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Highly selective semi-hydrogenation of alkynes with a Pd nanocatalyst modified with sulfide-based solid-phase ligands

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ABSTRACT

Soluble small molecular/polymeric ligands are often used in Pd-catalyzed semi-hydrogenation of alkynes as an efficient strategy to improve the selectivity of targeted alkene products. The use of soluble ligands requires their thorough removal from the reaction products, which adds significant extra costs. In the paper, commercially available, inexpensive, metallic sulfide-based solid-phase ligands (SPL8-4 and SPL8-6) are demonstrated as simple yet high-performance insoluble ligands for a heterogeneous Pd nanocatalyst (Pd@$CaCO_3$) toward the semi-hydrogenation of alkynes. Based on the reactions with a range of terminal and internal alkyne substrates, the use of the solid-phase ligands has been shown to markedly enhance the selectivity of the desired alkene products by efficiently suppressing over-hydrogenation and isomerization side reactions, even during the long extension of the reactions following full substrate conversion. A proper increase in the dosage or a reduction in the average size of the solid-phase ligands enhances such effects. With their insoluble nature, the solid-phase ligands have the distinct advantage in their simple, convenient recycling and reuse while without contaminating the products. A ten-cycle reusability test with the SPL8-4/Pd@$CaCO_3$ catalyst system confirms its well-maintained activity and selectivity over repeated uses. A mechanistic study with x-ray photoelectron spectroscopy indicates that the solid-phase ligands have electronic interactions with Pd in the supported catalyst, contributing to inhibit the binding and further reaction of the alkene products. This is the first demonstration of solid-phase ligands for highly selective semi-hydrogenation of alkynes, which show strong promise for commercial applications.

Introduction

Catalytic semi-hydrogenation of alkynes to alkenes is an important chemical reaction in widespread use for the fine synthesis of alkene building blocks and purification of alkene monomers (such as styrene, ethylene, propylene, etc.) by removal of alkyne impurities. Heterogeneous Pd nanocatalysts, with Pd nanoparticles (size < ca. 10 nm) immobilized on various supports, are most selective, most active, and most used for semi-hydrogenation of alkynes [1,2]. The Lindlar catalyst (Pd nanoparticles supported on $CaCO_3$ modified with Pb and/or quinoline) developed in 1952 is the classical example and still has wide industrial uses [3]. In the design of high-performance catalysts for industrial-scale alkyne semi-hydrogenation, one major goal is to maximize the selectivity of the desired alkene product at high alkyne conversions (for example, > 99 %) while at maintained high catalyst activity. This is challenging as over-hydrogenation and isomerization of the alkene product often occurs, giving rise to the corresponding alkane and isomerized alkene byproducts, respectively. The occurrence of over-hydrogenation is especially pronounced at high alkyne conversations due to the enhanced alkene adsorption on active sites at lowered alkyne concentrations and is often more severe with terminal alkyne substrates than internal ones due to higher reactivity of the former [4].

Several catalyst design strategies have been developed to suppress over-hydrogenation. In one strategy, Pd nanocatalysts are modified with another alloying element (other metals [5–9], as well as light elements [10–13]). Therein, alloying leads to the isolation of active Pd sites and improves alkene selectivity to a certain extent but compromises catalytic activity. Moreover, for most alloy catalysts, the enhancement in alkene

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selectivity is often insufficient, typically with severe selectivity drops observed for terminal alkynes at high conversions or after full conversion. In particular, with respect to the Lindlar catalyst, the use of toxic Pb also poses serious problems as its leaching contaminates the alkene products.

Another strategy involves the modification of Pd nanocatalysts with soluble organic modifiers/ligands containing coordinating atoms (N, S, or P). Organic ligands can reversibly bind to the Pd active sites, modify the electronic state of active sites, and alter the relative adsorption strength of alkyne/alkene. With the binding ability of ligands often intermediate between alkyne and alkene (weaker than alkyne but stronger than alkene), their binding can effectively block alkene adsorption, thus suppressing over-hydrogenation [1,2]. Many organic ligands in both small molecules [4,14–22] and macromolecules [20,23] have been reported to effectively improve the alkene selectivity. However, their use poses serious issues for practical applications. Used often at excessive quantities [4], the soluble organic ligands are undesired contaminants to the alkene products; their thorough removal from the products adds significant extra costs. Meanwhile, permanent modification of the Pd catalysts with these ligands is impossible due to their reversible binding. As such, re-modification of the recycled catalysts with a fresh dosage of ligands is needed for replenishment in a following cycle of reaction, which is inconvenient for practical applications. To address the issues with soluble ligands, one alternative approach is to covalently immobilize the organic ligand on an inorganic support, which requires sophisticated synthesis [24,25]. For example, silica with covalently tethered polyethyleneimine (PEI) has been used to support Pd nanocatalysts, where PEI serves as immobilized ligand for the Pd active sites to suppress over-hydrogenation [25]. Though effective in the semi-hydrogenation of diphenylacetylene as an internal alkyne, its performance towards phenylacetylene as a terminal alkyne is still rather restricted with serious over-hydrogenation observed even well before the full conversion of the substrate.

Tackling the issues with existing organic ligands, a solid-phase ligand technology based on inexpensive inorganic metal sulfides has recently been developed and commercialized by Zhejiang Superior Technology Corporation (China) for the highly selective liquid-phase alkene semi-hydrogenation [26]. Under common reaction conditions for liquid-phase semi-hydrogenation, the solid phase ligands, as stable inorganic powders, are insoluble or have only extremely low solubility in the organic reaction systems, but highly efficient in markedly enhancing alkene selectivity at high alkyne conversions by suppressing over-hydrogenation. With the unique solid-phase feature, the solid-phase ligand, together with the heterogeneous Pd nanocatalyst, can be conveniently separated from the reaction solution by simple filtration/sedimentation/centrifugation. This advantageously facilitates easy yet efficient recycling and reuse of the catalyst/ligand system without contamination of the reaction products by ligands. To verify the outstanding performance of the solid-phase ligand technology, we report herein a systematic study on the semi-hydrogenation of a broad range of alkyne substrates, including both internal and terminal alkynes, with the use of a supported Pd nanocatalyst ($Pd@CaCO_3$) modified with the proprietary solid-phase ligands. The reusability of the catalyst/ligand system has also been investigated over 10 cycles of recycle/reuse. The underlying mechanism of the solid-phase ligands in enhancing alkene selectivity has also been studied. This work confirms the strong promise of this solid-phase ligand technology in industrial applications for reusable, highly active, highly selective liquid-phase semi--hydrogenation of alkynes.

Experimental section

Materials

Na_2PdCl_4 was obtained Shanghai Tuosi Chemical Co. Ltd. (China). A $Pd@CaCO_3$ catalyst, with Pd nanoparticles (5 wt%) supported on $CaCO_3$, was synthesized according to a literature procedure [17]. Two optimized metallic sulfide-based solid-phase ligands (SPL8-4 and SPL8-6 with the average particle size of around 5 and 17 μm, respectively) were provided by Zhejiang Superior Technology Corporation (China). Two commercial Lindlar catalysts (LC1 and LC2, both with 5 wt% of Pd on $CaCO_3$, poisoned with lead at different contents) were purchased from Shaanxi Rock New Materials Co. Ltd. (China) and Aladdin Co. Ltd. (China), respectively. All alkyne substrates, including 2-methyl-3-butyn-2-ol (98 %), phenylacetylene (97 %), 4-ethynylbenzonitrile (≥99.7 %), 1-ethynylcyclohexene (>98 %), 1-heptyne (97 %), diphenylacetylene (99 %), 1-phenyl-1-propyne(>98 %), 4-octyne (99 %), and 1, 4-butynl-diol (98 %), were obtained from Aladdin Co. Ltd. (China) and were used directly. Other regents, including methanol, *n*-hexane (anhydrous, 99 %), tetrahydrofuran (THF) and ethanol (anhydrous, ≥99.7 %) were purchased from Sinopharm Chemical Reagent Co. Ltd. and were used as received.

General procedure of alkyne hydrogenation

Liquid phase alkyne hydrogenation reactions were conducted in a rubber septum-sealed 50/100 ml flask immersed in a water bath maintained at prescribed temperatures. The flask, containing prescribed amounts of Pd catalyst ($Pd@CaCO_3$ or Lindlar catalysts), solid-phase ligand, alkyne substrate, and solvent, was firstly evacuated under vacuum and then filled with H_2 to start the hydrogenation reaction. A hydrogen balloon was attached to the reaction flask to maintain the hydrogen atmosphere and vigorous stirring was applied to avoid mass transfer limitations. To monitor the reaction kinetics, the reaction solution was withdrawn at prescribed times. The sampled solution was diluted with methanol, filtered through a syringe filter (0.22 μm PTFE), and then analyzed with gas chromatography (GC). GC analysis was performed on a HP GC-5890II instrument equipped with a flame ionization detector. Depending on the alkyne substrate, the GC columns with different polarities were used, including a supelcowax®10 capillary column (30 m × 0.2 mm ×0.2 μm), Agilent J&W DB-1 capillary column (30 m ×0.32 mm ×0.3 μm), and Agilent J&W DB-5 capillary column (50 m ×0.2 mm ×0.33 μm). Alkene selectivity was calculated from the GC results as the percentage of alkenes produced among all the products. For internal olefin products, the molar fraction of *E*-olefin, $E/(Z+E)$, was also calculated from the GC results.

Results and discussion

A Pd nanocatalyst ($Pd@CaCO_3$) with Pd nanoparticles (5 wt%) supported on $CaCO_3$ microparticles (average size: 16 μm) is used in this study for the semi-hydrogenation of a broad range of alkyne substrates as shown below. Two inexpensive proprietary solid-phase ligands (SPL8-4 and SPL8-6) in the form of fine powders, developed and commercialized by Zhejiang Superior Technology Inc., are employed in this study to demonstrate the efficiency of the solid-phase ligand technology. Both solid-phase ligands are air- and moisture-stable. The latter has a smaller average particle size (about 5 vs. 17 μm) than the former. The particle size is expected to affect the performance given their solid-phase

nature. Different dosages of the solid-phase ligands have been applied at prescribed mass ratios relative to Pd@$CaCO_3$ catalyst in the reactions. In all reactions, the ligand and catalyst particles are simply mixed in the reaction system by magnetic stirring. Control experiments have also been undertaken with Pd@$CaCO_3$ catalyst alone in the absence of any solid-phase ligand. Meanwhile, hydrogenation reactions of some representative alkyne substrates have also been carried out with two Lindlar catalysts (LC1 and LC2) as industry benchmark catalysts for comparison.

Semi-hydrogenation of terminal alkynes

Phenylacetylene (PA)

Selectivity control in semi-hydrogenation of terminal alkynes is more difficult than internal alkynes due to the significantly higher reactivity of the former. Hydrogenation of PA was first undertaken as a terminal aromatic alkyne substrate commonly employed to evaluate the performance of semi-hydrogenation catalysts [4]. Fig. 1 shows the kinetic curves (PA conversion and the selectivity of styrene as the targeted product vs. time) with Pd@$CaCO_3$ catalyst in the presence of each solid-phase ligand at different mass ratios relative to Pd@$CaCO_3$, as well as those of the control runs with Pd@$CaCO_3$ or Lindlar catalysts. The reactions were all undertaken at identical conditions with $[PA]_0 = 0.5$ M and Pd loading of 1000 mol ppm relative to PA at 25 °C. In the control run with Pd@$CaCO_3$, the hydrogenation proceeds fast with PA conversion increasing quickly from 36 % at 15 min to 80.9 % at 35 min, and to >99.9 % (no observable PA signal in GC) at 47 min. This is accompanied with a slight decrease of styrene selectivity from 99.9 % to 97.9 % and to 92.5 %, respectively, indicative of the increasing occurrence of over-hydrogenation with the increase of conversion. The time to reach the full conversion (>99.9 %) of the alkyne substrate is the indicator of the catalytic activity. The relatively high alkene selectivity values (≥92.5 %) achieved prior to the full conversion of PA result from the significant presence of the alkyne substrate of a much stronger binding capability to the active centers than alkene, which inhibits over-hydrogenation. Following the full conversion of PA, a further extension of the reaction leads to a drastic drop of styrene selectivity to only 29.5 % at 90 min, suggesting the severe occurrence of over-hydrogenation after the consumption of PA. Such a trend of change in alkene selectivity is commonly seen in reactions facilitated with most Pd catalysts with no/limited suppression of over-hydrogenation [4]. The slope of the selectivity curve in the latter period is thus the sensitive indicator of the catalyst's ability in suppressing over-hydrogenation, with a higher slope suggesting the faster over-hydrogenation.

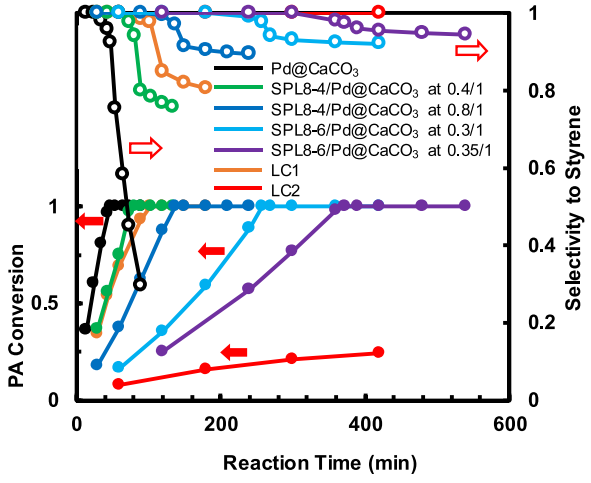


Fig. 1. Kinetic curves of hydrogenation reactions of phenylacetylene with Pd@$CaCO_3$ catalyst in the presence of solid-phase ligands at different mass ratios, and with only Pd@$CaCO_3$ and Lindlar catalysts (LC1 and LC2). Other conditions: $[PA]_0$ = 0.5 M in *n*-hexane, 0.1 mol% of Pd loading relative to substrate, 1 atm H_2 by balloon, and 25 °C.

In contrast to the control run, the addition of SPL8-4 or SPL8-6 markedly improves styrene selectivity and meanwhile reduces catalytic activity. With the increase of their dosage, such effects are enhanced. In the case with SPL8-4, the time for reaching the full conversion of PA (>99.9 %) is postponed to 81 and 138 min at the mass ratios of 0.4 and 0.8, respectively, indicative of decreasing catalytic activities. Prior to the full conversion of PA, styrene selectivity is well maintained at around 99.9 % in both runs. At the full conversion of PA, styrene selectivity values are 94.1 % and 97.1 %, respectively. After that, the further extension of the reaction at the mass ratio of 0.4 leads to the obvious drop of styrene selectivity to 78.3 % and 75.6 % at 105 and 135 min, respectively, which are still much better than those in the control run. In the other run at the higher mass ratio of 0.8, the selectivity drop and the slope of the selectivity curve after the full PA conversion are further reduced. After the full conversion of PA at 138 min, a small but quick drop of styrene selectivity to 91.5 % is observed at 150 min, followed with relatively stable selectivity values (90.5–89.5 %) maintained up to 240 min. In the other two runs with SPL8-6 (mass ratios of 0.3 and 0.35), a similar trend of effects is observed, with even more pronounced improvements in styrene selectivity. In the run with SPL8-6 at the mass ratio of 0.3, the full conversion of PA is reached at 258 min with a styrene selectivity of 97.8 %. After that, styrene selectivity is maintained within 94.1 % (270 min) to 92 % (420 min) upon extension of the reaction for up to additional 162 min (*i.e.*, total time of 420 min). In the other run at the mass ratio of 0.35, the time for reaching full conversion of PA is further postponed to around 372 min, at which the styrene selectivity is 97.3 %. Upon the extension of the reaction for additional 168 min, selectivity values are maintained high and strikingly stable within 96 % (390 min) to 94.6 % (540 min), which are the highest selectivity values with the least slope of drop among the four runs with solid-phase ligands.

Relative to the control run, these runs with both solid-phase ligands confirm the high efficiency of the solid-phase ligands in improving styrene selectivity of the catalyst by suppressing the over-hydrogenation. This is reasoned to result from the stronger binding strength of the ligands towards the active centers than styrene. The reduced activities with the postponed full conversion of PA results from the blocking effect of the ligands, which compete with PA for site binding. Similar effects are commonly seen with soluble small molecular ligands [4]. Particularly, SPL8-6 with a smaller average size shows stronger binding effects than SPL8-4 with the better suppression of over-hydrogenation and more reduction in activity even at a lower mass ratio. This should be attributed to the higher surface area and thus more sulfur binding sites on the surface for binding with the Pd active centers.

The Pd@$CaCO_3$/solid-phase ligand systems also outperform the two Lindlar catalysts (LC1 and LC2) in terms of the alkene selectivity. With LC1, the full conversion of PA is reached at 102 min with a styrene selectivity of 97.6 %. After that, an obvious selectivity drop is observed upon extension of the reaction, with the values of 85 % and 80.5 % at 120 and 180 min, respectively. This selectivity profile is clearly inferior to those in above three runs, the run with SPL8-4 at the mass ratio of 0.8 and the other two with SPL8-6. With LC2, the PA conversion reached after 400 min is only 12 %, indicating its extremely low activity due to excessive Pb poisoning.

In terms of the styrene selectivity, the Pd@$CaCO_3$/solid-phase ligand catalyst systems also outperform some high-performance catalyst systems reported in the literature for semi-hydrogenation of PA. For example, the yolk-shell nanostructured composite catalyst with Pd nanoparticles and PEI ligand confined within hollow silica spheres (Pd + PEI(L)@HSS) showed a styrene selectivity of only 88 % at the PA conversion of about 96 % [25]. With the extension of the reaction following the full conversion of PA for 200 min, the selectivity dropped to ca. 76 % therein. In another study, a Pd-Pb alloy nanocrystal catalyst with the optimized octahedra crystal structure and tailored composition showed

a styrene selectivity of 91.4 % at the full conversion of PA, followed with a drop of the selectivity to about 90 % upon extension of the reaction for additional 900 min [9]. In terms of the catalytic activity, a comparison of these different catalyst systems is, however, not possible given the different reaction conditions applied in these studies.

2. -Methyl-3-butyn-2-ol (MBY)

Liquid-phase semi-hydrogenation of MBY as an alkynol to the corresponding alkenol (2-methyl-3-buten-2-ol, MBE) is a key step in the industrial fine synthesis of Vitamin E [27]. Herein, we also demonstrate the superior performance of the solid-phase ligands in suppressing over-hydrogenation in the semi-hydrogenation of MBY with Pd@$CaCO_3$. Fig. 2 shows the kinetic curves of the reactions with Pd@$CaCO_3$ in the presence of SPL8-4/SPL8-6 at different mass ratios, as well as those of the control runs for comparison. The reactions were all undertaken in the absence of any solvent, which is desired for industrial processes due to the elimination of subsequent solvent removal step for product purification. In the control run with Pd@$CaCO_3$, the full conversion of MBY is reached at 81 min, with an MBE selectivity of only 88.5 %. This is followed with a fast drop of the selectivity to the low value of 20.6 % upon the extension of the reaction for additional 69 min (total 150 min). The use of the two Lindlar catalysts in the other two control runs does not show an obvious improvement in the alkene selectivity. LC2 shows a much lower activity (375 min to reach full conversion) compared to Pd@$CaCO_3$ (81 min) and LC1 (97 min). At the full conversion of MBY, the MBE selectivity values achieved with LC1 and LC2 are 92 % and 97.5 %, respectively, which are slightly better than that with Pd@$CaCO_3$. However, drastic drops in alkene selectivity are also seen with low values of 1% and 25.1 % retained after the extension of the reactions for additional 33 and 165 min, respectively. These control runs also suggest the poor performance of the three catalysts in suppressing over-hydrogenation in the semi-hydrogenation of MBY. Any slight delay in quenching the reaction following the full conversion MBY may lead to an appreciable drop in alkene selectivity and thus undermine the product purity, which can pose serious issues in large-scale industrial processes.

Upon the use of SPL8-4 with Pd@$CaCO_3$, significantly enhanced MBE selectivity accompanied with reduced catalytic activity can be seen. At the three different SPL8-4/Pd@$CaCO_3$ mass ratios (0.4, 0.8, and 1.2), the full conversion of MBY is achieved at 75, 96, and 135 min, respectively, with the corresponding MBE selectivity values of 97 %, 97.4 %, and 97.7 %, which are significantly higher than those in the control runs.

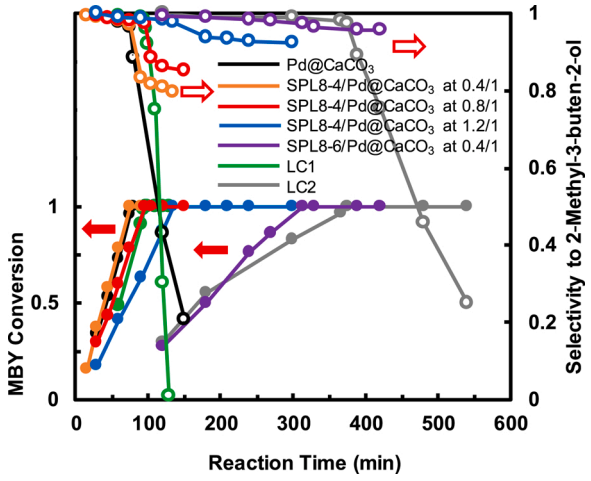


Fig. 2. Kinetic curves of hydrogenation reactions of 2-methyl-3-butyn-2-ol with Pd@$CaCO_3$ catalyst in the presence of solid-phase ligands (SPL8-4/SPL8-6) at different mass ratios, and with only Pd@$CaCO_3$ and Lindlar catalysts (LC1 and LC2). Other conditions: pure substrate with no solvent used, 0.2 mol% of Pd loading relative to substrate, 1 atm H_2 by balloon, and 40 °C.

Moreover, the rate of drop in MBE selectivity following the full conversion of MBY is markedly lowered as shown in Fig. 2. In the runs at the mass ratios of 0.4 and 0.8, MBE selectivity values of 79.5 % and 85.1 %, respectively, are maintained after the extension of the reaction by additional 60 min (total time of 135 and 150 min, respectively). In the other run at the highest mass ratio of 1.2, MBE selectivity remains very stable with only a minor drop to 92.5 % even after the extension of the reaction for 165 min (total time of 300 min). With SPL8-6 at the mass ratio of 0.4, the improvement in MBE selectivity is even more significant. In the run, the full conversion of MBY is reached at 314 min with an MBE selectivity of 97.4 %. After that, the selectivity remains nearly unchanged with a remarkably high value of 95.6 % maintained after extension of the reaction for 106 min (total time 420 min). In agreement with the results above with PA, increasing the ligand/catalyst mass ratio or decreasing the size of the solid-phase ligand from SPL8-4 to SPL8-6 enhances the selectivity performance of the catalyst due to the availability of more surface binding sites on the ligands for coordinating with Pd active centers.

When compared to some high-performance catalysts reported in the literature for the semi-hydrogenation of MBY, the performance achieved herein with the use of the solid-phase ligand technology is also superior. For example, with an intermetallic PdZn alloy catalyst immobilized on a hybrid ZnO/nitrogen-doped carbon support, the MBE selectivity was only about 96 % at the low MBY conversion of 20 % and it dropped to about 92 % at the conversion of 95 % [28]. In another study with the use of shape- and size-optimized Pd nanocrystals with poly(vinylpyrrolidone) as both the stabilizer and modifier, the highest MBE selectivity values achieved at MBY conversions of 50 % and 95 % were about 96 % and 94 %, respectively [29]. In both studies, no selectivity data was reported following the full conversion of MBY. In an additional study with an optimized Pd nanocatalyst supported on carbon decorated with oxygen-deficient TiO_2, an MBE selectivity of 94 % was rendered at the full conversion of MBY [30]. A further extension of the reaction for additional 50 min led to the drop of MBE selectivity to 88 %. Though the reaction conditions are not identical to those used in the literature studies, the selectivity values we achieve herein with SPL8-4 and SPL8-6 are distinctly higher and more stable, confirming the better suppression of over-hydrogenation with the use of the sulfide solid-phase ligand technology.

1. -Heptyne

Semi-hydrogenation of 1-heptyne as a representative aliphatic alkyne has also been undertaken with Pd@$CaCO_3$ in combination of SPL8-6 at a mass ratio of 0.2. Fig. 3 shows the kinetic curves of the reaction as well as those of the control run with Pd@$CaCO_3$. In the semi-hydrogenation of a terminal aliphatic alkyne, the isomerization of the resulting terminal alkene to internal alkene isomers are often observed as additional side reactions, beside the over-hydrogenation, forming the saturated alkane. Due to the formation of isomer byproducts, the selectivity to the targeted 1-alkene is expected to be lower than those seen above in the semi-hydrogenation of PA and MBY. The compositions of the reaction products in both runs are summarized in Table S1 in Supporting Information. In both runs, 1-heptene is the predominant product (selectivity within 98–100 %) prior to the full conversion (99.9 %). In addition, a small amount of 1-heptane (up to ca. 2%) is also formed with the content increasing upon the increase of time, but with no alkene isomers observed. Clearly, the presence of 1-heptyne suppresses efficiently both over-hydrogenation and isomerization of 1-heptene due to the site blocking effect of 1-heptyne, which has significantly stronger binding ability to the active centers than 1-heptene. In the control run, the full conversion of 1-heptyne is reached at 26 min with the selectivity to 1-heptene of 73 %. Two internal alkene isomers (total molar content: 13.3 %) are observed at this time, in addition to 1-heptane (13.7 %). After that, the 1-heptene selectivity drops drastically to only 28.8 % upon the extension of the reaction for additional 19 min (total time 45 min), with the contents of 1-heptane and isomers

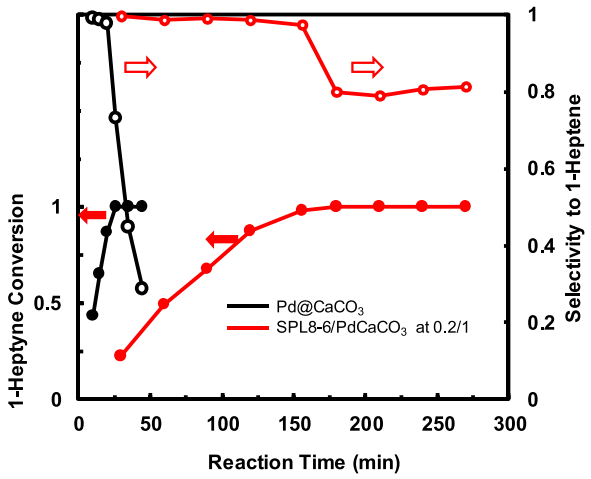


Fig. 3. Kinetic curves of hydrogenation reactions of 1-heptyne with Pd@$CaCO_3$ catalyst in the presence of SPL8-6 and with only Pd@$CaCO_3$. Other conditions: $[1\text{-heptyne}]_0 = 0.5$ M in *n*-hexane, 0.1 mol% of Pd loading relative to substrate, 1 atm H_2 by balloon, and 25 °C.

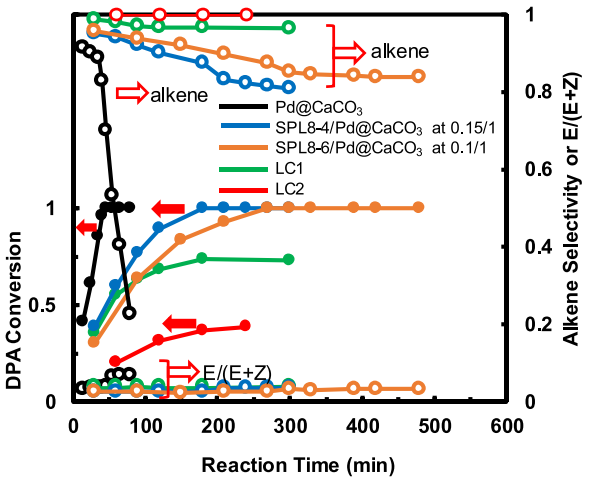


Fig. 4. Kinetic curves of hydrogenation reactions of DPA with Pd@$CaCO_3$ catalyst in the presence of solid-phase ligands (SPL8-4 or SPL8-6), and with only Pd@$CaCO_3$ or Lindlar catalysts (LC1 and LC2). Other conditions: $[DPA]_0 = 0.5$ M in *n*-hexane, 0.1 mol% of Pd loading relative to substrate, 1 atm H_2 by balloon, and 25 °C.

increasing sharply to 34.1 % and 37.1 %, respectively (see Table S1). This indicates the drastic loss of control on 1-heptene selectivity upon the full consumption of 1-heptyne.

In the other run with the use of SPL8-6, the full conversion of 1-heptyne is postponed to 180 min, at which the selectivity to 1-heptene is 79.9 % with 11.3 % of 1-heptane and 8.8 % of isomers. Relative to the high 1-heptene selectivity of 97.6 % at 156 min (conversion = 98.4 %), it appears that there is a sudden drop in 1-heptene selectivity when the 1-heptyne conversion approaches close to 100 %. However, the further extension of the reaction for additional 90 min (total 270 min) afterwards shows no distinct changes in the product composition, with 1-hexene selectivity maintained nearly constant at around 80 % throughout the period. In sharp contrast to the control run, 1-heptene selectivity achieved in this run is not only significantly higher with much lowered over-hydrogenation and isomerization but also markedly more stable after the full consumption of 1-heptyne. This confirms that the use of SPL8-6 efficiently reduces both side reactions.

In addition to the above three, we have also undertaken semi-hydrogenation reactions of two other terminal alkyne substrates, including 4-ethynylbenzonitrile and 1-ethynylcyclohexene, with Pd@$CaCO_3$ in combination with SPL8-6 at a SPL8-6/Pd@$CaCO_3$ mass ratio of 0.1. The results are summarized in Figs. S1 and S2 in Supporting Information. Compared to the corresponding control runs, similar findings as above can be seen in the presence of SPL8-6, with higher alkene selectivities at the full conversion of the substrates, significantly reduced selectivity drops upon further extension of the reaction, and reduced catalytic activities.

Semi-hydrogenation of internal alkynes

Diphenylacetylene (DPA)

In the semi-hydrogenation of internal alkynes, both *cis*- (*Z*-) and *trans*- (*E*-) internal alkenes are produced, with the former as the targeted thermodynamically favored product and the latter as another by-product in addition to alkane by over-hydrogenation. As such, both alkene selectivity (the total fractions of both *Z*- and *E*-alkenes in the product) and *E*-alkene fraction, *E*/(*E*+*Z*), are monitored in the reactions. Fig. 4 shows kinetic curves of the hydrogenation reactions of DPA as a common internal alkyne with the use of different catalyst systems under identical conditions. In the control run with Pd@$CaCO_3$, the conversion of DPA increases quickly from 41.8 % at 15 min to >99.9 % at 45 min. Concomitantly, alkene selectivity decreases from 91.5% to 70.1%, along with a slight increase of *E*/(*Z*+*E*) from 0.032 to 0.038. Further extension of the reaction leads to a drastic drop in alkene selectivity to 22.6 % at 80 min and the increase of *E*/(*Z*+*E*) to 0.07, indicating the occurrence of severe over-hydrogenation along with obvious isomerization after the full consumption of DPA. With both Lindlar catalysts (LC1 and LC2), only low conversions (73 % and 19 %, respectively) are achieved after 300 and 240 min, respectively, with no tendency of further increase. This also indicates the low activity of both Lindlar catalysts toward internal alkynes of relatively lower reactivity due to the excessive poisoning by lead.

The use of either SPL8-4 or SPL8-6 (mass ratios of 0.15 and 0.1, respectively) enhances efficiently the performance of Pd@$CaCO_3$ in *Z*-alkene selectivity, while reducing catalytic activity. Relative to those for PA, the required dosages of both SPL8-4 and SPL8-6 are significantly lower for DPA due to the relatively weaker binding ability of the internal alkyne to active sites. Particularly, due to its smaller average particle size, SPL8-6 shows more pronounced effects than SPL8-4 despite the slightly lower dosage, which agrees well with the results found above for terminal alkynes. Upon the use of SPL8-6, the time to achieve full conversion of DPA is postponed to *ca.* 270 min. Prior to the full conversion of DPA, alkene selectivity decreases from 95.8 % at 30 min (DPA conversion = 30 %) to 87.4 % at 270 min, but their values are significantly greater than the corresponding ones in the control run at similar DPA conversions. Upon extension of the reaction after the full conversion of DPA, alkene selectivity is maintained quite stable within 85.2 % (300 min) and 83.8 % (480 min) with only marginal decreases. Throughout the reaction, *E*/(*E*+*Z*) increases only slightly from 0.025 at 30 min to 0.028 at 270 min and to 0.033 at 480 min. Compared to the control run with Pd@$CaCO_3$, the *Z*-alkene selectivity of the catalyst is markedly improved.

1. ,4-Butyne diol (BYD)

Fig. 5 shows the hydrogenation reactions of BYD as an alkynol with an internal alkyne group. In the control run with Pd@$CaCO_3$, a fast drop in alkene selectivity (from 99.9% to 21%) along with a drastic increase in *E*/(*E*+*Z*) (from 0.06 to 0.95) is observed upon extending the reaction after the full conversion of BYD at 12 h to 20.5 h. In sharp contrast, over-hydrogenation is completely inhibited and isomerization is dramatically reduced in the presence of SPL8-6 at a low dosage (mass ratio of 0.1). Alkene selectivity is well maintained at >99.9 % with no drop at all throughout the whole reaction period of 24 h (full conversion of BYD at 16 h). *E*/(*E*+*Z*) shows only a small increase from 0.038 at 16 h to 0.067 at 24 h.

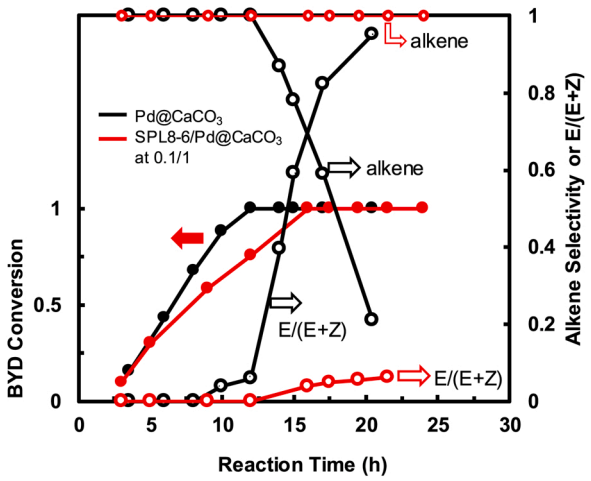


Fig. 5. Kinetic curves of hydrogenation reactions of BYD with Pd@$CaCO_3$ catalyst in the presence of SPL8-6 and with only Pd@$CaCO_3$, respectively. Other conditions: $[BYD]_0$ = 0.5 M in ethanol, 0.1 mol% of Pd loading relative to substrate, 1 atm H_2 by balloon, and 70 °C.

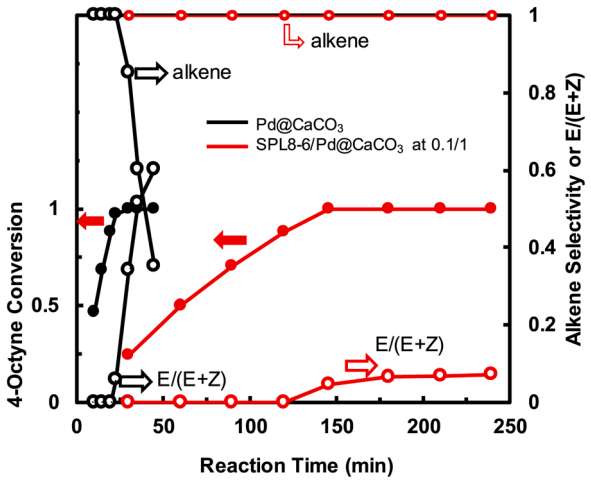


Fig. 6. Kinetic curves of hydrogenation reactions of 4-octyne with Pd@$CaCO_3$ catalyst in the presence of SPL8-6 and with only Pd@$CaCO_3$, respectively. Other conditions: $[4\text{-octyne}]_0$ = 0.5 M in *n*-hexane, 0.1 mol% of Pd loading relative to substrate, 1 atm H_2 by balloon, and 25 °C.

4. -Octyne

We have further examined the effect of SPL8-6 on the semi-hydrogenation of 4-octyne as an internal aliphatic alkyne substrate. As shown in Fig. 6, the use of SPL8-6 at a mass ratio of 0.1 also completely inhibits over-hydrogenation and markedly reduces isomerization, with the alkene selectivity of >99.9 % and $E/(E+Z)$ within 0.045–0.072 maintained after the full conversion of BYD. In sharp contrast, the over-hydrogenation and isomerization occur rapidly after the full conversion of BYD in the control run, with a fast drop in alkene selectivity and a sharp increase in $E/(E+Z)$.

Besides the above internal alkynes, the hydrogenation of 1-phenyl-1-propyne as an additional substrate was also undertaken with SPL8-6/Pd@$CaCO_3$ at a mass ratio of 0.1 (see Fig. S3 in Supporting Information). Similarly, compared to the control run with Pd@$CaCO_3$, alkene selectivity is much better maintained after the full conversion of the alkyne substrate, along with dramatically reduced $E/(E+Z)$, confirming the high efficiency of the solid-phase ligand in improving the selectivity toward the *Z*-alkene product.

Mechanistic study

The results above for all alkyne substrates confirm the high efficiency of solid-phase ligands (SPL8-4 and SPL8-6) in enhancing alkene selectivity in the semi-hydrogenation of various alkyne substrates despite their solid-phase nature, by reducing over-hydrogenation and isomerization reactions. This is accompanied with the reduced catalytic activity. An increase in the dosage of the solid-phase ligands generally enhances such effects. However, an excessive dosage will lead to over-reduced catalytic activity and thus insufficient substrate conversion. In practical applications, the dosage should thus be optimized to balance the selectivity and activity. The overall catalytic performance achieved herein with the use of solid-phase ligands is significantly better than those of the two Lindlar catalysts and outperforms some elegant high-performance catalysts reported in the literature that often require sophisticated synthesis.

The effects of the solid-phase ligands on the reactions resemble those commonly seen with soluble small molecular ligands. With a soluble ligand, the enhancement in alkene selectivity can result from its modification of electronic states of active sites, which reduces over-hydrogenation by promoting alkyne adsorption over alkene and suppresses isomerization. Meanwhile, the site-blocking effects by its preferential binding over alkene can also contribute to suppress over-hydrogenation [4]. To understand the mechanism by which the solid-phase ligands affect the reactions, we first need to rule out the possibility that some trace soluble sulfide species leached from the solid phase ligands may play the actual role in affecting the catalytic performance. For this purpose, an MBY/SPL8-4 suspension at the mass ratio of 19.75 : 1 (equivalent to the reaction with SPL8-4 at a mass ratio of 0.4 relative to Pd@$CaCO_3$ in Fig. 2) was stirred overnight to leach out the possible soluble species in SPL8-4. It was then filtered to remove the solid powders to render MBY after soaking with the solid-phase ligand, which was subsequently used as the substrate for the reaction with Pd@$CaCO_3$ with no additional solid-phase ligand added. Visually, there was no color change with MBY after the soaking. If the soluble active species leached out from SPL8-4, similar kinetic curves as those seen in the control run with fresh MBY and SPL8-4/Pd@$CaCO_3$ (mass ratio: 0.4) would yield to give similar effects on the reaction. We chose MBY instead of other nonpolar alkyne substrates for this experiment as it should better facilitate the leaching, if present, with its relatively high polarity.

Fig. 7 shows the kinetic curves of the reaction, along with those for the control run. The curves of the two runs are nearly overlapping with

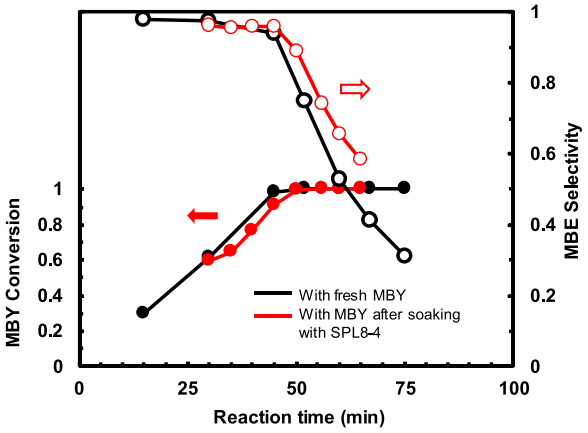


Fig. 7. Kinetic curves of hydrogenation reactions of 2-methyl-3-butyn-2-ol (fresh or soaked with SPL8-4) with Pd@$CaCO_3$ catalyst. Other conditions: no solvent, 0.2 mol% of Pd loading relative to substrate, 1 atm H_2 by balloon, and 40 °C.

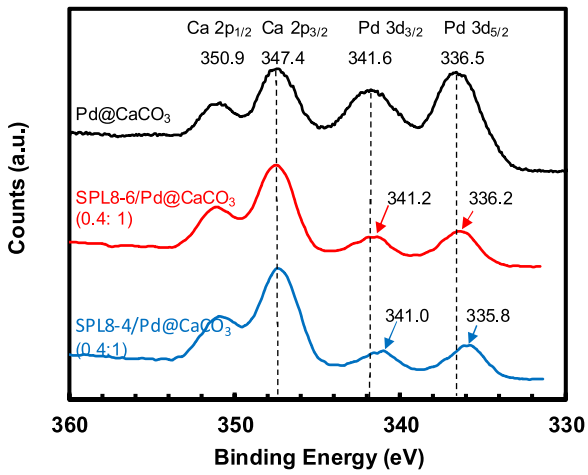


Fig. 8. Pd and Ca core level XPS spectra of $Pd@CaCO_3$, and mixtures of SPL8-4/$Pd@CaCO_3$ and SPL8-6@$CaCO_3$ at a mass ratio of 0.4. The spectra have been aligned in reference to the Ca $2P_{3/2}$ peak at 347.4 eV.

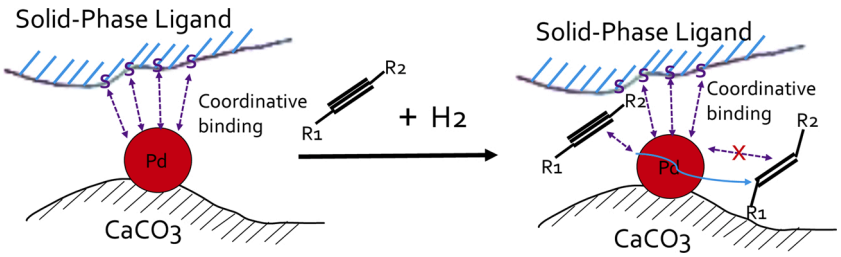
only minor differences within experimental variation range. The time to reach full MBY conversion is very close in both runs, indicative of the similar catalytic activity. Like the control run, MBE selectivity drops quickly from 89 % at 50 min (full conversion of MBY reached) to 58 % at 65 min in the run with MBY after soaking with SPL8-4. This differs distinctly from the corresponding run with fresh MBY but with SPL8-4/$Pd@CaCO_3$ (see Fig. 2; mass ratio of 0.4), where a stable MBE selectivity at about 80 % is well maintained within 1 h following the full conversion of MBY. The comparison thus precludes the possibility that leached soluble active species from SPL8-4 plays the role in affecting the catalytic behavior.

XPS characterization has been undertaken to reveal the interactions between the solid-phase ligands and Pd nanoparticles in $Pd@CaCO_3$. Fig. 8 compares the high-resolution XPS spectra of Pd and Ca elements of $Pd@CaCO_3$, and solid mixtures of SPL8-4/$Pd@CaCO_3$ and SPL8-6/$Pd@CaCO_3$ at the same mass ratio of 0.4. Both mixtures were prepared by wet mixing in methanol for 1 h, followed by vacuum drying. $Pd@CaCO_3$ shows Pd $3d_{3/2}$ and $3d_{5/2}$ peaks at 341.6 and 336.5 eV, respectively. The binding energy of the latter peak confirms the predominant presence of Pd in the form of Pd(0) nanoparticles since Pd(II) often has a $3d_{5/2}$ peak at an appreciably higher binding energy (around 338 eV) [31,32]. With the two mixtures, clear shifts of both Pd peaks to lower binding energies are observed, 341.0 and 335.8 eV for SPL8-4/$Pd@CaCO_3$, and 341.2 and 336.2 eV for SPL8-6/$Pd@CaCO_3$. Such peak shifts are strong evidence confirming the presence of electronic interactions between SPL8-4/SPL8-6 and the Pd nanoparticles in $Pd@CaCO_3$ [33–35]. Particularly, the lowered binding energies suggest the increased electronic density of Pd with the transfer of electrons from the solid-phase ligands to the Pd nanoparticles [35]. We reason such electronic interactions are responsible for the enhanced alkene selectivity and reduced activity observed herein upon the use of the solid-phase ligands.

The concept of strong metal-support interactions (SMSI) has been well demonstrated with metal nanoparticle catalysts immobilized on specific inorganic oxide supports [36], including Pd nanoparticle catalysts supported on titania (TiO_2) [30,33,34] and hydrotalcite [35] with improved alkene selectivity performance for alkyne semi-hydrogenation. Therein, metal nanoparticles are in direct contact with the inorganic solid support to yield strong electronic interactions between the two. It is generally considered that an atomic layer or two of the inorganic support forms across the surfaces of the metal nanoparticles [36]. In our case with the solid-phase ligands herein, there are rare chances for direct contact between the Pd nanoparticles and the solid-phase ligands as the former are supported on $CaCO_3$ support of sizes about 16 μm and the latter are solid particles with sizes about 2–40 μm. Though the precise mechanism is unknown yet, we hypothesize that the observed electronic interactions result from the longer-range interactions that sulfur elements on the surface of solid-phase ligands exert on the Pd nanoparticles without the requirement of direct physical contact (see Scheme 1). This is ascribed to the strong coordinating ability of sulfur towards Pd. Small molecular or polymeric sulfur-containing ligands are long-known highly effective ligands to improve the alkene selectivity of Pd nanocatalysts [4,16–18,23]. Featured with significantly stronger coordinating ability compared to N- and P-containing ligands, sulfur-containing soluble ligands require only trace loadings (as low as ppm levels relative to Pd) to achieve marked enhancements in alkene selectivity [4]. We found that, upon the addition of elemental sulfur at an extremely low dosage of about 2 mol ppm relative to Pd, the $Pd@CaCO_3$ catalyst was completely poisoned with no catalytic activity at all toward the hydrogenation of PA. Relative to the soluble ligands, sulfur in the solid-phase ligands should have significantly lowered coordinating ability due to steric reasons arising from their insoluble solid-phase nature and electronic reasons given their confinement within the sulfide salt. Moreover, only the sulfur elements on the surfaces of the solid-phase ligands can show active coordinating effects on the Pd catalytic centers. As such, relative to soluble ligands, significantly higher dosages of the solid-phase ligands are required to achieve equivalent enhancements in alkene selectivity for the semi-hydrogenation.

Reusability study

The distinct advantage of the solid-phase ligand technology is the convenient separation of the solid-phase ligands along with the heterogeneous Pd catalyst from the reaction solution via simple filtration/sedimentation/centrifugation. To verify the reusability of the solid-phase ligands, we have undertaken ten consecutive semi-hydrogenation reactions of MBY with SPL8-4/$Pd@CaCO_3$ (mass ratio of 0.8; other conditions identical to those in Fig. 2) as a demonstration. Each reaction, except the 10th one, was stopped at reaching approximately the full conversion (close to 99.9 %) of MBY without further extension. In each run except the 10th reaction, only at the terminal point were MBY conversion and MBE selectivity determined without additional sampling. The SPL8-4/$Pd@CaCO_3$ catalyst system was then recycled via centrifugation. Following quick wash with methanol and drying, the catalyst system was subsequently applied for the next reaction. In the final 10th reaction, the reaction was extended after reaching the full conversion of MBY and the full kinetic curves were obtained by sampling and analyzing the reaction solution throughout the whole reaction period. Fig. 9(a) compares MBY conversion and MBE selectivity of the ten runs. Upon reuse, the time for reaching the full conversion shows a trend of slight increase, along with only minor variations in MBE selectivity (within 94.4–97.4 %). To reveal the catalytic characteristics of the reused catalyst system, Fig. 9(b) shows the kinetic curves of the 10th run with the reused catalyst system, in comparison with those of the fresh catalyst system and control run with $Pd@CaCO_3$. The time to reach the full conversion of MBY is slightly shortened (88 min vs. 100 min for the fresh catalyst system) in the 10th run with the reused catalyst. Meanwhile, the rate of drop in MBE selectivity after the full conversion of MBY is also slightly enhanced but is still significantly lower compared to the control run with $Pd@CaCO_3$. Other than the minor changes, the well retained activity and MBE selectivity confirm the excellent reusability of the catalyst system incorporating the solid-phase ligand.



Scheme 1. Proposed mechanism for the interactions between solid-phase ligand and Pd nanoparticles in the reaction.

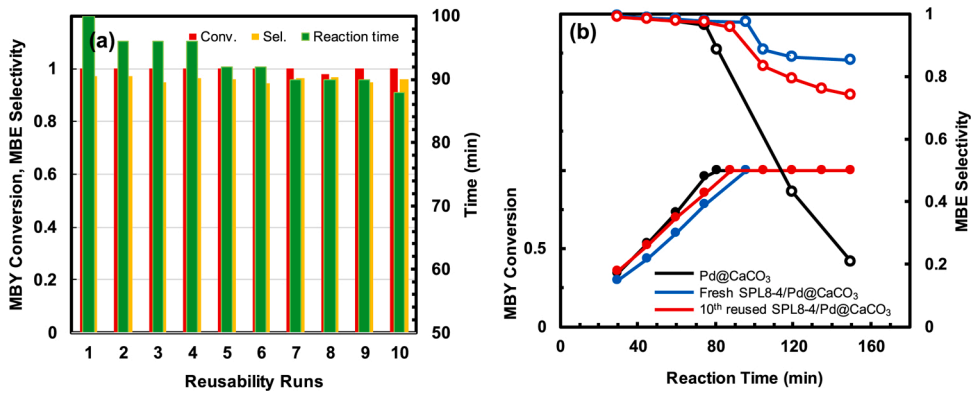


Fig. 9. Reusability test results with SPL8-4/Pd@$CaCO_3$ (mass ratio of 0.4): (a) the reaction time, MBY conversion, and MBE selectivity of ten cycles of reactions; (b) kinetic curves of the 10th reaction, in comparison with those with fresh SPL8-4/Pd@$CaCO_3$ and control run with Pd@$CaCO_3$.

Conclusions

Two sulfide-based solid-phase ligands (SPL8-4 and SPL8-6) have been demonstrated to facilitate highly selective semi-hydrogenation of a range of terminal and internal alkyne substrates catalyzed with Pd@$CaCO_3$. For all the alkyne substrates investigated, their addition in the reactions markedly improves the selectivity of the targeted alkene products by efficiently suppressing over-hydrogenation and isomerization reactions, along with reduced activities. Through XPS, both ligands have been demonstrated to electronically interact with Pd in Pd@$CaCO_3$ despite their solid-phase nature. Such electronic interactions are reasoned to suppress the binding of alkene products for further side reactions. The reusability test confirms the high stability of the SPL8-4/Pd@$CaCO_3$ catalyst system with well retained selectivity and activity performance over 10 cycles of repeat reactions. With their low cost, high-performance in improving alkene selectivity, and convenient recycling while without contamination of the products, this solid-phase ligand technology shows the strong promise for applications in commercial liquid-phase semi-hydrogenation of alkynes.

CRediT authorship contribution statement

The experimental work was undertaken exclusively by **Lingqi Huang**, **Kecheng Hu**, and **Ganggang Ye** at Zhejiang Superiority Technology Corporation (China). **Lingqi Huang**, **Ganggang Ye**, and **Zhibin Ye** conceptualized the research. **Lingqi Huang**, **Kecheng Hu**, and **Zhibin Ye** analyzed the results. **Lingqi Huang** and **Zhibin Ye** wrote the manuscript.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

A Chinese Patent Application (CN201910983739.1) partially based on this work has been filed.

Acknowledgements

The experimental work was undertaken exclusively by L. H., K. H., and G. Y. at Zhejiang Superiority Technology Corporation (China). L. H., G. Y., and Z. Y. conceptualized the research. L. H., K. H., and Z. Y. analyzed the results. L. H. and Z. Y. wrote the manuscript.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2021.111535.

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