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Polyhedral Cu_2O Crystals for Diverse Aryl Alkyne Hydroboration Reactions

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Abstract: Cu_2O cubes, octahedra, and rhombic dodecahedra were used to examine facet-dependent catalytic activity toward aryl alkyne hydroboration reaction. Although the reaction can proceed using ethanol and other alcohols as solvents, use of 1,4-dioxane gave the best product yield. All particle shapes gave exclusively the (*E*)-product, but rhombic dodecahedra exposing the {110} surfaces are consistently far more reactive than the other particle morphologies. A product yield of 99% has been achieved using Cu_2O rhombic dodecahedra to catalyze phenylacetylene hydroboration at 60 ℃ for 5 h. The rhombic dodecahedra have been shown to catalyze a variety of substituted aryl alkynes, demonstrating their potential as a versatile catalyst.

Introduction

The development of synthetic conditions for the growth of sharp-faced cuprous oxide cubes, octahedra, and rhombic dodecahedra has enabled the exploration of their facet-dependent electrical conductivity, photocatalytic, organocatalytic, and optical properties.[1–3] In contrast to the facet-dependent electrical, photocatalytic, and optical properties of semiconductors, which are described in terms of tunable degrees of surface band bending, organocatalysis by metal oxides is mainly concerned with surface atoms interacting with substrate molecules without the need to consider their band structures.[4–6] Previously, Cu_2O cubes, octahedra, and rhombic dodecahedra exposing respectively {100}, {111}, and {110} faces have been demonstrated to exhibit facet-dependent catalytic activities toward multicomponent click reactions forming 1,2,3-triazoles and [3 + 2] cycloaddition reactions yielding 3,5-disubstituted isoxazoles.[7–9] Rhombic dodecahedra have been found to be most catalytically active for these reactions, attributed to the fully exposed copper atoms on the (110) planes of Cu_2O, while Cu_2O cubes are least catalytically active with their copper atoms partially blocked by the uppermost layer of oxygen atoms.[7] The {111}

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surfaces of Cu_2O octahedra have both fully and partially exposed copper atoms and have displayed an intermediate catalytic activity. In addition, Cu_2O cubes have been employed to catalyze Ullmann coupling between aryl halides and phenols, and Cu/Cu_2O loaded on reduced graphene has shown good activity for Sonogashira cross-coupling reactions.[10,11] Furthermore, high-temperature gas-phase propylene oxidation reactions have been carried out using Cu_2O cubes, octahedra, and rhombic dodecahedra forming different products.[12] These polyhedral Cu_2O crystals are an excellent model material for further study of their facet-dependent organocatalytic properties. After surveying, we have found that their catalytic activities toward aryl alkyne hydroboration have not been reported before.[13] Previously, commercial micro copper powder was used for ligand-free hydroboration of terminal and internal alkynes, but the same amount of Cu_2O powder gave only 10% yield for internal alkyne hydroboration.[14] Cu_2O particles of undefined shapes dispersed on carbon black support and copper nanoparticles were also employed for borylation of alkyl bromides.[15,16] We have also explored the use of copper nanocubes for aryl alkyne hydroboration reactions in ethanol at 50 ℃ for 2 h giving exclusive (*E*)-product selectivity and 82–95% yields.[17] Terminal alkyne hydroboration using designed homogeneous catalysts is an active research topic in the organic community because of the great utility of the generated products.[18–21]

In this study, we have used Cu_2O cubes, octahedra, and rhombic dodecahedra to catalyze aryl alkyne hydroboration primarily in 1,4-dioxane at 60 ℃ for 5 h giving exclusively (*E*)-product selectivity. Clear facet-dependent catalytic performance has been observed, showing rhombic dodecahedra as the best catalyst. A range of substituted aryl alkynes were also tested to illustrate the versatility of Cu_2O rhombic dodecahedra for this important reaction.

Results and Discussion

Cu_2O cubes, octahedra, and rhombic dodecahedra were synthesized following our reported procedures.[22,23] Table S1 in the Supporting Information provides the reagent amounts used. Scheme S1 gives the illustration of the experimental procedure. Briefly, an aqueous mixture of $CuCl_2$ and sodium dodecyl sulfate (SDS) surfactant was prepared, followed by the addition of NaOH and $NH_2OH{\cdot}HCl$ reductant, and aged the resulting solution at room temperature or 31 ℃ for 30–50 min to form various polyhedral Cu_2O crystals. Particle shape control was achieved mainly by adjusting the amount of reducing agent introduced, showing particle shape evolution is governed by the reaction cell potential (E), which relates to changes in the Gibbs free energy ($\Delta G = -nFE$) or the reaction driving force.[24] Figure 1 presents scanning electron microscopy (SEM) images of the synthesized Cu_2O cubes, octahedra, and rhombic dodecahedra. The particles all have well-defined structures and sharp faces with fairly monodisperse sizes. Figure S1 provides the size distribution histograms of the three samples. Their average sizes and standard deviations are available in Table S2. The average edge length of the cubes is 208 nm, while the average opposite corner distance of octahedra is 423 nm. For rhombic dodecahedra, their average opposite face distance is 361 nm. X-ray diffraction (XRD) patterns of the synthesized cubes, octahedra, and rhombic dodecahedra are given in Figure S2 with all the peaks matched to those of Cu_2O. Earlier studies using Fourier-transform infrared (FT-IR) and X-ray photoelectron spectroscopy techniques have shown that the Cu_2O polyhedra are free of surfactant after a couple cycles of washing, so these clean crystals were subsequently used to catalyze aryl alkyne hydroboration reactions.[7,9,25]

Phenylacetylene was chosen as the model molecule to test the reactivity of different Cu_2O crystals and optimize the reaction conditions. Initially, 0.1 mmol of phenylacetylene, bis(pinacolato)diboron (B_2pin_2), and triphenylphosphine (PPh_3) as a base were mixed in various solvents in the presence of Cu_2O rhombic dodecahedra to carry out hydroboration reaction at 60 ℃ for 5 h. Table S3 offers the NMR yields of the sole product trans-2-phenylvinylboronic acid pinacol ester in 1,4-dioxane (99%), ethanol (85%), isopropanol (83%), *tert*-butanol (77%), and water (0%). Figures S3 to S7 give the ^{1}H NMR spectra of the (*E*)-product formed. Although good product yields have been obtained using various alcohols, the best yield was achieved employing 1,4-dioxane as the solvent. Thus, 1,4-dioxane was used throughout the study. Next, the reaction temperature was varied from room temperature to 80 ℃. The highest conversion yield of 99% was recorded at 60 ℃, so later reactions were all carried out at this temperature (see Table S4).

After optimizing the reaction conditions, different amounts of Cu_2O cubes, octahedra, and rhombic dodecahedra, having approximately the same total particle surface area, were used to compare their catalytic performance. The hydroboration conditions and the phenylacetylene conversion yields are presented in Table 1. Figures S8 and S9 are the crude ^{1}H NMR spectra of the product formed using Cu_2O cubes and octahedra as the catalysts. From the appearance of only the doublet peaks at ~ 6.2 ppm for all the samples, the (*E*)-product has been exclusively synthesized.[17] The absence of the doublet appearing at ~ 5.6 ppm indicates that the *cis*- or (*Z*)-product was not formed.[26] Figure S10 provides the ^{1}H and ^{13}C NMR spectra of the silica gel column-purified hydroboration product using Cu_2O rhombic dodecahedra as the catalyst. Rhombic dodecahedra have the best reactivity, giving 99% yield as compared to cubes (62%) and octahedra (73%). After the hydroboration reaction, the rhombic dodecahedra appeared to maintain their morphology integrity, suggesting their possible use as a recyclable catalyst (Figure S11). To confirm the superior reactivity of Cu_2O rhombic dodecahedra, 3-chloro-1-ethynylbenzene was also used for catalytic comparison. Table 2 offers the product yields of 3-chloro-1-ethynylbenzene hydroboration reaction employing different Cu_2O crystal catalysts and the same reaction conditions used for phenylacetylene. Figure S12 to S14 display ^{1}H NMR spectra of the crude product formed using these Cu_2O crystal catalysts. Again rhombic dodecahedra showed the best catalytic efficiency with a conversion yield of 85%, while cubes and octahedra recorded product yields of 54% and 69%, respectively. These results have revealed clear facet effects. Consistent with previous observations, the {110} faces of Cu_2O are most catalytically active due to their fully exposed copper atoms for binding of the deprotonated alkyne group to the crystal surface in the first step of catalytic process, as demonstrated previously for Au and Cu nanocrystal-catalyzed click reactions through the FT-IR spectral characterization.[27,28] Figure S15 depicts a possible reaction mechanism of phenylacetylene binding to the {110} surface of Cu_2O on the basis of known deprotonated alkyne intermediate formation on the crystal surface.

To prove the heterogeneous nature of this catalytic reaction, 2 mg of Cu_2O rhombic dodecahedra were first heated in 2 mL of 1,4-dioxane for 5 h at 60 ℃, and the 1,4-dioxane solution after particle removal was subsequently used for phenylacetylene hydroboration using the same amounts of reagents. Figure S16 shows no product was formed as judged from the solution ^{1}H NMR spectrum. Thus, no metal ion leaching has occurred and the hydroboration reaction proceeds via heterogeneous catalysis. Inductively coupled plasma mass spectral analysis (ICP-MS) has been performed on the real catalytic solution at 60 ℃ using Cu_2O rhombic dodecahedra as the catalyst. A copper ion concentration of just 2.861 ppm, or equivalent of 0.002861 mg of Cu ion in 1 mL of the product solution, was detected. The result proves that copper ion leaching did not happen. Actually, the colorless hydroboration product solution already indicates that no leaching of copper ions from Cu_2O rhombic dodecahedra has occurred (Figure S17). In contrast, a brown solution results by dispersing $CuCl_2$ in 1,4-dioxane. Recyclability of the Cu_2O rhombic dodecahedra was also examined. After completing one run of phenylacetylene hydroboration reaction, the same crystals were used to carry out another cycle of the reaction. A crude product yield of 74% was obtained after 5 h of reaction (see Figure S18). The particle shape was also maintained, proving the rhombic dodecahedra can be used as a recyclable catalyst. However, the low cost in the synthesis of Cu_2O crystals means recycling may not make good economic sense.

Next, the substrate scope of this catalytic reaction using various substituted aryl alkynes containing electron donating and withdrawing groups (-F, -Cl, $-OCH_3$, $-CH_3$, and -NH_2) was evaluated. Again Cu_2O rhombic dodecahedra and the same reaction conditions were used. Figures S19 to S23 provide the ^1H NMR spectra of the various products formed. Table 3 indicates that the yields are generally good ranging from 69% to 95% for the substituted aryl alkynes, demonstrating the great value of Cu_2O rhombic dodecahedra to make diverse vinylboronates.

Conclusion

This work explores the use of Cu_2O cubes, octahedra, and rhombic dodecahedra as catalysts toward aryl alkyne hydroboration reactions. Although the reaction can proceed in ethanol, use of 1,4-dioxane offers the highest product yield. All particle shapes gave exclusively the (*E*)-product, but rhombic dodecahedra consistently showed the best catalytic activity with a product yield of 99% for phenylacetylene hydroboration. The crystals have been demonstrated to be recyclable heterogeneous catalyst. The Cu_2O rhombic dodecahedra were employed to catalyze hydroboration of a number of substituted aryl alkynes, showing they are versatile catalyst.

Experimental Section

Cu_2O crystal-catalyzed aryl alkyne hydroboration reactions

Under an argon atmosphere, phenylacetylene (11 μL, 0.1 mmol, 1.0 equiv.), triphenylphosphine (0.02622 g, 0.1 mmol, 1.0 equiv.), and bis(pinacolato)diboron (B_2pin_2, 0.0253 g, 0.1 mmol, 1.0 equiv.) were added to a vial containing 3 mL of 1,4-dioxane. Previously, Cu_2O cubes, octahedra, and rhombic dodecahedra prepared following the same procedure and nearly identical reagent amounts gave respective particle surface areas of 2.84, 0.56, and 1.35 m^2/g, so 1, 5, and 2 mg of Cu_2O cubes, octahedra, and rhombic dodecahedra were respectively introduced into the vial, such that all samples have approximately the same total surface area for catalytic activity comparison.[7] Subsequently, the mixture was heated to 60 ℃ with stirring for 5 h. Then the mixture was centrifuged at 8000 rpm for 3 min to remove the nanocrystals. The solvent was then removed under reduced pressure. The filtrate was subjected to evaporation to obtain the crude compound. To evaluate the extent of versatility of the catalyst, the same hydroboration reaction was performed with different substituted aryl alkynes. Cu_2O rhombic dodecahedra were chosen as the catalyst in these reactions.

Use of the catalyst for multiple hydroboration reactions

The performance of Cu_2O rhombic dodecahedra as recyclable catalyst has been examined. After completing one run of reaction, the reaction mixture was centrifuged. The solution containing the product was removed, leaving behind the nanocrystal precipitate. Fresh 1,4-dioxane solution, phenylacetylene, PPh_3, and B_2pin_2 of the same amounts as before were added. The reaction mixture was heated to 60 °C with stirring for 5 h.

Instrumentation

SEM images of the samples were obtained using a JEOL JSM-7000F electron microscope. XRD patterns were recorded on a Shimadzu XRD-6000 diffractometer with Cu K_α radiation. A Varian Mercury NMR spectrometer was used to collect ^1H NMR spectra (400 MHz) and ^{13}C NMR spectra (100 MHz). UV–vis absorption spectra were collected using a JASCO V-670 spectrophotometer. ICP-MS analysis of Cu ions in the solution was performed on an Agilent 7500ce mass spectrometer.

Acknowledgements

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Conflict of interest

The authors declare on conflict of interest.

Keywords: cuprous oxide, facet-dependent properties, heterogeneous catalysis, hydroboration, nanocrystals

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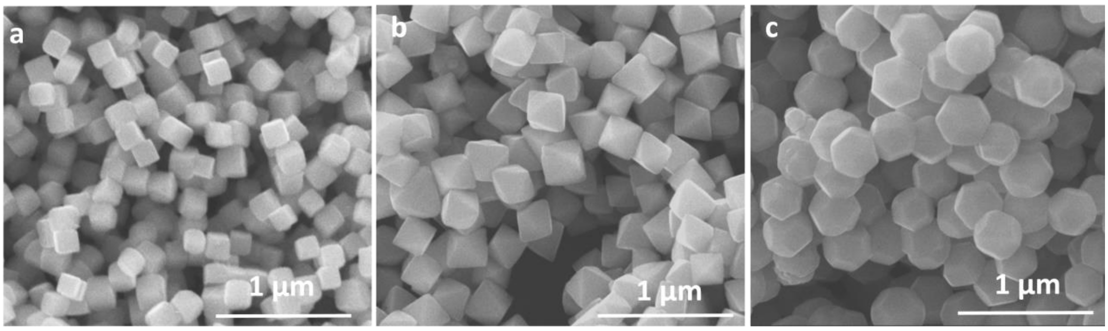
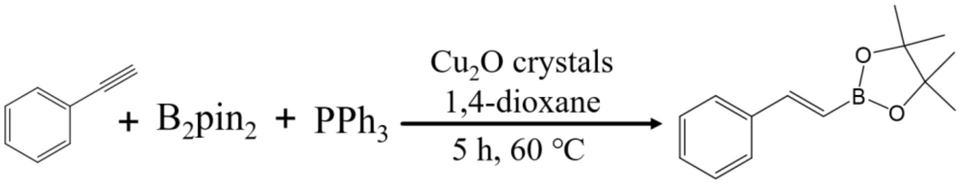


Figure 1. SEM images of the synthesized Cu_2O a) cubes, b) octahedra, and c) rhombic dodecahedra.

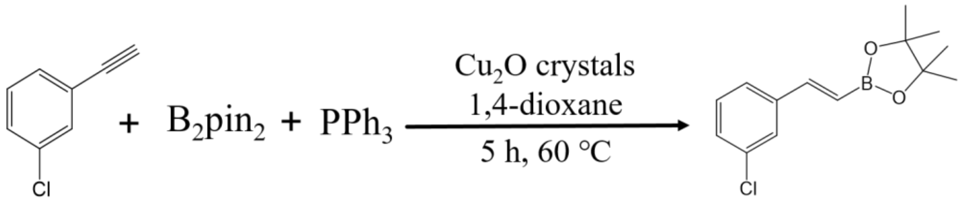
Table 1. Product yields of phenylacetylene hydroboration reaction using different Cu_2O crystals as the catalysts.



Catalyst	Yield (%)
Cu_2O cubes	62
Cu_2O octahedra	73
Cu_2O rhombic dodecahedra	99

Reagent amounts: PhC≡CH (0.1 mmol), B_2Pin_2 (0.1 mmol), PPh_3 (0.1 mmol), and 1,4-dioxane (2 mL).

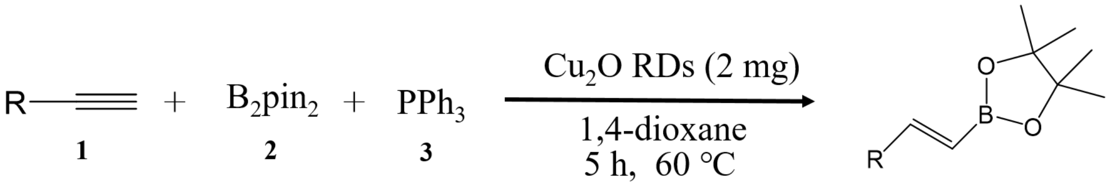
Table 2. Product yields of 3-chloro-1-ethynylbenzene hydroboration reaction using different Cu_2O crystals as the catalysts.

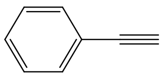
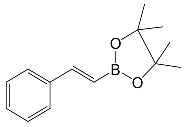
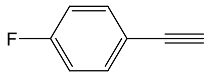
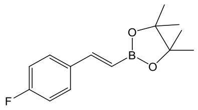
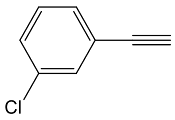
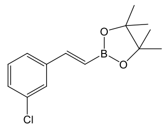
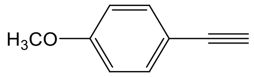
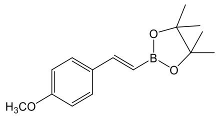
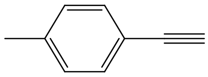
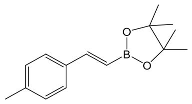
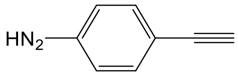
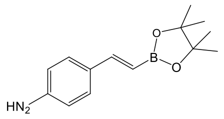


Catalyst	Yield (%)
Cu_2O cubes	54
Cu_2O octahedra	69
Cu_2O rhombic dodecahedra	85

Reagent amounts: PhC≡CH (0.1 mmol), B_2Pin_2 (0.1 mmol), PPh_3 (0.1 mmol), and 1,4-dioxane (2 mL).

Table 3. Use of Cu_2O rhombic dodecahedra as the catalyst for diverse aryl alkyne hydroboration reactions and the product yields.



Entry	Alkyne	Product	Yield (%)
2a			99
2b			95
2c			86
2d			81
2e			71
2f			69

Reagents and conditions: 1 (0.1 mmol), 2 (0.1 mmol), and 3 (0.1 mmol) in 1,4-dioxane (2 mL) at 60 ℃.

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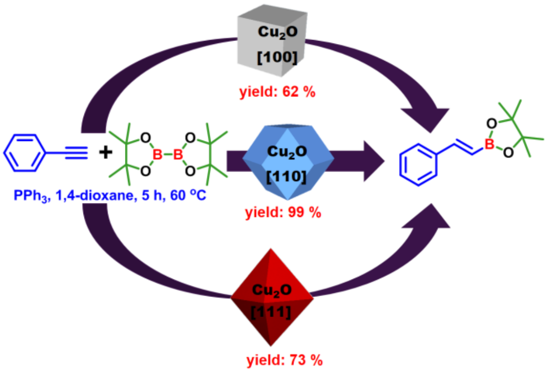

TOC Graphic

Polyhedral Cu_2O crystals display facet-dependent catalytic properties toward aryl alkyne hydroboration giving exclusive (*E*)-product selectivity. Rhombic dodecahedra exposing the {110} faces are most catalytically active for hydroboration of various substituted aryl alkynes.