Electronic Supplementary Material (ESI) for Nanoscale.

A Nano-reactor Based on PtNi@Metal-Organic Framework Composites Loading Polyoxometalates for Hydrogenation–Esterification Tandem Reactions

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Contents

1. Experimental Section

1.1. Synthesis of PtNi alloy branched NPs. The PtNi alloy branched NPs were synthesized following the procedure published in a previous report.[S1] In a typical synthesis, platinum (II) 2,4-pentanedionate ($Pt(acac)_2$) (40 mg) and nickel (II) 2,4-pentanedionate ($Ni(acac)_2$) (62.8 mg) were dissolved in an oleylamine (36 mL) and oleic acid (4 mL) solution. After injecting the formaldehyde solution (3.2 mL), the mixture was stirred until it became clear. The resulting mixture was transferred to a Teflon-lined stainless-steel autoclave with a capacity of 80 mL. The sealed autoclave was heated from room temperature to 220 °C for 70 min and kept at 220 °C for 12 h. After reaction, the products were collected by centrifugation and washed with a mixture of ethanol and hexane several times. Finally, the products were dried under vacuum at 120 °C overnight to remove the residual surfactant.

1.2. Synthesis of pure MOF-74(Ni). Pure MOF-74(Ni) was synthesized under modified conditions described elsewhere.[S2] DOT (0.75 mmol) was dissolved in tetrahydrofuran (THF, 2.5 mL) and $Ni(Ac)_2{\cdot}4H_2O$ (1.5 mmol) was dissolved in deionized water (25 mL). Then, the two solutions were stirred until well mixed. The resulting solution was transferred to a 25 mL Teflon-lined stainless-steel autoclave. The sealed vessel was then heated at 110 °C in a preheated oven for 72 h. Finally, the products were collected by centrifugation and washed with deionized water and ethanol three times.

2. Supplementary Results

Table S1 The actual Pt and W contents of catalysts according to the ICP measurements.

Element contents%	PtNi@MOF-74	PtNi@MOF-74-POM-5	PtNi@MOF-74-POM-10	PtNi@MOF-74-POM-20
Pt%	4.3	4.0	3.9	3.7
W%	-	2.4	4.9	11.3

Table S2 The catalytic results of benzocaine synthesis using different catalysts.

catalyst	Conversion %	Selectivity %			
		Benzocaine (P_T)	4-aminobenzoic acid (P_H)	Ethyl 4-nitrobenzoate (P_E)	else
blank	2.3	100.0	-	-	-
PtNi	100.0	-	87.4	-	12.6
MOF-74(Ni)	16.1	-	100.0	-	-
PtNi@MOF-74	100.0	7.8	90.8	-	2.4
PtNi@MOF-74-POM -5	100.0	63.7	36	-	0.3
PtNi@MOF-74-POM-10	100.0	81.4	17.4	1.2	-
PtNi@MOF-74-POM-20	97.4	64.9	6.4	26.0	-
PtNi@MOF-74+POM	97.0	32.8	64.2	-	
PtNi@MOF-74-PMo-10	100.0	75.4	23.6	1.0	
PtNi@MOF-74-SiW-10	100.0	62.7	37.0	0.3	

Table S3 The surface areas of catalysts.

Sample name	PtNi alloy	PtNi@MOF-74	PtNi@MOF-74 -POM-5	PtNi@MOF-74 -POM-10	PtNi@MOF-74 -POM-20
Surface area m^2/g	3.76	20.01	19.25	17.86	14.32

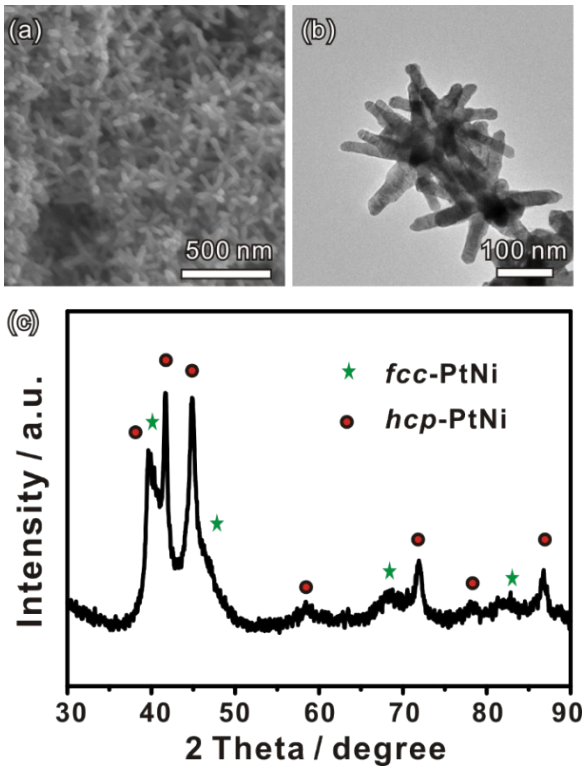

Fig. S1 (a) SEM image, (b) low-magnification TEM image and (c) XRD pattern of PtNi alloy branched nanoparticles.

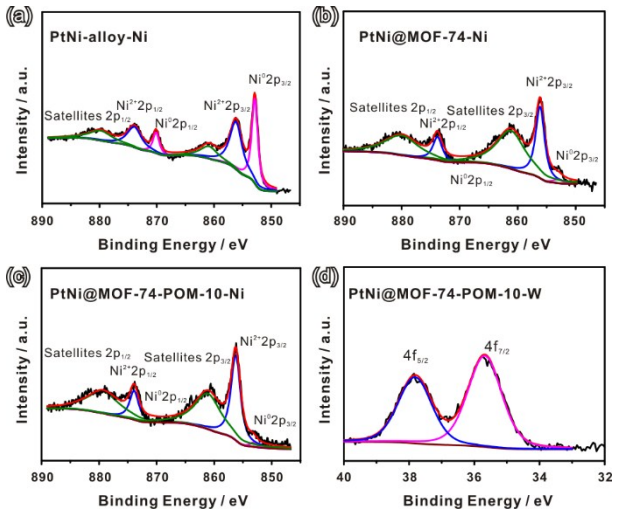

Fig. S2 XPS spectrum of Ni 2p of (a) pure PtNi alloy, (b) PtNi@MOF-74, and (c) PtNi@MOF-74-POM-10, (d) XPS spectrum of W 4f of PtNi@MOF-74-POM-10.

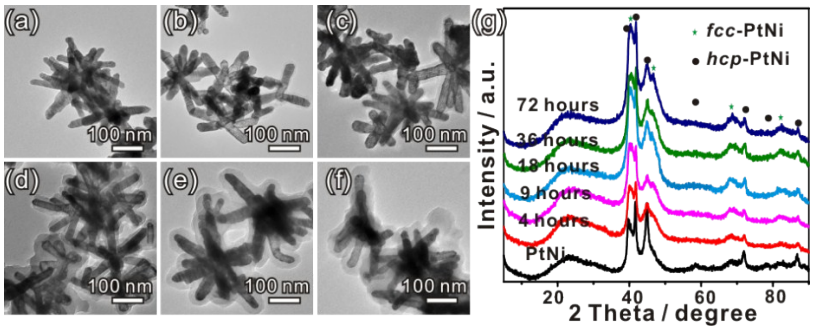

Fig. S3 Low magnification TEM images of (a) PtNi alloy branched nanoparticles and (b~f) the product after reaction with DOT at 110 °C for 4, 9, 18, 36, and 72 hours, respectively. (g) XRD patterns of samples.

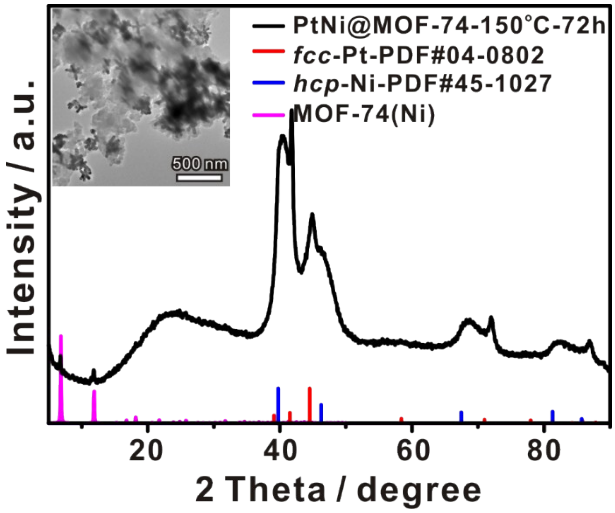

Fig. S4 XRD patterns of the product after PtNi alloy branched nanoparticles were reacted with DOT at 150 °C for 72 hours. Inset is corresponding TEM image.

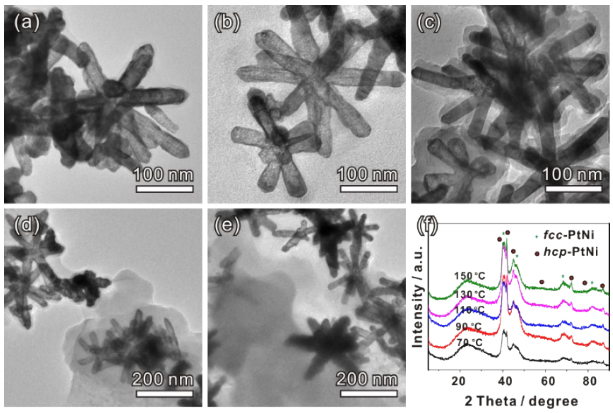

Fig. S5 TEM images of PtNi alloy branched nanoparticles after reaction with DOT at (a) 70 °C, (b) 90 °C, (c) 110 °C, (d) 130 °C and (e) 150 °C for 18 hours. (f) XRD patterns of samples.

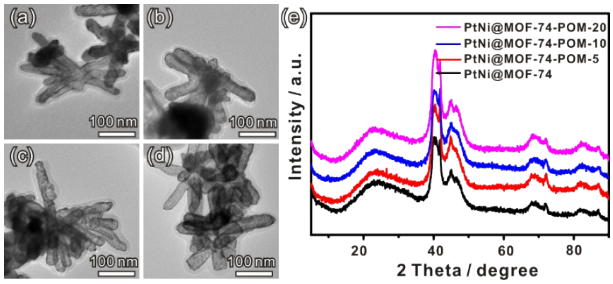

Fig. S6 TEM images of (a) PtNi@MOF-74, (b) PtNi@MOF-74-POM-5, (c) PtNi@MOF-74-POM-10, and (d) PtNi@MOF-74-POM-20. (e) XRD patterns of samples.

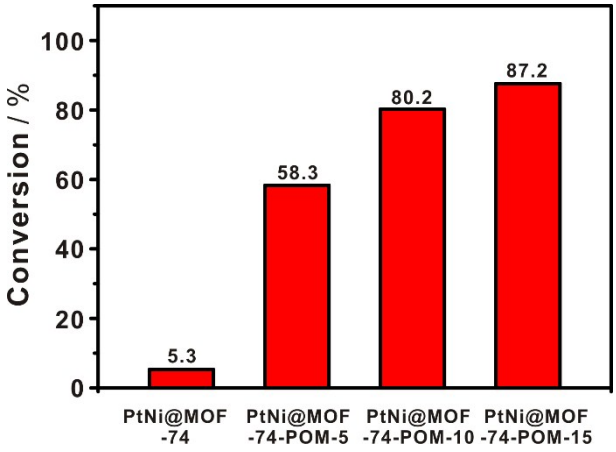

Fig. S7 The catalytic results of esterification reaction, using as-prepared catalysts. Reaction condition: 1.2 mmol 4-nitrobenzoic acid, 5 mL alcohol, stirred reaction for 8 hours at 80 °C.

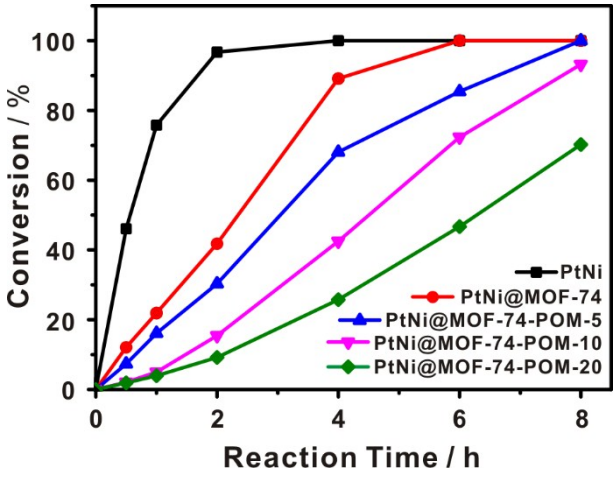

Fig. S8 The time-dependent conversion of hydrogenation of nitrobenzene. Reaction condition: 1.2 mmol nitrobenzene, 5 mL alcohol, stirred reaction for 8 hours in 0.1 Mpa H_2 atmosphere at 80 °C.

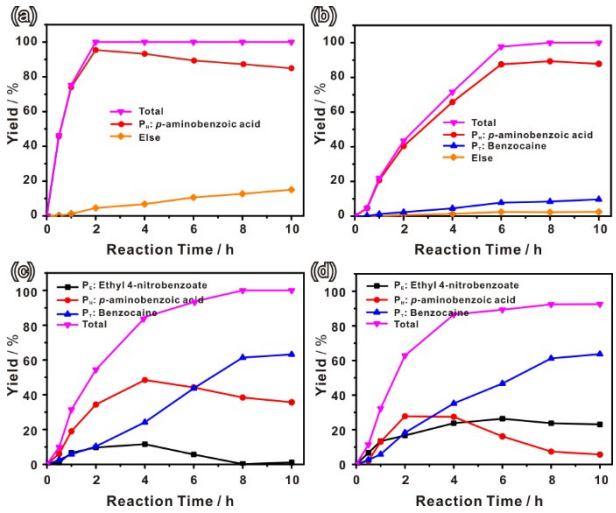

Fig. S9 Yield of different products on (a) pure PtNi alloy, (b) PtNi@MOF-74, (c) PtNi@MOF-74-POM-5 and (d) PtNi@MOF-74-POM-20 as a function of time. Reaction conditions: 1.2 mmol *p*-nitrobenzoic acid, 5 mL alcohol, stirred reaction for 8 h in 0.1 MPa H_2 atmosphere at 80 °C.

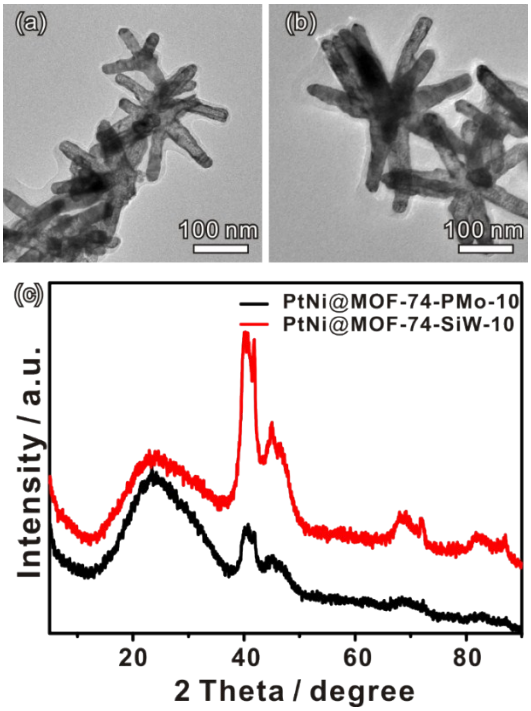

Fig. S10 TEM images of (a) PtNi@MOF-74-PMo-10 and (b)PtNi@MOF-74-SiW-10. (c) XRD patterns of samples.

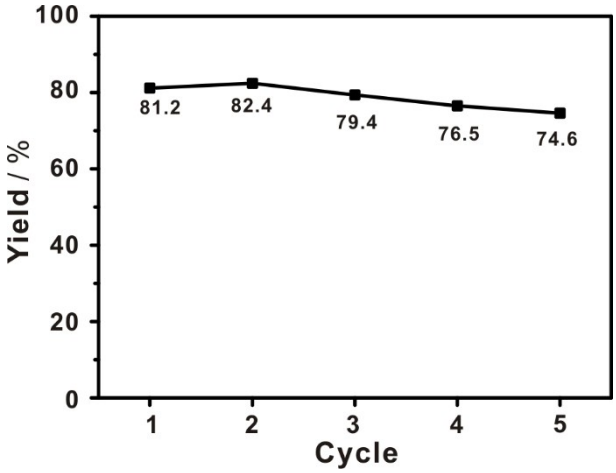

Fig. S11 The yield of benzocaine for five cycling catalytic reactions using PtNi@MOF-74-POM-10 as catalyst. Reaction condition: 1.2 mmol 4-nitrobenzoic acid, 5 mL alcohol, stirred reaction for 8 hours in 0.1 Mpa H_2 atmosphere at 80 °C.

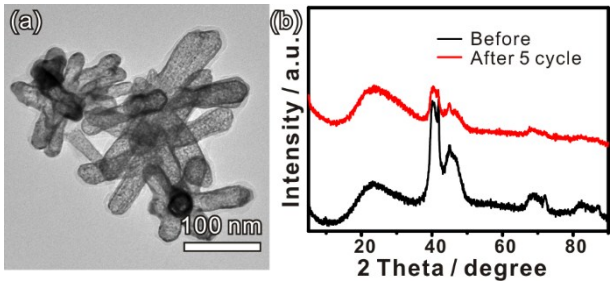

Fig. S12 (a) TEM images and (b) XRD patterns of PtNi@MOF-74-POM-10 after the five cycling catalytic reaction.

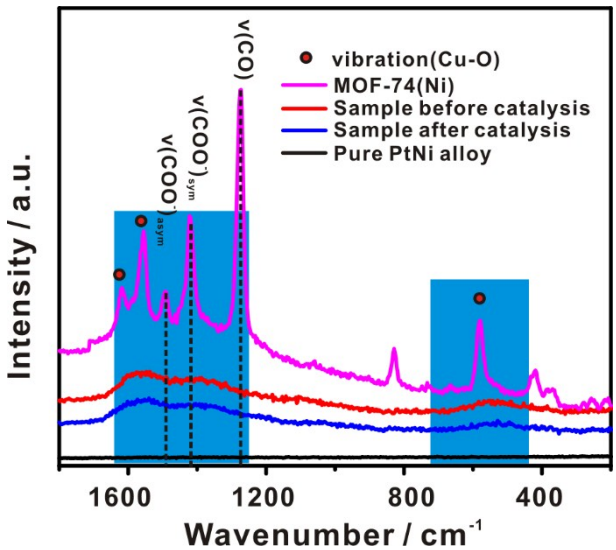

Fig. S13 Raman spectra of MOF-74(Ni), pure PtNi alloy, PtNi@MOF-74-POM-10 before and after cycling reaction. The peaks signed by cycles are assigned to stretching vibrations and ring deformation vibrations from the benzene ring.

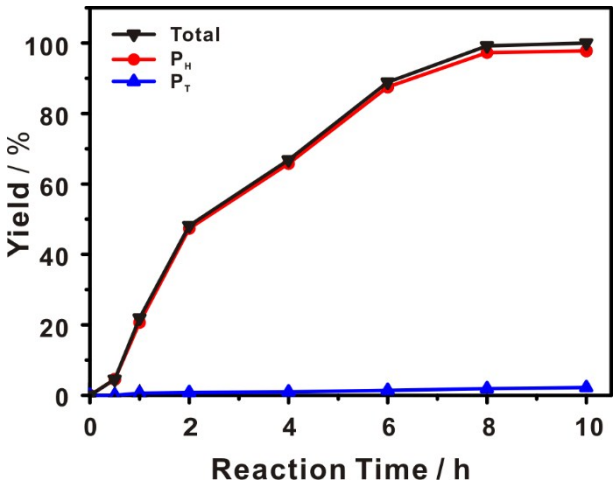

Fig. S14 Yield of different products on PtNi@MOF-74-POM-10 as a function of time. Reaction conditions: 1.2 mmol *p*-nitrobenzoic acid, 5 mL Benzyl alcohol, stirred reaction for 8 h in 0.1 MPa H_2 atmosphere at 80 °C.

3. Reference

[S1] Z. Cao, H. Li, C. Zhan, J. Zhang, W. Wang, B. Xu, F. Lu, Y. Jiang, Z. Xie, L. Zheng, *Nanoscale,* 2018, **10**, 5072.

[S2] C. Prestipino, L. Regli, J. G. Vitillo, F. Bonino, A. Damin, C. Lamberti, A. Zecchina, P. L. Solari, K. O. Kongshaug, S. Bordiga, *Chem. Mater.,* 2006, **18**, 1337-1346.