



# Propane dehydrogenation over supported Pt-Sn nanoparticles

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## ABSTRACT

The influences of support ( $\text{SiO}_2$  versus  $\text{Al}_2\text{O}_3$ ), synthesis method (impregnation versus colloidal synthesis) and Sn loading on the performance of Sn-promoted Pt nanoparticles for propane dehydrogenation to propene at 773 K were explored. Catalysts were characterized extensively by X-ray diffraction, temperature-programmed reduction/oxidation, chemisorption, electron microscopy, X-ray photoelectron spectroscopy, and DRIFTS of adsorbed CO. Catalyst stability and selectivity to propene were correlated with extent of Pt-Sn interactions within the nanoparticles, which was favored at high Sn loading, and when the particles were supported on a weakly interacting carrier such as silica. However, oxidative regeneration irreversibly deactivated bimetallic nanoparticles on silica relative to those on alumina. The extended performance of Sn-promoted Pt catalysts is an optimization of the Pt-Sn interactions with the ability to oxidatively redisperse the metals during regeneration.

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## 1. Introduction

Improvements to fracking technology have increased the availability of natural gas and natural gas liquids thus decreasing the cost of chemicals production [1]. The abundant supply of light hydrocarbons has motivated the development of processes for on-purpose dehydrogenation of light alkanes to alkenes that are key building-block molecules in the plastics and specialty chemicals industries [1,2]. Several processes that have been commercialized utilize chromium-based catalysts, which suffer from environmental concerns [2,3], or platinum-based catalysts [2]. Supported Pt catalysts in particular are highly active for the dehydrogenation of light alkanes, including the conversion of propane to propene. Unfortunately, Pt is also known to catalyze hydrocarbon hydrogenolysis and coke formation at the conditions required for alkane dehydrogenation [2,4–8]. Platinum is therefore typically promoted by a second metal such as Ga [9], Cu [10], Zn [11,12], and Sn [2,5].

Tin is a well-known promoter of Pt group metals that has been studied in a wide variety of reactions [13–27]. For example, the addition of Sn to Pt propane dehydrogenation catalysts increased selectivity to propene while decreasing catalyst deactivation due to coke formation [5,7,8,28–30]. The promotional role of Sn on Pt catalysts has been attributed to both electronic and geometric effects [2,5,31–34]. Electronic promotion is proposed to occur by

the donation of electronic charge from Sn to Pt, which decreases the heat of ethene [32,34] and propene [31] adsorption as well as increases the barrier for dissociative adsorption of light alkanes [31], which is postulated to be the rate determining step for the dehydrogenation of propane on Pt [2,5,35–37]. As an increased barrier of the dissociative chemisorption of propane will slow the rate of propane dehydrogenation, there is a trade-off between catalytic activity and stability of Pt-Sn alloys with varying Sn content. Density-functional theory was used to determine that the binding strength of 1-propyl, a key surface intermediate during the dehydrogenation of propane, decreases with increasing Sn-alloy content in the following series:  $\text{Pt}(1\ 1\ 1) > \text{Pt}_3\text{Sn} > \text{Pt}_2\text{Sn} > \text{PtSn}_2$  [31]. The decrease in binding energy of dehydrogenated species on the Pt surface lowers the steady state coverage of these unsaturated molecules, inhibiting deep dehydrogenation and coke formation.

The geometric effect of adding Sn to Pt results from the dilution of Pt ensembles. Large ensembles of Pt surface atoms are required for some undesired side reactions including deep dehydrogenation, which leads to coke formation, and hydrogenolysis. Thus, surface dilution of Pt ensembles is thought to enhance selectivity to propene during propane dehydrogenation while decreasing coke formation [2,4,28–30,32,37]. The presence of Sn atoms has also been suggested to improve the regeneration of deactivated Pt/ $\text{Al}_2\text{O}_3$  by acting as nucleation sites for mobilized Pt atoms during oxidative treatments [4,30,38,39].

The mode and extent of Sn promotion of Pt depends on many factors including synthesis method and catalyst support. For example, co-impregnation of an acidic solution containing  $\text{SnCl}_2$  and  $\text{H}_2\text{PtCl}_6$  forms the bimetallic  $\text{PtCl}_2(\text{SnCl}_3)_2^{2-}$  complex that

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results in a high degree of Pt–Sn interaction during the post-synthesis thermal treatment [5,30,40]. Direct reduction of Pt–Sn/SiO<sub>2</sub> prepared by incipient wetness impregnation was more active than analogous samples treated in inert gas or air prior to reduction [41]. Additionally, the composition of the catalyst support influences the interactions between Pt and Sn. A support such as SiO<sub>2</sub>, which interacts weakly with the metals, allows for a greater extent of metal interaction with themselves, resulting in a higher degree of alloy formation [2,5,42,43]. On the contrary, a support such as Al<sub>2</sub>O<sub>3</sub>, which interacts strongly with Sn, stabilizes the promoter in an oxidized state [2,5,8,44]. Alloy formation has only been observed on Al<sub>2</sub>O<sub>3</sub>-supported PtSn catalysts with high Sn loadings [44,45]. The Sn is typically found near the Pt–Al<sub>2</sub>O<sub>3</sub> interface or on Pt defect sites as determined by FTIR spectroscopy utilizing CO as a probe molecule [46].

Advanced synthesis techniques have been employed recently to produce a narrow size distribution of nanoparticles as well as specific Pt:Sn ratios within those nanoparticles. Particle size is known to influence catalyst stability and product selectivity for monometallic Pt catalysts [47,48] and bimetallic PtSn catalysts [32]. Step sites on monometallic Pt catalysts, which dominate the activity on smaller particles [48], bind propene more strongly and can lead to the formation of deep dehydrogenation products during propane dehydrogenation [31]. A narrow particle size distribution for the monometallic and bimetallic catalysts can be achieved using colloidal synthesis techniques [15,32,49–52]. In addition, manipulation of nanoparticle composition will influence the alloy phases that are produced. For example, increasing the atomic Sn content from 97:3 (Pt:Sn) to 75:25 has been shown to increase the content of Pt<sub>3</sub>Sn alloy as evidenced by powder X-ray diffraction [52].

In the present study, the dehydrogenation of propane to propene was investigated over Pt and PtSn catalysts. In particular, the influence of the catalyst support (SiO<sub>2</sub> versus Al<sub>2</sub>O<sub>3</sub>) and the Sn loading on the catalyst stability and selectivity were investigated, with and without co-fed H<sub>2</sub>. The performance of colloidal PtSn nanoparticles synthesized using a modified polyol method is compared to those synthesized by incipient wetness impregnation. The influence of Sn and the support on the regeneration of catalysts was also explored.

## 2. Materials and methods

### 2.1. Catalyst synthesis

Nominal 1 wt% Pt/SiO<sub>2</sub>, denoted as 1Pt/SiO<sub>2</sub>, was synthesized via incipient wetness impregnation (IWI) using H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (>37.5% Pt, Sigma-Aldrich) dissolved in distilled, deionized (DI) water. The catalyst was supported on Davisil 636 SiO<sub>2</sub> (Sigma-Aldrich). Following impregnation, the catalyst was dried overnight in air at 393 K and treated in 100 cm<sup>3</sup> min<sup>-1</sup> H<sub>2</sub> (99.999%, GTS-Welco) at 923 K for 3 h following a 1 K min<sup>-1</sup> ramp rate. Alumina-supported nominal 1 wt% Pt/Al<sub>2</sub>O<sub>3</sub>, denoted as 1Pt/Al<sub>2</sub>O<sub>3</sub>, was synthesized by IWI utilizing Al<sub>2</sub>O<sub>3</sub> with a mixed phase (pore size 58 Å, ~150 mesh, Sigma-Aldrich 267740) and H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O. Following impregnation, the catalyst was dried overnight in air at 393 K and treated in 100 cm<sup>3</sup> min<sup>-1</sup> air (medical grade, GTS-Welco) at 773 K for 3 h following a 1 K min<sup>-1</sup> ramp rate. After cooling to room temperature, the 1Pt/Al<sub>2</sub>O<sub>3</sub> catalyst was reduced in 100 cm<sup>3</sup> min<sup>-1</sup> H<sub>2</sub> at 923 K for 3 h following a 1 K min<sup>-1</sup> ramp rate.

Bimetallic Pt–Sn/SiO<sub>2</sub> catalysts were synthesized by IWI using H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O and SnCl<sub>2</sub> (98%, Sigma-Aldrich) precursors and Davisil 636 SiO<sub>2</sub> (Sigma-Aldrich) as the catalyst support. The Pt and Sn precursors were co-impregnated in an HCl (ACS reagent, 37%, Sigma-Aldrich) solution diluted in DI water with an HCl to SnCl<sub>2</sub>

molar ratio of 3 to 1. The catalysts were dried overnight in air at 393 K and then treated in 100 cm<sup>3</sup> min<sup>-1</sup> H<sub>2</sub> at 923 K for 3 h following a 1 K min<sup>-1</sup> ramp rate. The bimetallic catalysts had a nominal loading of Pt of 1 wt% and a nominal loading of Sn ranging from 0.2 wt% to 2.4 wt%. These catalysts were denoted as 1Pt<sub>x</sub>Sn/SiO<sub>2</sub> where x is the nominal Sn weight loading.

Bimetallic Pt–Sn/Al<sub>2</sub>O<sub>3</sub> catalysts were synthesized by IWI using H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O and SnCl<sub>2</sub> precursors and the mixed phase Al<sub>2</sub>O<sub>3</sub> support. The Pt and Sn precursors were co-impregnated in an HCl solution utilizing the same dilution and HCl:SnCl<sub>2</sub> molar ratio as the bimetallic SiO<sub>2</sub>-supported catalysts. The bimetallic samples were subsequently treated in air and H<sub>2</sub> following the same protocol used to prepare monometallic Pt/Al<sub>2</sub>O<sub>3</sub>. The bimetallic Al<sub>2</sub>O<sub>3</sub>-supported catalysts were denoted as 1Pt<sub>x</sub>Sn/Al<sub>2</sub>O<sub>3</sub> where x is the nominal Sn weight percent.

A bimetallic nominal 1 wt% Pt and 0.6 wt% Sn supported on SiO<sub>2</sub> catalyst was also synthesized by a modified polyol method [49]. In summary, 0.18 g NaOH (reagent grade ≥98%, Sigma-Aldrich) was dissolved in 50 cm<sup>3</sup> ethylene glycol (99.8%, anhydrous, Sigma-Aldrich) at 323 K. The solution was cooled to room temperature followed by the addition of 0.053 g PtCl<sub>4</sub> (99.99%, Sigma-Aldrich) and 0.030 g SnCl<sub>2</sub>. The metal precursor solution was stirred for 1 h at room temperature before 2.952 g of SiO<sub>2</sub> was added under stirring conditions. The slurry was then rapidly heated to 463 K where it was held for 2 h and stirred under reflux. The mixture was cooled to room temperature, thoroughly washed with DI water, and dried under vacuum. The catalyst was dried overnight in air at 393 K. Lastly, the catalyst was treated in 100 cm<sup>3</sup> min<sup>-1</sup> air (medical grade, GTS-Welco) at 723 K for 1 h to remove any remaining ethylene glycol, cooled to room temperature, and then treated in 100 cm<sup>3</sup> min<sup>-1</sup> H<sub>2</sub> (99.999%, GTS-Welco) at 773 K for 3 h. All ramp rates were 1 K min<sup>-1</sup>. This polyol-synthesized bimetallic catalyst was denoted as 1Pt0.6Sn/SiO<sub>2</sub>-P.

A second bimetallic catalyst synthesized by the polyol method composed of 1 wt% Pt and 0.6 wt% Sn supported on Al<sub>2</sub>O<sub>3</sub> was also prepared [49]. For this sample, 0.30 g NaOH was dissolved in 50 cm<sup>3</sup> ethylene glycol (99.8%, anhydrous, Sigma-Aldrich) at 323 K. The higher concentration of NaOH, relative to that used for 1Pt0.6Sn/SiO<sub>2</sub>-P synthesis, was utilized to ensure that the solution pH was above the point of zero charge for Al<sub>2</sub>O<sub>3</sub>. The solution was then cooled to room temperature followed by the addition of 0.053 g PtCl<sub>4</sub> and 0.030 g SnCl<sub>2</sub>. The solution containing the metal precursors was stirred for 1 h at room temperature before 2.952 g of Al<sub>2</sub>O<sub>3</sub> was added under stirring conditions. The slurry was then rapidly heated to 463 K and stirred for 2 h under reflux. The recovered solid was treated the same way as the 1Pt0.6Sn/SiO<sub>2</sub>-P catalyst. The polyol-synthesized Al<sub>2</sub>O<sub>3</sub>-supported bimetallic catalyst was denoted as 1Pt0.6Sn/Al<sub>2</sub>O<sub>3</sub>-P.

Catalyst compositions of some of the samples were analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES) provided by Galbraith Laboratories, Inc. (2323 Sycamore Drive, Knoxville, TN 37921).

### 2.2. Catalyst characterization

#### 2.2.1. Chemisorption of H<sub>2</sub> and CO

The number of exposed Pt surface sites was estimated by H<sub>2</sub> and CO chemisorption using a Micromeritics ASAP 2020 automated adsorption analyzer. All IWI-synthesized catalysts were heated ex situ at 923 K (or 773 K for polyol-synthesized catalysts), in flowing H<sub>2</sub> for 3 h prior to chemisorption analysis. The catalysts were heated in situ at 1 K min<sup>-1</sup> to 723 K under H<sub>2</sub> (99.999%, GTS-Welco) and held at temperature for 2 h. The samples were then cooled to 473 K and evacuated for 2 h before being cooled to 308 K for H<sub>2</sub> chemisorption. This sequence was repeated for CO chemisorption using the same sample without exposure to air.

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