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Three-dimensionally ordered macroporous $\text{CeO}_2/\text{Al}_2\text{O}_3$ -supported Au nanoparticle catalysts: Effects of CeO_2 nanolayers on catalytic activity in soot oxidation

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ABSTRACT

A series of catalysts consisting of three-dimensionally ordered macroporous (3DOM) $x\text{-CeO}_2/\text{Al}_2\text{O}_3$ -supported Au nanoparticles ($x = 2, 10, 20$, and $40 \text{ wt}\%$) were successfully synthesized using a reduction-deposition method. These catalysts were characterized using scanning electron microscopy, the Brunauer-Emmett-Teller method, X-ray diffraction, transmission electron microscopy, ultraviolet-visible spectroscopy, and temperature-programmed reduction by H_2 . Au nanoparticles of mean particle size 5 nm were well dispersed and supported on the inner walls of uniform macropores. The 3DOM structure improved the contact efficiency between soot and the catalyst. An Al-Ce-O solid solution was formed in the multilayer support, i.e., $x\text{-CeO}_2/\text{Al}_2\text{O}_3$, by the incorporation of Al^{3+} ions into the CeO_2 lattice, which resulted in the creation of extrinsic oxygen vacancies. Strong interactions between the metal (Au) and the support (Ce) increased the amount of active oxygen species, and this promoted soot oxidation. The catalytic performance in soot combustion was evaluated using a temperature-programmed oxidation technique. The presence of CeO_2 nanolayers in the 3DOM $\text{Au}/x\text{-CeO}_2/\text{Al}_2\text{O}_3$ catalysts clearly improved the catalytic activities in soot oxidation. Among the prepared catalysts, 3DOM $\text{Au}/20\%\text{CeO}_2/\text{Al}_2\text{O}_3$ showed high catalytic activity and stability in diesel soot oxidation.

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1. Introduction

Catalysis plays an important role in environmental pollution control [1–3]. Soot particles generated by diesel combustion are hazardous to human health and the environment [4–8], and their elimination has attracted much attention. Governments

have legislated to limit diesel exhaust emissions [9]. In recent years, various catalysts, including precious metals [10], transition-metal oxides [11], alkali-metal oxides [12,13], perovskite-type oxides [14], and CeO_2 -based oxides [15–17], have been investigated and found to give good catalytic performance in diesel soot combustion.

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CeO₂-based materials are promising candidate catalysts because of the high oxygen storage capacity, *f*-electron orbitals, and excellent redox properties of CeO₂ [18]. However, pure CeO₂ is rarely used in practical applications because of its low textural stability [19]. CeO₂ is easily sintered at high temperatures because of its poor mechanical strength. It is therefore important to improve its mechanical strength while maintaining its other properties. In this context, CeO₂ doping with various ions, e.g., Zr [20,21], La [22], Ga [23], and K [12,24] ions, has been investigated. Al₂O₃ is generally a good support for catalysts and has the advantages of thermal and chemical stabilities, a high surface area, and an amphoteric character [25]. CeO₂ deposited on Al₂O₃ has been successfully used to catalyze many reactions and shown high thermal stability [26]. The interactions between CeO₂ and Al₂O₃ are closely related to the Ce loading. At low loadings, the CeO₂ crystallites are well dispersed, but agglomerations can occur at higher loadings. The properties of dispersed CeO₂ crystallites differ from those of large CeO₂ aggregates. Aggregates have properties similar to those of bare, unsupported CeO₂. In the presence of Al₂O₃, an Al–Ce–O solid solution can be formed, and this can stabilize the CeO₂ surface against sintering at high temperatures [27]. The dispersion of rare-earth-metal oxides on Al₂O₃ can reduce the amount of rare-earth metal used. This lowers the price and therefore has a wide range of potential applications in catalysis.

Although CeO₂-based catalysts have many advantages in soot oxidation, they have poor low-temperature activities, therefore it is necessary to find appropriate alternatives. A supported Au catalyst with high activity in soot combustion, especially at low temperatures, was recently reported. We reported that a Au/Ce_{0.8}Zr_{0.2}O₂ catalyst gave the lowest ignition temperature in soot combustion under loose contact conditions at 218 °C [28]. The efficiency of supported Au nanoparticles in low-temperature reactions depends on various factors, including the size and shape of the Au particles, the role of the support, the oxidation state of the active Au species (i.e., metallic, Au⁺, or Au³⁺), the cluster-support interactions, the oxygen supply pathways, and the preparation procedures and pretreatment conditions.

In addition to the intrinsic catalytic activity, the contact between the catalyst and soot can affect the catalytic performance [29–31]. The average diameter of model soot particles is about 25 nm, and that of conventional catalysts is less than 10 nm. It is therefore difficult for soot to enter the inner pores of these catalysts. Soot combustion is inhibited because of restricted soot-catalyst contact and the low number of active sites. Recently, three-dimensionally ordered macroporous (3DOM) materials with uniform pore sizes (>50 nm) and ordered macroporous structures have attracted much attention for use in heterogeneous catalysis [28,31–34]. In this work, 3DOM Al₂O₃ was prepared using a colloidal crystal template method. Because of the well-defined macroporous structure of the catalyst, soot particles were able to enter the inner pores easily, and were transferred to the inner areas of the catalyst, enabling flexible access to the active sites. The soot-catalyst contact efficiency was greatly enhanced. Another advantage of 3DOM Al₂O₃ is that it has adequate mechanical strength. The design of

the multilayer support and 3DOM structure is similar to that of an industrial wall-flow type monolith. Studies of this catalyst are therefore important.

A combination of the advantages of Au, CeO₂, and Al₂O₃, e.g., high activity, good redox properties, and high surface area, can be used to design low-cost and highly effective catalysts for soot combustion. The aim of this study was to develop an efficient catalyst with Au and CeO₂ as the active components and 3DOM Al₂O₃ as the support for use in soot oxidation. We investigated the catalytic performance (activities, selectivities, and stabilities) of Au/*x*-CeO₂/Al₂O₃ catalysts with various CeO₂ loadings (*x*, mass fraction) in soot oxidation and examined how the interactions between Au and CeO₂ varied with the CeO₂ loading and affected the catalytic activity.

2. Experimental

2.1. Catalyst preparation

2.1.1. Synthesis of 3DOM Al₂O₃ support

The synthesis of monodispersed poly(methyl methacrylate) (PMMA) microspheres, template assembly, and preparation of the 3DOM Al₂O₃ and CeO₂ catalyst using a colloidal crystal template method were performed using previously reported methods [24,32]. The dried sample was calcined using the following temperature program: the temperature was increased linearly to 310 °C at a rate of 1 °C/min and held for 4 h, and then linearly increased to 800 °C at a rate of 1 °C/min in air for 5 h.

2.1.2. Synthesis of 3DOM *x*-CeO₂/Al₂O₃

Various amounts of CeO₂ were loaded on an Al₂O₃ support by micropore-diffused precipitation (MDP), using ammonia solution as the precipitating agent [28]. The catalysts with various amounts of CeO₂ are denoted by 3DOM *x*-CeO₂/Al₂O₃. A typical preparation was performed as follows. A solution (100 mL) of Ce(NO₃)₃·6H₂O was placed in a precursor tank (Beaker I). Ammonia solution was placed in another tank (Beaker II). The precursor solution (Beaker I) was diffused into a membrane reactor through holes (40 nm) distributed on the walls of ceramic membrane tubes, using a constant-flow pump. Ce³⁺ was precipitated in the membrane reactor, yielding Ce(OH)₃. The slurry was filtered, dried, and calcined at 550 °C for 4 h in static air to give 3DOM *x*-CeO₂/Al₂O₃.

2.1.3. Synthesis of 3DOM Au/*x*-CeO₂/Al₂O₃ catalysts

3DOM Au/*x*-CeO₂/Al₂O₃ catalysts were synthesized using a reduction-deposition method. A typical preparation was performed as follows. Poly(*N*-vinyl-2-pyrrolidone) solution, which was used as a stabilizer, was added to HAuCl₄ solution. The mixture was vigorously stirred for 5 min, and then a reductant solution (KBH₄) was added dropwise to reduce the Au³⁺ ions (the KBH₄/Au molar ratio was 5). The slurry became red-violet. The support (0.3 g, as prepared 3DOM Al₂O₃ or *x*-CeO₂/Al₂O₃) was added to the solution. The reaction system was vigorously stirred for 4 h. The product was removed by filtration and washed several times with distilled water and ethanol. The

resulting material was dried at 50 °C for 24 h. Water and stabilizer were removed from the product by calcining in a furnace at 350 °C for 1 h to give the desired 3DOM Au/Al₂O₃ and Au/*x*-CeO₂/Al₂O₃ samples.

2.2. Catalyst characterization

X-ray diffraction (XRD) was performed using a powder X-ray diffractometer (Shimadzu XRD 6000) with Ni-filtered Cu K α radiation ($\lambda = 1.54184$ Å). The diffraction data (2θ values) were recorded at 40 kV and 10 mA at a rate of 4°/min.

Raman spectra of the catalysts were recorded at room temperature using an inVia Reflex spectrometer (Renishaw). The sample was excited at 532 nm and a laser power less than 0.06 mW was applied to the sample.

Scanning electron microscopy (SEM) was performed using a Quanta 200 F instrument at an accelerating voltage of 5 kV. The catalyst samples were dusted on conducting resin and coated with Au prior to the observations.

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained using a JEOL JEM 2100 electron microscope at an accelerating voltage of 200 kV.

Temperature-programmed reduction by H₂ (H₂-TPR) was performed using a conventional flow apparatus connected to a thermal conduction detector. The sample (0.1 g) was pretreated by calcination at 300 °C for 1 h and then cooled to 50 °C in an air flow (20 mL/min). A 10% H₂/Ar flow (40 mL/min) was passed over the catalyst bed while the temperature was ramped from 100 to 900 °C at a heating rate of 10 °C/min.

Temperature-programmed desorption of O₂ (O₂-TPD) was performed using a Quantachrome Autosorb Iq instrument. The catalyst (100 mg) was placed in an O₂ flow (60 mL/min) at 300 °C for 30 min and then cooled to 50 °C in a He flow to purge residual O₂. The catalyst was heated from 30 to 900 °C at 10 °C/min under a He flow (60 mL/min). The desorbed oxygen was detected using a thermal conduction detector.

The Brunauer-Emmett-Teller (BET) technique was used to determine the surface areas of the catalysts based on N₂ adsorption-desorption using a Micromeritics ASAP 2020 analyzer.

Ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS) was performed using a UV-vis spectrophotometer (Hitachi U-4100) with the support as a reference in the range 200–800 nm.

2.3. Catalytic activity tests

The catalytic activities were evaluated based on temperature-programmed oxidation (TPO) in a quartz-tube ($\Phi = 8$ mm) fixed-bed reactor. The reaction temperature was increased from 150 to 650 °C at 2 °C/min. Soot with a particle diameter of ca. 25 nm (Printex-U) was purchased from Degussa. The catalyst and soot (total mass 0.11 g) were mixed in a mass ratio of 10:1 using a spatula to simulate practical condition. The simulated reaction gases contained 10% O₂, 0.2% NO, and balance Ar. During the TPO process, the mixed gases (50 mL/min) were passed over a mixture of the catalyst and soot. The outlet gas compositions were determined using a gas chromatography

system (Sp-3420, Beijing) with flame ionization detectors. The catalytic activities of the catalysts were evaluated based on T_{10} , T_{50} , and T_{90} , the temperatures at which 10%, 50%, and 90%, respectively, of the soot was oxidized during the TPO procedure. The selectivity for CO₂ (S_{CO_2}) was expressed by the equation $S_{CO_2} = C_{CO_2}/(C_{CO} + C_{CO_2})$, where C_{CO} and C_{CO_2} are the CO and CO₂ outlet concentrations, respectively; $S_{CO_2}^{max}$ was defined as the S_{CO_2} at which the CO₂ concentration was maximum.

3. Results and discussion

3.1. XRD results

The XRD patterns of the prepared catalysts, pure Al₂O₃, and CeO₂ are shown in Fig 1. For pure Al₂O₃, the main peaks, at 37.3°, 45.8°, and 66.8°, are assigned to the (311), (400), and (440) lattice faces, respectively, of crystalline γ -Al₂O₃ (PDF: 50-0741). The CeO₂ diffraction peaks at 28.5°, 33.2°, 47.5°, and 56.4° correspond to the (111), (200), (220), and (311) lattice faces, respectively, of face-centered cubic fluorite-type CeO₂ (PDF: 65-2975). For the catalyst with a CeO₂ loading of 2%, the diffraction peaks from crystalline CeO₂ were almost invisible and the pattern was almost identical to that of pure Al₂O₃. When the CeO₂ loading was greater than 10%, diffraction peaks attributed to CeO₂ appeared and the peak intensity increased with increasing CeO₂ loading. The diffraction peaks for *x*-CeO₂/Al₂O₃ shifted to slightly higher angles compared with those of CeO₂. This is attributed to contraction of the lattice cell parameter caused by substitution of Al³⁺ (0.057 nm) for Ce⁴⁺ (0.097 nm) in the fluorite lattice [35–37]. Such replacement could lead to the formation of Al–Ce–O bonds and the formation of oxygen vacancies. The intensities of the *x*-CeO₂/Al₂O₃ catalyst diffraction peaks were much lower than those of bulk CeO₂, indicating that the average CeO₂ crystal particle size decreased. Table 1 lists the crystal sizes of the *x*-CeO₂/Al₂O₃ catalysts. The average crystal size was determined using the Scherrer formula. The crystal size of the 10%CeO₂/Al₂O₃ catalyst was only ca. 3 nm. At a CeO₂ loading of 40%, the CeO₂ crystal size

Fig. 1. XRD patterns of 3DOM samples. (1) Al₂O₃; (2) 2%CeO₂/Al₂O₃; (3) 10%CeO₂/Al₂O₃; (4) 20%CeO₂/Al₂O₃; (5) 40%CeO₂/Al₂O₃; (6) CeO₂; (7) Au/Al₂O₃; (8) Au/2%CeO₂/Al₂O₃; (9) Au/10%CeO₂/Al₂O₃; (10) Au/20%CeO₂/Al₂O₃; (11) Au/40%CeO₂/Al₂O₃.

Table 1

Data of crystal phase, FWHM and crystal size of 3DOM CeO₂ and x-CeO₂/Al₂O₃ catalysts.

Catalyst	Crystal face	2 θ (°)	FWHM (°)	D (nm)
CeO ₂	(111)	28.48	0.752	10.78
10%CeO ₂ /Al ₂ O ₃	(111)	28.50	2.399	3.38
20%CeO ₂ /Al ₂ O ₃	(111)	28.59	2.108	3.85
40%CeO ₂ /Al ₂ O ₃	(111)	28.65	1.718	4.72

increased to ca. 5 nm. The crystal size of bulk CeO₂ was about 11 nm. Small crystalline nanoparticles promote adsorption of active oxygen.

Fig. 1 shows that no characteristic diffraction peaks for Au (e.g., at 38.2°) were observed in the supported Au catalysts, suggesting that the Au particles were very small and highly dispersed on the 3DOM x-CeO₂/Al₂O₃ support surface. The Au nanoparticles on the 3DOM x-CeO₂/Al₂O₃ surface therefore had less impact on the crystalline phase and crystallinity of the 3DOM x-CeO₂/Al₂O₃ catalyst. It should be noted that a diffraction peak from Au/x-CeO₂/Al₂O₃ can be observed at 37.3°. This peak may arise because of phase separation between γ -Al₂O₃ and CeO₂ after calcination during Au loading on the support. However, it could also come from the presence of broad Au diffraction peaks assigned to superimposed γ -Al₂O₃ phases.

3.2. Raman results

Raman spectroscopy is a powerful technique that can be used to study the mobility of oxygen atoms in a CeO₂ lattice [36]. The Raman spectra of 3DOM x-CeO₂/Al₂O₃, pure Al₂O₃, and CeO₂ were therefore recorded. Fig. 2(a) shows that the Raman spectrum of CeO₂ had a clear peak at ~464 cm⁻¹, which can be attributed to the triply degenerate F_{2g} mode and the symmetric breathing of oxygen atoms around Ce ions [38,39]. Fig. 2(b) shows that in the spectra of the x-CeO₂/Al₂O₃ catalysts, the peak shifted to lower wavenumbers compared with that for 3DOM CeO₂; for example, the main peak was located at ca. 457 cm⁻¹ for 10%CeO₂/Al₂O₃, ca. 459 cm⁻¹ for 20%CeO₂/Al₂O₃, and ca. 461 cm⁻¹ for 40%CeO₂/Al₂O₃. This peak migration is attributed to the replacement of Al³⁺ in the CeO₂ lattice. The intensities of the peaks in the Raman spectra increased with increasing amount of CeO₂. These results agree with the XRD

Fig. 3. SEM images of the 3DOM catalyst samples. (a) Al₂O₃; (b) 2%CeO₂/Al₂O₃; (c) 10%CeO₂/Al₂O₃; (d) 20%CeO₂/Al₂O₃; (e) 40%CeO₂/Al₂O₃; (f) 3DOM CeO₂; (g) Au/Al₂O₃; (h) Au/2%CeO₂/Al₂O₃; (i) Au/10%CeO₂/Al₂O₃; (j) Au/20%CeO₂/Al₂O₃; (k) 3DOM Au/40%CeO₂/Al₂O₃.

patterns. In addition, compared with those for pure CeO₂, the Raman peaks for x-CeO₂/Al₂O₃ broadened because of Ce-Al interactions arising from strain modification caused by the incorporation of Al³⁺, which increased the vibration frequency of the metal-anion bond. The incorporation of Al³⁺ also increased the number of oxygen vacancies in the structure, indicating the presence of Ce³⁺ ions, which favors oxygen mobility. Fig. 2(b) shows the presence of weak bands at ~330 cm⁻¹ in the spectra of x-CeO₂/Al₂O₃ (x = 10%, 20%, and 40%). This peak is ascribed to γ -Al₂O₃. The enlarged Raman spectrum of γ -Al₂O₃ (Fig. 2(c)) has a clear peak at ~330 cm⁻¹.

3.3. SEM results

Fig. 2. Raman spectra of 3DOM samples. (a) CeO₂; (b) (1) Al₂O₃, (2) 2%CeO₂/Al₂O₃, (3) 10%CeO₂/Al₂O₃, (4) 20%CeO₂/Al₂O₃, (5) 40%CeO₂/Al₂O₃; (c) Al₂O₃.

Fig. 3 shows SEM images of 3DOM $x\text{-CeO}_2/\text{Al}_2\text{O}_3$ synthesized using an MDP method and $\text{Au}/x\text{-CeO}_2/\text{Al}_2\text{O}_3$ synthesized using a reduction-deposition method. The pores of the 3DOM catalysts had the inverse opal structure of the template, indicating that the spherical pores were occupied by PMMA beads before calcination. The images show that the 3DOM materials had closely packed uniform ordered macropores. The macropore size for the Al_2O_3 catalyst was about 260 nm, which is smaller than the original PMMA colloidal microsphere template (350 nm). This shrinkage is attributed to melting of the polymer templates and sintering of the produced metal oxides. The highly ordered 3DOM is connected to its 12 neighbors by small windows. This interconnected structure promotes mass transfer [40]. In addition, it can be seen that Au loading did not change the morphologies of the 3DOM samples. The 3DOM $\text{Au}/x\text{-CeO}_2/\text{Al}_2\text{O}_3$ catalysts also had perfect macroporous structures. This indicates that the 3DOM Al_2O_3 had good mechanical strength and the 3DOM structure was not damaged even by vigorous stirring.

3.4. TEM results

Fig. 4 shows TEM images of all the prepared catalysts. These images show that the prepared catalysts retained a well-defined macroporous structure. In addition, the TEM images of the 3DOM materials show different postures from different angles. Every macropore resembles a football or tracery. This depends on the arrangement of PMMA microspheres in the template. In the images, the macropore framework is black, and the pores are white. This macroporous structure provides suitable sites for gas-solid-solid reactions. The average pore size of the support is ca. 260 nm, which is big enough to allow soot particles to enter the inner pores easily. Macropores can therefore reduce mass-transfer resistance. They can also in-

Fig. 4. TEM images of the 3DOM catalysts. (a) Al_2O_3 ; (b) 2% $\text{CeO}_2/\text{Al}_2\text{O}_3$; (c) 10% $\text{CeO}_2/\text{Al}_2\text{O}_3$; (d) 20% $\text{CeO}_2/\text{Al}_2\text{O}_3$; (e) 40% $\text{CeO}_2/\text{Al}_2\text{O}_3$; (f) CeO_2 ; (g) $\text{Au}/\text{Al}_2\text{O}_3$; (h) $\text{Au}/2\%\text{CeO}_2/\text{Al}_2\text{O}_3$; (i) $\text{Au}/10\%\text{CeO}_2/\text{Al}_2\text{O}_3$; (j) $\text{Au}/20\%\text{CeO}_2/\text{Al}_2\text{O}_3$; (k) 3DOM $\text{Au}/40\%\text{CeO}_2/\text{Al}_2\text{O}_3$.

crease the number of contact points between solid reactants. The voids are interconnected by open windows of diameter 60 nm. This is in consistent with the SEM results.

3.5. HRTEM results

The particle sizes and morphological structures of the CeO_2 and Au nanoparticles on the support surfaces were further investigated using HRTEM. The HRTEM images of 3DOM $x\text{-CeO}_2/\text{Al}_2\text{O}_3$ and the supported Au catalyst are shown in Fig. 5. Fig. 5(a)–(d) shows that CeO_2 crystalline particles were uniformly dispersed on the surface of the Al_2O_3 support. The CeO_2 particles in 40% $\text{CeO}_2/\text{Al}_2\text{O}_3$ were larger than those in $x\text{-CeO}_2/\text{Al}_2\text{O}_3$ ($x = 2\%, 10\%, \text{ and } 20\%$); this is in accordance with the XRD results. Agglomeration occurred with increasing CeO_2 loading. Too high a CeO_2 loading is therefore not favorable for soot combustion. Spherical Au nanoparticles were highly dispersed across the entire support (Fig. 5(e)–(i)). The features of the particles in all the $x\text{-CeO}_2/\text{Al}_2\text{O}_3$ substrates were similar. A high CeO_2 loading makes it difficult to differentiate the Au particles on the $x\text{-CeO}_2/\text{Al}_2\text{O}_3$ catalyst. However, the apparent contrast in TEM images is related to the atomic number. The higher the atomic number, the greater the mass thickness, and this leads to a greater apparent contrast. It can therefore be inferred that the Au nanoparticles were darker than the CeO_2 crystal particles, based on the difference between their atomic numbers. The CeO_2 and Au nanoparticles on the Al_2O_3 surface were in close contact with each other. This promotes interactions between Au and CeO_2 and could improve adsorption and activation of oxygen.

3.6. H_2 -TPR results

Fig. 6 shows the H_2 -TPR profiles for the 3DOM $x\text{-CeO}_2/\text{Al}_2\text{O}_3$ catalysts. Fig. 6(a) shows that the Al_2O_3 catalyst gave no significant H_2 reduction peaks during the reduction process. The H_2 -TPR profile of bare CeO_2 indicates stepwise reduction of CeO_2 , similar to previously reported results [7,32]. Bare CeO_2 gave three reduction peaks, at ca. 404, 523, and 744 °C. These

Fig. 5. HRTEM images of the prepared 3DOM samples. (a) 2% $\text{CeO}_2/\text{Al}_2\text{O}_3$; (b) 10% $\text{CeO}_2/\text{Al}_2\text{O}_3$; (c) 20% $\text{CeO}_2/\text{Al}_2\text{O}_3$; (d) 40% $\text{CeO}_2/\text{Al}_2\text{O}_3$; (e) $\text{Au}/\text{Al}_2\text{O}_3$; (f) $\text{Au}/2\%\text{CeO}_2/\text{Al}_2\text{O}_3$; (g) $\text{Au}/10\%\text{CeO}_2/\text{Al}_2\text{O}_3$; (h) $\text{Au}/20\%\text{CeO}_2/\text{Al}_2\text{O}_3$; (i) $\text{Au}/40\%\text{CeO}_2/\text{Al}_2\text{O}_3$.

Fig. 6. H₂-TPR profiles of 3DOM *x*-CeO₂/Al₂O₃ catalysts (a) and 3DOM Au/*x*-CeO₂/Al₂O₃ catalysts (b). (1) 0%; (2) 2%; (3) 10%; (4) 20%; (5) 40%; (6) bulk CeO₂.

are attributed to the reduction of surface-absorbed oxygen, the outermost layer of Ce⁴⁺, and inner lattice oxygen, respectively [41]. For the *x*-CeO₂/Al₂O₃ catalysts, the sample with 2% CeO₂ (Fig. 6(a)) gave no CeO₂ reduction peak. This may be because the amount of CeO₂ was too low and the CeO₂ was highly dispersed on the 3DOM Al₂O₃ and beyond the detection limit. The *x*-CeO₂/Al₂O₃ samples with higher loadings (*x* ≥ 10%) also gave three reduction peaks, but they were shifted to significantly lower temperatures compared with those for bare CeO₂. The main reason is that reduction of the smaller CeO₂ crystallites in the *x*-CeO₂/Al₂O₃ catalyst is easier than reduction of bulk CeO₂ because of the interactions between Al₂O₃ and CeO₂. Note that the first TPR peak for 40%CeO₂/Al₂O₃ appeared at a higher temperature than those for 10%CeO₂/Al₂O₃ and 20%CeO₂/Al₂O₃. This is mainly because agglomeration was easy and the average size of the CeO₂ crystallites increased when the CeO₂ loading was high. The surface energy of the larger CeO₂ crystallites is small, which decreases the oxygen-transfer capability and redox activity of the catalyst. However, for the supported CeO₂ catalyst, the second and third peaks shifted to lower temperatures with increasing CeO₂ loading. The XRD results showed that the formation of an Al–Ce–O solid solution generated a large number of lattice defects, facilitating transfer of lattice oxygens and improving the redox activities of the catalysts.

Fig. 6(b) shows the H₂-TPR profiles for the Au/*x*-CeO₂/Al₂O₃ catalysts with different amounts of CeO₂ (0% to 40%). The presence of Au clearly affects TPR of the supports. There was no low-temperature reduction peak for the Au/Al₂O₃ catalyst, suggesting that the Au nanoparticles were stable and no H₂ was consumed. However, a peak appeared at about 565 °C for the Au/Al₂O₃ catalyst; it can be assigned to the reduction of isolated patches of AuO_x on Al₂O₃. The shape of the H₂-TPR profile was closely related to the CeO₂ loading and the interactions between Au and the support. The Au/2%CeO₂/Al₂O₃ catalyst gave a weak peak at ca. 315 °C. The peak intensity gradually increased with increasing CeO₂ loading. This suggests that Au supported on the *x*-CeO₂/Al₂O₃ surface weakened the Ce–O bonds, creating more oxygen vacancies and improving the re-

dox activity of the catalyst. The presence of Au could also enhance the oxygen-storage capacity of CeO₂ via mutual interactions. The catalysts containing small Au nanoparticles can easily adsorb and activate more oxygen, which improves the low-temperature reduction ability of the catalyst. The first peak shifted slightly to higher temperature for Au/40%CeO₂/Al₂O₃, indicating that excess CeO₂ did not increase the catalyst reducibility and that the large CeO₂ crystallites limited active oxygen transfer. Unlike that for 2%CeO₂/Al₂O₃, the TPR profile for the Au/2%CeO₂/Al₂O₃ catalyst clearly showed two weak peaks at 623 and 670 °C, arising from reduction of bulk CeO₂ and formation of Ce₂O₃. The appearance of these peaks suggests strong interactions between Au and CeO₂/Al₂O₃, which could increase the mobility of lattice oxygens. The higher-temperature TPR peak can be attributed to residual chlorine, from the Au precursor, which could weaken the hydrogen chemisorption capacity of CeO₂. According to the literature, during reduction with H₂, chloride can replace oxygen ions in the CeO₂ lattice and form CeOCl or Ce(OH)Cl species [42,43]. When the amount of CeO₂ reached 10%, the second and third peaks shifted to lower temperatures compared with those for Au/2%CeO₂/Al₂O₃, indicating that the interactions between Au and the support became stronger with increasing CeO₂ loading. The shapes of the H₂-TPR profiles for Au/20%CeO₂/Al₂O₃ and Au/40%CeO₂/Al₂O₃ showed clear changes. The two peaks combined at high temperatures, and the peak shifted to lower temperatures. Reduction of the bulk catalyst occurs close to the surface at high CeO₂ loadings. However, the Au nanoparticles can activate the lattice oxygens in the catalyst, and this promotes migration of inner lattice oxygens to the surface and increases the overall H₂ consumption. These observations suggest that the CeO₂ loading in Au/*x*-CeO₂/3DOM Al₂O₃ catalysts can significantly affect the redox activity of the catalyst. There are strong interactions at the interface between Au and CeO₂, which is the active site of oxygen adsorption and activation.

3.7. O₂-TPD results

O₂-TPD studies can help to evaluate the catalytic activities of

Fig. 7. O₂-TPD profiles of 3DOM *x*-CeO₂/Al₂O₃ catalysts (a) and 3DOM Au/*x*-CeO₂/Al₂O₃ catalysts (b). (1) 0%; (2) 2%; (3) 10%; (4) 20%; (5) 40%.

the prepared catalysts. O₂-TPD was used to study the surface and bulk oxygen species in the catalysts; the results are shown in Fig. 7. For all the samples, three desorption regions were observed at the temperature ranges 100–300, 300–550, and 550–900 °C. The oxygen species desorbed in the first region are weakly physisorbed and/or chemisorbed oxygen molecules on the surface, which can be readily removed at low temperatures. The oxygen species desorbed in the second region are over-stoichiometric oxygen in the prepared catalyst; this can be represented by the equation $4\text{Ce}^{4+} + 2\text{O}^{2-}(\gamma) \rightarrow 4\text{Ce}^{3+} + \text{O}_2$, where the excess oxygen charge is compensated for by cation vacancies (γ). The oxygen species desorbed in the highest-temperature region may be associated with the migration of lattice oxygens in the catalysts. The O₂-TPD profiles of the 3DOM Au/*x*-CeO₂/Al₂O₃ catalysts differed significantly from those of the *x*-CeO₂/Al₂O₃ catalysts. As Fig. 7 shows, the intensity of the α desorption peak was weaker. This may be because the presence of Au enhances the interactions between the catalyst and molecular oxygen, resulting in chemical adsorption rather than physical adsorption. However, the intensities of the β and γ desorption peaks increased significantly. The reason may be that interactions between Au and CeO₂ weaken the Ce–O bond, creating a large number of oxygen vacancies, which could increase the amount of reactive oxygen species (O[•]) on the surface. O[•] species are important in catalytic soot oxidation. The larger the amount of chemisorbed oxygen, the higher the activity of the catalyst is. The γ desorption peak became stronger, indicating that Au promoted lattice oxygen migration, creating structural defects and oxygen vacancies, thus facilitating adsorption and activation of molecular oxygen. Fig. 7(b) shows that the intensities of the β and γ desorption peaks for Au/40%CeO₂/Al₂O₃ were weaker than those for Au/20%CeO₂/Al₂O₃. This may be because of agglomeration at high CeO₂ loadings, which hinders adsorption and activation of oxygen species. These results are consistent with the H₂-TPR results.

3.8. BET results

The specific surface areas of the *x*-CeO₂/Al₂O₃ and support-

ed Au catalysts are reported in Table 2. The data show that the introduction of CeO₂ on Al₂O₃ significantly increased the BET specific surface area, from 76 m²/g for the Al₂O₃ support to 142 m²/g for the 20%CeO₂/Al₂O₃ catalyst. This increase may be the result of abundant intergrain pores. The CeO₂ loadings ranged from 2% to 40%. It can be speculated that the CeO₂ particles or crystallites were packed together on the macropore walls. The pH during synthesis could also affect the specific surface area. The formation of Ce(OH)₄ species (from the reaction between ammonia and Ce(NO₃)₃) etches the Al₂O₃ surface, which contributes to the high BET surface area [44]. For the 40%CeO₂/Al₂O₃ catalyst, the surface area decreased to 126 m²/g. This may be because the CeO₂ crystallites are larger at high loadings and sintering occurs. This is in accordance with the HRTEM results. The data in Table 2 show that Au nanoparticle loading did not change the BET surface areas.

The N₂ adsorption isotherms for the *x*-CeO₂/Al₂O₃ and supported Au catalysts are shown in Fig. 8. The hysteresis loops correspond to the H3-type loops of mesopores, according to the International Union of Pure and Applied Chemistry classification. The mesopore size is 7–10 nm. H3-type hysteresis occurred in the p/p_0 range 0.5–1.0 and was much greater than that for pure Al₂O₃, indicating that the 3DOM *x*-CeO₂/Al₂O₃ catalyst had more mesopores within the macropore wall than did 3DOM Al₂O₃. This is in accordance with the BET surface areas. In addition, the type II isotherms observed in the low-pressure

Table 2

Physicochemical properties of as prepared 3DOM catalysts.

Catalyst	Surface area ^a (m ² /g)	Total pore volume ^b (cm ³ /g)	Pore size ^c (nm)
Al ₂ O ₃	76	0.20	9.3
2%CeO ₂ /Al ₂ O ₃	102	0.21	8.0
10%CeO ₂ /Al ₂ O ₃	128	0.26	7.7
20%CeO ₂ /Al ₂ O ₃	142	0.28	7.8
40%CeO ₂ /Al ₂ O ₃	126	0.25	7.6
Au/20%CeO ₂ /Al ₂ O ₃	149	0.29	7.2
Au/40%CeO ₂ /Al ₂ O ₃	131	0.23	7.6

^a Calculated by BET method. ^b Calculated by BJH adsorption cumulative volume of pores between 1.7 and 300 nm diameter. ^c Calculated by BJH adsorption average pore diameter.

Fig. 8. Nitrogen adsorption-desorption isotherms of as-prepared 3DOM catalysts. (1) Pure Al_2O_3 ; (2) 2% $\text{CeO}_2/\text{Al}_2\text{O}_3$; (3) 10% $\text{CeO}_2/\text{Al}_2\text{O}_3$; (4) 20% $\text{CeO}_2/\text{Al}_2\text{O}_3$; (5) 40% $\text{CeO}_2/\text{Al}_2\text{O}_3$; (6) $\text{Au}/20\%\text{CeO}_2/\text{Al}_2\text{O}_3$; (7) $\text{Au}/40\%\text{CeO}_2/\text{Al}_2\text{O}_3$.

portion were nearly linear in the middle because of unrestricted monolayer-multilayer adsorption. This indicates that the sample was a non-porous or macroporous adsorbent. Adsorption increased significantly with increasing relative pressure, which is characteristic of a wall composed of tenuously assembled solid solution clusters, i.e., the presence of many mesopores within the macropore wall [32,45]. Fig. 8(6) and (7) show that the textural properties of the support did not change significantly after Au deposition on the walls of the 3DOM $x\text{-CeO}_2/\text{Al}_2\text{O}_3$ catalysts. This is supported by the SEM and TEM results.

3.9. UV-vis DRS results

The UV-vis DR spectra of 3DOM $x\text{-CeO}_2/\text{Al}_2\text{O}_3$ were recorded using the Al_2O_3 support as a reference; the spectra are shown in Fig. 9(a). The spectra show an intense adsorption band with a maximum at ca. 300 nm, corresponding to $\text{Ce}^{3+} \leftarrow \text{O}^{2-}$ charge transfer and overlapping of the $\text{Ce}^{4+} \leftarrow \text{O}^{2-}$ charge transfer and interband transitions; this is in accordance with literature reports [46]. The intensity increased with in-

creasing CeO_2 content and the adsorption band red shifted, indicating that the CeO_2 crystallites became larger [46].

The presence of plasmon surface resonance is a good evidence of Au nanoparticle deposition on the $x\text{-CeO}_2/\text{Al}_2\text{O}_3$ materials. The UV-vis DR spectra of the 3DOM $\text{Au}/x\text{-CeO}_2/\text{Al}_2\text{O}_3$ catalysts, using 3DOM $x\text{-CeO}_2/\text{Al}_2\text{O}_3$ as a reference sample, were also recorded. Fig. 9(b) shows that a surface plasmon resonance maximum appeared at around 550 nm. Changes in the band intensity or shifts to higher energies were not observed. We can therefore assume that the Au nanoparticles on Al_2O_3 and $x\text{-CeO}_2/\text{Al}_2\text{O}_3$ were all similar in size. This is in accordance with the HRTEM results. The frequency and strength of the resonance are affected by various factors such as the particle size and shape and the dielectric properties of the surrounding medium [47]. In this study, a shoulder peak at 430 nm appeared on addition of CeO_2 . This indicates that 3DOM $x\text{-CeO}_2/\text{Al}_2\text{O}_3$ had strong chemical interactions with the Au nanoparticles on the catalyst surface, leading to changes in the electronic structure of the catalyst. These strong interactions are closely correlated with the CeO_2 loading. The intensity of the shoulder peak increased with increasing amount of CeO_2 . The strong interactions between Au and CeO_2 may also increase the redox potential of the catalyst and increase the catalytic activity. Similar results were obtained using UV-vis DRS in our previous work [28,47]. When the amount of CeO_2 increased to 40%, the shoulder peak did not change, suggesting that excess CeO_2 did not enhance the interactions. This is in line with H_2 -TPR and O_2 -TPD results.

3.10. TPO reaction results

Catalytic soot combustion is a typical heterogeneous reaction with solid particles as a reactant. Soot oxidations in the absence and presence of Au were investigated based on TPO reactions, using a NO/O_2 mixture as the oxidizing agent; the results are listed in Table 3. For comparison, the TPO results for soot alone (i.e., without a catalyst) are also presented; the T_{10} , T_{50} , T_{90} , and S_{CO_2} values were 449, 558, and 605 $^{\circ}\text{C}$, and 39.4%, respectively. As expected, all the catalysts lowered the soot combustion temperature compared with that for non-catalytic

Fig. 9. UV-Vis DRS spectra of 3DOM $x\text{-CeO}_2/\text{Al}_2\text{O}_3$ catalysts (a) [(1) 2%, (2) 10%, (3) 20%, (4) 40%) and 3DOM $\text{Au}/x\text{-CeO}_2/\text{Al}_2\text{O}_3$ catalysts (b) [(1) 0%, (2) 10%, (3) 20%, (4) 40%).

Table 3

Catalytic activities of 3DOM catalysts for soot combustion.

Catalyst	$T_{10}/^{\circ}\text{C}$	$T_{50}/^{\circ}\text{C}$	$T_{90}/^{\circ}\text{C}$	$S_{\text{CO}_2^{\text{m}}}/\%$
Soot	449	558	605	39.4
Al_2O_3	362	530	586	57.5
2% $\text{CeO}_2/\text{Al}_2\text{O}_3$	283	408	478	73.5
10% $\text{CeO}_2/\text{Al}_2\text{O}_3$	292	393	440	80.9
20% $\text{CeO}_2/\text{Al}_2\text{O}_3$	291	384	430	73.7
40% $\text{CeO}_2/\text{Al}_2\text{O}_3$	293	379	425	79.6
CeO_2	318	379	418	92.8
$\text{Au}/\text{Al}_2\text{O}_3$	298	453	513	96.9
$\text{Au}/2\%\text{CeO}_2/\text{Al}_2\text{O}_3$	278	412	469	96.7
$\text{Au}/10\%\text{CeO}_2/\text{Al}_2\text{O}_3$	281	384	438	97.3
$\text{Au}/20\%\text{CeO}_2/\text{Al}_2\text{O}_3$ -first	267	372	426	96.7
$\text{Au}/40\%\text{CeO}_2/\text{Al}_2\text{O}_3$	273	364	412	97.6
$\text{Au}/20\%\text{CeO}_2/\text{Al}_2\text{O}_3$ -second	293	386	440	94.3
$\text{Au}/20\%\text{CeO}_2/\text{Al}_2\text{O}_3$ -third	294	387	444	91.2

combustion. For the catalysts without Au, the catalytic activity increased with increasing CeO_2 loading. The relationship between the increase in the amount of CeO_2 and the improvement in the activity was examined. When the theoretical amount of CeO_2 was doubled, i.e., from 20% $\text{CeO}_2/\text{Al}_2\text{O}_3$ to 40% $\text{CeO}_2/\text{Al}_2\text{O}_3$, the T_{50} value for 40% $\text{CeO}_2/\text{Al}_2\text{O}_3$ only decreased by 5 $^{\circ}\text{C}$ compared with that for 20% $\text{CeO}_2/\text{Al}_2\text{O}_3$. This suggests that excess CeO_2 did not play a major role. This is also in line with the H_2 -TPR and O_2 -TPD results. In addition, the activities of all the prepared multilayer $x\text{-CeO}_2/\text{Al}_2\text{O}_3$ catalysts were better than that of bulk CeO_2 . This further illustrates that small crystallites and an appropriate amount of CeO_2 provide advantages, and may promote interactions between Al_2O_3 and CeO_2 . The multilayer support can also be designed to reduce the amount of rare-earth metal used, which would lower the price, and is therefore important in practical applications.

Oxygen adsorption and activation on Au are easy [48]. Au nanoparticle loading on the catalysts increases the production of highly oxidizing active oxygen species. Such species are also produced by oxygen exchange between Au and the CeO_2 -based catalyst. The data in Table 3 show that the activities of the catalysts after Au nanoparticle loading increased significantly; in particular, the T_{10} values decreased. The T_{10} values of the 3DOM $\text{Au}/\text{Al}_2\text{O}_3$ and $\text{Au}/20\%\text{CeO}_2/\text{Al}_2\text{O}_3$ catalysts decreased significantly, by 64 and 24 $^{\circ}\text{C}$, respectively, compared with the values for the corresponding catalysts without Au. The T_{50} and T_{90} values for 3DOM $\text{Au}/x\text{-CeO}_2/\text{Al}_2\text{O}_3$ also decreased with increasing amount of CeO_2 . This is mainly because interactions between Au nanoparticles and CeO_2 increase the amount of surface active oxygen. The activity did not increase significantly from $\text{Au}/20\%\text{CeO}_2/\text{Al}_2\text{O}_3$ to $\text{Au}/40\%\text{CeO}_2/\text{Al}_2\text{O}_3$. This may be because the CeO_2 crystallite size increased at high CeO_2 loadings. Large CeO_2 crystallites are not beneficial for the adsorption and activation of reactive oxygen species; this was confirmed by the H_2 -TPR, O_2 -TPD, and UV-vis DRS results.

The stabilities of the 3DOM $\text{Au}/x\text{-CeO}_2/\text{Al}_2\text{O}_3$ catalysts were investigated by performing three cycles of soot oxidation. The results are shown in Table 3. The catalytic activity decreased after one cycle, especially the T_{10} value. However, the T_{50} and

T_{90} values did not change significantly. It can be concluded that the introduction of CeO_2 improved the catalytic activity in soot oxidation and increased the stability of the Au catalyst.

The $S_{\text{CO}_2^{\text{m}}}$ values for the 3DOM Al_2O_3 -supported Au and $\text{Au}/x\text{-CeO}_2/\text{Al}_2\text{O}_3$ catalysts in soot combustion (>90%) were also much higher than that for the Al_2O_3 catalyst (<60%). The high $S_{\text{CO}_2^{\text{m}}}$ values are ascribed to the supported Au nanoparticles, which show high catalytic activities in CO oxidation [48]. This ensures that the CO gas produced from vehicle exhausts is rapidly removed under practical conditions.

3.11. Discussion

3.11.1. Effects of CeO_2 nanolayers on Al_2O_3

The textural properties of the support are crucial in determining the performance of a catalyst. The N_2 physisorption results for the 3DOM $x\text{-CeO}_2/\text{Al}_2\text{O}_3$ catalysts show that the BET surface areas of the catalysts increased with increasing CeO_2 loading on the 3DOM Al_2O_3 support. A high surface area is important in catalytic oxidation. The increased surface area increases the contact area between the soot and the catalyst, and this improves the catalytic activity. However, the surface area decreased when the loading of CeO_2 reached 40%. The CeO_2 crystallite sizes listed in Table 1 and the HRTEM images in Fig. 5 show that the CeO_2 crystallite size in the 40% $\text{CeO}_2/\text{Al}_2\text{O}_3$ catalyst was larger and the intergranular pores were smaller compared with those in the other catalysts. A high CeO_2 loading was therefore unfavorable for the dispersion of crystal grains. For all the prepared $x\text{-CeO}_2/\text{Al}_2\text{O}_3$ samples, the XRD and Raman results showed the formation of an Al-Ce-O solid solution formed by diffusion of Al^{3+} ions into the CeO_2 lattice. The introduction of Al^{3+} into the CeO_2 lattice can increase the amount of oxygen vacancies. At the interface between CeO_2 and Al_2O_3 , some Al^{3+} ions replace Ce^{3+} ions because they have the same valence states. This leads to the creation of additional oxygen vacancies in the $x\text{-CeO}_2/\text{Al}_2\text{O}_3$ system; this is in agreement with the H_2 -TPR results. Fig. 6 shows that the reduction peaks of $x\text{-CeO}_2/\text{Al}_2\text{O}_3$ shifted to lower temperatures compared with that of bulk CeO_2 , suggesting a significant increase in the mobility of lattice oxygen species, which could improve the catalytic performances of $x\text{-CeO}_2/\text{Al}_2\text{O}_3$.

TEM is a useful method for examining the surface properties of materials. HRTEM images of the 3DOM $x\text{-CeO}_2/\text{Al}_2\text{O}_3$ catalysts showed that the amount of CeO_2 crystallites on the support surface increased with increasing CeO_2 loading. These CeO_2 crystallites formed a CeO_2 layer that covered the support surface. CeO_2 nanolayers are tenuous at low CeO_2 loadings but dense at high CeO_2 loadings. The catalytic activity results show that the introduction of CeO_2 crystal grains on the surface of the 3DOM support significantly affected soot oxidation. This layered structure may improve electron mobility between Al_2O_3 and CeO_2 . However, if the amount of CeO_2 was excessive, the CeO_2 crystallites on the Al_2O_3 surface were easily sintered, which suppressed the catalytic activity. The above results show that CeO_2 nanolayers promote soot oxidation.

3.11.2. Effects of Au on CeO_2 nanolayers

The presence of a noble metal improves the redox properties of CeO_2 , and CeO_2 promotes the reduction of noble metals [49–51]. In the $\text{Au}/x\text{-CeO}_2/\text{Al}_2\text{O}_3$ catalysts, interactions between Au and CeO_2 increase the activity and stability of the catalyst. The H_2 -TPR profiles show that addition of 2% Au increased the reducibility. CeO_2 is an excellent promoter when combined with Au, Al_2O_3 , and other metal oxides, and has been used in many reactions, e.g., oxidation of benzene [52], total oxidation of propene [53], and catalytic oxidation of CO [46]. The high-temperature performance of Au is not as good as those of the Pt group metals. However, supported Au catalysts show high activities in low-temperature reactions. Improvement of catalytic performance in soot combustion at low temperatures is still a challenge. In this work, Al_2O_3 was chosen as the first layer of the support, and small CeO_2 crystalline grains were the second layer. Au nanoparticles were supported on the surfaces of $x\text{-CeO}_2/\text{Al}_2\text{O}_3$ catalysts. HRTEM images show that the CeO_2 and Au nanoparticles on the Al_2O_3 surface were in close contact each other, and this promotes interactions between Au and CeO_2 . In terms of CeO_2 dispersion, it has been reported that the CeO_2 nanosize is closely related to the excellent performance of Au catalysts. Fu et al. [54] found that the reactivity of surface oxygen in Au- CeO_2 catalysts was determined by the nanosize of CeO_2 . These results are associated with the catalytic activity data. The TPO results show that Au nanoparticles supported on $x\text{-CeO}_2/\text{Al}_2\text{O}_3$ catalysts had higher activities than those on Al_2O_3 . The T_{10} value for $\text{Au}/20\%\text{CeO}_2/\text{Al}_2\text{O}_3$ was lower than that of $\text{Au}/40\%\text{CeO}_2/\text{Al}_2\text{O}_3$. This shows that CeO_2 crystallite agglomeration is not beneficial to the interaction between Au and CeO_2 . In addition, we propose that the active sites in the soot combustion reaction can be represented as a complex, i.e., $\text{Au}^\delta\text{Ce}^{3+}$ (δ is an oxygen vacancy); enhanced electron transfer from the support to the small Au particles through oxygen vacancies occurs and is the key reason for the higher activity. The presence of Au nanoparticles greatly modifies CeO_2 . This leads to the formation of abundant oxygen vacancies and enhanced electron transfer between Au and Ce^{3+} [52]. This is consistent with our suggestion that the $x\text{-CeO}_2/\text{Al}_2\text{O}_3$ support plays an active role in supported Au catalysts and explains the superior performances of Au nanoparticles on $x\text{-CeO}_2/\text{Al}_2\text{O}_3$ catalysts.

3.11.3. Mechanism of 3DOM $\text{Au}/x\text{-CeO}_2/\text{Al}_2\text{O}_3$ catalysis of soot combustion

Fig. 10 shows a possible reaction pathway for soot combustion. Catalytic soot combustion involves a solid catalyst, a solid reactant (soot), and gaseous reactants (O_2 and NO). It should be noted that the presence of Ce^{3+} and $\text{Au}^{\delta+}$ was confirmed by our previous work [55]. Gas-phase O_2 cannot directly react with soot during catalytic soot oxidation. Gas-phase O_2 fills the oxygen vacancies created on the oxide. Then active oxygen species on the $\text{Au}/x\text{-CeO}_2/\text{Al}_2\text{O}_3$ surface are transferred to soot, or oxidize NO to NO_2 , and promote the next step in the reaction (generation of CO_2). The oxidizing ability of NO_2 is much stronger than that of O_2 [31,56–58]. The presence of NO_2 promotes soot particle oxidation to CO or CO_2 .

Because it is a heterogeneous reaction with a solid reactant,

Fig. 10. Mechanism illustration of 3DOM $\text{Au}/\text{CeO}_2/\text{Al}_2\text{O}_3$ catalysts for soot combustion.

the contact efficiency between the catalyst and soot strongly influences the catalytic activity. The number of contact points is closely related to the catalyst concentration, therefore the activity increases with increasing contact area. Many studies have shown that excellent catalytic activity is achieved in soot combustion when there is tight contact between the soot particles and the catalyst. However, under practical conditions, they are in loose contact [24]. It is therefore important to design and prepare new catalysts that have high activities in soot combustion under loose contact conditions.

Previously, we reported that a 3DOM structure was perfect for diesel soot combustion catalysts [32]. The pore size of 3DOM materials is greater than 50 nm [28,31–34,59], which allows soot particles to enter the inner pores of the 3DOM catalyst easily. As a result, the number of contact points between the soot and the catalyst is high. However, the contact efficiency is only an exterior factor in the control of soot combustion. The intrinsic activity of the catalyst is the other major influencing factor. Soot combustion is a deep oxidation reaction. The catalytic reaction is a redox process. The redox properties of the catalyst crucially affect its intrinsic activity. The layer structures of $x\text{-CeO}_2/\text{Al}_2\text{O}_3$ catalysts and the Au nanoparticle active components have strong redox abilities. The Ce-based support acts as an oxygen reservoir in the oxidation reaction, which facilitates metal (Au)-support (Ce) interactions. These interaction can lead to transfer of lattice oxygens and the adsorption of oxygen on oxygen vacancies at low temperatures. The 3DOM $\text{Au}/x\text{-CeO}_2/\text{Al}_2\text{O}_3$ catalysts therefore have excellent intrinsic activities. The TPO results show that the selectivities for CO_2 of supported Au catalysts are significantly higher than those of $x\text{-CeO}_2/\text{Al}_2\text{O}_3$ catalysts, enabling avoidance of secondary pollution and reduction of CO emissions. Thus, 3DOM $\text{Au}/x\text{-CeO}_2/\text{Al}_2\text{O}_3$ catalysts are appropriate for soot combustion under loose contact conditions.

4. Conclusions

The effects of the CeO_2 loading (2–40 wt% CeO_2) on the catalytic properties in soot combustion with an NO -assisted reaction gas were examined. The $x\text{-CeO}_2/\text{Al}_2\text{O}_3$ catalysts, which were obtained using an MDP method, had high specific surface areas and chemical stabilities. The characterization results suggest that CeO_2 crystallites formed nanolayers on the surface

Graphical Abstract

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Three-dimensionally ordered macroporous CeO₂/Al₂O₃-supported Au nanoparticle catalysts: Effects of CeO₂ nanolayers on catalytic activity in soot oxidation

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A mixed oxide catalyst containing Au, CeO₂, and Al₂O₃ combines the benefits of high activity, good redox properties, and high surface area, and provides a highly effective catalyst for soot oxidation.

3DOM Al₂O₃. x-CeO₂/Al₂O₃ was a good support for dispersed Au nanoparticles. The presence of CeO₂, even in low amounts, enhanced the catalytic activity compared with that of Au on bare Al₂O₃. The Au nanoparticles were well dispersed on the surface of the x-CeO₂/Al₂O₃ substrate. No crystalline Au was detected using XRD. The interactions between the dispersed Au nanoparticles and CeO₂ increased the amounts of oxygen vacancies and active oxygen species, which is crucial for improving the catalytic activity.

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CeO₂纳米层对多层载体x-CeO₂/3DOM Al₂O₃负载纳米Au催化剂催化柴油炭烟燃烧活性的影响

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摘要: 与汽油车相比, 柴油车具有CO₂排放低、寿命长和经济性好等优点, 所以近年来受到广泛关注并被大量使用。但是, 柴油车在使用过程中会产生大量炭烟颗粒物(PM), 对大气环境和人类健康造成很大威胁。因此, 开展这方面的基础研究具有重要的科学意义及环境保护意义。催化柴油炭烟燃烧反应是一个气-固-固多相深度氧化反应, 由于PM的粒径远大于传统催化剂, 导致PM不能进入催化剂孔道内部, 造成催化剂活性比表面积利用率较低。设计并制备大孔径的三维有序大孔结构(3DOM)的催化剂, 能够减小反应扩散阻力, 增加催化剂与炭烟颗粒物的有效接触, 加快反应进行。另外, 可以通过在3DOM氧化物表面负载其它活性组分, 提高催化剂的氧化还原性能, 进而提高其活性。

CeO₂有很好的储放氧性能, 在柴油车尾气净化催化剂中较为常见, 但是单一的CeO₂热稳定性较差, 高温下容易烧结, 使得比表面积减小, 并且失去储氧能力, 造成催化剂失活。文献中较常见的解决办法是在CeO₂中掺杂其它阳离子, 如Zr⁴⁺, Pr³⁺, Al³⁺, La³⁺及Y³⁺等离子, 以提高CeO₂的抗高温烧结能力。此外, 研究报道的催化剂对催化柴油炭烟颗粒物燃烧的峰值温度已经远低于炭烟颗粒物的自燃温度, 但是对颗粒物的起燃温度仍普遍较高。我们前期研究结果表明, 负载纳米Au颗粒催化剂能够显著降低炭烟燃烧的起燃温度。

本文采用胶体晶体模板法制备了3DOM Al₂O₃载体, 利用微孔膜-氨沉淀法负载不同量的活性组分CeO₂, 制备出一种负载型x-CeO₂/3DOM Al₂O₃催化剂, 它既可减少稀土元素用量, 降低成本, 又因为Al₂O₃的机械强度较高, 还能保证催化剂的机械强度足够好。为了进一步降低催化剂催化炭烟燃烧的起燃温度, 利用还原沉积法在多层载体x-CeO₂/3DOM Al₂O₃上负载纳米Au催化剂, 制备出不同厚度的CeO₂纳米层负载Au催化剂(Au/x-CeO₂/3DOM Al₂O₃)。利用X射线衍射、扫描电镜、透射电镜、H₂程序升温还原和O₂程序升温脱附等方法研究了催化剂的结构及物化性质与催化剂活性之间的关系, 提出了消除PM反应的可能机理。

结果表明, Al³⁺离子能够部分进入到CeO₂中, 形成Al-Ce固溶体。由于Al离子半径小于Ce离子, Al³⁺掺杂后能引起CeO₂

晶格发生畸变,产生大量缺陷,形成大量氧空位,促进晶格氧的移动,从而使催化剂具有更大的储放氧能力.在Au/x-CeO₂/3DOM Al₂O₃催化剂中,CeO₂担载量过高时,氧化铈纳米层较厚,活性组分容易烧结,不利于催化剂活性提高;而CeO₂担载量过低,则CeO₂纳米层较稀薄,催化剂的氧化还原性能受限,催化剂活性也不高.因此,CeO₂的担载量应适当.此外,Au和CeO₂之间的强相互作用能够增加Au纳米颗粒表面活性氧物种的数量,从而促进柴油炭烟燃烧反应.活性测试结果表明,担载纳米Au颗粒后,催化剂催化柴油炭烟燃烧的起燃温度均明显降低,在所制备的系列催化剂中Au/20%CeO₂/3DOM Al₂O₃催化剂展示了最高的催化活性, T_{10} , T_{50} 和 T_{90} 分别为267, 372和426 °C.

关键词: 三维有序大孔材料; 纳米金催化剂; 多层载体; 氧化铈纳米层; 炭烟燃烧

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