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Supporting Information for:

Gas-phase Organometallic Catalysis in MFM-300(Sc) Provided by Switchable Dynamic Metal Sites

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S1. Experimental details

Chemicals

Scandium triflate ($Sc(SO_3CF_3)_3$, 99 %), biphenyl-3,3′,5,5′-tetracarboxylic acid (H_4BPTC ≥ 99.7 %), tetrahydrofuran anhydrous (THF ≥ 99.9 %), N,N-dimethylformamide (DMF, 99.8 %), hydrochloric acid (HCl, 36.5%), and acetone (ACE, HPLC, ≥ 99.8%) were supplied by Sigma-Aldrich. Hydrogen gas (H_2, 99%) was supplied by Infra. All reagents, gases, and solvents were used as received from commercial suppliers without further purification.

Synthesis of MFM-300(Sc)

MFM-300(Sc) was synthesized following a previously reported procedure.[1] Then, 30 mg (0.061 mmol) of $Sc(SO_3CF_3)_3$ and 10 mg (0.030 mmol) of H_4BPTC were mixed using 4 mL of THF, 3 mL of DMF, 1 mL of water, and 2 drops of HCl. The resultant slurry mixture was stirred until complete dissolution occurred. The solution was then placed in a pressure tube and heated in an oil bath to 75 °C for 72 h. The tube was cooled down to room temperature. The colourless crystalline product was separated by filtration, washed with 5 mL of DMF (three times), and dried in air.

Analytical instruments

Powder X-Ray Diffraction Patterns (PXRD)

The PXRD were recorded on a Rigaku Diffractometer, Ultima IV with Cu-Kα1 radiation (λ = 1.5406 Å) using a nickel filter, the patterns were recorded in the range 2–50° 2θ with a step scan of 0.02° and a scan rate of 0.10° min^{-1}.

Fourier-transform infrared spectroscopy (FT-IR)

The FT-IR spectra were obtained in the range of 4000-500 cm^{-1} on a Shimadzu IRTracer-100 spectrometer using KBr pellets.

Thermal gravimetric analysis (TGA)

The TGA was performed using a TA Instruments Q500HR analyzer, under an N_2 atmosphere using the high-resolution mode (dynamic rate TGA) at a scan rate of 2 °C/min, from room temperature to 640 °C.

Nitrogen adsorption-desorption

Nitrogen adsorption-desorption isotherms were measured by a volumetric method using a Micromeritics ASAP 2020 gas sorption analyzer. The sample mass was 65.0 mg. Free space correction measurements were performed using ultra-high purity He gas (UHP grade 5, 99.999% pure). Nitrogen isotherms were measured using UHP-grade Nitrogen. All nitrogen analyses were performed using a liquid nitrogen bath at 77 K. Oil-free vacuum pumps were used to prevent contamination of sample or feed gases.

Catalysis experiments

Prior to the catalytic experiments, MFM-300(Sc) was acetone-exchanged for 3 days and dried at 120 °C under a vacuum. After that, MFM-300(Sc) was compacted and meshed to have a defined particle size (0.425-0.850 mm), using 1 TON m^{-2} of pressure. The catalytic test for the ACE conversion by MFM-300(Sc) was carried out using a Micro activity Effi reactor system (Figure S1), with a continuous flow fixed bed microreactor (9 mm i.d.), which was loaded with 15 mg of the catalyst. Before the catalytic test, the sample was activated under an N2 (25 mL min^{-1}) atmosphere for 4 h at 150°C. For the reaction, a flow of 0.1 ml min^{-1} of ACE was introduced using a micro syringe pump, and a gas flow of H_2 of 25 mL min^{-1}. Both flows were introduced to an evaporator at 150 ° C to ensure a homogenous gas-phase mix before entering the reactor. The flowing gas was regulated through a pre-calibrated mass flow controller with digital read-out units (MKS Instruments). The chemical reaction was carried out at atmospheric pressure and two temperatures were selected (80 and 180 °C) for 4h. The reaction products were recovered in a Peltier condenser cooled at 4 °C (Figure S2). The reactant and products concentrations were measured using a gas chromatograph (Clarus 480 chromatograph PerkinElmer) containing a Supelcowax fused silica capillary column (30 m × 0.25 mm, 0.25µm film thickness) connected to a flame ionization detector.

Figure S1. Microactivity Effi system.

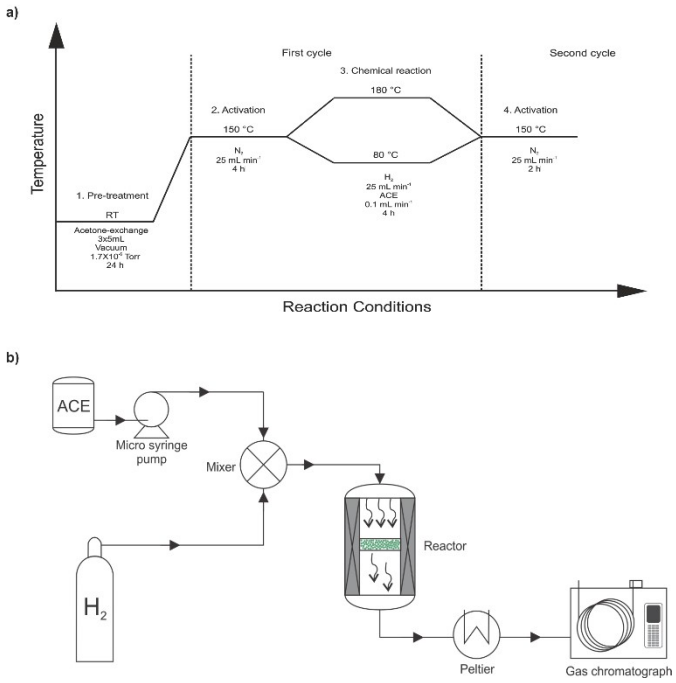

Figure S2. a) Diagram of the catalytic progress of the reaction and b) scheme of the reaction system.

S2. Results and Discussions

Synthesis of MFM-300(Sc)

PXRD

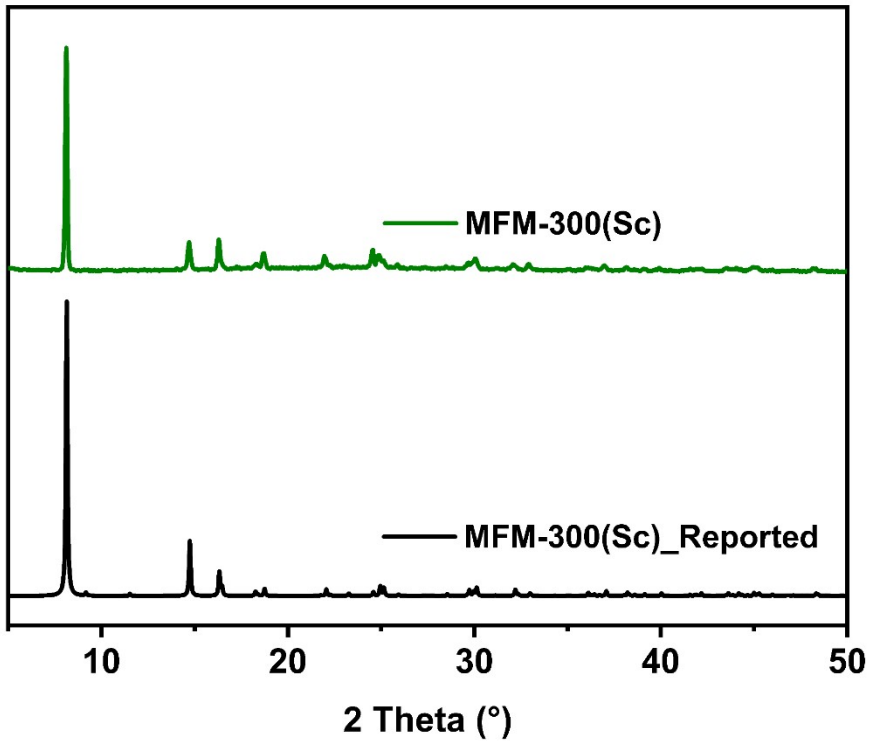

Figure S3. PXRD pattern of MFM-300(Sc) reported (black line), and MFM-300(Sc) as-synthetized (green line).

FTIR

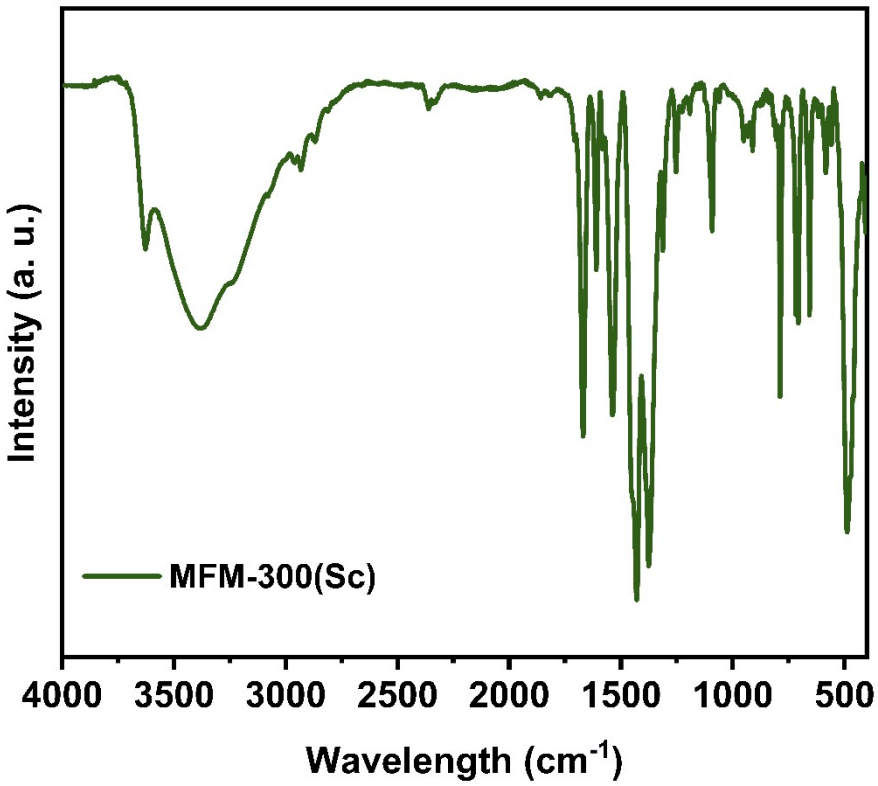

Figure S4. FTIR spectra of MFM-300(Sc) as-synthetized.

TGA

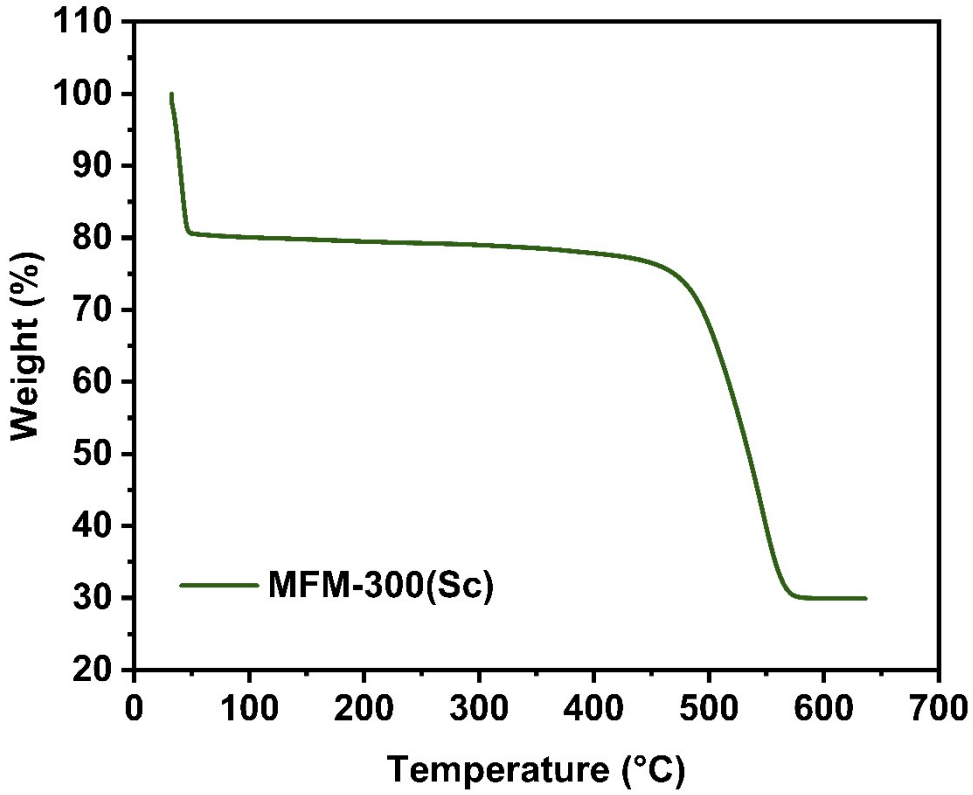

Figure S5. TGA spectra of MFM-300(Sc) as-synthetized.

Nitrogen adsorption-desorption

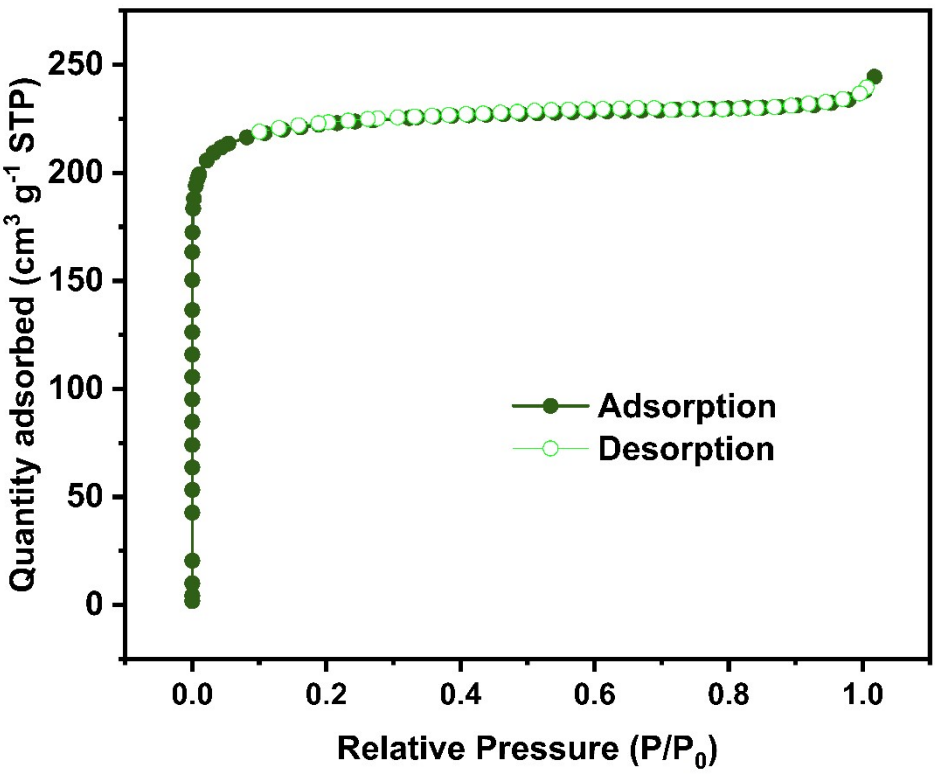

Figure S6. Nitrogen isotherm of MFM-300(Sc) as-synthetized: adsorption (dark green close line) and desorption (light green open line).

Table S1. Comparative table of the catalytic activity of different materials on the hydrogenation of acetone.					
Material	T (°C)	P(atm)	Conversion (%)	Yield (%)	References
0.1%Pd/HT	118	27	38	32	[2]
TiO_2−SiO_2/SiO_2	200	2	65.5	41.6	[3]
Pd/S(PS-GO)	160	20	59.6	33.5	[4]
Ni/MgO–Al_2O_3	160	1	63.9	19.8	[5]
Pd@MIL-101(Cr)	180	7.4	73.5	48.1	[6]
Pd/UiO-66	120	1	25.3	23.8	[7]
MFM-300(Sc)	180	1	27.7	27.2	**This work**

Table S2. TON number and yield of the reaction.			
Experiment	Temperature (°C)	Yield (%)	TON*
Initial test	180	27.2	710
Cycle (Spent catalyst reuse)	180	26.9	706
Reproducibility test	180	26.1	683
Low-temperature test	80	13.4	353
*TON was calculated based on the total metal of the material, which is considered an apparent number, due to the dynamics of the metal center.			

PXRD after the defined particle size, and after catalysis

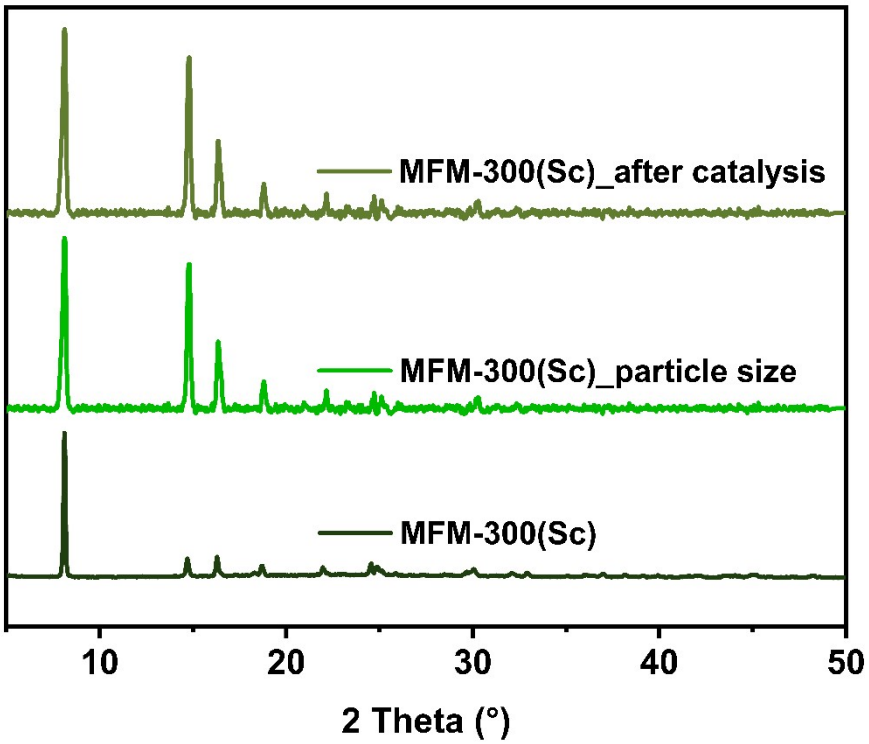

Figure S7. PXRD pattern of MFM-300(Sc) (dark green line), the particle size of MFM-300(Sc) (green line), and MFM-300(Sc) after catalysis (light green).

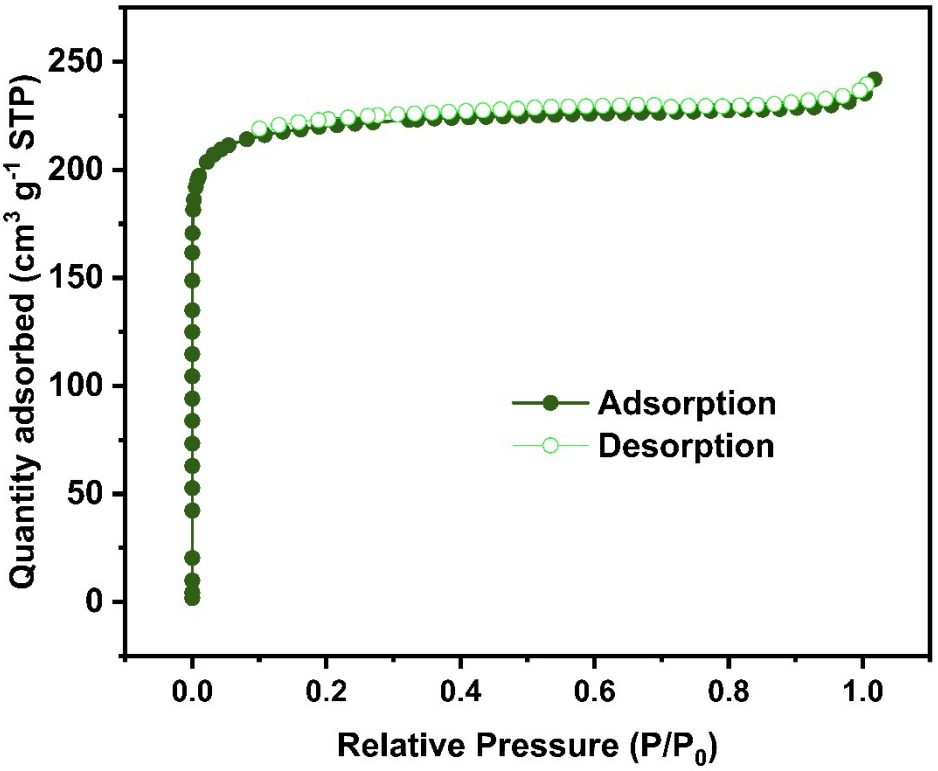

Figure S8. Nitrogen isotherm of MFM-300(Sc) post-catalysis with a BET surface area and pore volume of 1340 $m^2 g^{-1}$ and 0.56 $cm^3 g^{-1}$ respectively, in excellent agreement with the previously reported values (1390 $m^2 g^{-1}$ and 0.58 $cm^3 g^{-1}$, respectively).[8]

S3. References

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