## **Supporting Information**

## Highly Active, Durable and Recyclable Ordered Mesoporous Magnetic Organometal Catalysts Promoted Organic Reactions in Water

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Scheme S1 Schematic illustration of the synthetic procedure of (a) M-PPh<sub>2</sub>-SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub> and (b) M-PPh<sub>2</sub>-MCM-41 catalysts ( $M = Pd^{2+}$  or Rh<sup>+</sup>).



Scheme S2 Dependence of the coordination model on the P/M ratio of different catalysts.

Sample	Pd Loading	P content	Particle Size	$\mathbf{S}_{\text{BET}}$	$D_P$	$V_P$
	(mmmol/g)	( mmmol/g)	(nm)	(m <sup>2</sup> /g)	(nm)	(cm <sup>3</sup> /g)
Pd-PPh <sub>2</sub> -SiO <sub>2</sub> @Fe <sub>3</sub> O <sub>4</sub>	0.0109	0.110	440	35	1.0	0.030
PPh2-MCM-41@SiO2@Fe3O4	/	0.380	/	268	2.9	0.43
Pd-PPh <sub>2</sub> -MCM-41@SiO <sub>2</sub> @Fe <sub>3</sub> O <sub>4</sub>	0.0723	0.503	520	240	2.8	0.37
Pd-PPh <sub>2</sub> -MCM-41	0.161	0.516	10~1500	551	2.5	0.60
Pd-PPh <sub>2</sub> -MCM-41@SiO <sub>2</sub> @Fe <sub>3</sub> O <sub>4</sub> <sup>a</sup>	0.0683	0.290	530	170	2.8	0.21
Pd-PPh <sub>2</sub> -SiO <sub>2</sub> @Fe <sub>3</sub> O <sub>4</sub> <sup>a</sup>	0.00896	0.195	445	31	1.0	0.030
Pd-PPh <sub>2</sub> -MCM-41 <sup>a</sup>	0.150	0.560	10~1500	510	2.5	0.57
Rh-PPh <sub>2</sub> -MCM-41@SiO <sub>2</sub> @Fe <sub>3</sub> O <sub>4</sub>	0.0765	0.496	530	170	2.8	0.21
Rh-PPh <sub>2</sub> -SiO <sub>2</sub> @Fe <sub>3</sub> O <sub>4</sub>	0.0120	0.108	445	31	1.0	0.030
Rh-PPh <sub>2</sub> -MCM-41	0.167	0.510	10~1500	510	2.5	0.57

## Table S1 Elemental analysis and structural parameters of different catalysts

<sup>a</sup> The catalysts after being reused for 8 times.



Figure S1 Wide-angle XRD patterns of  $Fe_3O_4$  and Pd-PPh<sub>2</sub>-MCM-41@SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub>.



Figure S2 FT-IR spectra of  $Fe_3O_4$ ,  $SiO_2@Fe_3O_4$ ,  $PPh_2$ -MCM-41@SiO\_2@Fe\_3O\_4, and Pd-PPh\_2-MCM-41@SiO\_2@Fe\_3O\_4 samples.



Figure S3 XPS spectra of Pd-PPh<sub>2</sub>-MCM-41@SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub>, Pd-PPh<sub>2</sub>-SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub>, and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>.



Figure S4 XPS spectra of  $RhCl(PPh_3)_3$  and  $Rh-PPh_2-MCM-41@SiO_2@Fe_3O_4$  catalysts.



Figure S5 (a) Low-angle XRD pattern and (b)  $N_2$  sorption isotherm of the Rh-PPh<sub>2</sub>-MCM-41@SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub>. The attached is the HRTEM image.



Figure S6 XPS spectra of the Pd-PPh<sub>2</sub>-MCM-41@SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub> catalyst after being reused repetitively for 8 times.



Figure S7 Low-angle XRD pattern (a) and  $N_2$  adsorption-desorption curve (b) of the Pd-PPh<sub>2</sub>-MCM-41@SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub> catalyst after being reused repetitively for 8 times.