Temperature-programmed reduction and CO oxidation studies over Ce–Sn mixed oxides

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Received 12 June 2000; accepted 1 November 2000

The reduction behaviour of Ce–Sn mixed oxides has been studied by a temperature-programmed hydrogen reduction technique and compared with that of pure SnO_2 and CeO_2. The mixed oxides were found to reduce at lower temperature as compared to that of individual oxides. Carbon monoxide oxidation studies showed that mixed oxides have better activity for CO oxidation reaction than the constituent oxides, which is in conformity with their surface reduction behaviour. The improved oxidation activity is attributed to a synergetic effect existing in these mixed oxides.

KEY WORDS: Ce–Sn mixed oxide; TPR; CO oxidation; X-ray diffraction; ^{119}Sn MAS NMR

1. Introduction

Ceria-based mixed oxides have been extensively studied for their redox behaviour as they can regulate the oxygen partial pressure in the automobile exhaust by undergoing $Ce^{4+} \leftrightarrow Ce^{3+}$ redox reaction [1–5]. Attempts have been made to improve the low-temperature reducibility and enhance the oxygen storage capacity of CeO_2 by substituting part of Ce^{4+} by other suitable cations. Substitution of a part of Ce^{4+} by other reducible or non-reducible cations of same valency like Zr^{4+}, Ti^{4+}, etc. [3,6] or lower valent cations like Gd^{3+}, Ca^{2+}, Mn^{3+}, etc. [2,7] has been done to obtain these characteristics. In all these cases, the substitution has helped in bringing down the reduction temperature of ceria and different mechanisms have been proposed for this observed low-temperature reduction and better oxygen storage properties. These oxides are found to be good catalysts for oxidation reactions.

A number of mixed oxides are reported to exhibit better catalytic activity for oxidation reactions as compared to their constituent oxides due to a synergetic effect. Such effect has been reported for systems like MoO_3–Sb_2O_4, $Bi_2Mo_3O_{12}$–Bi_2MoO_6, Mn_2O_3–SnO_2, etc. [8–10] where, although individual oxides retained their crystal structure, the mixed oxides exhibited better catalytic activity. The existence of synergetic effect in mixed oxides has been demonstrated by improved catalytic activity particularly at lower temperatures and reduction in the value of activation energy for the reaction under consideration [10].

SnO_2 has been widely used as an oxidation catalyst as it can reversibly undergo the $Sn^{4+} \leftrightarrow Sn^{2+}$ reaction at relatively lower temperature (∼200 °C). Hence, it was of interest to study a mixed oxide system of CeO_2 and SnO_2 where SnO_2 can catalyse the oxidation reaction at relatively lower temperatures as compared to ceria. In the present study, the reduction behaviour of Ce–Sn mixed oxides has been studied and correlated with the CO oxidation activity of these mixed oxides.

2. Experimental

The mixed oxides of Ce–Sn, ($(CeO_2)_{1-x}(SnO_2)_x$, $x = 0.2$ and 0.7 represented as $Ce_{80}Sn_{20}$ and $Ce_{30}Sn_{70}$, respectively) were prepared by a co-precipitation method. Sn metal dissolved in HCl and a cerous nitrate solution were thoroughly mixed followed by their precipitation using NH_4OH. The precipitate was repeatedly washed and dried in an oven at 175 °C for 16 h and calcined at 300 °C in air for 18 h in a furnace. SnO_2 was prepared from a solution of Sn metal dissolved in HCl and CeO_2 from cerous nitrate solution using the same procedure as mentioned above.

Total surface area of the samples heated at 300 °C for 18 h was measured by BET technique using N_2 gas. Powder X-ray diffraction patterns were recorded on a Philips 1820 diffractometer using Cu K_α radiation.

TPR experiments were carried out from room temperature to 950 °C using an indigenously fabricated instrument. 25 mg sample was put in a quartz tube and heated at 15 °C/min in $H_2 + Ar$ stream (8% H_2 by volume). All samples were given an *in situ* pretreatment of heating in Ar flow at 300 °C for 2 h followed by cooling to room temperature, before a TPR run. Change in H_2 concentration in the effluent gas due to the reduction of samples, was monitored by a thermal conductivity detector. Water produced during the reaction was trapped in a silica gel column placed between the reactor and the thermal conductivity detector. No

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1011-372X/01/0100-0069$19.50/0

attempt was made to estimate the extent of water formed and the signals depicted in the TPR curves are indicative of the volume of hydrogen consumed during reduction.

CO oxidation experiments were carried out in a quartz tubular reactor using 0.20 g of oxides. 50 μl pulses of CO or CO + O_2 mixture (2 : 1 by volume) were injected to samples kept at different temperatures from 100 to 500 °C with a temperature increment of 25 °C. The effluent gas was analysed by a gas chromatograph equipped with a Porapak-Q column and a thermal conductivity detector. Helium was used as the carrier gas for these experiments. The samples were given a pretreatment of heating in He gas at 300 °C for 2 h before doing CO oxidation experiments.

With a view to look for the distribution of Sn^{4+} in the mixed oxide samples, ^{119}Sn MAS NMR spectra of SnO_2 as well as mixed oxides, heated at different temperatures, were recorded using a Bruker Avance DPX 300 machine with ^{119}Sn basic frequency of 111.817 MHz. Typical 90° pulse is of the order of 4 μs with a delay time of 5 s. The side band suppression was carried out using a modified version of the TOSS pulse program suggested by Dixon et al. [11].

The surface species formed on these oxides during exposure to CO were monitored *in situ* using IR spectroscopy in transmission mode. The details of a high-pressure and high-vacuum IR cell fitted with calcium fluoride windows and that of the instrumentation employed for this study are given elsewhere [12]. A self-supporting sample wafer of 25 mm diameter (~100 mg) was evacuated at 250 °C for 30 h before exposure to 100 Torr of CO at a desired temperature.

3. Results and discussion

XRD patterns of $Ce_{80}Sn_{20}$ and $Ce_{30}Sn_{70}$ heated at 300 and 500 °C in air for 18 h are shown in figure 1. From this figure it can be seen that the $Ce_{30}Sn_{70}$ sample exhibited a diffraction pattern where the different peaks could be assigned to both SnO_2 and CeO_2. In case of $Ce_{80}Sn_{20}$, even though the pattern looks like that of single phase CeO_2, small peaks characteristic of SnO_2 can still be discerned from it. The low intensity of SnO_2 peaks arises due to its poor crystallinity. The diffraction peaks corresponding to SnO_2 in $Ce_{80}Sn_{20}$ become clearer for the sample heated at 500 °C. It can also be noted that the SnO_2 phase has poor crystallinity even after heating at 500 °C for 18 h indicating its poor sintering behavior and lesser reduction in its surface area.

The BET surface areas of these oxide samples are given in table 1. It can be seen that the Sn-rich composition has higher surface area than the ceria-rich composition, which is consistent with the XRD patterns of these samples and also from the surface area values of pure SnO_2 and CeO_2.

Figure 2 shows the side band suppressed NMR spectra of these mixed oxide samples. The spectra show two peaks out of which one is very intense whose chemical shift is around −605 ppm and the other one is very weak around −650 ppm. The chemical shift of the intense peak matches with that of pure SnO_2. The small peak seen towards more negative side is due to a small amount of SnO_2 dissolved in the CeO_2 matrix. The increased shielding around the Sn nucleus dissolved in CeO_2 can be attributed to the change in coordination number of Sn from 6 to 8 in the ceria structure.

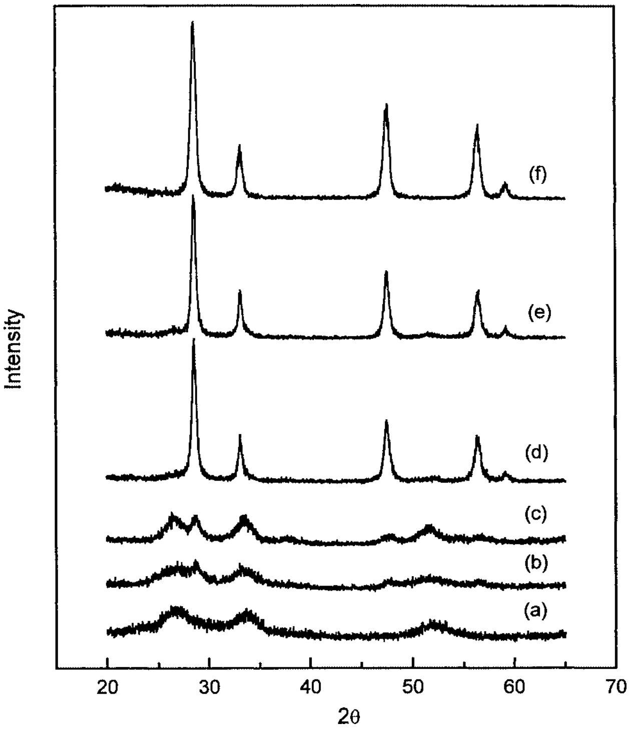

Figure 1. XRD patterns of samples heated in air for 18 h, (a) SnO_2 at 500 °C, (b) $Ce_{30}Sn_{70}$ at 300 °C, (c) $Ce_{30}Sn_{70}$ at 500 °C, (d) $Ce_{80}Sn_{20}$ at 300 °C, (e) $Ce_{80}Sn_{20}$ at 500 °C and (f) CeO_2 at 500 °C.

Table 1
Total surface area of oxide samples measured by BET technique and calculated values of activation energy for CO oxidation.

Compound	Surface area (m^2/g)	Approximate value of E_a (kcal/mol)
CeO_2	32	13.2
$Ce_{80}Sn_{20}$	53	1.6
$Ce_{30}Sn_{70}$	80	2.4
SnO_2	121	4.7

Figure 3 shows the TPR profiles of the mixed oxides along with that of pure oxides. From this figure it is clear that the main contribution to the intensity of TPR peaks is from SnO_2. Two main peaks are seen in the TPR patterns for all samples among which the first low-temperature peak can be assigned to the surface reduction of SnO_2 and the high-temperature peak is due to its bulk reduction. The assignment of the lower temperature peak to surface reduction is justified from figure 4, where the TPR profiles of SnO_2 heated in air at 300 and 800 °C are compared. The low-temperature peak is absent in a sample heated at 800 °C, which may be attributed to sintering of the sample resulting in the reduction of its surface area. Two low-intensity peaks seen in figure 3(d) correspond to the surface and bulk reduction of CeO_2, which is in conformity with the result reported

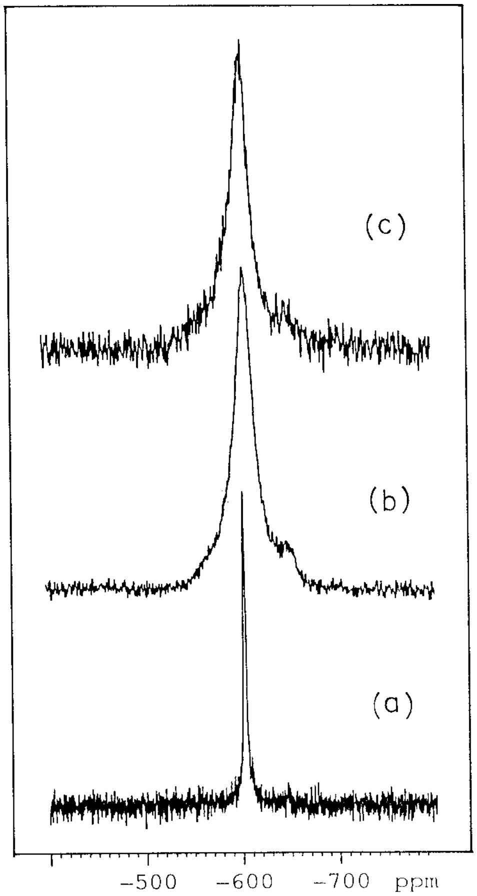

Figure 2. ^{119}Sn MAS NMR spectra of samples heated in air for 18 h (a) SnO_2 at 800 °C, (b) $Ce_{30}Sn_{70}$ at 300 °C and (c) $Ce_{80}Sn_{20}$ at 300 °C.

earlier [13]. The inset of figure 3 shows the lower temperature portion of the TPR curve after normalization to the same contents of tin and assuming that CeO_2 is not reduced over this temperature region, as is apparent from figure 3(d). From this inset, it is clear that the area under this curve is in the increasing order for SnO_2, $Ce_{30}Sn_{70}$ and $Ce_{80}Sn_{20}$ although the BET surface area is maximum for SnO_2. This suggests the possibility of the existence of some kind of synergism between the two types of oxides during their surface reduction process. Another important feature of figure 3 is that the bulk reduction peak of the mixed oxide has shifted to lower temperature as compared to the constituent oxides. The total volume of hydrogen consumed during TPR experiments corresponds to complete reduction of SnO_2 to its metallic state. The formation of Sn metal is clearly seen in the XRD patterns of these samples recorded after TPR experiments. A small peak seen around 775 °C for $Ce_{80}Sn_{20}$ is due to the bulk reduction of CeO_2, which is not resolved from the SnO_2 reduction peak in the case of $Ce_{30}Sn_{70}$.

In figure 5, the amount of CO reacted and CO_2 formed are plotted for different temperatures when 50 μl pulses of CO were injected over these oxides. It can be seen that the amount of CO reacted is higher for mixed oxides than for individual oxides. From this figure, it is clear that in mixed oxide samples, CO oxidation occurs at relatively lower tem-

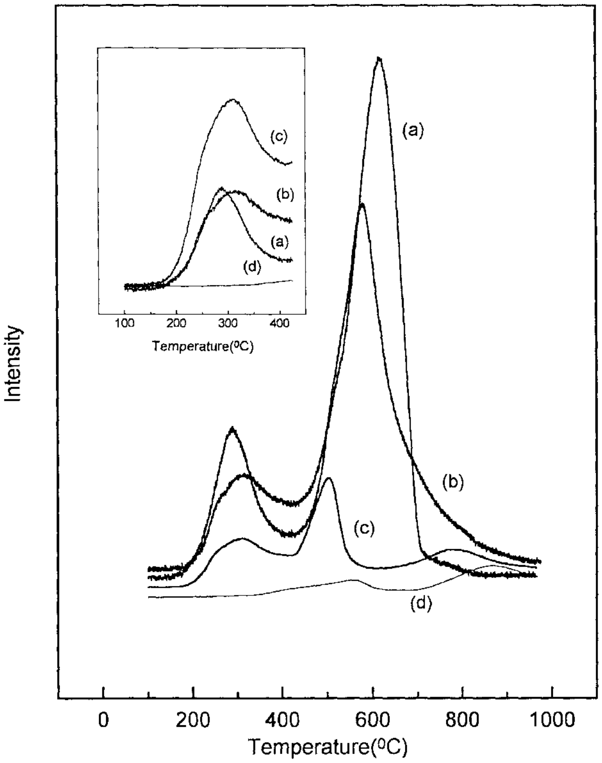

Figure 3. TPR patterns of (a) SnO_2, (b) $Ce_{30}Sn_{70}$, (c) $Ce_{80}Sn_{20}$ and (d) CeO_2. Inset shows the low-temperature region of the same figure with Sn content normalised to the same values for all samples.

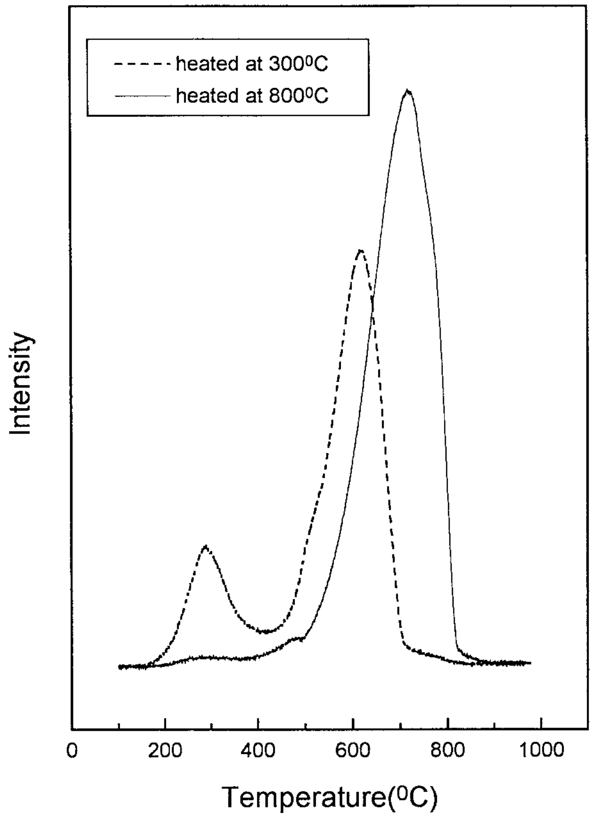

Figure 4. TPR curves of SnO_2 samples heated at two different temperatures in air for 18 h.

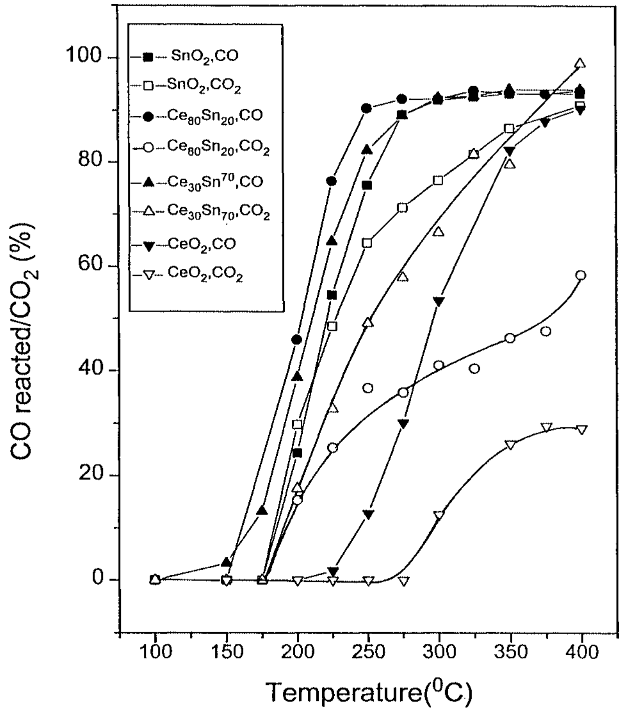

Figure 5. Percentage of CO reacted and CO_2 formed on different oxides when 50 μl pulses of CO gas were injected.

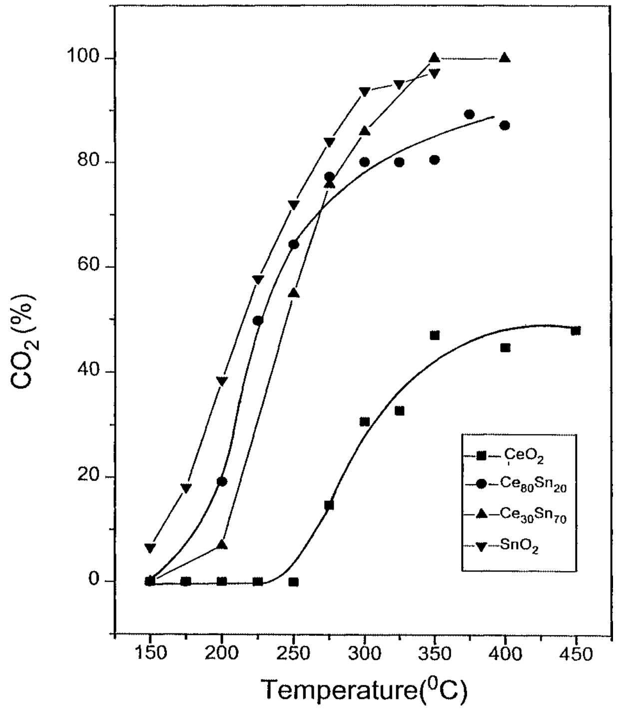

Figure 6. CO_2 formed on different oxides when 50 μl pulses of CO + O_2 gas mixture were injected at different temperatures.

peratures as compared to individual oxides; this correlates well with the low-temperature reduction behavior of these mixed oxides (see figure 3). This reaction occurs through lattice oxygen incorporation, as has been seen from our earlier studies where the formation of SnO in SnO_2 samples treated with CO under similar experimental conditions, has been demonstrated [14]. A comparative estimation of the activation energy values for CO oxidation over these samples was obtained by monitoring the extent of CO reacted at different temperatures under almost equilibrium conditions. This was achieved by injecting a number of pulses at each temperature such that the amount of CO reacted attained a constant value. The values of activation energy are listed in table 1. A significant reduction in the activation energy for the CO oxidation reaction for mixed oxides is indicative of the ease of availability of lattice oxygen in these samples.

For Ce-containing oxides, the volume of CO_2 eluted out is significantly less than the volume of CO reacted due to the reaction of CO_2 over the surface as carbonate species (figure 5) as revealed by their IR spectra. The IR spectrum of a $Ce_{80}Sn_{20}$ sample, after 5 min of exposure to CO, revealed the formation of CO_2 at room temperature in addition to bidentate carbonate species at 1593, 1323 and 1050 cm^{-1} and bridged carbonate species at 1401 and 1219 cm^{-1}. This is in agreement with the frequencies of these carbonate bands reported in literature [15,16]. The formation of stable carbonate species on the surface of CeO_2 due to CO interaction has been reported in a number of earlier studies [17,18]. Presence of SnO_2 leads to less stable carbonate species and therefore evolution of higher yields of CO_2 in a lower temperature range (figures 5 and 6).

Figure 6 shows the amount of CO_2 eluted when 50 μl pulses of a CO + O_2 mixture is used as reactant gas. It can be seen that the amount of CO_2 eluted is higher for SnO_2 than for mixed oxides and CeO_2. The higher catalytic activity of these mixed oxides is not observed here, due to the reaction of the product, namely CO_2, with the catalyst as mentioned above.

The higher oxidation activity and lower values of activation energy of mixed oxides as compared to SnO_2 and CeO_2 suggest the existence of a synergetic effect between the two oxides for the CO oxidation reaction. From XRD patterns and NMR spectra, it is seen that the mixed oxides exist in different phases characteristic of individual phases. Hence, the synergetic effect arises due to the "remote control mechanism" as proposed by Weng et al. [8]. It is proposed that SnO_2, being easily reducible, gives out its lattice oxygen for the CO oxidation reaction, which possibly gets rejuvenated by abstracting oxygen from the adjacent CeO_2 molecules. The properties of low-temperature reducibility and the existence of the synergetic effect in Ce–Sn mixed oxides offer them better scope as oxidation catalyst than CeO_2 and SnO_2, particularly for low-temperature reactions.

Acknowledgement

The authors are thankful to Mr. V. Sudarsan for help in recording the NMR spectra and Dr. A.D. Belapurkar for help in the initial stages of the work related to TPR measurements. Thanks are also due to Ms. Arati Sahasrabudhe for recording IR spectra.

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