

# Electronic Supplementary Material

## Metal size effects over metal/zeolite bifunctional catalysts in the selective hydroalkylation of benzene

Junjie Li<sup>1</sup>, Chuang Liu<sup>1</sup>, Zhenlong Jia<sup>1</sup>, Yingchun Ye<sup>1</sup>, Dawei Lan<sup>1</sup>, Wei Meng<sup>1</sup>, Jianqiang Wang<sup>1</sup>, Zhendong Wang<sup>1,2</sup>, Yongfeng Hu (✉)<sup>1</sup>, Weimin Yang (✉)<sup>1,2,3</sup>

1 Shanghai Research Institute of Petrochemical Technology, SINOPEC, Shanghai 201208, China

2 State Key Laboratory of Green Chemical Engineering and Industrial Catalysis, Shanghai 201208, China

3 School of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

E-mails: [yangwm.sshy@sinopec.com](mailto:yangwm.sshy@sinopec.com) (Yang W); [yhu08544@yahoo.com](mailto:yhu08544@yahoo.com) (Hu Y)

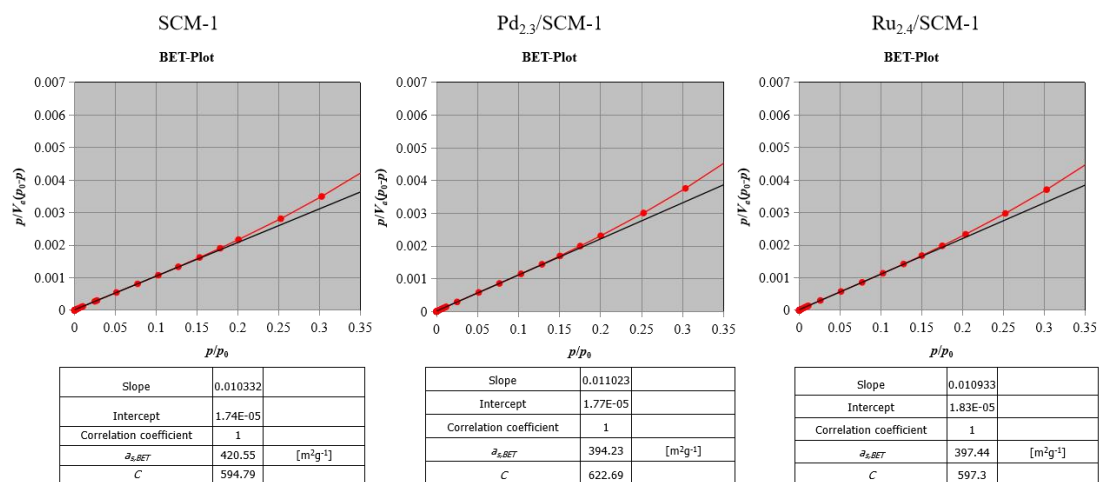
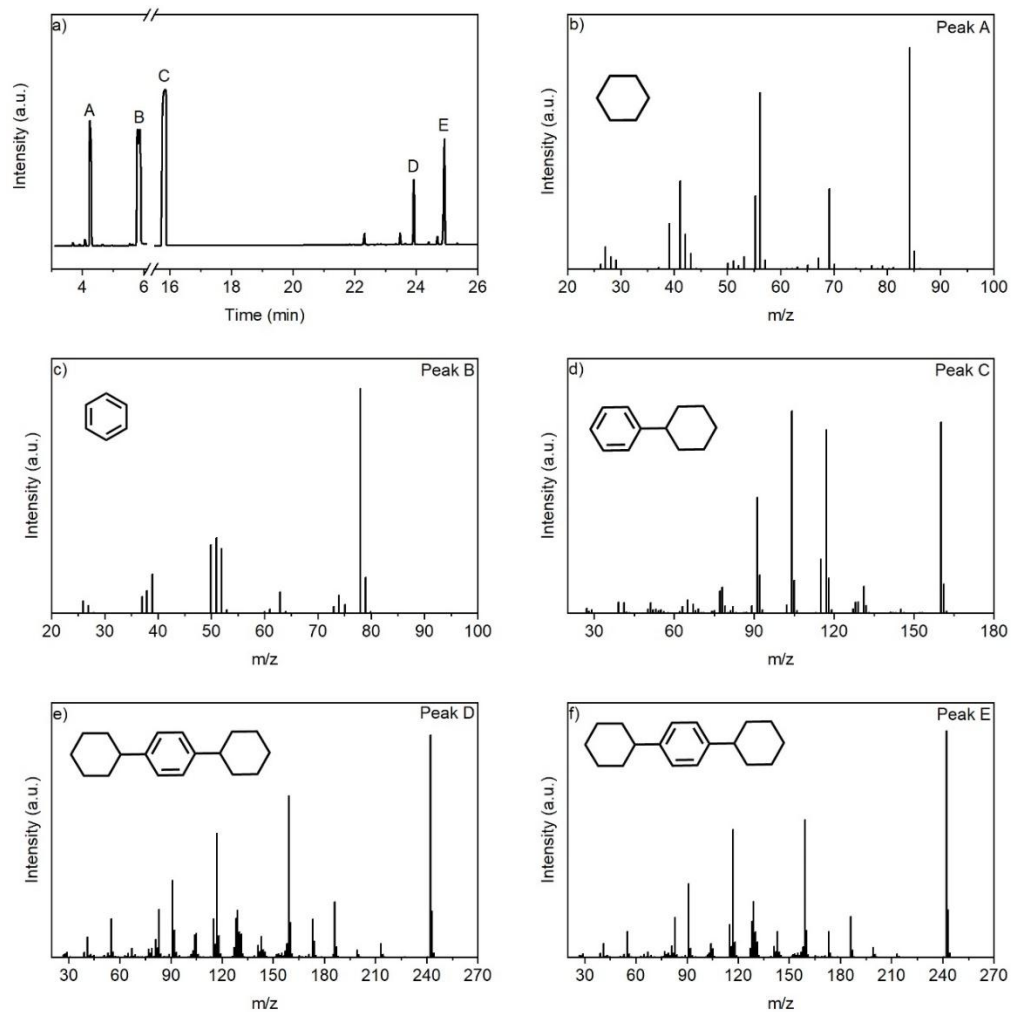
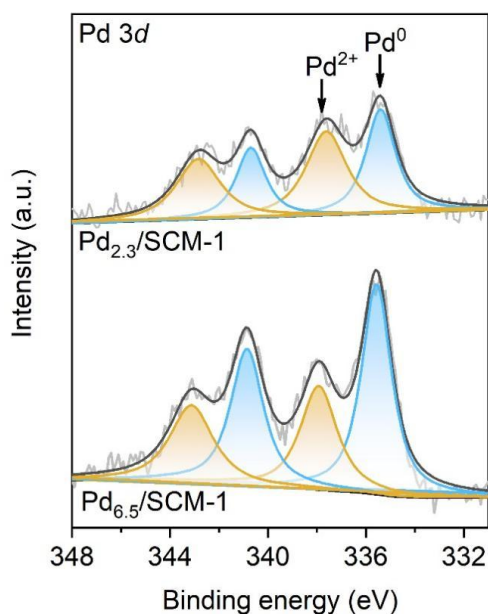


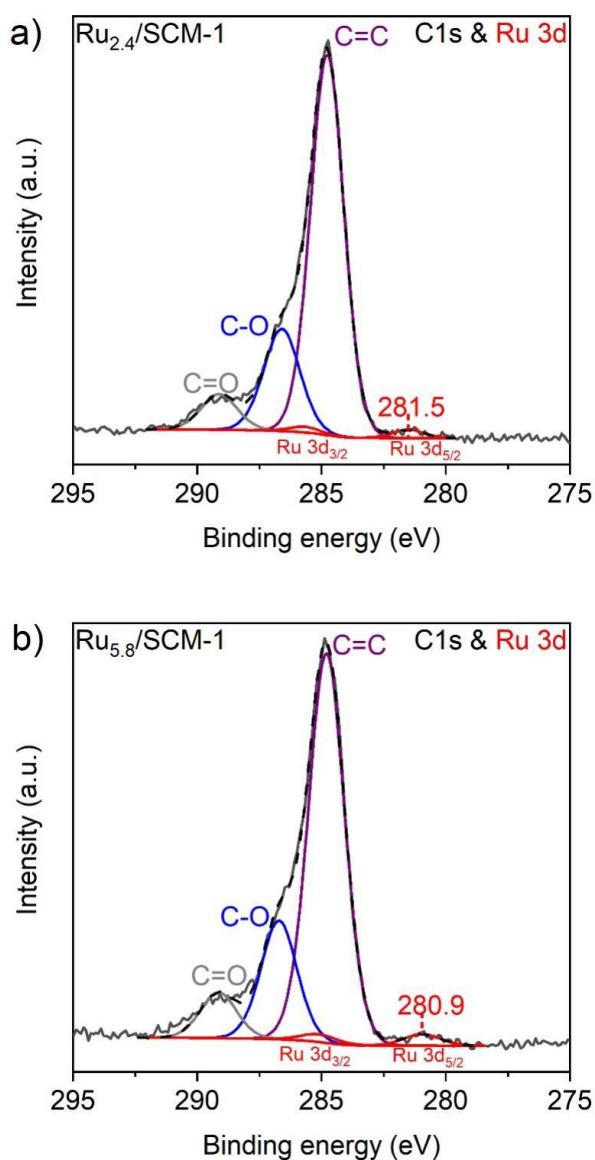
Fig. S1 Plots of BET results on SCM-1, Pd<sub>2.3</sub>/SCM-1 and Ru<sub>2.4</sub>/SCM-1 catalysts.



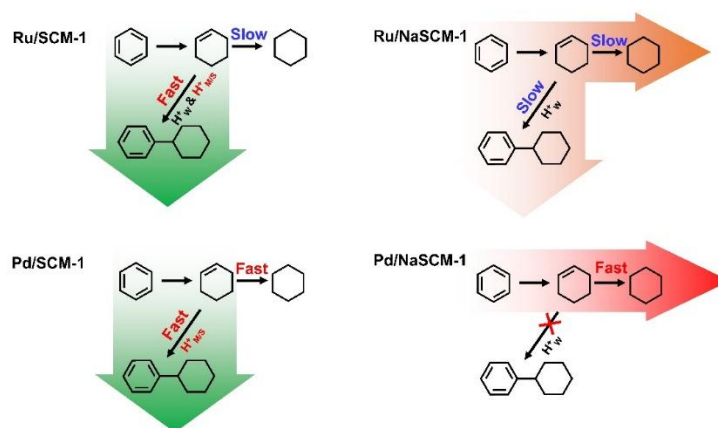
**Fig. S2** GC-MS spectrum of possible products after the hydroalkylation of benzene.



**Fig. S3** XPS spectra of the Pd<sub>2.3</sub>/SCM-1 and Pd<sub>6.5</sub>/SCM-1 catalysts in the Pd 3d region.

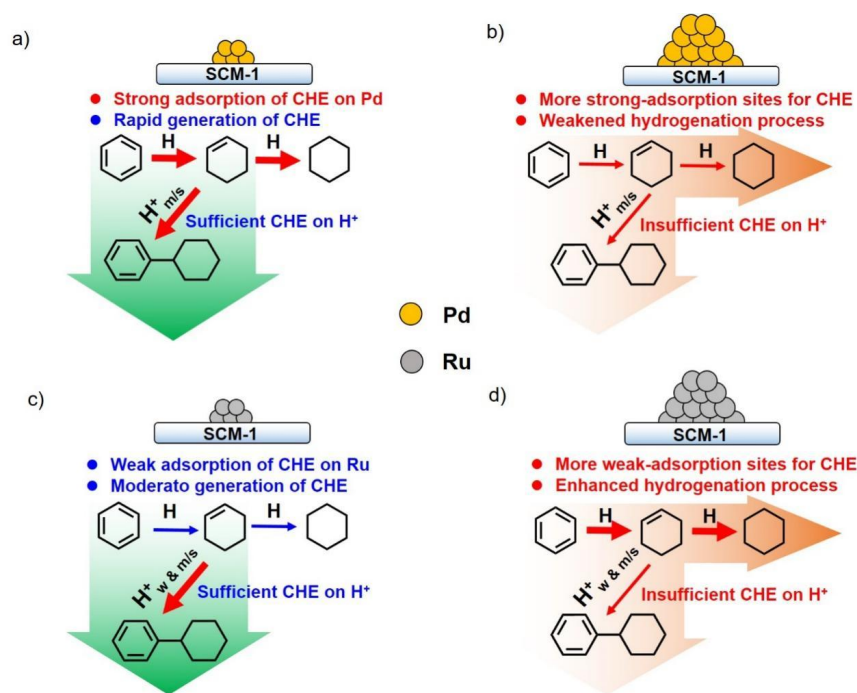


**Fig S4** XPS spectra of the  $\text{Ru}_{2.4}/\text{SCM-1}$  and  $\text{Ru}_{5.8}/\text{SCM-1}$  catalysts in the Ru 3d / C 1s region.



**Fig. S5** Illustration of the different catalytic behaviors between metal/SCM-1 and

metal/NaSCM-1 in the hydroalkylation of benzene.



**Fig. S6** Illustration of the different catalytic behaviors between differently sized metal/SCM-1 in the hydroalkylation of benzene.

**Table S1** BET of various materials.

	$S_{\text{BET}}$ (m <sup>2</sup> /g)	Total pore volume (cm <sup>3</sup> /g)
SCM-1	420	0.968
Pd <sub>2.3</sub> /SCM-1	394	0.926
Ru <sub>2.4</sub> /SCM-1	397	0.956

**Table S2** Hydroalkylation of benzene over various catalysts

Catalyst	Conversion of Benzene (%)	Selectivity (%)				Yield of CHB (%)
		CHA	CHB	DCHB	Others	
Ru <sub>2.4</sub> /SCM-1	41.8	15.4	72.4	10.4	1.8	30.3
Ru <sub>3.2</sub> /SCM-1	35.0	23.1	69.2	6.5	1.2	24.2
Ru <sub>3.7</sub> /SCM-1	29.5	40.3	53.1	5.3	1.3	15.7
Ru <sub>5.8</sub> /SCM-1	19.8	59.4	38.4	1.1	1.1	7.6
Pd <sub>2.3</sub> /SCM-1	35.7	25.4	64.2	8.8	1.6	22.9
Pd <sub>2.9</sub> /SCM-1	25.8	45.7	50.4	2.7	1.2	13.0
Pd <sub>3.8</sub> /SCM-1	25.0	74.7	24.3	0.5	0.5	6.0

<b>Pd<sub>6.5</sub>/SCM-1</b>	19.0	78.5	21.2	0.1	0.2	4.0
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Reaction conditions: 2.0 MPa H<sub>2</sub>, 150°C, 4 h, 0.3 g catalyst.

CHA, cyclohexane; CHB, cyclohexylbenzene; DCHB, dicyclohexyl.