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Cyclopropane Hydrogenation vs Isomerization over Pt and Pt–Sn Intermetallic Nanoparticle Catalysts: A Parahydrogen Spin-Labeling Study

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ABSTRACT: Hyperpolarized propane produced by heterogeneous hydrogenation of cyclopropane with parahydrogen has been proposed as a safe inhalant for sensitivity-enhanced in vivo magnetic resonance imaging. The present studies were initially motivated by the possibility to improve the pairwise selectivity of hydrogenation using Pt–Sn intermetallic nanoparticle catalysts which achieved a record high pairwise selectivity in the hydrogenation of propene. The performance of the Pt₃Sn catalysts is found to be comparable to that of the Rh/TiO₂ catalyst employed in a recent publication. However, significant amounts of propene are also produced by isomerization over the Pt–Sn catalysts. The isomerization is promoted by weakening of the propene–surface binding energy and depletion of the H adatom density. While this is a remarkable finding from the perspective of catalysis science, the isomerization to propene over the Pt–Sn catalysts negates the advantages of using cyclopropane rather than propene as the safer reactant for in vivo use.

PISn(110) PI₂Sn(111) PI(111) propene X HP propane Y propane Y HP propane Y PISN(110) PI₂Sn(111) PI(111) PI₂Sn(111) PI(11

INTRODUCTION

In the PASADENA and ALTADENA effects, transformation of the proton singlet spin order of parahydrogen into NMRobservable hyperpolarization is initiated by pairwise addition of parahydrogen $(p-H_2)$ to an unsaturated substrate molecule.¹⁻³ The resulting high-field NMR signal enhancements, which can exceed 4 orders of magnitude, depending on the pairwise selectivity of hydrogenation, can enable molecular magnetic resonance imaging for disease detection and monitoring. Pairwise hydrogenation, where both of the added protons originate from the same dihydrogen molecule, can be performed by either homogeneous or heterogeneous catalysis,^{2,5} but only the latter affords facile isolation of products, scalability, and compatibility with continuous-flow production of hyperpolarized fluids. Metal nanoparticle catalysts offer high stability without leaching of metal into solution.^{6–8} However, hydrogenation over catalytically active metals (e.g., Pt, Rh, Ir) occurs mainly by a stepwise transfer, favoring random rather than pairwise addition. For applications, high catalytic activity (i.e., conversion) with high pairwise selectivity is desirable, and chemoselectivity is also an important consideration, especially for hyperpolarized adducts destined for in vivo use.

Albert et al. recently demonstrated that thermally polarized propane can be used as an inhalation agent to acquire high-quality ¹H images in the lungs of live rats.⁹ This could assist in the diagnosis, staging, and treatment of pulmonary diseases.

However, the imaging sensitivity remains relatively low for propane due to the low spin density in gases and small population differences among spin states governed by the Boltzmann distribution. Hyperpolarized propane produced by hydrogenation of propene with p-H₂ can yield NMR signal enhancement factors of up to 3600 (extrapolated to 100% p-H₂ enrichment).8 However, a significant amount of unreacted propene in the product stream renders it unsuitable for clinical use. Salnikov et al. recently proposed a comparatively safe technique to produce hyperpolarized propane by the hydrogenation of cyclopropane with p-H₂. The unreacted cyclopropane is nontoxic and scentless.¹⁰ Using 82% para-enriched H_{2} , hydrogenation of cyclopropane over 118 mg of a Rh/TiO₂ catalyst yielded propane CH₂ peak signal enhancements (at 9.4 T) in the neighborhood of 480 (1.6% ¹H polarization) with <0.3% conversion, depending on catalyst loading, temperature, and flow rate.¹⁰ The present studies were inspired by the possibility to achieve even higher conversion and pairwise

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selectivity in the hydrogenation of cyclopropane over Pt–Sn intermetallic nanoparticles (iNPs).

Bimetallic catalysts, particularly those with ordered intermetallic phases with precise stoichiometry and ordered surface structures, can be tuned to increase catalytic performance.¹¹ By combining a metal that is catalytically active for such hydrogenations (e.g., Pt, Pd) with an inactive metal that can function as a catalytic promotor (e.g., Sn, In, Au), a higher pairwise selectivity can be achieved in comparison to monometallic nanoparticles containing only the active metal.^{8,12-14} We recently reported that the pairwise selectivity in the hydrogenation of propene to propane can be dramatically increased using Pt₃Sn@mSiO₂ and PtSn@mSiO₂ iNPs (where mSiO₂ denotes an MCM-41-like mesoporous silica encapsulation shell). The results were attributed to the effects of interrupting the contiguous 3-fold Pt hollow sites that comprise the Pt(111) surface upon incorporation of Sn into the lattice of the Pt seed particles, as illustrated in the model surfaces in Figure 1.



Figure 1. Computer models of Pt(111), $Pt_3Sn(111)$, and PtSn(110) surfaces. Orange (gray) spheres represent Pt (Sn) atoms. White triangles indicate the 3-fold Pt hollow sites.

Parahydrogen-enhanced NMR can provide information on the kinetics and mechanism of hydrogenation through the analysis of pairwise and nonpairwise addition products.^{8,15–17} Parahydrogen spin labeling is akin to the deuterium methodology employed by Bond et al.^{18,19} The catalytic mechanism can be inferred from the D-atom distribution in the products in reactions run with D₂.^{19,20} Path *i* in Scheme 1 is our adaptation of Bond's mechanism to the representative reactions of pairwise addition of parahydrogen.

A fundamental difference between parahydrogen spin labeling and isotopic labeling is that pairwise selectivity cannot

Scheme 1. Representative Reactions in the Mechanism for Pairwise Hydrogenation and Isomerization of Cyclopropane



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be inferred from reactions with deuterium. On the other hand, observation of parahydrogen-enhanced NMR signals is proof of pairwise addition. Furthermore, parahydrogen-induced hyperpolarization is observed only for propane molecules formed by pairwise incorporation into the chemically inequivalent CH_2 and CH_3 groups. Parahydrogen addition into the magnetically equivalent C1 and C3 sites yields adduct spin states that are invisible to NMR. Thus, parahydrogen-enhanced NMR experiments can reveal aspects of the surface interactions, hydrogenation, and isomerization that cannot be seen in experiments with deuterium.^{16,17}

EXPERIMENTAL SECTION

ALTADENA Hydrogenation. Hydrogenations of cyclopropane were performed with 50% para-enriched H₂ in ALTADENA (Adiabatic Longitudinal Transfer After Dissociation Engenders Net Alignment)³ mode, where the gaseous hydrogenation products formed at low field (ca. 5 mT) were adiabatically transported in a continuous flow to 9.4 T for NMR detection. The 50% para-enriched H₂ was produced by passing normal H_2 (n-H₂) through a coiled 3/16" i.d. copper tube filled with 30-50 mesh iron(III) oxide (Sigma-Aldrich, SKU 371254) immersed in liquid nitrogen. The p-H₂/N₂/ cyclopropane reaction mixture was prepared by combining the three outputs of the mass flow controllers (Alicat Scientific) programmed with flow rates of 120/70/210 mL/min at 1 bar. The reaction mixture was fed into a u-tube reactor containing 15 mg of Pt@mSiO₂, Pt₃Sn@mSiO₂, or PtSn@mSiO₂ iNPs. The u-tube reactor was placed in a ceramic heating element, and the reaction temperature was stabilized with feedback from a thermocouple inserted directly into the catalyst bed. After reaching a steady-state reaction condition, 400 MHz proton NMR spectra of the flowing reactor effluent were acquired by accumulating 32 transients using a 2 s recycle delay. Each experiment was repeated with n-H₂. ALTADENA difference spectra were obtained by subtracting the spectra acquired with n-H₂ from the spectra collected with p-H₂. A cubic spline baseline correction was applied to remove the H₂ residual peak due to the difference of orthohydrogen content in 50%enriched p-H₂ and n-H₂. By stopping the gas flow and sealing the reaction effluent in the NMR sample loop, the thermally polarized spectra at Boltzmann equilibrium under nonflowing conditions for cyclopropane hydrogenations were acquired by accumulating 512 transients with a recycle delay of 6 s.

Platinum and Platinum-Tin Nanoparticles. To synthesize Pt@mSiO2, tetraethyl orthosilicate (TEOS) was polymerized around the tetradecyltrimethylammonium bromidecapped (TTAB-capped) Pt cores at room temperature followed by removal of TTAB in the subsequent calcination. Pt₃Sn@mSiO₂ and PtSn@mSiO₂ intermetallic nanoparticles were obtained by the heterogeneous reduction and nucleation of Sn in mSiO₂-protected Pt NPs. Details of their synthesis and characterization were already published and are also included in the Supporting Information.^{8,21} The mesoporous silica shell around the metal cores significantly enhances catalyst stability against aggregation in the annealing process up to 750 °C while not preventing the diffusion of small reactants/products in the catalyzed reactions. Table S1 presents the metal loadings, particle sizes, Pt dispersions, and surface Pt site densities for the three mesoporous silica-encapsulated nanoparticles.

RESULTS AND DISCUSSION

The chemical bonding and reactivity of cyclopropane have intrigued chemists for many decades. In the 1950s, Bond and Turkevich showed that the reaction of D₂ with cyclopropane over supported Pt catalysts yielded propane molecules with 1-8 deuterons depending on temperature.¹⁹ The reaction mechanism they inferred from the distribution bears on the outcome of hydrogenation with parahydrogen. Kinetic studies of cyclopropane hydrogenation over group 10 metals showed that the reaction is zero order for hydrogen and first order for cyclopropane, indicating that the metal surface is easily saturated with hydrogen while cyclopropane is weakly adsorbed.²² Hydrogenation of cyclopropane to propane over Pt and Pd occurs without hydrogenolysis to methane and ethane.²³ High-vacuum surface-science techniques have been applied to the reaction over Ir and sulfided Ni surfaces, where in addition to propane, hydrogenolysis and isomerization products are also observed.^{24,25} A few studies have examined the reactions over bimetallic catalysts such as NiCu,²⁶ RuAu,² and RhIr.²⁸ While neither the adsorption of cyclopropane nor its chemical reactions with hydrogen on Pt-Sn bimetallic catalysts have been previously studied, the catalytic properties can be expected to be dramatically altered by addition of the Sn (inactive for hydrogenation but well known as a catalytic promotor) into Pt nanoparticles.

Figure 2 shows the thermal equilibrium and ALTADENA difference spectra acquired at a reactor temperature of 300 $^\circ \rm C$



Figure 2. Thermally polarized (top) and ALTADENA difference (bottom) spectra acquired using 120/70/210 mL/min of $H_2/N_2/$ cyclopropane at 300 °C for (A) PtSn@mSiO₂, (B) Pt₃Sn@mSiO₂, and (C) Pt@mSiO₂. ALTADENA and thermally polarized spectra were acquired with 32 and 512 transients, respectively. ALTADENA difference spectra were vertically scaled 16 times for normalized signal comparison. Vertical expansions of the thermally polarized spectra are shown in the dashed frame (peaks a–f).

using the mSiO₂-encapsulated Pt, Pt₃Sn, and PtSn catalysts. Spectra acquired at other temperatures ranging from 150 to 450 °C are included in Figures S1 and S2 in the SI. The appearance of resonances "e" and "f" provides clear evidence for the conversion of cyclopropane to propane for all three catalysts. Consistent with previous studies in the literature, no

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products of hydrogenolysis such as methane or ethane were observed.

As seen in Figure 2, both $Pt_3Sn@mSiO_2$ and $PtSn@mSiO_2$ yielded intense propane ALTADENA NMR signals. Tables S2, S3, and S4 provide the conversions, enhancement factors, and pairwise selectivities for the cyclopropane + H₂ reactions over $Pt@mSiO_2$, $Pt_3Sn@mSiO_2$, and $PtSn@mSiO_2$, respectively, at a series of different temperatures (details of parameter calculations are provided in the S1). The temperature dependences of these variables are plotted in Figure 3. Catalyst turnover frequencies (TOFs) were also calculated from the conversions and are reported in Table S5.



Figure 3. (A) Percent conversions φ_{PE} (conversion of cyclopropane to propene) and φ_{PA} (conversion of cyclopropane to propane) in the cyclopropane hydrogenation over Pt@mSiO₂, Pt₃Sn@mSiO₂, and PtSn@mSiO₂ at temperatures from 150 to 450 °C. Percent conversions are calculated using peak integrals of propene, propane, and cyclopropane in the thermally polarized spectra. (B) Signal enhancement factors (left vertical axis) and pairwise selectivity (right vertical axis) of Pt₃Sn@mSiO₂ and PtSn@mSiO₂ for the hydrogenation of cyclopropane to propane at temperatures from 150 to 450 °C. Signal enhancement factors are obtained by the integral ratio of the propane CH₃ peak in ALTADENA and thermally polarized spectra. Pairwise selectivities are obtained by the ratio of experimental and theoretical signal enhancement factors.

For Pt@mSiO₂, conversion of cyclopropane to propane was highest at 150 °C and monotonically decreased with increasing temperature, presumably due to formation of carbonaceous deposits in the flow reactor.²⁸ No ALTADENA signals could be detected using Pt@mSiO₂, consistent with a very low pairwise selectivity of hydrogenation.

The reader may have noticed a second set of resonances, in addition to the propane peaks, in the thermally polarized spectra of Figures 2 and S2 (labeled a–d) for the reactions of cyclopropane over the PtSn and Pt₃Sn catalysts. These unexpected signals reveal the presence of gaseous propene in the effluent, indicative of isomerization to propene. Notably, isomerization was not catalyzed by the Pt nanoparticles. As seen in Figure 3A, the relative production of propene and propane was temperature dependent. As seen in Figure 3B, pairwise selectivity initially increased and then decreased with increasing temperature above 200 °C for Pt₃Sn@mSiO₂, while for PtSn@mSiO₂, pairwise selectivity initially increased and then decreased and then decreased with increasing temperature above 350 °C.

For $Pt_3Sn@mSiO_2$, propane was the main product at temperatures between 150 and 250 °C, while above 250 °C, conversion to propane remained low while isomerization to propene sharply increases with temperature. For $PtSn@mSiO_2$, the propene isomerization product dominates at all temperatures and increases rapidly above 350 °C, while the minor product propane is observed only at elevated temperatures above 300 °C. To test if the propene isomerization product depends on the presence of surface hydrogen, experiments were performed with and without H_2 under otherwise identical conditions. The resulting thermally polarized spectra for the Pt and Pt_3Sn catalysts are presented in Figure 4. For Pt_3Sn , the



Figure 4. Thermally polarized spectra acquired using 120/70/210 mL/min of $H_2/N_2/cyclopropane$ (top) and 190/210 mL/min of $N_2/cyclopropane$ (bottom) for (A) Pt@mSiO₂ at 200 °C and (B) Pt₃Sn@mSiO₂ at 300 °C. The dashed frame contains the vertical expansion of the propene peaks (peaks a–d).

same amount of propene was formed in each experiment, consistent with the complete absence of PASADENA signals (which necessarily involves exchange or addition of H_2) for this species (Figure S2B). For Pt, no propene could be observed in experiments with or without H_2 at any temperature. Propene did not exhibit ALTADENA NMR signals for any of the catalysts. While ALTADENA propene signals stemming from pairwise replacement catalysis (PRC)¹⁷ have been reported in our previous studies utilizing these Pt–Sn catalysts with propene as the reactant,⁸ the PRC signals (ca. 100× weaker). Considering the S/N ratio of the propane ALTADENA signals in Figure 4, the propene pairwise replacement signals would be well below the noise level in this spectrum.

As a guide to the interpretation of our results, we turn to Bond et al., who employed mass spectrometry to quantify the products of reactions of D₂ with cyclopropane over supported Pt catalysts.¹⁹ As noted above, the reaction mechanism was inferred from the D distribution of propane- d_x with x = 1-8, where an increase in x with temperature was observed. The aspects of this mechanism that are pertinent to pairwise hydrogenation is shown in Scheme 1. The possibility that hydrogenation proceeds through an adsorbed propene intermediate formed by isomerization of cyclopropane was considered in ref 19. However, propene was not observed in the gaseous products, and the reaction through this intermediate was shown to be inconsistent with the D distribution in propane- d_x . The first step in path *i* in Scheme 1 is abstraction of an H (or D) adatom from the Pt surface to form a transient propyl radical which can adsorb onto the metal or abstract a second H (or D) adatom to yield gaseous propane. Formation of adsorbed propyl intermediate in the hydrogenation of cyclopropane on Pt(111) surface has been confirmed by in situ soft X-ray techniques.²⁹ Exchange of H atoms between the surface and the adsorbed propyl radical occurs through the reversible formation of di- σ -bonded species. At lower reaction temperatures, propane- d_2 with C1–C3 deuteration (Scheme 1, path i) involves the fewest number of reaction steps and is the dominant product. However, the analogous pairwise addition of parahydrogen into these magnetically equivalent sites produces no ALTADENA signals. Formation of C1-C2 deuterated products requires additional surface transformations, including reversible H/D exchange between the surface and the adsorbate molecule. At higher temperatures, there is an initial increase in the pairwise addition into C1-C2 sites of the product, but as temperature is further increased, an increasing number of exchange steps with statistics favoring nonpairwise addition become thermally activated, a process that is consistent with the decrease in pairwise selectivity observed in the hydrogenation of cyclopropane to propane.

Previously, we proposed a model to explain how conversion and pairwise selectivity of hydrogenation of propene were affected by incorporation of Sn into the Pt(111) surface. For the PtSn iNPs, where the 3-fold Pt hollow sites are absent, the high barrier to H₂ dissociation can reduce the density of surface H adatoms, and direct molecular addition has been proposed to account for the very high pairwise selectivity of this catalyst.^{8,30} On the $Pt_3Sn(111)$ surface where the 3-fold Pt sites are vertex connected, facile H₂ dissociation can occur; however, the activation barrier to H adatom diffusion is nearly an order of magnitude higher than on Pt(111).³¹ Our present results demonstrate that the catalytic properties are also drastically affected by the incorporation of Sn. While no ALTADENA signals and no isomerization of cyclopropane to propene are observed on Pt, both processes are clearly enhanced with propene dominating the products for the PtSn@mSiO₂ and Pt₃Sn@mSiO₂ catalysts at elevated temperatures (Figure 3A).

Experimental studies of the uncatalyzed gas-phase thermal isomerization of cyclopropane to propene date back to 1922. The activation energy for the gas-phase isomerization is 270 kJ/mol.³² Theoretical studies suggested that isomerization of cyclopropane to propene is a concerted process involving ring opening and C–C bond breaking, H-atom migration, and outer methylene group rotation.³³ The now generally accepted pathway, confirmed by Zewail et al. in 1994, proceeds through

the trimethylene biradical.³⁴ Engstrom and Goodman also discussed the possibility of 1,2-di- σ -bound C₃H₆ (trimethylene biradical) as a reaction intermediate in the observation of cyclopropane isomerization to propene on the carburized Ir(111) surface.²⁴ The cyclopropane to propene isomerization, which was favored in the presence of monolayer carbon deposits, was attributed to the decrease in binding energy of the adsorbed hydrocarbon intermediate in combination with a decrease in the density of the H adatom concentration. Notably, the dramatic shift in the selectivity from hydrogenolysis to isomerization, due in this case to "self-poisoning" of the metal surface by the reactants, appears to be similar to the reaction of cyclopropane and H_2 on a sulfide Ni(111) surface.²⁵ Since the isomerization of cyclopropane to propene does not require the presence of hydrogen on the surface, we propose a mechanism analogous to the gas-phase process, as shown in path *ii* of Scheme 1. After formation of π -bonded propene, either hydrogenation or desorption of propene can follow. In the presence of hydrogen, the propene can be subsequently hydrogenated with a high pairwise selectivity, as demonstrated in our previous work.8 To the extent that pathway *i* of Scheme 1 also contributes to the products, the overall pairwise selectivity for hydrogenation of cyclopropane to propane will be diminished, which can account for lower pairwise selectivity of hydrogenation of cyclopropane vs propene as substrate.

CONCLUSION

In summary, silica-encapsulated Pt-Sn@mSiO₂ iNPs can deliver significant signal enhancement of propane formed by hydrogenation of cyclopropane. The pairwise selectivity of 2.8% (2.2% without relaxation correction) obtained using the Pt₃Sn@mSiO₂ catalyst is comparable to the highest level obtained in the literature for the Rh/TiO₂ catalyst (280 mg at 6 bar). Furthermore, the variation in the performance with Pt-Sn composition reveals the existence of different reaction pathways in the ring-opening hydrogenation and isomerization. Analogous to the effects reported for carburized Ir(111) and Sdoped Ni(111) surfaces under high-vacuum conditions, we conclude that the relative importance hydrogenation versus isomerization is governed by the availability of H adatoms to the adsorbed alkane at the catalytic active sites and weakening of the propene binding, both of which would be affected by the presence of Sn on the surface. The isomerization of cyclopropane to propene does not require the presence of hydrogen and is not observed on the monometallic Pt@mSiO₂ catalyst where Sn is absent. In the presence of hydrogen, propene formed by isomerization can be hydrogenated to propane with pairwise addition to the C2 and C1 or C3 sites. In accordance with the typical inverse relationship between pairwise selectivity and catalyst activity, the high polarization levels obtained with PtSn@mSiO2 and Pt3Sn@mSiO2 suffer from the relatively low conversion of less than 1% under our reaction conditions. Higher conversion can be realized by the usage of larger amounts of catalyst and elevated substrate pressures. Unfortunately, the presence of significant amounts of propene produced by isomerization over the Pt-Sn catalysts negates the advantages of using cyclopropane as the safer reactant (rather than propene) for the production of hyperpolarized propane for in vivo use, an outcome that we did not anticipate at the outset of this work.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.0c02493.

Additional NMR spectra, tables of conversion, enhancement factor and pairwise selectivity, and details of hydrogenation reaction and calculation (PDF)

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Author Contributions

Y.D. completed all of the ALTADENA NMR experiments and calculations. R.B., R.M.-G., and M.C. provided $Pt-Sn@mSiO_2$ intermetallic nanoparticles and catalyst characterization. The manuscript was written by Y.D. and C.R.B. with revisions from all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

iNPs, intermetallic nanoparticles; p-H₂, 50% para-enriched H₂

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