## **Supplementary Information for**

## Highly efficient and robust Cu/SiO<sub>2</sub> catalyst prepared by ammonia evaporation hydrothermal method for glycerol hydrogenolysis to 1,2-

## propanediol

Shanhui Zhu,<sup>a,\*</sup> Xiaoqing Gao,<sup>b</sup> Yulei Zhu,<sup>a,b,\*</sup> Weibin Fan,<sup>a</sup> Jianguo Wang,<sup>a</sup> and

Yongwang Li<sup>a,b</sup>

<sup>a</sup>State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, PR China <sup>b</sup>Synfuels China Co. Ltd., Taiyuan 030032, PR China

Preparation methods	Operation	T (°C)	Р	Conversion	Selectivity	Stability	Reference
			(MPa)	(%)	(%)		
Ion exchange	continuous	245	1.5	92	86	-	1
Impregnation	batch	240	8	10	83.6	deactivation	2
Homogeneous deposition-	batch	180	9	22.1	98.0	deactivation	3
precipitation							
Heterogeneous	batch	180	9	35.0	93.7	deactivation	3
deposition-precipitation							
Precipitation-gel	batch	180	9	73.4	94.3	200 h <sup>a</sup>	4
Precipitation-gel <sup>b</sup>	batch	200	8	73.3	92.2	deactivation <sup>a</sup>	5
Precipitation-gel	continuous	200	5	62.1	89.5	deactivation <sup>c</sup>	6
Ammonia evaporation	continuous	200	5	100	98.3	300 h	this work
hydrothermal method							

**Table S1** Comparison for  $Cu/SiO_2$  catalysts prepared by different preparationmethods in glycerol hydrogenolysis to 1,2-PDO.

<sup>a</sup> Performed in fixed-bed reactor; solvent was 10 wt% water and 50 wt% methanol.

b Cu/SiO2 calcined at 450 °C

c 90 wt% water as solvent.

The catalytic performances of Cu/SiO<sub>2</sub> catalysts with different preparation methods are summarized in Table S1. Compared to previous catalysts, the AEH method presented higher glycerol conversion and 1,2-PDO selectivity. Notably, most of the previous Cu/SiO<sub>2</sub> catalysts (except precipitation-gel method) deactivated rapidly due to the serious agglomeration of copper nanoparticles. The Cu/SiO<sub>2</sub> prepared by precipitation-gel method stabilized 200 h, while our AEH presented 300 h long-term performance.<sup>4</sup> The above results indicated that AEH method was highly efficient for fabricating active, selective and robust Cu-based catalyst for glycerol hydrogenolysis to 1,2-PDO.



**Fig. S1** Thermogravimetric analysis in oxidative atmosphere of the spent 25Cu/SiO<sub>2</sub>-IM catalyst during long-term test.



Fig. S2 NH<sub>3</sub>-TPD profiles of various catalysts.

## Reference

- 1 A. Bienholz, H. Hofmann, P. Claus, Appl. Catal., A: Gen. 2011, 391, 153-157.
- 2 E. S. Vasiliadou, A. A. Lemonidou, Appl. Catal., A: Gen. 2011, 396, 177-185.
- 3 Z. Huang, F. Cui, J. Xue, J. Zuo, J. Chen, C. Xia, Catal. Today 2012, 183, 42-51.
- 4 Z. Huang, F. Cui, H. Kang, J. Chen, X. Zhang, C. Xia, Chem. Mater. 2008, 20, 5090-5099.
- 5 Z. Huang, H. Liu, F. Cui, J. Zuo, J. Chen, C. Xia, Catal. Today 2014, 234, 223-232.
- 6 S. Zhu, X. Gao, Y. Zhu, Y. Zhu, H. Zheng, Y. Li, J. Catal. 2013, 303, 70-79.