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Probing different effects of surface MO_y and M^{n+} species ($M = Cu$, Ni, Co, Fe) for $xMO_y/Ce_{0.9}M_{0.1-x}O_{2-\delta}$ catalysts in CO oxidation

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ABSTRACT

A series of $xMO_y/Ce_{0.9}M_{0.1-x}O_{2-\delta}$ ($M = Cu$, Ni, Co, Fe) catalysts (Ce-M) were prepared by a sol–gel method and corresponding $Ce_{0.9}M_{0.1-x}O_{2-\delta}$ catalysts (HCe-M) were obtained with an acid treatment. It was found that the Ce-M catalysts contained surface MO_y species and $Ce_{0.9}M_{0.1-x}O_{2-\delta}$ solid solution, as confirmed by the results of X-ray diffraction and Raman spectra, respectively. While the HCe-M catalysts only contained $Ce_{0.9}M_{0.1-x}O_{2-\delta}$ solid solution. CO oxidation over these catalysts revealed that the activities followed an order of Ce-Cu > Ce-Ni > Ce-Co > Ce-Fe, but were remarkably higher than the corresponding HCe-M samples. The activities of the HCe-M catalysts were closely related to their reducibility originated from the oxygen vacancies in these samples. The most active HCe-Cu catalyst had the highest content of oxygen vacancies and thus was the most reducible. For the Ce-M catalysts, the enhanced catalytic performance was due to a synergy between the surface MO_y species and the Ce-M-O solid solution, as the former provided sites for CO chemisorption and the latter promoted the activation of oxygen.

1. Introduction

Ceria (CeO_2) is one of the most reactive rare-earth oxides and attracted much attention due to its unique application in catalysis [1], solid oxide fuel cells [2,3], luminescence [4], UV-adsorbents [5] and semiconducting metal oxide gas sensor [6,7]. The successful applications of CeO_2 as catalytic materials are related to the facile redox cycling between trivalent and tetravalent Ce ions and the high mobility of bulk oxygen species which allows ceria to behave as an oxygen buffer [8]. It is commonly accepted that the redox property of ceria is controlled by the type, size, and distribution of oxygen vacancies as the most relevant surface defects [9]. The catalytic properties of ceria are considered to originate from the Ce^{4+}/Ce^{3+} redox cycle and affected by various structural factors, such as composition modification, large surface area, and preferential exposure of reactive facets and surface defects of oxygen vacancies [10–14]. In addition, doping of ceria with different cations, such as Zr [15], Zn [16], Pr, Sn [17–19], Y, La [20], Sc, Nd, Sm, Gd, Dy, Lu [20], Pd [21] could improve the redox properties or increase the amount of oxygen vacancies and thus enhancing the catalytic activities of ceria. Compared to pure CeO_2, the reducibility increases with the decrease in the ionic radius of the dopant associated with the structural distortion [22]. Also, the electronic and catalytic properties of CeO_2 can be modified by metal ion substitution in CeO_2, provided its fluorite structure is retained with higher thermal stability [23].

CO oxidation is of great practical and academic importance [24–26]. Catalytic oxidation is one of the most effective methods to remove the CO by converting CO to CO_2 [27]. Although supported noble metals (Au [28], Pt [29,30], Pd [31,32], and Ir [33]) have regarded as the most effective oxidation catalysts to eliminate CO, the high price and low availability limit their applications. Therefore, much attention has been paid to catalysts based on transition metal mixed oxides and thus become the subject of intense focus [34–36]. For example, doped-ceria with undersized lower valence ions such as Fe^{3+} have shown enhanced oxidation activity and catalytic properties through the formation of surface structural defects and a ceria-like solid solution [37,38]. Luo et al. [39] synthesized several nanosized catalysts Co_3O_4-CeO_2 with varying compositions and found that the catalysts, especially the ones promoted with Pd, showed markedly enhanced CO oxidation activity even at room temperature. Jung et al. [40] prepared a series of CuO-CeO_2 catalysts by a co-precipitation method and found that the best activity was obtained when the catalyst was calcined at 700 °C because a

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most stable Cu-Ce-O solid solution was formed on which CO could chemisorb reversibly. Luo et al. [41] studied Pd-doped mixed oxides MO_x-CeO_2 (M = Mn, Fe, Co, Ni, Cu) for CO oxidation. The results showed that a synergism effect exists between even trace amounts of exposed Pd and 3d-transition metal oxides for CO oxidation and the synergistic essential for CO oxidation should be the interaction-assisted generation of active oxygen species between Pd and MO_x.

We have previously studied the synergetic effects of PdO species on CO oxidation over PdO-CeO_2 catalysts [42]. The results showed that the activity was closely related to the catalyst structure/composition. While for the transition metals (Cu, Ni, Co, Fe) doped CeO_2 catalysts, the effect of catalyst compositions including surface MO_y (M = Cu, Ni, Co, Fe) species and M^{n+} cations in $Ce_{1-x}M_xO_y$ solid solutions on CO oxidation is worth further investigation.

In this work, a series of $xMO_y/Ce_{0.9}M_{0.1-x}O_{2-\delta}$ catalysts were prepared using the sol–gel method, and a comprehensive study of their catalytic performances for low-temperature oxidation of CO was conducted. After the acid treatment, surface MO_y species on the catalysts could be removed, and thus, the roles of surface MO_y species and M^{n+} cations in solid solution could be clearly distinguished. Various characterizations were performed to correlate the catalytic behaviors with the natures of the catalysts. Based on these examinations, the effects of surface MO_y species and M^{n+} cations in $Ce_{0.9}M_{0.1-x}O_{2-\delta}$ solid solution were discussed.

2. Experimental

2.1. Catalyst preparation

In the experiment, all the chemicals are of analytic grade and purchased from Sinopharm Chemical Reagent Co., Ltd., which are used without further purification.

$xMO_y/Ce_{0.9}M_{0.1-x}O_{2-\delta}$ (M = Cu, Ni, Co, Fe) catalysts were prepared by a citrate sol–gel method. $Ce(NO_3)_3{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$ were used as the precursors, and the molar ratio of Ce and M is 9:1. Taking $xCuO/Ce_{0.9}Cu_{0.1-x}O_{2-\delta}$ catalyst as an example, $Ce(NO_3)_3{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, and citric acid with twice moles of the metal ions were dissolved in deionized (DI) water. The mixture was heated at 90 °C under stirring until it became a viscous gel and then dried overnight at 120 °C. The resulting solid was calcined at 800 °C for 4 h with a heating rate of 10 °C min^{-1} to obtain the final material $xCuO/Ce_{0.9}Cu_{0.1-x}O_{2-\delta}$. Catalysts with other dopants were prepared in a similar manner. The catalysts were denoted as Ce-Cu, Ce-Ni, Ce-Co and Ce-Fe.

The obtained Ce-Ni, Ce-Cu catalysts were subjected to nitric acid treatment for comparison. Taking Ce-Cu catalyst as an example, the catalyst was immersed and stirred in concentrated nitric acid (HNO_3, 30 ml, 15.2 mol/L) at 100 °C for 4 h then filtered. The above process was repeated for three times. Finally, the obtained solid was washed with plenty of deionized water to remove the residual nitric acid and dried at 90 °C. The Ce-Co, Ce-Fe catalysts were treated by hydrochloric acid (HCl, 30 ml, 12.4 mol/L) in a similar manner as the Ce-Ni, Ce-Cu catalysts. The treated Ce-Co, Ce-Fe catalysts were washed thoroughly with deionized water until these samples were free of Cl^-, as evidenced with an aqueous solution of $AgNO_3$ (0.1 mol/L). The catalysts were denoted as HCe-Cu, HCe-Ni, HCe-Co and HCe-Fe.

Supported CuO/HCe-M (M = Cu, Ni, Co, Fe) and CuO/CeO_2 catalysts with a CuO loading of 5 wt.% were prepared using a conventional impregnating method. In a typical process, 0.24 g $Cu(NO_3)_2{\cdot}3H_2O$ was dissolved in deionized water (1 ml), and then 1.5 g of the support was immersed in the solution for 12 h. The mixture was heated at 90 °C and then dried overnight at 120 °C. The resulting solid was calcined at 300 °C for 4 h in air to yield the final catalysts. The catalysts were denoted as CuO/HCe-Cu, CuO/HCe-Ni, CuO/HCe-Co, CuO/HCe-Fe and CuO/CeO_2. Pure CeO_2 powder was obtained by direct thermal decomposition of $Ce(NO_3)_3{\cdot}6H_2O$ at 800 °C for 4 h.

2.2. Characterizations

X-ray diffraction (XRD) patterns were collected on a PANalytical X'Pert PRO MPD powder diffractometer using Cu Kα radiation ($\lambda = 0.15418$ nm). The working voltage was 40 kV and the working current was 40 mA. The patterns were collected in a 2θ range from 10 to 90°. The mean crystallite size were determined from line-broadening measurements on the (1 1 1) peak of CeO_2, using the Scherrer equation: $D = K\lambda/\beta\cos\theta$, where λ is the synchrotron wavelength ($\lambda = 0.154178$ nm), K is the particle shape factor, taken as 0.94 for spherical particles, β is the full-width at half maximum height (FWHM) in radians. The β-values were carefully determined by a least-square fit of a Gaussian function. The lattice parameter was determined by the Rietveld method using JADE 6.5 software.

Elemental compositions of the catalysts were determined by X-ray fluorescence (XRF) analysis, on an ARL ADVANT'X Intelli Power 4200 scanning X-ray fluorescence spectrometer. The results were analyzed using UniQuant non-standard sample quantitative analysis software.

Raman spectra were recorded on a Renishaw RM1000 with a confocal microprobe Raman system using an excitation laser line of 325 nm, in a range from 350 to 1000 cm^{-1}.

Reducibility of the catalysts was measured by the hydrogen temperature-programmed reduction (H_2-TPR) technique. 50 mg of the sample was placed in a quartz reactor connected to a homemade TPR apparatus and the reactor was heated from 40 to 800 °C with a heating rate of 10 °C min^{-1}, in a reducing atmosphere of mixed H_2 (5 vol.%) and N_2 (95 vol.%) with a total flow rate of 30 ml min^{-1}. The amount of H_2 uptake during the reduction was measured by a thermal conductivity detector (TCD), calibrated by using a known amount of pure CuO powder. The water produced in TPR was trapped on a 5 Å molecular sieve.

Diffuse reflectance infrared Fourier transform (DRIFT) spectra of the samples were recorded using a Nicolet 6700 spectrometer equipped with a mercury–cadmium–tellurium (MCT) detector and a diffuse reflectance cell (Harrick CHC-CHA-3), with a resolution of 4 cm^{-1}. An accumulation of 64 scans was used for collecting the spectra. About 20 mg of the catalyst was placed in the cell and pretreated at 300 °C for 1 h in a flow of Ar (30 ml min^{-1}) in order to remove water and carbonate in the catalyst. Subsequently, the system was cooled down to 30 °C and the background spectrum was recorded. After the introduction of the gas mixture (1 vol.% CO in Ar, 30 ml min^{-1}) for 30 min, the catalyst was purged with Ar for 30 min to remove the gaseous and physisorbed CO, and then a spectrum was collected.

2.3. Catalytic testing

CO oxidation experiments were conducted in a packed bed quartz tube (i.d. = 6 mm and length = 35 cm) operated isothermally at atmospheric pressure, in the temperature range of 80–500 °C. 200 mg of the catalyst was loaded into the reactor and the reaction temperature was monitored by a thermocouple placed at the center of the catalyst bed. A mixture of 1 vol.% CO and 1 vol.% O_2 balanced with N_2 was introduced as the reactants. The total flow rate was 40 ml min^{-1} and the space velocity was 12,000 ml g^{-1} h^{-1}. The catalyst was directly exposed to the reaction without any pretreatment. The CO concentration in the reactor effluent was analyzed using an Agilent 6850 gas chromatograph equipped with a thermal conductivity detector (TCD) and an HP PLOT (30 m × 0.32 mm × 12 μm)