

FTIR Study of Bimetallic Pt-Sn/Al<sub>2</sub>O<sub>3</sub> Catalysts

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A series of Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts supported on Degussa nonporous alumina were characterized by infrared spectroscopy of adsorbed CO. The nominal platinum loading was kept constant in the catalysts at 1 wt% and the nominal amount of tin was varied from 0 to 5 wt%. At room temperature it was found that there was a general trend for the linearly adsorbed CO band to shift to lower frequencies with increasing amounts of tin in the catalyst, except for one of the catalysts (1.0 Pt-1.0 Sn/Al<sub>2</sub>O<sub>3</sub>) where a particle size effect seemed to be dominant. The amount of bridge-bonded CO species was very small and became undetectable in the case of large tin loadings (1 and 5 wt% Sn). Thermal desorption infrared spectroscopy was used to determine the vibration frequency of the isolated CO molecule and hence observe if there were any indications of electronic interactions between tin and platinum. For the monometallic 1.0 Pt/Al<sub>2</sub>O<sub>3</sub> sample the singleton vibration frequency was 2041 cm<sup>-1</sup>. For all the Pt-Sn bimetallic samples it was found that the singleton vibration frequency lay within the range 2041 ± 6 cm<sup>-1</sup>. This suggests that the electronic effect of Sn on Pt in our Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts is not very large. © 1992 Academic Press, Inc.

## INTRODUCTION

Supported bimetallic catalysts are widely used in reforming reactions in the petroleum industry. The advantage of these catalysts as compared to monometallic platinum is that they provide an increased selectivity to high-octane products and better activity maintenance and resistance to coking. Bimetallic catalysts can also be used at more severe reaction conditions than the monometallic platinum catalyst (1-3). The Pt-Sn/Al<sub>2</sub>O<sub>3</sub> system is an interesting system to study because of its potential for use in reforming reactions (4, 5). The main questions that have to be addressed to understand the behavior of this system are: (a) in what way does tin influence the behavior of platinum and to what extent do Pt-Sn alloys form, and (b) what is the nature of the interaction between tin and the alumina support?

Previous XPS data on the Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts that were used in this study showed that most of the tin on the surface of all the samples was present in an Sn (II) or Sn (IV) state after reduction in hydrogen

at 673 K (6). A possible structure would be an "egg-shell" of tin aluminate stabilized by its interaction with the alumina support (7, 8). This form of tin in an oxidation state greater than zero is not a bulk tin oxide (8). It is of interest to determine how this type of tin species could affect the catalytic behavior of platinum particles that are situated nearby on the alumina support. By determining the CO singleton vibration frequency one can determine whether there is a geometric effect, electronic effect, or a combination of both effects that becomes operational when tin is added to a catalyst. There are two ways that one can determine the CO singleton vibration frequency or the frequency of the isolated CO molecule free from any dipole-dipole coupling effect.

One method is isotopic dilution as described in detail by Toolenaar *et al.* (9), while the other method is thermal desorption as described by Primet (10). In the case of the isotopic dilution method (9), diluting <sup>12</sup>CO with increasing amounts of <sup>13</sup>CO at full surface coverage results in a decrease in dipole-dipole coupling. At infinite dilution

one can get the vibration frequency of the isolated CO molecule, also known as the CO singleton vibration frequency. If one were to plot the  $^{12}\text{CO}$  peak position versus percentage of  $^{12}\text{CO}$  in the isotopic mixture for a monometallic Pt/ $\text{Al}_2\text{O}_3$  sample and for a bimetallic sample, one could envision three possible manifestations of metal-metal interactions. If the second metal were to have a purely electronic effect on the platinum leading to a change in the adsorbed C-O bond strength, then the curve for the bimetallic sample would be parallel to the curve for the monometallic Pt sample. If a pure geometric effect was present with the second metal diluting the Pt ensembles, the two curves should converge to the same point at infinite dilution. If both electronic and geometric effects were present then the appearance of the curves would be something in between the two extreme cases and the difference in  $^{12}\text{CO}$  singleton vibration frequency would give the upper limit for any existing electronic effect in the Pt-Sn system.

The other method used to determine the vibration frequency of the isolated  $^{12}\text{CO}$  molecule is the thermal desorption method (10).  $^{12}\text{CO}$  is adsorbed at 298 K on the sample and then the sample is evacuated. It is assumed that the CO surface coverage on the catalyst is unity (i.e., a monolayer) after desorption of the weakly held species at 298 K. Then the catalyst is heated under dynamic vacuum and the spectra are recorded at increasing temperatures. The CO surface coverages at the higher temperatures are determined by taking the ratio of the optical density of the band at the higher temperature to the optical density of the band obtained after desorption at 298 K. Then the adsorbed CO vibration frequency is plotted against the CO surface coverage. On extrapolating this curve to zero surface coverage the vibration frequency of the isolated CO molecule can be obtained. Primet (10) carried out detailed experiments to determine the frequency of the isolated  $^{12}\text{CO}$  molecule on a 5% Pt/ $\text{Al}_2\text{O}_3$  sample using both the ther-

mal desorption method and the isotopic dilution method. The frequencies of the isolated  $^{12}\text{CO}$  molecule that were obtained in both cases lay within  $1\text{ cm}^{-1}$  of each other.

In our work on bimetallic Pt-Sn/ $\text{Al}_2\text{O}_3$  catalysts, we decided to use the thermal desorption method for determining the value of the singleton vibration frequency of the  $^{12}\text{CO}$  molecule. By comparing these values with the corresponding value obtained on the monometallic Pt/ $\text{Al}_2\text{O}_3$  sample, the extent of electronic interactions between Sn and Pt could be ascertained.

There have been some prior infrared studies on the Pt-Sn/ $\text{Al}_2\text{O}_3$  system (11-13). Palazov *et al.* (11) studied the adsorption of CO at room temperature on Pt-Sn catalysts supported on  $\delta$ -alumina. The results of Palazov *et al.* were presumably obtained after complete coverage of the catalyst surface with CO. In the case of the monometallic 5% Pt sample a band of large intensity was found at  $2090\text{ cm}^{-1}$ . This band was assigned to CO linearly adsorbed on Pt sites. The 5% Pt-2% Sn sample, on the other hand, had a peak at  $2060\text{ cm}^{-1}$ . On adding more tin (5% Pt-5% Sn) the peak shifted to  $2053\text{ cm}^{-1}$ . Hence, with increase in the amount of tin the CO adsorption band shifted to lower frequencies. This shift has been attributed to an electronic modification of the platinum surface by tin. Donation of electrons from tin to platinum could lead to a lowering of the CO vibration frequency. Additional evidence for a possible electronic effect of tin was that the intensity of the CO infrared band was enhanced in the bimetallic Pt-Sn samples as compared to the monometallic Pt sample. In the case of the monometallic Pt sample a second peak of low intensity was found at  $1850\text{ cm}^{-1}$  corresponding to bridge-bonded CO. This peak was not found in the case of the bimetallic samples.

Kogan *et al.* (12) found that as the Sn/Pt atomic ratio was increased from 0 to 11 the CO vibration band frequency shifted towards higher wavenumbers, except at relatively high surface coverages of CO. At low surface coverages where one deals with

stronger adsorption sites, the difference in peak position between the monometallic Pt sample and the bimetallic samples became more prominent. At low surface coverages, an electronic effect due to the shift of the electron density from the Pt to the Sn was stated to be a likely reason for the increase in the CO band vibration frequency with increasing Sn content. The researchers also found that the energy homogeneity of the catalytic surface tended to increase as the amount of tin in the catalyst was increased.

Bastein *et al.* (13) studied alloys of Pt-Sn, Pt-Pb, and Pt-Re supported on  $\gamma$ -alumina using the isotopic dilution method. They found that in the case of the Pt-Pb alloys on infinite dilution of <sup>12</sup>CO by <sup>13</sup>CO there was a significant residual effect that could not be attributed to a simple geometric dilution effect. This residual effect tended to increase with the concentration of lead in the Pt-Pb alloy. In the case of the Pt-Sn and Pt-Re alloys, the effect of the second metal seemed to be mainly a geometric one and the residual effect was much smaller in comparison to the Pt-Pb alloys. The researchers concluded that the desirable catalytic properties of bimetallic Pt-Re and Pt-Sn alloy catalysts are probably due to a dilution effect of the platinum combined with the activity of the second metal component. On the basis of this work, it seems that the electronic modification effect of Pt by Sn may not be significant for catalysts supported on  $\gamma$ -alumina.

In this study, the effect of tin on the adsorptive behavior of platinum is studied for a series of Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by traditional impregnation techniques. The catalysts were characterized, after *in-situ* reduction treatment and high-temperature evacuation, using FTIR spectroscopy with CO as the probe molecule. Previous studies on the same catalyst series have included the following methods: chemisorption and XPS (6), *n*-hexane reactions and detailed microstructural characterization by high-resolution and analytical electron microscopy (14), and neopentane reactions (15).

## EXPERIMENTAL

### (a) Catalyst Preparation

The details of catalyst preparation have been given elsewhere (6, 14, 15). The Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by coimpregnation of Degussa non-porous aluminum oxide C (BET surface area of 90 m<sup>2</sup>/g) with hydrogen hexachloroplatinate (IV) hydrate and tin (II) chloride, obtained from Aldrich Chemicals. While the nominal platinum loading was kept constant at 1 wt%, the nominal amount of tin was increased from 0–5 wt%. In addition, a monometallic 2.0 Sn/Al<sub>2</sub>O<sub>3</sub> sample and a blank Al<sub>2</sub>O<sub>3</sub> sample were studied to determine the nature of CO adsorption on the second metal alone and on the blank support. Subsequent to the impregnation step, the catalysts were dried at 393 K in flowing air and calcined in air for 2 h at 773 K. After calcination, a portion of each sample was reduced for 5 h in flowing hydrogen (15 SCCM) at 673 K. These pre-reduced samples were then used to prepare the IR wafers. The actual metal compositions and the amount of chlorine were determined by neutron activation analysis. These results are summarized in Table 1.

### (b) IR Spectroscopy

A high-temperature IR cell (HTC-100, Harrick Scientific Corporation) was used in this work (16). This cell was made out of stainless steel 316 and could be heated to around 773 K. It consisted of a cell body into which the catalyst wafer could be mounted. The sample was held in place by a spacer and a clamping screw. Ports were provided on the cell so that vacuum and gas lines could be connected. A 2- $\frac{3}{4}$ " conflat flange was attached to one side of the cell body. This arrangement made it possible to replace the sample without having to remove the IR windows each time. Sodium chloride IR windows were used in the cell. An iron-constantan thermocouple connected to an Omega Temperature Controller measured the temperature in the heating block of the cell. The cell was heated with the help

TABLE I  
Component Loadings in the Pt-Sn/Al<sub>2</sub>O<sub>3</sub> Catalysts

Catalyst	Nominal loading (component wt%)		Loading as determined by neutron activation analysis <sup>a</sup> (component wt%)		
	Pt	Sn	Pt	Sn	Cl
1.0 Pt/Al <sub>2</sub> O <sub>3</sub>	1.00	—	0.99	—	0.72
1.0 Pt-0.1 Sn/Al <sub>2</sub> O <sub>3</sub>	1.00	0.10	0.96	0.14	0.97
1.0 Pt-0.5 Sn/Al <sub>2</sub> O <sub>3</sub>	1.00	0.50	1.00	0.53	1.00
1.0 Pt-1.0 Sn/Al <sub>2</sub> O <sub>3</sub>	1.00	1.00	0.89	0.99	0.97
1.0 Pt-5.0 Sn/Al <sub>2</sub> O <sub>3</sub>	1.00	5.00	0.94	3.25	0.48
2.0 Sn/Al <sub>2</sub> O <sub>3</sub>	—	2.00	—	1.90	0.87

<sup>a</sup> After impregnation the catalysts were dried in flowing air at 393 K, calcined in flowing air at 773 K, and reduced in flowing hydrogen at 673 K.

of three cartridge heaters that were inserted into cavities in the cell. Cooling water ports were provided to cool the exterior of the cell and keep the IR windows from getting too hot during high-temperature operation. Research grade gases were used for all the IR experiments. An oil diffusion pump and a mechanical pump were used to evacuate the IR cell. A liquid-nitrogen baffle on top of the diffusion pump and a liquid-nitrogen trap between the foreline and the mechanical pump were used to prevent backstreaming of pump oil. The infrared spectrometer was a Digilab FTS 20/C FTIR. The spectra were collected at a resolution of 2 cm<sup>-1</sup>.

The pretreatment procedure of catalyst powders for IR experiments consisted of the following steps: 110 mg of prereduced sample was pressed into a thin wafer between 1" stainless steel dies at 4000 psi for 1 min. After mounting the pellet in the cell, the cell was evacuated and the temperature was raised to 673 K and kept under dynamic vacuum for 4 h. The catalyst pellet was reduced for 16 hours under 1 atm of static H<sub>2</sub> (1 atm = 101.3 kPa). Then, the cell was evacuated at 693 K for 4 hr, and then the heating was turned off. While the cell was cooling down reference spectra were obtained at 673, 623, 573, 523, 473, 423, 363, and finally at 298 K.

After collecting a reference spectrum at 298 K, the pellet was exposed to 1 atm of CO for 1 hr. Then spectra were collected immediately after removal of the gas phase, and after evacuation with the diffusion pump at room temperature for an hour. By this evacuation step all the weakly adsorbed CO species could be removed. It was assumed that the surface coverage of CO was unity after evacuation at 298 K, in agreement with CO chemisorption results (6). The sample was then heated under dynamic vacuum to the temperatures at which reference spectra had been previously collected. After 10 min of evacuation at these temperatures spectra were again collected. This step was repeated at higher temperatures until the CO vibration frequency became too small to be accurately determined. The CO surface coverages at the higher temperatures were obtained by dividing the total integrated area of the CO vibration band at each temperature by the total integrated area obtained after room temperature evacuation. Then the CO vibration frequencies were plotted against the CO surface coverage and by back extrapolating the curve to zero surface coverage, the CO singleton vibration frequency was obtained. Only the band due to CO linearly adsorbed on Pt sites was used to calculate the area as the amount

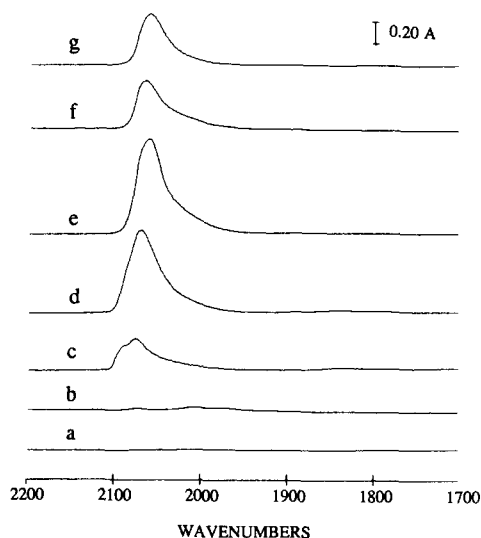


FIG. 1. Infrared spectra of linearly bonded CO at 298 K for catalysts of the Pt-Sn/Al<sub>2</sub>O<sub>3</sub> series (spectra obtained after removal of gas phase CO): (a) blank Al<sub>2</sub>O<sub>3</sub>; (b) 2.0 Sn/Al<sub>2</sub>O<sub>3</sub>; (c) 1.0 Pt/Al<sub>2</sub>O<sub>3</sub>; (d) 1.0 Pt-0.1 Sn/Al<sub>2</sub>O<sub>3</sub>; (e) 1.0 Pt-0.5 Sn/Al<sub>2</sub>O<sub>3</sub>; (f) 1.0 Pt-1.0 Sn/Al<sub>2</sub>O<sub>3</sub>; and (g) 1.0 Pt-5.0 Sn/Al<sub>2</sub>O<sub>3</sub>.

of bridge-bonded species in all the catalysts was negligibly small.

#### RESULTS AND DISCUSSION

Figure 1 shows the CO adsorption peak corresponding to CO linearly adsorbed on Pt sites for the different catalysts belonging to the Pt-Sn/Al<sub>2</sub>O<sub>3</sub> series at 298 K. These spectra were obtained by removing the gas phase CO after exposing the reduced and evacuated sample to CO gas. In this and all the other spectra shown the corresponding reference spectrum is subtracted. In this figure, no bridge-bonded CO species are noticeable. However, when the intensity scale of this region is magnified (Fig. 2), the presence of very small amounts of bridge-bonded CO can be observed. Figure 3 displays a typical sequence of spectra for the linearly adsorbed CO peaks obtained at various temperatures of desorption for the 1.0 Pt-1.0 Sn/Al<sub>2</sub>O<sub>3</sub> catalyst. Similar sequences of spectra were obtained for all the other catalysts. A summary of the CO peak posi-

tions as a function of the CO coverage is given in Fig. 4 for the various catalysts. The points on this plot were obtained from the thermal desorption experiments. The curves for each catalyst were extrapolated to zero surface coverage to determine the vibration frequency of the isolated CO molecule or the singleton vibration frequency. The 298-K data shown in Figs. 3 and 4 correspond to CO strongly adsorbed (obtained after evacuation with the diffusion pump), while the data shown in Figs. 1 and 2 correspond to total CO adsorption at 298 K, just after removal of gas-phase CO.

At 298 K no significant infrared peaks are visible on the blank Al<sub>2</sub>O<sub>3</sub> sample and on the monometallic 2.0 Sn/Al<sub>2</sub>O<sub>3</sub> sample (Figs. 1 and 2). In the case of the monometallic 1.0 Pt/Al<sub>2</sub>O<sub>3</sub> sample the main peak corresponding to CO linearly adsorbed on Pt sites is present at 2073 cm<sup>-1</sup>. There is a shoulder on this main peak on the high frequency side at around 2086 cm<sup>-1</sup>. Haaland (17) in his infrared investigation of a 1.0 Pt/Al<sub>2</sub>O<sub>3</sub> sample found that on adsorbing CO on the sam-

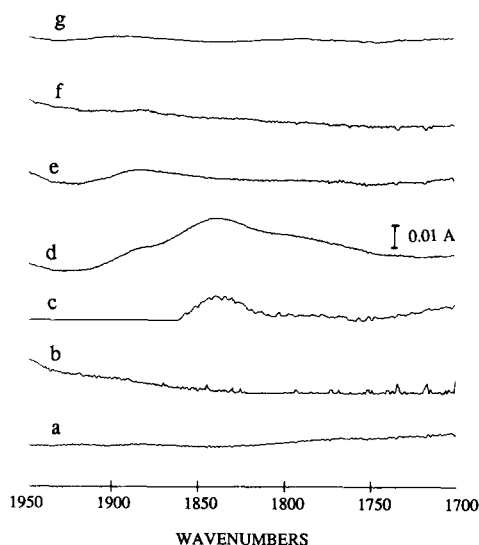


FIG. 2. Infrared spectra of multiply bonded CO on at 298 K for catalysts of the Pt-Sn/Al<sub>2</sub>O<sub>3</sub> series (spectra obtained after removal of gas phase CO): (a) blank Al<sub>2</sub>O<sub>3</sub>; (b) 2.0 Sn/Al<sub>2</sub>O<sub>3</sub>; (c) 1.0 Pt/Al<sub>2</sub>O<sub>3</sub>; (d) 1.0 Pt-0.1 Sn/Al<sub>2</sub>O<sub>3</sub>; (e) 1.0 Pt-0.5 Sn/Al<sub>2</sub>O<sub>3</sub>; (f) 1.0 Pt-1.0 Sn/Al<sub>2</sub>O<sub>3</sub>; and (g) 1.0 Pt-5.0 Sn/Al<sub>2</sub>O<sub>3</sub>.

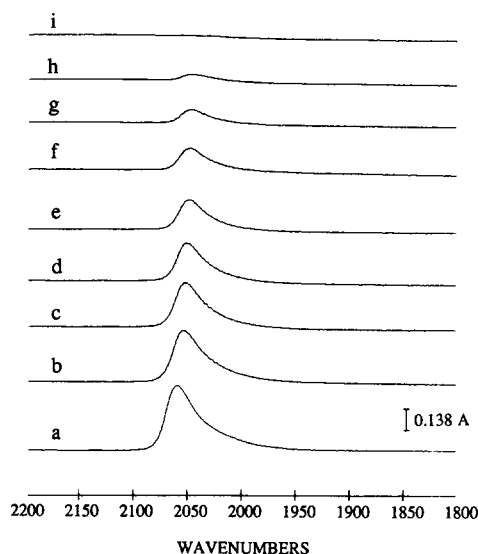


FIG. 3. Thermal desorption infrared spectra of linearly bonded CO for the 1.0 Pt-1.0 Sn/Al<sub>2</sub>O<sub>3</sub> catalyst with spectra obtained at the following desorption temperatures: (a) 298 K, (b) 363 K, (c) 423 K, (d) 473 K, (e) 523 K, (f) 573 K, (g) 623 K, (h) 673 K, and (i) 723 K.

ple at 300 K a main infrared peak was found at close to 2075 cm<sup>-1</sup>. This peak possessed a low energy shoulder at around 2025 cm<sup>-1</sup>. He attributed the peak doublet to CO linearly adsorbing on two different types of platinum surface sites. The peak at 2075 cm<sup>-1</sup> was said to correspond to CO linearly adsorbed on the flat terraces of the platinum particles while the broad shoulder at 2025 cm<sup>-1</sup> was attributed to the adsorption of CO on Pt atoms situated on high-Miller-index steps or corners of the platinum particles (17). Barth *et al.* (18) conducted detailed CO adsorption infrared studies on platinum supported on alumina. They found that on adsorbing CO at room temperature on a 1.0 Pt/Al<sub>2</sub>O<sub>3</sub> sample, the main CO adsorption band at 2060 cm<sup>-1</sup> possessed a shoulder at a higher frequency (2078 cm<sup>-1</sup>). In our work a similar result has been observed. The main CO adsorption band that was obtained by Barth *et al.* (18) was attributed to CO adsorption on platinum particles that do not possess extended crystal faces as a result of either the platinum particle morphology or

due to the very small size of the particles. The high frequency shoulder was said to be possibly due to CO adsorption on extended crystalline planes of platinum. The presence of peaks at very low frequencies (~2025 cm<sup>-1</sup>) was said to be formed by CO adsorption on platinum that interacts with the support (18). Hence based on these previous studies (17, 18) one can assign the 2073 cm<sup>-1</sup> peak obtained in our work to CO adsorption on platinum particles that do not possess extended crystal faces, and the 2086 cm<sup>-1</sup> shoulder can be attributed to CO adsorbed on well-defined platinum crystal faces. It should be reasonable to assume that this sample possesses a particle size distribution that is broad, since both the peaks were present in the CO adsorption spectra. Electron microscopy (14) showed that there were many particles smaller than 20 Å, though the particle size distribution extended to about 100 Å. Hydrogen chemisorption experiments (6) gave a surface average particle size of 29 Å. From Fig. 2 one can observe that there is a peak corresponding to bridge-bonded CO on the Pt/Al<sub>2</sub>O<sub>3</sub> sample located at 1838 cm<sup>-1</sup>. This peak is much lower in intensity as compared to the peak corresponding to CO linearly adsorbed on Pt sites. Hence the amount of CO in the bridge-bonded mode is much smaller as

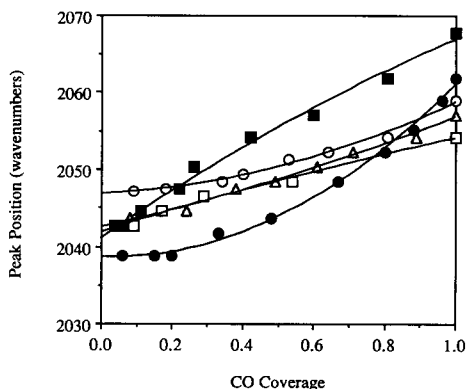


FIG. 4. Infrared peak positions of linearly bonded CO for varying CO surface coverages for catalysts of the Pt-Sn/Al<sub>2</sub>O<sub>3</sub> series. (■) 1.0 Pt/Al<sub>2</sub>O<sub>3</sub>; (●) 1.0 Pt-0.1 Sn/Al<sub>2</sub>O<sub>3</sub>; (△) 1.0 Pt-0.5 Sn/Al<sub>2</sub>O<sub>3</sub>; (○) 1.0 Pt-1.0 Sn/Al<sub>2</sub>O<sub>3</sub>; and (□) 1.0 Pt-5.0 Sn/Al<sub>2</sub>O<sub>3</sub>.

compared to the amount in the linearly adsorbed mode.

In the case of the bimetallic sample having small amounts of tin (1.0 Pt-0.1 Sn/Al<sub>2</sub>O<sub>3</sub>) the linearly adsorbed CO adsorption peak is present at 2068 cm<sup>-1</sup> and it is also of a larger intensity as compared to the peak for the monometallic 1.0 Pt/Al<sub>2</sub>O<sub>3</sub> sample. The high-frequency shoulder attributed to CO adsorption on extended Pt crystal faces is not visible in this sample. This suggests that Pt might be dispersed to a larger extent on the alumina support as compared to the monometallic Pt sample, in agreement with hydrogen and CO chemisorption results (6). Clearly, the CO peak has shifted to lower frequencies as compared to the monometallic 1.0 Pt/Al<sub>2</sub>O<sub>3</sub> sample. A similar shift towards lower wavenumbers by adding tin to platinum at room temperature has been reported previously by Palazov *et al.* (11). This type of shift has been noted before for other supported bimetallic systems containing platinum as the primary metal, and a host of second components like Au (19), Cu (9), Pb (20), Re (13), and MoO<sub>3</sub> (21). From Fig. 2 the presence of small amounts of bridge-bonded species is detected. The amount of tin might not have been sufficient to block all the sites corresponding to bridge-bonded CO on platinum sites. On the addition of more tin (1.0 Pt-0.5 Sn/Al<sub>2</sub>O<sub>3</sub>), the amount of bridge-bonded CO has decreased significantly. On further addition of tin (1.0 Pt-1.0 Sn/Al<sub>2</sub>O<sub>3</sub> and 1.0 Pt-5.0 Sn/Al<sub>2</sub>O<sub>3</sub>) the presence of bridge-bonded CO on Pt is no longer detected. Palazov *et al.* (11) also noted that addition of tin prevented the formation of bridge-bonded CO. Hence, when more and more tin is added the geometric effect of tin becomes predominant making it less likely to find sites consisting of contiguous ensembles of Pt atoms.

On comparison with 1.0 Pt-0.1 Sn/Al<sub>2</sub>O<sub>3</sub>, it is clear that in the 1.0 Pt-0.5 Sn/Al<sub>2</sub>O<sub>3</sub> sample there is a further shift in the linearly adsorbed CO peak towards lower frequencies (Fig. 1). Now the peak is present at 2059 cm<sup>-1</sup>. On further addition of tin (1.0 Pt-1.0

Sn/Al<sub>2</sub>O<sub>3</sub>) the peak shifts to a slightly higher frequency (2062 cm<sup>-1</sup>). This shift could be due to a particle size effect (22, 23) which could be dominating over other effects. Solomennikov *et al.* (22) found in their work on CO adsorption on alumina and silica supported platinum that, on increasing the temperature of reduction of the catalysts from 673 K to 973 K, the band due to CO linearly adsorbed on platinum shifted towards higher frequencies. The platinum metal dispersion on the other hand dropped on increasing the temperature of reduction. Hence they showed that the main reason for the increase in CO adsorption peak frequency with an increase in average particle size was due to the dominating effect of the so-called "geometric factor." As the average platinum particle size increased this had the effect of increasing the coordination number of the surface platinum atoms resulting in a lesser degree of back-donation of electrons into the antibonding  $\pi^*$  orbitals of CO. This would tend to increase the C-O bond strength hence causing a high frequency shift of the CO band. This effect would dominate over the metal-support electronic interaction effect that would tend to move the infrared band in the opposite direction (22). Toolenaar *et al.* (23) in their work on Ir/Al<sub>2</sub>O<sub>3</sub> catalysts also noticed a similar shift of the band due to CO adsorption with change in average particle size. In our work we find that for the 1.0 Pt-1.0 Sn/Al<sub>2</sub>O<sub>3</sub> catalyst the CO adsorption band lies at slightly higher frequency (3 cm<sup>-1</sup>) than in the case of the 1.0 Pt-0.5 Sn/Al<sub>2</sub>O<sub>3</sub> catalyst. Electron microscopy results (14) show that in the case of the 1.0 Pt-1.0 Sn/Al<sub>2</sub>O<sub>3</sub> sample there are more particles lying in the size range greater than 80 Å than in the case of the 1.0 Pt-0.5 Sn/Al<sub>2</sub>O<sub>3</sub> sample. Here two effects are simultaneously taking place. One effect is the effect of the second metal (Sn) shifting the infrared peak towards lower frequencies, while the opposing particle size effect tends to shift the infrared band towards higher frequencies. Since the particle size effect is dominating it is observed that there is a net shift in the infrared band

towards higher frequencies, though the shift is not very significant. On adding more tin (1.0 Pt–5.0 Sn/Al<sub>2</sub>O<sub>3</sub>) the CO adsorption peak shifts to lower frequencies and is detected at 2058 cm<sup>-1</sup>. The total integrated intensity of the linearly adsorbed CO band increases with the addition of small amounts of tin. The intensity increase can be explained by the hydrogen and CO chemisorption results (6). Both hydrogen and CO adsorption data showed an initial increase in the gas uptake with addition of small amounts of tin. This means that the amount of Pt exposed on the surface increases with the addition of small amounts of tin. This increase of surface Pt atoms leads to an increase in the intensity of the CO adsorption band as more CO gas is adsorbed on the catalytic surface. In the samples with higher tin loading, the integrated intensity of the CO band starts to decrease, in agreement with decreasing CO gas uptake values obtained in chemisorption experiments.

Figure 3 shows what happened to the linearly adsorbed CO band as the 1.0 Pt–1.0 Sn/Al<sub>2</sub>O<sub>3</sub> sample was heated to temperatures higher than 298 K while simultaneously applying a dynamic vacuum. Similar series of spectra were obtained for all the catalysts. From Fig. 3 two changes in the nature of the IR band can be observed as a result of increasing temperatures of desorption, namely, shifts in peak position and changes in integrated peak intensities. As the temperature of desorption is increased the position of the IR band shifts to lower frequencies. In the case of the 1.0 Pt–1.0 Sn/Al<sub>2</sub>O<sub>3</sub> sample the CO adsorption peak after desorption at 298 K is present at 2059 cm<sup>-1</sup> and this peak shifts to 2047 cm<sup>-1</sup> at 673 K. It is also observed that there is a decrease in the total integrated intensity of the bands, indicating a decrease in the CO surface coverage with increasing temperature. As the surface coverage decreases there is a decrease in the dipole–dipole coupling of the adsorbed CO molecules and the band shifts towards lower frequencies. Ultimately at temperatures >673 K the CO ad-

sorption band almost completely disappears as all the CO on the catalyst surface is desorbed.

From Fig. 4 the CO singleton vibration frequencies were obtained. In the case of the monometallic 1.0 Pt/Al<sub>2</sub>O<sub>3</sub> sample the singleton vibration frequency was 2041 cm<sup>-1</sup>. In the case of all the Pt–Sn bimetallic samples it was found that the vibration frequency lay within the range 2041 ± 6 cm<sup>-1</sup>. This deviation of 6 cm<sup>-1</sup> is not a very large one. Hence it is obvious that if there is an electronic effect of Sn on Pt in our Pt–Sn/Al<sub>2</sub>O<sub>3</sub> catalysts then it is not very large. Ponc and co-workers (13) had also noted in their work on Pt–Sn/Al<sub>2</sub>O<sub>3</sub> samples that the residual electronic effect was very small (5–10 cm<sup>-1</sup>) and hence it seems that the electronic or ligand effect does not play a big role in alumina-supported Pt–Sn catalysts.

In conclusion, infrared spectroscopy results indicate that there does not seem to be evidence of much electronic interactions between tin and platinum in reduced Pt–Sn/Al<sub>2</sub>O<sub>3</sub> catalysts. Though microscopy work (14) indicated the presence of a few Pt–Sn alloy particles in the case of the high-tin-loading bimetallic samples, most of the platinum was present in form of monometallic particles, some of them situated in proximity to ionic tin. It is clear from XPS results (6) that the tin on the catalytic surface is mainly present in the Sn (II, IV) form after reduction. This form of tin could be stabilized by interacting with the alumina support. The interaction between this ionic tin and platinum particles situated nearby could be the reason for the positive bimetal effects that have been observed in this catalytic system, namely, a lower rate of deactivation and a greater selectivity to products that increase the octane number.

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## REFERENCES

1. Sinfelt, J. H., in "Catalysis Science and Technology" (J. R. Anderson and M. Boudart, Eds.), Vol. 1, p. 257. Springer-Verlag, New York, 1981.
2. Gates, B. C., Katzer, J. R., and Schuit, G. C. A., "Chemistry of Catalytic Processes," p. 184. McGraw-Hill, New York, 1979.
3. Burch, R., and Garla, L. C., *J. Catal.* **71**, 360 (1981).
4. Adkins, S. R., Davis, B. H., and Völter, J., *J. Catal.* **89**, 371 (1984).
5. Völter, J., Lietz, G., Uhlemann, M., and Hermann, M., *J. Catal.* **68**, 42 (1981).
6. Balakrishnan, K., and Schwank, J., *J. Catal.* **127**, 287 (1991).
7. Srinivasan, R., De Angelis, R. J., and Davis, B. H., *J. Catal.* **106**, 449 (1987).
8. Adkins, S. R., and Davis, B. H., *J. Catal.* **89**, 371 (1984).
9. Toolenaar, F. J. C. M., Stoop, F., and Ponec, V., *J. Catal.* **82**, 1 (1983).
10. Primet, M., *J. Catal.* **88**, 273 (1984).
11. Palazov, A., Bonev, Ch., Shopov, D., Lietz, G., Sárkány, A., and Völter, J., *J. Catal.* **103**, 249 (1987).
12. Kogan, S. B., Podkletnova, N. M., Oranskaya, O. M., Semenskaya, I. V., and Bursian, N. R., *Kinet. Katal.* **22**(3), 663 (1981).
13. Bastein, A. G. T. M., Toolenaar, F. J. C. M., and Ponec, V., *J. Catal.* **90**, 88 (1984).
14. Sachdev, A., Ph.D. Thesis, University of Michigan, 1989.
15. Balakrishnan, K., and Schwank, J., *J. Catal.* **132**, 451 (1991).
16. Conner Jr., Wm. C., Cevallos-Candau, J. F., Shah, N., and Haensel, V., in "Spillover of Adsorbed Species," (G. M. Pajonk, S. J. Teichner, and J. E. Germain, Eds.), p. 31. Elsevier, Amsterdam, 1983.
17. Haaland, D. M., *Surf. Sci.* **185**, 1 (1987).
18. Barth, R., Pitchai, R., Anderson, R. L., and Verykios, X. E., *J. Catal.* **116**, 61 (1989).
19. Balakrishnan, K., Sachdev, A., and Schwank, J., *J. Catal.* **121**, 441 (1990).
20. Palazov, A., Bonev, Ch., Kadinov, G., Shopov, D., Lietz, G., and Völter, J., *J. Catal.* **71**, 1 (1981).
21. Primet, M., and Meriaudeau, P., *Appl. Catal.* **52**, 263 (1989).
22. Solomennikov, A. A., Lokhov, Yu. A., Davydov, A. A., and Ryndin, Yu. A., *Kinet. Katal.* **20**(3), 714 (1979).
23. Toolenaar, F. J. C. M., Bastein, A. G. T. M., and Ponec, V., *J. Catal.* **82**, 35 (1983).