

# A thermally stable and easily recycled core-shell Fe<sub>2</sub>O<sub>3</sub>@CuMgAl catalyst for hydrogenolysis of glycerol

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## 1 Experimental

FeCl<sub>3</sub>·6H<sub>2</sub>O (AR, Sinopharm Chemical Reagent Co., Ltd, China, 13.5 g), NaAc·3H<sub>2</sub>O (AR, Sinopharm Chemical Reagent Co., Ltd, China, 36.0 g) and **polyethylene glycol** (AR, Sinopharm Chemical Reagent Co., Ltd, China, 10.0 g) were dissolved together in 400 mL ethylene glycol (AR, Sinopharm Chemical Reagent Co., Ltd, China). After stirred vigorously for 30 min, a stable suspension was formed. Then the mixture was sealed in a stainless autoclave (500 mL capacity) with a Teflon inner layer. The autoclave was kept at 200 °C for 8 h under gentle stirring and then cooled to room temperature. The resulting products were separated by an external magnetic field, washed several times with ethanol and water and dried at 60 °C overnight, giving the black ferroferric oxide powder.

Magnetic Fe<sub>2</sub>O<sub>3</sub>@CuMgAl catalysts were prepared in coprecipitation. First, a certain amount of Fe<sub>3</sub>O<sub>4</sub> nanoparticles were dispersed in 150 ml methanol solution in ultrasonic bath (200 w) for 30 min to give a uniform suspension. Calculated amount of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (AR, Sinopharm Chemical Reagent Co., Ltd, China) were dissolved together in 100 mL methanol-water solution ( $V_{\text{methanol}}/V_{\text{water}}=1/19$ ), which was referred as solution A. Solution B was the mixed aqueous solution of Na<sub>2</sub>CO<sub>3</sub> and NaOH (AR, Sinopharm Chemical Reagent Co., Ltd, China) with concentrations of 0.1 and 0.2 mol/L, respectively. Solution A and B were simultaneously added into the solution with pretreated Fe<sub>3</sub>O<sub>4</sub> microspheres under vigorous stirring at room temperature and a pH value of 9.5. The obtained slurry was aged overnight at room temperature. Then the precipitate was separated by an external magnetic field, washed thoroughly with deionized water until the effluent was neutral. The fresh precipitate was then dried at 80 °C overnight and identified as (x%)Fe<sub>3</sub>O<sub>4</sub>@Cu<sub>0.4</sub>Mg<sub>5.6</sub>Al<sub>2</sub>(OH)<sub>16</sub>CO<sub>3</sub>, in which x% represented the mass ratio of

$\text{Fe}_3\text{O}_4/\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_2(\text{OH})_{16}\text{CO}_3$ . Secondly,  $(x\%)\text{Fe}_3\text{O}_4@\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_2(\text{OH})_{16}\text{CO}_3$  were calcined at 400 °C in a stationary air for 4 h and the calcined product catalysts were identified as  $(x\%)\text{Fe}_2\text{O}_3@\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_2\text{O}_9$ . After hydrogen reduction at 300 °C for 1 h, these catalysts were denoted as  $(x\%)\text{Fe}_2\text{O}_3@\text{Cu}_{0.4}/\text{Mg}_{5.6}\text{Al}_2\text{O}_{8.6}$ .

## 2 Characterization

The elemental compositions of Cu, Mg, Al and Fe of the catalysts were detected on inductively coupled plasma-atomic emission spectroscopy equipment (ICP, plasma-Spec-II spectrometer, Perkin-Elmer Optima 2000 instrument). X-ray diffraction (XRD) patterns were detected at room temperature on a Rigaku D/WAX-2500 diffractometer using Cu K $\alpha$  radiation ( $\lambda=1.5406 \text{ \AA}$ ) with a  $2\theta$  step of 0.02°. Scanning electronic images (SEM) images of these hydrotalcite-like samples were taken on a microscope (Leo Series VP 1430, Germany) having silicon detector equipped with energy-dispersive X-ray (EDX) facility (Oxford instruments). Samples were coated with gold using sputter coating to avoid charging. Analysis was carried out at an accelerating voltage of 15 kV. X-ray photoelectron spectra (XPS) were recorded on a Perkin-Elmer PHI ESCA System. X-ray source was Mg standard anode 146 (1253.6 eV) at 12 kV and 300 W. N<sub>2</sub> 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. Magnetic properties of the samples were investigated by a superconducting quantum interference device magnetometer (SQUID, MPMS-XL-5).

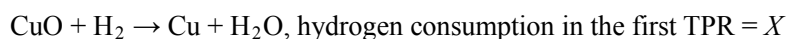
Transmission electron microscopy (TEM) images of reduced catalysts were recorded using an accelerating voltage of 200 kV (JEOL-2010 F). TG-DSC (Thermogravimetry-Differential scanning calorimetry) was carried out on a Netzsch STA 409 thermo-balance. Analysis was done from 30 to 850 °C at a heating rate of 10 °C/min under nitrogen (30 mL/min).

Temperature programmed reduction (TPR) studies were carried out in a quartz reactor. Samples were first pretreated at 400 °C for 1 h under N<sub>2</sub> at a flow rate of 30 mL/min and cooled to room temperature. A reduction agent (10% H<sub>2</sub>/N<sub>2</sub> 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 was recorded by TCD. The amount of reduced Cu in these samples was calibrated with pure CuO (AR, Sinopharm Chemical Reagent Co., Ltd, China) of known amount.

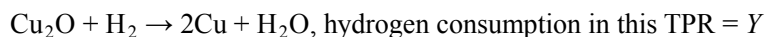
It was confirmed that all Cu species in these samples could be reduced in the temperature ranged from 50 to 450 °C.

The number of surface metallic copper sites was determined by N<sub>2</sub>O oxidation and followed H<sub>2</sub> titration using the procedure described by Van Der Grift et al.<sup>1</sup>. Catalysts were first reduced in the procedure described in above TPR experiment in 10% H<sub>2</sub>/N<sub>2</sub> 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<sub>2</sub>O/N<sub>2</sub> (30 mL/min) was shifted to oxidize the surface copper atoms to Cu<sub>2</sub>O 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<sub>2</sub>/N<sub>2</sub> at a flow rate of 30 mL/min. Hydrogen consumption in the second TPR was denoted as *Y*. The dispersion of the surface Cu was calculated according to these equations reported by Van Der Grift et al.<sup>1</sup>, which are shown below:

Reduction of all copper atoms:



Reduction of surface copper atoms only:



And the dispersion was calculated as:

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

### 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 H<sub>2</sub> at 300 °C for 1 h. The reaction mixture included 10.90 mmol glycerol in ethanol solution, and 0.085 mmol Cu. Then the autoclave was purged with H<sub>2</sub> 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 separated by an external magnetic field 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 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.

## Supplementary Results

### XRD

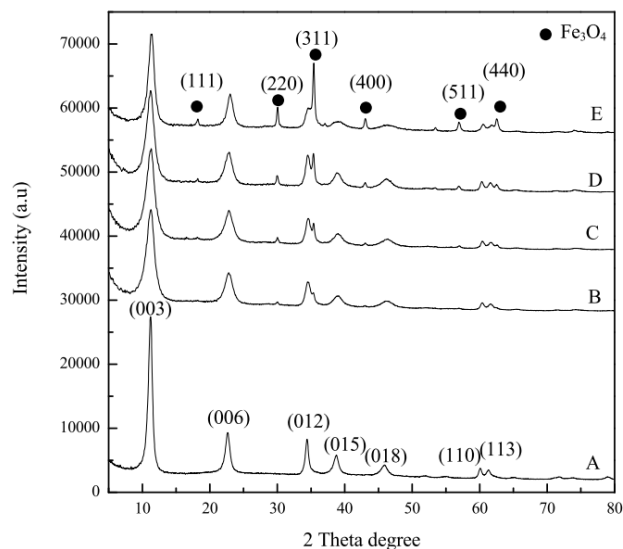


Fig.S1 XRD pattern of  $\text{Fe}_3\text{O}_4@ \text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_2(\text{OH})_{16}\text{CO}_3$

(A) pure  $\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_2(\text{OH})_{16}\text{CO}_3$ ; (B) (4.2%) $\text{Fe}_3\text{O}_4@ \text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_2(\text{OH})_{16}\text{CO}_3$ ; (C) (8.3%) $\text{Fe}_3\text{O}_4@ \text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_2(\text{OH})_{16}\text{CO}_3$ ; (D) (16.7%) $\text{Fe}_3\text{O}_4@ \text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_2(\text{OH})_{16}\text{CO}_3$ ; (E) (33.3%) $\text{Fe}_3\text{O}_4@ \text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_2(\text{OH})_{16}\text{CO}_3$ .

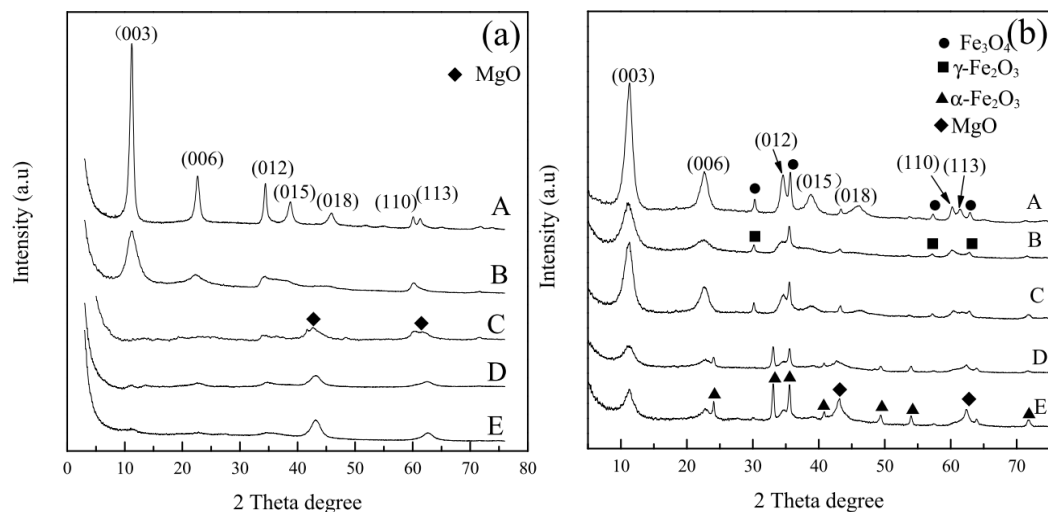


Fig. S2 XRD patterns of  $\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_2(\text{OH})_{16}\text{CO}_3$  (a) and

(16.7%) $\text{Fe}_3\text{O}_4@ \text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_2(\text{OH})_{16}\text{CO}_3$  (b) calcined at different temperatures.

(A) uncalcined catalyst; (B) calcined at 300 °C, 4 h; (C) calcined at 400 °C, 4 h; (D) calcined at 500 °C, 4 h; (E) calcined at 600 °C, 4 h.

## TG-DSC

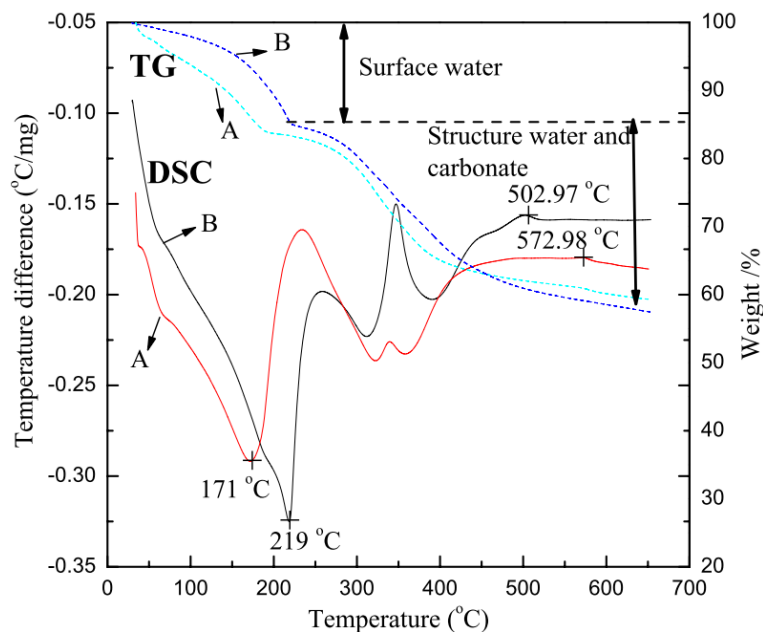


Fig. S3 TG-DSC curves of  $\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_2(\text{OH})_{16}\text{CO}_3$  (A) and  $(16.7\%)\text{Fe}_3\text{O}_4@\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_2(\text{OH})_{16}\text{CO}_3$  (B).

## H<sub>2</sub>-TPR

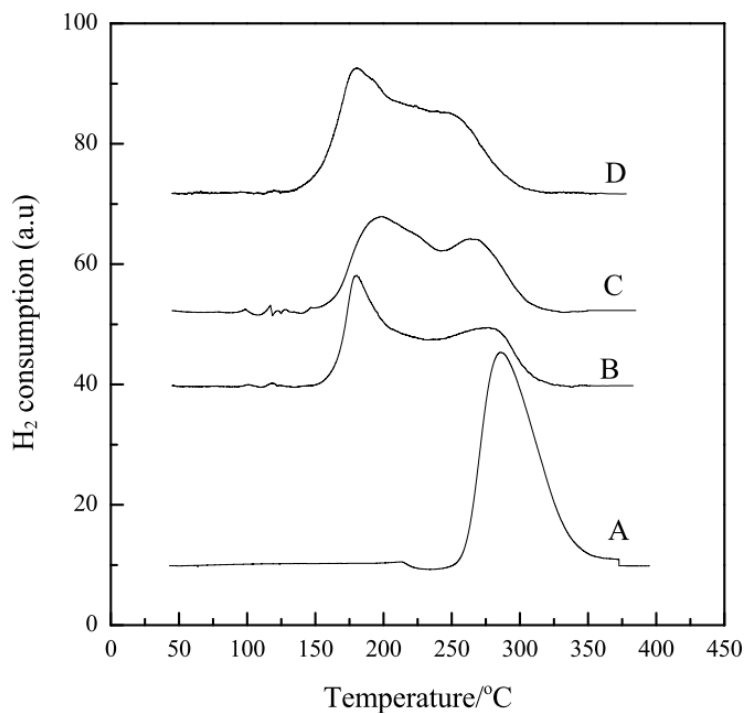


Fig. S4 H<sub>2</sub>-TPR profiles of calcined samples.  
(A)  $\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_2\text{O}_9$ ; (B)  $(8.3\%)\text{Fe}_2\text{O}_3@\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_2\text{O}_9$ ; (C)  $(16.7\%)\text{Fe}_2\text{O}_3@\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_2\text{O}_9$ ; (D)  $(33.3\%)\text{Fe}_2\text{O}_3@\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_2\text{O}_9$

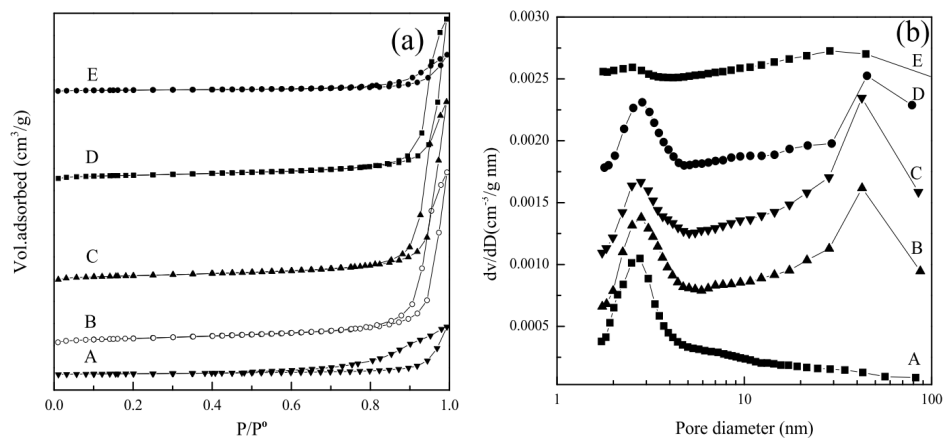


Fig. S5  $N_2$  adsorption (a) and pore size distribution (b) of the reduced catalyst. (A) pure  $Cu_{0.4}/Mg_{5.6}Al_2O_{8.6}$ ; (B) (4.2%) $Fe_2O_3@Cu_{0.4}/Mg_{5.6}Al_2O_{8.6}$ ; (C) (8.3%)  $Fe_2O_3@Cu_{0.4}/Mg_{5.6}Al_2O_{8.6}$ ; (D) (16.7%) $Fe_2O_3@Cu_{0.4}/Mg_{5.6}Al_2O_{8.6}$ ; (E) (33.3%) $Fe_2O_3@Cu_{0.4}/Mg_{5.6}Al_2O_{8.6}$ .

#### Images of magnetic separation

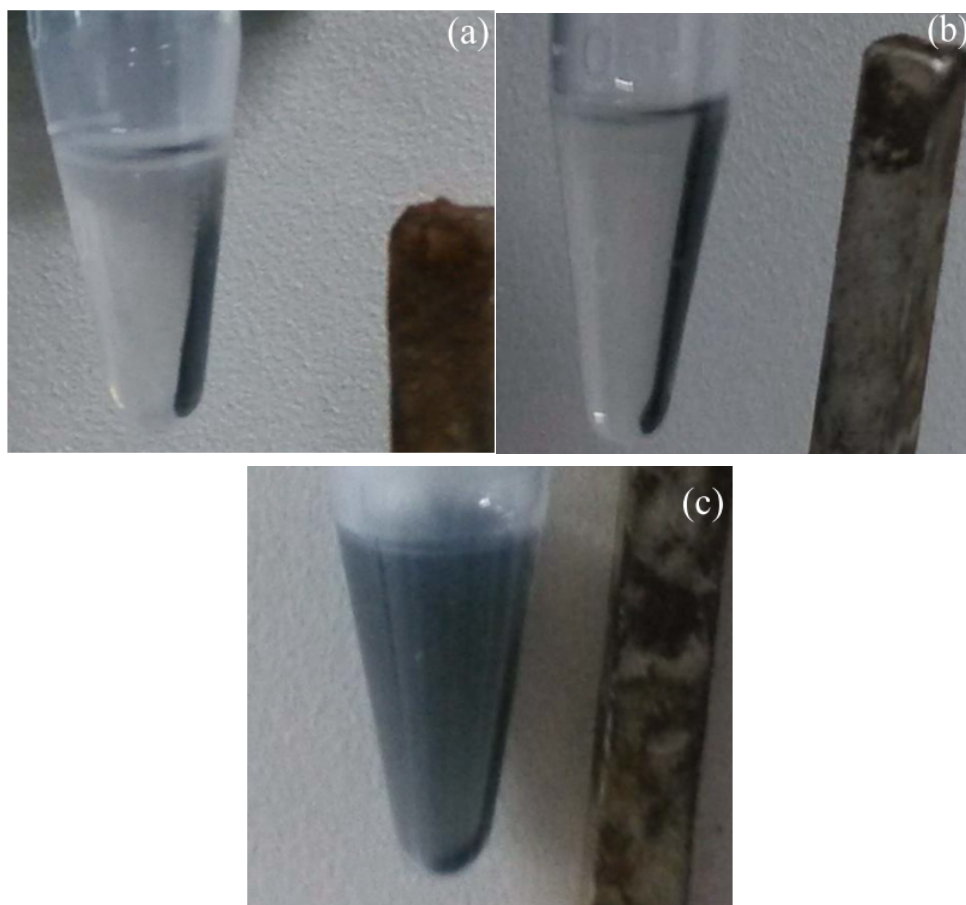


Fig. S6 Images of magnetic separation of the catalysts.

(a) (33.3%)Fe<sub>2</sub>O<sub>3</sub>@Cu<sub>0.4</sub>/Mg<sub>5.6</sub>Al<sub>2</sub>O<sub>8.6</sub>; (b) (16.7%)Fe<sub>2</sub>O<sub>3</sub>@Cu<sub>0.4</sub>/Mg<sub>5.6</sub>Al<sub>2</sub>O<sub>8.6</sub>; (c)  
 (8.3%)Fe<sub>2</sub>O<sub>3</sub>@Cu<sub>0.4</sub>/Mg<sub>5.6</sub>Al<sub>2</sub>O<sub>8.6</sub>

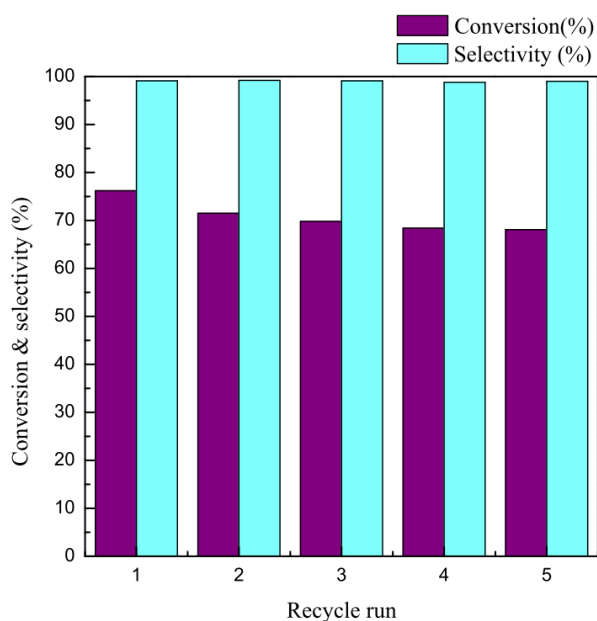


Fig. S7 Recycled usages of (16.7%)Fe<sub>2</sub>O<sub>3</sub>@Cu<sub>0.4</sub>/Mg<sub>5.6</sub>Al<sub>2</sub>O<sub>8.6</sub> catalyst. (Reaction conditions: 10.90 mmol glycerol, 0.085 mmol Cu in ethanol solution, 190 °C, 10 h, 2.0 MPa H<sub>2</sub>.)

Table S1 Surface composition of (x%)Fe<sub>2</sub>O<sub>3</sub>@Cu<sub>0.4</sub>Mg<sub>5.6</sub>Al<sub>2</sub>O<sub>9</sub> detected in XPS.

Catalysts	Surface mole concentration (%)					Relative atomic percentage (%)
	O	Fe	Al	Cu	Mg	Cu/(Cu+Mg+Al)
(4.2%)Fe <sub>2</sub> O <sub>3</sub> @Cu <sub>0.4</sub> Mg <sub>5.6</sub> Al <sub>2</sub> O <sub>9</sub>	35.3	0.08	5.8	0.6	7.9	4.2
(16.7%)Fe <sub>2</sub> O <sub>3</sub> @Cu <sub>0.4</sub> Mg <sub>5.6</sub> Al <sub>2</sub> O <sub>9</sub>	35.7	0.06	3.4	0.46	4.1	5.8
(33.3%)Fe <sub>2</sub> O <sub>3</sub> @Cu <sub>0.4</sub> Mg <sub>5.6</sub> Al <sub>2</sub> O <sub>9</sub>	41.5	1.7	4.9	0.44	3.9	4.8

Table S2 The structure and Cu dispersion of reduced catalysts <sup>a</sup>

Catalysts	S <sub>BET</sub> (m <sup>2</sup> /g)	Pore size (nm)	Pore volume (cm <sup>3</sup> /g)	Dispersion <sup>b</sup> (%) <sup>c</sup>
Cu <sub>0.4</sub> /Mg <sub>5.6</sub> Al <sub>2</sub> O <sub>8.6</sub>	127.9	2.7; --	0.61	43.2 (±6%)
(4.2%)Fe <sub>2</sub> O <sub>3</sub> @Cu <sub>0.4</sub> /Mg <sub>5.6</sub> Al <sub>2</sub> O <sub>8.6</sub>	144.5	2.8; 42.4	1.21	58.1(±6%)
(8.3%)Fe <sub>2</sub> O <sub>3</sub> @Cu <sub>0.4</sub> /Mg <sub>5.6</sub> Al <sub>2</sub> O <sub>8.6</sub>	141.7	2.8; 42.9	1.26	62.8 (±6%)
(16.7%)Fe <sub>2</sub> O <sub>3</sub> @Cu <sub>0.4</sub> /Mg <sub>5.6</sub> Al <sub>2</sub> O <sub>8.6</sub>	125.5	2.8; 44.7	1.13	59.1 (±6%)
(33.3%)Fe <sub>2</sub> O <sub>3</sub> @Cu <sub>0.4</sub> /Mg <sub>5.6</sub> Al <sub>2</sub> O <sub>8.6</sub>	37.3	2.8; 44.3	0.25	56.1(±6%)

<sup>a</sup> All catalysts are reduced in H<sub>2</sub> at 300 °C, 1 h.

<sup>b</sup> Calculated from N<sub>2</sub>O chemical adsorption after the catalysts were reduced in H<sub>2</sub> at 300 °C.

<sup>c</sup> Data in parentheses are estimated standard deviation that were calculated on the deviation of H<sub>2</sub> consumption.

Table S3 The amount of adsorbed CO<sub>2</sub> over catalyst detected by TG-DSC.

Catalysts	mCO <sub>2</sub> (mg) <sup>a</sup>
Cu <sub>0.4</sub> Mg <sub>5.6</sub> Al <sub>2</sub> O <sub>9</sub>	0.045254
(8.3%)Fe <sub>2</sub> O <sub>3</sub> @ Cu <sub>0.4</sub> Mg <sub>5.6</sub> Al <sub>2</sub> O <sub>9</sub>	0.052219
(16.7%)Fe <sub>2</sub> O <sub>3</sub> @Cu <sub>0.4</sub> Mg <sub>5.6</sub> Al <sub>2</sub> O <sub>9</sub>	0.063424
(33.3%)Fe <sub>2</sub> O <sub>3</sub> @Cu <sub>0.4</sub> Mg <sub>5.6</sub> Al <sub>2</sub> O <sub>9</sub>	0.031702

<sup>a</sup> defined as the amount of adsorbed CO<sub>2</sub> over per mg Cu<sub>0.4</sub>Mg<sub>5.6</sub>Al<sub>2</sub>O<sub>9</sub>.

Table S4 Glycerol hydrogenolysis over different catalysts <sup>a</sup>.

Catalysts	Cu dispersion (%)	Conversion (%)	Activity of surface Cu (h <sup>-1</sup> ) <sup>b</sup>
Cu <sub>0.4</sub> /Mg <sub>5.6</sub> Al <sub>2</sub> O <sub>8.6</sub>	43.2	18.6	5.5
Pd <sub>0.04</sub> Cu <sub>0.4</sub> /Mg <sub>5.56</sub> Al <sub>2</sub> O <sub>8.56</sub>	46.0	39.1	10.8
Rh <sub>0.02</sub> Cu <sub>0.4</sub> /Mg <sub>5.6</sub> Al <sub>1.98</sub> O <sub>8.57</sub>	47.4	50.4	13.6
Cu <sub>0.4</sub> /Zn <sub>0.6</sub> Mg <sub>5.0</sub> Al <sub>2</sub> O <sub>8.6</sub>	49.4	45.6	11.8
(16.7%)Fe <sub>2</sub> O <sub>3</sub> @Cu <sub>0.4</sub> /Mg <sub>5.6</sub> Al <sub>2</sub> O <sub>8.6</sub>	59.1	76.2	16.5

<sup>a</sup> Reaction conditions: 10.9 mmol glycerol in ethanol solution (413 mmol), and 0.085 mmol Cu, 2.0 MPa H<sub>2</sub>, 190 °C, 10 h. <sup>b</sup> Defined as (mol of converted glycerol)/(mol of exposed Cu atom)/(reaction time, h).



Table S5 Compositions of fresh and recycled (16.7%)Fe<sub>2</sub>O<sub>3</sub>@Cu<sub>0.4</sub>/Mg<sub>5.6</sub>Al<sub>2</sub>O<sub>8.6</sub> catalysts<sup>a</sup>

Sample	Composition (mol %)			
	Cu	Mg	Al	Fe
Fresh	4.59 (4.58)	64.08 (64.10)	22.85 (22.90)	8.48 (8.42)
Used <sup>b</sup>	4.63 (4.58)	63.96 (64.10)	22.96 (22.90)	8.45 (8.42)

<sup>a</sup> The values in parentheses are controlled values.

<sup>b</sup> The used (16.7%)Fe<sub>2</sub>O<sub>3</sub>@Cu<sub>0.4</sub>/Mg<sub>5.6</sub>Al<sub>2</sub>O<sub>8.6</sub> 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.