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Microcalorimetric, Spectroscopic, and Kinetic Studies of Silica-Supported Pt and Pt/Sn Catalysts for Isobutane Dehydrogenation

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Kinetic, microcalorimetric, and Mössbauer spectroscopic studies were conducted to investigate the factors controlling the selectivity of isobutane conversion over silica-supported Pt and Pt/Sn catalysts. Kinetic studies show that addition of Sn to Pt enhances the selectivity for isobutylene formation at temperatures near 700 K. Mössbauer spectroscopic studies show that Sn interacts with Pt to produce a Pt/Sn alloy. Microcalorimetric investigations show that addition of Sn reduces the number of sites that strongly interact with hydrogen or carbon monoxide. The elimination of stronger adsorption sites may be caused by preferential blocking of sites by tin or weakening of sites due to ligand effects. However, strong adsorption sites are present on a Pt/Sn catalyst that exhibits high dehydrogenation selectivity. Microcalorimetric studies of ethylene adsorption suggest that addition of Sn inhibits the formation of highly dehydrogenated surface species. These results suggest that high dehydrogenation selectivity achieved by addition of Sn to Pt is caused by a decrease in the size of surface Pt ensembles.

INTRODUCTION

Catalytic dehydrogenation processes are of increasing importance because of growing demand for olefins such as propylene and isobutylene. Isobutylene is in particularly high demand as a feedstock for the production of oxygenated compounds required in reformulated gasoline, such as methyl-*tert*-butyl ether (MTBE), ethyl-*tert*-butyl ether (ETBE), and *tert*-butyl alcohol (TBA).

Supported platinum is a good dehydrogenation catalyst (1). Since the dehydrogenation of isobutane to isobutylene is an endothermic reaction, high temperatures are required to achieve high conversions. However, the rates of isomerization, hydrogenolysis, and coking reactions become significant at these higher temperatures. Accordingly, the selectivity for dehydrogenation becomes low at the high temperatures required for favorable dehydrogenation thermodynamics.

Catalyst systems that employ Pt/Sn on a neutral support have been reported to exhibit high dehydrogenation selectivity and catalyst stability for dehydrogenation of light paraffins at elevated temperatures (2–4). Likewise, addition of tin to Pt/alumina naphtha-reforming catalysts is known to promote desired reforming reactions such as aromatization and inhibit coking reactions. The role of tin on these catalysts has been studied by several investigators (5–9). These studies have suggested that tin modifies the catalytic behavior of supported Pt-reforming catalysts through ensemble and/or ligand effects.

In the present study, silica-supported Pt and Pt/Sn catalysts were investigated in kinetic, microcalorimetric, and Mössbauer spectroscopic studies. The kinetic studies show that addition of tin to a supported platinum catalyst enhances the dehydrogenation selectivity for isobutane conversion to isobutylene. Mössbauer spectroscopic studies show that tin interacts with platinum to produce a Pt/Sn alloy. Microcalorimetric investigations show that the addition of tin reduces the strength of interaction of platinum with hydrogen, carbon monoxide, and ethylene. The combination of results from these studies suggests that strong adsorption sites are required for isobutane conversion, and addition of tin increases the selectivity for dehydrogenation reactions primarily by decreasing the size of the surface Pt ensembles.

EXPERIMENTAL

The 0.04 and 1.2 wt% Pt/Cab-O-Sil catalysts investigated in this study were prepared by ion exchange, using the method of Benesi *et al.* (10). These authors prepared silica-supported Pt catalyst with Pt loadings up to 4.5 wt% through the exchange of $Pt(NH_3)_4^{2+}$ with H^+ on the silica surface. The degree of exchange was controlled by adjusting the pH of the silica slurry. An aqueous, basic solution of $Pt(NH_3)_4(OH)_2$ was added periodically to maintain the slurry at the desired pH. The resulting material was filtered, washed with deionized water, and dried overnight in air at 390 K. Both the 0.04 and the 1.2 wt% Pt catalyst are highly dispersed, as determined by hydrogen chemisorption, which is in agreement with the results of Benesi *et al.* (10) for similar catalysts. While Pt particles

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sizes were not measured directly, it is thought that the 0.04 wt% Pt catalyst contained smaller platinum particles than the 1.2 wt% Pt catalyst.

Tin was added to the 1.2 wt% Pt catalyst by evaporative impregnation of a tributyltinacetate/pentane solution. This method was used to produce catalysts with Pt : Sn atomic ratios of 6 : 1, 1 : 1, and 1 : 3. After impregnation with tin, the catalysts were dried overnight in air at 390 K and treated with flowing oxygen at 573 K for 2 h, followed by reduction for 2 h in flowing hydrogen at 773 K. The results of elemental analyses (Galbraith Laboratories, Inc.) of these catalysts and the corresponding Pt/Sn atomic ratios are shown in Table 1.

Kinetic studies were conducted using a stainless-steel apparatus and a quartz, down-flow reactor. Helium (Liquid Carbonic) was employed as a carrier gas, and it was purified by passage through copper turnings at 473 K, followed by activated molecular sieves (13×) at 77 K. Isobutane (Matheson, 99.5%) was treated by passage through a molecular sieve trap at 298 K. Hydrogen (Liquid Carbonic) was treated by passage through a Deoxo unit (Engelhard) and a bed of molecular sieves (13×) at 77 K. The reactor outlet gases were sampled via an eight-port valve with matching sample loops. These gases were analyzed by a HP-5890 gas chromatograph with FID detector and a 10-ft 15% Squalane Chromsorb PAW column held at 323 K.

Mössbauer spectra were collected using an Austin Science Associates Model S-600 Mössbauer spectrometer, connected to a microcomputer with a PCAII data collection board. The spectrometer was operated in the constant-acceleration mode, with a 10-mCi single-line γ-ray source of $Ca^{119m}SnO_3$ (Amarsham). Detection of the 23.88-keV γ rays was achieved with a $Xe–CO_2$ proportional counter. A 0.05-mm-thick Pd foil was placed between the source and detector to filter 25.04- and 25.27-keV X rays from the source. A 50/50 mixture of $BaSnO_3$ and β-tin powder was used to calibrate the magnitude and linearity of the Doppler velocity for our system. Chemical shifts are reported relative to $BaSnO_3$ at room temperature.

Differential heats of adsorption for hydrogen, carbon monoxide, and ethylene were measured using a Tian-Calvet heat flow microcalorimeter (Setaram 80) connected to a gas handling system. A Baratron capacitance manometer was used to monitor the gas phase adsorbate pressure. A detailed description of this apparatus can be found elsewhere (11, 12). Hydrogen (Liquid Carbonic) was purified for these measurements by passage through a Deoxo unit (Engelhard), followed by molecular sieves (Davison) at 77 K. Carbon monoxide (Matheson 99.9%) was purified by passage through a heated trap (573 K) packed with quartz wool and dried by passage through molecular sieves at 77 K. The purified hydrogen and carbon monoxide were stored in 5-liter bulbs attached to the volumetric adsorption system. Ethylene (Matheson 99.5%) was placed in a glass cell connected to the vacuum apparatus, and it was purified by performing several freeze–pump–thaw cycles prior to each experiment.

TABLE 1

Summary of Pt/Sn/Cab-O-Sil Catalyst Compositions

Catalyst	Pt loading (wt%)	Sn loading (wt%)	Pt/Sn atomic ratio
0.04 wt% Pt	0.04	0.00	1 : 0
1.2 wt% Pt	1.23	0.00	1 : 0
6 : 1 Pt/Sn	1.22	0.12	6.2 : 1
1 : 1 Pt/Sn	1.22	0.67	1.1 : 1
1 : 3 Pt/Sn	1.23	2.07	1 : 2.8

RESULTS

Reaction Kinetic Studies

Steady-state kinetic studies were conducted to determine the activity and selectivity of the different catalysts at reaction conditions of 673 K, 12.5 Torr of isobutane, 75 Torr of hydrogen, and a total pressure of 760 Torr. All catalysts were first reduced with hydrogen at 773 K for 1 h and then cooled to 673 K before kinetic data were collected.

Table 2 shows reaction selectivities and isobutane conversions for the Pt and Pt/Sn catalysts. Hydrogenolysis and isomerization reactions are significant over the 1.2 wt% Pt catalyst, even at low conversions. For example, while dehydrogenation is the predominate reaction over the 1.2 wt% Pt catalyst at an isobutane conversion of 2.1%, significant amounts of methane, ethane, propane, and *n*-butane are also produced. At a higher isobutane conversion of 17%, the dehydrogenation selectivity is decreased since this reaction is limited by equilibrium. Accordingly, the isomerization and hydrogenolysis reactions predominate at higher conversions.

Table 2 shows that adding tin to the 1.2 wt% Pt catalyst has a significant effect on the hydrogenolysis and isomerization reaction rates. Over the 6 : 1 Pt/Sn catalyst, a lower space velocity was required to achieve 17% isobutane conversion. While the selectivities are similar to those observed for the 1.2 wt% Pt without tin, the addition of tin decreased the reaction rates of both the isomerization and the hydrogenolysis reactions. The dehydrogenation selectivity did not improve since the overall conversion is greater than the equilibrium conversion of 7% for the dehydrogenation reaction.

Increasing the amount of tin to produce a 1 : 1 Pt/Sn ratio further suppresses the hydrogenolysis and isomerization reactions and gave a catalyst with a dehydrogena-

TABLE 2

Isobutane Conversion and Selectivities over Pt and Pt/Sn Catalysts at 673 K, 12.5 Torr Isobutane, 75 Torr Hydrogen, and 760 Torr Total Pressure

Catalyst	1.2 wt% Pt	6 : 1 Pt/Sn	1 : 1 Pt/Sn	1 : 3 Pt/Sn	1.2 wt% Pt	0.04 wt% Pt
WHSV[a] (h^{-1})	6.52	3.91	3.88	3.82	324	11.8
Isobutane conversion (%)	17.0	17.1	4.8	4.5	2.1	3.5
CH_4 selectivity[b]	46.5	43.8	1.4	1.0	17.2	2.3
C_2H_6 selectivity[b]	14.7	12.5	0.1	0.2	4.8	0.2
C_3H_8 selectivity[b]	30.7	28.1	1.2	0.6	10.3	1.3
n-C_4H_{10} selectivity[b]	32.6	34.2	0.0	0.1	8.0	0.0
i-C_4H_8 selectivity[b]	25.4	27.5	98.7	99.1	77.5	98.0

[a] WHSV = (g isobutane/h)/(g catalyst).

[b] Selectivity = (100 × mol product)/(mol isobutane reacted).

tion selectivity of 98.7% at an overall isobutane conversion of 4.8%. The 1 : 3 Pt/Sn catalyst exhibited 99.1% selectivity for dehydrogenation at an isobutane conversion of 4.5%. The space velocities for kinetic studies of the 6 : 1, 1 : 1, and 1 : 3 Pt/Sn catalysts were essentially equal. In the latter two cases, the hydrogenolysis and isomerization reactions were inhibited and the isobutane conversion approached the equilibrium conversion for the dehydrogenation reaction.

Decreasing the platinum particle size also appears to suppress the hydrogenolysis and isomerization reactions. Table 2 shows that the highly dispersed 0.04 wt% Pt catalyst produces lower yields of hydrogenolysis and isomerization products at an isobutane conversion of 3.5% compared to the 1.2 wt% Pt catalyst at an isobutane conversion of 2.1%.

Catalytic activities were determined over the 1.2 wt% Pt and Pt/Sn catalysts under reaction conditions of 723 K, 12.5 Torr of isobutane, 75 Torr of hydrogen, and a total pressure of 760 Torr. For quantitative comparisons between catalysts, it was necessary to ensure that the kinetic data were not influenced by mass or heat transfer limitations. Computational criteria have been developed to test for these transport limitations for catalytic systems (13–16). Accordingly, all activity tests were performed on sieved catalysts (80–120 mesh) that were mixed with Cab-O-Sil at a dilution ratio greater than 19 : 1. In addition, isobutane conversions were maintained less than 10% of the equilibrium dehydrogenation conversion of 24.5%.

Figure 1 presents the turnover frequencies for isobutane conversion, based on the total number of platinum atoms in the catalysts. This figure shows that the 1.2 wt% Pt catalyst has the highest overall activity, and the activity decreases with increasing tin content. The 1.2 wt% Pt and 6 : 1 Pt/Sn catalysts exhibited dehydrogenation selectivities of 80 and 97%, respectively. The 1 : 1 and 1 : 3 Pt/Sn catalysts exhibited essentially 100% dehydrogenation selectivity. In addition, both the Pt and the 6 : 1 Pt/Sn catalysts showed significant deactivation, while deactivation of the 1 : 1 and 1 : 3 Pt/Sn catalysts was more moderate.

Tin Mössbauer Spectroscopy

Table 3 shows the Mössbauer parameters observed for the spectra of SnO, SnO_2 (Aldrich), and β-tin (Amersham). The observed chemical shifts for these materials are in good agreement with literature values (17, 18).

The 1 : 1 Pt/Sn catalyst was pressed between two 0.1-mm-thick, 25-mm-diameter glass fiber pads in a stainless-steel holder that was placed in a glass treatment cell. The catalyst was then treated with flowing hydrogen at 773 K for 24 h and cooled to ambient temperature. Figure 2 shows that the spectrum for this sample consists of a single dominant peak at a chemical shift of 1.83 mm/s. This spectrum shows no evidence for SnO_2 species and slight evidence for SnO. Gray and Farha (17) showed a linear relationship between tin content and the chemical shift in PtSn alloys and solid solutions. Accordingly, the

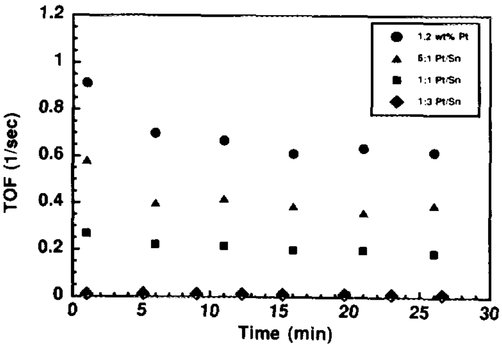

FIG. 1. Total isobutane turnover frequencies based on the total number of platinum atoms over silica-supported Pt and Pt/Sn catalysts. Reaction conditions are as follows: 723 K, 12.5 Torr isobutane, 75 Torr hydrogen, 760 Torr total pressure, and conversion less than 2.5%.

TABLE 3

Mössbauer Spectral Parameters for Tin Standard Materials at Room Temperature

Material	Chemical shift (mm/s)	Quadrupole splitting (mm/s)
$BaSnO_3$	0.00	—
β-Tin	2.56	—
SnO_2	0.09	—
SnO	2.66	1.37

chemical shift for the Pt/Sn alloy peak shown in Fig. 2 indicates an alloy with a tin content of 48 at.% Sn, which is in agreement with the elemental analysis data shown in Table 1.

Figure 3 shows the Mössbauer spectrum for the 1 : 3 Pt/Sn catalyst, following the treatment described above. This spectrum consists of a single peak with a chemical shift of 2.03 mm/s and a doublet indicating the presence of SnO. This spectrum shows no evidence for SnO_2 species. The chemical shift for the single peak suggests the formation of a Pt/Sn alloy with a tin content of 63 at.% Sn. The elemental analysis data shown in Table 1 indicate an overall content of 74 at.% tin. The appearance of SnO accounts for the additional tin shown in Fig. 3.

Microcalorimetric Studies

Catalyst samples were pretreated for microcalorimetric adsorption experiments by heating in the calorimeter cell under vacuum over a period of 3 h to 673 K, followed by evacuation at this temperature for 1 h. After cooling the cell to room temperature, 500 Torr of hydrogen was admitted into the system and the cells were heated to 723 K over a period of 3 h and held at this temperature for 2 h to reduce the catalyst. The gas in the cells was evacuated and replaced with fresh hydrogen several times during these reduction steps. Following reduction, the catalyst was outgassed at 673 K for 2 h. The calorimeter thermal block was subsequently raised around the cells and the system allowed to equilibrate overnight. Microcalorimetric measurements of the adsorption of hydrogen and carbon monoxide were conducted at 403 K, and measurements of the adsorption of ethylene were conducted at 323 K.

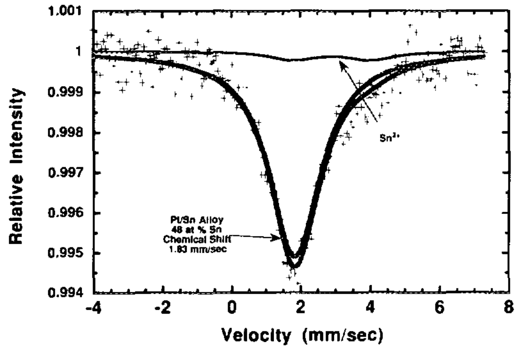

FIG. 2. Mössbauer spectrum of 1 : 1 Pt/Sn catalyst after reduction at 773 K for 24 h.

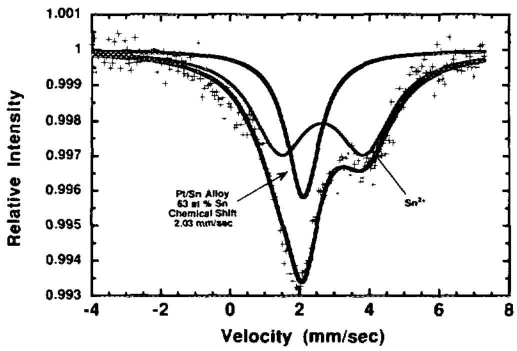

FIG. 3. Mössbauer spectrum of 1 : 3 Pt/Sn catalyst after reduction at 773 K for 24 h.

Figures 4 and 5 show plots of differential heat versus adsorbate coverage for hydrogen and carbon monoxide adsorption on the 1.2 wt% Pt and Pt/Sn catalysts. These figures show initial differential heats on the 1.2 wt% Pt catalyst of 93 and 144 kJ/mol for hydrogen and carbon monoxide adsorption, respectively. As the adsorbate coverages increase, the differential heats of adsorption decrease due to adsorption on weaker sites and/or interactions between adsorbed species. At higher coverages, the significant decreases in the differential heats of adsorption indicate saturation of the surface.

Figure 4 shows that the addition of tin decreases the saturation coverage of hydrogen on the catalyst. The initial differential heats are essentially the same for the 1.2 wt% Pt, 6 : 1 Pt/Sn, and 1 : 1 Pt/Sn catalysts; however, the 1 : 3 Pt/Sn catalyst shows a significantly lower initial heat. As with the adsorption of hydrogen, Fig. 5 indicates a decrease in the number of sites for carbon monoxide adsorption with increasing tin content. The 1 : 1 Pt/Sn

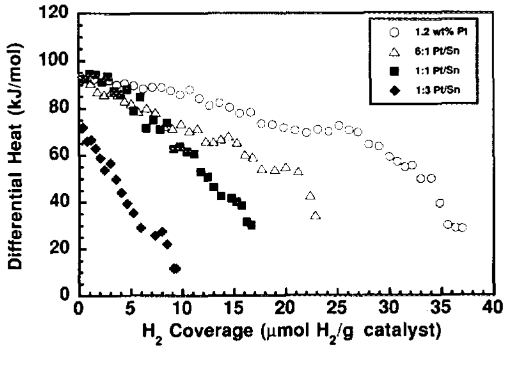

FIG. 4. Differential heats of hydrogen adsorption on silica-supported Pt and Pt/Sn catalysts at 403 K.

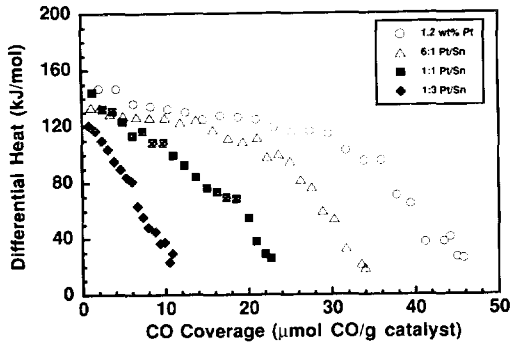

FIG. 5. Differential heats of carbon monoxide adsorption on silica-supported Pt and Pt/Sn catalysts at 403 K.

catalyst exhibited an initial heat comparable to that of the Pt catalyst, while the initial differential heat over the 1 : 3 Pt/Sn catalyst was significantly lower. The 6 : 1 Pt/Sn was degassed overnight at 403 K instead of for 2 h at 673 K, and the lower initial differential heat for carbon monoxide adsorption on this catalyst may be due to adsorbed hydrogen blocking the stronger adsorption sites.

Figures 6 and 7 show histograms of the differential heat distributions for adsorption of hydrogen and carbon monoxide on the Pt and Pt/Sn catalysts. These histograms were generated by first smoothing the differential heat data with a least-squares-fitted polynomial and then using this polynomial to determine the amount of adsorbate adsorbed within a given range of differential heats. As mentioned above, decreases in the differential heats of adsorption may be due to adsorption on weaker sites and/or interactions between adsorbed species.

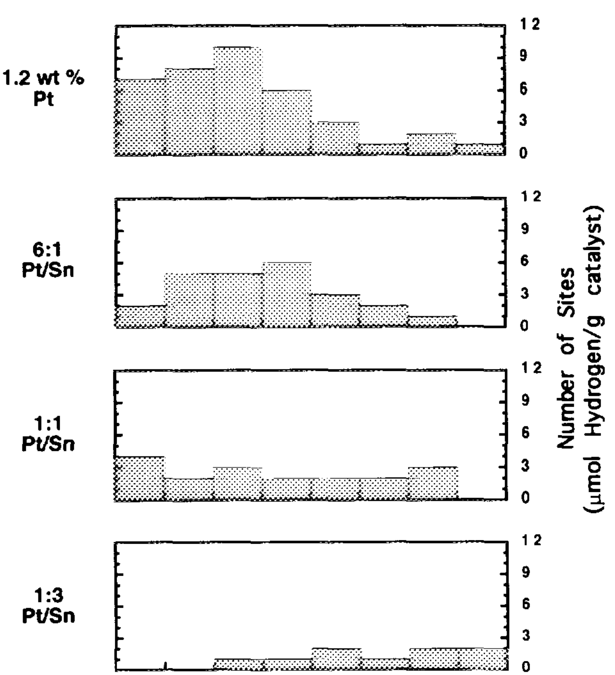

FIG. 6. Distribution of differential heats for hydrogen adsorption on silica-supported Pt and Pt/Sn catalysts at 403 K.

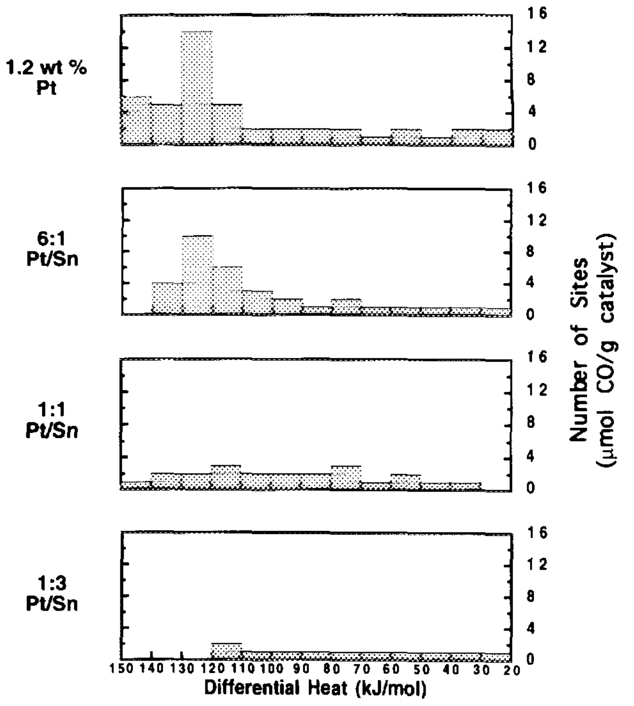

FIG. 7. Distributions of differential heats for carbon monoxide adsorption on silica-supported Pt and Pt/Sn catalysts at 403 K.

Figure 6 indicates that the 1.2 wt% Pt catalyst contains the largest number of sites for hydrogen adsorption, and the majority of the adsorbed hydrogen interacts with Pt to produce differential heats greater than 60 kJ/mol. The addition of tin decreases the amount of hydrogen adsorbed, and this effect appears to be more significant for those sites that interact with hydrogen more strongly. Figure 7 shows similar results for the adsorption of carbon monoxide. Specifically, the 1.2 wt% Pt catalyst contains the largest number of sites for carbon monoxide adsorption, and the majority of the carbon monoxide interacts with the platinum to produce differential heats greater than 100 kJ/mol. The addition of tin decreases the amount of carbon monoxide adsorbed, and this effect appears to be more significant for those sites that interact with carbon monoxide more strongly. It should be noted that addition of tin did not alter the CO/H ratio (~0.65 for all catalysts), indicating that spillover of atomic hydrogen from platinum to tin does not appear to be significant under the conditions of this study.

The adsorption of ethylene was investigated on Pt and a 1 : 1.5 Pt/Sn catalyst at 323 K. This 1 : 1.5 Pt/Sn catalyst was produced by impregnation of a tributyltinacetate/pentane solution onto a 0.86 wt% Pt/Cab-O-Sil catalyst. Figure 8 shows plots of the differential heats versus cover-

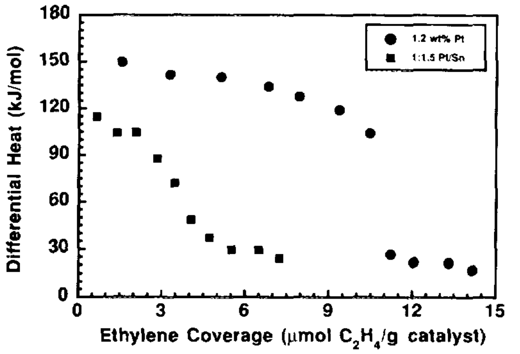

FIG. 8. Differential heats of ethylene adsorption on silica-supported Pt and Pt/Sn catalysts at 323 K.

age for ethylene on these two catalysts. The initial heat is equal to 150 kJ/mol for the Pt catalyst, and the saturation ethylene coverage was 11 μmol/g. The 1 : 1.5 Pt/Sn catalyst exhibited weaker ethylene adsorption, with an initial heat equal to 115 kJ/mol and a saturation coverage of 4.6 μmol/g. Ethylene adsorption stoichiometries were estimated using the number of surface platinum atoms determined from the saturation amount of adsorbed hydrogen at 403 K. On the Pt catalyst, one ethylene molecule appears to be associated with six platinum surface atoms, while the 1 : 1.5 Pt/Sn catalyst showed an adsorption stoichiometry of one ethylene molecule associated with four platinum surface atoms.

DISCUSSION

The reaction kinetics results of this study show that the addition of tin to platinum increases the selectivity for isobutane dehydrogenation. Table 2 indicates that the tin content of a 1 : 1 Pt/Sn catalyst is sufficient to inhibit almost completely the isomerization and hydrogenolysis reactions, while allowing the dehydrogenation reaction to proceed at a significant rate. The addition of tin also decreases the rate of catalyst deactivation. Table 2 shows lower yields of hydrogenolysis and isomerization products over the 0.04 wt% Pt catalyst compared to the 1.2 wt% Pt catalyst. This behavior suggests that the isomerization and hydrogenolysis reactions are also suppressed on smaller Pt particles. However, the enhanced dehydrogenation selectivity observed for the Pt/Sn catalysts is not due to particle size effects, since these catalyst were prepared from the 1.2 wt% Pt catalyst and pretreated in a similar manner.

The Mössbauer spectra in Figs. 2 and 3 are in agreement with previous Mössbauer spectroscopic and EXAFS investigations of silica-supported Pt/Sn catalysts (19, 20). For example, Li *et al.* (19) observed that a Pt/Sn alloy was the dominant species on a silica-supported catalyst containing equal amounts of platinum and tin. In addition, these investigators observed the formation of a Pt/Sn alloy as well as evidence of SnO on a silica-supported catalyst with a Pt : Sn atomic ratio of 1 : 2.8. The EXAFS investigation of Meitzner *et al.* (20) concluded that tin was present in the zero-valent state in reduced, silica-supported Pt/Sn catalysts, and these materials contained predominantly Pt/Sn alloy particles.

The differential heats for the adsorption of hydrogen and carbon monoxide on the Pt catalysts are in agreement with the work of Sharma *et al.* for Pt supported on silica and neutralized zeolites (21). These investigators reported initial differential heats for hydrogen and carbon monoxide adsorption on Pt at 403 K of 92 and 140 kJ/mol, respectively. In addition, the initial heat of hydrogen adsorption on the Pt/silica catalyst of the present study is in good agreement with published values of ca. 90 kJ/mol for supported and unsupported platinum catalysts (22–24).

Figures 4 and 5 show a decrease in the number of adsorption sites with increasing tin content for the adsorption of both hydrogen and carbon monoxide. In addition, Fig. 8 shows that the addition of tin decreases the number of adsorption sites and the heats of adsorption for ethylene. Verbeek and Sachtler (25) showed that the extents of adsorption for deuterium, carbon monoxide, and ethylene decreased on Pt/Sn alloy particles with increasing tin content.

Verbeek and Sachtler (25) used temperature-programmed desorption to show that Sn weakened the interaction of these compounds with the surface. In the present study, we have found that addition of tin affects the stronger sites for the adsorption of hydrogen and carbon monoxide, as seen in Figs. 6 and 7. In the case of the 1 : 3 Pt/Sn catalyst, the stronger sites were completely removed. It is not possible to rule out weakening of the stronger sites due to ligand effects caused by the formation of the Pt/Sn alloy. Accordingly, the elimination of the stronger sites may be due to preferential blocking of the stronger sites by tin or the weakening of adsorption sites due to ligand effects.

It is important to note that the 1 : 1 Pt/Sn catalyst contains a significant number of sites that interact strongly with hydrogen and carbon monoxide (see Figs. 6 and 7), since the hydrogenolysis and isomerization reactions are effectively inhibited over the 1 : 1 Pt/Sn catalyst (see Table 2). These results indicate that the inhibition by tin of the hydrogenolysis and isomerization reactions is not due solely to weakening of the platinum adsorption sites. Furthermore, Table 2 shows a decrease in yields of the hydrogenolysis and isomerization products over the 0.04 wt% Pt catalyst when compared to 1.2 wt% Pt. Moreover, Sharma *et al.* (21) indicated that particle size does not have a significant effect on the heats of hydrogen and carbon monoxide adsorption on platinum, even for cluster size particles supported in L-zeolite. These results suggest that the hydrogenolysis and isomerization reactions are suppressed over smaller Pt surface ensembles. Accordingly, the addition of tin appears to alter the reactivity primarily by decreasing ensemble size of the Pt surface sites.

The literature suggests that dehydrogenation reactions proceed on small ensembles of surface platinum atoms. For example, Biloen *et al.* (26) concluded that only one platinum atom is necessary for dehydrogenation reactions. In contrast, hydrogenolysis, isomerization, and coking reactions proceed through the formation of highly dehydrogenated species over multiple adsorption sites. For example, metal-catalyzed isomerization of isobutane has been shown to occur through a bond-shift mechanism (27–29) involving the formation of $\alpha\alpha\gamma$-diadsorbed intermediates bonded to two Pt surface atoms. Foger and Anderson (30) showed that the isomerization reaction of neopentane over Pt was structure sensitive and proceeded through a bond-shift mechanism over larger Pt particles. Anderson has proposed that the main route for isobutane hydrogenolysis is through a 1,3-diadsorbed species (28) that undergoes further dehydrogenation, forming multiple carbon–metal bonds. Analogous to the hydrogenolysis reaction, an ensemble of surface Pt atoms is required for decomposition reactions leading to coke formation.

The adsorption stoichiometries for ethylene adsorption were found in this study to be six Pt surface atoms for ethylene on Pt and four Pt surface atoms for ethylene on the 1 : 1.5 Pt/Sn catalyst. These stoichiometries are consistent with the results observed for the adsorption of ethylene on Pt(111) and Sn/Pt(111) single-crystal surfaces (31, 32). These single-crystal studies found that ethylene decomposes on Pt(111) to produce ethylidyne species and surface hydrogen atoms (32). However, decomposition was not observed over the Sn/Pt(111) surface, and the predominant adsorbed species was di-σ-adsorbed ethylene (32). Therefore, it appears that the addition of tin inhibits the formation of highly dehydrogenated species on platinum, while the formation of di-adsorbed species is not eliminated. Extending these results to the reaction of isobutane, we suggest that the addition of tin inhibits the formation of highly dehydrogenated surface species that are intermediates for hydrogenolysis, isomerization, and coking reactions. However, isobutane apparently is able to adsorb on a Pt/Sn surface to form di-adsorbed species that sequentially desorb as isobutylene.

The literature (26) suggests that dehydrogenation reactions may be structure insensitive, since they may proceed over a single Pt surface atom. Accordingly, the rate of isobutane dehydrogenation may be related simply to the number of Pt surface atoms. However, the catalytic activities for the 1 : 1 and 1 : 3 Pt/Sn catalysts are lower than those predicted from the saturation extents of hydrogen or carbon monoxide adsorption. Table 4 shows the initial turnover frequencies for isobutane dehydrogenation based on the total number of platinum atoms in the catalysts and the number of surface atoms determined from hydrogen and carbon monoxide adsorption. Table 4 shows that the dehydrogenation activity for the 1 : 3 Pt/Sn catalyst is markedly lower than that of the 1.2 wt% Pt catalyst, even when the turnover frequency is calculated using the number of sites determined by adsorption measurements. Figures 6 and 7 show that the strong sites for hydrogen and carbon monoxide adsorption are essentially absent for the 1 : 3 Pt/Sn catalyst. Accordingly, these results suggest that strong adsorption sites are more effective for isobutane dehydrogenation.

TABLE 4

Isobutane Dehydrogenation Turnover Frequencies Based on the Number of Sites Determined from the Total Number of Platinum Atoms and from Chemisorption Results

Catalyst	Dehydrogenation turnover frequencies (1/s) Total platinum	H_2 chemisorption	CO chemisorption
1.2 wt% Pt	0.72	0.72	1.10
6 : 1 Pt/Sn	0.57	0.82	1.28
1 : 1 Pt/Sn	0.27	0.61	0.89
1 : 3 Pt/Sn	0.01	0.06	0.09

CONCLUSIONS

The addition of tin to silica-supported platinum enhances the selectivity for the dehydrogenation of isobutane to isobutylene. In particular, a silica-supported 1 : 1 Pt/Sn catalyst exhibited approximately 98% selectivity for isobutane dehydrogenation. The Mössbauer spectrum of this catalyst showed that most of the tin was present with platinum in the form of Pt/Sn alloy particles. Microcalorimetric investigations showed that tin decreased the number of sites that strongly interact with hydrogen or carbon monoxide. However, these strong adsorption sites are still present on the 1 : 1 Pt/Sn catalyst that exhibited high dehydrogenation selectivity. These results suggest that ensemble effects are primarily responsible for the higher dehydrogenation selectivity of catalysts containing tin; i.e., tin decreases the size of surface Pt ensembles. Microcalorimetric results for the adsorption of ethylene suggest that the addition of tin inhibits the formation of highly dehydrogenated surface species. Accordingly, the addition of tin appears to attenuate the hydrogenolysis, isomerization, and coking reactions by inhibiting the formation of these highly dehydrogenated surface species.

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