

Article

Revisiting the Semi-Hydrogenation of Phenylacetylene to Styrene over Palladium-Lead Alloyed Catalysts on Precipitated Calcium Carbonate Supports

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Abstract: The quest for improved heterogeneous catalysts often leads to sophisticated solutions, which are expensive and tricky to scale up industrially. Herein, the effort to upgrade the existing inorganic nonmetallic materials has seldom been prioritized by the catalysis community, which could deliver cost-effective solutions to upgrade the industrial catalysts catalog. With this philosophy in mind, we demonstrate in this work that alloyed palladium-lead (Pd-Pb) deposited on novel precipitated calcium carbonate (PCC) supports could be considered an upgraded version of the industrial Lindlar catalyst for the semi-hydrogenation of phenylacetylene to styrene. By utilizing PCC supports of variable surface areas (up to 60 m²/g) and alloyed Pd-Pb loading, supported by material characterization tools, we showcase that achieving the “active-site isolation” feature could be the most pivotal criterion to maximize semi-hydrogenated alkenes selectivity at the expense of prohibiting the complete hydrogenation to alkanes. The calcite phase of our PCC supports governs the ultimate catalysis, via complexation with uniformly distributed alloyed Pb, which may facilitate the desired “active-site isolation” feature to boost the selectivity to the preferential product. Through this work, we also advocate increasing research efforts on mineral-based inorganic nonmetallic materials to deliver novel and improved cost-effective catalytic systems.

Keywords: heterogeneous catalysis; hydrogenation; alloyed catalyst; calcium carbonate; functionalization of C-C/C-H bonds



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1. Introduction

Semi-hydrogenation of carbon-carbon triple bond (C≡C) of alkyne to its corresponding alkene (C=C) is a reaction of high-industrial significance [1,2]. Among them, removing phenylacetylene from styrene feed, via such semi-hydrogenation, during styrene polymerization is essential because phenylacetylene, as an impurity above a concentration of 10 ppm, is poisonous to the polymerization catalysts and promotes quicker catalyst deactivation [3,4]. Therefore, the selective hydrogenation of phenylacetylene under benign conditions to the intermediate styrene is essential for the polymer industry. Styrene is a raw material for the polymer industry with an annual production of at least 30 million tons, including solid polystyrene (PS), expandable polystyrene (EPS), styrene-butadiene latex (SBL), acrylonitrile-butadiene-styrene/terpolymer (ABS), unsaturated polyester resins (UPR), and styrene-butadiene rubber (SBR) [5]. In addition, such alkynes semi-hydrogenation gives access to numerous target-oriented alkenes in organic synthesis, such as in fragrances, agrochemicals, and pharmaceuticals [6,7]. However, the major challenge here is, of course, to prohibit the complete hydrogenation to the corresponding alkane and maximize the semi-hydrogenated alkene product yields. Traditionally, the highly popular Lindlar catalyst, i.e., 5 wt% palladium (Pd) deposited on calcium carbonate (CaCO₃) and partially poisoned/alloyed with external substance (e.g., lead (Pb), mercury (Hg),

quinoline), is the most used catalytic material in the (petro-)chemical industry for semi-hydrogenation processes [2,8]. Since the surface of unmodified supported Pd catalyst is truly over-hydrogenated toward undesired alkanes, these active sites could be modified by “poisonous” alloyed Pb, via avoiding excessive Pd agglomeration and subsequent formation of “Pd-H” species in close proximity, which in turn pauses the reaction to deliver semi-hydrogenated alkenes (Figure 1) [9–12].

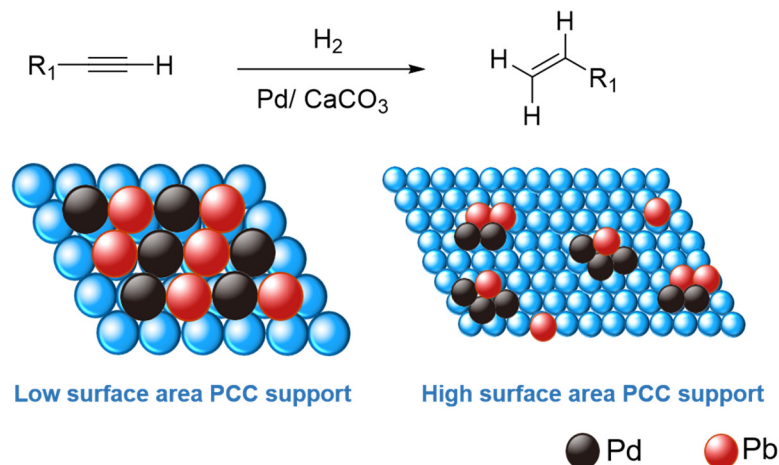


Figure 1. Simplistic illustration of “active-site isolation” concept over low- and high-surface-area precipitated CaCO_3 (PCC) supports.

Mechanistically, the key is to control the substrate adsorption on the metal active sites to promote selectivity toward alkene formation [13,14]. Herein, the catalysis community is seeking alternative pathways to deal with this challenge by developing environmentally friendly catalysts via emphasizing forming “isolated” metal sites to prevent agglomeration and, consequently, over-hydrogenation [13–15]. With this objective in mind, a wide variety of Pd/Pt-based advanced catalytic materials have been designed and screened for the semi-hydrogenation of alkynes: for example, (Lindlar-type) soluble or solid-supported $\text{Pd}(\text{CaCO}_3)_n$ clusters and supported on biogenic CaCO_3 ([14,16]), as well as fabricated bimetallic catalysts (i.e., using non-Pb second elements: B, Cu, Zn, Mg, Cd, Ru, Fe, Ag [17–25]), carbonaceous-supported or confined catalysts (including carbides, carbon nanotubes and graphenes [13,26–30]), silica/alumina/ TiO_2 /zeolite supported catalysts [13,31–34], colloidal catalysts [35], metal-organic framework (MOF)-derived catalysts [36], single-atom catalysts [37–39], and even solar-driven photocatalysts [40]. Although all these (non-poisoned) catalysts have delivered interesting reactivity and selectivity, these materials are unable to replace the traditional Lindlar catalysts in the industry, possibly because of their expensive nature that limits their potential industrial application, both in terms of cost and upscaling.

The major thrust of this research arena has been devoted to tuning catalytic metal sites, with a particular emphasis on providing “active-site isolation” to prevent over-hydrogenation [41,42]. In a typical hydrogenation process over heterogeneous catalysts, the impact of subsurface hydride species is often crucial in controlling the final product’s selectivity, which tends to promote over-hydrogenated products. Therefore, building an alloy via adding a second element (e.g., Pb in the traditional Lindlar catalyst) is a prominent way to deliver such “active-site isolation”. Such a strategy directly impacts the adsorption and activation of reactants, i.e., alkyne, which is also a typical π -ligand in organometallic chemistry [43]. The interaction between the alkyne reactant and the surface of a catalyst could proceed via either ethynylidyne or π -complex modes [44]. To facilitate the semi-hydrogenation to alkene products from alkyne, the relatively weaker π -bonding adsorption mode should be preferred. That could be achieved by isolating active catalytic sites to avoid further hydrogenation [45]. Therefore, to upgrade the commercial Lindlar

catalyst, an alternative strategy is required to deliver such an “active-site isolation”, to avoid any potential agglomeration of catalytically active metal sites.

With this objective in mind, we turned our attention toward upgrading the CaCO_3 support of the Lindlar catalyst. Herein, our original hypothesis was to enhance the surface area of CaCO_3 supports to facilitate such an “active-site isolation” philosophy. It is worth mentioning that commercial Lindlar catalysts or the analogous commercial Pd/Pt-supported CaCO_3 catalysts have limited surface areas (typically $< 10 \text{ m}^2/\text{g}$). Hypothetically, it can be anticipated that an increased surface area of the catalyst support could be an alternate strategy to achieve the desired site isolation. Here in this work, we have screened numerous precipitated CaCO_3 (PCC) supports with variable surface areas (up to $60 \text{ m}^2/\text{g}$) and commercial Lindlar catalysts for the semi-hydrogenation of alkyne substrates. This work unexpectedly demonstrates the beneficial effect of low-surface area PCC supports. Additionally, our Pd-Pb/PCC catalyst delivered superior performance vis-à-vis its commercial counterpart, under lower catalyst loading and using optimized reaction conditions. For example, our catalyst (i.e., 5 wt% Pd on low-surface area PCC support) and commercial 5 wt% Pd-based Lindlar catalyst delivered 81% and 66% of selectivity toward styrene, respectively, after the semi-hydrogenation of phenylacetylene. Interestingly, an almost similar selectivity ($\sim 79\%$) was also obtained upon lowering the catalyst loading, i.e., using 1 wt% Pd on low-surface area PCC support, advocating the concept of “active-site isolation” over our PCC-based catalyst supports. These interesting catalytic results have also been well corroborated with an in-depth characterization using multi-modal spectroscopic and analytical techniques, including X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), scanning calorimetry (TGA-DSC), X-Ray photoelectron spectroscopy (XPS), and nitrogen physical adsorption and desorption (N_2 -BET). Such characterization has also been extended to the commercial Lindlar catalysts to establish their structure–reactivity relationships and provide a rationalization of the fundamental difference in the catalysis results reported in this work.

2. Results and Discussion

2.1. Catalyst Preparation and Characterization

This work introduces three different precipitated calcium carbonate (PCC) supports with variable surface areas: PCC-04, PCC-30, and PCC-60, where the number denotes their respective BET surface area in m^2/g (see Table 1 for the physicochemical parameters' comparison). In this work, we evaluated the performance of both Pb-modified and unmodified catalytic materials, representing Pd-Pb/PCC-xy and Pd/PCC-xy (xy: respective BET surface area in m^2/g , see Table 1, Figures S1 and S2). For the sake of comparison with the commercial Lindlar catalysts, all catalytic materials were synthesized as originally reported by Lindlar and Dubuis [46].

Table 1. The comparison of physical parameters between our PCC supports and catalysts vis-à-vis their commercial counterparts.

Materials	Surface Area (m^2/g) ^a	Mean Pore Size (nm) ^b	Mean Pore Volume (cm^3/g) ^b	Grain Size (nm) ^c
PCC-04	4.4	15.3	0.02	58.1
PCC-30	30.7	27.2	0.24	36.1
PCC-60	60.7	18.2	0.32	17.3
CaCO_3 ^d	1.0	33.7	0.01	86.3
Pd-Pb/PCC-04 ^e	4.3	38.4	0.03	-
Pd-Pb/PCC-30 ^e	27.5	33.8	0.28	-
Pd-Pb/PCC-60 ^e	46.2	24.7	0.32	-
Pd-Pb/ CaCO_3 ^f	7.2	28.6	0.04	-

^a Surface area (S_{BET}) measured by N_2 -physical adsorption. ^b Determined by BJH method. ^c Measured by TEM.

^d A commercial calcium carbonate. ^e All materials are loaded with 5 wt% of Pd and BET measurements were performed after Pb upgrading the materials. ^f Commercial Lindlar Pd-Pb catalyst (cf. also Pd 5 wt% loading).

The physicochemical properties of our PCC supports and their commercial counterpart are illustrated in Figure 2. X-ray powder diffraction (XRD) has been performed to identify the phases of each material. PCC-04 and PCC-30 demonstrated responses at 2θ of 22.9° , 29.3° , 35.8° , 39.3° , 43.0° , 47.5° , 48.4° , and 57.2° , which belong to the diffraction peaks of (012), (104), (110), (113), (202), (018), (116), and (122) crystal planes, respectively (Figures 2a,b and S3) [47], which corresponds to the calcite phase, the most stable polymorph of CaCO_3 . XRD of PCC-60 showed mixed phases of both calcite and aragonite CaCO_3 (Figures 2b and S3): diffraction peaks (i) at 23.2° , 29.44° , 36.13° , 43.3° , 47.7° , and 48.7° at 2θ could be attributed to (012), (014), (110), (202), (018), and (116) crystal planes, respectively (i.e., consistent with the standard card JCPDS: 85-0849 for calcite CaCO_3) and (ii) at 26.35° , 27.21° , 33.12° , 37.88° , 45.85° , 48.44° , and 48.61° corresponds to (111), (021), (012), (112), (221), and (202), respectively (i.e., consistent with the standard card JCPDS: 41-1475 for aragonite CaCO_3). Hence, PCC-60 comprises the trigonal stable calcite and orthorhombic (relatively) unstable aragonite phases [48]. Moreover, the lack of impurity within the XRD spectrum exhibits the high purity of our PCC supports.

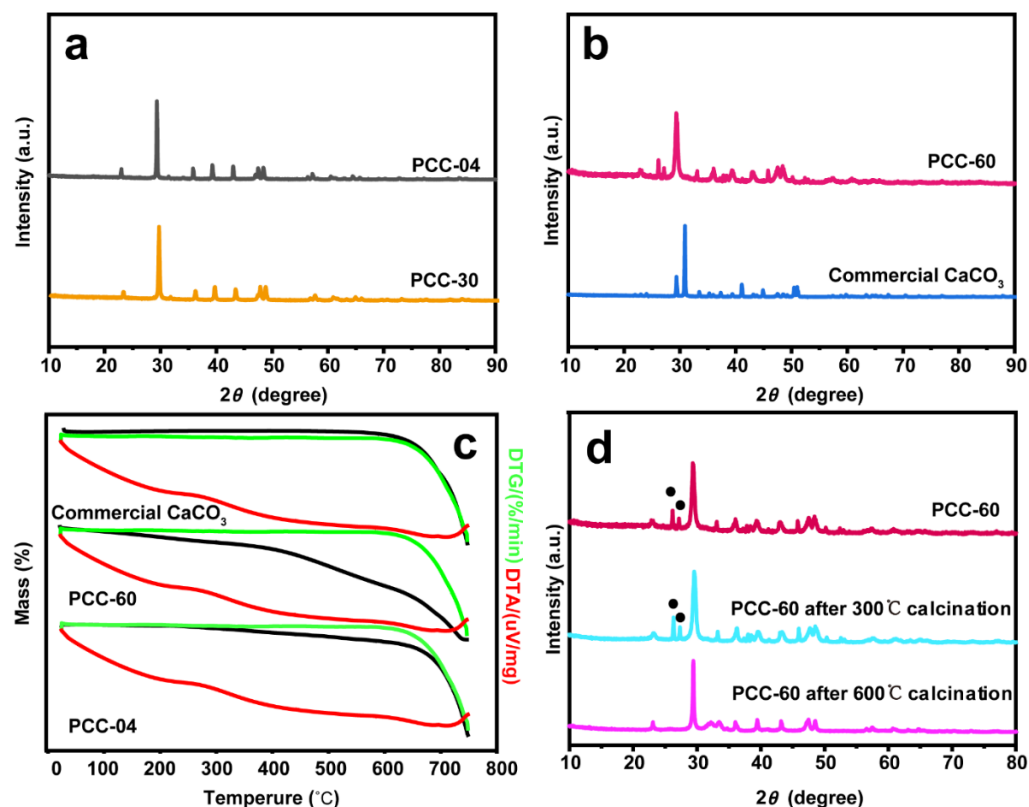


Figure 2. X-ray powder diffraction (XRD) patterns of standalone (a) PCC-04 and PCC-30, as well as (b) PCC-60 and commercial CaCO_3 , indicate the existence of mixed phases (aragonite and calcite) in PCC-60 sample. (c) Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of standalone PCC-04, PCC-60, and commercial CaCO_3 supports, demonstrating higher mass loss in the PCC-60 sample only. (d) XRD pattern of standalone PCC-60 support after the calcination at 300 $^\circ\text{C}$ and 600 $^\circ\text{C}$ highlights the transformation from the relatively unstable aragonite phase to a more stable calcite phase (The black dots refer to the diffraction peak of the aragonite phase). We refer to Figures S3–S5 for additional characterization data.

Since PCC-60 is composed of an aragonite phase, thermogravimetric analysis (TGA) has been performed to verify the material's phase transition during the gradual heating process (Figures S4 and S5). Figure 2c shows that the commercial CaCO_3 began to decompose to CaO at $> 600^\circ\text{C}$, while PCC-60 and PCC-04 began to decompose continuously from $> 200^\circ\text{C}$ and $> 100^\circ\text{C}$, respectively, probably attributed to the presence of $\text{Ca}(\text{OH})_2$ [49].

Herein, the extent of decomposition was significantly greater over PCC-60 (Figure S4c). At the temperature region between 300 °C and 450 °C, the aragonite phase in PCC-60 transformed into calcite, which could explain the higher mass loss [50]. To support this observation, XRD has been performed on the standalone PCC-60 support after calcining the sample at 300 °C, and 600 °C (Figure 2d). Both calcite and aragonite crystal phases were detected at 300 °C, but only calcite was observed when PCC-60 was thermally treated at 600 °C, which supports the mutual transformation between the two crystal forms of CaCO_3 [51].

Next, we turned our attention to understanding the morphology of the CaCO_3 -based supports and their corresponding Pd catalysts, using both scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) (Figures 3 and S6–S12). Using SEM, the standalone PCC-04 support exhibited a distinct fusiform shape, with a length of about 2 μm , and displayed a crisscross structure (Figures 3a and S6). The standalone PCC-30 showed a dense granular shape (Figure S7). In contrast, the PCC-60 support displayed a more organized network structure with a porous nature (Figures 3b and S8). The commercial calcium carbonate exhibited a lamellar structure (Figures 3c and S9).

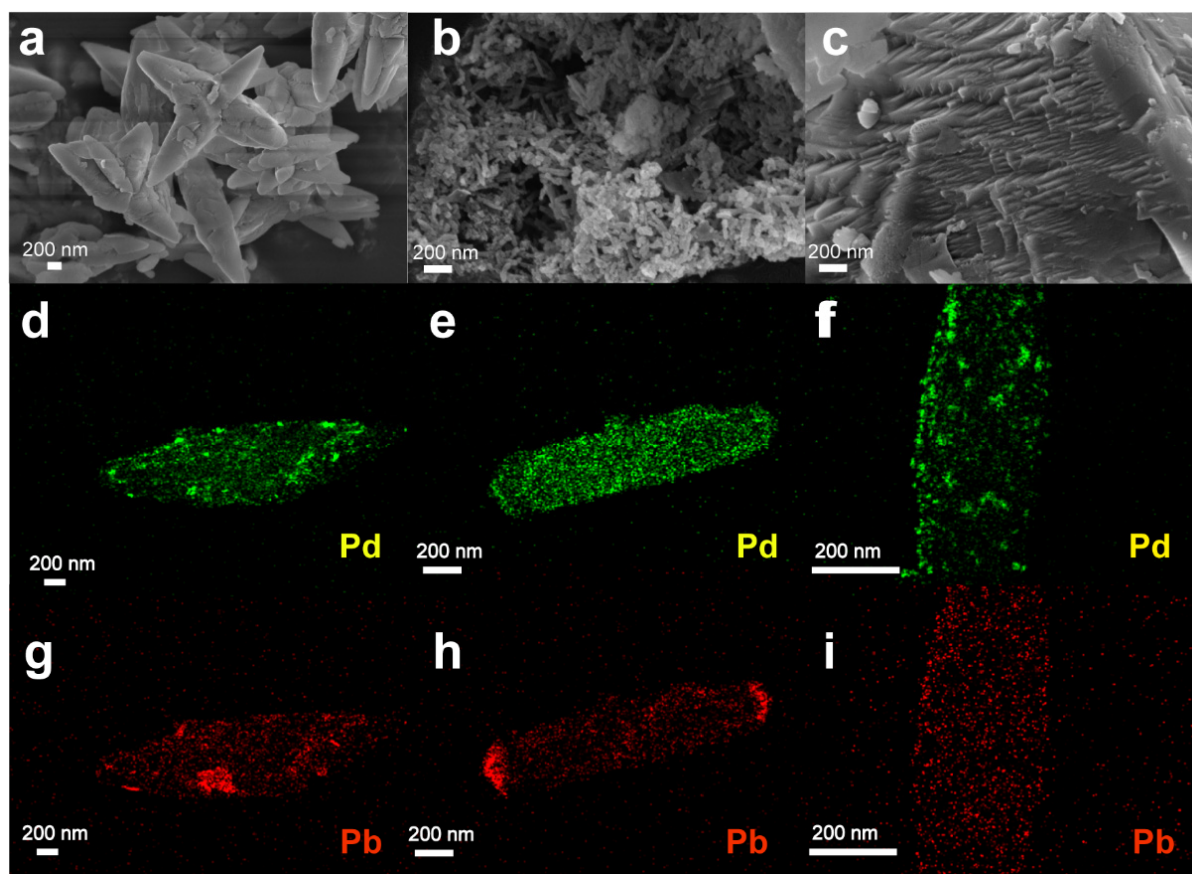


Figure 3. (a–c) Scanning electron microscope (SEM) image of standalone (a) PCC-04, (b) PCC-60, and (c) commercial CaCO_3 supports. (d–f) Pd and (g–i) Pb mapping by high-resolution transmission electron microscopy (HRTEM) on (d,g) 5 wt% Pd-Pb/PCC-04, (e,h) 5 wt% Pd-Pb/PCC-60, and (f,i) commercial 5 wt% Pd-Pb Lindlar catalysts. We refer to Figures S6–S12 for additional characterization data.

HRTEM analysis was performed on Pd-Pb loaded materials to analyze the dispersion of the Pd and Pb particles (Figures 3c and S10). TEM-mapping on Pd-Pb/PCC-04 material presented a (relatively) uniform distribution of the Pb particles on the catalyst surface; in contrast, the Pd particles were situated primarily on the edges (Figure S10). In the case of the Pd-Pb/PCC-60 material, the Pd particles displayed “zonal clusters” throughout the

material (Figure S11). The benchmark Lindlar catalyst reveals mixed characteristics: the uniform distribution of the Pb particles was visible (cf. similar to PCC-04 support), but with higher agglomeration/clustering of the Pd particles (cf. almost similar to PCC-60 support) (Figures 3f and S12). The alloyed nature derived from Pd and Pb was visualized in all materials, including the commercial catalysts. However, the Pd-Pb alloyed nature and distribution are dissimilar and heterogeneous in nature (including the commercial catalyst).

X-ray photoelectron spectroscopy (XPS) was performed to probe the catalyst's surface, especially the local environment of palladium and oxygen (Figures 4 and S13–S15). Herein, we restrict our discussion to the following three key materials: Pd-Pb/PCC-04 (i.e., Pd on low-surface area calcite CaCO_3), Pd-Pb/PCC-60 (i.e., Pd on high-surface-area calcite and aragonite CaCO_3), and commercial Lindlar catalyst (Pd-Pb/ CaCO_3) materials. Figure 4 demonstrates each material's high-resolution XPS spectrum of the fitted Pd 3d peak. Regarding Pd, two species (Pd^0 and Pd^{2+}) were observed in all three catalysts, confirming the co-existence of Pd^0 and Pd^{2+} on their surfaces, including the commercial samples. Herein, the Pd 3d spectrum consists of two main doublets after Gaussian fitting, indicating two distinct Pd states: $\text{Pd}^0 3d_{5/2}$ (335.2–335.4 eV), $\text{Pd}^{2+} 3d_{5/2}$ (336.4–336.6 eV), $\text{Pd}^0 3d_{3/2}$ (340.5 eV) and $\text{Pd}^{2+} 3d_{3/2}$ (341.7 eV). The oxidized Pd state is predominant on the low specific surface area supports (both PCC-04 and commercial catalysts), which could be attributed to the size effect or the strong chemical interaction between Pd and CO_3^{2-} [52]. Over the high specific surface area support (PCC-60), the metallic feature of Pd is apparent due to its larger Pd particle size and lack of interaction with CO_3^{2-} . As previously mentioned, it may eventually explain its “zonal clustering” feature (Figures S13–S15). Hence, it was speculated that the Pd particles formed on the low specific surface area CaCO_3 could preferentially be in the vicinity of the (alloyed) Pb particles, which led to superior site-isolation features. On the contrary, the higher specific surface area PCC support contains fewer Pb atoms in the vicinity of the Pd atoms since the surface of the PCC support was “stretched”. The calculated $\text{Pd}^0/\text{Pd}^{2+}$ on the three carriers are 0.77 (PCC-04), 1.86 (PCC-60), and 0.56 (commercial catalyst), indicating that Pd-Pb/PCC-04 could have a moderate reducing ability and may have the best semi-hydrogenation effect along with the commercial catalyst. It can be seen that different CaCO_3 -based supports could significantly impact the ratio of the $\text{Pd}^0/\text{Pd}^{2+}$ species, especially on the high-surface area PCC supports.

2.2. Catalysis: Study on Semi-Hydrogenation of Phenylacetylene

All materials were screened in the semi-hydrogenation of phenylacetylene, as a model substrate to rationalize the understanding of our material characterization (Table 2). Generally, all non-Pb alloyed catalysts lead to the fully hydrogenated ethyl benzene as a sole product, indicating the over-hydrogenated nature of all catalysts in the absence of Pb. Upon Pb-alloying, all materials delivered a complete conversion with semi-hydrogenated styrene as a major product. Moreover, 5 wt% Pd-Pb catalysts on PCC-04 and PCC-30 delivered a similar selectivity (~80%), while 5 wt% Pd-Pb catalysts on PCC-60 and the commercial Lindlar catalyst delivered similar styrene selectivity (~67%) under our reaction conditions. However, over the 1 wt% Pd-Pb catalysts, complete conversion was also achieved, where the higher selectivity to styrene could be maintained over all the PCC-supported catalysts (Table S1). Upon lowering the Pd loading, the superior “site-isolation” feature could be obtained over the PCC supports, which might explain the similar performance achieved at lower Pd loading.

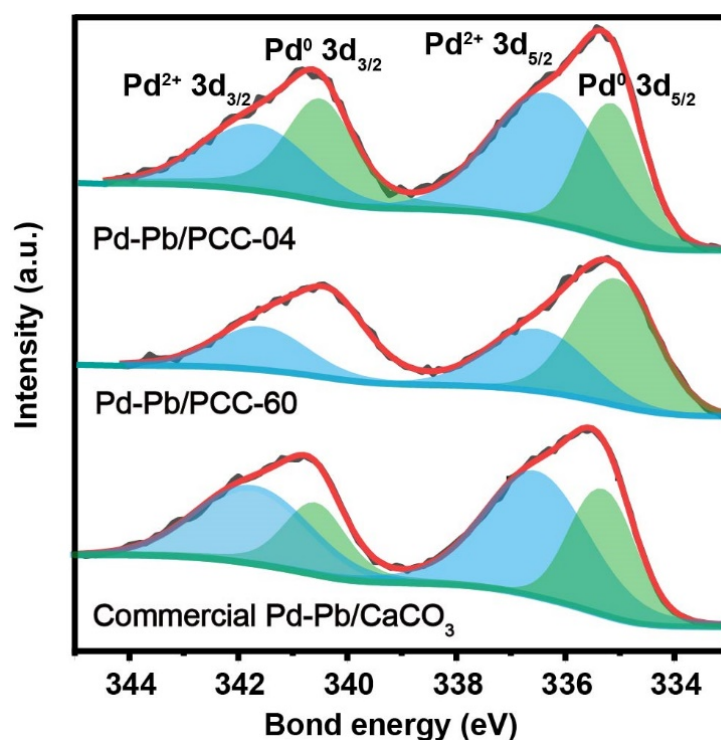


Figure 4. X-ray photoelectron spectroscopy (XPS) profile of Pd 3d on 5 wt% Pd-Pb/ PCC-04, 5 wt% Pd-Pb/PCC-60, and commercial 5 wt% Pd-Pb/CaCO₃. We refer to Figures S13–S15 for additional characterization data.

Table 2. Catalysts screening with phenylacetylene as a model substrate ^a.

phenyl acetylene		styrene	ethylbenzene
Catalyst	Con. (%)	Styrene (%)	Ethylbenzene (%)
Pd/PCC-04	>99	0	92
Pd/PCC-30	>99	0	98
Pd/PCC-60	>99	0	100
Pd-Pb/PCC-04	>99	81	3
Pd-Pb/PCC-30	>99	79	3
Pd-Pb/PCC-60	>99	68	18
Pd-Pb/CaCO ₃	>99	66	24

^a Dimerized styrene has also been identified as a remaining product besides semi-hydrogenated styrene and fully hydrogenated ethylbenzene.

Although complete conversions were achieved within 30 min of reaction, longer reaction times were also carried out to test the over-hydrogenated nature of our optimized catalysts (i.e., 5 wt% Pd-Pb/PCC-04 and commercial 5 wt% Pd-Pb Lindlar catalyst). As seen in Figure S16, the selectivity toward over-hydrogenated ethylbenzene has not been increased over time using our 5 wt% Pd-Pb/PCC-04 catalytic material. Herein, the selectivity toward the desired styrene products remained almost constant after 6 h of reaction. However, a different reaction profile was obtained over the commercial Lindlar catalyst, using our optimized reaction conditions: the gradual decrease in (semi-hydrogenated) styrene selectivity at the expense of the increasing selectivity to (over-hydrogenated) ethylbenzenes

over time. Such a sharp contrast of the time-monitored reaction profile unequivocally supports our PCC-derived catalytic material's superior, stable, and robust performance compared to its commercial counterpart (Table S2).

2.3. Mechanistic Hypothesis and Post-Reacted Catalyst Characterization

Based on the above-mentioned material characterization and their catalytic performance, we argue that the nature and type of the CaCO_3 support hold the key to delivering superior “active-site isolation”, which promotes the formation of the semi-hydrogenated products. Both the PCC-04 supported and the commercial catalysts provided excellent selectivity, while the higher surface area of PCC-60 has surprisingly limited added value. Although it was initially anticipated that a higher surface area could facilitate catalytic active-site isolation, such a phenomenon has not been reflected in the materials' characterization or catalytic performance. Contrarily, it indicates that a strong metal-support interaction (SMSI) might play a decisive role in governing catalysis [53]. The SMSI phenomenon is typically a function of numerous physicochemical properties, including charge transfer and the adsorption between nanoparticles and carriers [53,54]. Depending on the catalyst and the reaction involved, some phenomena will dominate, as demonstrated in this case. Changes in the oxidation state of the metal atoms of the nanoparticles or carrier metal ions may accompany it. XPS shows that in the same 5 wt% Pb catalysts, Pd electron transfer occurs when the carrier changes. It indirectly justifies in favor of the existence of SMSI in the present case. Herein, XRD analysis revealed that PCC-60 comprises an almost equal volume of aragonite and calcite crystal forms (Figure S3c). Hence, we hypothesize that the bonding of the Pd particles to the aragonite crystals might be unstable or absent. Since the stronger interaction between the Pd particles and calcite is well established (i.e., strong SMSI) and influential for the catalysis (see Figure 5), we argue that the presence of the aragonite phase is detrimental to the catalysis (or has limited impact). Alternatively, our PCC-04-supported Pd-based catalyst delivered superior product selectivity and robustness compared to the commercial Lindlar catalyst. Next, we performed TEM studies over post-reacted catalytic materials: 5 wt% Pd-Pb/PCC-04 and Commercial 5 wt% Pd-Pb/ CaCO_3 (Figure 6). Interestingly, both materials delivered similar features after the reaction: the uniform distribution of the Pb and Pd clustering or agglomeration is noticed in both cases. Such an agglomeration of Pd particles after the reaction is not uncommon [55]; therefore, the catalytically relevant “active-site-isolation” feature is well suited for PCC-04 support compared to the other catalysts used in this study. It implies that Pb might also be preferentially combined with calcite forms (possibly through the complexation as confirmed by its homogeneous distribution before or after the reaction) (Figures 5 and 6), inhibiting the interaction between the alkyne substrate and the catalytically active sites. However, the similar Pb loading spread across the lower-surface area samples may significantly enhance the desired site-isolation features, leading to improved alkene selectivity.

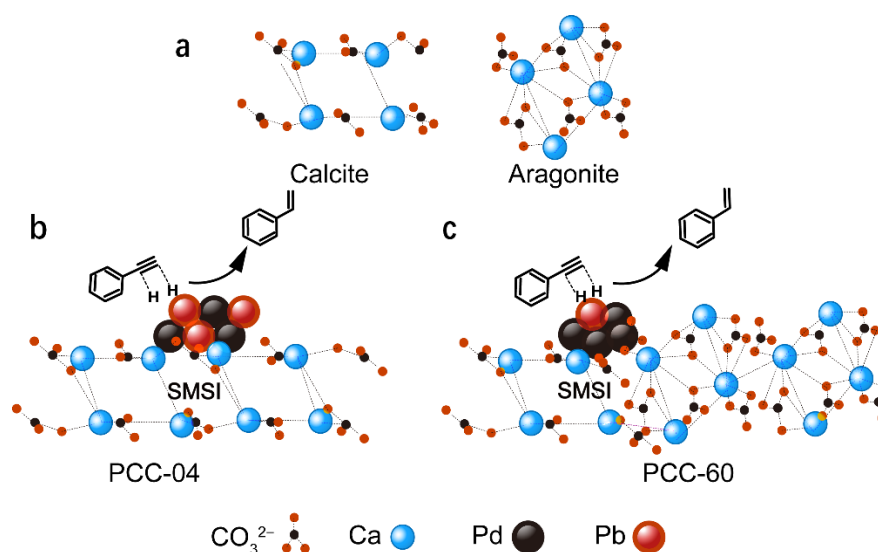


Figure 5. Simplified illustration of our PCC-derived catalysts' working hypothesis: (a) crystal model diagram of calcite and aragonite. A model reaction diagram of the semi-hydrogenation of phenylacetylene over (b) PCC-04 (i.e., consists of calcite phase only) and (c) PCC-60 (i.e., contains both calcite and aragonite phases) support. Only the calcite phase is catalytically relevant and delivers a strong metal-support interaction (SMSI), which allowed uniform distribution of Pd/Pb, presumably through complexation, key criteria to provide the “active-site isolation”, a feature necessary for the catalysis presented in this study.

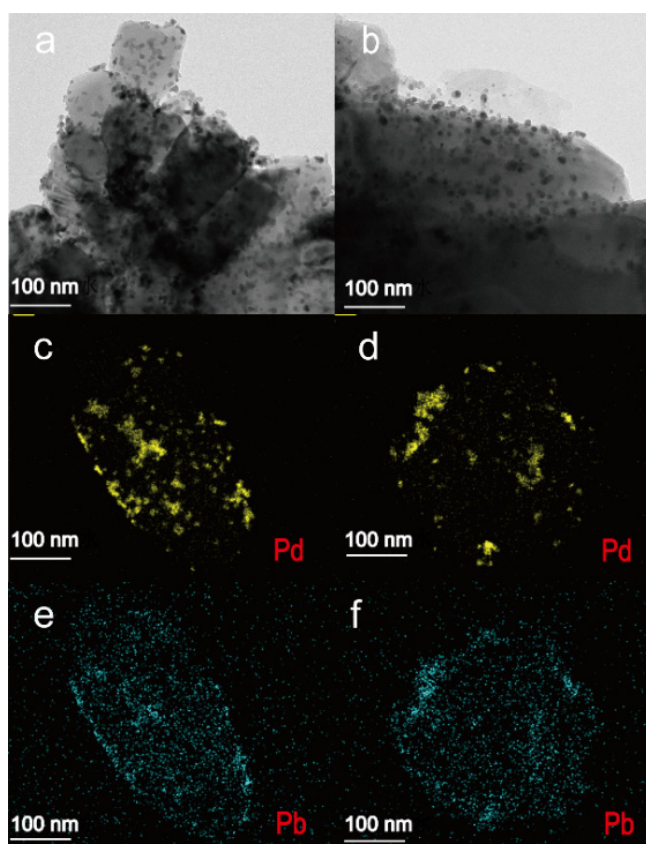


Figure 6. Transmission electron microscopic (TEM) images of post-reacted (a) Pd-Pb/PCC-04 and (b) commercial Pd-Pb/CaCO₃ catalytic material. (c,d) Pd and (e,f) Pb mapping on (c,e) Pd-Pb/PCC-04 and (d,f) commercial Pd-Pb Lindlar catalysts.

3. Materials and Methods

All chemicals and materials were purchased in the highest purity grade available and used without further purification: Phenylacetylene (Alfa Aesar, Haverhill, MA, USA, 98+%), diphenylacetylene (Energy Chemical, ZeSheng, Anhui, China, 98%), 1-heptene (Alfa Aesar, Haverhill, MA, USA, 98+%), 3-phenyl-2-propyn-1-ol (HEOWNS, TianJin, China, 96%), biphenylacetylene (Energy Chemical, ZeSheng, Anhui, China, 98%), 4-ethynyltoluene (HEOWNS, TianJin, China, 98%), 4-ethynylanisole (Bide, ShangHai, China, 98%), 4-fluorophenylacetylene (Energy Chemical, ZeSheng, Anhui, China, 98%), 4-ethynylbenzaldehyde (Bide, ShangHai, China, 98%), cyclohexane (Innochem, Beijing, China, 99.5%), ethanol (Innochem, Beijing, China, AR, 95%), tetrahydrofuran (Innochem, Beijing, China, 99%, AR), mesitylene (Alfa Aesar, Haverhill, MA, USA, 98+%), ethyl acetate (Sinopharm, ShangHai, China, AR), methanol (Innochem, Beijing, China, AR, 99.5%), deuterated chloroform (Innochem, Beijing, China, 99.8 atom % D), palladium chloride (Bide, ShangHai, China, 99%), hydrochloric acid (Sinopharm, ShangHai, China, 37%), sodium formate (Macklin, ShangHai, China, 99.5%), lead acetate (Aladdin, ShangHai, China, 99%), 5 wt% Pd/CaCO₃ Lindlar catalyst (Strem Chemicals Inc, North of Boston, MA, USA), commercial CaCO₃ (Macklin, ShangHai, China, 99%). All precipitated CaCO₃ (PCC) supports were obtained from Omya International.

Powder X-ray diffraction (XRD) analysis was performed using a Bruker D8 ADVANCE X diffractometer (Bruker, Karlsruhe, Germany) using a Cu K α radiation source ($\lambda = 0.154$ nm). Diffraction patterns are collected in the 2θ range between 10° and 80° with a step size of $4^\circ/\text{min}$. The catalysts' lattice constant and average grain size is analyzed using JADE software to analyze the recorded data. Scanning electron microscopy (SEM) images were acquired on a thermal field emission scanning electron microscope model Zeiss SIGMA (Carl Zeiss AG, Oberkochen, Germany). High-resolution transmission electron microscope (HRTEM) images were obtained using a Tecnai G3 F30 S-TWIN (FEI, Hillsboro, OR, USA). Thermal gravimetric analysis (TGA-DSC/TGA-DTA) was performed using a NETZSCH 449 F5/F3 Jupiter (NETZSCH, Selb, Germany) synchronous thermal analyzer. Under the N₂ atmosphere, the temperature increased from room to 800°C at $10^\circ\text{C}/\text{min}$: temperature stability 0.1°C , balance sensitivity $0.1\ \mu\text{L}$. The Brunauer–Emmett–Teller (BET) is measured by a nitrogen physical adsorption (ASAP 2460 Micrometrics) (Micromeritics, Norcross, GA, USA). Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) was performed on an Agilent ICPOES730 (Agilent, Palo Alto, CA, USA) instrument. X-ray photoelectron spectroscopy (XPS) was performed using a non-monochromatic Thermo ESCALAB 250Xi X spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) to generate Al K α radiation ($h\nu = 1486.6\ \text{eV}$) (10^{-10} Torr) under ultra-high vacuum. The charging effect is corrected relative to the carbon peak C 1s ($284.8\ \text{eV}$). The deconvolution of the peak spectrum is performed by XPSPEAK41 software [56], using Gaussian–Lorentzian linear and Shirley background subtraction.

3.1. Synthesis of Pd/PCC and Pd-Pb/PCC-Based Catalytic Materials

The synthesis protocol of catalytic materials is similar to the originally reported by Lindlar et al. [46,57]. In a typical synthesis, $0.46\ \text{mmol}$ of PdCl₂ was taken into a $10\ \text{mL}$ Erlenmeyer flask to achieve 5 wt% loadings and followed by $0.2\ \text{mL}$ of 37% hydrochloric acid. The flask was stirred at approximately 30°C until the PdCl₂ was completely dissolved. Next, the resultant acidic solution was transferred to a $10\ \text{mL}$ beaker filled with $2.5\ \text{mL}$ of distilled water, where $3\ \text{mol/L}$ aqueous sodium hydroxide solution was slowly added to bring the pH of the solution to $4.0\text{--}4.5$. Next, the above solution was immersed in a water bath and heated at 85°C . Next, $1\ \text{g}$ of CaCO₃ support (PCC-04, PCC-30, PCC-60, commercial CaCO₃) was added, and the temperature was held until all the Pd precipitated, which took approximately $15\ \text{min}$. While keeping the mixture at 85°C , $330\ \mu\text{L}$ HCOONa solution ($0.47\ \text{g}$ of HCOONa was added to $10\ \text{mL}$ water to form a $0.7\ \text{mol/L}$ solution) was added and stirred for $40\ \text{min}$, followed by the addition of $250\ \mu\text{L}$ HCOONa solution and stirring for $40\ \text{min}$. Then, it was washed by centrifugation with the addition of deionized

water and dried in an oven at 60 °C. The final catalytic materials were labeled as Pd/PPC-04, Pd/PPC-30, Pd/PPC-60, and commercial Pd/CaCO₃. In order to obtain the products Pd-Pb/PPC-04, Pd-Pb/PPC-30, Pd-Pb/PPC-60, and commercial Pd-Pb/CaCO₃, the above non-centrifugally dried products were retained. Next, 3.3 mL of deionized water and 1 mL of 7.7% (CH₃COO)₂Pb solution (0.45 g of (CH₃COO)₂Pb was added to 5 mL water to form a solution) were added to the above mixture and stirred for 40 min. Finally, it was washed by centrifugation with the addition of deionized water and dried in an oven at 60 °C.

3.2. Catalytic Testing

All catalytic hydrogenations were performed in a 250 mL Wattcas autoclave (WP-MSAR-250A). In a typical experiment, 1 mmol of alkyne substrate, 5 wt% catalyst, and 3 mL of cyclohexane (as solvent) were added to the reactor. After purging three times with H₂, H₂ was filled to 20 bar at ambient temperature. The reaction temperature and time were kept according to the need under strong magnetic stirring. After the reaction, the batch reactor was cooled to room temperature, and the product was separated from the catalyst by filtration through a microporous membrane. Next, mesitylene was added as an internal standard and then diluted with ethyl acetate. Finally, the collected sample solution was identified by a gas chromatograph–mass spectrometer combination (GCMS-QP2010 SE) and quantified by a gas chromatograph (GC-2014) with HPINNOWAX capillary column (30 m × 0.250 mm × 0.25 µm) or NMR spectroscopy. The GC detecting conditions were as follows: nitrogen was used as carrier gas; injection port temperature: 350 °C; detector (FID) temperature: 300 °C; column temperature: 50 °C, heating to 250 °C with a heating rate of 6 °C/min. ¹H NMR data were recorded with Bruker Advance III (400 MHz) spectrometer with internal standard (mesitylene). The purified product was added with 1 mmol of mesitylene as the internal standard and mixed thoroughly. Moreover, 50 µL of internal standard containing reaction solution was added into 0.75 mL deuterium chloroform (CDCl₃) for analysis.

4. Conclusions

With an aim to upgrade the industrial Lindlar catalyst for the semi-hydrogenation of phenyl acetylene to styrene, we demonstrated that newly derived precipitated CaCO₃ (PCC) holds the critical criteria to deliver superior catalytic performance compared to the commercial Lindlar catalyst. Herein, our low-surface area PCC-derived Pd-Pb catalytic material provided superior catalytic performance, stability, and robustness compared to its two counterpart materials: i.e., Pd-Pb over both high-surface area PCC materials and the commercial Lindlar catalyst. Our low-surface area Pd-Pb/PCC could deliver similar reactivity and selectivity even after lowering the metallic loading, indicating that the “active-site isolation” and “strong metal-support interaction” (SMSI) features are possibly among the contributing factors that may impact the catalysis. A diverse characterization technique has been employed to understand the catalytic performance from the material perspective. The uniform metallic distribution was accomplished through complexation between the alloyed Pb and calcite phase, delivering the desired active-site isolation necessary for the catalysis. Owing to the superior catalytic performance, stability, and robustness, we represent our PCC-derived catalyst as a promising candidate to upgrade the current state of Lindlar catalysts in the chemical industry. Through this work, we also advocate to actively research cost-effective inorganic supports or minerals instead of providing (mainly) elegant and expensive solutions. We certainly believe that this alternative research approach could eventually deliver better performance and also be easier to scale up for a potential industrial application.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal13010050/s1>. Figure S1: The physical adsorption spectrum of the (a) PCC-04, (b) PCC-30, (c) PCC-60, and (d) commercial CaCO₃; Figure S2: The physical adsorption spectrum of 5 wt% (a) Pd-Pb/PCC-04, (b) Pd-Pb/PCC-30, (c) Pd-Pb/PCC-60, and (d) commercial Pd-Pb/CaCO₃ (Lindlar catalyst). Figure S3: The XRD spectrum of the (a) PCC-04, (b)

PCC-30, (c) PCC-60, and (d) commercial CaCO_3 ; Figure S4: Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of (a) PCC-04, (b) PCC-30, (c) PCC-60, and (d) commercial CaCO_3 ; Figure S5: Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the commercial 5 wt% Pd-Pb/ CaCO_3 material (Lindlar catalyst); Figure S6: (a–d) Scanning electron microscope (SEM) images of standalone PCC-04 support, including mapping of (e) oxygen and (f) calcium; Figure S7: (a–d) Scanning electron microscope (SEM) images of standalone PCC-30 support, including mapping of (e) oxygen and (f) calcium; Figure S8: (a–d) Scanning electron microscope (SEM) images of standalone PCC-60 support, including mapping of (e) oxygen and (f) calcium; Figure S9: (a–d) Scanning electron microscope (SEM) images of standalone commercial CaCO_3 support, including mapping of (e) oxygen and (f) calcium; Figure S10: (a–d) Transmission Electron Microscope (TEM) images of standalone 5 wt% Pd-Pb/PCC-04, including (e) electronic image, (f) overlapping mapping of key elements, as well as individual mapping of (g) carbon, (h) oxygen, (i) calcium (j) palladium, and (k) lead. Figure S11: (a–d) Transmission Electron Microscope (TEM) images of standalone 5 wt% Pd-Pb/PCC-60, including (e) electronic image, (f) overlapping mapping of key elements, as well as individual mapping of (g) carbon, (h) oxygen, (i) calcium (j) palladium, and (k) lead; Figure S12: (a–d) Transmission Electron Microscope (TEM) images of commercial 5 wt% Pd-Pb/ CaCO_3 (i.e., Lindlar), including (e) electronic image, (f) overlapping of key elements, as well as individual mapping of (g) carbon, (h) oxygen, (i) calcium (j) palladium, and (k) lead; Figure S13: X-ray photoelectron spectroscopy (XPS) profiles of 5 wt% Pd-Pb/PCC-04 material, including (a) full spectrum, (b) C 1s, (c) Ca 2p, (d) O 1s, and (e) Pd 3d; Figure S14: X-ray photoelectron spectroscopy (XPS) profiles of 5 wt% Pd-Pb/PCC-60, including (a) full spectrum, (b) C 1s, (c) Ca 2p, (d) O 1s, and (e) Pd 3d; Figure S15: X-ray photoelectron spectroscopy (XPS) profiles of commercial Pd-Pb/ CaCO_3 (i.e., Lindlar catalyst), including (a) full spectrum, (b) C 1s, (c) Ca 2p, (d) O 1s, and (e) Pd 3d; Figure S16: Time-monitored data of (a) 5 wt% Pd-Pb/PCC-04, (b) 5 wt% Commercial 5 wt% Pd-Pb/ CaCO_3 ; Table S1: The catalyst screening with phenyl acetylene as a model substrate; Table S2: Comparison of semi-hydrogenation performance of alkyne over Pd-based catalysts. References [10,16,18,22–26,29,36–38] are cited in Supplementary Materials.

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