

Supporting Information for

Hydrophobic Core/Hydrophilic Shell-Structured Catalysts: A General Strategy for Improving the Reaction Rate in Water

Hengquan Yang,* Xuan Jiao, and Shuru Li

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1. Chemicals

Tetramethyl orthosilicate (TMOS), $(\text{MeO})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ (APTS), cetyltrimethylammonium chloride (CTAC), most of olefins and nitroarene were purchased from Aladdin Company. $(\text{MeO})_3\text{Si}(\text{CH}_2)_2\text{CF}_3$ (TFPS) was obtained from Zhejiang Chem-tech Group CO. Ltd. $\text{Pd}(\text{OAc})_2$ was purchased from Shanghai Boka Company (China). H_2PtCl_6 was obtained from Tianjin Chemical Reagent Research Institute (China).

2. Material synthesis

Hydrophobic core/hydrophilic shell-structured mesoporous silica nanospheres were synthesized according to the delayed condensation strategy (Ref. 7). The total amount of siliceous precursor was kept at 10.10 mmol. Take **MF@MN** for example, a mixture of tetramethyl orthosilicate (TMOS, 42.5 mol%) and 3,3,3-trifluoropropyltrimethoxysilane (7.5 mol%) was added into a cetyltrimethylammonium chloride solution containing 400 mL of deionized water, 505 mL of methanol and 2.5 mL of NaOH (1mol/L) under stirring. After stirring for 2 h, the other mixture of TMOS (47.5 mol%) and 3-aminopropyltrimethoxysilane (2.5 mol%) was added into above system. After further stirring for 12 h and aging overnight, the precipitation was isolated and washed with water. After being dry, the powder was extracted with hot ethanol (12 h, repeated three times), leading to fluoro-functionalized core/mesoporous amine-functionalized shell-structured silica nanospheres (denoted as **MF@MN**).

For **MN@MF**. The silica precursors were added through two steps. A mixture of 0.7315g of TMOS (47.5mol%) and 0.0453 g of APTS (2.5 mol%) was added to above CTAC solution for constructing the core. After stirring for 2 h, a mixture of 0.6545 g of TMOS (42.5 mol%) and 0.1654 g of TFPS (7.5 mol%) was added for constructing the shell. After further stirring for 12 h and then aging overnight, the precipitation was isolated, washed with water and dried under air. Afterward, the solid powder was extracted with hot ethanol (12 h, repeated 3 times), and dried under vacuum.

For **MF/MN**. MF/MN was synthesized through one-step of condensation instead of the delayed condensation. A mixture of 1.3860 g of TMOS (90 mol%), 0.0453 g of APTS (2.5 mol%) and 0.1654 g of TFPS (7.5 mol%) was added into above CTAC solution. After further stirring for 12 h and then aging overnight, the precipitation was isolated, washed with water and dried under air. Afterward, the solid powder was extracted with hot ethanol (12 h, repeated 3 times), and then dried under vacuum.

For **MN**. MN was synthesized through one-step of condensation instead of the delayed condensation. A mixture of 1.5015 g of TMOS (97.5mol%) and 0.0453 g of APTS (2.5 mol%) was added into above CTAC solution. After stirring for 12 h and then aging overnight, the precipitation was isolated, washed with water and dried under air. Afterward, the solid powder was extracted with hot ethanol (12 h, repeated 3 times), and then dried under vacuum.

For **M@MN**. The silica precursors were added through two steps. In the first step, 0.7700 g of TMOS (50 mol%) was added dropwise to above CTAC solution for the formation of the core. After stirring for 2 h, the other mixture of 0.7315 g of TMOS (47.5 mol%) and 0.0453 g of APTS (2.5 mol%) was added for constructing the shell. The hydrolysis and condensation proceeded for 12 h under stirring. After aging overnight, the precipitation was isolated and washed with

water. Afterward, the solid powder was extracted with hot ethanol (12 h, repeated 3 times), and then was dry under vacuum.

For **MF2.5@MN** and **MF12.5@MN**. The synthesis procedures are similar to **MF@MN**. A mixture of tetramethyl orthosilicate (47.5 mol% or 37.5 mol%) and 3,3,3-trifluoropropyltrimethoxysilane (2.5 mol% or 12.5%) was added into a cetyltrimethylammonium chloride solution containing 400 mL of deionized water, 505 mL of methanol and 2.5 mL of NaOH (1M) under stirring. After stirring for 2 h, the other mixture of TMOS (47.5 mol%) and 3-aminopropyltrimethoxysilane (2.5 mol%) was added into above system. After further stirring for 12 h and aging overnight, the precipitation was isolated and washed with water. After being dry, the powder was extracted with hot ethanol (12 h, repeated three times). The obtained materials were named as MF2.5@MN and MF12.5@MN, respectively.

Loading Pd. 0.3 g of MF@MN was added to a toluene solution containing 0.0108 g of Pd(OAc)₂. After stirring for 4 h, the toluene was removed. The Pd-adsorbed solid was reduced with NaBH₄ in a mixture of toluene and ethanol (V/V=20/1). After being washed with ethanol and being dry, the catalyst with a Pd loading of 1.70 wt% was obtained (denoted as Pd/MF@MN). The UV-vis spectroscopy measurement of the Pd(OAc)₂ concentration in solution before and after adsorption revealed that Pd(OAc)₂ was completely adsorbed by the solid materials. ICP-AES analysis of the metal-supported catalysts also disclosed that the used Pd(OAc)₂ was fully loaded on the supports.

Loading Pt. 0.3 g of MF@MN was added to 9 mL of H₂PtCl₆ aqueous solution. Other procedures are the same as the Pd catalysts.

Recycling test. A typical hydrogenation was set up. At the end of reaction, the product was extracted with ether and then analyzed with GC. The catalyst was recovered through centrifugation and repeatedly washed with ether. After being dry under vacuum, the solid catalyst was weighted again (It was found the weight of the solid catalyst decreased during the recovery to some extent. To obtain the reused catalyst, the other set of reaction was simultaneously carried out to provide the reused catalyst each reaction cycle). In the next reaction cycle, the amounts of substrate, catalyst and solvent, and reaction conditions were all kept constant (as the same as the first reaction).

3. Characterization

The small-angle X-ray powder diffraction analysis was performed on Rigaku D/max rA X-Ray diffractometer (at 40 kV and 30 mA with CuK α radiation). N₂ physical adsorption was measured by using an ASAP2020 volumetric adsorption analyzer. Before measuring, all samples were outgassed at 120 °C under vacuum for 6 h. Surface area was calculated from the adsorption branch in the relative pressure range of 0.05–0.15 using Brunauer-Emmett-Teller (BET) equation. Pore diameters were determined from the adsorption branch of the isotherm using BJH method. The total pore volume was calculated at a relative pressure of P/P₀>0.99. FT-IR spectra were performed on Thermo-Nicolet-Nexus 470 infrared spectrometer. Transmission electron microscope (TEM) images were obtained on a JEM-2000EX (operated at 200 kV). 300 MHz spectrometer: for ¹³C CP-MAS NMR experiments, 75.4 MHz resonant frequency, 4 kHz spin rate,

4 s pulse delay. 1.0 ms contact time, hexamethyl benzene as a reference compound; for ^{13}Si MAS NMR experiments, 79.6 MHz resonant frequency, 4 kHz spin rate, 4.0 s pulse delay, TMS as a reference compound. Thermal gravimetric analysis (TG) was performed with a NETZSCH TG analyzer (Germany) under nitrogen atmosphere from room temperature to 900 °C with a heating rate of 20 °C/min. Pd content was analyzed with an inductively coupled plasma-atomic emission spectrometry (ICP-AES, AtomScan16, TJA Co.). C and N content analysis was conducted on Vario EL (Elementar). Metal content analysis was carried out on an inductively coupled plasma-atomic emission spectrometry (ICPAES, AtomScan16, TJA Co.). X-ray photoelectron spectra (XPS) were recorded on a Kratos Axis Ultra DLD, and the C1S line at 284.8 eV was used as a reference. GC analysis was conducted on Agilent 7890A.

Table S1. The results for elemental analysis of the Pd-supported catalysts

Samples	N (wt%)		C (wt)%	
	Found	Cacul.	Found	Cacul.
Pd/MN	0.96	0.56	17.47	1.94
Pd/M@MN	1.04	0.56	18.10	1.94
Pd/MF/MN	0.97	0.49	18.55	6.83
Pd/MF@MN	0.92	0.49	17.74	6.83
Pd/MN@MF	0.98	0.49	17.88	6.83

Notes: Due to the template molecules residing in the mesopores, the specific surface areas and pore volumes of these composites determined by N₂ sorption are as low as 30-40 m²/g. It should be noted that N₂ sorption analysis is conducted at -196 °C. Template molecules are so rigid (frozen) that N₂ may not access the unique interior of template-containing mesopores under the measuring conditions. It should be also noted that the pore volume of the template-free mesoporous materials is *ca.* 0.6~0.80 g/cm³, determined by N₂ sorption. Assuming that the template molecules inside mesopores stack closely like them in solid state (without void), the whole weight contributed by templates would reach as high as *ca.* 40~50 wt% (considering the density of template in solid state is 0.97 g/cm³). However, in fact, elemental analysis indicates that the weight contributed by the template is only 18-20 wt%. These differences suggest that there must be some void spaces in the template-containing mesopores, which cannot be determined by N₂ sorption. In spite of containing template molecules, the pores still exhibit good adsorption of organic compounds.^{7b-e}

In our experiments, it was found that the template-containing mesopores owned high adsorption capacity toward Pd(OAc)₂ and H₂PtCl₆, and the added Pd(OAc)₂ and H₂PtCl₆ were completely adsorbed by template-containing mesoporous materials.

Moreover, the presence of templates in the mesopore is proven to be helpful to stabilize metal nanoparticles.^{7a} We also found that although the extraction with NH₄NO₃ ethanol or aqueous NaCl methanol solution could remove most of the templates, the activity of the solid catalyst considerably decreased. It is possible that the NH₄NO₃, NaCl affect the metal dispersion or surface properties of metal nanoparticles.

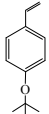
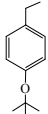
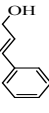
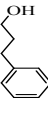
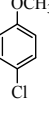
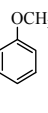
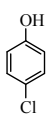
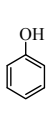
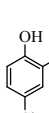
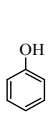
Table S2. The results of surface elemental compositions of the Pd-supported catalysts determined by XPS

Molar ratios	Pd/MN	Pd/MF/MN	Pd/MF@MN	Pd/MN@MF
F/Si (%)		36	29	42
Pd/Si (%)	1.86	1.60	1.66	1.43
N/Si (%)	6.37	5.85	5.95	5.77

Table S3. The results of surface elemental compositions of the Pt-supported catalysts determined by XPS

Molar ratios	Pt/MN	Pt/MF/MN	Pt/MF@MN	Pt/MN@MF
F/Si (%)	-	18.8	17.1	20.4
Pt/Si (%)	1.70	1.51	1.53	1.30
N/Si (%)	4.95	4.27	5.63	3.61

Table S4. The results of hydrogenations over Pd/M@MN and Pd/C

Entry	Substrate	Product	Conv.(%) over Pd/M@MN	Conv.(%) ^f over Pd/C
1 ^a			61	37
2 ^b			26	37
3 ^c			67	39
4 ^d			72	60
5 ^e			73	59

^a 2 mmol of substrate, 0.1 mol% Pd (with respect to substrate), 4.5 mL of water, 25 °C, 0.15 MPa of H₂, 1.5 h.

^b 1 mmol of substrate, 0.2 mol% Pd, 2 mL of water, 40 °C, ambient H₂ pressures, 1.5 h. ^c 1 mmol of substrate, 0.2

mol% Pd, 4.5 mL of water, 50 °C, 0.3 MPa of H₂, 1 h. ^d 1.6 mmol of substrate, 0.1 mol% Pd, 4.5 mL of water, 50

°C, 0.3 MPa of H₂, 1 h. ^e 1 mmol substrate, 0.2 mol% Pd, 10 mL of water 50 °C, 0.3 MPa of H₂, 1 h. ^f The results

were obtained over Pd/C (1 wt% Pd, Sigma), and the reaction conditions were the same as those for other catalysts.

Table S5. The recycling results of hydrogenations of cinnamyl alcohol over Pd/MF@MN^a









Reaction cycles	Run1	Run 2	Run3	Run4	Run5
Conv. ^b (%)	84	79	83	85	74

^a1 mmol of substrate, 0.2 mol% Pd, 2 mL of water, 40 °C, ambient H₂ pressures, 1.5 h. ^bdetermined by GC.

Table S6. The results of the elemental analysis of the reused Pd/MF@MN

Pd/MF@MN	fresh catalyst		After being used twice		After being used five times	
	N (wt%)	C (wt%)	N (wt%)	C (wt%)	N (wt%)	C (wt%)
Weight %	0.92	17.74	0.69	11.63	0.68	9.8

Table S7. The results of the aqueous-phase hydrogenations over different Pt catalysts

Entry	substrates	product	Conversions over different Pt catalyst(%)				
			Pt/MN	Pt/M@MN	Pt/MN/MF	Pt/MF@MNN	Pt/MN@MF
1 ^a			38	49	64	87	73
2 ^b			29	73	67	94	25
3 ^c			41	45	56	78	49
4 ^d			43	48	58	99	43

^a 1.5 mmol of substrate, 0.1 mol% Pt (with respect to substrate), 4.5 mL of water, 40 °C, 0.3 MPa of H₂, 3 h. ^b 1 mmol of substrate, 0.2 mol% Pt, 4.5 mL of water, 35 °C, 0.6 MPa of H₂, 4 h. ^c 1 mmol of substrate, 0.2 mol% Pt, 5 mL of water, 25 °C, 0.6 MPa of H₂, 40 min. ^d 1 mmol of substrate, 0.2 mol% Pt, 5 mL of water, 25 °C, 0.6 MPa of H₂, 2 h.

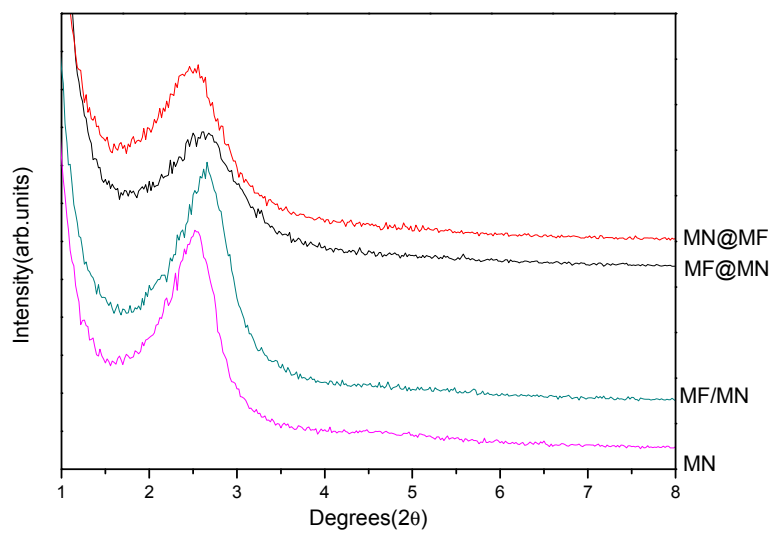


Fig.S1. The XRD patterns of the synthesized samples.

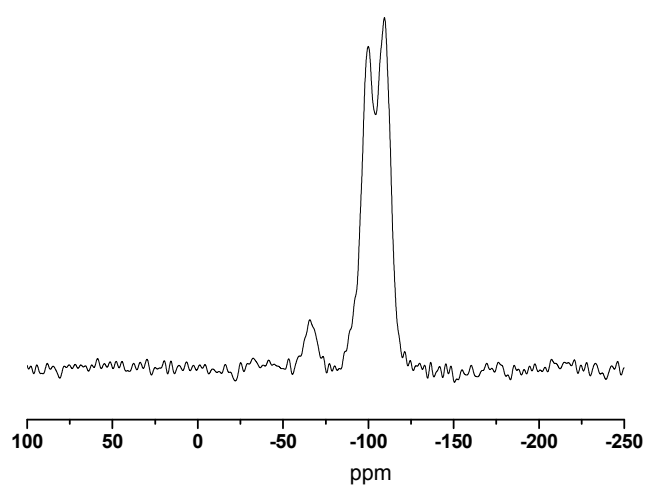


Fig. S2. The ^{29}Si MAS NMR spectrum of MF@MN.

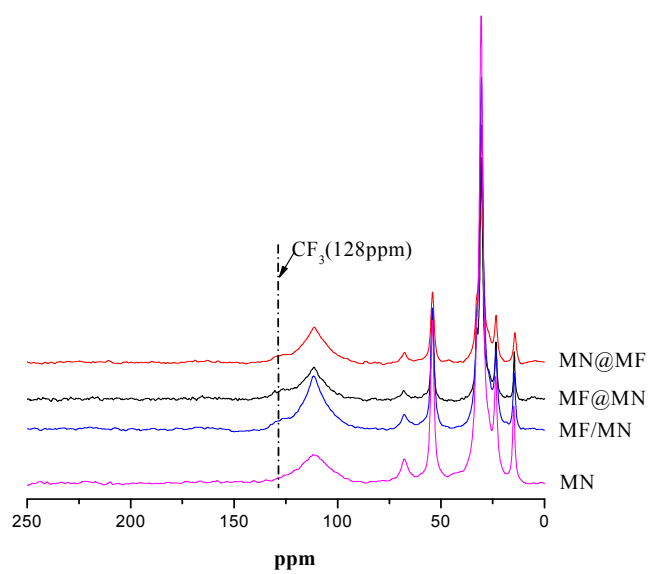


Fig. S3. The ^{13}C CP MAS NMR spectra of the synthesized samples.

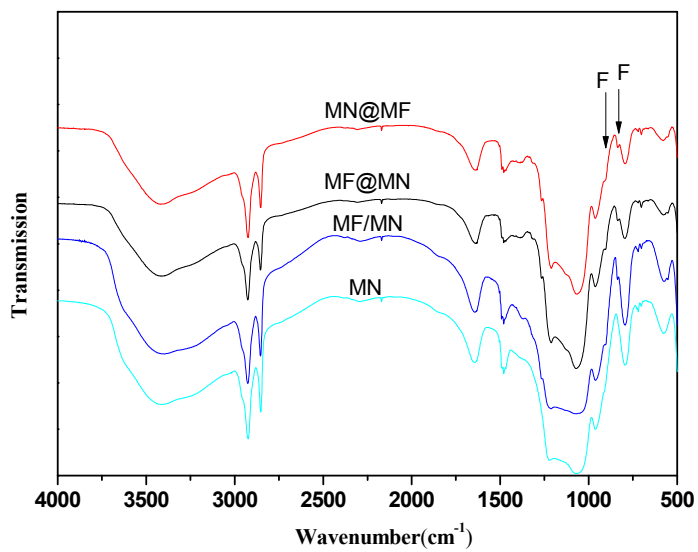


Fig. S4. The FT-IR spectra of the synthesized materials.

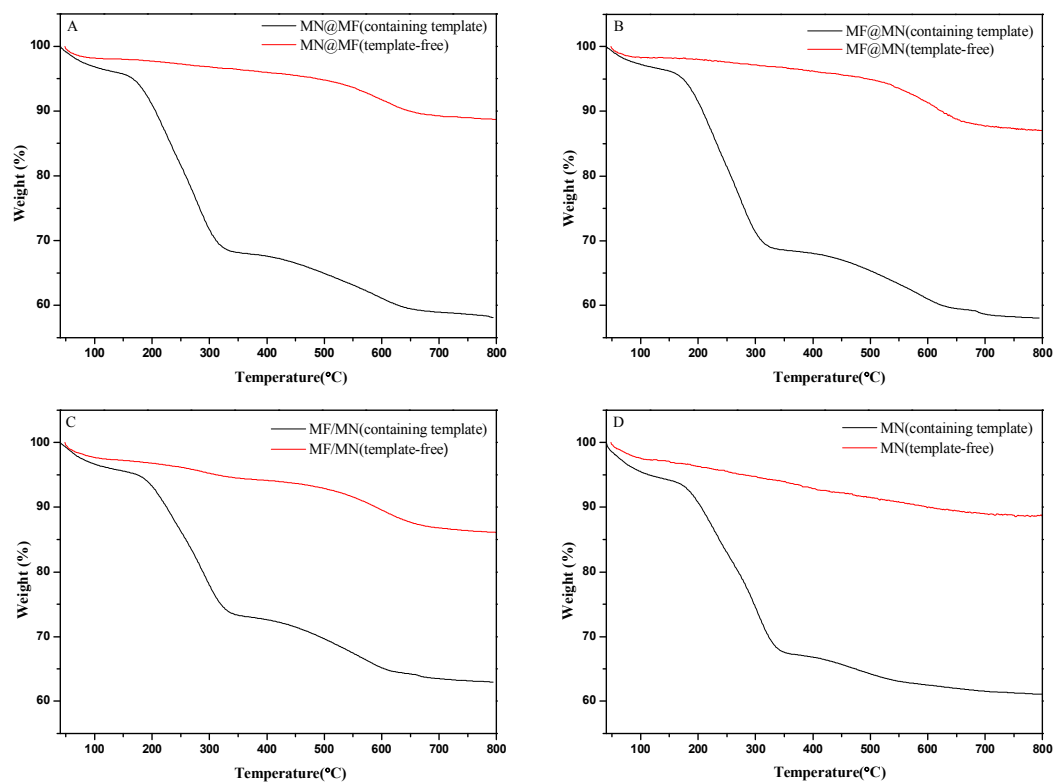


Fig. S5. TG curves of the synthesized materials containing templates and without templates (treated with a $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ solution containing NaCl).

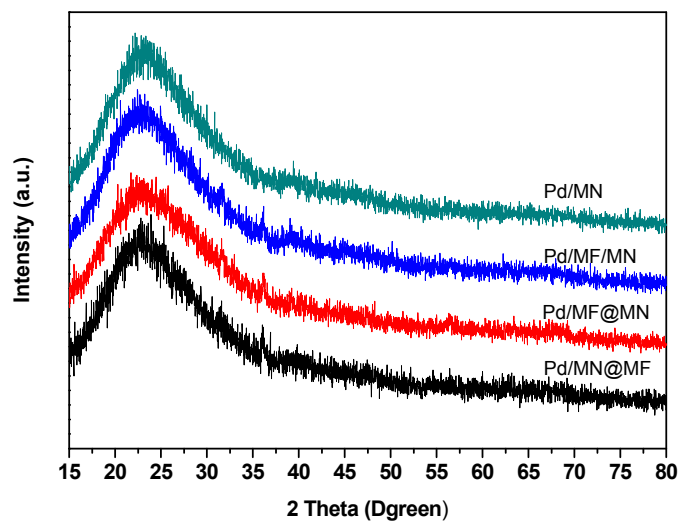


Fig. S6. Wide angle XRD patterns of the Pd-supported catalysts.

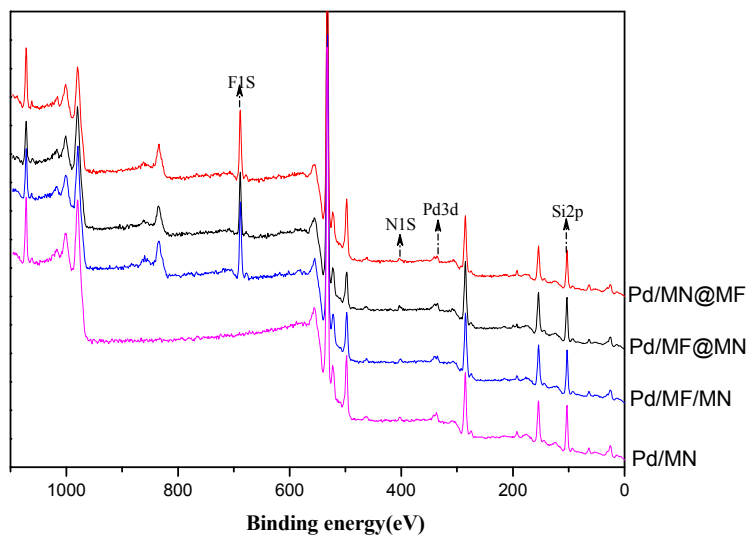


Fig. S7. XPS spectra of the Pd-supported catalysts.

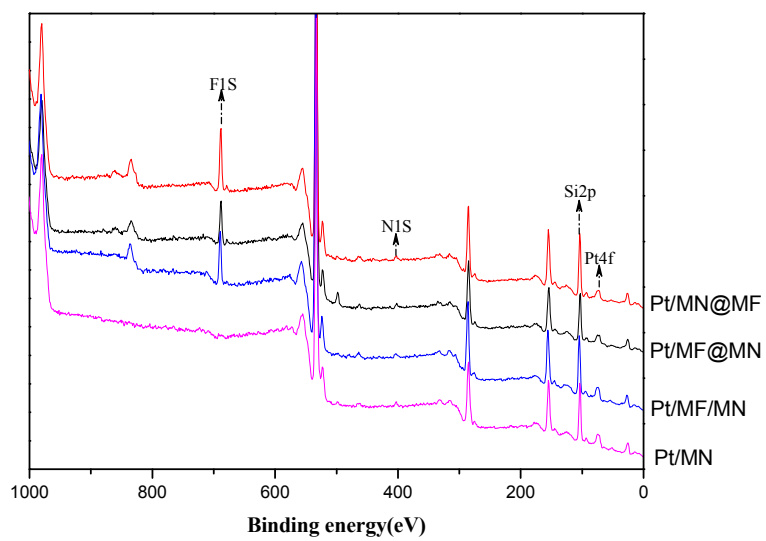


Fig. S8. XPS spectra of the Pt-supported catalysts.

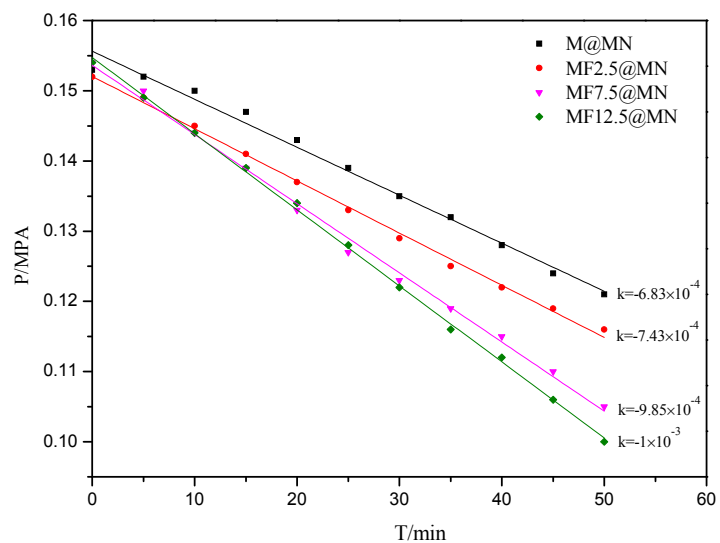


Fig. S9. The reaction kinetics of the hydrogenation of 4-*tert*-butoxystyrene over Pd/MFx@MN in water. Reaction conditions: 3.2 mmol of 4-*tert*-butoxystyrene, 8 mL of water as solvent, 0.15 MPa of H₂ pressure, 0.2 mol% Pd with respect to substrate, fixing stirring rate. K represents the slope of the pressure drop.

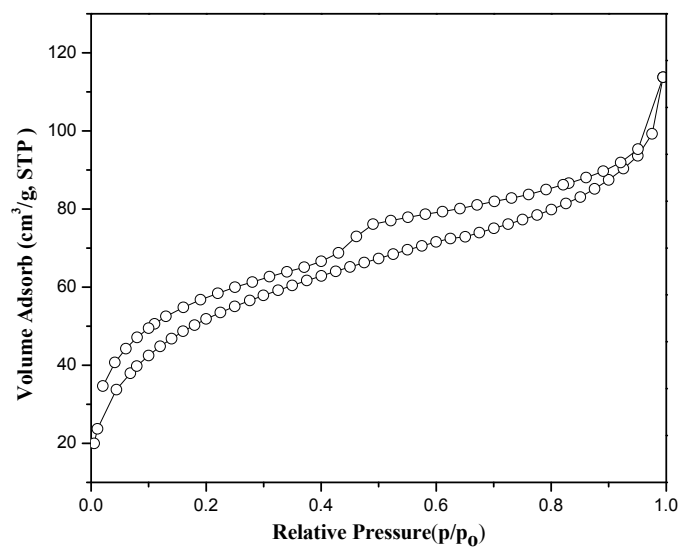


Fig.S10 N_2 sorption isotherm of Pd/MF@MN used 5 times. The specific surface area and pore volume are as high as $195 \text{ m}^2/\text{g}$ and $0.18 \text{ cm}^3/\text{g}$, respectively.