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An efficient noble-metal-free supported copper catalyst for selective nitrocyclohexane hydrogenation to cyclohexanone oxime†

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It was shown for the first time that cyclohexanone oxime (CHO) can be selectively produced by heterogeneous copper-catalyzed hydrogenative transformation of nitrocyclohexane (NC). The combination of Cu⁰ and Cu⁺ and their cooperative interaction with weakly acidic SiO₂ supports elicited a significantly unique and selective catalysis in the hydrogenation of NC to CHO.

The development of an innovative methodology for the production of bulk and commodity chemicals, in particular one that takes account of resource utilization and waste minimization, becomes more and more important in industrial chemistry worldwide. Cyclohexanone oxime (CHO) is a privileged raw material for the production of nylon 6 fibers, which are widely used in synthesis of polymers for advanced technologies.[1,2] Currently, CHO is mainly synthesized through the catalytic oxidation of cyclohexane to cyclohexanone (CHone) followed by reaction with hydroxylamine sulfate,[3,4] the limitation of traditional CHO synthetic methodologies such as production of ammonium sulfate and the use of hazardous chemicals[5–8] has stimulated considerable interest in developing new, efficient, catalytic methods for the synthesis of CHO. In this context, the direct hydrogenation of nitrocyclohexane (DHNC) to give CHO is particularly attractive because NC can now be readily prepared from the corresponding cyclohexane.[9,10] Converting NC into CHO, however, can be challenging because DHNC can undergo several reduction pathways, which compete with each other (Scheme 1), and the chemo-selectivity of these reactions must therefore be strictly controlled to avoid the formation of undesirable byproducts.

Over the last decade, a number of supported noble metals, notably palladium, have been shown to facilitate NC to CHO transformation, with a maximum yield of *ca.* 90%.[6,11–14] From
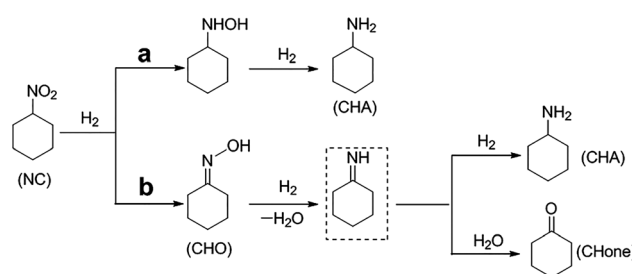
Scheme 1 The proposed reaction mechanism for the hydrogenation of nitrocyclohexane.

an economical and practical point of view, the development of a reusable and less expensive base-metal catalyst is highly desirable. In our pursuit of new cost-effective catalysts that can offer efficient alternatives to traditional noble metals, we found that a simple non-noble-metal-based catalyst system comprising copper dispersed in a SiO₂ matrix can efficiently catalyze the controlled and selective hydrogenation of NC. Copper-containing catalysts have been extensively employed in the past few decades for the selective elimination of NO$_x$,[15] water-gas shift reactions,[16] and synthesis and steam reforming of methanol.[17,18] Moreover, it is also established that copper catalysts are very selective for the hydrogenation of dimethyl oxalate[19] and diethyl oxalate[20] due to their favorableness as related to the capacity for hydrogenation in a controlled manner. Herein, we reveal that Cu⁰ nanoparticles (NPs) with partially reduced Cu⁺ entrapped in a SiO₂ matrix can efficiently catalyze the controlled and highly selective hydrogenation of NC for the first time. To the best of our knowledge, this novel Cu-mediated catalysis represents the most convenient, efficient and cost-effective catalytic system for the selective conversion of NC to CHO.

We began our study by synthesizing a series of Cu/SiO₂ with the same Cu loading of 15 wt% by different preparation methods, including ammonia evaporation hydrothermal method (AE), conventional precipitation–deposition method (DP), sol–gel method (SG) and traditional incipient wet impregnation method (Imp).[19,21] The as-prepared Cu/SiO₂ precursors were calcined in air at 600 °C

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Table 1 Physicochemical properties and catalytic performance[a]

Entry	Catalyst	Conv. (%)	Sel. (%) 2	3	4	S_{BET} (m^2 g^{-1})	$S_{Cu}{}^b$ (m^2 $g_{catal}{}^{-1}$)	$S_{Cu}{}^b$ (m^2 $g_{Cu}{}^{-1}$)
1	15Cu/SiO$_2$-DP	50	70	18	12	162	22	148
2	15Cu/SiO$_2$-Imp	7	67	1	32	176	8	55
3	15Cu/SiO$_2$-SG	8	64	1	35	186	9	59
4	15Cu/SiO$_2$-AE	74	92	3	5	352	39	261
5	10Cu/SiO$_2$-AE	32	76	6	18	428	22	220
6	30Cu/SiO$_2$-AE	66	77	8	15	265	39	130
7	50Cu/SiO$_2$-AE	41	65	12	23	164	16	33
8	15Cu/ZrO$_2$	19	49	28	23	50	11	73
9	15Cu/Al$_2$O$_3$	55	53	—	47	300	24	160
10	15Cu/CeO$_2$	29	77	5	18	90	15	100
11	15Ni/SiO$_2$	19	59	20	21	382	—	—
12	15Fe/SiO$_2$	8	25	—	75	373	—	—
13	15Co/SiO$_2$	4	12	—	88	359	—	—

[a] Nitrocyclohexane 0.77 mmol, catalyst 20 mg, ethylenediamine 5 mL, time 3 h, H$_2$ pressure 1 MPa. [b] Dispersion of copper species and copper surface area determined by the N$_2$O titration method.

for 4 h, followed by reduction with 5 vol% H$_2$/Ar at 300 °C for 2 h, which were denoted as 15Cu/SiO$_2$-AE, 15Cu/SiO$_2$-SG, 15Cu/SiO$_2$-DP and 15Cu/SiO$_2$-Imp, respectively. The reduced-Cu/SiO$_2$ hybrid materials were then tested for the DHNC under 1 MPa H$_2$ at 100 °C for 3 hours. To our delight, it was found that 15Cu/SiO$_2$-AE gave the highest catalytic activity with an excellent selectivity of CHO of 92% among all the samples tested under identical conditions (Table 1, entries 1–4), which could be ascribed to its highly porous surface texture as inferred from the N$_2$ adsorption isotherms (Fig. S1, ESI†), highly exposed, properly assembled acid sites (Fig. S2, ESI†), N$_2$O titration and Brunauer–Emmett–Teller (BET) surface areas (Table 1), and H$_2$ temperature-programmed reduction (TPR) (Fig. S3, ESI†), respectively. Indeed, the number of accessible surface Cu atoms was reported to account for the catalytic hydrogenation performance.[21]

To further understand the origin of the catalytic reactivity over Cu/SiO$_2$ catalysts, we then set out to optimize Cu/SiO$_2$-AE by altering the Cu content during the preparation procedure. Table 1 shows that the 15Cu/SiO$_2$-AE (entries 4–7) catalyst exhibited superior catalytic reactivity in comparison to the others. To gain more detailed insight into the reaction performed with 15Cu/SiO$_2$-AE, the time-course plot for the above-mentioned DHNC to CHO transformation was examined (Fig. S4, ESI†). The reaction proceeded smoothly and was completed within 4 h. During the whole reaction process, cyclohexylamine (CHA) and cyclohexanone (CHone) were the only by-products with very low selectivity and without detecting any other intermediates. After 4 h, the yield of CHO approached 92% at full NC conversion, with unwanted byproducts essentially being prevented to be formed during the reaction. Furthermore, in a series of additional studies examining the effect of pressure, it was revealed that the reaction time was greatly shortened from 4 to 1 h as P_{H_2} was increased from 1 to 4 MPa (Table S1, ESI†). Subsequent experiments focused on the effect of the reaction temperatures

revealed that under otherwise identical reaction conditions the 15Cu/SiO$_2$-AE catalyst exhibited rather low activity at 60 °C (Table S2, entry 4, ESI†). Notably, at an elevated temperature of 120 °C, prominent formation of CHO can be attained within 1.5 h (Table S2, entry 1, ESI†).

To further confirm the effectiveness of the present system, hydrogenation of NC was carried out on a 50 mmol scale. The DHNC proceeds efficiently, and the corresponding CHO could be obtained in 91% yields (ESI†). After completion of the first hydrogenation, the 15Cu/SiO$_2$-AE catalyst was readily separated from the reaction mixture through simple filtration. For each successive use, the filtered catalyst was subjected to calcination in air at 600 °C for 4 h, and then reduced with 5% H$_2$/Ar at 300 °C for 2 h. After this treatment, the recovered catalyst can also be reused at least three times without an appreciable loss of activity on this scale. Moreover, catalyst leaching was not observed, as indicated by the absence of copper ions in the product solution after each catalyst reuse (the Cu contents of the catalysts and solutions were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis).

Imaging the nanocomposites of 15Cu/SiO$_2$-AE after reduction in H$_2$/Ar flow at 300 °C using TEM (Fig. 1A) reveals the high dispersity of partially reduced CuO$_x$ particles with uniform morphology embedded in the SiO$_2$ matrix. The CuO$_x$ particles have an average size of ∼3 nm and a narrow size distribution (Fig. 1B) and the elemental mapping (Fig. 1C and D) results confirmed the homogeneous elemental dispersion. It is interesting to find two sets of lattice fringes in the 15Cu/SiO$_2$-AE from the HRTEM image (Fig. 1E); the lattice spacing of ∼0.208 and ∼0.24 nm presented in the picture corresponds to the Cu(111) (JCPDS 04-0836) and
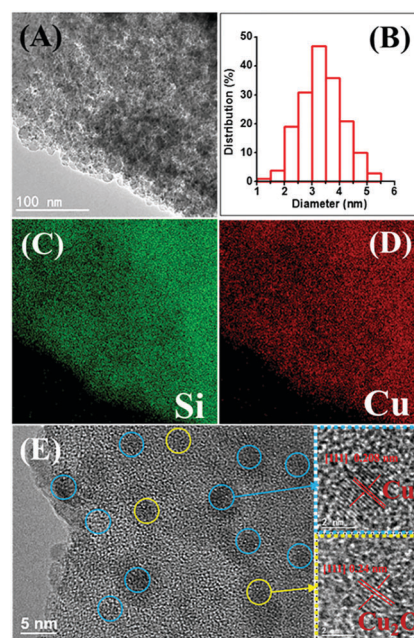

Fig. 1 (A) TEM image of the 15Cu/SiO$_2$-AE catalyst, (B) the corresponding particle size distributions and the corresponding (C) Si, and (D) Cu elemental mapping of the 15Cu/SiO$_2$-AE catalyst. (E) HRTEM images of 15Cu/SiO$_2$-AE catalysts.

$Cu_2O(111)$ (JCPDS 05-0667) planes, respectively.[22] The XRD patterns of the Cu/SiO_2-AE samples after calcination are shown in Fig. S5(A) (ESI†). In agreement with the TEM results, no diffraction peaks of any crystalline phase of copper species were observed when the Cu loading was lower than 15%, revealing that an excellent component dispersion can be readily achieved *via* the present simple one-pot method. The results of reduced samples in Fig. S5(B) (ESI†) show that there are no obvious diffraction peaks at $2\theta = 43.3°$ corresponding to Cu(111) for lower Cu/SiO_2 loading ($<15\%$), which also suggests the presence of a well dispersed metal phase. The Cu LMM XAES (Fig. S6 and S7, ESI†) results revealed that the Cu species on the reduced Cu/SiO_2 catalysts are Cu^0 and Cu^+, these findings imply that the metallic copper and Cu_2O coexisted in the working catalyst, which confirmed the HRTEM results.[23]

To gain further insight into the effect of the chemical state of Cu on the selective hydrogenation of NC to CHO, we examined the effect of Cu loading on the CHO yield and the mass specific activity of Cu (MAS_{Cu}, the NC consumption rate by mol h^{-1} g_{Cu}^{-1}) of NC as a function of $Cu^0/(Cu^0 + Cu^+)$ (Fig. 2) or the copper metal surface area (Fig. S8, ESI†). It was revealed that the MAS_{Cu} of NC did not exhibit monotonous variation upon increasing the copper metal surface area but was concerned with the surface $Cu^0/(Cu^0 + Cu^+)$ ratio, and the MAS_{Cu} of NC increased steadily at low $Cu^0/(Cu^0 + Cu^+)$, reaching a property of $Cu^0/(Cu^0 + Cu^+)$ at $15Cu/SiO_2$-AE, then decreasing upon further increases in Cu loading (Fig. 2B). Therefore, the optimal MAS_{Cu} of NC on the $15Cu/SiO_2$-AE catalyst could be related to its higher surface Cu^0 site density (Table 1) as well as the cooperative effect of Cu^0 and Cu^+ species. The critical role of $Cu^0/(Cu^0 + Cu^+)$ was further confirmed by comparing the catalytic performance of $15Cu/SiO_2$-AE, $15Cu/SiO_2$-Imp and $15Cu/SiO_2$-SG with their structural parameters, wherein it was found that $15Cu/SiO_2$-AE possessing a suitable $Cu^0/(Cu^0 + Cu^+)$ ratio showed the highest CHO yield. Taken together, these results demonstrate that, as a result of an optimal cooperative interaction between Cu^0 and Cu^+ species, the $15Cu/SiO_2$-AE sample afforded the highest catalytic activity and selectivity for the hydrogenation of NC

to CHO. It is very likely that Cu^0 species dissociate H_2, and Cu^+ sites function as electrophilic sites to polarize the nitro groups, similar to the hydrogenation of dimethyl oxalate.[23,24] The balanced Cu^0 and Cu^+ sites can improve the activity and selectivity.

Besides SiO_2, ZrO_2, Al_2O_3 and CeO_2 were also used as supporting substrates for the DHNC reaction. As shown in Table 1 entries 8–10, Al_2O_3 was chosen as a representative acidic oxide support, and ZrO_2 and CeO_2 were selected as amphoteric and weakly basic oxide supports. Cu/CeO_2, Cu/Al_2O_3, and Cu/ZrO_2 catalysts possess lower activities than the Cu/SiO_2 catalyst, which could be ascribed to the lower CuO_x dispersions and limited exposure of surface Cu atoms as seen from Table 1. The fact that these catalysts can only afford very limited selectivity toward CHO formation further confirms that an optimal balance of the different catalytically active sites is essential to maximize the efficacy of CHO production and minimize undesired CHone generation. A clear advantage of the Cu/SiO_2 catalyst over other abundant metals was also noticed when the reaction was performed using Ni/SiO_2, Fe/SiO_2 or Co/SiO_2 under otherwise identical conditions (Table 1, entries 11–13). It is important to remark that the performances of Cu/SiO_2 were comparable to or even higher than those of the typical noble metal catalysts or Cu salts.[6,11–14] These results indicate that the cooperation of SiO_2 supports and copper plays a key role in enabling high performance *via* maintaining high copper dispersion and weak surface acidity.

During the hydrogenation of NC, it is generally believed that CHA and CHone require several reaction steps to be produced from NC and they were expected to appear as the secondary products.[4,11,14] In fact, one could consider that while CHA could be produced by consecutive hydrogenation reactions (see Scheme 1a),[25,26] CHone could be produced by hydrolysis of CHO[27–30] with the formation of water during the first hydrogenation step. Generally, it is well known that this reaction may be catalyzed either by Brönsted or Lewis acid sites.[27–29] In order to check if CHone is directly formed by the hydrolysis of CHO over $15Cu/SiO_2$-AE, CHO was reacted either in the presence of stoichiometric amounts of water and/or in the absence of H_2. The results in Table S3 (ESI†) show that when this reaction was carried out with the $15Cu/SiO_2$-AE catalyst, only 0.5% conversion of the CHO is observed after 3 h, indicating that this compound is stable against hydrolysis especially in the absence of H_2, inferring that the very weak acid character of $15Cu/SiO_2$-AE is essential for this beneficial effect.[12]

We therefore checked the effect of water on the hydrogenation of NC under otherwise identical hydrogenative conditions. The results in Table S4 (ESI†) show that the introduction of water would lead to the formation of appreciable amounts of CHone, with the selectivity of CHone increased up to 35% upon increasing the amount of water to 20 equivalents. All these results proved that the formation of CHone during the hydrogenation of NC must occur through a catalytic route other than the direct hydrolysis of CHO by water. At this point, it should be mentioned that CHO can also be reduced with H_2 in the presence of certain metal-based catalysts, forming either CHA or CHone.[31–33] So it is reasonable that CHone may be initially reduced to an unstable intermediate (presumably cyclohexylimine), which
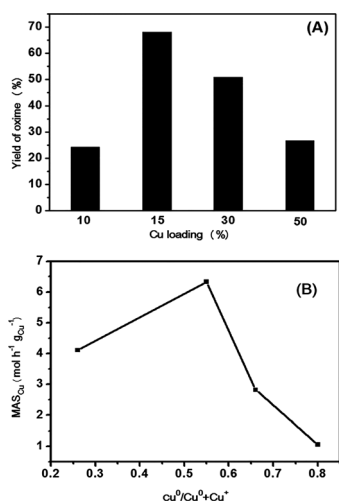

Fig. 2 (A) Yield of CHO as a function of Cu loading. (B) Correlation of the MAS_{Cu} of NC with $Cu^0/(Cu^0 + Cu^+)$.

could be further hydrogenated to give an amine, or hydrolyzed giving a cyclic ketone as the reaction product.[12] Taken together, it appears that the formation of CHA, and CHone over 15Cu/SiO$_2$-AE may proceed mainly *via* the reaction pathway given in Scheme 1b.

In summary, we have demonstrated that a highly active and robust catalyst based on a simple non-noble Cu/SiO$_2$-based catalyst can be used to convert NC into CHO under mild hydrogenative conditions in excellent yields. It was observed that the optimal combination of partially reduced CuO$_x$ NPs and weakly acidic SiO$_2$ supports is essential for attaining excellent selectivity for CHO in the hydrogenation of nitrocyclohexane. The present finding forms the basis for cost-competitive production of CHO from NC and the development of a new sustainable, economically affordable process for the production of bulk and commodity chemicals that are typically mediated by catalysts containing precious metals.

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