

Intermetallic $\text{Pd}_x\text{In}_y/\text{Al}_2\text{O}_3$ catalysts with isolated single-atom Pd sites for one-pot hydrogenation of diphenylacetylene into *trans*-stilbene

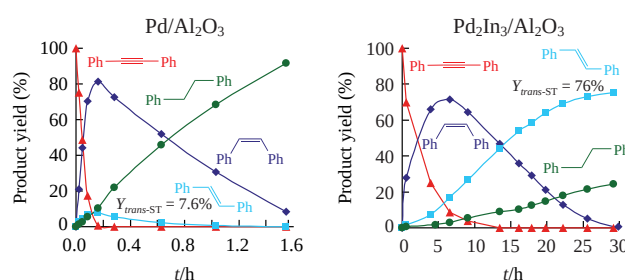
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Novel one-pot synthesis of *trans*-stilbene comprises hydrogenation of diphenylacetylene into *cis*-stilbene followed by its hydroisomerization, over the catalyst being intermetallic $\text{Pd}_x\text{In}_y/\text{Al}_2\text{O}_3$ system with isolated single-atom Pd_1 sites. The hydroisomerization rate in the process is comparable or exceeds the over-hydrogenation into 1,2-diphenylethane thus providing 76% yield of *trans*-stilbene in the case of $\text{Pd}_2\text{In}_3/\text{Al}_2\text{O}_3$ catalyst. This result presumably stems from the formation of ordered single-atom Pd_1 sites with favorable hydroisomerization ability on the surface of Pd_xIn_y catalysts.



Keywords: indium, palladium, single-atom site, *trans*-alkenes, stilbene, hydrogenation, isomerization, alkynes, intermetallic systems.

Selective semihydrogenation of alkynes for the synthesis of *cis*- and *trans*-alkenes has important application in both industry and laboratory.¹ The catalytic hydrogenation of substituted alkynes to *cis*-alkenes is rationalized as *syn* addition of hydrogen to the adsorbed alkyne moiety; the Lindlar-type catalysts being commonly used for this purpose. On the other hand, the synthesis of *trans*-alkenes is a more challenging task.² The Birch reduction used for the synthesis of *trans*-alkenes from alkynes³ requires stoichiometric amount of a base and harsh reductive reaction conditions along with the use of alkali metals in liquid ammonia. This procedure is also incompatible to functionalized alkynes with base-labile or reducible moieties.

Catalytic hydrogenation using molecular hydrogen seems to be a good alternative to the Birch reduction. Recently, several transition metal homogeneous catalysts containing Rh, Ru, Ir, Ni, and Pd have been reported to be promising for *trans*-hydrogenation of alkynes.^{2,4–8} However, homogeneous catalysts are difficult to implement in industry since separation of such catalysts from the reaction mixture remains a serious problem. From this viewpoint, heterogeneous catalysis is preferable to homogeneous. To date, the number of reports concerning selective hydrogenation of alkynes to *trans*-alkenes over heterogeneous catalysts is scarce. The tandem catalytic system comprising the mixture of intermetallic $\text{Pd}_3\text{Bi}/\text{SiO}_2$ and H-USY zeolite was proposed for the preparation of *trans*-stilbene (*trans*-ST) by hydrogenation of diphenylacetylene (DPA).⁹ Therein, *cis*-hydrogenation of DPA proceeded over $\text{Pd}_3\text{Bi}/\text{SiO}_2$ while Brønsted acid sites of H-USY were responsible for *cis*–*trans* isomerization of stilbene. Later, RhSb/SiO_2 intermetallic catalyst was found to provide the favorable *cis*–*trans* hydroisomerization.¹⁰ That catalyst was effective in one-pot *trans*-ST synthesis from DPA providing a significant yield (58%) of *trans*-ST along with the alkane (*ca.* 38%) and *cis*-stilbene

(*cis*-ST) (*ca.* 4%).^{10,11} High selectivity to *trans*-alkene and low over-hydrogenation rate originated from the specific atomic arrangement of RhSb/SiO_2 active sites with single Rh atoms isolated by inactive Sb atoms on the RhSb intermetallic surface. This type of catalysts is called single-atom catalysts (SACs) or single-atom alloys (SAAs).¹² Note that the catalytic systems mentioned above (PdBi and RhSb) are of limited use in food and pharmaceutical industry since they contain toxic bismuth and antimony. Therefore, a development of new environmental friendly heterogeneous system for *trans*-alkene synthesis is of high priority. Since favorable combination of hydrogenation/hydroisomerization functions was attributed to a specific surface structure of single-atom active sites of RhSb/SiO_2 , one can expect that other intermetallic catalysts with isolated active sites may be promising for *trans*-alkene synthesis.

Earlier we synthesized supported intermetallic Pd_1In_1 nanoparticles with the surface atomic arrangement similar to RhSb .¹³ Characterization of the catalyst by XRD and FTIR-CO revealed the formation of an ordered Pd_1In_1 intermetallic structure with Pd atoms completely isolated from each other by inactive In atoms (Pd_1 sites) on the surface of PdIn nanoparticles. Such type of Pd active sites surface arrangement is similar to the arrangement of Rh atoms on RhSb intermetallic surface. A similar structure of active sites in PdIn and RhSb gives hope for similar performance in alkyne hydrogenation. Indeed, in alkyne hydrogenation Pd_1In_1 catalyst demonstrated excellent overall selectivity to alkene due to the pronounced deceleration of the undesired alkene-to-alkane over-hydrogenation.¹³ It should be noted that the low rate of over-hydrogenation is a crucial parameter, since minimization of the hydrogenation rate compared with the rate of hydroisomerization is a prerequisite for achieving a high *trans*-alkene yield. Therefore, due to low over-hydrogenation rate and specific surface structure

PdIn intermetallic catalysts can be considered as promising environmentally friendly candidates for *trans*-hydrogenation of alkynes. However, hydroisomerization performance of PdIn intermetallics was not studied by now.

In this work, we examined efficiency of PdIn intermetallic nanoparticles with Pd:In ratios of 1:1 and 2:3 in *trans*-hydrogenation of DPA. A higher In loading was applied to provide effective spatial separation of Pd₁ active sites thus improving its overall performance.¹⁴ The obtained catalysts are designated as follows: Pd/ α -Al₂O₃-Pd, PdIn/ α -Al₂O₃-Pd₁In₁, Pd₂In₃/ α -Al₂O₃-Pd₂In₃ (see Online Supplementary Materials for details of preparation procedure). The synthesized catalysts were characterized by transmission electron microscopy (TEM), powdered X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and diffuse reflectance infrared Fourier transform spectroscopy of adsorbed CO (DRIFTS CO). The micrographs and particle size distribution of the Pd₁In₁ and Pd₂In₃ catalysts (Figure S1, see Online Supplementary Materials) indicate that the catalysts contain almost spherical well-distributed PdIn bimetallic particles with the average size of 14 nm.

XRD patterns of the synthesized Pd, Pd₁In₁, Pd₂In₃ catalysts and the parent α -Al₂O₃ support are plotted in Figure 1 for the range of $2\theta = 34$ – 42° . The parent α -Al₂O₃ exhibits characteristic narrow reflexes at 2θ of ca. 35.3 and 37.9° , indicating a highly-crystalline structure of the carrier.¹⁵ For monometallic Pd characteristic diffraction peak was detected at 2θ of ca. 40.2° attributed to the Pd (111).¹⁶ XRD profile of bimetallic Pd₁In₁ catalyst with Pd:In ratio of 1:1 exhibits a peak at 39.2° , assigned to a 110 diffraction of cubic CsCl structure of Pd₁In₁, indicating the formation of Pd₁In₁ intermetallic nanoparticles in a single phase.¹⁷ Neither metallic Pd nor In typical reflexes were observed. For the In-enriched catalyst with Pd:In ratio of 2:3, the XRD patterns reveal coexisting of two Pd_xIn_y intermetallic phases with different stoichiometry. Peak fitting analysis of the XRD profile reveals four reflexes. The one at 39.1° is characteristic of In(110) indicating the presence of metallic In. Two intensive peaks at 2θ of ~ 39.7 and 39.9° were assigned to 110 and 012 facets of Pd₂In₃ intermetallic phase of hexagonal structure.¹⁸ The low-intensive peak at 2θ of $\sim 40.4^\circ$ suggests the formation of a minor amount of Pd₃In₇ phase. The signal at 2θ of 36.3° stems from the presence of metallic In.¹⁹

XPS study of Pd, Pd₁In₁ and Pd₂In₃ catalysts provides additional evidences of PdIn intermetallic compound formation (Figure S2, see Online Supplementary Materials). Thus, Pd3d_{5/2} for Pd₁In₁ is shifted toward high binding energy by 0.9 eV relative to Pd catalysts (335.8 and 334.9 eV, respectively). The observed shift of Pd3d_{5/2} line is indicative of PdIn IMC formation and pronounced perturbation of Pd electronic structure due to Pd^{δ+}-In^{δ-} charge transfer.²⁰ For Pd₂In₃ catalyst, Pd3d_{5/2} line shifts further to 336.0 eV,

which corresponds to the increase in Pd/In ratio and formation of In-enriched Pd₂In₃ intermetallic phase. It is important that curve fitting analysis of Pd3d_{5/2} line in Pd₁In₁ and Pd₂In₃ did not reveal any signal typical of metallic Pd (334.9 eV). This observation indicates the absence of monometallic Pd nanoparticles in Pd₁In₁ and Pd₂In₃ samples, which is in agreement with the XRD data.

The DRIFTS CO technique was used for studying the surface structure. Figure 2 shows the DRIFT spectra of CO adsorbed on monometallic Pd, and bimetallic Pd₁In₁ and Pd₂In₃ catalysts in the carbonyl stretching vibrations region of 1800–2200 cm⁻¹. The IR spectrum of adsorbed CO for monometallic Pd exhibits two broad asymmetric absorption bands. The one with maximum at 2089 cm⁻¹ corresponds to linear bonded CO on palladium atom, whereas intensive asymmetric peak in the range of 2000–1800 cm⁻¹ is attributable to multiple adsorbed CO.²¹ The high intensity of this peak suggests the presence of large well-crystallized palladium particles. Maximum at 1990 cm⁻¹ corresponds to bridge-bonded CO, adsorbed on (100) facet. A shoulder with maximum at 1944 cm⁻¹ indicates the presence of bridge-bonded CO adsorbed on (111) facet of metallic palladium.

In contrast, the spectrum of freshly reduced Pd₁In₁ catalyst exhibit the intense single peak with maximum at 2064 cm⁻¹ attributable to CO linearly adsorbed on metallic Pd. The absence of other characteristic bands within the multibonded CO range (2000–1800 cm⁻¹) provides strong evidence for the formation of intermetallic PdIn structure with isolated Pd₁ atoms capable of binding only linear CO. The absence of bridging and hollow adsorbed CO presumably stems from the increase of Pd–Pd interatomic distances caused by surrounding of Pd sites by In atom similarly to PdGa compositions.²²

It should be noted that the linearly adsorbed CO band on Pd₁In₁ (2064 cm⁻¹) is shifted toward lower frequency by 25 cm⁻¹ as compared to monometallic Pd (2089 cm⁻¹). The red shift can be explained by two effects. First, it caused by the pronounced back-donation of electron density from the Pd atom to the anti-bonding π -orbital of the adsorbed CO molecule and a concomitant weakening of the C–O bond indicating the modification of the Pd electronic states by covalent bonding in Pd–In.^{23,24} Similar effect was also reported for PdGa intermetallics.²⁵ Second, this shift may possibly stem from a reduced lateral interaction between linearly adsorbed CO molecules due to isolation of Pd atoms by In ones.²⁵

The spectrum of Pd₂In₃ also exhibits the single band with maximum shifted to 2052 cm⁻¹. Indium tends to segregate on the surface of indium-rich intermetallic compounds, thus this shift can be related to presence of large amount of indium on upper layers of nanoparticles.¹⁴ Another explanation may be that Pd₂In₃ IMC has a different structure, so CO molecules can be adsorbed on another facet, unlike PdIn.

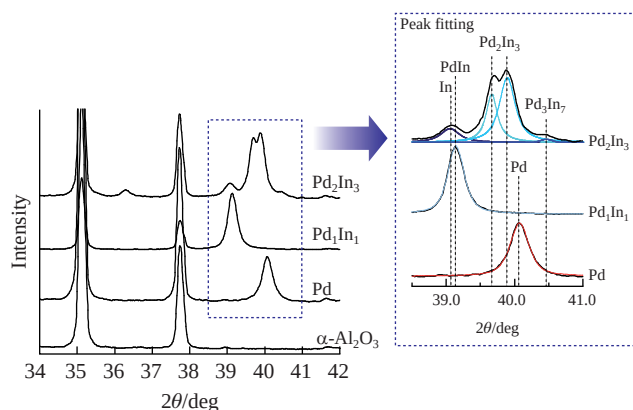


Figure 1 XRD patterns for parent α -Al₂O₃, monometallic Pd, Pd₁In₁ and Pd₂In₃ catalysts.

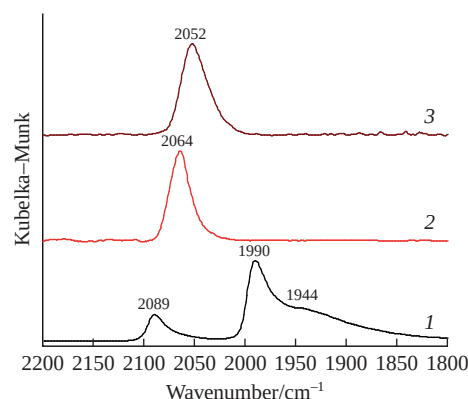


Figure 2 DRIFT spectra of adsorbed CO collected for (1) Pd, (2) Pd₁In₁ and (3) Pd₂In₃ catalysts.

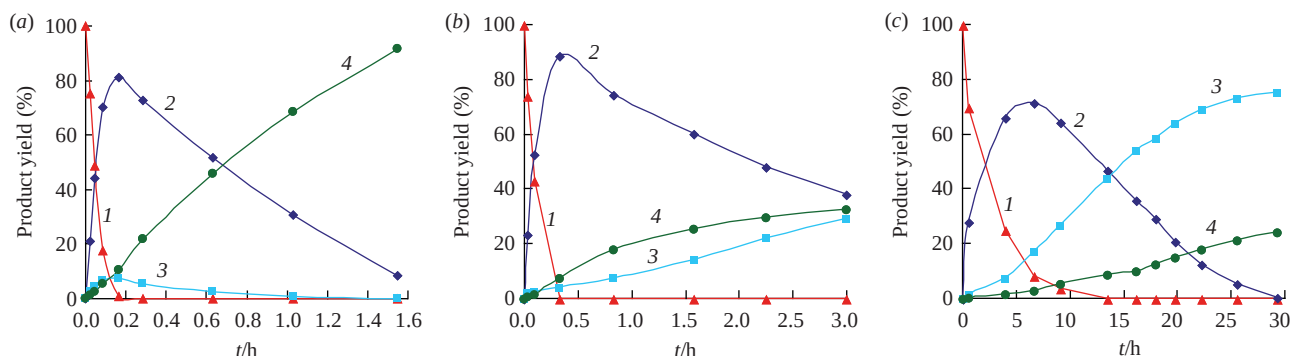
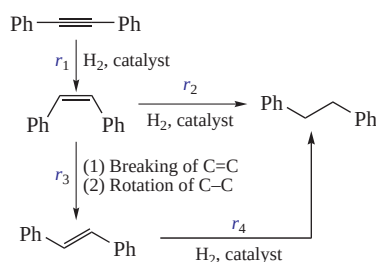


Figure 3 Time course of product concentrations in the hydrogenation of DPA over (a) Pd, (b) Pd₁In₁ and (c) Pd₂In₃ catalysts; (1) DPA, (2) *cis*-ST, (3) *trans*-ST, and (4) DPE.

The catalytic properties of the synthesized catalysts were studied in liquid-phase hydrogenation of DPA (Scheme 1). Figure 3 depicts the time course of the product yields for Pd, Pd₁In₁ and Pd₂In₃ catalysts. The volcano-type shape of *cis*-ST ‘yield vs. time’ profile for monometallic Pd catalyst implies the consecutive hydrogenation mechanism. In the first step, an alkyne molecule adsorbed on Pd surface undergoes syn addition with dissociated hydrogen resulting in the rapid formation of *cis*-ST with a maximum yield at 81%. After complete conversion of DPA, the yield of *cis*-ST gradually decreases, while the amount of 1,2-diphenylethane (DPE) grows continuously, indicating over-hydrogenation of the stilbene intermediate. The reaction rate of stilbene hydrogenation is ~8 times slower than that of DPA. The formation of *trans*-ST over monometallic Pd is minor and the amount does not exceed 8%.

Similarly to the monometallic Pd, hydrogenation of DPA over Pd₁In₁ catalyst leads to *cis*-ST as the primary product with the maximum yield of 89%. After full consumption of DPA, amount of *cis*-ST passes through the maximum and gradually decreases. Unlike monometallic Pd catalyst, the decrease in *cis*-ST amount is accompanied by the increase in both DPE yield and amount of *trans*-ST. Apparently, the further transformation of *cis*-ST proceeds via two pathways, namely, its over-hydrogenation and isomerization, with the rate of over-hydrogenation being ca. 40 times slower compared to the rate of DPA hydrogenation. This suggests significant inhibition of the Pd₁In₁ activity in over-hydrogenation compared to monometallic Pd catalyst. The close rates of *trans*-ST and DPE formation point out the improved isomerization performance of Pd₁In₁ since the yield of *trans*-ST surpasses 30%.

In the case of Pd₂In₃ with higher content of In component, the rate of *trans*-ST formation exceeds the rate of over-hydrogenation by a factor of 5, namely, the yield of *trans*-ST yield approaches 76%, with the yield of DPE being essentially lower as 24%. For the previously reported¹⁰ best single-component Rh₂Sb/SiO₂ catalyst, the yield of *trans*-ST was 58%. The higher yield of 88% was achieved by moving to the more expensive [RhSb/SiO₂ + Pd₃Bi/SiO₂] tandem catalytic system, while the other tandem system of [Pd₃Bi/SiO₂ + H-USY] provided 74% yield of *trans*-ST.⁹



Scheme 1

Scheme 1 suggests a primary formation of *cis*-alkene followed by its subsequent conversion via two pathways: over-hydrogenation to alkane and the isomerization to *trans*-alkene.^{10, 26} The *cis*–*trans* isomerization of olefin can proceed via the breaking of a C=C bond into the corresponding C–C single bond followed by rotation about the C–C axis.¹⁰ Thus, addition of one hydrogen atom to the C=C bond results in its semi-hydrogenation and breaking of a double bond. As a next step, the elimination of the hydrogen with the corresponding C–C bond rotation enables a thermodynamically stable *trans*-isomer formation.¹⁹ In parallel to isomerization, over-hydrogenation of *cis*- and *trans*-alkenes proceeds with the formation of undesired alkane. By this reaction network, the maximal *trans*-ST yield is dictated by the ratio of isomerization to over-hydrogenation rates [$r_3/(r_2 + r_4)$].

The increase in *trans*-isomer yield at isolated Pd₁ centers can be explained by two factors. Firstly, it is conceivable that the adsorption energy of *cis*-ST and *trans*-ST is reduced on isolated Pd₁ sites compared to multiatomic centers of monometallic Pd, which favors alkene desorption, thereby, lowering r_2 and r_4 rates and inhibiting over-hydrogenation. This suggestion is supported by DFT study of C₂H₄ adsorption on Pd₁In₁ intermetallic surface, which indicated the C₂H₄ coordinates on Pd₁ site surrounded by In atoms via weak π -bonding with low adsorption energy.²⁷ Secondly, by analogy with RhSb intermetallic compound,²⁸ specific atomic arrangements of isolated Pd site permits primary addition of hydrogen atom enabling rotation along C–C bond but inhibits the secondary addition and favors elimination of hydrogen followed by desorption of thermodynamically stable *trans*-ST, thus enhancing r_3 isomerization rate. It is remarkable, that the improvement of *trans*-ST yield over Pd₂In₃ compared to that over Pd₁In₁ indicates that both factors become more pronounced with increasing degree of isolation of Pd₁ centers.

In conclusion, PdIn intermetallic nanoparticles exhibit favorable catalytic performance providing 76% yield of *trans*-ST upon hydrogenation of DPA, which is drastically different to the performance of monometallic Pd. Comparison of the catalytic results with characterization data suggests that the specific catalytic performance originates from the formation of single atom Pd₁ sites isolated by In atoms on the surface of intermetallic Pd_xIn_y nanoparticles. Specific atomic arrangement of Pd₁ centers lowers over-hydrogenation activity and enables *cis*–*trans* isomerization thus favoring production of *trans*-isomer. The data obtained suggest that Pd_xIn_y ($y > x$) intermetallic catalysts can be promising candidates for the *trans*-alkenes synthesis via one-pot selective hydrogenation/hydroisomerization of disubstituted alkynes.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.07.020.

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