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Effects of Potassium on Silica-Supported Pt and Pt/Sn Catalysts for Isobutane Dehydrogenation

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Isobutane conversion was studied over silica-supported Pt, Pt/Sn, and Pt/Sn/K catalysts at temperatures from 673 to 773 K. The addition of tin to Pt/SiO$_2$ suppresses isobutane isomerization and hydrogenolysis reactions, and decreases to a smaller extent the activity for isobutane dehydrogenation. The addition of potassium to Pt/Sn/SiO$_2$ promotes isobutane dehydrogenation, increases the dehydrogenation selectivity, and improves resistance of the catalyst to deactivation. The additions of tin and potassium lead to the formation of smaller ensembles of surface platinum atoms, and the hydrogenolysis, isomerization, and coking reactions are thereby suppressed. Microcalorimetric measurements of hydrogen and carbon monoxide adsorption indicate that the addition of potassium to Pt/SiO$_2$ and Pt/Sn/SiO$_2$ does not significantly alter the heats of adsorption of these molecules, whereas potassium increases the saturation extent of hydrogen adsorption and decreases the extent of carbon monoxide adsorption. The rate of isobutane dehydrogenation becomes zero order with respect to hydrogen pressure over Pt/SiO$_2$ at hydrogen pressures lower than 75 Torr, and dissociative adsorption of isobutane appears to control the dehydrogenation rate. The dehydrogenation reaction is negative order with respect to hydrogen over both Pt/Sn/SiO$_2$ and Pt/Sn/K/SiO$_2$ catalysts, indicating a higher coverage of hydrogen at the active sites. The increased dehydrogenation rate over Pt/Sn/K/SiO$_2$ may be attributed to the increased number of sites available for removal of hydrogen from adsorbed isobutane and perhaps also to the stabilization of molecularly adsorbed isobutane.

INTRODUCTION

Catalytic dehydrogenation processes are of increasing importance because of growing demand for olefins such as propylene and isobutylene. For example, isobutylene is a feedstock for the production of oxygenated compounds required in reformulated gasoline, such as methyl *tert*-butyl ether, ethyl *tert*-butyl ether, and *tert*-butyl alcohol.

The addition of tin to platinum-based catalysts increases the selectivity for dehydrogenation of isobutane to isobutylene (e.g., (1–4)). In agreement with other studies of the Pt/Sn/SiO$_2$ system (5, 6), we showed in our previous investigation that tin interacts with silica-supported platinum to form Pt/Sn alloy particles (1). This addition of tin decreases the size of surface Pt ensembles, thereby inhibiting the formation on the surface of highly dehydrogenated hydrocarbon species required for hydrogenolysis, isomerization, and coking reactions. Accordingly, the attenuation of these reactions enhances the selectivity for the dehydrogenation reaction that can proceed over small ensembles of surface Pt atoms.

While Pt/Sn/SiO$_2$ catalysts can exhibit high selectivity for isobutane dehydrogenation, the addition of tin to Pt/SiO$_2$ also reduces the activity for isobutane dehydrogenation (1). We show in the present paper that addition of potassium to Pt/Sn/SiO$_2$ catalysts promotes the dehydrogenation of isobutane to isobutylene. Furthermore, Pt/Sn/K/SiO$_2$ catalysts exhibit higher dehydrogenation selectivity and greater resistance to deactivation compared to Pt/Sn/SiO$_2$.

EXPERIMENTAL

Two silica-supported platinum catalysts were used in this present investigation, a 1.2 wt% Pt/SiO$_2$ catalyst employed in our previous study (1) and a 0.93 wt% Pt/SiO$_2$ catalyst. Both catalysts were prepared by ion-exchange, using the method of Benesi *et al.* (7). The resulting material was filtered, washed with deionized water, and dried overnight in air at 390 K.

Potassium was added to the 1.2 wt% Pt/SiO$_2$ catalyst by incipient wetness impregnation with an aqueous solution of KOH (Alfa 99.995% KOH). The resulting Pt/K/SiO$_2$ catalyst was dried in air at 390 K. The Pt/SiO$_2$ and Pt/K/SiO$_2$ catalysts were subsequently treated in flowing oxygen at 573 K for 2 h, followed by reduction for 2 h in flowing hydrogen at 673 K.

Tin was added to the 1.2 wt% Pt catalyst by evaporative impregnation of a solution of tributyltinacetate in pentane. This method was used to produce catalysts with Pt : Sn atomic ratios of 1 : 1 and 1 : 2.8. After impregnation with

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tin, the catalysts were dried overnight in air at 390 K, treated with flowing oxygen at 573 K for 2 h, followed by reduction for 2 h in flowing hydrogen at 773 K.

Tin was added to the 0.93 wt% Pt catalyst by evaporative impregnation of a tributyltinacetate/pentane solution to produce a catalyst with Pt : Sn atomic ratios of 1 : 1. After impregnation with tin, the catalyst was dried overnight in air at 390 K. Potassium was added to the dried $Pt/Sn/SiO_2$ catalyst by incipient wetness impregnation with an aqueous solution of KOH. The resulting $Pt/Sn/K/SiO_2$ catalyst was dried in air at 390 K. The $Pt/Sn/SiO_2$ and $Pt/Sn/K/SiO_2$ catalysts (0.93 wt% Pt) were treated with flowing oxygen at 673 K for 2 h, followed by reduction for 7 h in flowing hydrogen at 773 K. Table 1 shows elemental analyses (Galbraith Laboratories, Inc.) of the catalysts investigated in this present study.

Kinetic studies of isobutane conversion were conducted using 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 (13X) at 77 K. Isobutane (Liquid Carbonic, 99.5%) was treated by passage over beds of reduced Oxytrap (Alltech) and reduced Ni on alumina at 373 K to remove oxygen and sulfur impurities, respectively. Hydrogen (Liquid Carbonic) was treated by passage through a Deoxo unit (Engelhard) and a bed of molecular sieves (13X) at 77 K. The reactor inlet and outlet gases were analyzed by a HP-5890 gas-chromatograph with FID detector and a 10-ft 15% Squalane Chromsorb PAW column held at 318 K. Turnover frequencies were calculated from the kinetic data based on the number of surface platinum atoms determined by the saturation uptakes of hydrogen at 403 K.

Differential enthalpy changes 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 detailed description of this apparatus can be found elsewhere (8, 9). In short, the differential enthalpy changes of adsorption, ΔH_{ads}, versus adsorbate coverage were obtained by measuring the heat evolved from sequential doses of the adsorbate gas (0.5–2.0 μmol) onto the catalyst until the surface was saturated by adsorbed species. These values of ΔH_{ads} are negative, and it is convenient to define the heat of adsorption as being equal to $-\Delta H_{ads}$. 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. Ethylene (Matheson 99.5%) was purified by performing several freeze–pump–thaw cycles prior to each experiment.

TABLE 1

Compositions of Silica-Supported Pt, Pt/Sn, and Pt/Sn/K Catalysts

Catalyst	Pt loading (wt%)	Sn loading (wt%)	K loading (wt%)	Pt/Sn/K (atomic ratio)
Pt/SiO_2	1.2	—	—	1:0:0
$Pt/K/SiO_2$	1.2	—	0.7	1:0:2.9
$Pt/Sn/SiO_2$	1.2	0.67	—	1:0.9:0
$Pt/Sn/SiO_2$	1.2	2.1	—	1:2.8:0
$Pt/Sn/SiO_2$	0.93	0.51	—	1:0.9:0
$Pt/Sn/K/SiO_2$	0.93	0.51	0.5	1:0.9:2.7

RESULTS

Reaction Kinetic Studies

Table 2 shows the initial isobutane reactivities over the silica-supported Pt, Pt/K, Pt/Sn, and Pt/Sn/K catalysts. The reaction conditions for these measurements were 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. The equilibrium conversion of isobutane to isobutylene is 7.0% at these conditions.

Table 2 shows the isobutane reactivities over the Pt/SiO_2 catalyst at two isobutane conversions, 19.0 and 2.1%. This table shows that the Pt/SiO_2 catalyst exhibits the highest production rates of methane, ethane, propane, and *n*-butane, and these rates are slightly higher at the lower isobutane conversion. The turnover frequencies for formation of the hydrogenolysis and isomerization products are 2–4 times lower over the $Pt/K/SiO_2$ catalyst compared to the Pt/SiO_2 catalyst.

In agreement with our previous investigation (1), Table 2 indicates that the addition of Sn to Pt/SiO_2 suppresses the hydrogenolysis and isomerization reactions. The turnover frequencies for production of methane, ethane, propane, and *n*-butane decrease with increasing tin content. The addition of potassium to $Pt/Sn/SiO_2$ further decreases the rates for production of methane, ethane, propane, and *n*-butane. Accordingly, higher dehydrogenation selectivities are observed over $Pt/Sn/SiO_2$ and $Pt/Sn/K/SiO_2$ at isobutane conversions greater than 3.4% compared to the Pt/SiO_2 catalyst at an isobutane conversion of 2.1%.

Figure 1 shows dehydrogenation reaction rates measured at 723 K, 12.5 Torr of isobutane, 75 Torr of hydrogen, and a total pressure of 760 Torr over sieved catalyst fractions (80–120 mesh) of the various platinum-based catalysts mixed with Cab-O-Sil at a dilution ratio greater than 19 : 1. These conditions were chosen to ensure that the dehydrogenation rates were not influenced by transport limitations (10–12). Isobutane conversions were main-

TABLE 2

Isobutane Reactivity at 673 K, 12.5 Torr Isobutane, 75 Torr Hydrogen, and 760 Torr Total Pressure

Catalyst	Pt/SiO_2	Pt/SiO_2	$Pt/K/SiO_2$	$Pt/Sn/SiO_2$	$Pt/Sn/SiO_2$	$Pt/Sn/K/SiO_2$
Wt% Pt	1.2	1.2	1.2	1.2	0.93	0.93
Pt/Sn/K ratio	1:0:0	1:0:0	1:0:3	1:2.8:0	1:1:0	1:1:2.7
WHSV[a] (h^{-1})	6.5	324	8.0	3.8	7.3	7.4
Isobutane conversion (%)	19.0	2.1	7.7	4.5	3.4	3.4
Isobutane conversion TOF[b]	8.0×10^{-2}	3.7×10^{-1}	3.5×10^{-2}	4.3×10^{-2}	5.2×10^{-2}	3.0×10^{-2}
CH_4 TOF[b]	4.1×10^{-2}	6.4×10^{-2}	1.7×10^{-2}	5.2×10^{-4}	6.1×10^{-3}	2.4×10^{-3}
C_2H_6 TOF[b]	1.4×10^{-2}	1.8×10^{-2}	4.4×10^{-4}	1.3×10^{-4}	1.3×10^{-3}	2.2×10^{-5}
C_3H_8 TOF[b]	2.6×10^{-2}	3.8×10^{-2}	1.6×10^{-2}	4.5×10^{-4}	5.3×10^{-3}	1.7×10^{-4}
n-C_4H_{10} TOF[b]	2.8×10^{-2}	3.0×10^{-2}	5.4×10^{-3}	3.6×10^{-4}	4.9×10^{-3}	1.8×10^{-4}
i-C_4H_8 selectivity[c] (%)	19.5	77.5	36.1	99.1	78.9	96.9

[a] WHSV = (g isobutane/h)/(g catalyst).
[b] TOF = (molecules of product)/(molecules of surface Pt) (s).
[c] Selectivity = (100 × moles of product)/(moles of isobutane reacted).

tained at less than 10% of the equilibrium dehydrogenation conversion of 24.5%.

At the low conversions of these kinetic measurements, the silica-supported Pt/K, Pt/Sn, and Pt/Sn/K catalysts exhibit dehydrogenation selectivities higher than 95%. In contrast, the Pt/SiO_2 catalyst exhibits an initial dehydrogenation selectivity of 80%. Figure 1 shows that the initial dehydrogenation turnover frequency over $Pt/K/SiO_2$ is about 70% of the value for Pt/SiO_2. In agreement with our previous investigation (1), the dehydrogenation turnover frequencies are significantly lower over the $Pt/Sn/SiO_2$ catalyst. Importantly, the addition of potassium to $Pt/Sn/SiO_2$ leads to a significant increase of the dehydrogenation turnover frequency. Figure 1 also shows that the dehydrogenation turnover frequencies over Pt/SiO_2 and $Pt/K/SiO_2$ decrease with time under reaction conditions, while only modest deactivation is observed over the $Pt/Sn/SiO_2$ and $Pt/Sn/K/SiO_2$ catalysts.

Figure 2 presents turnover frequencies for the production of isobutylene at 773 K, 109 Torr of isobutane, and 651 Torr of helium (i.e., without hydrogen in the feed). The $Pt/Sn/SiO_2$ and $Pt/Sn/K/SiO_2$ catalysts exhibit essentially 100% selectivity for dehydrogenation at these low conversions. Figure 2 indicates that the addition of potassium to $Pt/Sn/SiO_2$ improves both the initial dehydrogenation activity and the resistance of the catalyst to deactivation under these reaction conditions. While the $Pt/Sn/SiO_2$ catalyst shows essentially no activity after 6 h under reaction conditions, the $Pt/Sn/K/SiO_2$ catalyst exhibits significant dehydrogenation activity and maintains high dehydrogenation activity after 24 h of operation. Figure 2 also shows the dehydrogenation turnover frequency versus time for the 1:2.8 $Pt/Sn/SiO_2$ catalyst (1.2 wt% Pt). It can be seen

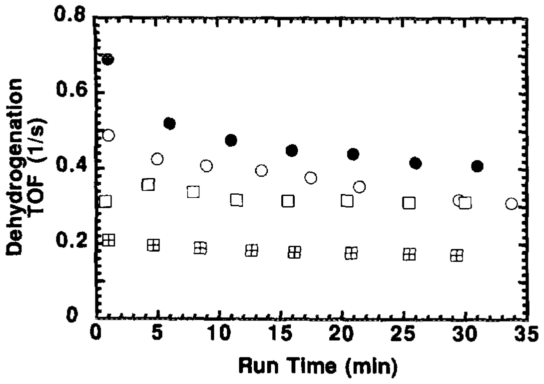

FIG. 1. Turnover frequencies for isobutylene production over silica-supported catalysts at 723 K, 12.5 Torr isobutane, 75 Torr hydrogen, 760 Torr total pressure, and isobutane conversions less than 2.5%. ●, Pt/SiO_2 (1.2% Pt); ○, 1:2.9 $Pt/K/SiO_2$ (1.2% Pt); ⊞, 1:1 $Pt/Sn/SiO_2$ (0.93% Pt); □, 1:1:2.7 $Pt/Sn/K/SiO_2$ (0.93% Pt).

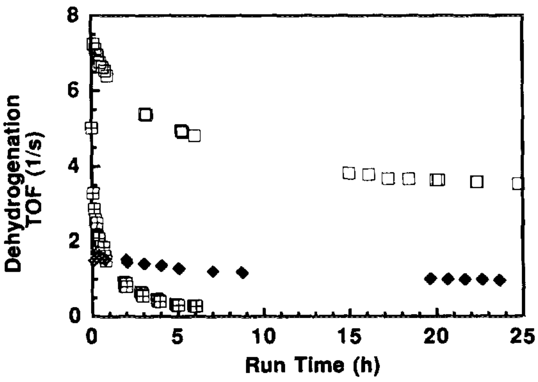

FIG. 2. Turnover frequencies for isobutylene production over silica-supported catalysts at 773 K, 109 Torr isobutane and 651 Torr helium. ⊞, 1:1 $Pt/Sn/SiO_2$ (0.93% Pt); □, 1:1:2.7 $Pt/Sn/K/SiO_2$ (0.93% Pt); ◆, 1:2.8 $Pt/Sn/SiO_2$ (1.2% Pt).

TABLE 3

Activation Energies for Isobutane Dehydrogenation at 12.5 Torr Isobutane Pressure, 75 Torr Hydrogen Pressure, and Total Pressure of 760 Torr

Catalyst	*Ea* (kJ/mol)
1.2 wt% Pt/silica	44
1 : 1 Pt/Sn/silica (1.2 wt% Pt)	76
1 : 2.8 Pt/Sn/silica (1.2 wt% Pt)	76
1 : 1 : 2.7 Pt/Sn/K (0.9 wt% Pt)	70

that the further addition of Sn to Pt leads to a lower initial dehydrogenation activity and a slower rate of catalyst deactivation.

Kinetic studies were conducted to determine activation energies and kinetic orders for isobutane dehydrogenation over the Pt/SiO_2, $Pt/Sn/SiO_2$, and $Pt/Sn/K/SiO_2$ catalysts. These catalysts were sieved and diluted with Cab-O-Sil, as described above, to avoid transport limitations. All data were collected at dehydrogenation conversions less than 15% of the equilibrium values. Table 3 shows the apparent activation energies for isobutane dehydrogenation determined at temperatures between 673 and 773 K, and at 12.5 Torr isobutane, 75 Torr hydrogen, and a total pressure of 760 Torr. Table 4 lists the hydrogen reaction orders determined at various temperatures and hydrogen pressures for the silica-supported catalysts at an isobutane pressure of 12.5 Torr. At the low conversions of these kinetic investigations, the reaction orders with respect to isobutane pressure were found to be nearly first order at a hydrogen pressure of 75 Torr and over a range of isobutane pressures between 5 and 100 Torr.

TABLE 4

Hydrogen Reaction Orders at 12.5 Torr Isobutane Pressure

Catalyst	Temperature (K)	H2 pressure range (Torr)	Hydrogen order
1.2 wt% Pt/Silica	723	25-350	0.0
	673	25-75	−0.1
	673	75-350	−0.5
1 : 1 Pt/Sn/silica (1.2 wt% Pt)	673	25-75	−0.7
	673	75-600	−1.0
	723	25-75	−0.6
	723	75-600	−0.7
	773	25-600	−0.5
1 : 2.8 Pt/Sn/silica (1.2 wt% Pt)	673	25-75	−0.5
	673	75-600	−1.0
	723	25-75	−0.3
	723	75-600	−0.6
	773	25-75	−0.1
	773	75-600	−0.4
1 : 1 : 2.7 Pt/Sn/K (0.9 wt% Pt)	673	25-75	−0.5
	673	75-450	−0.6
	723	25-75	−0.4
	723	75-450	−0.7
	773	25-450	−0.3

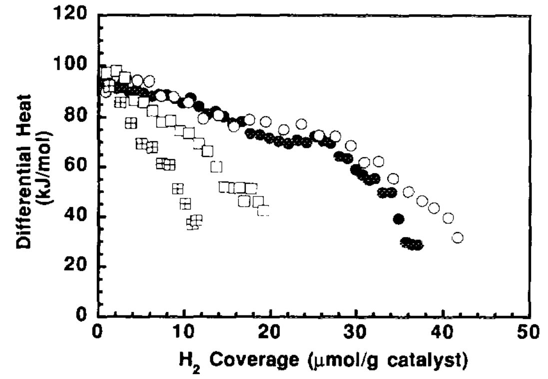

FIG. 3. Differential heats of hydrogen adsorption on silica-supported catalysts at 403 K. ●, Pt/SiO_2 (1.2% Pt); ○, 1 : 2.9 $Pt/K/SiO_2$ (1.2% Pt); ⊞, 1 : 1 $Pt/Sn/SiO_2$ (0.93% Pt); □, 1 : 1 : 2.7 $Pt/Sn/K/SiO_2$ (0.93% Pt).

Microcalorimetric Studies

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. The samples were pretreated using the procedure reported elsewhere (1).

Figures 3 and 4 show plots of differential heat versus adsorbate coverage for the adsorption of hydrogen and carbon monoxide, respectively. Table 5 lists the initial heats of hydrogen and carbon monoxide adsorption on the four catalysts of this investigation and shows that the additions

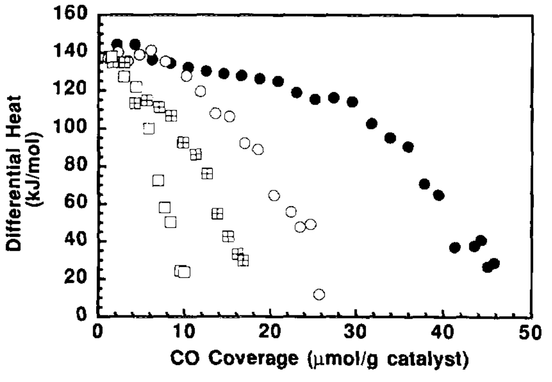

FIG. 4. Differential heats of carbon monoxide adsorption on silica-supported catalysts at 403 K. ●, Pt/SiO_2 (1.2% Pt); ○, 1 : 2.9 $Pt/K/SiO_2$ (1.2% Pt); ⊞, 1 : 1 $Pt/Sn/SiO_2$ (0.93% Pt); □, 1 : 1 : 2.7 $Pt/Sn/K/SiO_2$ (0.93% Pt).

TABLE 5

Initial Heats of Adsorption for Hydrogen, Carbon Monoxide, and Ethylene on Silica-Supported Catalysts

Catalyst	wt% Pt	Heats of adsorption (kJ/mol) H_2	CO	C_2H_4
Pt	1.2	93 ± 2	144 ± 3	145 ± 5
1:2.9 Pt/K	1.2	95 ± 2	140 ± 3	140 ± 5
1:1 Pt/Sn	0.93	92 ± 2	135 ± 3	115 ± 5
1:1:2.7 Pt/Sn/K	0.93	97 ± 2	138 ± 3	110 ± 5

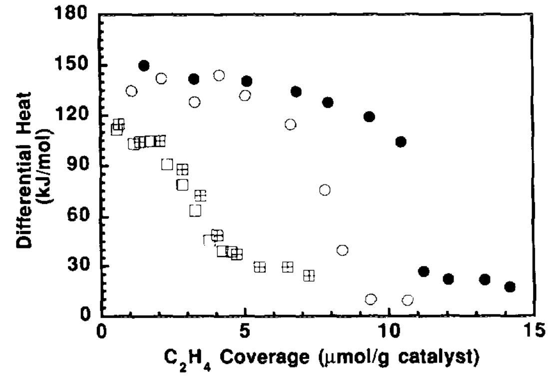

FIG. 5. Differential heats of ethylene adsorption on silica-supported catalysts at 323 K. ●, Pt/SiO$_2$ (1.2% Pt); ○, 1:2.9 Pt/K/SiO$_2$ (1.2% Pt); ⊞, 1:1 Pt/Sn/SiO$_2$ (0.93% Pt); □, 1:1:2.7 Pt/Sn/K/SiO$_2$ (0.93% Pt).

of tin and potassium have no significant effect on these initial heats. The initial heats for the adsorption of hydrogen and carbon monoxide on the Pt/SiO$_2$ catalyst are in agreement with values reported by Sharma *et al.* (13) for Pt supported on silica and neutralized zeolites.

Figure 3 shows that the addition of potassium increases the extent of hydrogen adsorption on the Pt/SiO$_2$ and Pt/Sn/SiO$_2$ catalysts. The saturation coverages of hydrogen and carbon monoxide on the four catalysts investigated are tabulated in Table 6. It can be seen therein that the addition of potassium to the Pt/Sn/SiO$_2$ catalyst increases the saturation extent of hydrogen adsorption from 11 to 19 μmol/g, while potassium increases the extent of hydrogen adsorption on Pt/SiO$_2$ from 37 to 41 μmol/g. In contrast to the adsorption of hydrogen, Fig. 4 and Table 6 show that the addition of potassium to Pt/Sn/SiO$_2$ decreases the saturation extent of carbon monoxide adsorption from 16 to 10 μmol/g, and the addition of potassium to Pt/SiO$_2$ decreases the extent of carbon monoxide adsorption from 46 to 26 μmol/g. Table 6 also shows that the CO/H ratio of saturation coverages decreases upon adding potassium to the supported catalysts, whereas the addition of tin to Pt/SiO$_2$ does not significantly alter the CO/H ratio. This latter finding is in agreement with results from our previous investigation of silica-supported Pt/Sn catalysts (1).

Figure 5 shows plots of the differential heat versus coverage for the adsorption of ethylene at 323 K. The addition of tin to Pt/SiO$_2$ leads to a significant decrease in initial heat of ethylene adsorption. However, the addition of potassium does not influence the initial heats of ethylene adsorption on the Pt/SiO$_2$ or Pt/Sn/SiO$_2$ catalysts. The ethylene saturation coverages shown in Table 6 indicate that the addition of potassium to Pt/SiO$_2$ decreases the saturation extent of ethylene adsorption from 11 to 8.5 μmol/g, while the addition of potassium to Pt/Sn/SiO$_2$ only slightly decreases the extent of ethylene adsorption.

DISCUSSION

The kinetic data of the present study show that the addition of tin to Pt/SiO$_2$ enhances the selectivity for isobutane dehydrogenation (Table 2) but decreases the dehydrogenation activity (Fig. 1), in agreement with results reported elsewhere (1). However, the present investigation also shows that the addition of potassium to Pt/Sn/SiO$_2$ increases the dehydrogenation activity (Fig. 1), enhances the dehydrogenation selectivity (Table 2), and improves the resistance of the catalyst to deactivation (Fig. 2).

Alumina-supported Pt/Sn/K catalysts are known to be

TABLE 6

Saturation Extents of Hydrogen, Carbon Monoxide, and Ethylene Adsorption at 403 K on Silica-Supported Catalysts

Catalyst	wt% Pt	Adsorption μmol/g H_2	CO	C_2H_4	CO/H	H/C_2H_4	H/Pt
Pt	1.2	37 ± 1	46 ± 1	11 ± 0.5	0.62	6.7	1.18
1:2.9 Pt/K	1.2	41 ± 1	26 ± 1	8.5 ± 0.5	0.32	9.6	1.31
1:1 Pt/Sn	0.93	11 ± 0.5	16 ± 0.5	4.5 ± 0.5	0.73	4.0	0.51
1:1:2.7 Pt/Sn/K	0.93	19 ± 1	10 ± 0.5	4.5 ± 0.5	0.26	8.4	0.89

selective for dehydrogenation reactions (3). In this system, potassium is added primarily to neutralize the acid sites of alumina and thereby to inhibit hydrocarbon cracking on the support. Imai and Hung (3) observed improved isobutane conversions over an alumina-supported Pt/Sn dehydrogenation catalyst containing amounts potassium in excess of that required to neutralize the support. In addition, this alumina-supported Pt/Sn/K catalyst exhibited lower extents of coke formation.

Table 6 shows that the addition of potassium to Pt/SiO_2 and Pt/Sn/SiO_2 decreases the saturation extent of carbon monoxide adsorption, while the addition of potassium substantially increases the uptake of adsorbed hydrogen on Pt/Sn/SiO_2 and increases slightly the extent of hydrogen adsorption on Pt/SiO_2. Accordingly, the CO/H ratio decreases with the addition of potassium to both the Pt/SiO_2 and the Pt/Sn/SiO_2 catalysts. Similar decreases in the CO/H ratio have been observed when basic oxides were added to silica-supported rhodium catalysts (14, 15). Kesraoui *et al.* (14) suggested that potassium decreased the CO/H ratio of silica-supported rhodium by blocking carbon monoxide adsorption. Underwood and Bell (15) indicated that the addition of lanthana to silica-supported rhodium had little effect on the amount of adsorbed hydrogen but significantly decreased the amount of adsorbed CO. These authors suggested that lanthana blocked sites for CO adsorption on Rh and provided sites for spilled-over H atoms.

Table 6 shows that the addition of tin to Pt/SiO_2 does not significantly alter the CO/H ratio, indicating that tin blocks platinum surface sites in a different manner than potassium. Ogletree *et al.* (16) have shown that CO adsorbs at low coverages on a-top sites of Pt(111) and forms bridge bonds with twofold coordination at higher coverages. In contrast, atomic hydrogen occupies threefold hollow sites (17, 18). The addition of tin to Pt(111) forms substitutional surface alloys (19, 20), and it has been shown that tin interacts with platinum on silica to form a Pt/Sn alloy (1, 5, 6). Accordingly, the substitution of tin in the platinum surface would alter the bonding with atomic hydrogen of threefold hollow sites and would decrease the number of onefold and twofold sites for bonding with CO.

At the treatment conditions of the present study, potassium is expected to be present as an hydroxide (21). The potassium hydroxide may well be associated with the tin atoms present within the platinum surface of the Pt/Sn/K/SiO_2 catalyst. In particular, tin has a stronger affinity for oxygen than does platinum (22), and tin may thus have a stronger affinity for the oxygen atom of KOH than platinum. This association between tin and KOH may lead to a reconstruction of the supported Pt/Sn particles, thereby weakening the influence of tin on the threefold hollow sites of platinum and allowing the bonding of atomic hydrogen to these sites.

Table 2 shows that the addition of tin to Pt/SiO_2 reduces the rates of hydrogenolysis and isomerization reactions, and the addition of potassium to Pt/Sn/SiO_2 further decreases the hydrogenolysis and isomerization reaction rates. As discussed elsewhere, it has been suggested that the isomerization, hydrogenolysis, and coking reactions proceed through the formation of highly dehydrogenated species over larger ensembles of surface Pt atoms (1). The microcalorimetric results in Fig. 5 and Table 6 show that the addition of Sn to Pt/SiO_2 alters the interaction of ethylene with Pt. The initial heat for ethylene adsorption on Pt/SiO_2 is 145 kJ/mol and the apparent adsorption stoichiometry is six Pt surface atoms for each ethylene molecule. In contrast, ethylene adsorbs on the Pt/Sn/SiO_2 catalyst with an initial heat of 115 kJ/mol and an apparent adsorption stoichiometry of four Pt surface atoms for each ethylene molecule. These adsorption stoichiometries and differential heats are consistent with the results observed for ethylene on Pt(111) and Sn/Pt(111) single-crystal surfaces (19, 23). Specifically, ethylene decomposes on Pt(111) to produce ethylidyne species and surface hydrogen atoms (23), while di-σ-adsorbed ethylene is the predominant adsorbed species on the Sn/Pt(111) surface (19). Extending these results to isobutane, we suggest that the addition of tin to platinum inhibits the formation of highly dehydrogenated surface species that are intermediates for hydrogenolysis, isomerization, and coking reactions. The lower isomerization and hydrogenolysis reaction rates (Table 2) over the Pt/Sn/K/SiO_2 catalyst suggest that the addition of potassium further decreases the size of the surface Pt ensembles. In contrast to hydrogenolysis, isomerization, and coking reactions, the literature suggests that dehydrogenation reactions can proceed on small ensembles of surface platinum atoms (24). Accordingly, the decreased size of the surface Pt ensembles caused by the additions of tin and potassium leads to high selectivity for isobutane dehydrogenation to isobutylene.

While the Pt/Sn/K/SiO_2 catalyst exhibits low production rates of methane, ethane, propane, and *n*-butane, Table 2 indicates that the addition of potassium to Pt/SiO_2 is not sufficient to significantly suppress the isomerization and hydrogenolysis reactions. In contrast to the behavior of tin, the addition of potassium to Pt/SiO_2 decreases the uptake of ethylene but does not decrease the initial heat of ethylene adsorption. These results suggest that while potassium blocks surface Pt sites for ethylene adsorption, it does not effectively suppress the decomposition of ethylene to form ethylidyne species. Thus, we see an important difference between the effects of adding tin and potassium to Pt/SiO_2. The origin of this difference may be related to the incorporation of tin into the surface of platinum through the formation of a substitutional alloy, while potassium may be present on top of the platinum surface.

Figures 3 and 4 show that the addition of potassium to Pt/SiO_2 and $Pt/Sn/SiO_2$ does not significantly alter the initial heats of hydrogen and carbon monoxide adsorption. Whereas the interaction strengths of these molecules with the surface are generally observed to be enhanced by the addition of metallic potassium to platinum single crystals (25–29), the effects on hydrogen and carbon monoxide adsorption of potassium hydroxide are expected to be much weaker. For example, Ertl and co-workers (30, 31) indicated that the addition of oxygen to metallic potassium on iron increased the thermal stability of the adsorbed potassium but weakened the promotional effect for dissociative adsorption of nitrogen. Spiewak *et al.* (32) found that while the addition of metallic K or Cs to nickel increases the heat of CO adsorption by 80–85 kJ/mol, smaller promotional effects on the heat of CO adsorption were observed when these samples were exposed to air followed by treatment in hydrogen. Accordingly, at the treatment conditions of the present study, potassium is expected to be present as a hydroxide and promotional effects are expected to be weak compared to metallic potassium.

Figure 1 shows that the addition of tin to Pt/SiO_2 decreases the catalytic activity for isobutane dehydrogenation, and the addition of potassium to $Pt/Sn/SiO_2$ increases the dehydrogenation activity. While $Pt/Sn/K/SiO_2$ has a higher hydrogen uptake (see Table 6), Fig. 1 shows that $Pt/Sn/K/SiO_2$ still exhibits higher dehydrogenation activity based on the number of hydrogen adsorption sites. In contrast to the behavior of $Pt/Sn/SiO_2$, Fig. 1 shows that the addition of potassium to Pt/SiO_2 has no effect on the dehydrogenation activity based on the number of sites determined by the uptake of hydrogen. These results suggest that the addition of potassium to $Pt/Sn/SiO_2$ promotes the dehydrogenation reaction over the active site.

A general scheme for isobutane dehydrogenation over small ensembles of surface platinum atoms is shown below.

$$C_4H_{10} + 2^* \rightarrow C_4H_9^* + H^* \qquad \text{[step 1]}$$

$$C_4H_9^* + {}^* \rightleftharpoons C_4H_8^* + H^* \qquad \text{[step 2]}$$

$$C_4H_8^* \rightleftharpoons C_4H_8 + {}^* \qquad \text{[step 3]}$$

$$H_2 + 2^* \rightleftharpoons 2H^* \qquad \text{[step 4]}$$

It was found that deuterium is readily incorporated into isobutylene in flowing gas mixtures of isobutane/D_2 and isobutylene/D_2 over silica-supported Pt and Pt/Sn catalysts at 723 K (33). These results suggest that step 1 is rate limiting and steps 2, 3, and 4 are equilibrated. The following rate expression is appropriate for this case:

$$\text{rate} = \frac{k_1 P_{C_4H_{10}}}{(1 + \sqrt{K_4 P_{H_2}})^2}$$

According to this expression, the dehydrogenation reaction has a hydrogen order of −1.0 when the surface coverage by hydrogen is high. At low hydrogen pressures, this rate expression suggests that the dehydrogenation reaction will be zero order in hydrogen, and the rate expression reduces to the following form:

$$\text{rate} = k_1 P_{C_4H_{10}}.$$

Table 4 shows that the dehydrogenation reaction over 1.2 wt% Pt/SiO_2 is nearly zero order with respect to hydrogen at 673 and 723 K for a hydrogen pressure of 75 Torr. The apparent activation energy was 44 kJ/mol, as shown in Table 3. The above rate expression suggests that the activation energy is equal to the activation energy for step 1. It has been generally observed that the activation energy for alkane-deuterium exchange over transition metals such as platinum is 40 to 50 kJ/mol (34, 35).

The lower dehydrogenation reaction rates over $Pt/Sn/SiO_2$ suggest that the addition of tin to Pt/SiO_2 decreases the rate of dissociative adsorption of isobutane. Xu *et al.* (20) showed that the presence of tin in the surface layer of Sn/Pt(111) surface alloys decreases the binding energy of molecular isobutane in comparison to Pt(111). The decrease in binding energy of this molecularly adsorbed precursor would decrease the sticking coefficient for the dissociative adsorption of isobutane.

The negative orders with respect to hydrogen for isobutane dehydrogenation over the $Pt/Sn/SiO_2$ catalysts, as shown in Table 4, suggest that the addition of Sn to Pt/SiO_2 increases the hydrogen coverage on the dehydrogenation sites. Paffett *et al.* (36) showed that the presence of tin suppressed both the adsorption and desorption rates of hydrogen on Pt(111) surface. The higher apparent dehydrogenation activation energies over the $Pt/Sn/SiO_2$ catalysts, shown in Table 3, may thus be attributed to the larger influence of hydrogen pressure over $Pt/Sn/SiO_2$ catalysts.

It is suggested that the addition of potassium to $Pt/Sn/SiO_2$ promotes the dissociation of isobutane. Figure 3 shows that the addition of potassium increases the number of sites for hydrogen adsorption. Accordingly, potassium may increase the isobutane dehydrogenation turnover frequency by increasing the number of sites for hydrogen removal from adsorbed isobutane. In addition, potassium may also increase the rate of isobutane dissociation through stabilization of molecularly adsorbed isobutane.

CONCLUSIONS

The addition of tin to Pt/SiO_2 enhances the selectivity for dehydrogenation of isobutane to isobutylene but also decreases the dehydrogenation rate over the exposed platinum. However, the addition of potassium to $Pt/Sn/SiO_2$

enhances the isobutane dehydrogenation activity, improves the dehydrogenation selectivity, and decreases the rate of catalyst deactivation.

The addition of tin to Pt/SiO_2 suppresses hydrogenolysis, isomerization, and coking reactions by decreasing the size of the surface Pt ensembles. These reactions are suppressed more completely over small Pt ensembles than is the dehydrogenation reaction, and the dehydrogenation selectivity is thereby enhanced over these smaller Pt ensembles. The results of kinetics studies suggest that the dissociative adsorption of isobutane controls the dehydrogenation, and addition of tin to Pt/SiO_2 decreases the rate of dissociative adsorption of isobutane.

It is suggested that the addition of potassium to Pt/SiO_2 and $Pt/Sn/SiO_2$ also reduces the size of the surface platinum ensembles, since the rates of hydrogenolysis and isomerization reactions are suppressed by this additive. Microcalorimetric studies of hydrogen, carbon monoxide, and ethylene adsorption show that potassium does not significantly alter strengths of interaction between these adsorbates and the supported metal. However, potassium increases the saturation extent of hydrogen adsorption and decreases the extent of carbon monoxide adsorption on Pt/SiO_2 and $Pt/Sn/SiO_2$. The dehydrogenation rate increases upon addition of potassium to $Pt/Sn/SiO_2$ due to an increase in the number of sites available for hydrogen removal from adsorbed isobutane. The increased dehydrogenation activity may also be due to the stabilization by potassium of molecularly adsorbed isobutane.

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