Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Applying MOF$^+$ technique to in-situ prepare hybrid material for hydrogenation reaction

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Materials and Physical Measurements. All the reagents used in this work are purchased from Alfa without any purification. X-ray powder diffraction were collected by a Bruker AXSD8 Discover powder diffractometer at 40 kV, 40 mA for Cu Kα, (λ = 1.5406Å). The simulated powder patterns were calculated by Mercury 1.4. The purity of the bulk products were determined by comparison of the simulated and experimental PXRD patterns. The TEM and HRTEM were performed using a JEM-2010 transmission electron microscope operating at 200 kV.XPS experiments were performed in a Theta probe (Thermo Fisher) using monochromated Al Kα x-rays at *h*ν=1486.6 eV. The Pd concentration was determined by inductively coupled plasma-mass spectroscopy (ICP-MS, NexION 300X).The catalytic reaction were traced and identified by gas chromatography (GC, Agilent 7890A with a 0.25 mm × 30 m DB-5 capillary column) using an internal standard technique.

The gas sorption isotherms were collected on a Belsorp-max. Ultrahigh-purity-grade (>99.999%) N_2 and H_2 gases were used in this adsorption measurement. To maintain the experimental temperatures liquid nitrogen (77 K) and temperature-programmed water bath (293 K) were used respectively.

Before carrying out adsorption experiments, the samples used in this work (150 mg) were immerged in CH_3OH for three days, then degassed automatically in Belsorp-max at 180ºC for 24 h to generate the activated samples.

Catalyst Preparation.

Synthesis of Zn-MOF-74.A mixture of $Zn(NO_3)_2{\cdot}6H_2O$ (0.0604 g, 0.203 mmol), 2,5-dihydroxy terephthalic acid (0.0191 g, 0.096 mmol), N,N-dimethylformamide (DMF) (2ml), isopropyl alcohol (0.1 mL) and H_2O (2 mL) was placed in a closed 25 ml Teflon reactor and heated at 105°C for 1200 min, in turn cooled to room temperature, produced brown needle-shaped crystals were got and dried naturally at room temperature.

Synthesis of Zn-MOF-74@Fe_2O_3. The synthesis of it is referred to the reported method.[13] 12 mg $FeSO_4{\cdot}7H_2O$ is dissolved in 5 mL H_2O, after then, 150 mg Zn-MOF-74 was added, then shake for 1 min. The resultant solid was isolated by filtration, and then washed by water (5 mL) for three times, then dried naturally.

Synthesis of Zn-MOF-74@(Pd@Fe_2O_3). Typically, 12mg $FeSO_4·7H_2O$ is dissolved in 5 ml H_2O, then 5 ml 500ppm Pd solution is relaxedly added at room temperature. When a flocculation appears in solution, 150 mg Zn-MOF-74 are added immediately and shake for 1 min. The resultant solid samples were separated using centrifugal separation, and washed three times with distilled water, then dried naturally.

Synthesis of Pd@Fe_2O_3. The samples were prepared by co-precipitation method.[18] Typically, $PdCl_2$ and $Fe(NO_3)_3$ were firstly dissolved in 60 mL de-ionic water and stirred for 30 min. Then, the mixture was slowly dropped into Na_2CO_3 aqueous solution at 338 K under vigorous stirring. The pH of the solution was maintained 8. After aged for 2 h, the brown precipitate was filtrated and washed by hot water for several times until the chloride ions were undetected by silver nitrate. The finally obtained slurry was dried at 373 K overnight and calcined for 4 h at 573 K.

Catalytic Activity Characterization.

GC. The liquid products were analyzed by an Agilent GC7890 A gas chromatograph equipped with flame ionization detector and DB-5 capillary column (30.0 m × 250 μm × 0.25 μm).

The injector temperature was set at 260 °C, and the detector column temperature was increased from 80 to 150 °C with a ramp rate of 5 °C min. The experimental errors for the conversions and selectivity were less than 3% obtained according to at least 3 parallel experiments.

Typical reaction procedure.

A typical reaction procedure for hydrogenation of olefins (or semihydrogenation of phenylacetylene) using the catalysts in this work was as follows. Catalyst (10 mg) was placed in a reaction vessel connected to a gas bag filled with 1 atm of H_2. Next, EtOH (2 mL) and olefins (0.3 mmol) were added to the reaction vessel, then the flask was purged with H_2 for several times to allow pure H_2 atmosphere for the reaction. Next, the mixture was stirred at setted temperature. The conversion of the products were determined by GC.

Reuse experiment.

For the catalytic recycling/durability experiments, the same amount of styrene was added into the flask to initiate the reaction. Next, the mixture was stirred at setted temperature. The conversion of the products were determined by GC.

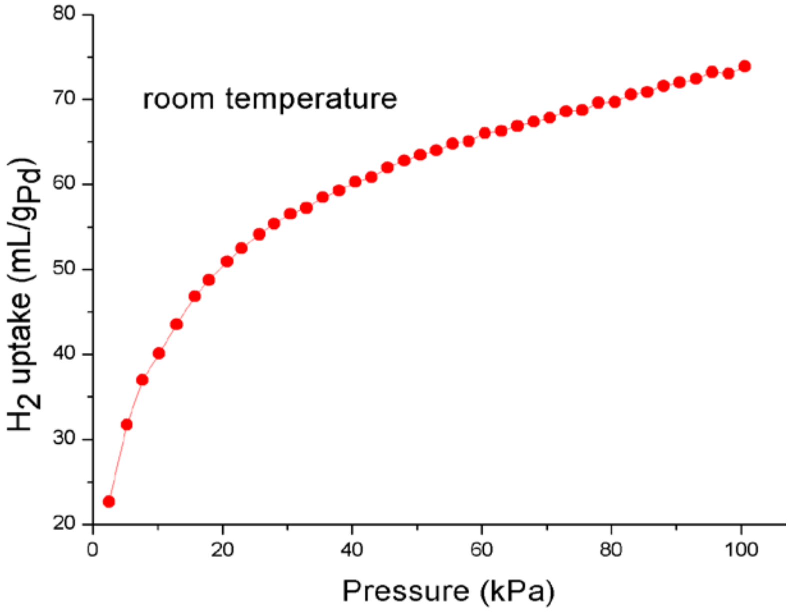

Fig. S1 H_2 uptake of Zn-MOF-74@(Pd@Fe_2O_3) at room temperature.

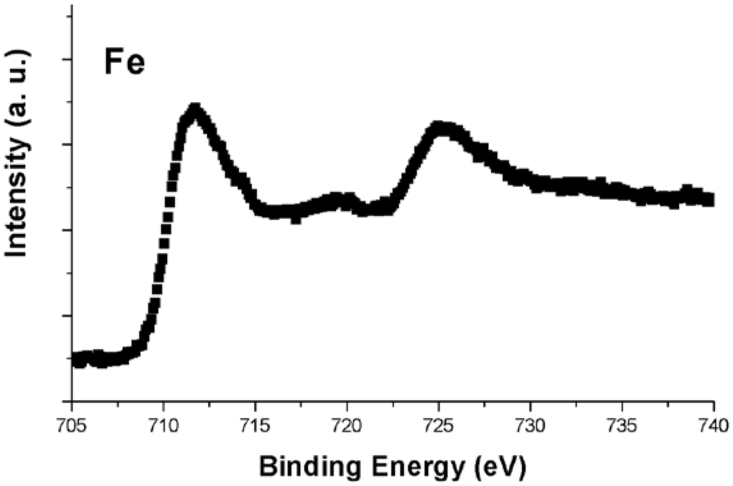

Fig. S2 The HRXPS data of Fe element for Zn-MOF-74@(Pd@Fe_2O_3) samples.

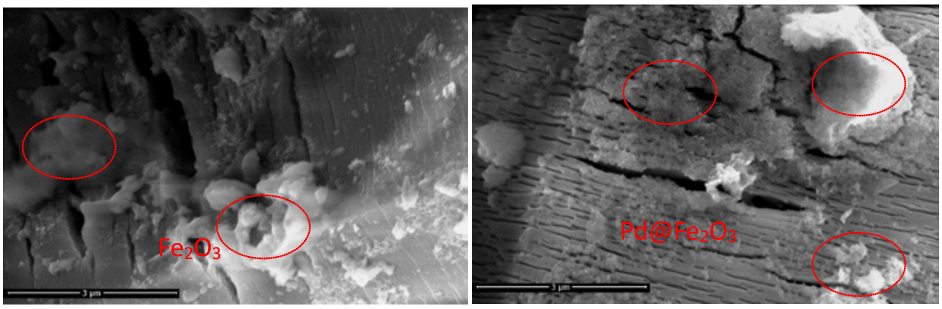

Fig. S3 The SEM image of Zn-MOF-74@Fe_2O_3 and Zn-MOF-74@(Pd@Fe_2O_3). The highlight is Fe_2O_3 and Pd@Fe_2O_3, respectively.

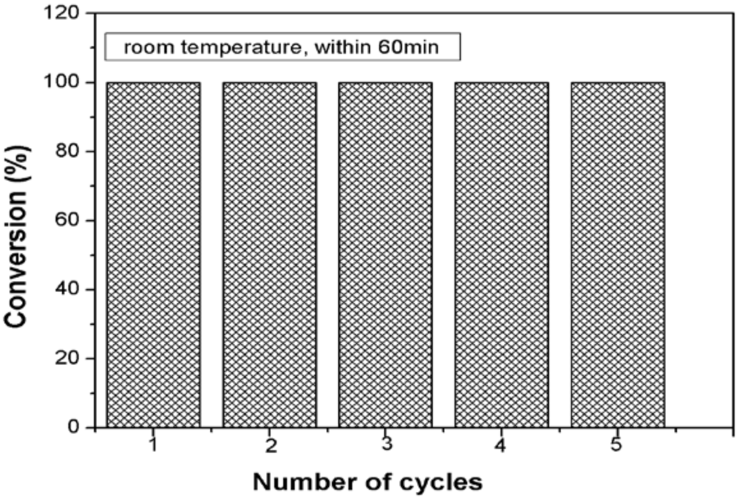

Fig. S4 Recyclability of Zn-MOF-74@(Pd@Fe_2O_3) for the hydrogenation reaction on styrene at room temperature and 1 atm H_2 within 60 min.

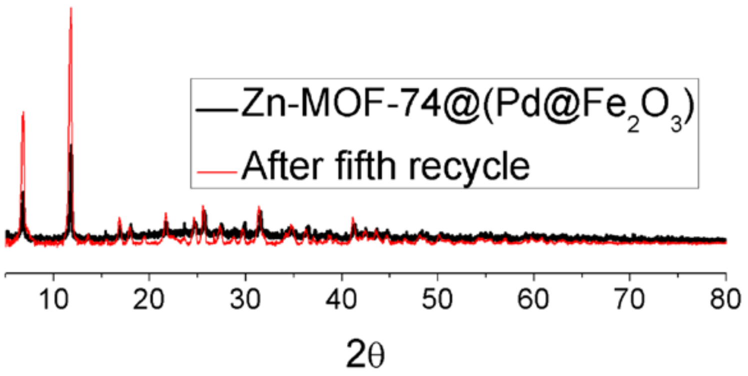

Fig. S5 A comparison of PXRD patterns between Zn-MOF-74@(Pd@Fe$_2$O$_3$) and it after fifth recycle. It is clear that a well match between them is observed, indicative of its good durability for reuse.

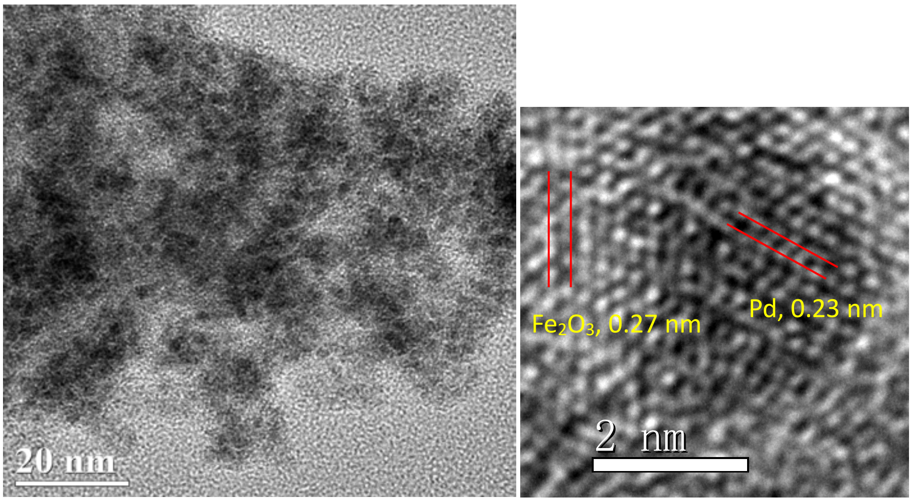

Fig. S6 TEM and HRTEM images of the Zn-MOF-74@(Pd@Fe_2O_3) samples after fifth recycle. It is cleat that the Pd NPs do not aggregate together.

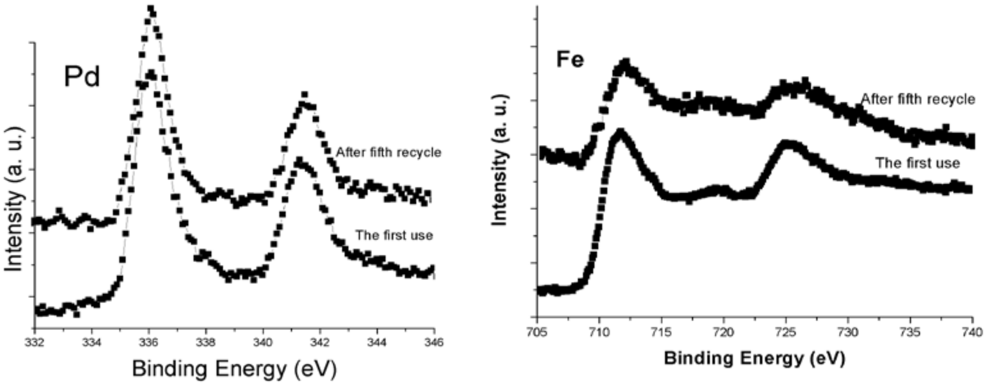

Fig. S7 The XPS data of Zn-MOF-74@(Pd@Fe$_2$O$_3$) samples after fifth recycle. It is cleat that the XPS spectra for the samples after fifth recycle is comparable with as-synthesized Zn-MOF-74@ (Pd@Fe$_2$O$_3$) samples, indicative of its good durability for reuse.

Table S1. A comparison with other reported catalysts for hydrogenation reaction.

Catalyst	Substrate	Time (h)	H_2 pressure(bar)	Conversion(%)	Selectivity(%)	Ref
Pd/UiO-66	styrene	4.2	1	100		17
Pd/UiO-66@PDMS-60	styrene	1		100		17
Lindlar catalyst	phenylacetylene	3.5	1	100	56	8c
Pd/$MgAl_2O_4$	phenylacetylene	3.5	1	100	49	8c
PdIn/$MgAl_2O_4$	phenylacetylene	3.5	1	92	97	8c
Pd@Ag-0.20	phenylacetylene	3	50	>99	>99	7a
(Pd@Ag)@CeO_2	phenylacetylene	12	15	97	>99	7b
Zn-MOF-74@(Pd@Fe_2O_3)	styrene	0.83	1	100		This work
Zn-MOF-74@(Pd@Fe_2O_3)	phenylacetylene	1	1	82.6	92.6	This work