

Communication

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Room-Temperature Chemoselective Reduction of 3-Nitrostyrene to 3-Vinylaniline by Ammonia Borane over Cu Nanoparticles

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ABSTRACT: We report a new strategy of controlling catalytic activity and selectivity of Cu nanoparticles (NPs) for ammonia borane-initiated hydrogenation reaction. Cu NPs are active and selective for chemoselective reduction of nitrostyrene to vinylaniline under ambient conditions. Their activity, selectivity, and more importantly, stability is greatly enhanced by their anchoring on WO_{2.72} nanorods, providing a room temperature full conversion of nitrostyrene selectively to vinylaniline (>99% yield). Compared with all other catalysts developed thus far, our new Cu/WO_{2.72} catalyst shows much-enhanced hydrogenation selectivity and stability without using the pressured hydrogen. The synthetic approach demonstrated here can be extended to prepare various M/WO_{2.72} catalysts (M = Fe, Co, Ni) with M being stabilized for many chemical reactions.

Selective reduction of functional aryl nitro (Ar-NO₂) to amine (Ar-NH₂) group is an important step towards preparation of a wide variety of organic compounds for pharmaceutical, polymer, herbicidal, and fine chemical applications.¹⁻³ Nanosized transition metals/metal oxides have shown great potential as heterogeneous catalysts for the -NO₂ reduction because of their high activity, ease of separation, and recyclability.⁴ However, what is difficult to achieve is selective reduction of Ar-NO2 without affecting other reducible groups under the catalytic condition. In particular, the selective reduction of Ar-NO2 over a vinyl group (Ar-C=C) in an aromatic compound remains to be challenging due to the uncontrolled hydrogenation of both Ar-NO2 and Ar-C=C.5-10 Since Corma and Serna first reported that Au-based catalysts can show good selectivity in the reduction of 3-nitrostyrene in 2006,⁵ much progress has been made in using Au,^{6, 11-12} Pt,¹³⁻¹⁶ Ag,¹⁷ Pd,⁹ and Ru¹⁰ catalysts for the selective reduction process. Recently, using non-noble metals to catalyze the same reaction also attracted much attention: Ni/TiO2 showed 90 % selectivity of 3-vinylaniline at 93 % conversion under 723 K and 15 bar of H₂;¹⁶ Fe₂O₃-based catalyst gave 93 % selectivity on 100 % conversion under 393 K and 50 bar of H₂ after 16 h;¹⁸ and Co₃O₄-based catalyst was even more efficient at 383 K, 50 bar H_2 , 6 h with 91 % selectivity and > 99 % conversion.¹⁹ Despite the progress made in non-noble metal catalysts for the selective hydrogenation process,²⁰⁻²¹ the catalytic reaction generally requires > 373 K temperature, high pressure of H₂ and hours of reaction time to complete.

Ammonia borane (AB) is regarded as a safe material for hydrogen storage (19.6 wt % hydrogen) and transport (solid at room temperature). In the presence of a transition metal catalyst, H₂ can be released from AB under ambient conditions,²²⁻²³ and AB has been used widely for hydrogenation reaction in milder reaction conditions to reduce nitrobenzenes to their amine derivatives.²⁴⁻²⁷ However, this hydrogenation process can become complicated when there exists a second reducible functional group in the aromatic structure as the competition between two reduction reactions often causes poor selectivity. Herein, we report copper (Cu) nanoparticles (NPs) as a new nonnoble catalyst to catalyze AB for selective reduction of 3nitrostyrene to 3-vinylaniline in ethanol at room temperature under atmospheric pressure. When Cu NPs are coupled to $WO_{2.72}$ nanorods (NRs), they show much improved activity and stability for both AB ethanolysis and nitrostyrene hydrogenation to vinylaniline with > 99 % chemoselectivity from 100 % conversion within 1.5 h at 298 K. Alloying Cu with Ni or Pd increased its catalytic power, but lost its selectivity as 3-nitrostyrene was fully converted to 3-ethylaniline.

Cu NPs were synthesized by reductive decomposition of copper (I) acetate (CuOAc).²⁸⁻³⁰ Figure 1A is the transmission electron microscopy (TEM) image of Cu NPs with an average size of $7.0\pm$ 0.4 nm. They are uniform in size and shape, and tend to selfassemble into a 2D superlattice array (Figures 1A & S1). The highresolution TEM (HRTEM) image (inset of Figure 1A) shows clear lattice fringes of Cu NPs with a spacing distance of 0.21 nm, which corresponds to the interplanar spacing of (111) planes of facecentered cubic (fcc) Cu. The Cu NPs were deposited on the carbon or silica support to give Cu/C or Cu/SiO₂ catalysts (Figure S2). The WO_{2 72} NRs with an average length of 80 nm and width of 6 nm (Figure 1B) were prepared by reacting WCl₄ with oleic acid (OAc) and oleylamine (OAm) in 1-octadecene (ODE) at 553 K for 10 h.31 The average inter-fringe spacing of WO_{2.72} NRs is 0.38 nm (Inset of Figure 1B), matching the 0.378 nm of (010) interplanar distance of monoclinic WO_{2.72}. To deposit Cu NPs on WO_{2.72} NRs, we mixed Cu NPs and WO_{2.72} NRs in OAm and OAc under an Ar atmosphere and heated the mixture solution at 553 K for 0.5 h to give Cu/WO_{2 72}, as shown in the representative TEM image (Figures 1C & S3). After coupling Cu NPs with WO_{2.72} NRs, the inter-fringe distance of Cu NPs slightly expands from initial 0.21 nm to 0.23 nm (inset of Figure 1C). The X-ray diffraction (XRD) patterns of both Cu NPs and Cu/WO₂₇₂ NRs (Figures 1D & S4) show (111) diffraction peaks of Cu, as well as Cu₂O due to the surface oxidation of Cu NPs. The (111) peak in Cu/WO_{2.72} slightly shifts to the low diffraction angle. Both TEM and XRD show that Cu NPs "swell" a little once coupled to WO_{2.72}, indicating that there exists a strong coupling between Cu NPs and WO_{2 72} NRs in the Cu/WO_{2.72} structure.



Figure 1. TEM (inset HRTEM) images of (A) Cu NPs; (B) WO_{2.72} NRs; (C) Cu/WO_{2.72} composites, and (D) XRD patterns of Cu NPs, WO_{2.72} NRs and Cu/WO_{2.72} composites.

The electronic structure of Cu NPs and Cu/WO2.72 was characterized by X-ray photoelectron spectroscopy (XPS). Once Cu NPs are coupled with WO2.72 NRs, the binding energy of Cu⁺/Cu⁰ (2p_{3/2} and 2p_{1/2}) becomes slightly larger and new peaks corresponding to Cu²⁺ species show up (2p_{3/2}: 932.14 eV for Cu, 932.26 eV for Cu/WO_{2.72}; 2p_{1/2}: 952.05 eV for Cu, 952.48 eV for $Cu/WO_{2,72}$), indicating the decrease of surface electron density on Cu NPs (Figure 2A). The change is similar to what was reported.³² Correspondingly, the binding energies of W4f in Cu/WO_{2.72} show negative shifts compared with free WO_{2.72} NRs, suggesting the possible negative charge transfer from Cu NPs to WO_{2.72} NRs. We further studied the surface electrochemistry of Cu/WO₂₇₂ in CH₂Cl₂ by cyclic voltammograms (Figures S5). Compared to those in the Cu/C, Cu NPs in the Cu/WO_{2.72} structure are more difficult to be oxidized while the oxidized Cu NPs are also more difficult to be reduced due to the electron polarization from Cu to WO_{272} , which is consistent with what is concluded in the XPS data analysis. The XPS spectra of Cu/SiO2 or Cu/C are identical with that of free Cu NPs, indicating that there is no charge transfer between Cu NPs and SiO₂ or C support.



Figure 2. XPS spectra of (A) Cu 2p of Cu NPs and Cu/WO_{2.72} and (B) W 4f of WO_{2.72} NRs and Cu/WO_{2.72}.

We first tested the AB hydrogen evolution reaction in ethanol solution catalyzed by Cu NPs deposited on different supports at 298 K (Figure S6). The Cu/WO_{2.72} is much more active than Cu/SiO₂ and Cu/C due likely to the increased affinity of Cu^{δ+} to AB, and WO_{2.72} to "H" in the Cu/WO_{2.72} structure.^{31, 33} Moreover, Cu/WO_{2.72} demonstrates a superb stability for AB ethanolysis

(Figure S7), which is supported by the previous report that $WO_{2.72}$ NRs can stabilize Cu component in the CuPd alloy structure after its strong coupling to $WO_{2.72}$.³² SiO₂ support can also improve the activity of Cu NPs to a certain degree as compared with the carbon support due to the stronger AB adsorption power of the hydrophilic SiO₂ surface.³⁴

Next, we investigated the Cu NP catalysis for chemoselective hydrogenation of Ar-NO₂ into Ar-NH₂ in the presence of Ar-C=C, which is one of the most competitive and demanding selective reduction reactions leading to the formation of functional amines. We tested Cu/C, Cu/SiO₂, or Cu/WO_{2.72} for AB-initiated hydrogenation of a mixture of nitrobenzene and styrene at 298 K (Table S1). They are all active and selective to the reduction of - NO_2 while -C=C in the styrene structure is intact, inferring that the Cu NPs activate only Ar-NO₂, not Ar-C=C. Cu/WO_{2.72} shows the best hydrogenation activity among the three Cu NP catalysts studied due to its more evident synergistic effect between Cu and WO_{2.72}. Then, we chose 3-nitrostyrene as a model molecule to further study the chemoselectivity of Cu NPs. From our tests (Table 1), we can see that the Cu NPs show high selectivity to the reduction of -NO2 to -NH2 in AB-initiated hydrogenation of 3nitrostyrene. Particularly, Cu/WO2.72 demonstrates an outstanding chemoselectivity (> 99 %) to 3-vinylaniline at full conversion of 3nitrostyrene within 1.5 h at 298 K. No other byproducts were detected. SiO₂- and C-supported Cu NPs exhibit excellent selectivity as well (98 % for SiO₂-Cu, 95 % for C-Cu) after longer time of reaction. Our Cu NPs are much superior to other non-noble metal catalysts reported previously (Table S2). We tested the Cu/WO_{2 72} catalyst for its hydrogenation of other nitroarenes that contain vinyl or other reducible groups (Table S3). All these nitroarenes are selectively hydrogenated. We further compared Cu NP catalysis with CuNi²⁶ and CuPd³⁵ alloy NPs (Figure S8) that are more active for AB hydrogen evolution than pure Cu NPs to evaluate the hydrogenation of 3-nitrostyrene under the same condition (Table 1). Both CuNi and CuPd NPs show poor selectivity, catalyzing the hydrogenation of 3-nitrostyrene directly to 3-ethylaniline (> 99 % yield within 1.5 h) (Table 1, Entries 4 & 5). However, when Ar-C=O co-exists with Ar-NO₂, our Cu/WO₂₇₂ catalyst did not show the desired chemoselective reduction of Ar- NO_2 due most likely to the high reducing power AB to Ar-C=O.³⁶

 Table 1. Hydrogenation of 3-nitrostyrene with different Cu-based catalysts.

NO ₂	AB, Ethanol Cat.	A H	H B	+	C
Entry	Cat.	Yield / %			Time /
		Α	В	С	- h
1	Cu/WO _{2.72}	>99	0	0	1.5
2	Cu/SiO ₂	98	0	2	2.5
3	Cu/C	95	5	0	3
4	CuNi/SiO2	0	0	>99	1.5
5	$CuPd/SiO_2$	0	0	>99	1.5
6	None	1	15	3	1.5

Reaction conditions: 3-nitrostyrene (1 mmol), Cu-based catalysts (6 mole % Cu), ethanol (10 ml), AB (3 mmol), 298 K. Complete conversion was observed in the cases of 1-5. Conversion and yields were determined by GC-MS using dodecane as an internal standard.

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Finally, we conducted stability tests of Cu NPs catalysts in the reaction solution leading to chemoselective hydrogenation of 3nitrostyrene. The catalysts were recovered by simple centrifugation followed by washing with water/ethanol. The Cu/C suffers a huge loss in both activity and selectivity during the cycles (Figure S9). The Cu NPs on carbon support were seen heavily aggregated on the C surface after the fourth catalytic reaction (Figure S10), similar to what have been observed.³⁷⁻³⁸ The Cu/SiO₂ shows an improved stability due to the stronger binding between Cu NPs and SiO₂, similar to the case of Ni/SiO₂ for AB hydrolysis,³⁴ but is still not as robust as the Cu/WO₂₇₂, which is the most stable catalyst, maintaining its initial activity and selectivity after six catalytic cycles (Figure 3) without showing any noticeable morphology change (Figure S11). This stability test further confirms that strong interfacial interaction between Cu NPs and WO_{2.72} is essential to activate and stabilize Cu NPs for their active and selective hydrogenation of nitrostyrene to vinylamine.



Figure 3. Recycling test of hydrogenation of 3-nitrostyrene to 3-vinylamine by Cu/WO_{2.72} catalyst.

In summary, we have reported Cu NPs as a new catalyst for active and selective hydrogenation of nitrostyrene to vinylaniline in the presence of AB under ambient conditions. Among three different Cu NP catalysts Cu/C, Cu/SiO2 and Cu/WO2.72 studied in this paper, Cu/WO_{2 72} is the most efficient catalyst, achieving >99% selectivity for the formation of vinylaniline at 100% conversion of 3-nitrostyrene within 1.5 h of reaction time at room temperature. The high efficiency of the $Cu/WO_{2.72}$ is attributed to the strong interfacial Cu-WO_{2.72} interactions, rendering Cu NPs electron deficient. This, coupled with the "H"-affinity of WO₂₇₂, provides the desired synergistic effect on hydrogen release from AB and preferred hydrogenation of Ar-NO2 over Ar-C=C at room temperature and at atmospheric pressure. As a comparison, catalytically more active CuNi and CuPd NPs hydrogenate nitrostyrene to ethylaniline. The reported synthetic approach to Cu/WO_{2 72} is not limited to Cu and its alloys, but can be extended to other transition metals, such as, Fe, Co, Ni, and their alloys, providing a general method to stabilize and activate transition metal NP catalysts for chemical reactions with desired selectivity and activity.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Materials and experimental methods, Figures S1–S11, and Tables S1–S3.

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Author Contributions

M.S and H.L contributed equally to this study.

Notes

The authors declare no competing financial interests.

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