## Highly Efficient and Robust Aerobic Co-oxidation of Olefins and Aldehydes over $CoO_x$ Dispersed within Hierarchical Silicalite-1 Zeolites

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## **Analysis method**

Both substrates and products were analyzed by a GC-MS instrument (Agilent 7890B) equipped with capillary flow splitter, which can divide the injection flow into two flows. One flow can be analyzed by mass spectrometer (MS) detector (5977 MSD) for identifying the structure of substrates and products, while the other flow is simultaneously quantified by the flame ionization detector (FID) of GC for quantifying detailed composition.

The Agilent 7890B instrument was equipped with an Agilent HP-5 column (30 m×0.25 mm×0.25  $\mu$ m). 0.4  $\mu$ L of sample was injected into the GC with a split ratio of 50:1, and the carrier gas (nitrogen) flow rate was 25 mL/min. The flow rates of air and hydrogen were 300 mL/min and 30 mL/min, respectively. The temperatures of the injector and the detector were 280 °C and 300 °C, respectively. The oven temperature program consisted of a 2 min soak at 50 °C, followed by a 10 °C/min ramp up to 250 °C, and then by a 50 °C/min ramp to 300 °C, which was held for one minute.

The reaction activity was expressed as conversion rate (Conv, %) and selectivity (Selec, %), which are defined as followed:

$$Conv.(\%) = \frac{c_0 - c}{c_0}$$
  
Selec.(\%) =  $\frac{c_{product}}{c_0 - c}$ 

where  $c_0$  is referred to the molar concentration of olefins and aldehydes before reaction, c is referred to the molar concentration of olefins and aldehydes after reaction, and  $c_{product}$  is referred as to the molar concentration of the product after reaction.

In addition, to precisely quantify catalytic performance, all data in this manuscript were reexamined by standard curve method, with Naphthalene ( $C_{10}H_8$ , 99%) as the specific internal standard compound under the same GC detection conditions, as described in analysis method of SI.

Firstly, to obtain standard epoxy products of two configurations, the epoxidation of both Econfiguration (Methyl trans-9-Octadecenoate, 98%, purchased from TCI Co., China) and Zconfiguration MO substrates was carried out by using peroxy acid as oxidant, according to the reference (Green Chem., 2017, 19, 3535-3541). Then, those two epoxy products were quantified by <sup>1</sup>H NMR spectroscopy, as shown and highlighted in **Fig. S6**. It is confirmed that the <sup>1</sup>H-NMR spectra of two as-made epoxy products agree well with those reported in literature (Green Chem., 2016, 18, 3775-3788).

After that, as shown in **Fig. S7**, GC-FID spectra were constructed by altering mass ratio of methyl oleate (and as-made epoxy products with two configurations) to internal standard Naphthalene, with  $CH_3CN$  as solvent. The standard curve is obtained by correlating the ratio of the integral area of the standard to the integral area of the internal standard with the weight ratio of the standard to the integral area of the internal standard with the weight ratio of the standard to the integral area of the integral area of the integral area of the standard to the standard.

To confirm the configuration of the raw material, both Z-configuration MO and E-configuration MO samples were detected by <sup>1</sup>H NMR spectroscopy, as shown in **Fig. S11a** and **b**. Obviously, Z-configuration MO is of a characteristic peak at around 5.24 ppm, while that of E-configuration MO is totally different, which is at around 5.34 ppm in <sup>1</sup>H NMR spectra in the lower field region, according to the reference (Org. Lett., 2021, 23, 6895–6899).

On the other hand, to judge the isomerization of MO under the effect of catalyst in the absence of aldehyde, the mixture after blank experiment were also tested by <sup>1</sup>H NMR spectroscopy, as shown in **Fig. S11c** and **d**. It is obvious that there is no product generated, and the remained MO is of

almost the same peaks as that of fresh Z-configuration MO we used. Consequently, it strongly suggests no olefin-H migration and C=C double bond isomerization occur during the blank experiment under this mild conditions.

A full picture of a representative gas chromatogram was presented in Fig. S12.



**Fig. S1** XPS spectra of as-synthesized  $1\%CoO_x/S-1$  (a) and  $1\%CoO_x/h-S-1$  (b) and  $1\%CoO_x/h-S-1$  after calcination (c).



Fig. S2 H<sub>2</sub>-TPR profile of Co<sub>3</sub>O<sub>4</sub>.



**Fig. S3** Peak fit (a-d) of the band of 460 and 740 nm in the UV-Vis spectrum of  $Y\%CoO_x/h$ -S-1 (Y =1-7); Peak area (e) and peak area proportion (f) obtained by peak fitting *versus* Co content. The positions of the three peaks are 520, 590 and 660 nm.



**Fig. S4** Fourier transform (FT) magnitude of the  $k^2$ -weighted  $\chi(k)$ -function EXAFS spectra of Co

foil.

The reaction mixture of aerobic co-oxidation of IBA and MO after filtration and solvent removal was tested by <sup>1</sup>H NMR method, which were recorded at room temperature on a Bruker AVANCE III-400 spectrometer and referenced to the residual deuterated solvent signals (CDCl<sub>3</sub> 7.26 ppm). All reported NMR values are given in parts per million (ppm).

Notably, as shown in **Figure. S5**, both *trans*-isomer and *cis*-isomer can be confirmed by the peaks at around 2.9 ppm and 2.6 ppm, respectively, agreeing well with that of GC-MS analysis and those data in the reference (Green Chem., 2016, 18, 3775-3788), although there is a very slight shoulder peak ascribed to the proton on  $\alpha$ -carbon of isobutyric acid (J. Org. Chem., 2006, 71, 9291-9296). Meanwhile, the <sup>1</sup>H NMR data of two as-prepared epoxy products in **Fig. S6** is highly relevant with the GC-FID analysis with different retention time in **Fig. S7**.

Furthermore, there are no peaks ascribed to oligomers in <sup>1</sup>H-NMR spectrum, which means all products can be well gasified and detected by GC-FID instrument for quantification. That may be due to the huge steric resistance of methyl oleate and corresponding derivatives, especially within confined channels of zeolite. Therefore, the combined GC-MS and GC-FID method allows well quantifying the amount of both raw materials and products in this aerobic oxidation system.



**Fig. S5** <sup>1</sup>H NMR spectrum of the reaction mixture of aerobic co-oxidation of IBA and MO after filtration and solvent removal.

(a) <sup>1</sup>H NMR spectrum of epoxy product of *cis*-configuration



(b) <sup>1</sup>H NMR spectrum of epoxy product of *trans*-configuration



Fig. S6 <sup>1</sup>H NMR of epoxy products of different configurations.



Fig.S7 The representative gas spectrum for establishing the standard curve.

The differences of *trans-/cis-* ratios ( $\alpha$  value) in the same experiments may be majorly ascribed to the slight difference of oxygen pressure of balloon in different experiment, because of the rate-limitation of dissolution and transfer of dioxygen molecules during aerobic oxidation. In the same batch of reaction, various glass reactors were connected to the same balloon, as shown in **Fig. S8**.



Fig. S8 Multiple parallel reactions at the same time by oxygen balloon shunt.



Fig. S9 The standard curve using naphthalene as internal standard.



Fig. S10 XPS spectra of fresh and used 1%CoO<sub>x</sub>/h-S-1 samples.





(b) <sup>1</sup>H NMR spectrum of E-configuration raw material





(c) <sup>1</sup>H NMR spectrum of the product of blank experiment using Z-configuration MO as raw material

(d) Zoomed-in region (5.17-5.41 ppm) of superimposed <sup>1</sup>H NMR spectra of (a), (b) and (c).



**Fig. S11** <sup>1</sup>H NMR of raw materials of different configurations ((a) and (b)) and the product of blank experiment using Z-configuration raw material (c) and Zoomed-in region (5.17-5.41 ppm) of superimposed <sup>1</sup>H NMR spectra of (a), (b) and (c).



**Fig. S12** The gas chromatogram of the crude reaction mixture of aerobic co-oxidation of IBA and MO.

	⊥ <sub>сно</sub> + €	COOCH3	Catalyst, O <sub>2</sub> CH <sub>3</sub> CN			COOCH <sub>3</sub>
		Isobutyraldehyde		Selec.	(%)	
Entry	v Catalyst	Conv. (%)	Isobutyric	Isobutyric	Isopropyl	Isopropyl
			acid	anhydride	formate	ether
1	blank	41.9	93.8	0	6.2	0
2	<i>h</i> -S-1	62.2	96.2	0	3.8	0
3	Co $Pc^b$	95.6	82.2	17.3	0	0.5
4	CoO	96.7	86.8	12.6	0	0.6
5	Co <sub>3</sub> O <sub>4</sub>	96.1	98.1	1.4	0	0.5
6	1%CoO <sub>x</sub> / <i>h</i> -S-1	90.0	95.9	1.2	1.6	1.3
7	3%CoO <sub>x</sub> / <i>h</i> -S-1	90.9	97.2	1.4	0	1.4
8	5%CoO <sub>x</sub> / <i>h</i> -S-1	92.5	95.8	1.1	1.5	1.6
9	7%CoO <sub>x</sub> / <i>h</i> -S-1	95.0	95.9	1.0	1.1	2.0

## Table S1 Catalytic Conversion of MO by Co-oxidation with IBA<sup>a</sup>

"Reaction condition: methyl oleate (MO) = 1 mmol, isobutyraldehyde (IBA) = 3 mmol, acetonitrile = 2.5 mL; Catalyst = 50 mg 1%  $CoO_x/h$ -S-1, under an O<sub>2</sub> atmosphere (1.0 atm), reaction temperature = 25 °C, time = 6 h. <sup>b</sup>Co Pc: Phthalocyanine cobalt(II).

<b>F</b> (	Temperature	Time		Oledfin	n(aldehyde)	Aldeheyde	Carboxylic acid
Entry	(°C)	(h)	Aldehyde	derivatives	/n(oledfin)	conv. (%)	selec. (%)
1	25	6	IBA	cyclohexene	3	96.1	97.5
2	25	6	IBA	cyclooctene	3	91.6	97.2
3	25	6	IBA	1,5- hexadiene	3	97.3	97.6
4	25	6	IBA	1-hexene	3	98.2	97.4
5	25	6	IBA	1-octene	3	98.0	98.4
6	25	6	IBA	1-decene	3	98.3	96.9
7	25	6	IBA	МО	3	95.6	97.3
8	25	6	acetaldehyde <sup>b</sup>	МО	3	70.6	8.5
9	60	12	acetaldehyde <sup>b</sup>	МО	2	100	9.0
10	25	6	propanal	МО	3	95.0	100
11	25	6	3,5,5-trimethyl-hexanal	МО	3	95.9	94.6
12	25	6	benzaldehyde	МО	3	8.4	100
13	25	6	o-chlorobenzaldehyde	МО	3	0	-
14	25	6	o-nitrobenzaldehyde	МО	3	0	-
15	60	6	benzaldehyde	МО	2	32.3	88.7
16	60	6	p-ethylbenzaldehyde	МО	2	93.2	94.7
17	60	6	o-chlorobenzaldehyde	МО	2	3.0	100
18	60	6	o-nitrobenzaldehyde	МО	2	0	-

## Table S2 The Aerobic Co-oxidation of Aldehydes and Olefins<sup>a</sup>

20	60	12	benzaldehyde	МО	2	41.3	100
21	60	12	o-chlorobenzaldehyde	МО	2	2.3	100
22	60	12	o-nitrobenzaldehyde	МО	2	0	-

<sup>*a*</sup>Olefin = 1 mmol, acetonitrile = 2.5 mL, catalyst = 50 mg 1%CoO<sub>x</sub>/*h*-S-1, under an O<sub>2</sub> atmosphere

(1.0 atm).  $^{b}$ Paraldehyde is the main byproduct.

	Catalyst amount		Selec. (%)				
Entry	(ma/mmal MO)	Conv. (%)	Isobutyric	Isobutyric	Isopropyl	Isopropyl	
	(mg/mmol MO)		acid	anhydride	formate	ether	
1	0	41.9	93.8	0	6.2	0	
2	10	97.1	96.1	1.2	1.4	1.3	
3	30	95.1	97.0	0.9	0.9	1.2	
4	50	92.8	96.5	1.3	0.8	1.4	
5	100	95.7	97.0	1.4	0.5	1.1	

Table S3 Catalytic Conversion of MO by Co-oxidation with IBA over 1%CoO<sub>x</sub>/h-

<b>S-1</b>	of	Diff	erent	Amo	unts <sup>a</sup>
<b>S-1</b>	01	Diff	erent	Amo	unts"

"MO = 1 mmol, IBA = 3 mmol, acetonitrile = 2.5 mL; Catalyst = 50 mg 1%CoO<sub>x</sub>/h-S-1, under

an  $O_2$  atmosphere (1.0 atm), reaction temperature = 25 °C, time = 6 h.