Supplementary Information

A Noble-Metal free Cu-catalyst derived from hydrotalcite for highly efficient hydrogenation of biomass-derived furfural and levulinic acid

Kai Yan*[1], Jiayou Liao, Xu Wu, Xianmei Xie*

Institute of Chemistry and Chemical Engineering, Taiyuan University of Technology, Yingze Street No. 79, Taiyuan, 030024, China.

Tel: 86-351-6018564; E-mail: yankai0553@sina.com, xxmsxty@sina.com

1: Present address: Department of Chemistry, Lakehead University, P7B 5E1, ON, Canada

Experimental section

Catalyst synthesis

The hydrotalcite precursors were prepared by a modified co-precipitation method similarly as our previous studies.[1] Generally two solutions, one solution (A) containing the desired amount of metal nitrates 1 mol/L $Fe(NO_3)_3 \cdot 9H_2O$ (or 1 mol/L $Al(NO_3)_3 \cdot 9H_2O$ or1 mol/L $Cr(NO_3)_3 \cdot 9H_2O$) and 1 mol/L $Cu(NO_3)_2 \cdot 3H_2O$ with different Cu^{2+}/Fe^{3+} (or Al^{3+}or Cr^{3+}) ratio of 2.0 and the other (B) with precipitating agents aqueous NaOH (1M), were added simultaneously under argon atmosphere, and the pH value was maintained around 5.5-6.0 under vigorous stirring at room temperature. The slurry was aged for 30 min under vigorous stirring and then was transferred into Teflon-lined autoclave. The autoclave was sealed and maintained at 120 ^{o}C for 6h. Thereafter the light green precipitate was collected by centrifugation and rinsed for three times using distilled water followed by absolute ethanol. Finally, the obtained powder was dried at 60 °C for 12 h and calcinated at 950 °C for 10 h in the air oven. The hydrotalcite precursor is transferred to the corresponding mixed oxide by heating to a certain temperature, which often involves dehydration (1), dehydroxylation (2), decomposition of anions (3), oxide and spinel formation (4) in series or in overlapping manner.[2]

(1) Dehydration: $[Cu^{2+}_{1-x}Fe^{3+}_{x}(OH)_2]^{x+}(NO_3^{-1})_x\cdot mH_2O\rightarrow[Cu^{2+}_{1-x}Fe^{3+}_{x}(OH)_2]^{x+}(NO_3^{-1})_x$

(2) Dehydroxylation: $[Cu^{2+}_{1-x}Fe^{3+}_{x}(OH)_2]^{x+}(NO_3^{-1})_x\rightarrow[Cu^{2+}_{1-x}Fe^{3+}_{x}O]^{x+}(NO_3^{-1})_x$

(3) Decomposition of anion: $[Cu^{2+}_{1-x}Fe^{3+}_{x}O]^{x+}(NO_3^{-1})_x\rightarrow[Cu^{2+}_{1-x}Fe^{3+}_{x}O_{1+x/2}](NO_y)$

(4) Oxide and spinel reformation: $[Cu^{2+}_{1-x}Fe^{3+}_{x}O_{1+x/2}](NO_y)\rightarrow CuO/CuFe_2O_4+NO_y$

References

1. (a) X. M. Xie, K. Yan, J. P. Li and Z. Wang, *Catal. Commun.*, 2008, **9**, 1128-1131; (b) X. M. Xie, X. An, K. Yan, J. L. Song and Z. Wang, *J. Natural Gas Chem.*, 2010, **19**, 77-80.
2. Z. P. Xu, J. Zhang, M. O. Adebajo, H. Zhang and C. H. Zhou, *Appl. Clay Sci.*, 2011, **53**, 139-150.

Catalyst Characterization

The powder X-ray diffraction (XRD) patterns for qualitative phase analysis were collected on a Rigaku D/Max2500 in transmission geometry with a primary monochromator and a linear position sensitive detector, with Cu$K\alpha_1$: 1.5418 Å as a radiation source. The data were collected in the range of 5-85° with a step width of 8° (2θ).

Inductively coupled plasma (ICP) spectrometry was performed on Australian Labtam Co. Labtam8410. Samples were dried at 100 °C for 24 h prior to analysis, and solutions were prepared by dissolving the samples in dilute HCl (1:1). The rate of cooling gas was 10.5 L/min and the flue rate of the carrier gas was 1.0 L/min.

Scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDX) were obtained with Japanese JSM-6360LV operating at an acceleration voltage of 10 kV.

Transmission electron microscopy (TEM) was used to investigate textural features of the catalysts with a JEOL 2010 instrument.

Selective hydrogenation of furfural

The hydrogenation of furfural was performed in a micro-autoclave. 2.1 mL furfural was added in 5 mL octane followed by addition of 0.1 g catalyst into the solution under continuous stirring condition. To remove the air inside, the autoclave was flushed with argon before it was pressurized with hydrogen. Reaction time t_0 was defined for the moment when the inner temperature of the autoclave reached the desired temperature. After reaction, the autoclave was cooled down to room temperature in a controlled manner using an ice water bath. The product mixture was firstly centrifuged for 30 min, and then filtrated over neutral aluminum oxide, followed by a second filtration and dilution by dichloromethane. The subsequent samples were analysis by GC (Shimadzu 2014, column: 30 m SE-54 G/17, FID). The column temperature was raised from 40 to 250 °C with a heating rate 5 °C/min. The injector temperature was set to 350 °C, which was loaded with a sampling volume of 1 μL.

Selective hydrogenation of levulinic acid

The hydrogenation of levulinic acid was performed in a micro-autoclave. Under continuous stirring (1000 rpm), 1.02 g levulinic acid was dissolved in 5 mL H_2O followed by addition of 0.1 g catalyst into the solution. In order to remove most of the air, the autoclave was flushed with argon before it was pressurized with hydrogen. Reaction time t_0 was defined for the moment when the inner temperature of the autoclave reached desired temperature. After reaction, the autoclave was cooled down to room temperature in a controlled manner using an ice water bath. The product mixture was firstly centrifuged for 30 min, and then filtrated over neutral aluminum oxide, followed by a second filtration and dilution by dichloromethane. The subsequent samples were analysis by GC (Shimadzu 2014, column: 30 m DBWax, FID). The column temperature was raised from 40 to 250 °C with a heating rate of 5 °C/min. The injector temperature was set to 350 °C, which was loaded with a sampling volume of 1 μL.

Table S1 Properties of the potential fuel components.

Terms	ethanol	2-methylfuran	GVL
Mass Weight /g mol^{-1}	46.07	82.10	100.12
Carbon /wt %	52.2	73.15	60
Hydrogen /wt %	13.1	7.37	8
Oxygen /wt %	34.7	19.49	32
Boiling point /^{o}C	78	64	207
Melting point /^{o}C	-114	-89	-31
Flash Point /^{o}C	13	-22	96
Density /g ml^{-1}	0.789	0.91	1.046
Solubility in water / mg/ml	miscible	3	>=1
Enthalpy of vaporization/ kJ/kg	912	357	442.36

References in Table S1

1. (a) I. T. Horvath, H. Mehdi, V. Fabos, L. Boda and L. T. Mika, *Green Chem.,* 2008, **10**, 238-242; (b) V. Fábos, G. Koczó, H. Mehdi, L. Boda and I. T. Horváth, *Energy Environ. Sci.,* 2009, **2**, 767-769; (c) H. E. Hoydonckx, W. M. Van Rhijn, W. V. Rhijn, D. E. De Vos and P. A. Jacobs, Furfural and derivatives in ullmann's encyclopedia of industrial chemistry. 2000, Wiley-VCH, Weinheim; (d) K. J. Zeitsch: "Sugar Series", in The Chemistry and Technology of Furfural and its Many By-products, 2000, V13, 1st ed., Elsevier Science, Amsterdam.

Table S2. Representaive works for the hydrogenation of levulinic acid (LA) to γ-valerolactone using the solid catalysts[a].

No.	Catalyst	Reaction conditions	Conv./%	Yield/%	Refs.
1	5% Ru/C	130 °C, 1.2 Mpa H_2, 160 min, methanol solvent	92.36	91.3	1
2	Raney Ni	130 °C, 1.2 Mpa H_2, 160 min, methanol solvent	18.88	6.0	1
3	5% Ru/Al_2O_3 + A70	70 °C, 3.0 Mpa H_2, acid-assisted, H_2O solvent	57	56.2	2
4	5% Ru/C + A70	70 °C, 3.0 Mpa H_2, acid-assisted, H_2O solvent	100	~100	2
5	5 wt% Ru/C	180 °C, WHSV=1.2, propyl guaiacol solvent, formic acid	100	93	3
6	5 wt% Ru/C	150 °C, 5.5 Mpa H_2, 1,4-dioxane solvent	80	72	4
7	5% Ru/SiO_2	$ScCO_2$, 200 °C, H_2 (3 equivalent)	>99	>99	5
8	1 mol % Au/ZrO_2	150 °C, 6 h, equimolar amount of LA and formic acid	>99	>99	6
9	Ru/ZrO_2	150 °C, 6 h, equimolar amount of LA and formic acid	<2%	<2%	6
10	Ru/C	150 °C, 6 h, equimolar amount of LA and formic acid	<2%	<2%	6
11	5 wt% Pt/C	265 °C, 0.1 Mpa H_2, 160 min, methanol solvent	100	30	7
12	5 wt% Pd/C	265 °C, 0.1 Mpa H_2, 160 min, methanol solvent	100	90	7
13	5 wt% Ru/C	130 °C, 1.2 Mpa H_2, methanol solvent	92	91.1	8
14	5 wt% Pd/C	130 °C, 1.2 Mpa H_2, methanol solvent	17	6.5	8
15	5 wt% Cu/SiO_2	265 °C, 1 Mpa H_2	>99	>99	9
This study	**Cu-Cr catalyst**	**200 °C, 70 bar H_2, 10 h, water solvent**	**>99**	**90.7**	This study

[a] Reaction note: WHSV (weight hourly space velocity); Conv.: conversion of levulinic acid; the yield was calculated using the conversion multiply the selectivity; Refs.: references number.

References in Table S2.

1. Y. Gong, L. Lin and Z. P. Yan, *BioResources* 2011, **6**, 686-699.
2. A. M. R. Galletti, C. Antonetti, V. De Luise and M. Martinelli, *Green Chem.,* 2012, **14**, 688- 694.
3. P. Azadi, R. Carrasquillo-Flores, Y. J. Pagán-Torres, E. I. Gürbüz, R. Farnood and J. A. Dumesic, *Green Chem.,* 2012, **14**, 1573-1576.
4. L. E. Manzer, *Appl. Catal. A* 2004, **272** (1-2), 249-256.
5. R. A. Bourne, J. G. Stevens, J. Ke and M. Poliakoff, *Chem. Commun.,* 2007, **44**, 4632-4634.
6. X. L. Du, L. He, S. Zhao, Y. M. Liu, Y. Cao, H. Y. He and K. N. Fan, *Angew. Chem. Int. Ed.,* 2011, **50** (34), 7815-7819.
7. P. P. Upare, J. M. Lee, D. W. Hwang, S. B. Halligudi, Y. K. Hwang and J. S. Chang, *J. Ind. Eng. Chem.,* 2011, **17**, 287-292.
8. Z. P. Yan, L. Lin and S. J. Liu, *Energy Fuels* 2009, **23**, 3853-3858.
9. P. P. Upare, J. M. Lee, Y. K. Hwang, D. W. Hwang, J. H. Lee, S. B. Halligudi, J. S. Hwang and J. S. Chang, *ChemSusChem* 2012, **4**, 1749-1752.

Table S3. Representative works from literatures for the hydrogenation of furfural to furfuryl alcohol[a].

No.	Catalyst	Reaction conditions	Conv./%	Yield/%	Refs.
1	5% Pt/C	175 °C, 80 bar H_2, 0.5 h, n-butanol solvent	99.3	47.86	1
2	5% Pt/C	175 °C, 80 bar H_2, 0.5 h, n-decanol solvent	94.5	26.34	1
3	5% Pd/C	150 °C, 20 bar H_2, 4h, acetic acid-assisted	41.2	14.4	2
4	5% Pd/ $Al_2(SiO_3)_3$	150 °C, 20 bar H_2, 4h, acetic acid-assisted	56.9	30.0	2
5	5% Cu/ $Al_2(SiO_3)_3$	150 °C, 20 bar H_2, 4h, acetic acid-assisted	26.1	7.80	2
6	5% Ni/ $Al_2(SiO_3)_3$	150 °C, 20 bar H_2, 4h, acetic acid-assisted	23.9	6.2	2
7	Ni-Fe-B	200 ^{o}C, 10 bar H_2, 4 h, 30 mL ethanol	100	100	3
8	$Cu_{11.2}Ni_{2.4}$-MgAlO	300 ^{o}C, 10 bar H_2, 90 mL ethanol	89.9	87.0	4
9	5% Pt/C	175 ^{o}C, 30 bar H_2, 1 h, 20 mL H_2O solvent H_3PO_4 (85%)	100	27.0	5
10	2% Ir/TiO_2	90 ^{o}C, 6.2 bar H_2, n-heptane/ethanol	30	30	6
11	Cu/MgO	GHSV =0.05 mol h^{-1} g catalyst^{-1}	98	98	7
12	$PtSn/SiO_2$	100 ^{o}C, 8h, 10 bar H_2, 50 mL 2-propanol	~85	~83.5	8
13	1% Pd/SiO_2	250 °C, H_2/Feed ratio =25, 1 atm H_2, TOS =15 min	69	10	9
14	10%Cu/ SiO_2	230 °C, H_2/Feed ratio =25, 1 atm H_2, 5 min	69	67.6	9
15	2 wt% Pt / TiO_2/MgO	200 °C, HLSV =2, H_2/furfural =2 mol/mol)	33.6	7.7	10
16	MoNiB/γ-Al_2O_3	80 ^{o}C, 3 h, 50 bar, methanol solvent	99	91	11
17	Cu-MgO	200 °C, 6 h, H_2/furfural =2.5, GHSV= 0.05 mol h^{-1} g catalyst^{-1}	71.6	71.6	12
18	CuO +$CuCr_2O_4$	300 ^{o}C	60	21-42	13
19	$Ni_{74.5}P_{12.1}B_{13.4}$	250 psi H_2, 80 °C, furfural/ethanol =2 mL/170 mL	~95	~77.9	14

20	$PtSn_{0.2}$/ SiO_2	100 °C, 8 h, 10 MPa H_2, 50 mL of propan-2-ol solvent	100	96	15
21	1 wt% Pt/ SiO_2	100 °C, 8 h, 10 MPa H_2, 50 mL of propan-2-ol solvent	46	45.5	15
22	2 wt% Ni/ SiO_2	100 °C, 8 h, 10 MPa H_2, 50 mL of propan-2-ol solvent	31	23.6	15
This study	**Cu-Fe catalyst**	**160 °C, 90 bar H_2, 5 h**	**91.0**	**89.5**	This study

[a] Reaction note: LHSV (Liquid hourly space velocity); GHSV (Gas hourly space velocity); Conv.: conversion of furfural; Refs.: reference number.

References in Table S3:

1. M. Hronec and K. Fulajtarová, *Catal. Commun.,* 2012, **24**, 100-104.
2. W. J. Yu, Y. Tang, L. Y. Mo, P. Chen, H. Lou and X. M. Zheng, *Bioresource Technol.,* 2011, **102**, 8241–8246.
3. H. Li, H. Luo, L. Zhuang, W. Dai and M. Qiao, *J. Mol. Catal. A* 2003, **203**, 267-275.
4. C. H. Xu, L. K. Zheng, J. Y. Liu and Z. Y. Huang, *Chin. J. Chem.,* 2011, **29**, 691-697.
5. M. Hroneca, K. Fulajtarováa and T. Liptaj, *Appl. Catal. A* 2012, **437-438***,* 104-111.
6. P. Reyes, D. Salinas, C. C. M. Oportus, J. Murcia, H. R. G. Borda and J. L. G. Fierro, *Quim. Nova* 2010, **33**, 777-780.
7. B. M. Nagaraja, V. Siva Kumar, V. Shasikala, A. H. Padmasri, B. Sreedhar, B. D. Raju and K. S. Rama Rao, *Catal. Commun.,* 2003, **4**, 287–293.
8. A. B. Merlo, V. Vetere, J. F. Ruggera and M. L. Casella, *Catal. Commun.,* 2009, **10**, 1665-1669.
9. S. Sitthisa and D.E. Resasco, *Catal. Lett.,* 2011, **141**, 784–791.
10. J. Kijenski, P. Winiarek, T. Paryjczak, A. Lewicki and A. Mikołajska, *Appl. Catal. A* 2002, **233**, 171–182.
11. S. Q. Wei, H. Y. Cui, J. H. Wang, S. P. Zhuo, W. M. Yi, L. H. Wang and Z. H. Li, *Particuology* 2011, **9**, 69-74.
12. B. M. Nagaraja, A. H. Padmasri, B. D. Raju and K. S. R. Rao, *Int. J. Hydrogen. Energ.,* 2011, **36**, 3417-3425.
13. R. Rao, A. Dandekar, R. T. K. Baker and M. A. Vannice, *J. Catal.,* 1997, **171,** 406-419.
14. S. P. Lee and Y. W. Chen, *Ind. Eng. Chem. Res.,* 1999, **38**, 2548-2556.
15. V. Vetere, A. B. Merlo, J. F. Ruggera and M. L. Casella, *J. Braz. Chem. Soc.,* 2010, **21**, 914-920.

Table S4. Representaive works in the hydrogenation of furfural to 2-methylfuran (MF) using the solid catalysts[a].

No.	Catalyst	Reaction conditions	Conv./%	Yield/%	Refs.
1	5% Pt/C	175 °C, 80 bar H_2, 30 min, n-butanol solvent	99.3	40.43	1
2	5% Pt/C	175 °C, 80 bar H_2, 30 min, n-decanol solvent	94.5	23.17	1
3	5% Pt/C	175 °C, 80 bar H_2, 30 min, n-Butanol/water (1:1 vol)	99.7	30.84	1
4	5% Pd/C + $Al_2(SiO_3)_3$	150 °C, 20 bar H_2, 4h, acetic acid-assisted	69.4	17.9	2
5	5% Pd/C	150 °C, 20 bar H_2, 4h, acetic acid-assisted	41.2	8.90	2
6	5% Pt/C	160 ^{o}C, 30 bar H_2, 1 h, 20 mL H_2O solvent	96.5	4.9	3
7	5% Pt/C	175 ^{o}C, 30 bar H_2, 1 h, 20 mL H_2O solvent H_3PO_4 (85%)	100	36.6	3
8	Cu-Zn-Al	225 ^{o}C, 6 h, LHSV=0.7 h^{-1}	99.9	93.0	4
9	2 wt% $Pt/TiO_2/SiO_2$	150 °C, HLSV =2 h^{-1}, H_2/furfural =2 mol/mol)	68.3	12.5	5
10	2 wt% $Pt/TiO_2/MgO$	250 °C, HLSV =2 h^{-1}, H_2/furfural =2 mol/mol)	50.4	3.0	5
11	2 wt% $Pt/TiO_2/\gamma$-Al_2O_3	200 °C, HLSV =2 h^{-1}, H_2/furfural =2 mol/mol)	33.2	1.6	5
12	Cu-Mn-Si	279 ^{o}C, 8 h, 1 atm, n(H_2): n(CHL + FFA) =10:1, LHSV=0.49 h^{-1}	99.8	93.7	6
13	Cu/Zn/Al/Ca/Na = 59:33:6:1:1	250 ^{o}C, LHSV =0.3 h^{-1}, H_2:furfural =25 (molar ratio)	99.7	87	7
14	Cu/Zn/Al/Ca/Na = 59:33:6:1:1	300 ^{o}C, LHSV = 0.3 h^{-1}, H_2:furfural =25 (molar ratio)	99.7	77.6	7
15	Cu/Cr/Ni/Zn/Fe = 43:45:8:3:1	200 ^{o}C, LHSV =0.3 h^{-1}, H_2:furfural =25 (molar ratio)	99.6	67.0	7
This study	**Cu-Fe catalyst**	**220 ^{o}C, 90 bar H_2, 14 h**	**99.4**	**51.1**	This study

[a] Reaction note: LHSV (Liquid hourly space velocity); GHSV (Gas hourly space velocity); Conv.: conversion of furfural; the yield was calculated using the conversion multiply the selectivity; Refs.: reference number.

References in Table S4

1. M. Hronec and K. Fulajtarová, *Catal. Commun.,* 2012, **24**, 100-104.

2. W. J. Yu, Y. Tang, L. Y. Mo, P. Chen, H. Lou and X. M. Zheng, *Bioresource Technol.,* 2011, **102**, 8241-8246.

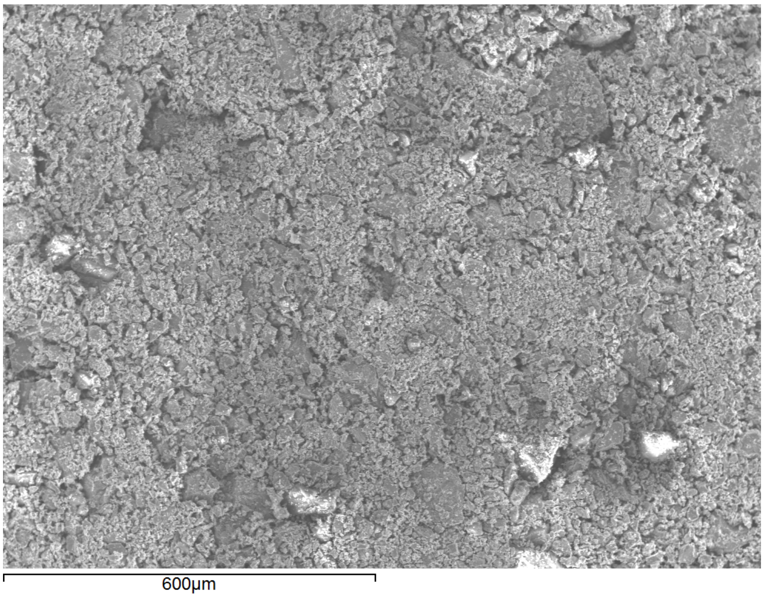
3. M. Hronec, K. Fulajtarová and T. Liptaj, *Appl. Catal. A* 2012, **437-438**, 104-111.

4. J. Yang, H.Y. Zheng, Y. L. Zhu, G. W. Zhao, C. H. Zhang, B. T. Teng, H. W. Xiang and Y. W. Li, *Catal. Commun.,* 2004, **5**, 505-510.

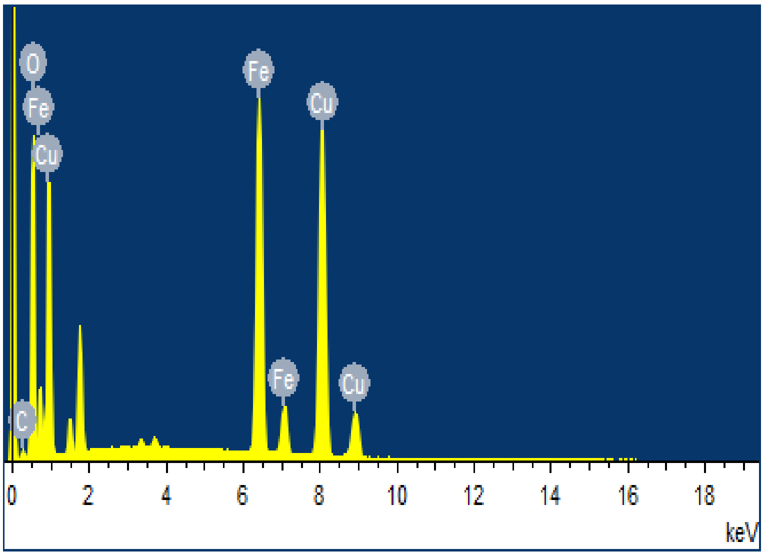
5. J. Kijenski, P. Winiarek, T. Paryjczak, A. Lewicki and A. Mikołajska, *Appl. Catal. A* 2002, **233**, 171-182.

6. H. Y. Zheng, Y. L. Zhu, L. Huang, Z. Y. Zeng, H. J. Wan and Y. W. Li, *Catal. Commun.,* 2008, **9**, 342-348.

7. H. Y. Zheng, Y. L. Zhu, B. T. Teng, Z. Q. Bai, C. H. Zhang, H. W. Xiang and Y. W. Li, *J. Mol. Catal. A* 2006, **246**, 18-23.



(a) The chosen area of EDX analysis

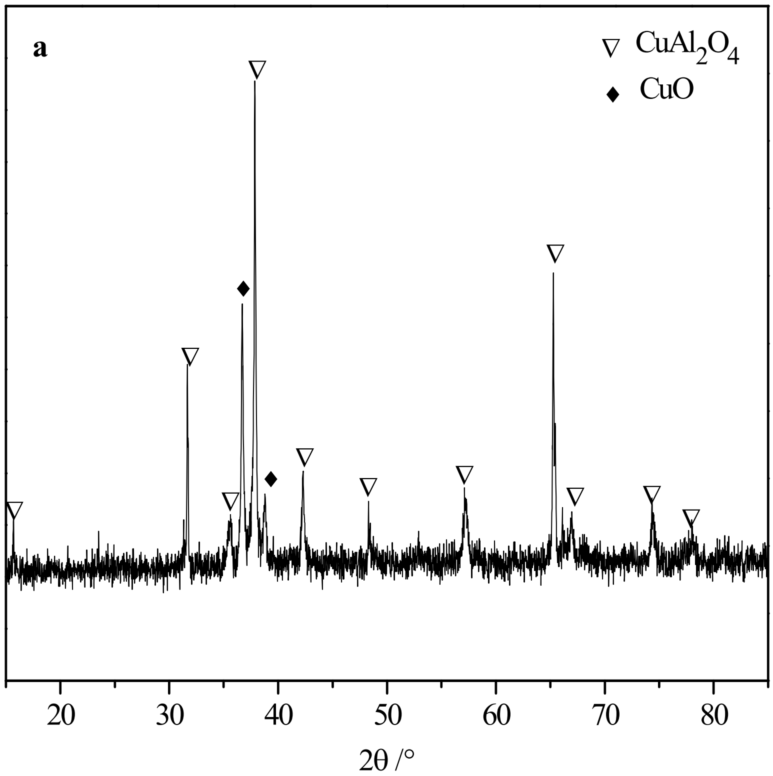


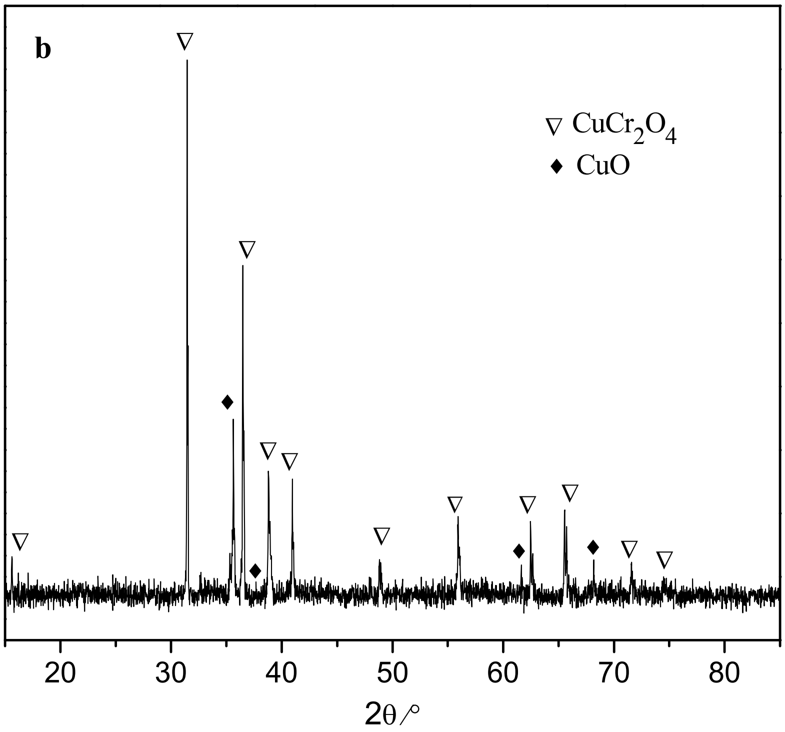
(b) EDX spectroscopy

Element	Weight Mass%	Atom%
O K	25.40	56.30
Fe K	26.77	17.00
Cu K	47.83	26.70
Total	100.00	

(c) numeric analysis results of EDX

Fig. S1 EDX plus SEM analysis of the chosen example of Cu-Fe catalyst.


a
▽ CuAl2O4
◆ CuO
20
30
40
50
60
70
80
2θ /°


b
▽ CuCr2O4
◆ CuO
20
30
40
50
60
70
80
2θ /°

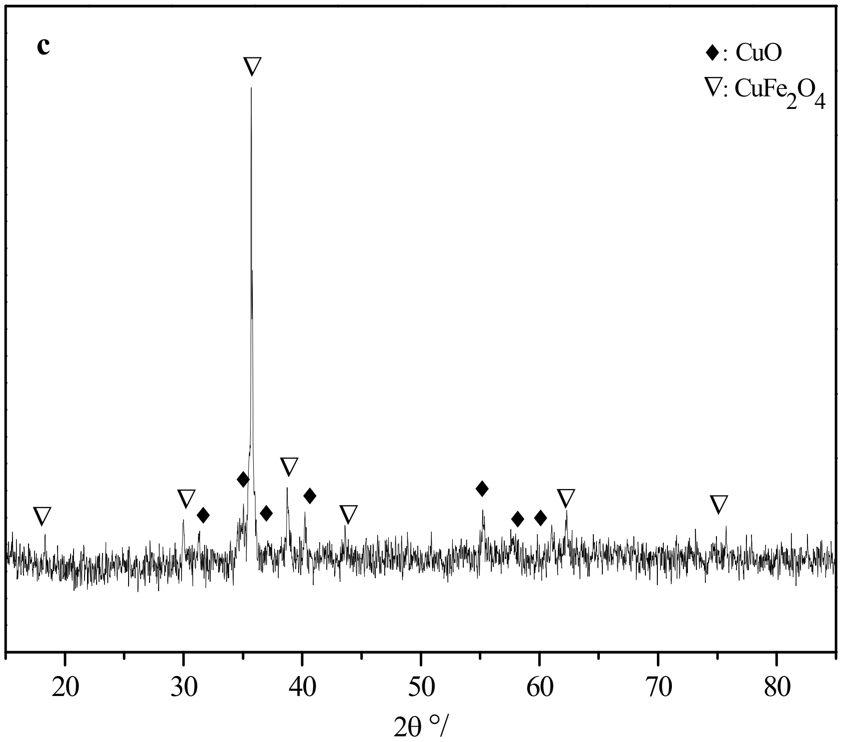


Fig. S2 XRD analysis of the resulting Cu-catalysts: (a) Cu-Al; (b) Cu-Cr; (c) Cu-Fe.

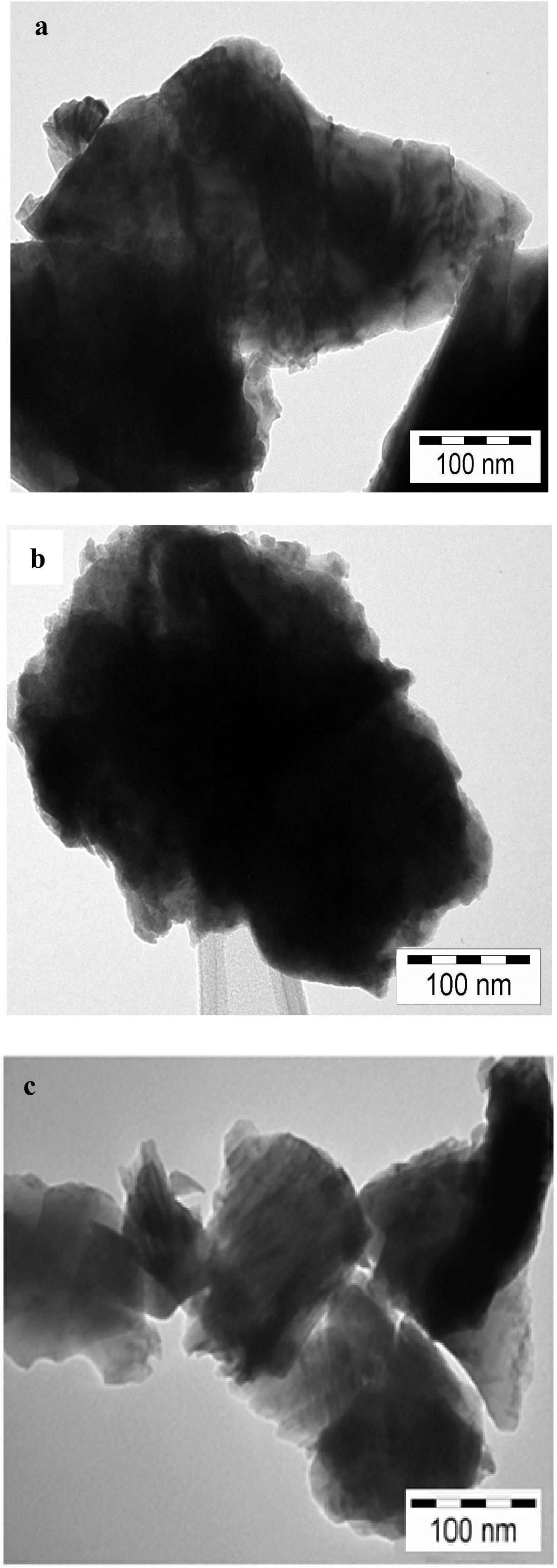


Fig. S3 TEM analysis of Cu-catalysts: (a) Cu-Al; (b) Cu-Cr; (c) Cu-Fe.

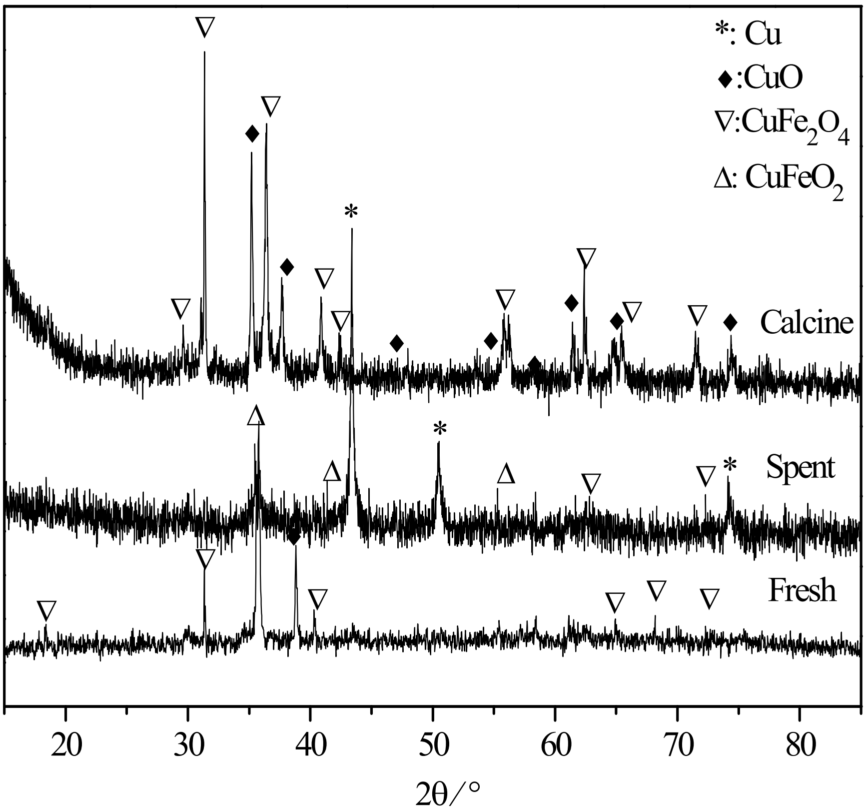


Fig. S4 XRD analysis of the fresh, spent and calcinated Cu-Fe catalyst.