

## Supplementary Information

### Selective hydrogenolysis of furfural into fuel-additive 2-methylfuran over rhenium-promoted copper catalyst

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**Table S1** Mass balance of the liquid product after reaction (200 °C, 2 h, and 20 bar H<sub>2</sub>) over the Cu, Cu<sub>1</sub>Re<sub>0.14</sub>, and Re catalysts.

Sample	Mass balance (%)
Cu	99.2
Cu <sub>1</sub> Re <sub>0.14</sub>	99.7
Re	99.3

**Table S2** Liquid product composition by GC-MS analysis obtained from the reaction using Cu and Cu<sub>1</sub>Re<sub>0.14</sub> catalysts at reaction temperature of 200°C, initial H<sub>2</sub> pressure of 20 bar and time for 2 h.

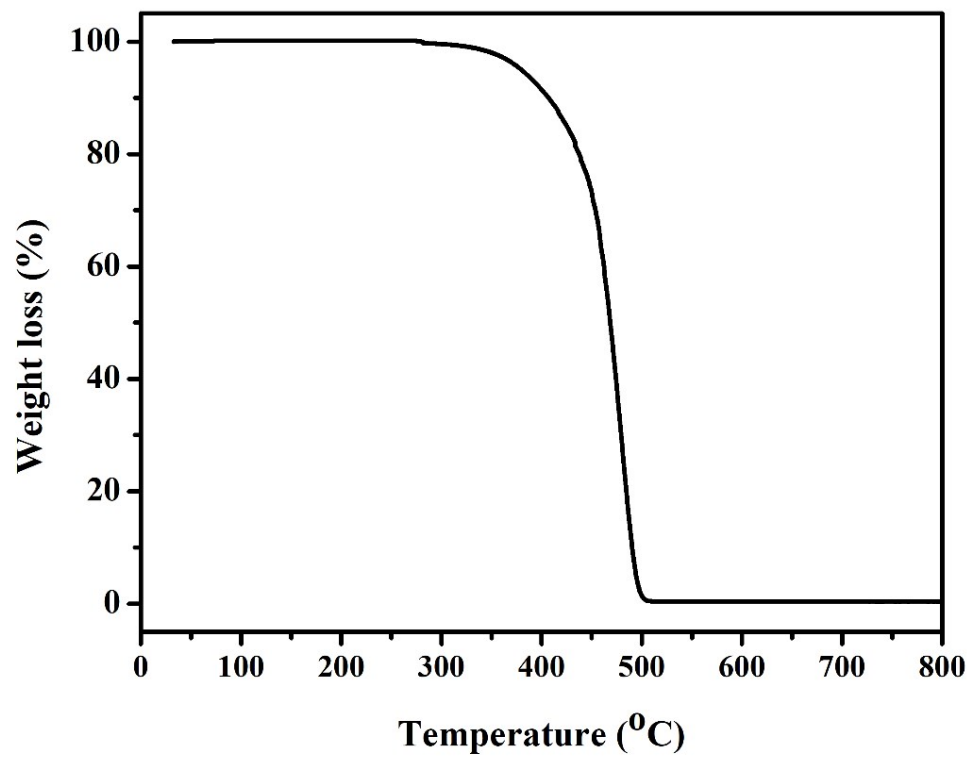
Product	% Area by GC-MS analysis	
	Cu	Cu <sub>1</sub> Re <sub>0.14</sub>
2-Methylfuran	31.8	46.1
2-Methyltetrahydrofuran	6.4	11.6
1-Pentanol	2.8	3.2
Furfuryl alcohol	34.5	10.9
Tetrahydrofurfuryl alcohol	1.8	1.8
1,2-Pentanediol	6.2	6.3
1,4-Pentanediol	8.5	14.6
Isopropyl furfuryl ether	8.0	5.6

**Table S3** Metal contents of the catalysts as determined by XRF analysis.

Sample	Metal content		Re/Cu
	Re	Cu	mole ratio
(wt.%)			
Cu	0	12.8	-
Cu <sub>1</sub> Re <sub>0.04</sub>	1.4	11.3	0.04
Cu <sub>1</sub> Re <sub>0.14</sub>	4.0	9.6	0.14
Cu <sub>1</sub> Re <sub>0.34</sub>	7.2	7.2	0.34
Re	15.7	0	-

**Table S4** Metal content by SEM-EDS analysis of the fresh and spent  $\text{Cu}_1\text{Re}_{0.14}$  catalysts after the reaction test at a reaction temperature of 200 °C, initial  $\text{H}_2$  pressure of 20 bar, and reaction time for 2 h.

Sample	Metal content by SEM-EDS analysis	
	Cu	Re
	(wt.%)	
Fresh $\text{Cu}_1\text{Re}_{0.14}$	9.5	4.4
Spent $\text{Cu}_1\text{Re}_{0.14}$	10.1	4.5



**Fig. S1** TGA profile of the  $\text{NH}_4\text{ReO}_4$  precursor decomposition in air.

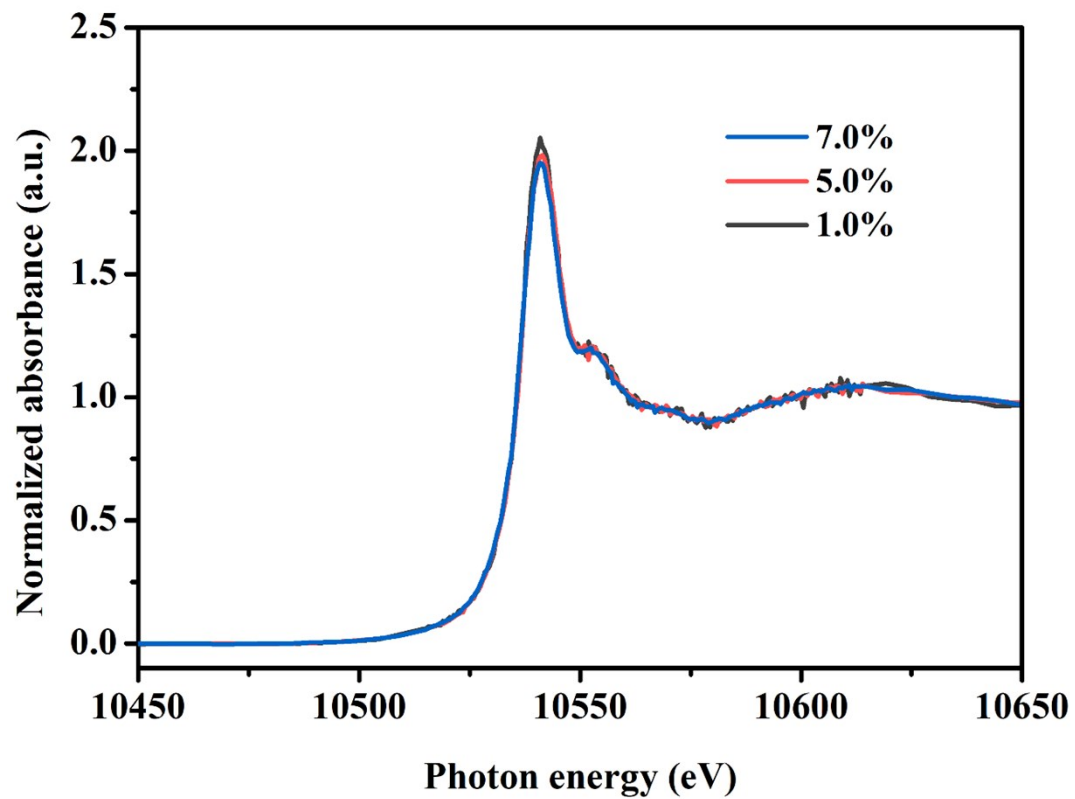
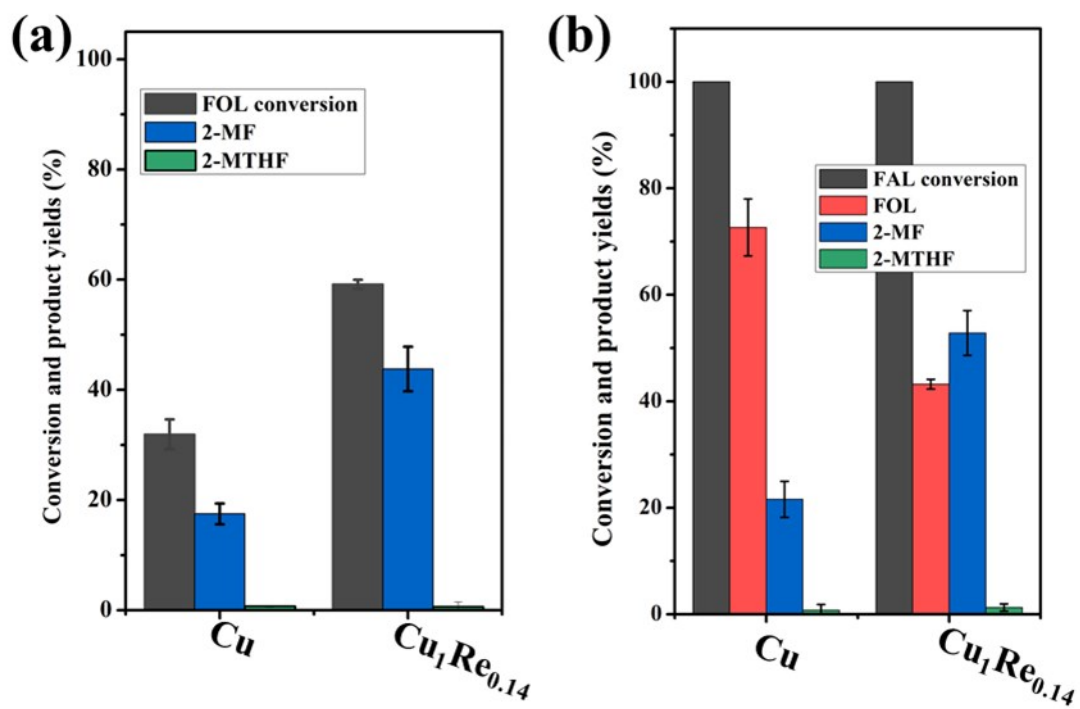
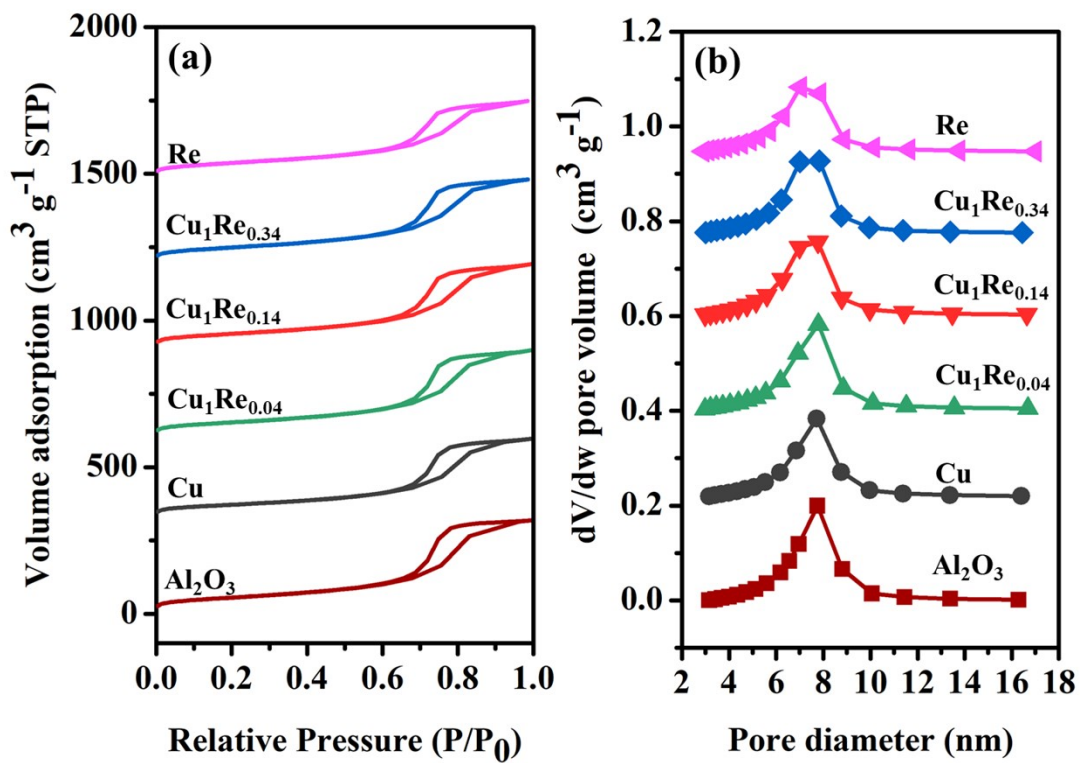


Fig. S2 Representative normalized Re L<sub>3</sub>-edge XANES spectra of the NH<sub>4</sub>ReO<sub>4</sub> standard with different Re contents.

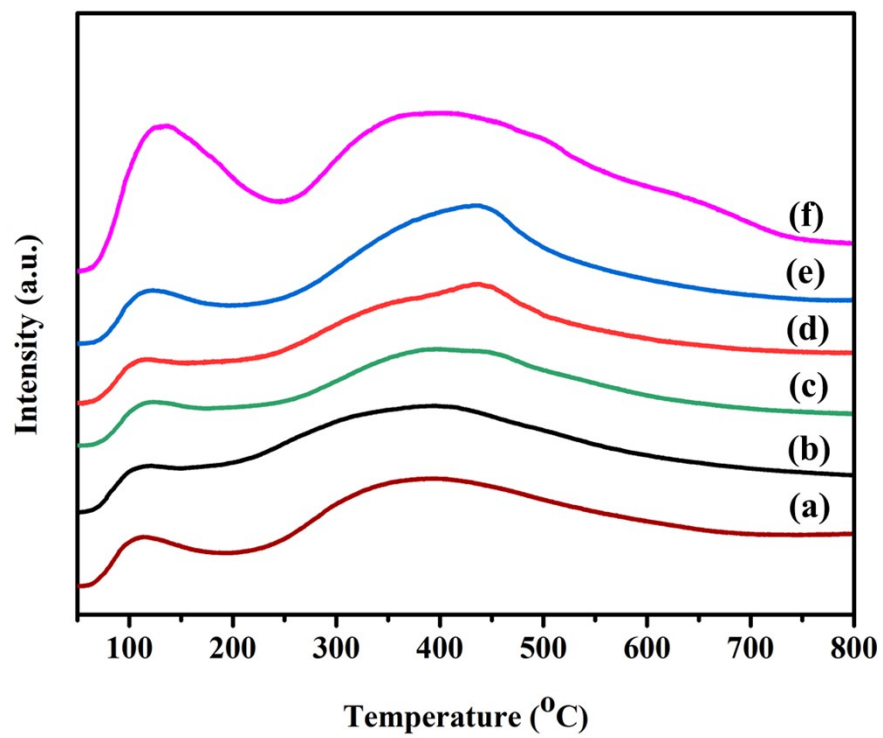


**Fig. S3** Comparative study of Cu and Cu<sub>1</sub>Re<sub>0.14</sub> catalysts using (a) a primary intermediate FOL and (b) FAL as the reactants to generate the target 2-MF at a reaction temperature of 200 °C, initial H<sub>2</sub> pressure of 20 bar, and reaction time for 30 min. The catalyst loading was 20 wt.% based on initial mass of FAL.

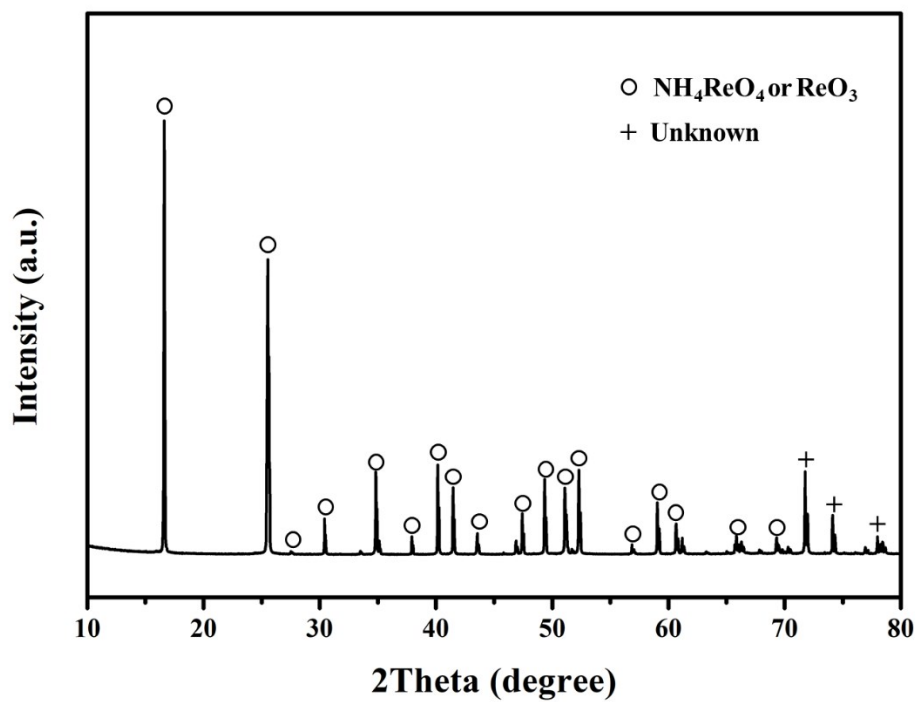




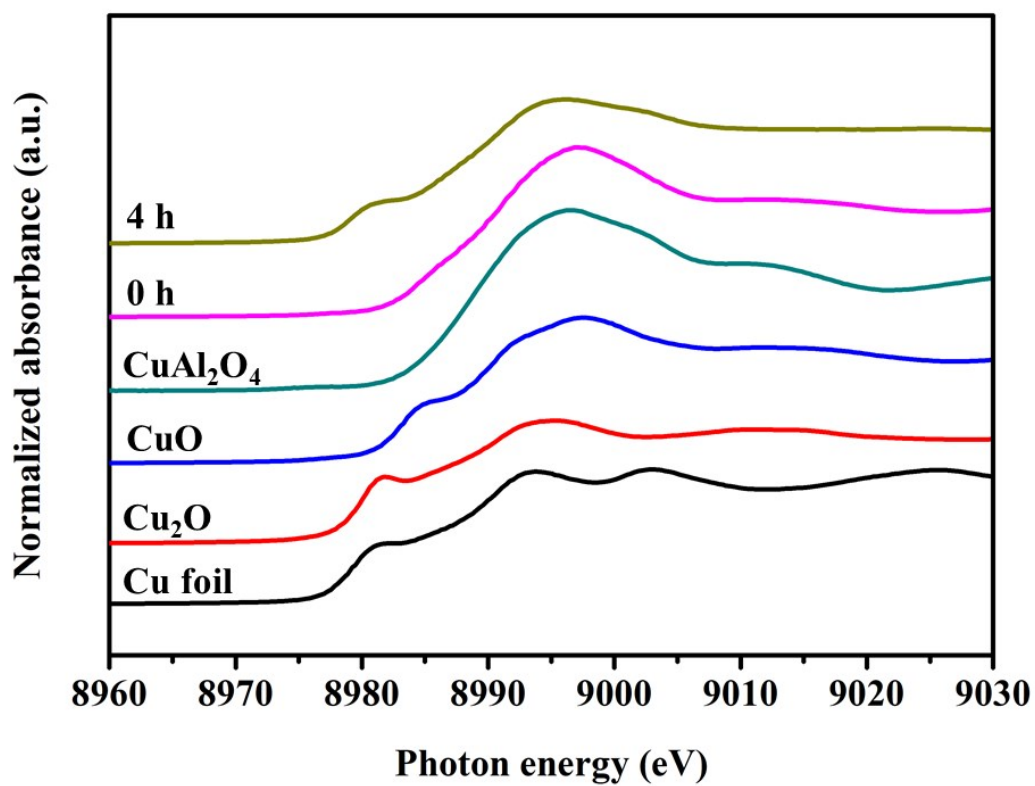
**Fig. S4** (a) N<sub>2</sub> adsorption and desorption isotherms and (b) pore size distribution of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and the calcined Cu, Cu<sub>1</sub>Re<sub>0.04</sub>, Cu<sub>1</sub>Re<sub>0.14</sub>, Cu<sub>1</sub>Re<sub>0.34</sub>, and Re samples.



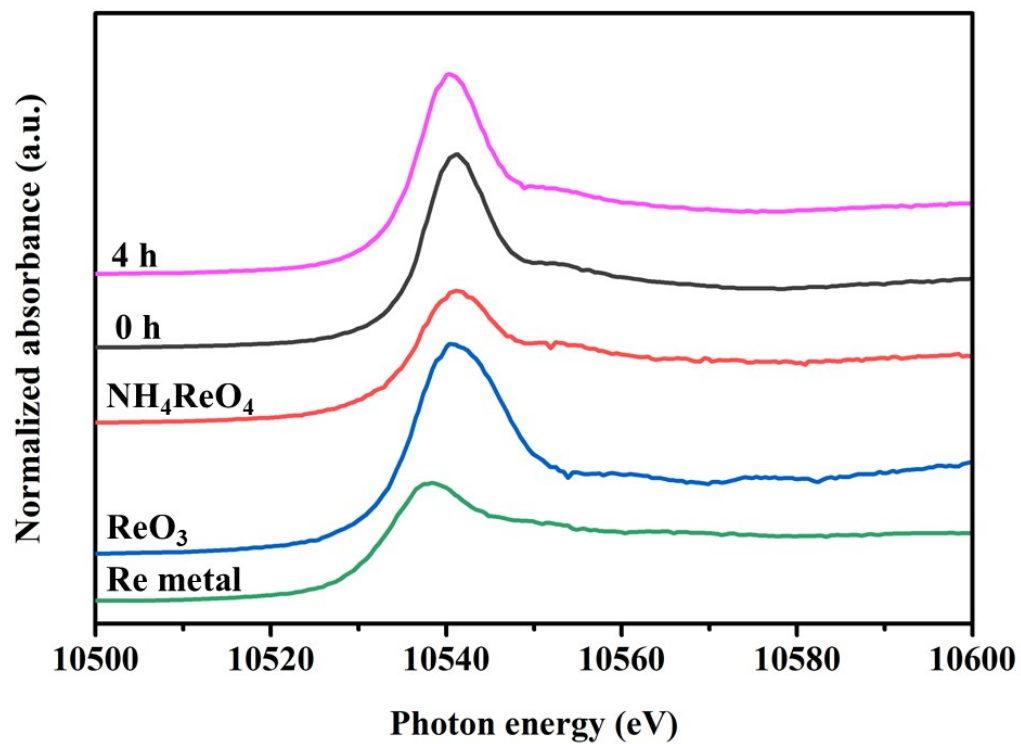
**Fig. S5** NH<sub>3</sub>-TPD profiles of the fresh (a)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (b) Cu, (c) Cu<sub>1</sub>Re<sub>0.04</sub>, (d) Cu<sub>1</sub>Re<sub>0.14</sub>, (e) Cu<sub>1</sub>Re<sub>0.34</sub>, and (f) Re catalysts.



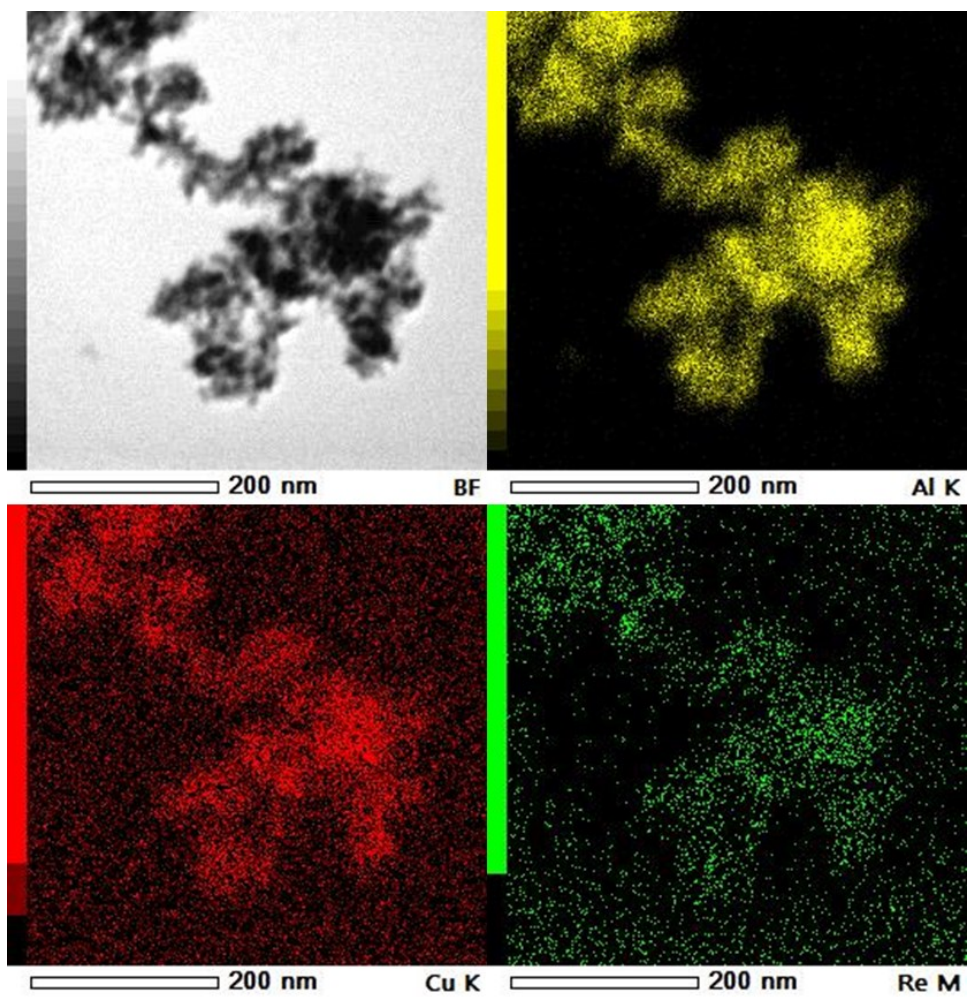
**Fig. S6** XRD pattern of the  $\text{NH}_4\text{ReO}_4$  precursor calcined at 300 °C for 3 h.



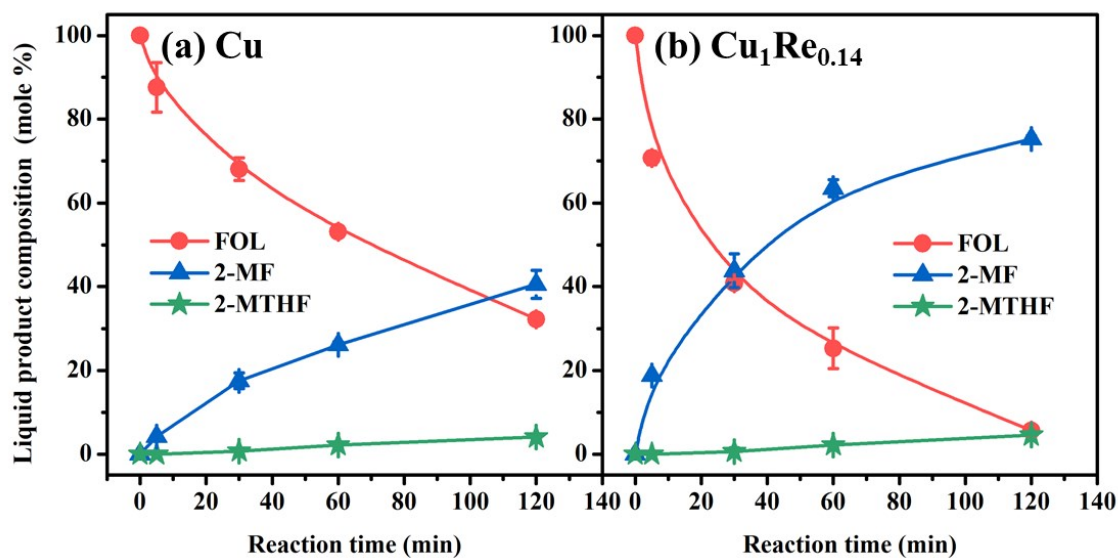
**Fig. S7** The *ex situ* normalized Cu K-edge XANES spectra of the Cu catalyst with different reaction times (0 and 4 h) at a reaction temperature of 200 °C and initial H<sub>2</sub> pressure of 20 bar, and the Cu foil, Cu<sub>2</sub>O, CuO, and CuAl<sub>2</sub>O<sub>4</sub> standards.



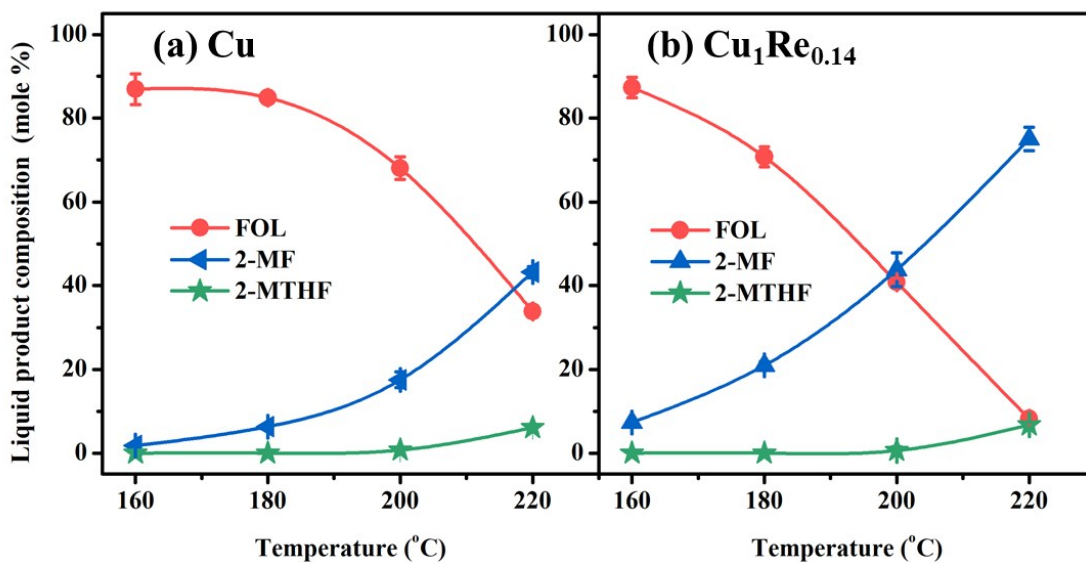
**Fig. S8** The *ex situ* normalized Re L<sub>3</sub>-edge XANES spectra of the Re catalyst with different reaction times (0 and 4 h) at a reaction temperature of 200 °C and initial H<sub>2</sub> pressure of 20 bar, and the Re metal, ReO<sub>3</sub>, and NH<sub>4</sub>ReO<sub>4</sub> standards.



**Fig. S9** Representative EDS mapping of the spent  $\text{Cu}_1\text{Re}_{0.14}$  catalyst.

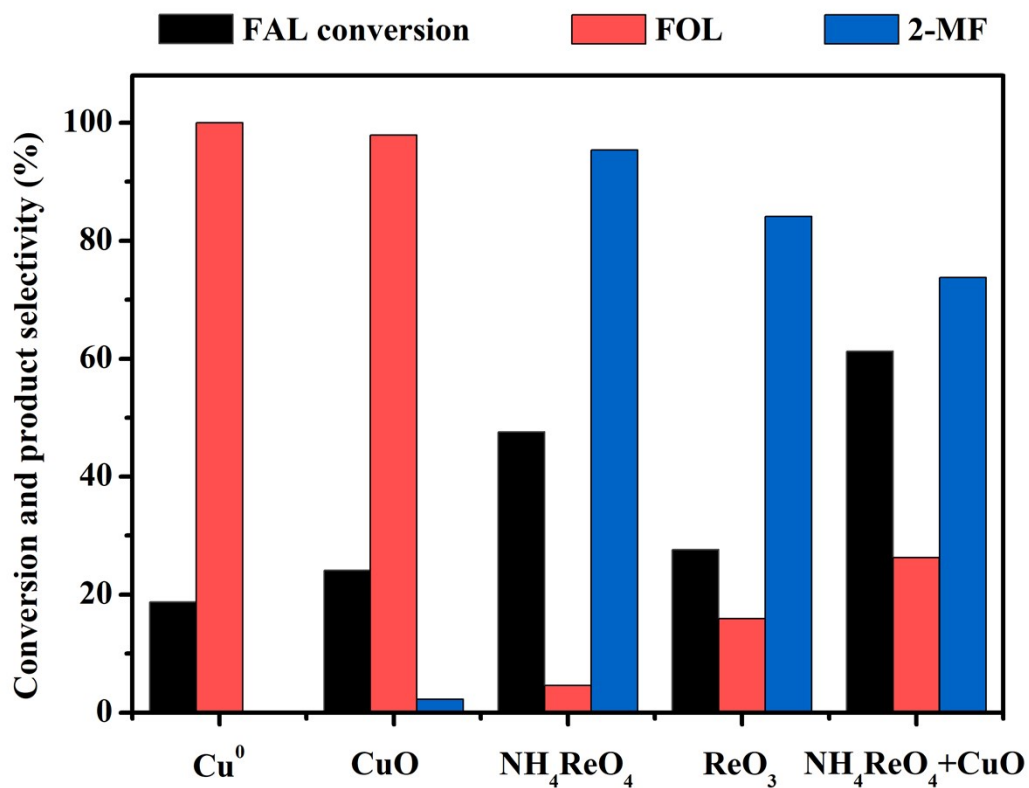


**Fig. S10** Influence of the reaction time (5–120 min) on the liquid product composition for the FOL hydrogenolysis at 200 °C over the (a) Cu and (b) Cu<sub>1</sub>Re<sub>0.14</sub> catalysts. The catalyst loading was 20 wt.% based on initial mass of FAL.

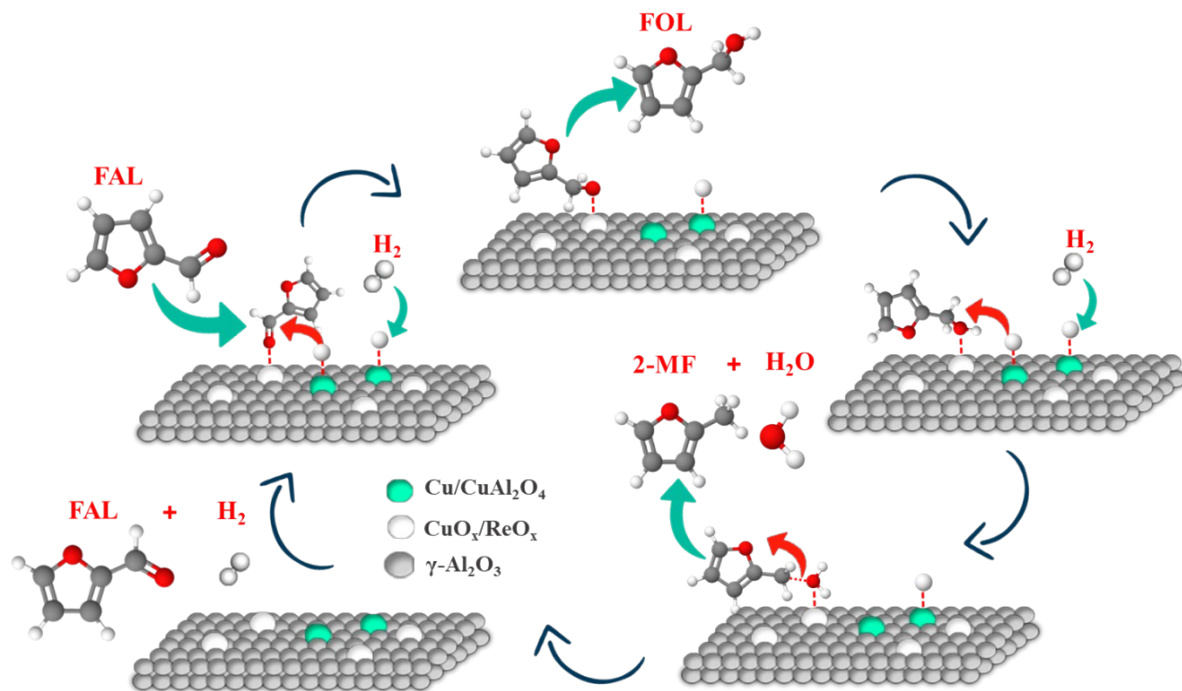


**Fig. S11** Influence of the reaction temperature (160-220 °C) on the liquid product composition in the FOL hydrogenolysis for 30 min over the (a) Cu and (b) Cu<sub>1</sub>Re<sub>0.14</sub> catalysts. The catalyst loading was 20 wt.% based on initial mass of FAL.





**Fig. S12** Catalytic performance for FAL hydrogenolysis over Cu, CuO, ReO<sub>3</sub>, NH<sub>4</sub>ReO<sub>4</sub>, and mixed NH<sub>4</sub>ReO<sub>4</sub>-CuO species at a reaction temperature of 200 °C, initial H<sub>2</sub> pressure of 20 bar, and reaction time for 30 min. The catalyst loading was 20 wt.% based on initial mass of FAL.



**Fig. S13** Proposed reaction mechanism for FAL hydrogenolysis over the  $\text{Cu}_1\text{Re}_{0.14}$  catalyst.

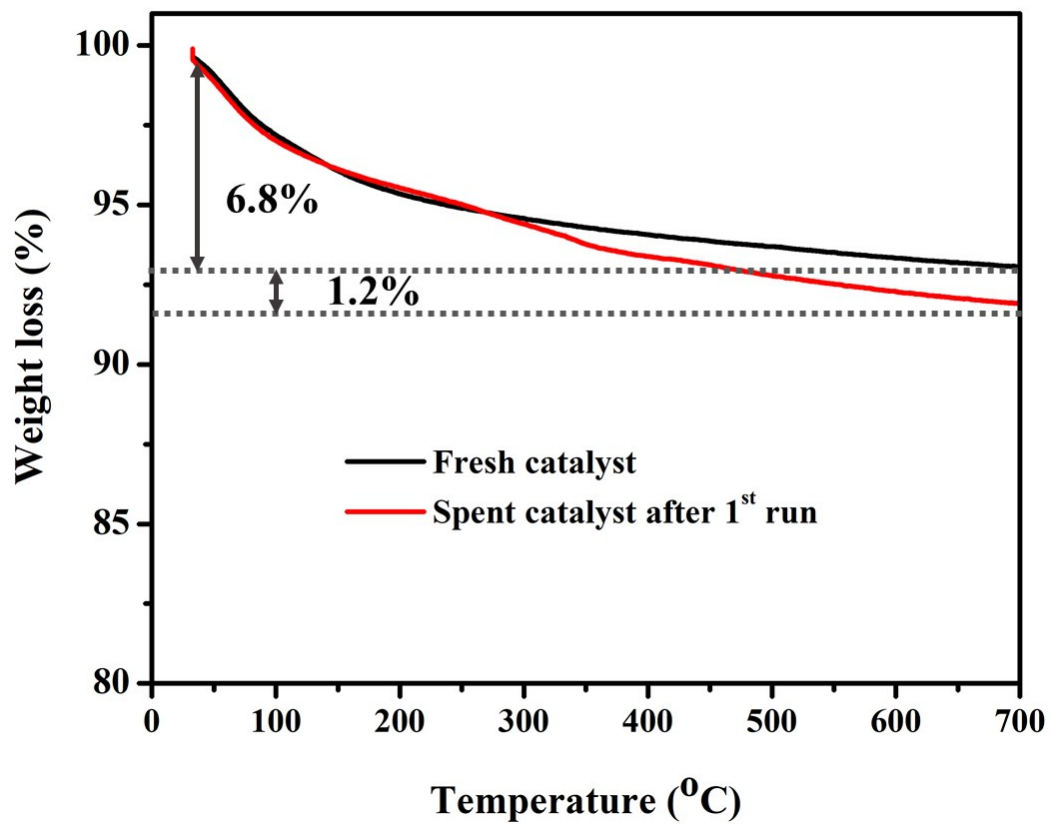


Fig. S14 TGA profiles of the fresh and spent Cu catalyst in air.