Electronic Supplementary Information

Cyclohexene esterification–hydrogenation for efficient production of cyclohexanol

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Table S1 Summary of the industrial data for the calculation of the atom economy and per pass yield of cyclohexanol/cyclohexanone through three typical industrial processes. The pilot-scale data of the novel cyclohexene esterification–hydrogenation process are presented for comparison.

Process	Reaction	Conv. (%)	Product	Sel. (%)	Atom economy (%)	Product	Sel. (%)	Per pass yield (%)	Per pass yield of cycohexanol/ cyclohexanone (%)
Cyclohexane oxidation (industrial data from Baling Petrochemical)	Benzene → cyclohexane	100	Cyclohexane	100	**83.7**	Cyclohexane	100	100	**3.7**
	Cyclohexane → cyclohexyl peroxide	4.5	Cyclohexyl hydroperoxide	93		Cyclohexyl hydroperoxide	93	4.2	
	Cyclohexyl hydroperoxide → Cyclohexanone/ cycohexanol	99	Cyclohexanone and cycohexanol	90		Cyclohexanone and cyclohexanol	90	89.1	
Cyclohexene hydration	Benzene → cyclohexene[1]	60	Cyclohexane and cyclohexene	100	**99.3**	Cyclohexene	67	40.2	**5.1**
	Cyclohexene →	12.7	Cyclohexanol	99.3		Cyclohexanol	99.3	12.6	

	cyclohexanol[2]								
Phenol hydrogenation	Benzene → cumene[3]	98	Cumene and polyisopropyl benzenes	98	**95.5**	Cumene	84.9	83.2	**14.9**
	Cumene → cumene hydroperoxide	25	Cumene hydroperoxide and dimethylphenyl-carbinol	98		Cumene hydroperoxide	90	18	
	Cumene hydroperoxide → phenol[4]	100	Phenol	99.5		Phenol	99.5	99.5	
	Phenol → cyclohexanol[5,6]	99.9	Cyclohexanol	99.9		Cyclohexanol	99.9	99.9	
Cyclohexene esterification–hydrogenation	Benzene → cyclohexene	60	Cyclohexane and cyclohexene	100	**99.4**	Cyclohexene	67	40.2	**34.6**
	Cyclohexene → cyclohexyl acetate	87	Cyclohexyl acetate	99.7		Cyclohexyl acetate	99.7	86.7	
	Cyclohexyl acetate	99.5	Cyclohexanol	99.7		Cyclohexanol	99.7	99.2	

	→ cyclohexanol								

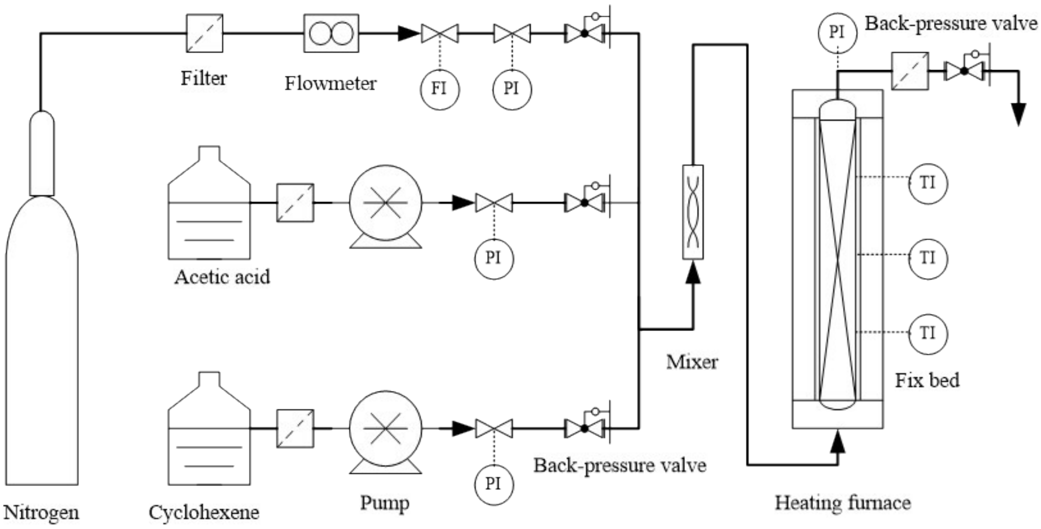

Fig. S1 Experimental set-up for intrinsic kinetic evaluation of the esterification of cyclohexene with acetic acid.

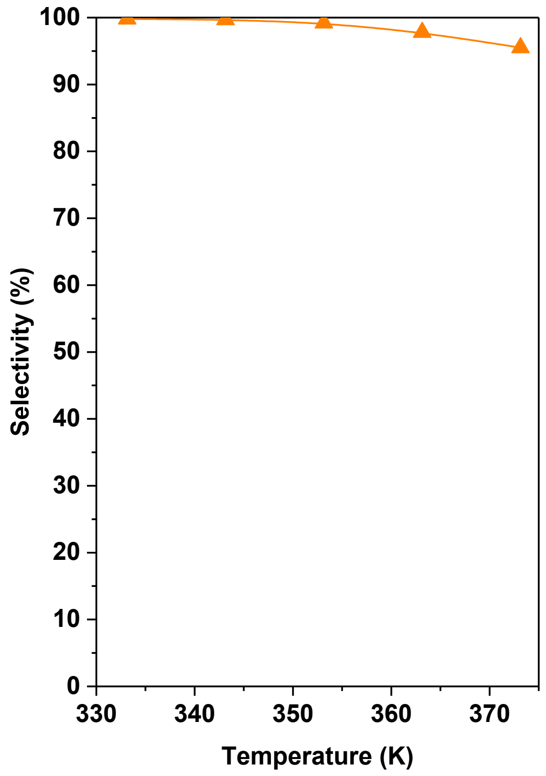

Fig. S2 Effect of reaction temperature on cyclohexyl acetate selectivity in cyclohexene esterification at HAc/cyclohexene molar ratio of 2: 1.

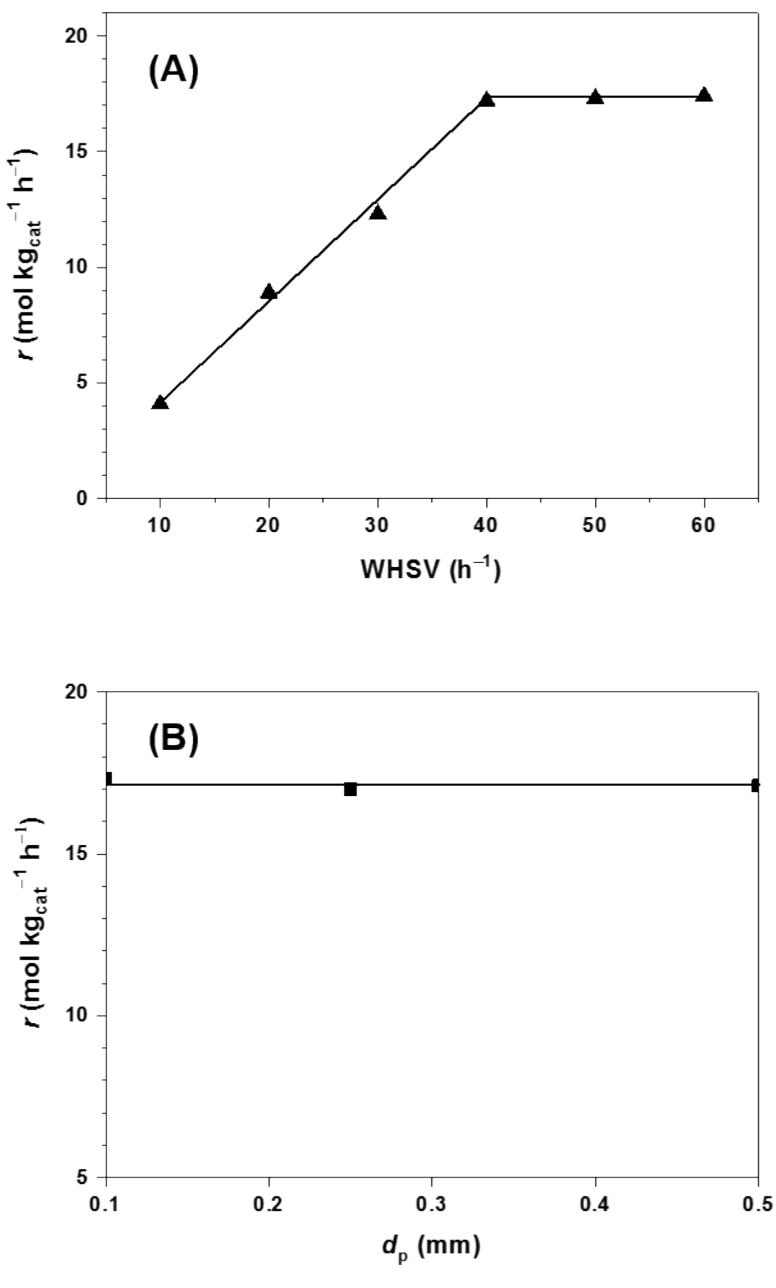

Fig. S3 (A) Effect of weight hourly space velocity (WHSV) on the reaction rate in cyclohexene esterification. Other reaction conditions: temperature of 353 K, N_2 pressure of 0.3 MPa, HAc/cyclohexene molar ratio of 2: 1, and catalyst particle size d_p< 0.5 mm, and (B) effect of catalyst particle size d_p on the reaction rate. Other reaction conditions: N_2 pressure of 0.3 MPa, HAc/cyclohexene molar ratio of 2: 1, and WHSV of 45 h^{-1}.

Table S2 Parameters of the esterification of cyclohexene with acetic acid derived from the LHHW-type kinetics model.

$$r_{\mathrm{C6E}} = m_{\mathrm{cat}} 1.43 \times 10^{14} \exp(-60000/RT) \frac{a_{\mathrm{HAC}} a_{\mathrm{C6}} - a_{\mathrm{C6E}}/K_{\mathrm{eq}}}{(1 + 99.9 a_{\mathrm{HAC}} + a_{\mathrm{C6}} + 14.9 a_{\mathrm{C6E}})^2}$$

Parameter	Unit	Fitted value
A	mol $\mathrm{kg_{cat}}^{-1}$ h^{-1}	1.43×10^{14}
E_a	kJ mol^{-1}	60.0
b_{HAC}	/	99.9
b_{C6}	/	1.0
b_{C6E}	/	14.9

Table S3 The textural and basic properties of the $Cu_1Zn_1Si_2$ and $Cu_1Zn_1Si_2La_{0.1}$ catalysts after reduction.

Catalyst	S_{BET} (m^2 g^{-1})	V_{pore} (cm^3 g^{-1})	d_{pore} (nm)	Base content ($mmol_{CO2}$ g_{cat}^{-1})
$Cu_1Zn_1Si_2$	100	0.61	24.3	3.47
$Cu_1Zn_1Si_2La_{0.1}$	106	0.61	23.0	4.22

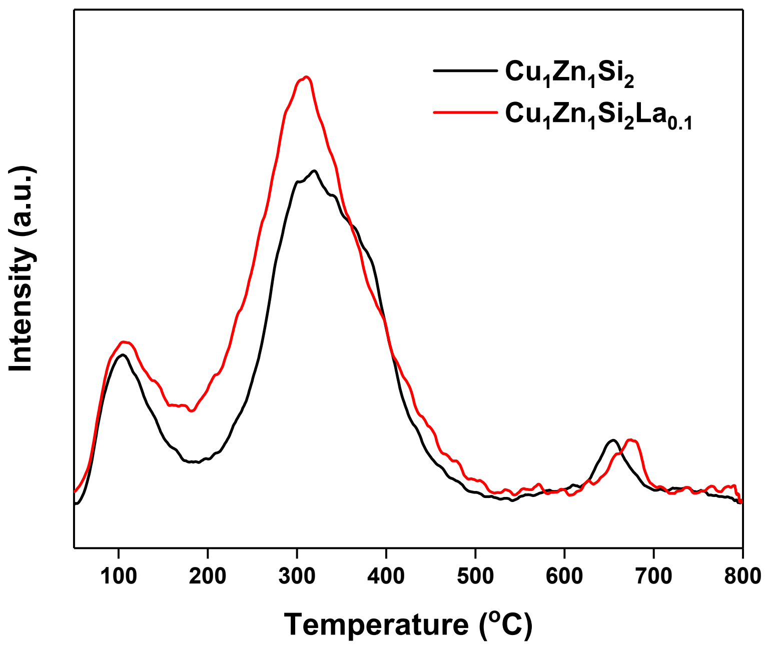

Fig. S4 CO_2-TPD profiles of the $Cu_1Zn_1Si_2$ and $Cu_1Zn_1Si_2La_{0.1}$ catalysts.

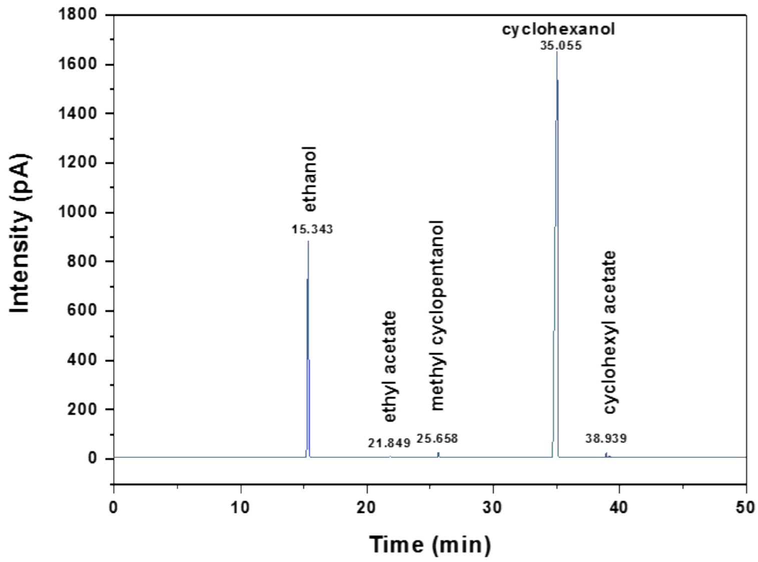

Fig. S5 The chromatogram of the hydrogenation products of cyclohexyl acetate over the $Cu_1Zn_1Si_2La_{0.1}$ catalyst.

Table S4 The characteristics and operation parameters of the reactive distillation column.

Parameter	Value
Height (m)	3
Inner diameter (m)	0.12
Reboiler capacity (L)	15
Reboiler power (W)	1050
Catalytic section	0–2 m (from column top)
Stripping section	2–3 m (from column top)
Operation pressure (MPa)	0.1
Catalyst weight (kg)	2.65

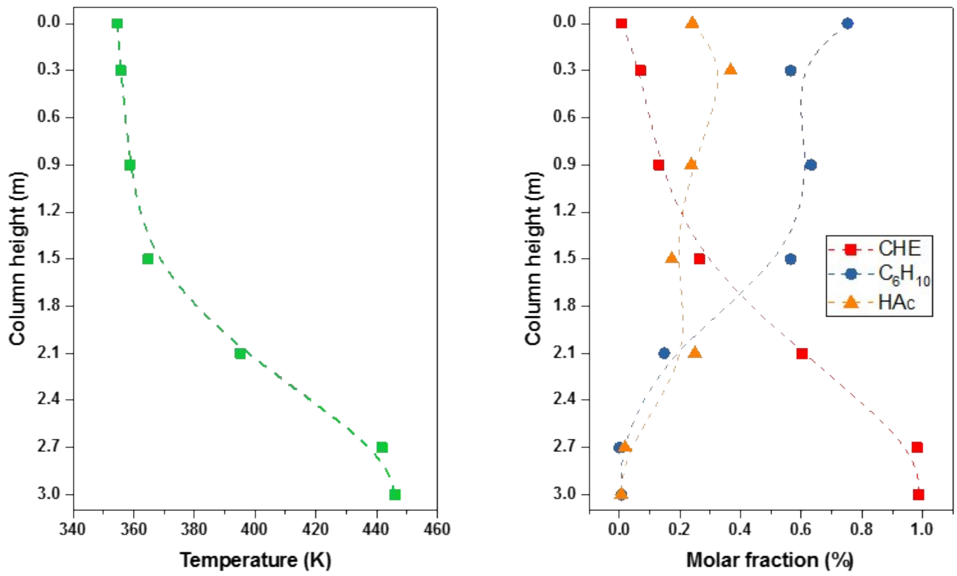

Fig. S6 The temperature (left) and composition (right) profiles in the reactive distillation column operated under the conditions indicated in Table S4.

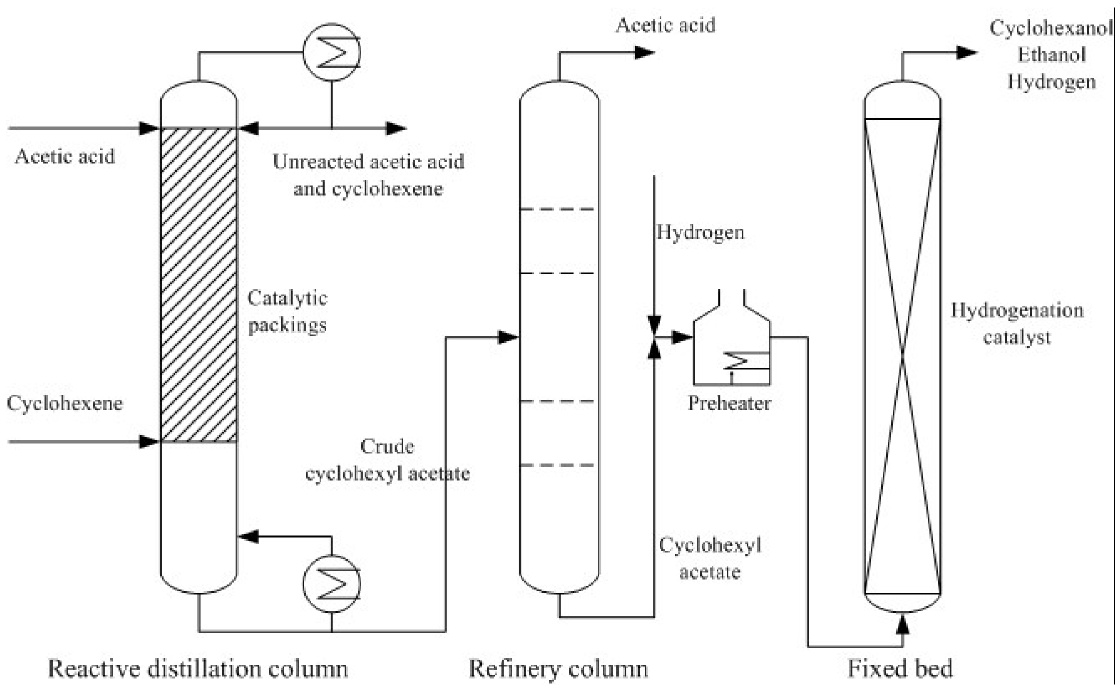

Fig. S7 The flow chart (top) and photograph (bottom) of a pilot-scale reactor with a reactive-distillation reactor in conjugation with a fixed-bed reactor for continuous cyclohexene esterification and ester hydrogenation.

References

1. H. Nagahara, M. Ono, M. Konishi and Y. Fukuoka, *Appl. Surf. Sci.*, 1997, **121/122**, 448–451.

2. H. Ishida, *Catal. Surv. Jpn.*, 1997, **1**, 241–246.

3. T. F. Degnan Jr., C. M. Smith and C. R. Venkat, *Appl. Catal. A*, 2001, **221**, 283–294.

4. R. J. Schmidt, *Appl. Catal. A*, 2005, **280**, 89–103.

5. J. He, X. H. Lu, Y. Shen, R. Jing, R. F. Nie, D. Zhou and Q. H. Xia, *Mol. Catal.*, 2017, **440**, 87–95.

6. A. Q. Li, K. Shen, J. Y. Chen, Z. Li and Y. W. Li, *Chem. Eng. Sci.*, 2017, **166**, 66–76.