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Tuning the Catalytic Performance for the Semi-hydrogenation of Alkynols by Selectively Poisoning the Active Sites of Pd Catalysts

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Abstract

Semi-hydrogenation of alkynols to alkenols with Pd-based catalysts, is of great significance in fine chemical industries. Industrial Lindlar catalysts, employing Pb to modify the Pd nanoparticles for higher selectivity toward alkenols, however, generally suffer from both severely activity decrease and environment pollution caused by using

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heavy metal Pb and additives. Therefore, how to overcome the selectivity a controllable paradox remains a great challenge in industry. Here, we reported a controllable strategy for semi-hydrogenation catalysts synthesis, which successfully improves the catalytic performance through selectively poisoning the edge and corner sites of Pd nanoparticles. When integrity of the crystal face is reserved, both higher activity (~1340 h⁻¹) and selectivity (~95% at 99% conversion) are achieved in the semi-hydrogenation of 2-methyl-3-butyn-2-ol (MBY) in ethanol, an industrial important intermediate product for synthesis of Vitamin E, without adding any toxic additives. What's more, the yield could exceed 98% at 99% conversion under no solvent and organic adsorbate conditions, which had never been achieved before. This work provides a different perspective to design and develop high performance catalysts for semi-hydrogenation of alkenols or even substituted alkynes.

Keywords

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semi-hydrogenation, selectively poison, Lindlar catalyst, Vitamin E,

2-methyl-3-butyn-2-ol

1. Introduction

The semi-hydrogenation of alkynols to alkenols is critical for many important manufacturing processes of bulk and fine chemicals including vitamins, drugs, fragrances and synthetic material such as corrosion inhibitor and artificial fiber etc.^{1, 2} Among them, the synthesis of Vitamin E involves various alkenol such as isophytol, linalool and 2-methyl-3-buten-2-ol (MBE). Generally, these alkenols are achieved via semi-hydrogenation of alkynols.³⁻⁶ Pd-based catalysts are frequently used in

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semi-hydrogenation reaction of alkynes in industry. However, they usually suffer and the suffice of the suffice of the suffice of the suffice active sites at a certain degree.⁸ One of the most famous cases is Lindlar catalysts,⁹ in which Pd/CaCO₃ is modified with Pb and quinoline. However, the addition of Pb leads to serious heavy metal pollution and activity loss.¹⁰ Therefore, developing lead-free catalysts with higher performance for selective hydrogenation is highly desired. Based on this idea, much work has been focused on the isolation of the active sites by forming metal compounds or alloys,¹¹⁻¹³ single-atom catalysts¹⁴⁻¹⁶ and so on¹⁷⁻¹⁹.

The semi-hydrogenation of alkynols is structure-sensitive.^{20, 21} The activity and selectivity are strongly influenced by both the size and shape of Pd nanoparticles (NPs), since the ratio of different types of active sites (e.g., facet, corner and edge) on the surface varies.²² In 2011, Xia²² et al. synthesized uniform Pd nanocrystals of different shapes with different ratios of low-coordinated sites (edge and corner atoms) through a solution-phase method with poly(vinyl pyrrolidone) (PVP) serving as a stabilizer, and then tested them in the hydrogenation of MBY (Scheme 1). In view of the mechanism, the direct route with MBY being hydrogenated to MBA straightly occurred on the conditions that the adsorption of MBE was stronger than that of MBY. In this way, adsorbed MBE intermediate would not be replaced by MBY on the catalytic surface, and then was further hydrogenated to 2-methyl-butan-2-ol (MBA). Otherwise, MBE would desorb into the solvent as the semi-hydrogenation product

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Scheme 1. Reaction scheme of 2-methyl-3-butyn-2-ol (MBY) hydrogenation.

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route. The results from Xia demonstrate that the reaction mainly proceeded along the sequential route on Pd catalysts and that the facet sites are the main active sites for the transformation of alkynols to alkenols in semi-hydrogenation reaction, while the corner and edge sites are responsible for over-hydrogenation.²³⁻²⁵ However, the influence of PVP on catalytic performance cannot be ruled out. In our group, a PdZn/CN@ZnO catalyst was recently utilized for the semi-hydrogenation of MBY.²⁶ The selectivity to MBE was significantly improved over PdZn/CN@ZnO catalyst compared with that over the monometallic Pd/CN catalyst. Density functional theory (DFT) calculation results demonstrate that it is the decrease of corner and edge Pd atoms caused by Zn doping, rather than planar poisoning, that was responsible for the enhanced selectivity. However, it is hard to control the degree of Zn doping since PdZn alloy are easily formed. This unselective doping would dramatically reduce the catalytic activity due to the excessive poisoning of the surface active-sites (e.g. TOF = 434 h^{-1} and Sel./% = 92% for PdZn/CN@ZnO with 1 wt% Pd loading). One would be

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easily trapped into a mindset that the isolation of the Pd sites is pre-requisite to prevent the polymerization of alkynes during the catalyst preparation since organic adsorbates are always used.^{27, 28} However, our previous investigation suggests that the OH group in alkynols/alkenols actually bind to the Pd sites upon adsorption.²⁶ This reactant induced self-poisoning or self-isolation effect may suppress the polymerization, and then the isolation of the Pd sites through Pb poisoning or organic absorbates may no longer be neccessay.

In this work, a controllable strategy is adopted to fabricate catalysts in which only corner and edge Pd atoms can be blocked. The synthesized catalysts were proved to be highly efficient for the selective hydrogenation of MBY to MBE in ethanol (TOF = 1340 h⁻¹ and Sel./% = 95% with 0.3 wt% Pd loading). What's more, to the best of our knowledge, higher than 98% yield at 99% conversion were firstly achieved under no solvent and organic adsorbate conditions, while commercial Lindlar catalysts only gave ~1/4 activity and 93% selectivity under the same conditions. The enormous improved performance of this catalyst originates from the appropriate poisoning degree of Pd NPs, which can be precisely controlled by reduction temperatures. Besides, the catalysts could be reused at least ten times without significant loss of activity and selectivity. We believe this work would shed light on another insight to design and synthesize efficient catalysts for industrial semi-hydrogenation of alkenols or even substituted alkynes.

2. Experimental

2.1 Materials

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Indium oxide (50 nm, Macklin), In(NO3)₃, NaBH₄ (Sinopharm Chemical Reagent Co. Ltd), SiO₂ (Alfa Aesar), PdPb/CaCO3 (5 wt% Pd, Lindlar catalyst) and 2-methyl-3-butyn-2-ol (98%) were used as received from Aladdin Chemistry Co., Ltd. Palladium(II) nitrate dehydrate purchased from Energy Chemical. was Dehydrolinalool and dehydronerolidol were purchased from NHU Co., Ltd. All chemicals were used as purchased.

2.2 Catalyst synthesis

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A series of Pd catalysts were prepared by wetness impregnation method. The prepared catalysts were named as Pd-In/In₂O₃-x (x stands for reduction temperature). 1.00 g In₂O₃ support was impregnated with a certain amount of palladium nitrate aqueous solution to achieve 0.3 wt% Pd loading. After magnetic stirring at 70 °C for 12 h, the precursor was dried at 70 °C in an oven overnight, followed by reduction at various temperatures from 200 to 350 °C in H₂ for 1 h. The solid was ground before use.

The prepared catalysts with no coating upon Pd particles, denoted as Pd/In₂O₃, were prepared by an ultrasound reduction method, which was tested as contrast sample. In detail, 1.00 g In₂O₃ support was dispersed in 30 mL deionized water in a beaker by shaking it with the assistance of ultrasound, and 300 uL Pd(NO₃)₂ aqueous solution (0.01 g mL⁻¹) was added into this suspension with ultrasound for 30 min. Then, 10 mL newly prepared NaBH₄ solution (1 mg mL⁻¹) was added into this system quickly, and the mixture was shaken for another 30 min. Next, the solution was centrifuged to get the gray residue. The residue was washed several times with deionized water. After

drying in vacuum oven at 40 °C overnight, the catalyst was obtained. Pd/SiO₂ catalyst ^{COGCO1356C} with 0.3 wt.% Pd loading was also prepared by wetness impregnation method. PdIn/Al₂O₃ catalyst with 0.3 wt.% Pd and 0.3 wt.% In was prepared by co-impregnation method with reduction temperature of 400 °C.

2.3 Characterizations

High-resolution transmission electron microscopy (HRTEM) was performed on a Field Emission Transmission Electron Microscopy with an acceleration voltage of 200 kV. The samples to be tested were ultrasonically dispersed in ethanol. A drop of the solution was deposited onto a carbon-coated copper grid, followed by evaporation for TEM, HRTEM characterization and elemental mapping.

The IR spectra of CO adsorbed on solid samples were performed on a Bruker Vector 22. All spectra were obtained at room temperature (25 °C). Before the tests, the as-synthesized catalysts (150 mg) were purged for 1 h with He at preset temperatures to remove the vapor and impurities. After cooled to room temperature, the background spectrum was recorded and a feed gas (5 vol% CO in He) was introduced into the sample cell with flow rate at 30 mL/min for 1h. Then, He was introduced with flow rate at 30 mL/min for 30 min to remove the physically absorbed CO, and the IR spectra were collected.

After water removal under Ar atmosphere at 120 °C, H_2 temperature programmed reduction (TPR) was conducted in a quartz reactor connected to a thermal conductivity detector (TCD) under an atmosphere of 10% H_2 /Ar from room temperature to 500 °C at a heating rate 10 °C/min. Temperature programmed desorptions of CO (CO-TPD) and H_2 -TPD were conducted with a TCD under pure CO and Ar respectively with H_2 in situ reduction pretreatment at a heating rate 10 °C/min from room temperature for 2 h before calcining at 250 °C for 3 h.

The X-ray photoelectron spectra (XPS) were obtained on an ESCALAB_MARK^{tew Arcle Online} II spherical analyzer with an aluminum anode (1486.6 eV) X-ray source, and the binding energy was calibrated by C1s peak (284.5 eV). Powder X-ray diffraction (PXRD) was performed using a wide-angle X-ray diffractometer (D/tex-Ultima TV) with Cu K α raiation ($\lambda = 1.54$ Å) (tube operating at 40 kV and 40 mA). The Pd content in the prepared catalysts was analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Perkin-Elmer 3300 DV). Scanning electron microscopy (SEM) study was performed on Hitachi SU8010 microscopy. The textual properties were collected on Micromeritics ASAP 2020 HD88 instrument. The specific surface area was calculated by the Brunauer–Emmett-Teller (BET) method. Prior to analysis, the samples were degassed in vacuum at 573 K for 12 h.

2.4 Catalytic tests

In a typical reaction, 1.25 mmol MBY, 5 mL ethanol, and 20 mg freshly-prepared catalysts were added into a 50 mL 3-necked round bottom flask and thoroughly mixed. A balloon filled with H₂ was connected to the flask, and the flask was purged with H₂ for three times before reaction. Then, the reaction was maintained at 30 °C under vigorous stirring. To track the reaction progress, the reaction mixture was collected with a syringe at a certain time interval. After sampling and centrifugation, the product distribution of the solution was analyzed by gas chromatography-flame ionization detector (GC-FID), while the products were identified by gas chromatography-mass spectrometer (GC-MS). By utilizing isopropanol as the internal standard, the mass ratios of MBE, MBY, and MBA were eventually calculated.

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The conversion, selectivity, and mass balance of the reaction can be calculated as following equations. These formulae imply that no components other than MBY, MBE and MBA were obtained, which was confirmed by the carbon balance of $100 \pm 2\%$ for all reactions.

Conv.%= 1-m(MBY),

Sel.%= m(MBE)-m(MBY),

Mass balance= m(MBY)+m(MBE)+m(MBA)

where m(MBY), m(MBE), and m(MBA) are the mass ratios of MBY, MBE, and MBA in the reaction system.

2.5 TOF calculations

The calculation method of TOF values in this article is reported in our earlier work.²⁶ To be specifically, it could be denoted as follows:

$$\mathrm{TOF} = \frac{n_{MBY}}{n_{Pd}} \times \frac{\mathrm{Conv.}}{T},$$

Where n_{MBY} is the moles of MBY, n_{Pd} is the moles of Pd in the catalyst, Conv. and T are conversion and reaction time of MBY respectively. Conv./T is the value of the slope taken from the T-Conv. curves of MBY in the kinetic regime.

2.6 Catalyst reusing

In order to examine the stability of the catalysts, they were recycled in repeated runs. Parallel experiments were conducted during the recycle test. One 50 ml 3-necked round bottom flask, with a balloon filled with 1 Bar H₂, contained 120 uL MBY, 5 mL ethanol and 20 mg Pd-In/In₂O₃-250. Another, with a balloon filled with 1 Bar H₂, contained 30 mg Pd-In/In₂O₃-250 with proportional amplified substrate and

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solvent and was used as catalyst supplier for the first flask. The catalytic hydrogenation was carried out at 30 °C for 1 h separately. After each run, the recovered catalyst was washed several times with ethanol and dried overnight at 40 °C under vacuum and stored in the vacuum desiccator for no more than 1 day before the next run. The mass loss of the catalyst in the first flask was supplied from the second flask before the next run. Subsequent reusability tests were carried out following the same procedures as stated above.

3. Results and discussion

The Pd-In/In₂O₃-x catalysts with 0.3 wt% Pd loading were prepared by wetness impregnation method. X-ray diffraction (XRD) patterns of all these catalysts exhibit diffraction peaks indexed to only In₂O₃ (Figure 1A). No Pd diffraction peaks were detected because of the low metal content. The representative images and corresponding size distribution of Pd NPs are presented in Figure S1. It clearly shows that the Pd NPs sizes in all samples are similar. No obvious particle sintering is observed. The average particle size is about 3.9 nm, which is just in the optimum size range (3–5 nm) of Pd nanoparticles for high performance of semi-hydrogenation of MBY.²² Besides, the hemispherical shape of the Pd NPs indicates the existence of interaction between Pd and In_2O_3 . High resolution transmission electron microscopy (HRTEM) images show that the Pd NPs on the catalysts are covered by a thin layer except for



Figure 1. The compositions and Structures of the catalysts. (A) XRD pattern for Pd/In_2O_3 , $Pd-In/In_2O_3-200$, $Pd-In/In_2O_3-250$ and $Pd-In/In_2O_3-300$. (B) H_2 TPR files of $Pd-In_2O_3$ and In_2O_3 without reduction.

reduction temperature. One can observe that the carrier gradually migrated onto the Pd-In/In₂O₃-200. The degree of coverage is different and closely depends on the surfaces of Pd NPs (Figure 2A-D) under H₂ atmosphere. In addition, the lattice spacing of the thin cover layer is 0.29 nm which is consistent with the (222) plane of In_2O_3 , as revealed

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Figure 2. The interaction between Pd NPs and In₂O₃ under different reduction conditions. HRTEM images of (A) Pd-In/In₂O₃-200, (B) Pd-In/In₂O₃-250, (C) Pd-In/In₂O₃-300, (D) Pd-In/In₂O₃-350. (E) Pd 3d XPS spectra of the catalysts for (A), (B) and (C). (F) An enlarged view of Pd-In/In₂O₃ -250.

in Figure 2D. Element mapping analysis also confirms the composition of the cover layer (Figure S2). The above results fully prove the migration process of the carriers to the surface of Pd NPs.

The interaction between Pd NPs and In₂O₃ was then studied using H₂-temperature programmed reduction (H₂-TPR) and the results are shown in Figure

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1B. For In_2O_3 , the reduction starts at around 170 °C. Two broad peaks centered at 250^{°COCC01356C} °C and 410 °C are assigned to the reduction of surface In_2O_3 .²⁹ For sample impregnated with Pd precursor, H₂-TPR shows one peak centered at about 100 °C, which can be attributed to the reduction of Pd^{2+,30} Two reduction peaks located at 240 °C and 400 °C can be attributed to the reduction of surface In_2O_3 . And another small peak centered at about 140 °C, which is not present in the sample In_2O_3 , can be attributed to the reduction of surface In_2O_3 by the spillover hydrogen from Pd NPs.³¹

To further verify the electronic interaction between Pd and In_2O_3 , X-ray photoelectron spectroscopy (XPS) investigation was performed for samples Pd-In/In₂O₃-200, Pd-In/In₂O₃-250 and Pd-In/In₂O₃-300 (Figure 2E). Two peaks at the binding energy of 335.4 and 340.8 eV are observed for Pd-In/In₂O₃-200, in accordance with the values for metallic Pd 3d^{5/2} and 3d_{3/2}.³² For samples Pd-In/In₂O₃-250 and Pd-In/In₂O₃-300, the peaks of Pd 3d^{5/2} and 3d^{3/2} gradually shift to lower binding energies with the increase of reduction temperature. Meanwhile, the layer over the Pd NPs becomes thicker (Figure 2A-D). The negative shift of Pd 3d may indicate the electron transfer from reduced In to Pd. However, no obvious difference for the binding energies of In 3d^{5/2} and 3d^{3/2} are observed for the three samples (Figure S3) due to the existence of massive bulk In₂O₃. According to previous researches, in the strong metal-support interaction (SMSI) state which occurred under reductive condition, the Fermi level of the partially reduced metal oxide support becomes higher than that of the metal NPs.³³ Therefore, we surmise that

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the electron might transfer from the support to the metal NPs in order to attain the Fermi-level equilibration at the interfaces. In our case, when pretreated with H₂, the Fermi level of species containing In which located on the top surface of Pd NPs is higher than that of Pd NPs, which would facilitate the electron transfer from the support to Pd NPs.34

To demonstrate the effect of poisoning degree on tuning the catalytic performance, MBY semi-hydrogenation reaction was used as a probe reaction, as shown in Figure 3A. The possible mass-transfer limitations has been minimized as seen in Figure S4 and the involved discussion. When the reduction temperature is below 200 °C, the reaction activity for MBY hydrogenation gerenarally remains unchanged, but the selectivity toward MBE rises. As reduction temperature further enhances, the activity for MBY hydrogenation decreased significantly, while the selectivity toward MBE continues to rise. Until the reduction temperature is beyond 250 °C, the selectivity toward MBE begins to decline. Combined with Figure 1, the above results illustrate that an appropriate poisoning extent is responsible for the excellent selectivity. By comparing the selectivity of these catalysts, we found that Pd-In/In₂O₃-250 was the optimal (Figure 3A). The yield of MBE could reach above 95% at 99% conversion, without adding any toxic additives such as heavy metal Pb or organic ligand quinoline. Nearly twice higher activity (TOF = 1340 h^{-1}) with identical selectivity are achieved compared with our

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Figure 3. The catalytic performance of different catalysts. (A) Comparison of the catalytic performance among different catalysts. Reaction conditions: 20 mg catalysts, 120 uL substrate, 5 mL ethanol, 30 °C, 1 atm H₂, stirring rate of 1000 rpm. (B) The proposed catalyst model. And infrared spectroscopy of CO adsorption (C) and CO-TPD spectra (D) on various Pd samples.

industrial catalyst PdZn/CN@ZnO.26

As a control experiment, the Pd/In_2O_3 sample reduced by NaBH₄ without decoration on the surface of Pd NPs, which can be clearly proved by TEM images (Figure S5 and S6), was tested. As shown in Figure 3A and S7A, the selectivity of Pd-In/In₂O₃-250 catalyst is much better than that of Pd/In₂O₃ during the whole reaction process. Since the particle size of Pd/In₂O₃ is close to that of Pd-In/In₂O₃-250

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samples (Figure S8), the different performance cannot be attributed to the particle⁰S128^{CCOCCO1336CC} simply. Note that different reducing temperature may change the morphology of the Pd NPs, which may also cause the different catalytic performance. Therefore, we also choose SiO₂, always seen as an inert oxide, as the carrier to probe the possibility of the above affection. According to previous researches, the surface of SiO₂ could not be activated even when loaded with noble metals at nearly 400 °C upon H₂ atmosphere.^{1, 35} A series of Pd/SiO₂ (0.3 wt% Pd loading) catalysts reduced at various temperatures were tested (Figure S7B). Results showed that in contrast to Pd-In/In₂O₃, the selectivity of Pd/SiO₂ catalysts improved little with the change of reduction temperature. So the proper surface decoration or poisoning of Pd NPs is the key for Pd-In/In₂O₃-250 to achieve higher MBE selectivity while maintaining a remarkable activity.

Different degree of poisoning on the surface of NPs would result in the structural changes of active sites, further influence the catalytic performance.^{36, 37} So in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) with CO as the probe molecule was carried out to explore the relationship between the structure of active sites and catalytic performance. As shown in Figure 3C, the peaks at 2000-2050 cm⁻¹ could be attributed to the adsorption of CO linearly bound to (111)/(111) and (111)/(100) particle edges.³⁸⁻⁴¹ The bands at appropriately 2079 cm⁻¹ could be assigned to the adsorption of linear CO bound to corner atoms of Pd NPs.⁴¹ The peaks appearing below 2000 cm⁻¹ are generally attributed to the CO species bound to the facet sites of the Pd NPs. Specifically, the bands at 1950 cm⁻¹, 1900 cm⁻¹ and 1850

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cm⁻¹ can be assigned to compressed-bridge bonded CO, isolated-bridge bonded CO^{POL10}CO^{COGC01356C} and threefold-hollow bonded CO on facets of Pd NPs, respectively.^{7, 39}.

Compared with other samples, the intense peaks only appear on Pd/In₂O₃ at appropriately 2051 cm⁻¹ could be assigned to the adsorption of linear CO bound to the edge atoms of Pd NPs, which indicates the existence of a large number of edge sites on the Pd NPs. However, only the peaks for bridge-bonded CO adsorption are observed on Pd-In/In₂O₃-200 sample. The disappearance of the signals for linear-bonded CO adsorption under He purging conditions suggests that the edge and corner sites of Pd NPs are blocked. In theory, it is thermodynamically feasible for these low-coordinated atoms to preferentially bond with carriers which migrate onto the surface of Pd NPs.⁴²⁻⁴⁴ In contrast to Pd/In₂O₃, the selectivity of Pd-In/In₂O₃-200 has been enhanced. According to our density functional theory (DFT) results (Table S1), the major active sites for the semi-hydrogenation from MBY to MBE are facet sites, while the edge and corner sites are responsible for the over-hydrogenation to product MBA.²⁶ Therefore, as the reduction temperature gradually rises, the improved selectivity of Pd-In/In₂O₃-200 mainly ascribes to the selective poisoning of edge and corner sites by carrier migration. CO-temperature programmed desorption (CO-TPD) also corroborates the above conclusion. As shown in Figure 3D, the peak attributed to facet sites (50 ~ 100 °C) remained, while the peak corresponding to edge and corner sites $(150 \sim 200 \text{ °C})^{45}$ disappeared when raising the reduction temperature. The preservation of high activity further confirms that the facet sites are responsible for semi-hydrogenation of alkynols. It can be concluded that there is no necessary to

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poison facet sites. Further raising the reduction temperature to 250 °C, the signal intensity for bridge-adsorbed CO adsorption (Pd-In/In₂O₃-250) is attenuated, accompanied with the appearance of a stretching peak at 2070 cm⁻¹, which is attributed to the linear-bonded CO adsorption at facet sites.⁴¹ It implies that partial facet sites have been alloyed with In, resulting in the break of the Pd-Pd bond and the poisoning of the facet sites. The additional peak at 140 °C (Figure 1B) and the binding energy shift of Pd 3d for Pd-In/In₂O₃-250 (Figure 2E) also corroborate the above deduction. The sharp decline in activity is then well expected as shown in Figure 3A. The continual rise of selectivity toward MBE beyond 250 °C may be caused by the continual blocking of the remained small fraction of edge and corner sites (Figure 2F), which is beyond the detectability of instrument. This detectable limitation factor can be confirmed in the case of Pd-In/In₂O₃-300. After reduced at 300 °C, the signal of bridge-bonded CO adsorption on the facet sites disappears, which means the further poison of facet sites. In fact, no valid signals were detected at all on Pd-In/In₂O₃-300. However, this catalyst still shows activity, which means the partial exposure of facet active sites. The selectivity decline for catalysts reduced beyond 250 °C means poisoning the facet sites by breaking the Pd-Pd bond is detrimental to the semi-hydrogenation of alkynols. Therefore, it is feasible to achieve both intriguing catalytic activity and selectivity for semi-hydrogenation of alkynols by selectively blocking corner and edge Pd sites in the synthesized catalysts as illustrated in Figure 2B.

One would suspect that may be it is the progressive inhibition of Pd-hydride

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formation with increased reduction temperatures that actually dominated improved selectivity since several work has disclosed the impact of Pd-hydride to the catalytic performance of semi-hydrogenation of alkynes.^{7, 46} In particular, bimetallic PdIn/Al₂O₃ catalyst, with conventional Lindlar's concept, has been successful in the semi-hydrogenation of Acetylene, where Pd-hydride was entirely suppressed.⁴⁷ Then H₂-TPD was conducted for the involved catalysts reduced at different temperatures. As shown in Figure S9, a progressive inhibition of hydride formation was indeed observed as the reduction temperature increased in that the released amount of H₂ decreased monotonously along with the increase of the reduction temperature. And the desorption temperature of H₂ increased gradually as well. However, the selectivity for the semi-hydrogenation of MBY went through a volcano, rather than a linear decline. Therefore, the impact of Pd-hydride was not thought to be a dominant role to the selectivity of MBY semi-hydrogenation. To further confirm this, supported PdIn alloy (PdIn/Al₂O₃), which has been proved to completely inhibit the formation of Pd-hydride,⁴⁷ was used for the semi-hydrogenation of MBY. The results in Figure 3A, yet, showed that this catalyst was totally inactive on these conditions, which also rules out the possible contribution to the improved selectivity by surface facet Pd-In intermixing on the above Pd-In/In₂O₃ catalysts, i.e., PdIn is not the active phase for MBY semi-hydrogenation under this condition. In addition, the formation of Pd-hydride, together with the CO-IR results in Figure 3C clearly showed the early stage for selectively covering the edge/corner sites in order when increasing the reduction temperature (< 200 °C), and the late stage for surface Pd-In intermixing at

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facet sites when the reduction temperature went beyond 200 °C.

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Note that solvent would also influence the selectivity and no solvent conditions are actually used in industry.^{3, 48} The catalytic performance of Pd-In/In₂O₃-250 in pure MBY were evaluated to make a comparison with the dominated commercial Lindlar catalyst PdPb/CaCO₃. As shown in Figure 4, the reaction rate on Pd-In/In₂O₃-250 (TOF =44208 h⁻¹) is 5.5 times higher than that on PdPb/CaCO₃ (TOF =8034 h⁻¹). What's more, the selectivity of MBE were well maintained in the whole process, achieveing unexpected more than 98% yield at 99% conversion for Pd-In/In₂O₃-250. However, the selectivity decreased sharply at the late conversion stage for PdPb/CaCO₃ (~93% at 99% conversion). The superior catalytic performance for Pd-In/In₂O₃-250 clearly demonstrates the validity of the proposed catalyst design strategy.

In addition, other industrially relevant alkynols, such as dehydrolinalool (D1) and



Figure 4. The comparison of the catalytic performance on Pd-In/In₂O₃-250 and PdPb/CaCO₃ for the semi-hydrogenation of MBY. (A) The time-conversion profile;

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(B) A comparison of selectivity vs. conversion. Reaction conditions: 2.77×10^{-20} and $^{1039/C9GC01356C}$ 4.16×10⁻² wt.% of Pd for Pd-In/In₂O₃-250 and PdPb/CaCO₃ respectively, 5 mL substrate, 80 °C, 1 Bar H₂, stirring rate of 1000 rpm. The amount of catalyst loaded is referred to previous work to ensure reasonable evaluation conditions.⁴⁸

dehydronerolidol (D2), which play an important role in the synthesis of Vitamin E, were also tested in ethanol (Table 1 and Figure S10). Their semi-hydrogenation products were named linalool (L) and nerolidol (N), respectively. As expected, for semi-hydrogenation of D1, the selectivity to L increases from 89.6% to 95% at a conversion of over 99%. And for semi-hydrogenation of D2, the selectivity to N increases from 84% to 89% at a conversion of over 94%. Above results indicate the general scope of this catalyst in semi-hydrogenation of alkynols.

The recycling experiment of $Pd-In/In_2O_3-250$ at both high and middle conversions

Table 1. Result of hydrogenation reaction on dehydrolinalool anddehydronerolidol by Pd/In2O3 and Pd-In/In2O3-250.



	– Pd-In/In ₂ O ₃ -250	99	95	View Article Online DOI: 10.1039/C9GC01356C
D2	Pd/In ₂ O ₃	94	84	
	Pd-In/In ₂ O ₃ -250	94	89	

Reaction condition: 20 mg catalysts, 2 mmol substrate, 5 mL ethanol, 30 °C, 1 atm H₂, stirring rate of 1000 rpm.

for MBY semi-hydrogenation was conducted due to the importance of reusability for catalyst in industrial application (Figure 5A and S11). It was observed that MBE selectivity stay unchanged even after ten recycle runs. Slightly activity decline was observed after seven recycle runs. According to the ICP results, there is no leaching of Pd (Table S2). XRD patterns for the recycled catalyst after ten runs also show no obvious changes (Figure 5B). Considering the sticking effect in Figure S4B, we



Figure 5. The reusability evaluation. The reusability (A) and XRD results after recycling (B) of Pd-In/In₂O₃-250. (C) Evolution of reactant and product concentrations during hydrogenation over Pd-In/In₂O₃-250. Reaction condition: 20 mg catalysts, 120 uL substrate, 5 mL ethanol, 30°C, 1atm H₂, stirring rate of 1000 rpm.

suspected the activity loss would be caused by the decreased agglomerative sizes of the catalysts during the long-term stirring in the recycle process. Besides, the stability is much better than the newly-developed Pd/ZnO/SMF catalyst.^{25, 49} The good stability of the catalyst may be attributed to the protection of the cover layer outside the Pd NPs from SMSI. And the time-conversion curve in Figure 5C suggested a typical sequential hydrogenation mechanism.

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4. Conclusions

Through the selective poisoning of the edge and corner sites of the Pd NPs responsible for over-hydrogenation, both much better selectivity and activity of the Pd- based catalysts were achieved. The comparable selectivity and much better activity on barely Pd-In/In₂O₃-250 catalysts, compared with that on PdZn/CN@ZnO or other Pd-based Lindlar catalysts with additives, suggests that the integrality of the facet sites is necessary when the self-poisoning or self-isolation effects induced by reactants are considered. This work offers a distinctive insight to solve the selectivity-activity paradox on Pd-based Lindlar catalysts for the semi-hydrogenation of alkynols or even other substituted alkynes.

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