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Mesoporous silica encapsulated metal nanoparticles in catalysis

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Mesoporous silica encapsulated metal nanoparticles in catalysis

by

Yuchen Pei

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY

Major: Analytical Chemistry

Program of Study Committee:
Wenyu Huang, Major Professor
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The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this dissertation. The Graduate College will ensure this dissertation is globally accessible and will not permit alterations after a degree is conferred.

Iowa State University
Ames, Iowa
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Always, to my parents and grandparents with my most sincere appreciation who give me love, courage, and kindness to inspire me to pursue my goals.
Nanosized particles can demonstrate dramatic performance in comparison to bulk materials in heterogeneous catalysis, due to their high density of under coordinate sites associated with altered electronic properties. The structural and compositional design of bimetallic nanoparticles can further afford the precise control of activity and selectivity via the geometric and electronic effects of secondary metals. Intermetallic compounds are one of the special alloys with defined stoichiometry and ordered crystal structure, which exemplifies them as ideal model catalysts for structure-property studies in catalysis. Direct colloidal synthesis of intermetallic nanoparticles requires the presence of organic capping agents, which limits the thermal stability of nanoparticles and complicates their surface structures. Mesoporous silica shells can be used to encapsulate monometallic and bimetallic nanoparticles with high sinter-resistance for high-temperature treatment, and enables their applications for harsh reaction conditions and fundamental mechanism studies. Several examples of silica-encapsulated nanoparticles have been demonstrated in this thesis to study their catalytic properties.
CHAPTER 1. GENERAL INTRODUCTION

1.1 Catalysis in the Nanometer

Catalysis of nanomaterials is an emerging research area in developing active and selective catalysts as well as in demonstrating the fundamental reaction mechanism.\textsuperscript{1,2} As the size of catalysts decreases to nanometer range, their structural and electronic properties can be largely different in comparison to bulk materials. Extensive studies have been demonstrated to control the size of catalysts ranging from bulk,\textsuperscript{3} nanometers,\textsuperscript{2} and even single atomic level\textsuperscript{4} with unique catalytic performances. Nanocatalysts have thus been considered to bridge the homogeneous catalysis of single molecules and the heterogeneous catalysis related to atom ensembles,\textsuperscript{5-8} however, to understand the true active sites and associated mechanisms in reactions are still challenging.\textsuperscript{9,10}

One interesting story of nanocatalysts is the discovery of gold catalysis,\textsuperscript{11} evidencing the dramatically catalytic enhancement of nanosize gold particles. Gold has been considered as a less active element in comparison to other precious metals,\textsuperscript{11} which puzzled researcher for a long time. Early reports show that gold can have limited hydrogenation activity.\textsuperscript{12} However, the gold catalysis was re-explored later accompanied with a new gold rush in catalysis,\textsuperscript{13} since nanosize gold nanoparticles have been first utilized as a very active catalyst for the carbon monoxide oxidation at surprisingly low temperature\textsuperscript{14} and the hydrochlorination of ethylene to vinyl chloride.\textsuperscript{15} More studies have further demonstrated the unique electronic structures of nanosize gold clusters in enhancing their activity,\textsuperscript{16-18} turning down the previous commonsense of inert gold.
Many breakthroughs in the synthesis of well-defined nanomaterials have evidenced the improved properties of nanosize materials expanding from optical,\textsuperscript{19} electronic,\textsuperscript{20} magnetic,\textsuperscript{21} and bio-related research fields\textsuperscript{22}, and catalysis is merely one example. Small Au clusters have discrete structures behaving as homogeneous complexes with size effects in catalysis, known as magic numbers.\textsuperscript{18,23,24} The shape effect of metallic nanomaterials can be further extended to study the facet-catalysis relationship.\textsuperscript{25,26} Specifically focused on nanosized porous oxides, the shape selectivity\textsuperscript{27} and surface functionalization\textsuperscript{28,29} in zeolites/mesoporous silica widely improve the traditional bulk catalysts in the synthesis of petroleum-related products. The introduction of metal and oxides nanohybrids provide enormous platforms for the tandem reactions\textsuperscript{30} utilizing metal-support interactions and multiple interfaces. Supported single site catalysts further scale down the size scope of metal nanocatalysts to even resemble to homogeneous complexes.\textsuperscript{4} Even catalysis is a narrow research branch concerning the broad applications of nanomaterials, considerable efforts have been exerted and are still worthwhile for in-depth understandings of their catalytic mechanism in molecular level.\textsuperscript{1,2}

1.2 Synthesis of Metallic Nanocatalysts, and Their Structure-Property Relationship

The synthesis development of metallic nanocatalysts is accompanied with endeavors to understand their structure-catalysis relationships. Size control and morphology control are two directions for the synthesis of nanocatalysts. The smaller size and even smaller sizes of nanocatalysts have been continuously discovered on monometallic and bimetallic compositions.\textsuperscript{25,26} The state-of-art concepts of anchored single atomic catalysts have even served as the nowadays benchmark.\textsuperscript{4} As the size of nanomaterials decreases, the high surface
to volume ratios of nanocatalysts enhances the usage of active sites on the surface. Exposure of defect sites can also promote the activity and selectivity of nanocatalysts, because these low coordinated sites, positioned at edge, corner, and kink, have been demonstrated to affect the adsorption of substrates, either in geometry or strength, leading to their unique catalytic performance.\textsuperscript{26,31} The correlation of structural defect sites to their catalysis has emerged as another research fields. Many morphological nanoparticles have been synthesized with defined facets, controlled shapes, and precise surfaces,\textsuperscript{26,32,33} serving as model catalysts for studying their structure-property relationship.

The colloidal synthesis of monometallic NPs starts from the reduction of metal precursors with reducing agents.\textsuperscript{34} The growth of NPs follows the general La Mer model including nucleation stage and growth stage.\textsuperscript{35,36} Controlling a fast nucleation speed during the initial reduction can ensure the dominance of small nucleus. However, the direct reduction cannot easily control a monodisperse size of NPs. Several methods have thus been developed to complement the size control of NPs, such as gel electrophoresis,\textsuperscript{37} diafiltration,\textsuperscript{38} and size exclusion chromatography.\textsuperscript{39} Seeded growth method can further narrow the size distribution of NPs during the colloidal synthesis.\textsuperscript{40} Pre-synthesized seeds are utilized in seeded growth method, where their size and concentration can be adjusted. Secondary metal precursors can thus be controllably deposited on these seeds. Seed growth method also enables the facet control induced by the original facet of seeds.\textsuperscript{41}

Among the colloidal synthesis, organic capping agents serve indispensable roles.\textsuperscript{42} First, smaller NPs associated with low coordination sites have high surface energy, and thus they are prone to aggregate. Organic capping agents can stabilize these facets via electrostatic and steric stabilization.\textsuperscript{43} Moreover, organic capping agents can selectively concentrate and
passivates the growth of specific facet resulting in shape control of NPs. Third; organic capping agents can assemble on NPs in the preferential orientation via the self interaction between the functional moieties (e.g., carbon chains) of organic capping molecules. The favorable assembly of adsorbed organic capping agents can influence the adsorption configuration of reaction substrates, leading to a shape selectivity in catalysis. However, the presence of organic capping agents can also poison the surface active sites that will be further discussed in Chapter 1.3.

Besides the synthesis of free monometallic NPs, the chemical and structural properties of supports can suppress the aggregation of supported NP. Wetness or incipient wetness impregnation are commonly used to prepare supported small NPs in a facile way. The support and metal precursors are mechanically mixed by drop-casting, soaking, or solid phase grinding, and subsequent chemical treatments (i.e., oxidation and reduction) can induce the formation of supported NPs. The interactions between metal precursor and supports can confine the growth of NPs and in turn alter the local properties of supports, known as strong metal-support interactions (SMSI). SMSI can largely affect the electronic structures of supported metal NPs as well as their dispersion and structure. Heterogeneous catalysis desires precise controls of SMSI. Even though the fundamental guidelines of SMSI have not been well understood, it is seen that the variance of supports can tune the selectivity and activity of supported metals.

One cutting-edge research field is the synthesis of single atomic catalysts which exemplifies the SMSI in stabilizing metallic atoms on supports. Many reports have demonstrated the high dispersion and isolation of single metal atoms anchored on supports to stabilize the atoms in meta-states among metallic atoms and metallic ions (usually as analogs
of oxides and nitrides). The single atom catalysts show exceptional selectivity and activity, likely due to their unique catalytic behaviors and high atomic efficiency of active sites. In single site catalysts, active sites are remarkably deposited as single atoms on the support surface which can maximize the atom efficiency of every atom. These single atoms have low oxidation states and low coordinations fulfilling their unique catalysis. Wetness impregnation has been mostly used in preparing single site catalysts, where the control of low loadings (<1 wt.%) and metal-support interactions are two keys to survive isolated atoms from aggregations. Platinum is the most reported active site in single site catalysts, whereas the oxygen (O) can usually contribute to stabilize the highly mobile Pt atoms by the Pt(δ⁺)-O(δ⁻) interaction. Several O-rich supports have been studied such as SiO₂ associated with a NaOH promoter, Fe(OH)ₓ, and phosphomolibdic acid functionalized active carbons. Carbon (C) and nitrogen (N) also possess similar chemical properties to O, affording various carbides and nitrides as advanced supports. These supported atoms resemble homogeneous complex; however, confined in the 2-dimensional support surfaces, such as Co-N or Fe-N moieties as active sites over metal-supported carbon catalysts. Further studies of metallic dimers or trimers are desirable to investigate their structure-property relationship because dimers have certainly been theoretically concluded as active sites for many reactions but lack experimental supports, such as 3d transition metal dimers in CO₂ electrochemical reduction.

Bimetallic NPs are advantageous in tailoring their electronic and structural properties for catalysis in comparison to monometallic NPs, as well as in reducing the usage of precious metals. The general synthesis of bimetallic NPs is similar to that of monometallic NPs. Coreduction is a facile method by simultaneously or subsequently reducing two metal
precursors. Because two metal precursors may have different reduction potentials, it is interesting to mention that the co-reduction method usually requires a careful selection of metal precursors, solvent, temperature and reducing agent. The co-reduced bimetallic NPs have composition and morphology varying from well-mixed alloy, \textsuperscript{62} core-shell\textsuperscript{63} to branched structures. \textsuperscript{64} Seeded growth method can also be used to prepare many core-shell based bimetallic NPs, which overcomes the uncertain morphology control in many co-reduction methods. A post-annealing process is often applied to convert the core-shell structures into alloy or sublayer alloy NPs.

The surface structures of alloy NPs may not always reflect their bulk composition.\textsuperscript{65} Several surface modification methods have been readily developed to create and manipulate the bimetallic surface or sublayer. Under-potential deposition can electrochemically deposit a few atom layers on pre-synthesized NPs,\textsuperscript{66} which largely saves the plated metal and the very thin top-layers have shown improved electrocatalytic performance. Similarly, galvanic replacement\textsuperscript{67} is another scale-up method to dope secondary metals and as well as to change the bimetallic structures. For example, Pt shells can be readily deposited on PtCu NPs to prepare a Pt shell/PtCu alloy structure beneficial for oxygen reduction reaction.\textsuperscript{68} The galvanic replacement can also be applied to the synthesis of hollow or caged NPs, such as hollow PtPd nanoboxes,\textsuperscript{69} hollow PtCu NPs,\textsuperscript{70} and AuPtNi nanocages\textsuperscript{71}, etc. These hollow structures can efficiently utilize edge and corner sites to enhance their catalytic performances.

In comparison to monometallic NPs, bimetallic NPs have complicated compositional and structural tunability due to the difference in electronic properties and the atomic radius of two metals. Well-mixed alloys are more easily obtained in metals with similar size and
electronic configuration. Lattice strain and tension have also been studied with catalytic promoters in many bimetallic NPs with two largely different metals.

Synergistic effect of bimetallic NPs can cause the corporation of two metals with unique catalysis in comparison to the respective monometallic composition.\textsuperscript{72} Au@Pd core-shell NPs have been studied with a shell-thickness dependent activity in benzyl alcohol oxidation due to the optimal electronic donations from Au to Pd.\textsuperscript{73} Core-shell Ru@Pt NPs have also been reported with highest activity and selectivity in preferential CO oxidation among Ru-Pt alloys, physical mixtures, Ru, and Pt NPs.\textsuperscript{74} Even tension and strain are not desirable for the formation of homogeneous alloys,\textsuperscript{59} the associated defect structures are advantageous to be highly active sites in catalysis. Dumbbell Ru NPs have been synthesized by adding Co to create Ru lattice strain, which readily leads to a high selectivity in the hydrogenation of nitrostyrene.\textsuperscript{75} A dealloying process has also been applied to PtCu NPs to quantitatively correlate the degree of lattice tension to their activity in oxygen reduction reaction.\textsuperscript{76} Moreover, the addition of secondary metals can geometrically dilute the major metal sites diverting the original selectivity of contiguous major metals, known as a geometric effect.\textsuperscript{77} Examples are the formation of PdGa for acetylene semi-hydrogenation,\textsuperscript{78} RhIn for nitrostyrene hydrogenation,\textsuperscript{79} and PdAu for vinyl acetate synthesis.\textsuperscript{80} Diluted major metals can induce preferential adsorption of desirable functional groups\textsuperscript{81} as well as suppress over hydrogenation pathways favored on major metals.\textsuperscript{52} The secondary metals can also tune an optimal distance between surface active sites adjusting a proper contact angle/length of two reactants.

Shape control is evident for promoting catalysis in well-mixed bimetallic alloys added to the three aforementioned effects.\textsuperscript{82} Monodispersed PtPd with cubic and octahedral
shapes have been prepared to expose respective (100) and (111) facets. Pt and Pd have minimum lattice mismatch leading to a homogeneous mixture of PtPd NPs. (111) facets in PtPd NPs show a higher activity compared to that in (100) facets, likely due to the electronic properties and higher active sites density on (111) facets.

Bimetallic NPs usually have complicated catalysis associated multiple electronic and geometric factors. It is thus essential but challenging to establish the structure-property relationship to elucidate how the bimetallic composition, structure, and morphology can affect their catalysis.

1.3 Mesoporous Silica Confined Nanocatalysts

Organic capping agents have been realized with multiple functions in both synthesis and catalytic applications. As mentioned in Chapter 1.2, organic capping agents play essential roles to stabilize the high energy facets of NPs, and they can also manipulate a facet control of NPs. In catalytic rationale, organic capping agents can assemble on the metal surface to induce a preferential geometry for adsorbed molecules. Oleylamine-capped PtCo have been studied to show a carbon-chain-length dependent selectivity and activity in cinnamaldehyde hydrogenation where the assembly of carbon chains can adopt cinnamaldehyde molecules to a straight-up geometry to restrict the efficient contact of C=O to PtCo bimetallic surface. The similar surface assembly of thiol modifier has also been discovered on Pd surface to facilitate the formation of furfuryl alcohol in furfural hydrogenation due to the preferential blockage of terrace Pd sites.

Even organic capping agents are indispensable in the colloidal synthesis of NPs; they readily have limitations for broader applications. Organic capping agents often lead the
surface uncertainty via the interaction between organic capping agents and the metal surface. One major concern is the blockage of active sites, such as thiol group showing strong interactions on precious metal sites.\textsuperscript{84} Even the selective adsorption of organic modifiers can enhance the selectivity of capped NPs; they are often accommodated with a loss of activity. Another synthesis challenge is the surface reconstruction induced by the organic capping agents. For examples, the ligand can readily chelate and change the surface structure of many quantum dots (i.e., CdSe),\textsuperscript{85} and phosphor ligands have also been reported to migrate into the inner space of NiCo NPs.\textsuperscript{86} Thermostability of many organic ligand-capped NPs also limits their applications under high temperature reactions of harsh conditions. The decomposition of organic capping agents, such as polyvinylpyrrolidone (PVP), have been studied with sum-frequency generation spectroscopy.\textsuperscript{87} Upon different temperatures, PVP can decompose to cover surface active sites impacting reaction activity.\textsuperscript{88} Many ionic organic capping molecules have counter ions, such as chlorine negative ions\textsuperscript{89} and IA metal positive ions,\textsuperscript{90} that as well affect the catalysis of organic molecule capped NPs.

The use of supports is one strategy to prevent the usage of the organic capping agents in synthesis (i.e., wetness impregnation method).\textsuperscript{46} To further promote the size control and expose more active sites of NPs, the encapsulation of metal NPs with oxides can collect advantages of supported catalysts and free colloidal NPs.\textsuperscript{91} Many efforts have been addressed to coat a variety of oxides (e.g., silica,\textsuperscript{91} alumina,\textsuperscript{92} and ceria\textsuperscript{93}) on metallic cores.

Mesoporous silica is one of the most reported oxides serving as inorganic shells. Mesoporous silica has high thermal stability, and the encapsulation provides the three-dimensional protection of metallic NPs from aggregations. The porosity of mesoporous silica allows the diffusion of molecules as well as provide a size and shape selectivity to substrates
as reported widely in zeolite catalysts. By utilizing oxides from relatively inert silica to reactive supports (i.e., alumina, ceria, zeolites, etc.), these oxide shells can provide anchored acid, base sites as well as the SMSI to enhance reactivity and enable tandem reactions. Moreover, surface functionalization of oxide shells is possible to vary their surface properties, such as hydrophobicity/hydrophilicity and acidity, tuning proper adsorption of substrates as well as the local chemical environment.

However, the encapsulation of metal NPs with oxide shells still has limitations that need to be addressed by further studies. For example, the encapsulation approach can block some surface sites and lower the efficient usage of metals. The encapsulation of oxide shells is also time-consuming in comparison to wetness impregnation method developed for supported catalysts, restricting the industrial application of oxide-encapsulated NPs. The surface compatibility also brings difficulties to generalize synthesis condition to a wide choice of oxides and metals.

1.4 Intermetallic Compounds as Advanced Bimetallic Catalysts

Intermetallic compounds are growing as series of alternative catalysts to random bimetallic alloys. Intermetallic compounds feature defined stoichiometry and ordered structures, and these structures are relatively stable at high temperatures and harsh chemical environment. Owing to their high structural stability easier to be characterized, intermetallic compounds are ideal catalyst platforms to study the fundamental structure-property relationship.

In catalytic aspects, intermetallic compounds have defined structures rendering them ideal catalyst templates. Intermetallic PdIn and PdGa catalysts have been developed to
show high selectivity to semi-hydrogenation of acetylene. Similarly, intermetallic PtZn NPs\textsuperscript{100,101} have been synthesized as selective catalysts for nitroarenes hydrogenation and methanol electro-oxidation. Generally speaking, electronic and geometric effects contribute two major factors to rationalize the high activity and selectivity of intermetallic compounds in selective hydrogenations. These two factors have been extensively concluded in alloys and intermetallic compounds can be extended as more rational examples compared to many alloys. Electronic effects have been studied over Rh-based intermetallic compounds for the selective hydrogenation of nitrostyrene where methanol was used as the reducing agent.\textsuperscript{102} The more electronegativity of secondary metals in many Rh systems can enhance the O-H dissociation in methanol promoting the activity of Rh based intermetallic compounds. More importantly, the geometric effects of intermetallic compounds can ensure complete elimination of major metal ensembles due to their intrinsic structures addressing the dilution effect of major metals.\textsuperscript{81,103,104} It has been reported that an optimal distance of Au-Pd in AuPd alloys can lead to the high activity and selectivity in viny acetate synthesis.\textsuperscript{80} The dilution of Zn to Pd has been studied in intermetallic PdZn catalysts with essential geometric roles leading to high selectivity in semi-hydrogenation of acetylene.\textsuperscript{105} Intermetallic PdZn can eliminate the active Pd-Pd sites, weaken the \( \pi \)-bonding of ethylene on single Pd sites, and thus lower their capability to hydrogenate ethylene. However, the Pd-Zn-Pd patterns can provide two adjacent Pd isolated sites for a moderate \( \sigma \)-bonding of acetylene, leading to a high acetylene hydrogenation activity. Similar geometric interactions have also been demonstrated on intermetallic PtZn\textsuperscript{102} and RhIn\textsuperscript{79} in hydrogenation of nitroarens, intermetallic PtSn\textsuperscript{104} in hydrogenation of furfural, and NiIn\textsuperscript{106} in the hydrogenation of cinnamaldehyde. The isolated patterns of major metals diluted by inert metals can adopt the
substrates to a preferential adsorption of polar groups (such as nitro group and aldehyde group), playing essential roles for suppressing the undesirable hydrogenation of other functional groups. Intermetallic compounds have also been studied as a structural template to induce the formation of CNTs with specific chiral orientation due to their high melting points and special crystal structures, such as tungsten-based intermetallic compounds.\textsuperscript{107}

To synthesize intermetallic compounds, the control of metallic composition is essential because of the discrete stoichiometry of intermetallic compounds.\textsuperscript{108} Intermetallic PtZn has a relatively wide range of atomic Zn/Pt (0.47-1) to tolerate the intermetallic formation,\textsuperscript{109} however, intermetallic PtSn is mere a line compound.\textsuperscript{110} An annealing process is also general to ensure adequate migration of atoms to reach the desirable structure of intermetallic compounds. The colloidal synthesis of intermetallic NPs has thus not been fully developed because many NPs cannot resist high-temperature annealing. A few intermetallic NPs can be synthesized directly by polyol reduction or by a gentle post-annealing process of alloy NPs, such as Au-Cu (AuCu, AuCu\textsubscript{3})\textsuperscript{111} and Pt-Sn (PtSn, Pt\textsubscript{3}Sn, and PtSn\textsubscript{2}) systems.\textsuperscript{110,112} Supported intermetallic compounds are more generally reported ranging from Pt,\textsuperscript{113} Pd,\textsuperscript{114} and Rh\textsuperscript{102} systems, because of a more accessible compositional control based on the addition of metal precursors, and the high thermal stability of supports. However, the supporting method has limited controls to obtain a homogeneous distribution of intermetallic NPs in size, structure, and compositions.

1.5 Perspectives on Each Chapter

This thesis is composed of eight chapters. Chapter 1 is a brief introduction of nanosize catalysts and their synthesis. We especially focus on the synthesis of mesoporous
silica encapsulated nanoparticles, and the structure-catalytic property relationship of intermetallic compounds. Chapter 2-6 introduce the synthetic advantages and catalytic studies of silica encapsulated intermetallic NPs. Chapter 7-8 introduce the synthesis of silica confined monometallic NPs and the silica pore induced nanoconfinement effect in catalysis. Specifically, Chapter 2 has been published in *Nanoscale*, and we studied the seeded growth method in preparing mesoporous silica encapsulated Pt-based bimetallic nanoparticles. These nanoparticles have high thermal stability due to the silica encapsulation, and their composition is highly tunable. We demonstrate an etching mechanism to explain the deposition and growth of secondary metals on Pt seeds accommodated by etching the inner space of silica shells. Chapter 3 has been published in *Journal of Catalysis*. We further used the seeded growth method described in Chapter 1 to synthesize Pt-based intermetallic NPs encapsulated in silica. We demonstrated a structure-catalysis relationship that the defined intermetallic PtSn structure can induce a non-dissociative hydrogenation pathway leading to the high selectivity in the hydrogenation of nitroarenes. The alternation of hydrogenation is due to the elimination of Pt threefold sites on intermetallic PtSn preferring molecular hydrogen as surface species. Chapter 4 has further utilized intermetallic PtSn as selective hydrogenation catalyst to preferentially produce the cis-alkenes, due to the structural effect that intermetallic PtSn prefers the adsorbed molecular H\textsubscript{2}. Molecular H\textsubscript{2} can thus be more easily added into alkynes in a pairwise fashion associated with a high cis-selectivity of alkenes. Chapter 5 has discussed the surface composition-dependent catalysis of PtSn intermetallic nanoparticles in selective hydrogenations. We varied Pt/Sn ratios from slightly Pt-rich to Sn-rich, and the reduction temperatures can readily induce the formation of different surface structures responsible for their unique catalysis. In Chapter 6-7, we
introduce a sandwiched structure to encapsulate metal nanoparticles between amino-functionalized silica cores and mesoporous silica outer shells, as a complement to the metal nanoparticle/silica core-shell structure mentioned in Chapter 2-5. Chapter 6 has been published in *Surface Science*. Chapter 6 focuses on the synthesis using an annealing treatment to enhance the metal loading efficiency and dispersion on amino-functionalized silica. Chapter 7 has been published in *Nature Catalysis* as a continuing work of Chapter 6 with catalytic mechanism studies. We further coated the Pt loaded silica spheres as described in Chapter 6 with well-defined mesoporous silica shells. Thanks to our collaborators Dr. Bin Dong and Prof. Ning Fang at Georgia State University, this sandwiched structure can be used as a template catalyst for single-molecule fluorescent studies. We precisely varied pore lengths of mesoporous silica shells to study the diffusion and catalytic kinetic mechanism of fluorescent molecules confined in shells. An enhanced activity has been observed as we increased the pore lengths evidencing the catalytic nanoconfinement effect. The diffusion and kinetic parameters of fluorescent molecules in confined space have also been quantified in single-molecular and single-particle level. Chapter 8 concludes these synthesis and catalysis studies of silica-encapsulated nanoparticles as well as provides perspectives to future catalytic directions on specific intermetallic compounds.
CHAPTER 2. AN INORGANIC CAPPING STRATEGY FOR THE SEEDED GROWTH OF VERSATILE BIMETALLIC NANOSTRUCTURES

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2.1 Abstract

Metal nanostructures have attracted great attention in various fields due to their tunable properties through precisely tailored sizes, compositions and structures. Using mesoporous silica (mSiO2) as the inorganic capping and encapsulated Pt nanoparticles as the seeds, we developed a robust seeded growth method to prepare uniform bimetallic nanoparticles encapsulated in mesoporous silica shells (PtM@mSiO2, M = Pd, Rh, Ni and Cu). Unexpectedly, we found that the inorganic silica shell is able to accommodate an eight–fold volume increase in the metallic core by reducing its thickness. The bimetallic nanoparticles encapsulated in mesoporous silica shells showed enhanced catalytic properties and thermal stabilities compared with those
prepared with organic capping agents. This inorganic capping strategy could find a broad application in the synthesis of versatile bimetallic nanostructures with exceptional structural control and enhanced catalytic properties.

2.2 Introduction

Uniform and tunable metal nanostructures have been extensively investigated as advanced materials in imaging, drug delivery, and heterogeneous catalysis. Among them, bimetallic nanoparticles (NPs) have been attractive paradigms to study their tunable electronic and chemical properties resulting from synthetic advances that enable size, composition and morphology control. Seeded growth approaches are commonly applied in colloidal chemistry to synthesize diverse bimetallic nanostructures such as core–shell, alloy, and hollow structures in a predictable and controllable manner. In general colloidal synthesis, organic surfactants are indispensable to prevent the aggregation of NPs, functioning as capping agents. However, NPs capped with organic surfactants would aggregate under harsh reaction or pretreatment conditions. Moreover, organic capping agents can stymie the access of reactants to the surface of NPs, and thus limit their catalytic performance. Thermal treatment can remove organic capping agents, but usually leads to undesired aggregation of the NPs. To enhance the stability of NPs, oxides and carbon materials (e.g. Al₂O₃, SiO₂, and functionalized graphene) have been used as supports to immobilize them. Unfortunately, the sintering of supported NPs is still unavoidable under high temperature treatments. To further enhance the thermal stability of NPs, another strategy is to encapsulate them within inorganic shells, such as mesoporous silica (mSiO₂), which can provide a robust three–dimensional protection against NP sintering.
In the synthesis of bimetallic@mSiO$_2$ core–shell NPs, the traditional strategy relies on the pre–synthesis of bimetallic NPs followed by coating mSiO$_2$ \cite{43,44} where organic capping agents still play key roles in the synthesis of bimetallic NPs, resulting in the challenging removal of organic surfactants bound to the surface of the bimetallic NPs. Inspired by the structural similarities between NPs capped with organic surfactants and inorganic shells, we hypothesized that the inorganic shell can be directly used as a stabilizer or “capping agent” for the growth of uniform bimetallic NPs from monometallic NP seeds encapsulated within this inorganic shell.

We explored this inorganic stabilizer concept for the first time using mSiO$_2$ as a robust inorganic shell for the synthesis of various Pt–based bimetallic@mSiO$_2$ NPs (PtM@mSiO$_2$). Pt NPs encapsulated in mSiO$_2$ shells (Pt@mSiO$_2$) were used as seeds where mSiO$_2$ functioned as an inorganic “capping agent”. We then introduced a secondary metal (Pd, Rh, Ni, or Cu) onto Pt@mSiO$_2$ via seeded growth as illustrated by the first step in Scheme 1. The increase in the metal core volume due to the deposition of secondary metals is accommodated by the decrease in the mSiO$_2$ shell thickness. This suggests that the mSiO$_2$ shell is not a rigid coating and can be easily deformed to accommodate the expansion of the encapsulated metal core during the seeded growth. We demonstrated that four different nanostructures could be easily synthesized using this inorganic capping strategy. Initially, the deposited secondary metal forms a shell in between the original metal core and the deformed mSiO$_2$ shell under the employed synthesis conditions. Upon further annealing, the bimetallic core could be converted to an alloy. We could also selectively etch away the original metal core or the secondary metal shell leading to a mSiO$_2$–encapsulated nanobox or yolk–shell structure, respectively. Moreover, the mSiO$_2$ shell permits the access of reactants to the clean
metal surface after bimetallic seeded growth in the absence of strong organic capping agents. We found that PtPd bimetallic NPs capped with mSiO$_2$ shells showed superior catalytic properties compared to those capped with organic capping agents.

### 2.3 Experimental

**Synthesis of bimetallic PtPd@mSiO$_2$ NPs**

In a typical synthesis of PtPd@mSiO$_2$ NPs, as–synthesized Pt@mSiO$_2$ seeds (10 mg Pt, stored in methanol) and K$_2$PdCl$_4$ (16.7 mg, as Pt/Pd=1) precursor were well dispersed in 80 mL TEG with sonication. The mixed solution was placed in vacuum to remove residual methanol, after which argon was backfilled into the flask. Under argon protection, the mixture was heated at 180 °C for 2 hrs (ramping rate: 2.5 °C·min$^{-1}$) from 30 °C and subsequently heated at 280 °C for another 2 hrs (ramping rate: 1.7 °C·min$^{-1}$) with vigorous stirring. After cooling down to room temperature, 80 mL of acetone was added into the solution to help separate PtPd@mSiO$_2$ NPs. PtPd@mSiO$_2$ NPs were then collected by centrifuge and further washed with methanol three times. As–synthesized PtPd@mSiO$_2$ NPs were stored in methanol for future use.

**Yolk–shell Pt@mSiO$_2$ and hollow Pt@mSiO$_2$ nanoboxes**

Yolk–shell and hollow Pt@mSiO$_2$ were derived from their respective PtPd bimetallic nanostructures by preferential etching of Pd by HNO$_3$. Yolk–shell Pt@mSiO$_2$ was obtained by placing 0.5 mg PtPd@mSiO$_2$ powder (Pt core/Pd shell) in 5 mL concentrated HNO$_3$ and stirring for 18 hrs at room temperature. Before HNO$_3$ etching, PtPd@mSiO$_2$ samples were pre–dried in vacuum at room temperature and further dried at 120 °C in an oven overnight. Hollow
Pt@mSiO₂ was obtained by placing 2 mg PdPt@mSiO₂ (Pt shell/Pd core) in 10 mL concentrated HNO₃ under reflux for 18 hrs.

Control experiment for mSiO₂ etching

TEG blank (control i) was conducted using Pt@mSiO₂ (10 mg Pt) directly in 80 mL TEG under the same temperature ramping conditions as that for the synthesis of PtPd@mSiO₂. KCl treatment (control ii) was conducted using Pt@mSiO₂ (10 mg Pt) in 80 mL TEG with the addition of four molar equivalents of KCl (comparing to Pt).

Characterization

Surface analysis of Pt@mSiO₂ and PtPd₁.₁@mSiO₂ was performed by nitrogen adsorption isotherms using Micromeritics 3Flex surface characterization analyzer at 77 K. PXRD patterns of the samples were acquired by a STOE Stadi P powder diffractometer using Cu Kα radiation (40 kV, 40 mA, λ = 0.1541 nm). TEM, EDS line scans and elemental mapping analysis for the morphology of Pt@mSiO₂, Pd@mSiO₂ and PtM@mSiO₂ were investigated using TEM recorded on a Tecnai G2 F20 electron microscope with EDS analysis (Oxford INCA EDS) operated at 200 kV. ICP–MS (X Series II, Thermo Scientific) was performed to determine the actual metal loadings of Pt@mSiO₂ and Pd@mSiO₂ ahead of the introduction of the secondary metal precursor, and to determine metal ratios of PtM@mSiO₂ after synthesis. Samples were first dissolved in a mixture of 100 µL HF and 5 mL aqua regia to dissolve the mSiO₂ shell for efficient digestion of metals. After evaporating the solution containing HF under 250 °C, the remaining solids were further dissolved in 5 mL aqua regia to achieve a clear solution with metal ions, and diluted appropriately for ICP–MS detection.
Nitrobenzene hydrogenation

PtPd@mSiO₂ catalysts were collected from their methanol suspension solution and then dried under vacuum. The compositions of Pt and Pd of catalysts were measured by ICP–MS. The catalysts were calcined at 350 °C in air for 4 hrs and reduced at 300 °C for 2 hrs in 5 % H₂/He flow before reaction. Typically, calculated amounts of dried catalyst powder (2.6×10⁻³ mmol Pt + Pd) were weighed in a 20 mL glass vial, followed by the addition of 410 μL nitrobenzene, 1.5 mL H₂O and 300 μL ethylene glycol as the internal standard. The vial was then sealed with a rubber cap equipped with a needle to aid H₂ diffusion. Then 2 or 3 vials were placed inside a Parr autoclave charged with 4 MPa H₂ after suction and flushing was carried out several times. The reaction was conducted under room temperature (~ 25 °C) with vigorous stirring. All contents (nitrobenzene, nitrosobenzene, phenylhydroxylamine, aniline, and azoxybenzene) after reaction were analyzed directly by an Agilent 6890N/5975 gas chromatograph mass spectroscopy (GS–MS) equipped with a HP–5ms capillary column (30 m × 0.25 mm × 0.25 μm) and a flame ionization detector.

2.4 Results and Discussion

Pt NPs encapsulated in mSiO₂ shells (Pt@mSiO₂) were prepared as reported earlier.⁴² To form PtM@mSiO₂ (M = Pd, Rh, Ni, Cu) bimetallic NPs, Pt@mSiO₂ seeds and a secondary metal precursor were dispersed and reduced in tetraethylene glycol (TEG) at elevated temperatures under argon atmosphere (Scheme 1).⁴⁵ To avoid the formation of isolated NPs by the fast nucleation of the secondary metal precursor, we adjusted the reduction temperature for different metal precursors. For 3d metal precursors (NiCl₂ and CuCl₂), the reduction
temperature was kept at 280 °C, while 180 °C was used to reduce noble metal precursors (K$_2$PdCl$_4$ and RhCl$_3$). At the appropriate reduction temperature, the secondary metal prefers to deposit on the Pt core encapsulated in mSiO$_2$ due to the relatively lower nucleation energy barrier required for seeded growth as opposed to forming independent nuclei. Pt NPs can also catalyze the dehydrogenation of TEG, generating hydrogen species on the surface of Pt that could localize the reduction and thus the selective deposition of the secondary metal.

Prior to the synthesis of bimetallic PtM@mSiO$_2$ NPs from Pt@mSiO$_2$ seeds, we were wondering if the limited space within the mSiO$_2$ shell would restrict the growth of bimetallic NPs from Pt cores. We first performed the seeded growth with K$_2$PdCl$_4$ precursor and Pt@mSiO$_2$ seeds. After reduction at 180 °C for 2 hrs, the overall particle size (including the mSiO$_2$ shell) and the mSiO$_2$ shell morphology of final PtPd$_{1.1}$@mSiO$_2$ NPs (overall size: 36.3 ± 1.9 nm) show no obvious change compared with those of Pt@mSiO$_2$ seeds (overall size: 36.1 ± 1.8 nm), though the metal core expands to 17.7 ± 1.2 nm from 13.6 ± 1.0 nm as shown by the transmission electron microscopy (TEM) images in Figure 2.1a and 2.1b. To accommodate the metal core expansion, the thickness of the mSiO$_2$ shell decreases to 9.3 ± 1.1 nm from 11.3 ± 1.1 nm. We speculate that the mSiO$_2$ shell is either etched or compressed specifically from the inner surface. Specific surface areas and pore volumes of Pt@mSiO$_2$ and PtPd$_{1.1}$@mSiO$_2$ are shown in Table S2.1 and Figure S2.1 in the Supporting Information measured by N$_2$ physisorption. The specific surface area and pore volume of PtPd$_{1.1}$@mSiO$_2$ decrease accompanied by a slight increase in pore size, compared with those of Pt@mSiO$_2$. Considering the unchanged sizes of the overall particles, decreased surface areas, and nearly intact pore sizes, we suggest the loss of mSiO$_2$ during seeded growth of PtPd@mSiO$_2$, likely
etched by ions in TEG during synthesis. It has also been reported that some inorganic ions can etch amorphous silica.\textsuperscript{50}

To illustrate the etching of the mSiO\textsubscript{2} shell by ions, we conducted two control experiments under the same synthesis conditions: (i) Pt@mSiO\textsubscript{2} seeds were heated in TEG; (ii) KCl was added to hot TEG that contained Pt@SiO\textsubscript{2} seeds. In the first control experiment (Figure S2.2a and S2.2b), we found that the overall size of Pt@mSiO\textsubscript{2} is \(~35\) nm and the Pt core is \(~13\) nm, which conforms to that of the original Pt@mSiO\textsubscript{2} (overall size: \(36.1 \pm 1.8\) and Pt core: \(13.6 \pm 1.0\) nm). The specific area of Pt@mSiO\textsubscript{2} in control (i) is \(594.8\) cm\(^2\)-g\(^{-1}\) with a pore size of \(2.5\) nm. This is also similar to that of the original Pt@mSiO\textsubscript{2} (specific area: \(503.4\) cm\(^2\)-g\(^{-1}\) and pore size: \(2.4\) nm). This blank control serves to show the mSiO\textsubscript{2} shell is stable without obvious deformation in TEG during our seeded growth. In the second control experiment, 4 equivalents of KCl were added to the hot TEG solution that contained Pt@mSiO\textsubscript{2} to study the capacity of KCl to etch mSiO\textsubscript{2} under our synthesis conditions. The amount of KCl is comparable to the added K\textsubscript{2}PdCl\textsubscript{4} precursor in a typical synthesis. The diameter of Pt core and overall size (including the mSiO\textsubscript{2} shell) in Pt@mSiO\textsubscript{2}–KCl (control ii) are \(13.3 \pm 0.8\) nm and \(31.3 \pm 1.7\) nm respectively. The 5 nm decrease in overall size of Pt@mSiO\textsubscript{2}–KCl and the relatively intact Pt core size suggests the etching of the mSiO\textsubscript{2} shell in presence of KCl. We also used N\textsubscript{2} adsorption to characterize Pt@mSiO\textsubscript{2}–KCl control. Due to etching by the KCl, the specific area of Pt@mSiO\textsubscript{2}–KCl decreased to \(442.0\) cm\(^2\)-g\(^{-1}\) from \(503.4\) cm\(^2\)-g\(^{-1}\) in the original Pt@mSiO\textsubscript{2}. Pore size distribution of Pt@mSiO\textsubscript{2}–KCl in Figure S2d also shows a bump at \(4.9\) nm besides the peak at \(2.6\) nm, which indicates that the well–defined pore structure of mSiO\textsubscript{2} was partially destroyed in presence of KCl. The etching of mSiO\textsubscript{2} was also supported by the increase of Si content in the supernatant of the solution after synthesis (Table S2.2). We
speculate that the localized production of ions during the reduction of metal precursors (e.g. $H^+$, $K^+$ and $Cl^-$ in the case of $K_2PdCl_4$) would occur predominantly at the inner surface of mSiO$_2$, near the metal NP cores, where Pd is being nucleated on the surface of Pt NPs during seeded growth. The heat of the reaction or the high local concentration of ions, produced *in situ* during synthesis, could induce the etching of mSiO$_2$ at this interface.

Since the etching mechanism of mSiO$_2$ shell could allow the PtPd metal core to expand, we sequentially reduced 10 batches of $K_2PdCl_4$ on Pt@mSiO$_2$ seeds to test how much the metal core can expand (Figure 2.2). Surprisingly, we obtained PtPd metal cores with an average size of $25.5 \pm 3.0$ nm after 10 growth cycles of Pd addition. Comparing to the original Pt core ($12.4 \pm 1.3$ nm), the mSiO$_2$ shell is capable of accommodating an 8–fold volume expansion of the inner metal core. As more Pd deposited, it is also clearly seen that PtPd metal cores expand consistently and the mSiO$_2$ shell becomes thinner. More detailed mechanism studies about the changes in the mSiO$_2$ shell are underway. Nevertheless, the flexibility of mSiO$_2$ shell allows us to increase the metal core size without destroying the inorganic shell.

To show the versatility of our method, we demonstrated that monodisperse bimetallic NPs can be synthesized using mSiO$_2$ as the inorganic capping shell, when we used different metal precursors ($H_2PtCl_6$, $K_2PtCl_4$, Pd(acac)$_2$ and $K_2PdCl_4$), solvents (oleylamine, denoted as OAm, and TEG), and reduction orders (Pd on Pt@mSiO$_2$ and Pt on Pd@mSiO$_2$). As summarized by (i)–(v) in Table 2.1, uniform PtPd@mSiO$_2$ NPs were formed regardless of diverse synthetic conditions. Even though bare PtPd NPs have been reported with spatial and structural controls via co– or sequential reduction of Pd or Pt precursors in polyol and/or oleylamine solvents, these synthetic methods are specifically dependent on a delicate choice of precursors, solvents, capping agents, temperatures, and reduction orders.$^{51-54}$ In the absence
of the mSiO₂ shell encapsulation, under our synthetic conditions using TEG, we found that uniform PtPd NPs could hardly be synthesized by the direct deposition of Pd on Pt NPs. Even with the additional introduction of polyvinylpyrrolidone (PVP, Mw ~ 29000) as an organic capping agent to stabilize PtPd NPs in TEG, we still cannot synthesize uniform PtPd NPs (vi and vii, Table 2.1).

Figure 2.1. TEM images showing the morphology of (a) Pt@mSiO₂; (b) PtPd₁.₁@mSiO₂; (c) PtPd₁.₆@mSiO₂; (d) Linear relationship between volumetric ratios of PtPd/Pt metal core and Pd/Pt molar ratios; (e) hollow Pt nanobox@mSiO₂ from PdPt₀.₄₈@mSiO₂ after etching Pd by HNO₃; (f) yolk–shell Pt@mSiO₂ by etching Pd in PtPd@mSiO₂.
Figure 2.2. TEM images of PtPd@mSiO$_2$ after sequential addition of Pd to Pt@mSiO$_2$. The average sizes of (a) original Pt and PtPd metal core after (b) 3, (c) 5, (d) 8 and (e) 10 cycles of Pd addition are summarized as 12.4 ± 1.3 nm, 17.9 ± 1.1 nm, 20.2 ± 1.5 nm, 21.9 ± 2.2 nm and 25.5 ± 3.0 nm, respectively (based on 200 particles in each case). After each cycle of Pd precursor addition, as–synthesized PtPd@mSiO$_2$ NPs were washed and redispersed as seeds for the next cycle.

Oleylamine was then inspected as a stronger capping agent than PVP, and flower–like Pd@Pt NPs with Pd clusters forming around Pt cores were attained as previously reported (viii, Table 2.1). However, when we reversed the reduction order to deposit Pd(acac)$_2$ on Pt NPs, flower–like Pt@Pd NPs were not obtained, instead Pd nucleated independently of the available Pt seeds (ix, Table 2.1). These results demonstrate that the mSiO$_2$ shell is more robust as an inorganic stabilizer for seeded growth and renders our method less sensitive to synthetic conditions when accounting for other general organic capping agents.

To test the versatility of our method in regulating bimetallic compositions, we chose the PtPd@mSiO$_2$ system for detailed studies. By tuning the ratio of K$_2$PdCl$_4$ precursor to Pt@mSiO$_2$ seeds, various PtPd@mSiO$_2$ samples ranging from the Pt–rich to the Pd–rich region were synthesized, denoted as PtPd$_{0.50}$@mSiO$_2$, PtPd$_{0.74}$@mSiO$_2$, PtPd$_{1.1}$@mSiO$_2$ and PtPd$_{1.6}$@mSiO$_2$. We also used Pd@mSiO$_2$ as seeds and reduced Pt precursor (K$_2$PtCl$_4$) on them under similar synthetic conditions as described for introducing the Pd precursor to
These bimetallic NPs prepared using Pd@mSiO₂ as seeds are denoted as PdPt₀.₄₈@mSiO₂ and PdPt₁.₁@mSiO₂. We utilized inductively coupled plasma mass spectroscopy (ICP–MS) to measure final Pd/Pt ratios. Measured Pd/Pt ratios agree well with those calculated from the starting materials (Table S2.3), which demonstrates the efficient incorporation of K₂PdCl₄ in bimetallic PtPd@mSiO₂ NPs. Additionally, the TEM images (Figure S2.4) show that no isolated metal NPs formed in all PtPd@mSiO₂ samples with various Pd/Pt ratios, even when 1.6 equivalents of Pd were introduced to Pt@mSiO₂. We also measured the average sizes of metal cores in Pt@mSiO₂, PtPd₀.₅₀@mSiO₂, PtPd₀.₇₄@mSiO₂, PtPd₁.₁@mSiO₂, and PtPd₁.₆@mSiO₂ as 13.6 ± 1.0 nm, 15.5 ± 1.3 nm, 16.7 ± 1.2 nm, 17.7 ± 1.2 nm, and 19.1 ± 1.1 nm, respectively (Figure S2.5). Overall particle sizes (including the mSiO₂ shell) in all PtPd@mSiO₂ samples experienced no obvious change. The measured PtPd metal core sizes agree with the theoretical values assuming no Pt loss during the seeded growth (Figure 2.1d and Equation S2.1). Together with ICP–MS results in Table S2.3, it is evident that the robust confinement afforded by mSiO₂ ensured the successful introduction of Pd upon Pt@mSiO₂ seeds with tunable Pd/Pt ratios and high incorporation efficiency.

The morphology of the PtPd metal core in as–synthesized PtPd@mSiO₂ was characterized by TEM coupled with energy dispersive X–ray spectroscopy (EDS) as shown in Figure 2.3 and Figure S2.6. The core–shell structure of the PtPd metal core can be observed in PtPd₁.₁@mSiO₂ with the darker Pt core visualized within a lighter Pd shell (Figure 2.3a). After the deposition of Pd, the PtPd metal core in PtPd₁.₁@mSiO₂ also illustrates a spherical shape, which differs from the more cubic–like Pt core in the original Pt@mSiO₂ seeds (Figure 2.1b and 2.1a). The Pt core/Pd shell structure in PtPd₁.₁@mSiO₂ was further confirmed in Figure 2.3c and 2.3e–h under EDS line scan and elemental mapping. We observed Pt was localized...
in the inner position, while Pd was distributed around the Pt core as a ~ 5 nm shell. When we reversed the reduction order to form PdPt_{1.1}@mSiO$_2$ by introducing Pt on Pd@mSiO$_2$ seeds, a Pd core/Pt shell structure was also evident as expected (Figure 2.3b, 2.3d, and 2.3i–l). However, we could not exclude the deposition of secondary metal within the mSiO$_2$ network due to the limited sensitivity and resolution of EDS.

Table 2.1. The effect of different synthetic conditions, including solvent, precursor, capping agent, and reduction order on the morphology of synthesized bimetallic NPs.

<table>
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<th>items</th>
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<th>solvent</th>
<th>capping agent</th>
<th>results</th>
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<td>Pt@mSiO$_2$</td>
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<td>Fig. 2.1b</td>
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<td>Fig. S2.3b</td>
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<td>uniform PtPd@mSiO$_2$</td>
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<td>isolated Pd clusters</td>
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Figure 2.3. TEM images, EDS line scans, and elemental mappings: TEM images of the representative (a) as–synthesized PtPd$_{1.1}$@mSiO$_2$ NP to discern Pt core/Pd shell structure and (b) as–synthesized PdPt$_{1.1}$@mSiO$_2$ NP with Pd core/Pt shell structure; EDS line scans of (c) PtPd$_{1.1}$@mSiO$_2$ and (d) PdPt$_{1.1}$@mSiO$_2$; (e)–(l) are elemental mapping images of Pt (green) and Pd (red) signals. The scale bars in (e)–(h) are all 5 nm, and in (i)–(l) are 10 nm.

To further illustrate the core–shell structure, PdPt$_{0.48}$@mSiO$_2$ was obtained by coating the Pd core with a thin Pt shell, and placed in concentrated HNO$_3$ to engender the preferential chemical etching of Pd. Hollow Pt shell–like nanoboxes encapsulated in mSiO$_2$ were derived for the first time after etching away inner Pd cores in PdPt$_{0.48}$@mSiO$_2$ (Figure 2.1e). Starting with a Pd shell deposited on Pt@mSiO$_2$ core, we hypothesize that a Pt yolk–shell structure encapsulated in mSiO$_2$ (yolk–shell Pt@mSiO$_2$) can also be acquired when removing the deposited Pd layer in between the original Pt core and the etched mSiO$_2$ shell. To prove this, we used HNO$_3$ to etch Pd in dried PtPd@mSiO$_2$ powders with a 21.9 nm PtPd core. As shown in Figure 2.1f, the metal cores decreased to ~ 13 nm, which is comparable to the original 12.4
nm Pt core, and the void space between the metal core and the mSiO$_2$ shell was clearly observed. Interestingly, if we directly etched Pd in as–synthesized PtPd@mSiO$_2$ without drying, we could not observe any yolk–shell structure (Figure S2.2e).$^{55}$ Based on these experiments, we envisage that the mSiO$_2$ shell can perform as a universal inorganic stabilizer enabling the synthesis of versatile nanostructures.

Under the protection of the mSiO$_2$ shell, PtPd@mSiO$_2$ experiences enhanced thermal stability, which facilitates the high–temperature treatment to convert the core–shell structure of PtPd metal cores into alloy phases. The high–temperature also helps remove organic remnants that could hinder the catalytic performance of PtPd metal cores. As–synthesized PtPd@mSiO$_2$ NPs were then calcined at 350 °C in air and reduced at 300 °C under 5% H$_2$/Ar flow. We then utilized powder X–ray diffraction (PXRD) to clarify the formation of PtPd alloy phases in PtPd@mSiO$_2$ after thermal treatment (Figure 2.4). The characteristic diffraction peaks (e.g. major peak around 39.7°) in all PtPd@mSiO$_2$ samples after thermal treatment shift to higher diffraction angles towards Pd@mSiO$_2$ peak positions as the Pd/Pt ratio increases. Meanwhile, all characteristic diffraction peaks in pure Pt@mSiO$_2$ and Pd@mSiO$_2$ are aligned with that of the respective Pt and Pd bulk metal standards. This coherent trend of angle shift suggests the formation of PtPd alloy phases.$^{56}$ The formation of PtPd alloy phase is also confirmed with EDS line scan and elemental mapping (Figure S2.8). TEM images show that the mSiO$_2$ shell morphology was maintained and no aggregation of PtPd metal cores was observed in all PtPd@mSiO$_2$ samples after thermal treatment (the TEM image of PtPd$_{1.1}$@mSiO$_2$ annealed at 350°C is shown in Figure S2.9h).
Figure 2.4. PXRD patterns of PtPd@mSiO$_2$ with Pt/Pd ratios after calcination and reduction

Table 2.2. Catalytic properties of PtPd@mSiO$_2$ and oleylamine-capped PtPd in nitrobenzene hydrogenation.

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<th>Catalyst</th>
<th>Conversion (%)</th>
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</tbody>
</table>

a. Catalysts experienced 350 °C calcination in air for 4 hrs and reduced at 300 °C under 5% H$_2$/Ar for 2 hrs before reaction except for PdPt$_{0.50}$ NPs; b. Aniline (AN), nitrosobenzene (NOB), azoxybenzene (AB) and phenylhydroxylamine (PHA) are four major products detected.

Nitrobenzene hydrogenation was used to evaluate the catalytic activity of PtPd@mSiO$_2$. Since both Pt and Pd are hydrogenation catalysts, the total metal amount (Pt+Pd) was kept constant for all reaction studies. For PtPd$_{1.1}$@mSiO$_2$ and PdPt$_{0.48}$@mSiO$_2$ catalysts (after annealing to form alloys), high conversion of nitrobenzene and high selectivity
to aniline was obtained with less by-products detected (Table 2.2). Notably, no obvious mSiO₂ shell destruction was observed after the reaction (Figure S2.10a). To further illustrate the difference in catalytic properties between mSiO₂-encapsulated PtPd NPs (PtPd@mSiO₂) prepared using this new inorganic capping strategy and general organic-stabilizer capped PtPd NPs, we investigated the catalytic performance of flower-like PdPt NPs synthesized in oleylamine for nitrobenzene hydrogenation (Table 2.2). When capped with oleylamine, PdPt NPs show decreased conversion and poor selectivity in contrast to PtPd@mSiO₂. This suggests that oleylamine molecules may partially block surface active sites of metal NPs for the hydrogenation reaction. The oleylamine covered PdPt NP surface also complicates the product distribution likely due to the variation in electronic and steric characteristics of the metal surface. To help remove oleylamine from the metal surface, PdPt NPs were then loaded on silica gel and treated by calcination and reduction (PdPt/SiO₂). However, the conversion and selectivity of PdPt/SiO₂ were not improved and significant aggregation of the PtPd NPs were observed as shown in Figure S2.3h. Hence the mSiO₂ shell can promote the thermal stability of PtPd nanocatalysts with no distinct retardation to reactant/product diffusion for nitrobenzene hydrogenation. The reusability of PtPd@mSiO₂ was evaluated with high activity and selectivity achieved for 6 runs (Figure S2.11 and Table S2.4). We did observe that the mSiO₂ shell became thinner and partially damaged (Figure S2.10b) after 6 recycle runs, which could be due to the formation of the basic reaction product, aniline. Aniline could etch mSiO₂ over time and finally led to the aggregation of unprotected PtPd NPs and the decrease of their activity.

In order to extend this strategy to other bimetallic NPs of PtM@mSiO₂, Ni, Cu and Rh were introduced into Pt@mSiO₂ seeds to form PtNi@mSiO₂, PtCu@mSiO₂ and
PtRh@mSiO₂, respectively. The molar ratios of the secondary metals to original Pt were measured by ICP–MS (Table S2.3). The compositions of as–synthesized PtM@mSiO₂ (M = Ni, Cu and Rh) revealed that the secondary metals have been successfully introduced into Pt@mSiO₂. From Figure S2.9a–c, the diameter increase in the metal core and the preserved mSiO₂ shell after introducing the secondary metals confirm the induced growth of additive metal precursors on Pt@mSiO₂ seeds. The elemental mappings and EDS line scans of PtNi@mSiO₂ and PtRh@mSiO₂ also suggest the successful introduction of secondary metals (Figure S2.12 and S2.13). We thereupon applied high–temperature annealing to induce alloy phases as confirmed by PXRD patterns of PtM@mSiO₂ before and after annealing in Figure S2.14. All PtM@mSiO₂ after annealing clearly show consistent peak shifts to higher diffraction angles with peak positions in between Pt and corresponding secondary bulk metal standards. In addition, mSiO₂ shells in all PtM@mSiO₂ NPs were retained after annealing with no aggregation of metal NPs being observed (Figure S2.9e–g).

2.5 Conclusions

In summary, we have demonstrated the versatility of the inorganic capping strategy in the seeded growth of various bimetallic PtM@mSiO₂ NPs. Unique structures (core–shell, alloy, box, and yolk–shell) were synthesized using this strategy starting from Pt@mSiO₂ or Pd@mSiO₂ seeds. With the assistance of the mSiO₂ shell as an inorganic stabilizer, our method provides tunability in bimetallic composition and structure, promoted thermal stability, as well as desirable size control of bimetallic NPs. We believe that this synthetic route can be extended to a broad spectrum of alloy and intermetallic nanostructures for structural and catalytic studies.
2.6 Supporting Information

Figure S2.1. a) Nitrogen adsorption isotherms and b) Pore size distributions of Pt@mSiO$_2$ and PtPd@mSiO$_2$.

Figure S2.2. a) TEM image of Pt@mSiO$_2$ blank control in TEG; b) Pore size distributions of Pt@mSiO$_2$ (hollow circles) and Pt@mSiO$_2$–blank control (russet triangles); c) TEM image of Pt@mSiO$_2$ with the addition of 4 equivalents of KCl in TEG using the same heating program employed for the synthesis of PtPd@mSiO$_2$; and d) Pore size distributions of Pt@mSiO$_2$ (hollow circles) and Pt@mSiO$_2$–KCl control (black down triangles); and e) PtPd@mSiO$_2$ after Pd etched by HNO$_3$ when using the fresh PtPd@mSiO$_2$ in ethanol solution without drying as the starting materials.
Figure S2.3. TEM images of a) PtPd@mSiO₂ synthesized by reducing Pt@mSiO₂ with Pd(acac)₂ in TEG; b) PdPt@mSiO₂ synthesized by reducing Pd@mSiO₂ and H₂PtCl₆ in TEG (slightly isolated NPs observed); c) PdPt@mSiO₂ by reducing Pd@mSiO₂ and H₂PtCl₆ in oleylamine; d) Pt NPs and K₂PdCl₄ directly reduced in TEG without the addition of organic capping agents and without mSiO₂ shell protection; e) Pt NPs, K₂PdCl₄ and additional PVP (80 equivalent molar ratio to Pt) reduced in TEG; f) Flower–like PdPt NPs by reducing Pd NPs and H₂PtCl₆ in oleylamine; g) Pt NPs and Pd(acac)₂ reduced in oleylamine; h), i) Flower–like PdPt NPs supported on silica gel after 350 °C calcination and 300°C reduction.
Figure S2.4. TEM images of a) Pt@mSiO$_2$; b) Pd@mSiO$_2$; c) PtPd$_{0.50}$@mSiO$_2$; d) PtPd$_{0.74}$@mSiO$_2$; e) PtPd$_{1.1}$@mSiO$_2$; f) PtPd$_{1.6}$@mSiO$_2$; g) PdPt$_{0.48}$@SiO$_2$; and h) PdPt$_{1.1}$@mSiO$_2$ NPs.

Figure S2.5. Particle size distributions are acquired by counting 300 particles in TEM images of corresponding samples as shown in Figure S4, a) Pt@mSiO$_2$ (13.6 ± 1.0 nm); b) PtPd$_{0.50}$@mSiO$_2$ (15.5 ± 1.3 nm); c) PtPd$_{0.74}$@mSiO$_2$ (16.7 ± 1.2 nm); d) PtPd$_{1.1}$@mSiO$_2$ (17.7 ± 1.2 nm); e) PtPd$_{1.6}$@mSiO$_2$ (19.1 ± 1.1 nm); and f) PdPt$_{0.48}$@mSiO$_2$ (15.4 ± 1.3 nm).
Equation S2.1. Mathematical conversion of measured (black circles) and theoretical slopes (grey triangles) in the above figure pertaining to Pd/Pt molar ratios and the volumetric increase of PtPd bimetallic cores.

Calculation details in equation S2.1:

Assuming both Pt and PtPd core are spherical in shape, the volume increase of PtPd core due to Pd contents depositing on Pt core can be interpreted based on metal core diameters as below, which is also the increase along the y–axis.

\[
\frac{V_{\text{measured}}}{V_{\text{measured}}} = \frac{V_{\text{Pd}}}{V_{\text{Pt}}} = \frac{D_{\text{measured}}^3 - D_{\text{Pt}}^3}{D_{\text{Pt}}^3} \sim \frac{n_{\text{Pd}}}{n_{\text{Pt}}}
\]

And thus, it is possible to find the relationship between volume increase and Pd to Pt ratios in the above figure.

\[
\frac{D_{\text{PtPd}}^3}{D_{\text{Pt}}^3} = \frac{n_{\text{Pd}}}{n_{\text{Pt}}}
\]

The fitted linear relationship of measured data (black circles) is described as:

\[
\frac{D_{\text{PtPd}}^3}{D_{n}^3} = 1.1 \frac{n_{\text{Pd}}}{n_{\text{Pt}}} + 1.0
\]

The slope of the theoretical line (grey triangles) was calculated based on bulk Pt and Pt metal density as above:
The theoretical slope can be described as:

\[
\text{Theoretical Slope} = \frac{V_{\text{Pd}}}{V_{\text{Pt}}} = \frac{n_{\text{Pd}}}{n_{\text{Pt}}} = \frac{M_w(\text{Pt}) d_m}{M_w(\text{Pd}) d_m} = \frac{195.1 \text{ g mol}^{-1} \cdot 12 \text{ g cm}^{-3}}{106.4 \text{ g mol}^{-1} \cdot 21.4 \text{ g cm}^{-3}} \approx 1.0
\]

So we can describe the theoretical line above as:

\[
\frac{D_{\text{Pd}}}{D_{\text{Pt}}} = 1.0 \frac{n_{\text{Pd}}}{n_{\text{Pt}}} + 1.0
\]

The slopes of the theoretical line (1.0) and measure line (1.1) are fairly close, which indicates that Pd contents are introduced into Pt@mSiO₂ seed with high efficiency.

Figure S2.6. The Pt, Pd and Si elemental mappings of a) The elemental mappings of PtPd@mSiO₂; and b) PdPt@mSiO₂. The scale bars in a) are all 5 nm and in b) are all 10 nm. From a) and b), PtPd cores are almost resident within the mSiO₂ shell.
Figure S2.7. PXRD patterns of PtPd@mSiO₂ samples with various Pt/Pd ratios after calcination and reduction.

Figure S2.8. EDS line scans and elemental mappings of alloy PtPd@mSiO₂. The scale bars in elemental mappings figure are all 10 nm.
Figure S2.9. TEM images of as–synthesized PtM@mSiO₂: a) PtNi@mSiO₂; b) PtCu@mSiO₂; c) PtRh@mSiO₂; and d) PtPd₁.₁@mSiO₂, and PtM@mSiO₂ after thermal treatment: e) PtNi@mSiO₂ after 350°C annealing; f) PtCu@mSiO₂ after 350 °C annealing; g) PtRh@mSiO₂ after 500 °C annealing; and h) PtPd₁.₁@mSiO₂ after 350°C annealing.

Figure S2.10. TEM image of a) PtPd@mSiO₂ after 350 °C calcination, 300 °C reduction and collected after reaction; and b) PtPd@mSiO₂ after 6 runs before catalyst deactivation.
Figure S2.11. Conversion and selectivity of PtPd@mSiO₂ catalyst with 7 runs for nitrobenzene hydrogenation.

Figure S2.12. EDS line scans and elemental mappings of PtNi@mSiO₂. The scale bars in elemental mappings figure are all 10 nm. Ni is dominant around the area of the original Pt core, however some Ni signals are observed preading within the mSiO₂ framework.
Figure S2.13. EDS line scans and elemental mappings of PtRh@mSiO₂. The scale bars in elemental mappings figure are all 10 nm. Rh is deposited on the Pt core to form the Pt core/Rh hell structure. Rh signals are mixed well with Pt at 10-25 nm region, which indicates that PtRh alloy phase is also present.

Figure S2.14. PXRD patterns of as–synthesized and annealed PtM@mSiO₂ samples: a) PtNi@mSiO₂; b) PtCu@mSiO₂; and c) PtRh@mSiO₂.
Table S2.1. Summary of BET specific area, average pore size and pore volume of Pt@mSiO$_2$ and PtPd@mSiO$_2$.

<table>
<thead>
<tr>
<th>Items $^a$)</th>
<th>Specific area /cm$^2$·g$^{-1}$</th>
<th>Pore size /nm $^b$)</th>
<th>Pore volume /cm$^3$·g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt@mSiO$_2$</td>
<td>503.4</td>
<td>2.4</td>
<td>0.66</td>
</tr>
<tr>
<td>PtPd@mSiO$_2$</td>
<td>396.0</td>
<td>2.5</td>
<td>0.59</td>
</tr>
</tbody>
</table>

$^a$) All samples were calcined at 350 °C in air for 4 hrs and reduced at 300 °C in 5% Ar/H$_2$ for 2 hrs before BET characterization; $^b$) Pore sizes were determined from BJH pore size distribution.

Table S2.2. ICP-MS results of all PtM@mSiO$_2$ nanostructures (M=Pd, Ni, Cu and Rh).

<table>
<thead>
<tr>
<th>Items</th>
<th>Added Pt/M, molar</th>
<th>Major metal /wt%</th>
<th>Secondary metal /wt%</th>
<th>Actual M/Pt, molar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt@mSiO$_2$</td>
<td>–</td>
<td>42% Pt</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Pd@mSiO$_2$</td>
<td>–</td>
<td>38% Pd</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>PtPd$_{0.50}$@mSiO$_2$</td>
<td>1:0.5 Pt/Pd</td>
<td>28% Pt</td>
<td>7.5% Pd</td>
<td>1:0.50 Pt/Pd</td>
</tr>
<tr>
<td>PtPd$_{0.74}$@mSiO$_2$</td>
<td>1:0.7 Pt/Pd</td>
<td>28% Pt</td>
<td>11% Pd</td>
<td>1:0.74 Pt/Pd</td>
</tr>
<tr>
<td>PtPd$_{1.1}$@mSiO$_2$</td>
<td>1:1 Pt/Pd</td>
<td>31% Pt</td>
<td>18% Pd</td>
<td>1:1.1 Pt/Pd</td>
</tr>
<tr>
<td>PtPd$_{1.6}$@mSiO$_2$</td>
<td>1:1.6 Pt/Pd</td>
<td>30% Pt</td>
<td>27% Pd</td>
<td>1:1.67 Pt/Pd</td>
</tr>
<tr>
<td>PdPt$_{0.48}$@mSiO$_2$</td>
<td>0.5:1 Pt/Pd</td>
<td>19% Pt</td>
<td>22% Pd</td>
<td>0.48:1 Pt/Pd</td>
</tr>
<tr>
<td>PdPt$_{1.1}$@mSiO$_2$</td>
<td>1:1 Pt/Pd</td>
<td>–</td>
<td>–</td>
<td>1:1.1 Pt/Pd</td>
</tr>
<tr>
<td>PtPd$_{1.6}$@mSiO$_2$– Pd(acac)$_2$</td>
<td>1:1 Pt/Pd</td>
<td>–</td>
<td>–</td>
<td>1:(0.5 – 0.7) Pt/Pd</td>
</tr>
<tr>
<td>PtNi@mSiO$_2$</td>
<td>1:1 Pt/Ni</td>
<td>28% Pt</td>
<td>8.0% Ni</td>
<td>1:0.96 Pt/Ni</td>
</tr>
<tr>
<td>PtCu@mSiO$_2$</td>
<td>1:1 Pt/Cu</td>
<td>31% Pt</td>
<td>6.8% Cu</td>
<td>1:0.68 Pt/Cu</td>
</tr>
<tr>
<td>PtRh@mSiO$_2$</td>
<td>1:1 Pt/Rh</td>
<td>22% Pt</td>
<td>12% Rh</td>
<td>1:1.1 Pt/Rh</td>
</tr>
</tbody>
</table>
Table S2.3. The resuablity of PtPd@mSiO\textsubscript{2} in nitrobenzene hydrogenation. \textsuperscript{a)

<table>
<thead>
<tr>
<th>Run number</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>&gt;99</td>
<td>&gt;99</td>
</tr>
<tr>
<td>2</td>
<td>&gt;99</td>
<td>&gt;99</td>
</tr>
<tr>
<td>3</td>
<td>&gt;99</td>
<td>&gt;99</td>
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<tr>
<td>4</td>
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</tr>
<tr>
<td>5</td>
<td>&gt;99</td>
<td>&gt;99</td>
</tr>
<tr>
<td>6</td>
<td>95.4</td>
<td>96.5</td>
</tr>
<tr>
<td>7</td>
<td>69.5</td>
<td>91.7</td>
</tr>
</tbody>
</table>

\textsuperscript{a) All reaction conditions were controlled the same, and the catalyst was centrifuged down and used directly for the next cycle.}

2.7 References


44. S. Zhao, Y. Chen and Z. Liu, RSC Adv., 2015, 5, 33299–33305.
CHAPTER 3. INTERMETALLIC STRUCTURES WITH ATOMIC PRECISION FOR SELECTIVE HYDROGENATION OF NITROARENES

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3.1 Abstract

Bridging the structure-properties relationship of bimetallic catalysts is essential for the rational design of heterogeneous catalysts. Different from random alloys, intermetallic compounds (IMCs) present atomically-ordered structures, which is advantageous for catalytic
mechanism studies. We used Pt-based intermetallic nanoparticles (iNPs), individually encapsulated in mesoporous silica shells, as catalysts for the hydrogenation of nitroarenes to functionalized anilines. With the capping-free nature and ordered atomic structure, PtSn iNPs show >99% selectivity to hydrogenate the nitro group of 3-nitrostyrene albeit with a lower activity, in contrast to Pt$_3$Sn and Pt NPs. The geometric structure of PtSn iNPs in eliminating Pt threefold sites hampers the adsorption/dissociation of molecular H$_2$ and leads to a non-Horiuti-Polanyi hydrogenation pathway, while Pt$_3$Sn and Pt surfaces are saturated by atomic H. Calculations using density functional theory (DFT) suggest a preferential adsorption of the nitro group on the intermetallic PtSn surface contributing to its high selectivity.

3.2 Introduction

Engineering catalytically active sites is critical to establish a molecular understanding of structure-property relationships, and thus guide the design of highly active and selective catalysts. Bimetallic alloys composed of noble metals are efficient catalysts for selective hydrogenations. However, correlating the atomic structures of alloy catalysts with their catalytic properties is challenging owing to the random arrangement of atoms in most alloy structures. Intermetallic compounds (IMCs) are special alloys featuring atomically-ordered and thermodynamically stable structures with defined stoichiometry, which render IMCs ideal platforms to study mechanisms of catalytic reactions in comparison to random alloys $^{1-3}$. IMCs can manipulate the adsorption energy and geometry of reactants and intermediates that could vary catalytic pathways. Moreover, the addition of inexpensive metals to noble metal-based IMCs can efficiently utilize noble metals through a homogenous dilution. The isolation of noble metal sites can significantly improve the selectivity by suppressing over-hydrogenated
products in many selective hydrogenation reactions. Therefore, the synthetic development of intermetallic catalysts with homogeneous composition and structure becomes essential for the bottom-up design of intermetallic catalysts and their mechanism studies. To improve the precision in the preparation of catalysts apart from the traditional wetness impregnation method, our group demonstrated a seeded-growth method and obtained series of Pt-based intermetallic nanoparticles (iNPs) individually encapsulated in mesoporous silica shells (PtM@mSiO₂, M = Sn, Zn, and Pb). These iNPs have well-defined intermetallic structure, precise composition, capping-free surface, and high thermal stability that provide an optimal platform to elucidate the unique catalytic properties of IMCs.

The selective hydrogenation of nitroarenes constitutes an important industrial process for the production of functionalized anilines widely used as pharmaceuticals, herbicides, and pigments. The challenge of this reaction is to selectively hydrogenate the nitro group in the presence of other reducible/leaving groups (e.g., C=C, C=O, C≡N, and halides). Commercial synthesis of functionalized anilines requires a stoichiometric addition of reducing agents (i.e. Zn-NH₃ and Na₂S₂O₄) and generates excessive waste. Nobel metal-based heterogeneous catalysts are thus developed for this reaction and used in an eco-friendly manner. Using alloys is an effective strategy to suppress noble metal ensembles and thus the over-hydrogenation capability of noble metals, which enhances their selectivity in hydrogenation reactions. In regards of the atomically ordered IMCs, limited compositions have been reported as selective catalysts in comparison to a variety of alloys. It is intriguing if the high selectivity in the hydrogenation of nitroarenes can be extended to other IMCs, and further structural studies are essential to elucidate the origin of this high selectivity on IMCs with homogeneous compositions and well-defined structures.
Pt-containing IMCs have shown high activity and selectivity in selective hydrogenations\textsuperscript{21-23}, such as PtSn iNPs in the hydrogenation of furfural to furfuryl alcohol\textsuperscript{8}. Herein, we report the selective hydrogenation of 3-nitrostyrene using PtM@mSiO\textsubscript{2} iNPs (M = Sn, Zn, and Pb). To tune the degree of Pt dilution by Sn, we synthesized PtSn and Pt\textsubscript{3}Sn iNPs. Different from Pt and Pt\textsubscript{3}Sn@mSiO\textsubscript{2}, PtSn@mSiO\textsubscript{2} demonstrates >99\% nitro hydrogenation selectivity due to the preferential adsorption of the nitro group on the intermetallic PtSn surface. The high selectivity is universal to various functionalized nitroarenes over PtSn@mSiO\textsubscript{2} and other PtM typed iNPs such as PtZn and PtPb iNPs. An abrupt drop in activity on PtSn@mSiO\textsubscript{2} was also observed in contrast to Pt and Pt\textsubscript{3}Sn@mSiO\textsubscript{2}, which cannot be explained solely by the decrease of Pt density on the surface. We conferred a non-Horiuti-Polanyi (HP) mechanism over intermetallic PtSn where hydrogenations proceed likely with molecular H\textsubscript{2} as opposed to atomic H. The variance of hydrogenation pathway is readily determined by the geometric structures of intermetallic PtSn because the elimination of threefold Pt sites on intermetallic PtSn inhibits H\textsubscript{2} dissociation\textsuperscript{24-27}. This work exemplifies the relationship between intermetallic structures and their unique catalytic performance in heterogeneous catalysis.

3.3 Experimental

Synthesis of Pt\textsubscript{3}M/PtM@mSiO\textsubscript{2} (M = Sn, Zn, and Pb)

In a typical synthesis of Pt\textsubscript{3}M/PtM@mSiO\textsubscript{2} NPs, as-synthesized Pt@mSiO\textsubscript{2} seeds (containing 10 mg Pt, stored in methanol) and secondary metal precursor (SnCl\textsubscript{2}•2H\textsubscript{2}O, Pb(CH\textsubscript{3}COO)\textsubscript{2}•3H\textsubscript{2}O, and Zn(acac)\textsubscript{2}•xH\textsubscript{2}O) were well dispersed in 80 mL tetraethylene glycol (TEG) via sonication (for Zn precursor, 45 mL oleylamine and 15 mL oleic acid was used).
The reaction flask was sealed with a septum, and the solution was subjected to vacuum to remove methanol. Under argon protection, the mixture was heated to 280 °C and stayed for 2 h with vigorous stirring (350 °C was used for the synthesis of PtZn and Pt₃Zn). After allowing the solution to cool down to room temperature, 80 mL of acetone was added to the reaction solution. Pt₃M/PtM@mSiO₂ NPs were collected by centrifugation and washed with methanol 3 times. All Pt₃M/PtM@mSiO₂ NPs were calcined at 500 °C for 4 h to burn off organic remnants and reduced at certain temperatures in 10% H₂/Ar (total flow rate: 50 mL/min) to form the corresponding intermetallic phases. PtSn and PtPb were reduced at 300 °C for 2 h. PtZn, Pt₃Zn, and Pt₃Sn were reduced at 600 °C for 6 h. The Pt@mSiO₂ control sample was treated with the same procedure as PtSn@mSiO₂. Alloy PtSn₀.₃@mSiO₂ was used after washing and vacuum drying from the wet synthesis.

Catalytic evaluation

Typically, 1-2 mg catalysts, 50 mg 3-nitrostyrene and 2 mL toluene were mixed in a 5 mL vial. 20 mg xylene was then added as an internal standard. The vial was placed in a Parr 4740 high-pressure/high-temperature vessel. After exchanging the atmosphere with H₂, the high-pressure vessel was charged with 20 bar H₂ and maintained at 80 °C with a stirring speed set at 1200 rpm for the reaction. The products after the reaction were diluted and analyzed by an Agilent 6890N/5975 gas chromatograph mass spectrometer (GC–MS) equipped with an HP–5ms capillary column (30 m × 0.25 mm × 0.25 μm) and a flame ionization detector (FID). For kinetic studies, the vial was placed back into the high-pressure vessel and charged with high-pressure H₂ after sampling at atmospheric pressure.
Characterization

For ambient pressure (AP)-XPS analysis, all samples were dispersed in ethanol and then dropped on pyrolytic graphite. The reduction treatments to all samples were carried out in an incorporated high-pressure cell in the vacuum chamber of the AP-XPS, in which 0.2 Torr H₂ was introduced at different temperatures to study the surface composition of the PtSn@mSiO₂. After the treatment, H₂ was purged out, and the sample was taken out to a manipulator in ultrahigh vacuum for AP-XPS analysis. A flux of low energy electrons (8.5 eV, 60 mA) generated by a flood gun was used for each analysis to remove the surface charging effects due to the existence of mSiO₂ shell. All spectra were calibrated by Pt 4f₇/₂ at 71.2 eV. High resolution (HR)-TEM, high-angle annular dark field scanning TEM (HAADF-STEM), and elemental mapping analysis were investigated using a Tecnai G2 F20 electron microscope equipped with an EDS detector (Oxford INCA EDS) and a Titan Themis 300 probe corrected TEM with a Super-X EDS detector. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was conducted using an Agilent Cary 670 Fourier transform infrared spectroscopy equipped with a linearized HgCdTe (MCT) detector, a Harrick diffuse reflectance accessory, and a Praying Mantis high-temperature reaction chamber. CO was used as the probe molecule, and 10-20 wt.% sample was diluted with KBr. H₂/D₂ exchange experiments were conducted under ambient pressure using H₂/D₂ = 10/10 mL/min as the feed gas, where H₂/HD/D₂ signals were monitored using a mass spectrometer (Agilent 5975). The cyclic voltammetry (CV) curves were measured using a potentiostat (VSP-300, Bio-Logic Science Instruments). 5 mg catalysts were first immersed in 2 mL hydrazine hydrate (78-82%) for overnight to gently remove the insulating mSiO₂ shell together with active carbon substrate (10 wt.% Pt). After washing with water for 3 times, etched catalysts were dispersed in a mixture
of H₂O: isopropanol:5% Nafion solution (4:1:0.025) to prepare a 0.5 mg/mL ink. 20 µL catalyst ink was transferred onto the rotational ring-disk working electrode (RRDE, 5 mm diameter). A platinum wire and a saturated Ag/AgCl electrodes were used as the counter and the reference electrodes, respectively. The experiment was conducted in 0.1 M HClO₄ under an argon atmosphere with a scan speed of 50 mV/s. The water used in experiments was Millipore ultrapure water (18.2 MΩ•cm).

Density Functional Theory (DFT) calculations

All DFT calculations have been carried out with PBE for 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 is modeled as a three-layer slab with a surface supercell of (2√3×3). The PtSn(1120) surface is modeled as a four-layer slab with a surface supercell of (2×2). Various flat and tilt configurations with different molecular orientations of 3-nitrostyrene on the surfaces have been tried to search for the most stable adsorption configurations on the surfaces. All the atoms except for the bottom two layers in the slab (fixed at bulk positions) are relaxed till the absolute values of forces are below 0.02 eV/Å. A kinetic energy cutoff of 400 eV for the plane wave basis set and a (5×5×1) k-point mesh with a Gaussian smearing of 0.05 eV have been used.

3.4 Results and Discussion

Intermetallic PtM@mSiO₂ (M = Sn, Zn, and Pb) and Pt₃M@mSiO₂ (M = Sn and Zn) were prepared by following a “ship-in-a-bottle” strategy. These iNPs were calcined at 500 °C to completely remove capping agents and reduced at temperatures of 300 or 600 °C to form
the corresponding intermetallic phases. Figure S3.1 in the Supporting Information shows the representative TEM images of these iNPs. Even after 600 °C reductions, all iNPs were isolated and well encapsulated within the mSiO₂ shell, which highlights the robust nature of the mSiO₂ shell against the aggregation of the encapsulated iNPs. With previous studies in our group, this ship-in-a-bottle strategy can maintain a precise control of the secondary metals, and the growth of the bimetallic cores are facilitated by the etching of the inner interface of mSiO₂ shells likely by the ion species produced during the TEG reduction. The mSiO₂ shells have an average pore size of ca. 2.5 nm, which allows the free access of small organic molecules, such as furfural and nitrobenzene. Most of the iNPs are single crystals with well-ordered structures as shown in the HR-TEM images (Figure 3.1a, f, and S3.1). The measured lattice distances correspond well with specific crystal facets associated with the corresponding intermetallic phases. We also acquired PXRD patterns to confirm the formation of the desired intermetallic phases for all iNPs (Figure S3.2). The exact ratios of Pt to the secondary metal M are in good agreement with the theoretical values measured via ICP-MS (Table S3.1).

We evaluated the catalytic properties of these iNPs in the selective hydrogenation of 3-nitrostyrene. 3-nitrostyrene is composed of a nitro group and a vinyl group. The major hydrogenation products range from desired 3-aminostyrene (1), undesired 3-ethylnitrobenzene (2) and over-hydrogenated 3-ethylaniline (3). It is challenging to exclusively hydrogenate nitro group in the presence of more reducible C=C group over Pt-based catalysts. One effective strategy to fulfill the high selectivity in hydrogenating nitro group is to downsize Pt contiguous sites that can suppress C=C hydrogenation. The addition of secondary metals in many alloys can dilute Pt contiguous sites and modify the adsorption geometry of 3-nitrostyrene on bimetallic surfaces. DFT calculation suggests that the catalytic mechanism for reducing
nitroarenes over these bimetallic alloys is the preferential adsorption of nitro group on the isolated Pt sites. It is thus reasonable to hypothesize from the geometric consideration that eliminating Pt contiguous sites is essential and likely universal to achieve a high selectivity to the hydrogenation of the nitro group over Pt-containing bimetallic catalysts.

Even though Pt-based alloys are selective for reducing nitroarenes, inconsistent results have been reported \(^{28-31}\). This ambiguous catalysis on bimetallic alloys is likely due to their random geometry that cannot ensure the elimination of contiguous noble metal sites on the surface, and thus leads to the low nitro hydrogenation selectivity. Proper IMCs with ordered structure could completely remove the contiguous noble metal sites and lead to high selectivity in nitro hydrogenation. However, only limited compositions (PtZn, PtGa, and RhIn) have been studied over ordered IMCs \(^{19,20,29}\). In this work, we endeavor to utilize more structurally ordered and thermodynamically stable IMCs to study the structure-property relationship in selective hydrogenations, especially the effect of eliminating Pt contiguous sites. We choose PtSn iNPs as a model because previous work has shown that bimetallic PtSn alloys/H-WO\(_3\) exhibited 75% selectivity to 3-nitrostyrene hydrogenation in comparison to Pt controls \(^{28}\). PtSn with 1:1 atomic ratio can form a NiAs-type IMC with hexagonal \(hP4\) cells. We examined the low index facets of intermetallic PtSn(11\(\overline{2}\)0), (0001), and (11\(\overline{2}\)1) facets that are most likely present in spherical iNPs (Figure S3.3) \(^{32-35}\). On all those facets, contiguous Pt sites (specifically threefold sites) are eliminated due to the highly ordered nature of iNPs. Based on these reasons, intermetallic PtSn@mSiO\(_2\) is a promising model to study the structure-property relationship in the selective hydrogenation of 3-nitrostyrene. As a comparison, we also prepared Pt\(_3\)Sn iNPs that contain Pt contiguous sites on their surfaces.
To visualize the homogeneous structures of our Pt₃Sn@mSiO₂ and PtSn@mSiO₂, HAADF-STEM images were acquired as shown in Figure 3.1. Figure 3.1b-c depict the $P6_3/mmc$ PtSn iNPs oriented in the [010] direction, consistent with the uniform hexagonal FFT diffraction pattern. The lattice spacing of 0.416 nm agrees with the theoretical value of the PtSn(10 1 0) facet. Figure 3.1g-h show the $Pm-3m$ Pt₃Sn along [011] orientation, which correlates with the distorted hexagonal FFT diffraction pattern. As illustrated in Figure S3.3, the ideal Pt₃Sn(110) is arranged with staggered Pt chains and alternating Pt/Sn chains. This arrangement is seen in Figure 3.1h when scanning the inner areas of Pt₃Sn iNPs (Pt chains are observed as brighter dots, and Pt/Sn chains are slightly darker) 36. The lattice spacing was measured as 0.285 nm, conforming to the theoretical values of the Pt₃Sn(110) facet. The elemental mappings of PtSn and Pt₃Sn iNPs are also listed (Figure 3.1e and 3.1g, and both PtSn and Pt₃Sn demonstrate the evenly distributed Pt and Sn through the respective iNPs.

![Figure 3.1. HRTEM and HAADF-STEM images of a-c) PtSn@mSiO₂, and f-h) Pt₃Sn@mSiO₂; insets in c) and h) are, respectively, fast Fourier transform (FTT) patterns from [0001] direction for PtSn@mSiO₂ and [110] direction for Pt₃Sn@mSiO₂; and elemental mappings of d-e) PtSn@mSiO₂, and i-j) Pt₃Sn@mSiO₂](image-url)
The catalytic performance of intermetallic PtSn@mSiO₂ in the selective hydrogenation of 3-nitrostyrene is summarized in Table 3.1. PtSn@mSiO₂ shows a significantly high selectivity to desired 3-aminostyrene 1 (>99%). To prove that both high conversion and selectivity can be achieved without over-hydrogenation, we extended the reaction time to 12 h after obtaining a full conversion. The byproducts (2 and 3) were still not detected, which proves the remarkable nitro hydrogenation selectivity of intermetallic PtSn. To further investigate how intermetallic geometry can impact the selectivity, we evaluated Pt@mSiO₂ and Pt₃Sn@mSiO₂. Intermetallic compounds typically have discrete stoichiometric compositions with crystal structures, setting them apart from those random alloys with tunable compositions and randomly arranged constituent atoms. Intermetallic Pt₃Sn@mSiO₂ has the Cu₃Au-type structure (cP4 cells) with face-centered cubic (fcc) packing of Pt and Sn atoms³⁷,³⁸, which is similar to the structure of monometallic fcc Pt but differs significantly from hexagonal hP4 PtSn. Pt@mSiO₂ and Pt₃Sn@mSiO₂ demonstrate higher activity with respective 50- and 21-fold faster reaction rates compared to PtSn@mSiO₂. However, Pt@mSiO₂ directs the reaction to undesired C=C hydrogenation product 2 and over-hydrogenated product 3. Although Pt₃Sn@mSiO₂ gives 40.4% selectivity to the hydrogenation of the nitro group (1) at the initial stage, this selectivity could not be maintained and rapidly shifted to over-hydrogenated product 3. These catalysis results prove that PtSn@mSiO₂ is unique in its’ high selectivity to the hydrogenation of the nitro group in 3-nitrostyrene. We subsequently investigated the scope of PtSn@mSiO₂ in the hydrogenation of nitroarenes with bromo, iodo, formyl and methoxy groups (Table 3.2). High selectivities to their corresponding functionalized anilines were achieved, demonstrating the general applicability of PtSn iNPs in the hydrogenation of various nitroarenes substrates.
Table 3.1. Selective hydrogenation of 3-nitrostyrene over Pt NPs and Pt-based iNPs.\textsuperscript{a}

![Diagram of selective hydrogenation with products: 3-aminostyrene, 3-ethyllnitrobenzene, and 3-ethylaniline.]

| Catalyst       | Time (h) | Rate (g \textsubscript{Pt} \textsuperscript{-1} h\textsuperscript{-1}) | TOF (h\textsuperscript{-1}) | Conversion (%) | Selectivity | | 1 | 2 | 3 |
|----------------|----------|-------------------------------------------------|----------------------------|---------------|-------------|---|---|---|
| Pt@mSiO\textsubscript{2} | 0.16     | 471.4                                           | 9491                       | 18.2          | —           | 23.8 | 76.2 |
|                 | 1.0      |                                                  |                            | 99.2          | —           | 2.0   | 98.0 |
| PtSn@mSiO\textsubscript{2} | 6        | 40.8                                            |                             | >99           | >99         | —     | —   |
|                 | 9        | 9.3                                             | 676                        | >99           | >99         | —     | —   |
|                 | 12       | >99                                             |                             | >99           | >99         | —     | —   |
| Pt\textsubscript{3}Sn@mSiO\textsubscript{2} | 0.16     | 201.1                                           | 9274                       | 62.2          | 40.4        | —     | 59.6 |
|                 | 1        |                                                  |                            | >99           | —           | —     | >99 |
| PtZn@mSiO\textsubscript{2} | 12       | 0.93                                            |                             | 31.1          | >99         | —     | —   |
| Pt\textsubscript{3}Zn@mSiO\textsubscript{2} | 1        |                                                  |                            | 76.5          | 88.8        | —     | 11.2 |
|                 | 3        | 101.1                                           |                             | >99           | 88.9        | —     | 11.1 |
|                 | 6        | >99                                             |                             | 37.9          | —           | 62.1  | —   |
| PtPb@mSiO\textsubscript{2} | 12       | 5.0                                             |                             | 97.5          | >99         | —     | —   |

\textsuperscript{a}. Reaction condition: 1 mg catalyst, 50 mg 3-nitrostyrene, 20 mg xylene as internal standard, 2 mL toluene as solvent, 80 °C, and 20 bar H\textsubscript{2}; b. Reaction rates were calculated by maintaining the conversion less than 20%, and Pt loadings were measured by ICP-MS; c. Turnover frequency (TOF) values were calculated based on specific Pt dispersions measured by CO chemisorption (6.5% for Pt@mSiO\textsubscript{2}, 1.8% for PtSn@mSiO\textsubscript{2} and 2.8% for Pt\textsubscript{3}Sn@mSiO\textsubscript{2}).
Table 3.2. Selective hydrogenation of substituted nitroarenes over PtSn@mSiO2 iNPs.a

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Product</th>
<th>Time (h)</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br-NO₂</td>
<td>Br-NH₂</td>
<td>12</td>
<td>84.6</td>
<td>&gt;99</td>
</tr>
<tr>
<td>I-NO₂</td>
<td>I-NH₂</td>
<td>18</td>
<td>18.5</td>
<td>&gt;99</td>
</tr>
<tr>
<td>OHC-NO₂</td>
<td>OHC-NH₂</td>
<td>9</td>
<td>&gt;99</td>
<td>&gt;99</td>
</tr>
<tr>
<td>C-NHO₂</td>
<td>C-NH₂</td>
<td>9</td>
<td>&gt;99</td>
<td>76.3 b</td>
</tr>
<tr>
<td>H₂CO-NO₂</td>
<td>H₂CO-NH₂</td>
<td>18</td>
<td>31.2</td>
<td>&gt;99</td>
</tr>
</tbody>
</table>

a. Reaction condition: 1 mg catalyst, 0.4 mmol nitroarenes, 20 mg xylene as internal standard, 2 mL toluene as solvent, 80 °C, and 20 bar H₂; b. Selectivity includes the partially intra-condensation product with incomplete reduced hydroxylamino group and formyl group.

It is intriguing to explore how the specific intermetallic structures in Pt-Sn systems can result in different catalytic behavior. To characterize the surface properties of intermetallic PtSn and Pt₃Sn, we conducted ambient pressure X-ray photoelectron spectroscopy (AP-XPS) with in situ reductions to study the surface evolution of catalysts when exposed to a reducing atmosphere at different temperatures. The catalysts were pre-calcined at 500 °C and reduced at proper temperatures to form intermetallic phases (300 °C for PtSn and 600 °C for Pt₃Sn), which have been denoted as fresh samples. AP-XPS spectra in Figure 3.2 illustrates the surface composition for PtSn@mSiO₂ and Pt₃Sn@mSiO₂. High reduction temperatures are beneficial to induce the formation of metallic Sn and decrease the concentration of surface SnOₓ species. Meanwhile, Pt majorly remains in the metallic state. The Pt/Sn atomic ratios of PtSn@mSiO₂ in fresh, 300, and 500 °C reduced samples are 0.91, 0.91 and 0.94, respectively. These similar Pt/Sn atomic ratios indicate the relatively stable surface composition of intermetallic PtSn under a reducing atmosphere up to 500 °C. Fresh Pt₃Sn@mSiO₂ have Pt/Sn atomic ratios of
2.78, which increases to 3.31 and 3.21 after in situ reductions at 300 and 500 °C. A higher reduction temperature can introduce a slight segregation of Pt to the surface of Pt$_3$Sn iNPs. Except for the native Pt threefold sites on Pt$_3$Sn(111) (Figure S3.3b), the Pt-rich surface can contain more contiguous Pt sites speeding the over-hydrogenation pathways. The AP-XPS results support that the 300 °C reduction for PtSn and 600 °C reduction for Pt$_3$Sn can maintain their surface composition closed to their respective theoretical values. The AP-XPS results demonstrate that both the surfaces of PtSn and Pt$_3$Sn iNPs closely reflect their bulk stoichiometric composition.

![Figure 3.2](image.png)

Figure 3.2. AP-XPS spectra of a) Pt 4f, b) Sn 3d in PtSn@mSiO$_2$, and c) Pt 4f, and d) Sn 3d in Pt$_3$Sn@mSiO$_2$ NPs.

With the atomically ordered intermetallic Pt$_3$Sn and PtSn, we attribute the dramatically diverse catalytic pathways of Pt, Pt$_3$Sn, and PtSn to their surface structures. Previous DFT calculations showed that Pt(111), Pt$_3$Sn(111), and PtSn(1120) hold the lowest surface energies.
As shown in Figure 3.3a-c and S3.3, both Pt(111) and Pt_{3}Sn(111) contain contiguous Pt threefold sites. PtSn(11\textsubscript{2}0) only presents bridge Pt sites, where the staggered Sn atoms disrupt the Pt threefold geometry. To further probe the surface Pt arrangement, we employed a CO-DRIFTS study for Pt, Pt\textsubscript{3}Sn, and PtSn as shown in Figure 3.3d. Two major absorption peaks were observed in regions of 2050-2070 cm\textsuperscript{-1} and 1850-1870 cm\textsuperscript{-1} on Pt and Pt\textsubscript{3}Sn@mSiO\textsubscript{2}. The first intense peak is ascribed to atop CO linearly adsorbed on a single Pt atom, and the weak peak corresponds CO adsorbed over the bridge Pt sites. Pt and Pt\textsubscript{3}Sn have similar CO atop adsorption at ~2070 cm\textsuperscript{-1}, corresponding to their abundance of Pt threefold sites with a strong affinity to CO. The atop CO absorption shifts to low wavenumber region over the PtSn iNPs due to the electron donation from Sn to Pt. However, the reduced CO dipole-dipole coupling effect cannot be completely ruled out. The addition of Sn in PtSn also shows a significant suppression of the bridge CO peak compared to Pt/Pt\textsubscript{3}Sn, demonstrating that PtSn has different bridge Pt sites likely due to the interruption of the staggered Sn atoms. The intensity decrease of bridge CO and the peak shift of atop CO illustrate the decrease of Pt threefold sites (Pt>Pt\textsubscript{3}Sn>>PtSn). Correlating CO-FTIR results to the catalytic activities, the reaction rate of Pt@mSiO\textsubscript{2} progresses 2- and 50-fold faster than Pt\textsubscript{3}Sn@mSiO\textsubscript{2} and PtSn@mSiO\textsubscript{2}. We also normalized the reaction rate to the accessible Pt sites by Pt dispersion. The TOF of PtSn@SiO\textsubscript{2} is still 14-fold less than that of Pt@mSiO\textsubscript{2}. The TOF of Pt\textsubscript{3}Sn@mSiO\textsubscript{2} (9274 h\textsuperscript{-1}) is close to that of Pt@mSiO\textsubscript{2} (9491 h\textsuperscript{-1}), confirming the catalytically identical Pt threefold sites on these two catalysts. The decreasing activity (Pt>Pt\textsubscript{3}Sn>>PtSn) is consistent with the reduction of Pt threefold sites.
Figure 3.3 Ideal atomic geometry of a) Pt(111), b) Pt₃Sn(111), c) PtSn(1120), where Pt (white circles) Sn (orange circles) are indicated; d) DRIFTS spectra of Pt@mSiO₂, Pt₃Sn@mSiO₂, and PtSn@mSiO₂ using CO as the probe molecule. Pt 3-fold sites (red triangle in a and b) and Pt bridge sites (red rectangle in c) are marked.

The Pt threefold site is critical for the dissociative adsorption of H₂ molecules. The elimination of Pt threefold sites on intermetallic PtSn inhibits the H₂ adsorption/dissociation to form atomic H species, which hinders the activity in hydrogenation reactions using molecular H₂.⁴⁴,⁴⁶,⁴⁷ To validate the different behaviors of H₂ adsorption/dissociation on Pt and intermetallic PtSn, we employed H⁺ electro-reduction, H₂ chemisorption, and H/D exchange experiments. The CV scans of intermetallic PtSn@mSiO₂ (after removing mSiO₂ shell) in 0.1 M HClO₄ show flat features from -0.25 to 0.15 V (vs Ag/AgCl). H⁺ electro-reduction (2H⁺ ⇌ H₂) is clearly observed over Pt/Vulcan and Pt@mSiO₂ (-0.2-0 V in Figure S3.4)⁴⁸. The two tails (-0.25 V) in the forward/backward scan on Pt@mSiO₂ demonstrate the adsorption and desorption of H₂.⁴⁹ However, only H₂ desorption tail during the backward scan was observed over intermetallic PtSn@mSiO₂ sourced from the reduction of H⁺. The absence of H₂ adsorption tail in the forward scan indicates a weak H₂ adsorption over PtSn in the liquid phase at room temperature. Negligible chemisorbed H₂ was observed on intermetallic PtSn@mSiO₂ either, similar to a previously report on alloy Sn/Pt (111).⁵⁵ H/D exchange
results further revealed the dramatically higher temperature (150 °C) required for H2/D2 exchange on PtSn@mSiO2, compared to Pt@mSiO2 (25 °C). This inability of H2/D2 dissociation has also been reported over intermetallic PtGe and PtSn/SiO2. Therefore, it is seen that intermetallic PtSn is ineffective at adsorption and dissociation of H2. We thus propose that the hydrogenation on intermetallic PtSn could largely proceed in a non-Horiuti-Polanyi (HP) pathway where molecular H2 directly participates in the hydrogenations. Although the HP pathway involving atomic H is well-accepted on precious metals with a nearly barrierless H2 dissociation, some catalysts have been reported with obstacles to breaking H-H bonds. Here, the intermetallic PtSn is exemplified as an exception to the traditional HP pathway in hydrogenations where a deficiency of atomic H was induced as a consequence of the elimination of Pt threefold sites. We endeavor to demonstrate that the physical state of H2 can play important roles in hydrogenations, which has not been given significant emphasis.

Comparative DFT studies of the adsorption of 3-nitrostyrene on Pt(111) vs. PtSn(1120) were also performed to elucidate the origin of the nitro selectivity. On Pt(111) as shown in Figure 3.4a, 3-nitrostyrene prefers to adsorb in a flat configuration with both the center of the benzene ring and the vinyl group sitting on Pt bridge sites. This flat configuration maximises the number of C=C bonds interacting with the neighboring Pt bridge sites, while the nitro group is tilted away from the surface, which agrees with early DFT studies. The strong band hybridization between Pt d and C p orbitals gives an adsorption energy of ~2.08 eV. In contrast, on PtSn(1120) in Figure 3.4b without the contiguous Pt sites, the flat adsorption configuration is not preferred anymore, and the band hybridization between Pt d and C p orbitals becomes much weaker due to charge transfer from Sn to Pt that lowers the Pt d-band center. Additionally, 3-nitrostyrene prefers to adsorb in a vertical configuration with the two O atoms.
in the nitro group sitting on top of Sn atoms. The interaction is mostly of ionic character with a charge transfer from Sn to O, resulting in a weak adsorption energy of -0.58 eV. We also varied the geometry of 3-nitrostyrene molecules on Pt(111) and PtSn(1120) facets to accommodate the contact of the benzene ring, C=C, and –NO2 groups on these two facets as shown in Figure S3.5. Pt(111) facet gives the adsorption energy of -2.08, -1.16 and -0.19 eV for the respective benzene ring, C=C and –NO2 group. Due to the straight-up geometry of the 3-nitrostyrene molecule on PtSn(1120), the adsorption energy of C=C and –NO2 group was calculated as -0.12 and -0.58 eV. Such distinctively different adsorption configurations mean that the vinyl group is more accessible to the hydrogenation on Pt(111) or surfaces with contiguous Pt sites, while the nitro group can be hydrogenated selectively on PtSn(1120). These different adsorption geometries of 3-nitrostyrene on Pt(111) and PtSn(1120) explain the observed selectivity difference 19,55,56.

Figure 3.4. Most preferred adsorption configuration for 3-nitrostyrene: a) flat on Pt(111) and b) vertical on PtSn(1120) surfaces. Large grey (brown) spheres are Pt (Sn) atoms in the surfaces; small gray, blue, red and white spheres are C, N, O and H atoms in 3-nitrostyrene. The top (bottom) panel is the top (side) view. c-d) product distribution of 3-nitrostyrene hydrogenation over c) Pt@mSiO2 and d) PtSn@mSiO2.
We summarized the kinetic studies and product selectivity in Figure 3.4c-d and S3.6. In the liquid phase, H\textsubscript{2} molecules need to dissolve in the solvent and then contact catalytic surfaces to initiate reactions. To better evaluate the relationship between intermetallic catalysts and their catalysis, the dissolution factor of H\textsubscript{2} should be investigated. We acquired a volcano-shaped dependence between TOFs and H\textsubscript{2} pressure for both Pt@mSiO\textsubscript{2} and PtSn@mSiO\textsubscript{2} (Figure S3.6). Within the H\textsubscript{2} pressure ranging from 1-10 bar for Pt@mSiO\textsubscript{2} and 1-20 bar for PtSn@mSiO\textsubscript{2}, a positive dependence was observed indicating that the H\textsubscript{2} dissolution kinetically controls the reaction. A negative dependence was observed with the further increase of the H\textsubscript{2} pressure. Later kinetic discussion is based on the results at the high-pressure region. For Pt@mSiO\textsubscript{2}, the hydrogenation of 3-nitrostyrene was not highly dependent on either substrate concentration (168-503 mM, 20 bar H\textsubscript{2}, slope = 0.08) or H\textsubscript{2} pressure (10-40 bar, 160 mM, slope = −0.43), which can be attributed to the strong adsorption of 3-nitrostyrene molecules over the Pt surface as revealed by the DFT calculation. Figure 3.4c shows the product distributions over Pt@mSiO\textsubscript{2} for the hydrogenation of 3-nitrostyrene. We noticed that vinyl groups readily underwent faster hydrogenation giving 3-ethyl nitrobenzene (2) in comparison to the hydrogenation of nitro groups giving 3-ethylaniline (3) over Pt@mSiO\textsubscript{2}, experimentally confirming the flat adsorption geometry of 3-nitrostyrene and the slower catalytic hydrogenation kinetics of tilted nitro groups. The slightly negative dependence of H\textsubscript{2} reaction order indicates the slight competition of atomic H and 3-nitrostyrene molecules on active Pt sites.

Looking into intermetallic PtSn@mSiO\textsubscript{2}, a similar non-dependence of 3-nitrostyrene (168-503 mM, 20 bar H\textsubscript{2}, slope = 0.02) was observed. However, unlike pure Pt, DFT calculations conjecture a weak adsorption of 3-nitrostyrene vertically adsorbed on the
intermetallic PtSn surface due to the elimination of contiguous Pt sites. The vertically adsorbed 3-nitrostyrene has a weak interaction with PtSn (-0.58 eV) through the nitro group, and the vinyl group largely deviates from the PtSn surface. Such weak adsorption of nitro groups also agrees on the catalytic preference that the non-HP pathway of hydrogenation is more preferential on a polar group with a weak adsorption, which has been suggested by the previous DFT calculations for the selective hydrogenation of acrolein over Au sites. When increasing the H$_2$ pressure, we observed a steeply negative dependence of H$_2$ pressure (20-40 bar H$_2$, 168 mM, slope = -1.25), indicating that a higher H$_2$ concentration has an adverse impact on the reaction. Noting that H$_2$ molecules are not likely dissociative over the intermetallic PtSn surface, such impedance can be explained solely by a significant competitive adsorption of both weakly adsorbed molecular H$_2$ and 3-nitrostyrene. It is worth to note that PtSn@mSiO$_2$ is almost inactive under 5 bar H$_2$, and thus a switch-on H$_2$ pressure is critical to initiate the reaction through the non-HP pathway. In addition to the geometry of 3-nitrostyrene, we performed control experiments using either styrene or nitrobenzene as substrates to evaluate the hydrogenation of single vinyl and nitro groups over PtSn@mSiO$_2$. The TOFs of nitrobenzene and styrene were relatively close, at 194 and 150 h$^{-1}$ respectively when 40 bar H$_2$ was employed. When both styrene and nitrobenzene were present in one-pot to test the competitive hydrogenation in the presence of the same 40 bar H$_2$, intermetallic PtSn@mSiO$_2$ can only hydrogenate nitrobenzene (TOF = 61 h$^{-1}$), while largely hampered the hydrogenation of styrene. These results confirmed the preferential adsorption of nitro groups over vinyl groups in intermetallic PtSn@mSiO$_2$, which is consistent with the molecular adsorption geometry from DFT calculations. Similar catalytic trends were also reported by using single site-based Pt/FeO$_x$ catalysts, confirming that the absence of contiguous Pt sites in the well-
ordered structure of intermetallic PtSn@mSiO₂ catalysts is beneficial to the selective hydrogenation of the nitro group.

Confirming that the structures of Pt, Pt₃Sn, and PtSn can alter the catalytic pathway and selectivity, we endeavored to validate whether such structure-property correlations in the hydrogenation of 3-nitrostyrene can be used as a probe reaction to study structure evolution in Pt-Sn systems. During the synthesis of Pt₃Sn iNPs, we initially achieved an alloy phase in TEG solution at 280 °C (denoted as PtSnₐ.₃@mSiO₂) as shown in Figure S3.7, and post-annealing in reducing atmosphere at 600 °C is necessary to transition the alloy to the intermetallic phase (denoted as Pt₃Sn@mSiO₂). The catalytic performances of fresh alloy (PtSn₀.₃) and annealed IMC (Pt₃Sn) samples in the hydrogenation of 3-nitrostyrene are different as summarized in Table S2. PtSn₀.₃@mSiO₂ NPs show a high selectivity and low activity, while Pt₃Sn iNPs show a decreased selectivity and increased activity. Based on the aforementioned structure-property relationship, the fresh PtSn₀.₃@mSiO₂ would likely have an intermetallic PtSn surface, likely due to the lower formation energy of intermetallic PtSn in comparison to Pt₃Sn in the wet TEG synthesis. The annealing treatment can reconstruct the surface of the fresh PtSn₀.₃ to intermetallic Pt₃Sn. To observe this transition of surface composition, we performed an in situ AP-XPS on fresh PtSn₀.₃@mSiO₂ and annealed it to 500 °C (Figure S3.8). The fresh PtSn₀.₃@mSiO₂ indeed has a Pt/Sn surface ratio (1.33) closer to intermetallic PtSn, largely deviating from their bulk Pt/Sn ratio (3.0), and the annealed Pt₃Sn@mSiO₂ presents a matching composition (Pt/Sn = 2.78) to intermetallic Pt₃Sn.

We further extended the intermetallic composition to Zn and Pb as shown in Table 1. For Pt₃Zn@mSiO₂, the cP4 structure of intermetallic Pt₃Zn reflects high activity and poor selectivity, which is similar to their isostructural Pt₃Sn counterpart. All PtM@mSiO₂ (M = Sn,
Zn, and Pb) demonstrated similar slow rates and high selectivity, indicating similar non-HP reaction mechanism. Intermetallic PtPb has the specific hP4 unit cell as intermetallic PtSn, and intermetallic PtZn has a tP2 unit cell. We examined the low index facets including (110), (111), and (100) for PtZn and (1120), (1121) and (0001) for PtPb. No typical Pt threefold site presents in all these facets. The high selectivity of intermetallic PtSn, PtZn, and PtPb commonly corresponds to the absence of Pt threefold sites. In retrospect, the reaction rates follow the trend PtZn<PtPb<PtSn. However, this activity order agrees neither the trend of the atomic radius nor electronegativity (radius: Zn~Pt<Sn<Pb and electronegativity: Zn<Sn<Pt~Pb). These results confer that the geometric effect of IMC structures can more significantly affect the catalytic selectivity in hydrogenation. Nevertheless, the electronic and size effect of IMCs can also alter the activity and selectivity \(^{29}\), which is challenging to address while providing tremendous research opportunities in future.

3.5 Conclusion

In summary, we synthesized a series of intermetallic PtM- and Pt\(_3\)M-type catalysts (M = Sn, Pb, and Zn). The atomically-ordered intermetallic structures of these catalysts are elaborately correlated to their catalytic properties in the hydrogenation of 3-nitrostyrene. All PtM-type intermetallic compounds (IMCs) show high selectivity to 3-aminostyrene in the hydrogenation of 3-nitrostyrene, in contrast to pure Pt and Pt\(_3\)M-type catalysts. Intermetallic PtSn@mSiO\(_2\) is also highly selective for the hydrogenation of nitro group in nitroarenes in the presence of bromo, iodo, formyl and methoxy groups. Kinetic studies over Pt, PtSn, and Pt\(_3\)Sn revealed that the hydrogenation pathways could be altered due to changes in the surface structure of IMCs. Intermetallic PtSn facilitates a unique non-Horiuti-Polanyi pathway, where
the elimination of Pt threefold site inhibits the \( \text{H}_2 \) dissociative adsorption and, in turn, decreases the reaction rate. DFT calculations and competitive reactions ascribe the high selectivity to the preferential adsorption of nitro groups in 3-nitrostyrene over intermetallic PtSn surfaces. This work demonstrates a molecular engineering of intermetallic structures to tune and elucidate the catalytic mechanism for selective hydrogenations. We anticipate that the geometric effect of IMCs in heterogeneous catalysis can be generalized to instruct the exploration of advanced intermetallic systems for heterogeneous catalysis.

3.6 Supporting Information

Figure S3.1. TEM images and HRTEM images of a), b) PtSn@mSiO\(_2\); c), d) Pt\(_3\)Sn@mSiO\(_2\); e), f) PtZn@mSiO\(_2\); g), h) Pt\(_3\)Zn@mSiO\(_2\); i), j) Pt@mSiO\(_2\); and k), l) PtPb@mSiO\(_2\)
Figure S3.2. PXRD patterns of a) Pt@mSiO$_2$; b) Pt$_3$Sn@mSiO$_2$; c) PtSn@mSiO$_2$; d) Pt$_3$Zn@mSiO$_2$; e) PtZn@mSiO$_2$; and f) PtPb@mSiO$_2$ with corresponding standard patterns.

Figure S3.3. Surface structures of ideal a) Pt(111), b) Pt$_3$Sn(111), (110) and (100), and c) PtSn(1120), (0001), and (1121). Pt (white circles) and Sn atoms (yellow circles) are shown, along with Pt threefold sites (red triangles and rhombus in b), fourfold sites, and bridge sites (red rectangle in c) and single Pt (circle in c).
Figure S3.4. CV spectra of H⁺ electro-reduction for intermetallic PtSn@mSiO₂, Pt@mSiO₂ and commercial Pt/Vulcan. H₂ Electro-reaction of evolution (2H⁺ + 2e ⇌ H₂) occurs at -0.2-0.1 V region (vs. Ag/AgCl) for both forward and backward scans, and the subsequent H₂ desorption and adsorption due to this electro-reaction occurs at ~ 0 V. In -0.2 ~ 0.1 V, commercial Pt/Vulcan and Pt@mSiO₂ are both active for the H⁺ electro-reduction reaction. Pt@mSiO₂ has weaker peak intensity and some voltage shift compared to commercial Pt/Vulcan, likely due to the large sizes of Pt@mSiO₂ (14 nm) presenting low surface area-to-volume ratio and less undercoordinated Pt at corner, edge and kink sites. Specifically, Pt@mSiO₂ sample has two tails (~ 0 V) in forward and backward scans, corresponding the H₂ adsorption and desorption. Intermetallic PtSn@mSiO₂ shows only one tail as the backward scan corresponding the desorption of H₂ from the electro-reaction, but the absence of the adsorption tail indicates a negligible H₂ adsorption capability on PtSn surfaces in the liquid phase at room temperature.
Figure S3.5. DFT results of 3-nitrostyrene adsorption on Pt(111) and PtSn(1120) in different configurations. Pt (Sn) in surfaces are given by light grey (brown) spheres; C, N, O and H atoms in 3-nitrostyrene are shown by small gray, blue, red and white spheres. Top (bottom) panel is the top (side) view.
Figure S3.6. For Pt@mSiO$_2$: the dependence of reaction rate on a) 3-nitrostyrene (NS) concentration, and b) H$_2$ pressure. The slope in a) is 0.08, indicating a near zero reaction order, and the slope in b) is -0.43. For PtSn@mSiO$_2$: c) the dependence of reaction rate on 3-nitrostyrene concentration, and d) H$_2$ pressure. The slope in c) is 0.02, indicating a near zero order reaction, and the slope in d) is -1.25, showing a near negative first reaction order to H$_2$.

For Pt, nitrostyrene substrate varies from 50, 75, 100, 125, and 150 mg; H$_2$ pressure ranges from 10, 20, 30 and 40 bars. For PtSn, nitrostyrene substrate varies from 50, 75, and 100 mg; H$_2$ pressure ranges from 20, 30, and 40. All other reaction conditions were controlled as the same: 2 mL toluene as a solvent, 20 mg xylene as internal standard and 80 °C. The reaction rate was calculated at the initial reaction time.
Figure S3.7. PXRD patterns of alloyed PtSn_{0.3}@mSiO$_2$ alloy (black curve, directly after synthesis), and intermetallic Pt$_3$Sn@mSiO$_2$ (red curve, after annealing). The diffraction peaks of alloy PtSn$_{0.3}$ slightly shift to lower angle due to lattice expansion by addition of Sn. The intermetallic Pt$_3$Sn agrees well with the Pt$_3$Sn standard. Intermetallic phase shifts more to the lower angles in contrast to the alloy phase.

Figure S3.8. AP-XPS spectra of PtSn$_{0.3}@$mSiO$_2$ during in situ reductions. Pt stays as a metallic state in both fresh and reduced samples. The fresh sample has SnO$_x$ peaks and transitions to metallic state after high-temperature reduction. The SnO$_x$ on the fresh sample can be formed during the sample handling. However, they may readily exist during the TEG reduction. Atomic Pt/Sn ratios of fresh, reduced in 300°C, and reduced in 500 °C are respectively 1.33, 1.90 and 2.28.
Table S3.1. ICP results of all PtM@mSiO$_2$ NPs (M=Sn, Zn, and Pb).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Pt (wt.%)</th>
<th>Secondary metal (wt.%)</th>
<th>Actual Pt/M in molar ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt@mSiO$_2$</td>
<td>46.0</td>
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<td>–</td>
</tr>
<tr>
<td>PtSn@mSiO$_2$</td>
<td>27.5</td>
<td>16.3</td>
<td>1.02</td>
</tr>
<tr>
<td>Pt$_3$Sn@mSiO$_2$</td>
<td>57.8</td>
<td>10.6</td>
<td>3.3</td>
</tr>
<tr>
<td>PtZn@mSiO$_2$</td>
<td>41.9</td>
<td>12.7</td>
<td>1.1</td>
</tr>
<tr>
<td>Pt$_3$Zn@mSiO$_2$</td>
<td>43.0</td>
<td>4.3</td>
<td>3.3</td>
</tr>
<tr>
<td>PtPb@mSiO$_2$</td>
<td>36.0</td>
<td>34.7</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Table S3.2. Catalytic results of fresh and annealed PtSn$_{0.3}$@mSiO$_2$ for the selective hydrogenation of 3-nitrostyrene.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Time (h)</th>
<th>Conversion (%)</th>
<th>Selectivity</th>
</tr>
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<tr>
<td>1</td>
<td>Fresh</td>
<td>1</td>
<td>3.2</td>
<td>&gt;99</td>
</tr>
<tr>
<td></td>
<td>PtSn$_{0.3}$@mSiO$_2$</td>
<td>9</td>
<td>63.3</td>
<td>&gt;99</td>
</tr>
<tr>
<td>2</td>
<td>Annealed</td>
<td>0.5</td>
<td>&gt;99</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>Pt$_3$Sn@mSiO$_2$</td>
<td>1</td>
<td>&gt;99</td>
<td>—</td>
</tr>
</tbody>
</table>

a. Reaction condition: 1 mg catalyst, 50 mg 3-nitrostyrene, 20 mg xylene as internal standard, 2 mL toluene as solvent, 80 °C, and 20 bar H$_2$. 
3.7 References


CHAPTER 4. NON-DISSOCIATION HYDROGENATION PATHWAY DRIVEN CIS-SELECTIVITY OVER INTERMETALLIC PLATINUM-TIN CATALYSTS

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4.1 Introduction

The hydrogenation of alkynes to alkenes is one of the most important reactions to remove the trace amount of alkynes from large alkene feeds.\textsuperscript{1-4} For example, the trace amount of acetylene can lower the catalyst efficiency for the polymerization of ethylene.\textsuperscript{5} Another interest of this reaction is to modulate the stereoselectivity of alkene products targeting different applications in pharmaceutical and synthetic chemistry.\textsuperscript{6} Because trans-alkenes are more thermodynamically stable than cis-alkenes, it is thus interesting and challenging to maintain the high stereoselectivity of cis-alkenes during the chemoselective hydrogenation of alkynes.

The use of Lindlar catalyst and Birch reduction are two general strategies to synthesize respective cis- and trans-alkenes effectively. Specifically, Lindlar catalysts\textsuperscript{3,7} can adopt a \textit{syn} addition style of alkynes, where supported palladium is deactivated on purpose to
lower its hydrogenation capability to avoid the formation of alkanes. In contrast, Birch reduction\textsuperscript{8} can produce a stoichiometric amount of trans-alkenes over alkali metals in liquid ammonia, and the free radical anions are considered as the reduction intermediates. Even though these catalysts are effective in controlling stereoselectivity, the hydrogenation mechanisms have not been well understood. The Zaera group\textsuperscript{9} has demonstrated that the transformation of trans-alkenes to cis-alkenes is favored on H-saturated Pt(111) compared to more open Pt structures likely due to their different adsorption strength and steric effect. The Komatsu group\textsuperscript{10,11} has further demonstrated the structural effect of bimetallic alloys in the preferential production of trans-alkenes compared to monometallic catalysts. Bimetallic structures can also prevent the over-hydrogenation pathway maintaining high chemoselectivity to alkenes. The steric effect of trans-alkenes is likely less accessible to atomic hydrogen on these bimetallic structures in comparison to cis-alkenes, leading a high trans-stereoselectivity.

Among these studies, the catalyst surface is saturated with atomic hydrogen associated with strong hydrogen spillover, similarly to the mechanism of Birch type reduction. It is thus interesting to study if the physical state of hydrogen, such as molecular H\textsubscript{2}, can modulate their cis-stereoselectivity following a \textit{syn} addition fashion. Intermetallic PtSn surface has been demonstrated with both weak H\textsubscript{2} adsorption and weak H\textsubscript{2} dissociation capability due to the structural elimination of Pt threefold sites.\textsuperscript{12} We have also evidenced a pairwise addition of para-H\textsubscript{2} to propene induced by the PtSn intermetallic surface.\textsuperscript{13} Using PtSn intermetallic structures, we anticipate a selective addition of H\textsubscript{2} to alkyne substrates through a \textit{syn} addition fashion (pairwise addition), leading to a high stereoselectivity to cis-alkene products (Figure 4.1).
Figure 4.1 Schematic illustration of the pairwise addition of molecular H₂ to alkynes (i.e., diphenylacetylene) in the production of cis-alkenes. The large grey (yellow) dots represent Pt (Sn) atoms on PtSn(110) facets where one dimensional Pt chains can be observed in the elimination of Pt threefold sites. The small white and blue dots present respective hydrogen and carbon atoms in diphenyl acetylene molecules. The small red dots represent the active molecular hydrogen in pairwise geometry.

4.2 Results, Discussion and Perspectives

The model catalyst of PtSn intermetallic NPs (iNPs) was prepared by a seeded-growth method as described in Chapter 2 and 3. These PtSn iNPs demonstrate advantageous of capping-free nature, high thermal stability and homogeneous structures through most of individual iNPs. Our PtSn iNPs also feature defined structure and the surface Pt contiguous sites were not significantly observed in PtSn iNPs as probed by CO-DRIFTS (Figure 3.3d). We thus evaluate the cis-stereoselectivity and chemoselectivity of PtSn iNPs in the alkyne semi-hydrogenation. Two substrates of dimethyl acetylenedicarboxylate and diphenylacetylene were evaluated as model substrates for PtSn iNPs. As shown in Table 4.1, the hydrogenation of dimethyl acetylenedicarboxylate has three major products from full
hydrogenated product dimethyl succinate 1, semi-hydrogenated cis-maleate 2, and trans-fumarate 3. At a low temperate of 50 °C, Pt starts to show a significant amount of over-hydrogenated product 1. After 99% conversion was achieved, we used nuclear magnetic resonance (400 MHz, Bruker) to quantify cis-maleate and trans-fumarate. Pt shows no stereoselectivity with a molar ratio of trans-fumarate/cis-maleate as 1/2 and the trans-fumarate is dominant likely due to the thermodynamically stable nature of trans alkenes. However, PtSn iNPs has different catalysis with both high chemoselectivity to semi-hydrogenated products (2 and 3) of ca. 90% and high stereoselectivity to cis-maleate of over 99%. The dilution effect of noble metals by secondary atoms (i.e., diluted Pt by Sn in PtSn iNPs) can suppress the hydrogenation of C=C bonds (alkenes) in comparison to alkyne substrates, resulting in high chemoselectivity in hydrogenation.\textsuperscript{12,14-16} It is noteworthy to address that negligible trans-fumarate product 3 was observed on PtSn iNPs, evidencing the high syn addition fashion likely due to the non-dissociative pairwise hydrogen addition to alkynes on PtSn surface as we expected. To evaluate the thermodynamic cis-stereoselectivity of PtSn iNPs, we evaluated reaction temperature to 110 °C, and PtSn iNPs still show a high cis-stereoselectivity over 99% and the chemoselectivity to the semi-hydrogenated product is also as high as 80%.

As the steric effect of functional groups in acetylene derivatives can largely determine the stereoselectivity in the transformation of cis- to trans-alkenes, we further used diphenyl acetylene as a substrate with more bulky phenyl groups over Pt NPs and PtSn iNPs as shown in Table 4.2. The steric effect is significant when Pt was used as catalysts, and Pt shows a much higher cis-stereoselectivity. Pt surface is saturated with atomic H, because of the barrierless hydrogenation dissociation on Pt.\textsuperscript{12} The atomic H can attack either carbon end of
triple bonds and induce a semi-hydrogenated olefin intermediates, whereas the steric effect can define the rotation of tilted bulky groups in the olefin intermediate and lead to the retard preference of trans-olefins. However, the chemoselectivity cannot be maintained in pure Pt resulting the over-hydrogenation pathways at increased reaction times. This steric effect of Pt indicates that the kinetically controlled semi-hydrogenation of alkynes on Pt surface. Because Pt surface is mostly saturated with atomic H, atomic H can be more accessible to the cis-configuration product considering a flat geometry of adsorbed alkynes. When the cis-alkenes transform to trans-alkenes, this transformation involves a bond rotation, and the bulky groups will retard the free rotation prohibiting the formation of trans-alkenes. Retrospection of PtSn iNPs, this steric effect was not observed on PtSn iNPs with a slightly lower cis-stereoselectivity of trans-stilbene in comparison to a less bulky dimethyl acetylenedicarboxylate at similar condition (ethanol, 50 °C, 20 bar H2). However, PtSn iNPs can still show a relatively high cis-stereoselectivity around 90% regardless of solvents (ethanol/toluene) and reaction temperatures (50°C or 80 °C). We increased the reaction time to 35 hrs after the 100% conversion was obtained, and observed a slow increase of cis-stilbene. To further validate the structure-catalysis of PtSn iNPs, we on purpose prepared a Pt-rich PtSn-1.1 with Pt/Sn molar ratio as 1.1:1. The Pt-rich PtSn-1.1 cannot maintain the high cis-stereoselectivity when the reaction completed and a rapid cis- to trans-transformation was also observed, likely due to the presence of surface contiguous Pt sites on PtSn-1.1 iNPs.

Even the cis-stereoselectivity of PtSn iNPs can be originated from the syn addition involved the molecular H2, the direct evidence of the pairwise adduct intermediate of alkynes is ongoing with more spectroscopic studies. Since the kinetic mechanism of the syn addition
is not clear with preliminary results in this study, we tried to study the isotope effect by only supplying D\(_2\) as feed gas instead of H\(_2\) for the diphenylacetylene hydrogenation over PtSn. A negligible apparent reaction rate (k\(_D\)) was readily observed when D was used in hydrogenation with negligible D-substituted stilbene in comparison to that of k\(_H\), likely indicating a tunneling hydrogenation pathway involved the molecular H\(_2\) considering the large k\(_D\)/k\(_H\) (usually over 30) associated with the D\(_2\) inhibition effect. The similar isotope effect was also observed in the 3-nitrostyrene hydrogenation over PtSn iNPs (as mentioned in Chapter 3). The kinetic isotope experiments were also employed using D\(_2\) or D\(_2\)/H\(_2\) as feed gas on both Pt NPs and PtSn iNPs. Pt shows k\(_H\)/k\(_D\)=1.7, and partially D-substituted-3-ethyl nitrobenzene and 3-ethylaniline were both observed in GC-MS in the case of Pt NPs (k\(_H\) denotes the apparent reaction rate when H\(_2\) was used as the feed gas, and k\(_D\) denotes the apparent reaction rate when D\(_2\) was used as the feed gas). This result indicates that the Pt surface shows strong dissociation of H\(_2\) (D\(_2\)) and good H/D exchange capability. Considerably, PtSn iNPs show dramatically reduced reaction rate as k\(_H\)/k\(_D\)=30. Even charging H\(_2\)/D\(_2\) mixture (10 bar/10 bar), k\(_H\)/K\(_H\)-D is still as high as 10 (K\(_H\)-D denotes the apparent reaction rate when H\(_2\)/D\(_2\) mixture was used as the feed gas). We propose that overall H/D exchange capability is limited on PtSn, which can rise the hydrogenation energy barrier. The large kinetic isotope effects and inactive D\(_2\) on intermetallic PtSn may indicate the H\(_2\) tunneling effects\(^{17,18}\) consistent with the high energy barrier for H\(_2\)/D\(_2\) dissociation on such PtSn intermetallic surface.
Table 4.1 Catalytic results for semi-hydrogenation of dimethyl acetylenedicarboxylate over Pt NPs and PtSn iNPs.

![Reaction scheme](image)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T (°C)</th>
<th>Time (h)</th>
<th>Conversion (%)</th>
<th>Chemoselectivity (%)</th>
<th>Stereoselectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1, C-C</td>
<td>2+3, C=C</td>
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<tr>
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<td>50</td>
<td>0.5</td>
<td>42.9</td>
<td>33.0</td>
<td>67.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>&gt; 99</td>
<td>63.7</td>
<td>36.3</td>
</tr>
<tr>
<td>PtSn@mSiO₂</td>
<td>50</td>
<td>16</td>
<td>12.4</td>
<td>12.1</td>
<td>87.9</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>3</td>
<td>9.4</td>
<td>8.8</td>
<td>91.2</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>79.8</td>
<td>17.3</td>
<td>17.3</td>
<td>82.7</td>
</tr>
</tbody>
</table>

reaction condition: 20 mg dimethyl acetylenedicarboxylate, 2 mL ethanol, 20 mg n-decane as an internal standard, 5 bar H₂/100 °C or 20 bar H₂/50 °C.

Accepting that the non-dissociative hydrogenation pathway on PtSn iNPs is due to the elimination of Pt threefold sites, we endeavor to generalize this geometric structure-property relationship into broader metallic scopes. Several intermetallic compounds were synthesized using the similar seeded growth method including PdCu (fcc and bcc), AuCu (fcc), Pd₃Sn₂ (hP6), and Pd₂Sn (oP12) iNPs. Diphenylacetylene hydrogenation was used as a probe reaction to study their chemoselectivity and stereoselectivity as shown in Figure 4.3. It is clearly seen that only Pd₃Sn₂ shows high chemoselectivity to alkenes together with a cis-stereoselectivity, and other iNPs can lead the reaction to either over hydrogenated product 3 or a mixture of cis- and trans-stilbene. We examined the low index facets of all these iNPs to
investigate the presence of contiguous metal sites, especially metal threefold sites. Different to all other iNPs, typical threefold metal sites are only absent on Pd$_3$Sn$_2$ intermetallic structures agreeing to their high cis-stereoselectivity.

Table 4.2 Semi-hydrogenation of diphenyl acetylene over Pt NPs and PtSn iNPs.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Time (h)</th>
<th>T (°C)</th>
<th>Solvent</th>
<th>Conversion (%)</th>
<th>selectivity /%</th>
<th>1, cis-C=C</th>
<th>2, trans-C=C</th>
<th>3, C-C</th>
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</thead>
<tbody>
<tr>
<td>Pt</td>
<td>1</td>
<td>50</td>
<td>ethanol</td>
<td>40</td>
<td>91.9</td>
<td>8.1</td>
<td>--</td>
<td></td>
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<tr>
<td></td>
<td>3</td>
<td></td>
<td></td>
<td>77</td>
<td>91.0</td>
<td>9.0</td>
<td>--</td>
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</tr>
<tr>
<td></td>
<td>6</td>
<td>&gt; 99</td>
<td></td>
<td></td>
<td>9.8</td>
<td>94.8</td>
<td>5.2</td>
<td>93.7</td>
</tr>
<tr>
<td>PtSn-1.0</td>
<td>23</td>
<td>50</td>
<td>ethanol</td>
<td>9.8</td>
<td>94.8</td>
<td>5.2</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>hP4</td>
<td>6</td>
<td></td>
<td>toluene</td>
<td>71.5</td>
<td>90.9</td>
<td>9.1</td>
<td>--</td>
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<tr>
<td></td>
<td>20</td>
<td></td>
<td></td>
<td>87.0</td>
<td>86.7</td>
<td>13.3</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>80</td>
<td>toluene</td>
<td>93.1</td>
<td>91.2</td>
<td>8.8</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td></td>
<td>35</td>
<td></td>
<td></td>
<td>&gt; 99</td>
<td>83.4</td>
<td>16.6</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>PtSn-1.1</td>
<td>6</td>
<td>80</td>
<td>toluene</td>
<td>43.5</td>
<td>91.2</td>
<td>8.8</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>hP4</td>
<td>12</td>
<td></td>
<td></td>
<td>69.5</td>
<td>91.7</td>
<td>8.3</td>
<td>--</td>
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</tr>
<tr>
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<td>35</td>
<td></td>
<td></td>
<td>&gt; 99</td>
<td>64.6</td>
<td>35.4</td>
<td>--</td>
<td></td>
</tr>
</tbody>
</table>

reaction condition: 50 mg diphenyl acetylene, 2 mL toluene or ethanol, 20 mg xylene as an internal standard in use of toluene as a solvent or 20 mg n-decane as an internal standard in use of ethanol as solvent, and 20 bar H$_2$. 
Table 4.3 Semi-hydrogenation of diphenylacetylene over other intermetallic NPs.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Time (h)</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>1, cis-C=C</th>
<th>2, trans-C=C</th>
<th>3, C-C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdCu (bcc, fcc)</td>
<td>1</td>
<td>97.5</td>
<td>47.2</td>
<td>—</td>
<td>—</td>
<td>52.8</td>
</tr>
<tr>
<td>AuCu (fcc)</td>
<td>12</td>
<td>2.5</td>
<td>52.0</td>
<td>48.0</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Pd$_2$Sn$_2$ (hP6)</td>
<td>6</td>
<td>54.0</td>
<td>92.9</td>
<td>7.1</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>64.0</td>
<td>93.2</td>
<td>6.8</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>78.1</td>
<td>92.5</td>
<td>7.5</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>Pd$_2$Sn (oP12)</td>
<td>1</td>
<td>&gt; 99</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>&gt; 99</td>
</tr>
</tbody>
</table>

reaction condition: 50 mg diphenyl acetylene + 2 mL toluene + 20 mg xylene, 20 bar H$_2$.

In summary, we have demonstrated a structure-property relationship that the PtSn iNPs can show a high cis-stereoselectivity in the semi-hydrogenation of alkynes. The intrinsic structure of intermetallic PtSn eliminates the presence of Pt threefold sites, which leads to a non-dissociate hydrogenation pathway. Molecular H$_2$ can only be added into alkynes by a pairwise geometry on PtSn iNPs surface ensuring the preferential production of cis-alkenes. The future direction is essential to extend the substrate scope to more alkynes with different functional groups. More spectroscopic studies on the kinetic mechanism of this pairwise addition over intermetallic compounds can also be valuable to contribute a
molecular level understanding by visualizing the intermediates between an adsorbed alkyne and adsorbed molecular H₂ species. We anticipate engineering the well-ordered structure of intermetallic compounds for satisfying high selectivity and activity in catalytic reactions.

4.3 References


CHAPTER 5. FINELY TUNING THE COMPOSITIONS OF PLATINUM-TIN INTERMETALLIC NANOPARTICLES AS CHEMO-SELECTIVE HYDROGENATION CATALYSTS

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5.1 Introduction

Surface or sublayer structures are essential to determine the catalytic behaviors of heterogeneous catalysts, because their geometric and electronic properties directly affect the configuration and strength of adsorbed molecules.\textsuperscript{1,2} Designing efficient heterogeneous catalysts thus relies on the fundamental understanding of the structure-property relationship to correlate heterogeneous surfaces to their catalytic properties. However, the near-surface structures of many heterogeneous catalysts are different from their bulk composition, and state-of-art techniques cannot easily characterize these thin surfaces under reaction conditions. Developing well-ordered catalyst platforms and in situ structural probes are two strategies to elucidate the catalytic dependence on the surface structure at a molecular level.
Alloy nanoparticles are mostly studied bimetallic catalysts for the ease to tune their bulk compositions satisfying high catalytic activity and selectivity.\textsuperscript{3-6} To a limit extent, the bulk composition of bimetallic nanoparticles can synthetically reflect that of their surface structure.\textsuperscript{7-8} The direct modification techniques of the alloy surfaces are advantageous to provide more structural controls, such as colloidal galvanic replacement,\textsuperscript{9-11} electrochemically under-potential deposition,\textsuperscript{12-14} and reaction-driven gas pretreatment.\textsuperscript{2, 8} However, the random structures of many alloys retards the establishment of structure-property relationships. Atoms in alloys can also migrate from surface to bulk phase and vice versa,\textsuperscript{15} resulting to the unpredictable surface segregation\textsuperscript{16-18} associated with heterogeneous distributions of atoms through nanoparticles. Moreover, organic capping agents are often present in free alloy nanoparticles prepared in colloidal methods, which complicates the structural clarification of their surface.

Intermetallic compounds, featuring atomic-ordered structures and precise stoichiometry, are thus ideal platforms for studying the structural-catalytic property relationship in comparison to random alloys.\textsuperscript{19-21} Because intermetallic compounds have defined stoichiometry, the fine-tuning of the bulk composition can readily deviate their native structures in a more controllable manner, leading to a quantitative correlation of compositional effect in heterogeneous catalysis. Intermetallic PtSn is chosen as the model catalyst platform in this study because intermetallic PtSn is a line compound\textsuperscript{22} where Pt/Sn can maintain mere 1:1 stoichiometry to form accurate intermetallic structure. In catalytic rationale, we have revealed that PtSn intermetallic nanoparticles (iNPs) are compositionally dependent in gas-phase furfural hydrogenation,\textsuperscript{23} where the extra Pt in PtSn iNPs can lower their selectivity. In liquid-phase nitrostyrene hydrogenation,\textsuperscript{24} the surface sensitivity effect
has also been studied over Pt NPs, Pt$_3$Sn iNPs, and PtSn iNPs correlated to their different catalysis. It is thus desirable to quantitatively correlate the composition factors of intermetallic PtSn catalysts to their unique catalysis by using these surface-sensitive reactions as \textit{in situ} probes. We expect to vary the bulk Pt/Sn ratios in intermetallic PtSn iNPs and apply different reduction temperatures to trigger respective surface reconstructions of PtSn iNPs. Chemoselective hydrogenations can be used as probe reactions to investigate the surface structures of PtSn iNPs in real reaction conditions.

To synthesize the PtSn intermetallic candidates, our group has developed a ship-in-a-bottle method of preparing Pt-based iNPs encapsulated in mesoporous silica shells (mSiO$_2$).$^{23,25-26}$ As-prepared PtSn iNPs can maintain the capping free nature, high thermal stability and structural ordering of intermetallic compounds. This ship-in-a-bottle method also enables the precise composition control of the incorporated metal precursors ending up in the iNPs. Herein, we demonstrated a structure-catalysis relationship over PtSn iNPs catalysts with Pt/Sn ratio slightly deviate from 1:1. The surface structure evolution induced by reduction temperatures were demonstrated by two probe reactions, furfural hydrogenation and acetylene semi-hydrogenation. In comparison to monometallic Pt and less-ordered PtSn alloys, ordered intermetallic PtSn phase is thermodynamically favored at high reduction temperatures on the surface of iNPs with enhanced hydrogenation selectivity.

5.2 Experimental

Synthesis of PtSn iNPs with various ratios

Synthesis of Pt@mSiO$_2$ seeds follows by literature, and as-prepared Pt@mSiO$_2$ seeds were stored in ethanol before use. The Pt mass concentrations of Pt@mSiO$_2$ seeds
solution were measured by ICP-MS to ensure an accurate estimate for the addition of Sn in preparing PtSn iNPs. A proper amount of Pt@mSiO$_2$ seeds (ca. 10 mg) was taken out and re-dispersed in a small amount of acetone (2-3 mL) by centrifugation (12000 rpm, 10 min). The Pt@mSiO$_2$ seeds-acetone solution was transferred to 80 mL tetraethylene glycol (TEG) with the addition of according amount of SnCl$_2$·2H$_2$O based on the desired Pt/Sn molar ratios in the ending PtSn iNPs (0.9, 1.0 and 1.2). The resulting TEG solution was protected in argon, then brought to 260 °C in 45 min, ramped to 280 °C in 20 min, and maintained at 280 °C for another 2 hrs. After cooling to room temperature, 80 mL acetone was added to resulting PtSn iNPs in TEG solution, and PtSn iNPs was centrifuged down at 12000 rpm for 10 min. After washing 3 times with ethanol, PtSn iNPs was dried in vacuum at room temperature and calcined at 500 °C in air for 4 hrs to clean off the remaining capping agents on PtSn iNPs surface. The PtSn iNPs were then reduced at 300 °C for 2 hrs in 10% H$_2$/Ar (a total flow of 50 mL min$^{-1}$), denoted at PtSn-300 iNPs. 300 °C reduced PtSn iNPs were continuing reduced at 500 °C for another 2 hrs, denoted as PtSn-500 iNPs. The exact Pt/Sn ratios of as-prepared PtSn iNPs with different ratios were confirmed by ICP-MS.

The catalytic evaluation of PtSn iNPs

For furfural hydrogenation, typical 1-2 mg of PtSn iNPs were diluted with 200 mg quartz sand and placed into a U-shaped quartz reactor. A gas feed of furfural(He)/H$_2$ was maintained as 8.6/11.4 mL/min where 8.6 mL He flow went through a bubbler containing furfural with an actual furfural/H$_2$ flow as 0.023/11.4 mL min$^{-1}$. The gas contents were monitored and quantified using a HP 5890 gas chromatography equipped with a capillary column (DB-5, 30 m × 0.32mm × 0.25 µm) and a flame ionization detector. For acetylene
semi-hydrogenation, a similar amount of PtSn iNPs and set-up of the gas-flow reactor was applied at for furfural hydrogenation. A gas feed of C$_2$H$_2$/C$_2$H$_4$/H$_2$/He was controlled as 3.0/15/1.5/10.5 mL min$^{-1}$. The gas contents were monitored and quantified using a HP 5890 gas chromatography equipped with a capillary column (HP PLOT Q, 30 m × 0.25 mm × 0.25 mm) and a flame ionization detector. Before the catalytic reaction, all PtSn iNPs catalysts were calcined at 500 °C in air for 4 hrs, and either i) reduced in situ at 300 °C for 2 hrs or ii) reduced in situ at 300 °C for 2 hrs and then 500 °C for another 2 hrs in 10% H$_2$/He (a total flow of 50 mL min$^{-1}$).

Characterization

PXRD patterns of the samples were acquired by a STOE Stadi P powder diffractometer and a Bruker D8 Advance Twin diffractometer. X-ray absorption fine structure spectroscopy (XAFS) spectra were measured in transmission mode (Pt $L_3$ edge = 11564 eV and Sn $K$ edge = 23220 eV) at 9-BM-B and 20-BM-B beamlines of the Advanced Photon Source at Argonne National Laboratory. XAFS of reference samples were collected using pure finely ground powders homogeneously dispersed on polyimide Kapton tape. While the PtSn iNPs (dilute with boron nitride) were pressed into a pellet fit to a hole embedded in a sample holder, reference platinum was acquired simultaneously with each measurement for energy calibration. The Athena program, which is an interface to IFEFFIT and FEFFIT, was used for smoothing raw data and converting energy spectra to $k$ space. The XAFS data were fitted in $R$ space by Artemis program from the same package using quick shell theory of related Pt and Sn coordination. All the EXAFS data fittings were performed with a $k^3$ weight in $R$ space.
5.3 Results and Discussion

Bulk Pt/Sn ratios of PtSn iNPs have been finely tuned with extra Pt or Sn departing from the theoretical 1:1 stoichiometry. We varied the extra metal ratios from 10-20 mol.% capable of covering the whole surfaces of a 20 nm spherical particle (theoretical dispersion: 7 mol.% surface atoms). Due to the high incorporation efficiency of secondary metal in the ship-in-a-bottle method, the molar ratios of Pt seed/secondary precursors can be well maintained in the final bimetallic NPs depending on that of respective precursors. We thus prepared Pt$_{1.2}$Sn, Pt$_{1.0}$Sn and Pt$_{0.9}$Sn iNPs with precise Pt/Sn ratios, and their bulk compositions were confirmed by ICP-MS as 1.16, 0.98 and 0.91, closed to the precursor ratios (Table S5.1 in Supporting Information). In the ship-in-a-bottle method, Pt seeds are essential facilitating the reduction of secondary metal precursors in tetraethylene glycol. Specifically to alloy NPs, PtPd alloy NPs synthesized by this method can have flexible Pd/Pt ratios from 0.5 to 2.0, and even higher. However, we observed restricted bimetallic ratios in intermetallic PtSn catalysts. For Sn-rich PtSn iNPs, the excess of Sn (>10%) cannot be deposited on Pt seeds to further increase extra Sn contents, likely due to that the deficiency of surface Pt sites on the as-formed Sn-rich surface. Following Pt-rich PtSn iNPs, the major phase can fall into intermetallic Pt$_3$Sn in the case of Pt/Sn ratios more closed to 3/1. This restricted composition tunability of PtSn iNPs in Pt-rich samples exemplifies the ordering effects of intermetallic compounds in comparison to random alloys.

Due to the synthesis advantages using mesoporous silica shells, these PtSn iNPs have high thermal stability against aggregations (Figure 5.1a). Our previous studies have demonstrated the formation of ordered intermetallic PtSn in bulk phase through most of individual Pt$_{1.0}$Sn$_{1.0}$ iNPs reduced at 300 °C. We first calcined Pt-Sn iNPs at 500 °C in the
air to remove surface capping agents leaving phase-segregated Pt and SnO$_2$ particles (Pt-SnO$_2$ particles). The intermetallic PtSn phase can form together with surface restructuring depending on the Pt/Sn ratio after we reduced these Pt-SnO$_2$ particles at different temperatures. Two reduction sequences were applied for the reconstruction of PtSn iNPs as i) 300 °C reduction, and ii) 300 °C and then 500 °C. These PtSn iNPs reduced at respective two temperature sequences were denoted as $\text{Pt}_x\text{Sn}$-300 and $\text{Pt}_x\text{Sn}$-500 ($x=0.9$, 1.0 and 1.2). Powder X-ray diffraction (PXRD) patterns of PtSn iNPs reduced under different temperatures were acquired as shown in Figure 5.1b. It is seen that the major phase of intermetallic PtSn was formed in all PtSn iNPs under either 300 or 300/500 °C reductions. The Pt-rich $\text{Pt}_{1.2}\text{Sn}$-300 iNPs display monometallic Pt phase, and the Pt phase in $\text{Pt}_{1.2}\text{Sn}$-500 was suppressed after being reduced at higher temperatures. Only intermetallic PtSn patterns were identified for accurate $\text{Pt}_{1.0}\text{Sn}$ and Sn-rich $\text{Pt}_{0.9}\text{Sn}$ iNPs regardless of the different reduction temperatures. Unlike alloys, the PXRD patterns show that Pt and intermetallic PtSn fractions in our PtSn iNPs can be differentiated with a small compositional difference (10%), demonstrating the essential roles of the defined stoichiometry of intermetallic compounds.

To demonstrate the structural difference of PtSn iNPs in a function of composition and reduction temperature, we first tried to acquire the compositional information of PtSn iNPs using the elemental mappings and energy dispersive X-ray spectroscopy (EDS) line scans under high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) as shown in Figure 5.3. The Pt/PtSn core/shell structure was observed in $\text{Pt}_{1.2}\text{Sn}$ iNPs (Figure 5.3b). After reduced at a higher temperature, $\text{Pt}_{1.2}\text{Sn}$-500 iNPs have a more homogeneous mixing of Pt and Sn; even Pt signal was slightly observed to concentrate in core areas of iNPs (Figure 5.3d). $\text{Pt}_{0.9}\text{Sn}$-300 iNPs have similar Pt core/PtSn shell
structures as to Pt$_{1.2}$Sn-500 iNPs, even if the Pt is less concentrated in core areas (Figure 5.3f). Upon the reduction of 500 °C, Pt$_{0.9}$Sn-500 iNPs show the homogeneous distribution of Pt and Sn signals through the entire nanoparticle (Figure 5.3h). The HAADF-STEM results show the heterogeneity of Pt/Sn distributions in Pt-rich Pt$_{1.2}$Sn samples in comparison to Sn-rich Pt$_{0.9}$Sn-500. It is also noticeable to emphasize that Pt is more favorable to maintain in the core area in comparison to PtSn showing that intermetallic PtSn phase is more thermodynamically stable compared to monometallic Pt and Sn species.

Figure 5.1. (a) Transmission electronic microscopy (TEM) images of Pt$_{1.0}$Sn iNPs after calcination at 500 °C and reduction at 300 °C without observable aggregation. The inserted figure is the high-resolution TEM images of a typical Pt$_{1.0}$Sn iNPs demonstrating one lattice orientation through the entire nanoparticle. (b) PXRD patterns of Pt$_{0.9}$Sn, Pt$_{1.0}$Sn, and Pt$_{1.2}$Sn iNPs reduced at 300 °C and 300/500 °C. Blue and red triangles represent characteristic diffraction peaks in respective Pt and intermetallic PtSn standard patterns.

We also acquired X-ray absorption fine structure (XAFS) spectra at Pt L$_3$ and Sn K edges for PtSn iNPs as shown in Figure S5.1-2 and Table S5.2-3. Even though the 10% mol. difference in PtSn cannot be well distinguished in XAFS, we used XAFS to obtain the
ensemble information and validate the HAADF-STEM results. The energy position of white lines in all PtSn iNPs at Pt \( L_3 \) edge shows a high-energy shift in comparison to that of Pt, due to the formation of PtSn phase (Figure S5.1a). The white lines of all PtSn iNPs at Sn \( K \) edge position at similar energy in comparison to that of Sn foil (Figure S5.1b). In Pt \( L_3 \) edge, Pt\(_{1.0}\)Sn and Sn-rich Pt\(_{0.9}\)Sn iNPs have respective Pt-Pt and Pt-Sn coordination number closing to 2 and 4, as well as that the Sn-Sn coordination number closed to 6 in Sn \( K \) edge. The XAFS fittings of Pt\(_{1.0}\)Sn and Sn-rich Pt\(_{0.9}\)Sn iNPs relatively matched to theoretical PtSn intermetallic compounds indicating the formation of ordered PtSn in Pt\(_{1.0}\)Sn and Pt\(_{0.9}\)Sn iNPs regardless of reduction temperatures. The significant deviation was observed in Pt\(_{1.2}\)Sn samples. As the presence of monometallic Pt cores in Pt\(_{1.2}\)Sn-300 iNPs observed in HAADF-STEM images, the Pt-Pt (Pt \( L_3 \) edge), Pt-Sn (Pt \( L_3 \) edge) and Sn-Pt (Sn \( K \) edge) coordination was fitted as respective 4.6(0.3), 3.3(0.1) and 4.5(0.2). The large deviation of Pt-Pt and Pt-Sn coordination number indicates the significant Pt and Sn aggregates in bulk phase of Pt\(_{1.2}\)Sn-300 iNPs, in comparison to their theoretical values of 2 and 6. Upon reduction at 500 °C (i.e. Pt\(_{1.2}\)Sn-500 iNPs), the Pt-Pt (Pt \( L_3 \) edge), Sn-Pt (Pt \( L_3 \) edge) and Sn-Pt (Sn \( K \) edge) coordination was fitted as respective 2.7(0.3), 4.0(0.2) and 5.5(0.2), more closed to their theoretical values of 2, 6 and 6, indicating a more homogenous distribution of PtSn intermetallic structures at higher reduction temperatures.

The XAFS, EDS and PXRD results demonstrate the ordering effect facilitated by high-temperature reductions. However, these bulk characterizations cannot provide detailed information of their surface structures. Despite Pt rich cores in Pt\(_{1.2}\)Sn-300, all rest catalysts cannot show a major structural difference. We further considered of using furfural hydrogenation as a reaction probe to investigate these PtSn iNPs. It is to our surprise that
these four catalysts were readily beheld with different catalysis as shown in Figure 5.4 and Figure S5.3. In the previous report, we had demonstrated that Pt_{1.0}Sn-300 °C iNPs are highly active and selective (>99%) in the hydrogenation of furfural to furfuryl alcohol due to the straight-up geometry of furfural molecules adsorbed on well-ordered PtSn intermetallic structures.\textsuperscript{23} Interestingly, Pt_{1.2}Sn and Pt_{0.9}Sn iNPs show composition and reduction temperature-dependent catalytic properties in furfural hydrogenation. Pt-rich Pt_{1.2}Sn iNPs have high activity and 90% selectivity to furfuryl alcohol after reduction at 300 and 300/500 °C. Sn-rich Pt_{0.9}Sn iNPs have different catalytic properties depending on the reduction temperature. Pt_{0.9}Sn-300 has high activity and 90% selectivity similar to that of Pt_{1.2}Sn iNPs. However, the higher temperature reduction (i.e., 300/500 °C) can largely suppress the activity of Pt_{0.9}Sn-500 iNPs with enhanced selectivity (>99%). We further summarized the apparent activation energy and turn-over-frequency (TOF) of PtSn iNPs for furfural hydrogenation in Figure 5.4a and Figure S5.4-7 to quantify the different catalysis. Two sets of catalysts can be classified based on their apparent activation energy values: i) Pt-rich Pt_{1.2}Sn-300, Pt_{1.2}Sn-500, and Sn-rich Pt_{0.9}Sn iNPs-300 iNPs have activation energy closed to that of Pt control (10-18 kJ mol\(^{-1}\)), and they are all not highly selective to furfuryl alcohol (90% selectivity at 220 °C). Pt_{1.2}Sn-500 °C iNPs show lowest activation energy among all PtSn iNPs samples. ii) Differently, Sn-rich Pt_{0.9}Sn-500 iNPs have almost identical activation energy and high selectivity in comparison to Pt_{1.0}Sn-300 iNPs with well-ordered intermetallic structures. Among these four catalyst, the TOF follows in order of Pt_{1.2}Sn-300 > Pt_{1.2}Sn-300 > Pt_{1.0}Sn-300 ~ Pt_{0.9}Sn-300 > Pt-300 >> Pt_{0.9}Sn-500 (Figure S5.7). We thus speculate that the reduction temperature can induce the reconstruction of the extra metals in PtSn iNPs endowing different surface structures.
Figure 5.3. Elemental mappings of HAADF-STEM images and EDS line scan of representative Pt$_{0.9}$Sn and Pt$_{1.2}$Sn iNPs reduced under 300 °C and 300/500°C. The scale bar is 5 nm. The EDS line scans of (b) Pt$_{0.9}$Sn-300, (d) Pt$_{0.9}$Sn-500, (f) Pt$_{1.2}$Sn-300, and (h) Pt$_{1.2}$Sn-500. The red dots and blue triangles are Pt and Sn signals. The inserted is HAADF-STEM images of (a) Pt$_{0.9}$Sn-300, (c) Pt$_{0.9}$Sn-500, (e) Pt$_{1.2}$Sn-300, and (g) Pt$_{1.2}$Sn-500.

Table 5.1. XAFS summary of Pt-Pt, Pt-Sn, and Sn-Pt coordination numbers (CNs) of PtSn iNPs with different compositions and reduction temperatures.$^a$

<table>
<thead>
<tr>
<th>Samples</th>
<th>Pt$_{L3}$ edge</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pt-Pt CNs</td>
<td>Pt-Sn CNs</td>
<td>Sn-Sn CNs</td>
<td>Sn-O CNs</td>
<td></td>
</tr>
<tr>
<td>Pt$_{1.2}$Sn-300</td>
<td>4.6 (0.3)</td>
<td>3.3 (0.2)</td>
<td>4.5 (0.2)</td>
<td>0.8 (0.2)</td>
<td></td>
</tr>
<tr>
<td>Pt$_{1.2}$Sn-500</td>
<td>2.7 (0.3)</td>
<td>4.0 (0.2)</td>
<td>5.5 (0.3)</td>
<td>0.5 (0.3)</td>
<td></td>
</tr>
<tr>
<td>Pt$_{1.0}$Sn-300</td>
<td>2.1 (0.4)</td>
<td>4.4 (0.2)</td>
<td>6.4 (1.1)</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>Pt$_{1.0}$Sn-500</td>
<td>2.0 (0.4)</td>
<td>4.2 (0.5)</td>
<td>5.9 (0.3)</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>Pt$_{0.9}$Sn-300</td>
<td>2.0 (0.5)</td>
<td>4.5 (0.2)</td>
<td>5.7 (0.2)</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>Pt$_{0.9}$Sn-500</td>
<td>2.0 (0.5)</td>
<td>4.2 (0.4)</td>
<td>5.8 (0.4)</td>
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a. The value in each parenthesis is the error during the fittings. The Pt-Pt coordination in Pt foil in 10.2 in terms 12-coordinated Pt environments, and this value was used to estimate all Pt-Pt, Pt-Sn, and Sn-Sn coordination numbers. $k^3$ weight was used in all fittings.
Figure 5.4. (a) Apparent activation energy of furfural hydrogenation over Pt@mSiO$_2$, Pt$_{0.9}$Sn, Pt$_{1.0}$Sn and Pt$_{1.2}$Sn iNPs reduced at 300 °C and 300/500 °C. 0.3-0.5 mg catalyst was used in furfural hydrogenation with a gas feed of furfural/H$_2$=0.023/11.4 mL min$^{-1}$. A He flow of 8.6 mL min$^{-1}$ carries furfural vapor in a bubbler. (b) CO-DRIFTS spectra for Pt@mSiO$_2$, Pt$_{0.9}$Sn, Pt$_{1.0}$Sn and Pt$_{1.2}$Sn iNPs reduced at 300 °C and 300/500 °C. (c) proposed structural models for Pt$_{1.2}$Sn-300, Pt$_{1.2}$Sn-500, Pt$_{1.0}$Sn, Pt$_{0.9}$Sn-300, and Pt$_{0.9}$Sn-500 iNPs. The white (yellow) dots represent Pt (Sn) atoms, and the blue dots exclusively represent the Pt atoms located in the core areas.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used to investigate the surface structures of PtSn iNPs where CO serves as the probe molecule (Figure 5.4b). In all DRIFTS spectra of PtSn iNPs, only one mode of atop CO band was observed. However, the respective peak shifts can be readily categorized into two sets matching well to the activation energy set in furfural hydrogenation. Due to the electron
donation from Sn to Pt, accurate intermetallic PtSn (i.e., Pt_{1.0}Sn-300 iNPs) have a low wavenumber shift (2068 cm\(^{-1}\)) in comparison to Pt, which agrees to our previous studies.\(^{24}\)

We also reduced the same Pt\(_{1.0}\)Sn-300 iNPs to 500 °C, and the peak position of as-formed Pt\(_{1.0}\)Sn-500 iNPs almost remains despite a weak intensity being observed. The unmoved peak position demonstrates that accurate Pt\(_{1.0}\)Sn iNPs can have a stable surface structure derived from the well-ordering intermetallic structures. The wavenumber of atop CO band in Pt and accurate Pt\(_{1.0}\)Sn can serve as two benchmarks to evaluate the surface structures of Pt- and Sn-rich PtSn iNPs. The CO adsorption features of Sn-rich Pt\(_{0.9}\)Sn iNPs-500 iNPs resemble that of Pt\(_{1.0}\)Sn iNPs, indicating the presence of accurate PtSn intermetallic structures due to ordering effect at the higher reduction temperatures. Different to accurate Pt\(_{1.0}\)Sn iNPs, Pt-rich Pt\(_{1.2}\)Sn-300, Pt\(_{1.2}\)Sn-500, and Sn-rich Pt\(_{0.9}\)Sn iNPs-300 iNPs show high wavenumber shifts, demonstrating the presence of contiguous Pt sites on surface responsible for their high activity but lower selectivity in furfural hydrogenation. It is noteworthy that Pt-rich Pt\(_{1.2}\)Sn-500 has the highest wavenumber shift surpassing that in monometallic Pt@mSiO\(_2\). In retrospect to the lowest activation energy of Pt\(_{1.2}\)Sn-500, we suspect a unique structure of Pt\(_{1.2}\)Sn-500 can be present particularly favored in the furfural hydrogenation.

Heterogeneous catalysis is highly dependent on the surface structure of catalysis. We have probed surface information of PtSn iNPs from DRIFTS and reaction results of the furfural hydrogenation. EDS, line scan, and XAFS studies also contribute to deriving the bulk information of these PtSn iNPs. We thus proposed the structural models of these four catalysts as shown in Figure 5.4c. The accurate Pt\(_{1.0}\)Sn iNPs have homogeneous distributed Pt and Sn atoms. Differently, Pt\(_{1.2}\)Sn-300 iNPs will have Pt or Sn aggregates on the surface with Pt cores, explaining to their resembled catalysis to pure Pt. After reduced at 500 °C,
Pt$_{1.2}$Sn-500 iNPs will have smaller Pt cores and Pt distribution can become more homogeneous, leading to the formation of Pt-rich top-layer over a PtSn intermetallic sublayer with even higher activity than pure Pt. Similar Pt/PtSn core/shell structures$^{31}$ have been reported with enhanced electrochemical activity, as well as other highly active intermetallic Pt-rich shelled Pt/PtZn$^{32}$ and Pt skinned Pt/Pd NPs.$^{33-34}$ For Sn-rich samples, Pt$_{0.9}$Sn-300 iNPs have similar Pt(Sn) aggregate on the surface. However, the 500 °C reduction can homogenize the structure of Pt$_{0.9}$Sn-500 iNPs with a well-ordered PtSn surface due to high coverage of Sn, agreeing to their closed activation energy but much lower activity in comparison to intermetallic PtSn (Figure 5.4 and S5.7).

To validate these structural models, especially to investigate the surface homogeneity, we further used acetylene semi-hydrogenation as a probe reaction. Acetylene semi-hydrogenation is sensitive to the ensemble Pt sites (aggregates) widely studied over the single site, and intermetallic catalysts.$^{35-37}$ The desired product in acetylene semi-hydrogenation is ethylene, which is more favorable on diluted Pt sites in these single site catalysts and intermetallic compounds. The side pathway of C=C hydrogenation (i.e., ethylene) can lower the selectivity to ethylene in the acetylene conversion, but allow the formation of over-hydrogenated ethane, which is significantly favored on contiguous Pt sites.$^{38}$ We listed the reaction results in Figure 5.5a, b, and Figure S5.8. It is seen that the presence of Pt contiguous sites on Pt$_{1.2}$Sn-300, Pt$_{1.2}$Sn-500, and Pt$_{0.9}$Sn-300 iNP, which leads to higher conversion and a lower selectivity to ethylene as a function of increasing temperature. On the contrary, Pt$_{0.9}$Sn-500 shows a dramatically enhanced selectivity due to the homogeneous dilution of Pt in the intermetallic PtSn structures. The low activity in Pt$_{0.9}$Sn-500 also confirms the presence of Sn coverage on the surface Pt$_{0.9}$Sn-500 iNPs. The
reaction results of furfural hydrogenation and acetylene semi-hydrogenation readily agree to the proposed structural models. We demonstrate the structure-property relationship that chemical reactions can be used as sensitive probes to investigate the surface structures of heterogeneous catalysts in situ reaction conditions.

Figure 5.5. Temperature-dependent conversion and selectivity trends of acetylene semi-hydrogenation over Pt$_{0.9}$Sn and Pt$_{1.2}$Sn iNPs reduced at 300 °C (a) and 300/500 °C (b). 1-2 mg catalyst was used in acetylene semi-hydrogenation with a gas feed of C$_2$H$_2$/C$_2$H$_4$/H$_2$/He=3.0/15.0/1.5/10.4 mL min$^{-1}$. Black triangles and blue dots in Fig. (a and b) represent the catalysis of Pt$_{0.9}$Sn and Pt$_{1.2}$Sn iNPs, respectively. The solid/empty legends of these triangles and dots represent respective conversion and selectivity.

5.4 Conclusion

In summary, we finely tuned the Pt/Sn ratios in PtSn iNPs with three sets of Pt-rich, 1:1, and Sn-rich PtSn iNPs. These PtSn iNPs were reduced under either 300 °C and 300/500 °C to induce the respective surface reconstruction. Furfural hydrogenation and acetylene semi-hydrogenation were used as probe reactions to study the structure-catalysis relationship.
of PtSn iNPs. Pt-rich Pt$_{1.2}$Sn iNPs shows higher activity but lower selectivity due to the presence of Pt heterogeneous sites on surface regardless of reduction temperatures. Meanwhile, Sn-rich Pt$_{0.9}$Sn-300 iNPs have similar Pt contiguous sites on the surface, but higher reduction temperature can induce the reconstruction of the well-ordered PtSn surface with high selectivity in Pt$_{0.9}$Sn-500 iNPs. The composition- and reduction temperature-dependent surface reconstruction was also validated by DRIFTS, associated with HAADF-STEM imaging and XAFS. This study demonstrates that the composition effect in intermetallic compounds can significantly affect their surface structure and catalytic properties. We anticipate that the well-ordered intermetallic structures can be extended to hydrogenation reactions with appropriate structural designs in a more predictable manner.

5.5 Supporting Information

Figure S5.1. X-ray absorption near edge spectra (XANES) of (a) Pt L3 edge and (b) Sn K edge of all PtSn iNPs. The XANES of Pt foil, PtO$_2$, Sn foil, SnO$_2$ samples were provided in respective (a) and (b) as standard references.
Figure S5.2. Fourier-transformed XAFS fittings of Pt $L_3$-edge: (a) Pt$_{0.9}$Sn-300, (b) Pt$_{0.9}$Sn-500, (c) Pt$_{1.0}$Sn-300, (d) Pt$_{1.0}$Sn-500 °C, (e) Pt$_{1.2}$Sn-300, and (f) Pt$_{1.2}$Sn-500 in $R$ space using a $k^3$ weight. Fourier-transformed XAFS fittings of Sn $K$-edge: (g) Pt$_{0.9}$Sn-300, (h) Pt$_{0.9}$Sn-500, (i) Pt$_{1.0}$Sn-300, (j) Pt$_{1.0}$Sn-500, (k) Pt$_{1.2}$Sn-300, and (l) Pt$_{1.2}$Sn-500 in $R$ space using a $k^3$ weight. The grey dots are measured spectra and the red curves are fittings.

Figure S5.3. The time-of-stream results of the conversion and selectivity of (a) Pt$_{1.2}$Sn-300, (b) Pt$_{1.2}$Sn-500, (c) Pt$_{0.9}$Sn-300, and (d) Pt$_{0.9}$Sn-500 iNPs as a function of reaction temperature in furfural hydrogenation.
Figure S5.4. Arrhenius plot of turn-over-frequency (TOF) as a function of temperature over (a) Pt$_{0.9}$Sn-300, Pt$_{0.9}$Sn-500, Pt$_{1.2}$Sn-300, and Pt$_{1.2}$Sn-500 iNPs. The slope is linearly fitted. The respective activation energy is thus calculated as 16.6, 11.4, 17.4, and 28.6 kJ mol$^{-1}$ for Pt$_{0.9}$Sn-300, Pt$_{0.9}$Sn-500, Pt$_{1.2}$Sn-300, and Pt$_{1.2}$Sn-500 iNPs using the fitted slopes.

Figure S5.5. (a) The time-of-stream results of the conversion and selectivity of Pt$_{1.0}$Sn-300 as a function of reaction temperature in furfural hydrogenation. 0.3 mg catalyst was used in furfural hydrogenation with a gas feed of furfural/H$_2$=0.023/11.4 mL min$^{-1}$. (b) Arrhenius plot of turn-over-frequency (TOF) as a function of temperature over Pt$_{1.0}$Sn-300. The slope is linearly fitted as -3.48, and the activation energy is calculated as 28.9 kJ mol$^{-1}$. 
Figure S5.6. (a) The time-of-stream results of the conversion and selectivity of Pt@mSiO$_2$ as a function of reaction temperature in furfural hydrogenation. 0.3 mg catalyst was used in furfural hydrogenation with a gas feed of furfural/H$_2$=0.023/11.4 mL min$^{-1}$. (b) Arrhenius plot of turn-over-frequency (TOF) as a function of temperature over Pt@mSiO$_2$. The slope is linearly fitted as -2.21, and the activation energy is calculated as 18.3 kJ mol$^{-1}$.

Figure S5.7. The turn-over frequency (TOF) results of Pt$_{1.2}$Sn-300, Pt$_{1.2}$Sn-500, Pt$_{0.9}$Sn-300, Pt$_{0.9}$Sn-500, Pt$_{1.0}$Sn-300 iNPs, and Pt-300 NPs at 220 °C in furfural hydrogenation.
Figure S5.8. The time-of-stream results of the conversion and selectivity of (a) Pt$_{1.2}$Sn-300, (b) Pt$_{1.2}$Sn-500, (c) Pt$_{0.9}$Sn-300, and (d) Pt$_{0.9}$Sn-500 iNPs as a function of reaction temperature in acetylene semi-hydrogenation. 1-2 mg catalyst was used in acetylene semi-hydrogenation with a gas feed of C$_2$H$_2$/C$_2$H$_4$/H$_2$/He=3.0/15.0/1.5/10.4 mL min$^{-1}$.

Table S5.1. ICP-MS results of PtSn iNPs with different Pt/Sn ratios.

<table>
<thead>
<tr>
<th>samples</th>
<th>desirable molar</th>
<th>Pt/Sn</th>
<th>measured Pt$<em>{194}$/Sn$</em>{117}$</th>
<th>Pt (wt.%)</th>
<th>Sn (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt$_{0.9}$Sn iNPs</td>
<td>0.90</td>
<td>0.91</td>
<td>30.8</td>
<td>20.0</td>
<td></td>
</tr>
<tr>
<td>Pt$_{1.0}$Sn iNPs</td>
<td>1.00</td>
<td>0.97</td>
<td>36.0</td>
<td>22.8</td>
<td></td>
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<tr>
<td>Pt$_{1.2}$Sn iNPs</td>
<td>1.20</td>
<td>1.24</td>
<td>31.0</td>
<td>15.6</td>
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Table S5.2. Detailed Pt $L_3$ edge XAFS fittings of Pt$_{1.2}$Sn-300, Pt$_{1.2}$Sn-500, Pt$_{0.9}$Sn-300, Pt$_{0.9}$Sn-500, Pt$_{1.0}$Sn-300, and Pt$_{1.0}$Sn-500 iNPs.$^a$

<table>
<thead>
<tr>
<th>items</th>
<th>Pt$_{0.9}$Sn-300</th>
<th>Pt$_{0.9}$Sn-500</th>
<th>Pt$_{1.0}$Sn-300</th>
<th>Pt$_{1.0}$Sn-500</th>
<th>Pt$_{1.2}$Sn-300</th>
<th>Pt$_{1.2}$Sn-500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-Pt CNs</td>
<td>2.0 (0.5)</td>
<td>2.0 (0.5)</td>
<td>2.1 (0.4)</td>
<td>2.0 (0.5)</td>
<td>4.6 (0.3)</td>
<td>2.7 (0.3)</td>
</tr>
<tr>
<td>Energy (eV)</td>
<td>6.0 (1.1)</td>
<td>4.2 (1.1)</td>
<td>4.4 (0.2)</td>
<td>5.0 (1.1)</td>
<td>3.9 (0.9)</td>
<td>4.0 (1.0)</td>
</tr>
<tr>
<td>$R_{\text{Pt-Pt}}$ (Å)</td>
<td>2.73</td>
<td>2.72</td>
<td>2.72</td>
<td>2.72</td>
<td>2.77</td>
<td>2.76</td>
</tr>
<tr>
<td>Pt-Sn CNs</td>
<td>4.5 (0.2)</td>
<td>4.2 (0.4)</td>
<td>3.6 (0.2)</td>
<td>4.2 (0.5)</td>
<td>3.3 (0.2)</td>
<td>4.0 (0.2)</td>
</tr>
<tr>
<td>$R_{\text{Pt-Sn}}$ (Å)</td>
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<td>2.71</td>
<td>2.71</td>
<td>2.71</td>
<td>2.72</td>
<td>2.72</td>
</tr>
<tr>
<td>DW factor$^b$</td>
<td>0.0053</td>
<td>0.0053</td>
<td>0.0047</td>
<td>0.0065</td>
<td>0.0069</td>
<td>0.0068</td>
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<tr>
<td>R factor ($\times 10^{-6}$)</td>
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<td>8.2</td>
<td>4.6</td>
<td>20</td>
<td>66</td>
<td>20</td>
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</table>

$^a$ The value in each parenthesis is the fitting errors. The Pt-Pt coordination in Pt foil in 10.2 in 12-coordinated Pt environments, and this value was used to estimate all Pt-Pt and Pt-Sn coordination numbers. $k = 1.4-13.9$, $R = 1.3-3.6$. $k^3$ weight was used in all fittings. $^b$ Debye-Waller factor (DW) was defined as mentioned values.

Table S5.3. Detailed Sn $K$ edge XAFS fittings of Pt$_{1.2}$Sn-300, Pt$_{1.2}$Sn-500, Pt$_{0.9}$Sn-300, Pt$_{0.9}$Sn-500, Pt$_{1.0}$Sn-300, and Pt$_{1.0}$Sn-500 iNPs.

<table>
<thead>
<tr>
<th>items</th>
<th>Pt$_{0.9}$Sn-300</th>
<th>Pt$_{0.9}$Sn-500</th>
<th>Pt$_{1.0}$Sn-300</th>
<th>Pt$_{1.0}$Sn-500</th>
<th>Pt$_{1.2}$Sn-300</th>
<th>Pt$_{1.2}$Sn-500</th>
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</thead>
<tbody>
<tr>
<td>Sn-Sn CNs</td>
<td>5.7 (0.2)</td>
<td>5.8 (0.4)</td>
<td>6.4 (1.1)</td>
<td>5.9 (0.2)</td>
<td>4.5 (0.2)</td>
<td>5.5 (0.2)</td>
</tr>
<tr>
<td>Energy (eV)</td>
<td>2.2 (1.1)</td>
<td>2.6 (0.7)</td>
<td>6.7 (1.5)</td>
<td>5.7 (1.2)</td>
<td>4.8 (1.2)</td>
<td>6.2 (1.3)</td>
</tr>
<tr>
<td>$R_{\text{Sn-Pt}}$ (Å)</td>
<td>2.71</td>
<td>2.71</td>
<td>2.71</td>
<td>2.72</td>
<td>2.74</td>
<td>2.73</td>
</tr>
<tr>
<td>Sn-O CNs</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.8(0.2)</td>
<td>0.5 (0.3)</td>
</tr>
<tr>
<td>$R_{\text{Sn-O}}$ (Å)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2.1</td>
<td>2.0</td>
</tr>
<tr>
<td>DW factor$^b$</td>
<td>0.007</td>
<td>0.0079(36)</td>
<td>0.0071(12)</td>
<td>0.0082</td>
<td>0.004</td>
<td>0.006</td>
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<tr>
<td>R factor ($\times 10^{-5}$)</td>
<td>36</td>
<td>15</td>
<td>16</td>
<td>8.2</td>
<td>8.2</td>
<td>16</td>
</tr>
</tbody>
</table>

$^a$ The value in each parenthesis is the fitting errors. The Pt-Pt coordination in Pt foil in 10.2 in 12-coordinated Pt environments, and this value was used to estimate all Sn-Sn and Sn-O coordination numbers. $k = 1.5-13.0$, $R = 1.2-3.3$. $k^3$ weight was used in all fittings. $^b$ Debye-Waller factor (DW) was defined as mentioned values except for two values with parenthesis, and the value in each parenthesis is the error during the fittings.
5.6 References


CHAPTER 6. TUNING SURFACE PROPERTIES OF AMINO-FUNCTIONALIZED SILICA FOR METAL NANOPARTICLE LOADING: THE VITAL ROLE OF AN ANNEALING PROCESS

*Modified from a publication in the Surface Science


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6.1 Abstract

Metal nanoparticles (NPs) loaded on oxides have been widely used as multifunctional nanomaterials in various fields such as optical imaging, sensors, and heterogeneous catalysis. However, the deposition of metal NPs on oxide supports with high efficiency and homogeneous dispersion still remains elusive, especially when silica is used as the support. Amino-functionalization of silica can improve loading efficiency, but metal NPs often aggregate on the surface. Herein, we report that a facial annealing of amino-functionalized silica can significantly improve the dispersion and enhance the loading efficiency of various
metal NPs, such as Pt, Rh, and Ru, on the silica surface. A series of characterization techniques, such as diffuse reflectance infrared Fourier transform spectroscopy (DRIFT), Zeta potential analysis, UV-vis spectroscopy, thermogravimetric analysis coupled with infrared analysis (TGA-IR), and nitrogen adsorption, were employed to study the changes of surface properties of the amino-functionalized silica before and after annealing. We found that the annealed amino-functionalized silica surface has more cross-linked silanol groups and relatively lesser amount of amino groups, and less positively charges, which could be the key to the uniform deposition of metal NPs during the loading process. These results could contribute to the preparation of metal/oxide hybrid NPs for the applications that require uniform dispersion.

6.2 Introduction

Hybrid NPs, endowed with two or more unique properties, have been the focus of growing attention as advanced nanoarchitectures in a wide spectrum of applications, such as optical and magnetic imaging, drug delivery, energy harvesting, and heterogeneous catalysis. Of specific interest are inorganic hybrid NPs that metal NPs (Au, Ru, Pt, Pd etc.) decorated on well-designed metal oxides (SiO₂, Al₂O₃ and Fe₃O₄). For example, Au/SiO₂ with tunable sizes is effectively utilized in surface-enhanced Raman spectroscopy (SERS) and surface plasmon resonance (SPR). Replacing the SiO₂ support with magnetic Fe₃O₄, the obtained hybrid Au/Fe₃O₄ NPs have been considered as promising candidates for in-vivo diagnostic tests that include both optical detection and targeting capabilities under an external magnetic field. Using Rh, Pt, and Pd NPs, the design of versatile supported heterogeneous oxide-supported metal hybrid NPs can also be achieved, such as Rh/SiO₂, Pd/Al₂O₃ and Pt/CeO₂. The assembly of metal NPs on oxides possesses exceptional advantages ranging from the
size control of metal NPs, enhanced thermal stabilities provided by oxide supports, and the utilization of metal-oxide interactions. These evince the metal/oxide hybrid NPs as multifunctional catalysts for a number of reactions.

The dispersion homogeneity and size uniformity of these hybrid NPs are highly desirable, due to the size and shape-dependent properties in practical applications. For catalytic purposes, the aggregation of NPs would significantly deactivate catalysts, due to the decreased surface area. Well-dispersed and separated metal NPs on oxide supports are thus beneficial to relieve the aggregation tendency of NPs during thermal pretreatment and harsh catalytic reaction conditions. Monodispersity and size homogeneity of hybrid NPs are also regarded as important criteria in the fabrication of efficient light harvesting materials and solar cell films. Surface smoothness, interparticle spacing and uniformity of the self-assembled NPs are also highly demanded for high quality optical detection and magnetic resonance imaging.

Several conventional strategies have been studied to obtain various metal/oxide hybrid NPs: i) growth of metal components on oxides or reversed approach, such as reduction of metal ions on preformed oxides NPs, decomposition of one metal precursor on other preformed metal NPs followed by oxidation, and chemical-triggered phase segregation of alloy NPs; and ii) direct deposition of preformed metal NPs on oxides via colloidal method. Strategy i) is challenging to accomplish the uniform growth of metal NPs on other surfaces. Strategy ii) provides a more advantageous platform to prepare metal/oxide hybrid NPs with precise controls in size and geometry by isolating the synthesis of metal NPs and oxide substrates in advance of the colloidal deposition. Among the direct deposition, charged metal NPs can be well dispersed on various substrates due to the electrostatic repulsion between metal NPs. Hydrophobic/hydrophilic interactions also play
important roles in instances that involve loading ligand-protected neutral metal NPs onto substrates. Nevertheless, the direct assembly of metal NPs on bare oxides with uniform dispersion and high loading efficiency is still challenging due to the complicated surface compatibility of metal/oxide interfaces derived from diverse synthetic methods. Chemical functionalization of the oxides is an alternative strategy to enhance metal NP-oxide interactions utilizing the chemical bonding. Amino-, thiol- and carboxylic-terminated alkyl groups are commonly functionalized on the surface of silica to anchor various ligand-capped precious metal NPs through strong coordinating interactions, such as Au, Pt, Rh and Pd. However, the general mechanism of assembly remains unsolved leading to the empirical endeavors in the fabrication of metal/oxide hybrid NPs.

Recent studies have revealed that the pretreatment steps on oxide substrates, such as heating and drying, can tune the surface characteristics and thus likely improve the uniformity of the coating material on such substrate. For example, a mild thermal treatment of SiO$_2$ was found to be advantageous to obtain conformal CeO$_2$ coatings in the synthesis of SiO$_2$@CeO$_2$ NPs. In this article, we have used amino-functionalized silica spheres (NH$_2$-SiO$_2$) as a model system to study the loading of metal NPs on them. We demonstrate herein that the annealing process performed on NH$_2$-SiO$_2$ can largely improve both the dispersion and loading efficiency of diverse precious metal NPs. We explored the surface variance of NH$_2$-SiO$_2$ pertaining to this annealing process, zeroing in on the most important factors that affect the loading of metal NPs. This annealing process can be easily executed, thus broadening its technical applications for the efficient manufacture of various metal/oxide nanostructures.
6.3 Experimental

The synthesis of 200 nm SiO$_2$ spheres with uniform particle size (deviation <5%)

200 nm SiO$_2$ spheres were synthesized by a four-step seeded growth approach.$^{44}$ 24 nm SiO$_2$ seeds: 18.2 mg L-arginine and 13.9 mL of ultrapure water were mixed thoroughly. Then 0.9 mL of cyclohexane was added gently to the water-arginine solution without disturbing the two-layer solution. The solution was heated to 60.0 ± 0.2 °C for 30 min at 300 rpm. 1.10 mL of TEOS was added to the mixture. The reaction was kept for 20 hrs at 60 °C. After reaction, the bottom layer was taken out and kept in the refrigerator (Sample A).

45 nm SiO$_2$ seeds: 4 mL of the 24 nm seeds (Sample A) was taken and diluted with 14.4 mL ultrapure water after which 2 mL cyclohexane was added. The mixture was brought to 60 °C for 30 min at 300 rpm. Then 1.408 mL TEOS was added to the top layer immediately, and the mixture was kept at 60°C for 30 hrs. After reaction, the bottom layer was taken out and kept in refrigerator (Sample B).

82 nm SiO$_2$ seeds using Stöber method

1 mL of the 45 nm seeds (Sample B) was taken and diluted with 2.6 mL deionized water and 18 mL ethanol. Subsequently, 1.7 mL NH$_3$·H$_2$O (~28%) was added. The solution was mixed at ~ 500 rpm for 1 hr at room temperature. Total 0.8 mL TEOS was added to the solution dropwise, three times at intervals of 30 mins. The solution was stirred for 6 hrs and later kept in the refrigerator (Sample C)

200 nm SiO$_2$ spheres using Stöber method

1 mL of the 82 nm seeds (Sample C) was taken and diluted with 2.6 mL deionized
water and 18 mL ethanol. 1.7 mL NH$_3$H$_2$O (~28%) was added. The solution was mixed at ~500 rpm for 1 hr. A total volume of 0.44 mL TEOS was added to the solution dropwise twice at intervals of 30 mins. After 6 hrs, 200 nm SiO$_2$ spheres (Sample D) were obtained and kept in the refrigerator for further use. This step could be easily scaled up. In our lab, >10 g silica spheres could be obtained in one batch. The size deviation is typically within ±10 nm.

The purification of SiO$_2$ spheres was conducted by washing them 5 times with an ethanol/water solution (50/50 v/v). The purified SiO$_2$ spheres were stored in ethanol.

The synthesis of 5 nm Pt, 4 nm Rh, and 1.8 nm Ru NPs

All metal NPs were synthesized according to previously reported literature with modifications.\textsuperscript{45}

5 nm Pt NPs: 41.5 mg K$_2$PtCl$_4$, 505 mg C$_{14}$TAB and 222 mg PVP (K30) were mixed in 20 mL EG with sonication. Under argon protection, the mixed solution was heated to 140 °C for 2 hrs. After reaction, Pt NPs were precipitated by adding excessive acetone (acetone:EG = 9:1). The precipitate was further washed 5 times with an ethanol/hexane mixture (1/4 v/v). Purified 5 nm Pt NPs were dispersed in 20 mL ethanol.

4 nm Rh NPs and 1.8 nm Ru NPs: The synthetic conditions and purification procedure are the same as 5 nm Pt NPs except for using 20.7 mg RhCl$_3$·xH$_2$O and 20.7 mg RuCl$_3$·xH$_2$O respectively as starting materials.

The synthesis of NH$_2$-SiO$_2$\textsuperscript{3,59}

1.0 g SiO$_2$ spheres (1.0 g) were centrifuged from the original ethanol solution and re-dispersed in 175 mL isopropanol. 200 μL APTS was dissolved in 25 mL isopropanol and mixed
with the above SiO$_2$-isopropanol solution. A round-bottom flask containing the mixed solution was heated to 80 °C. The reaction was stopped after 2 hrs. NH$_2$-SiO$_2$ spheres were separated, washed with ethanol 3 times and stored in 20 mL ethanol.

The annealing process of NH$_2$-SiO$_2$

As-synthesized NH$_2$-SiO$_2$ spheres were taken out from their ethanol solution and dried in vacuum at room temperature. The dried solids were annealed in an oven in air at 100 °C for 5 hrs, then cooled down to room temperature naturally.

The preparation of metal NPs (M) loaded on NH$_2$-SiO$_2$ (M/NH$_2$-SiO$_2$)

Typically, 200 mg NH$_2$-SiO$_2$ (fresh or annealed) spheres were taken out and dispersed in 60 mL ethanol. The appropriate amount of the metal NPs solution was taken out according to the desired metal loading and diluted to a final volume of 110 mL with ethanol. The 110 mL diluted metal NPs solution was added to 60 mL NH$_2$-SiO$_2$ solution dropwise with vigorous magnetic stirring. After addition, the resulting M/NH$_2$-SiO$_2$ solution was further sonicated for 30 min. After separation, the M/NH$_2$-SiO$_2$ precipitate was washed with ethanol 5 times and stored in ethanol.

Characterization

Zeta potential analysis was conducted in neutral ethanol solvent under a Malvern Zetasizer Nano ZS90 with MPT-2 autotitrator. The amount of amine sites on modified silica spheres was determined by titration: 150 mg of NH$_2$-SiO$_2$ was dispersed in 5.0 g ultrapure water with sonication. The solution was neutralized with 0.1 M NaOH solution first, and then
back titrated with 0.1 M HCl solution in the presence of bromothymol blue indicator. The surface area measurements were performed with N₂ adsorption/desorption isotherms at −196 °C on a Micromeritics 3Flex instrument. Before the analysis, the samples were evacuated under vacuum (~5–10⁻⁵ Torr) for 12 hrs at room temperature. The diffuse reflectance UV-Vis spectra and transmission UV-Vis spectra were acquired using StellaNet Black-Comet C-SR-100 spectrometer and Varian Cary 50 Bio UV-Visible spectrophotometer respectively. TGA-IR experiments were performed on Netzsch DSC/TGA-MS/IR in O₂/N₂ flow (10/40 mL/min).

6.4 Results and Discussion

We utilized the general colloidal method to load metal NPs on NH₂-SiO₂ spheres. Uniform metal NPs and monodisperse 200 nm NH₂-SiO₂ spheres were synthesized following reported literatures⁴⁴,⁴⁵ and diluted to certain volumes before the loading process. The colloidal solution of metal NPs was added dropwise into the solution of NH₂-SiO₂ under vigorous stirring. The annealing process was found to be essential to obtain well-dispersed metal NP loadings. After vacuum drying them at room temperature, the as-made NH₂-SiO₂ powders were annealed at 100 °C in air for 5 hrs, denoted as “annealed NH₂-SiO₂”. We also loaded metal NPs on fresh NH₂-SiO₂ spheres without the annealing process as experimental controls. Other synthetic conditions related to the dispersion of metal NPs loadings were carefully controlled to be constants, such as dropping rate, stirring rate, and the total volume of metal NPs and NH₂-SiO₂ solutions. We used three precious metal NPs including Pt, Rh and Ru to illustrate the dispersion of metal NPs on NH₂-SiO₂. These samples are denoted as 5 nm Pt/NH₂-SiO₂, 4 nm Rh/NH₂-SiO₂ and 1.8 nm Ru/NH₂-SiO₂. With 5 wt% target loadings of Pt, Rh and Ru NPs, the actual loading amounts of metal to NH₂-SiO₂ were determined by ICP-MS.
TEM images of 5 nm Pt, 4 nm Rh and 1.8 nm Ru NPs on fresh and annealed NH$_2$-SiO$_2$ are shown in Figure 6.1. The dispersion of metal NPs on annealed NH$_2$-SiO$_2$ was significantly improved compared to fresh NH$_2$-SiO$_2$. For 5 nm Pt, 4 nm Rh and 1.8 nm Ru NPs, it is clearly seen that many domains of NP aggregations were observed when loaded on fresh NH$_2$-SiO$_2$. These domains comprise of several NPs piled on each other and lead to some NH$_2$-SiO$_2$ agglomerations. Even though some separated NPs were found on the surface of fresh NH$_2$-SiO$_2$, they were not distributed evenly. After treating the fresh NH$_2$-SiO$_2$ with the annealing process, all metal NPs can be loaded uniformly and clearly appear to be separated on the annealed NH$_2$-SiO$_2$ surface. It is evident that the annealing process is crucial in achieving the exceptional uniform dispersion of metal NPs on the NH$_2$-SiO$_2$ surface.

To investigate the key role of the annealing process in the dispersion of metal loadings, we used nitrogen adsorption, acid-base titration, TGA-IR, DRIFT and Zeta potential analysis to study the surface characteristics of both fresh and annealed NH$_2$-SiO$_2$. The surface area of NH$_2$-SiO$_2$ was measured with N$_2$ adsorption performed at $-196^\circ$C. As shown in Figure 6.2, the isotherms of both fresh and annealed NH$_2$-SiO$_2$ samples show type II characteristics. The detailed results are summarized in Table 6.1. BET surface areas of fresh and annealed NH$_2$-SiO$_2$ were determined to be 14.0 and 14.4 m$^2$·g$^{-1}$, respectively. For fresh and annealed samples, the respective micropore volume is 0.0016 and 0.0019 m$^3$·g$^{-1}$. The BET surface areas are intrinsically the same to the theoretical value (14.4 m$^2$·g$^{-1}$), using the following equation:

$$A = \frac{6000}{\rho d}$$

Where $\rho$ is the density of amorphous silica (2.08 g·cm$^{-3}$) and $d$ is the diameter of the silica spheres (200 nm). These results suggest that the fresh and annealed NH$_2$-SiO$_2$ spheres are non-porous. However, we should point out that we only activated NH$_2$-SiO$_2$ under vacuum
at room temperature for 12 hrs, which could still leave micropores (if any) filled with solvent molecules and thus cannot be detected by N$_2$ physisorption.

Amino groups attached to NH$_2$-SiO$_2$ spheres are vital to bind metal NPs. The amount of amino groups was determined by acid-base titration, as shown in Table 6.2. The number of amino sites per square nanometer was measured to be 12.1 ± 0.6 for the fresh NH$_2$-SiO$_2$. This number is higher than the typical concentration of surface silanol groups on silica surface (3-7 ea·nm$^{-2}$). However, it is known that preparation and pretreatment methods could lead to such changes, and it possibly implies that dangling oligomers of amino-polysiloxanes could present during the amino functionalization of silica spheres. Also, we noticed that measured BET surface areas of NH$_2$-SiO$_2$ sphere were likely lower than the actual surface areas due to the insufficient degas process performed at room temperature. Using the underestimated silica surface area in amino group density calculation could lead to a higher than expected value. After the annealing process, the number of amino groups dramatically dropped to 0.29 ± 0.05 ea·nm$^{-2}$. We speculate that the reduction of accessible amino sites on the surface could be due to the chemical decomposition or the cleavage of the oligomers of amino-polysiloxanes during the annealing process. This was confirmed using the TGA-IR technique and is discussed later.

The quantity difference of surface amino groups on fresh NH$_2$-SiO$_2$ and annealed NH$_2$-SiO$_2$ were further determined by spectrometric methods using Rhodamine B as the probe molecule. We mixed the Rhodamine B with NH$_2$-SiO$_2$, where the carboxylic groups on Rhodamine B can react with surface amino groups to be anchored on the NH$_2$-SiO$_2$ spheres. We separated the Rhodamine B modified fresh NH$_2$-SiO$_2$ and annealed NH$_2$-SiO$_2$ from solution by centrifugation. Free Rhodamine B molecules were washed away thoroughly until the supernatant was clear. The Rhodamine B modified fresh NH$_2$-SiO$_2$ and annealed NH$_2$-SiO$_2$
were dried at room temperature and measured under diffuse reflectance UV-Vis spectrometry as shown in Figure 6.3. The adsorption of free Rhodamine B was determined using a transmission UV-Vis spectrometer in ethanol, with a peak being observed at 544 nm (Figure S6.1). Based on the Rhodamine B adsorption, it is clearly seen in Figure 6.3 that both Rhodamine B modified fresh NH$_2$-SiO$_2$ and annealed NH$_2$-SiO$_2$ demonstrate a broad peak at 540 nm, which is attributed to the anchored Rhodamine B molecules. The fresh NH$_2$-SiO$_2$ presents a more intense adsorption of Rhodamine B, comparing to the annealed NH$_2$-SiO$_2$. This serves to indicate that more surface amino groups are present on fresh NH$_2$-SiO$_2$ than annealed NH$_2$-SiO$_2$, which has been confirmed earlier by the titration results. Comparing with the acid-base titration results to reveal the significant difference of amino groups between fresh and annealed NH$_2$-SiO$_2$, the difference of the anchored Rhodamine B peak between the fresh and annealed samples is smaller. This could be attributed to the different sizes of proton and Rhodamine B molecules. Because the concentration of surface amino groups is very high in the fresh sample, Rhodamine B could occupy the space of several amine sites.

In DRIFTS, we examined bare SiO$_2$, fresh NH$_2$-SiO$_2$ and annealed NH$_2$-SiO$_2$ in air at room temperature, as shown in Figure 6.4a. Significant differences were found with the broad features in 3100-3700 cm$^{-1}$ region. For bare SiO$_2$, we observed a bump at around 3120 cm$^{-1}$, which is designated as the hydrogen bonded SiO–H groups together with physically adsorbed water.$^{49}$ This revealed the hydrophilic nature of bare SiO$_2$. Bare SiO$_2$, fresh NH$_2$-SiO$_2$ and annealed NH$_2$-SiO$_2$ displayed a broad peak in the 3300-3400 cm$^{-1}$ region with a shoulder at around 3650–3700 cm$^{-1}$. The first broad peak can be ascribed to the SiO–H stretching and N–H vibrations; meanwhile the latter region is ascribed to free silanol groups. Typically, free N-H stretching was reported comprising of two peaks at around 3300 cm$^{-1}$ and 3200 cm$^{-1}$,
respectively. In our cases, N-H vibrations are not well resolved from the broad SiO–H stretching. However, both fresh and annealed NH$_2$-SiO$_2$ exhibits similar widening and stronger intensity of the 3300-3400 cm$^{-1}$ peak in contrast to bare SiO$_2$. This may be due to the contribution of N-H vibrations from the surface amino groups. When comparing annealed NH$_2$-SiO$_2$ with fresh NH$_2$-SiO$_2$, the intensity of 3300 cm$^{-1}$ peak increased with a slight shift to higher wavenumber region and the hydrogen bonded SiO–H peak (3120 cm$^{-1}$) disappeared. This shift indicates the dehydration and dehydroxylation of SiO–H groups, which evinces that the annealing process can induce the cross-link of the SiO–H groups. The intense doublet peaks at 1000-1250 cm$^{-1}$ are designated as Si-O-Si (1130-1000 cm$^{-1}$) and Si-R (R=alkyl or ethoxyl groups, 1200-1250 cm$^{-1}$) groups, respectively. C-N vibrations are also reported within this region even though they are not clearly resolved in our observations. The intensity of the first 1000 cm$^{-1}$ partial peak (Si-O-Si groups) in annealed NH$_2$-SiO$_2$ also increased, comparing to that of both fresh NH$_2$-SiO$_2$ and bare SiO$_2$. This further illustrates the condensation of silanol groups due to the annealing process.

The multi-peak features around 1300-1500 cm$^{-1}$ and 2900-3000 cm$^{-1}$ were observed in all three samples with no obvious difference in intensity, which can be attributed to C-H vibrations. This may be due to the residual solvent such as ethanol or the incomplete hydrolysis of TEOS during the synthesis of silica spheres. We conducted two control experiments to figure this out. We heated the sample to 300°C in He, but still observed the same peak with no significant changes in the intensity. Thus it is not likely to be from residual ethanol (Figure S6.2). While in the control to exhibit the C-H vibration of TEOS, we drop-casted pure TEOS in KBr pellets. C-H vibrations of TEOS were observed with the similar contour and at the same wavenumber region as shown in all SiO$_2$ samples (Figure S6.3).
Figure 6.1. TEM images of (a) 5 nm Pt NPs; (b) 5 nm Pt/fresh NH$_2$-SiO$_2$; (c) 5 nm Pt/annealed NH$_2$-SiO$_2$; (d) 4 nm Rh NPs; (e) 4 nm Rh/fresh NH$_2$-SiO$_2$; (f) 4 nm Rh/annealed NH$_2$-SiO$_2$; (g) 1.8 nm Ru NPs; (h) 1.8 nm Ru/fresh NH$_2$-SiO$_2$; (i) 1.8 nm Ru/annealed NH$_2$-SiO$_2$.

We also conduct a time-dependent in situ DRIFTS analysis to study the kinetics of surface characteristics via the annealing process. Fresh NH$_2$-SiO$_2$ sample was heated at 100 °C for 5 hrs under He flow. As shown in Figure 6.4b, we observed a similar shift of the broad 3300 cm$^{-1}$ peak to the high wavenumber region, indicating the more cross-linked
characteristics of SiO–H groups. In this time-dependent control, a bump at 3650-3700 cm\(^{-1}\) is clearly observed, arising gradually during heating, ascribed as free single silanol groups (3747 cm\(^{-1}\)).\(^{51}\) It is known that the dehydroxylation of single silanol groups is difficult.\(^{55,56}\) The exposure of free silanol groups due to the dehydroxylation of hydrogen bonded SiO–H groups (3120 cm\(^{-1}\)) would release the free silanol neighbors during heating.\(^{49}\) The increasing intensity of this free silanol peak can serve as an important indication for the more cross-linked surface characteristics. Supported by these DRIFTS results, we suggest that the annealing process of NH\(_2\)-SiO\(_2\) can result in the decrease of hydrogen bonded SiO–H groups on NH\(_2\)-SiO\(_2\) surface due to the dehydroxylation under high temperatures.

Table 6.1. Nitrogen adsorption of amino-functionalized silica spheres\(^a\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m(^2)·g(^{-1}))</th>
<th>Langmuir Surface area (m(^2)·g(^{-1}))</th>
<th>Microporous surface area (m(^2)·g(^{-1})) (b)</th>
<th>External surface area (m(^2)·g(^{-1})) (b)</th>
<th>Micropore volume (m(^3)·g(^{-1})) (b)</th>
<th>Calculated surface area (m(^2)·g(^{-1})) (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh NH(_2)-SiO(_2)</td>
<td>14.0</td>
<td>17.1</td>
<td>3.5</td>
<td>10.4</td>
<td>0.0016</td>
<td>14.4</td>
</tr>
<tr>
<td>Annealed NH(_2)-SiO(_2)</td>
<td>14.4</td>
<td>17.1</td>
<td>3.5</td>
<td>10.9</td>
<td>0.0019</td>
<td>14.4</td>
</tr>
</tbody>
</table>

\(^a\) Approximately 500 mg SiO\(_2\) was used in each experiment. \(^b\) Obtained from t-plot analysis between the range 5.1-7.8 Å, which is a straight line. \(^c\) A diameter of 200 nm and a density of 2.08 g·cm\(^{-1}\) was assumed for the silica spheres.

To further illustrate the surface difference of NH\(_2\)-SiO\(_2\) during the annealing process, we utilized TGA-IR measurements to study the weight loss of fresh NH\(_2\)-SiO\(_2\) after a temperature ramping process from room temperature to 100 °C under 20% O\(_2\)/N\(_2\) flow. The evolved gas phase products were monitored \textit{in situ} by IR during the temperature ramping process. As shown in Figure 6.5a, the 1 % mass loss was observed when temperature reached
100 °C. For the *in situ* IR analysis, we monitored the products in the airflow when the temperature reached 100 °C. We observed significant ethanol and water peaks with increasing intensity at longer annealing time (Figure 6.5b, see ethanol standard spectra in Figure S6.4). This confirmed that the loss of water during annealing as well as shown in the DRIFT spectra. Notably, we observed the N-H bending and stretching vibrations at 931, 966, and 3334 cm⁻¹, respectively, in the enlarged IR spectra in Figure 6.5c and d (see NH₃ standard spectra in Figure S6.4). With longer annealing time, the intensity of N-H vibration increased gradually, indicating the consistent loss of N-H groups during the annealing process. Using *in situ* TGA-IR, we demonstrated that fresh NH₂-SiO₂ sample would lose water, ethanol and –NH₂ groups under high temperatures. We thus suggest that annealed NH₂-SiO₂ would present more cross-linked silanol groups and less accessible NH₂ groups compared to fresh NH₂-SiO₂.

![Image of N₂ adsorption-desorption isotherms](image)

Figure 6.2. N₂ adsorption-desorption isotherms of fresh NH₂-SiO₂ and annealed NH₂-SiO₂

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amount of Amino groups (mol·g⁻¹)</th>
<th>Concentration of amino groups (ea·nm⁻²)ᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh NH₂-SiO₂</td>
<td>2.8 ± 0.1×10⁻⁴</td>
<td>12.1 ± 0.6</td>
</tr>
<tr>
<td>Annealed NH₂-SiO₂</td>
<td>7.0 ± 1.1×10⁻⁶</td>
<td>0.29 ± 0.05</td>
</tr>
</tbody>
</table>

ᵃ Approximately 150 mg SiO₂ sample was used in each experiment. ᵇ Measured BET surface area was used in the calculations.
Figure 6.3. Diffuse reflectance UV-Vis spectra of the Rhodamine B modified fresh NH$_2$-SiO$_2$ and annealed NH$_2$-SiO$_2$.

Figure 6.4. (a) DRIFT spectra of bare SiO$_2$, fresh NH$_2$-SiO$_2$ and annealed NH$_2$-SiO$_2$ at room temperature; (b) time-dependent DRIFT spectra of fresh NH$_2$-SiO$_2$ at 100 °C for 5 hrs in 20 mL/min He flow. The band in the range of 2800-3000 cm$^{-1}$ is due to residual ethoxyl groups introduced from TEOS.

To further illustrate the surface difference of NH$_2$-SiO$_2$ during the annealing process, we utilized TGA-IR measurements to study the weight loss of fresh NH$_2$-SiO$_2$ after a
temperature ramping process from room temperature to 100 °C under 20% O₂/N₂ flow. The evolved gas phase products were monitored in situ by IR during the temperature ramping process. As shown in Figure 6.5a, the 1 % mass loss was observed when temperature reached 100 °C. For the in situ IR analysis, we monitored the products in the airflow when the temperature reached 100 °C. We observed significant ethanol and water peaks with increasing intensity at longer annealing time (Figure 6.5b, see ethanol standard spectra in Figure S6.4). This confirmed that the loss of water during annealing as well as shown in the DRIFT spectra. Notably, we observed the N-H bending and stretching vibrations at 931, 966, and 3334 cm⁻¹, respectively, in the enlarged IR spectra in Figure 6.5c and d (see NH₃ standard spectra in Figure S6.4). With longer annealing time, the intensity of N-H vibration increased gradually, indicating the consistent loss of N-H groups during the annealing process. Using in situ TGA-IR, we demonstrated that fresh NH₂-SiO₂ sample would lose water, ethanol and –NH₂ groups under high temperatures. We thus suggest that annealed NH₂-SiO₂ would present more cross-linked silanol groups and less accessible NH₂ groups compared to fresh NH₂-SiO₂.

Based on the previous results from DRIFT, UV-Vis, TGA-IR and titration, the numbers of surface silanol and accessible NH₂ groups were greatly reduced after annealing. This may lead to the changes in surface charge. We then conducted Zeta potential (ζ) analysis for bare SiO₂, fresh NH₂-SiO₂, annealed NH₂-SiO₂, metal NPs and M/NH₂-SiO₂ (M = Pt, Rh, Ru). The results are summarized in Table 6.3. All samples were diluted with ethanol in a neutral environment for analysis. Bare SiO₂ has a negative value of ζ as -25.9 mV, conformed to the non-functionalized SiO₂ surface covered by strong negatively charged SiO–H groups. After amino functionalization, a positive value of ζ was observed for fresh NH₂-SiO₂ at 27.9 mV. This indicates that the amino-functionalized NH₂-SiO₂ surface attained a strong positively
charged characteristic, derived from the coverage of -NH₂ groups or -NH₃⁺ groups. After annealing, the ζ value of bare silica increased to −14.7 mV, which could be caused by the dehydroxylation of silanol groups. It is noteworthy that the ζ value of NH₂-SiO₂ decreased to 17.2 mV. This can only be explained by the loss of both accessible amino groups and silanol groups on the surface, which is consistent with previous results indicating the presence of less surface amino groups from UV-Vis, TGA-IR and titrations and less silanol groups detected from DRIFT.

Figure 6.5. (a) TGA spectra of fresh NH₂-SiO₂ heated in 20% O₂/N₂; (b) Time-dependent in situ IR spectra of evolved gas phase products when the temperature reaches 100 °C; (c) and (d) the enlarged IR spectra to clearly see the increased intensity of N-H vibrations at 900-1000 cm⁻¹ and 3300-3500 cm⁻¹ regions.

Differing from strongly charged SiO₂ surface, Pt, Rh and Ru NPs have a slightly negative ζ of −1.4, −5.4 and -0.8 mV, respectively. The negative charged characteristics could
come from the electron donation interactions between metal and the capping agent, PVP, previously observed in Au-PVP NPs.\textsuperscript{59,60} This suggests that electrostatic interactions between metal NPs and NH\textsubscript{2}-SiO\textsubscript{2} can affect metal NPs loadings together with coordinating interactions between metal NPs and amino groups.

Table 6.3. The summary of Zeta potential (\(\zeta\)) values.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Loading amount /wt %</th>
<th>(\zeta)/mV</th>
<th>(\Delta\zeta)/mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>bare SiO\textsubscript{2}, fresh</td>
<td>-</td>
<td>-25.9</td>
<td>2.7</td>
</tr>
<tr>
<td>bare SiO\textsubscript{2}, annealed</td>
<td>-</td>
<td>-14.7</td>
<td>2.0</td>
</tr>
<tr>
<td>NH\textsubscript{2}-SiO\textsubscript{2}, fresh</td>
<td>-</td>
<td>27.9</td>
<td>2.3</td>
</tr>
<tr>
<td>NH\textsubscript{2}-SiO\textsubscript{2}, annealed</td>
<td>-</td>
<td>17.2</td>
<td>1.2</td>
</tr>
<tr>
<td>5 nm Pt/NH\textsubscript{2}-SiO\textsubscript{2}, fresh</td>
<td>1.3</td>
<td>23.7</td>
<td>2.2</td>
</tr>
<tr>
<td>5 nm Pt/NH\textsubscript{2}-SiO\textsubscript{2}, annealed</td>
<td>2.0</td>
<td>14.2</td>
<td>0.8</td>
</tr>
<tr>
<td>4 nm Rh/NH\textsubscript{2}-SiO\textsubscript{2}, fresh</td>
<td>0.8</td>
<td>6.6</td>
<td>0.3</td>
</tr>
<tr>
<td>4 nm Rh/NH\textsubscript{2}-SiO\textsubscript{2}, annealed</td>
<td>1.0</td>
<td>2.1</td>
<td>0.6</td>
</tr>
<tr>
<td>1.8 nm Ru/NH\textsubscript{2}-SiO\textsubscript{2}, fresh</td>
<td>1.2</td>
<td>1.4</td>
<td>0.3</td>
</tr>
<tr>
<td>1.8 nm Ru/NH\textsubscript{2}-SiO\textsubscript{2}, annealed</td>
<td>1.3</td>
<td>-1.4</td>
<td>0.3</td>
</tr>
<tr>
<td>5 nm Pt NPs</td>
<td>-</td>
<td>-1.4</td>
<td>0.3</td>
</tr>
<tr>
<td>4 nm Rh NPs</td>
<td>-</td>
<td>-5.4</td>
<td>0.5</td>
</tr>
<tr>
<td>1.8 nm Ru NPs</td>
<td>-</td>
<td>-0.8</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Recalling the above results, the annealed NH\textsubscript{2}-SiO\textsubscript{2} has both less positively charged surface and less accessible amino groups compared to the fresh NH\textsubscript{2}-SiO\textsubscript{2} surface, which leads to the better dispersion of metal NPs. Interestingly, this surface characteristic of annealed NH\textsubscript{2}-SiO\textsubscript{2} with weak electrostatic and coordinating interactions can also induce better metal loading efficiency compared to that of fresh NH\textsubscript{2}-SiO\textsubscript{2} as shown in Table 6.3. We thus proposed a
possible mechanism concerning the interactions of metal NPs with NH$_2$-SiO$_2$ surface, as shown in Scheme 6.1. When free metal NPs approach NH$_2$-SiO$_2$ surface, electrostatic interaction is predominant between them due to their charged nature. The less positively charged surface of annealed NH$_2$-SiO$_2$ might slow down the loading process of metal NPs due to the weaker electrostatic interactions. The slower loading rate could allow a “pick up” mechanism wherein the silica sphere grabs individual metal NP from an assembly of a bunch of metal NPs interconnected with PVP. Since NH$_2$-SiO$_2$ and metal NPs move freely in the solution, the docking position of metal NPs would be random. Moreover, the binding of the metal NP to NH$_2$-SiO$_2$ surface led to a lower surface charge at the docking position compared to other places. Thus, the next metal NP may prefer other docking positions far away from an occupied one because these possess higher positive charge and more accessible amino groups. Appropriate amount of amino groups on silica spheres could be the key leading to uniform dispersion of metal NPs.

Scheme 6.1. Proposed mechanism of loading metal NPs onto NH$_2$-SiO$_2$ spheres. a) Fast loading process on fresh NH$_2$-SiO$_2$; b) slow loading process (pick-up mechanism) on annealed NH$_2$-SiO$_2$ NPs.
6.5 Conclusion

In this work, we presented a facile annealing process of NH$_2$-SiO$_2$ for efficient metal NP loadings. This method was demonstrated to be robust to load common metal NPs on NH$_2$-SiO$_2$ spheres, such as Pt, Rh and Ru NPs. A series of experiments, including DRIFT, UV-Vis, TGA-IR, acid-base titration and Zeta potential analysis, were conducted to elucidate the surface variance of NH$_2$-SiO$_2$ due to this annealing process. The results revealed that annealed NH$_2$-SiO$_2$ surface possessed more cross-linked silanol groups, much less amino groups, and less positive charges. A “pick up” mechanism was proposed to elucidate the loading process of metal NPs onto the annealed NH$_2$-SiO$_2$ surface. Reduced density of surface amino groups is the key to facilitate the relatively slow “pick-up” of metal NPs by the NH$_2$-SiO$_2$ spheres, thus leading to the uniform NP dispersion.

6.6 Supporting Information

Figure S6.1. Transmission UV-Vis spectra of Rhodamine B in ethanol with different concentrations.
Figure S6.2. DRIFT spectra of bare SiO$_2$, fresh NH$_2$-SiO$_2$ and annealed NH$_2$-SiO$_2$ samples heated up to 300 °C for 1 hr in He flow. The C-H vibrations around 3000 cm$^{-1}$ were still observed with no obvious intensity difference among all three samples.

Figure S6.3. DRIFT spectra of TEOS control by drop-casting TEOS on KBr pellets.
Figure S6.4. Standard spectra of ethanol and NH$_3$, acquired from

6.7 References

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CHAPTER 7. IN SITU QUANTITATIVE SINGLE-MOLECULE STUDY OF DYNAMIC CATALYTIC PROCESSES IN NANOCONFINEMENT

Modified from a publication in the Nature Catalysis


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Contribution Notation: Bin Dong at Georgia State University conduct single molecule study and Yuchen Pei contributed most of catalyst synthesis.

7.1 Abstract

Understanding the fundamental catalytic principles when the catalytic center is confined in nanoscale space that is dimensionally comparable to the reactant molecule is crucial for designing high-performance catalysts. Theoretical studies with simplified model systems and ensemble experimental measurements have shown that chemical reactions in nanoconfined environments are largely different compared to those in bulk solution. Here we
design a well-defined platform with catalytic centers confined in the end of nanopores with controlled lengths to study the *in situ* dynamic behavior of catalytic processes under nanoconfinement at the single-molecule and single-particle level. Variable single molecular mass transport behavior reveals the heterogeneity of the confined environment in the nanopores. With the capability of decoupling mass transport factors from reaction kinetics in the well-defined platform, we uncovered a confinement-induced enhancement quantitatively in the activity of Pt nanoparticles inside the nanopores. The combination of the unique model catalyst and the single-molecule super-localization imaging technique paves the way to understand the nanoconfinement effects in catalysis.

### 7.2 Introduction

Molecules confined in nanoreactors, either synthetically generated or those native to biological structures, can bring significant changes to their physical and chemical properties. For example, the confinement can alter the Raman response of molecules in a single-wall carbon nanotube, the binding constant between ligands and receptors in a nanochannel, and the proton conductance inside a protein nanotube. In catalysis, nanoconfinement could dramatically change molecular transport and chemical conversion in porous materials, such as zeolites, mesoporous silica, carbon nanotubes, and metal-organic frameworks. The importance of heterogeneous catalytic processes based on these porous materials demands a thorough understanding of the nanoconfinement effects for the rational design of high-efficiency catalysts. Theoretical studies using simplified model systems, along with ensemble experimental measurements, have led to a limited understanding of the confinement factors, including the size, shape, and surface chemical properties of the pores on reaction kinetics. A
significant breakthrough will be the development of single-molecule approaches to acquire
direct experimental evidence and achieve quantitative understandings of the nanoconfinement
effects at the single-molecule and single-nanopore level.

In the past decade, molecular diffusion in nanopores have been visualized at the single-molecule level,\textsuperscript{84-89} and single turnover events on individual nanocatalysts such as layered double hydroxides (LDHs),\textsuperscript{90} zeolites,\textsuperscript{91-95} metal nanoparticles,\textsuperscript{96-99} and semiconductors\textsuperscript{100-103} have been mapped with nanometer precision by super-resolution microscopy imaging. Furthermore, intraparticle diffusion limited catalytic activity of porous materials\textsuperscript{104,105} have also been studied at the single-molecule level recently. However, mass transport of reactant molecules and reaction kinetics of catalytic active sites in nanopores have never been measured together experimentally due to seemingly insurmountable technical challenges of tracking single molecules dynamically in complex nanoporous structures under reaction conditions.

In the present work, a model nanocatalyst platform has been designed to enable the catalytic study of the nanoconfinement effects at the single-molecule and single-particle level. After decoupling the mass transport factors from reaction kinetics, we quantitatively demonstrate the heterogeneous behaviour of the single molecular mass transport confined in nanopores. Catalytic reaction rate constants and absorption equilibrium constants were measured experimentally on the model nanocatalysts. The specially designed nanocatalysts are proven to be a versatile platform for future studies on different aspects of the catalytic nanoconfinement effects, such as surface chemical properties and nanopore morphology.
7.3 Selected Results and Discussion

Design and characterization of nanocatalyst platform. The nanocatalyst platform (Figure 7.1) has highly tunable structures with well-defined geometry that consists of platinum nanoparticles (NPs) sandwiched between an optically-transparent solid SiO$_2$ core and a mesoporous SiO$_2$ shell (mSiO$_2$) with aligned nanopores. The synthesis of the nanocatalysts are discussed in detail in Supplementary Methods. This structure of nanocatalyst provides a restricted pathway for reactant molecules in the bulk solution to diffuse a uniform distance through the nanopores to access active sites on confined Pt NPs at the bottom of the nanopores. Encapsulating Pt NPs in mSiO$_2$ shells provides many advantages, such as stabilizing the particle morphology and avoiding the aggregation of particles during removal of surfactant ligands (Figure S7.2 and S7.3).\textsuperscript{106} In the current experiments, the average diameter of the solid SiO$_2$ cores (105.0 ± 2.1 nm) and the thickness of mSiO$_2$ shells (83.1 ± 9.0 nm and 118.5 ± 9.5 nm) were controlled (Figure S7.4), which could keep all Pt NPs within the excitation depth (~300 nm) of total internal reflection fluorescence (TIRF) microscopy (Figure S7.5). The average diameter of the nanopores was measured as ca. 2.3 nm from the size distribution derived from the desorption branch using the Barret-Joyner-Halenda method and the cross-sectional profile in transmission electron microscopy (TEM) images of the nanocatalysts (Figure S7.6-S7.7). The sandwiched Pt NPs had an average size (5.1 ± 1.0 nm) larger than the nanopore diameter, and their locations were secured during the synthetic process and imaging experiments. Thicker mesoporous shells (Figure S7.8-S7.10) were also prepared for validating the nanoconfinement effects through ensemble experiments.
Catalytic modelling of the nanoconfinement (Dr. Bin Dong independently collected data in this part, and detailed calculation and experiment description can be referred to the original publication). Catalytic kinetics on the heterogeneous surface generally conforms to the Langmuir-Hinshelwood (LH) model when the reaction rate is purely chemical conversion limited (Figure 7.2). We fitted the kinetics data of a control sample without nanopores (100 nm SiO$_2$@ 5 nm Pt without mSiO$_2$ shells) with the LH model in Figure 7.2i. When there are no nanoconfinement effects on catalysis, it gives the chemical conversion rate constant of $k_{\text{eff}} = 0.074 \pm 0.006$ s$^{-1}$ particle$^{-1}$ and absorption-desorption equilibrium constant $K_{AR} = 6.2 \pm 1.5$ µM$^{-1}$, respectively. However, the LH model cannot be directly used to determine the chemical reaction kinetic parameters when the nanoconfinement effects exist, because mass transport plays an inevitable role in controlling the catalytic reaction rate. Herein, we established the diffusion-limited LH (DLH) kinetics model based on the steady-state assumption to correct the
mass transport factor on measuring the chemical reaction kinetics when the catalytic reaction is affected by nanoconfinement. Fitting the reaction kinetics data in Figure 7.2e with the DLH model gives $k_{\text{eff}} = 0.53 \pm 0.08 \, \text{s}^{-1} \, \text{particle}^{-1}$ and $K_{AR} = 3.0 \pm 0.9 \, \text{µM}^{-1}$, respectively. These results show that the $k_{\text{eff}}$ increases by a factor of $\sim 7$, while the $K_{AR}$ is $\sim 2$ times smaller for Pt NPs confined in nanopores (Figure 7.3).

The enhanced activity of Pt NPs confined in the nanopores could be explained by either the increased effective concentration of amplex red in a nanoscale space$^{64}$ or the nanoconfinement effect that helps to stabilize intermediate species/states.$^{71}$ Furthermore, the highly restricted space in the nanopores could constrain the molecular adsorption, and thus decreasing the adsorption strength of amplex red. The heterogeneous catalytic activity enhances with an optimal adsorption strength of reactive species on catalytic centers.$^{64}$ The results here suggest that the nanoconfinement effects can potentially tune the adsorption strength of molecules.

There are a few possible reasons for the nanoconfinement effects explaining the much smaller diffusion rate of resorufin in the nanopores. First, the nanopore diameter (ca. 2.3 nm) is comparable to the hydrodynamic size of resorufin ($R_H$, ca. 0.51 nm). Second, the viscosity of the medium has been reported to increase dramatically when confined in small space,$^{107}$ which severely reduce the diffusion rate of trapped molecules. In this study, the viscosity of medium (H$_2$O) inside the nanopores was estimated to be $67.6 \pm 8.4$ Pa s, which is around 4 orders of magnitude higher than that of normal aqueous solution (0.89 mPa s at 25 °C). Third, the adsorption of resorufin on the hydrophilic surface of the nanopores (silanol groups) also hinders the mass transport rate (Figure 7.2, c1).$^{89}$
Figure 7.2. Study catalytic activities at the single-molecule single-particle level with turnover resolution. (a) Segment of a typical fluorescence intensity trajectory from a single nanoparticle at a temporal resolution of 50 ms. $\tau_{on}$ and $\tau_{off}$ correspond to the resident time of resorufin in nanopores and the interval time between two consecutive catalytic events, respectively. (b) Distribution of catalytic events on a nanocatalysts particle. (c-f) Diffusion rate estimated from Fick’s first law (d) and reaction kinetics measured from single molecule single particle experiments of 100 nm SiO$_2$@5 nm Pt@120 nm mSiO$_2$ (e). (f) shows the ratio of measured reaction rate over diffusion rate. (g-j) The same reaction kinetic study performed on 100 nm SiO$_2$@5 nm Pt as those shown in (c-f). Error bars in (e) and (i) were calculated as
Similar single-molecule and ensemble measurements were carried out on another nanocatalyst with the same design but a thinner shell thickness of ~80 nm. The measured $D_{app}$ ($0.010 \pm 0.004 \text{ µm}^2 \text{s}^{-1}$) was virtually identical to $D_{app}$ for 120 nm shell ($0.011 \pm 0.003 \text{ µm}^2 \text{s}^{-1}$), confirming that the diffusional behavior of tracked molecules was independent of the pore length. As shown in Figure 7.3, $K_{AR}$ were also similar for both shell thicknesses, suggesting similar absorption/desorption strength of amplex red on Pt NPs in the nanopores with the same diameter and surface properties but different pore length. Furthermore, $k_{eff}$ for 80 nm shell
(0.39 ± 0.09 s\(^{-1}\) particle\(^{-1}\)) was about half of that for 120 nm shell (0.074 ± 0.006 s\(^{-1}\) particle\(^{-1}\)), which may be explained by the pore-length-dependent enhancement of the effective concentration of amplex red near Pt NPs. Ensemble measurements (Figure S7.11) also agree with the single-molecule data.

The nanoconfinement effects on catalytic processes are truly complicated and worth continued efforts to achieve a better understanding. The well-defined nanocatalysts used in the present study involves a multilayered structure, with which the composition, structure, and surface properties of the solid core, aligned porous shell, and sandwiched metal NPs can be customized independently. Therefore, it provides us with a highly versatile platform to study many aspects of nanoconfinement, especially pathway-dependent chemical processes and tandem reactions. For example, the catalytic effects of surface chemical properties (hydrophobic vs. hydrophilic) and the nanopore morphology\(^{105}\) (pore size, length, and geometry) can be revealed \textit{in situ} in the nanoscale-confined environment. This work opens a research direction where it is possible to quantitatively differentiate, evaluate, and understand the complex nanoconfinement effects on dynamic catalytic processes, thus guiding the rational design of high-performance catalysts.

### 7.4 Conclusion

A well-defined catalyst platform with nanoporous structures have been designed, which enables the quantitative study on the nanoconfinement effects. Single-molecule super-localization based imaging technique was applied to reveal and differentiate the heterogeneous molecular transport and dynamic catalytic reaction kinetics in nanopores at the single-molecule and single-particle turnover resolution under \textit{in situ} conditions. Results show that the reaction
rate is significantly increased in the presence of nanoconfinement, while the adsorption of reactant molecules on the Pt NPs surface is weakened due to the restricted molecular adsorption.

7.5 Supporting Information

Preparation of 100 nm SiO$_2$@5 nm Pt@120 nm mSiO$_2$ nanocatalysts

100 nm SiO$_2$@5 nm Pt NPs were prepared by the similar method as mentioned in Chapter 6. To coat a 120 nm mSiO$_2$ shell, 25 mg (to the mass of pure SiO$_2$ cores) 100 nm SiO$_2$@5 nm Pt was dispersed in 10 mL ethanol under ultrasonication for 30 min. 165 mg hexadecyltrimethylammonium bromide (C$_{16}$TAB), 50 mL H$_2$O and 16.3 mL ethanol were then added to the 100 nm SiO$_2$@5 nm Pt solution and ultrasonicated for another 30 min. After adding 550 µL NH$_3$·H$_2$O (~28%), the above solution was moderately stirred at room temperature for 30 min. 900 µL TEOS was premixed with 5 mL ethanol and added dropwise into the solution by 3-4 times per 30 min. After stirring for 6 hrs in total and washing for 3 times with ethanol, raw 100 nm SiO$_2$@5 nm Pt@120 nm mSiO$_2$ spheres were obtained. To remove the pore-directing agent C$_{16}$TAB, as-synthesized 100 nm SiO$_2$@5 nm Pt@120 nm mSiO$_2$ spheres were dispersed in a mixture of 15 mL methanol and 1 mL concentrated HCl. The mixture was refluxed at 80 °C for 24 hrs. After washing 6 times with ethanol, 100 nm SiO$_2$@5 nm Pt@120 nm mSiO$_2$ spheres were obtained and stored in ethanol. The thickness of mSiO$_2$ shells can be varied by changing the amount of C$_{16}$TAB and TEOS as shown in Table S7.1. When increasing the amount of TEOS to grow thicker shells, we need to add 0.5 to 1 mL TEOS-ethanol solution for 2-5 times in 30 min intervals.
Optical setup for single molecule imaging (Conducted by Dr. Bin Dong)

Figure S7.5 shows the total internal reflection fluorescence (TIRF) microscopy setup for the single molecule and single particle imaging experiments. An adjustable 50-mW 532-nm CW laser (Uniphase, San Jose, CA) was first collimated using a pair of lens and then focus on the interface between aqueous sample and quartz slide by a long working distance lens. An extra quarter wave plate (WPMQ05M-532, Thorlabs, Newton, NJ) was introduced into the optical path to switch the linear polarized laser beam into a circular polarized laser profile. The fluorescence signal was collected by a 60× water immersion objective (Olympus, N.A. = 1.2) and focused onto the Andor iXonEM+ 897 camera (Belfast, Northern Ireland: 512 × 512 imaging array, 16 µm × 16 µm pixel size). A fluorescence filter set composed of a 532-nm longpass filter, a 532-nm notch filter and a 568/40 bandpass filter (Semrock, Rochester, NY) was inserted before the camera to reject scattering signal from the sample. There is an extra magnification of ×1.25 after the imaging objective in the microscope giving an effective imaging pixel size of 213 nm.

The incident angle of the laser beam at the interface was determined by the angle of the last mirror (controlled by a galvanometer), which was also in conjunction with a motorized linear stage (MAA-PP, Newport, Irvine, CA). The optimal illumination conditions were achieved when the laser spot overlapped perfectly with the view field of the objective by scanning the vertical position of the final mirror. All of the parameters were recorded by the in-house program for later use. Through this automatic calibration procedure, we can fully optimize the imaging conditions to achieve maximum illumination depth while maintaining high signal-to-noise ratio (SNR) for every sample. It is worthwhile to notice that the whole process of optimization only takes a few minutes.
Figure S7.1. Preparation of the model catalyst, Pt NPs sandwiched in between a solid SiO$_2$ core and a mesoporous mSiO$_2$ shell with aligned channels. APTS: 3-minopropyltriethoxysilane; TEOS: tetraethyl orthosilicate; C$_{16}$TAB: hexadecyltrimethyl-ammonium bromide.

Figure S7.2. TEM images of nanocatalysts. Representative TEM images of (a, b) 5 nm Pt NPs; (c, d) 100 nm SiO$_2$@5 nm Pt spheres. (e, f) nanocatalysts of SiO$_2$@5 nm Pt SiO$_2$@120 nm mSiO$_2$.

Figure S7.2 shows TEM images of 5 nm Pt NPs and the multilayer nanocatalysts with and without mSiO$_2$ shells. These TEM images show that 5 nm Pt NPs are evenly distributed on the surface of 100 nm SiO$_2$ spheres. After coated with 120 nm mSiO$_2$ shells, the nanocatalyst had a uniform morphology of the sandwich structure.
The DRIFTS spectrum of the 100 nm SiO$_2$@5 nm Pt sample without mSiO$_2$ shell (Figure S7.3 spectrum c) shows the C-H vibration of PVP-K30, which aligns well with the PVP K-30 standards. The mSiO$_2$ shell coating process introduces a significant amount of C$_{16}$TAB as pore directing agents (Figure S7.3 spectrum d). Even though we cannot distinguish the vibrations of C$_{16}$TAB and PVP K-30, the intensity of C-H vibrations (2600-3000 cm$^{-1}$, attributed to C$_{16}$TAB and PVP-K30) decreases during the methanol-HCl reflux, indicating the removal of surfactant ligands. After the methanol-HCl reflux (Figure S7.3 spectrum f), the presence of PVP-K30 and C$_{16}$TAB can be barely seen compared to the sample before the reflux.
The 5 nm Pt NPs had an average diameter of 5.1 ± 1.0 nm. 100 nm SiO$_2$ cores had an average diameter of 105.0 ± 2.1 nm. The average diameter of the overall sizes of SiO$_2$@5 nm Pt SiO$_2$@120 nm mSiO$_2$ was 342.2 ± 9.7 nm, which introduced an average thickness of mSiO$_2$ as 118.5 ± 9.5 nm. These diameters were calculated by counting random 300 particles.

Figure S7.4. Diameter calculation of nanocatalysts. (a) 5 nm Pt NPs; (b) 100 nm SiO$_2$ cores

Figure S7.5. TIRF microscope for single molecule imaging experiments.
The BET surface area of 100 nm SiO$_2$@5 nm Pt@120 nm mSiO$_2$ was measured as 1080 m$^2$ g$^{-1}$. Mesoporosity was determined by the BJH method, which is suitable for the mesoporous pores. The mesoporous volume is 0.85 cm$^3$ g$^{-1}$ from the desorption branch and 0.97 cm$^3$ g$^{-1}$ from the adsorption branch. Pore size was determined by BJH method using the thickness curve of Harkins and Jura with standard correction. The pore size calculated from the adsorption and desorption branch is consistent as 2.3 nm (Figure S7.6).

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Figure S7.6. (a) Nitrogen isotherm and (b) pore size distribution of 100 nm SiO$_2$@5 nm Pt@120 nm mSiO$_2$ nanocatalysts.

Figure S7.7. (a, b) TEM images of 100 nm SiO$_2$@5 nm Pt@120 nm mSiO$_2$ nanocatalysts to show nanopore structures; (c, d) cross-sectional profile analysis of nanopore structures at selected areas.
The aligned nanopores structure of mSiO$_2$ shells was seen from the TEM images (Figure S7.7a, b) with the staggered changes of the contrast. The pore sizes of nanocatalysts were also measured from the cross-sectional profile analysis of two areas as 2.42 and 2.47 nm (Figure S7.7c, d), which are very close to that obtained from the BJH analysis.

Figure S7.8. TEM images of nanocatalysts with variable mesoporous shell thickness. (a) 100 nm SiO$_2$@5 nm Pt@80 nm mSiO$_2$; (b) 100 nm SiO$_2$@5 nm Pt@120 nm mSiO$_2$; (c) 100 nm SiO$_2$@5 nm Pt@140 nm mSiO$_2$; and (d) 100 nm SiO$_2$@5 nm Pt@200 nm mSiO$_2$.

We also prepared the 5 nm Pt NPs loaded nanocatalysts of different mSiO$_2$ shell thickness (80, 140, and 200 nm), denoted as 100 nm SiO$_2$@5 nm Pt SiO$_2$@80 nm mSiO$_2$, 100 nm SiO$_2$@5 nm Pt SiO$_2$@140 nm mSiO$_2$, 100 nm SiO$_2$@5 nm Pt SiO$_2$@200 nm mSiO$_2$. We used the same batches of the 100 nm SiO$_2$@5 nm Pt particles, so the core size is 105.0 ± 2.1 nm. Their TEM images and size calculations are shown in Figure S7.8 and S7.9. Their shell thickness values are thus calculated as 83.1 ± 9.0, 132.8 ± 12.0, and 199.1 ± 6.6 nm.
Figure S.7.9. Size distributions for the mesoporous shell of nanocatalysts with different mesoporous shell thickness. (a) 100 nm SiO$_2$@5 nm Pt@80 nm mSiO$_2$; (b) 100 nm SiO$_2$@5 nm Pt@140 nm mSiO$_2$; and (c) 100 nm SiO$_2$@5 nm Pt@200 nm mSiO$_2$. The shell thicknesses in (a), (b) and (c) are 83.1 ± 9.0, 132.8 ± 12.0, and 199.1 ± 6.6 nm.

Figure S7.10. Characterization of the nanopore size. (a) isotherms of 5 nm Pt NPs loaded nanocatalysts with different shell thickness, (b) BJH pore size distributions using the adsorption branch for 5 nm Pt NPs loaded nanocatalysts with different shell thickness, and (c) BJH pore size distributions using the desorption branch for 5 nm Pt NPs loaded
We also measured the BET surface area and calculated the BJH pore size distributions for nanocatalysts with different shell thickness (80, 140 and 200 nm). Their isotherms and pore size distributions are shown in Supplementary Figure S7.10.

Figure S7.11. Comparison of the catalytic activities of nanoparticles w/wo nanoconfinement effects at ensemble level. Fluorescence intensity of resorufin at 583 nm was measured every 12 seconds. The reaction solution contained 2.0 µM of amplex red, 20 mM of H₂O₂ and same amount of Pt NPs (~ 10^{14} particles mL⁻¹). Data were collected by Dr. Bin Dong.

The effects of nanoconfinement (w/wo mSiO₂ shell) on the catalytic activities of nanocatalysts were also tested with ensemble measurements. The fluorescence emission signal from the product resorufin at 583 nm was measured at different time points under same reaction conditions for all the catalysts by a fluorometer. As shown in Figure S7.11, the activities of the catalysts with mesoporous shell (80 nm, 120nm, 140 nm, 200 nm) were much higher than 100 nm SiO₂@5 nm Pt (no shell), which agrees with the results from single molecule single particle catalysis experiments. Both single-molecule and ensemble data support the increase of catalytic activity of Pt NPs in the presence of the nanoconfinement effects.
Table S7.1. The amounts of C_{16}TAB and TEOS for preparing 5 nm Pt NPs loaded nanocatalysts with different mSiO_{2} shell thickness.

<table>
<thead>
<tr>
<th>Thickness of mSiO_{2} shells (nm)</th>
<th>80</th>
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<th>140</th>
<th>200</th>
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<tr>
<td>C_{16}TAB (mg)</td>
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<td>515</td>
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<tr>
<td>TEOS (µL)</td>
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<td>900</td>
<td>1550</td>
<td>3050</td>
</tr>
</tbody>
</table>

7.6 References


CHAPTER 8. CONCLUSION

Among chapter 1-8, we introduced two structures of mesoporous silica encapsulated metal NPs. The seeded growth method has been developed to prepare bimetallic and intermetallic NPs encapsulated in mesoporous silica shells as one catalyst platform. These encapsulated intermetallic NPs show high thermal stability, capping-free nature and well-ordered structure, enabling their catalytic applications for selective reactions and fundamental mechanism studies. However, it is challenging to architecture intermetallic NPs with uniform shapes to study the facet-property dependence of intermetallic catalysts. The synthesis of intermetallic NPs usually requires the annealing process which bring difficulties to maintain high surface energy facets. The low temperature synthesis of morphologically controlled intermetallic NPs are thus essential for further breakthroughs for broader intermetallic compositions. The sandwiched structure of metal NPs encapsulated in between silica cores and mesoporous silica shells serves as the second catalyst platform. We can tune the pore length, silica core size and metal size of this platform for the single-molecule fluorescence spectroscopy studying dynamic catalytic process under nanoconfinement. The further modifications of pore size and surface functionality can enable in-depth understandings on the diffusion behaviors and reaction kinetic mechanism of confined molecules in molecular level. In summary, we anticipate to contribute endeavors of nanocatalyst synthesis and their fundamental studies to broader applications.
LITERATURE CITED


