NOTE

Infrared Study of the Interaction between Tin and Platinum Supported on Alumina

A previous study showed that at metal loadings of 3 wt% platinum and 3 wt% tin, co-impregnated onto a low area γ-alumina, there was a synergistic effect which strongly increased coke deposition and decreased chemisorption of carbon monoxide on the platinum (1). These effects were detectable at a metal loading of 0.6 wt% but were not detected at loadings of 0.3%. A single metal loading of 3.0 wt% tin decreased coke deposition and a single metal loading of 3.0 wt% platinum produced only a small increase in coke deposition. A study of bimetallic loadings in the 0.3 to 3.0 wt% range suggested that the synergistic interaction occurs when the capacity of alumina to complex tin is exceeded. This is consistent with the findings of Dautzenberg *et al.* who, on the basis of reduction studies, concluded that 0.6 wt% tin could be complexed by high area alumina (2).

The coke deposition and chemisorption results, observed with the low surface area alumina support, raise the question of whether studies at high metal loadings are pertinent to the lower metal loadings which are used in commercial platinum–tin reforming catalysts. Because of the significance of this question, the current study was undertaken using a high area γ-alumina as the support. A 0.3 wt% metal loading, supported on Cab-O-Sil, was also studied on the premise that complexing of tin by the support would be minimal.

The available literature on platinum–tin bimetallics is complicated. A summary of results from a variety of experimental approaches has been published (3).

The infrared spectra of chemisorbed carbon monoxide was observed with a Mattson Sirius 100 FTIR. An inverted T-shaped pyrex cell was wound with heating tape. The two ends of the five-inch short arm of the T were fitted with CaF$_2$ windows which were sealed with Apiezon W wax and cooled with flowing water. The long arm of the cell was connected to diffusion pump vacuum and gas handling systems. The spectra of chemisorbed carbon monoxide were observed at 100°C with a pressure of 1 Torr (1 Torr = 133.3 Nm^{-2}) of Union Carbide Specialty Grade carbon monoxide in the cell.

All samples were prepared by incipient wetness impregnation using water solutions which contained the desired amounts of chloroplatinic acid or tin chloride. The bimetallic samples were prepared by co-impregnation. The samples were pressed into discs which had a face area of 2.6 cm^2. These discs weighed between 48 and 60 mg. The absorbance scales were normalized to 50 mg when spectra from different samples were compared. The samples were evacuated at 350°C for 1 h in the infrared cell and then reduced at 350°C for 18 h. Static hydrogen, which had been purified by passage through a Fisher DEOXO unit, was used at one atmosphere pressure with three changes of hydrogen during the course of the reduction.

Two γ-alumina samples are compared. The low area Degussa Aluminum Oxide-C has a surface area of 100 m^2/g and the high area Norton alumina has a surface area of 270 m^2/g. The surface area of the single Cab-O-Sil sample has a surface area of 100 m^2/g. In all bimetallic supported platinum–tin samples the weight percent loadings are the same for both metals, i.e., 3 wt% Pt–Sn/Al$_2$O$_3$ has a weight loading of 3% platinum and 3% tin.

Spectrum A of Fig. 1 has a band at 2079 cm^{-1} which is attributable to carbon monoxide chemisorbed on 3 wt% Pt/Al$_2$O$_3$. A small bridged carbon monoxide band in the 1860 cm^{-1} region is not shown. In all cases the bridged carbon monoxide bands are relatively small and proportional to the bands of the linear carbon monoxide. Therefore, comparisons of adsorbed carbon monoxide are made on the basis of the linear bands. In spectrum A of Fig. 1 the integrated area of the 2079 cm^{-1} band is 58 cm^{-1}. Spectrum B of Fig. 1 shows the linear carbon monoxide band for 3 wt% Pt–Sn/Al$_2$O$_3$. This band at 2077 cm^{-1} has an integrated area of 37 cm^{-1}. Previous work has shown that there is no chemisorption of carbon monoxide on tin under the conditions of Fig. 1 (1).

Spectrum A of Fig. 2 was observed for 0.3 wt% Pt/Al$_2$O$_3$. The peak is at 2064 cm^{-1} and the band area is 5.3 cm^{-1}. Spectrum B of Fig. 2 was observed for 0.3 wt% Pt–Sn/Al$_2$O$_3$. The peak is at 2064 cm^{-1} and the band area is 5.0 cm^{-1}.
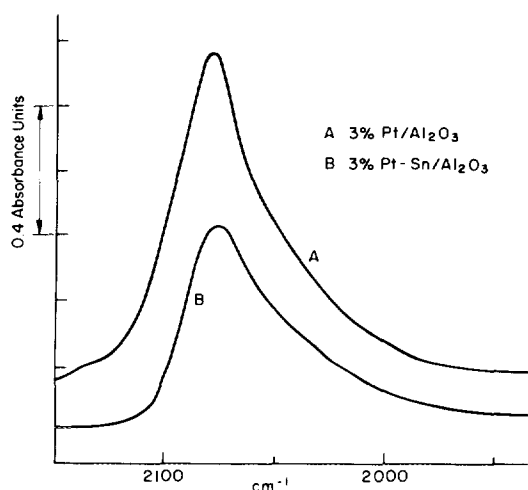
FIG. 1. Spectrum A: Carbon monoxide on 3% Pt/Al_2O_3; spectrum B: Carbon monoxide on 3% $Pt-Sn/Al_2O_3$.

The spectra for 1.0 and 0.6 wt% samples are not shown. For 1 wt% Pt/Al_2O_3 the band peak is at 2072 cm^{-1} and the band area is 17 cm^{-1}. For 1 wt% $Pt-Sn/Al_2O_3$ the band peak is also at 2072 cm^{-1} and the band area is 13 cm^{-1}. The band peak for 0.6 wt% Pt/Al_2O_3 is at 2068 cm^{-1} and the area is 12 cm^{-1}. For 0.6 wt% $Pt-Sn/Al_2O_3$ the peak is at 2068 cm^{-1} and the area is 12 cm^{-1}.

There is a decrease from 2079 to 2064 cm^{-1} in peak frequencies of platinum samples as loadings decrease from 3.0 to 0.3 wt%. This shift would probably not merit mention if the patterns were not consistent for all four samples. This shift is difficult to explain because it is in the opposite direction of what would be expected if the shifts were due to interaction with the alumina support. It may be related to chlorine which would shift the frequencies toward the higher range.

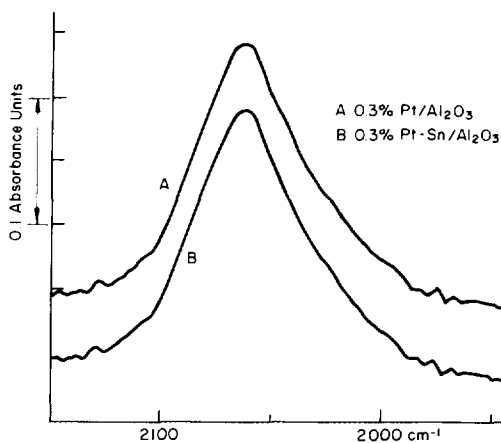The 0.3 wt% platinum on Cab-O-Sil produced a band at 2077 cm^{-1} with a band area of 3.4 cm^{-1}. The 0.3 wt%

FIG. 2. Spectrum A: Carbon monoxide on 0.3% Pt/Al_2O_3; spectrum B: Carbon monoxide on 0.3% $Pt-Sn/Al_2O_3$.

platinum–tin on Cab-O-Sil produced a band at 2077 cm with an area of 1.2 cm^{-1}. Thus, at 0.3 wt% loadings, tin decreased the platinum capacity for chemisorption of carbon monoxide to about 35% of the original value.

In Table 1 the results for the various metal loadings on the high area Norton alumina are compared with the previously reported low area Aluminum Oxide-C. This table shows the percentage of chemisorption capacity retained on the samples which contain both platinum and tin. For example, in Fig. 1 the band for the 3 wt% Pt/Al_2O_3 samples on the high area Norton alumina has an area of 58 cm^{-1} while the 3% $Pt-Sn/Al_2O_3$ band has an area of 37 cm^{-1}. Thus, 64% of the chemisorption capacity is retained in the Pt–Sn sample.

The data in Table 1 show that there is no appreciable platinum–tin interaction, with resultant inhibition of carbon monoxide chemisorption, for 0.3 and 0.6 wt% platinum–tin on Norton γ-alumina. Table 1 also supports the expectation that the platinum–tin interaction is related to the surface area of the alumina with the higher surface area having a larger capacity for complexing tin. The data of Table 1 are also consistent with the XRD observations of Srinivasan et al. (4). These workers found that at low concentrations of tin there was some platinum that was not present as a platinum–tin alloy for catalysts containing 1 wt% Pt and Sn to Pt ratios from 1 to 8. They also mention the possibility that the platinum–tin alloy is not catalytically active for hydrocarbon conversions.

Table 1 shows that the platinum–tin interaction, as detected by decreases in carbon monoxide chemisorption, becomes evident at loadings between 0.6 and 1.0 wt%. This implies that, at higher loadings, the bimetallic systems are a complicated mixture involving platinum and tin which have interacted and platinum and tin which have not interacted. The bimetallic interaction component is detected only at metal loadings which are higher than the loadings used in commercial platinum–tin/alumina reforming catalysts. For the low area alumina the chemisorption results were supplemented by coke deposition studies (1). It was found that the decrease in carbon monoxide chemisorption paralleled the enhancement of coke deposition. Neither the chemisorption decrease nor the increase in coke formation are proven indicators of com-

TABLE 1

Percentage of Platinum Chemisorption Retained after Interaction with Tin

Loading	Aluminum Oxide-C	Norton
3%	35	64
1%	39	76
0.6%	73	100
0.3%	103	94

mercial performance. However, the two approaches lend credence to the questions of whether the species produced by interaction of platinum and tin has any significantly beneficial role in the performance of commercial catalysts.

The low weight loadings (0.3 wt%) at which platinum-tin interaction predominates on Cab-O-Sil and the effect of alumina surface area on the appearance of interactions between platinum and tin are supportive of the view that the alumina has a finite capacity to complex tin and that this complexed tin does not interact with platinum. The specific nature of the alumina–tin complex is not amenable to study by carbon monoxide chemisorption because there is no difference between platinum and platinum-tin at low metal loadings. It is possible that XPS using a high performance instrument such as Lehigh's Scienta ESCA-300 may have value with low metal loading samples. Preliminary results indicate that the tin is complexed with low surface area alumina at 0.3 wt% loading of calcined samples while tin oxide is observed at higher loadings (5). After reduction the detectable tin–platinum ratio for all metal loadings is 0.5 compared with the 0.6 expected from the 1 : 1 weight ratios used in preparing the samples. This constant value of 0.5 suggests that the decrease in chemisorption capacity of the platinum is due to formation of a bulk platinum–tin species rather than being due to the platinum being covered by a layer of tin.

ACKNOWLEDGMENTS

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