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Selective hydrogenation of quinolines over a CoCu bimetallic catalyst at low temperature



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ABSTRACT

Quinoline derivatives are widely exist in the environment, and mainly separated from the coal tar pitch fraction. Hydrogenation of these compounds to 1,2,3,4-tetrahydroquinolines, an important class of natural products and medicinal agents, is a significant transformation of waste to valuable chemicals. In the present work, we developed a cheap and highly efficient $Co_3Cu_1O_x$ bimetallic catalyst and used it for the hydrogenation of quinolines at a temperature down to 60 °C. The introduction of Cu into Co catalyst changed the physical and chemical features of Co catalyst, which was characterized by Raman spectra, N₂-adsorption/desorption isotherms, H₂-TPR and H₂-TPD tests. The recycling experiments indicated the catalyst was stable and possessed good reusability. Importantly, the gram-scale experiment provided a high yield (92%) to the target product, demonstrating that the catalytic system has a potential practical application.

1. Introduction

N-containing heterocycle compounds are common intermediates in pharmaceutical and biological active molecules [1,2]. For example, 1,2,3,4-terthydrogenquinoline derivatives (THQs) are very important chemicals in organic synthesis, pharmaceuticals, biologically active natural products *etc* [3]. The hydrogenation of quinolines which are the by-products of petroleum refining processes, is considered to be a promising strategy to generate THQs in view of the high atom efficiency [3,4–6]. However, the reaction is difficult for the highly unsaturated feedstocks and the potential poisoning on the metal catalysts [2,5]. Despite great progresses have been achieved in the last decades, the efficient hydrogenation of quinolines to THQs still remains challenge able.

A variety of homogeneous and heterogeneous catalysts have been developed for the titled reaction. The homogeneous catalysts such as Ir [7], η 6-arene/TsDpen-Ru(II) [8] and metal-free catalyst [9] *etc.* were active for the titled reaction. However, the difficulties in separation of the catalyst from reaction mixtures and the high cost inhibited their further applications. The heterogeneous catalysts always involved precious metals, for example, Ru/ordered mesoporous N-doped carbon [10,11], Au/HSA-TiO₂ (HSA denoted as high surface area) [3], nanoporous Au catalyst [12], Ru/HAP (HAP is hydroxyapatite) [13], Ru/

 ZrO_2xH_2O [14], RuCu nanocages and Cu@Ru nanocrystals [15], Ru NPs immobilized on PVP [16], multimetallic nanoparticle catalysts [4], Pt/TiO₂ [17], Ru-SiO₂@mSiO₂ [18], Pd NPs [19–21] and PEG-stabilized Rh NPs [22] *etc.* The precious catalysts are unfavorable for industrial applications, while the base metal catalysts, especially Cobased catalysts, are potential substitutions for these precious catalysts. Recently, Co-based catalysts were developed and utilized to catalyze hydrogenation of quinolines, however, the reaction operated at elevated temperature (> 120 °C) [23–25].

The bimetallic catalysts have caught much attention due to some individual properties originated from the regulable electronic, structure and chemical effects between two metals [26,27]. Consequently, developing a cheap bimetallic catalyst with precious metal-free and high efficiency is extremely desirable. In recent years, lots of bimetallic catalysts were developed in hydrogenation [28], hydrogen generation [29], C–C and C–X coupling reactions [26], furan transformation [30], energy and environmental applications [31], CO hydrogenation [32] *etc.* However, to the best of our knowledge, it is rare for hydrogenation of quinolines. Herein, we developed a CoCu bimetallic catalyst ($Co_3Cu_1O_x$) and applied in the titled reaction under relatively low temperature conditions. The stable $Co_3Cu_1O_x$ catalyst, which could be magnetically separated from the reaction mixtures, exhibited a high efficiency for the selective hydrogenation of unsaturated aromatic

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amines. The catalytic performances and characterization of catalysts suggested that a synergistic effect existed between Co and Cu species.

2. Experimental section

2.1. Materials and methods

Co(NO₃)₂·6H₂O (99.0%), Cu(NO₃)₂·3H₂O (99.0%) were provided by Adamas-Beta. Ni(NO₃)₂·6H₂O (\geq 98.0%) was obtained from Tianjin Beilian Fine Chemicals Development Co., Ltd. Fe(NO₃)₃·6H₂O (\geq 98.5%) and tetrahydrofuran (99%) were afforded by Guangdong Guanghua Sci-Tech Co., Ltd. Na₂CO₃ was purchased from Tianjin Sheng'ao Chemicals Development Co., Ltd. Quinoline (96.0%) was gained by Aladdin Industrial Corporation. N₂ (99.999%), CO₂ (99.995%) and H₂ (99.99%) were purchased from Xi'an Teda Cryogenic Equipment Co., Ltd. All other chemicals were obtained from commercial companies and used without further purification.

2.2. Catalyst preparation

The catalysts were prepared by a simple co-precipitation method. The Co₃Cu₁O_x catalyst was manufactured as follows: Co(NO₃)₂·6H₂O (0.873 g, 3.0 mmol), Cu(NO₃)₂·3H₂O (0.242 g, 1.0 mmol) were dissolved in 20 mL of deionized water and the mixture was stirred for 1 h until Co²⁺ and Cu²⁺ were well dispersed. Then the solution was dropped slowly to 0.5 M of Na₂CO₃. Meanwhile, the precipitate was formed and the mixture was stirred for another 16 h at room temperature. The solid was filtrated and washed with 500 mL of deionized water to remove Na⁺ and CO₃²⁻. After that, the solid was calcined in a muffle furnace in air from room temperature to 500 °C with a heating rate of 5 °C/min and kept at 500 °C for 3 h. The catalyst was further reduced in a tube furnace under pure H₂ from room temperature to 500 °C with the same rate and kept at 500 °C for 2 h, after reduction, the catalyst was passivated by 1% O₂/N₂ at room temperature for 30 min to avoid the over-oxidation.

Other Co-Cu catalysts with different compositions were synthesized by the same procedures as the above, and the catalysts of the pure Co and Cu, $Co_3Zn_1O_x$, $Co_3Mn_1O_x$, $Co_3Fe_1O_x$, $Co_3Ni_1O_x$ and $Co_3Ce_1O_x$ were also prepared by the above co-precipitation method with corresponding nitrate salts as precursors.

2.3. Catalyst characterization

The as prepared catalysts were characterized by TEM, XRD, XPS, Raman, H₂-TPR and H₂-TPD, and N₂-adsorption/desorption. The TEM images of the catalysts were measured using a JEM-2100 electron microscope operated at 200 kV. The XRD was carried out on Rigaku D/ max 2500 with nickel filtered Cu-K α (λ = 0.154 nm) operated at 40 kV and 20 mA. The XPS spectra were performed using an ESCALab 220I-XL electron spectrometer from VG Scientific using 300 W AlK α radiation with a hemispherical energy analyzer. The Raman spectra were tested on a Laser microscopic Raman imaging spectrometer (Thermo Fisher, USA) equipped with a 532 nm Ne laser and a high-grade Leica microscope (long working distance objective 50). The single crystal silicon was used for the position correction.

The H₂-TPR tests were performed on a chemisorption analyzer (Autochem II 2920, Micromeritics). Before the test, the catalyst was pretreated at 300 °C for 30 min in He with a flow rate of 50 mL/min, and then was cooled down to 50 °C. Then a mixture gas of 10%H₂-90%Ar was passed through the catalysts with a flow of 50 mL/min. The temperature was linearly raised from 50 °C to 700 °C at a heating rate of 10 °C/min. The effluent gas was analysed using a thermal conductivity detector (TCD). The H₂-TPD analysis was carried out as follows: the catalyst was heated to 400 °C in He for 30 min, and then was cooled to 50 °C. After that, the catalyst was saturated with the 10%H₂-90%Ar mixture gas for 1 h. Then the purging in He with a flow rate of 50 mL/

min was performed to remove residual H₂ from the surface of catalysts. H₂ adsorption test was conducted from 50 to 600 °C at a heating rate of 10 °C/min and maintained at 600 °C for 30 min with 50 mL/min of He. The desorption amount of H₂ was tested by using a TCD detector.

2.4. Hydrogenation of quinolines

The hydrogenation reactions of quinolines were carried out in 16 mL stainless steel autoclaves with a Teflon inner container in a batch mode of operation [33,34]. In a typical reaction, quinoline (0.129 g, 1 mmol), catalyst 20 mg and THF (1 mL) were added into the inner container, which was transferred into the autoclave. The reactor was sealed and charged with 1 MPa of H₂ to remove the air for three times. After that, it was charged with 4 MPa of H₂ and heated to 60 °C and stirred for 15 h. Upon completion of reaction, the solid catalyst was separated using an extra magnet, and the liquid was analysed on a gas chromatograph (GC9720, Zhejiang Fuli Analytical Instruments Co., Ltd., China) equipped with a flame ionization detector and a HP-5 capillary column (30 m × 0.32 mm × 0.25 µm) with toluene as an internal standard and GC–MS (Agilent 6890N-5975) with a HP-5 capillary column (30 m × 0.32 mm × 0.25 µm).

2.5. The reusability of the catalyst and the hot filtration tests

After the reaction, the solid catalyst was separated by an extra magnet and washed with THF for five times, and then it was used in the next run. Other operations were the same as mentioned. The hot filtration test was carried out as follows: after the reaction proceeded for 9 h, the catalyst was filtrated and the solution was kept under the catalytic conditions for another 6 h. After the reaction completion, the solution was analyzed by GC.

3. Results and discussion

Cat

Initially, we chose the abundant and cheap quinoline as the substrate to screen the catalyst, and the results are summarized in Table 1. The reaction did not occur spontaneously in the absence of the catalyst (entry 1). The pure Co catalyst gave THQ with the yield of only 2%. The pure Cu showed a low activity even prolonged the time to 20 h, which gave 2% yield. The results revealed that Co and Cu were both inactive

Table 1

Hydrogenation of quinoline over divers catalysts.^a.

$ \begin{array}{c} & & \\ & & $						
Entry	Catalyst	Time (h)	Conv. ^b (%)			
1	-	15	0			
2	pure Co	15	2			
3	pure Cu	20	2			
4	Co ₃ Cu ₁ O _x	15	97			
5	Co ₁ Cu ₆ O _x	15	7			
6	$Co_1Cu_3O_x$	15	23			
7	$Co_1Cu_1O_x$	15	27			
8	Co ₂ Cu ₁ O _x	15	15			
9	Co ₄ Cu ₁ O _x	15	40			
10	Co ₅ Cu ₁ O _x	15	8			
11	Co ₆ Cu ₁ O _x	15	5			
12	Co ₃ Zn ₁ O _x	15	0			
13	$Co_3Mn_1O_x$	15	0			
14	$Co_3Fe_1O_x$	15	< 1			
15	$Co_3Ni_1O_x$	15	< 1			
16	$Co_3Ce_1O_x$	15	2			

 a Reaction conditions: catalyst 20 mg, quinoline 1 mmol, THF 1 mL, H $_{2}$ 4 MPa, 15 h, 60 °C.

 $^{\rm b}$ Conversion was detected by GC with toluene as an internal standard, and the selectivity of THQ was > 99% in all cases.

for the reaction (entries 2 and 3). Interestingly, the CoCu bimetallic catalyst with the molar ratio of 3/1, denoted as Co₃Cu₁O_x exhibited a 97% conversion of quinoline and > 99% selectivity to THQ, which were much higher than that of pure Co and Cu (entry 4). Importantly, the high catalytic activity was obtained at a low temperature (60 °C), which is within an acceptable temperature range in industry. The catalyst was synthesized by a simple co-precipitation method, and the details are given in the Supporting Information. Interestingly, the other CoCu catalysts with different molar ratios such as Co₁Cu₆O_x, Co₁Cu₃O_x, Co1Cu1Ox, Co2Cu1Ox, Co4Cu1Ox, Co5Cu1Ox, Co6Cu1Ox etc. showed lower yields to THQ (entries 4 vs 5–11), which was probably due to the complex properties of structure and electronic of bimetallic catalyst. The Co/Cu molar ratios were confirmed by ICP-OES (Table S1). For comparison, the Co catalysts combined with other metals were also evaluated. All of them exhibited low activities, for example, the Co₃Zn₁O_x and Co₃Mn₁O_x catalysts could not catalyse the reaction at all (entries 12 and 13), while Co₃Fe₁O_x, Co₃Ni₁O_x and Co₃Ce₁O_x bimetallic catalysts yielded trace amounts of desirable product (entries 14-16). Based on these results, the outstanding performances were probably due to the existence of a synergistic effect between Co and Cu metals in $Co_3Cu_1O_x$ catalyst.

It is well known that the catalytic performances of the catalyst are related closely to the structures. The N₂ adsorption/desorption isotherms indicated the BET surface area of the fresh $Co_3Cu_1O_x$ catalyst $(41 \text{ m}^2/\text{g})$ was smaller than that of the pure Co catalyst $(77 \text{ m}^2/\text{g})$. The pore sizes of $Co_3Cu_1O_x$ and Co catalysts calculated from the distribution curves were approximately 50 and 46 nm, respectively, which were mainly formed through particle accumulation (Fig. S1 and Table S2 in supporting information). This was also confirmed by SEM image, which showed the nanoparticles were aggregated (Fig. S2a). The EDS spectrum of the fresh catalyst was also tested, and the result revealed the Co/Cu/O surface atom ratio was 71.7/20.5/7.8 (Fig. S2b and Table S3). TEM images showed that the fresh $Co_3Cu_1O_x$ catalyst was mostly aggregated by nanoparticles with the size of approximately 60–100 nm (Fig. 1a). The HR-TEM images of fresh catalyst showed the lattice



Fig. 2. XRD patterns of the as-synthesized catalysts (a, pure Co, \blacklozenge), (b, pure Cu, \blacklozenge), (c, the fresh Co₃Cu₁O_x), (d, the unreduced Co₃Cu₁O_x), (e, the used Co₃Cu₁O_x), (f, Co standard JCPDS:15-0806), (g, Cu, JCPDS:04-0836), (h, CuO, \blacklozenge , JCPDS:48–1548) and (i, Co₃O₄, JCPDS:42–1467).

fringes of the planes with a D-spacing of 1.8 Å, 2.4 Å and 2.0 Å, corresponding to Cu (200), CoO (111) and Co (002) (Fig. 1c-d), respectively. The HR-TEM tests indicated the fresh catalyst was composed of Co°, Cu°



Fig. 1. TEM images of the fresh $Co_3Cu_1O_x$ catalyst (a), the used catalyst (b) and HR-TEM images of fresh catalyst (c-e).



Fig. 3. XPS tests of the fresh catalyst (a, Co), (b, Cu), the used catalyst Co₃Cu₁O_x, (c, Co) (d, Cu), and the unreduced catalyst (e, Co), (f, Cu).

and CoO species. The Co $^\circ$ and Cu $^\circ$ species were also confirmed by the XRD tests.

The bulk phase of these nanoparticles was mainly composed of Co[°] and Cu[°] species, which were confirmed by the XRD patterns (Fig. 2) [35]. XRD patterns of different catalysts are shown in Fig. 2. Compared with the unreduced catalysts, fewer peaks were found in the fresh catalyst. The peaks at 44.3°, 51.7°, and 75.8° were ascribed to the (111), (200), and (220) of Co[°] (JCPDS file No. 15-0806), respectively (2c *vs* 2a and 2f) [35]. The peaks around 43.3° and 50.6° were attributed to (111) and (200) of Cu[°] (JCPDS file No. 04-0836), respectively (2c *vs* 2b and 2 g) [35]. The peaks at 19.0°, 31.3°, 36.9°, 38.6°, 44.9°, 59.4° and 65.3°

of the unreduced catalyst were in good agreement with that of Co_3O_4 (JCPDS file No. 42-1467) (Fig. 2d vs Fig. 2i) which were indexed as (111), (220), (311), (222), (400), (511) and (400) diffraction lines, respectively (2d vs 2i) [36]. The weak peaks at 35.5° and 38.8° are assigned to (002) and (111) of CuO (JCPDS file No. 48-1548) (2d vs 2 h) [5,35].

To investigate the surface atomic composition, the catalysts were examined by XPS (Fig. 3). The peaks of Co species in the unreduced catalyst were attributed to Co_3O_4 , which was verified by the weak shake-up satellite structure of from the minor Co^{2+} component (Fig. 3e) [37]. The surface Cu atom of the unreduced catalyst mainly was Cu^{2+}



Fig. 4. Raman spectra of the pure Co catalyst (pink), $Co_3Cu_1O_x$ catalyst (green) and the pure Cu (red) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

species (Fig. 3f). In the fresh catalyst, the binding energy of the Co 2p peaks observed at 782.0 eV and 796.5 eV could be assigned to Co^{3+} 2p 3/2 and Co^{3+} 2p 1/2, respectively. The peaks at 781.3 eV and 797.4 eV could be attributed to Co^{2+} 2p 3/2 and Co^{2+} 2p 1/2, and the peaks at 778.0 eV and 795.3 eV could be designated to Co° 2p 3/2 and Co° 2p 1/2, respectively. Small amount of Co° species was found because it was easily oxidized to CoO in air at room temperature (Fig. 3a), which was further confirmed by the strong shake-up peaks [37]. The peaks at 932.9 eV and 934.8 eV could be assigned to $Cu^{0/+}$ and Cu^{2+} species, respectively (Fig. 3b). It is difficult to distinguish between Cu° and Cu^{+} species based on their Cu 2p binding energies, which are almost indistinguishable [38]. The XPS spectra of used catalyst were nearly the same as the fresh one, which indicated the surface of catalyst stayed stable after using.

Raman scattering is very sensitive to the microstructure of nanocrystalline materials [39], and the pure Co, Cu and the fresh $Co_3Cu_1O_x$ catalysts were examined (Fig. 4). The peaks at 190, 470, 514, 607 and 676 cm⁻¹ in the pure Co catalyst were attributed to F_{2g} , E_g , F_{2g} , F_{2g} and A_{1g} mode of Co_3O_4 , respectively [35]. Notably, Co_3O_4 was formed from partial oxidization of CoO by local laser heating [39]. The pure Cu catalyst showed no obvious peak in the range of 100-1000 cm⁻¹. Compared with the pure Co catalyst, the intensities of $Co_3Cu_1O_x$ decreased remarkably, meanwhile, the peak of Co_3O_4 was broadened for the structural disorder. The Raman spectra indicated the lattice defects were created in Co_3O_4 *via* the penetration of Cu atoms [35].

The results of Raman spectra indicated that the $Co_3Cu_1O_x$ catalyst probably possessed a strong interaction between Co and Cu species. To further substantiate this, the fresh catalyst, the pure Co and Cu catalysts

were characterized by H2-TPR and H2-TPD tests (Fig. 5). In H2-TPR tests, two peaks emerged around 282 and 375 °C in the pure Co catalyst, which could be attributed to the reduction of Co₃O₄ to CoO and CoO to Co°, respectively [40,41]. These corresponding temperatures were reduced to 180 and 221 °C in Co3Cu1Ox catalyst. The TPR curve of CuO showed a wide peak at 208 °C and two shoulder peaks at 139 and 262 °C, which were assgined to the reduction of isolated CuO to Cu₂O, the reduction of surface CuO clusters and the reduction of Cu₂O to Cu[°], respectively (Fig. 5a). The results demonstrated the addition of Cu could reduce the reduction temperature of Co catalyst. In H₂-TPD tests, the $Co_3Cu_1O_x$ catalyst exhibited two peaks presented at approximately 120 and 600 °C, respectively. The H₂ adsorption quantities were calculated from the curves, which were 0.25 and 0.44 mmolH₂: g_{cat}^{-1} , respectively. However, for the pure Co and Cu catalysts, both of them were much less than that of Co₃Cu₁O_x, which were only 0.14 and $0.10 \text{ mmolH}_2 \cdot \text{g}_{\text{cat}}^{-1}$, respectively. The results indicated the Cu and Co gave the strong synergistic effect for adsorption of H₂, which probably contributed to the outstanding catalytic performances in hydrogenation of quinoline.

Effects of reaction conditions such as the reaction temperature, pressure of H₂ and reaction time on the catalytic performances were investigated and the results are given in Fig. 6. The temperature affected the catalytic efficiency remarkably (Fig. 6a). The reaction did not occur at 40 °C, while it proceeded smoothly at 50 °C. Interestingly, the conversion increased to 97% at 60 °C. The pressure of $\rm H_2$ also affected the reaction obviously (Fig. 6b). The conversion of quinoline increased with increasing the pressure of H₂. The dependence of reaction time on the conversion and selectivity was given in Fig. 6c, which showed the conversion increased with prolonging the time to 18 h. For example, the conversion of quinoline at 13 h was 20%, which increased remarkably to 97% at 15 h. The reason for this rapid increase was speculated to exist of an activation period between the catalyst and substrate. During the period, the surface of oxidized catalyst was in-situ reduced to Co° species under H₂ in THF. The dependence of solvent on the catalytic performances was listed in Table S4. Among the solvents tested, THF was considered to be the best solvent for the reaction (Table 1, entry 4). Cyclohexane and toluene gave THQ with a moderate yield of 77% and 67%, respectively. Water, DMF, DMI (1,3-dimethyl-2- imidazolidinone) and DCM (dichloromethane) exhibited low activities for the reaction. The reasons for these divers activities were probably due to the low solubility of substrate in water, strong coordination between solvent, Co₃Cu₁O_x catalyst and substrate.

The reusability of $Co_3Cu_1O_x$ catalyst in hydrogenation of quinoline was also studied (Fig. 7a). The results showed that it could be used at least 5 times without significant loss in activity, indicating that it possessed a good stability in the recycling tests, which was confirmed by the TEM, XRD, XPS and ICP-OES results. TEM image of the used catalyst displayed that it was mainly nano-particles with the size in the range of 60–100 nm, which was the same as the fresh catalyst (Fig. 1a vs 1b).



Fig. 5. (a) H_2 -TPR tests of Co_3O_4 (pink), bimetallic $Co_3Cu_1O_x$ catalyst (green) and CuO (red); (b) H_2 -TPD studies of the $Co_3Cu_1O_x$ (green), the Co (pink) and the Cu (blue) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).



Fig. 6. Effects of temperature (a), the pressure of H₂ (b) and the reaction time (c) on the catalytic performances (catalyst 20 mg, quinoline 1 mmol, THF 1 mL).

The XRD patterns of the used catalyst were the same as the fresh one (Fig. 2e vs 2c), and the XPS results showed the used catalyst were the same as the fresh catalyst (Fig. 3c vs 3a, and 3d vs 3b). The ICP-OES test of the used catalyst showed the same molar ratio of Co/Cu (3.16) as the fresh one (Table S1). These characterizations indicated the catalyst possessed good stability during the reaction. The $Co_3Cu_1O_x$ catalyst could be easily separated from the reaction mixture by an extra magnet (Fig. S3). The hot-filtration experiments indicated that the yield of 1,2,3,4-tetrahydroquinoline did not increase after the catalyst was filtrated, indicating that the catalyst was performed in a true heterogeneous way (Fig. 7b).

Subsequently, we evaluated the substrate scope of the reaction over $Co_3Cu_1O_x$ bimetallic catalyst and the results are given in Table 2. The substrates bearing with an electron-donating group, such as CH_3 - and CH_3O - groups on the 6-position of quinoline, worked well under the given conditions (entries 1 and 2). CH_3 - group at the 8-position of quinoline, afforded the target product in excellent yield (up to 99%) under 120 °C (entry 3). Electron-withdrawing groups such as chloride, bromide at the 6-position of the quinoline structure showed 77% and 23% yield (entries 4 and 5). No corresponding product was detected when nitro- group at 7-position of quinoline (entry 6). Isoquinoline was tolerated in the present protocol, which produced 1,2,3,4-tetrahydrogenisoquinoline with a 99% yield (entry 7). Interestingly, the gram-scale experiment was also conducted, and a satisfying yield of 92% for THQ was obtained (entry 9), indicating that the catalyst has great potential application in industry.

4. Conclusions

In summary, we have developed a highly efficient bimetallic



Hydrogenation of various substrates over Co₃Cu₁O_x catalyst.^a.

Co₃Cu₁O_x

N N	H ₂	N H		
Entry	R	Time (h)	Temp. (°C)	Yield ^b
1	6-CH ₃	15	80	> 99
2	6-OCH ₃	15	80	> 99
3	8-CH ₃	15	120	> 99
4	6-Cl	15	80	77
5	6-Br	15	130	23
6	$7-NO_2$	15	130	0
7 ^c	Н	24	130	> 99
8 ^d	Н	15	80	92

 $^{\rm a}$ Reaction conditions: catalyst 20 mg, solvent 1 mL, substrate 1 mmol, ${\rm H}_2$ 4 MPa.

^b GC vield.

^c isoquinoline was used as the substrate.

^d gram-scale experiment, quinoline 10 mmol, solvent 10 mL, catalyst 200 mg.

 $Co_3Cu_1O_x$ catalyst for hydrogenation of quinolines to 1,2,3,4-tetrahydroquinolines under low temperature. The catalyst could be simply fabricated by a co-precipitate method, reused for several times and worked in a heterogeneous way. The high efficiency was partly proved to be originated from the strong adsorption of H₂ over Co₃Cu₁O_x catalyst. The gram-scale experiment indicated the catalyst had a great potential application in industry. The developed approach demonstrates the technical feasibility of replacing precious metal catalysts by non-precious bimetallic catalysts, and we expect this protocol will



Fig. 7. The reusability and the hot filtration tests for Co₃Cu₁O_x catalyst. Reaction conditions were similar to that of entry 4, Table 1.

extend the utilization in hydrogenation of analogous core structure.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2019.04.005.

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