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Selective dehydrogenation of isobutane over supported Pt/Sn catalysts

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Abstract

Catalytic dehydrogenation of isobutane is important because of growing demand for isobutene as a precursor for the production of oxygenates required in reformulated gasoline. It was found that supporting tin and platinum in K-L-zeolite produces catalysts that exhibit high activity and selectivity for isobutane dehydrogenation. Furthermore, Pt/Sn/K-L-zeolite catalysts exhibit high resistance to deactivation at conditions conducive to high dehydrogenation conversions. Fundamental investigations of silica-supported Pt/Sn catalysts show that tin interacts with platinum to form Pt/Sn alloy particles, which reduces the size of surface Pt ensembles and inhibits the formation of highly dehydrogenated surface species required for the competing isomerization, hydrogenolysis, and coking reactions. Similarly, the addition of potassium to Pt/Sn/SiO_2 increases the selectivity for isobutane dehydrogenation by further reducing the size of surface Pt ensembles. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Dehydrogenation; Isobutane; Pt/Sn catalysts

1. Introduction

Platinum-based materials are employed extensively as catalysts for the reforming of hydrocarbon streams in the production of petrochemicals and gasoline [1,2]. It has been shown that modifications of platinum-based materials result in catalysts that exhibit high selectivity for the dehydrogenation of isobutane to isobutene at elevated temperatures (e.g. [3–10]). Catalytic dehydrogenation of isobutane is important because of the growing demand for isobutene as a precursor for the production of oxygenates required in reformulated gasoline [10].

Recently, it was shown that supporting tin and platinum in the potassium form of L-zeolite produces a unique material that exhibits high activity and selectivity for isobutane dehydrogenation to isobutene [7,9,11,12]. The favorable properties of this material are caused by a unique combination of metal, modifiers, and support. The importance of these different components on the reactivity of isobutane has been elucidated in various studies of silica- and L-zeolite-supported Pt/Sn catalysts [6–9,11,13]. This present paper discusses the results from diverse experimental techniques employed in our studies of different Pt/Sn-based materials (e.g. steady-state kinetics, isotopic tracing kinetics, microcalorimetry, Mössbauer spectroscopy, temperature programmed oxidation, and transmission electron microscopy). Furthermore, these results are combined to develop a quantitative understanding of how the different components of Pt/Sn/K-L-zeolite allow this system to be highly selective and stable for isobutane dehydrogenation.

2. Summary of experimental studies

The strategy of our investigations was to determine the selectivities for the reactions of isobutane

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over a variety of silica- and L-zeolite supported Pt/Sn catalysts. These Pt/Sn catalysts were characterized using tin Mössbauer spectroscopy to determine the extent of interaction of tin with the platinum and the support. Transmission electron microscopy (TEM) investigations were conducted to determine the size and location of metal particles on the catalytic supports. Microcalorimetric investigations of the adsorption of hydrogen, ethylene, and isobutene were performed to determine the number of surface sites and the interaction strengths of these probe molecules with the surface sites. Detailed kinetic studies and deuterium tracing investigations were performed to elucidate the kinetically significant steps and to develop a quantitative description of the catalytic chemistry. Finally, deactivation kinetic studies were combined with temperature programmed oxidation investigations to elucidate possible deactivation mechanisms. Based on the results of the deactivation studies, kinetic studies were conducted at lower temperatures in the absence of feed hydrogen to demonstrate that Pt/Sn/K-L-zeolite can be used under conditions where catalyst deactivation is minimal (i.e. rates of metal sintering and carbon deposition are slow).

2.1. Catalyst preparation

Silica-supported Pt/Sn catalysts were prepared by sequential impregnation [6,8]. Platinum was added to Cab-O-Sil (Cabot) by ion-exchange using the method of Benesi et al. [14]. Tin was added to the Pt/SiO_2 catalyst by evaporative impregnation of a solution of tributyltin acetate in pentane. After impregnation with tin, the catalysts were dried at 390 K, treated with flowing oxygen at 573 K, followed by reduction in flowing hydrogen at 773 K. Silica-supported Pt/Sn/K catalysts were prepared by impregnating the Pt/Sn/SiO_2 catalysts with a KOH aqueous solution using the incipient wetting technique [8]. Pt/Sn/K-L-zeolite catalysts were prepared by the sequential impregnation of tin and platinum [7,9]. Tosoh L-zeolite with a silica to alumina ratio of 6.2 and a potassium content of 13.6 wt.% was used as the support. After calcining the support, an incipient wetness impregnation with a solution of tributyltin acetate in methanol was done in a dry nitrogen atmosphere. This procedure was followed by drying in air and calcining at 573 K before impregnation with an aqueous solution of platinum tetraammine nitrate. The catalysts were then dried at 573 K and reduced at 773 or 873 K for 6 h. Catalysts were sent for elemental analyses (Galbraith Laboratories) to determine the loadings of platinum, tin, and potassium. Additionally, the number of surface platinum sites were determined by hydrogen chemisorption at 403 K or by CO chemisorption at 298 K.

Catalysts are named according to the atomic ratios of Pt, Sn and K (i.e. a 1 : 1 : 2.5 Pt/Sn/K/SiO_2 catalyst has atomic ratios of Pt : Sn : K of 1 : 1 : 2.5 and a 1 : 2.5 Pt/Sn/L catalyst has an atomic ratio of Pt : Sn of 1 : 2.5). All of the catalysts used in these studies had between 0.5 and 2.5 wt.% Pt.

2.2. Reaction kinetic studies

Reaction kinetic studies of isobutane conversion 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 (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 an HP-5890 gas-chromatograph with FID detector and a 10 foot 15% Squalane Chromsorb PAW column at 323 K.

Initial isobutane reactivities were measured over the various catalysts at 673 K, 0.016 atm of isobutane, 0.098 atm of hydrogen and a total pressure of 1 atm. The catalysts were first reduced with hydrogen at 773 K for 1 h and then cooled to 673 K before kinetic data were collected. The results of these measurements are summarized in Table 1. The turnover frequencies are based on the number of surface platinum atoms determined from saturation hydrogen uptakes at 403 K, as reported in Table 1.

Table 1 shows that the addition of Sn to Pt/SiO_2 suppresses the hydrogenolysis and isomerization reactions, and the turnover frequencies for the produc-

Table 1
Isobutane reactivity at 673 K, 0.016 atm isobutane pressure, 0.098 atm hydrogen pressure, and 1 atm total pressure

Catalyst	1 : 0 Pt/SiO_2	1 : 1 Pt/Sn/SiO_2	1 : 3 Pt/Sn/SiO_2	1 : 1 : 2.7 Pt/Sn/K/SiO_2	1 : 0 Pt/L	1 : 2.5 Pt/Sn/L	1 : 3.5 Pt/Sn/L
H_2 uptakes μmol H_2/g of catalyst	37 ± 2	11 ± 1	9 ± 1	19 ± 1	22 ± 2	2 ± 0.5	3.5 ± 0.5
WHSV[a] (h^{-1})	6.5	7.3	3.8	7.4	24.9	3.88	8.2
Isobutane conversion(%)	19.0	3.4	4.2	3.4	22.5	6.4	3.0
Isobutane conversion TOF[b]	0.080	0.052	0.043	0.030	0.64	0.17	0.17
CH_4 TOF[b]	0.041	0.0061	0.00052	0.0024	0.45	0.013	0.0014
C_2H_6 TOF[b]	0.014	0.0013	0.00013	0.00002	0.10	0.00033	0
C_3H_8 TOF[b]	0.026	0.0053	0.00045	0.00017	0.31	0.012	0.0037
n-C_4H_{10} TOF[b]	0.028	0.0049	0.00035	0.00018	0.16	0	0
i-C_4H_8 selectivity[c] (%)	19.5	78.9	97.9	96.9	14.1	92.6	98.2

[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).

tion of methane, ethane, propane, and *n*-butane decrease with increasing tin content (e.g., the propane production turnover frequency decreases from 0.026 to 0.00045 s^{-1} as the Pt/Sn ratio changes from 1 : 0 to 1 : 3). The suppression of isomerization and hydrogenolysis reactions over the Pt/Sn catalysts leads to an enhancement in the selectivity for production of isobutene, and the overall isobutane conversion is limited to the dehydrogenation equilibrium conversion to isobutene (ca., 7% for the reaction conditions) [6]. Table 1 shows that the addition of potassium to 1 : 1 Pt/Sn/SiO_2 catalyst further decreases the rates for production of methane, ethane, propane, and *n*-butane. The further suppression of the isomerization and hydrogenolysis reaction upon addition of potassium results in a higher isobutane dehydrogenation selectivity [8].

It can be seen in Table 1 that a Pt/L-zeolite catalyst exhibits significantly higher activity for isobutane conversion compared to the Pt/SiO_2 catalyst. Specifically, the Pt/L-zeolite catalyst exhibits turnover frequencies for conversion of isobutane and for production of methane, ethane, propane, and *n*-butane that are an order of magnitude higher than the Pt/SiO_2 catalyst. The addition of tin to L-zeolite-supported platinum significantly lowers turnover frequencies for the conversion of isobutane and for production of methane, ethane, propane, and *n*-butane, as shown in Table 1. Similar to the silica-supported system, the hydrogenolysis and isomerization reaction rates decrease with increasing tin content of the Pt/Sn/K-L-zeolite catalysts, and the isobutane conversion is limited over these Pt/Sn/K-L-zeolite catalysts by the equilibrium conversion of isobutane to isobutene [7].

2.3. Mössbauer spectroscopy

Room temperature Mössbauer spectra of ^{119}Sn were collected using an Austin Science Associates Model S-600 Mössbauer spectrometer, connected to a microcomputer with a PCAII data collection board [6,7]. The spectrometer was operated in the constant-acceleration mode, with a 10 mCi single-line γ-ray source of $Ca^{119m}SnO_3$ (Amarsham). Chemical shifts are reported relative to $BaSnO_3$ at room temperature.

Fig. 1a shows the room temperature Mössbauer spectrum for the 1 : 1 Pt/Sn/SiO_2 catalyst after treatment with flowing hydrogen at 773 K. This spectrum consists of a single dominant peak at a chemical shift of 1.83 mm/s [6]. This spectrum shows no evidence for SnO_2 species and slight evidence for SnO. Based on Mössbauer spectroscopy data for Pt/Sn alloys and solutions reported by Gray and Farha [15], the chemical shift of this single peak indicates that the tin is zero valent and is alloyed with platinum. The chemical shift for the Pt/Sn alloy peak shown in Fig. 1a indicates an alloy with a tin content of 48 atom % Sn, which is in agreement with the elemental analysis data.

Fig. 1b shows the Mössbauer spectrum collected for the 1 : 3.5 Pt/Sn/K-L-zeolite catalyst after treatment in H_2 at 773 K for 8 h. This spectrum exhibits a singlet

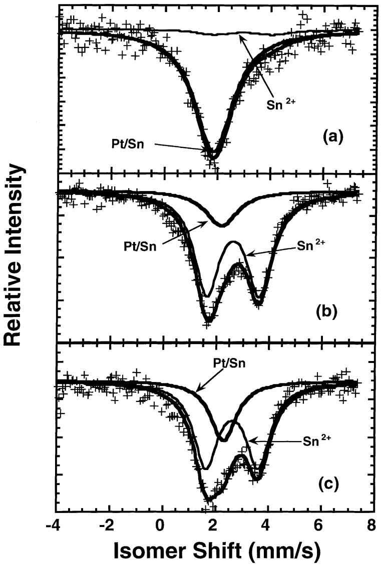

Fig. 1. Mössbauer spectrum collected at 298 K of (a) 1 : 1 Pt/Sn/SiO_2 after 12 h reduction at 773 K, (b) 1 : 3.5 Pt/Sn/K-L-zeolite after 8 h reduction at 773 K, and (c) 1 : 3.5 Pt/Sn/K-L-zeolite after 1 h reduction at 873 K.

peak attributed to formation of Pt/Sn alloy particles, but it also shows a predominant doublet attributed to Sn^{2+}. Reduction of the 1 : 3.5 Pt/Sn/K-L-zeolite catalyst at a higher temperature (873 K for 10 h) appears to further reduce the tin, as shown in Fig. 1c. The Mössbauer spectrum in this figure shows a decrease in the relative intensity of the doublet compared to the singlet with increased temperature. Accordingly, the higher temperature reduction appears to reduce the Sn^{2+} species to a zero-valent tin species which is mostly likely alloyed with platinum.

2.4. Electron microscopy

Transmission electron microscopic studies were conducted using a high resolution microscope (Phillips CM 200 equipped with a LaB_6 filament) at a point resolution of 0.2 nm and a magnification range of 25× to 1.6 M×. A spot size of 120 nm was used to minimize electron beam damage to the specimens.

Fresh catalysts were analyzed to determine if the Pt and Sn were located within the pores of the zeolite. Fig. 2a is a typical micrograph of a fresh catalyst. Lattice fringes from the L-zeolite are visible but few if any particles are visible on the external surface of the zeolite. After extended periods of exposure to high temperature, however, particles appear on the catalyst surface. Fig. 2b shows the presence of a few 5 nm particles as well as several 1–2 nm particles. This micrograph is of a 1 : 2.5 Pt/Sn/K-L-zeolite catalyst which had been exposed to reaction conditions of 0.67 atm hydrogen and 0.33 atm isobutane for 4 h at 873 K. For this sample, 1–2 nm particles were visible on the majority of the external surface of the zeolite. As the catalysts are held at high temperature for longer times, the size and number of particles generally increase. On Pt/K-L-zeolite catalysts, however, the particle sizes do not increase to the same extent as on a Sn-modified catalyst, i.e. only 1–2 nm sized particles are visible on a Pt/K-L-zeolite catalyst after 4 h reaction at 873 K with 0.67 atm hydrogen and 0.33 atm isobutane [12].

Mössbauer spectroscopy has shown that Pt and Sn form alloy clusters in L-zeolite, but the majority of the Sn is present as Sn^{2+} [7]. Studies on Pt/Sn/alumina [16,17] and Pt/Sn/NaY-zeolite [18] have shown that the proportion of tin in metallic particles increased with metal particle size. Furthermore, Merlen et al. [16] have suggested that metallic tin cannot be stabilized in small particles. Thus, the Sn^{2+} in the Pt/Sn/K-L-zeolite catalyst may slowly become reduced in the presence of hydrogen during isobutane dehydrogenation at 873 K and migrate to the Pt/Sn alloy particles, resulting in surface enrichment with metallic Sn, particle agglomeration, and the loss of accessible Pt sites.

The sintering of the catalyst can be reduced significantly by changing the reaction conditions. TEM analyses of catalysts before and after reaction in isobutane (in the absence of hydrogen) at 798 K indicate that little, if any, particle agglomeration occurs after 4 h of reaction [12].

2.5. Microcalorimetry

Differential enthalpy changes of hydrogen, ethylene, and isobutene adsorption were measured over various Pt/Sn based materials using heat flux microcalorimetry at several temperatures [6–8,19–21]. Fig. 3 shows the differential heats of adsorptions for ethylene and isobutene over a 2.5 wt.% Pt/SiO_2 catalyst and a 2 : 1 Pt/Sn/SiO_2 (2.5 wt.% Pt) catalyst at 303 K [19]. Values of the differential enthalpy

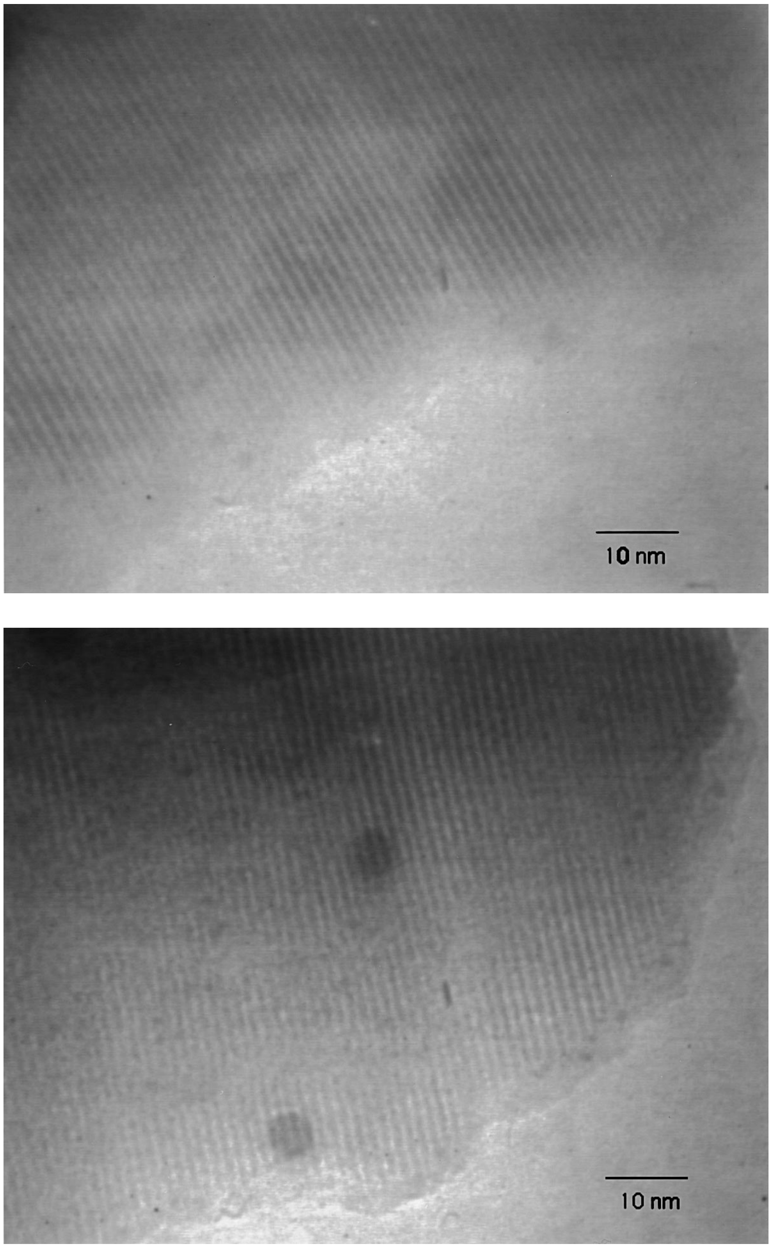

Fig. 2. TEM micrographs of 1 : 2.5 Pt/Sn/K-L-zeolite (a) before reaction, and (b) after 4 h reaction at 873 K in 0.33 atm isobutane and 0.67 atm hydrogen.

changes of adsorption, ΔH_{ads}, are negative, and it is convenient to define the heat of adsorption as being equal to $-\Delta H_{\text{ads}}$.

This figure shows that the addition of tin to silica-supported platinum reduces the initial heat of ethylene adsorption. Similar effects of adding tin to supported platinum on the heats of ethylene adsorption have been observed in related investigations [6,8,20]. Spectroscopic investigations suggest that ethylene dissociatively adsorbs on platinum surfaces

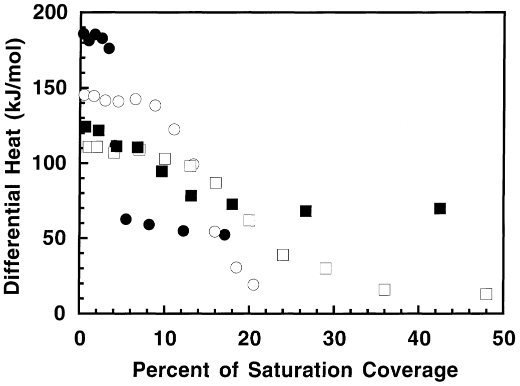

Fig. 3. Differential heat of adsorption for ethylene and isobutene at 303 K. ●, i-C_4H_8 on Pt/SiO_2; ○, C_2H_4 on Pt/SiO_2; ■, i-C_4H_8 on Pt/Sn/SiO_2 ; □, C_2H_4 on Pt/Sn/SiO_2.

at room temperature to form ethylidyne species and adsorbed atomic hydrogen, but the addition of tin suppresses the formation of ethylidyne species such that molecularly-adsorbed ethylene is also present at room temperature on tin-modified platinum surfaces [20,22,23]. Accordingly, the combined results of spectroscopic and microcalorimetric investigations suggest that the higher initial heat (ca. 150 kJ/mol) for ethylene adsorption on platinum surfaces at room temperature may be attributed to the dissociation of ethylene to form ethylidyne species and adsorbed hydrogen [6,19–21]. Furthermore, the combined results of these techniques suggest that the addition of tin suppresses the decomposition of ethylene, and the observed lower initial heat of adsorption (ca. 115 kJ/mol) may be in part attributed to the formation of only molecularly-adsorbed ethylene [6,19,20]. It appears that the decomposition of ethylene to form ethylidyne requires larger platinum ensembles compared to molecularly-adsorbed ethylene.

In a recent study [20], the combined results of microcalorimetric and infrared spectroscopic experiments indicate that Sn suppresses the formation of ethylidyne and also weakens the interaction of molecularly-adsorbed ethylene with the catalyst. Results from density functional theory calculations on Pt/Sn clusters suggest that besides geometric blocking effects, there is also an electron charge transfer from tin to platinum. Accordingly, the addition of tin to platinum reduces the effective size of surface platinum ensemble through either geometric and/or electronic effects and suppresses the formation of more-highly dehydrogenated surface species.

Fig. 3 shows that the addition of tin to Pt/SiO_2 decreases the initial heat of isobutene adsorption from 185 kJ/mol on Pt/SiO_2 to 125 kJ/mol on Pt/Sn/SiO_2. Similar to the adsorption of ethylene, the higher heat for isobutene adsorption on Pt/SiO_2 can be attributed to the decomposition of isobutene to an isobutylidyne species and surface hydrogen atoms. The lower heat of adsorption on Pt/Sn/SiO_2 may be attributed to molecularly adsorbed olefin. Accordingly, the addition of tin to supported platinum appears to suppress the decomposition of adsorbed olefins to more highly-dehydrogenated species.

2.6. Hydrogenation/dehydrogenation kinetics

Kinetic studies were conducted to determine reaction rates and kinetic orders for isobutane dehydrogenation and isobutene hydrogenation over 1 : 1 Pt/Sn/SiO_2, 1 : 1 : 2.5 Pt/Sn/K/SiO_2, and 1 : 2.5 Pt/Sn/K-L-zeolite catalysts at 673, 723, and 773 K [11,13]. All data were collected at a total flow rate of 304 cm^3(STP)/min and the catalyst amounts were adjusted to maintain conversions less than 15% of the equilibrium values. At these low conversions, the catalysts exhibited dehydrogenation selectivities greater than 98%. 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 (22 ± 1, 38 ± 1, and 4.0 ± 0.5 mmol surface Pt/g for the Pt/Sn/SiO_2, Pt/Sn/K/SiO_2, and Pt/Sn/K-L-zeolite catalysts, respectively).

Fig. 4a shows the effect of temperature on the rates of isobutane dehydrogenation at 0.016 atm isobutane and 0.098 atm hydrogen over the three investigated catalysts. This figure shows that the addition of potassium to Pt/Sn/SiO_2 nearly doubles the dehydrogenation rate, and the dehydrogenation rates are more than an order of magnitude higher over Pt/Sn/K-L-zeolite compared to Pt/Sn/SiO_2 or Pt/Sn/K/SiO_2. Fig. 4b shows the effect of temperature on the rates of isobutene hydrogenation at 0.013 atm isobutene and 0.13 atm hydrogen partial pressures over the three catalysts. As with the dehydrogenation reaction, the addition of potassium to Pt/Sn/SiO_2 significantly increases the hydrogenation rate, and the hydrogena-

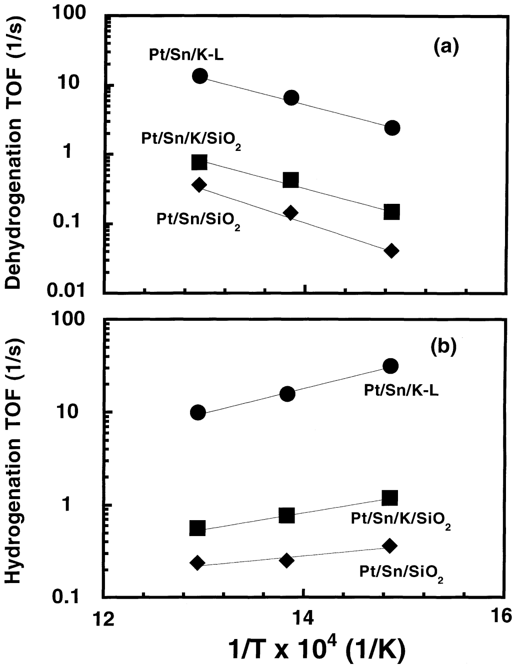

Fig. 4. Turnover frequency for (a) isobutane dehydrogenation at 0.016 atm isobutane and 0.098 atm hydrogen and (b) isobutene hydrogenation at 0.013 atm isobutene and 0.13 atm hydrogen [●, Pt/Sn/K-L-zeolite; ■, Pt/Sn/K/SiO$_2$; and ◆ Pt/Sn/SiO$_2$].

tion reaction rates are over an order of magnitude higher more than Pt/Sn/K-L-zeolite compared to the silica-supported catalysts.

The average hydrogenation/dehydrogenation reactions rates were 2.5 times faster over Pt/Sn/K/SiO$_2$ and 50 times faster over Pt/Sn/K-L-zeolite compared to Pt/Sn/SiO$_2$ [11] when the turnover frequencies are based on the number of surface platinum atoms. If the turnover frequencies are based on the total number of platinum atoms present on these catalysts, then the factor for Pt/Sn/K/SiO$_2$ would increase from 2.5 to 4.3, and the factor would decrease from 50 to 24 for Pt/Sn/K-L-zeolite. Importantly, these turnover frequencies are still considerably higher over the Pt/Sn/K-L-zeolite catalyst when the rates are based on total platinum.

2.7. Deuterium tracing studies

Deuterium tracing studies were conducted to determine the extent of deuterium incorporation into isobutane and isobutene during the isobutane dehydrogenation and isobutene hydrogenation reactions [13]. The reactor effluent was analyzed with a gas chromatograph (Perkin–Elmer Sigma 3B with a thermoconductivity detector), and the separated gases from the GC were directed to a mass spectrometer (EAI Quad 250B) for analysis. Mass spectroscopic measurements were conducted on the separated isobutane and isobutene fractions in the reactor effluent over the mass range of the parent peaks (54–68 amu for isobutene and 54–70 amu for isobutane). Results of deuterium tracing studies for isobutane dehydrogenation over both Pt/Sn/SiO$_2$ and Pt/Sn/K/SiO$_2$ show that perdeuterated isobutene is the predominate product species and the average number of deuterium atoms incorporated into the isobutene is greater than 6 over both catalysts. Additionally, little deuterium is incorporated into isobutane, as the average number of deuterium atoms incorporated into isobutane was 1.4 and 1.9 for Pt/Sn/SiO$_2$ and Pt/Sn/K/SiO$_2$, respectively [13].

2.8. Kinetic analyses of isobutane dehydrogenation and isobutene hydrogenation

The combined results from hydrogenation/dehydrogenation kinetics studies, microcalorimetric measurements of hydrogen and isobutene adsorption, and deuterium tracing during isobutane dehydrogenation and isobutene hydrogenation can be explained by a Horiuti–Polanyi mechanism shown below [11,13]:

$$C_4H_{10} + 2_* \rightleftharpoons C_4H_{9*} + H_* \qquad \text{(Step 1)}$$

$$C_4H_{9*} + 2_* \rightleftharpoons C_4H_{8**} + H_* \qquad \text{(Step 2)}$$

$$C_4H_{8**} \rightleftharpoons C_4H_8 + 2_* \qquad \text{(Step 3)}$$

$$H_2 + 2_* \rightleftharpoons 2H_* \qquad \text{(Step 4)}$$

Based on the deuterium tracing results, it appears that the dissociative adsorption of isobutane is the slow step in this process [13]. Therefore, we may assume that Steps 2, 3, and 4 are quasi-equilibrated for the experimental conditions of the present study, leading to the following rate expression for the hydrogenation-dehydrogenation reactions:

$$r_{\mathrm{DH}} = k_1\theta_*^2\left[P_{i\text{-}\mathrm{C_4H_{10}}} - \frac{P_{i\text{-}\mathrm{C_4H_8}}P_{\mathrm{H_2}}}{K_{\mathrm{eq}}}\right] \qquad (1)$$

where r_{DH} is the net dehydrogenation rate, k_1 is the rate constant for the dissociative adsorption of isobutane, K_{eq} is the overall equilibrium constant for isobutane dehydrogenation, and θ_* is the fraction of sites that is free of adsorbed species. The latter term, θ_*, is dependent on the quasi-equilibrated adsorption/desorption for hydrogen and isobutene [11,13]. Accordingly, the dehydrogenation/hydrogenation reactions are dependent on the values of forward rate constant of Step 1 (k_1) and the equilibrium constants for Steps 3 and 4. The equilibrium constants may be described in terms of standard entropy changes (ΔS_3 and ΔS_4) and enthalpy changes (ΔH_3 and ΔH_4) for the adsorption of isobutene and hydrogen. These standard entropy changes can be expressed in terms of known gaseous entropies and entropies of the surface species – adsorbed H atoms, adsorbed isobutene, and the activated complex for Step 1. The number of adjustable parameters is reduced to four by fixing the heats of isobutene and hydrogen adsorption (ΔH_3 and ΔH_4) using the results of microcalorimetric experiments [13,19]. The entropies for adsorbed isobutene and hydrogen were determined from analysis of the kinetic data from the studies of isobutane dehydrogenation and isobutene hydrogenations. Results from this analysis suggest that on all the catalysts the adsorbed isobutene is immobile and adsorbed atomic hydrogen has one degree of translational freedom [11].

Furthermore, results from analyses of the kinetic data show that the free energy change to form the activation complex for Step 1 at 723 K decreases in the following order:

$$\underset{(167\,\text{kJ/mol})}{\text{Pt/Sn/SiO}_2} > \underset{(160\,\text{kJ/mol})}{\text{Pt/Sn/K/SiO}_2} > \underset{(136\,\text{kJ/mol})}{\text{Pt/Sn/K-L-zeolite}}$$

This trend suggests that the activated complex of Step 1 is stabilized over Pt/Sn/K/SiO$_2$ and Pt/Sn/K-L-zeolite, compared to Pt/Sn/SiO$_2$. Therefore, the higher reactions rates over Pt/Sn/K-L-zeolite and Pt/Sn/K/SiO$_2$ may be attributed to stabilization of the transition-state for the dissociative adsorption of isobutane by the presence of potassium as well as by the zeolite micropores [9,13].

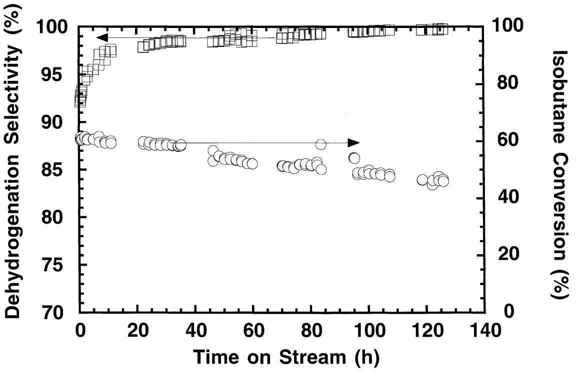

Fig. 5. Isobutane conversions (○) and dehydrogenation selectivities (☐) over 1 : 2 Pt/Sn/K-L-zeolite at 873 K, 0.33 atm isobutane and 0.67 atm hydrogen, and a WHSV of 13.2 h^{-1}.

2.9. High conversion kinetics data at 873 K

High conversion kinetic data was obtained at 873 K, 0.33 atm isobutane pressure, 0.67 atm hydrogen pressure, and a WHSV of 13.2 h^{-1} over a 1 : 2 Pt/Sn/K-L-zeolite catalyst. At these reaction conditions the equilibrium conversion to isobutene is 58%. These kinetic studies were performed with 20–35 mesh catalyst particles packed between quartz glass plugs in a narrow quartz U-tube reactor. This reactor configuration eliminated gas-phase reactions as confirmed via kinetic testing of an empty reactor. The catalyst was pretreated at 873 K for 1 h in pure H$_2$. Fig. 5 shows that the Pt/Sn/K-L-zeolite catalyst exhibits an initial isobutane dehydrogenation selectivity of 92% at an isobutane conversion of 61%. This kinetic study was run for 126 h in view of the slow deactivation. After 126 h, the isobutane conversion decreased to 46% and the dehydrogenation selectivity had increased to 99.8%.

2.10. Deactivation investigations

As Fig. 5 shows, the Pt/Sn/K-L-zeolite catalyst deactivates in the presence of hydrogen at 873 K. Therefore, TEM analysis (discussed above), and temperature programmed oxidation (TPO) studies were performed to determine the origin of deactivation [12]. In the TPO studies, the investigated catalysts were first exposed to reaction conditions (873 K, 0.33 atm isobutane and 0.67 atm hydrogen) for 4 h, cooled to

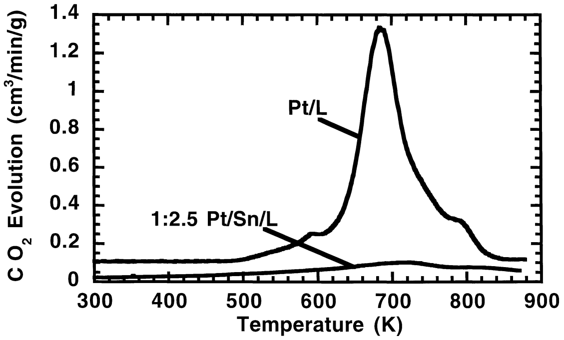

Fig. 6. Temperature programmed oxidation spectra of L-zeolite supported Pt catalysts after 4 h reaction at 873 K in 0.33 atm isobutane and 0.67 atm hydrogen.

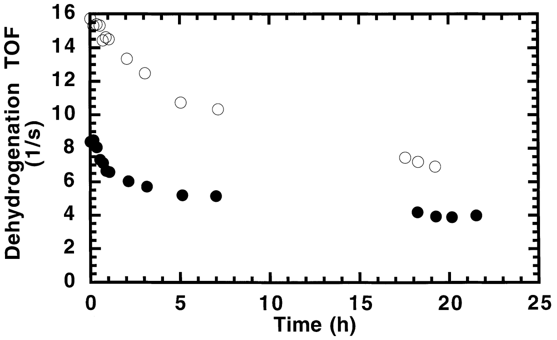

Fig. 7. Effect of reduction time on isobutane dehydrogenation reaction rates at 873 K, 0.33 atm isobutane and 0.67 atm hydrogen over 1 : 2.5 Pt/Sn/K-L. (○) 1 h reduction and (●) 16 h reduction.

298 K in helium, and then heated from 298 to 873 K at 10 K/min in a flowing mixture of 2% oxygen in helium. The exit gas from the reactor was analyzed for H_2O, CO and CO_2 using a mass spectrometer (EAI Quad 250B residual gas analyzer). Calibration of the mass 44 signal was achieved using a gas mixture of 5% carbon dioxide in helium (AGA).

Fig. 6 shows that the addition of tin to L-zeolite-supported platinum decreases the amount of deposited carbon. This shows that the evolution of CO_2 is significantly decreased with the addition of tin. Furthermore, the peak for the 1 : 2.5 Pt/Sn/K-L-zeolite catalyst is shifted to higher temperature compared to the Pt/K-L-zeolite catalyst. Similar results were observed when tin was added to silica-supported platinum [12]. It has been shown that the lower temperature peaks in TPO spectra generally correspond to carbon on Pt, while the higher temperature peaks correspond to carbon on the support [24–28]. Thus, the observed temperature shift suggests that the small amount of deposited carbon on the Pt/Sn/K-L-zeolite catalyst may be associated with the support. Lin et al. [26] reported a similar effect when tin was added to alumina-supported platinum. These investigators observed that Sn decreased the ratio of the carbon deposited on the metal to the total carbon deposited [26]. It has been suggested that Sn transports coke from the active sites to the support on Pt/Sn/alumina catalysts [26,29,30]. Lieske et al. [30] proposed a drain-off mechanism to explain the stabilizing effect of Sn on Pt/alumina catalysts. As suggested above, the presence of Sn decreases the size of the surface Pt ensembles so that the hydrocarbon cannot readily form multiple carbon-metal bonds. Because the adsorbed species is attached less strongly to the metal surface, it may be more mobile and it may more easily migrate to the support.

The combined results of Mössbauer spectroscopic, TEM, and kinetic investigations show that extended reduction of Pt/Sn/K-L-zeolite at 873 K has detrimental effects on the catalytic performance of this material. Mössbauer spectroscopic results show that extended reduction at 873 K leads to enhanced Pt/Sn alloy formation (see Fig. 1) and TEM indicates that significant particle growth occurs on catalysts reduced for 16 h at 873 K [12]. In conjunction with the spectroscopic results, Fig. 7 shows a significant decrease in the isobutane dehydrogenation reaction rate with increased reduction time at 873 K. The isobutane dehydrogenation reaction rates were determined at 873 K, 0.33 atm isobutane pressure, and 0.67 atm hydrogen pressure over a 1 : 2.5 Pt/Sn/K-L-zeolite catalyst after 1 and 16 h pretreatments in flowing hydrogen at 873 K. The lower initial rate of isobutane dehydrogenation after a 16 h pretreatment is significantly lower than after a 1 h pretreatment and, in fact, the rate is similar to the dehydrogenation rate of the catalyst pretreated for 1 h followed by 16 h under reaction conditions. These results suggest that under reducing conditions, reduction of oxidized tin and/or an increase in the metal-alloy particle size with time at 873 K is a significant factor in the deactivation of the catalyst.

Since TPO investigations show that the addition of tin and potassium to supported platinum significantly decreases the amount of deposited carbon

[12], the presence of hydrogen may not be critical for inhibiting deactivation attributed to coking. In fact, results from kinetic investigations conducted without hydrogen in the feed show that Pt/Sn/K-L-zeolite catalysts exhibit high activity, selectivity, and stability for isobutane dehydrogenation [7,12]. At 773 K, a 1 : 3.5 Pt/Sn/K-L-zeolite catalyst maintained isobutane dehydrogenation activity over 45 h on stream with no hydrogen in the feed [7]. Furthermore, this investigation showed that the addition of excess potassium to Pt/Sn/K-L-zeolite further enhanced the stability of the catalyst in the absence of hydrogen. At 798 K, kinetic studies show that Pt/K-L-zeolite deactivates rapidly in the absence of feed hydrogen, whereas a 1 : 2.5 Pt/Sn/K-L-zeolite maintains significant activity under the same reaction conditions [12]. Furthermore, little or no particle migration occurred on the Pt/Sn/K-L-zeolite catalyst under reducing conditions at 798 K. Isobutane dehydrogenation over Pt/Sn/K-L-zeolite catalysts at lower hydrogen partial pressures and lower temperatures has several advantages including: (1) higher equilibrium conversion for the dehydrogenation reaction at lower hydrogen partial pressures; (2) decreased reduction of oxidized tin at lower hydrogen partial pressures and lower temperatures; and (3) decreased particle migration and growth at lower temperatures.

3. Summary

Results from previous reaction kinetics studies of isobutane conversion showed that hydrogenolysis and isomerization reactions are suppressed over small platinum particles [6]. It is generally accepted that hydrogenolysis requires the alkane molecule to undergo successive dehydrogenation processes prior to the rate-limiting C–C bond breaking step [31–33]. In addition, the bond-shift mechanism for metal-catalyzed isomerization requires that the alkane molecule undergo successive dehydrogenation processes before the rate-limiting bond-shift step. For example, Anderson and Avery [34] suggested a bond-shift mechanism involving a $\alpha\alpha\gamma$-tri-adsorbed intermediate bonded to two adjacent metal atoms. In short, hydrogenolysis and isomerization reactions require surface ensembles containing at least several Pt atoms, and these reactions are inhibited over small metal particles that lack these surface ensembles. Analogous to the hydrogenolysis reaction, a fairly large ensemble of surface Pt atoms is required for reactions leading to coke formation [35]. In contrast, kinetic results suggest that dehydrogenation reactions can proceed on small ensembles of surface platinum atoms [6,36].

The results of our kinetics studies show that the addition of tin to Pt/SiO_2 suppresses the isomerization and hydrogenolysis of isobutane, and enhances the dehydrogenation selectivity. Mössbauer spectroscopic results show that tin interacts with supported platinum to produce a Pt/Sn alloy. Microcalorimetric results show that the addition of tin to Pt/SiO_2 inhibits ethylidyne formation from the adsorption of ethylene. The combined results of these studies suggest that tin reduces the size of the surface Pt ensembles on Pt/Sn alloy particles, suppresses the isomerization and hydrogenolysis reactions, and enhances the selectivity for isobutane dehydrogenation to isobutene [6].

Furthermore, it has been shown that the addition of potassium to Pt/Sn/SiO_2 increases the isobutane dehydrogenation rate, enhances the dehydrogenation selectivity, and improves the resistance of the catalyst to deactivation [8]. Results from this investigation suggest that potassium further reduces the size of surface platinum ensembles on Pt/Sn/SiO_2 which further suppresses isomerization and hydrogenolysis reactions of isobutane and enhances the dehydrogenation selectivity. The addition of potassium may also increase the dehydrogenation reaction rate by stabilizing reactive intermediates on the surface of the Pt/Sn/K/SiO_2 catalyst [11].

It has been shown that Pt/Sn/K-L-zeolite catalysts exhibit high dehydrogenation activity, high dehydrogenation selectivity, and high resistance to catalyst deactivation [7,9,11–13]. The properties of this highly selective dehydrogenation catalyst may be attributed to the stabilization of small Pt/Sn particles in the L-zeolite pore in the presence of potassium. Results from deactivation studies show that Pt/Sn/K-L-zeolite catalysts exhibit tolerance to deposited carbon, and the predominate modes of deactivation are enrichment of the Pt/Sn alloy particle surface with tin and/or sintering of the metal particles under reducing conditions and high temperatures. Accordingly, Pt/Sn/K-L-zeolite materials are selective and stable isobutane dehydrogenation catalysts at conditions of low hydrogen partial pressures and moderate temperatures (i.e., <800 K).

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