Multiwall carbon nanotube-pillared layered Cu_{0.4}/Mg_{5.6}Al₂O_{8.6}: an

efficient catalyst for hydrogenolysis of glycerol

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1 Experimental

1.1 Pretreatment of MWCNTs

MWCNTs with the diameter range of 20-45 nm that prepared by a conventional CVD method were purchased from Shenzhen Nanotech Port Co., Ltd. And before catalyst preparation, MWCNTs were first pretreated in HNO₃ (65-68 wt%). The slurry was stirred and kept refluxing at 75 °C for 11 h. Then the solid was filtered out and washed with distilled water until the pH of effluent reached 7.0. The pretreated MWCNTs were dried in vacuum at 80 °C for 10 h.

1.2 Preparation of MWCNT-pillared layered Cu_{0.4}/Mg_{5.6}Al₂O_{8.6}

MWCNT-pillared layered $Cu_{0.4}/Mg_{5.6}Al_2O_{8.6}$ was prepared by a coprecipitation method. Calculated amount of $Cu(NO_3)_2 \cdot 3H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$ (AR, Sinopharm Chemical Reagent Co., Ltd, China) were dissolved together in 400 mL deionized water, which was referred as solution A. Solution B was the mixture of Na_2CO_3 and NaOH (AR, Sinopharm Chemical Reagent Co., Ltd, China) with concentrations of 0.25 and 0.8 mol/L, respectively. A certain amount of pretreated MWCNTs were first dispersed in 200 ml deionized water in ultrasonic bath (200 w) for 30min. Solution A and B were simultaneously added into the solution with pretreated MWCNTs under vigorous stirring at room temperature and a pH value of 9.5. The obtained slurry was aged overnight at the room temperature, filtered off, and washed thoroughly with deionized water. The fresh precipitate was then dried at 80 °C overnight and identified as (x%)MWCNT-Cu_{0.4}Mg_{5.6}Al₂(OH)₁₆CO₃, where x% represented mass percentage of MWCNT/Cu_{0.4}Mg_{5.6}Al₂(OH)₁₆CO₃.

Secondly, (x%)MWCNTs-Cu_{0.4}Mg_{5.6}Al₂(OH)₁₆CO₃ were calcined at 400 °C in a stationary air

for 4 h and the calcined product catalysts were identified as $(x\%)MWCNT-Cu_{0.4}Mg_{5.6}Al_2O_9$. After hydrogen reduction at 300 °C for 1 h, these catalysts were denoted as $(x\%)MWCNT-Cu_{0.4}/Mg_{5.6}Al_2O_{8.6}$.

2 Characterization

The elemental compositions of Cu, Mg and Al of the catalysts were detected on an inductively coupled plasma-atomic emission spectroscopy equipment (ICP, plasma-Spec-II spectrometer, Perkin-Elmer Optima 2000 instrument). N₂ adsorption was measured at its normal boiling point using an ASAP 2010 analyzer (Micromeritics) after pretreated at 250 °C for 4 h in vacuum. Surface area and pore size distribution were calculated using their adsorption isotherms. X-ray diffraction (XRD) patterns were detected at room temperature on a Rigaku D/WAX-2500 diffractometer using Cu K*a* radiation (λ =1.5406 Å) with a 20 step of 0.02°.

Temperature programmed reduction (TPR) studies were carried out in a quartz reactor. Samples were first pretreated at 400 °C for 1 h under N_2 at a flow rate of 30 mL/min and cooled to room temperature. A reduction agent (10% H₂/N₂ mixture, 30 mL/min) was shifted and the reactor was heated to 450 °C at a ramp of 10 °C/min. Effluent gas was dried by powder KOH and the consumption of hydrogen were recorded by thermal conductivity detector (TCD). Calibration of the instrument was carried out with CuO (AR, Sinopharm Chemical Reagent Co., Ltd, China) of known amount.

The number of surface metallic copper sites was determined by N_2O oxidation and followed H_2 titration using the procedure described by Van Der Grift et al.¹ Catalysts were first reduced in the procedure described in above TPR experiment in 10% H_2/N_2 mixture at a flow rate of 30 mL/min until 450 °C. The amount of hydrogen consumption in the first TPR was denoted as *X*. And then the reactor was purged with He to 50 °C. 20% N_2O/N_2 (30 mL/min) was shifted to oxidize surface copper atoms to Cu₂O at 50 °C for 0.5 h. The reactor was flushed with He to remove the oxidant. Finally, another TPR experiment was performed in 10% H_2/N_2 at a flow rate of 30 mL/min. Hydrogen consumption in the second TPR was denoted as *Y*. The dispersion and surface area of the surface Cu were calculated according to these equations reported by Van Der Grift et al., which are shown below:

Reduction of all copper atoms:

 $CuO + H_2 \rightarrow Cu + H_2O$, hydrogen consumption in the first TPR = X

Reduction of surface copper atoms only:

 $Cu_2O + H_2 \rightarrow 2Cu + H_2O$, hydrogen consumption in this TPR = Y

And the dispersion and surface area of the surface Cu were calculated as:

 $D = (2 \times Y/X) \times 100\%$

 $S = 2 \times Y \times N_{av}/(X \times M_{Cu} \times 1.4 \times 10^{19}) = 1353 \times Y/X \text{ (m}^2\text{-}Cu/g\text{-}Cu)$

In these equations, N_{av} is the Avogadro's constant, M_{Cu} is the relative atomic mass of copper (63.46 g/mol), 1.4×10^{19} is the number of copper atom of per square meter because the average surface area of copper atom is assigned to 7.11×10^{-2} nm².

Average volume-surface diameter can be expressed as a function:

 $d_{v.s.} = 6/(S \times \rho_{Cu}) \approx 0.5 \times X/Y \text{ (nm)}$

 ρ_{Cu} in above equation is the density of copper (8.92 g/cm³).

The H₂ activation activities of the reduced catalysts were carried out via temperature-programmed desorption of H₂ (H₂-TPD). Sample was first reduced at 350 °C in H₂ flow of 30 mL/min for 1 h, purged by purified Ar and further treated at 450 °C for 0.5 h in Ar. And then the reactor was cooled to 50 °C in Ar, exposed to 10% H₂/Ar for 30 min, purged by Ar for 5 h at 50 °C in order to eliminate the physically adsorbed H₂. Temperature-programmed desorption (TPD) was conducted by ramping to550 °C and H₂ (*m/e*=2) in effluent was detected and recorded as a function of temperature on a quadrupole mass spectrometer (OmniStarTM, GSD301, Switzerland).

3 Catalytic reactions

Hydrogenolysis of glycerol was performed in a custom-designed 50 mL stainless steel autoclave equipped with a thermoelectric couple. Before reaction, catalyst was pretreated in a stream of H₂ at 300 °C for 1 h. The reaction mixture included an aqueous solution of glycerol (60 wt%) 5.0 g and 0.2 g reduced catalyst. Then the autoclave was purged with H₂ to 2.0 MPa and placed in an oil bath preheated to required temperature and maintained at that temperature for a given time under vigorously stirring with a magnetic stirrer (MAG-NEO, RV-06 M, Japan). After reaction, the reactor was cooled to room temperature. Vapor phase was collected by a gas-bag and analyzed with a gas chromatograph (Shimadzu, 8 A) with TCD detector, liquid phase was centrifuged to remove solid catalyst powder and analyzed using a FID gas chromatograph (Shimadzu, 14 B) equipped with a 30 m capillary column (DB-WAX 52 CB, USA). All products

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detected in liquid were verified by a gas chromatography and mass spectrometry system (GC-MS, Agilent 6890) and quantified via external calibration method. The selectivity of products was calculated on carbon basis. Solid catalyst was collected by **centrifugation, and** washed with a mixed ethanol/water (2/1 in mol) solution several times to remove residual glycerol, and then it was added in the reaction mixture again.

Supplementary Results

XRD



Fig. S1 XRD patterns of fresh (x%)MWCNT-Cu_{0.4}Mg_{5.6}Al₂(OH)₁₆CO₃.

(A) $Cu_{0.4}Mg_{5.6}Al_2(OH)_{16}CO_3$; (B) (1.5%)MWCNT- $Cu_{0.4}Mg_{5.6}Al_2(OH)_{16}CO_3$; (C) (3%)MWCNT- $Cu_{0.4}Mg_{5.6}Al_2(OH)_{16}CO_3$; (D) (6%)MWCNT- $Cu_{0.4}Mg_{5.6}Al_2(OH)_{16}CO_3$; (E) pure MWCNT



- Fig. S2 XRD patterns of calcined catalysts

TEM images



Fig.S3 TEM images of reduced (3%)MWCNT-Cu_{0.4}/Mg_{5.6}Al₂O_{8.6} catalyst (a-b).

H₂-TPR



Fig.S4 The reducibility profile of calcined catalysts.

(A) $Cu_{0.4}Mg_{5.6}Al_2O_9$; (B) (1.5%)MWCNT- $Cu_{0.4}Mg_{5.6}Al_2O_9$; (C) (3%)MWCNT- $Cu_{0.4}Mg_{5.6}Al_2O_9$; (D) (6%)MWCNT- $Cu_{0.4}Mg_{5.6}Al_2O_9$







(A) $Cu_{0.4}/Mg_{5.6}Al_2O_{8.6}$; (B) (1.5%)MWCNT- $Cu_{0.4}/Mg_{5.6}Al_2O_{8.6}$; (C) (3%)MWCNT- $Cu_{0.4}/Mg_{5.6}Al_2O_{8.6}$; (D) (6%)MWCNT- $Cu_{0.4}/Mg_{5.6}Al_2O_{8.6}$

Time course



Fig.S6 Time course of glycerol hydrogenolysis over (3%)MWCNT-Cu_{0.4}/Mg_{5.6}Al₂O_{8.6} catalyst

Recycles	Conversion	Activity of surface Cu	Selectivity (%)	
	(%)	$(h^{-1})^{b}$	1,2-PDO	Others ^c
1	64.8	17.2	99.3	0.7
2	47.5		99.1	0.9
3	42.4		98.8	1.2
4	42.2		98.7	1.3
5	41.8	16.6	98.8	1.2

Table S1 Hydrogenolysis of glycerol on recycled (3%)MWCNT-Cu_{0.4}/Mg_{5.6}Al₂O_{8.6} catalysts^a

^{*a*} Reaction conditions: 5 g glycerol aqueous solution (60 wt%), 180 $^{\circ}$ C, 2.0 MPa H₂, 0.2 g reduced catalyst, 10 h.

^b defined as (mol of converted glycerol)/(mol of exposed Cu atom)/(reaction time, h).

^c Ethylene glycol, methanol and 1-propanol

Sample —	Composition (mol %)			
	Cu	Mg	Al	
Fresh	5.17 (5.00)	69.52 (70.00)	25.31 (25.00)	
Used ^b	5.03 (5.00)	69.81 (70.00)	25.16 (25.00)	

Table S2 Compositions of fresh and recycled (3%)MWCNT-Cu_{0.4}/Mg_{5.6}Al₂O_{8.6} catalysts^{*a*}

^{*a*} The values in parentheses are controlled values.

^b The used (3%)MWCNT-Cu_{0.4}/Mg_{5.6}Al₂O_{8.6} catalyst has been recycled five times.

References:

1. C. J. G. Van Der Grift, A. F. H. Wielers, B. P. J. Jogh, J. Van Beunum, M. De Boer, M. Versluijs-Helder and J. W. Geus, *J. Catal.*, 1991, 131, 178-189.