Supporting Information

Platinum and cobalt intermetallic nanoparticles confined within MIL-101(Cr) for enhanced selective hydrogenation of the carbonyl bond in α, β-unsaturated aldehydes: synergistic effects of electronically-modified Pt sites and Lewis acid sites

Muhammad Zahid [a], Jiang Li [a], Ahmed Ismail [a], Francisco Zaera [b]*, Yujun Zhu [a]*

[a] Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education of the People's Republic of China, Heilongjiang University, Harbin, 150080, China.

[b] Department of Chemistry and UCR Center for Catalysis, University of California, Riverside, 900 University Avenue, Riverside, California 92521, United States

*Corresponding author. Tel: +86-45186609650; E-mail address: yujunzhu@hlju.edu.cn (YJ Zhu), zaera@ucr.edu (F Zaera)

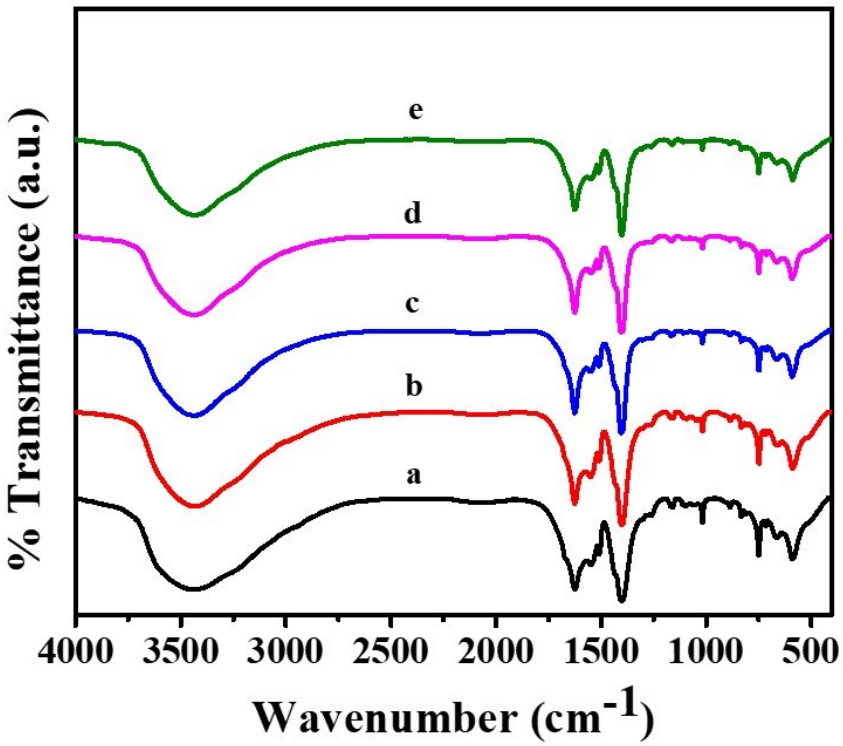

Fig. S1 FTIR spectra of (a) MIL-101(Cr), (b) 3%Pt/MIL-101(Cr), (c) 3%Pt1%Co/MIL-101(Cr), (d) 3%Pt3%Co/MIL-101(Cr), and (e) 3%Pt5%Co/MIL-101(Cr).

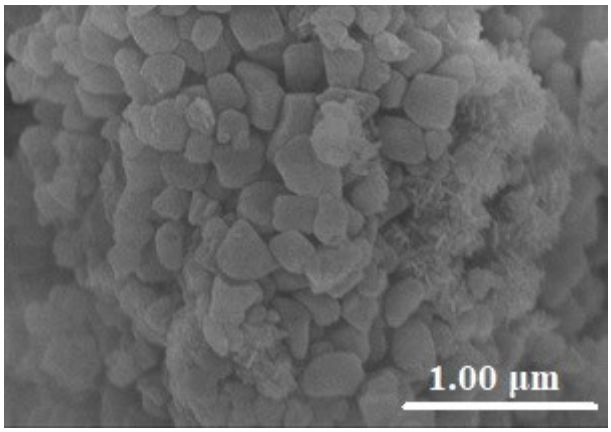

Fig. S2 SEM image of MIL-101(Cr)

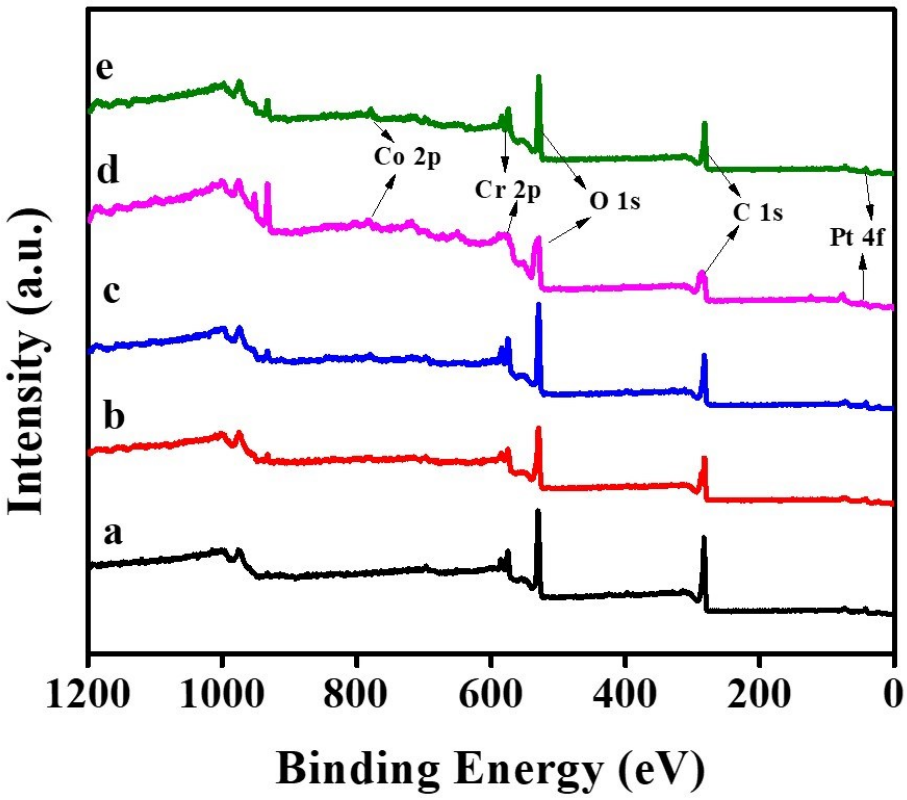

Fig. S3 XPS survey scans for (a) 3%Pt/MIL-101(Cr), (b) 3%Pt1%Co/MIL-101(Cr), (c) 3%Pt3%Co/MIL-101(Cr), (d) 3%Pt5%Co/MIL-101(Cr), and (e) Used-3%Pt3%Co/MIL-101(Cr)

Table S1 Pt $4f_{7/2}$ XPS peak positions for the different catalysts reported here (binding energies, BE, in eV)

Catalyst	Pt(0)	Pt(II)	Pt(IV)
3%Pt/MIL-101(Cr)	70.80	73.65	75.55
3%Pt1%Co/MIL-101(Cr)	71.35	73.65	75.55
3%Pt3%Co/MIL-101(Cr)	71.15	73.45	75.35
3%Pt5%Co/MIL-101(Cr)	71.05	73.50	75.50
Used-3%Pt3%Co/MIL-101(Cr)	71.35	74.45	75.70

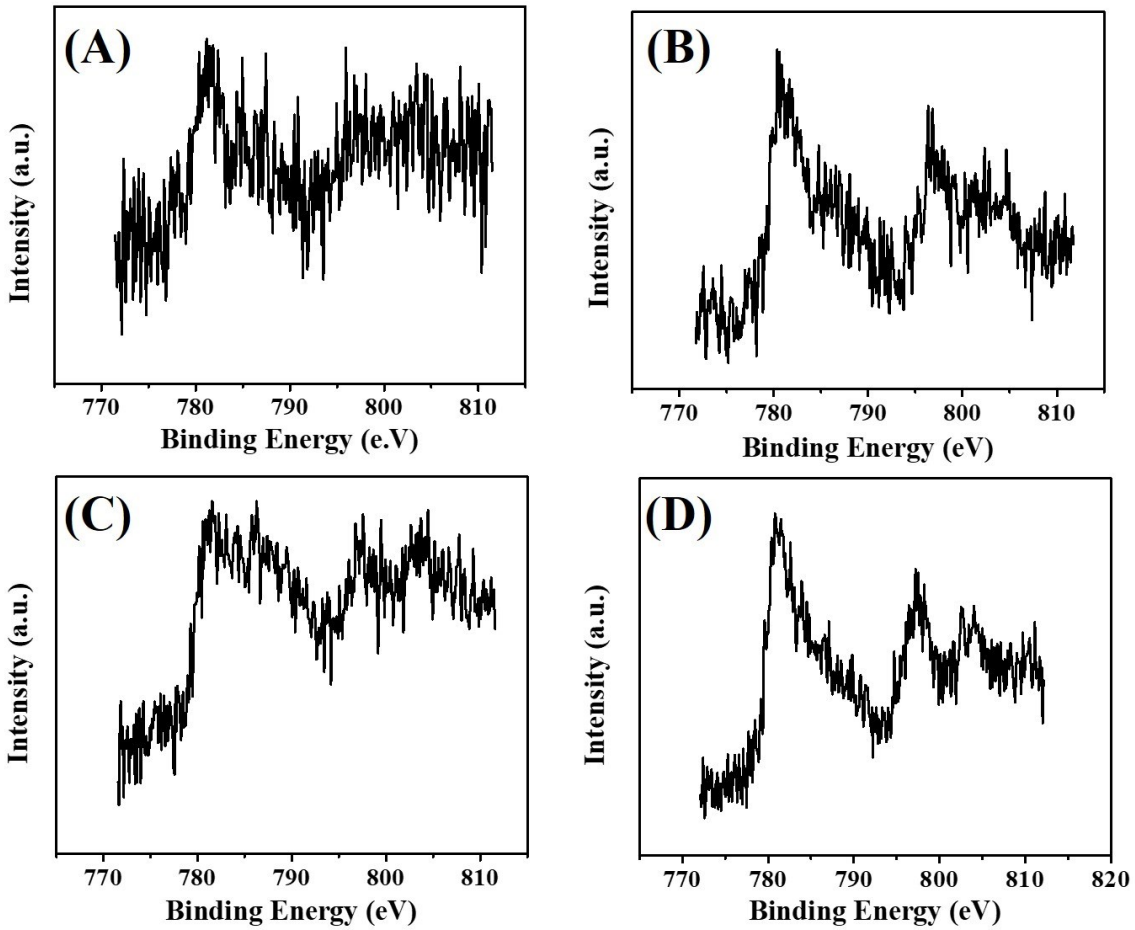

Fig. S4 Co 2p XPS spectra for (A) 3%Pt1%Co/MIL-101(Cr), (B) 3%Pt3%Co/MIL-101(Cr), (C) 3%Pt5%Co/MIL-101(Cr), and (D) Used-3%Pt3%Co/MIL-101(Cr)

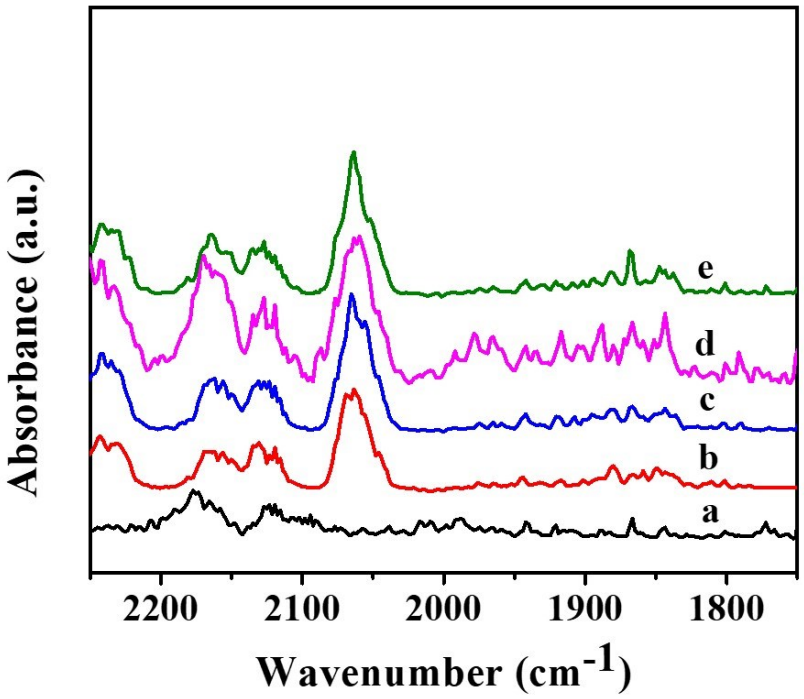

Fig. S5 FTIR spectra of CO adsorbed on (a) MIL-101(Cr) (b) 3%Pt/MIL-101(Cr), (c) 3%Pt1%Co/MIL-101(Cr), (d) 3%Pt3%Co/MIL-101(Cr), and (e) 3%Pt5%Co/MIL-101(Cr)

Table S2 Peak positions for the C–O stretching mode of carbon monoxide linearly adsorbed on Pt^0 sites in the different catalysts reported here

Catalyst	Wavenumber (cm^{-1})
MIL-101	-
3%Pt/MIL-101(Cr)	2068
3%Pt1%Co/MIL-101(Cr)	2065
3%Pt3%Co/MIL-101(Cr)	2059
3%Pt5%Co/MIL-101(Cr)	2063

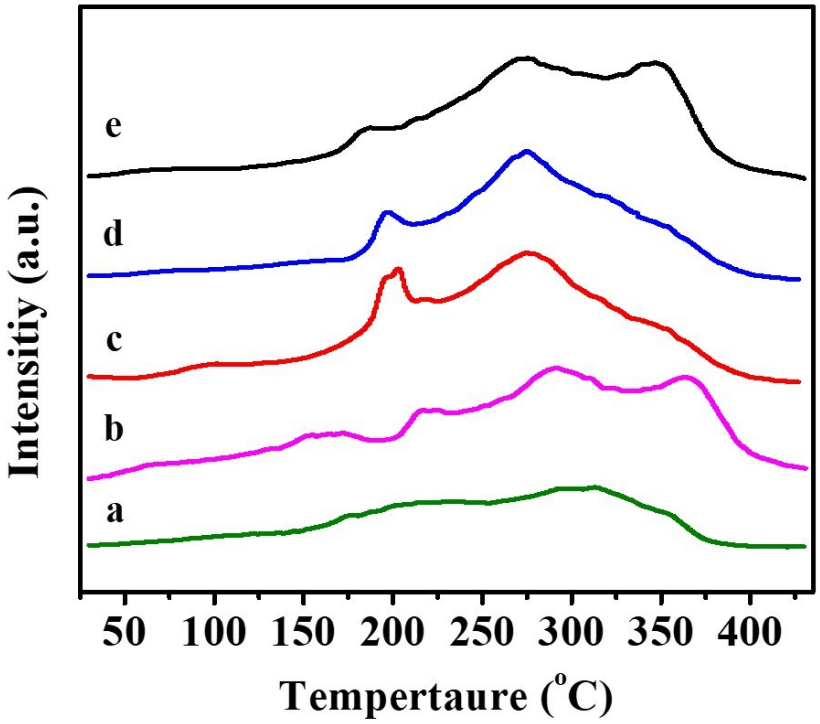

Fig. S6 NH_3-TPD profiles from (a) MIL-101(Cr), (b) 3%Pt/MIL-101(Cr), (c) 3%Pt1%Co/MIL-101(Cr), (d) 3%Pt3%Co/MIL-101(Cr), and (e) 3%Pt5%Co/MIL-101(Cr)

Table S3 EXAFS fitted parameters for 3%Pt/MIL-101(Cr) and 3%Pt3%Co/MIL-101(Cr).

Catalysts	shell	CN[a]	R[b]	σ^2 (10^{-3} Å^2) [c]	ΔE_0 (eV) [d]	R [e]
3%Pt/MIL-101(Cr)	Pt–O	1.00 ± 0.01	2.00 ± 0.02	2.65 ± 0.2	9.87	0.003
	Pt–Pt	4.27 ± 0.02	2.74 ± 0.01	8.98 ± 0.2	4.91	
3%Pt3%Co/MIL-101(Cr)	Pt–O	0.81 ± 0.03	1.98 ± 0.02	0.97 ± 0.1	6.31	0.001
	Pt–Pt	5.28 ± 0.07	2.73 ± 0.01	10.2 ± 0.2	3.71	
Pt-foil	Pt-Pt	12	2.76±0.05	5.63±0.3	5.90	0.0018

[a] Coordination number; [b] Distance between absorber and backscatterer atoms; [c] Debye–Waller factor; [d] Inner potential correction; [e] Correlation coefficient.

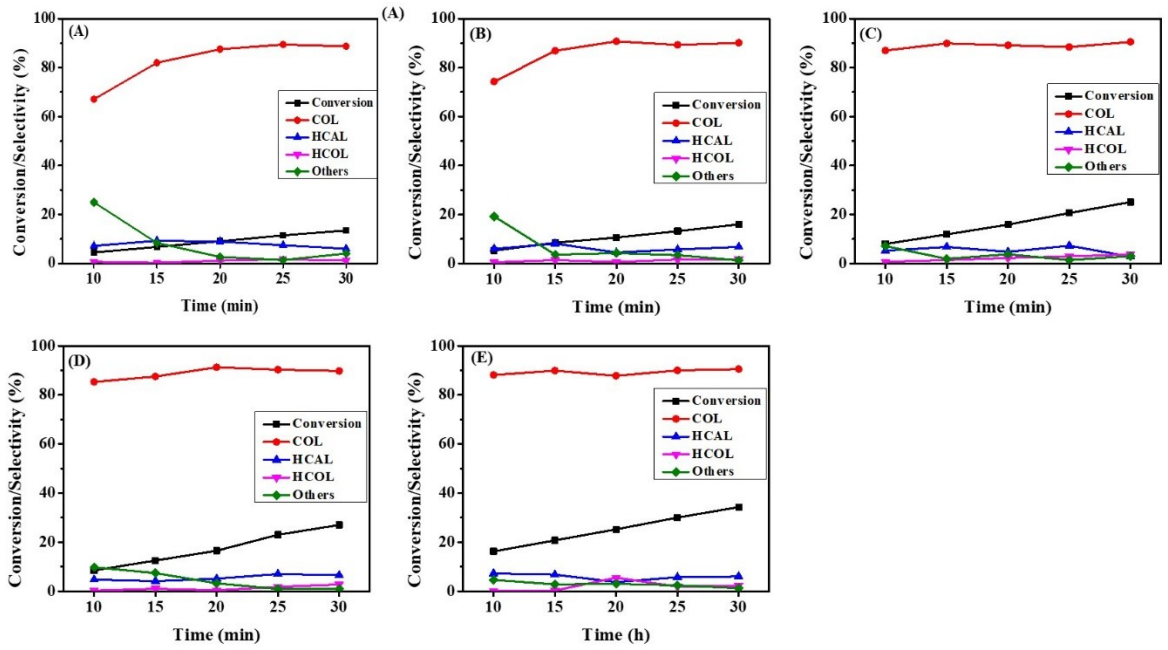

Fig. S7 Kinetic data for the conversion of CAL using a 3%Pt3%Co/MIL-101(Cr) catalyst at (A) 30 ^{o}C (B) 45 ^{o}C (C) 60 ^{o}C (D) 70 ^{o}C and (E) 80 ^{o}C. Reaction conditions: 1 MPa H_2 pressure, 0.2525 g CAL, 20 mg catalysts, 15 mL isopropanol, 800 rpm.

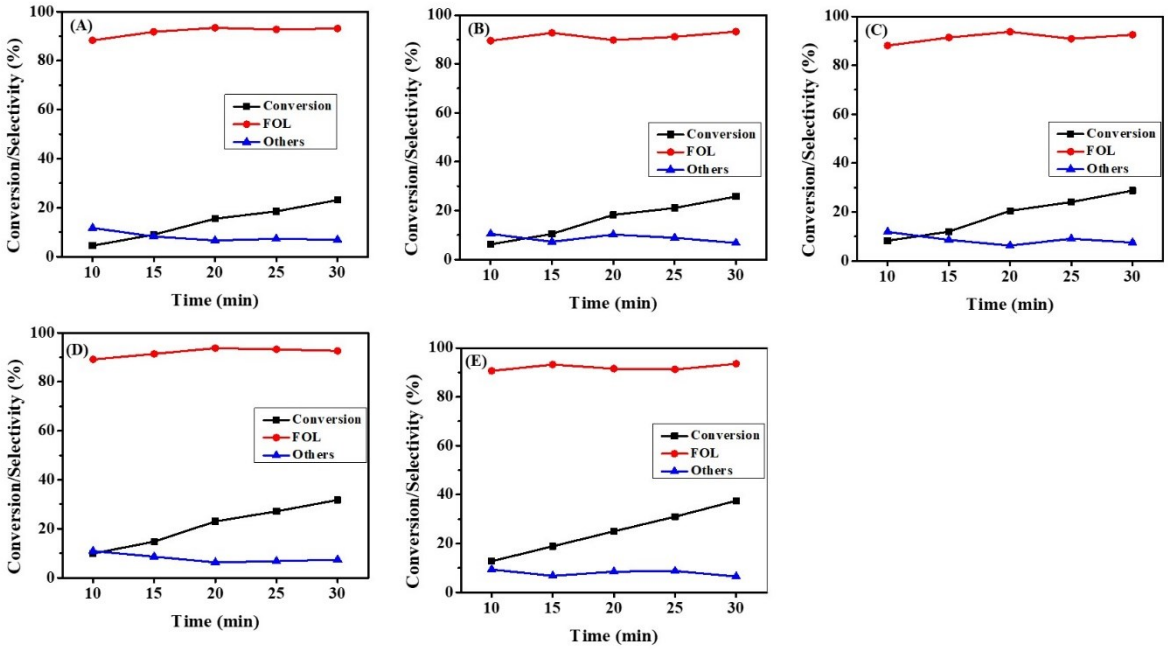

Fig. S8 Kinetic data for the conversion of FFL using a 3%Pt3%Co/MIL-101(Cr) catalyst at (A) 30 ^{o}C (B) 45 ^{o}C (C) 60 ^{o}C (D) 70 ^{o}C and (E) 80 ^{o}C. Reaction conditions: 1 MPa H_2 pressure, 0.2525 g CAL, 20 mg catalysts, 15 mL isopropanol, 800 rpm.

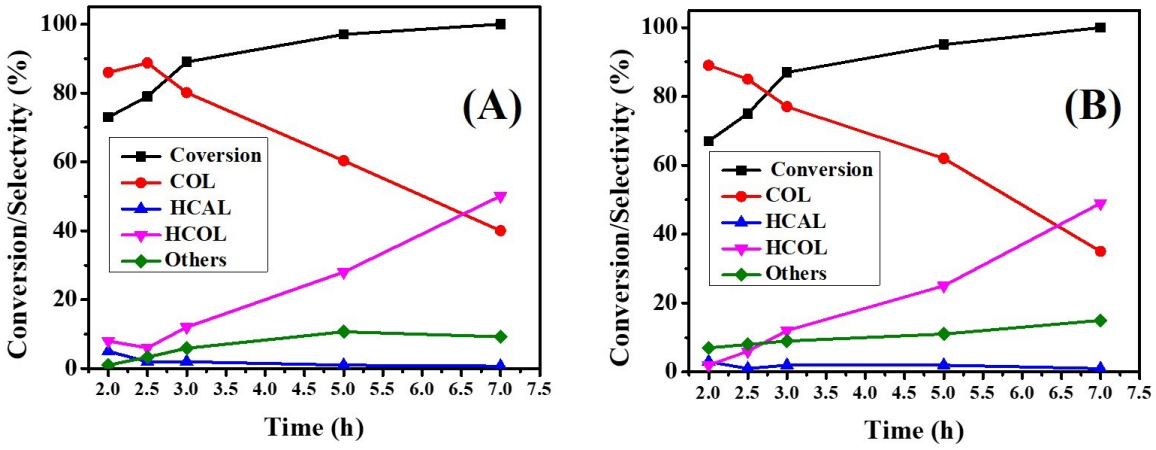

Fig. S9 Selective hydrogenation of CAL as a function of reaction time over the (A) 3%Pt1%Co/MIL-101(Cr) and (B) 3%Pt5%Co/MIL-101(Cr) catalysts (Reaction conditions: 60 ^{o}C, 1 MPa H_2 pressure, 0.2525 g CAL, 20 mg catalysts, 15 mL isopropanol, 800 rpm).

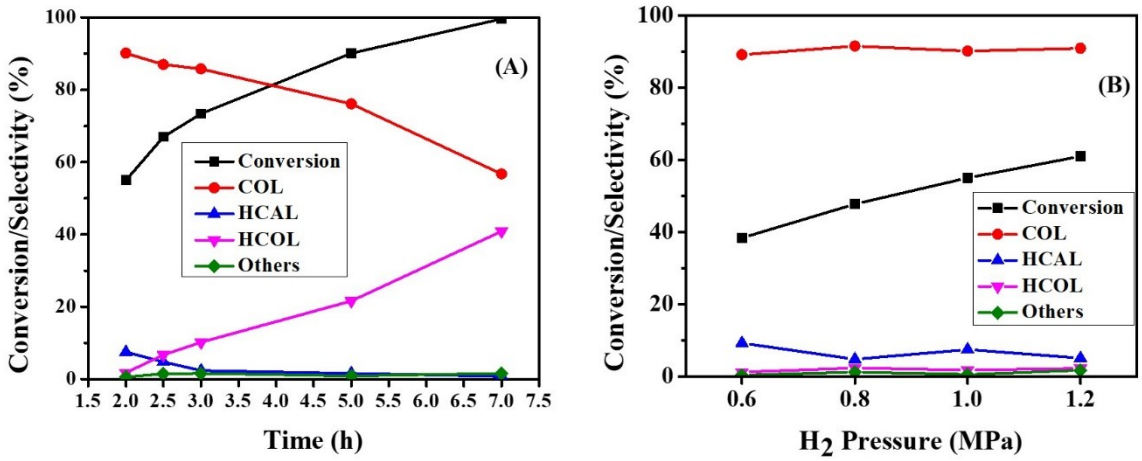

Fig. S10 (A) Kinetic data for the conversion of CAL using a 3%Pt3%Co/MIL-101(Cr) catalyst at 30 °C, 1 MPa H_2 pressure, 0.2525 g CAL, 20 mg catalysts, 15 mL isopropanol, 800 rpm, (B) CAL total conversion and selectivity after 2 h of reaction versus H_2 pressure.

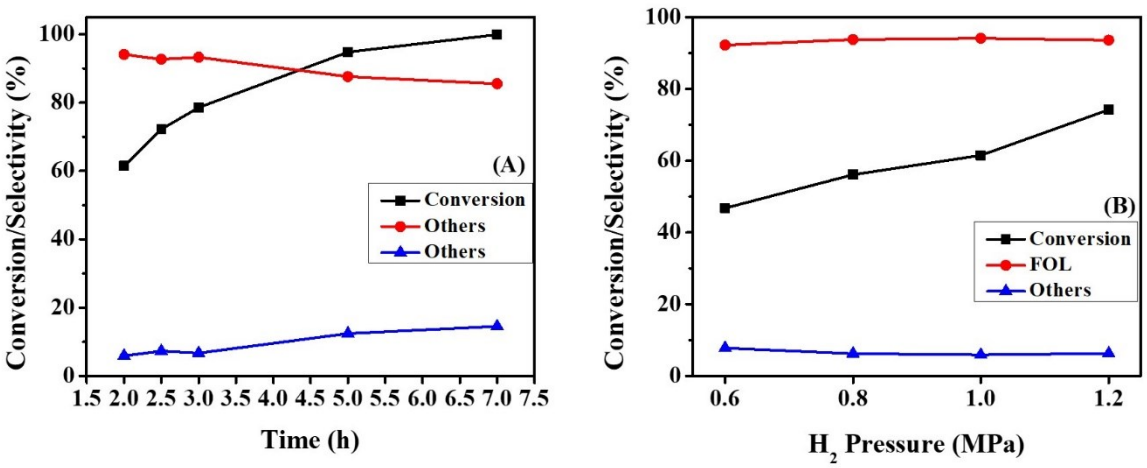

Fig. S11 (A) Kinetic data for the conversion of FFL using a 3%Pt3%Co/MIL-101(Cr) catalyst at 30 ^{o}C, 1 MPa H_2 pressure, 0.2525 g FFL, 20 mg catalysts, 15 mL isopropanol and 800 rpm. (B) FFL total conversion and selectivity after 2 h of reaction versus H_2 pressure.

Table S4 Comparison of catalytic performance for the hydrogenation of cinnamaldehyde (CAL) of 3%Pt3%Co/MIL-101(Cr) versus other reported Pt-based catalysts.

Catalysts	Conversion (%)	TOF	Time (h)	T (^oC) & $P(H_2)$ (MPa)	COL Selectivity (%)	Reference
3%Pt3%Co/MIL-101(Cr)	95	546 h^{-1}	2	60 & 1	91	Current work
3%Pt3%Co/MIL-101(Cr)	38.4	216 h^{-1}	2	30 & 0.6	89.1	Current work
$PtNi_{2.20}$ NWs@Ni/Fe_4-MOF	99.5	77.6 h^{-1}	2	40 & 3	83.3	1
10c-Co/2c-Pt/MWCNTs	93.3	-	12	80 & 1	93.4	2
3Pt0.05Sn/HPZSM-5	99.5	-	1	90 & 2	81.9	3
$PtFe_{0.25}/Al_2O_3$@SBA-15	77.4	1.54 s^{-1}	0.5	90 & 2	76.9	4
19 %wt Pt_3Co@$Co(OH)_2$	99.6	-	2	70 & 0.5	91.3	5
3wt% Pt-Mo_2N/SBA-15	85.8	423 h^{-1}	2	80 & 1	78	6
2 wt% Pt-Mo_2N/SBA-15	70.8	521 h^{-1}	2	80 & 1	76.9	6
Pt-Co/SBA-15-0.6	71	-	2	80 & 1	91	7
Pt_3Fe/CNT	62.1	-	0.5	60 & 2	97.2	8
Pt-FeOx/15TS	99.0	1.36 s^{-1}	1	90 & 4	84.5	9

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