Supporting Information for

Highly active Ce, Y, La modified Cu/SiO₂ catalysts for hydrogenation of methyl acetate to ethanol

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Table S1. Product analysis from GC-MS.

Time/min	Product	Molecular Weight
1.32	(structure: methanol)	32
1.4	(structure: ethanol, CH₃CH₂OH)	46
1.55	(structure: dimethyl ether)	46
1.58	(structure: methyl acetate)	74
1.7	(structure: 2-butanol)	74
1.78	(structure: 1-propanol)	60
1.88	(structure: 3-pentanol)	88
1.94	(structure: 2-methylpropanal)	72
2.06	(structure: ethyl acetate)	88
2.41	(structure: sec-butyl ethyl ether)	102
2.58	(structure: acetaldehyde methyl ethyl acetal)	104

Reaction condition: T=280 °C, P=2.5MPa, GHSV=3000 h⁻¹, LHSV=1 h⁻¹.

Main Side reaction:

$$CH_3COOCH_3 + CH_3CH_2OH \rightarrow CH_3COOC_2H_5 + CH_3OH \qquad (1)$$

$$CH_3CH_2OH \rightarrow CH_3CHO + H_2 \qquad (2)$$

$$CH_3CH_2OH \rightarrow CH_3CH_2 + H_2O \qquad (3)$$

$$CH_2CH_2 + H_2 \rightarrow CH_3CH_3 \tag{4}$$
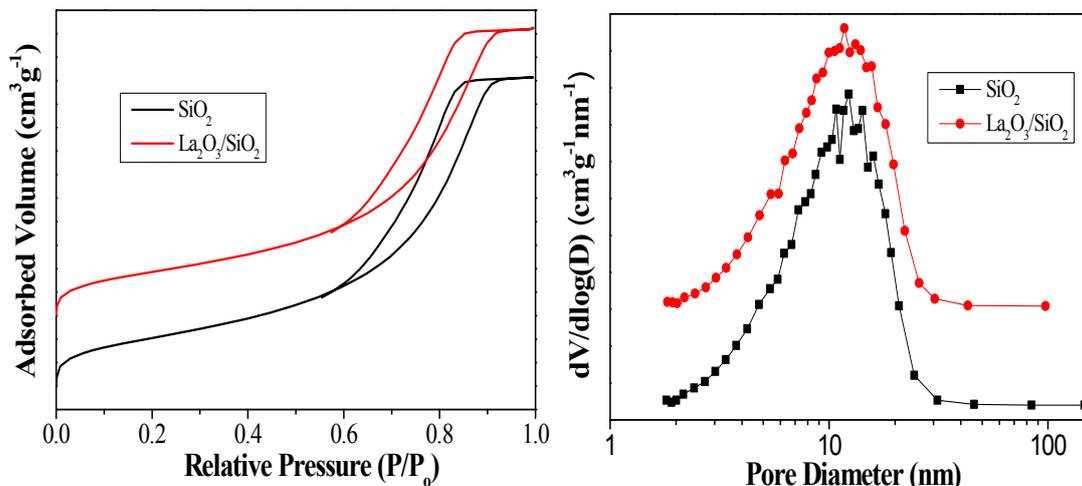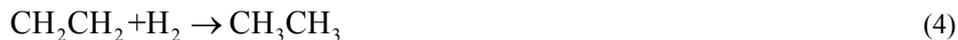
Fig. S1. N_2 adsorption-desorption isotherm and pore distribution of selected SiO_2 and La_2O_3/SiO_2.

Table S2. Grain size of the copper crystallite of different catalyst.

Catalyst	2θ of 111Crystal face (^{o})	d_{Cu} (nm)
Cu/SiO_2	43.4	4.5
Cu/SiO_2-5Ce	43.5	4.1
Cu/SiO_2-5Y	43.5	7.7
Cu/SiO_2-1La	43.5	3.6
Cu/SiO_2-5La	43.5	3.5
Cu/SiO_2-10La	43.5	7.1
Spent Cu/SiO_2	43.1	8.6
Spent Cu/SiO_2-5La	43.2	5.2
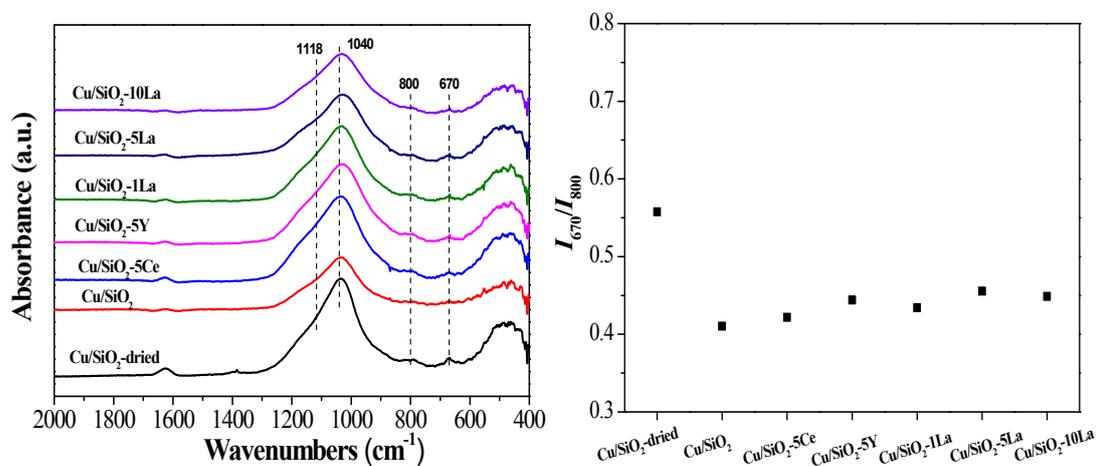
Fig. S2. FTIR spectra of Cu-SiO_2 and Cu/SiO_2-xM catalysts.

The IR bands of $\delta_{OH} = 670$ cm^{-1} and $\upsilon_{SiO} = 1040$ cm^{-1} could be suggested that the presence of copper phyllosilicate phase in all samples, while silica exhibits an asymmetric υ_{SiO} band at 1118 cm^{-1} and a symmetric υ_{SiO} band at 800 cm^{-1}. I_{670}/I_{800} is denoted the relative contents of copper phyllosilicate in different catalysts.[1-2] It could be found that the value of different calcined catalyst is almost the same, suggesting the amount of $Cu_2SiO_5(OH)_2$ in different catalyst has no big difference.

[1] T. Toupance, M. Kermarec, C. Louis, *J. Phys. Chem. B* 2000, **104**, 965–972.

[2] H. Yue, Y. Zhao, S. Zhao, B. Wang, X. Ma and J. Gong, *Nat. Commun.,* 2013, **4**, 2339–2345.

N$_2$O titration method

The copper surface area was calculated combined with the results of N$_2$O titration and Cu LMM XAES spectra according to previous report.[2-3] Typically, 50 mg of the calcined catalysts were reduced by the same H$_2$-TPR procedure described **in section 2.2** (denoted as total TPR). After cooling down to 60 °C, the reduced samples were exposed to a pure N$_2$O flow (60 mL/min, 1 h) to completely oxidize surface copper atoms into Cu$_2$O. Afterwards, the resulting surface oxidized samples underwent the second TPR run as the first one (denoted as surface TPR). The Cu dispersion (D$_{Cu}$), specific expose Cu surface area (S$_{Cu}$) were calculated by Eqs. (1) and Eqs. (2), by assuming 1.47×10^{19} copper atoms per square meter. Then the S$_{Cu}^+$ (S$_{Cu}^0$) could be calculated combined the values of S$_{Cu}$ and the Cu$^+$ (Cu^0) ratio from the results of Cu LMM XAES under the assumption that the Cu$^+$ ions and Cu^0 atoms occupy identical areas.

$$D_{Cu}(\%) = \frac{2 \times H_2 \text{ Consumption (surface TPR)}}{H_2 \text{ Consumption (total TPR)}} \times 100 \qquad (1)$$

$$S_{Cu}(m^2 g^{-1} Cu) = \frac{D_{Cu} \times N_{av}}{M_{Cu} \times 1.46 \times 10^{19}} \qquad (2)$$

Where N_{av}: Avogadro constant $= 6.02 \times 10^{23}$ (mol^{-1}); M_{Cu}: relative atomic mass $=63.55$ (g/mol).

[3] Y. Zhao, B. Shan, Y. Wang, J. Zhou, S. Wang and X. Ma, *Ind. Eng. Chem. Res.,* 2018, **57**, 4526–4534.

[4] P. Ai, M. Tan, P. Reubroycharoen, Y. Wang, X. Feng, G. Liu, G. Yang and N. Tsubaki, *Catal. Sci. Technol.,* 2018, **8***,* 6441–6451.
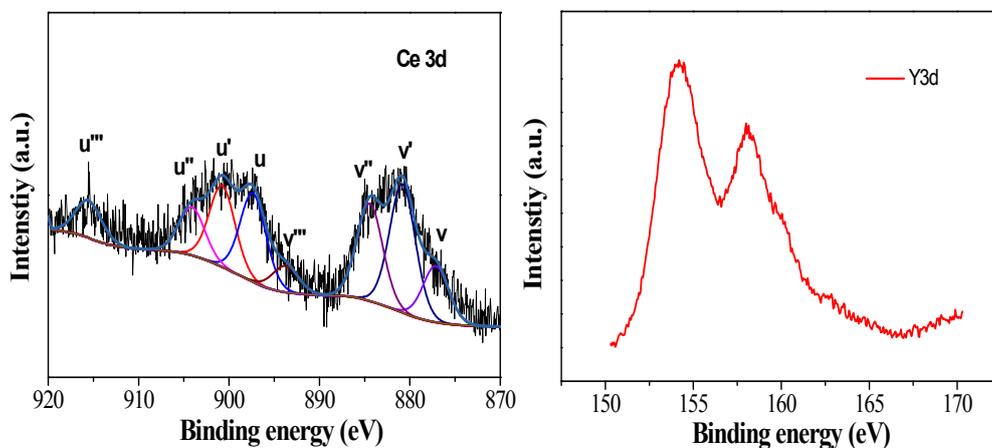
Fig. S3. XPS spectra of Ce 3d and Y 3d.
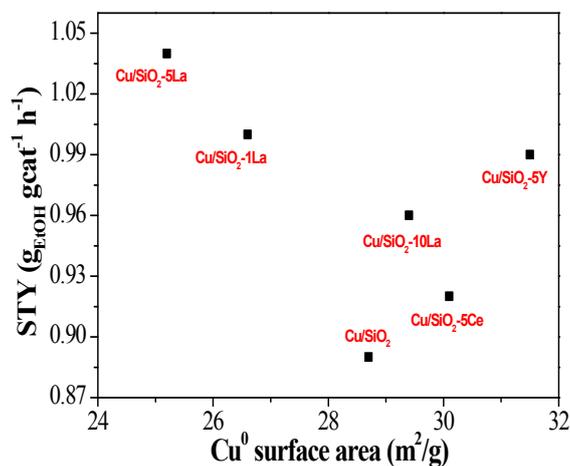
Fig. S4. Effects of Cu^0 surface area of $Cu-SiO_2$ and Cu/SiO_2-xM catalyst on the STY_{EtOH}.
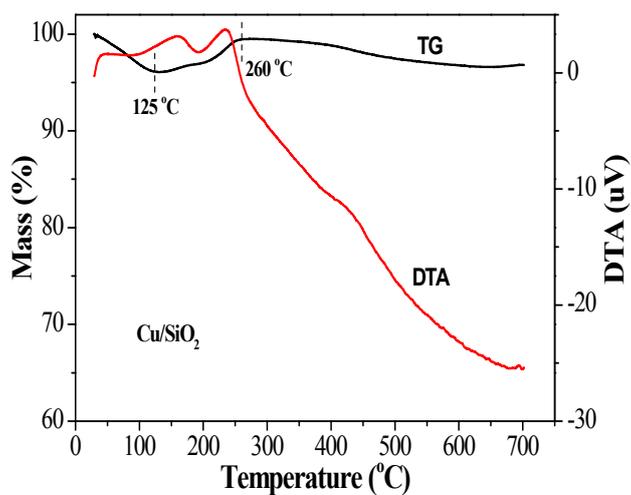
Fig. S5. TG and DTA analysis of spent Cu/SiO_2 after long-term stability test.

From the result of Figure S5, it could be found that there have three steps in the

whole stage. The first step before 125 °C is related to the weight loss of surface water. After that, the weight has increased might be due to the Cu^+ species oxidation when exposed to the air. The third step after 260 °C is probably corresponding to the decomposition of CuO. From previous literatures, the carbon deposit would be oxidized at 200-400 °C. But from our results, it could be inferred that the formation of carbon deposition is not obvious.
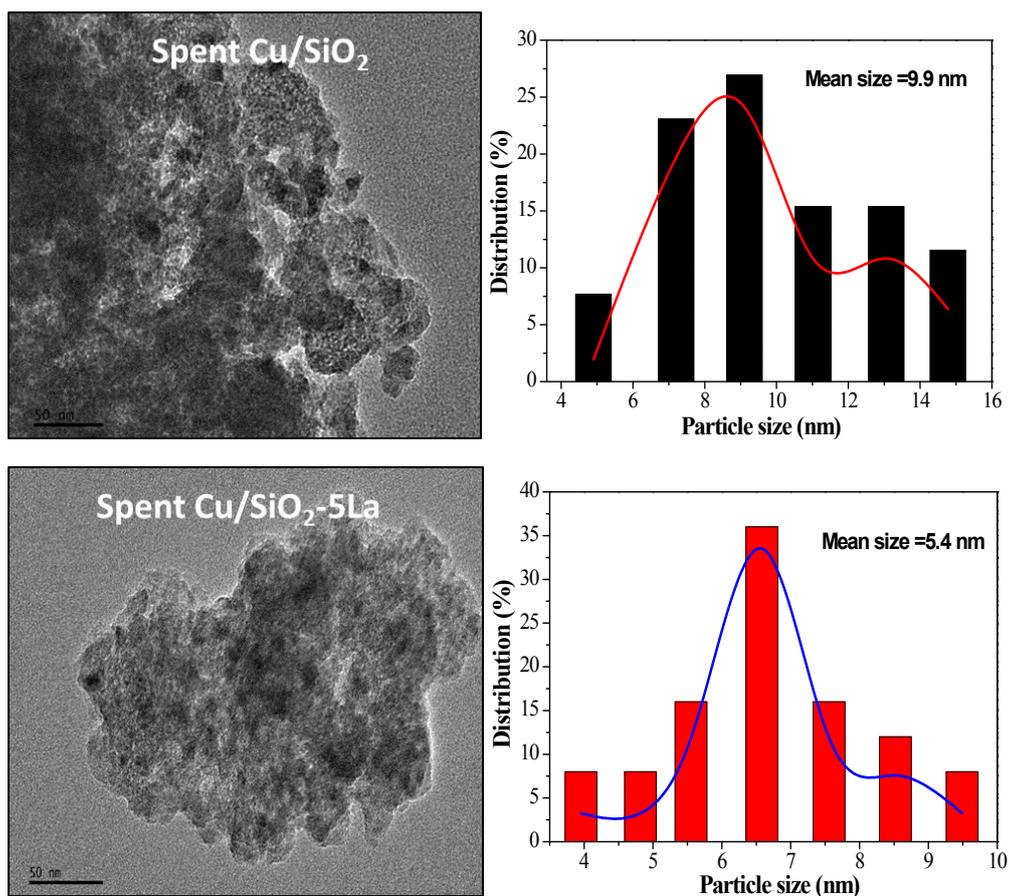
Fig. S6. TEM image of spent Cu/SiO_2 and $Cu-/SiO_2$-5La catalyst after long-term estimating.

Table S3. Summary of Cu-based catalysts for hydrogenation of MA to ethanol under different reaction conditions.

Catalyst	Pressure (Mpa)	LHSV (h^{-1})	H_2/MA	Reaction temperature (°C)	MA conversion (%)	Ref.
Cu/SiO$_2$-HP	2.5	2	15	250	86.8	This work
Cu/SiO$_2$-5La-HP	2.5	2	15	250	94.3	This work
Cu/SiO$_2$-AE	2	1	**40**	220	80.9	5
Cu/SiO$_2$-AE	**3**	2	**15**	250	83.7	6
Cu$_9$Zn$_1$/SiO$_2$	2	2	**20**	220	92	7
Cu$_{0.9}$Zn$_{0.1}$/SBA-15	2	2	**20**	220	85	8
Cu@CeO$_2$	2.5	**1**	**80**	215	99	9
Cu/9MgO-SiO$_2$	**3**	2	10	340	80.3	10
3Mn-Cu/SiO$_2$	**3**	2	15	250	96	11

HP: hydrolysis-precipitation method; AE: ammonia evaporation

[5] X. Dong, X. Ma, H. Xu and Q. Ge, *Catal. Sci. Technol.,* 2016, **6**, 4151–4158.

[6] Y. Zhang, C. Ye, C. Guo, C. Gan and X. Tong, *Chinese J Catal.,* 2018, **39**, 99–108.

[7] Y. Zhao, B. Shan, Y. Wang, J. Zhou, S. Wang and X. Ma, *Ind. Eng. Chem. Res.,* 2018, **57**, 4526–4534.

[8] Y. Wang, J Liao, J. Zhang, S. Wang, Y. Zhao and X. Ma, *AIChE J,* 2016, **63**, 2839–2849.

[9] Y. Wang, Y. Zhao, J. Lv and X. Ma, *ChemCatChem,* 2017, **9**, 2085–2090.

[10] H. Qin, C. Guo, C. Sun and J. Zhang, *J Mol. Catal. A,* 2015, **409**, 79–84.

[11] C. Ye, C. Guo, C. Sun and Y. Zhang, *RSC Adv.,* 2016, **6**, 113796–113802.