Electronic Supplementary Information

Catalytic chromium reduction using formic acid and metal nanoparticles immobilized in a metal-organic framework

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Experimental Section

Chemicals All chemicals were commercial and used without further purification. Formic acid (HCOOH, 98-100%, Kishida Chemicals Co. Ltd.), potassium dichromate ($K_2Cr_2O_7$, >99.5%, Kishida Chemical Co. Ltd), hydrogen hexachloroplatinate hexahydrate ($H_2PtCl_6·6H_2O$, >99%, Kishida Chemical Co. Ltd), palladium chloride ($PdCl_2$, 99.9%, Wako Pure Chemical Industries Ltd), hydrochloric acid (HCl, >35%, Kishida Chemical Co. Ltd), hydrogen tetrachloroaurate tetrahydrate ($HAuCl_4·4H_2O$, >99%, Kishida Chemicals Co. Ltd.,), rhodium trichloride ($RhCl_3·3H_2O$, 95%, Wako Pure Chemical Industries Ltd), terephthalic acid ($HOOCC_6H_4COOH$, 99%, Tri Chemical Laboratories Inc.), chromic nitrate nonahydrate ($Cr(NO_3)_3·9H_2O$, 99%, Sigma-Aldrich), aqueous hydrofluoric acid (HF, 46%, Kishida Chemical Co. Ltd), cyclohexane (C_6H_{12}, 99.5%, Kishida Chemicals Co. Ltd.) and ethanol (C_2H_5OH, 99%, Kishida Chemical Co. Ltd) were used as received.

Synthesis

Synthesis of MIL-101 MIL-101 was synthesized using the reported procedure.[1] Terephthalic acid (328 mg, 2.0 mmol), $Cr(NO_3)_3·9H_2O$ (800 mg, 2.0 mmol), aqueous HF (0.4 mL, 2.0 mmol) and de-ionized water (12 mL) were placed in a 20 mL Teflon-lined autoclave and heated at 220 °C for 8 h. After cooling, the resulting green powder of MIL-101 with formula $Cr_3F(H_2O)_2O[(O_2C)C_6H_4(CO_2)]_3·nH_2O$ ($n \leq 25$) was doubly filtered off using two glass filters with pore sizes between 40 and 100 μm to remove the unreacted crystals of terephthalic acid, and then further purified by solvothermal treatment in ethanol at 80 ^oC for 24 h. The resulting green solid was soaked in NH_4F (1.0 M) solution at 70 ^oC for 24 h to eliminate the terephthalic acid inside the pores of MIL-101 and immediately filtered, washed with hot water several times, and finally dried overnight at 150 °C under vacuum for further use.

Synthesis of M@MIL-101 (M = Pt, Pd, Au, and Rh) Supported Pt, Pd, Au, and Rh nanoparticles were prepared via double-solvents method. Typically, 150 mg of green MIL-101 powder activated by heating at 150 ^oC for 12 h under dynamic vacuum, which has a pore volume of 1.54 cm^3 g^{-1} as determined by N_2 sorption isotherm, was suspended in 30 mL of dry cyclohexane as hydrophobic solvent and the mixture was sonicated for 15 min until it became homogeneous. After stirring of 2 h, 0.15 mL of aqueous H_2PtCl_6 (0.10 M) solution, H_2PdCl_4 (0.19 M) solution (prepared by mixing 100 mg of $PdCl_2$, 308 μL aqueous HCl (35%) and 750 μL water), aqueous $HAuCl_4$ (0.10 M) solution or aqueous $RhCl_3$ (0.20 M) solution as the hydrophilic solvent was added dropwise over a period of 15 min with constant vigorous stirring. The resulting solution was continuously stirred for 2 h. After careful filtration, the green powder was dried in air at room temperature. These synthesized samples were further dried at 150 °C for 12 h, followed by treating in a stream of H_2/He (50 mL min^{-1}/50 mL min^{-1}) at 200 °C for 5 h to yield 2 wt% M@MIL-101 (M = Pt, Pd, Au, and Rh), respectively.

Catalytic reduction of aqueous solution of Cr(IV) To an aqueous solution (5 mL) of $K_2Cr_2O_7$ (29.4 mg, 1 mmol, 2 x 10^{-2} M) and HCOOH (0.3 mL), 2 wt% Pt@MIL-101 (27.5 mg, 0.0028 mmol), 2 wt% Pd@MIL-101 (15 mg, 0.0028 mmol), 2 wt% Au@MIL-101 (27.6 mg, 0.0028 mmol) or 2 wt% Rh@MIL-101 (14.4 mg, 0.0028 mmol) catalyst was added. The initial molar ratio of M/Cr is 1/710. After introducing the catalyst, the yellow solution gradually faded as the reaction proceeded and finally a colorless solution was obtained. UV-Vis spectra were recorded on a Shimadzu UV-2550 spectrophotometer at short intervals to monitor the progress of the reaction. The absorption spectra of the solution were measured in the range of 200-800 nm. Addition of an excess of sodium hydroxide solution to the above resulting colorless solution resulted in a green solution, confirming the presence of Cr(III) as the reduction product of Cr(VI).

Characterization Powder X-ray diffraction (PXRD) was performed on a Rigaku Rint 2000 X-ray diffractometer with Cu Kα. The surface area measurements were performed with N_2 adsorption/desorption isotherms at liquid-nitrogen temperature (77 K) using automatic volumetric adsorption equipment (Belsorp mini II) after pretreatment under vacuum at 150 °C for 12 h. The pore volume was calculated by a single point method at $P/P_0 = 0.99$. Transmission electron microscope (TEM, FEI TECNAI G^2) equipped with energy-dispersed X-ray detector (EDX) were applied for the detailed microstructure information.

References

1. G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé and I. Margiolaki, *Science*, 2005, **309**, 2040.

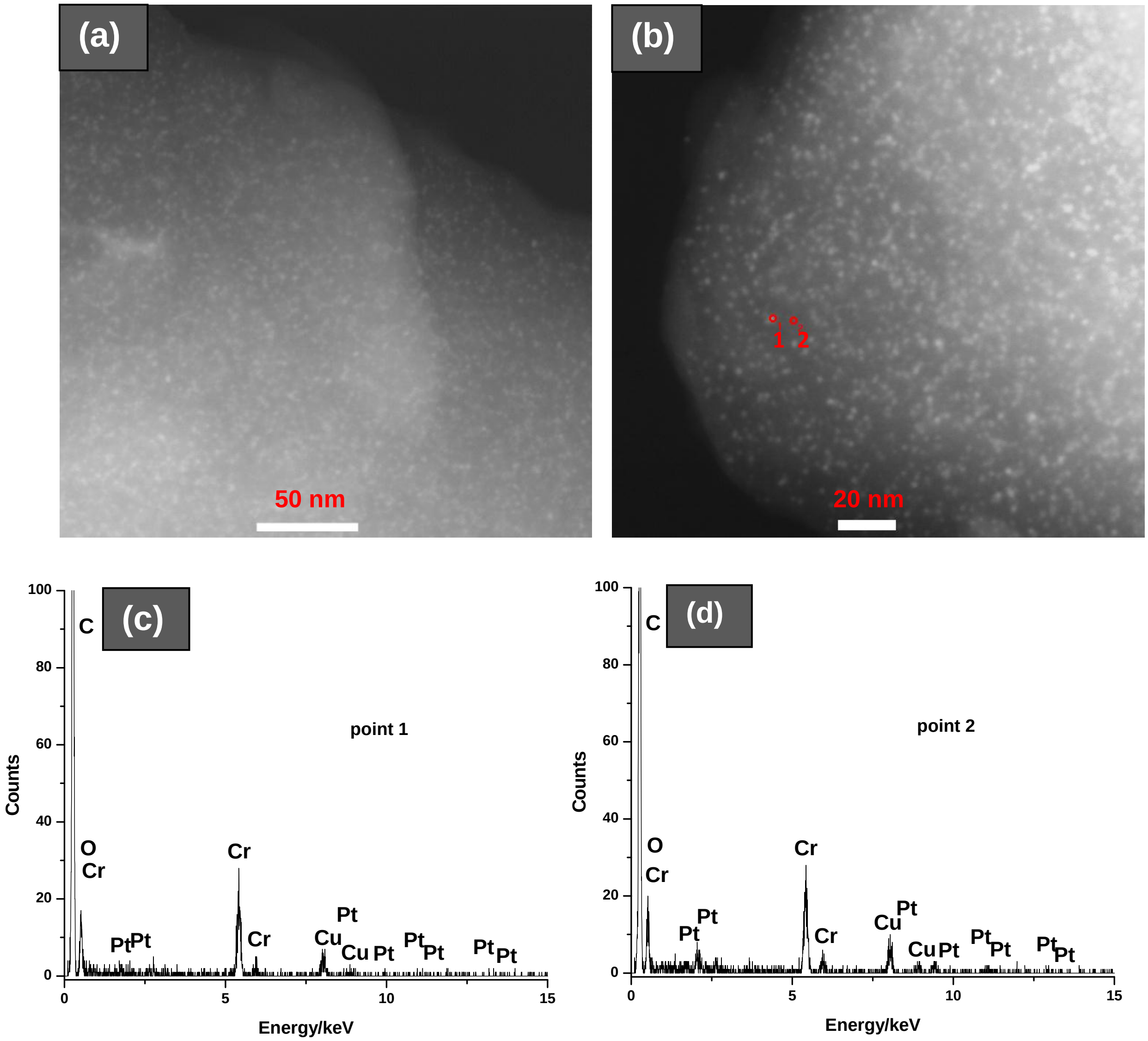

Fig. S1 Representative (a and b) HAADF-STEM images and (c and d) the corresponding EDX spectra (at points 1 and 2, respectively, in (b)) of 2 wt% Pt@MIL-101 after catalytic reaction.

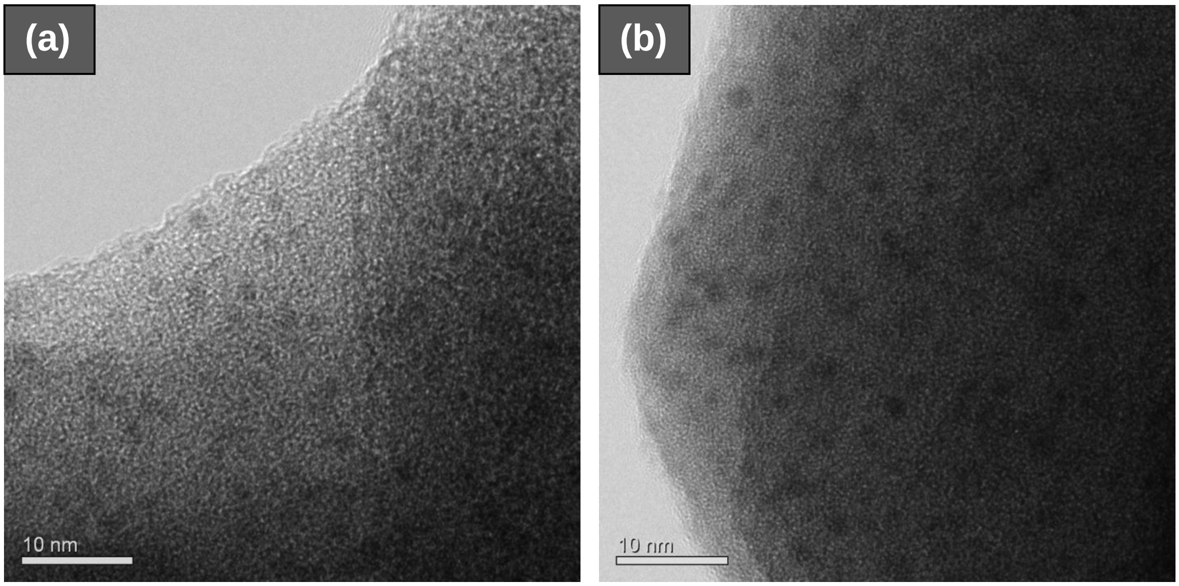

Fig. S2 Representative (a and b) HR-TEM images of 2 wt% Pt@MIL-101 after catalytic reaction.

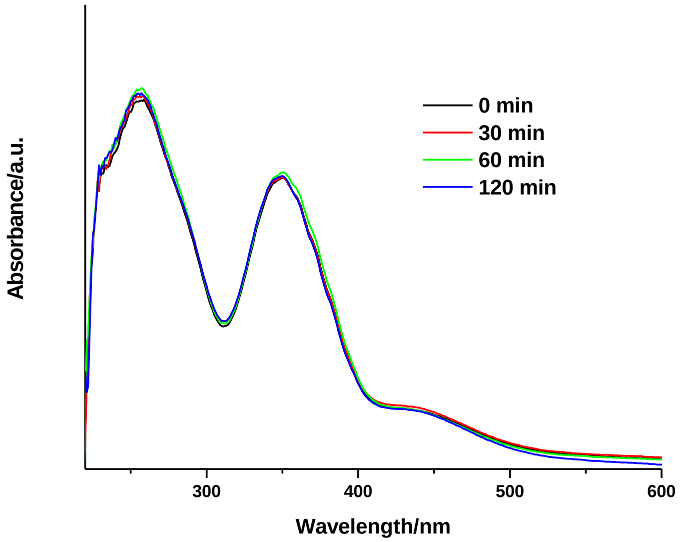

Fig. S3 Catalytic reduction of Cr(VI) using excess of formic acid over MIL-101 at 50 ^{o}C as monitored by UV-Vis spectroscopy.

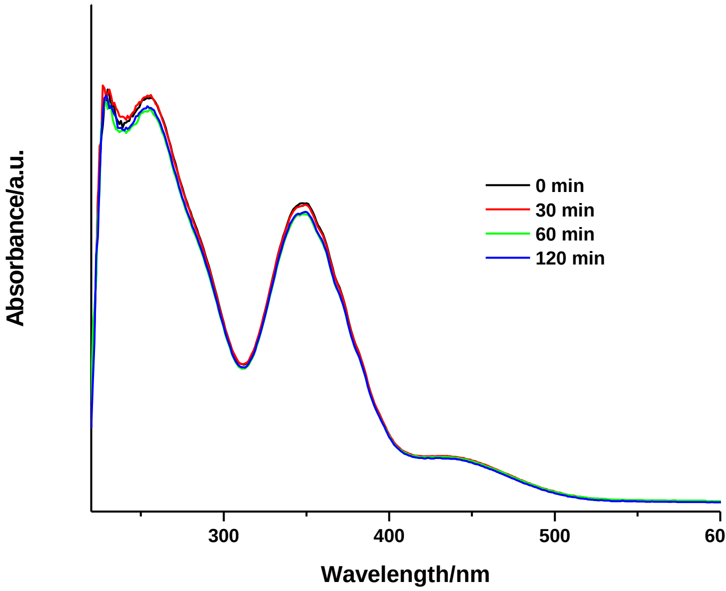

Fig. S4 Catalytic reduction of Cr(VI) using excess of formic acid over 2% Au@MIL-101 at 50 ^{o}C (Au/Cr = 1/710) as monitored by UV-Vis spectroscopy.

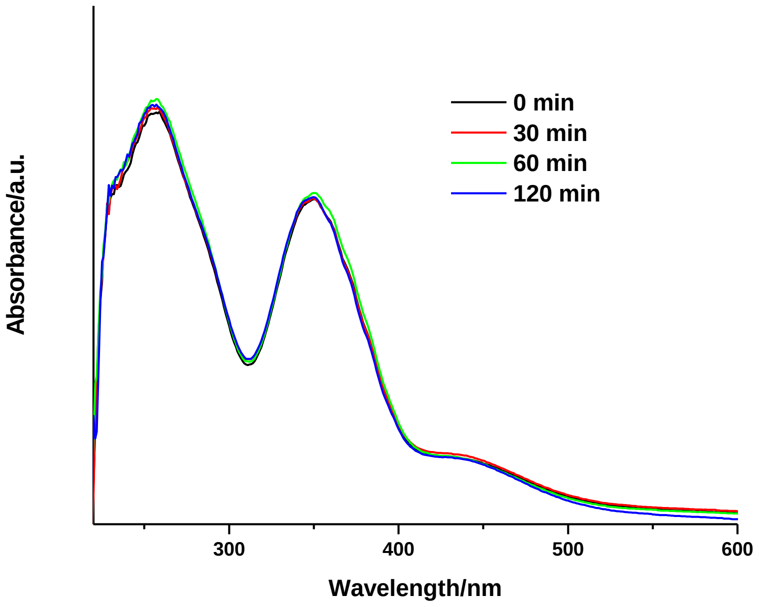

Fig. S5 Catalytic reduction of Cr(VI) using excess of formic acid over 2% Rh@MIL-101 at 50 °C (Rh/Cr = 1/710) as monitored by UV-Vis spectroscopy.