported for Cu and Zr-doped ceria materials [47,48].

Compared with pure ceria, the v' and u' peak intensities for the 3.8 atm% Ni-loaded PCO show insignificant change compared with those of the 5.7 atm% Ni-doped catalyst, which is in accordance with the Raman spectra results. The Ni contents on the catalyst surface (as detected by XPS) are listed in Table 1. There is no obvious Ni signal from the surfaces of the 1.1 atm% Ni-doped or 3.2 atm% Ni-doped catalysts, and the surface nickel content is 5.4 atm% for the 5.7 atm% Ni-doped sample, which is similar to the bulk nickel content. In contrast, the surface nickel content is 13.44 atm% for the Ni-loaded catalyst, which is three times higher than the actual composition of 3.8 atm%. This is consistent with the fact that the Ni particles are mostly dispersed on the surface of the 3.8 atm% Ni-loaded PCO sample. In addition, it is found that the peak at approximately 919.4 eV in the Ce 3d core level grows larger with increases in the doped Ni amount. This is clearly related to the nickel-doping behavior, and the same peak is not observed in the spectra of the 3.8 atm% Ni-loaded PCO. The Ni 2p spectra of the 5.7 atm% Ni-doped and 3.8 atm% Ni-loaded PCOs are compared in Fig. 4(b). In the Ni-loaded catalyst, there are two distinct peaks at ~855.3 and ~861 eV, which were assigned to Ni^{II}. The peak at approximately 861 eV does not present, and the peak at approximately 855.3 eV broadens. This indicates the different chemical environments surrounding the Ni in the loaded and doped catalysts.

The O 1s spectra of the samples are shown in Fig. 4(c). There are two peaks in the pure PCO and Ni-doped PCO samples and three peaks in the Ni-loaded PCO sample. The O 1s peaks at 529.25 and 531.75 eV in PCO, which are assigned to the ceria-related lattice oxygen, and the adsorbed oxygen species on the surface, respectively [49,50], shifted to 529.20 and 531.30 eV after 1.1 atm% Ni and 3.2 atm% Ni doping, and to 528.65 and 530.95 eV after 5.7 atm% Ni doping. The O 1s peaks at 528.10, 529.25, and 530.60 eV in the 3.8 atm% Ni-loaded samples and the new peak at 528.10 eV that was related to O²⁻

were also found in LaNiO₃ [51]. The surface O contents are listed in Table 1. They slightly increase from 77.27% to 79.18% after 1.1 atm% Ni or 3.2 atm% Ni doping, but rapidly reduce to 71.13% and 67.99% after 5.7 atm% Ni doping and 3.8 atm% Ni loading, respectively. The surface O content is closely related to the reduction of surface ceria [49]. According to the changes in the ratio of Ce to O on the surface, as listed in Table 1, it is clearly that the Ni loading and doping reduce the surface oxygen content. That is, they enhance the oxygen vacancy content on the surface. However, it is found that the Ce/O ratio in the 1.1 atm% Ni doping and 3.2 atm% Ni doping samples is a little lower than that in PCO. In these two samples, the doped nickel was not be detected using XPS. However, it is likely that the nickel combines with the oxygen on the surface, which contributes to the slightly lower Ce/O ratio of 26.30% in the 1.1 atm% Ni doping and 3.2 atm% Ni doping samples, compared with the value of 29.41% found for PCO. It is found that there are more oxygen vacancies on the surface of the 5.7 atm% Ni-doped sample compared with the 3.8 atm% Ni-loaded sample.

According to the XRD, Raman spectroscopy, and XPS results given here, the lattice shrinking of CeO₂ is induced after Ni doping. To suppress the structure deformation, more Ce^{III} is generated, since its ionic radius is larger than that of Ce^{IV}. This can explain the increases in the Ce^{III} concentration after Ni doping. According to the above results, the defect chemistry could be written in Kröger-Vink notation as follows:

3.2. TPR results

The 5.7 atm% Ni-doped PCO sample and the 3.8 atm% Ni-loaded PCO sample were selected to compare the influence of Ni doping and loading on the reduction properties of PCO. The TPR spectra are shown in Fig. 5 and the results are summarized in Table 1. Two peaks are identified. The peak at 380 °C (marked as P2) is attributed to the surface reduction of the ceria, and the second peak at 655 °C (marked as P3) is related to the bulk reduction of the ceria. The reduction temperatures are much lower than the reported temperatures of ~500 and

Fig. 5. TPR profiles for the selected samples. (1) Pure PCO; (2) 5.7 atm% Ni-doped PCO; (3) 3.8 atm% Ni-loaded PCO.

~800 °C [9,48]. When Ni is introduced, regardless of the doping or loading, the P2 and P3 shift to lower temperature. This shows that the presence of Ni promotes the reduction of ceria. In addition, the P1 below 300 °C in the spectra of the Ni-containing samples was assigned to the reduction of Ni [52]. For the 5.7 atm% Ni-doped PCO, the P1 may be related to the reduction of Ni in the ceria close to the surface. The P2 for the Ni-doped sample is at 315 °C, much lower than that for PCO, which is at 380 °C. The P2 peak consumes much more H₂ for reduction on the Ni doped PCO catalyst than that on PCO. This indicates that the Ni doping promotes the reduction of the ceria surface. The P2 for the 3.8 atm% Ni-loaded PCO decreases to 323 °C, indicating that interactions occur between the loaded Ni and the surface of the ceria. However, the H₂ consumption of the 3.8 atm% Ni-loaded PCO is lower than that of PCO. This is probably because the dispersion of Ni particles on the surface partly blocks the reduction of the ceria. The P3 associated with the reduction of the bulk ceria does not shift significantly for either the 5.7 atm% Ni-doped sample or the 3.8 atm% Ni-loaded sample, and the P3 peak area for the three samples is similar, which shows that the Ni loading and doping have no significant influence on the reduction of bulk ceria. Comparing the relative intensity of P1 to that of P2 and P3, it is quite clear that the amount of reducible Ni is higher in the 3.8 atm% Ni-loaded PCO sample than in the 5.7 atm% Ni-doped PCO. This is consistent with the XPS results showing that Ni is distributed uniformly within the lattice of the Ni-doped sample.

3.3. Catalytic activity

The CO oxidation results are shown in Fig. 6. All of the Ni-containing catalysts show higher activities compared to the pristine PCO. It is clear that this improvement effect is not related to changes in the specific surface area of the catalyst since the specific surface area of the pure PCO is above 100 m²/g [14,15], and is not significantly changed after small amounts of Ni loading or doping. The catalytic activity of the Ni-doped catalyst increases with the increasing of the Ni doping amount. The activity of the 3.8 atm% Ni-loaded PCO is lower than that of

Fig. 6. CO conversion for all Ni-doped and Ni-loaded PCO catalysts. The catalyst (50 mg) was loaded in the reactor using quartz wool. A feed with a constant CO:O₂:N₂ volume ratio of 2:3:95 was used. The total gas flow rate was 50 ml/min.

3.2 atm% Ni-doped PCO. To further clarify why the effects of the Ni doping is superior to those of the Ni loading, a sample of 13.4 atm% Ni-loaded PCO (actual composition) was also prepared using the impregnation method, and was tested for CO oxidation. The activity of the 13.4 atm% Ni-loaded PCO is also lower than the activity of the 3.2 atm% Ni-doped PCO and the 5.7 atm% Ni-doped PCO. Therefore, the Ni doping is more effective in enhancing the activity than the Ni-loading. It has been reported that the releasable lattice oxygen on the ceria surface could be the key reactant for the oxidation of the adsorbed CO [12,53–56]. As shown in the TPR profiles in Fig. 5, the 3.8 atm% Ni-loaded PCO has more reducible Ni, but less reducible surface ceria than the 5.7 atm% Ni-doped PCO sample. This result supports the findings from previous investigations that the surface reducibility of CeO₂ is an essential factor for CO oxidation, at least for ceria-based catalysts [12,53–56].

Data for the partial oxidation of methane is shown in Fig. 7. The CH₄ conversion ratio of the Ni-doped catalysts increases with the increasing of the doped Ni amount. The activity of PCO

Fig. 7. Partial oxidation of CH₄ on catalysts. The catalyst (50 mg) was loaded in the reactor, using quartz wool. A feed with a constant CH₄:O₂:N₂ volume ratio of 2:1:4 was used. The total gas flow rate was 49 ml/min.

is similar to that of the 3.2 atm% Ni-doped PCO for the temperature range tested, and is slightly higher than the activity shown by the 1.1 atm% Ni-doped PCO sample. The 5.7 atm% Ni-doped PCO shows a 20% conversion ratio at 350 °C. Compared with the Ni-doped PCO catalysts, the 3.8 atm% Ni-loaded PCO sample shows a much higher conversion ratio of 28% at 540 °C, which is also higher than the ratios shown by all of the doped and un-doped PCO samples. Ni metal sites are known for methane activation [10,57], and our results indicate that the reducible Ni plays an important role in the POM reaction. The methane conversion ratio begins to decrease at 480 °C and 540 °C on 5.7 atm% Ni-doped PCO and 3.8 atm% Ni-loaded PCO catalyst respectively. This is attributed to the degradation of the catalysts after the reaction, which likely occurs because of carbon formation and the coarsening of the PCO grain growth. This was confirmed by the XRD measurements performed after the POM tests (data not shown).

It is interesting to note that for the PCO-based catalysts, the onset temperature for CH₄ conversion is strongly influenced by the Ni doping. The reforming reaction starts at 400 °C for the PCO and the Ni-loaded PCO samples. It decreases to 360, 360, and 340 °C for the 1.1, 3.2, and 5.7 atm% Ni-doped PCO samples, respectively. These onset temperatures are much lower than those reported previously for Ni-loaded ceria catalysts, or catalysts with other supports [9,57–60]. The decreasing trend for the onset temperature in the POM reaction could be related to the oxygen vacancy generation, or the enhancement in the reduction of surface ceria, caused by the Ni doping. Due to the complicated reaction mechanism of POM, a clear understanding of this process will require further investigations.

4. Conclusions

Hierarchically nanostructured Ni-doped and Ni-loaded peony-like ceria materials have been successfully prepared, and show high activity for CO oxidation and the partial oxidation of methane. Ni doping is favorable for the formation of Ce^{III} in ceria, and enhances the reduction of surface ceria. The Ni-doped samples therefore show much higher activity for CO oxidation than the Ni-loaded samples. It is believed that the surface oxygen vacancy induced by Ni doping is essential for CO oxidation. The onset temperature for CH₄ conversion is highly dependent on the Ni doping amount. It decreases from 400 °C for the pure PCO and the 3.8 atm% Ni-loaded PCO sample, to 340 °C for the 5.7 atm% Ni-doped PCO sample. The 3.8 atm% Ni-loaded PCO sample realizes the highest CH₄ conversion ratio of 28% at 540 °C. It is thought that the exposed reducible Ni is more important for the partial oxidation of methane than the ceria surface or the doped Ni. The Ni-doped PCO samples show interesting effects for the oxidation of CO and the partial oxidation of methane, which should be useful for the design of catalysts and the understanding of catalytic mechanisms.

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Graphical Abstract

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Effect of Ni doping on the catalytic properties of nanostructured peony-like CeO_2

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Oxygen vacancies are generated in bulk ceria after Ni doping, which promotes the reducibility of peony-like CeO_2 , and hence enhances the catalytic activity for CO oxidation.

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Ni掺杂对纳米结构牡丹花状 CeO_2 材料催化特性的影响

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摘要: 制备了一种新型Ni掺杂多层纳米结构牡丹花状 CeO_2 材料, 研究了其催化性能, 同时与Ni负载牡丹花状 CeO_2 样品进行了比较. 结果表明, Ni掺杂 CeO_2 样品具有纳米晶粒和开放的介孔结构, 特殊的形貌使其在CO氧化和甲烷部分氧化反应中具有独特的催化特性. Ni掺杂后, CeO_2 中产生了多余氧空位, 同时其氧化还原活性也增强, 其在CO氧化反应中的催化活性明显高于纯 CeO_2 和Ni负载 CeO_2 样品; 在甲烷部分氧化反应中, 牡丹花状 CeO_2 负载3 atm% Ni催化剂样品上甲烷转化率高于所有Ni掺杂的催化剂样品. 但是在Ni负载型催化剂和花状 CeO_2 催化剂上, 甲烷的起始转化温度为400°C, 而5.7 atm% Ni的掺杂使其降至340°C.

关键词: 纳米结构氧化铈; 镍; 一氧化碳; 氧化; 甲烷; 部分氧化

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