

Structure and redox properties of $\text{Ce}_x\text{Sn}_{1-x}\text{O}_2$ mixed oxides

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A variety of $\text{Ce}_x\text{Sn}_{1-x}\text{O}_2$ mixed oxides has been synthesized and their structure and redox properties have been studied. The structure of $\text{Ce}_x\text{Sn}_{1-x}\text{O}_2$ mixed oxides depends on values of 'x' and calcination temperature. When $x=1.0\sim 0.8$, $\text{Ce}_x\text{Sn}_{1-x}\text{O}_2$ mixed oxides are in cubic phase; on decreasing x from 0.7 to 0.1, $\text{Ce}_x\text{Sn}_{1-x}\text{O}_2$ mixed oxides are observed to have cubic and tetragonal mixed phases; and single SnO_2 is in a tetragonal phase. Only small amounts of SnO_2 can be introduced into the CeO_2 lattice to form cubic phase, and excess SnO_2 is in tetragonal phase. Low calcination temperatures favour formation of $\text{Ce}_{0.7}\text{Sn}_{0.3}\text{O}_2$ solid solutions, while high calcination temperatures do not favour formation of solid solutions and lead to sample sinters. Combined with DTA result, we believe the $\text{Ce}_{0.7}\text{Sn}_{0.3}\text{O}_2$ mixed oxides are formed during the decomposition of the dried sample at about 300 °C. The mixed oxides have three reduction peaks (α , β and γ). The peak α is attributed to the reduction of the easily reducible surface Sn^{4+} . The peak β is attributed to the overlapping peak of the reduction of bulk oxygen of SnO_2 and the easily reducible surface Ce^{4+} . The peak γ is ascribed to the reduction of bulk CeO_2 . The intensity and temperature of reduction peaks are affected by x values and calcination temperatures.

Cerium oxide has come under intense scrutiny as catalyst and as structural and electronic promoter of heterogeneous catalytic reactions, especially as a key component of a three-way catalyst for the treatment of exhaust gas from automobiles. In recent years, its excellent catalytic applications have aroused interest of many research workers. Its catalytic application relies primarily on the high efficiency of the reduction/oxidation cycles by shifting between Ce^{4+} (CeO_2) under oxidizing conditions and Ce^{3+} (Ce_2O_3) under reducing conditions, respectively¹. The capabilities of the redox couple Ce^{4+} - Ce^{3+} are strongly enhanced if other elements are introduced into the CeO_2 lattice by forming solid solutions²⁻⁵. It has been reported that ceria-zirconia mixed oxides show enhanced thermal, redox and catalytic properties compared to those of pure CeO_2 ^{2-4,6-8}.

Many workers have reported that SnO_2 is a fine support for the CO oxidation catalyst in the low temperature region. Hoflund and coworkers have found that Pt/SnO_2 has excellent oxidation

property^{9,10}. In order to evaluate the role played by the oxidation of Pd and Sn in the overall oxidation, Tripathi *et al.*¹¹ have also reported CO adsorption and CO- O_2 reaction over Pt/SnO_2 . As SnO_2 is a fine support for the CO oxidation catalyst, the Sn element was inserted to modify the property of CeO_2 .

In the present work, we have synthesized $\text{Ce}_x\text{Sn}_{1-x}\text{O}_2$ mixed oxides and studied their structure and redox properties to obtain better catalytic support.

Materials and Methods

$\text{Ce}_x\text{Sn}_{1-x}\text{O}_2$ samples ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$ and 1.0) were prepared according to the following steps: A certain amount of Sn powder was reacted with HNO_3 solution; followed by addition of a mixture of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and citric acid ($n_{\text{citric acid}} = n_{\text{Ce}} + n_{\text{Sn}}$) when a transparent and viscous gel was obtained. The solution was evaporated and the gel dried in an oven at 100 °C to get a white solid. The solid was finally calcined at 650°C for 4 h to obtain a yellow powder.

The reduction properties of $\text{Ce}_x\text{Sn}_{1-x}\text{O}_2$ mixed oxides were measured by means of temperature-programmed reduction (TPR) technique. Samples of $\text{Ce}_x\text{Sn}_{1-x}\text{O}_2$ (10 mg) were placed in a quartz reactor, which was connected to a conventional TPR apparatus¹². The reactor was heated from room temperature to 950 °C at a heating rate of 20 °C min⁻¹.

The purpose of the reoxidation treatment was to reveal the oxidation properties of the reduced sample. Before reoxidation, the sample was reduced in a flow of $\text{H}_2\text{-N}_2$ (5:95) mixed gas at a heating rate of 20 °C min⁻¹ up to 950 °C. Subsequently, the sample's temperature was decreased to a desired value (500, 300 or 100 °C), and the gas flow was simultaneously switched to oxygen for 0.5 h. The temperature of the sample was then decreased to 20 °C. Finally, TPR of reoxidation samples was performed.

X-ray diffraction (XRD) patterns were collected on a Rigaku D/max-III B powder diffractometer, using $\text{Cu K}\alpha$ radiation.

Results and Discussion

Figure 1 shows the XRD patterns of $\text{Ce}_x\text{Sn}_{1-x}\text{O}_2$ ($x = 1.0\sim 0$) mixed oxides calcined at 650 °C. Pure CeO_2 is in cubic phase and pure SnO_2 is in a tetragonal phase. $\text{Ce}_{0.9}\text{Sn}_{0.1}\text{O}_2$ and $\text{Ce}_{0.8}\text{Sn}_{0.2}\text{O}_2$ are in cubic phases, and the crystal lattice parameters for both are 5.409 Å, smaller than that of pure CeO_2 (5.417 Å). It may be due to the insertion of Sn atom into the CeO_2 crystal lattice and since the radius of Sn^{4+} ion is smaller than that of the Ce^{4+} , it reduces CeO_2 crystal lattice parameter. On decreasing x from 0.7 to 0.1, the XRD diffraction peaks due to CeO_2 become weak and SnO_2 phases are observed. We propose that only small amounts of SnO_2 can be introduced into the CeO_2 lattice to form solid solutions, and excess SnO_2 remains in a tetragonal phase.

Figure 2 shows the TPR profiles of fresh $\text{Ce}_x\text{Sn}_{1-x}\text{O}_2$ ($x = 1.0\sim 0$) mixed oxides. Pure CeO_2 shows two peaks at about 570 and 900 °C. The former at 570 °C is strongly dependent on surface and is generally attributed to the reduction of the easily reducible surface Ce^{4+} , and the latter at 900 °C is due to bulk oxygen removal⁵. Pure SnO_2 shows two reduction peaks, α and β . Peak γ (~ 330 °C) is quite weak and β peak (~700 °C) is quite strong. We

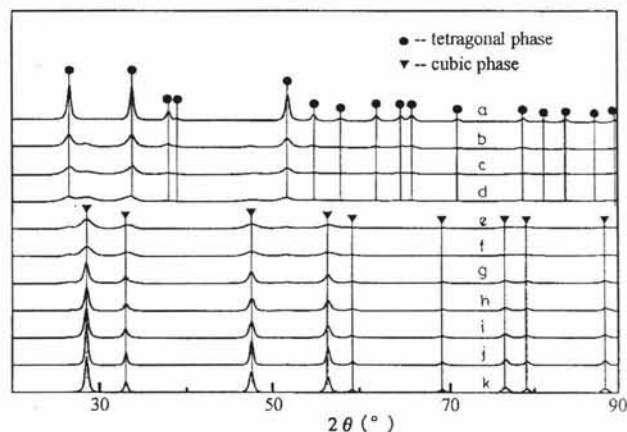


Fig. 1 — XRD patterns of $\text{Ce}_x\text{Sn}_{1-x}\text{O}_2$ ($x = 1.0\sim 0$) mixed oxides calcined at 650 °C [a, SnO_2 ; b, $\text{Ce}_{0.9}\text{Sn}_{0.1}\text{O}_2$; c, $\text{Ce}_{0.8}\text{Sn}_{0.2}\text{O}_2$; d, $\text{Ce}_{0.7}\text{Sn}_{0.3}\text{O}_2$; e, $\text{Ce}_{0.6}\text{Sn}_{0.4}\text{O}_2$; f, $\text{Ce}_{0.5}\text{Sn}_{0.5}\text{O}_2$; g, $\text{Ce}_{0.4}\text{Sn}_{0.6}\text{O}_2$; h, $\text{Ce}_{0.3}\text{Sn}_{0.7}\text{O}_2$; i, $\text{Ce}_{0.2}\text{Sn}_{0.8}\text{O}_2$; j, $\text{Ce}_{0.1}\text{Sn}_{0.9}\text{O}_2$; and k, CeO_2]

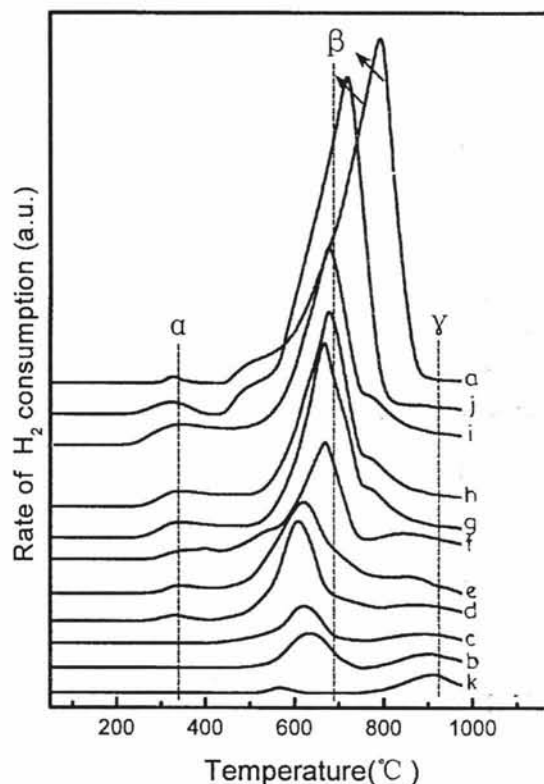


Fig. 2 — TPR profiles of fresh $\text{Ce}_x\text{Sn}_{1-x}\text{O}_2$ ($x = 0\sim 1$) mixed oxides [Legends same as for Fig.1]

believe peak α may be due to the reduction of surface Sn^{4+} in SnO_2 , while peak β may be due to the reduction of bulk SnO_2 . The mixed oxides have three reduction peaks (α , β and γ). But for $\text{Ce}_{0.9}\text{Sn}_{0.1}\text{O}_2$ and $\text{Ce}_{0.8}\text{Sn}_{0.2}\text{O}_2$, only two reduction peaks are observed,

β peak ($\sim 630^\circ\text{C}$) and γ peak ($\sim 900^\circ\text{C}$). When x decreases, β peak grows larger and shifts to higher temperatures, while γ peak weakens and finally diminishes. Peak α only begins to form when x is less than 0.8. Combined with the XRD results, the reason for this observation may be as follows: when Sn is in lesser proportion, Sn enters the cell of CeO_2 forming solid solution and there is nearly no surface Sn^{4+} left. On increasing Sn proportion, some of Sn atoms enter the cell of CeO_2 , while others do not. According to TPR profiles of single SnO_2 , α peak is attributed to the reduction of the easily reducible surface Sn^{4+} ; β peak is contributed by the overlapping peak of the reduction of bulk oxygen of SnO_2 and the easily reducible surface Ce^{4+} ; while γ peak is ascribed to the reduction of bulk CeO_2 in the high-temperature region. Table 1 lists the hydrogen consumption of $\text{Ce}_x\text{Sn}_{1-x}\text{O}_2$ ($x=1.0\sim 0$) mixed oxides. The hydrogen consumption of $\text{Ce}_x\text{Sn}_{1-x}\text{O}_2$ mixed oxides ($x=0.9\sim 0$) is higher than that of pure CeO_2 . When x decreases from 0.8 to 0.7, the hydrogen consumption of $\text{Ce}_x\text{Sn}_{1-x}\text{O}_2$ changes dramatically. The hydrogen consumptions of $\text{Ce}_{0.8}\text{Sn}_{0.2}\text{O}_2$ and $\text{Ce}_{0.7}\text{Sn}_{0.3}\text{O}_2$ are respectively 24 and 68 ml g^{-1} , the latter value being almost three times of the former. This difference may be associated with the cubic phase for the $\text{Ce}_{0.8}\text{Sn}_{0.2}\text{O}_2$ sample, and cubic and tetragonal mixed phases for the $\text{Ce}_{0.7}\text{Sn}_{0.3}\text{O}_2$ sample.

Figure 3 shows the XRD patterns of $\text{Ce}_{0.7}\text{Sn}_{0.3}\text{O}_2$ samples calcined at 400, 500, 650, 800 and 950 $^\circ\text{C}$, respectively. From Fig. 3, it can be seen that the intensity of peak increases and the width of the peak narrows with increasing the calcination temperature. The samples calcined at 400 and 500 $^\circ\text{C}$ are in CeO_2 phases, and no SnO_2 phase is observed. After being calcined at 650, 800 and 950 $^\circ\text{C}$, peaks due to CeO_2 phase and a weak diffraction peak due to SnO_2 phase are observed. It indicates that low temperature calcination favours formation of $\text{Ce}_{1-x}\text{Sn}_x\text{O}_2$ solid solutions, while high temperature calcination sinters the sample, which hinders the formation of $\text{Ce}_{1-x}\text{Sn}_x\text{O}_2$ solid solutions.

Figure 4 shows the TPR profiles of the $\text{Ce}_{0.7}\text{Sn}_{0.3}\text{O}_2$ samples calcined at 400, 500, 650, 800 and 950 $^\circ\text{C}$, respectively. All the samples have three reduction peaks (α , β and γ). The intensity of β peak increases with increasing calcination temperature, γ peak is almost constant, while α peak becomes weak. This indicates that high-temperature calcination

Table 1 — H_2 consumption of $\text{Ce}_x\text{Sn}_{1-x}\text{O}_2$ calcined at different temperatures

x	H_2 consumption ^a (ml g^{-1})
0	258(12.9)
0.1	255(12.8)
0.2	210(10.5)
0.3	201(10.1)
0.4	127 (6.4)
0.5	83 (4.2)
0.6	79 (4.0)
0.7	68 (3.4)
0.8	24 (1.2)
0.9	20 (1.0)
1.0	14 (0.7)

^a H_2 consumption was calculated by integration of the TPR; the error is reported in parentheses.

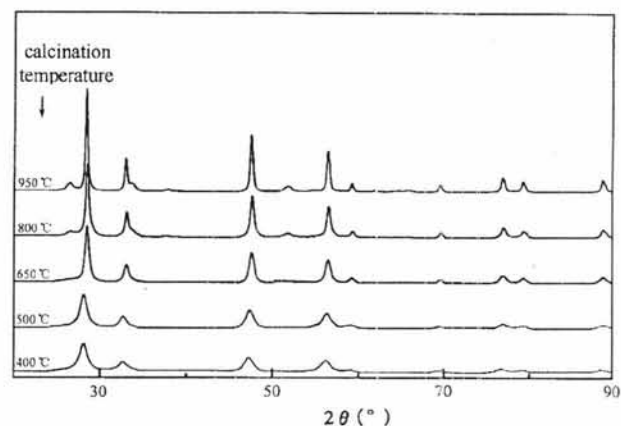


Fig. 3 — XRD patterns of $\text{Ce}_{0.7}\text{Sn}_{0.3}\text{O}_2$ sample calcined at different temperatures

enhances the reduction of bulk SnO_2 , and has little effect on the reduction of bulk CeO_2 . Table 2 lists the hydrogen consumption of $\text{Ce}_{0.7}\text{Sn}_{0.3}\text{O}_2$ mixed oxides calcined at different temperatures. From Table 2, we can see that the hydrogen consumption increases with the increase in calcination temperature. This indicates that high temperature calcination favours the reduction of $\text{Ce}_x\text{Sn}_{1-x}\text{O}_2$ mixed oxides.

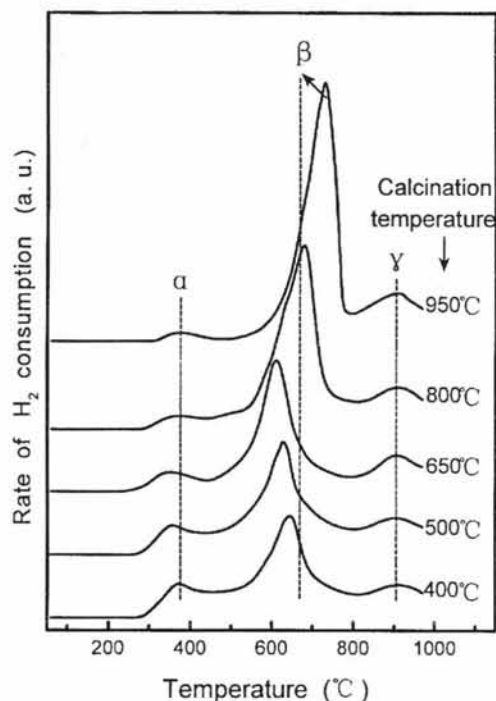


Fig. 4 — TPR profiles of $\text{Ce}_{0.7}\text{Sn}_{0.3}\text{O}_2$ calcined at different temperatures

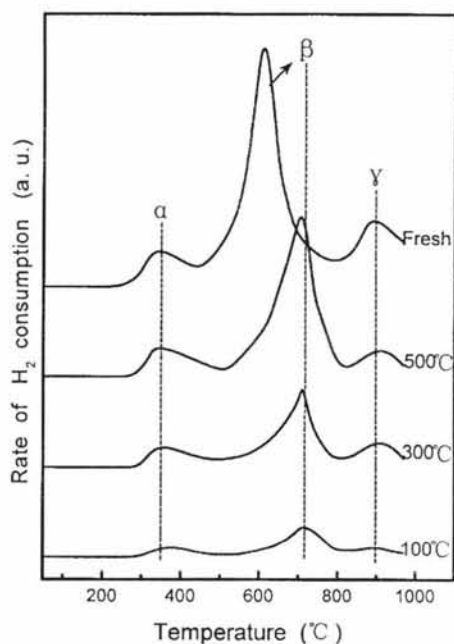


Fig. 5 — TPR profiles of $\text{Ce}_{0.7}\text{Sn}_{0.3}\text{O}_2$ reoxidised at different temperatures

The TPR profiles of the fresh $\text{Ce}_{0.7}\text{Sn}_{0.3}\text{O}_2$ and the effects of reoxidation temperature are shown in Fig. 5. The reoxidation temperature affects the redox

Table 2 — H_2 consumption of $\text{Ce}_{0.7}\text{Sn}_{0.3}\text{O}_2$ calcined at different temperatures

Calcination temperature (°C)	H_2 consumption ^a (ml g ⁻¹)
400	56 (2.8)
500	64 (3.2)
650	68 (3.4)
800	96 (4.8)
950	102 (5.1)

^a H_2 consumption was calculated by integration of the TPR; the error is reported in parentheses.

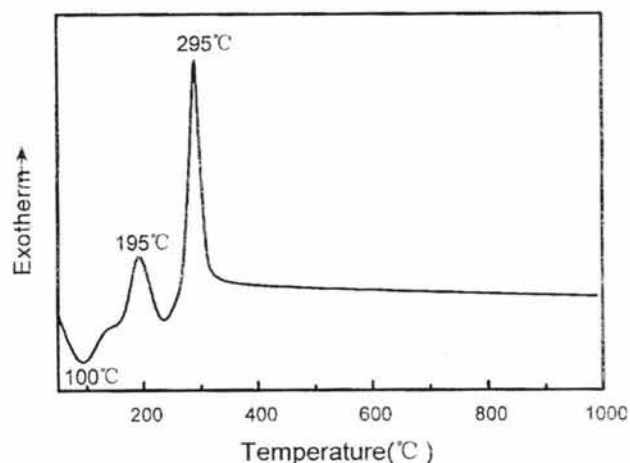


Fig. 6 — DTA patterns of $\text{Ce}_{0.7}\text{Sn}_{0.3}\text{O}_2$ sample before calcination in the stream of air

properties of the samples. After reoxidation at different temperatures, the highest peak at around 630 °C shifts to 700 °C, while the peaks at around 330 °C and 900 °C do not change. With the increasing reoxidation temperature, all these peaks become weak. Hydrogen consumption of the sample calcined at 500, 300 and 100 °C is respectively 65, 38 and 17 ml g⁻¹ which is lower than that of the fresh sample (68 ml g⁻¹). We propose that this trend is observed because it is not easy for the reoxidized samples to recover oxygen at low temperatures.

Figure 6 shows differential thermal analysis (DTA) curve of the dried $\text{Ce}_{0.7}\text{Sn}_{0.3}\text{O}_2$ sample in the stream of air. Similar DTA curves are also observed for other compositions. In the DTA curve, an endothermic peak appearing from room temperature to about 100 °C is due to elimination of water. Two exothermic peaks appearing at 195 and 295 °C are attributed to the decomposition of the sample. From 350 to 900 °C, no DTA peak is observed. Combined

with the XRD results, these results indicate that the $\text{Ce}_{0.7}\text{Sn}_{0.3}\text{O}_2$ mixed oxides are formed during the decomposition of the dried sample at about 300 °C.

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