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$Ce_{1-x}La_xO_y$ solid solution prepared from mixed rare earth chloride for soot oxidation

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Abstract: $Ce_{1-x}La_xO_y$ solid solution was simply prepared using mixed rare earth chloride ($RECl_3 \cdot xH_2O$, RE=Ce, La>99%, containing unseparated Ce and La from rare earth metallurgical industry) as precursor by ultrasonic-assisted co-precipitation method with different ultrasonic frequencies (CL*f*, *f*=200, 400, 600, 800, 1000 Hz). A compared $Ce_{1-x}La_xO_y$ solid solution (CL^*) was also prepared by the same mothod with 10% less precipitant. X-ray diffraction results confirmed the formation of $Ce_{1-x}La_xO_y$ solid solution, and the crystal structures of these catalysts were not very sensitive to ultrasonic frequency and precipitant amount. However, both of the factors had obvious effect on morphology and surface area of CL, and precipitant amount seem to play a more crucial role than ultrasonic frequency for $Ce_{1-x}La_xO_y$ solid solution preparation. When soot and catalyst were tight contacted, the peak temperature (T_{peak}) of soot oxidation and oxygen reducing temperature for CL*f* catalysts decreased linearly with increasing surface area. Under loose contact condition, the T_{peak} had obvious negative correlation with H_2 consumption. It was inferred that good reducibility of the $Ce_{1-x}La_xO_y$ solid solution favored the soot oxidation reaction. The $Ce_{1-x}La_xO_y$ solid solution prepared from unseparated rare earth chloride showed a good soot oxidaiton activity. Controlling the preparation conditions to prepare a CL catalyst would high surface area will enhance its reducibility and activity.

Keywords: $Ce_{1-x}La_xO_y$ solid solution; soot oxidation; mixed rare earth chloride; ultrasonic-assisted method; co-precipitation

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During the last few decades, diesel engines have attracted more and more attentions, but the emitted exhausts contain a large amount of soot, which has been considered as one of the hazardous materials causing environmental pollutions and human health problems[1–3]. The combination of traps and oxidation catalysts appeared to be one of the most efficient after-treatment techniques for decreasing soot emission[4,5]. Several kinds of catalysts such as precious metals, alkaline metal oxides, perovskite or perovskite-like type oxides and ceria-based materials have been studied for diesel soot combustion[6]. Among them, ceria-based catalyst got great significance and serious interest from researchers owing to its two important properties: (i) the redox couple, (Ce^{3+}/Ce^{4+}) with its ability to shift between Ce_2O_3 and CeO_2 under oxidizing and reducing conditions respectively, and (ii) the ease of formation of labile oxygen vacancies and oxide ion storage[7–9]. However, under elevated conditions ceria became inefficient with time and many innate properties could be affected, hence ceria was commonly combined with other metal ions to form solid solutions with improved properties[10].

It is now well established that Zr^{4+} incorporation greatly enhances the surface area, thermal stability and oxygen storage/release capacity (OSC) of ceria, resulting in superior catalytic performance, and has been used as an important material in soot oxidation[11–15]. However, Reddy and co-workers systematically investigated the relative efficacies of zirconium and lanthanum promoters in ceria solid solutions and demonstrated that compared to $Ce_{1-x}Zr_xO_2$, the $Ce_{1-x}La_xO_y$ sample showed a high OSC, better thermal stability and enhanced soot oxidation activity[16]. La doping greatly increased the OSC value of ceria because more oxygen vacancies were created by substitution of Ce^{4+} cations with La^{3+} cations to keep charge neutrality[17,18]. These newly generated defects were expected to induce larger number of surface active oxygen species and improve the diffusion rate of bulk oxygen to the surface and exchange of oxygen with the environment thereby making progress in the catalytic performance[19]. The $Ce_{1-x}La_xO_y$ solid solution frequently exhibited enhanced surface area, catalytic activity and stability toward sintering, which increased its application in soot oxidation[20,21].

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Our previous work showed that the proper La/(Ce+La) molar ratio is 20 mol.%–50 mol.% of $Ce_{1-x}La_xO_y$ solid solution supported Rh catalysts for ethanol oxidative steam reforming reaction[22]. The similar phenomenon was also found in water-gas shift and combustion of methane reaction[23,24]. Surprisingly the actual La/(Ce+La) molar ratio in rare earth ore is coincidentally in the range mentioned above. For example, Ce:La is about 5:3 in the typical bastnasite (Bayan Obo, China). In rare earth metallurgical industry, mixed rare earth chloride ($RECl_3·6H_2O$) can be conveniently produced from bastnasite or/and monazite by hydrochloric acid chlorination. After separation of other more useful and expensive rare earth elements such as Pr, Nd and Sm, the $RECl_3·6H_2O$ turned to be a cheap industrial raw and processed materials containing highly purified mixed Ce and La (RE=Ce and La, >99%). However, Ce and La separation is a complicate process because of their similar physical and chemical properties. Therefore, we are inspired that the $Ce_{1-x}La_xO_y$ solid solution prepared from mixed rare earth chloride ($RECl_3·6H_2O$, RE=Ce and La, >99%) directly will save plenty of instruments, materials, energy and time, which is a great improvement in environmental and economic view.

$Ce_{1-x}La_xO_y$ solid solution (CL) can be prepared by many methods, but Ce and La would exhibit phase segergation with La loading and calcination temperature increasing, and the range limits could be affected by the preparation method[25]. It was reported that thermal decomposition of $Ce_{1-x}La_x(OH)CO_3$ (precipitates from co-precipitation method) favored the formation of CL and keeping unsegergation[26]. Our previous work reported that the precipitation conditions greatly affected the properties of CL, and ultrasonic-assisted method was reported to be more controlable than traditional strring[27,28].

Inspired by all of the above, in this work, $Ce_{1-x}La_xO_y$ solid solution was prepared by ultrasonic-assisted co-precipitation method using mixed rare earth chloride ($RECl_3·6H_2O$, RE=Ce and La, >99%) as precursor and Na_2CO_3 as precipitant. The catalytic properties of $Ce_{1-x}La_xO_y$ solid solution for soot oxidaiton were tested, and the effects of ultrasonic frequency and amount of precipitant were investigated.

1 Experimental

1.1 Catalysts preparation

$Ce_{1-x}La_xO_y$ solid solution were prepared by ultrasonic-assisted co-precipitation method using mixed rare earth chloride ($RECl_3·6H_2O$, RE=Ce, La, 99 wt.%, La/(Ce+La)=38 mol.%, Baotou Xinye) as precursor. Typically, 30 g $RECl_3·6H_2O$ was dissolved in 200 mL of water. Then, 0.1 mol Na_2CO_3 solution was added into the mixed solution drop by drop during turbulence with a variation ultrasonic frequency (f=200, 400, 600, 800, 1000 Hz). The precipitate was dried at 60 ºC for 12 h, and then thermally treated in a furnace at 800 ºC for 3 h in air. The obtained powder was denoted as CLf. A compared $Ce_{1-x}La_xO_y$ solid solution (CL^*) with f=200 Hz using 0.09 mol Na_2CO_3 was also prepared. CeO_2 was prepared by the samilar method as a reference in the crystal structure analysis.

1.2 Catalysts characterization

The chemical compositions of the catalysts were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using an OPTIMA 2000DV spectrometer. The BET (Brunauer, Emmett, and Teller) surface areas of catalysts were determined on Quantasorb-18 automatic equipment by physical adsorption measurements with N_2 at –196 ºC. Prior to N_2 physical sorption, the samples were degassed at 300 ºC for 3 h.

X-ray powder diffraction (XRD) patterns were measured using a PANalytical X’Pert Pro diffractometer with Cu Kα (λ=0.15406 nm) radiation. Data of 2θ were collected from 10º to 80º with step size of 0.01º. The particle size was estimated from predominant crystalline planes by the Scherrer equation and cell parameter “a” of CLf and CL^* catalysts. The structure refine by Rietveld analysis was used.

The surface morphologies of catalysts were studied by a JSM-7001F field emission scanning electron microscope (FE-SEM). Powder samples were mounted directly on aluminum sample holders and placed in the SEM chamber without gold sputter coating.

Hydrogen temperature-programmed reduction (H_2-TPR) measurements were carried out in a conventional set-up equipped with a thermal conductivity detector (TCD). Samples (200 mg) were heated from room temperature to 900 ºC in a reducing gas mixture (10 vol.% H_2/He, 50 mL/min) with a ramp rate of 10 °C/min.

1.3 Activity test for soot oxidation

The soot oxidation activities of $Ce_{1-x}La_xO_y$ solid solution catalysts were measured by thermo-gravimetric (TG) and differential thermo-gravimetric (DTG) analysis (STARe system METTLER TOLEDO) methods. Oxidation experiments consisted of heating the soot-catalyst mixtures at 10 ºC/min from 30 to 800 ºC in a 100 mL/min flow of air. The mass ratio of soot:catalyst was 1:4 and 20 mg of each sample was tested in each run. The model soot used in this work was a carbon black from Degussa S.A. (Printex-U). Because contact between soot and catalyst is a key factor in this process, experiments in loose and tight contact conditions were both performed. For loose contact experiments, soot and catalyst were mixed with a spatula, whereas for tight contact tests the two components were intimately mixed in a mortar. A blank experiment was conducted in absence of catalyst