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Facile Synthesis of Copper-Based Metal Oxide Nanoparticles with Exceptional Catalytic Activity for the Selective Oxidation of Styrenes into Benzaldehydes

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The development of highly efficient catalysts for the selective oxidation of styrene to benzaldehyde has attracted great attention in recent years because of its significance in synthetic chemistry. In this study, two different kinds of copper-based metal oxide nanoparticles (NPs), namely, CuO and CuO/Co_3O_4 NPs, were synthesized by a simple and scalable method, and these nanoparticles demonstrated efficient catalytic abilities for the selective oxidation of styrene and its derivatives to the corresponding aldehydes in the presence of *tert*-butyl hydroperoxide (TBHP) under mild reaction conditions in excellent yields. Importantly, both of the heterogeneous catalysts can be recycled up to five runs while still maintaining their high catalytic activity.

Introduction

Styrene oxidation is of considerable importance in both academic and commercial sectors for the synthesis of benzaldehyde, which has wide applications in various fields as a crucial intermediate, such as pharmaceuticals, dyestuffs, spices, and so forth.[1,2] Traditionally, this transformation was performed using organic peracid as the oxidant,[3] the wide application of which was hindered because of it nocuous nature, high costs, and the generation of undesirable by-products. However, taking into account low catalytic activity, stability, and difficulty with homogeneous catalyst separation, as well as the production of many waste products during the reaction process, many efforts have been devoted to develop valid and recyclable heterogeneous catalysts and safer oxidizing agents such as *tert*-butyl hydroperoxide (TBHP), hydrogen peroxide, or molecular oxygen to catalyze styrene selective oxidation.[4–6]

As a consequence, the design of novel and more effective catalysts combined with clean oxidants to replace traditional strategies is extremely urgent from an environmental point of view. For example, Dapurkar et al. found that supported gold nanoparticle catalysts could efficiently catalyze the oxidation of benzylic compounds at 1 atm O_2.[7] Luque's group reported that iron oxide nanoparticles supported on the mesoporous aluminosilicates exhibited high catalytic activity for the oxidation of styrene under mild conditions.[8] Although a large variety of supported catalysts have been well developed, catalysts without supports have drawn more investigative attention on account of their numerous advantages, such as making full use of the effective reactive center of catalysts. Lambert et al. adopted ultrasmall gold nanoclusters as catalyst, which exhibited relatively high catalytic activity and selectivity for styrene oxidation under molecular oxygen.[9] Gu's group reported that ultrathin gold nanowires (GNWs) appeared much more active for the oxidation of benzylic compounds under molecular oxygen than the gold nanoclusters above.[10]

Copper oxide, an inexpensive and simple transition-metal oxide, has also attracted much attention as novel nanocatalyst in a variety of organic transformations such as dye degradation[11] and ring opening.[12] It demonstrated good catalytic performance.

Herein, we describe the use of copper oxide (CuO) nanoparticles and bimetal oxide (CuO/Co_3O_4) nanoparticles as nonsupported catalysts for the selective oxidation of styrene to benzaldehyde under mild conditions. In this study, metal oxide nanocatalysts were synthesized by a calcination treatment of metal–ligand complexes, which were achieved by means of a coordination-driven aggregation process. The reaction was performed in acetonitrile and using *tert*-butyl hydroperoxide (TBHP) as the oxidant. The results revealed that our metal oxide nanoparticles showed high catalytic activities and the overall yield of benzaldehyde was as high as 80 %. These inexpensive and unsupported catalysts were found to be more active than our previously reported $Pt@Fe_2O_3$ NWs catalysts.[13] Furthermore, compared with a Cu-Ni-Co/γ-Al_2O_3 system, our CuO and CuO/Co_3O_4 compounds provided higher conversion and selectivity.[14] It was noted that CuO NPs displayed complete conversion of styrene and its derivatives, whereas CuO/Co_3O_4 NPs exhibited higher selectivity for the corresponding al-

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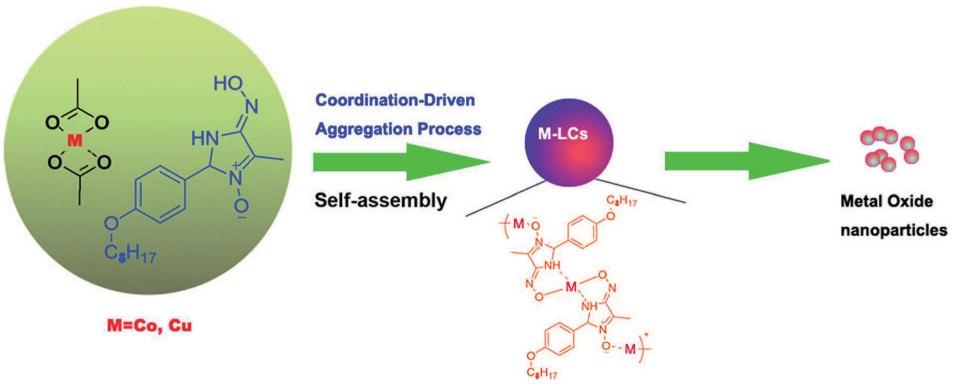
dehydes. Importantly, these metal oxide NPs could be recycled multiple times without any notable decrease in activity.

Results and Discussion

The metal oxide spheres were synthesized according to our previous reported method.[15] As illustrated in Scheme 1, organic ligands ((*Z*)-4-amino-5-(hydroxyimino)-2-(4-*n*-octyloxyphenyl)-2,5-dihydro-1*H*-imidazole-3-oxide (AHODIO)) were mixed with metal acetate (copper(II) acetate and cobalt(II) acetate) in a 2:1 molar ratio to form metal–ligand complexes (M–LCs) by means of a coordination-driven aggregation process (CDAP). Figure 1 shows the SEM image of as-prepared Cu-based MLCs, which clearly indicated that the precipitate consisted of spheres with a diameter of about 1.5 μm and exhibited extensive corrugation with deep cavities at the surface. The chemical composition of Cu–LCs was determined by energy-dispersive X-ray spectroscopy (EDS; Figure S1 in the Supporting Information). These particles were calcinated at 500 °C, and the color of the products changed from yellowish-brown into brownish-black, which resulted in the formation of the CuO nanoparticles. The typical SEM of the CuO NPs sample (Figure 1b) showed that the shape and size were very different from the Cu–LCs. The particles almost can be separated from each other, which could be further confirmed by the corresponding TEM image (Figure S2). It was clear that the CuO NPs were very uniform solid nanospheres with perfectly smooth surfaces and diminishing sizes from about 1.5 μm to 150 nm in diameter. This could be attributed to the successive release and loss of CO_2 and H_2O during the thermal decomposition. The corresponding EDS further proved the removal of released organic ligands (Figure S3). In addition, the crystalline structure and phase purity of the as-prepared CuO were analyzed by XRD in Figure 1c. All the diffraction peaks were satisfactorily indexed to the standard XRD data card of CuO (JCPDS card no. 48-1548).[16] Clearly, no additional peaks were detected, thus indicating the absence of any other impurities such as Cu_2O and Cu in the XRD patterns.



Scheme 1. Preparation of copper-based metal oxide nanoparticles.

According to the above procedure, CuO/Co_3O_4 nanoparticles were synthesized by calcination treatment of Cu/Co–ligand complexes under the same temperature. The size of Cu/Co–LCs (Figure 2a) was approximately 100 nm, whereas the size of CuO/Co_3O_4 (Figure 2b) was less than 50 nm. This size reduction came from the release of the organic ligands. The XRD patterns (Figure 2c) illustrate the pure mixed-crystalline structure,

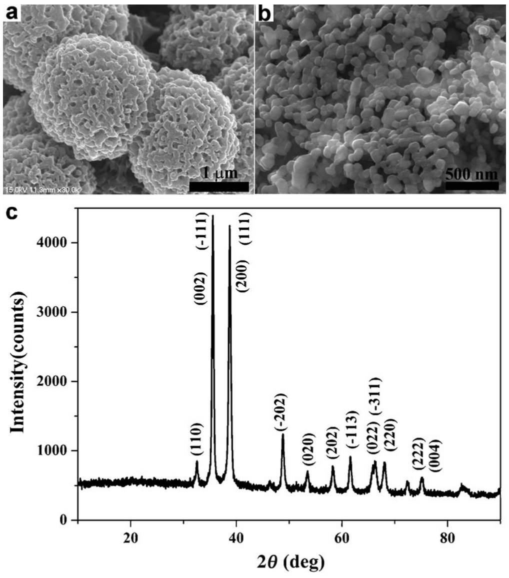


Figure 1. SEM images of as-prepared (a) Cu–LCs and (b) CuO NPs. (c) XRD patterns of the CuO NPs.

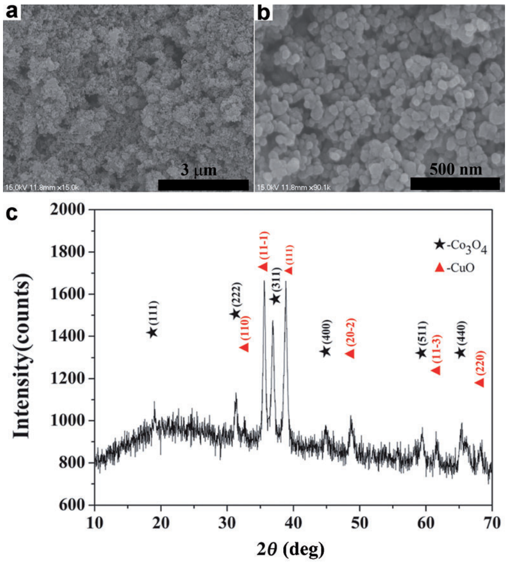
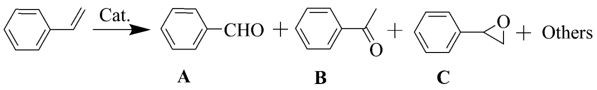


Figure 2. SEM image of as-prepared (a) Cu-Co–LCs and (b) CuO/Co_3O_4 NPs. (c) XRD patterns of the CuO/Co_3O_4 NPs.

which consisted of CuO and Co_3O_4. Moreover, the chemical composition of complexes was also determined by EDS (Figures S4 and S5). The measured Brunauer–Emmett–Teller (BET) pore volume and specific surface area of the CuO NPs and CuO/Co_3O_4 NPs are described in Table S1.

The test of the catalytic activity of the CuO NPs was performed by using styrene as the model substrate under air in the presence of TBHP (Scheme 2). Table 1 shows the results of the selective oxidation of styrene under different reaction conditions. The reactions in *N*,*N*-dimethylformamide (DMF) and tetrahydrofuran (THF) exhibited complete conversions with relatively lower selectivity towards benzaldehyde. Compared to other solvents, $CHCl_3$ offered excellent yield for the oxidation of styrene, but its real application is hindered by its high toxicity. When using water as solvent, the yield of benzaldehyde was 57.3% (Table 1, entry 10). It was found that acetonitrile was one of the best solvents for the reactions, and the yield of benzaldehyde was 74.9% over eight hours (Table 1, entry 2).



Scheme 2. Styrene oxidation with CuO NPs for the generation of the benzaldehyde and other by-products.

Table 1. The optimization of the different solvents for styrene oxidation to benzaldehyde.[a]

Entry	Solvent	Conversion [%][b]	Yield [%][b]
1	$CHCl_3$	96	77
2	CH_3CN	96	74
3	toluene	55	34
4	isopropanol	92	53
5	ethanol	64	56
6	DMF	100	48
7	THF	100	63
8	1,4-dioxane	81	38
9	methanol	60	43
10	H_2O	76	57

[a] Reaction conditions: styrene (1 mmol), TBHP (2.5 mmol), CuO NPs (5 mg), solvent (2 mL), 70 °C, 8 h. [b] Determined by GC analysis.

The time-dependent conversion of styrene to benzaldehyde was based on the GC analysis, which is illustrated in Table 2. Styrene (1 mmol) was oxidized at 70 °C under an air atmosphere by using CuO nanoparticles (5 mg) as catalyst, *tert*-butyl hydroperoxide (2.5 mmol) as oxidizing agent, and acetonitrile (2 mL) as solvent. As shown in Table 2, after one hour, the reaction afforded benzaldehyde in a yield of 70.4%, and the selectivity towards acetophenone was 12.9%. When the reaction time increased, the yields of benzaldehyde remained unchanged. In addition, styrene oxide started to appear and was gradually reduced as time went on. The highest yield of benzaldehyde was achieved after ten hours and reached as high as 82.1%. Compared with the selectivities of benzaldehyde over the entire reaction, the values were between 74 and 87.1%, which suggested that the benzaldehyde was formed by the direct oxidative cleavage of C=C of styrene, and one of the by-products, styrene oxide, can be further oxidized to form benzaldehyde.[17]

Table 2. Time-conversion data for benzaldehyde formation from the oxidation of styrene using CuO NPs as catalyst.[a]

Time [h]	Conversion [%][b]	Selectivity [%][b] A/B/C	Yield [%][b]
1	80	87:13:0	70
3	87	82:14:4	71
5	96	74:18:6	70
6	96	76:16:6	73
7	95	78:15:6	74
8	96	77:14:7	74
10	97	85:13:3	82
12	98	82:16:3	80
24	100	81:16:0	81

[a] Reaction conditions: styrene (1 mmol), TBHP (2.5 mmol), CuO NPs (5 mg), CH_3CN (2 mL), 70 °C. [b] Determined by GC analysis.

To further evaluate the catalytic activity of CuO nanoparticles, we conducted further studies to screen other factors including different temperatures, oxidants, and the amount of oxidants and catalysts. The reactions were carried out in the presence of different oxidizing agents, such as TBHP, air, oxygen, hydrogen peroxide, or benzoyl peroxide (BPO), respectively (entries 1–5, Table S2). Among these, no benzaldehyde was achieved in air, O_2, or hydrogen peroxide. BPO gave relatively high conversion but quite low selectivity for benzaldehyde. When the amount of TBHP was increased, the conversion for styrene was higher. The styrene could be fully converted and the selectivity was as high as 84.4% when using 4 mmol of TBHP (Table 3, entry 7). Furthermore, it was found that the conversion for styrene was 100% and the selectivity for benzaldehyde was 86.4% when adding 7 mg CuO NPs as the catalyst for the oxidation of styrene (Table S3).

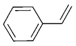
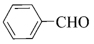
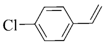
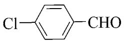
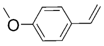
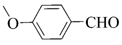
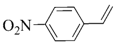
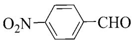
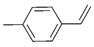
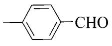
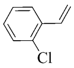
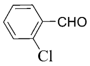
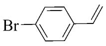
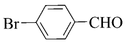
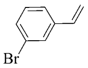
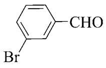
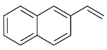
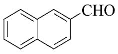
The general applicability of the catalytic oxidation was tested with styrene derivates under the optimized conditions, and the results are summarized in Table 4. Clearly, all the substrates can be completely converted with an overall yield be-

Table 3. The different ratios of TBHP and styrene for styrene oxidation to benzaldehyde.[a]

Entry	TBHP [mmol]	Conversion [%][b]	Yield [%][b]
1	0.5	39	32
2	1.0	66	46
3	1.5	83	72
4	2.0	91	73
5	2.5	97	82
6	3.0	100	70
7	4.0	100	84
8	5.0	100	74

[a] Reaction conditions: styrene (1 mmol), CuO NPs (5 mg), CH_3CN (2 mL), 70 °C, 10 h. [b] Determined by GC analysis.

Table 4. Selective oxidation of styrene and its derivatives to the corresponding aldehydes.

Entry	Substrate	Product	CuO[a]		CuO/Co_3O_4[b]	
			Conv. [%][c]	Selectivity [%][c]	Conv. [%][c]	Selectivity [%][c]
1			100	86	100	84
2			100	37	99	84
3			100	54	100	51
4			100	73	96	56
5			100	62	100	91
6			100	77	97	75
7			100	56	94	73
8			100	34	100	66
9			100	46	96	71

[a] Reaction conditions: styrene (1 mmol), TBHP (4 mmol), CuO NPs (7 mg), CH_3CN (2 mL), 70 °C, 10 h. [b] Reaction conditions: styrene (1 mmol), TBHP (3 mmol), CuO/Co_3O_4 NPs (5 mg), CH_3CN (2 mL), 70 °C, 5 h. [c] Conversion and selectivity determined by GC analysis.

tween 34.8 and 86.4% (Table 4, entries 1–9). Furthermore, we examined the possibility of the nanoparticles to catalyze 2-vinyl naphthalene to the corresponding 2-naphthaldehyde, which was generated with a yield of 46.1% (Table 4, entry 9).

Encouraged by the above results, we tested the catalytic activities of bimetal oxide (CuO/Co_3O_4). When CuO/Co_3O_4 was used as the catalyst for the selective oxidation of styrene, these two kinds of catalysts provided different catalytic activity. In acetonitrile, the conversion of styrene by the CuO/Co_3O_4 over five hours was 100% and the yield of benzaldehyde was 84.4%, a little lower than that of CuO (86.4%).

The time-conversion profile for the oxidation of styrene is shown in Table S4. After one hour, 66.2% of styrene conversion was observed with 88.2% selectivity of benzaldehyde at 70 °C. The highest yield (73.9%) was obtained after five hours with 94.8% styrene conversion. The conversion was able to reach 100% after 24 hours, but the selectivity gradually decreased. Temperature-dependent analysis revealed that the selectivity of benzaldehyde was decreased as the conversion of styrene increased while the reaction temperature was raised from 40 to 100 °C.

A series of styrene derivates could also converted to their corresponding aldehyde under the optimized reaction conditions (Table 4). Compared to the catalytic performance of CuO NPs, not all substrate could be completely converted except for 4-methoxystyrene (Table 4, entry 3), 4-methylstyrene (Table 4, entry 5), and 3-bromostyrene (Table 4, entry 8). Similarly, the yields of the selective oxidation for the electron-rich and electron-withdrawing substrates to the corresponding aldehydes ranged from 51.4 to 91.2% and were relatively higher than that of CuO. It was reported that CuO shows greater Brønsted acidity than Co_3O_4, whereby the oxidant was adsorbed on the surface. The Co_3O_4 displayed high Lewis basicity, whereby the oxygen was desorbed from the oxidant. As a result, the reactive sites would be favorable for the formation of benzaldehyde in view of the catalytic reaction that probably adopts an approach similar to the Eley–Rideal mechanism.[14]

Our CuO and CuO/Co_3O_4 catalysts could be easily recycled and reused over five times and exhibited excellent stability (Figure 3). The yields were able to be maintained (over 65%) and the conversion and selectivity could basically remain unchanged after five cycles.

Conclusion

In summary, we have synthesized M–LCs by means of a coordination-driven aggregation process, and we obtained two kinds of inexpensive copper-based metal oxide (CuO, CuO/Co_3O_4) NPs after calcination treatment. As heterogeneous catalysts, the as-prepared copper-based metal oxide NPs exhibited exceptional catalytic performance for the selective oxidation of styrene and its derivatives to the corresponding aldehydes with TBHP as oxidant under mild reaction conditions, thereby resulting in yields as high as 86.4% for benzaldehyde from styrene. In comparison, CuO/Co_3O_4 NPs displayed relatively higher selectivity than that of CuO NPs for the generation of the corresponding aldehydes, whereas CuO NPs exhibited higher catalytic capability for the complete conversion of styrene and its derivates. Beyond these, the copper-based metal oxide NPs showed excellent cyclic stability over five runs. The oxidation process was environmentally friendly and demonstrated their potential for industrial application.

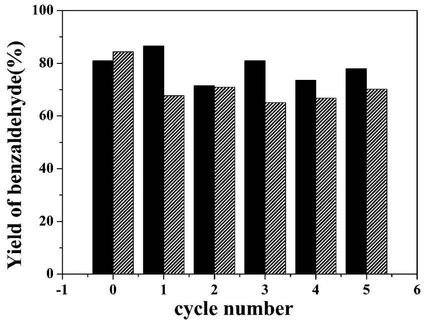


Figure 3. Catalytic stability of CuO NPs (black) and CuO/Co_3O_4 NPs (diagonal stripes) in the oxidation of styrene to benzaldehyde.

Experimental Section

An explosion stack (50 mL) was enclosed with styrene (1 mmol), CuO NPs (7 mg), TBHP (4 mmol), and CH_3CN (2 mL). Then the reaction was stirred for 10 h at 70 °C. When the reaction was stopped, the reaction mixtures were analyzed by GC using chlorobenzene as the internal standard. The catalysts were gained by the centrifugation and washing with acetonitrile. Under the same mild conditions, the catalyst was reused over five times.

An explosion stack (50 mL) was enclosed with styrene (1 mmol), CuO/Co_3O_4 NPs (5 mg), TBHP (3 mmol), and CH_3CN (2 mL). Then the reaction was stirred for 5 h at 70 °C. The following procedures were the same as the above.

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Keywords: copper · nanoparticles · oxidation · self-assembly · styrene

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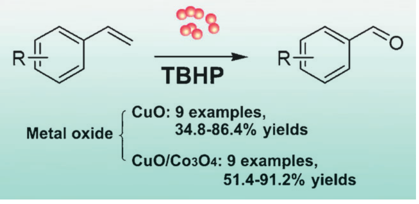
Facile Synthesis of Copper-Based Metal Oxide Nanoparticles with Exceptional Catalytic Activity for the Selective Oxidation of Styrenes into Benzaldehydes



Talkin′ about our generation: Copper-based metal oxide (CuO, CuO/Co_3O_4) nanoparticles have been synthesized from coordination-driven self-assembling aggregates and calcination treatment. They exhibited exceptional catalytic activity and stability for the selective oxidation of styrene and its derivatives to generate the corresponding aldehydes (see figure; TBHP = *tert*-butyl hydroperoxide).