

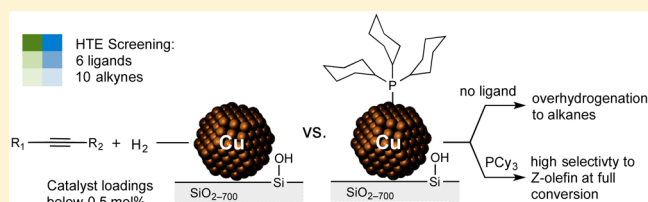
Silica-Supported Cu Nanoparticle Catalysts for Alkyne Semihydrogenation: Effect of Ligands on Rates and Selectivity

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S Supporting Information

ABSTRACT: Narrowly dispersed, silica-supported Cu nanoparticles (ca. 2 nm) prepared via surface organometallic chemistry from a mesityl complex $[\text{Cu}_5\text{Mes}_5]$ are highly active for the hydrogenation of a broad range of alkynes. High-throughput experimentation allows for identifying the optimal ligand and reaction conditions to turn these supported Cu nanoparticles into highly chemo- and stereoselective catalysts for the preparation of Z-olefins (overall, 23 examples). For instance, PCy_3 -modified Cu nanoparticles semihydrogenate 1-phenyl-1-propyne to *cis*- β -methylstyrene (20 bar H_2 , 40 °C) with turnover number and turnover frequency of ca. 540 and 1.9 min^{-1} , respectively, and with 94% selectivity at full conversion.



INTRODUCTION

Catalytic semihydrogenation of alkynes to alkenes is an important process in both industry and academia.^{1–7} For instance, Pd catalysts are utilized for selective semihydrogenation of acetylene in ethylene feeds prior to ethylene polymerization.⁸ Stereoselective semihydrogenation of internal alkynes to valuable Z-alkenes is a key step in the synthesis of vitamins and natural products.^{9,10} Developed in the 1950s, the heterogeneous Lindlar catalyst ($\text{Pd}/\text{CaCO}_3/\text{Pb}(\text{OAc})_2/\text{quinoline}$)¹¹ still remains a privileged system for Z-selective batch alkyne semihydrogenation.^{2–4,9} However, it relies on expensive and rare palladium metal, uses toxic Pb additive, and has other limitations such as narrow substrate scope, overhydrogenation to alkanes, Z/E isomerization, and double bond migration reactions of olefin products. Commercial lead-free Pd-based catalysts with increased utilization of palladium were developed only very recently.¹² Approaches to improve the chemoselectivity of Lindlar-type catalysts relied on addition of ligands, for instance, organosulfides.¹³ Semihydrogenation catalysts based on nanostructured Au^{14–19} and Ag^{20–22} were reported as well.

The scarcity and high price of noble metals has triggered the development of earth-abundant metal catalysts for alkyne semihydrogenation.^{23–26} In particular, catalysts that utilize molecular Cu precursors and reductants such as hydrosilanes,^{27–29} H_3PO_2 ,³⁰ or H_2 ^{31–33} have recently emerged as an alternative to the Lindlar catalyst. However, these transformations often require high catalyst loadings (5–10 mol %) and H_2 pressures. That said, while supported Cu nanoparticles (NPs) are well-known active catalysts for propyne semihydrogenation in the flow settings,^{34–38} the practical semihydrogenation of alkynes with Cu NPs in batch conditions remains underdeveloped.³⁹

Here we describe the synthesis and characterization of narrowly dispersed, silica-supported Cu nanoparticles prepared

via surface organometallic chemistry (SOMC) approach.⁴⁰ These recyclable Cu NPs are highly active in alkyne hydrogenation at low loadings. The addition of various ligands to these Cu NPs, which is a general approach to modulate selectivity and activity of supported nanoparticle catalysts,^{41–45} allows the improvement of the chemoselectivity of Cu alkyne semihydrogenation catalyst. In particular, PCy_3 -modified Cu particles feature high turnover numbers and frequencies in a broad range of substrates.

RESULTS AND DISCUSSION

Silica partially dehydroxylated at 700 °C (SiO_{2-700} , 0.34 $\text{mmol} \equiv \text{SiOH g}^{-1}$, 1.0 $\equiv \text{SiOH sites per nm}^2$, Figure 1a) reacts with a toluene solution of $[\text{Cu}_5\text{Mes}_5]$ ^{46,47} (0.95 equiv with respect to $\equiv \text{SiOH}$, Mes = mesityl) to give a yellow material $\text{Cu}_x\text{Mes}_{x-1}/\text{SiO}_{2-700}$ ($x = 2–5$). The mass balance analysis shows recovery of 0.27 equiv of $[\text{Cu}_5\text{Mes}_5]$ and infers 0.68 equiv of grafted $[\text{Cu}_5\text{Mes}_5]$. An NMR-scale grafting experiment in benzene- d_6 confirms this stoichiometry and also shows that the ratio of released Mes–H to reacted amount of $[\text{Cu}_5\text{Mes}_5]$ is ca. 1.3. This is explained by the equilibrium between $[\text{Cu}_5\text{Mes}_5]$ and $[\text{Cu}_2\text{Mes}_2]$ in solution⁴⁶ and a concomitant grafting of both species. The IR spectrum of the grafted material shows a nearly complete disappearance of the isolated $\equiv \text{SiOH}$ band at 3745 cm^{-1} upon treatment with $[\text{Cu}_5\text{Mes}_5]$ in toluene and appearance of new C–H bands at 3036, 2937, 2880, and 1600 cm^{-1} (Figure 1b). These observations infer grafting of $[\text{Cu}_5\text{Mes}_5]$, in contrast to $[\text{Au}_5\text{Mes}_5]$ that does not graft onto SiO_{2-700} under the same reaction conditions.⁴⁸ Subsequent treatment of $\text{Cu}_x\text{Mes}_{x-1}/\text{SiO}_{2-700}$ material under H_2 flow at 300 °C for 12 h gives a dark-brown $\text{Cu}/\text{SiO}_{2-700}$. Synthesis of $\text{Cu}/\text{SiO}_{2-700}$ can be easily performed on gram scale. The H_2

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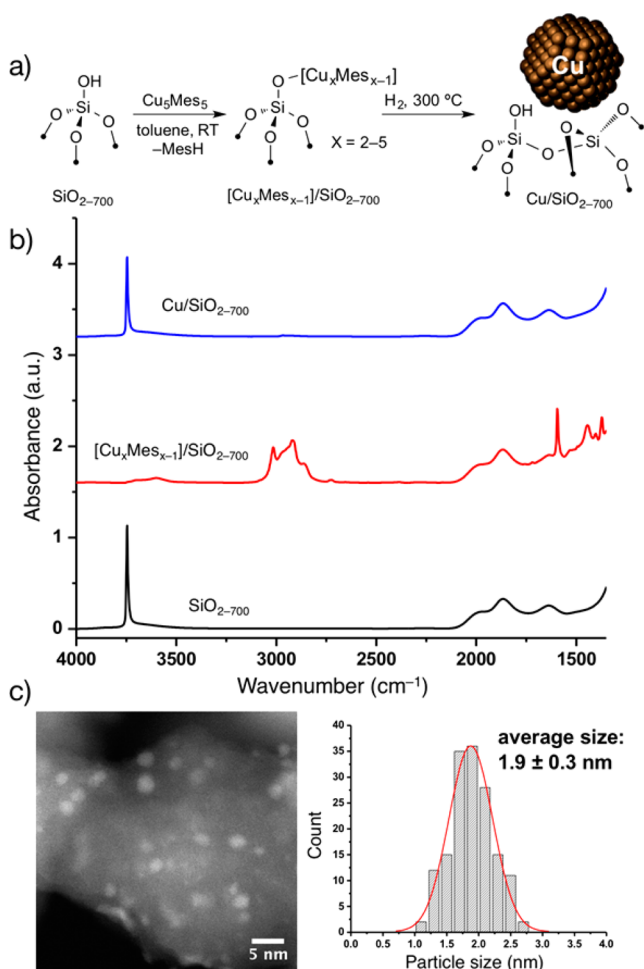


Figure 1. Synthesis (a), IR spectra (b), representative HAADF STEM micrograph and the corresponding particle size distribution of Cu/SiO₂₋₇₀₀ after slow oxidation in air at room temperature (c).

treatment regenerates surface silanols, while the C–H bands vanish (Figure 1b). Elemental analysis of Cu/SiO₂₋₇₀₀ reveals 5.5 wt % of Cu, corresponding to 3.5 Cu per ≡SiOH site in the dehydroxylated support, and only trace amount of carbon and hydrogen. High-angle annular dark field scanning transmission microscopy (HAADF STEM) reveals formation of narrowly dispersed Cu nanoparticles with an average size of 1.9 ± 0.3 nm, as determined after slow exposure to air (Figure 1c). Note that the size of Cu NPs prepared by other methods typically ranges from 5 to 15 nm.⁴⁹

Exposure of Cu/SiO₂₋₇₀₀ to 12.7 mbar CO gives two strong bands in the IR spectrum at 2093 and 2057 cm⁻¹ (Figure S3). These bands disappear upon evacuation at room temperature, which is characteristic for CO adsorption on metallic copper nanoparticles.⁵⁰ H₂ chemisorption shows that amount of effective Cu surface (Cu_{active}) in Cu/SiO₂₋₇₀₀ is 0.31 mmol g⁻¹ (Figure S6).⁵¹

Activity of Cu/SiO₂₋₇₀₀ in semihydrogenation was tested with a set of 10 alkynes (1–10) at 60 °C in toluene under 50 bar H₂ for 24 h with 0.375 mol % Cu_{active} catalyst loading (Figure 2, entry 1, and Table S1). Cu/SiO₂₋₇₀₀ semihydrogenates 4-nonyne (1) and 5-decyne (2) to Z-olefins with good chemo- and stereoselectivity and high conversion. Replacement of a longer alkyl group in 1–2 by a methyl group in 2-nonyne (3) deteriorates the Z-selectivity (Z/E ratio = 0.6).

While the Z-content with 2,10-dodecadiyne is moderate, the conversion is low (4). Terminal 1-dodecyne (5) predominantly converts to dodecane instead of the olefin. Aryl alkyl and silyl alkynes (6–9) are overhydrogenated to alkanes under these reaction conditions. No reduction of aromatics (or solvent) was observed. Interestingly, the chemo- and stereoselectivity is greatly improved with electron-depleted ethyl phenylpropiolate (10). A possible explanation for this increase in selectivity is the lower reactivity of the thus-formed olefin or the poisoning of unselective Cu sites via the binding of the ester group.

A crucial component of the Lindlar catalyst is quinoline that poisons unselective Pd sites.¹¹ We therefore examined if addition of ligands can enhance the selectivity to Z-olefins. The ligands tested included phosphines (PPh₃, (HO)PPh₂, PCy₃), a phosphine oxide PCy₃(=O), an N-heterocyclic carbene (IMes = (1,3-bis(2,4,6-trimethylphenyl)imidazolide), as well as N,N-dimethylaminopyridine (DMAP) (L1-6, Figure 2, entries 2–7). These ligands were added to H₂-treated Cu/SiO₂₋₇₀₀ in ca. 5.3-fold excess with respect to the effective Cu surface area.

Overall, the addition of ligands resulted in significant improvement of chemo- and stereoselectivity to Z-olefins, albeit at the expense of mass activity (per Cu_{total}) with some substrates. Compared to other ligands, phosphines yield higher Z-selectivity while maintaining high conversion of alkynes. Among phosphines tested, PCy₃ gives higher yields of Z-olefins. DMAP typically affords more alkanes, possibly due to the weaker binding to the Cu surface. PCy₃(=O) generally improves selectivity towards Z-alkenes with alkyl alkynes, but is not very effective with electron-rich aryl-substituted alkynes. Secondary phosphine oxide (HO)PPh₂ and strongly donating and bulky IMes ligand are generally not efficient, but are selective with 1-phenyl-1-hexyne and 1-phenyl-1-propyne. Interestingly, PCy₃ and PCy₃(=O) improve conversion of 10 compared to that of free Cu/SiO₂₋₇₀₀. In contrast, the Lindlar catalyst overhydrogenates all alkynes to alkanes under the same reaction conditions.

Since PCy₃ performed best among ligands screened, yielding corresponding Z-alkenes with high selectivity due to reduced amounts of overhydrogenated and oligomerized products, Cy₃P–Cu/SiO₂₋₇₀₀ was prepared by treating Cu/SiO₂₋₇₀₀ in pentane with 2.7-fold excess of PCy₃ per surface Cu_{active} followed by a removal of the unbound ligand by washing with pentane. By elemental analysis, Cy₃P–Cu/SiO₂₋₇₀₀ contains 0.6 wt % P and ratios of C/P and H/P are ca. 21 and 26, respectively. This corresponds to 1.45 P per surface Cu atom. However, the IR spectrum of Cy₃P–Cu/SiO₂₋₇₀₀ shows broadening of the silanol band indicating interaction of PCy₃ with ≡SiOH (Figure S3). This suggests that silanols compete with the Cu surface for the phosphine binding, making the actual Cu nanoparticle coverage lower than inferred from the nominal loading. Based on the projected surface area of PCy₃, ca. 70% of total Cu/SiO₂₋₇₀₀ surface is covered by the ligand.

Cross-polarization (CP) magic angle spinning (MAS) ³¹P NMR spectroscopy of Cy₃P–Cu/SiO₂₋₇₀₀ reveals broad peaks at 33 and 27 ppm and a relatively sharp peak at 57 ppm (Figure S4c). The latter two peaks are also found in PCy₃ adsorbed on SiO₂₋₇₀₀ (Figure S4b) and are therefore attributed to the strongly adsorbed phosphonium species such as [≡SiO–H···PCy₃] or [≡SiO···H–PCy₃⁺].⁵² The peak at 33 ppm is likely due to interactions of PCy₃ with Cu NPs. Notably, addition of CO (34.6 mbar) gives rise to two CO adsorption bands at 2084 and 2007 cm⁻¹, red-shifted compared to CO bands on Cu/SiO₂₋₇₀₀ (Figure S3). Intensities of these bands are much lower

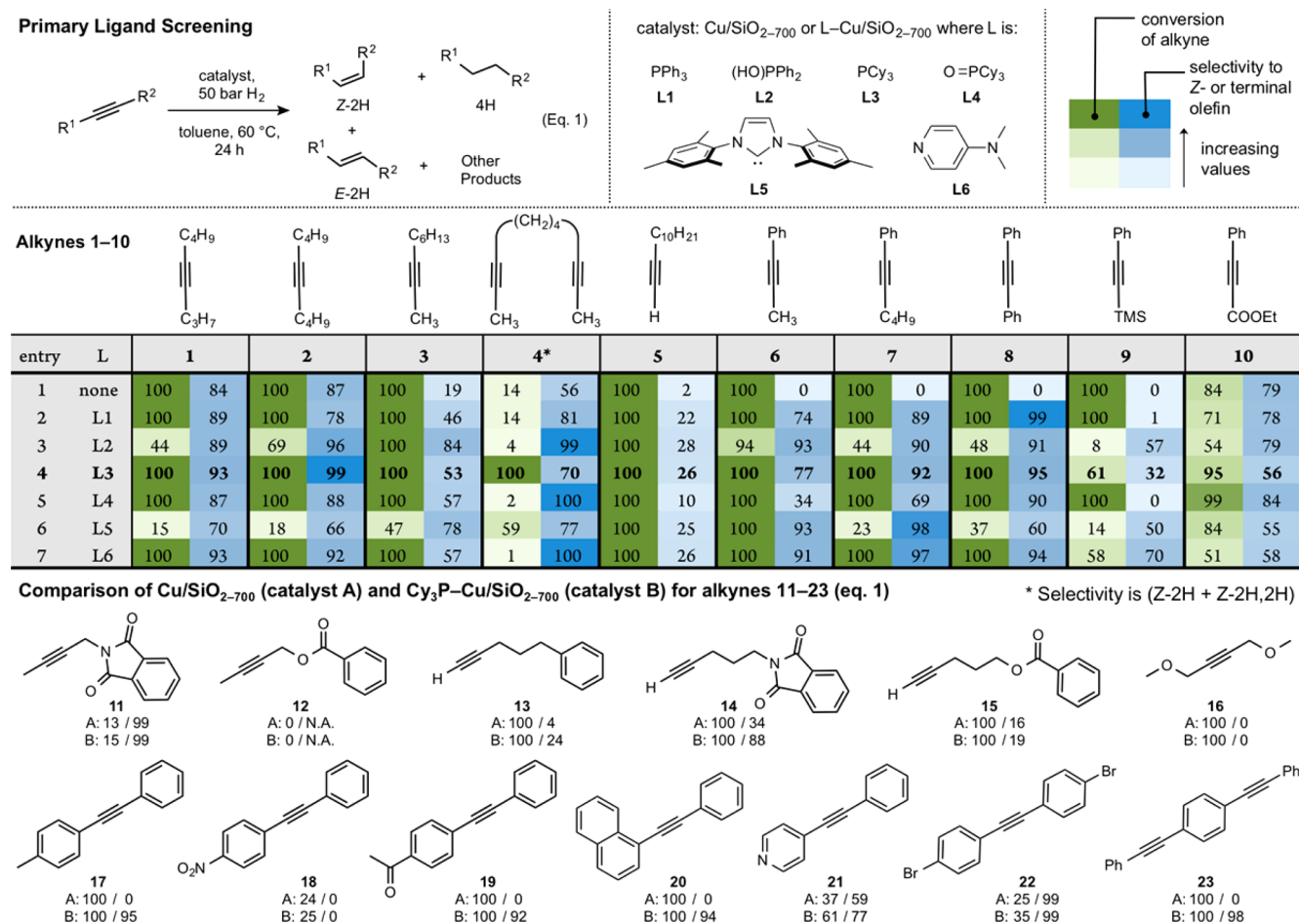


Figure 2. Top: identification of the optimal ligand for Cu/SiO₂₋₇₀₀-catalyzed hydrogenation with a selected set of 10 alkynes; bottom: Cu/SiO₂₋₇₀₀ and Cy₃P-Cu/SiO₂₋₇₀₀-catalyzed alkyne hydrogenation with an additional set of 13 alkynes. See Table S1 for details. Conditions were as follows: substrate (400 μmol), Cu/SiO₂₋₇₀₀ (5 mg, ca. 4.4 μmol Cu_{total}, 1.5 μmol Cu_{active}), L1–L6 (8 μmol) in 2 mL of toluene.

than those of unmodified Cu/SiO₂₋₇₀₀, consistent with the decreased number of available surface sites, and the red shift of the CO band points to an increase of the electron density on Cu due to the PCy₃ binding. H₂ chemisorption shows that Cy₃P-Cu/SiO₂₋₇₀₀ has an effective Cu surface area of 0.067 mmol g⁻¹ and a thermodynamic adsorption constant $K = 3.44$, corresponding to thermodynamic adsorption energy of -3 kJ mol⁻¹, as opposed to the effective surface area of 0.14 mmol g⁻¹ and $K = 948$ for unmodified Cu/SiO₂₋₇₀₀ (Figure S6). This data supports a much weaker interaction of Cu surface with hydrogen in the case of PCy₃-Cu/SiO₂₋₇₀₀.

An additional set of alkynes (13 substrates), including more challenging terminal alkynes,⁵³ was then submitted to Cu/SiO₂₋₇₀₀ and in situ prepared Cy₃P-Cu/SiO₂₋₇₀₀ under the standard reaction conditions and the same total Cu loading (Figure 2, bottom). Whereas hydrogenation of phthalimidyl alkyne **11** proceeds with low conversion and high Z-selectivity, 2-butyryl benzoate **12** shows no conversion. Terminal alkynes **13–15** are readily hydrogenated, however, while PCy₃ does improve the selectivity to olefins, especially with **13**; further optimization of pressure and temperature is necessary for these substrates. Higher reactivity of terminal alkynes compared to that of internal alkynes has been also observed for Pd/Al₂O₃ catalysts.⁵⁴ While both catalysts oligomerize **16**, switching to (HO)PPh₂ and IMes ligands, which proved generally inferior to PCy₃ in this study, allows for 88 and 70% selectivity to 16-Z-

2H, respectively (see Table S1). With exception of alkyne **18**, the triple bond of activated diaryl-substituted alkynes **17–23** is semihydrogenated to Z-alkenes with Cy₃P-Cu/SiO₂₋₇₀₀. The nitro group in **18** is selectively reduced to the amino without reduction of the triple bond, although with a modest yield. In contrast, the acetyl group in **19** is reduced by both catalysts along with the triple bond; with PCy₃ ligand, the latter reduction is chemoselective to the olefin product. Pyridine moiety in **21** can presumably act as a ligand, making Cu/SiO₂₋₇₀₀ catalyst more selective at the expense of activity. The C-Br bond in **22** is not reduced under the reaction conditions. The difficulty in the hydrogenation of alkynes with electron-deficient aryl substituent by Cu/SiO₂₋₇₀₀ is similar to what is observed with the Lindlar catalyst but is in contrast to gold-based catalysts.¹⁷ With diyne **23**, Cy₃P-Cu/SiO₂₋₇₀₀ selectively yields Z-reduction of both triple bonds. Increasing the amounts of **6** and **8** by a factor of 4 results in similar conversions or selectivities with Cu/SiO₂₋₇₀₀ and Cy₃P-Cu/SiO₂₋₇₀₀ (ca. 0.1 and 0.05 mol % Cu_{active}, respectively) as those shown in Figure 2.

To identify primary and secondary reaction products, we studied the progress of hydrogenation of 1-phenyl-1-propyne (**6**) at 40 °C under isobaric conditions (20 bar H₂) with Cu/SiO₂₋₇₀₀ and Cy₃P-Cu/SiO₂₋₇₀₀ catalysts using 0.375 and 0.18 mol % Cu_{active}, respectively (Figure 3, Table S2). Both catalysts show zero-order dependence on alkyne concentration indicat-

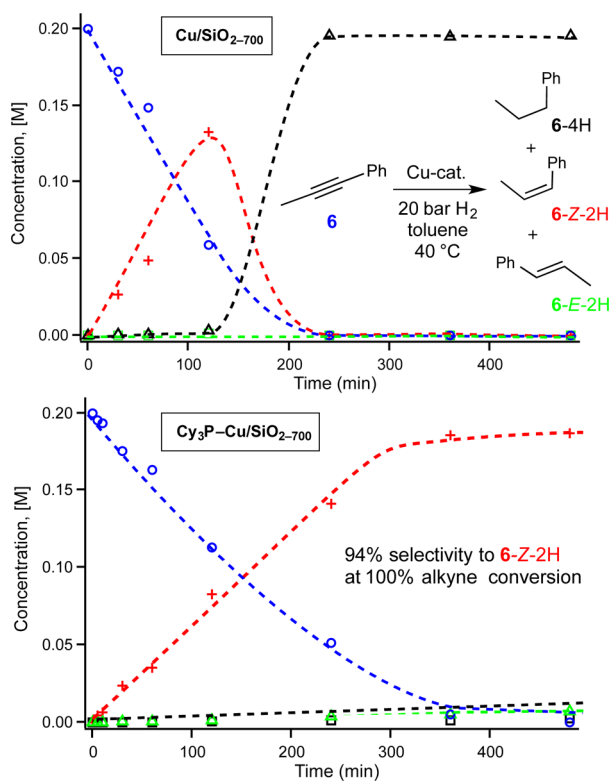


Figure 3. Evolution of concentration with time for the hydrogenation of 1-phenyl-1-propyne with Cu/SiO₂₋₇₀₀ (0.375 mol %, top) and Cy₃P-Cu/SiO₂₋₇₀₀ (0.18 mol %, bottom) with dotted lines added to guide an eye.

ing a strong alkyne adsorption onto the Cu surface.⁵³ The unmodified catalyst Cu/SiO₂₋₇₀₀ is selective to *cis*- β -methylstyrene (6-Z-2H) until at least 70% conversion (120 min) and produces phenylpropane with 98% selectivity after 240 min. This demonstrates that overhydrogenation to alkane is a secondary process,²⁴ which is also confirmed by an in situ IR spectroscopy (see Supporting Information for details). In contrast, Cy₃P-Cu/SiO₂₋₇₀₀ provides 6-Z-2H with 94% selectivity at full conversion of 6. The rates of Z-selective semihydrogenation of 1-phenyl-1-propyne to 6-Z-2H for the unmodified and phosphine modified Cu catalysts are 1.2×10^{-3} and 7×10^{-4} M s⁻¹, which corresponds to TOF values corrected for the number of active sites determined by H₂ chemisorption of 1.5 and 1.9 min⁻¹, respectively. Since poisoning of the most active but unselective sites by added ligands typically decreases reaction rates of heterogeneous catalysts, this increase in TOF observed for Cy₃P-Cu/SiO₂₋₇₀₀ compared to Cu/SiO₂₋₇₀₀ indicates a ligand-accelerated catalysis,⁵⁵ a highly desirable and actively researched phenomenon in heterogeneous systems.^{44,56-60} The aforementioned IR data on CO binding to the phosphine-modified Cu NPs suggests an increase in electron density on the surface Cu atoms. This modification of electronic structure of the catalyst is due to the donation of electron density from PCy₃ to Cu. Coordination of the phosphine probably reduces the strength of alkyne binding, which may be a reason for the enhanced rate with Cy₃P-Cu/SiO₂₋₇₀₀.

To confirm the difference in reactivity of Cy₃P-Cu/SiO₂₋₇₀₀ versus that of Cu/SiO₂₋₇₀₀ in hydrogenation of *cis*-olefins, we subjected pure *cis*- β -methylstyrene to hydrogenation under reaction conditions presented in Figure 3. Whereas unmodified

Cu/SiO₂₋₇₀₀ fully converted ca. 270 equiv of 6-Z-2H to 6-4H after 2 h, Cy₃P-Cu/SiO₂₋₇₀₀ was nearly inactive, converting only 3% of 6-Z-2H to 6-4H (Table S3). This data suggest that while the alkyne can displace the phosphine bound to Cu surface sites and thereby be hydrogenated to the Z-alkene the alkene is a too weak ligand for the Cu in the presence of phosphine.

We also examined if Cu/SiO₂₋₇₀₀ and Cy₃P-Cu/SiO₂₋₇₀₀ hydrogenate 1-phenyl-1-propyne at lower pressures and found that 6-Z-2H forms already at 2 bar although conversion after 360 min dropped from 100 and 97% at 20 bar to 21 and 17% at 2 bar, respectively, and selectivity decreased yielding higher amount of oligomers (selectivities to 6-Z-2H = ca. 65%, Table S2). Filtration tests were conducted as well and showed no further conversion of 6 after removal of Cu/SiO₂₋₇₀₀ or Cy₃P-Cu/SiO₂₋₇₀₀ from the reaction mixture, demonstrating no leaching of copper in both cases. Finally, recycling experiments with diphenylacetylene show that the catalytic ability of Cy₃P-Cu/SiO₂₋₇₀₀ is retained in the second run and gradually decreases to one-fourth after five cycles.

CONCLUSIONS

We reported that well-dispersed, silica-supported Cu NPs prepared in a highly controlled manner via surface organometallic chemistry are highly active for batch alkyne hydrogenation. The high-throughput ligand screening approach applied to a heterogeneous catalyst allowed identifying tricyclohexylphosphine as a potent ligand to increase the chemoselectivity of alkyne semihydrogenation. The optimal catalyst Cy₃P-Cu/SiO₂₋₇₀₀ is thus an efficient, practical, sustainable, and cheap alternative to the Lindlar catalyst. Modification of the electronic structure of the catalyst surface by PCy₃ ligand is reflected in the red-shifted stretching frequencies of Cu-bound CO probe molecule. Such ligand effect not only improved the chemoselectivity but also gave a more active catalyst, indicating ligand-accelerated catalysis⁵⁵ and serving as a guide for further development of better catalytic systems.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b10817.

Full experimental details and characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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