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General and Chemoselective Copper Oxide Catalysts for Hydrogenation Reactions

*Wu Li, Xinjiang Cui, Kathrin Junge, Annette-Enrica Surkus, Carsten Kreyenschulte, Stephan Bartling, and Matthias Beller**

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ABSTRACT. Copper oxide catalysts have been prepared by pyrolysis of copper acetate on aluminum oxide. The material resulting from pyrolysis at 800 °C allows for catalytic hydrogenations at low temperature of a variety of unsaturated compounds such as quinolines, alkynes, ketones, imines, polycyclic aromatic hydrocarbons, as well as nitroarenes with good to good activity and selectivity.

KEYWORDS. Copper, heterogeneous catalysis, Hydrogenation, Semihydrogenation, Aluminum oxide.

Introduction

Catalytic hydrogenations are arguably the most useful and widely applicable methodologies for the reduction of chemical substances, and have found numerous applications both in academic laboratories and industrial processes.[1] Today, most of the large scale hydrogenations make use of heterogeneous catalysts containing different metals. In general, materials based on precious metals such as platinum, palladium, rhodium, and ruthenium show good to excellent activities, selectivities, and even broad substrate scope.[2] However, for a number of applications, these metals are too expensive. Obviously, non-precious metal catalysts have substantial cost advantages, but they are often less active than their noble metal counter parts. A frequently used example includes Raney nickel and derivatives, which have been developed as economical alternatives.[3] Notably, with respect to toxicity, precious metals as well as nickel are known or suspected human carcinogens or show other poisonousness effects.[4] For example, their use in food, agrochemical, pharmaceutical as well as cosmetic applications is strictly regulated and those metals must be removed completely from the final products, resulting in additional expenses.[5] Therefore, using abundant metals with low or minimal safety concern, especially iron, zinc or copper for hydrogenation reactions is most desirable.[6] In this respect, in recent years significant attention focused on the development of iron-based hydrogenation catalysts and important progress has been achieved.[7] Somewhat surprisingly, copper-based catalysts were much less considered, although they are well-established in industry and the most prominent example is the ternary system Cu-ZnO-Al_2O_3 used in methanol synthesis from gas mixtures (H_2/CO_2/CO).[8] This process has been extensively studied due to its high industrial relevance since its first use in 1966. Furthermore, modified copper catalysts have been used for the hydrogenation of C=O bonds,[9] the hydrogenation/dehydroxylation of biomass (e.g. fructose, sorbitol, glycerol or furfural) to valuable diols,[10] photocatalytic H_2 production,[11] and methanol steam reforming.[12] However, supported copper catalysts for hydrogenation of other unsaturated functional groups are much less explored.[13] Notably, most copper-catalyzed hydrogenations are performed under relatively drastic conditions (temperatures >200 °C), which obviously limits their applications. To conclude a general Cu catalyst which works for several classes of substrates under milder conditions is basically unknown and would be desirable.

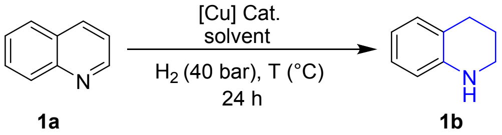
To date, the synthesis of supported metal nanoparticles (NPs) has become a useful tool for the development of new catalysts for advanced organic synthesis.[14] In the last decade, apart from precious metals, a large focus was given to more earth-abundant metals, specifically cobalt, nickel and iron, which were successfully employed in several redox reactions.[7, 15] In this respect, we became interested in the synthesis of copper-based materials for broad-scope catalytic hydrogenation reactions.

Results and Discussion

Following our previous work,[7, 16] $Cu(OAc)_2$ with or without additional ligands was immobilized on different supports and pyrolyzed at 600-1000 °C. All the resulting materials were tested in the hydrogenation of quinoline, which is of considerable interest in the fields of petrochemicals, specialty chemicals, and bio-active compounds, under comparably mild conditions (80 °C, 40 bar hydrogen, 2 mL toluene, 24 h).[17]

As shown in Table 1, using a copper catalyst prepared in the presence of 1,10- phenanthroline as ligand and carbon (Vulcan XC 72r), unfortunately no conversion to the desired product 1,2,3,4-tetrahydroquinoline (**1b**) was observed (Table 1, entry 1). Surprisingly, without any ligand the carbon-supported catalyst gave **1b** in 15% (Table 1, entry 2). Next, different supports such as γ-Al_2O_3, α-Al_2O_3, MgO, CeO_2 and Al_2O_3 (activated, neutral, Brockmann Activity I) were used for the preparation of the catalysts. While most of the supports did not create active catalysts, the Al_2O_3–based catalysts gave **1b** in 8-33% yield (Table 1, entries 3-7). Testing the best catalyst system in the presence of different solvents (1,4-dioxane, isopropanol, cyclohexane, and 2-methyltetrahydrofuran) unfortunately gave no improvement (Table 1, entries 8-11). Similarly, materials pyrolyzed at 500, 600, 900, and 1000 °C provided lower yields or did not exhibit any catalytic activity for quinoline hydrogenation (Table 1, entries 12−15). However, modifying the temperature ramp of the pyrolysis procedure from 25 °C/min to 10 °C/min led to significantly improved yield (94%) of **1b** (Table 1, entry 16). Finally, slowing down the pyrolysis procedure to 5 °C/min gave a quantitative yield of the desired product (Table 1, entry 17). Interestingly, the system is also active at 60 °C (Table 1, entry 18). Comparing the activity of our catalytic system with Cu/ZnO, a benchmark copper based methanol synthesis catalyst and with Raney nickel, the new material outperforms these commercially available catalysts (Table 1, entries 17 versus 19 and 20).

Table 1. Model reaction: Hydrogenation of quinoline.[a]



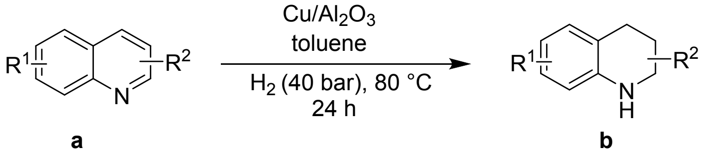
Entry	Catalyst	Pyrolyzed T (°C)	Solvent	T (°C)	Yield (%)[a]
1	Cu-Phen/Carbon	800	toluene	80	0
2	Cu/Carbon	800	toluene	80	15
3	Cu/γ-Al_2O_3	800	toluene	80	30
4	Cu/α-Al_2O_3	800	toluene	80	8
5	Cu/MgO	800	toluene	80	trace
6	Cu/CeO_2	800	toluene	80	0
7	Cu/Al_2O_3	800	toluene	80	33
8	Cu/Al_2O_3	800	1,4-dioxane	80	0
9	Cu/Al_2O_3	800	isopropanol	80	8
10	Cu/Al_2O_3	800	cyclohexane	80	12
11	Cu/Al_2O_3	800	2-MeTHF	80	10
12	Cu/Al_2O_3	1000	toluene	80	0
13	Cu/Al_2O_3	900	toluene	80	trace
14	Cu/Al_2O_3	600	toluene	80	31
15	Cu/Al_2O_3	500	toluene	80	27

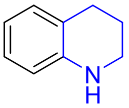
16	Cu/Al_2O_3	800[b]	toluene	80	94
17	**Cu/Al_2O_3**	**800[c]**	**toluene**	**80**	**>99**
18	Cu/Al_2O_3	800[c]	toluene	60	57
19	CuO/ZnO[d]		toluene	80	0
20	Raney nickel[e]		toluene	80	27

[a] Reaction conditions: 0.5 mmol quinoline, 40 mg catalyst (2.5 mol% Cu), *p* bar H_2, 2 mL solvent, T °C, 24 h. GC yield using *n*-dodecan as internal standard. [b] The furnace was heated to 800 °C at a rate of 10 °C per minute. [c] The furnace was heated to 800 °C at a rate of 5 °C per minute. [d] Copper based methanol synthesis catalyst (1.6 mg, 2.5 mol%). [e] 0.74 mg (2.5 mol%).

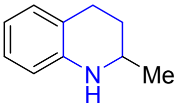
Based on the catalyst optimization, different substituted quinolines were tested under the standard conditions (2.5 mol% Cu/Al_2O_3, 2.0 mL toluene, 40 bar H_2, 24 h). As shown in

Table 2. Hydrogenation of various quinolines and isoquinoline.[a]

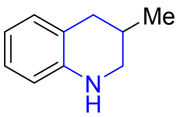




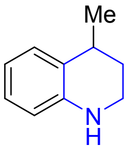
1b 92%



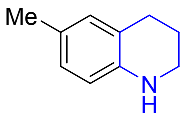
2b 96%



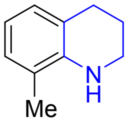
3b 92%



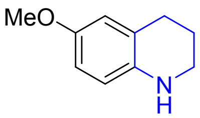
4b 92%



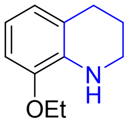
5b 98%[b]



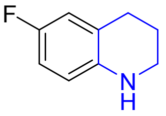
6b >99%



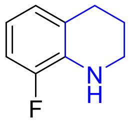
7b 98%[b]



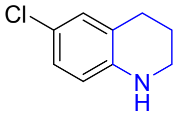
8b 98%[b]



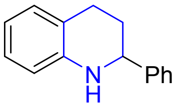
9b >99%[b]



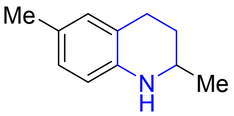
10b 93%[b]



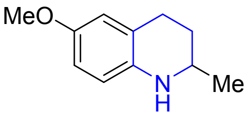
11b 98%[c]



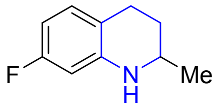
12b 90%



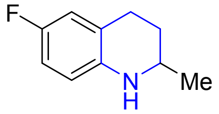
13b 98%



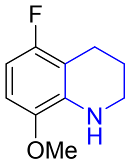
14b 99%



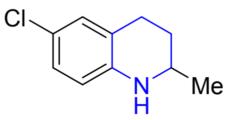
15b 90%



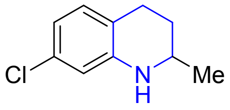
16b 94%



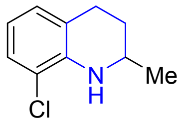
17b >99%[b]



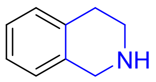
18b >99%



19b >99%[b]



20b >99%[b]



21b 92%[c]

[a] Reaction conditions: 0.5 mmol substrates, 40 mg catalyst (2.5 mol% Cu), 40 bar H_2, 2 mL toluene, 80 °C, 24 h. [b] 100 °C, 50 bar H_2. [c] 140 °C, 50 bar H_2. Isolated yields.

Table 2, quinolines containing electron-donating as well as electron-withdrawing groups are compatible with the catalytic system and the hydrogenated products (**2b-20b**) were isolated in excellent yields. Notably, groups substituted at the different positions on the aromatic ring had no significant influence on the product yields. For example, the methyl group in **2b**, **3b**, **4b, 5b, 6b**, **13b** and methoxy, ethoxy, and phenyl substituents in **7b**, **8b** and **12b** as well as halogens in **9b**, **10b**, and **11b** gave over 90% of the corresponding product. Di-substituted quinolines were also converted to 1,2,3,4-tetrahydroquinolines (**13b-20b**) in 90->99% yields. In addition, isoquinoline (**21a**) was hydrogenated selectively, albeit at higher temperature and hydrogen pressure.

Obviously, stability and recyclability are important parameters for the application of any heterogeneous catalyst, which are crucial performance metrics for efficient and cost-effective processes. Hence, the heterogenized Cu/Al_2O_3 catalyst was recycled up to seven times. As depicted in Figure 1, no significant loss of activity was observed and 89% of **1b** was still achieved after the seventh run. ICP measurements proved small amounts of copper leaching after first run (1.08 ppm) and second to sixth run (2.00 ppm) (Table S1, see Supporting Information).

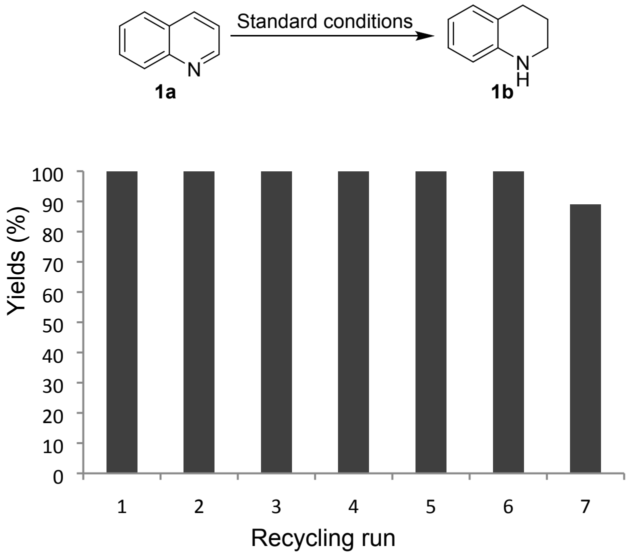
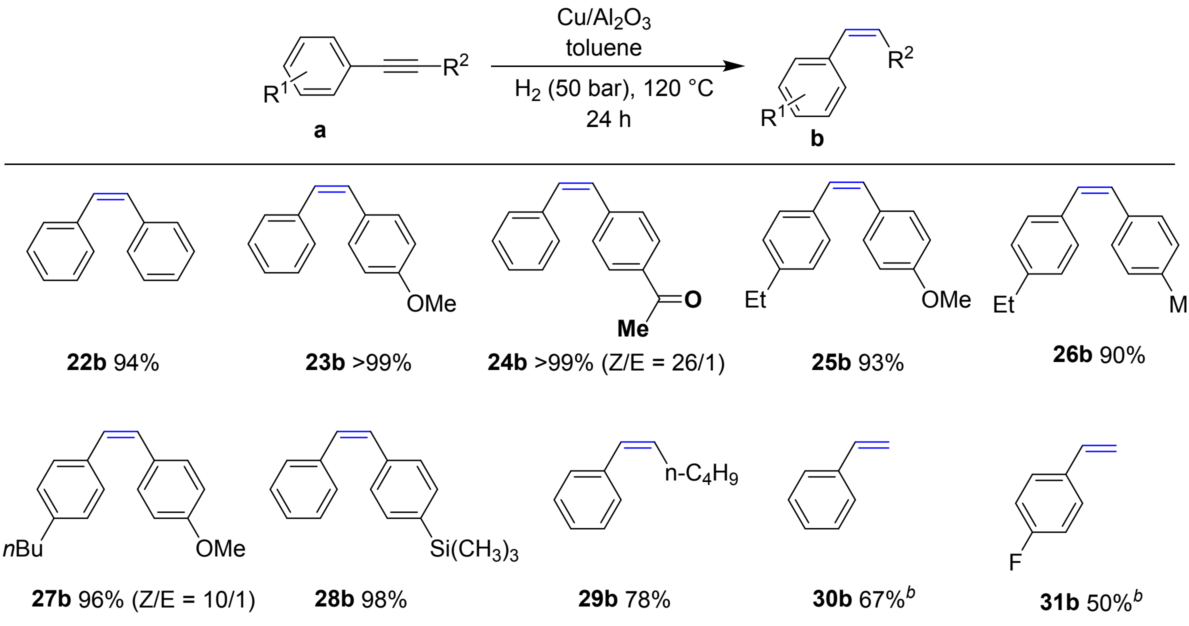


Figure 1. Recycling experiments using Cu/Al_2O_3 catalyst. Yields were determined by GC using *n*-dodecan as internal standard.

To demonstrate the general reactivity of this copper catalyst, several hydrogenations of other functional groups including alkynes, olefins, ketones, imines, nitriles, polycyclic aromatic hydrocarbons, as well as nitroarenes were investigated. For this purpose, we explored the semihydrogenation of several internal aryl alkynes using the Cu/Al_2O_3 catalyst under similar conditions at 120 °C (Table 3). Notably, the resulting *Z*-alkene scaffold is widely found in food, medical as well as cosmetic applications.[18] Until to date, Lindlar's catalyst is the most prominent material for industrial semihydrogenation of alkynes to generate *Z*-alkenes.[19] In general, good selectivity and excellent yields for the *Z*-isomer formation was achieved for diarylalkynes (**22b**, **23b**, **25b**, **26b**, **28b** and **29b**). Interestingly, substrate **24a** bearing a

Table 3. Copper-catalyzed semihydrogenation of various internal alkynes.[a]



22b 94% **23b** >99% **24b** >99% (Z/E = 26/1) **25b** 93% **26b** 90%

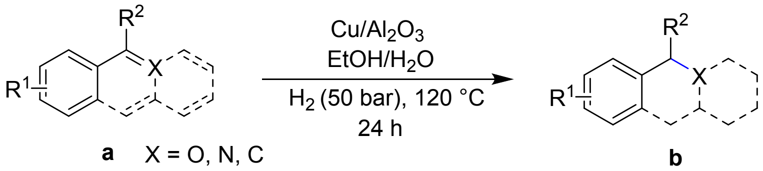
27b 96% (Z/E = 10/1) **28b** 98% **29b** 78% **30b** 67%[b] **31b** 50%[b]

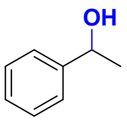
[a]Reaction conditions: 0.5 mmol substrates, 40 mg catalyst (2.5 mol% Cu), 50 bar H_2, 2 mL toluene, 120 °C, 24 h. Isolated yields. [b]Yield determined by GC using *n*-dodecan as the standard.

reducible carbonyl group is also compatible with these conditions. In addition to internal alkynes, terminal alkynes such as ethynylbenzene (**30a**) and 1-ethynyl-4-fluorobenzene (**31a**) gave the corresponding olefins with full conversion under standard conditions. Since no ethylbenzenes were detected, we propose poly- and/or oligomerization of the substrates as side reactions. However, using water as solvent instead of toluene, styrene was reduced to ethylbenzene quantitatively, demonstrating the possibility for olefin hydrogenation at different conditions.

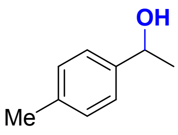
Hence, we performed the hydrogenation of C=O, C=N, and other C=C double bonds by using EtOH and H_2O as the solvents to explore the general applicability of the catalytic system further on (Table 4). Gratifyingly, all substrates were converted into the desired products with ≥90% yields. For example, the polycyclic aromatic hydrocarbon anthracene was easily hydrogenated in 98% yield to give **37b**. In addition, aromatic ketones were hydrogenated to benzyl alcohols (**32b-35b**) in high yields. In the case of *N*-benzylideneaniline, hydrogenation reaction also proceeded smoothly to **36b**. When using benzonitrile as substrate in water (50 bar H_2, 120 °C, 24), even nitrile reduction to the corresponding dibenzylamine took place with full conversion.

Table 4. Copper-catalyzed hydrogenation of ketones, imine and anthracene.*[a]*

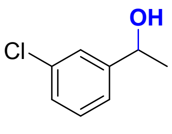




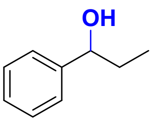
32b 96%



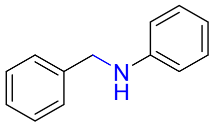
33b 90%



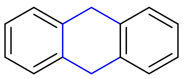
34b 94%



35b 94%



36b 96%*[b]*

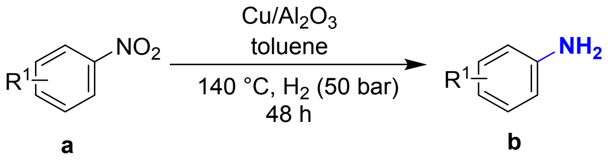


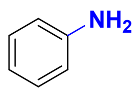
37b 98%

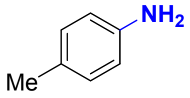
*[a]*Reaction conditions: 0.5 mmol substrates, 40 mg catalyst (2.5 mol% Cu), 50 bar H_2, EtOH/H_2O (1.5 mL/0.5 mL), 120 °C, 48 h. Isolated yields. *[b]*83 mg catalyst (5.0 mol%), toluene (2.0 mL), 140 °C, 48 h.

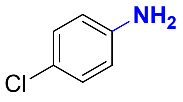
To finish the substrate scope, we investigated the hydrogenation of nitroarenes, a reaction frequently used in the industrial production of dyes, pigments, pharmaceuticals, agrochemicals and monomers for polyurethanes. As demonstrated in Table 5, the Cu/Al_2O_3 can be used for the reduction of a wide range of substrates containing diverse substituents. Using toluene as solvent, no dehalogenation was detected for chloro-substituted substrates (**40b** and **47b**). Interestingly, under these conditions the catalyst is also able to reduce the nitro group in the presence of reducible groups such as cyano and ketone, which showed reactivity in a different solvent system vide supra. Gratifyingly, full conversion was obtained without any detectable reduction of the unsaturated units (**41b**, **42b** and **44b**).

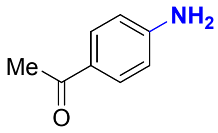
Table 5. Hydrogenation of various aromatic nitro compounds.*[a]*

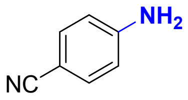



38b 92%[b]


39b 79%


40b 76%


41b 72%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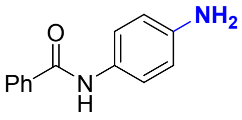
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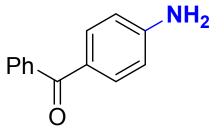
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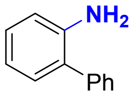
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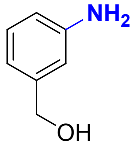
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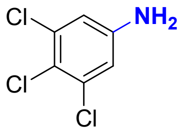
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[a] Reaction conditions: 0.5 mmol substrates, 40 mg catalyst (2.5 mol% Cu), 50 bar H_2, toluene 2.0 mL, 140 °C, 48 h.
[b] GC yield sing *n*-dodecan as internal standard.

Catalyst characterization

The presented optimal catalyst was prepared using $Cu(OAc)_2$ as the precursor and Al_2O_3 as the support (see Supporting Information). The Cu composition of the most active system (Cu/Al_2O_3) is 2.0 wt%, which is determined by elemental analysis. To elucidate the structure and morphology of the material and to get more insight into its chemical composition, scanning transmission electron microscopy (STEM) measurements have been performed. As can be seen from Figures 2a-b, the fresh catalyst contains mainly rather large particles of polycrystalline Cu containing particles. In agreement with this observation, STEM-HAADF image and the corresponding EDX spectra (Figure S1a) confirm that particles of similar morphology albeit different sizes contain Cu as indicated by the Cu signal. General morphology of these particles suggests the particles to be of Cu oxide, which could be confirmed by EDX analysis of a free hanging Cu containing particle (Figure S1b).

To obtain further information about the valence states of this copper catalyst, X-ray photoelectron spectroscopy (XPS) measurements were performed. The Cu2p region (Figure S4) contains two main peaks ($2p_{3/2}$ and $2p_{1/2}$) and a satellite featured around 944 eV characteristic for Cu^{2+}. The main peaks can be fitted with two components suggesting the presence of Cu^{1+} and Cu^{2+} according to their binding energies at 932.4 ± 0.3 eV and 934.3 ± 0.3 eV respectively, after pyrolysis at 800 °C (Figure S4a). To distinguish between Cu^{1+} and metallic Cu the Cu LMM region is shown in Figure S5a, revealing a broad peak at a binding energy of 570 eV characteristic for Cu^{1+}. No indications for metallic Cu at 568 eV are visible,[40] thus supporting the peak assignment in the Cu2p spectra. In the recycling experiments after one catalytic run the double peak structure of the Cu2p region was still visible while all peaks are shifted by about 2.5 eV to higher binding energies (Figure S4b). This shift correlates well

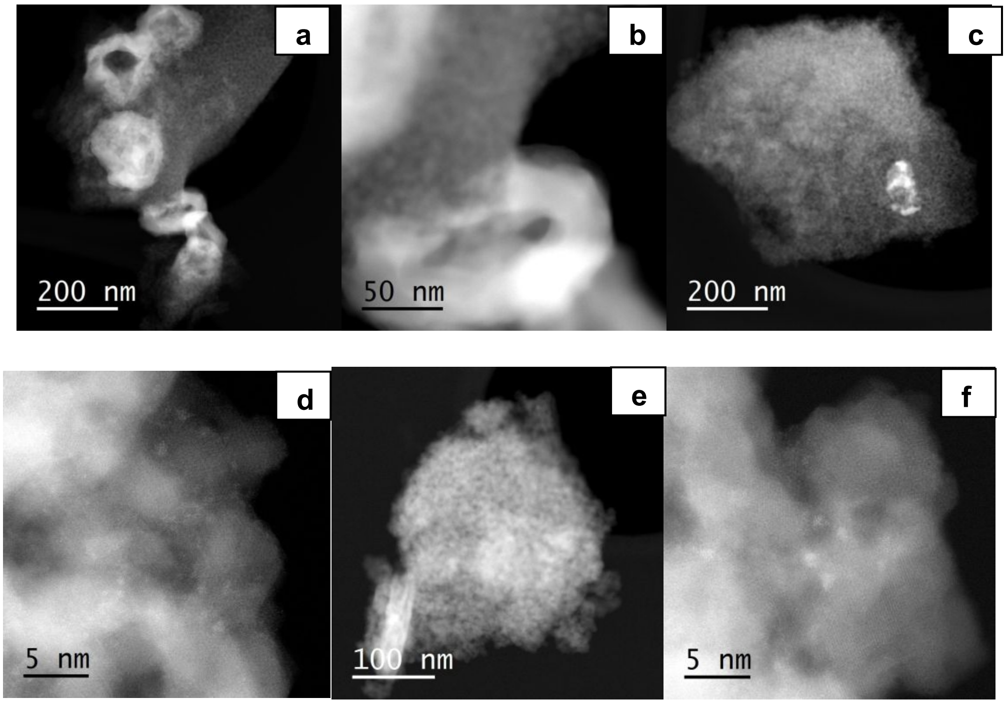

Figure 2. HAADF-STEM images of fresh Cu/Al_2O_3, (a) showing an overview and (b) giving a more detailed part of the Cu oxide on the Al_2O_3 (a, b). HAADF-STEM image of Cu/Al_2O_3 catalyst after 1 run (c, d) and after 7 runs (e, f) of the model reaction.

with the observed morphological changes to smaller Cu particles in STEM measurements and is known for Copper nanostructures.[20] The peak deconvolution reveals a dominating Cu^{1+} state which is also supported by the even smaller satellite peak of Cu^{2+} and the changes observable in the Cu LMM region (Figure S5).[21]

The STEM images of the copper catalyst after the first run and the seventh run are shown in Figure 2c-f. Interestingly, most of the original large copper oxide particles are gone after the first run. This reformation process seems to happen during the first run resulting in highly distributed copper atoms, clusters and small particles (Figure 2c-d). STEM-HAADF image and the corresponding EDX spectra of the once used Cu/Al_2O_3 catalyst shows the remnants of a larger Cu containing particle (Figure S2) indicated by the strong Cu signal, while the spectrum of a different area shows a much lower Cu signal, which can be attributed to a highly dispersed copper phase (Figure S2). The size and distribution of the copper phase is very different compared to the fresh one, although some of the large Cu oxide particles still exist. After the seventh run, a finely distributed Cu phase down to small clusters, even single atoms and particles showing crystal structures with sizes up to about 10 nm are observed (Figure 2e-f). STEM-HAADF image and the corresponding EDX spectra of the marked regions (Figure S3) of the seven times used Cu/Al_2O_3 catalyst show only a small Cu signal besides the Al_2O_3 signal indicating the highly distributed phase.

Conclusion

This work demonstrates for the first time that several classes of unsaturated compounds can be hydrogenated with one specific copper catalyst at comparably low temperature. For example, quinolines, alkynes, aromatic ketones, imines, a polycyclic aromatic hydrocarbon, as well as nitroarenes are reduced with high chemoselectivity (under different conditions) using the same catalyst. In case of diarylalkynes excellent selectivity for the *Z*-isomer formation was achieved. Upscaling and further applications using this heterogeneous copper catalyst are currently under way in our laboratory.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website at http://pubs.acs.org Experimental details, catalyst and recycled catalyst as well as organic compounds characterization, and NMR spectra (PDF) are provided in the Supporting Information.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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