## Modification of supported Pd catalysts by alkalic salts in the selective racemization and dynamic kinetic resolution of primary amines

Qianru Jin, <sup>a, b</sup> Guoqing Jia, <sup>a</sup> Yanmei Zhang, <sup>a</sup> and Can Li<sup>\*, a</sup>

<sup>a</sup>State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China

<sup>b</sup>Graduate University of Chinese Academy of Sciences, Beijing 100049, China

\*Corresponding author: Tel: 86-411-84379070. Fax: 86-411-84694447. Email: <u>canli@dicp.ac.cn</u>. <u>http://www.canli.dicp.ac.cn</u>



Fig. S1 The relation between concentration of Pd(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub> precursor and Pd loading.



Fig. S2 Line shape analysis of the XPS spectrum of 2.45 wt% Pd/MCF.



**Fig S3** The color change of bromothymol blue suspended with Li<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, Li<sub>3</sub>PO<sub>4</sub>, Na<sub>3</sub>PO<sub>4</sub>, and K<sub>3</sub>PO<sub>4</sub>.



Fig. S4 FT-IR of (a) Pd/MCF, (b) Pd/MCF impregnated with  $K_2CO_3$ , and (c) Pd/MCF mixed with

 $K_2CO_3$ 

Fig. S4 shows FT-IR of pristine and  $K_2CO_3$ -modified Pd/MCF. After the addition of  $K_2CO_3$  to Pd/MCF by incipient wetness impregnation (b) and mechanical mixing (c), there are obvious bands at 1402 cm<sup>-1</sup> and 1371 cm<sup>-1</sup> attributed to carbonate species of  $K_2CO_3$ , indicating the presence of  $K_2CO_3$  in the Pd/MCF catalysts. However, the signal intensity of carbonate species on sample b ( $K_2CO_3$ -Pd/MCF) is weaker than that on Sample c ( $K_2CO_3$ +Pd/MCF), indicating that most of carbonate species were introduced into the nanopores of Pd/MCF by incipient wetness impregnation method.



**Fig. S5** XRD pattern of (a) MCF, (b) Pd/MCF, (c) Pd/MCF mixed with K<sub>2</sub>CO<sub>3</sub>, and (d) Pd/MCF impregnated with K<sub>2</sub>CO<sub>3</sub>.

Fig. S5 shows XRD patterns of Pd/MCF in the presence of  $K_2CO_3$ . After the addition of  $K_2CO_3$ , there is an obvious shift occurring in the diffraction peak of MCF, probably indicating the effect of  $K_2CO_3$  on MCF. The XRD pattern of sample c ( $K_2CO_3$ +Pd/MCF) prepared by mechanical mixing of  $K_2CO_3$  and Pd/MCF exhibits the typical diffraction peak of  $K_2CO_3$ . However, peaks of  $K_2CO_3$  in the sample d ( $K_2CO_3$ -Pd/MCF) prepared by incipient wetness impregnation appear to shift to higher angles, probably due to the presence of Si-O-K compound.



Fig. S6 TEM images of (a) MCF; (b) SBA-15; (c) FDU-12; (d) Commercial SiO<sub>2</sub>.



Fig. S7 N<sub>2</sub> sorption isotherms of MCF, SBA-15, FDU-12 and commercial SiO<sub>2</sub>



Fig. S8 The effect of  $K_2CO_3$  content on the selectivity in the racemization of

(S)-1-phenylethylamine.

NH <sub>2</sub> Pd na	nocatalyst	+	Ph +
(S)-1-phenylethylamine	racemic 1-phenyle	thylamine	$\sim$
Serial number	<sup>b</sup> ee (%)	Conv. (%)	Select. (%)
Ideal	0	50	100
1	6	53	94
2	1	54	95
3	2	53	96
4	5	52	96
5	5	52	95
6	4	53	95
7	3	54	95
8	7	50	96
9	4	52	96
10	5	52	96
Average	4	53	95
Standard Deviation	1.83	1.29	0.82
Relative Standard Deviation	0.4676	0.0243	0.0009

Table S1 The reproducibility of  $K_2CO_3$ -Pd/MCF catalyst preparation with different batches.

(Standard reaction condition: 0.5 mmol of (S)-1-phenylethylamine (65  $\mu$ L), 0.22 mmol of hexadecane (65  $\mu$ L), toluene (4 mL), and catalyst: K<sub>2</sub>CO<sub>3</sub>-Pd/MCF (55 mg, 0.01mmol of Pd source, 2.5 mmol K<sub>2</sub>CO<sub>3</sub> per gram Pd/MCF), 0.01 MPa H<sub>2</sub>, 70 °C; Reaction time: 4 h. <sup>b</sup> Determined as corresponding acetamide using chiral GC)

$\begin{array}{c} & \overset{\mathrm{NH}_2}{\longrightarrow} & \overset{\mathrm{NH}_2}{\longrightarrow} & \overset{\mathrm{NH}_2}{\longrightarrow} & \overset{\mathrm{HN}}{\longrightarrow} & \overset$						
(S)-1-pnenyletnyla	imine racemic	1-pnenyletnylami	ne			
Scale	Serial number	<sup>b</sup> ee (%)	Conv. (%)	Select. (%)		
50 mg	1	21	40	99		
100 mg	1	23	39	98		
100 mg	2	19	41	99		
200 mg	1	24	38	99		
	2	27	37	99		
	3	17	41	98		
	4	19	40	99		
	5	27	37	99		
400 mg	1	17	42	99		
	2	21	39	98		
	3	25	38	99		
	4	21	40	99		
	5	20	40	98		
Average	22		39	99		
Standard Deviation	3.40		1.61	0.58		
Relative Standard Deviation	0.15		0.04	0.0059		

Table S2 The reproducibility of K<sub>2</sub>CO<sub>3</sub>-Pd/MCF catalyst preparation with different scales.

(Standard reaction condition: 0.5 mmol of (S)-1-phenylethylamine (65  $\mu$ L), 0.22 mmol of hexadecane (65  $\mu$ L), toluene (4 mL), and catalyst: K<sub>2</sub>CO<sub>3</sub>-Pd/MCF (70 mg, 0.01mmol of Pd source, 5 mmol K<sub>2</sub>CO<sub>3</sub> per gram Pd/MCF), 0.01 MPa H<sub>2</sub>, 70 °C; Reaction time: 4 h. <sup>b</sup> Determined as corresponding acetamide using chiral GC)

Samples	Surface area <sup>a</sup>	Pore volume	Pore size <sup>b</sup>	Window size <sup>b</sup>
	$(m^2 g^{-1})$	$(cm^3 g^{-1})$	(nm)	(nm)
MCF	438	2.28	36.1	17.9
SBA-15	715	0.68	8.5	
FDU-12	486	0.36	15.5	3.6
Commercial SiO <sub>2</sub> <sup>c</sup>	227	1.61	0.5	

Table S3. Physicochemical Properties of the synthesized materials.

<sup>a</sup> The BET surface area.

<sup>b</sup> The pore size and window size of the cages were calculated from the adsorption and desorption branches of the isotherms using the Barrett-Joyner-Halenda (BJH) method. <sup>c</sup> The pore sizes were calculated using the Horvath-Kawazoe (HK) method.

Catalyst	T (°C)	t (h)	ee (%)	Conversion (%)	Selectivity (%)
K <sub>2</sub> CO <sub>3</sub> -Pd/C -0	70	4	15	48	91
$K_2CO_3$ -Pd/C -1 <sup>st</sup>	70	4	23	44	91
K <sub>2</sub> CO <sub>3</sub> -Pd/C -2 <sup>nd</sup>	70	4	28	42	93
$K_2CO_3$ -Pd/C -3 <sup>rd</sup>	70	6	31	41	90
$K_2CO_3$ -Pd/C -4 <sup>th</sup>	70	24	54	31	91

Table S4 Recyclability of K<sub>2</sub>CO<sub>3</sub>-Pd/C catalyst.

(Standard reaction condition: 0.5 mmol of (S)-1-phenylethylamine (65 µL), 0.22 mmol of hexadecane (65 µL), toluene (4 mL), and catalyst: K<sub>2</sub>CO<sub>3</sub>-Pd/C (70 mg, 0.01mmol of Pd source, 5 mmol K<sub>2</sub>CO<sub>3</sub> per gram Pd/MCF), 0.01 MPa H<sub>2</sub>, 70 °C; Reaction time: 4 h. <sup>b</sup> Determined as corresponding acetamide using chiral GC)