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# Synergistic effects during CO oxidation over mixed oxides. Study of ($Fe_2O_3 + SnO_2$) and ($Mn_2O_3 + SnO_2$) systems

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Based on the comparative evaluation of the catalytic activity of $Fe_2O_3$, $Mn_2O_3$ and $SnO_2$ and their mixed oxides ($Fe_2O_3 + SnO_2$) and ($Mn_2O_3 + SnO_2$), it is shown that the system ($Mn_2O_3 + SnO_2$) shows strong synergistic effects during CO oxidation reaction. Such effects are not observed for the analogous system ($Fe_2O_3 + SnO_2$). Based on the calcination and reduction behaviour of these two mixed oxide systems and the redox potentials of the involved cations, the possible reasons for the observance of synergistic effects for the ($Mn_2O_3 + SnO_2$) system are discussed.

**Keywords:** synergistic effect; carbon monoxide; oxidation; mixed oxides; iron oxide; tin oxide; manganese oxide

## 1. Introduction

Mixed oxide catalysts have been used in industry for a variety of reactions like oxidative dehydrogenation [1], oxidative coupling [2], partial oxidation [3], etc. because of the possibility of synergistic effects [4] between constituent oxides. Two important suggestions proposed to explain the observed synergistic effects are (i) solid solution or compound formation between the constituent oxides and (ii) a remote control mechanism involving continuous regeneration of consumed sites by other oxide which rejuvenates itself from the feed gas mixture. Based on the studies carried out with mixed oxides to investigate [5,6] the role of individual metal ions during the oxidation process it is conjectured that the reducibility of different oxides depends on the value of the standard free energy change ($\Delta G^0$) involved during dissociation of the metal–oxygen bond. Aso et al. [7] have correlated the reducibility of various metal oxides with their standard free energy change and inferred that the higher the value of $\Delta G^0$, the more difficult is the reduction process. To understand the role played by different cations it is desirable to tailor make the isostructural catalyst systems with varying degree of synergistic effects and study a simple model oxidation reaction over these catalysts. In the present communication, we report the CO oxidation activity of $\alpha$-$Mn_2O_3 + SnO_2$ and $\alpha$-$Fe_2O_3 + SnO_2$ mixed oxide systems and their constituent oxides to ascertain the possible reasons for the observance of strong synergistic effects for the ($\alpha$-$Mn_2O_3 + SnO_2$) system as compared to that of ($\alpha$-$Fe_2O_3 + SnO_2$).

## 2. Experimental

$\alpha$-$Mn_2O_3 + SnO_2$ and $\alpha$-$Fe_2O_3 + SnO_2$ catalysts were prepared by the coprecipitation method from the respective solutions. To prepare the mixed oxides of ($Mn_2O_3 + SnO_2$), the mixed hydroxides of Mn and Sn were prepared by dissolving these metals (2 : 1 ratio) in concentrated HCl and precipitating with NaOH. Preparation of ($Fe_2O_3 + SnO_2$) was carried out as follows. Iron metal was directly dissolved in HCl and oxidised by the addition of nitric acid. Sn metal was first treated with nitric acid to form hydrated stannic oxide followed by its dissolution in diluted HCl. The two chloride solutions were mixed, diluted with water and coprecipitated at room temperature using $NH_4OH$ with constant stirring at pH $\approx 9.0$. For carrying out comparative studies, the individual oxides were also prepared in the same manner. These precipitates were washed thoroughly with water, dried in an oven at 375 K for 12 h and calcined at 825 K for 20 h. Before carrying out CO oxidation experiments, the catalyst was heated in situ in flowing helium at 625 K for 2 h to remove moisture and physisorbed gases. After this pretreatment the catalyst was cooled to the desired temperature in flowing helium. CO oxidation reaction was carried out over 0.5 g catalyst sample in a micro catalytic reactor. 100 $\mu$l pulses of the ($CO + O_2$) (1 : 1 volume) mixture or only CO were injected over the catalyst with helium as carrier gas (flow 30 ml/min) and effluent gases were analysed by a gas chromatograph using a Porapak Q column and a thermal conductivity detector. Pulse to pulse deactivation experiments were carried out using 500 mg of fresh catalyst at a constant temperature after giving the same pretreatment mentioned above.

Powder X-ray diffraction patterns of the individual

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oxides and their mixed oxides were recorded using Cu $K_\alpha$ radiation. The source used for recording $^{119}$Sn Mössbauer spectra was $Ba^{119}SnO_3$ and the spectra were least-squares fitted using Lorentzian line shape. The source used for recording $^{57}$Fe Mössbauer spectra was $^{57}$Co in Rh matrix.

The surface area of the individual oxides and their mixtures was measured by $N_2$ absorption method using the BET technique. $SnO_2$ was found to have a surface area of $\approx$ 84 $m^2/g$, which is significantly more than that of the other two oxides, $Fe_2O_3$ and $Mn_2O_3$, which showed an approximate area of 21 and 5 $m^2/g$ respectively. The total surface area for the mixed oxide systems, ($Mn_2O_3 + SnO_2$) and ($Fe_2O_3 + SnO_2$), is found to be 52 and 65 $m^2/g$ respectively.

## 3. Results and discussion

Fig. 1 (a, b and c) show the percentage yield of $CO_2$ at different temperatures when 100 μl pulses of CO were injected over α-$Mn_2O_3$, α-$Fe_2O_3$ and $SnO_2$ oxide catalysts. Fig. 1 (d, e and f) show the percentage yield of $CO_2$ when a mixture of ($CO + O_2$) was injected over these catalysts. A comparison of these results shows that of the three oxides, $SnO_2$ is the least active and CO oxidation is initiated at relatively higher temperature ($T_i \approx 550$ K). This reaction temperature is significantly decreased when both ($CO + O_2$) pulses were used as reactant gases. The other two oxides showed almost comparable activity for CO oxidation and initiation temperature is approximately 425 K. Further, the presence of oxygen in the reactant gas mixture did not significantly alter the CO oxidation reaction temperature. These results imply that in the matrix of α-$Fe_2O_3$ and α-$Mn_2O_3$, there is better mobility of oxygen as compared to that of $SnO_2$, CO oxidation is mainly occurring through lattice oxygen incorporation, and the oxygen depleted oxide surface gets rejuvenated due to the presence of oxygen in the reactant gas mixture. The results of CO oxidation over the surface of mixed oxide systems, ($Fe_2O_3 + SnO_2$) and ($Mn_2O_3 + SnO_2$) are shown in fig. 1 (g and h) when 100 μl pulses of CO alone were injected at different temperatures. From this figure it is also clear that the ($Mn_2O_3 + SnO_2$) system is significantly more active and CO oxidation is initiated at significantly lower temperature as compared to that of individual oxides. For the ($Fe_2O_3 + SnO_2$) system, the decrease in initiation temperature is only marginal. The presence of oxygen in the feed gas mixture further facilitates the CO oxidation reaction. The numbers of $CO_2$ molecules produced per unit area per pulse for ($Mn_2O_3 + SnO_2$) and ($Fe_2O_3 + SnO_2$) systems at different temperatures are given in table 1, which clearly shows that ($Mn_2O_3 + SnO_2$) is more active than the ($Fe_2O_3 + SnO_2$) system. For the ($Mn_2O_3 + SnO_2$) system, in the absence of oxygen in the feed gas, the CO oxidation activity was found to be slightly tapered off at relatively higher temperatures because of its higher activity at lower temperatures; thereby the surface gets depleted of its mobile oxygen. This feature is absent when oxygen was added to the reactant gas mixture. These observations suggest the existence of strong synergism between the constituent oxides of the ($Mn_2O_3 + SnO_2$) system which is absent for the ($Fe_2O_3 + SnO_2$) system.

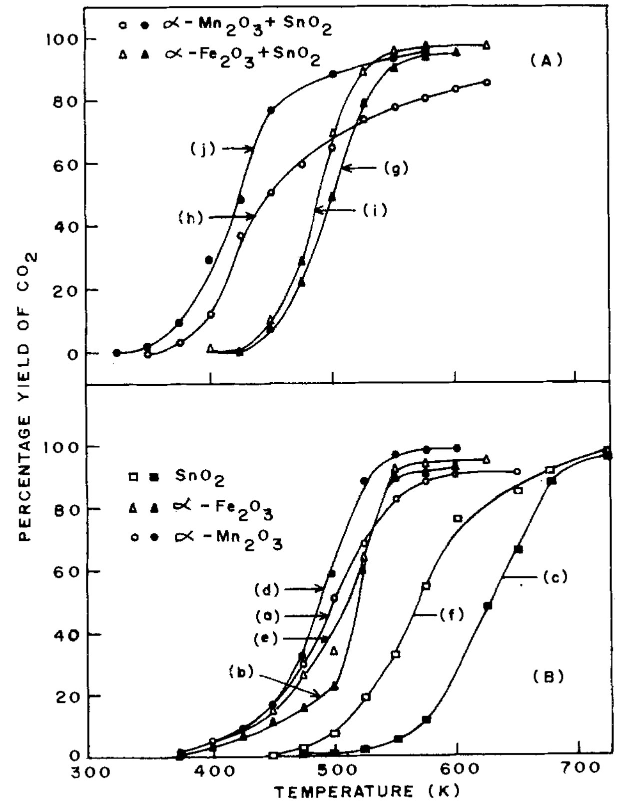

Fig. 1. Percentage of $CO_2$ yield when 100 μl pulses of CO were injected over (a) α-$Mn_2O_3$, (b) α-$Fe_2O_3$, (c) $SnO_2$, (g) α-$Fe_2O_3 + SnO_2$, (h) α-$Mn_2O_3 + SnO_2$ and when 100 μl $CO + O_2$ was injected over (d) α-$Mn_2O_3$, (e) α-$Fe_2O_3$, (f) $SnO_2$, (i) α-$Fe_2O_3 + SnO_2$ and (j) α-$Mn_2O_3 + SnO_2$.

The variation of catalytic activity of the mixed oxide

Table 1

Number of $CO_2$ molecules formed per unit area of the catalyst per pulse when $CO + O_2$ pulses were used as reactant gas over mixed oxide catalysts

| Temperature (K) | Number of $CO_2$ molecules /$m^2$ catalyst/pulse ($\times 10^{15}$) | |
|---|---|---|
| | $Fe_2O_3 + SnO_2$ | $Mn_2O_3 + SnO_2$ |
| 400 | – | 15 |
| 425 | – | 40 |
| 450 | 5 | 55 |
| 475 | 20 | 60 |
| 500 | 40 | 65 |
| 525 | 65 | 75 |
| 550 | 75 | 80 |
| 575 | 75 | 80 |

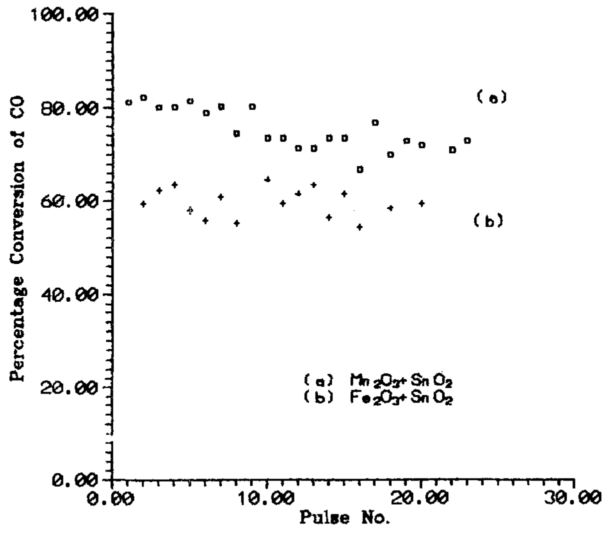

Fig. 2. Percentage yield of $CO_2$ with successive CO pulses at 575 K. (a) $Mn_2O_3 + SnO_2$, (b) $Fe_2O_3 + SnO_2$.

catalysts from pulse to pulse at 575 K is shown in fig. 2. ($Fe_2O_3 + SnO_2$), being less active than ($Mn_2O_3 + SnO_2$), exhibited lower conversion of CO as well as no deactivation with successive pulses of CO. Similar experiments carried out on the ($Mn_2O_3 + SnO_2$) system showed some deactivation due to its higher activity as compared to the ($Fe_2O_3 + SnO_2$) system.

The coprecipitated mixed oxide samples were characterised by powder X-ray diffraction and $^{119}Sn$ Mössbauer spectroscopic measurements to explore their crystallisation behaviour and the occurrence of any solid state reaction between the constituent oxides after calcination at different temperatures for a fixed duration of 20 h. The oven dried samples were found to be amorphous in nature and crystallisation of $\alpha$-$Mn_2O_3$ and $\alpha$-$Fe_2O_3$ occurred at about 775 and 875 K, respectively, in these mixed oxide systems (table 2). This suggests that the crystallisation of $\alpha$-$Fe_2O_3$ and $\alpha$-$Mn_2O_3$ is retarded in these mixed oxides as the individual oxides were found to be crystalline after calcination at 475 K. The $SnO_2$ phase was found to crystallise at $\approx$ 875 K for both these systems with rutile structure and sharp X-ray diffraction lines were observed for the samples calcined at ~ 975 K. Further, upto a calcination temperature of 1075 K, there is no chemical reaction between the constituent oxides of these two mixed oxide systems as can be seen from the X-ray diffraction patterns shown in fig. 3 neither of which exhibits any additional diffraction peak nor any change in the peak positions of individual oxides. The $^{119}Sn$ Mössbauer spectra recorded at room temperature for both mixed oxide systems showed an unresolved quadrupole doublet characterised with an isomeric shift $\delta = 0.01$ mm/s (with respect to $BaSnO_3$) and quadrupole splitting $\Delta E_q = 0.68$ mm/s which are characteristic of $SnO_2$ having rutile structure. The $^{57}Fe$ Mössbauer spectra of the ($Fe_2O_3 + SnO_2$) system also did not show the formation of any new phase in the crystalline or amorphous state. These observations rule out the involvement of any new phase during CO oxidation process which is responsible for the observance of the synergistic effect.

Further, the existence of strong synergistic effects for the ($Mn_2O_3 + SnO_2$) system as compared to that of ($Fe_2O_3 + SnO_2$) was also reflected during their hydrogen reduction behaviour. For the ($Mn_2O_3 + SnO_2$) system, $Mn_2O_3$ was directly reduced to the MnO form at about 625 K as compared to that of $\alpha$-$Mn_2O_3$ alone which is reduced to MnO at about ~ 725 K through the formation of $Mn_3O_4$ as the intermediate phase. Unlike this, $Fe_2O_3$, either alone or in mixed oxide form, was reduced to $Fe_3O_4$ at 675 K. As regards the reduction behaviour of the other constituent $SnO_2$, it was initiated at ~ 675 K for both the systems as revealed from the appearance of metallic tin or intermetallic $FeSn_2$ and FeSn for both these systems. The formation of SnO was not observed in either of the systems because of its strong reactivity with other reduced species. Unlike this, for $SnO_2$ alone the formation of SnO during hydrogen reduction has been well demonstrated [8]. The hydrogen reduction behaviour of these compounds provides an additional evidence for the existence of synergism in the ($Mn_2O_3 + SnO_2$) system. The reduction potentials for the three cations involved during CO oxidation are

$$Mn^{3+} + e^- \to Mn^{2+} \quad E_0 = +1.54 \text{ eV}$$

$$Fe^{3+} + e^- \to Fe^{2+} \quad E_0 = +0.77 \text{ eV}$$

$$Sn^{4+} + 2e^- \to Sn^{2+} \quad E_0 = +0.15 \text{ eV}.$$

From the above values of $E_0$, it is apparent that $Mn^{3+}$ should be the easiest to reduce and conversion of $Sn^{4+}$ to $Sn^{2+}$ is the most difficult process. This behaviour is consistent with the catalytic behaviour of the individual oxi-

Table 2

Temperatures for the initiation of crystallisation and hydrogen reduction for various oxides and mixed oxides

| Oxide system | Crystallisation temperature (K) | | | Reduction temperature (K) | | |
|---|---|---|---|---|---|---|
| | $Mn_2O_3$ | $Fe_2O_3$ | $SnO_2$ | $Mn_2O_3$ | $Fe_2O_3$ | $SnO_2$ |
| $Mn_2O_3 + SnO_2$ | 775 | – | 875 | 625 | – | 675 |
| $Fe_2O_3 + SnO_2$ | – | 875 | 875 | – | 675 | 675 |
| $Mn_2O_3$ | 475 | – | – | 725 | – | – |
| $Fe_2O_3$ | – | 475 | – | – | 675 | – |
| $SnO_2$ | – | – | 775 | – | – | 475 |

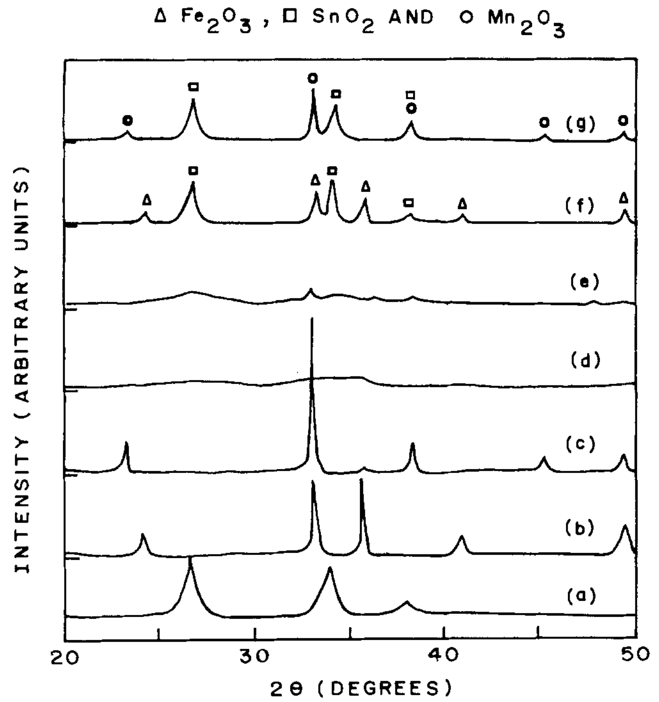

Fig. 3. X-ray diffraction patterns of samples calcined in air for 20 h. (a) $SnO_2$ at 775 K, (b) $\alpha$-$Fe_2O_3$ at 775 K, (c) $\alpha$-$Mn_2O_3$ at 775 K, (d) $\alpha$-$Fe_2O_3 + SnO_2$ at 775 K, (e) $\alpha$-$Mn_2O_3 + SnO_2$ at 775 K, (f) $\alpha$-$Fe_2O_3 + SnO_2$ at 1075 K and (g) $\alpha$-$Mn_2O_3 + SnO_2$ at 1075 K.

des of these systems and the observed values of initiation temperatures $T_i$. The observed catalytic behaviour of the individual oxides is also consistent with the values of $\Delta G$ reported [7] for the reduction of these cations due to loss of oxygen. The values of $\Delta G$, at 550 K which is in the region of CO oxidation temperature, for the individual oxides are

$$3Mn_2O_3 \rightarrow 2Mn_3O_4 + \tfrac{1}{2}O_2 \quad \Delta G = 13.753 \text{ kcal/mol}$$

$$3Fe_2O_3 \rightarrow 2Fe_3O_4 + \tfrac{1}{2}O_2 \quad \Delta G = 41.466 \text{ kcal/mol}$$

$$SnO_2 \rightarrow SnO + \tfrac{1}{2}O_2 \quad \Delta G = 57.746 \text{ kcal/mol}.$$

Based on X-ray diffraction and Mössbauer results reported here, it is clear that the synergism observed during CO oxidation over the surface of $(Mn_2O_3 + SnO_2)$ is not arising due to the formation of any new compound between the constituent oxides or the existence of a phase transformation. Hence, the remote control mechanism seems to be the most probable cause of observed synergism in presence of oxygen. Based on these results it may be inferred that the first step of the mechanism of CO oxidation over the mixed oxide $(SnO_2 + Mn_2O_3)$ is the reduction of $Mn^{3+}$ to $Mn^{2+}$. As the metal ion–oxygen bond strengths for $Mn^{3+}$–$O^{2-}$ and $Sn^{4+}$–$O^{2-}$ are 97 and 133 kcal/mol respectively [9], the breaking of the $Mn^{3+}$–$O^{2-}$ bond is favoured as compared to that of $Sn^{4+}$–$O^{2-}$. Further, the reoxidation of $Mn^{2+}$ to $Mn^{2+}$ is difficult due to the larger negative potential value; the direct oxidation with gaseous oxygen is difficult. Therefore the donation of oxygen from $Sn^{4+}$ to $Mn^{2+}$ takes place and $Sn^{4+}$ gets reduced to the $Sn^{2+}$ state. The oxidation of this $Sn^{2+}$ state is relatively easier because of the lower negative potential value as compared to that of $Mn^{2+}$ oxidation. Hence, tin cations act as oxygen carrier in the mixed system and thus a synergistic effect is observed:

$$CO + 2Mn^{3+}O^{2-} \rightarrow CO_2 + 2Mn^{2+}$$

$$2Mn^{2+} + Sn^{4+}O^{2-} \rightarrow 2Mn^{3+}O^{2-} + Sn^{2+}$$

$$O + Sn^{2+} \rightarrow Sn^{4+}O^{2-}$$

$$\overline{CO + O \rightarrow CO_2}$$

It may be mentioned that an essentially similar type of mechanism has been reported for the $Fe_2O_3 + Sb_2O_5$ system where antimony cations act as oxygen carrier [5].

In order to further ascertain the synergism between these oxides, the activation energy values for the individual oxides as well as the mixed oxides when $CO + O_2$ mixture or CO alone were used as reactants were calculated from the Arrhenius plots and are given in table 3. The activation energy value obtained for $Mn_2O_3+SnO_2$ is quite low as compared to those of the individual oxides, indicating strong synergism between these two oxides for CO oxidation reaction. Unlike this, for $Fe_2O_3 + SnO_2$, this value is almost the same as that of $Fe_2O_3$ which suggests that a similar synergistic effect is absent for this mixed oxide. The possible reason for not observing synergism in the $(Fe_2O_3 + SnO_2)$ system is the comparable values of $\Delta G$ observed for the loss of oxygen. Further, it is also clear from table 3 that, for $Mn_2O_3$ based catalysts, the activation energy is not affected by the presence of oxygen in the reactant gas mixture thereby implying that CO oxidation is occurring mainly due to the lattice oxygen because of its high degree of lability.

In conclusion it may be mentioned that a strong synergistic effect, during CO oxidation, has been observed for the $(Mn_2O_3 + SnO_2)$ system whereas such an effect is absent for the analogous $(Fe_2O_3 + SnO_2)$ system. The observed synergism for $(Mn_2O_3 + SnO_2)$ is

Table 3
Activation energy values of different oxides and mixed oxides for CO oxidation reaction when CO alone or $CO + O_2$ was used as reactant gas

| Catalyst | Activation energy (kcal/mol) | |
|---|---|---|
| | only CO | $CO + O_2$ |
| $Mn_2O_3$ | 9.1 | 9.8 |
| $SnO_2$ | 16.3 | 11.7 |
| $Fe_2O_3$ | 10.9 | 8.9 |
| $Mn_2O_3 + SnO_2$ | 3.6 | 3.0 |
| $Fe_2O_3 + SnO_2$ | 10.8 | 9.6 |

occurring possibly through a remote control mechanism arising due to the widely different values of $\Delta G$ involved in the reduction of the individual oxides of this mixed oxide system.

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