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CO oxidation over Pd/SnO_2 catalyst

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Abstract

Oxidation of CO over the surface of SnO_2 and Pd/SnO_2 catalysts has been investigated with a view to understand the role of Pd metal particles which are known to improve the catalytic activity. The reaction occurs through the incorporation of lattice oxygen and an oxidized surface of the catalyst facilitates the CO oxidation. For Pd/SnO_2 significant CO oxidation occurs even at room temperature as monitored by CO pulse injection technique. Disproportionation of CO into CO_2 and carbon has been observed in the region $350\ K \leq T \leq 425\ K$. From ^{119}Sn Mössbauer investigations the existence of Sn^{2+} species in the support matrix has been observed and its extent is affected by Pd incorporation. The effect of oxygen and/or hydrogen pretreatment of Pd/SnO_2 catalyst at different temperatures on its catalytic activity has been discussed.

Key words: carbon monoxide; oxidation; palladium; stannia; supported catalyst

Introduction

Low temperature catalytic oxidation of CO has attracted the attention of a large number of research workers because of its significance in closed-cycle CO_2 lasers and environmental pollution control processes as is apparent from the number of review articles [1–8] published during the past few years and a variety of reaction mechanisms proposed by different authors. Generally the oxides having variable oxidation state of metal ions, with and without impregnation of noble metal (such as Pd, Pt, Au, etc.), have been found to be active catalysts for this reaction. For oxides, without impregnation of noble metal, CO oxidation occurs through redox mechanism and lattice oxygen incorporation takes place during CO oxidation and the reduced surface of metal oxide is rejuvenated by taking oxygen from the feed mixture. For noble metal incorporated oxide catalysts, the CO oxidation occurs at relatively lower temperatures and a variety of suggestions have been made to explain this enhancement in catalytic activity at relatively lower temperatures, such as: (i) the activation of both CO and oxygen over the metal surface and spillover of these activated

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species to the support oxide [9]; (ii) the energy released during the chemisorption of CO and oxygen over the metal sites may give rise to localized temperature increase and thereby enhance the catalytic activity as reported for Pd supported on non-reducible oxides like SiO_2, Al_2O_3, MgO, etc. [10, 11]; (iii) disproportionation of CO to carbon and CO_2 on particles of metal [12–15]; (iv) recombination of chemisorbed CO and atomic oxygen over the surface of the metal [16–18]; and (v) the reaction of chemisorbed atomic or molecular oxygen with the CO molecules present in the gas phase [19–21].

Pd/SnO_2 and Pt/SnO_2 are interesting catalyst systems for CO oxidation because of the synergistic effect [22–24]. The order of the reaction and the apparent activation energy for CO oxidation over Pd/SnO_2 catalyst have been found to be quite different from those observed for polycrystalline Pd (or Pd/SiO_2 and Pd/Al_2O_3) and SnO_2 individually. Bond et al. [9] suggested that the spillover of both CO and atomic oxygen from metal sites to the support SnO_2 is responsible for the enhanced catalytic activity. These authors also suggested that $\simeq 2\%$ Pd concentration is sufficient to cover the entire surface of SnO_2. In contrast Sheintuch et al. [23] in a recent study suggested that the spillover of only CO is responsible for the synergistic effects and oxygen spillover is not consistent with their observations. Matolin et al. [25] on the other hand, have provided evidence for the partial disproportionation of CO on the surface of unsupported Pd and the formation of surface carbon as an intermediate species during the steady state CO oxidation process. The role of surface hydroxyl species during CO oxidation also has been emphasized by some authors [26, 27]. On the basis of microcalorimetry measurements Gangal et al. [28] have suggested that lattice oxygen plays an important role at all temperatures of reaction and the localized heat produced in the vicinity of metal sites due to chemisorption of the gases enhances the yield of CO_2 over Pt/SnO_2 catalyst. Thus there is some controversy about the mechanism of CO oxidation over Pt or Pd/SnO_2 and further investigations are desirable.

In the present communication we report the CO oxidation results on SnO_2 and Pd/SnO_2 catalyst samples which provide direct evidence for the lattice oxygen incorporation during CO oxidation over both SnO_2 and Pd/SnO_2 and the disproportionation of CO over the metal surface of Pd/SnO_2 catalyst even at less than 375 K.

Experimental

SnO_2 gel was prepared by precipitating hydrous tin oxide from $SnCl_4$ solution at 275 K using aqueous ammonia. The precipitated gel was washed and centrifuged repeatedly and finally dried at room temperature. The material thus obtained was redispersed in water to break large granules, filtered and again dried at room temperature followed by heating at 475 K. The powder X-ray diffraction pattern of the sample was found to be characteristic of tetragonal rutile structure with very broad diffraction peaks due to poor crystallinity. The 40–80 mesh fraction of SnO_2 particles having a surface area of $\simeq 150$ $m^2\ g^{-1}$ was used to impregnate 2% (by weight) palladium on its surface using $PdCl_2$ solution. The impregnated sample was dried at $\simeq 425$ K. The impregnated palladium chloride was reduced to palladium metal by heating in flowing hydrogen gas at 375 K for 2 h in-situ before the CO oxidation experiments. The catalytic reaction was carried out using pulse injection method after giving the desired pretreatment to 0.5 g catalyst placed in the tubular stainless steel reactor with 0.4 mm i.d. The effluent gases were analyzed by gas chromatography on a Porapak Q column using thermal conductivity detector. One of the following pretreatments was carried out on the catalyst: (i) heating at 625 K for 2 h in helium flow; (ii) heating at 625 K for 2 h in oxygen flow, followed by heating in helium at 625 K for 2 h to remove the adsorbed oxygen; or (iii) heating in hydrogen flow at 525 K for 2 h, followed by heating in helium at 625 K for 2 h to remove the chemisorbed hydrogen from metal surface. After such pretreatments, the catalyst sample was cooled to room temperature in helium stream. The CO oxidation reaction was carried out at variable temperatures by injecting 100 μl pulse of either CO or $(CO+O_2)$ (1:1) gas mixture under helium flow of 30 ml min^{-1}.

The catalyst samples were characterized by powder X-ray diffraction (XRD) and ^{119}Sn Mössbauer spectroscopy to monitor the changes in crystallinity and oxidation state of Sn during the catalytic reaction. ^{119}Sn Mössbauer spectra were recorded in an in situ cell at room temperature after different pretreatments. The source used was $Ba^{119}SnO_3$ and the absorber contained approximately 0.5 mg $^{119}Sn/cm^2$. These spectra were fitted by least squares using Lorentzian line shape to get the values of various Mössbauer parameters and to infer about the nature of the catalyst.

Results

Figure 1 shows the results of CO oxidation over the surface of plain SnO_2 catalyst after treating it in helium or oxygen at 625 K for 2 h when 100 μl pulses of either CO or $(CO+O_2)$ had been injected over the surface of the catalyst at variable temperatures. From this figure, three important inferences can be drawn: (i) There is no adsorption or chemisorption of unreacted CO over the surface of SnO_2 catalyst at reaction temperature ($450\ K \leq T \leq 775\ K$) as can be seen from Fig. 1 (b, b′, c and c′). (ii) The lattice oxygen is being used for CO oxidation as is apparent from complete conversion of CO to CO_2 (Fig. 1 (b and c)). (iii) Pretreatment of the catalyst by oxygen or addition of oxygen to the reaction gas mixture facilitates the oxidation of CO to CO_2 over the surface of SnO_2 as can be seen from the "lit-off" temperature of the reaction in Fig. 1 (a, b and c).

Figure 2 shows the results of CO oxidation over the surface of Pd/SnO_2

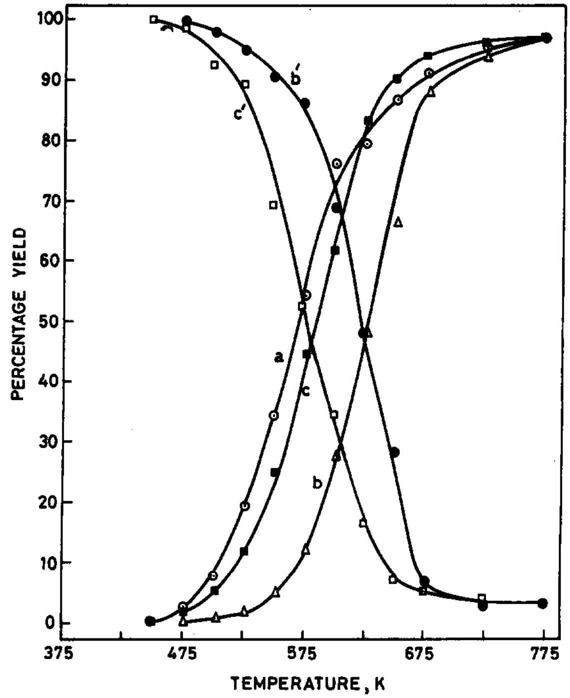

Fig. 1. Percentage yield of CO_2 over the surface of SnO_2, heated in helium at 625 K for 2 h when (a) $(CO+O_2)$ pulses were injected, (b) CO pulses were injected, and (c) CO pulses were injected over the surface of SnO_2 pretreated with oxygen (625 K, 2 h). The yields of unreacted CO corresponding to (b) and (c) are shown in (b′) and (c′).

catalyst after different types of pretreatments have been given to the catalyst. One of the important features of these curves is that in the region 350–425 K there is a clear discontinuity and decrease in the yield of CO_2 with increasing temperature of reaction, when pulses of CO or $(CO+O_2)$ have been injected over Pd/SnO_2 catalyst pretreated either in helium or oxygen followed by heating in helium. Such a clear discontinuity in the yield of CO_2 has not been reported earlier for Pd/SnO_2 or Pt/SnO_2 catalyst. Further, at lower temperatures, the total amount of CO_2 and unreacted CO eluted is not commensurate with the amount of CO injected over the catalyst as can be seen from Fig. 2 (b, b′, c and c′). Pd/SnO_2 catalyst was found to work at much lower temperature as compared to what has been observed for SnO_2. From the comparison of Fig. 2 (b, b′, and c, c′) it is observed that the oxygen pretreatment not only improved the yield of CO_2 but also the evolved unreacted CO was found to be more than that observed for the Pd/SnO_2 catalyst heated in helium alone. Figure 2(d) shows the percentage yield of CO_2 when 100 μl pulses of $(CO+O_2)$ mixture were injected over the Pd/SnO_2 catalyst which has been first heated in oxygen at 625 K for 2 h followed by sequential heating in hydrogen (at 525

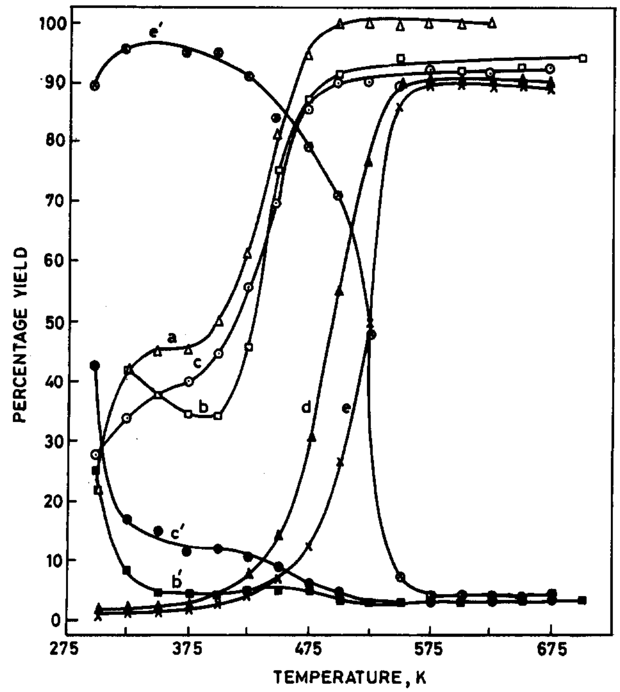

Fig. 2. Percentage yield of CO_2 when either CO or ($CO+O_2$) pulses were injected over the surface of Pd/SnO_2 after carrying out the following treatments in sequence. (a) Helium at 625 K for 2 h and ($CO+O_2$) pulses, (b) helium at 625 K for 2 h and CO pulses, (c) oxygen at 625 K for 2 h and CO pulses, (d) hydrogen at 525 K for 2 h and ($CO+O_2$) pulses, (e) hydrogen at 525 K for 2 h and CO pulses. The yield of unreacted CO corresponding to (b), (c), and (e) are shown in (b'), (c') and (e').

K for 2 h) and helium (at 625 K for 2 h) and cooled to room temperature in flowing helium. Fig. 2 (e and e') show the percentage yield of CO_2 and unreacted CO over the same catalyst as in Fig. 2(d) when only CO pulses were injected over the catalyst. Thus the behaviour of hydrogen treated catalyst sample is quite different from that observed for helium or oxygen pretreated catalyst. This observation is quite surprising as the hydrogen pretreatment is expected to generate clean Pd metal surface over which the chemisorption and disproportionation of CO should be enhanced and the discontinuity observed in the yield of CO_2 (viz. Fig. 2 (a, b and c)), should have been more pronounced. Like plain SnO_2, here also lattice oxygen is being incorporated during CO oxidation as can be seen from Fig. 2(e) where only CO pulses have been injected over the reduced catalyst and complete conversion of CO to CO_2 has been observed. Similarly the presence of oxygen in the reactant gas mixture or an oxidized surface of Pd/SnO_2 catalyst is found to facilitate the CO oxidation.

As the hydrogen pretreated Pd/SnO_2 catalyst behaved in a different manner for CO oxidation, detailed experiments were carried out for Pd/SnO_2 catalyst after heating it in hydrogen at different temperatures between 375 to 525 K for a fixed duration of two hours. Figure 3 shows the results of percentage yield of CO_2 and unreacted CO when 100 μl pulses of CO have been injected at variable temperatures. A clear discontinuity in the yield of CO_2 is observed for the catalyst sample pretreated in hydrogen at different temperatures. Further, the temperature region of the observed discontinuity in CO_2 yield is almost unaffected by hydrogen reduction of the catalyst at different temperatures. Heating Pd/SnO_2 catalyst at higher temperature in hydrogen was found to slightly reduce the catalytic activity. Analysis of these data suggest that at lower temperatures there is imbalance in the amount of CO injected and eluted CO and CO_2. These results are different from what has been shown in Fig. 2 (e and e′). The possible reason for this could be the oxygen pretreatment given to the catalyst sample of Fig. 2 (d and e). In order to ascertain the role of oxygen pretreatment, Pd/SnO_2 was first heated in oxygen (625 K, 2 h) followed by heating in helium at the same temperature for 2 h and cooled to room temperature and its catalytic activity was measured (Fig. 4(a)). The same catalyst was further heated in hydrogen (525 K, 2 h) and helium (625 K, 2 h) and cooled to room temperature in helium. The observed activity for CO oxi-

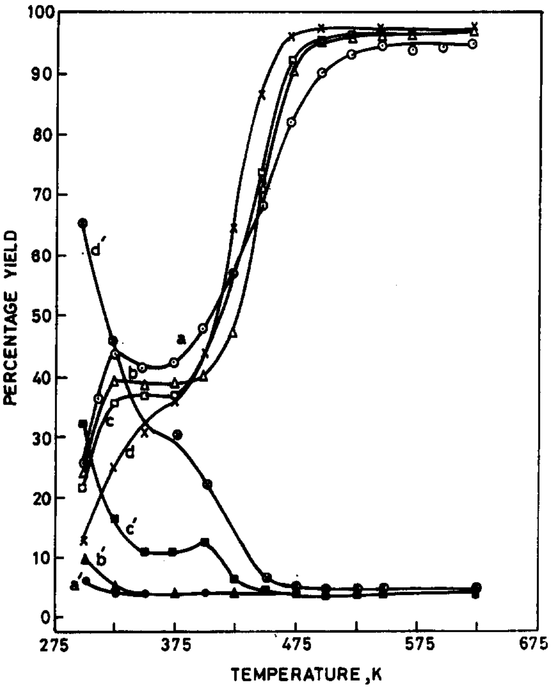

Fig. 3. Percentage yield of CO_2 when only CO pulses were injected over the surface of Pd/SnO_2 after giving hydrogen pretreatments at the following temperatures for 2 h in sequence. (a) At 375 K, (b) at 425 K, (c) at 475 K, and (d) at 525 K. The yield of unreacted CO corresponding to these figures are shown in (a′), (b′), (c′) and (d′).

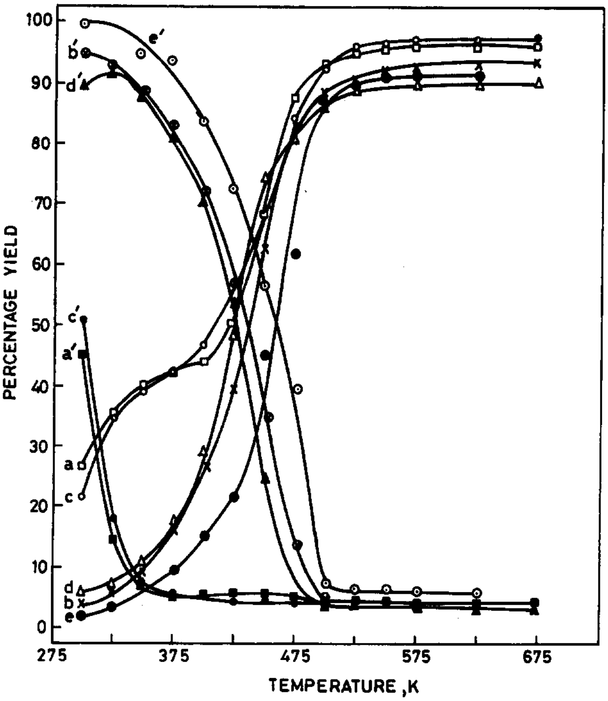

Fig. 4. Percentage yield of CO_2 when only CO pulses were injected over the surface of Pd/SnO_2 after carrying out the following pretreatments for 2 h in sequence. (a) Oxygen at 625 K, (b) hydrogen at 525 K, (c) oxygen at 625 K, (d) hydrogen at 525 K and (e) oxygen at 625 K followed by hydrogen at 525 K pretreatments of fresh Pd/SnO_2 catalyst. The yield of unreacted CO corresponding to these figures are shown in (a′), (b′), (c′), (d′) and (e′).

dation, after this pretreatment is shown in Fig. 4(b). Comparison of these two curves shows that the oxygen pretreatment followed by hydrogen pretreatment significantly affects catalytic behaviour. The results of Fig. 4(b) are quite similar to what has been reported in Fig. 2(e) under identical conditions. The results of repeated pretreatments in oxygen and hydrogen were found to be quite reproducible as can be seen from Fig. 4 where the results of the yield of CO_2 and the amount of unreacted CO are plotted. In order to further substantiate these observations, a fresh catalyst sample generated by heating in hydrogen at 375 K for 2 h was pretreated sequentially with oxygen and hydrogen similarly to that described above and the results of its catalytic activity for CO oxidation are plotted in Fig. 4(e) which are qualitatively similar to what is observed in Fig. 4(b) and (d) where the hydrogen pretreatment was carried out at 525 K.

In order to ascertain the formation of active carbon over the surface of Pd/SnO_2 catalyst due to CO disproportionation at lower temperature, another set of experiments were carried out from 300 K to 475 K, in which after each CO pulse injection and subsequent to the elution of unreacted CO and product

CO_2, 80 μl pulses of oxygen were injected and the yield of CO_2 was monitored. The results of these experiments are presented in Fig. 5, which clearly establishes the formation of CO_2 between 375 K and 425 K and beyond this temperature the formation of CO_2 could not be seen after the injection of oxygen pulses.

Figure 6 shows the ^{119}Sn Mössbauer spectra of the catalyst samples with and without Pd metal impregnation pretreated under reducing conditions by heating the samples in flowing hydrogen or CO for three hours each at 475 K. The unresolved quadrupole doublet shown in Fig. 6(a) corresponds to SnO_2 gel and is characterized by an isomeric shift $\delta = 0.0$ mm s^{-1} and quadrupole splitting $\Delta E_q = 0.69$ mm s^{-1}. These values are in good agreement with what has been reported earlier for SnO_2 catalyst samples [29]. Heating this sample in a reducing atmosphere of CO or hydrogen at 475 K for 3 h has resulted in the formation of Sn^{2+} species characterized by $\delta = 1.9$ mm s^{-1} and $\Delta E_q = 3.0$ mm s^{-1} which are characteristic of SnO [30] present on the surface of these samples. From this figure, it is also clear that Pd incorporation has facilitated the reaction of SnO_2 and the amount of Sn^{2+} formed is more than that observed for plain SnO_2. In contrast, the Mössbauer spectra of the sample heated in the

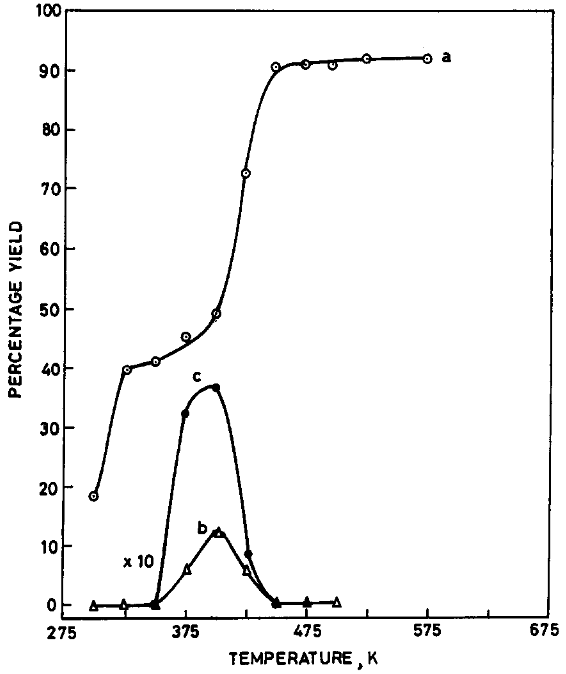

Fig. 5. (a) Percentage yield of CO_2 when only CO pulses were injected over Pd/SnO_2 catalyst pretreated in hydrogen at 425 K for 2 h. (b) The yield of CO_2 on injection of oxygen pulse after elution of CO_2 and unreacted CO. (c) The cumulative amount of CO_2 obtained when five pulses of oxygen were successively injected at a particular temperature.

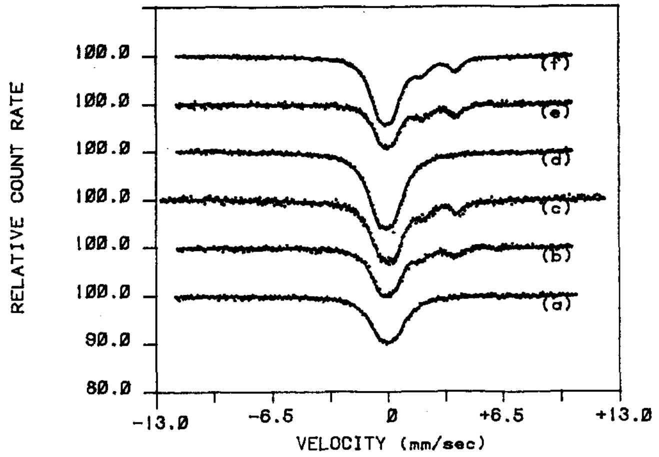

Fig. 6. ^{119}Sn Mössbauer spectra of (a) SnO_2 gel, (b) SnO_2 exposed to CO at 475 K for 3 h, (c) SnO_2 exposed to hydrogen at 475 K for 3 h, (d) SnO_2 exposed to $(CO+O_2)$ (1:1) mixture at 475 K for 3 h, (e) Pd/SnO_2 exposed to CO at 475 K for 3 h, and (f) Pd/SnO_2 exposed to hydrogen at 475 K for 3 h.

$(CO+O_2)$ mixture, did not show the formation of Sn^{2+} species as can be seen from Fig. 6(d). It may be mentioned that the powder X-ray diffraction pattern of these reduced samples did not show any change because of their surface nature.

Discussion

CO oxidation over SnO_2

A number of reducible oxides have been used for CO oxidation due to the presence of labile oxygen and SnO_2 is one such system for which a number of experiments have already been reported. From the results presented in this study it is clear that when a pulse of $(CO+O_2)$ is injected over the surface of SnO_2, the CO oxidation initiates at $\simeq 475$ K and is almost complete by $\simeq 650$ K (viz. Fig. 1(a)). In contrast, when only CO pulse has been injected, the CO oxidation although complete, occurs at a relatively higher temperature. A preoxidized surface of SnO_2 is found to facilitate CO oxidation. These results suggest that CO oxidation occurs through lattice oxygen abstraction and oxygen present in the feed mixture is used for the oxidation of the reduced catalyst surface. Thus the reaction involves two steps and oxygen withdrawal from the catalyst appears to be the rate determining step as suggested by Boreskov [6]. Mössbauer studies carried out on SnO_2 sample used for continuous flow experiments conducted with CO gas, showed the presence of Sn^{2+} which was absent for the sample treated with $(CO+O_2)$ gas (Fig. 6(b) and (d)). This provides direct evidence for the mechanism suggested. Since the oxidation of

of oxygen in the feed mixture or subsequent injection of oxygen transforms the carbon into CO_2 at slightly higher temperatures (Fig. 5(b), and $350\ K < T < 450\ K$). The CO_2 formed on injection of the oxygen pulse is only due to reaction of carbon with oxygen and not due to the reaction of chemisorbed CO and oxygen. This is supported by the fact that the $(CO+O_2)$ mixture when injected over Pd/SnO_2 catalyst, produces finite CO_2 even at room temperature, thereby suggesting that the chemisorbed CO, if any, would have produced CO_2 on oxygen injection at room temperature. Since we observed CO_2 formation only above 350 K, confirms the deposition of carbon on palladium sites and the disproportionation mechanism. At higher temperatures, the direct reaction of CO with lattice oxygen of SnO_2, becomes operative and is the most prominent mode of CO oxidation. As a result, the CO_2 yield shows a sharp increase above 450 K. This is further supported from the appearance of Sn^{2+} species in the Mössbauer spectra of SnO_2 and Pd/SnO_2 catalyst samples which were treated in CO at this temperature ($\simeq 475$ K) for 3 h. Further, the observation of enhanced Sn^{2+} for Pd containing catalyst as compared to SnO_2, provides clear evidence for the spillover of activated CO from Pd centers to the support oxide and its subsequent reaction with lattice oxygen to produce Sn^{2+} species. The presence of oxygen in the reactant gas mixture rejuvenates the oxygen-depleted catalyst. The addition of oxygen to the CO pulse or the pretreatment of the catalyst with oxygen did not prevent the disproportionation of CO over the Pd surface, as can be seen from Fig. 2(a) and (c) where the decrease in CO_2 yield is still seen although its magnitude is less than that in Fig. 2(b). This implies that the chemisorption of CO over Pd sites is preferential compared to oxygen. The pretreatment of Pd/SnO_2 catalyst in hydrogen at different temperatures did not affect the observed decrease in CO_2 yield at $\simeq 350$ K to 375 K as can be seen from Figs. 3 and 5. The yield of CO_2 in the high temperature region is not significantly affected by hydrogen pretreatment of the catalyst sample at $375\ K \leq T \leq 525\ K$ because of the availability of lattice oxygen by partial reduction of SnO_2. However, when Pd/SnO_2 was pretreated in hydrogen at 625 K, there was no yield of CO_2 as the SnO_2 is completely reduced to metallic state and forms an alloy with Pd metal.

The observed reduction in the catalytic activity of Pd/SnO_2, after the sequential pretreatment in oxygen and hydrogen, compared to that observed for the hydrogen and oxygen treatment alone, is an important result and can be understood in terms of blockages of Pd sites due to the formation of -OH species at the Pd sites and in its vicinity which affects the CO adsorption and its spillover. During oxygen pretreatment of the catalyst, PdO_x species are formed on the surface which, owing to partial reduction in subsequent hydrogen treatment, produce -OH species at Pd centers.

In conclusion, we would like to mention that in the present communication, we have reported the results of CO oxidation over the surface of Pd/SnO_2 which clearly establish the spillover of activated CO from Pd centers to the support and abstraction of lattice oxygen for CO oxidation. The results have also provided clear evidence for CO disproportionation over Pd surface to produce CO_2 and active carbon. A comparison of the Mössbauer spectra of Pd/SnO_2 and SnO_2 samples treated in CO, provided direct evidence for the reduction of SnO_2 support due to the reaction of the spilled over activated carbon monoxide with lattice oxygen. The reduced activity for Pd/SnO_2 catalyst sample when sequentially heated in oxygen and hydrogen, is understood in terms of the blockage of Pd sites by –OH species formed during partial reduction of PdO_x species.

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