A Ship-in-a-Bottle Strategy To Synthesize Encapsulated Intermetallic Nanoparticle Catalysts: Exemplified for Furfural Hydrogenation

Raghu V. Maligal-Ganesh
Iowa State University, raghuv96@iastate.edu

Chaoxian Xiao
Iowa State University, cxiao@iastate.edu

Tian Wei Goh
Iowa State University, jasongoh@iastate.edu

Lin-Lin Wang
Ames Laboratory, llw@ameslab.gov

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A Ship-in-a-Bottle Strategy To Synthesize Encapsulated Intermetallic Nanoparticle Catalysts: Exemplified for Furfural Hydrogenation

Raghu V. Maligal-Ganesh,† Chaoxian Xiao,† Tian Wei Goh,† Lin-Lin Wang,‡ Jeffrey Gustafson,† Yuchen Pei,† Zhiyuan Qi,† Duane D. Johnson,§ Shiran Zhang,#, Franklin (Feng) Tao,# and Wenyu Huang*,†,‡,§

†Department of Chemistry, Iowa State University, Ames, Iowa 50011, United States
‡Ames Laboratory, U.S. Department of Energy, Ames, Iowa 50011, United States
§Departments of Materials Science & Engineering and Chemical & Biological Engineering, Iowa State University, Ames, Iowa 50011, United States
#Department of Chemical & Petroleum Engineering, Department of Chemistry, University of Kansas, Lawrence, Kansas 66045, United States

Supporting Information

ABSTRACT: Intermetallic compounds are garnering increasing attention as efficient catalysts for improved selectivity in chemical processes. Here, using a ship-in-a-bottle strategy, we synthesize single-phase platinum-based intermetallic nanoparticles (NPs) protected by a mesoporous silica (mSiO₂) shell by heterogeneous reduction and nucleation of Sn, Pb, or Zn in mSiO₂-encapsulated Pt NPs. For selective hydrogenation of furfural to furfuryl alcohol, a dramatic increase in activity and selectivity is observed when intermetallic NPs catalysts are used in comparison to Pt@mSiO₂. Among the intermetallic NPs, PtSn@mSiO₂ exhibits the best performance, requiring only one-tenth of the quantity of Pt used in Pt@mSiO₂ for similar activity and near 100% selectivity to furfuryl alcohol. A high-temperature oxidation-reduction treatment easily reverses any carbon deposition-induced catalyst deactivation. X-ray photoelectron spectroscopy shows the importance of surface composition to the activity, whereas density functional theory calculations reveal that the enhanced selectivity on PtSn compared to Pt is due to the different furfural adsorption configurations on the two surfaces.

KEYWORDS: intermetallic compounds, site isolation, heterogeneous catalysis, core−shell, green chemistry

1. INTRODUCTION

Intermetallic compounds have been the subject of significant scientific interest as efficient catalytic materials with vastly improved activity and selectivity compared to their monometallic counterparts.1–4 The site isolation of the active metal in these ordered structures, as opposed to their random arrangement in alloys, affords geometric and electronic changes directed toward noticeable enhancement in activity, selectivity, and stability during catalysis.5 The synthesis of these intermetallic compounds, however, involves high temperatures in these ordered structures, as opposed to their random arrangement in alloys, affords geometric and electronic changes directed toward noticeable enhancement in activity, selectivity, and stability during catalysis.5 The synthesis of these intermetallic compounds, however, involves high temperatures in these ordered structures, as opposed to their random arrangement in alloys, affords geometric and electronic changes directed toward noticeable enhancement in activity, selectivity, and stability during catalysis.5 The synthesis of these intermetallic compounds, however, involves high temperatures in these ordered structures, as opposed to their random arrangement in alloys, affords geometric and electronic changes directed toward noticeable enhancement in activity, selectivity, and stability during catalysis.5 The synthesis of these intermetallic compounds, however, involves high temperatures in these ordered structures, as opposed to their random arrangement in alloys, affords geometric and electronic changes directed toward noticeable enhancement in activity, selectivity, and stability during catalysis.5 The synthesis of these intermetallic compounds, however, involves high temperatures in these ordered structures, as opposed to their random arrangement in alloys, affords geometric and electronic changes directed toward noticeable enhancement in activity, selectivity, and stability during catalysis.5 The synthesis of these intermetallic compounds, however, involves high temperatures in these ordered structures, as opposed to their random arrangement in alloys, affords geometric and electronic changes directed toward noticeable enhancement in activity, selectivity, and stability during catalysis.5

Furthermore, the use of popular supports (e.g., alumina and ceria) for the intermetallic NPs did not prevent aggregation completely.13 A layered double hydroxide (LDH) approach to obtain monodisperse nanoscale Ni–In intermetallic compounds for the enhanced chemoselective hydrogenation of α,β-unsaturated aldehydes has been reported.14 Without the incorporation of Al or Mg in the Ni–In LDHs, however, severe aggregation was observed in the intermetallics during their synthesis.

Here we report a unique and facile approach to synthesizing monodisperse nanoscale intermetallic compounds via seed NPs confined in a thermally robust inorganic capsule. Metal NPs encapsulated by inorganic shells have demonstrated enhanced stability at high temperatures compared to those capped with organic agents.15–18 Pt NPs encapsulated in mesoporous silica
shells (Pt@mSiO₂) demonstrated their stability against aggregation when annealed at 750 °C.¹⁹ Using the Pt@mSiO₂ as the Pt seeds and the metal precursor of the additional metal (salts of Sn, Pb, Zn), we synthesized intermetallic compound NPs within the mSiO₂ shell. Low-temperature solution chemistry methods²⁰,²¹ facilitated this ship-in-a-bottle conversion of Pt@mSiO₂ to the Pt-based intermetallic NPs, as shown in Figure 1. This approach addresses the biggest synthesis dilemma of intermetallic nanoparticles. Since the formation of intermetallic phase usually requires high temperature, the traditional methods using organic capping agents could not avoid the aggregation of nanoparticles during the high-temperature annealing. With the protection of the inorganic mSiO₂ shell, we could routinely anneal the bimetallic-structured nanoparticles at high temperature (600 °C), which will lead to the formation of intermetallic nanoparticle while preventing their aggregation at the same time. To the best of our knowledge, the hybridization of these two existing synthetic strategies—inorganic shell encapsulated thermally stable NPs and the heterogeneous nucleation of ions on these particles to synthesize intermetallic NPs—have not been reported before. Intermetallic NPs synthesized by this method were well-confined within the mesoporous silica environment. Moreover, the mesoporous silica encapsulation did not pose any hindrance during catalytic reactions.

We chose the hydrogenation of furfural to demonstrate the catalytic property of the Pt-based intermetallic compounds. Upon hydrogenation, furfural (2-furfuraldehyde), an important renewable chemical feedstock,²²–²⁴ produces furfuryl alcohol, among other derivatives. Furfuryl alcohol features prominently as an important precursor in the synthesis of a wide variety of chemicals.²⁵–²⁸ However, selectively hydrogenating furfural to furfuryl alcohol poses a considerable challenge.

Industrially, the toxic copper-chromite catalyst has been used to carry out vapor-phase selective hydrogenation of furfural to furfuryl alcohol with moderate yields. However, significant deactivation of the catalyst occurs due to coking and the migration of chromium on the catalyst, effectively blocking the active sites on reduced copper NPs.²⁹ Additionally, the catalyst poses an environmental (toxic chromium) hazard, and reinforces the need to find greener alternatives. Using noble metal catalysts, the selectivity to furfuryl alcohol is poor with the increased possibility for decarbonylation and ring hydrogenation, as opposed to the selective hydrogenation of the carbonyl bond to obtain furfuryl alcohol.³⁰ Variations in shape, size, supports, and surface modifiers have been reported for improved selectivity.³¹–³⁵ However, these still require delicate methodologies and careful design, narrowing the possibility to recycle the catalysts in their optimum state.

Using Pd NPs capped with self-assembled molecules, selectivity to furfuryl alcohol could be controlled by blocking active sites responsible for the undesired reactions.³⁶ Yet there is no enhancement in the activity of these catalysts to the desired product. In contrast, for the ship-in-a-bottle synthesized intermetallic compounds, especially PtSn@mSiO₂, activity was enhanced 10-fold in comparison with Pt@mSiO₂ at nearly 100% selectivity to furfuryl alcohol based on the total amount of Pt. We measured the Pt dispersion using chemisorption on the mSiO₂-encapsulated PtSn and Pt NPs, and we found the specific activity per surface Pt site on PtSn@mSiO₂ is 40 times that of Pt@mSiO₂. An additional advantage of the mSiO₂ protection is that a deactivated PtSn@mSiO₂ catalyst can be regenerated with a convenient oxidation-reduction treatment. No loss in activity and selectivity of the catalyst after six cycles of the regeneration treatment was observed.

2. EXPERIMENTAL SECTION

2.1. Materials and Synthesis. Synthesis of Pt@mSiO₂ Nanoparticles. Pt@mSiO₂ was prepared according to reported methods with a slight modification.³⁷ Around 5 mL of 10 mM K₃PtCl₆ (Acros Organics, 46–47% Pt) was added to 12.5 mL of a 400 mM aqueous solution of tetradecyltrimethylammonium bromide (TTAB, ≥ 99%, Sigma-Aldrich). Additionally, 29.5 mL of distilled water was added. After stirring for 10 min at room temperature, a cloudy solution was obtained, which was then heated in an oil bath at 50 °C for another 10 min resulting in a clear solution. A freshly prepared ice-cold 500 mM (3 mL) aqueous solution of sodium borohydride (Alfa Aesar, 98%) was then added. After the solution was stirred for 15–20 h at 50 °C, the result was a dark brown colloidal solution of Pt nanoparticles. This was centrifuged at 3000 rpm four times for 30 min, discarding the residue after each session. Finally, the supernatant was centrifuged at 14000 rpm for 15 min twice, collected, and dispersed in 35 mL of water. About 1 mL of a 0.05 M sodium hydroxide solution was added to obtain a pH between 11 and 12. While stirring, 500 μL of a 10% tetraethyloxysilicate (TEOS, Aldrich, reagent grade, 98%) solution was centrifuged and redispersed in 40 mL of methanol. After 24 h, the sample was centrifuged at 14000 rpm twice, and the coated particles (Pt@mSiO₂) were redispersed in methanol. The surfactant was removed via an acidic methanol refluxing session (6% hydrochloric acid solution) at 90 °C for 24 h. The platinum content in Pt@mSiO₂ was identified using ICP-MS.

Synthesis of Intermetallic-Pt@mSiO₂ Nanoparticles. For a typical synthesis of an intermetallic compound, the Pt@mSiO₂ solution was centrifuged and dispersed in 40 mL of tetraethylene glycol (Alfa Aesar, 99%) in a 100 mL two-neck flask. The amount of Pt in a typical synthesis of Pt@mSiO₂ particles was 0.18 mmol. The salt of the corresponding metal (Sn, Pb, or Zn) was then added prior to sonication of the mixture to obtain a homogeneous mixture. After removing air from the flask and refilling with Argon, the flask was heated using a temperature-controlled heating mantle for 2 h. PtSn@mSiO₂ was made by adding SnCl₂·2H₂O (Alfa Aesar, 98%), with a molar ratio of Pt:Sn = 1:1, heating the solution to 280 °C for 2 h. PtPb@mSiO₂ was made ensuring a Pt:Pb molar ratio of 3:1, heating the solution to 280 °C. The obtained alloy was centrifuged, washed, dried, and annealed at 600 °C in a 10% H₂/Ar flow in a tube furnace to obtain intermetallic Pt₃Sn@mSiO₂. PtPb@mSiO₂ utilized Pb(CH₂COO)₂·3H₂O
The as-obtained samples were washed, dried, and annealed in a 10% H2/Ar flow at 600 °C in a tube furnace to obtain the PtZn and Pt2Zn intermetallic phases. After their synthesis, inductively coupled plasma mass spectrometry (ICP-MS) measurements were also carried out on the powdered samples to confirm their stoichiometry as per the synthesis.

A control experiment was also carried out to synthesize PtSn supported on a mesoporous silica support, MCF-17. MCF-17 was synthesized according to a reported method. Pt colloids synthesized earlier were not coated with the silica shell and instead dispersed directly on MCF-17 to obtain loadings similar to Pt@mSiO2 (40–50%). The loading eventually obtained was around 38% of Pt in Pt/MCF-17. This was then dried and dispersed in tetraethylene glycol. Tin(II) Chloride was then added to the solution before heating it at 280 °C for 2 h. The resultant solution was then diluted with acetone for easier centrifugation.

Conventional incipient wetness impregnation method was carried out to synthesize another control sample, PtSn supported on MCF-17. The precursors, H2PtCl6 and SnCl2·2H2O (Acros Organics) and SnCl2·2H2O, were dissolved separately in the water required to fill up the pores of the MCF-17 (1.0 wt % Pt; Sn/Pt = 1.0, molar ratio). MCF-17 support was mixed with Pt precursor solution first with mortar and pestle. Then Sn precursor solution was added. The sample was dried at 100 °C for 3 h and calcined in air at 400 °C for 3 h. Finally, the sample was reduced under hydrogen at 350 °C for 3 h.

2.2. Instrumentation. Transmission electron microscopy (TEM) and energy dispersive X-ray spectrometry (EDS) analysis were carried out using a TECNAI G2 F20 with EDS analyzer (Oxford INCA EDS) at an acceleration voltage of 200 kV. TEM samples were prepared by the drop casting method. Around 200 particles were measured for each sample to get the overall particle size, the metal core diameter, and the silica shell thicknesses. Histograms were then made using these size measurements. Powder X-ray diffraction (PXRD) patterns were collected at room temperature using a STOE Stadi P powder diffractometer equipped with an image plate and a Cu Kα radiation source (λ = 1.5406 Å). ICP-MS measurements were carried out using a Thermo Fisher Scientific X Series 2 ICP-MS. Typically, powdered samples were dissolved in 5 mL of aqua regia to dissolve all metal content before the addition of around 100–300 μL 30% HF solution to dissolve the mesoporous silica completely. These samples were diluted with 2% nitric acid before the ICP-MS measurements. BET Surface area measurements of Pt@mSiO2 and PtSn@mSiO2 were performed by nitrogen sorption isotherms using a Micromeritics 3Flex surface characterization analyzer at 77 K. Prior to surface area measurements, both samples were calcined at 500 °C in air and reduced at 300 °C under 50 mL/min 10% H2/He. CO chemisorption was conducted at 35 °C using the same instrument. The samples were calcined at 500 °C for 4 h in air and reduced at 300 °C for 4 h in pure hydrogen flow. The first isotherm was performed after evacuation at 300 °C for 30 min using a turbomolecular pump. Subsequently, the second isotherm was conducted after evacuation at 35 °C for 1 h. The difference between the two isotherms extrapolated to zero pressure gave the amount of the irreversibly adsorbed CO. Exposed Pt was thus calculated using CO/Pt = 1.5.

X-ray photoelectron spectroscopy (XPS) measurements were performed using a PHI 5500 Multitechnique system (Physical Electronics, Chanhassen, MN) with a monochromatized Al Kα X-ray source (hv = 1486.6 eV). For both the Pt 4f and Sn 3d peaks, theoretical values for the peak area ratios were used (0.75 for the Pt peaks and 0.67 for the Sn peaks) while fitting using CasaXPS. Peak widths (fwhm values), when comparing samples for the same elements, were also made as similar as possible, keeping within acceptable limits of ±0.2 eV. For the Pt peaks, a peak width between 2.20 and 2.35 eV was maintained. For Sn peaks, a peak width was maintained between 2.35 and 2.45 eV.

Ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) was also carried out on PtSn@mSiO2. The sample was dispersed in ethanol and then dropped on pyrolytic graphite. The reducing treatments to the sample were carried out in an incorporated high-pressure cell in the vacuum chamber of AP-XPS, in which 0.2 Torr H2 was introduced at different temperatures for a certain amount of time. After the treatment, H2 was purged out, and the sample was taken out to a manipulator in ultrahigh vacuum for X-ray analysis. Due to the existence of SiO2 shell, significant surface charging was encountered. As a result, a flux of low-energy electrons (8.5 eV, 60 mA) generated by a flood gun was used for each analysis.

2.3. Catalysis Studies. Furfural (Acros Organics, 99%) was hydrogenated by dispersing the catalysts on 1.2 g of quartz sand and then loading them into a quartz-glass plug flow reactor. The Pt content in all catalysts was maintained at a fixed value (1.25 mg or 6.4 μmol). All the catalysts were calcined in an oven at 500 °C in air to remove any organic substances, such as solvent residues and surfactant, not been removed during the methanol reflux. Subsequently the catalysts were reduced in 10% H2 in situ (He = 45 mL/min, H2 = 5 mL/min) at an appropriate temperature, i.e., 300 °C for PtSn@mSiO2 and PtPb@mSiO2: 600 °C for PtSn@mSiO2, Pt3Zn@mSiO2, and PtZn@mSiO2 to regenerate the intermetallic phase. All the catalysts were reduced at 300 °C again for 4 h in 10% H2 before furfural hydrogenation was carried out. The reaction gas mixture was composed of 8.6 mL/min He through a bubbler containing furfural (actual furfural flow = 0.023 mL/min), and 11.4 mL/min H2 at 1 atm was passed through the catalyst bed in a fritted quartz U-tube flow reactor. The vapor from the reactor was monitored online using a HP 5890 gas chromatograph equipped with a capillary column (DB-S, 30 m × 0.32 mm × 0.25 μm) and a Flame Ionization Detector. The products were further identified using an online mass spectrometer (Agilent 5973N) connected to the outlet of the capillary column installed in the HP 5890. Additional analysis of products was done using a GC-MS (Agilent 6890N-5975N) to identify products from washed catalysts.

2.4. DFT Calculations. All density functional theory (DFT) calculations were performed with the Perdew, Burke, and Ernzerhof (PBE) exchange-correlation functional, a plane-wave basis set and projector augmented wave method, as implemented in the Vienna Atomic Simulation Package (VASP). The Pt(111) surface was modeled as a three-layer slab with a surface supercell of (2 × 3 × 3). The PtSn(110) and (100) surfaces (the lowest energy structure for these intermetallic compounds), are modeled as a four- and six-
layer slab with a surface supercell of (2 × 2), respectively. Various flat and tilt configurations with different molecular orientations of furfural on the surfaces were tested, and thermal annealing with ab initio molecular dynamics was used to search for the most stable adsorption configurations on each surface. All the atoms (except for the bottom two layers in the slab fixed at bulk positions) are relaxed until the absolute values of forces were below 0.02 eV/Å. A kinetic energy cutoff of 400 eV for the plane-wave basis and a (5 × 5 × 1) k-point mesh with a Gaussian smearing of 0.05 eV was used.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization. NiAs-type PtSn and PtPb intermetallic NPs were readily synthesized in tetraethylene glycol (TEG) and did not require further thermal treatment. PXRD of samples taken out at different times during synthesis of PtSn NPs indicated the formation of the intermetallic phase after 2 h at 280 °C (Figure S1). Cu3Au-type Pt3Sn NPs (Pt:Sn molar ratio = 3:1) were not formed in TEG, yielding alloy NPs instead. However, further annealing up to 600 °C resulted in the ordered intermetallic Pt3Sn NPs (Figure 2). Similarly, Cu3Au-type Pt3Zn and CuAu-type PtPb intermetallic NPs were readily synthesized in tetraethylene glycol (TEG), yielding alloy NPs instead. However, further annealing at 600 °C resulted in the ordered intermetallic Pt3Zn and PtPb intermetallic NPs (Figure S6). The sample was also measured after reaction by both TEM and PXRD, which indicated PtSn@mSiO2 after this calcination and reduction treatment, as observed by TEM and measured by PXRD, is still well encapsulated within the mesoporous silica shell. EDS line-scans carried out on single PtSn@mSiO2 particles show that Pt and Sn were predominantly in the metallic core of the composite NPs (Figure S3 and S4). Table S1 summarizes the observed size increase in the metal core going from Pt to intermetallic NPs seen in TEM, which also agrees with the theoretical values calculated from the corresponding crystal lattice constants assuming no loss of Pt. The decrease in mSiO2 shell thickness could be due to etching of less cross-linked internal silica under synthesis conditions. Park et al. reported the internal hollowing of silica spheres in aqueous media, suggesting that the relatively less cross-linked, high surface-energy inner environs are more reactive and susceptible to dissolution, especially in aqueous or basic media. Other reports have suggested a preferential internal etching of silica rather than at the periphery.

3.2. Catalysis—Vapor-Phase Furfural Hydrogenation.

Furfural hydrogenation was carried out in a gas-phase plug-flow reactor equipped with an online gas chromatograph. Pt@mSiO2 and PtSn@mSiO2 were calcined at 500 °C for 4 h in air to remove organic residues from synthesis followed by reduction at 300 °C for 4 h under 10% H2/He before catalysis studies. PtSn@mSiO2 after this calcination and reduction treatment, as observed by TEM and measured by PXRD, is still well encapsulated within the silica shell and maintains its pure intermetallic phase (Figure S6). The sample was also measured after reaction by both TEM and PXRD, which indicated PtSn@mSiO2 was not affected by the continuous vapor-phase hydrogenation of furfural (Figures S7). PtSn@mSiO2 exhibits greatly improved conversion and selectivity in furfural hydrogenation to furfuryl alcohol compared with Pt@mSiO2. Using PtSn@mSiO2 containing the same amount of Pt as in Pt@mSiO2, the conversion reaches 99% in the hydrogenation of furfural, while it is only 24% for Pt@mSiO2 (Figure 4a). In the case of PtSn@mSiO2, high selectivity (97%) was also obtained toward furfuryl alcohol—the desired product. In contrast, Pt@mSiO2...
mSiO2 generated many decomposition products, such as furan, tetrahydrofuran, and propane (see Figure S8 for product distributions).

Along with the greatly enhanced furfuryl alcohol selectivity on PtSn@mSiO2 compared to that on Pt@mSiO2, the intermetallic catalyst is very stable, giving close to 100% conversion over a time on stream study for 40 h. As the conversion is too high to evaluate the actual stability of PtSn@mSiO2, we decreased the amount of the catalyst (0.26 mg of PtSn@mSiO2 containing 0.124 mg Pt) to tune the furfural conversion to ∼20%. Again, the catalyst is stable for a 40 h-test after an initial deactivation (Figure 4b). Moreover, the low conversion data on PtSn@mSiO2 shows that only one-tenth the amount of Pt is needed in the intermetallic catalyst compared to the pure Pt catalyst to achieve similar conversion of furfural.

On the basis of CO chemisorption analysis (Table S2), the exposed Pt is 1.8% for PtSn@mSiO2, which is only about a quarter of that for Pt@mSiO2 (6.5%). Therefore, the specific activity per surface Pt site of PtSn@mSiO2 is about 40 times that on Pt@mSiO2.

This PtSn@mSiO2 intermetallic catalyst demonstrates that greatly enhanced activity and selectivity in the hydrogenation of furfural to furfuryl alcohol can be achieved compared to pure Pt NPs with largely reduced usage of the precious metal. All the other intermetallic catalysts were also tested for furfural hydrogenation. Like PtSn@mSiO2, they were first calcined at 500 °C after synthesis, but different reduction temperatures were used to generate the respective intermetallic catalysts. A reduction temperature of 300 °C was used for PtPb@mSiO2 (similar to the synthesis conditions in TEG), while 600 °C was used for PtSn@mSiO2, PtZn@mSiO2, and PtZn@mSiO2.

Prior to furfural hydrogenation, all the catalysts were reduced again in the reactor at 300 °C for 4 h in 10% H2/He. Intermetallic PtSn@mSiO2 containing the same amount of Pt, also showed around 95% selectivity to furfuryl alcohol but deactivated over time (Figure S9). However, it deactivated much slower in comparison to the unannealed PtSn alloy (Pt:Sn ratio = 3:1). We speculate that this is due to the greater degree of ordering in the intermetallic iteration of the compound than in the alloy. The other intermetallic catalysts, including PtZn, Pt3Zn, and PtPb were also tested (Figure S10).

All of them showed high selectivity to furfuryl alcohol; however, their conversions were lower than PtSn@mSiO2 and PtSn@mSiO2 for the same quantity of Pt employed. More detailed studies will be conducted to analyze these intermetallic compounds for furfural hydrogenation to explain their lower activity.

To indicate the importance of the mesoporous encapsulation, a control catalyst was also prepared by using MCF-17 as the porous silica support. Mesostructured siliceous foams, such as MCF-17 (pore diameter of ∼30−50 nm and connection window size of ∼17 nm), are porous silica materials commonly used as catalytic supports. As-synthesized colloidal Pt NPs (∼14 nm) were supported on MCF-17 and then converted to PtSn/MCF-17 using the same synthetic conditions used to prepare PtSn@mSiO2. The TEM images...
observed initially. However, the catalyst decays after 2 h (Figure 4).

Conversion and good selectivity are required for the hydrogenation of furfural, was also tested under our reaction conditions. High conversion and good selectivity are required for the hydrogenation of furfural, was also tested under our reaction conditions.

S14).

were carried out on the intermetallic PtSn@mSiO2. A point of importance of the surface for activity and stability, XPS studies showed almost complete conversion at the beginning but deactivated continuously during a 40 h reaction test (Figure S13). Copper chromite, the industrial catalyst used for the hydrogenation of furfural, was also tested under our reaction conditions. High conversion and good selectivity are observed initially. However, the catalyst decays after 2 h (Figure S14).

3.3. X-ray Photoelectron Spectroscopy Study of PtSn@mSiO2 for Furfural Hydrogenation. Focusing on the best catalyst for furfural hydrogenation to understand the importance of the surface for activity and stability, XPS studies were carried out on the intermetallic PtSn@mSiO2. A point of concern before we carried out XPS for the samples was the presence of the mesoporous silica shell (about 8 nm in thickness around the PtSn nanoparticle core). Technically, silica shell thickness affects XPS composition analysis because photoelectrons with different kinetic energies attenuate to a different extent upon traveling through the silica media. Referring to the NIST Electron Inelastic Mean Free Path Database for SiO2,11 the mean free paths of photoelectrons in silica emitted from Pt 4f and Sn 3d are 4.41 and 3.35 nm, respectively. Considering the silica shell thickness is 8 nm in average, Pt 4f signal intensity should remain at 16.3% and Sn 3d at 9.18% after penetrating through the silica shell. As a result, there is no difficulty in collecting Pt 4f and Sn 3d. The cross sections (probability of photoelectron emission) of Pt 4f and Sn 3d under illumination of Al Kα X-ray (1487 eV) are 0.24 and 0.34, respectively.22 Combining the cross section with intensity attenuation, we could get a relative sensitivity factor for Pt 4f and Sn 3d, where S(Pt 4f) = 0.24 × 16.3% = 3.91%, S(Sn 3d) = 0.34 × 9.18% = 3.12%, and their ratio is 3.91/3.12 = 1.25.

We used sensitivity factors from the Handbook of X-ray Photoelectron Spectroscopy in which S(Pt 4f) = 5.75, S(Sn 3d) = 4.725, S(Sn 3d)/S(Pt 4f) = 1.18. This number is quite similar to 1.25 with a deviation of 5.6%. As a result, we were still able to obtain a reasonable Pt/Sn ratio within the limit of experimental error. On the other hand, the similarity of the two ratios indicates that the silica shell thickness in the work carried out here does not significantly affect the compositional analysis. If the existence of the mesopores in the silica shell was further taken into account, the effect of silica shell would be even smaller. Consequently, our compositional analysis in XPS experiments is accurate within experimental error.

Furfural hydrogenation was carried out for a freshly reduced sample of PtSn@mSiO2 and a sample that had not been reduced prior to the reaction. The former showed higher conversion and greater stability compared to the latter. The latter was a sample that had undergone typical synthesis, followed by calcination and reduction and then stored in a vial for 2 weeks. Their selectivity to furfuryl alcohol was similar (96–98%) when furfural hydrogenation was carried out over a 10 h period (Figure 5). To understand the difference in their catalytic behavior, XPS analysis was carried out for freshly reduced PtSn@mSiO2 and the sample that had been in a vial for 2 weeks.

From the XPS spectra, the surface atomic concentration of Pt:Sn on the prereduced sample was 1:1.1, close to the stoichiometry of the intermetallic compound (Pt:Sn ICP-MS ratio = 1:1.02; Table 1), while the PtSn sample that had not been reduced before XPS had a lower surface atomic concentration of Pt relative to Sn (Pt:Sn = 1:1.3, Table 1). Platinum in both of the samples was in its metallic state, with a slight shift to higher binding energy (0.1–0.2 eV) for PtSn@mSiO2 that had been reduced before XPS (Figure 6a). From the Sn spectra (Figure 6b), however, it is evident that the oxide component is greater than metallic tin in the sample that had not been reduced just before the reaction. The percentage of reduced Sn on this sample is only 52% of the total Sn on the surface.

Figure 4. (a) Catalytic performance of Pt@mSiO2 vs PtSn@mSiO2. (b) Furfural hydrogenation by PtSn@mSiO2 with a lower amount of the catalyst (0.26 mg, Pt mass = 0.124 mg). Reaction conditions for furfural hydrogenation: Furfural/H2/He = 0.023/11.4/8.6 mL/min, 160 °C.

Figure 5. Conversion in furfural hydrogenation for reduced vs unreduced PtSn@mSiO2. Selectivity of both samples to furfuryl alcohol is 96–98%. Reaction conditions: Furfural/H2/He = 0.025/11.4/8.6 mL/min, 160 °C.
Sn has been known to segregate to the surface readily upon exposure to air in PtSn bimetallics due to its greater affinity for oxygen.43–46 A higher percentage of reduced Sn on the surface (84% of the total Sn on the surface, Table 1) and a surface atomic ratio that represents the stoichiometry of the intermetallic compound seemed to contribute to the enhanced conversion by the catalyst that was reduced prior to unfurual hydrogenation. This was further verified by initially running a freshly reduced catalyst for a short period, following which the catalyst was calcined in air. The conversion of furfural drops drastically from ∼100% to ∼30% after calculation (Figure S15). From the XPS measurements carried out on the calcined sample, Pt is still in the metallic state, while Sn exists solely as its oxides (Figure S17). The surface atomic ratio of Pt:Sn indicates that Sn is 5.5 times higher than Pt on the surface (Table 1).

Some reports we had resorted to for the synthesis of nanoscale intermetallic PtSn used significantly excess Sn.10,13 We wanted to observe the effect of adding slightly excess Sn during our synthesis of PtSn. PtSn1.1@mSiO2 with excess Sn (Pt:Sn = 1:1.12 measured by ICP-MS) was thus synthesized, and the PXRD measurement indicates the formation of the intermetallic PtSn (Figure S16b). We found that this 10% increase in the bulk Sn composition induced a 40% increase in the surface Sn concentration of the PtSn NPs, even when XPS was measured immediately after the sample had been reduced at 300 °C in 10% hydrogen (Pt:Sn surface atomic ratio by XPS = 1:1.4, Table 1).

As seen in the Sn XPS in Figure S18b, although reduction for PtSn1.1@mSiO2 was employed under similar conditions to PtSn@mSiO2, the oxide component was more prominent. Additionally, from Table 1, PtSn1.1@mSiO2 (Pt:Sn = 1:1.12) also had a lower fraction of reduced Sn on the surface at 75%, compared to 86% reduced Sn in PtSn@mSiO2 (Pt:Sn = 1:1) with respect to the total surface Sn. Increased surface Sn and a high percentage of oxidized Sn on the intermetallic surface may have contributed to the rapid decay in activity during unfurual hydrogenation (Figure S16a). Hence, although adding Sn was beneficial to the performance of the catalyst via the formation of intermetallic PtSn, Sn if added beyond the required amount would accumulate on the surface. The extra Sn on the intermetallic surface was susceptible to oxidation and detrimental for the stability of the catalyst in unfurual hydrogenation.

We also tried to measure if there is any surface segregation of Pt or Sn on the PtSn@mSiO2 using ambient pressure XPS, in which 0.2 Torr H2 was used to treat the intermetallic NPs under different temperatures. The atomic percentages of Pt and Sn, as well as their ratios to Si, could be found in Table S3. The atomic ratio of surface Pt to Sn (1:1) is consistent with the bulk ratio. Annealing PtSn@mSiO2 in H2 at elevated temperatures, the composition of Pt and Sn barely changes, suggesting there is no segregation of Pt or Sn in the PtSn core under these reduction conditions. The ratios of Pt and Sn to Si are rather small, consistent with the fact that PtSn nanoparticle is encapsulated in the SiO2 shell. The ratios of Pt and Sn to Si under these pretreatment conditions do not change much, indicating that the PtSn core still stays in the SiO2 shell after 500 °C reduction. AP-XPS measurements were, however, not carried out for unfurual hydrogenation on the Pt@mSiO2 and PtSn@mSiO2 catalysts to observe the evolution of the product based on the surface of the nanoparticles.

3.4 Catalyst Regeneration. A regeneration experiment was carried out to demonstrate the extra benefit of having the mSiO2 shell protection for the intermetallic NPs. As demonstrated in Figure S6, PtSn@mSiO2 can be calcined at 500 °C and reduced at 300 °C to regenerate its intermetallic phase. Performing the same treatment on deactivated catalysts due to carbon deposition, we should be able to remove the deposited carbon and regenerate the intermetallic catalysts. To test this hypothesis, PtSn@mSiO2 was first reduced at 300 °C in situ in the flow reactor using 10% H2/He, followed by unfurual hydrogenation for 35 min with the vapor composition being furfural/H2/He = 0.025/11.4/8.6 mL/min at 160 °C. Then the catalyst was deactivated intentionally by increasing the ratio of furfural to hydrogen such that furfural/H2/He = 0.025/2.86/17.2 mL/min. Following this deactivation, the catalyst was calcined at 500 °C for 30 min in air to remove deposited carbon and then reduced at 300 °C for 30 min. This constituted a single regeneration cycle, and the catalyst showed completely recovered activity in unfurual hydrogenation. In total, 6 cycles were carried out to demonstrate the ability to regenerate the catalyst (Figure 7).

3.5 DFT Studies. To explain the high hydrogenation selectivity toward unfurual alcohol on the PtSn NPs, we performed DFT-PBE calculations to compare the adsorption of unfurual on PtSn surfaces versus Pt(111). PtSn at 1:1 ratio forms an intermetallic compound of hexagonal NiAs structure with Pt–Pt atomic chains, which is more open than the close-packed face-centered cubic (fcc) structure. Among the three cleaving planes, we found that (110) and (100) have lower energy cost than (001) because the former preserves while the latter breaks the strong interaction in Pt–Pt chains. This behavior agrees with...
with our earlier study on PtPb and PtBi compounds in the same NiAs structure.47

For the adsorption of furfural, the most stable configurations on Pt(111) and PtSn(110) are shown in Figure 8a and b, respectively, with their corresponding projected density of states (PDOS) shown in (c). On Pt(111), the most preferred configuration is flat with the C=C bonds in the furan ring and the C=O bond sitting along three different Pt–Pt bridge sites, agreeing with other studies.48,49 The adsorption energy is 0.87 eV. In contrast, on PtSn(110), the most preferred configuration is tilted with the O in C=O group sitting on top of the Sn site. The PtSn(110) surface can be characterized as Pt–Pt chains decorated with Sn to form Pt–Pt–Sn trimers locally. Even though Pt–Pt bridge sites are still available, which can accommodate the adsorption of H and CO, the relatively larger furfural molecule does not have its C=C and C=O bond sit along these bridge sites (they are unstable) and become tilted after relaxation. The adsorption energy is reduced significantly to 0.33 eV. On the PtSn(100) surface, the adsorption energy for furfural is even weaker at 0.18 eV with also the tilt configuration being preferred on top of the protruded Sn atoms.

The reduction in adsorption energies is expected from our earlier study of H and CO adsorption on PtPb and PtBi surfaces47 having the same NiAs structure, because the Pt d-band center on (110) is pushed toward lower energy and further away from the Fermi level due to the charge transfer from the p-metals. From PDOS (Figure 8c), this is clearly shown by furfural on PtSn(110) retaining the molecular HOMO−1 (−3.5 eV), HOMO (−2.5 eV), LUMO (0.5 eV) and LUMO+1 (3.0 eV) states with part of the broadened LUMO-derived band shifted below the Fermi level and filled by charge transfer from Sn. In contrast, there is a strong band hybridization between furfural and Pt(111) in the flat configuration due to the direct C–Pt bonds. The tilt configuration on Cu(111) versus flat on Pd(111) has been used to explain49 the high selectivity toward hydrogenation on Cu(111) because the channel for the activation of C=C is effectively closed. Similarly here, enhanced selectivity for furfural hydrogenation with PtSn intermetallic NPs should be also due to its preferred tilted configuration on PtSn(110) and (100). To confirm, a future study will investigate the reaction pathway and kinetic barriers, including other surface terminations of PtSn.

■ CONCLUSIONS

Using this ship-in-a-bottle strategy, we have synthesized a series of monodisperse silica shell-encapsulated, Pt-based intermetallic NPs, including PtSn, Pt3Sn, PtPb, PtZn, and Pt3Zn. As demonstrated in the hydrogenation of furfural, the intermetallic PtSn@mSiO2 with molar ratio of Pt:Sn = 1:1 phase exhibited superior activity and selectivity to furfuryl alcohol in comparison to Pt@mSiO2. In intermetallic compounds, Pt benefits from an ordered environment and is deemed responsible for the observed high activity and selectivity. From XPS studies, a stoichiometric surface ratio of Pt-to-Sn is found to be the most optimal for catalyst longevity. Using AP-XPS, we find the surface Pt-to-Sn ratio remains constant under reduction conditions. DFT calculations suggest the enhanced furfuryl alcohol selectivity in furfural hydrogenation on PtSn over Pt is correlated to the different adsorption configuration of furfural in these two systems. Our work demonstrates that greatly enhanced activity and selectivity can be achieved using intermetallic NP catalysts, while reducing precious metal usage,
and silica encapsulation can effectively prevent aggregation of PtSn NPs during catalyst synthesis and regeneration. This ship-in-a-bottle strategy provides an easy route to synthesize efficient intermetallic NPs heterogeneous catalysts with a broad spectrum of compositions and uses.

**REFERENCES**

Experimental details about the synthesis of intermetallic compounds, catalysis measurements, size distribution of NPs, EDX measurements, nitrogen sorption, product distributions for Pt@mSiO$_2$ and PtSn@mSiO$_2$, furfural hydrogenation by the other intermetallic compounds, control catalysts and further XPS measurements (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail: whuang@iastate.edu.

**Notes**

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**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail: whuang@iastate.edu.

**Notes**

The authors declare no competing financial interest.