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Influence of an Fe promoter on silica-supported Pt/SnO_x catalysts used for low-temperature CO oxidation

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Silica-supported Pt/SnO_x catalysts used for low-temperature CO oxidation have been prepared without and with an Fe promoter. Reaction studies demonstrate that the addition of the Fe promoter results in higher catalytic activity in the presence of 8 at% CO_2 and a lower decay rate. Ion scattering spectroscopy (ISS) has been used to examine the outermost atomic layers of the promoted and nonpromoted catalysts before and after activation by a reductive pretreatment. The nonpromoted catalyst exhibits agglomeration of the platinized tin oxide film exposing the catalytically inactive silica support. This agglomeration does not occur when Fe is present, and a large catalytically active surface area is maintained during the reduction.

Keywords: CO oxidation; platinized tin oxide

1. Introduction

Over the last decade a substantial effort has been made to develop efficient low-temperature CO oxidation catalysts. The primary motivation has been for use in CO_2 lasers to reoxidize CO and O_2 formed in the electric discharge back to CO_2 in order to maintain a high power output [1]. However, these catalysts also will be useful in other applications such as air purification, low-temperature oxidation of hydrocarbons, and gas sensing.

Many different types of catalysts have been prepared and tested over the years for low-temperature CO oxidation. Most of the catalysts that exhibit high activity consist of one or more noble metals dispersed on a reducible oxide support (referred to as NMRO catalysts [2]). Stark and coworkers [3,4] first identified platinized tin oxide as a good catalyst for this application. Since then, there have been many improvements in Pt/SnO_x catalysts that have resulted in higher activities and better aging properties at lower temperatures. A high-purity, commercial 2 wt% Pt/SnO_x catalyst produced by Engelhard has been tested catalytically and characterized using Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS) and ion scattering spectroscopy (ISS) [5]. The effects of varying pretreatment conditions and adding moisture to the reaction gas mixture have been examined for this catalyst [6,7]. Generally, conditions that reduce but do not dehydrate the catalyst surface result in higher activities. This is believed to be due to an increased surface concentration of hydroxyl groups which play an important role in the mechanism [5,8]. In order to further increase the availability of surface hydroxyl groups, a Pt/SnO_x catalyst supported on a hydrated silica support was developed, tested and characterized [9–11]. This catalyst is more active than the Engelhard Pt/SnO_x catalyst [10].

Other types of NMRO catalysts have been prepared and studied by different groups. Haruta and coworkers have found that Au/α-Fe_2O_3 and Au/Co_3O_4 catalysts perform well for low-temperature CO oxidation [12–16]. Gardner et al. [17,18] prepared and tested a large number of NMRO catalysts and found that Au/MnO_x catalysts perform exceedingly well. A comparison of the performance of Au/MnO_x and Pt/SnO_x catalysts was made, and the Au/MnO_x catalysts are clearly superior for a stoichiometric feed containing no CO_2 [19]. Unfortunately, CO_2 is a poison for both Pt/SnO_x and Au/MnO_x catalysts in that it lowers their activities and increases their decay rates.

In this study various promoters including Cr, Sb, P, As and Fe have been added to silica-supported Pt/SnO_x catalysts. These catalysts were then tested to determine if they could counter the influence of CO_2. All of these promoters except Fe resulted in even poorer catalyst performance. The purpose of this paper is to describe the preparation and catalytic behavior of the Fe-promoted, silica-supported Pt/SnO_x catalyst and to provide a comparison with the nonpromoted, silica-supported Pt/SnO_x catalyst and an Au/MnO_x catalyst. Surface characterization studies were also carried out. Ion scattering spectroscopy (ISS) data provide insight into how the presence of Fe improves the performance of silica-supported Pt/SnO_x CO oxidation catalysts in the presence of CO_2. X-ray photoelectron spectroscopy (XPS) data were also collected in this study, but they are quite similar to the XPS data presented in the previous study of silica-supported Pt/SnO_x catalysts [11] so they are not presented here.

2. Experimental

2.1. CATALYST PREPARATION

Silica-supported platinized tin oxide catalysts were prepared by dissolving Sn powder in nitric acid and heating to dryness at 150°C in the presence of deaerated SiO_2 particles. Pt deposition was accomplished by reducing tetraaminoplatinum(II) hydroxide with formic acid in the presence of the deaerated SnO_x/SiO_2 support. The Pt concentration was 11.4 at% based on the Pt and Sn content. The resulting slurry was dried in air at 150°C. In the preparation of the promoted catalyst, $Fe(NO_3)_3$ was added to the impregnating solution such that it was 1 at% of the Pt plus Sn content. The BET surface area was about 157 m^2/g of catalyst.

The Au/MnO_x catalyst [17–19] was prepared by coprecipitation at 70°C from an aqueous solution containing tetrachloroauric acid, manganese(II) nitrate, and sodium carbonate. The Au-to-Mn at ratio was 10%. The precipitate was washed with hot water, dried in air at 110°C, and calcined at 400°C for 4 h. The BET surface area was about 132 m^2/g of catalyst.

2.2. REACTOR EXPERIMENTS

The reactions were carried out in a tubular reactor at 35°C using 250 mg of the silica-supported Pt/SnO_x catalysts. Of this 200 mg was silica. For comparison on a silica-free basis, 50 mg of the Au/MnO_x catalyst was used. The reaction mixture consisted of 1% CO, 0.5% O_2 and 8% CO_2 in He at a flow rate of 10 sccm and 1 atm total pressure. The reaction products were monitored using a gas chromatograph. The experimental procedure varied depending upon whether the catalyst was pretreated or not. The nonpretreated Au/MnO_x catalyst was exposed to 10 sccm of He for 1 h as the reactor temperature stabilized. The pretreated silica-supported Pt/SnO_x catalysts were heated in 10 sccm of pure He as the reactor temperature stabilized at 125°C, exposed to 10 sccm of the pretreatment gas (5 vol% CO in He) for 1 h at 125°C and cooled to 35°C in 10 sccm of He for 1 h. The reaction was begun by switching flow to the reaction mixture at which time product sampling was initiated.

2.3. SURFACE CHARACTERIZATION STUDIES

Surface characterization experiments were performed in an ultrahigh vacuum (UHV) system (base pressure $< 1 \times 10^{-10}$ Torr) containing multiple surface analytical techniques including ISS and XPS. In this study ISS and XPS were performed on the silica-supported Pt/SnO_x and silica-supported Fe-promoted Pt/SnO_x catalysts before and after reduction in 40 Torr of CO at 125°C for 1/2 h in a pretreatment chamber attached to the UHV system. The heater system used for the reductive treatment [20] did not dissociate the CO. The pressed powder samples were moved directly from the pretreatment chamber to the surface analysis chamber without exposure to air. Energy analysis for ISS was accomplished using a Perkin-Elmer PHI model 25-270 double-pass cylindrical mirror analyzer (CMA) with an internal, movable aperture which allowed for variation of the polar acceptance angle in ISS. ISS spectra were collected in the retarding mode using a 147° scattering angle and pulse counting detection [21]. A 100 nA, 1 keV $^4He^+$ primary beam was defocused over a 1 cm^2 area, and spectra collection periods of 90 s were used to minimize sputter damage yet achieve a reasonable signal-to-noise ratio.

3. Results and discussion

The catalytic activities of silica-supported Pt/SnO$_x$ with and without an Fe promoter and Au/MnO$_x$ for CO oxidation at 35°C in the presence of CO$_2$ are shown in fig. 1. The use of the Fe promoter significantly enhances the catalytic activity and lowers the decay rate of silica-supported Pt/SnO$_x$ for the reaction conditions tested. However, if more than 1% Fe is used, the improvement in catalytic performance is lessened, and at large Fe concentrations it behaves as a poison. For example, at 5% Fe the activity curve is similar to that of the nonpromoted catalyst except that it levels off at a value of 10% loss of CO. The activities of all catalysts decay slowly with time, but the activity of the Au/MnO$_x$ catalyst decays more rapidly over the time period tested in fig. 1. The complex decay behavior is composed of multiple processes and probably differs for the two catalysts. For all Pt/SnO$_x$ catalysts buildup of a surface carbonate species is partially responsible for the decay. This loss in activity can be regenerated by heating the catalyst or exposing the catalyst to vacuum to decompose the carbonate species. Evolved CO$_2$ can be observed during this process using a gas chromatograph or a mass spectrometer [7]. A portion of the decay is irreversible with a half life of several months. This may be due to a slow morphological change or enrichment of Sn at the surface.

The data obtained from pretreated, Fe-promoted silica-supported Pt/SnO$_x$ initially go through a dip in activity. The Au/MnO$_x$ and nonpromoted silica-supported Pt/SnO$_x$ data do not exhibit this type of behavior. For the commercially

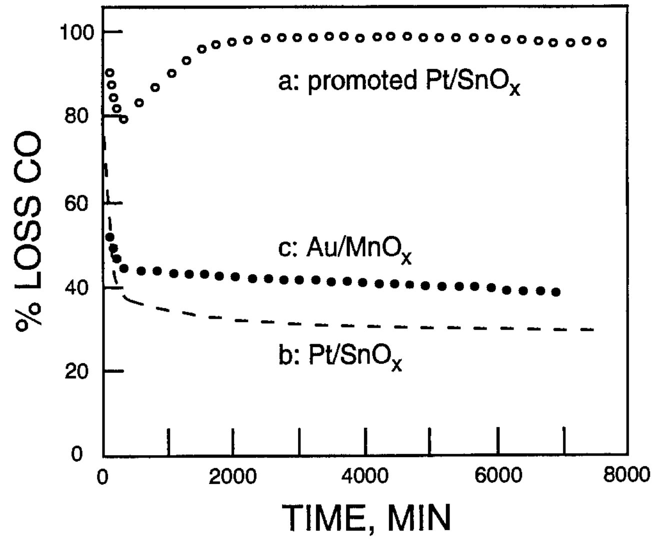

Fig. 1. Catalytic activity of (a) Fe-promoted, silica-supported Pt/SnO$_x$, (b) nonpromoted, silica-supported Pt/SnO$_x$ and (c) Au/MnO$_x$ catalysts. Both silica-supported Pt/SnO$_x$ catalysts were pretreated, and the Au/MnO$_x$ catalyst was not. The feed gas consisted of 10 sccm of 8% CO$_2$, 1% CO and 0.5% O$_2$ in He at 35°C and 1 atm. 50 mg of the Au/MnO$_x$ was used, and 250 mg of the Pt/SnO$_x$ catalysts were used. This 250 mg includes 200 mg of silica support material.

available Pt/SnO$_x$ catalysts, the dip in activity has been shown to be associated with the surface water content and does not appear when moisture is added to the feed gas [6,22]. The reason for the dip in activity of the Fe-promoted, silica-supported Pt/SnO$_x$ has not been investigated yet. The presence of this initial unsteady-state behavior makes it necessary to run the reaction studies long enough to get past the dip in order to assess long-term catalyst performance.

A direct comparison between the Pt/SnO$_x$ and Au/MnO$_x$ catalytic activities is complicated by the fact that the Pt/SnO$_x$ catalysts are supported on silica and this 200 mg is not included in the sample weights for the Pt/SnO$_x$ catalysts. If total weights of 50 mg of each catalyst were used instead of 250 mg for the silica-supported Pt/SnO$_x$ catalysts, the Au/MnO$_x$ catalyst would exhibit higher activity as observed previously without CO$_2$ in the feed gas [19]. A method of obtaining a more direct comparison of activities would be to place the Au/MnO$_x$ on an inactive support with a surface area similar to that of silica, but this has not been done. Furthermore, the silica is not just an inert support because it affects the activity of Pt/SnO$_x$ catalysts.

ISS is capable of providing important information regarding the role of the Fe promoter. Since ISS is sensitive only to the outermost atomic layer of a surface, it probes the region that is most important to catalysis. Therefore, an ISS study of the silica-supported Pt/SnO$_x$ catalysts with and without Fe was carried out before and after reduction of the catalysts. The results are shown in fig. 2 for the catalyst without promoter and in fig. 3 for the promoted catalyst.

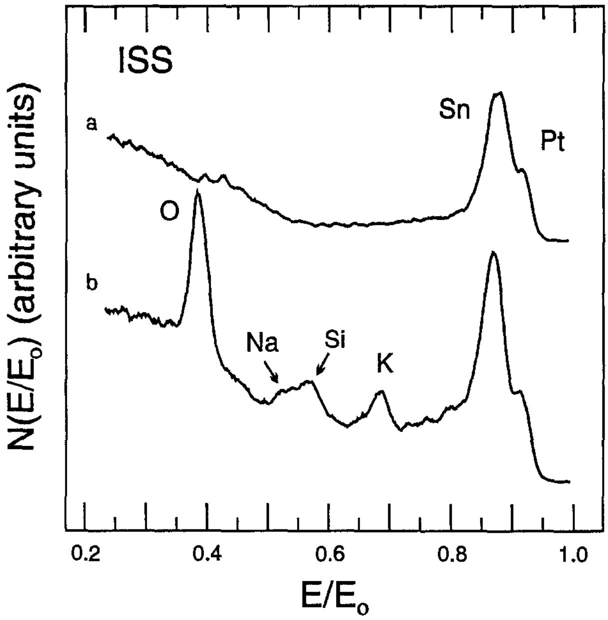

Fig. 2. ISS data obtained from nonpromoted, silica-supported Pt/SnO$_x$ (a) before and (b) after pretreatment in CO at 125°C.

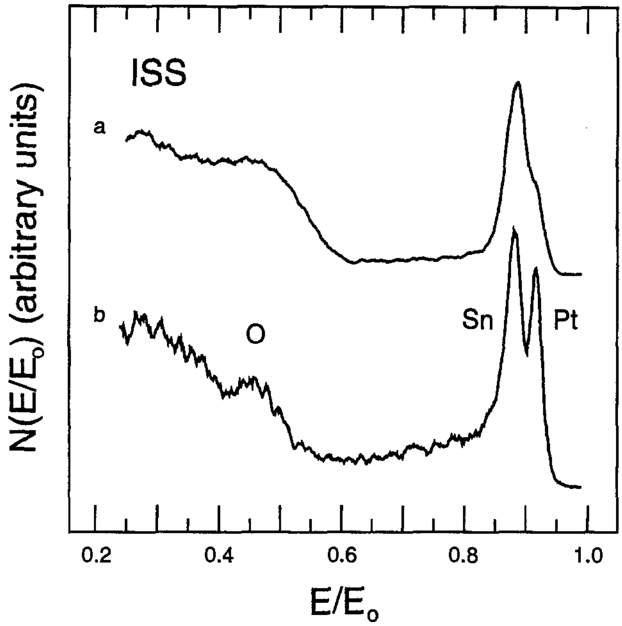

Fig. 3. ISS data obtained from Fe-promoted, silica-supported Pt/SnO$_x$ (a) before and (b) after pretreatment in CO at 125°C.

The ISS spectrum obtained from the as-prepared, silica-supported Pt/SnO$_x$ catalyst in fig. 2a exhibits peaks due to Sn and Pt and a small hump at an E/E_0 of about 0.4 due to O. This spectrum is characteristic of a tin oxide surface that is fairly heavily loaded with Pt [23]. Pretreatment results in significant changes in the ISS spectrum as shown in fig. 2b. The O peak is now very large, and peaks due to Na, K and Si are prominent. The Na and K are impurities in the Si that have been observed in a previous study of these catalysts [11], but the influence of the Na and K on activity has not been investigated. The large O, Na, K and Si peaks result from agglomeration of the Pt/SnO$_x$ overlayer into thicker patches and crystallites which exposes the underlying silica. The large O signal is attributed to oxygen in SiO$_2$ because oxygen-exposed silicon yields a large ISS O feature [24] while oxygen-exposed tin [25] or tin oxide surfaces [26] do not. Some of this surface oxygen is bonded to the Na and K. The Pt feature consists of a shoulder on the Sn peak. After reduction the Sn/Pt peak-height ratio is increased indicating that some of the Pt is covered by Sn (or perhaps Sn oxide) as the surface morphology changes. In a reaction mechanism study of CO oxidation over Pt/SnO$_x$ catalysts [8], arguments based on results of reactor and characterization studies are made that the Pt/Sn alloy surface formed during reduction is the active catalytic surface. The active catalyst sites are believed to consist of neighboring Pt and Sn atoms with an adsorbed hydroxyl group. Even though the loss of catalytically active surface area and the covering of Pt are detrimental effects regarding catalytic activity, the overall influence of reduction is positive due to chemical-state changes of the Pt and Sn induced by pretreatment. The chemical-state changes include reduction of Pt oxides, formation of $Pt(OH)_2$, and reduction of some Sn oxide to Sn metal which forms a Pt/Sn alloy [5,11].

ISS data have been collected from nonpromoted, silica-supported Pt/SnO_x surfaces before and after reduction in a previous study [11]. The catalyst examined in that study contained 19.5 at% Pt so the ISS Pt peak is larger than the ISS Sn peak in that study. Otherwise, similar conclusions can be drawn from the ISS data in that study and this study concerning these similar catalysts.

ISS spectra obtained from the Fe-promoted catalyst before and after reduction are shown in figs. 3a and 3b respectively. Peaks due only to O, Sn and Pt but not Fe are present in these spectra. The low E/E_0 portions of these spectra are large due to charging effects. This high background shifts the O feature from an elastic E/E_0 of 0.39 to about 0.45 as discussed previously [23]. The spectrum shown in fig. 3a is quite similar to the corresponding spectrum obtained from the nonpromoted catalyst (fig. 2a), but there are very large differences between the spectra obtained from the reduced Pt/SnO_x catalysts with and without promoter. In fig. 3b no peaks due to Na, Si or K are apparent indicating that the silica support is not exposed during reduction of the promoted catalyst. The Fe/Pt atom ratio is large enough that a distinct Fe peak would appear at an E/E_0 of 0.76 in the spectra shown in fig. 3 if Fe were located at the surface. This implies that Fe lies beneath the surface and most likely at the silica/platinized SnO_x interface. This important difference between the Fe-promoted and nonpromoted catalysts suggests that the role of the Fe is to provide adhesion between the catalytically active Pt/SnO_x overlayer and the silica so that the Pt/SnO_x does not agglomerate and expose the catalytically inactive silica.

The compositional changes of the outermost atomic layer during reduction are quite different for the promoted catalyst. The O feature is decreased due to reduction of Pt oxides to Pt metal and of Sn oxides to lower oxides and Sn metal. In this case the Pt-to-Sn ratio is increased very significantly as Sn oxide is reduced to Sn metal that alloys with the Pt [23,27]. This exposes more Pt at the surface resulting in a larger catalytically active surface area. A similar increase in the Pt-to-Sn ISS peak-height ratio has been observed during the reduction of a Pt_3Sn alloy [27]. Hence, the catalytically active surface area is greater for the Fe-promoted catalyst which explains its increased activity observed in fig. 1. Furthermore, the lower activity decay rate for the promoted catalyst is also believed to be due to the adhesion behavior of the Fe. The chemical interactions between the Fe, silica and tin oxide which are responsible for the observed differences are not understood and require investigation.

4. Summary

This study demonstrates that the addition of low concentrations of an Fe promoter to silica-supported Pt/SnO_x catalysts improves both their activities and decay rates for the low-temperature CO oxidation in the presence of large amounts of CO_2. ISS data suggest that Fe promoter acts as an adhesive between the silica support and the Pt/SnO$_x$ layer so that the catalytically active area is larger for the promoted catalyst after pretreatment and more resistant toward agglomeration.

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