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Supporting Information

Controlling catalytic dehydrogenation of formic acid over low-cost transition metal-substituted AuPd nanoparticles immobilized by functionalized metal-organic frameworks at room temperature

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1. Syntheses

1.1 Synthesis of MIL-101

According to the literature,[1] MIL-101 was prepared by reacting terephthalic acid (332 mg, 2.0 mmol) with $Cr(NO_3)_3.9H_2O$ (800 mg, 2.0 mmol) in the presence of aqueous HF (0.4 mL, 2.0 mmol) and deionized water (9.5 mL) at 200 °C for 8 h. The reaction produced microcrystalline green powder of MIL-101 with formula $Cr_3F(H_2O)_2O[(O_2C)C_6H_4(CO_2)]_3.nH_2O$ ($n \leq 25$). To eliminate the unreacted terephthalic acid, the crystalline MIL-101 product in the solution was doubly filtered off using two glass filters with pore sizes between 40 and 100 μm, and then further purified by solvothermal treatment in ethanol at 80 °C for 24 h and washed with hot ethanol. The resulting solid was soaked in NH_4F (1 M) solution at 70 °C for 24 h and immediately filtered, washed with hot water, and finally dried overnight at 150 °C under vacuum.

1.2 Synthesis of MIL-101-NO_2

According to the literature,[2] MIL-101-NO_2 was synthesized by nitration of MIL-101 using nitrating acid (HNO_3 conc. and H_2SO_4 conc.) for five hours under ice cooling and immediately filtered, washed with water, and finally dried overnight at 150 °C under vacuum.

1.3 Synthesis of MIL-101-NH_2

According to the literature,[2] MIL-101-NH_2 was synthesized by reduced the nitro groups of MIL-101-NO_2 to amino groups using $SnCl_2 \cdot 2H_2O$ and ethanol for 6 h at 70 °C and immediately filtered, washed with water, and finally dried overnight at 150 °C under vacuum.

1.4 Synthesis of MIL-101-SO_3H

According to the literature,[3] MIL-101-SO_3H was prepared by dissolving monosodium 2-sulfoterephthalic acid (3.35 g, 12.5 mmol), CrO_3 (1.25 g, 12.5 mmol), and concentrated aqueous hydrochloric acid (0.91 g, 25 mmol) in water (50 mL), then transferred to a Teflon-lined stainless steel autoclave. This highly acidic solution was heated at 453 K for 6 d under the hydrothermal conditions. The reaction product was washed three times with deionized water (400 mL) and methanol (100 mL), then dried in air.

1.5 Synthesis of MOF-5-NH_2

According to the literature,[4] MOF-5-NH_2 was prepared by reacting $Zn(NO_3)_2 \cdot 6H_2O$ (1.2 g, 4.04 mmol), 2-aminoterephthalic acid (0.24 g, 1.32 mmol) and DEF (40 mL) at 100 °C for 48 h. Cubic crystals were collected and immersed in DEF (20 mL) for 24 h (2×), followed by immersing the crystals in $CHCl_3$ (40 mL) for 24 h (3×). The solvent-exchanged product was vacuum-dried at 160 °C for 24 h.

1.6 Synthesis of MOF-5

According to the literature,[4] MOF-5 was prepared by reacting $Zn(NO_3)_2·6H_2O$ (1.2 g, 4.04 mmol), terephthalic acid (0.22 g, 1.32 mmol) and DEF (40 mL) at 100 °C for 48 h. Cubic crystals were collected and immersed in DEF (20 mL) for 24 h (2×), followed by immersing the crystals in $CHCl_3$ (40 mL) for 24 h (3×). The solvent-exchanged product was vacuum-dried at 160 °C for 24 h.

1.7 Synthesis of SBA-15-NH_2

According to the literature,[5] SBA-15 (0.3 g) was suspended in anhydrous toluene (30 ml), and then APTES (0.1 ml) was added to the mixture. The solution was refluxed for 24 h. After that, the solution was cooled down to room temperature, and the product was centrifuged, washed thoroughly with MeOH. The resulting product was placed under high vacuum to remove the remaining solvent in the mesopores.

1.8 Synthesis of SBA-15

According to the literature,[6] P123 (2 g) was stirred with 15 mL of deionized water at 35 ^oC until fully dissolved, followed by adding HCl solution (2 M, 30 g) and addition of TEOS (4.4 g). The mixture was allowed to stir at 35 ^oC for 24 h before transferring into a Teflon bottle sealed in an autoclave, which was then heated to 100 ^oC for 2 days in an oven. The solid was filtered off, washed three times with deionized water, and calcined at 500 ^oC for 4 h.

1.9 Synthesis of $Au_{0.28}Pd_{0.47}Co_{0.25}$/MIL-101-$NO_2$

$HAuCl_4·4H_2O$ (0.0115 g, 0.028 mmol), Na_2PdCl_4 (0.0138 g, 0.047 mmol) and $Co(NO_3)_2·6H_2O$ (0.0073 g, 0.025 mmol) were dispersed in deionized H_2O (4 mL). Then, activated MIL-101-NO_2 (0.04 g) was added into the solution with stirring for 2 h. After that, the deionized H_2O (2 mL) containing $NaBH_4$ (0.06 g) was added into the above mixture, which was vigorously stirred in Ar atmosphere for 2 h to obtain $Au_{0.28}Pd_{0.47}Co_{0.25}$/MIL-101-$NO_2$.

1.10 Synthesis of $Au_{0.28}Pd_{0.47}Co_{0.25}$/MIL-101-$SO_3H$

$HAuCl_4·4H_2O$ (0.0115 g, 0.028 mmol), Na_2PdCl_4 (0.0138 g, 0.047 mmol) and $Co(NO_3)_2·6H_2O$ (0.0073 g, 0.025 mmol) were dispersed in deionized H_2O (4 mL). Then, activated MIL-101-SO_3H (0.04 g) was added into the solution with stirring for 2 h. After that, the deionized H_2O (2 mL) containing $NaBH_4$ (0.06 g) was added into the above mixture, which was vigorously stirred in Ar atmosphere for 2 h to obtain $Au_{0.28}Pd_{0.47}Co_{0.25}$/MIL-101- SO_3H.

1.11 Synthesis of $Au_{0.28}Pd_{0.47}Co_{0.25}$/MIL-101

$HAuCl_4·4H_2O$ (0.0115 g, 0.028 mmol), Na_2PdCl_4 (0.0138 g, 0.047 mmol) and $Co(NO_3)_2·6H_2O$ (0.0073 g, 0.025 mmol) were dispersed in deionized H_2O (4 mL). Then, activated MIL-101 (0.04 g) was added into the solution with stirring for 2 h. After that, the deionized H_2O (2 mL) containing $NaBH_4$ (0.06 g) was added into the above mixture, which was vigorously stirred in Ar atmosphere for 2 h to obtain $Au_{0.28}Pd_{0.47}Co_{0.25}$/MIL-101.

1.12 Synthesis of $Au_{0.28}Pd_{0.47}Co_{0.25}$/MOF-5-$NH_2$

$HAuCl_4\cdot 4H_2O$ (0.0115 g, 0.028 mmol), Na_2PdCl_4 (0.0138 g, 0.047 mmol) and $Co(NO_3)_2\cdot 6H_2O$ (0.0073 g, 0.025 mmol) were dispersed in deionized H_2O (4 mL). Then, activated MOF-5-NH_2 (0.04 g) was added into the solution with stirring for 2 h. After that, the deionized H_2O (2 mL) containing $NaBH_4$ (0.06 g) was added into the above mixture, which was vigorously stirred in Ar atmosphere for 2 h to obtain $Au_{0.28}Pd_{0.47}Co_{0.25}$/MOF-5-$NH_2$.

1.13 Synthesis of $Au_{0.28}Pd_{0.47}Co_{0.25}$/MOF-5

$HAuCl_4\cdot 4H_2O$ (0.0115 g, 0.028 mmol), Na_2PdCl_4 (0.0138 g, 0.047 mmol) and $Co(NO_3)_2\cdot 6H_2O$ (0.0073 g, 0.025 mmol) were dispersed in deionized H_2O (4 mL). Then, activated MOF-5 (0.04 g) was added into the solution with stirring for 2 h. After that, the deionized H_2O (2 mL) containing $NaBH_4$ (0.06 g) was added into the above mixture, which was vigorously stirred in Ar atmosphere for 2 h to obtain $Au_{0.28}Pd_{0.47}Co_{0.25}$/MOF-5.

1.14 Synthesis of $Au_{0.28}Pd_{0.47}Co_{0.25}$/SBA-15-$NH_2$

$HAuCl_4\cdot 4H_2O$ (0.0115 g, 0.028 mmol), Na_2PdCl_4 (0.0138 g, 0.047 mmol) and $Co(NO_3)_2\cdot 6H_2O$ (0.0073 g, 0.025 mmol) were dispersed in deionized H_2O (4 mL). Then, activated SBA-15-NH_2 (0.04 g) was added into the solution with stirring for 2 h. After that, the deionized H_2O (2 mL) containing $NaBH_4$ (0.06 g) was added into the above mixture, which was vigorously stirred in Ar atmosphere for 2 h to obtain $Au_{0.28}Pd_{0.47}Co_{0.25}$/SBA-15-$NH_2$.

1.15 Synthesis of $Au_{0.28}Pd_{0.47}Co_{0.25}$/SBA-15

$HAuCl_4\cdot 4H_2O$ (0.0115 g, 0.028 mmol), Na_2PdCl_4 (0.0138 g, 0.047 mmol) and $Co(NO_3)_2\cdot 6H_2O$ (0.0073 g, 0.025 mmol) were dispersed in deionized H_2O (4 mL). Then, activated SBA-15 (0.04 g) was added into the solution with stirring for 2 h. After that, the deionized H_2O (2 mL) containing $NaBH_4$ (0.06 g) was added into the above mixture, which was vigorously stirred in Ar atmosphere for 2 h to obtain $Au_{0.28}Pd_{0.47}Co_{0.25}$/SBA-15.

1.16 Synthesis of $Au_{0.19}Pd_{0.56}Co_{0.25}$/MIL-101-$NH_2$

$HAuCl_4\cdot 4H_2O$ (0.0078 g, 0.019 mmol), Na_2PdCl_4 (0.0165 g, 0.056 mmol) and $Co(NO_3)_2\cdot 6H_2O$ (0.0073 g, 0.025 mmol) were dispersed in deionized H_2O (4 mL). Then, activated MIL-101-NH_2 (0.04 g) was added into the solution with stirring for 2 h. After that, the deionized H_2O (2 mL) containing $NaBH_4$ (0.06 g) was added into the above mixture, which was vigorously stirred in Ar atmosphere for 2 h to obtain $Au_{0.19}Pd_{0.56}Co_{0.25}$/MIL-101-$NH_2$.

1.17 Synthesis of $Au_{0.375}Pd_{0.375}Co_{0.25}$/MIL-101-$NH_2$

$HAuCl_4\cdot 4H_2O$ (0.0154 g, 0.0375 mmol), Na_2PdCl_4 (0.011 g, 0.0375 mmol) and $Co(NO_3)_2\cdot 6H_2O$ (0.0073 g, 0.025 mmol) were dispersed in deionized H_2O (4 mL). Then, activated MIL-101-NH_2 (0.04 g) was added into the solution with stirring for 2 h. After that, the deionized H_2O (2 mL) containing

$NaBH_4$ (0.06 g) was added into the above mixture, which was vigorously stirred in Ar atmosphere for 2 h to obtain $Au_{0.375}Pd_{0.375}Co_{0.25}$/MIL-101-$NH_2$.

1.18 Synthesis of $Au_{0.47}Pd_{0.28}Co_{0.25}$/MIL-101-$NH_2$

$HAuCl_4 \cdot 4H_2O$ (0.0194 g, 0.047 mmol), Na_2PdCl_4 (0.0082 g, 0.028 mmol) and $Co(NO_3)_2 \cdot 6H_2O$ (0.0073 g, 0.025 mmol) were dispersed in deionized H_2O (4 mL). Then, activated MIL-101-NH_2 (0.04 g) was added into the solution with stirring for 2 h. After that, the deionized H_2O (2 mL) containing $NaBH_4$ (0.06 g) was added into the above mixture, which was vigorously stirred in Ar atmosphere for 2 h to obtain $Au_{0.47}Pd_{0.28}Co_{0.25}$/MIL-101-$NH_2$.

1.19 Synthesis of $Au_{0.32}Pd_{0.53}Co_{0.15}$/MIL-101-$NH_2$

$HAuCl_4 \cdot 4H_2O$ (0.013 g, 0.032 mmol), Na_2PdCl_4 (0.0156 g, 0.053 mmol) and $Co(NO_3)_2 \cdot 6H_2O$ (0.0044 g, 0.015 mmol) were dispersed in deionized H_2O (4 mL). Then, activated MIL-101-NH_2 (0.04 g) was added into the solution with stirring for 2 h. After that, the deionized H_2O (2 mL) containing $NaBH_4$ (0.06 g) was added into the above mixture, which was vigorously stirred in Ar atmosphere for 2 h to obtain $Au_{0.32}Pd_{0.53}Co_{0.15}$/MIL-101-$NH_2$.

1.20 Synthesis of $Au_{0.24}Pd_{0.41}Co_{0.35}$/MIL-101-$NH_2$

$HAuCl_4 \cdot 4H_2O$ (0.01 g, 0.024 mmol), Na_2PdCl_4 (0.012 g, 0.041 mmol) and $Co(NO_3)_2 \cdot 6H_2O$ (0.01 g, 0.035 mmol) were dispersed in deionized H_2O (4 mL). Then, activated MIL-101-NH_2 (0.04 g) was added into the solution with stirring for 2 h. After that, the deionized H_2O (2 mL) containing $NaBH_4$ (0.06 g) was added into the above mixture, which was vigorously stirred in Ar atmosphere for 2 h to obtain $Au_{0.24}Pd_{0.41}Co_{0.35}$/MIL-101-$NH_2$.

1.21 Synthesis of $Au_{0.34}Pd_{0.56}Co_{0.1}$/MIL-101-$NH_2$

$HAuCl_4 \cdot 4H_2O$ (0.014 g, 0.034 mmol), Na_2PdCl_4 (0.016 g, 0.056 mmol) and $Co(NO_3)_2 \cdot 6H_2O$ (0.003 g, 0.01 mmol) were dispersed in deionized H_2O (4 mL). Then, activated MIL-101-NH_2 (0.04 g) was added into the solution with stirring for 2 h. After that, the deionized H_2O (2 mL) containing $NaBH_4$ (0.06 g) was added into the above mixture, which was vigorously stirred in Ar atmosphere for 2 h to obtain $Au_{0.34}Pd_{0.56}Co_{0.1}$/MIL-101-$NH_2$.

1.22 Synthesis of $Au_{0.26}Pd_{0.44}Co_{0.3}$/MIL-101-$NH_2$

$HAuCl_4 \cdot 4H_2O$ (0.011 g, 0.026 mmol), Na_2PdCl_4 (0.013 g, 0.044 mmol) and $Co(NO_3)_2 \cdot 6H_2O$ (0.087 g, 0.03 mmol) were dispersed in deionized H_2O (4 mL). Then, activated MIL-101-NH_2 (0.04 g) was added into the solution with stirring for 2 h. After that, the deionized H_2O (2 mL) containing $NaBH_4$ (0.06 g) was added into the above mixture, which was vigorously stirred in Ar atmosphere for 2 h to obtain $Au_{0.26}Pd_{0.44}Co_{0.3}$/MIL-101-$NH_2$.

1.23 Synthesis of $Au_{0.225}Pd_{0.375}Co_{0.4}$/MIL-101-$NH_2$

$HAuCl_4\cdot 4H_2O$ (0.0093 g, 0.0225 mmol), Na_2PdCl_4 (0.011 g, 0.0375 mmol) and $Co(NO_3)_2\cdot 6H_2O$ (0.0116 g, 0.04 mmol) were dispersed in deionized H_2O (4 mL). Then, activated MIL-101-NH_2 (0.04 g) was added into the solution with stirring for 2 h. After that, the deionized H_2O (2 mL) containing $NaBH_4$ (0.06 g) was added into the above mixture, which was vigorously stirred in Ar atmosphere for 2 h to obtain $Au_{0.225}Pd_{0.375}Co_{0.4}$/MIL-101-$NH_2$.

1.24 Synthesis of $Au_{0.75}Co_{0.25}$/MIL-101-NH_2

$HAuCl_4\cdot 4H_2O$ (0.031 g, 0.075 mmol) and $Co(NO_3)_2\cdot 6H_2O$ (0.0073 g, 0.025 mmol) were dispersed in deionized H_2O (4 mL). Then, activated MIL-101-NH_2 (0.04 g) was added into the solution with stirring for 2 h. After that, the deionized H_2O (2 mL) containing $NaBH_4$ (0.06 g) was added into the above mixture, which was vigorously stirred in Ar atmosphere for 2 h to obtain $Au_{0.75}Co_{0.25}$/MIL-101-NH_2.

1.25 Synthesis of $Au_{0.38}Pd_{0.62}$/MIL-101-NH_2

$HAuCl_4\cdot 4H_2O$ (0.0156 g, 0.038 mmol), Na_2PdCl_4 (0.0182 g, 0.062 mmol) were dispersed in deionized H_2O (4 mL). Then, activated MIL-101-NH_2 (0.04 g) was added into the solution with stirring for 2 h. After that, the deionized H_2O (2 mL) containing $NaBH_4$ (0.06 g) was added into the above mixture, which was vigorously stirred in Ar atmosphere for 2 h to obtain $Au_{0.38}Pd_{0.62}$/MIL-101-NH_2.

1.26 Synthesis of $Pd_{0.75}Co_{0.25}$/MIL-101-NH_2

Na_2PdCl_4 (0.022 g, 0.075 mmol) and $Co(NO_3)_2\cdot 6H_2O$ (0.0073 g, 0.025 mmol) were dispersed in deionized H_2O (4 mL). Then, activated MIL-101-NH_2 (0.04 g) was added into the solution with stirring for 2 h. After that, the deionized H_2O (2 mL) containing $NaBH_4$ (0.06 g) was added into the above mixture, which was vigorously stirred in Ar atmosphere for 2 h to obtain $Pd_{0.75}Co_{0.25}$/MIL-101-NH_2.

1.27 Synthesis of Au/MIL-101-NH_2

$HAuCl_4\cdot 4H_2O$ (0.0412 g, 0.1 mmol), were dispersed in deionized H_2O (4 mL). Then, activated MIL-101-NH_2 (0.04 g) was added into the solution with stirring for 2 h. After that, the deionized H_2O (2 mL) containing $NaBH_4$ (0.06 g) was added into the above mixture, which was vigorously stirred in Ar atmosphere for 2 h to obtain Au/MIL-101-NH_2.

1.28 Synthesis of Pd/MIL-101-NH_2

Na_2PdCl_4 (0.0294 g, 0.1mmol) were dispersed in deionized H_2O (4 mL). Then, activated MIL-101-NH_2 (0.04 g) was added into the solution with stirring for 2 h. After that, the deionized H_2O (2 mL) containing $NaBH_4$ (0.06 g) was added into the above mixture, which was vigorously stirred in Ar atmosphere for 2 h to obtain Pd/MIL-101-NH_2.

1.29 Synthesis of Co/MIL-101-NH_2

$Co(NO_3)_2\cdot 6H_2O$ (0.029, 0.1mmol) were dispersed in deionized H_2O (4 mL). Then, activated MIL-101-NH_2 (0.04 g) was added into the solution with stirring for 2 h. After that, the deionized H_2O (2 mL) containing $NaBH_4$ (0.06 g) was added into the above mixture, which was vigorously stirred in Ar atmosphere for 2 h to obtain Co/MIL-101-NH_2.

2. Calculation Methods

The turnover frequency (TOF) reported here is an apparent TOF value based on the number of metal atoms in catalyst, which is calculated from the equation as follow:

$$TOF = \frac{P_{\mathrm{atm}} V_{\mathrm{gas}} / RT}{2 n_{metal} t}$$

Where P_{atm} (88.8 kPa) is the atmospheric pressure in Hohhot of Inner Mongolia, V_{gas} is the volume of generated H_2 and CO_2, R is the universal gas constant (8.314 m^3 Pa mol^{-1} K^{-1}), T is the room temperature (298 K), n_{metal} is the total mole number of metal atoms in catalyst, and t is the reaction time.

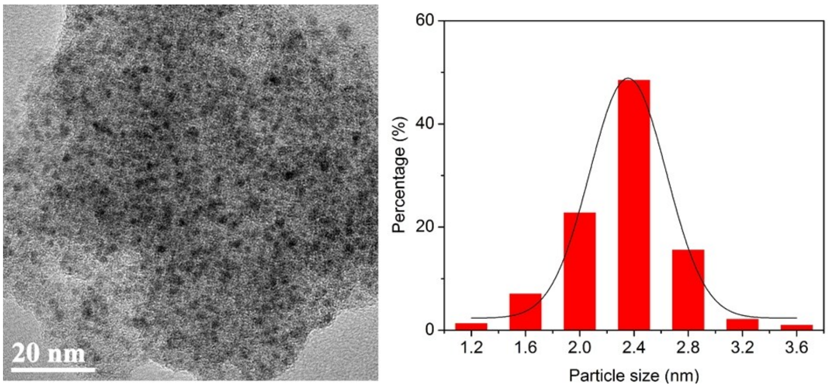

Fig. S1 TEM image of $Au_{0.28}Pd_{0.47}Co_{0.25}$/MIL-101-$NH_2$ and the corresponding size distribution histogram of AuPdCo NPs.

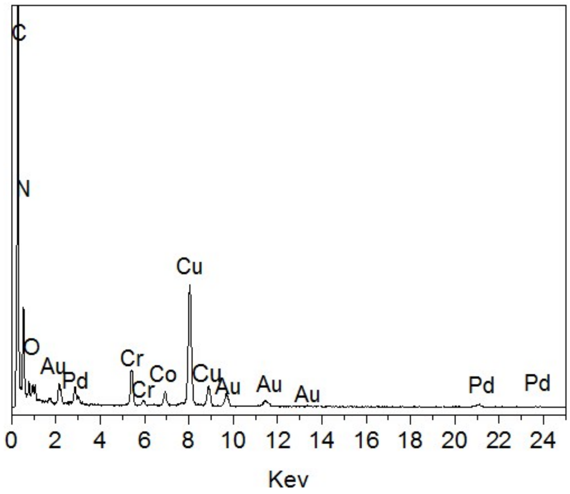

Fig. S2 EDS pattern of $Au_{0.28}Pd_{0.47}Co_{0.25}$/MIL-101-$NH_2$.

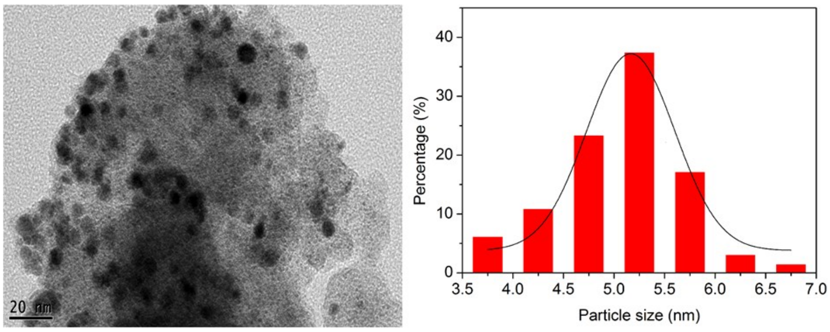

Fig. S3 TEM image of $Au_{0.28}Pd_{0.47}Fe_{0.25}$/MIL-101-$NH_2$ and the corresponding size distribution histogram of AuPdFe NPs.

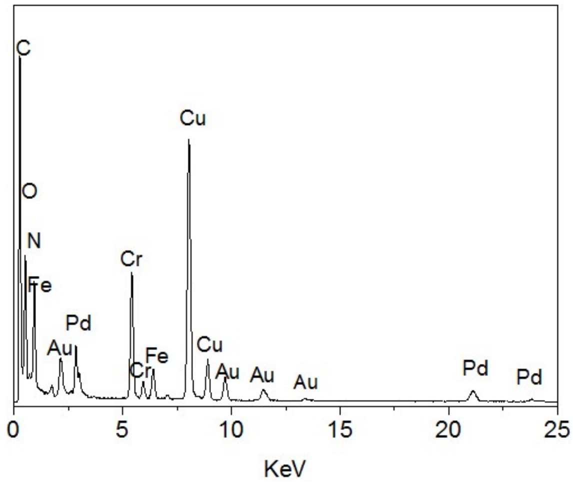

Fig. S4 EDS pattern of $Au_{0.28}Pd_{0.47}Fe_{0.25}$/MIL-101-$NH_2$.

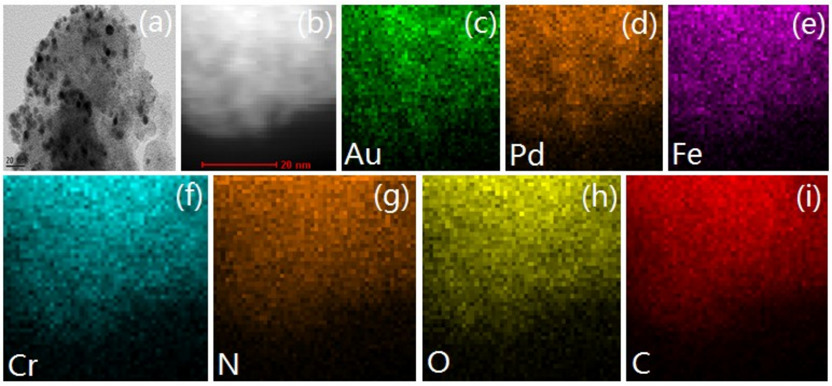

Fig. S5 (a) TEM, (b) HAADF-STEM images of $Au_{0.28}Pd_{0.47}Fe_{0.25}$/MIL-101-$NH_2$ and the corresponding elemental mappings for (c) Au, (d) Pd, (e) Fe, (f) Cr, (g) N, (h) O and (i) C.

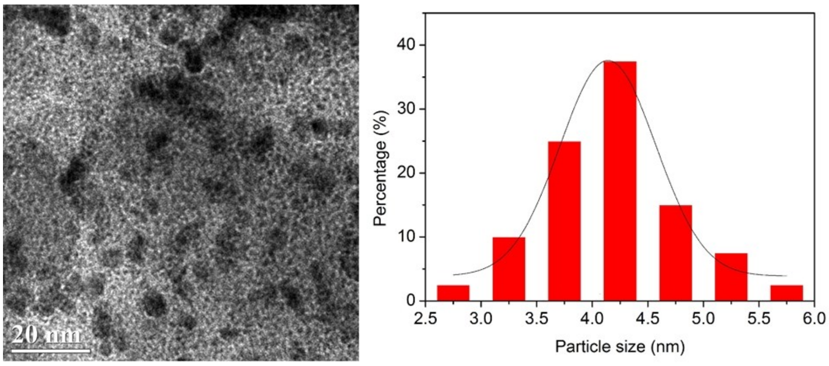

Fig. S6 TEM image of $Au_{0.28}Pd_{0.47}Ni_{0.25}$/MIL-101-$NH_2$ and the corresponding size distribution histogram of AuPdNi NPs.

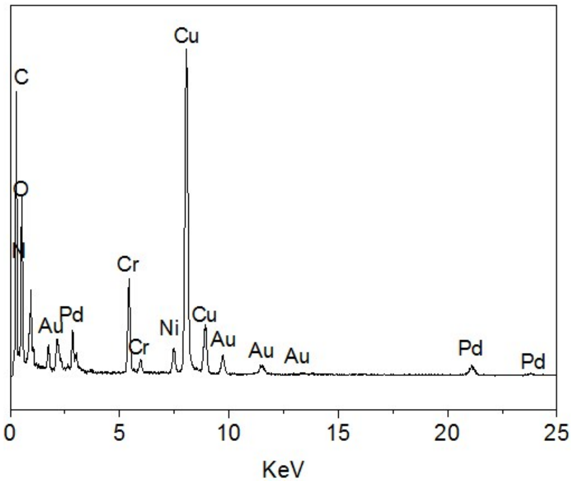

Fig. S7 EDS pattern of $Au_{0.28}Pd_{0.47}Ni_{0.25}$/MIL-101-NH$_2$.

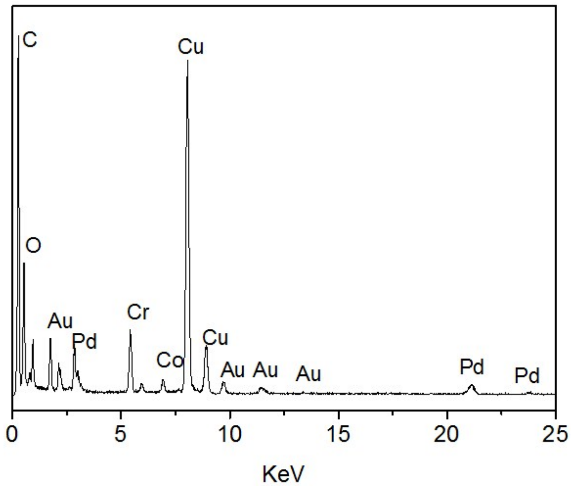

Fig. S8 EDS pattern of $Au_{0.28}Pd_{0.47}Co_{0.25}$/MIL-101.

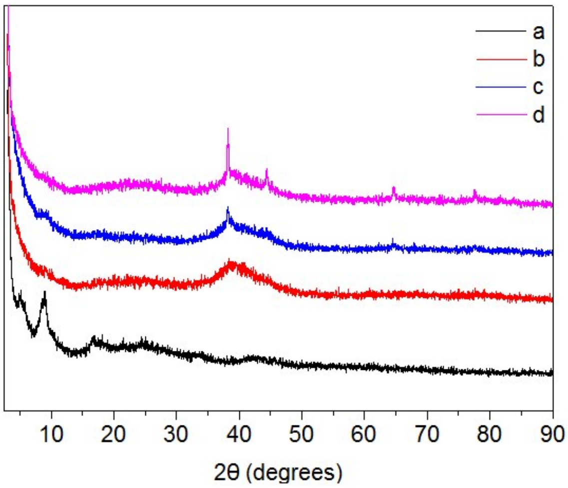

Fig. S9 PXRD patterns of (a) MIL-101-NH_2, (b) $Au_{0.28}Pd_{0.47}Co_{0.25}$/MIL-101-$NH_2$, (c) $Au_{0.28}Pd_{0.47}Fe_{0.25}$/MIL-101-$NH_2$ and (d) $Au_{0.28}Pd_{0.47}Ni_{0.25}$/MIL-101-$NH_2$.

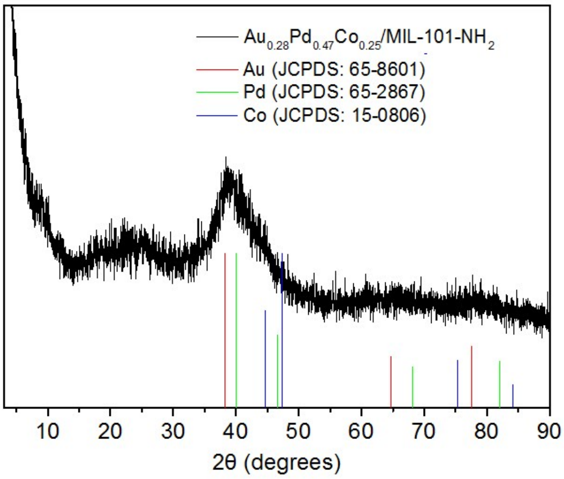

Fig. S10 PXRD patterns of $Au_{0.28}Pd_{0.47}Co_{0.25}$/MIL-101-$NH_2$ and Au, Pd and Co in JCPDS.

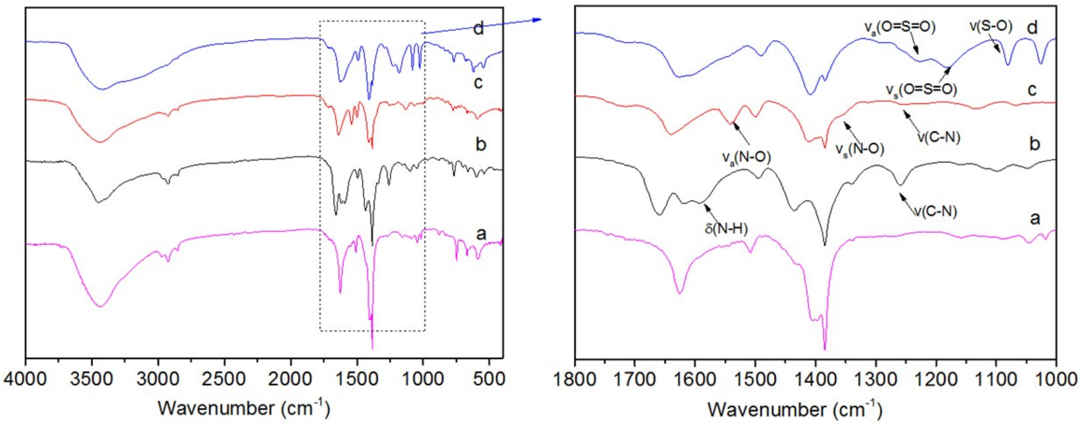

Fig. S11 IR spectra of (a) MIL-101, (b) MIL-101-NH_2, (c) MIL-101-NO_2 and (d) MIL-101-SO_3H.

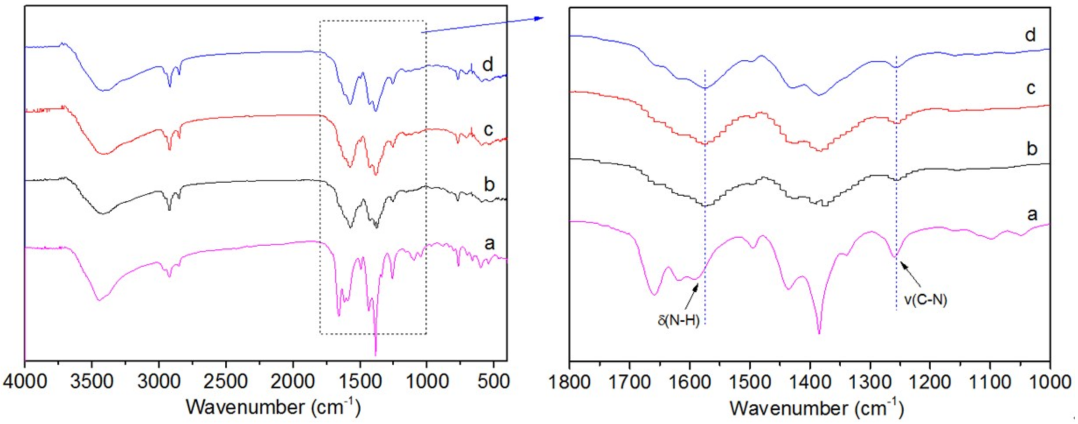

Fig. S12 IR spectra of (a) MIL-101-NH_2, (b) $Au_{0.28}Pd_{0.47}Co_{0.25}$/MIL-101-$NH_2$, (c) $Au_{0.28}Pd_{0.47}Fe_{0.25}$/MIL-101-$NH_2$ and (d) $Au_{0.28}Pd_{0.47}Ni_{0.25}$/MIL-101-$NH_2$.

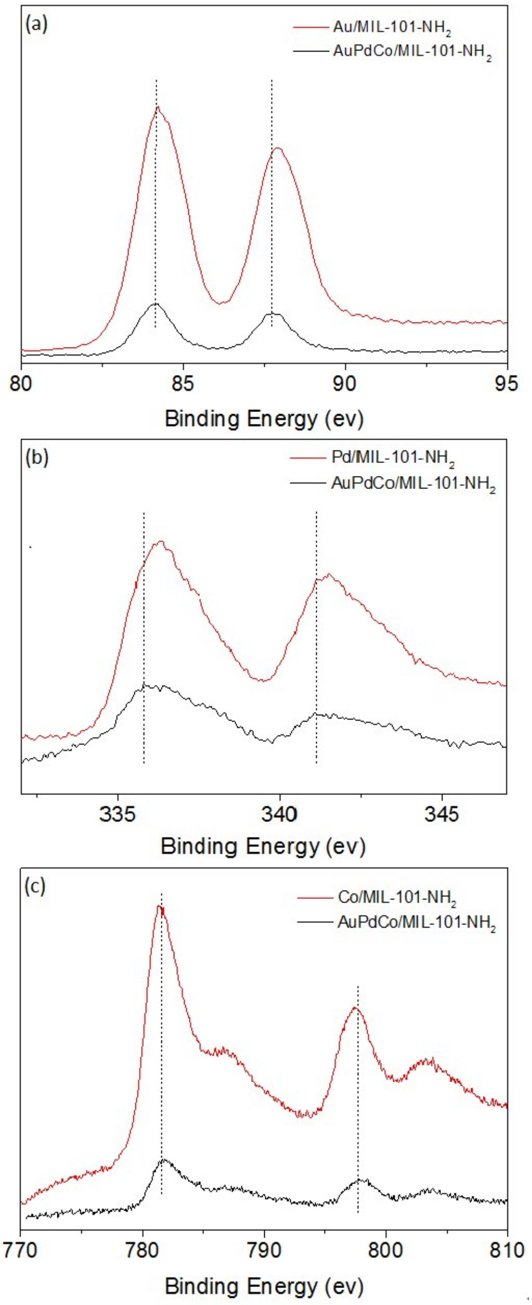

Fig. S13 XPS patterns in (a) Au 4f regions of Au/MIL-101-NH_2 and $Au_{0.28}Pd_{0.47}Co_{0.25}$/MIL-101-$NH_2$, (b) Pd 3d regions of Pd/MIL-101-NH_2 and $Au_{0.28}Pd_{0.47}Co_{0.25}$/MIL-101-$NH_2$ and (c) Co 2p regions of Co/MIL-101-NH_2 and $Au_{0.28}Pd_{0.47}Co_{0.25}$/MIL-101-$NH_2$.

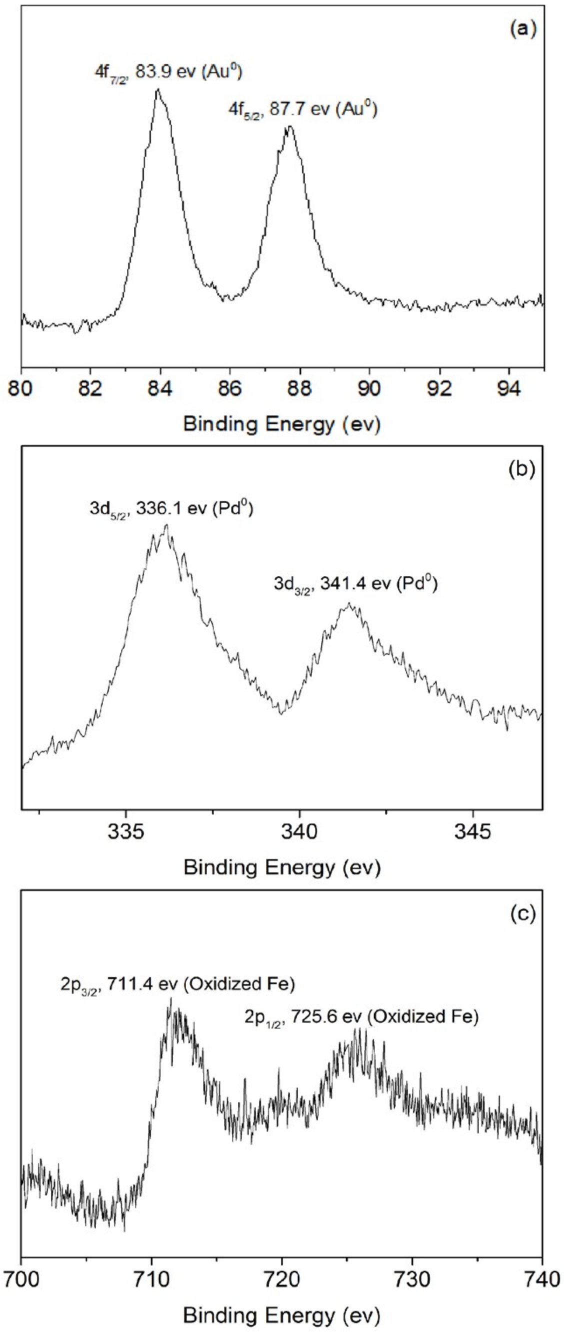

Fig. S14 XPS patterns for $Au_{0.28}Pd_{0.47}Fe_{0.25}$/MIL-101-$NH_2$.

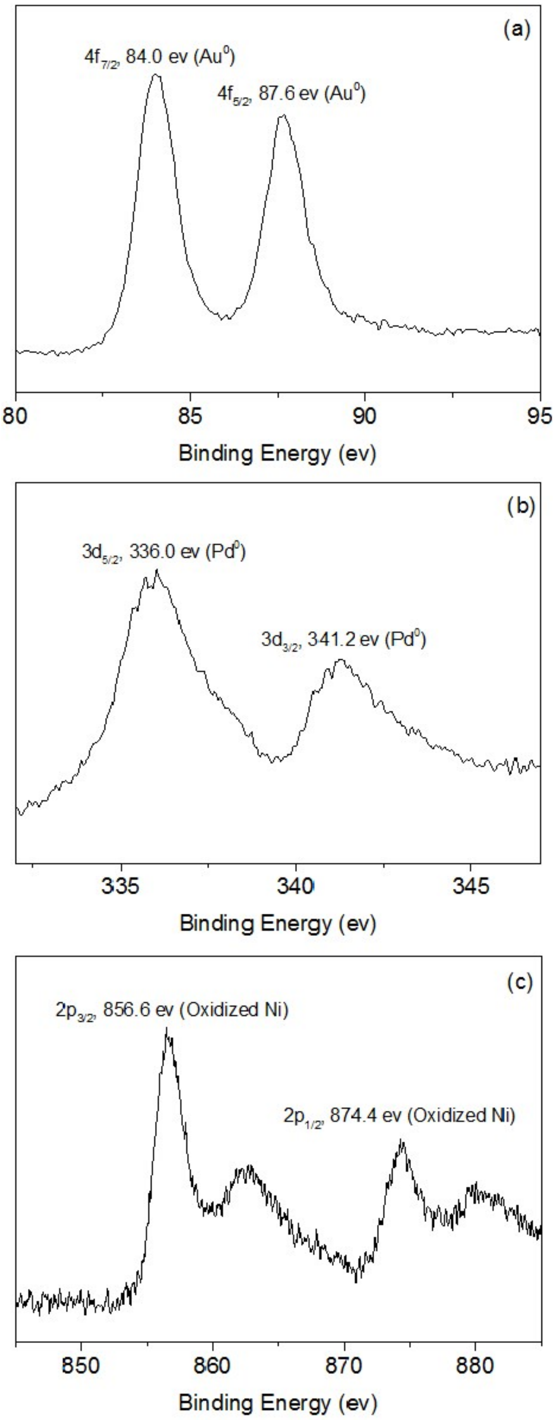

Fig. S15 XPS patterns for $Au_{0.28}Pd_{0.47}Ni_{0.25}$/MIL-101-$NH_2$.

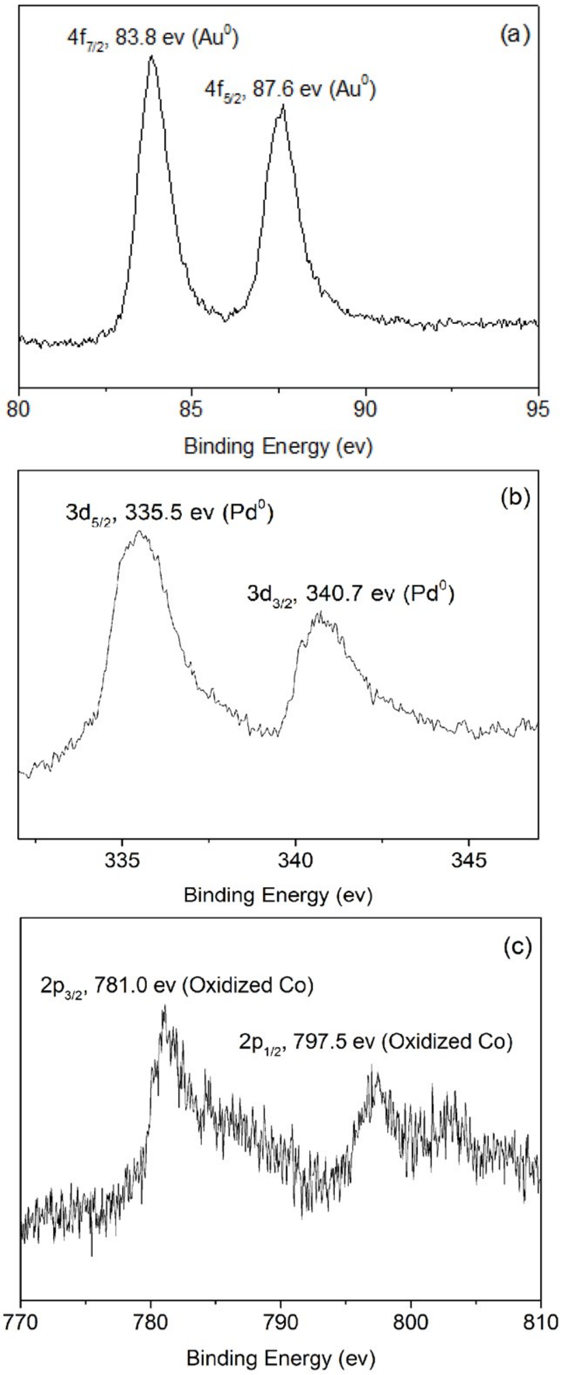

Fig. S16 XPS patterns for $Au_{0.28}Pd_{0.47}Co_{0.25}$/MIL-101-$NO_2$.

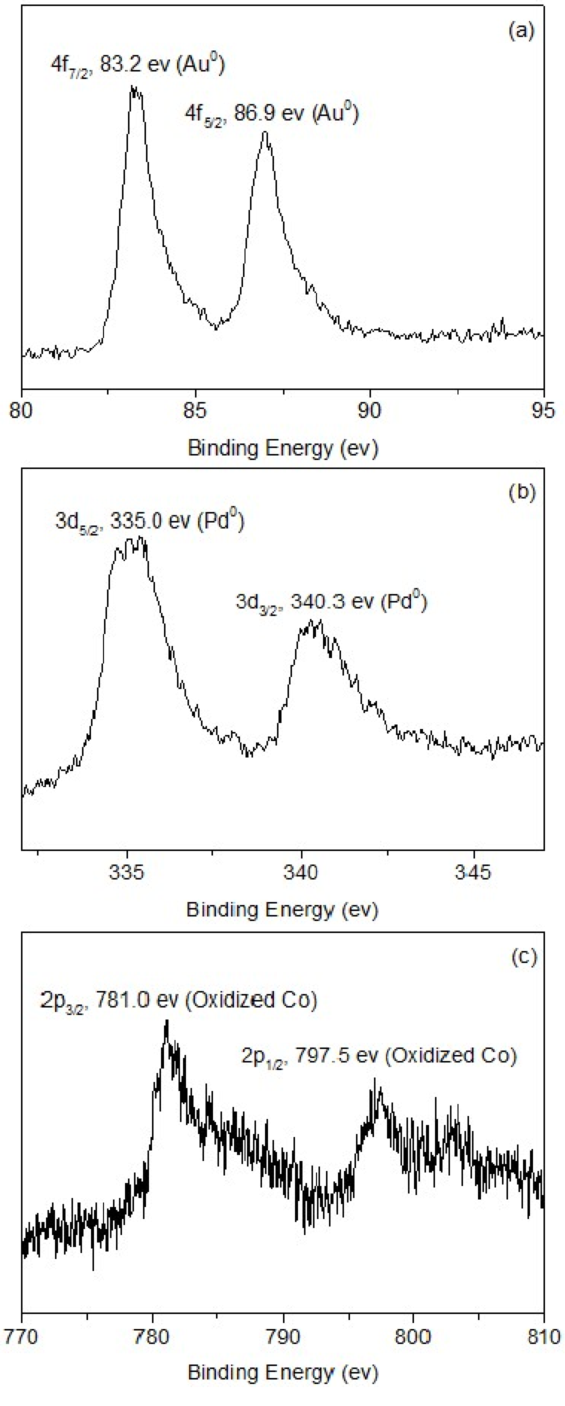

Fig. S17 XPS patterns for $Au_{0.28}Pd_{0.47}Co_{0.25}$/MIL-101-$SO_3H$.

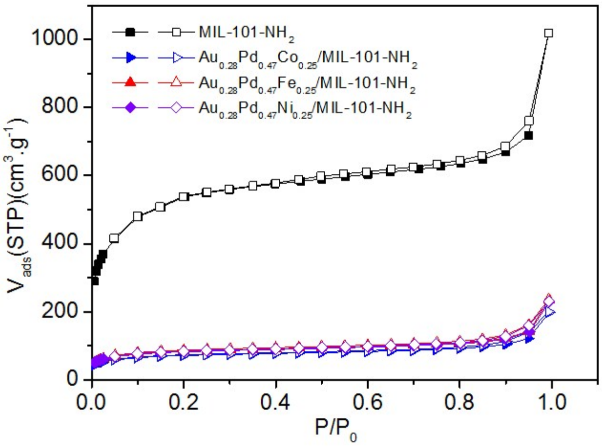

Fig. S18 N_2 adsorption-desorption isotherms of MIL-101-NH$_2$, Au$_{0.28}$Pd$_{0.47}$Co$_{0.25}$/MIL-101-NH$_2$, Au$_{0.28}$Pd$_{0.47}$Fe$_{0.25}$/MIL-101-NH$_2$ and Au$_{0.28}$Pd$_{0.47}$Ni$_{0.25}$/MIL-101-NH$_2$.

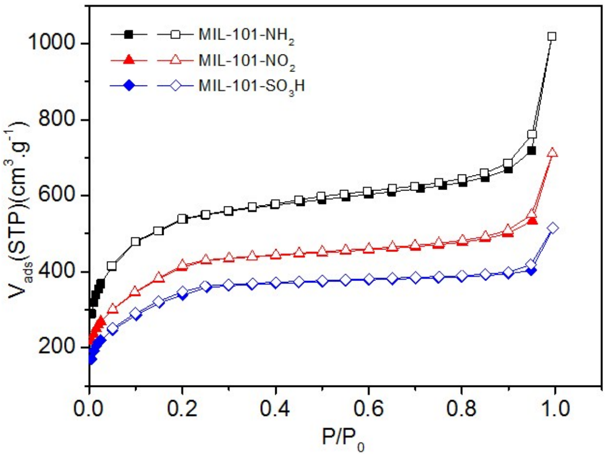

Fig. S19 N_2 adsorption-desorption isotherms of MIL-101-NH$_2$, MIL-101-NO$_2$ and MIL-101-SO$_3$H.

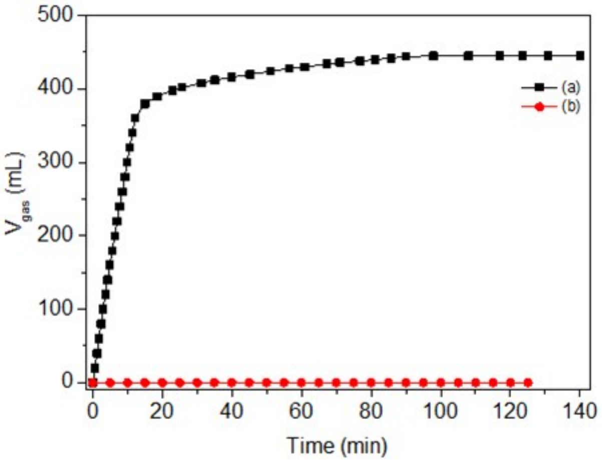

Fig. S20 Plots of time versus volume of the generated gas (H_2 and CO_2) from (a) FA-SF aqueous solution and (b) SF solution over $Au_{0.28}Pd_{0.47}Co_{0.25}$/MIL-101-$NH_2$ (n_{metal}/n_{FA} = 0.0125, n_{metal}/n_{SF} = 0.0125) at 298 K.

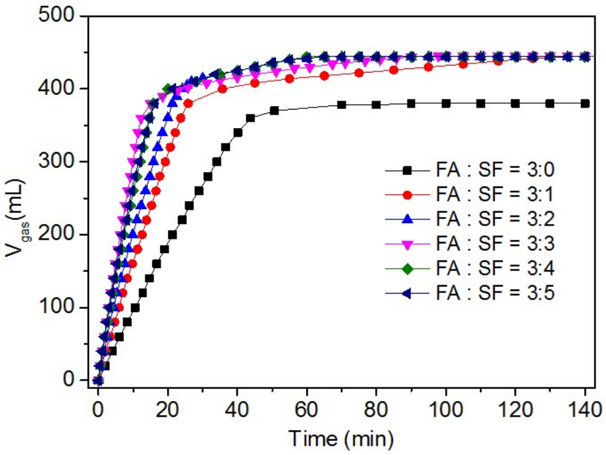

Fig. S21 Plot of time versus volume of the gas generated gas (H_2 and CO_2) from FA-SF aqueous solution with different FA/SF molar ratios over $Au_{0.28}Pd_{0.47}Co_{0.25}$/MIL-101-$NH_2$ (n_{metal}/n_{FA} = 0.0125) at 298 K.

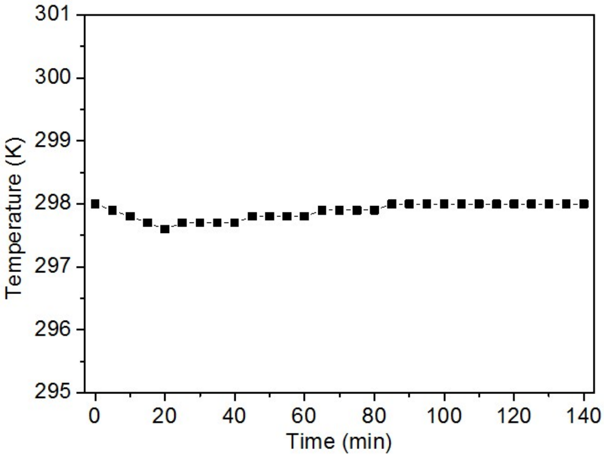

Fig. S22 Plot of time versus temperature during the decompositon of FA in the FA-SF aqueous solution over $Au_{0.28}Pd_{0.47}Co_{0.25}$/MIL-101-$NH_2$ (n_{metal}/n_{FA} = 0.0125, n_{metal}/n_{SF} = 0.0125).

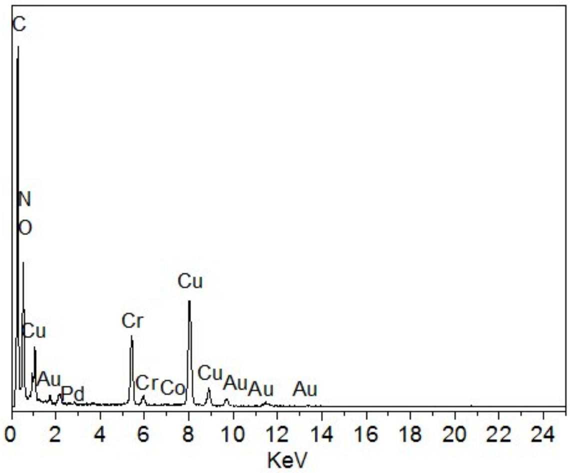

Fig. S23 EDS pattern of $Au_{0.28}Pd_{0.47}Co_{0.25}$/MIL-101-$NO_2$.

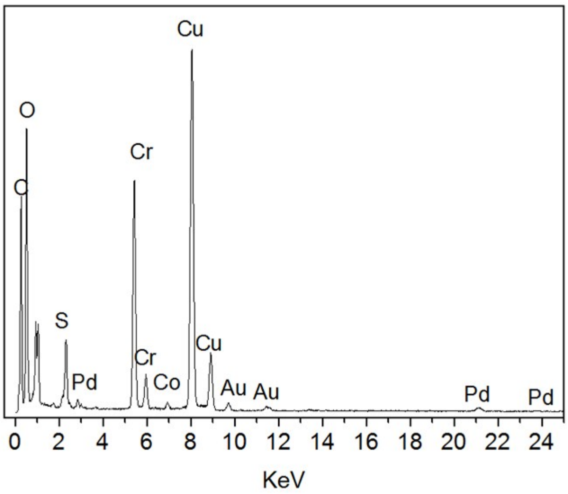

Fig. S24 EDS pattern of $Au_{0.28}Pd_{0.47}Co_{0.25}$/MIL-101-$SO_3H$.

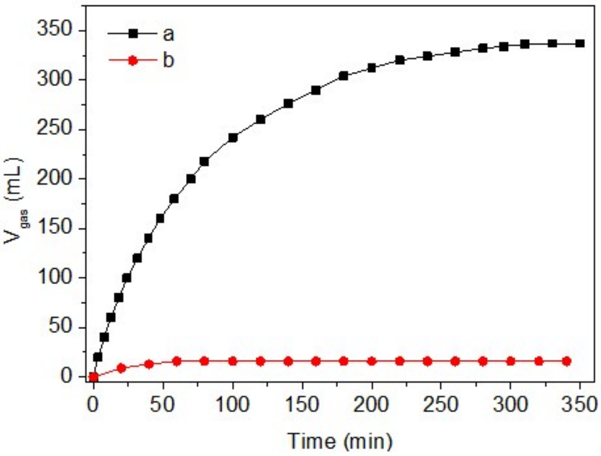

Fig. S25 Plot of time versus volume of the generated gas (H_2 and CO_2) from FA-SF aqueous solution over (a) $Au_{0.28}Pd_{0.47}Co_{0.25}$/MOF-5-$NH_2$ and (b) $Au_{0.28}Pd_{0.47}Co_{0.25}$/MOF-5 ($n_{metal}/n_{FA} = 0.0125$) at 298 K.

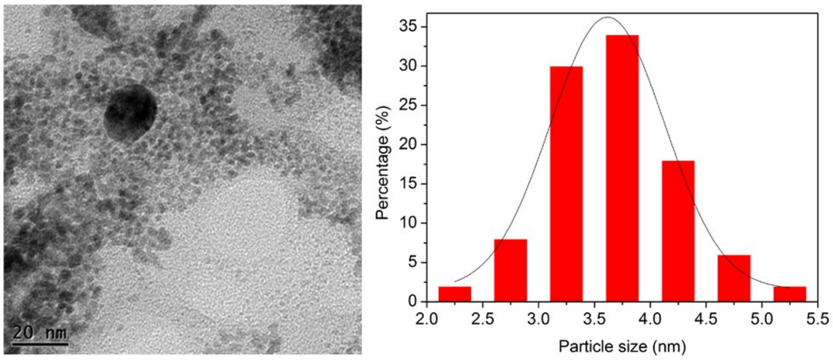

Fig. S26 TEM image of $Au_{0.28}Pd_{0.47}Co_{0.25}$/MOF-5-$NH_2$ and the corresponding size distribution histogram of AuPdCo NPs.

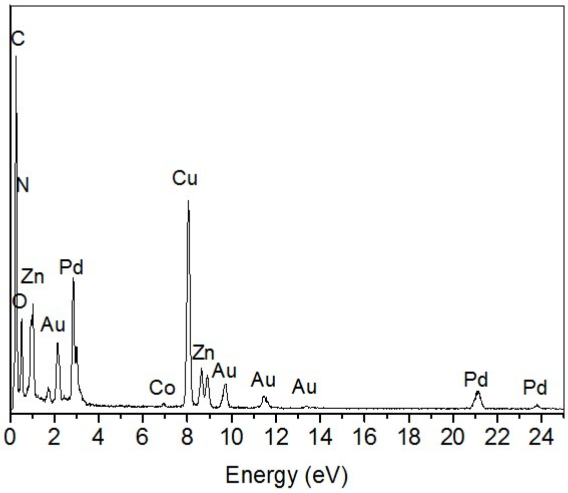

Fig. S27 EDS pattern of $Au_{0.28}Pd_{0.47}Co_{0.25}$/MOF-5-$NH_2$.

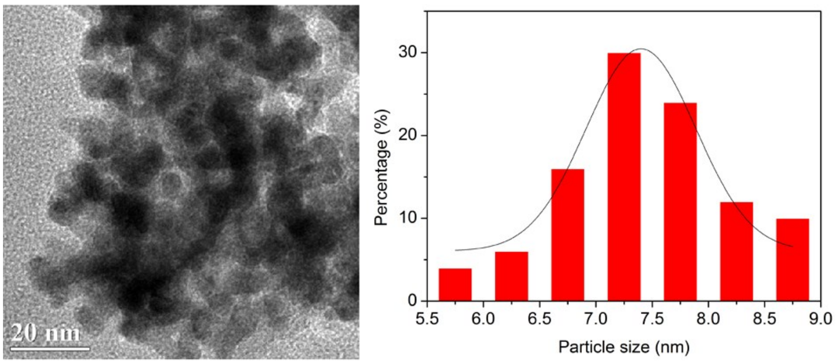

Fig. S28 TEM image of $Au_{0.28}Pd_{0.47}Co_{0.25}$/MOF-5 and the corresponding size distribution histogram of AuPdCo NPs.

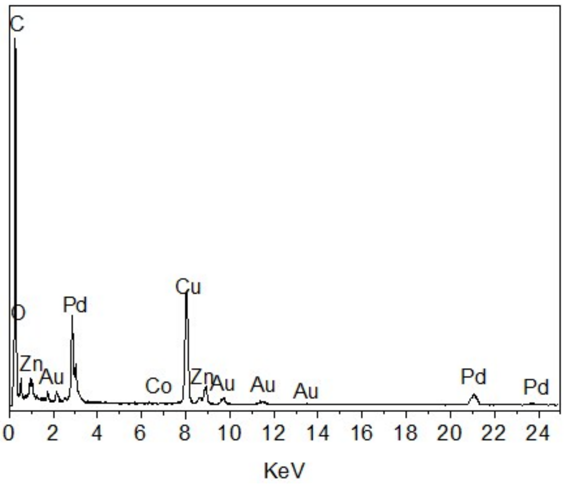

Fig. S29 EDS pattern of $Au_{0.28}Pd_{0.47}Co_{0.25}$/MOF-5.

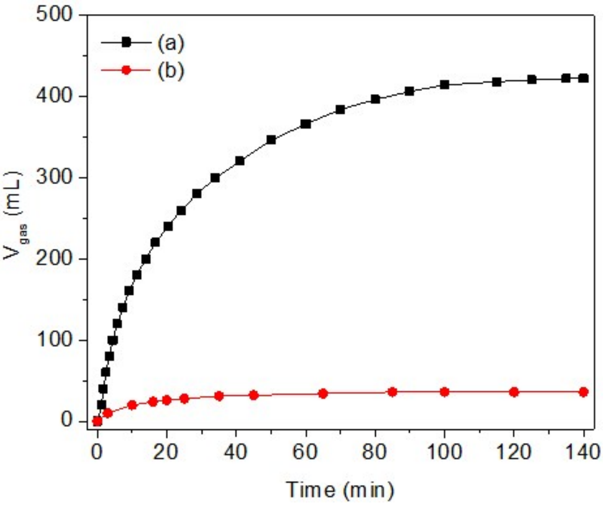

Fig. S30 Plot of time versus volume of the generated gas (H_2 and CO_2) from FA-SF aqueous solution over (a) $Au_{0.28}Pd_{0.47}Co_{0.25}$/SBA-15-NH$_2$ and $Au_{0.28}Pd_{0.47}Co_{0.25}$/SBA-15 ($n_{metal}/n_{FA}$ = 0.0125) at 298 K.

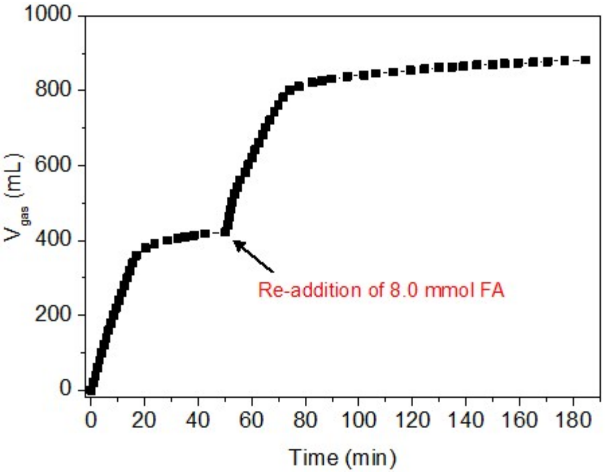

Fig. S31 Plot of time versus volume of generated gas (H_2 and CO_2) from FA-SF aqueous solution over $Au_{0.28}Pd_{0.47}Co_{0.25}$/MIL-101-NH$_2$ with re-addition of 8.0 mmol of FA at 298 K.

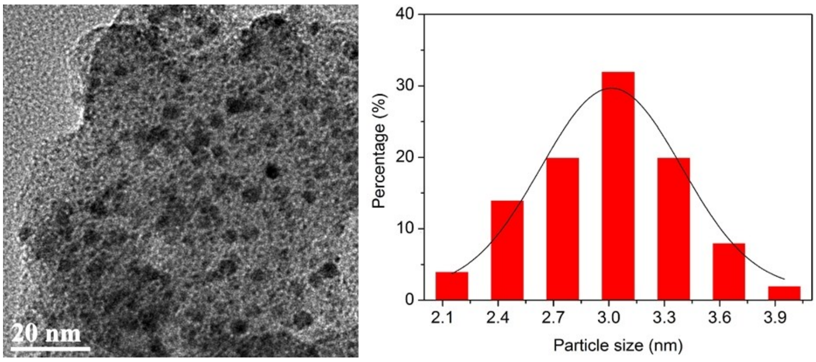

Fig. S32 TEM image of $Au_{0.28}Pd_{0.47}Co_{0.25}$/MIL-101-$NH_2$ after the decomposition of FA and the corresponding size distribution histogram of AuPdCo NPs.

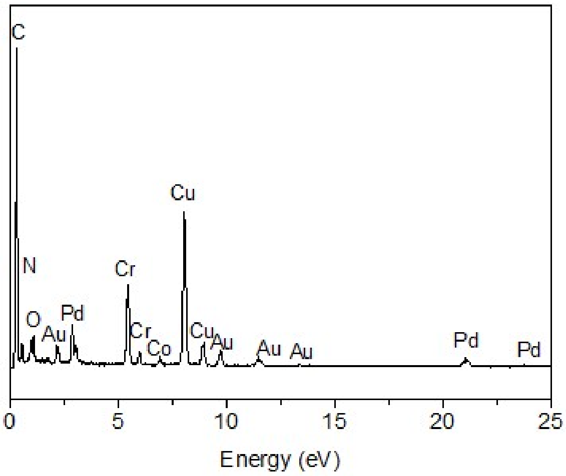

Fig. S33 EDS pattern of $Au_{0.28}Pd_{0.47}Co_{0.25}$/MIL-101-$NH_2$ after catalysis.

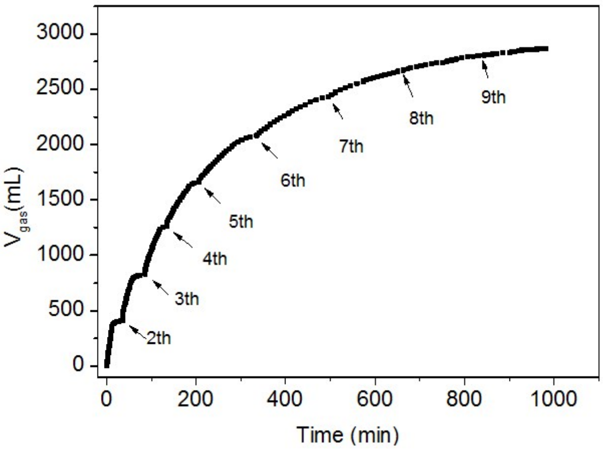

Fig. S34 Plot of time versus volume of generated gas (H_2 and CO_2) from FA-SF aqueous solution over $Au_{0.28}Pd_{0.47}Co_{0.25}$/MIL-101-NH$_2$ with re-addition of 64.0 mmol of FA at 298 K.

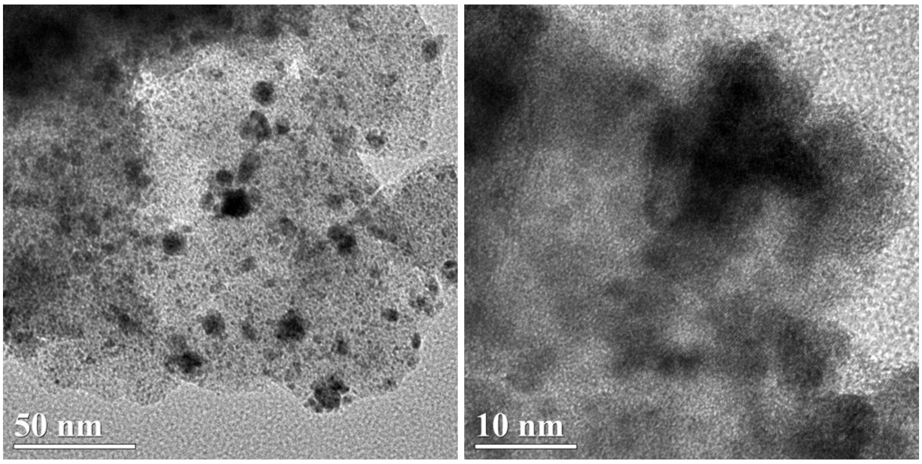

Fig. S35 TEM image of spent catalyst $Au_{0.28}Pd_{0.47}Co_{0.25}$/MIL-101-NH$_2$ after nine catalytic cycles.

Table S1 ICP analyses for the samples.

Sample	Metal content (wt %)	Atom ratio (Au:Pd:M)
$Au_{0.28}Pd_{0.47}Co_{0.25}$/MIL-101-$NH_2$	Au, 10.25; Pd, 9.31; Co, 2.65	0.283:0.467:0.25
$Au_{0.28}Pd_{0.47}Fe_{0.25}$/MIL-101-$NH_2$	Au, 10.31; Pd, 9.36; Fe, 2.55	0.281:0.473:0.246
$Au_{0.28}Pd_{0.47}Ni_{0.25}$/MIL-101-$NH_2$	Au, 10.28; Pd, 9.30; Ni, 2.59	0.284:0.475:0.241
$Au_{0.28}Pd_{0.47}Co_{0.25}$/MIL-101-$NO_2$	Au, 10.33; Pd, 9.21; Co, 2.62	0.285:0.472:0.243
$Au_{0.28}Pd_{0.47}Co_{0.25}$/MIL-101-$SO_3H$	Au, 10.22; Pd, 9.33; Co, 2.50	0.285:0.481:0.234
$Au_{0.28}Pd_{0.47}Co_{0.25}$/MIL-101	Au, 10.18; Pd, 9.30; Co, 2.55	0.284:0.479:0.237
$Au_{0.19}Pd_{0.56}Co_{0.25}$/MIL-101-$NH_2$	Au, 7.01; Pd, 11.32, Co, 2.56	0.193:0.573:0.234
$Au_{0.375}Pd_{0.375}Co_{0.25}$/MIL-101-$NH_2$	Au, 13.47; Pd, 7.24; Co, 2.49	0.383:0.381:0.236
$Au_{0.47}Pd_{0.28}Co_{0.25}$/MIL-101-$NH_2$	Au, 16.90; Pd, 5.27; Co, 2.47	0.484:0.279:0.237
$Au_{0.34}Pd_{0.56}Co_{0.1}$/MIL-101-$NH_2$	Au, 12.20; Pd, 10.87; Co, 1.00	0.343:0.562:0.095
$Au_{0.32}Pd_{0.53}Co_{0.15}$/MIL-101-$NH_2$	Au, 11.60; Pd, 10.29; Co, 1.56	0.323:0.531:0.146
$Au_{0.26}Pd_{0.44}Co_{0.3}$/MIL-101-$NH_2$	Au, 9.59; Pd, 8.70; Co, 3.21	0.263:0.442:0.295
$Au_{0.24}Pd_{0.41}Co_{0.35}$/MIL-101-$NH_2$	Au, 9.12; Pd, 8.31; Co, 3.80	0.245:0.413:0.342
$Au_{0.225}Pd_{0.375}Co_{0.4}$/MIL-101-$NH_2$	Au, 8.40; Pd, 7.60; Co, 4.40	0.226:0.378:0.396
$Au_{0.28}Pd_{0.47}Co_{0.25}$/MOF-5-$NH_2$	Au, 10.30; Pd, 9.33; Co, 2.52	0.286:0.480:0.234
$Au_{0.28}Pd_{0.47}Co_{0.25}$/ MOF-5	Au, 10.30; Pd, 9.26; Co, 2.49	0.288:0.479:0.233
$Au_{0.28}Pd_{0.47}Co_{0.25}$/SBA-15-$NH_2$	Au, 10.25; Pd, 9.35; Co, 2.53	0.285:0.480:0.235
$Au_{0.28}Pd_{0.47}Co_{0.25}$/ SBA-15	Au, 10.20; Pd, 9.28; Co, 2.50	0.285:0.481:0.234
$Au_{0.38}Pd_{0.62}$/MIL-101-NH_2	Au, 13.51; Pd, 11.89	0.38:0.62
$Pd_{0.75}Co_{0.25}$/MIL-101-NH_2	Pd, 15.68; Co, 2.69	0.764:0.236
Pd/MIL-101-NH_2	Pd, 20.28	/

Table S2 TOF values for dehydrogenation of FA catalysed by different catalysts.

Catalyst	T (K)	TOF (h^{-1})	Reference
$Au_{0.28}Pd_{0.47}Co_{0.25}$/MIL-101-$NH_2$	298	347	This work
$Au_{0.28}Pd_{0.47}Fe_{0.25}$/MIL-101-$NH_2$	298	261	This work
$Au_{0.28}Pd_{0.47}Ni_{0.25}$/MIL-101-$NH_2$	298	217	This work
$Au_{0.28}Pd_{0.47}Co_{0.25}$/MIL-101-$NO_2$	298	5	This work
$Au_{0.28}Pd_{0.47}Co_{0.25}$/MIL-101-$SO_3H$	298	4.9	This work
$Au_{0.28}Pd_{0.47}Co_{0.25}$/MIL-101	298	2	This work
$Au_{0.19}Pd_{0.56}Co_{0.25}$/MIL-101-$NH_2$	298	334	This work
$Au_{0.375}Pd_{0.375}Co_{0.25}$/MIL-101-$NH_2$	298	132	This work
$Au_{0.47}Pd_{0.28}Co_{0.25}$/MIL-101-$NH_2$	298	92	This work
$Au_{0.32}Pd_{0.53}Co_{0.1}$/MIL-101-$NH_2$	298	400	This work
$Au_{0.32}Pd_{0.53}Co_{0.15}$/MIL-101-$NH_2$	298	376	This work
$Au_{0.32}Pd_{0.53}Co_{0.3}$/MIL-101-$NH_2$	298	257	This work
$Au_{0.24}Pd_{0.41}Co_{0.35}$/MIL-101-$NH_2$	298	177	This work
$Au_{0.32}Pd_{0.53}Co_{0.4}$/MIL-101-$NH_2$	298	156	This work
PdAu/C-CeO_2	365	113.1	S7
AuPd/ED-MIL-101	363	106	S8
Ag@Pd/C	293	125	S9
Au/ZrO_2	298	252	S10
Pd/C	298	64	S11
$Ag_{0.1}Pd_{0.9}$/rGO	295	105.2	S12
$Co_{0.30}Au_{0.35}Pd_{0.35}$/C	298	80	S13
Pd@CN	288	71	S14
C-$Ag_{42}Pd_{58}$	323	382	S15
Pd/MSC-30	298	750	S16
Pd/C-$NaBH_4$	303	304	S17
Pd-B/C	303	1184	S17
$Ni_{0.40}Au_{0.15}Pd_{0.45}$/C	298	12.4	S18
AuPd-MnO_x/ZIF-8-rGO	298	382.1	S19
$Au_{0.75}Pd_{0.25}$/C-L-7.5	298	718	S20
PdAu-MnO_x/N-SiO_2	298	785	S21

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