

## **An efficient noble-metal-free CuO<sub>x</sub>/SiO<sub>2</sub> catalyst for Selective Nitrocyclohexane Hydrogenation to Cyclohexanone Oxime**

Qian-Qian Zhang<sup>a</sup>, Jing Dong<sup>a,b</sup>, Yong-Mei Liu<sup>a\*</sup>, Yong Cao<sup>a</sup>, He-Yong He<sup>a</sup>,  
Yang-Dong Wang<sup>b\*</sup>

<sup>a</sup> *Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, P. R. China*

<sup>b</sup> *SINOPEC Shanghai Research Institute of Petrochemical Technology, Shanghai 201208, P.R. China*

### **Experimental Section**

#### **1. General**

Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Zr(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>2</sub>·9H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Oxalic acid, Na<sub>2</sub>CO<sub>3</sub>, NaOH, NH<sub>3</sub>·H<sub>2</sub>O, tetraethyl orthosilicate (TEOS) and ethylenediamine (EDA) were purchased from Sinopharm Chemical Reagent Co., Ltd. silica sol (JN30) was purchased from Qingdao Haiyang Chem. Co., Ltd. Nitrocyclohexane (97 wt %) was purchased from Tokyo Chemical Industry Corporation Limited.

#### **2. Catalyst preparation**

##### **Preparation of Cu/SiO<sub>2</sub>-AE catalysts**

A series of Cu/SiO<sub>2</sub>-AE catalysts (Cu loading ranging from 10 to 50 wt %) were prepared by the AE method described as literature.<sup>S1</sup> Shortly, 15.25 g of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O was dissolved in 150 ml of deionized water. 46 ml of 28 % ammonia aqueous solution was added and stirred for 30 min. Then 40.0 g of silica sol was added to the copper ammonia complex solution and stirred for another 4 h. The initial pH of the suspension was 11-12. All the above operations were performed at room temperature. The suspension was transferred to an oil bath preheated at 90 °C, respectively, to allow for the evaporation of ammonia and the decrease of pH and consequently, the deposition of copper species on silica. When the pH value of the suspension decreased to 6-7, the evaporation process was terminated. The filtrate was

washed with 500 ml of deionized water five times and dried at 100 °C overnight. The catalyst precursors were calcined in static air at 600 °C for 4 h. Prior to the reaction, the calcined samples were pre-reduced with 5 vol. % H<sub>2</sub>/Ar at 300 °C for 2 h to obtain their reduced forms (denoted as xCu/SiO<sub>2</sub>-AE, where x represents the nominal copper loading).

#### **Preparation of reference 15Ni/SiO<sub>2</sub>, 15Fe/SiO<sub>2</sub>, 15Co/SiO<sub>2</sub> catalysts**

The three catalysts were prepared according to the method described in preparation of 15Cu/SiO<sub>2</sub>-AE catalysts.

#### **Preparation of reference 15Cu/SiO<sub>2</sub>-DP catalyst.**

The 15Cu/SiO<sub>2</sub>-DP catalyst was prepared by precipitation-deposition method. Typically, 2.83 g Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O was dissolved in 250 ml dissolved water and 12 ml silica sol was added dropwise simultaneously. After stirring at room temperature for 4 h, an aqueous solution of NaOH (2 mol/l) was added to the above suspension till PH = 9. Then the temperature was raised to 80 °C and kept at this temperature for 4 h. Then the resulted catalyst precursor was washed with deionized water until PH = 7 and then dried at 100 °C overnight. The catalyst precursors were calcined in static air at 600 °C for 4 h. Prior to the reaction, the calcined samples were pre-reduced with 5 vol. % H<sub>2</sub>/Ar at 300 °C for 2 h.

#### **Preparation of reference 15Cu/SiO<sub>2</sub>-Imp catalyst**

The 15Cu/SiO<sub>2</sub>-Imp catalyst was prepared by an incipient wetness impregnation method. In a typical procedure, 10 ml silica sol was added into the aqueous solution of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (1.415 g). After the mixture was stirred for 4 h at room temperature, it was stirred until the mixture became dry at 85 °C. Then samples were dried in the oven 100 °C overnight. The catalyst precursors were calcined in static air at 600 °C for 4 h. Prior to the reaction, the as-obtained materials were pre-reduced with 5 vol. % H<sub>2</sub>/Ar at 300 °C for 2 h.

#### **Preparation of reference 15Cu/SiO<sub>2</sub>-SG catalyst**

The 15Cu/SiO<sub>2</sub>-SG catalyst was prepared by sol-gel method according to previous literature.<sup>S2</sup> 52.608 g TEOS, 46.46 g ethanol and 50 g H<sub>2</sub>O were mixed. After stirring for 2 h, the above mixture was poured into a plastic container and 15 % NH<sub>3</sub> was added to adjusted the PH value to 11. The mixture was stirring homogeneously and kept at 50 °C for 5 h for gelation. Then the temperature was raised to 75 °C to evaporate most of

the ethanol and ammonia until no remarkable shrinkage was detected. The resulting gel was dried again by raising the temperature to 100 °C and maintaining for 24 h. The dried solid was fully washed with deionized water and again dried at 120 °C for 12 h. The catalyst precursors were calcined in static air at 600 °C for 4 h. Prior to the reaction, the as-obtained materials were pre-reduced with 5 vol. % H<sub>2</sub>/Ar at 300 °C for 2 h.

#### **Preparation of reference 15Cu/ZrO<sub>2</sub> catalyst**

Cu/ZrO<sub>2</sub> catalyst was prepared by an oxalate gel co-precipitation method previously developed by our group.<sup>S3</sup> In brief, 14.5 g Zr(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O and 3.2 g Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O were dissolved in 380 ml alcoholic solution. Then an alcoholic solution of 20 % excess of oxalic acid was injected rapidly into the above solution at room temperature under vigorous stirring. After 2 h stirring, the resultant gel-like precipitates were separated by filtration followed by air drying at 100 °C overnight. Then the as-obtained materials were calcined in a muffle oven at 600 °C for 4 h. Prior to the reaction, 15CuO/ZrO<sub>2</sub> was pre-reduced with 5 vol.% H<sub>2</sub>/Ar at 300 °C for 2 h to obtain their reduced forms.

#### **Preparation of reference 15Cu/CeO<sub>2</sub> catalyst**

The 15Cu/CeO<sub>2</sub> was prepared according to the procedure for preparation of 15Cu/ZrO<sub>2</sub> as described above.

#### **Preparation of reference 15Cu/Al<sub>2</sub>O<sub>3</sub> catalyst**

The 15Cu/Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by a conventional carbonate co-precipitation method. Typically, 1.5 g Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and 0.3 g Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O were dissolved in 50 ml aqueous solution. Then sodium carbonate (0.1 M) were added slowly and simultaneously at 80 °C under vigorous stirring. The pH was kept constant at 6.5-7.0. After 4 h stirring, the precipitates were separated by filtration followed by drying at 100 °C overnight. Then, the as-obtained material was calcined in a muffle oven at 600 °C for 4 h. Prior to the reaction, 15Cu/Al<sub>2</sub>O<sub>3</sub> was pre-reduced with 5 vol. % H<sub>2</sub>/Ar at 300 °C for 2 h to obtain their reduced forms.

### **3. Catalyst characterization**

**Elemental analysis:** The Cu loading of the catalyst was analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES; IRIS Intrepid).

**BET analysis:** The BET surface area (BET) was measured using N<sub>2</sub> physisorption at

77 K on a Micromeritics TriStar 3000 apparatus. Sample degassing was carried out at 120 °C prior to acquiring the adsorption isotherm.

**X-ray diffraction (XRD) analysis:** XRD analysis of the catalysts was carried out on a Germany Bruker D8Advance X-ray diffractometer using nickel filtered Cu K $\alpha$  radiation with a scanning angle ( $2\theta$ ) of 20–80°, a scanning speed of 2 ° min<sup>-1</sup>, and a voltage and current of 40 kV and 40 mA.

**X-ray photoelectron spectroscopy (XPS):** XPS data were recorded with a Perkin Elmer PHI 5000C system equipped with a hemispherical electron energy analyzer. The spectrometer was operated at 15 kV and 20 mA, and a magnesium anode (Mg K $\alpha$ ,  $h\nu$  = 1253.6 eV) was used. The C 1s line (284.6 eV) was used as the reference to calibrate the binding energies (BE).

**High resolution transmission electron microscopy (HRTEM):** HRTEM images for catalysts were taken with a JEM-2100F electron microscope operating at 200 kV. The samples for electron microscopy were prepared by grinding and subsequent dispersing the powder in ethanol and applying a drop of very dilute suspension on carbon-coated grids.

**Temperature-programmed reduction (TPR):** TPR profiles were obtained on a homemade apparatus loaded with 50 mg of catalyst. Prior to TPR test, the sample was pretreated in an Ar flow of 30 mL min<sup>-1</sup> at 120 °C for 1 h, then cooled down to room temperature and purged with a flow (50 mL/min) of 5 vol. % H<sub>2</sub>/Ar mixture and heated from room temperature to 500 °C at a ramp of 10 °C min<sup>-1</sup>. The H<sub>2</sub> consumption was monitored on-line by the chemical adsorption analyzer. The reduction peak was calibrated against that of the complete reduction of a known standard of powdered CuO (Aldrich, 99.995%).

**NH<sub>3</sub>-Temperature-programmed desorption (NH<sub>3</sub>-TPD):** Typically, the sample (50 mg) loaded in a quartz reactor was pretreated with high-purity Ar at 200 °C for 1 h.

After cooling the sample to 60 °C, NH<sub>3</sub> adsorption was performed by switching the Ar flow to a NH<sub>3</sub> gas until adsorption saturation. The gas-phase (and/or weakly adsorbed) NH<sub>3</sub>, was purged by Ar at the same temperature for about 1h. NH<sub>3</sub>-TPD was then performed in the Ar flow by raising the temperature to 700 °C at a rate of 10 °C min<sup>-1</sup>. The desorbed NH<sub>3</sub> molecules were monitored by an OmniStar mass spectrometer (QMS-200).

**N<sub>2</sub>O titration:** The specific surface area of metallic copper was measured by the adsorption and decomposition of N<sub>2</sub>O on the surface of metallic copper as follows<sup>[S4]</sup>: Shortly, 50 mg catalyst was reduced at 400°C in a 5 vol.% H<sub>2</sub>/Ar flow for 30 min using a 5°C/min heating rate. Then, it was exposed to 10 vol.% N<sub>2</sub>O/Ar flow (50 mL/min) for 1 h at 90°C to oxidize the surface Cu<sup>0</sup> to Cu<sub>2</sub>O. Finally, the sample was flushed with Ar and cooled to 40°C to start a H<sub>2</sub>-TPR program. Copper dispersion was calculated by dividing the amount of chemisorption sites into total supported copper atoms; the copper surface area was calculated by assuming spherical shape of the copper metal particles and  $1.47 \times 10^{19}$  copper atoms/m<sup>2</sup>.

#### 4. Catalytic activity measurements

##### **General procedure for selective hydrogenation of nitrocyclohexane**

Nitrocyclohexane hydrogenation was carried out in a 25 mL Teflon-lined stainless-steel autoclave equipped with temperature detector and pressure control. For hydrogenation of nitrocyclohexane, 0.77 mmol of nitrocyclohexane, 5 mL ethylenediamine solvent and 0.02 g catalyst were added into the autoclave. After being sealed, the reactors were flushed with H<sub>2</sub> and then pressurized at 1 MPa, and then heated to the required temperature (typically 100 °C). The catalysts were removed from the solution by filtration when the reaction was finished. Conversion and yields of products were determined by GC with WAX capillary column (Aliginet) using n-dodecane as an internal standard. The products were identified by GC–MS and by comparison with commercially pure products.

##### **Procedure for 50-mmol scale and recycling experiments**

A mixture of nitrocyclohexane (50 mmol), 0.5g 15Cu/SiO<sub>2</sub>-AE and 50 mL ethylenediamine solvent were charged into an autoclave (250 mL capacity). The

resulting mixture was vigorously stirred (1000 rpm with a magnetic stir bar) at 100 °C under H<sub>2</sub> atmosphere (2 MPa) for given reaction time. After the completion of the reaction, the reaction mixture was extracted with EtOH for 3 times and the catalyst was filtered and washed thoroughly with ethanol. The catalyst was dried under vacuum at room temperature for 12 h. Then it was subjected to calcination in air at 600 °C for 4 h and reduced with 5 vol. % H<sub>2</sub>/Ar at 300 °C for 2 h to obtain the reused catalyst. In the four successive cycles, the yields of CHO were 91%, 90%, 88%, 87% (GC analysis), respectively.

#### **Procedure for hydrogenation of cyclohexanone oxime**

A mixture of cyclohexanone oxime (0.77 mmol), 15CuSiO<sub>2</sub>-AE catalyst (20 mg) and ethylenediamine (5 ml) was put into a batch reactor (25 mL). After sealing the reactor, H<sub>2</sub> (1 MPa) was fed to the reactor via a gas inlet tube. The reaction mixture was stirred at 100 °C for 3 h. The conversion and product selectivity were periodically determined by GC with WAX capillary column (Alignet) using n-dodecane as an internal standard.

#### **Procedure for hydrogenation of cyclohexanone oxime in the presence of water**

A mixture of cyclohexanone oxime (0.77 mmol), 15CuSiO<sub>2</sub>-AE catalyst (20 mg), ethylenediamine (5 ml) and water (0.77 mmol) was put into a batch reactor (25 mL). After sealing the reactor, H<sub>2</sub> (1 MPa) was fed to the reactor via a gas inlet tube. The reaction mixture was stirred at 100 °C for 3 h. The conversion and product selectivity were periodically determined by GC with WAX capillary column (Alignet) using n-dodecane as an internal standard.

#### **Procedure for reaction of cyclohexanone oxime in the absence of hydrogen**

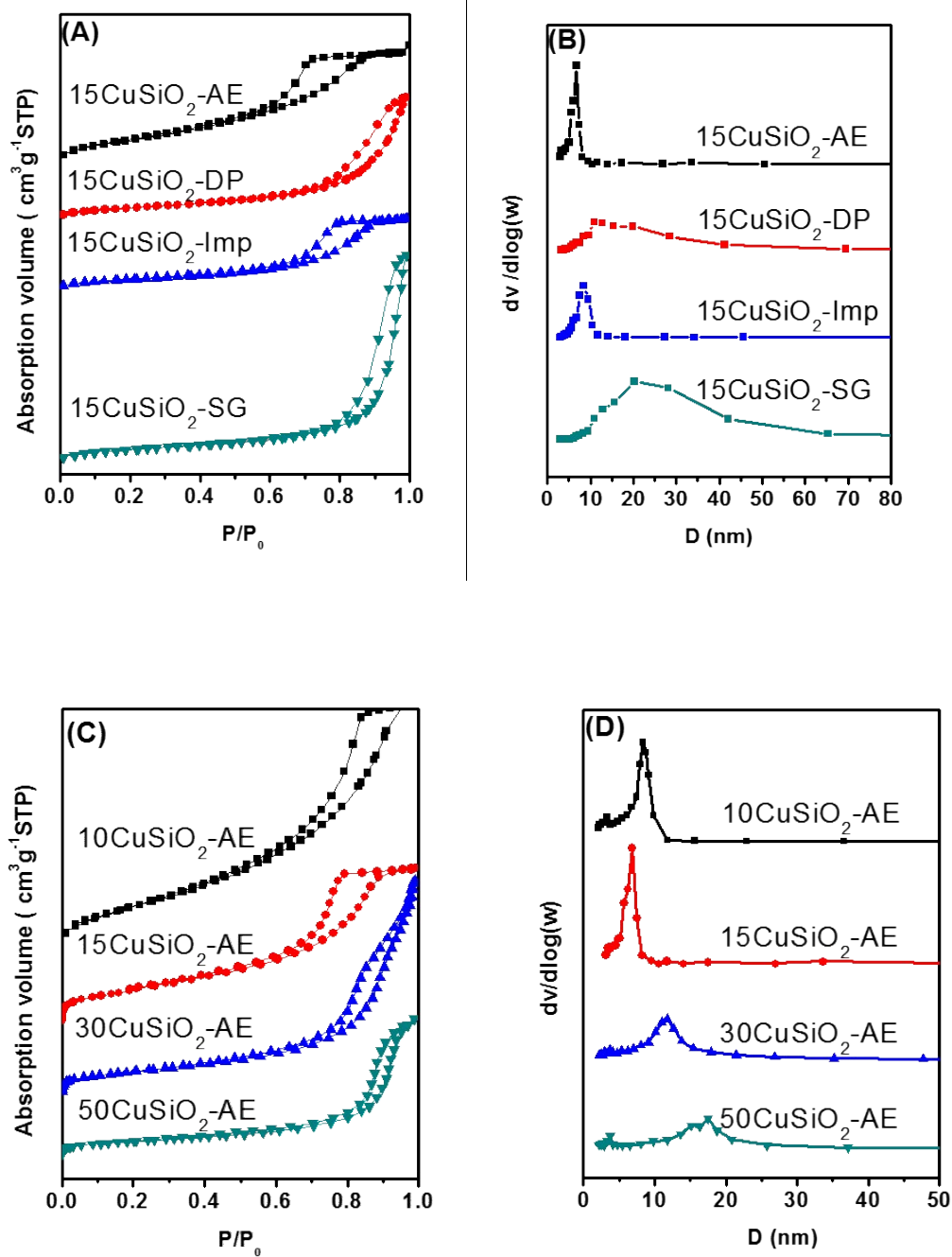
A mixture of cyclohexanone oxime (0.77 mmol), 15CuSiO<sub>2</sub>-AE catalyst (20 mg) and ethylenediamine (5 ml) was put into a batch reactor (25 mL). After sealing the reactor, the reaction mixture was stirred at 100 °C for 3 h. The conversion and product selectivity were periodically determined by GC with WAX capillary column (Alignet) using n-dodecane as an internal standard.

#### **Procedure for hydrogenation of nitrocyclohexane in the presence of water**

A mixture of cyclohexanone oxime (0.77 mmol), 15CuSiO<sub>2</sub>-AE catalyst (20 mg), ethylenediamine (5 ml) and water of different equivalent (0.5, 5 and 20 equivalent of nitrocyclohexane, respectively) was put into a batch reactor (25 mL). After sealing the

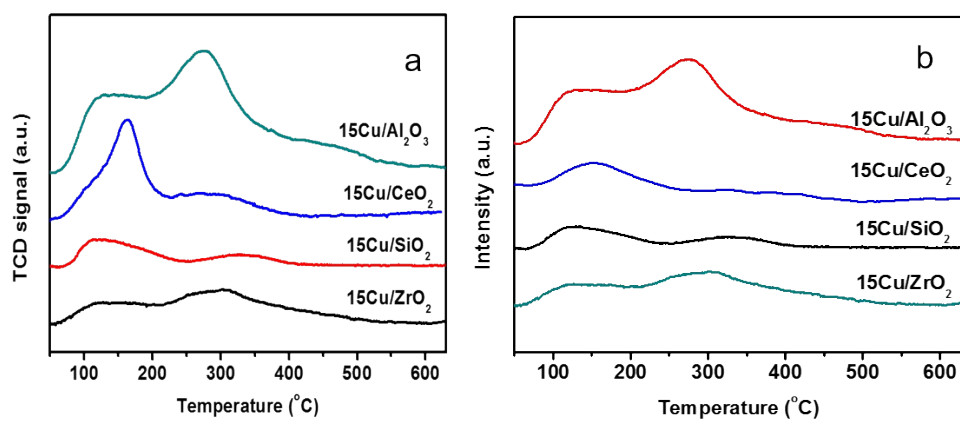
reactor, H<sub>2</sub> (1 MPa) was fed to the reactor via a gas inlet tube. The reaction mixture was stirred at 100 °C for 3 h. The conversion and product selectivity were periodically determined by GC with WAX capillary column (Aliginet) using n-dodecane as an internal standard

## 5. Results

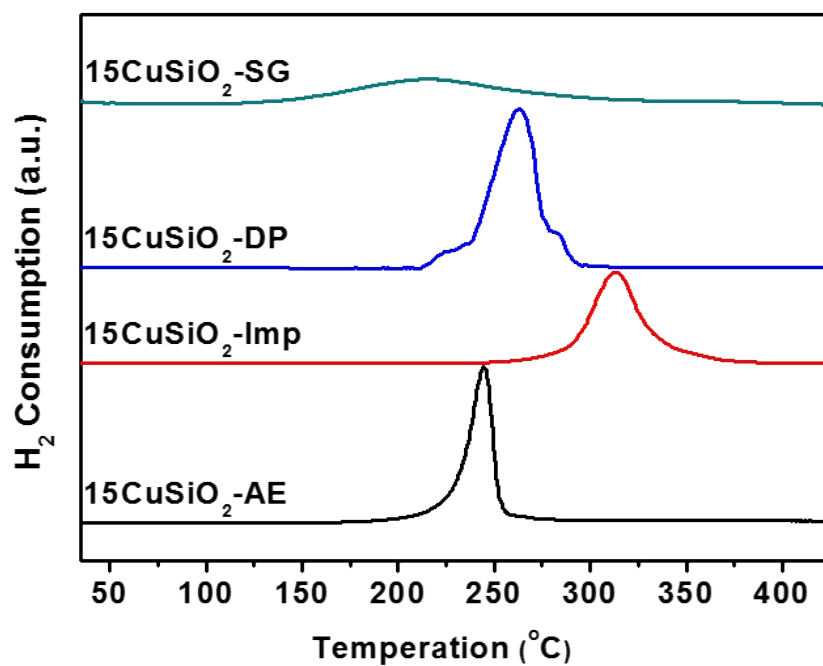


**Figure S1.** (A) N<sub>2</sub> adsorption-desorption isotherms and (B) pore size distribution curves of 15Cu/SiO<sub>2</sub> prepared by different methods. (C) N<sub>2</sub> adsorption-desorption isotherms and (D) pore size distribution curves of Cu/SiO<sub>2</sub>-AE catalysts with different Cu loading.

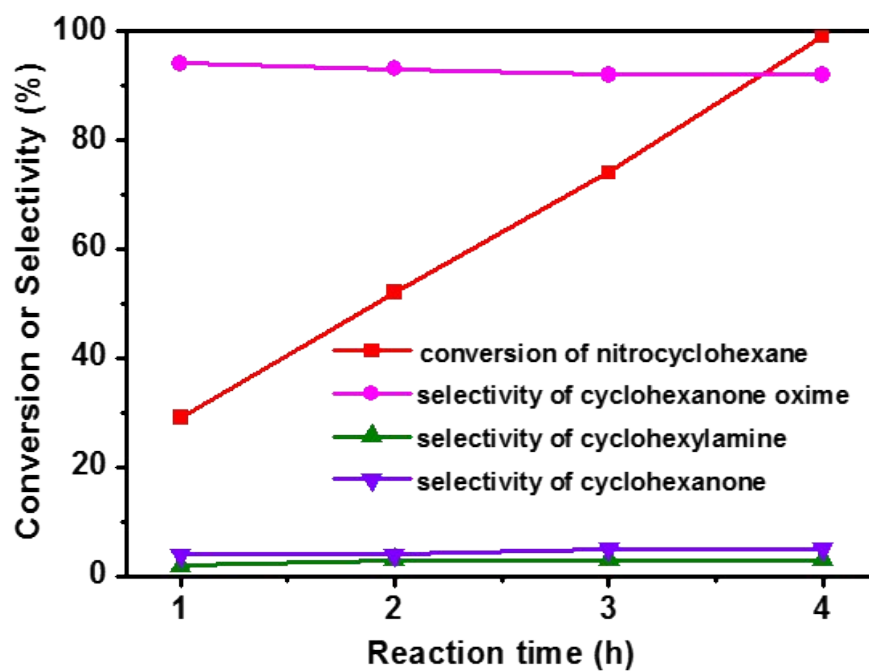




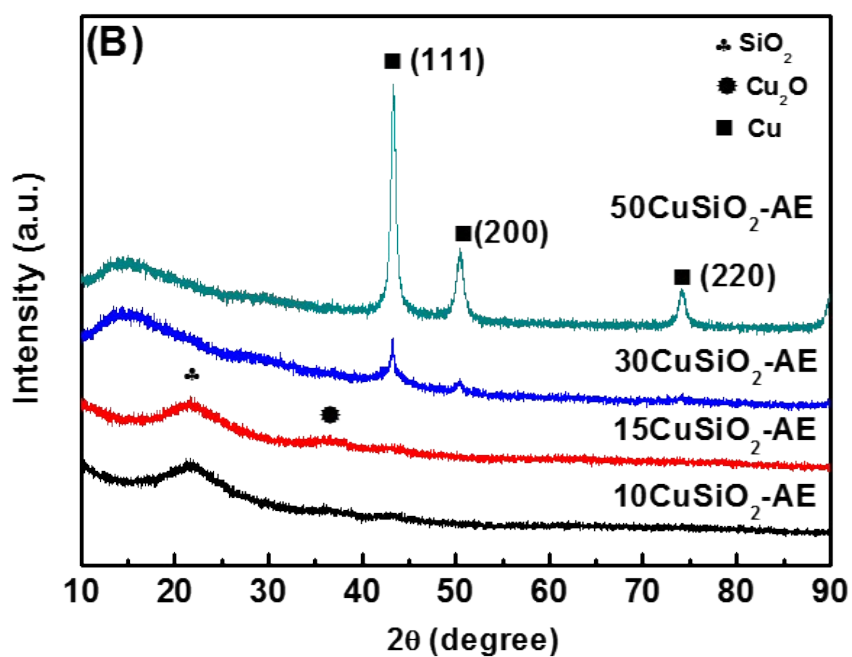
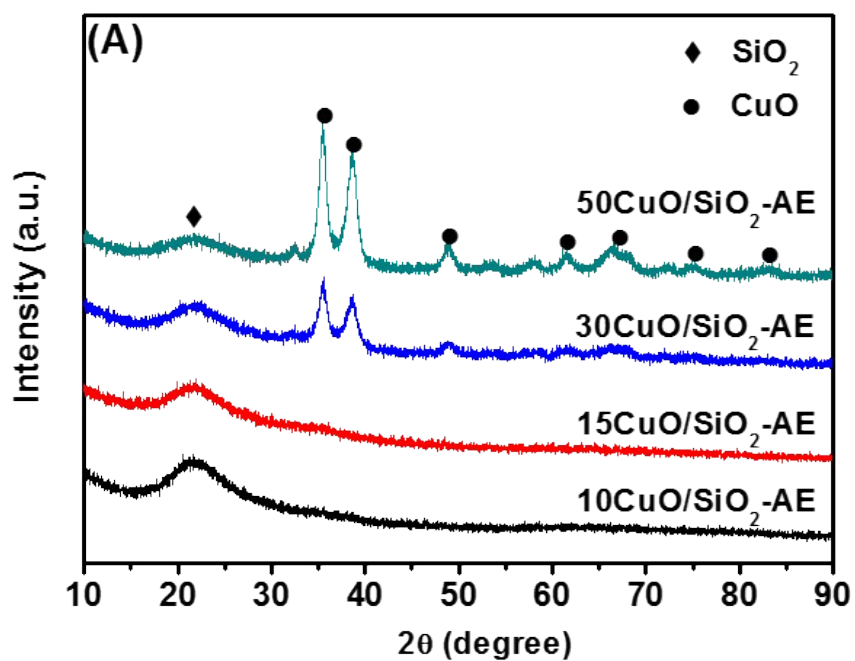
**Figure S2.** NH<sub>3</sub>-TPD profiles of the reduced Cu-based catalysts(a) TCD signal, (b) MS signal.



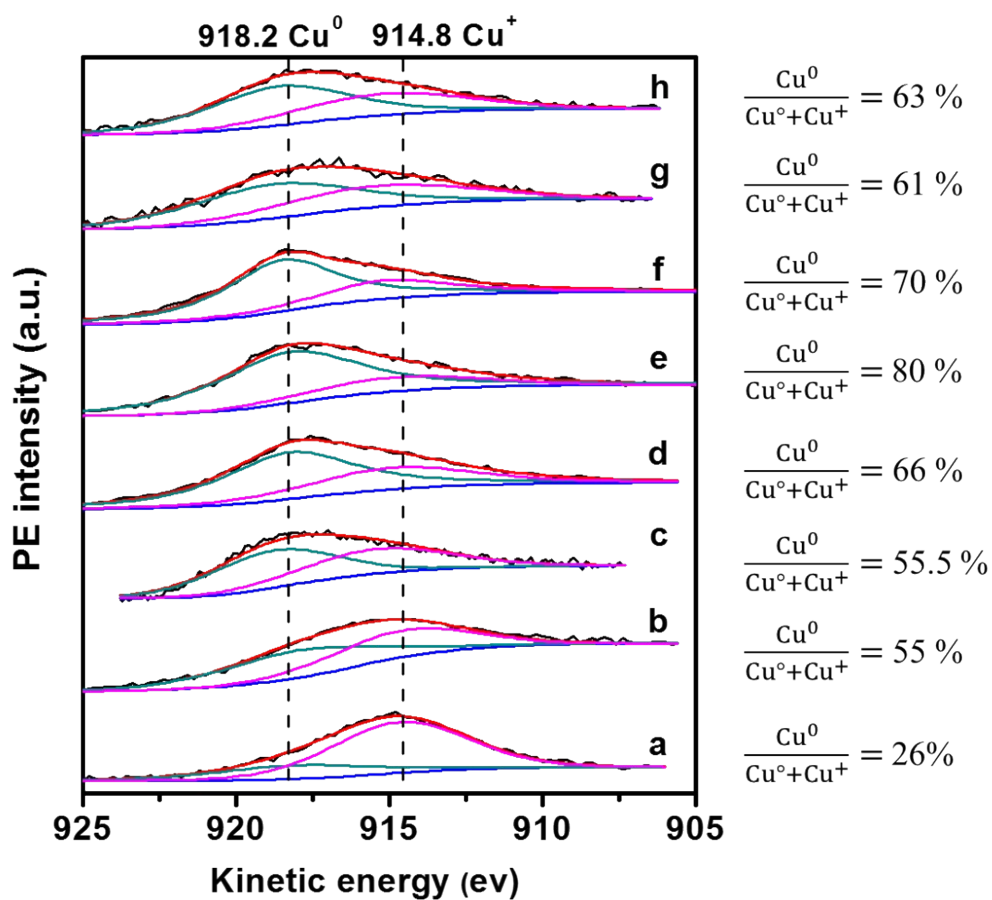
**Figure S3.** H<sub>2</sub>-TPR profiles of the unreduced 15Cu/SiO<sub>2</sub> catalysts prepared by different methods.



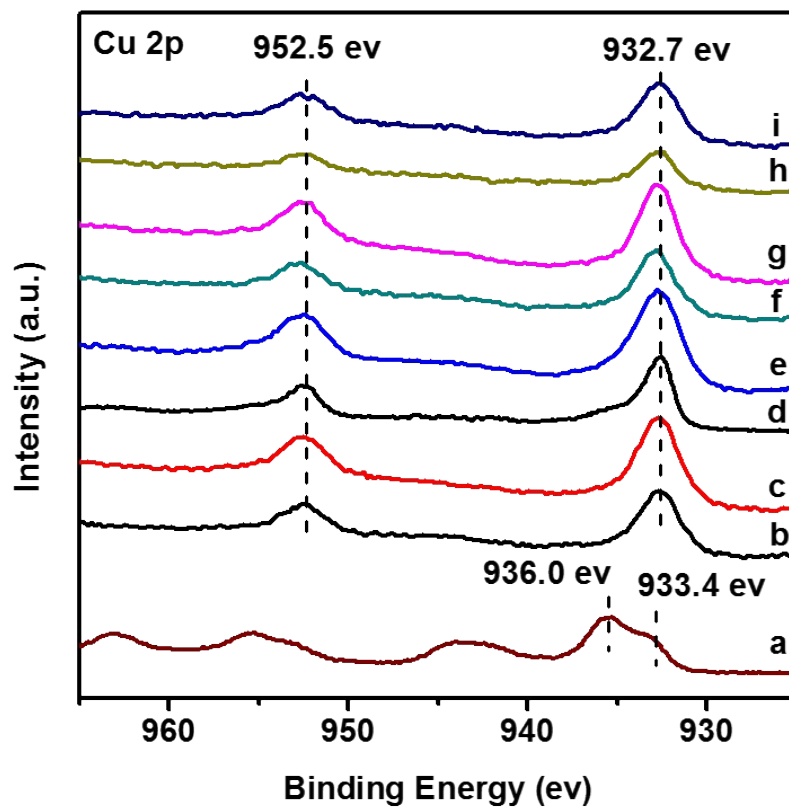
**Figure S4.** Effect of reaction time on nitrocyclohexane hydrogenation over 15Cu/SiO<sub>2</sub>-AE catalyst. Reaction conditions: nitrocyclohexane 0.77 mmol, catalyst 20 mg, ethylenediamine 5 mL, H<sub>2</sub> 1 MPa, reaction temperature 100 °C.



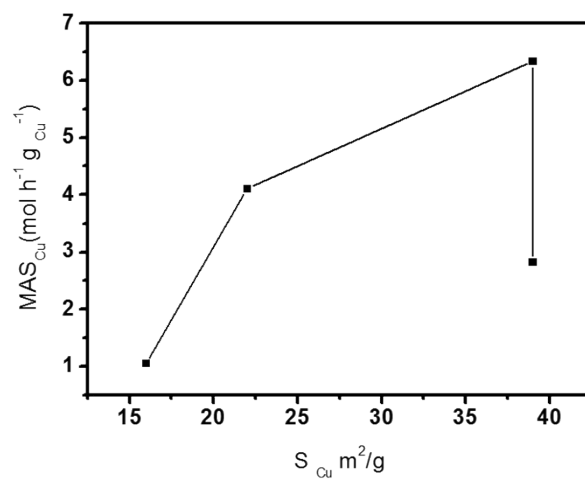
**Figure S5.** XRD Patterns of the prepared Cu/SiO<sub>2</sub>-AE catalysts with different Cu loading. A: after calcination and B: after reduction.



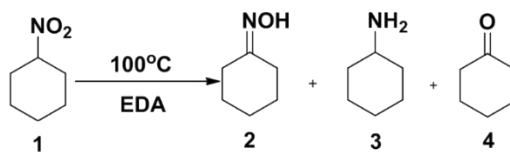
**Figure S6.** Cu LMM Auger spectra of the reduced Cu/SiO<sub>2</sub> catalysts. (a) 10Cu/SiO<sub>2</sub>-AE, (b) 15Cu/SiO<sub>2</sub>-AE, (c) 15Cu/SiO<sub>2</sub>-AE-used, (d) 30Cu/SiO<sub>2</sub>-AE, (e) 50Cu/SiO<sub>2</sub>-AE, (f) 15Cu/SiO<sub>2</sub>-DP, (g) 15Cu/SiO<sub>2</sub>-Imp and (h) 15Cu/SiO<sub>2</sub>-SG.



**Figure S7.** XPS spectra of (a) unreduced 15Cu/SiO<sub>2</sub>-AE sample and reduced Cu/SiO<sub>2</sub> catalysts: (b) 10Cu/SiO<sub>2</sub>-AE, (c) 15Cu/SiO<sub>2</sub>-AE, (d) 15Cu/SiO<sub>2</sub>-AE-used, (e) 30Cu/SiO<sub>2</sub>-AE, (f) 50Cu/SiO<sub>2</sub>-AE, (g) 15Cu/SiO<sub>2</sub>-DP, (h) 15Cu/SiO<sub>2</sub>-Imp and (i) 15Cu/SiO<sub>2</sub>-SG.



**Figure S8** Correlation of the MAS<sub>Cu</sub> of NC and Cu metal surface area.

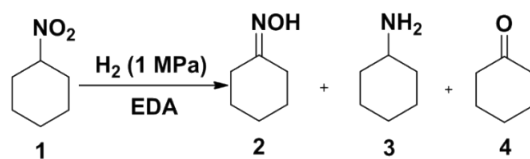
**Table S1** The effect of H<sub>2</sub> Pressure on the catalytic activity and selectivity of DHNC.<sup>a</sup>

Entry	H <sub>2</sub> Pressure (MPa)	Conversion (%)	Selectivity (%)		
			2	3	4
1 <sup>b</sup>	4	96	86	9	5
2	3.5	86	89	7	4
3	2	68	90	5	5
4	1	52	93	3	4
5	0.5	25	94	3	3

<sup>a</sup> nitrocyclohexane 0.77 mmol, 15CuSiO<sub>2</sub>-AE catalyst 20 mg, reaction temperature 100 °C, reaction time 2 h, ethylenediamine 5 mL, <sup>b</sup> Reaction time 1 h.



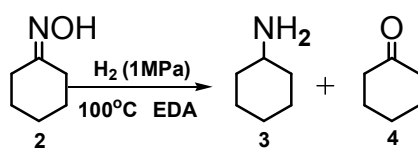
**Table S2** The effect of reaction temperature on the catalytic activity and selectivity of DHNC.<sup>a</sup>



Entry	Temperature (°C)	Conversion (%)	Selectivity (%)		
			2	3	4
1 <sup>b</sup>	120	93	88	7	5
2	100	52	93	3	4
3	80	15	94	3	3
4	60	10	96	2	2

<sup>a</sup> nitrocyclohexane 0.77 mmol, 15CuSiO<sub>2</sub>-AE catalyst 20 mg, H<sub>2</sub> 1 MPa, reaction time 2 h, ethylenediamine 5 mL. <sup>b</sup> Reaction time 1.5 h.

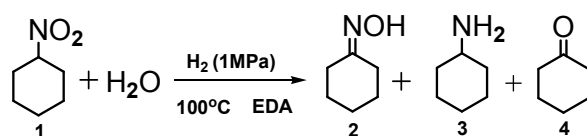
Table S3. The catalytic performance of cyclohexanone oxime as reactant.<sup>a</sup>



Entry	Catalyst	Conv. (%)	Sel. (%)	
			3	4
1	15Cu/SiO <sub>2</sub> -AE	8.8	-	100
2 <sup>b</sup>	15Cu/SiO <sub>2</sub> -AE	11.0	-	100
3 <sup>b,c</sup>	15Cu/SiO <sub>2</sub> -AE	0.5	-	100

<sup>a</sup> cyclohexanone oxime 0.77 mmol, 15CuSiO<sub>2</sub>-AE catalyst 20 mg, ethylenediamine 5 ml, reaction time 3 h. <sup>b</sup> Adding water (0.77 mmol). <sup>c</sup> Absence of hydrogen.

Table S4. The effect of water on the catalytic activity and selectivity of nitrocyclohexane hydrogenation.<sup>a</sup>



Entry	H <sub>2</sub> O <sup>b</sup> (eq)	Conv. (%)	Sel.(%)		
			2	3	4
1	0	74	92	3	5
2	0.5	60	82	5	13
3	5	28	70	6	24
4	20	13	56	9	35

<sup>a</sup> cyclohexanone oxime 0.77 mmol, 15Cu/SiO<sub>2</sub>-AE catalyst 20 mg, ethylenediamine 5 ml, reaction time 3 h. <sup>b</sup> The added amount of water (equivalent of nitrocyclohexane).

## 5. References

- [S1] (a) L. F. Chen, P. J. Guo, M. H. Qiao, S. R. Yan, H. X. Li, W. Shen, H. L. Xu and K. N. Fan, *J. Catal.*, 2008, **257**, 172; (b). J. Yuan, S.S. Li, L. Yu, Y.M. Liu, Y. Cao, H.Y. He, K.N. Fan, *Energy Environ. Sci.*, 2013, **6**, 3308.
- [S2] L. M. He, X. C. Chen, J. S. Ma, H. L. He, and W. Wang, *J. Sol-Gel. Sci. Technol.*, 2010, **55**, 285.
- [S3] L. C. Wang, Q. Liu, M. Chen, Y. M. Liu, Y. Cao, H. Y. He and K. N. Fan, *J. Phys. Chem. C*, 2007, **111**, 16549.
- [S4] (a) A. Gervasini, S. Bennici, *Appl. Catal. A: Gen.* 2005, **281**, 199-205; (b) B. Zhang, Y. Zhu, G. Ding, H. Zheng, Y. Li, *Appl. Catal. A: Gen.* 2012, **443-444**, 191-201.