Cu$_2$O-Supported Atomically Dispersed Pd Catalysts for Semihydrogenation of Terminal Alkynes: Critical Role of Oxide Supports

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Atomically dispersed catalysts have demonstrated superior catalytic performance in many chemical transformations. However, limited success has been achieved in applying oxide-supported atomically dispersed catalysts to semihydrogenation of alkynes under mild conditions. By utilizing various metal oxides (e.g., Cu$_2$O, Al$_2$O$_3$, ZnO, and TiO$_2$) as support for atomically dispersed Pd catalysts, we demonstrate herein the critical role of the oxidation state and coordination environment of Pd centers in their catalytic performance, thus leading to the discovery of an "oxide-support effect" on atomically dispersed metal catalysts. Pd atomically dispersed on Cu$_2$O exhibits far better catalytic activity in the hydrogenation of alkynes, with an extremely high selectivity toward alkenes, compared with catalysts on other oxides. Pd species galvanically displace surface Cu(I) sites on Cu$_2$O to create two-coordinated Pd(I), which is a critical step for the activation and heterolytic splitting of H$_2$ into Pd-H$^\delta^-$ and O-H$^\delta^+$ species for the selective hydrogenation of alkynes. Moreover, the adsorption of alkenes on H$_2$-preadsorbed Pd(I) is relatively weak, preventing deeper hydrogenation and increased selectivity during semihydrogenation. We demonstrate that the local coordination environment of active metal centers plays a crucial role in determining the catalytic performance of an oxide-supported atomically dispersed catalyst.

Keywords: atomically dispersed catalyst, support effect, palladium, semihydrogenation, selective hydrogenation, alkynes, heterolytic activation of hydrogen, galvanic displacement
Introduction

Supported metal catalysts play important roles in the chemical industry due to their applications in a wide range of catalytic reactions, for example, hydrogenation reactions. The metal-support interaction has been well documented as an important factor for controlling the overall catalytic performance of a supported metal catalyst. For instance, a few metal oxides, such as FeOx, CeOx, SiO2, and TiO2, have been recently demonstrated to create effective metal-support interfaces for promoting catalysis. For those systems with active metal-support interfaces, catalysts with enhanced performance are easily achieved by maximizing the metal-support interfaces. In this regard, due to the maximum utilization of metal atoms, atomically dispersing metals on oxide supports that can provide active metal-support interfaces would be an ideal strategy to optimize the catalytic performances of oxide-supported metal catalysts.

It is particularly interesting that, although atomically dispersed metal catalysts on nonmetal oxide supports have been widely demonstrated as efficient catalysts for hydrogenation, limited success has been achieved when metal oxides are used as supports. Surprisingly, a few atomically dispersed metal catalysts supported on metal oxides exhibited negligible activity toward the semihydrogenation of alkynes under mild conditions, which is in contrast to the catalytic behavior of the same metal in the form of clusters or nanoparticles. For instance, Rossell and co-workers reported that atomically dispersed Pd atoms on Fe3O4 show no activity in the hydrogenation of alkynes, whereas Pd clusters and nanoparticles are active. Gaining a deeper understanding of the role of the support in atomically dispersed catalysts is thus important.

This work aims to investigate how the nature of oxide supports influences the catalytic hydrogenation performance of atomically dispersed, surface metal catalysts. CuxO is demonstrated to readily create catalytically active and selective interfaces with atomically dispersed Pd atoms for the semihydrogenation of alkynes into alkenes, whereas many other oxides (e.g., Al2O3, ZnO, and TiO2) cannot. The atomically dispersed Pd catalyst on Cu2O (Pd1/Cu2O) is prepared by anchoring Pd atoms onto Cu2O via the galvanic displacement reaction between Pd0 and Cu+ on the support. With its unique Pd-(O-Cu)2 interface structure and the valence state of Pd at +1, Pd/Cu2O activates H2 in a heterolytic way, distinguishing it from the hemolytic dissociation on supported Pd nanoparticles (NPs). The Pd-O-Cu interface serves as the active site for semihydrogenation of terminal alkynes. However, the nature of the atomically dispersed Pd sites suppresses the full hydrogenation of styrene because the styrene is difficult to hydrogenate and easily desorbs from the catalytic sites. Based on this understanding, commercial Cu2O is regularly used as an active support for the preparation of atomically dispersed Pd catalysts for the semihydrogenation of terminal alkynes under mild conditions.

Experimental Methods

The Cu2O support used in this study was prepared by reducing Cu(OH)2 with hydrazine (Supporting Information Figures S1–S3). The precursor solution of Pd(CH3CN)2Cl2 was then added dropwise into the acetonitrile dispersion of Cu2O to allow deposition of Pd species on Cu2O by the galvanic displacement reaction (Cu+ + Pd2+ → Cu2+ + Pd0, ΔE° = +0.394 V). After 5 h of stirring at 50 °C under a N2 atmosphere, the Pd/Cu2O catalyst was washed three times with ethanol (Supporting Information Figure S4). As revealed using aberration-corrected scanning transmission electron microscopy (Figure 1a; Supporting Information Figure S5) and X-ray diffraction, no formation of Pd NPs was observed on the as-obtained Pd/Cu2O catalyst (Supporting Information Figure S6) when the loading content of Pd was 0.2 (wt %). The local chemical environment of Pd atoms on Pd/Cu2O was studied by the means of extended X-ray absorption fine structure (EXAFS) spectroscopy (Figure 1b; Supporting Information Figure S7). There was one notable peak in the region of 1-2 Å from the Pd-O contribution and a peak in the range 2.5-3.5 Å from the Pd-Cu contribution. No peak in the region of 2-3 Å from the Pd-Pd contribution was observed. These data suggested success in atomically dispersing Pd on Cu2O (Supporting Information Table S1). The low-intensity oscillations following the near-edge region also indicated that the isolated Pd sites on Cu2O had a low coordination number.

The CO adsorption behavior on Pd/Cu2O (Supporting Information Figure S8a) was investigated to further confirm that Pd was atomically dispersed on Cu2O. There was one notable peak at 2090 cm−1, which can be attributed to CO adsorption on the positively charged Pd in a top configuration. No signals attributed to bridge and hollow site adsorption were observed, which was distinct from those on supported Pd NP catalysts (Supporting Information Figure S8b). Considering Cu2O was easily reduced or oxidized, we also used the X-ray adsorption spectra to evaluate the valence state of Cu. Both X-ray absorption near-edge structure (XANES) and EXAFS analyses at the Cu K-edge of Pd/Cu2O confirmed that the valence of Cu remained unchanged (Figure 1c; Supporting Information Figure S9). More experimental details are available in Supporting Information.

Results and Discussion

Pd-Cu catalysts have been well documented to be effective for the semihydrogenation of alkynes into alkenes. We thus first evaluated the catalytic
performance of Pd₁/Cu₂O in the selective hydrogenation of phenylacetylene (PA), a terminal alkyne. As shown in Figure 1d, Pd₁/Cu₂O exhibited excellent catalytic performance with a high selectivity of 96.5% toward styrene at 100% conversion within 60 min. It was particularly impressive that no deeper hydrogenation of styrene into ethylbenzene took place even with increased hydrogenation time. Moreover, the catalytic performance of Pd₁/Cu₂O was maintained after six cycles with the same catalyst (Supporting Information Figure S10), suggesting that the atomically dispersed structure of Pd₁/Cu₂O was quite stable under the hydrogenation conditions. Both EXAFS fitting and CO adsorption behavior (Supporting Information Figures S11–S13 and Table S2) confirmed that the Pd species on Pd₁/Cu₂O was still atomically dispersed on the Cu₂O support. In comparison, atomically dispersing Pd on other oxides (i.e., TiO₂, ZnO, and Al₂O₃) using the similar protocol showed negligible activity under the same catalytic conditions (Supporting Information Figures S14, S15, and Table S3).

The observed support-dependent phenomena provided motivation to probe the underlying mechanism. The valence states of catalytic metal centers often determine the electronic structures and thus the overall catalytic potential of a supported metal catalysts. We thus performed XANES studies over the Pd catalysts supported on the different metal oxides to evaluate the valence state of Pd. Compared with those on TiO₂, ZnO, and Al₂O₃, as illustrated in Figure 2a, the Pd K-edge white line of Pd₁/Cu₂O shows a small shift toward lower energy, located in-between Pd foil and PdO. These results suggested that the valence state of Pd on Pd₁/Cu₂O was between 0 and +2, more likely +1, whereas the valence state of Pd on other the oxide-supported Pd catalysts was close to +2. The +1 oxidation state and local coordination environment of Pd on Pd₁/Cu₂O suggests that H₂ should prefer a heterolytic activation pathway over the catalyst.³⁴,³⁵

It should be noted that the heterolytic activation of H₂ has also been frequently demonstrated on heterogeneous metal catalysts with enriched metal–metal oxide

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Figure 1 | Structural characterizations of Pd₁/Cu₂O and its catalytic performance. (a) High-resolution, high-angle annular dark-field scanning transmission electron microscopy image of Pd₁/Cu₂O along zone axis of Cu₂O[111]. (b) FT-EXAFS spectra of Pd₁/Cu, bulk palladium foil, and PdO at the Pd K-edge. (c) FT-EXAFS spectra of Pd₁/Cu₂O, Cu₂O, and CuO at the Cu K-edge. (d) Catalytic performance of semihydrogenation of PA on Pd₁/Cu₂O compared with other atomically disperse Pd catalysts.

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Density functional theory (DFT) calculations (Figure 2b; Supporting Information Figures S16 and S17) confirmed that the H₂ adsorbed on Pd was readily split in two, with one H atom moving to a nearby oxygen to yield O-H⁻ and the other remaining on Pd as H⁻. This activation step was calculated to be 0.79 eV exothermic with a barrier of 0.33 eV. Experimentally, a large kinetic isotope effect (KIE) of 5.7 was observed, also confirming the heterolytic activation pathway of H₂ and thus the involvement of proton transfer in the subsequent hydrogenation steps (Figure 2c). In situ Fourier transform infrared spectroscopy (FT-IR) was applied to detect the activated D₂ species on Pd₁/Cu₂O. As shown in Figure 2d and Supporting Information Figure S18a, after introducing D₂, strong absorption peaks appeared at 2472 and 2627 cm⁻¹, corresponding to –OD stretching. Increasing the time of D₂ treatment resulted in a much stronger –OD signal, indicating the production of more –OD species on Pd₁/Cu₂O. In sharp contrast, no signals of –OD were observed on Cu₂O and other oxide-supported catalysts after similar D₂ treatment (Figure 2d; Supporting Information Figures S18b,c and S19). These results clearly demonstrate that the surface Cu(I) sites were replaced by Pd(I) to form a unique Pd–(O-Cu)₂ structure, where H₂ could heterolytically dissociate into Pd-H⁻ and O-H⁺ species. In contrast, the +2 valence state and four-coordinated Pd species anchored on other oxides could not activate the H₂.

To gain insight into the hydrogenation process, DFT calculations were performed. As shown in Figure 3a and Supporting Information Figure S20, with the adsorption of PA on the H₂-dissociated Pd site (PA adsorption energy = 0.30 eV) as the initial state, the hydrogenation of C≡C to C=O involved two transition states (TSs), TS₁ (H transfer from Pd-H to β-C) and TS₂ (H transfer from O-H to α-C), and a semihydrogenation intermediate. The reaction barriers for the first and second H additions were calculated to 0.45 and 0.81 eV, respectively. This was in accordance with the KIE results. In comparison, the desorption energy of styrene on the
surface with heterolytically activated H atoms was only 0.26 eV, which was smaller than the barriers of the following H addition steps, 0.32 and 1.26 eV. The high energy barrier of the second H addition on styrene implies that the styrene was difficult to hydrogenate, a result that is consistent with the experimental observations that the hydrogenation of PA on Pd1/Cu2O would stop at styrene.

To confirm the mechanism suggested by DFT calculations, in situ FT-IR and nuclear magnetic resonance (NMR) with deuterium-labeled reagents were performed to monitor the catalytic hydrogenation process. As shown in the FT-IR analysis (Supporting Information Figure S21), the signal of –OD on Pd1/Cu2O appeared with the 60 min D2 treatment, but gradually disappeared after the introduction of PA gas, indicating that O–D+ was involved directly in the semihydrogenation of PA. In addition, we used CD3OD instead of CH3OH as the reaction solvent and analyzed the hydrogenation products by H-NMR (Figure 3b). No signals of D-substituted hydrogenation products were detected, indicating the solvent would not participate into the hydrogenation. According to the mechanism, no proton exchange between Cu–O–H+ and CH3OH took place. The hydrogenation product in CH3OH under a D2 atmosphere should have D atoms added to both α– and β-C atoms as well, which was indeed confirmed by the H-NMR data (Supporting Information Figure S22).

In order to better illustrate the high catalytic selectivity of Pd1/Cu2-O for the semihydrogenation of alkynes, two experiments using styrene and a 1:1 mixture of PA and styrene as substrates were carried out (Supporting Information Figure S23). When only styrene was used, negligible ethylbenzene was produced, suggesting that the hydrogenation of styrene into ethylbenzene did not occur over Pd1/Cu2-O, which correlated well with the high reaction barrier determined in the DFT calculations. Moreover, the result with the hydrogenation carried out with a 1:1 mixture of PA and styrene demonstrated that the presence of styrene did not influence the semihydrogenation of PA into styrene. Styrene is typically bonded to metal centers with π electrons. The Pd(I) centers...
should thus weaken the binding of styrene and internal alkyynes with Pd1/Cu2O. Indeed, as clearly demonstrated by FT-IR analyses (Supporting Information Figure S24), the headsorption of PA on Pd1/Cu2O gradually disappeared with the introduction of H2, and no adsorption of styrene on the catalyst was detected. It should be pointed out that, in the absence of H2, styrene did adsorb on Pd1/Cu2O, which was confirmed by FT-IR. However, the signal disappeared when H2 was introduced (Figure 3c). These findings support the conclusion that the high selectivity was the result of the weak adsorption of styrene and the high barrier for deeper hydrogenation of styrene.

An additional interesting finding was that Pd1/Cu2O only catalyzes the terminal alkyynes and has negligible activity on internal alkyynes. When 1-phenyl-1-propyne was chosen as the model substance, no hydrogenation took place even after the reaction was prolonged to 100 min (Supporting Information Figure S25). No apparent differences were observed in IR spectra of Pd1/Cu2O containing preadsorbed 1-phenyl-1-propyne before and after H2 treatment (Supporting Information Figure S26a). The IR spectrum of Cu2O containing preadsorbed 1-phenyl-1-propyne was the same as that of Pd1/Cu2O (Supporting Information Figure S26b). These results indicated that the internal alkyne, 1-phenyl-propyne, was not adsorbed on Pd1/Cu2O.

With a deep understanding of why Cu2O is an effective support for the fabrication of atomically dispersed Pd catalysts, we expected that commercial Cu2O (Supporting Information Figure S27a) should also work well for the reaction. Commercial Cu2O was treated with Pd(CH3CN)2Cl2 at 50 °C for 5 h to prepare the practical Pd1/Cu2O catalyst (Supporting Information Figure S27b, c). Both FT-IR and X-ray absorption spectroscopy (XAS) measurements confirmed that Pd was atomically dispersed on commercial Cu2O (Supporting Information Figures S28, S29, and Table S4). Indeed, the obtained catalyst also exhibited high activity and selectivity for the semihydrogenation of PA into styrene (Supporting Information Figure S30). More importantly, the catalyst also displayed excellent catalytic performance in the semihydrogenation of other alkyynes, such as 1-octyne, 2-methyl-3-butyne-2-ol, trimethylsilylacetylene, 4-ethyl-2-nitrobenzylacetone, 4-(tert-butyl)phenylacetylene, and 4-chlorophenylacetylene, with selectivities of 96.2%, 94.7%, 96.0%, 90.5%, 95.3%, and 96.1%, respectively (Table 1; Supporting Information Figure S31), further demonstrating the wide applicability of the as-prepared atomically dispersed Pd catalyst.

**Conclusions**

In summary, we demonstrate in this work that Cu2O serves as an excellent support for the fabrication of an atomically dispersed Pd catalyst for the semihydrogenation of terminal alkyynes to alkenes. The excellent performance was ascribed to the unique Pd-(O-Cu)2 interfacial structure and the +1 oxidation state of the Pd atoms on Pd1/Cu2O. H2 underwent a heterolytic activation over Pd1/Cu2O, giving rise to Pd-Hδ− and O-Hδ+ species and facilitating the hydrogenation of terminal alkyynes. In contrast, the further hydrogenation of alkenes to alkanes is dramatically suppressed in the presence of Pd-Hδ− and O-Hδ+. We expect an atomic-level understanding of the effect of supports in the development of atomically dispersed metal catalysts would inspire further research to unveil the critical roles these supports have in catalysis.

**Supporting Information**

Supporting information is available including more experimental and computational details, and additional data.

**Conflicts of Interest**

The authors declare that they have no conflict of interest.

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