

A Proposed Mechanism for Pt/SnO_x-Catalyzed CO Oxidation

CO oxidation catalysts with high activity at or near room temperature are useful for several applications including closed-cycle CO₂ lasers and air purification (1). One such catalyst that has been extensively studied is platinumized tin oxide (Pt/SnO_x) (2). Although much is still uncertain or ambiguous and much else is still unknown, it is now possible to propose a mechanism for Pt/SnO_x-catalyzed CO oxidation which is consistent with a broad range of experimental observations.

Platinumized tin oxide has significantly higher catalytic activity for CO oxidation at low temperatures than does either Pt or SnO_x alone (3). The effect is clearly synergistic and apparently involves separate but complementary roles for the Pt and Sn components. The activity for CO oxidation of Pt/SnO_x catalysts increases with Pt loading until a maximum activity is reached at about 17% Pt by weight (4). A reductive pretreatment enhances the activity of Pt/SnO_x catalysts relative to no pretreatment or to pretreatment with O₂ or an inert gas (5). Both CO and H₂ are suitable gases for reductive pretreatment. Duration of the pretreatment can affect subsequent catalyst activity (5). For optimum results the effluent gases from the pretreatment should be analyzed and the pretreatment terminated when no additional significant yield of oxidation product gas (CO₂ or H₂O) is detected.

The temperature at which a Pt/SnO_x catalyst is pretreated can also affect its subsequent activity (5). Pretreatment at elevated temperatures may result in an initial dip in catalyst activity before the steady-state activity is achieved (5). If the catalyst is exposed to water vapor following pretreatment but prior to exposure to the reaction gas mixture, or if the reaction gas mixture is humidified, no initial dip in activity occurs

(5). In many cases water vapor not only eliminates the initial dip in catalyst activity, it also enhances the activity of the catalyst (5). In fact, addition of water vapor has been shown to increase the activity of an unpretreated Pt/SnO_x catalyst (2). This is believed to be due to conversion of surface oxides to more active surface hydroxyls.

The activity of Pt/SnO_x catalysts exhibits fairly rapid decay with time; the activity loss typically is a factor of 2 or more (2). Initial activity can be readily restored by outgassing the catalyst either by heating it or by exposing it to a vacuum or to an inert gas flow (2). In either case, restoration of activity is found to be associated with outgassing of CO₂ from the catalyst. Decay in activity occurs again when CO oxidation is resumed (2). An additional long-term decay which is not associated with CO₂ retention has also been observed. This decay is reversible by reduction of the catalyst (2).

The yield of CO₂ for a given catalyst sample and set of reaction conditions is increased by addition of O₂ to a stoichiometric CO-O₂ mixture and decreased by addition of CO to such a mixture (2). The reaction has been found to be approximately first order with respect to O₂ concentration. No simple reaction order has been found for CO and the true rate equation appears to be somewhat complex (2).

Reaction of C¹⁸O and ¹⁸O₂ on a common-isotope Pt/Sn¹⁶O₂ catalyst yields predominantly C¹⁸O₂ with only a small quantity of C¹⁸O¹⁶O. This indicates that the gaseous CO and O₂ chemisorb on the catalyst surface and react there in preference to reaction of chemisorbed CO with oxygen from the catalyst followed by reoxidation of the catalyst (6).

An unsupported commercial Pt/SnO_x cata-

lyst has been examined both unpretreated and pretreated with CO using ion scattering spectroscopy (ISS), Auger electron spectroscopy (AES), and electron spectroscopy for chemical analysis (ESCA). Following pretreatment, the O/Sn ratio is decreased, the platinum oxides are reduced to $\text{Pt}(\text{OH})_2$ and Pt, the surface hydroxyl group concentration is decreased, and a Pt/Sn alloy forms (7).

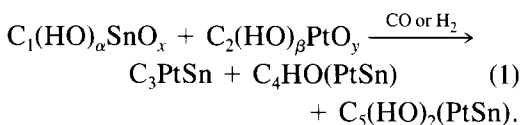
The experimental observations summarized above suggest the postulate that surface OH groups participate in the oxidation of CO chemisorbed on Pt sites. Although reductive pretreatment of the catalyst enhances its activity, pretreatment at elevated temperatures also dehydrates the catalyst surface and thereby may deplete the surface concentration of OH (8). The initial reaction which occurs when the catalyst is exposed to the test-gas mixture further depletes the surface concentration of OH and partially reoxidizes the surface. This results in the observed decline in catalyst activity. Rehydroxylation of the surface, probably by migration of H (or H^+) from the catalyst sub-surface, eventually restores the catalyst activity. The sequential decline and increase in catalyst activity result in the observed dip. If the OH concentration at the catalyst surface is restored by humidification of either the catalyst or the reaction gas, no dip is observed. Humidification of the catalyst surface may increase the OH concentration above the initial value and the activity of the catalyst may then be enhanced as reported in Ref. (2).

Two reaction pathways apparently occur simultaneously. In one reaction, CO chemisorbed on Pt reacts with an adjacent hydroxyl group to form CO_2 (possibly through a formate intermediate) which rapidly desorbs and escapes into the gas phase. In the other reaction, chemisorbed CO reacts with two adjacent hydroxyl groups to form a bicarbonate. This bicarbonate eventually undergoes decomposition, but until such decomposition occurs the bicarbonate species ties up OH sites and, thus, contributes to the observed decay in catalyst activity. Out-

gassing of CO_2 from the bicarbonate restores the catalyst activity.

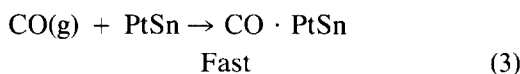
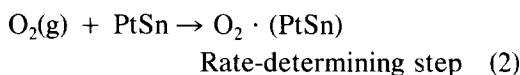
A reaction set which represents the foregoing proposed mechanism is

Pretreatment



The surface of the "tin oxide" and "platinum" phases of platinized tin oxide consists of complex hydroxy oxides which are represented here as $(\text{HO})_\alpha\text{SnO}_x$ and $(\text{HO})_\beta\text{PtO}_y$, respectively. Following reduction some metallic Pt and Sn are formed which are present predominantly as a PtSn alloy with some surface hydroxyl groups (7). Note that the alloy is represented herein by the formula PtSn although this may not indicate its true composition. Note also that when a given ligand may be attached to either a Pt or an Sn atom of the alloy, or both, or when it is not known to which atom it is attached, parentheses are used, e.g., $\text{HO}(\text{PtSn})$. The coefficients in Eq. (1) depend upon the composition of the alloy and the relative yield of the product species.

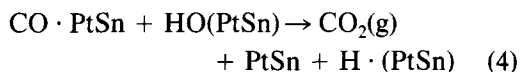
Chemisorption



CO chemisorbs readily on Pt but does not chemisorb on Sn; O_2 chemisorbs on both Pt and Sn (9), but its sticking coefficient on Pt is very low. It is assumed herein that these qualitative statements about the chemisorption properties of Pt and Sn are also true for these species in the PtSn alloy. This has been demonstrated experimentally in the case of O_2 (10) and is assumed to be so in the case of CO. A Pt surface exposed to a mixture of CO and O_2 at room temperature chemisorbs CO almost exclusively due to

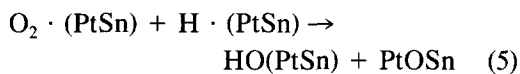
the low sticking coefficient of O_2 and the fact that each O_2 molecule requires a pair of adjacent vacant surface sites for chemisorption whereas CO molecules require only individual vacant sites (11). The presence of Sn atoms in the PtSn alloy component of a prerduced platinumized tin oxide catalyst significantly alters this situation. Each Pt atom on the PtSn alloy surface is adjacent to one or more Sn atoms which can chemisorb O_2 but not CO. This allows O_2 molecules to compete with CO molecules for chemisorption on vacant Pt atoms since adjacent Sn atoms provide the necessary second sites; adjacent Pt vacancies are not required as they would be if Sn atoms were not present. However, due to the low sticking coefficient of O_2 on Pt, surface coverage by CO still greatly exceeds that by O_2 for CO: O_2 ratios near stoichiometry. In fact, chemisorption of O_2 appears to be the rate-limiting step of this reaction set.

CO Oxidation

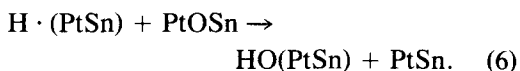


It is proposed that chemisorbed CO is oxidized predominantly by surface hydroxyls rather than by oxygen atoms. This is analogous to the situation in the gas-phase oxidation of CO (11, 12) and is consistent with the experimental results summarized herein.

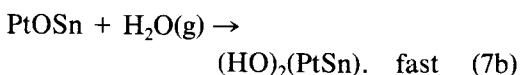
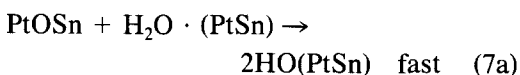
Surface Rehydroxylation



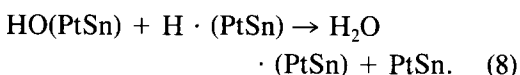
Although the oxidizing species, $HO(PtSn)$, is regenerated by reaction (5), the surface is also oxidized to $PtOSn$ by this step and, thus, partially deactivated. This may be the cause of the downward portion of the initial dip in activity when the catalyst has been dehydrated during pretreatment. It is possible that surface oxidation can be partially undone by



However, the experimental data suggest that conversion of surface oxide to surface hydroxyl is most readily accomplished by reaction with water:



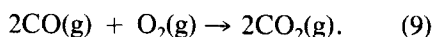
Although water may conceivably migrate from the catalyst subsurface to the surface to allow the catalyst to come out of the initial dip in activity via reaction (7a), it is more likely that the migrating species is H (or H^+) yielding surface H_2O via



Of course, if gaseous water is supplied continuously by humidifying the reaction gas mixture, OH groups are continuously regenerated by reaction (7b) and no dip in activity occurs. In this case, the activity of the catalyst may be enhanced, as observed experimentally (2), due to an increase in the concentration of surface hydroxyl groups.

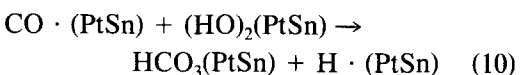
Steady-State Catalytic Cycle

The sum of reactions (2)–(5), (7a), and (8), with the appropriate coefficients, i.e., (2) + $2x(3)$ + $2x(4)$ + (5) + (7a) + (8), yields the overall reaction



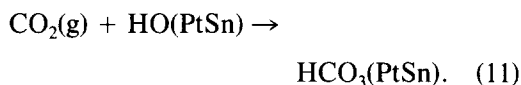
Therefore, these reactions, in theory, constitute a complete catalytic cycle for the steady-state Pt/SnO_x-catalyzed oxidation of CO to CO₂ by O₂.

Bicarbonate Formation and Decomposition



Although the oxidation of chemisorbed CO normally proceeds with the immediate release of CO₂(g), as in reaction (4), bicarbonate formation can occur when two OH groups are adjacent to a chemisorbed CO,

as in reaction (10). It is not known whether the bicarbonate group is on a Pt or an Sn site, or both, since either would effectively deactivate the catalyst. It is possible that bicarbonate formation can occur by reaction of surface hydroxyl species with gaseous CO₂:



It is not yet known whether bicarbonate decomposition is thermal or caused by reaction with surface hydrogen. Nevertheless, it is clear that a steady state eventually is attained in which bicarbonate is formed at the same rate at which it is decomposed. This steady state then limits the effective activity of the catalyst to a value less than its activity if no bicarbonate buildup occurred. In addition to the fairly rapid loss of activity due to bicarbonate buildup, a slow morphological change further deactivates the catalyst with a half-life of several months. This is probably due to coverage of alloy Pt atoms by Sn in the presence of O₂. (13).

The foregoing mechanism admittedly is speculative in many ways. Nevertheless, it is consistent with all experimental data currently available and it offers a point of departure for future studies of CO oxidation on Pt/SnO_x-based catalysts.

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