Optimization of Cu Catalysts for Nitrophenol Reduction, Click Reaction and Alkyne Coupling

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1. Chemicals and reagents

All commercial materials were used without further purification, unless indicated. Deionized water was prepared in the laboratory. Cupric sulfate, manganese sulfate, Cu₂O, CuO, SBA-15, activated carbon, potassium permanganate, nitric acid, 4-nitrophenol, 2,4-dinitrophenol, 4-nitrobenzene diazo tetrafluoroborate, and NaBH₄ were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China, <u>http://www.aladdin-e.</u> com/).

2. Instruments

XRD was recorded on a Rigaku Ultima IV (Rigaku, Japan) of Material Analysis and Testing Center, China Three Gorges University. Transmission electron microscopy (TEM) measurements were performed on a TECNAI F-20 electron microscope (JOEL 2100F, Netherlands) at an accelerating voltage of 200 kV. Surface analysis by XPS was performed in a Thermo SCIENTIFIC ESCALAB 250Xi (ThermoFischer, USA) system spectrometer in an ultra-high vacuum (UHV) chamber. Nitrogen adsorption-desorption measurements were performed at 76K using an ASAP 2020M analyzer utilizing the BET model for the calculation of specific surface areas. The element contents of samples were determined by ICP-AES (ContrAA 700). The reducibility of the catalysts was measured by the hydrogen temperature-programmed reduction (H₂-TPR) technique. A 50 mg of OMS-2, Cu-OMS-2 or CuO_x/OMS-2 was placed in a quartz reactor that was connected to a TPR apparatus and the reactor was heated from r.t. to 550 °C with a heating rate of 10 °C/min. The reducing atmosphere was the mixture of H₂ and N₂ with a total flow rate of 30 mL/min and the amount of H₂ uptake during the reduction was measured by a thermal conductivity detector (TCD).

3. Synthesis of OMS-2

First, 5.89 g of potassium permanganate in 100 mL of neat water was added to a solution of 30 mL of neat water containing 8.8 g manganese sulfate and 3 mL of concentrated nitric acid. The solution was refluxed at 100 °C for 1d. Then the product was filtered, washed, and dried at 120 °C for 8 hours. Finally, the dry OMS-2 was calcined in a muffle furnace at 350 °C for 2 hours. Then, the black powder, OMS-2, was obtained. Further OMS-2 has also been characterized by N_2 adsorption-desorption isotherms, transmission electron microscopy, X-ray diffraction and X-ray photoelectron spectroscopy.

4. Synthesis of CuO_x/OMS-2

First, 2 g OMS-2 and a solution of $Cu(NO_3)_2 \cdot 3H_2O(0.15 \text{ g})$ in neat water (10 mL) were added to a 50 mL roundbottom flask. Another neat water (10 mL) was added to wash down the sides of the flask. Then, the flask was submerged in an ultrasound bath for 3 h at r.t. and stirred for another 20 h at r.t. After that, water was distilled at 80 °C for 3 h. Finally, the black powder was dried in an oven at 110 °C for 4 hours, followed by calcination at 350 °C for 2 hours. The Inductive Coupled Plasma Optical Emission Spectrum showed that the Cu content was 1.31 wt%. First, 4.4 g of manganese sulfate and 0.3623 g of Cu(NO₃)₂·3H₂O in 20 mL of neat water is added to a solution of 30 mL of neat water containing 1.5 mL of concentrated nitric acid and 2.945 g of potassium permanganate. The solution is refluxed at 100 °C for 1d. Then the product is filtered, washed, and dried at 120 °C for 8 hours. Finally, the dry Cu-OMS-2 is calcined in a muffle furnace at 350 °C for 2 hours. Then, the black powder, Cu-OMS-2, was obtained. Cu-OMS-2 has also been characterized by BET, TEM, XRD and XPS.

6. Catalysis of 4-nitrophenol reduction

An aqueous solution (3 mL) containing 4-nitrophenol (2.5×10^{-4} mmol) and NaBH₄ (2.5×10^{-2} mmol) is prepared in a standard quartz cuvette (3 mL, path length: 1 cm). The CuO_X/OMS-2 (10 mg) is added into this solution, and the reaction progress is detected by UV-vis. spectroscopic analysis every min at 25 °C. 2,4-dinitrophenol, 4nitrobenzene diazo tetrafluoroborate are reduced in the same method.

7. The general procedure of the click reaction

The phenylacetylene (0.5 mmol), benzyl azide (0.6 mmol), CuO_X/OMS-2 (10 mg) and 2 mL H₂O are taken into a round bottom flask equipped with stirrer. The resulting mixture is stirred for 24 h at 30 °C. After cooling to room temperature and extraction with acetic ether (3×10 mL), the combined organic phases are washed with brine (2×5 mL), dried over anhydrous MgSO₄ and concentrated under reduced pressure. The residue is subjected to flash column chromatography with hexanes/EtOAc (5:1) as eluent to obtain the desired product as a light yellow solid (93 % yield).



Scheme S1. ¹H NMR spectrum of 1-benzyl-4-phenyl-1H-1,2,3-triazole. ¹H NMR (300 MHz, CDCl₃): δ: 7.80-7.82 (d, J=6.0Hz, 2H), 7.67 (s, 1H), 7.38-7.43 (m, 5H), 7.31-7.35 (m, 3H), 5.60 (s, 2H).

8. Homocoupling of terminal alkynes

0.5 mmol of alkyne, 20 mg of CuO_x/OMS-2, 1 mmol of Et_3N and 2 mL of toluene were taken into a flask equipped with stirrer. The resulting mixture was stirred for 12 h at 100 °C. The reaction mixture was separated with centrifugation and concentrated under reduced pressure. The residue was subjected to flash column chromatography with petroleum ether-EtOAc, (v/v=40:1) as eluent to obtain the desired product (97.7 % yield).



Scheme S2. ¹H NMR spectrum of 1,4-diphenylbuta-1,3-diyne. ¹H NMR (300 MHz, CDCl₃): δ: 7.44-7.47 (m, 5H), 7.26-7.28 (m, 5H),

9. Microscopy images and spectra



Figure S1. (a) STEM image, (b) combined (Cu, Mn, K and O) EDX compositional map, (c) O EDX compositional map, (d) K EDX compositional map, (e) Mn EDX compositional map and (f) Cu EDX compositional map of Cu-OMS-2;



Figure S2. XRD patterns of original OMS-2, CuOx/OMS-2 and Cu-OMS-2.



Figure S3. Consumption rate of 4-nitrophenol: $-\ln(C/C_0)$ vs. reaction time for CuO_x/OMS-2



Figure S4. Consumption rate of 4-nitrophenol $-\ln(C/C_0)$ versus reaction time for Cu-OMS-2



Figure S5. UV-vis. spectra of the degradation of 4-nitrophenol monitored at 25 °C for OMS-2



Figure S6. UV-vis. spectra of 4-nitrobenzene diazo tetrafluoroborate degradation monitored at 25 °C for $CuO_x/OMS-2$.



Figure S7. Consumption rate of 4-aminobenzene diazo tetrafluoroborate: $-\ln(C/C_0)$ versus reaction time for $CuO_x/OMS-2$



Figure S8. UV-vis. spectra of the degradation of 2,4-dinitrophenol monitored at 25 °C for CuO_x/OMS-2.



Figure S9. Consumption rate of 2,4-diaminophenol: -ln(C/C₀) versus reaction time for CuO_x/OMS-2



Figure S10. Possible reaction path for the CuO_x/OMS -2-catalyzed alkyne homocoupling via coupled electron-

transfer reactions.



Figure S11. The homocoupling reaction using the recycled $CuO_x/OMS-2$ for 5 times



Figure S12. UV-vis. spectra of the degradation of 4-nitrophenol monitored at 25 °C for CuO_x/OMS-2 at 2nd run.



Figure S13. UV-vis. spectra of the degradation of 4-nitrophenol monitored at 25 °C for CuO_x/OMS-2 at 3rd run.



Figure S14. UV-vis. spectra of the degradation of 4-nitrophenol monitored at 25 °C for CuO_x/OMS-2 at 4th run.



Figure S15. UV-vis. spectra of the degradation of 4-nitrophenol monitored at 25 °C for CuO_x/OMS-2 at 5th run.



Figure S16. UV-vis. spectra of the degradation of 4-nitrophenol monitored at 25 °C for CuO_x/OMS-2 at 6th run.



Figure S17. UV-vis. spectra of the degradation of 4-nitrophenol monitored at 25 °C for CuO_x/OMS-2 at 7th run.



Figure S18. UV-vis. spectra of the degradation of 4-nitrophenol monitored at 25 °C for CuO_x/OMS-2 at 8th run.



Figure S19. UV-vis. spectra of the degradation of 4-nitrophenol monitored at 25 °C for CuO_x/OMS-2 at 9th run.



Figure S20. UV-vis. spectra of the degradation of 4-nitrophenol monitored at 25 °C for CuO_x/OMS-2 at 10th run.