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Supplementary Information

Promotional effect of indium on Cu/SiO_2 catalysts for the hydrogenation of dimethyl oxalate to ethylene glycol

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Table S1. Textural Properties of CuxIn/SiO_2 Catalysts.

In (wt%)	Cu (wt%) [a]	In (wt%) [a]	S_{BET} (m^2/g) [b]	Vp (cm^3/g) [b]	Dp(nm) [b]
0	28.45	0	473	0.83	5.8
0.5	30.30	0.53	510	0.98	6.3
1	29.06	1.02	482	0.86	5.8
1.5	29.64	1.49	497	0.95	6.4

[a]Determined by ICP-OES analysis. [b]Determined by N_2 isotherm adsorption.

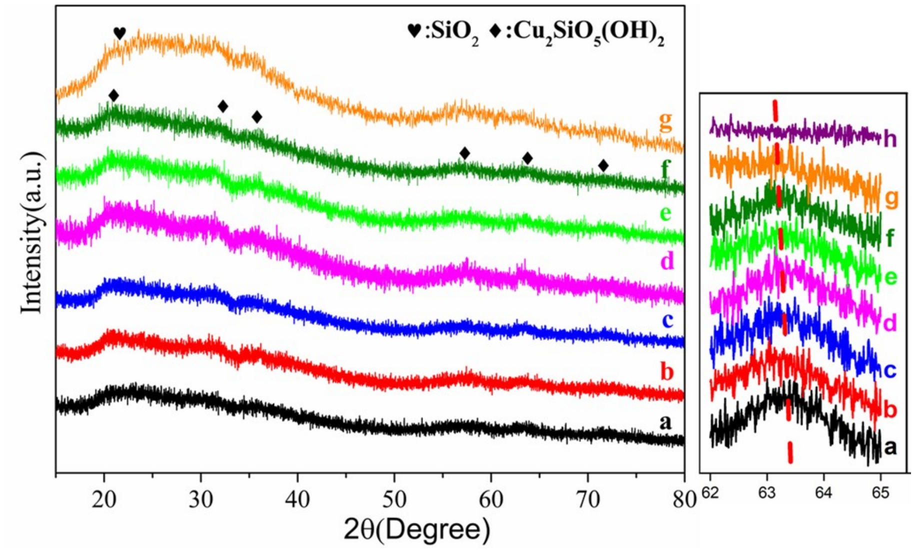

Figure S1. XRD for calcined catalysts and the fine scanning XRD at 62-65 degree for CuxIn/SiO_2 catalysts (a-g: x=0, 0.5, 1, 1.5, 2, 5, 10) and 6.7In/SiO_2 (h).

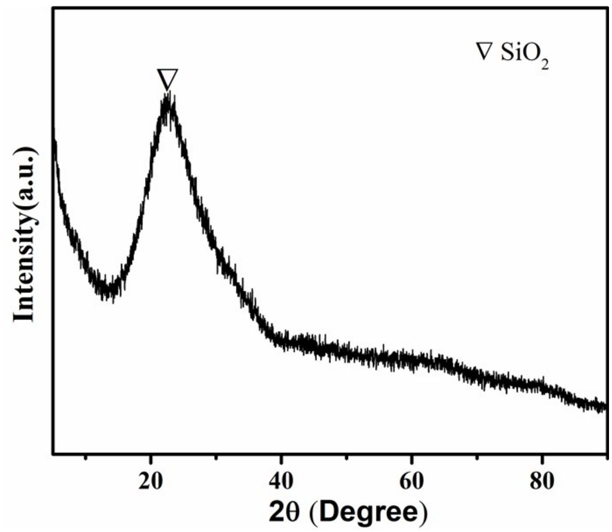

Figure S2. XRD for calcined 6.7In/SiO_2 catalyst

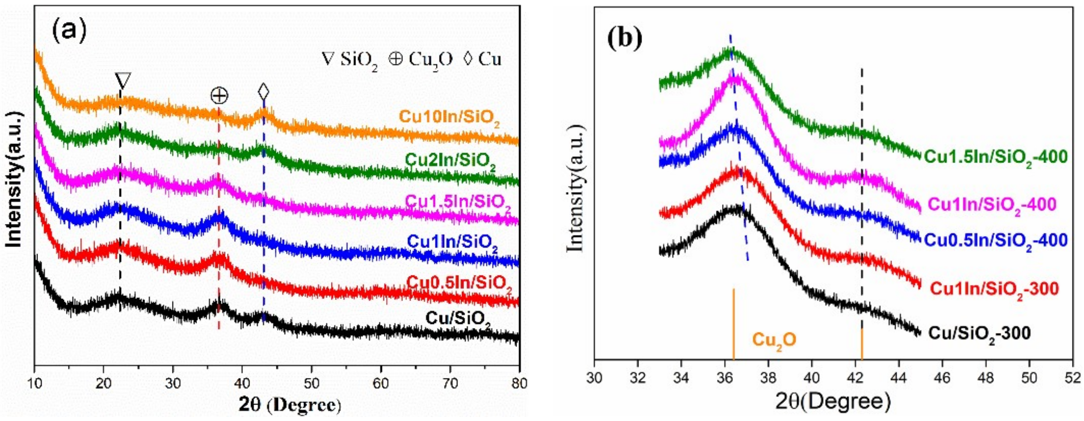

Figure S3. XRD patterns for reduced (a) and fine scanning XRD for reduced catalysts at 33-45 degree (b), Cu_2O (JCPDS: 05-0667) [1].

Table S2. Particle sizes calculated from XRD with reduced catalysts.

Catalysts	Reduced(nm)	
	Cu^+	Cu^0
Cu/SiO_2	2.3	2.6
$Cu0.5In/SiO_2$	2.1	-
$Cu1In/SiO_2$	2.2	-
$Cu1.5In/SiO_2$	2.2	-
$Cu2In/SiO_2$	1.9	2.2
$Cu10In/SiO_2$	-	3.3

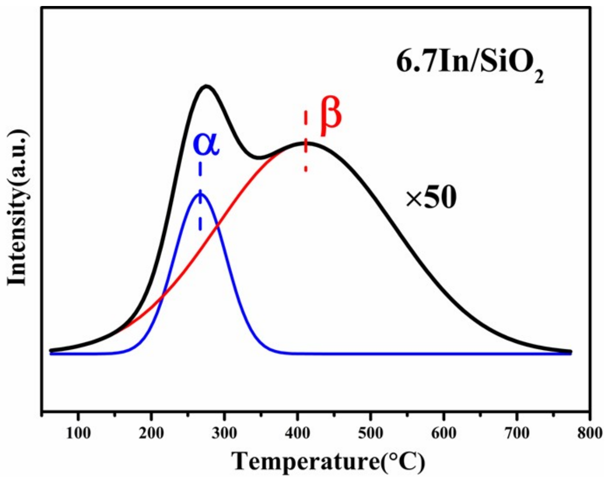

Figure S4. Deconvolution of the enlarged H_2-TPR curve of 6.7In/SiO_2.

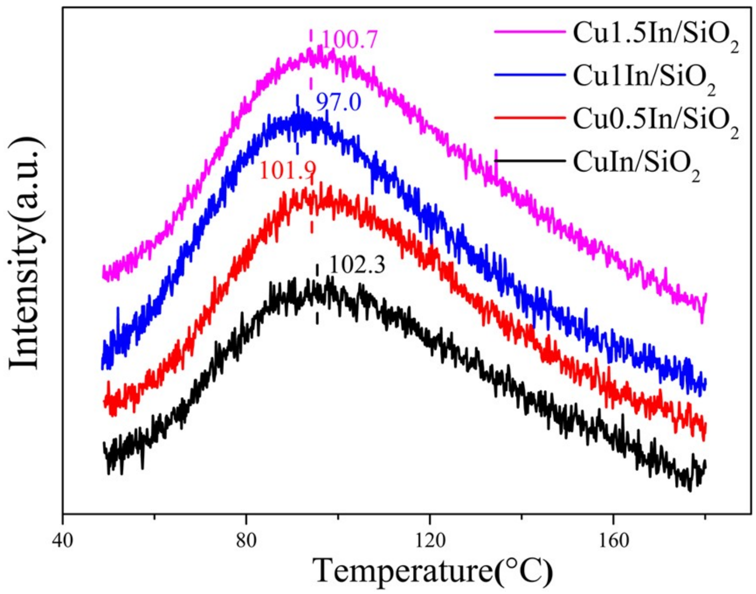

Figure S5. H_2-TPD curves of CuxIn/SiO_2 catalysts.

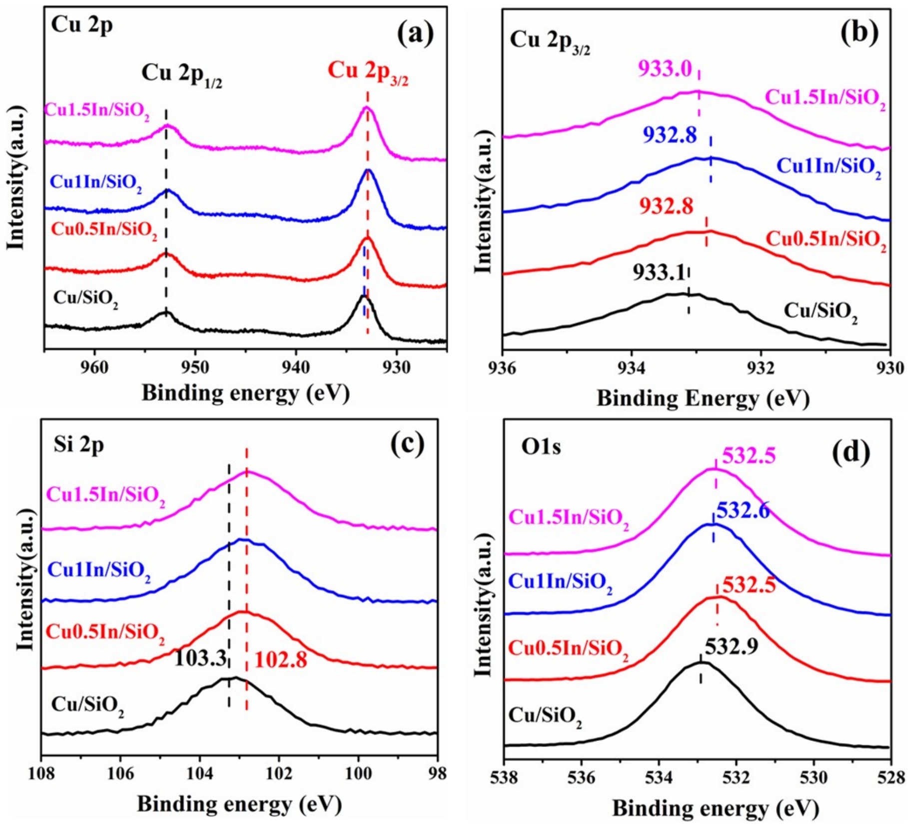

Figure S6. XPS for Cu 2p(a), Cu $2p_{3/2}$(b), Si 2p(c), O 1s(d).

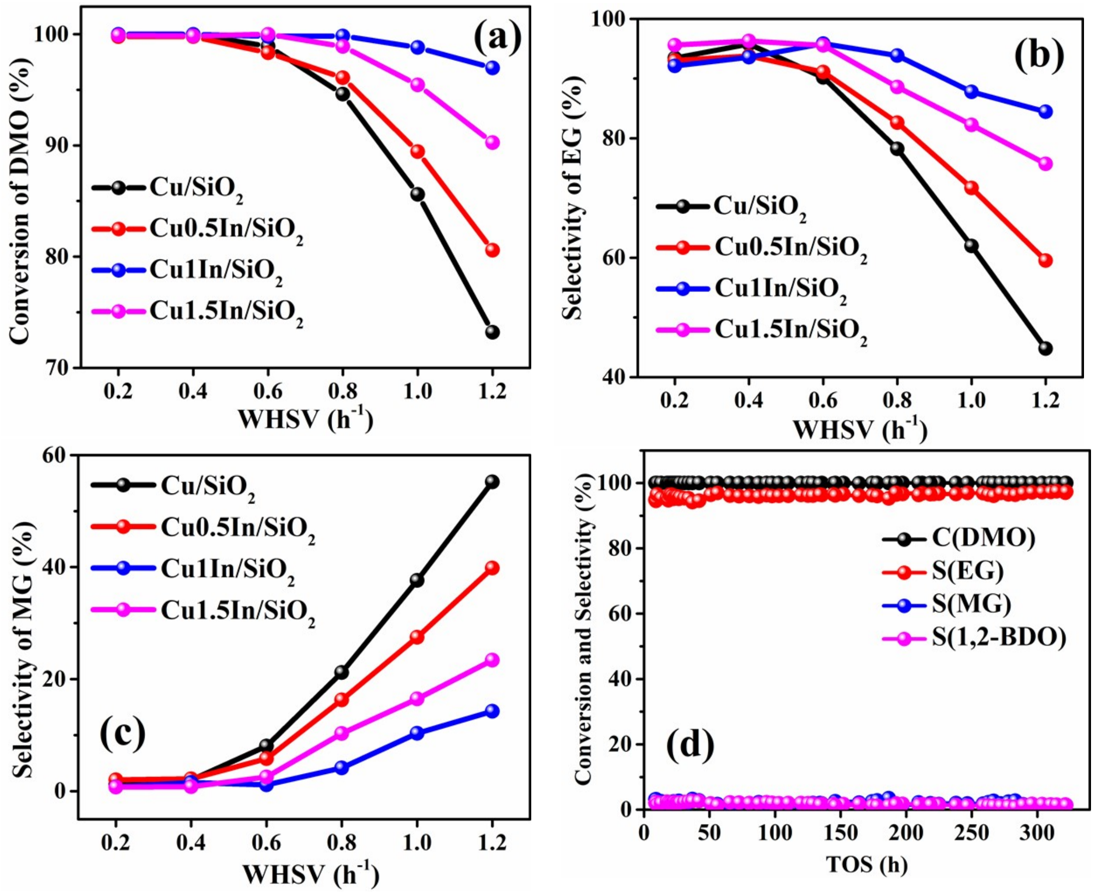

Figure S7. Activity evaluation of CuxIn/SiO_2 catalysts (x=0, 0.5, 1, 1.5), conversion of DMO (a), selectivity of EG (b), selectivity of MG (c) at reaction conditions of 2.5 MPa, 180 °C, H_2/DMO = 80 (mole) and stability evaluation of Cu1In/SiO_2 catalyst (d) at reaction conditions of 2.5 MPa, 180 °C, H_2/DMO = 80 (mole) and WHSV=0.8 h^{-1}.

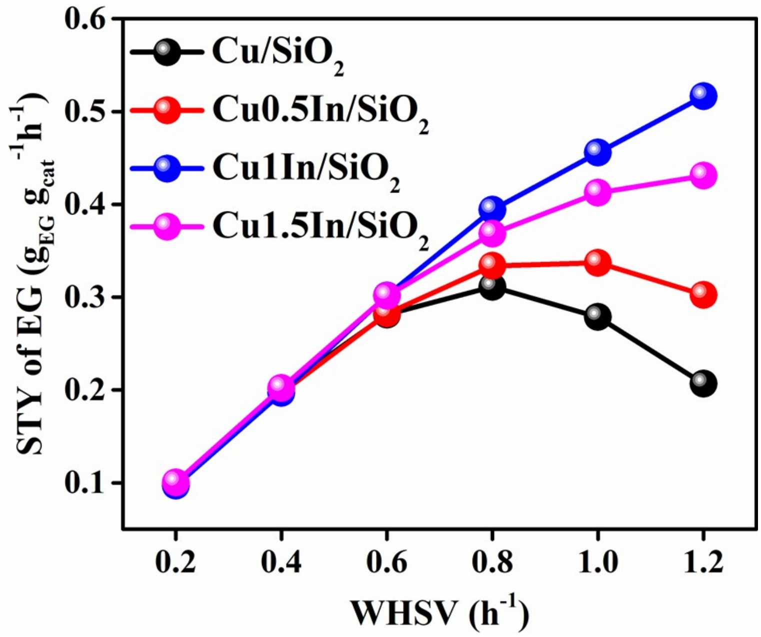

Figure S8. STY of EG at different WHSV, reaction conditions: 2.5 MPa, 180 °C, H_2/DMO = 80 (mole).

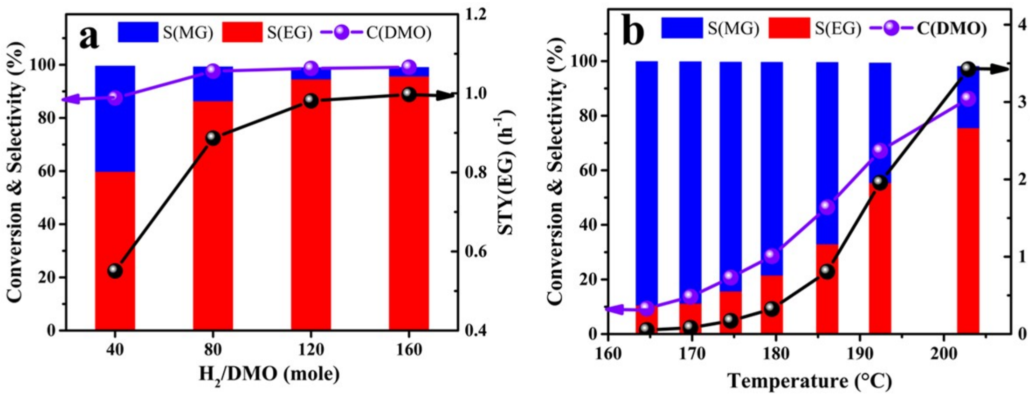

Figure S9. Catalytic performance of $Cu1In/SiO_2$ with different H_2/DMO (a) at 180 ºC, 2 h^{-1}, 2.5 MPa, and reaction temperature (b) at 10 h^{-1}, 2.5 MPa, H_2/DMO = 80 (mole).

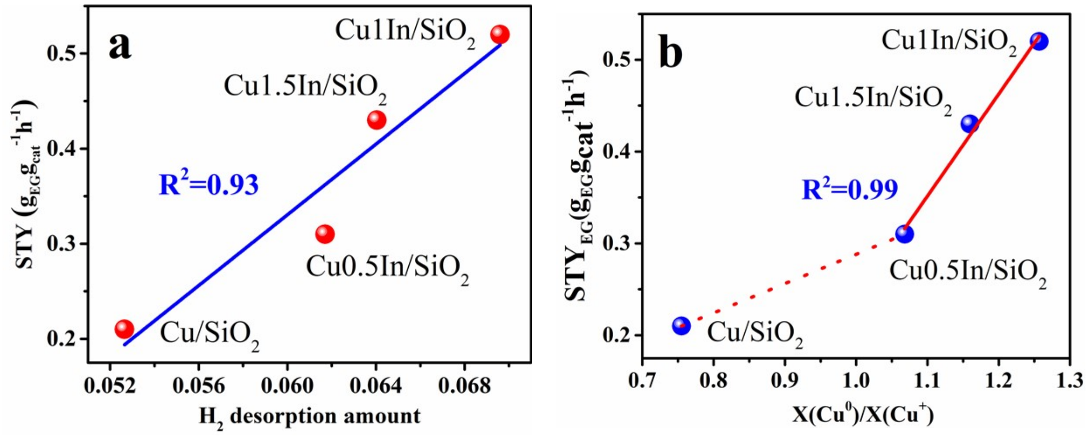

Figure S10. Relationship between STY_{EG} and H_2 adsorption amount (a) and ratio of Cu^0/Cu^+(b).

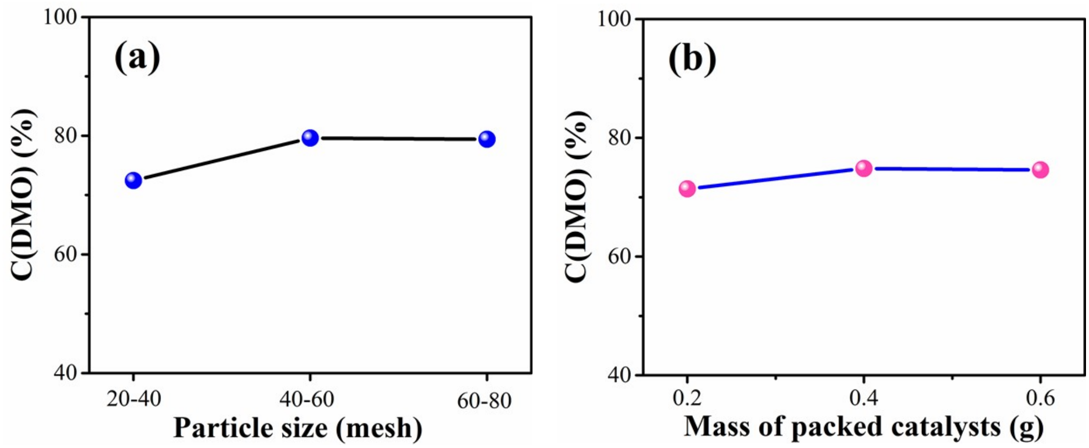

Figure S11. Madon-Boudart test[2] with Cu1In/SiO_2. Reaction conditions: 180 ºC, 2.5 MPa, WHSV = 3 h^{-1} and H_2/DMO = 80 (mole).

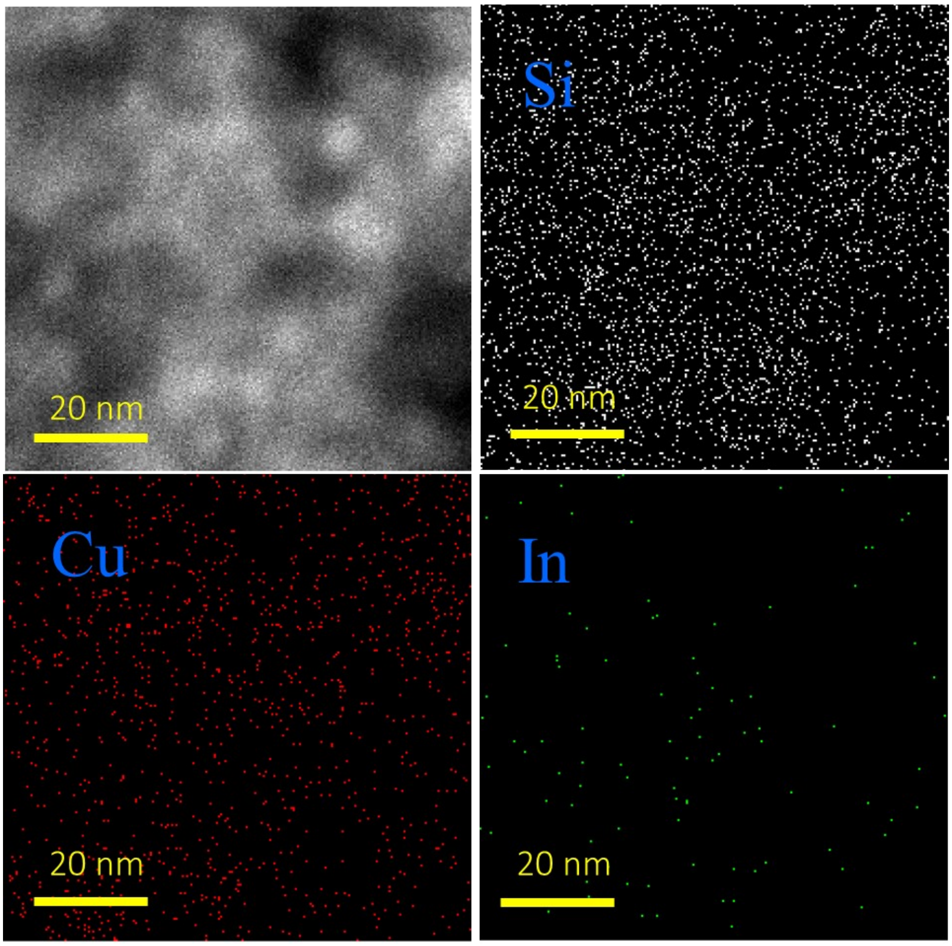

Figure S12. Elemental mapping of Si, O, Cu and In for Cu1In/SiO_2

Table S3. The evaluation results for Cu/SiO_2 when calculating the Ea.

T/ºC	WHSV/h^{-1}	C(DMO)/%	S(EG)/%
184.8	6	35.3	19.0
180.0	6	23.9	12.7
175.1	6	16.3	10.2
170.4	6	11.4	9.6
165.4	6	7.5	6.6

Table S4. The evaluation results for $Cu0.5In/SiO_2$ when calculating the Ea.

T/ºC	WHSV/h^{-1}	C(DMO)/%	S(EG)/%
184.3	10	27.7	14.9
180.9	10	20.8	13.6
175.2	10	13.4	10.1
170.1	10	9.3	7.9
164.8	10	6.2	5.2

Table S5. The evaluation results for $Cu1In/SiO_2$ when calculating the Ea.

T/ºC	WHSV/h^{-1}	C(DMO)/%	S(EG)/%
185.4	14	20.4	12.1
180.0	14	13.9	8.7
175.2	14	9.8	5.8
170.3	14	7.1	7.2
165.4	14	5.0	6.4

Table S6. The evaluation results for $Cu1.5In/SiO_2$ when calculating the Ea.

T/ºC	WHSV/h^{-1}	C(DMO)/%	S(EG)/%
185.3	10	24.2	15.9
180.6	10	16.4	11.2
175.8	10	11.4	8.8
169.9	10	7.7	8.3
165.0	10	5.1	6.5

Table S7 Catalytic performance of DMO hydrogenation for Cu5In/SiO_2 and Cu10In/SiO_2.

Catalysts	C(DMO)/%	S(EG)/%	S(MG)/%
Cu5In/SiO_2	41.5	16.9	83.1
Cu10In/SiO_2	24.4	5.7	94.3

Reaction conditions: 2.5 MPa, 180 °C, WHSV=0.4 h^{-1}, H_2/DMO = 80 (mole)

Table S8. Catalytic performance of copper-based catalysts in DMO hydrogenation to EG.

catalyst	C_{DMO}/%	S_{EG}/%	P/ MPa	T/ ºC	H_2/DMO	LHSV /h^{-1}	Yield/%	STY/ h^{-1}	TOF/h^{-1} (RT[a])
Cu/MMO-S3[3]	98.2	96.1	2	165	50	1	94.4	0.602	23.6(165)
20Cu-OMS[4]	100	98.2	2.5	180	80	1	98.2	0.477	-
Cu1In/SiO2(this work)	100	96	2.5	180	80	0.6	96	0.52	27.6(180)
6Cu1.9Au/SBA-15[5]	100	99.1	3	180	80	0.6	99	1.5	121(180)
Cu/ZrO2-x-S3[6]	100	99.5	2	180	50	2	99.5	1.05	42.4(180)
CuZr1/SiO2[7]	100	95	2.5	180	80	0.6	-	-	35.6(180)
1B-Cu-SiO2[8]	99.7	93	3	190	80	0.75	92.7	1.6	-
Cu@SiO2@CNT[9]	100	~99	3	190	100	0.6	99	-	22(190)
0.05D-Cu-SiO2[10]	99.9	96.9	2	190	50	1	96.8	-	11.4(160)
Cu-Ag0.05/SiO2[11]	100	97	3	190	80	0.6	97	-	20.6(190)
CuSiZr1-850[12]	100	99	3	190	150	0.3	99	-	30(190)
Cu/SiO2-3HZ-38	99.8	94.4	3	190	80	2	94.2	1.50	-
6Cu1-Pt0.1/SBA-15[13]	100	98	3	190	80	0.6	98	0.31	62.1(190)
Cu/SiO2[14]	100	95.0	2.5	200	200	2	95.0	-	-
Cu/SiO2[15]	95.0	90.0	3	200	80	0.6	85.5	-	-
Cu/10-SiO2[16]	100	94.7	2.5	200	120	2.5	94.7		30.6(195)
Cu-PSNT@m-SiO2[17]	100	98.0	3	200	80	2	98.0	-	40.6(200)
Cu/NAHS	100	95.0	2.5	200	20	2	95.0	-	160(200)
Cu-0.5%Pd/SiO2[18]	100	95.0	2.5	200	100	0.5	95	-	-
Cu-0.6%Sn/SiO2[19]	100	96.0	2.5	200	90	1	96	-	-
15CNTs-Cu-SiO2[20]	100	95.0	3	200	80	1.2	95.0	2.6	-
Cu/SiO2-TiO2[21]	100	97	3	200	100	0.3	97	-	-
Cu/H1S1[22]	100	98	2.5	200	100	1.5	98	-	1.89(200)
20Cu-HMS[23]	100	98	2.5	200	50	0.45	98	-	3.8
20Cu-MCM-41[24]	100	92	2.5	200	80	3	92	-	-
CuB/HMS(2/1)[25]	100	98	2.5	200	120	2.5	98	-	-
Cu3Ni/HMS[26]	100	98	2.5	200	100	1	98	-	19.7(200)
Cu-Ni/ZrO2-DBD[27]	100	96	2.5	200	120	0.3	96	-	-
Cu/SiO2-MOF[28]	99.9	95.0	2	210	50	0.82	94.9	0.424	19.3(190)
0.1CD-Cu-SiO2[29]	~99.9	~95.0	2	210	50	0.72	94.9	~0.36	11.4(170)
10%Cu-Co/HMS[30]	100	>95.0	3	220	150	1.2	95.0	-	5.5(220)
Cu/Al-ZrO2[31]	100	97.1	2.5	220	120	0.8	97.1	-	16.9(220)
CuZnAl-773[32]	100	>95.0	3	220	100	0.3	95.0	-	-
CuZnZr-0.2[33]	>95.0	>95.0	3	220	150	0.3	90	-	-
CoCu-ZnO-450[34]	100	93	2.5	220	110	2	93	-	-
CuZnAl-LDH[35]	100	94.7	2.5	220	160	0.3	94.7	-	-
20Cu/P25-823[36]	100	99	2.5	220	100	0.3	99	-	4.5(220)
Cu@CNTs-350[37]	99.4	87.4	2.5	240	200	0.2	86.9	-	-
20Cu/HAP[38]	100	90.0	2.5	240	150	0.4	90	0.72	14.6(210)

[a]RT: reaction temperature when calculating the TOF values.

References

[1] Xu C., Chen G., Zhao Y., Liu P., Duan X., Gu L., Fu G., Yuan Y., Zheng N., *Nat. Commun.*, 2018, **9**, 3367.

[2] M. Zhang, M. Wang, B. Xu, D. Ma, *Joule*, 2019, **3**, 2876-2883.

[3] G. Cui, X. Meng, X. Zhang, W. Wang, S. Xu, Y. Ye, K. Tang, W. Wang, J. Zhu, M. Wei, D. G. Evans, X. Duan, *Appl. Catal. B- Environ.*, 2019, **248**, 394-404.

[4] Y. Zhao, Y. Zhang, Y. Wang, J. Zhang, Y. Xu, S. Wang, X. Ma, *Appl. Catal. A- Gen.*, 2017, **539**, 59-69.

[5] Y.-n. Wang, X. Duan, J. Zheng, H. Lin, Y. Yuan, H. Ariga, S. Takakusagi, K. Asakura, *Catal. Sci. Technol.*, 2012, **2**.

[6] G. Cui, X. Zhang, H. Wang, Z. Li, W. Wang, Q. Yu, L. Zheng, Y. Wang, J. Zhu, M. Wei, *Appl. Catal. B- Environ.*, 2021, **280**.

[7] Y. Zhao, H. Zhang, Y. Xu, S. Wang, Y. Xu, S. Wang, X. Ma, *J. Energy Chem.*, 2020, **49**, 248-256.

[8] Z. He, H. Lin, P. He, Y. Yuan, *J. Catal.*, 2011, **277**, 54-63.

[9] J. Zheng, H. Fang, X. Duan, H. Lin, Y. Yang, Y. Yuan, *ACS Appl. Mater. Inter.*, 2020, **12**, 27268-27276.

[10] R.-P. Ye, L. Lin, J.-X. Yang, M.-L. Sun, F. Li, B. Li, Y.-G. Yao, *J. Catal.*, 2017, **350**, 122-132.

[11] Y. Huang, H. Ariga, X. Zheng, X. Duan, S. Takakusagi, K. Asakura, Y. Yuan, *J. Catal.*, 2013, **307**, 74-83.

[12] Y. Zhu, X. Kong, D.-B. Cao, J. Cui, Y. Zhu, Y.-W. Li, *ACS Catal.*, 2014, **4**, 3675-3681.

[13] X. Zheng, H. Lin, J. Zheng, H. Ariga, K. Asakura, Y. Yuan, *Top. Catal.*, 2014, **57**, 1015-1025.

[14] J. Gong, H. Yue, Y. Zhao, S. Zhao, L. Zhao, J. Lv, S. Wang, X. Ma, *J. Am. Chem. Soc.*, 2012, **134**, 13922-13925.

[15] J. Lin, X. Zhao, Y. Cui, H. Zhang, D. Liao, *Chem. Commun. (Camb)*, 2012, **48**, 1177-1179.

[16] C. Zhang, D. Wang, M. Zhu, F. Yu, B. Dai, *Catalysts*, 2017, **7**,75.

[17] C. Xu, G. Chen, Y. Zhao, P. Liu, X. Duan, L. Gu, G. Fu, Y. Yuan, N. Zheng, *Nat. Commun.*, 2018, **9**, 3367.

[18] C. Zhang, D. Wang, M. Zhu, F. Yu, B. Dai, *ChemistrySelect*, 2016, **1**, 2857-2863.

[19] C. Zhang, D. Wang, B. Dai, *Catalysts*, 2017, **7**,122.

[20] H. Lin, X. Duan, J. Zheng, X. Zheng, P. He, Y. Yuan, Y. Yang, *RSC Adv.*, 2013, **3**, 11782-11789.

[21] C. Wen, A. Yin, Y. Cui, X. Yang, W.-L. Dai, K. Fan, *Appl. Catal. A- Gen.*, 2013, **458**, 82-89.

[22] A. Yin, C. Wen, W.-L. Dai, K. Fan, *Appl. Sur. Sci.*, 2011, **257**, 5844-5849.

[23] An. Yin, X. Guo, W.-L. Dai, K. Fan, *J. Phys. Chem. C*, 2009, **113**, 11003–11013

[24] X. Ma, H. Chi, H. Yue, Y. Zhao, Y. Xu, J. Lv, S. Wang, J. Gong, *AIChE J.*, 2013, **59**, 2530-2539.

[25] A. Yin, J. Qu, X. Guo, W.-L. Dai, K. Fan, *Appl. Catal. A- Gen.*, 2011, **400**, 39-47.

[26] A. Yin, C. Wen, X. Guo, W.-L. Dai, K. Fan, *J. Catal.*, 2011, **280**, 77-88.

[27] C. Zhang, D. Wang, M. Zhu, F. Yu, B. Dai, *Catal. Commun.*, 2017, **102**, 31-34.

[28] R.-P. Ye, L. Lin, C.-C. Chen, J.-X. Yang, F. Li, X. Zhang, D.-J. Li, Y.-Y. Qin, Z. Zhou, Y.-G. Yao, *ACS Catal.*, 2018, **8**, 3382-3394.
[29] R.-P. Ye, L. Lin, C.-Q. Liu, C.-C. Chen, Y.-G. Yao, *ChemCatChem*, 2017, **9**, 4587-4597.
[30] C. Wen, Y. Cui, A. Yin, K. Fan, W.-L. Dai, *ChemCatChem*, 2013, **5**, 138-141.
[31] Q. Hu, G. Fan, L. Yang, F. Li, *ChemCatChem*, 2014, **6**, 3501-3510.
[32] C. Wen, F. Li, Y. Cui, W.-L. Dai, K. Fan, *Catal. Today*, 2014, **233**, 117-126.
[33] Y. Zhu, X. Kong, H. Zheng, Y. Zhu, *Mol. Catal.*, 2018, **458**, 73-82.
[34] X. Kong, X. Zhang, J. Chen, *Catal. Commun.*, 2015, **65**, 46-50.
[35] S. Zhang, Q. Liu, G. Fan, F. Li, *Catal. Lett.*, 2012, **142**, 1121-1127.
[36] B. Wang, Y. Cui, C. Wen, X. Chen, Y. Dong, W.-L. Dai, *Appl. Catal. A- Gen.*, 2016, **509**, 66-74.
[37] P. Ai, M. Tan, Y. Ishikuro, Y. Hosoi, G. Yang, Y. Yoneyama, N. Tsubaki, *ChemCatChem*, 2017, **9**, 1067-1075.
[38] C. Wen, Y. Cui, X. Chen, B. Zong, W.-L. Dai, *Appl. Catal. B- Environ.*, 2015, **162**, 483-493.