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An efficient noble-metal-free Supported Copper Catalyst for Selective Nitrocyclohexane Hydrogenation to Cyclohexanone Oxime

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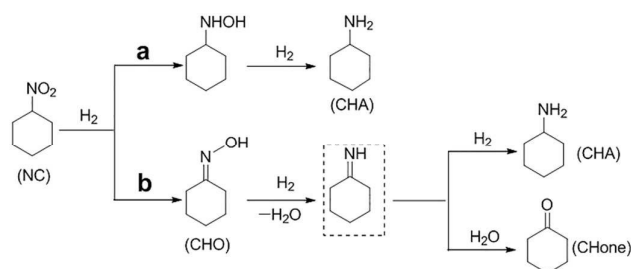
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It was shown for the first time that cyclohexanone oxime (CHO) can be selectively produced by heterogeneous copper-catalyzed hydrogenative transformation of nitrocyclohexane (NC). The combination of Cu⁰ and Cu⁺ and their cooperative interaction with weakly acidic SiO₂ supports elicited 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 is widely used in synthesis of polymers for advanced technologies^{1,2}. Currently, CHO is mainly synthesized through the catalytic oxidation of the cyclohexane to cyclohexanone (CHone) followed by reaction with hydroxylamine sulfate^{3,4}, the limitation of traditional CHO synthetic methodologies such as producing ammonium sulfate and the use of hazardous chemicals⁵⁻⁸, which 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 to 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% can be achieved^{6,11-14}. From 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 SiO₂ matrix can efficiently catalyze the controlled and selective hydrogenation of NC. Copper-containing catalysts have been extensively employed in past decades for the selective elimination of NOx¹⁵, water-gas-shift reactions¹⁶, synthesis and steam reforming of methanol.¹⁷⁻¹⁸ Moreover, it is also established that copper catalysts are very selective for the hydrogenation of dimethyl oxalate¹⁹ and diethyl oxalate²⁰ 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.



Scheme 1. The proposed reaction mechanism for the hydrogenation of nitrocyclohexane.

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 for 4 h, followed by reduction with 5 vol. % H₂/Ar at 300 °C for 2 h, which were denoted as 15Cu/SiO₂-AE, 15Cu/SiO₂-SG, 15Cu/SiO₂-DP and 15Cu/SiO₂-Imp, respectively. The reduced-Cu/SiO₂ hybrid materials were then tested for the DHNC under 1 MPa H₂ at 100 °C for 3 hours. To our delight, it was found that 15Cu/SiO₂-AE gave the highest catalytic activity with excellent selectivity of CHO of 92 %

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among all the samples tested under the identical conditions (Table 1, entry 1-4), which could be ascribed to its highly porous surface texture as inferred from the N_2 adsorption isotherms (Figure S1), highly exposed, properly assembled acid sites (Figure S2), N_2O titration and Brunauer-Emmett-Teller (BET) surface areas (Table 1), H_2 temperature-programmed reduction (TPR) (Figure S3), respectively. Indeed, the number of accessible surface Cu atoms was reported to account for the catalytic hydrogenation performance²¹.

To further understand the origin of the catalytic reactivity over Cu/SiO₂ catalysts, we then set out to optimize the Cu/SiO₂-AE by altering the Cu content during the preparation procedure. Table 1 shows that the 15Cu/SiO₂-AE (entry 4-7) catalyst exhibited superior catalytic reactivity in comparison with the others. To gain more detailed insight into the reaction performed with 15Cu/SiO₂-AE, the time-course plot for the above mentioned DHNC to CHO transformation was examined (Figure S4). 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). Subsequent experiments focused on the effect of the reaction temperatures revealed that under otherwise identical reaction conditions the 15Cu/SiO₂-AE catalyst exhibited rather low activity at 60 °C (Table S2, entry 4). Notably, at an elevated temperature of 120 °C, prominent formation of CHO can be attained within 1.5 h (Table S2, entry 1).

Table 1. Physicochemical properties and Catalytic Performance.^[a]

Entry	Catalyst	Conv (%)	Sel. (%)			S_{BET} (m ² g ⁻¹)	S_{Cu} (m ² g ⁻¹)	S_{Cu}^* (m ² g ⁻¹)
			2	3	4			
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 15Cu/SiO₂ 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 N_2O titration method.

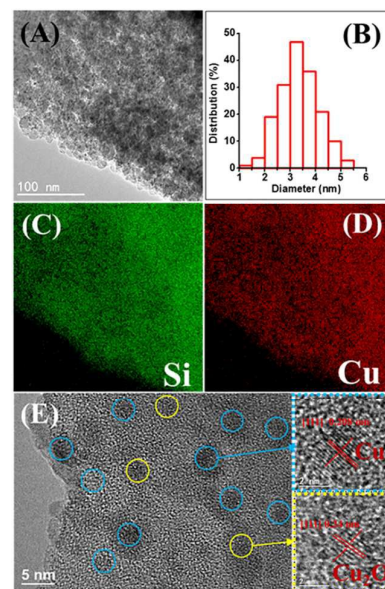


Figure 1. (A) TEM images of 15Cu/SiO₂-AE catalyst, (B) the corresponding particle size distributions and the corresponding (C) Si, (D) Cu elemental mapping of 15Cu/SiO₂-AE catalyst. (E) HRTEM images of 15Cu/SiO₂-AE catalysts.

To further confirm the effectiveness of the present system, a 50 mmol scale hydrogenation of NC was carried out. The DHNC proceeds efficiently, and the corresponding CHO could be obtained in 91% yields (supporting information). After completion of the first hydrogenation, the 15Cu/SiO₂-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 activity of 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 ion in the product solution after each catalyst reuse (the Cu content of the catalysts and solutions were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis).

Imaging the nanocomposites of 15 Cu/SiO₂-AE after reduction in H_2 /Ar flow at 300 °C using TEM (Figure 1A) reveals the high dispersity of partially reduced Cu_x particles with uniform morphology embedded in SiO₂ matrix. The Cu_x particles have an average size of ~3 nm and a narrow size distribution (Figure 1B) and the element mapping (Figure 1C, 1D) results confirmed the homogeneous elemental dispersion. It is interesting to find two sets of lattice fringes in the 15 Cu/SiO₂-AE from HRTEM image (Figure 2E), the lattice spacing of ~0.208 and ~0.24 nm presented in the picture corresponds to the Cu (111) (JCPDS 04-0836) and Cu₂O (111) (JCPDS 05-0667) plane, respectively²². The XRD patterns of the Cu/SiO₂-AE samples after calcination are shown in Figure S5 (A). 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 Figure S5 B show there are no obvious diffraction peaks at $2\theta=43.3^\circ$ corresponding to Cu(111) for the lower loaded Cu/SiO₂ (< 15%), which also suggests the presence of a well dispersed metal phase. The Cu LMM XAES (Figure S6 and S7) results revealed that the Cu species on the reduced Cu/SiO₂ catalysts are Cu⁰ and Cu⁺, these findings infer that the metallic copper and Cu₂O coexisted in the working catalyst, which confirmed the HRTEM results²³.

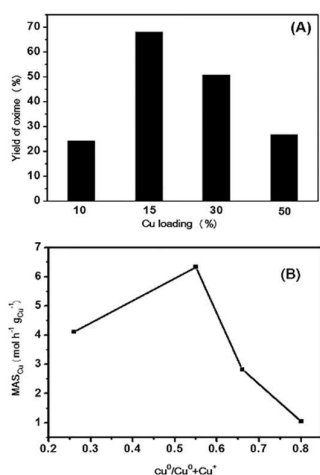


Figure 2. (A) Yield of CHO as a function of Cu loading. (B) Correlation of the MAS_{Cu} of NC with Cu⁰/(Cu⁰ + Cu⁺).

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 Cu⁰/(Cu⁰ + Cu⁺) (Figure 2) or copper metal surface area (Figure S8). It was revealed that MAS_{Cu} of NC did not exhibit monotonous variation with increasing the copper metal surface area but was concerned with the surface Cu⁰/Cu⁰+Cu⁺ ratio, and the MAS_{Cu} of NC increased steadily at low Cu⁰/(Cu⁰ + Cu⁺), reaching a property of Cu⁰/(Cu⁰ + Cu⁺) at 15Cu/SiO₂-AE, then decreasing upon further increases in Cu loading (Figure 2B). Therefore, the optimal MAS_{Cu} of NC on the 15Cu/SiO₂-AE catalyst could be related to its higher surface Cu⁰ site density (Table 1) as well as the cooperative effect of Cu⁰ and Cu⁺ species. The critical role of Cu⁰/(Cu⁰ + Cu⁺) was further confirmed by comparing the catalytic performance of 15Cu/SiO₂-AE, 15Cu/SiO₂-Imp and 15Cu/SiO₂-SG with their structural parameters, wherein it was found that 15Cu/SiO₂-AE possessing suitable Cu⁰/(Cu⁰ + Cu⁺) ratio showed the highest CHO yield. Taken together, these results demonstrate that, as a result of an optimal cooperative interaction between Cu⁰ and Cu⁺ species, the 15Cu/SiO₂-AE sample afforded the highest catalytic activity and selectivity for hydrogenation of NC to CHO. It is very likely that Cu⁰ species dissociate H₂, and Cu⁺ sites function as electrophilic sites to polarize the nitro groups, similar with the dimethyl oxalate hydrogenation^{23,24}. The balanced Cu⁰ and Cu⁺ sites can improve the activity and selectivity.

Besides SiO₂, ZrO₂, Al₂O₃ and CeO₂ were also used as supporting substrates for the DHNC reaction. As shown in Table 1 entry 8-10, Al₂O₃ was chosen as a representative acidic oxide support, and

ZrO₂ and CeO₂ were selected as amphoteric and weakly basic oxide supports. Cu/CeO₂, Cu/Al₂O₃, and Cu/ZrO₂ catalysts possess lower activities than the Cu/SiO₂ catalyst, which could be ascribed to the lower CuO_x dispersions, 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 the CHO production and minimize the undesired CHone generation. A clear advantage of the Cu/SiO₂ catalyst over other abundant metals was also noticed when the reaction was performed using Ni/SiO₂, Fe/SiO₂ or Co/SiO₂ under otherwise identical conditions (Table 1, entries 11-13). It is important to remark that the performances of Cu/SiO₂ 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 SiO₂ support and copper play a key role in enabling high performance via maintaining high copper dispersion and weak surface acidity.

During the hydrogenation of NC reaction, 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 CHO²⁷⁻³⁰ with the water formed during the first hydrogenation step. Generally, it is well known that this reaction may be catalyzed either by Brønsted or Lewis acid sites²⁷⁻²⁹. In order to check if the formation of CHone is directly formed by hydrolysis of CHO over 15Cu/SiO₂-AE, CHO was reacted under conditions either in the presence of stoichiometric amounts of water and/or in absence of H₂. The results in Table S3 show that when this reaction was carried out with the 15Cu/SiO₂-AE catalyst, only 0.5 % conversion of the CHO is observed after 3 h, indicating that this compound is stable against hydrolysis especially in absence of H₂, inferring that the very weak acid character of 15Cu/SiO₂-AE is essential for this beneficial effect.¹²

We therefore checked the effect of the water on hydrogenation of NC under otherwise identical hydrogenative conditions. Results in Table S4 show that the introduction of water would lead to formation of appreciable amounts of CHone, with the selectivity of CHone increased up to 35 % on increasing the amount of water to 20 equiv- alent. 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 H₂ 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 could be further hydrogenated to give the amine, or hydrolyzed giving the cyclic ketone as reaction product.¹² Taken together, it appears that the formation of CHA, and CHone over 15Cu/SiO₂-AE may proceed mainly via reaction pathway as given in Scheme 1b.

In summary, we have demonstrated that a highly active and robust catalyst based on a simple non-noble Cu/SiO₂-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 SiO₂ supports are essential for attaining excellent selectivity for CHO in the hydrogenation of nitrocyclohexane. The present finding forms the basis for cost-competitive producing CHO from NC and the development of new sustainable, economically affordable process for the

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production of bulk and commodity chemicals that are typically mediated by catalysts containing precious metals.

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