Supporting information

Preparation and performances of ZIF-67-derived FeCo bimetallic catalysts for CO_2 hydrogenation to light olefins

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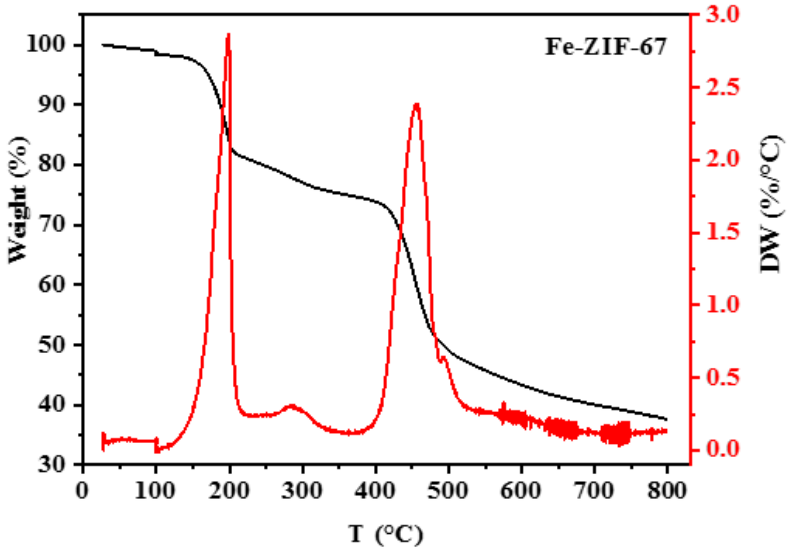

Figure S1. TG and DTG of Fe/ZIF-67

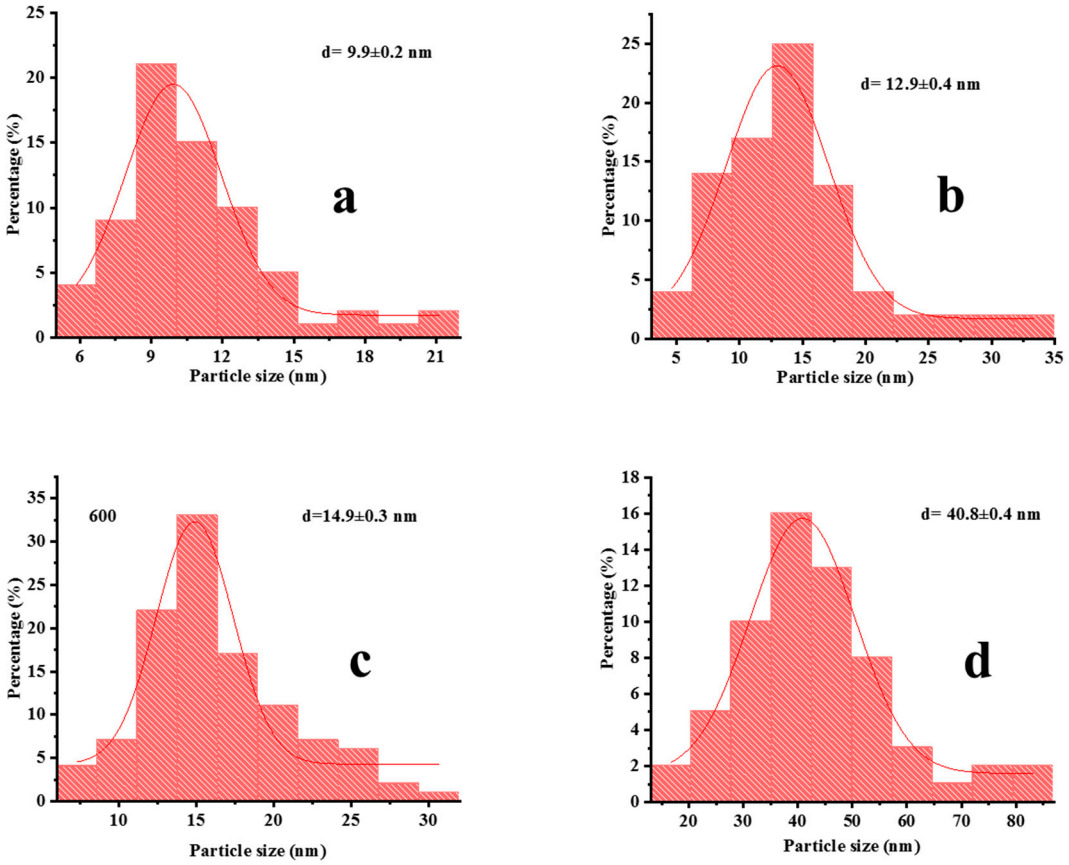

Figure S2. TEM particle size distribution images of (a) FeCo/NC-400; (b) FeCo/NC-500; (c) FeCo/NC-600; (d) FeCo/NC-700

Table S1. CO_2-TPD results of different samples.

Sample	Total CO2 uptake amount/mmol g^{-1}
FeCo/NC-400	0.124
FeCo/NC-500	0.109
FeCo/NC-600	0.059
FeCo/NC-700	0.037

Table S2 Hyperfine parameters of catalysts FeCo/NC-T obtained from the fittings of 57Fe Mössbauer spectra recorded at room temperature. Numbers in parentheses indicate the statistical uncertainty of the last digit(s).

Catalysts	T[a]	CS (mm/s)	QS (mm/s)	H (kOe)	Area (%)	Assignments
After reaction FeCo/NC-T	400	0.30(1)	0.79(2)		29(1)	SP doublet
		0.33(2)	-0.04(2)	499(2)	10(2)	Fe_3O_4-A
		0.54(7)	0.02(7)	462(5)	5(2)	Fe_3O_4-B
		0.03(2)	-0.01(2)	354(8)	39(2)	Fe-Co alloys
		0.17(3)	-0.09(3)	207(2)	13(3)	Fe_5C_2-I
		0.21(3)	-0.01(3)	182(2)	4(2)	Fe_5C_2-II
	500	0.30(9)	0.77(2)		30(1)	SP doublet
		0.33(4)	-0.02(4)	499(3)	7(2)	Fe_3O_4-A
		0.34(7)	0.05(6)	461(4)	7(3)	Fe_3O_4-B
		0.01(2)	-0.01(2)	345(8)	34(2)	Fe-Co alloys
		0.20(4)	-0.06(4)	205(3)	15(3)	Fe_5C_2-I
		0.17(3)	0.08(3)	178(2)	4(2)	Fe_5C_2-II
		0.19(5)	0.12(5)	99(3)	3(1)	Fe_5C_2-III
	600	0.27(7)	0.81(2)	-	26(1)	SP doublet
		0.27(6)	0.04(6)	499(4)	7 (2)	Fe_3O_4-A
		0.78(6)	0.04(6)	460(4)	2 (1)	Fe_3O_4-B
		0.04(3)	-0.02(3)	343(1)	23 (2)	Fe-Co alloys
		0.18(4)	-0.02(3)	206(4)	26(5)	Fe_5C_2-I
		0.31(4)	-0.08(3)	180(2)	8(4)	Fe_5C_2-II
		0.09(3)	0.02(3)	99(2)	8(1)	Fe_5C_2-III
	700	0.29(8)	0.70(2)		27(1)	SP doublet
		-0.02(2)	0.02(2)	342(9)	18(1)	Fe-Co alloys
		0.25(1)	-0.03(1)	201(2)	32(4)	Fe_5C_2-I
		0.25(2)	0.04(2)	179(1)	12(4)	Fe_5C_2-II
		0.21(3)	0.01(2)	92(2)	11(1)	Fe_5C_2-III
Before reaction FeCo/NC-T	600	0.12(5)	0.42(9)	-	4.3(9)	SP doublet
		0.013(2)	0.00(2)	339.5(2)	95.7(15)	Fe-Co alloys

a: pyrolysis temperature

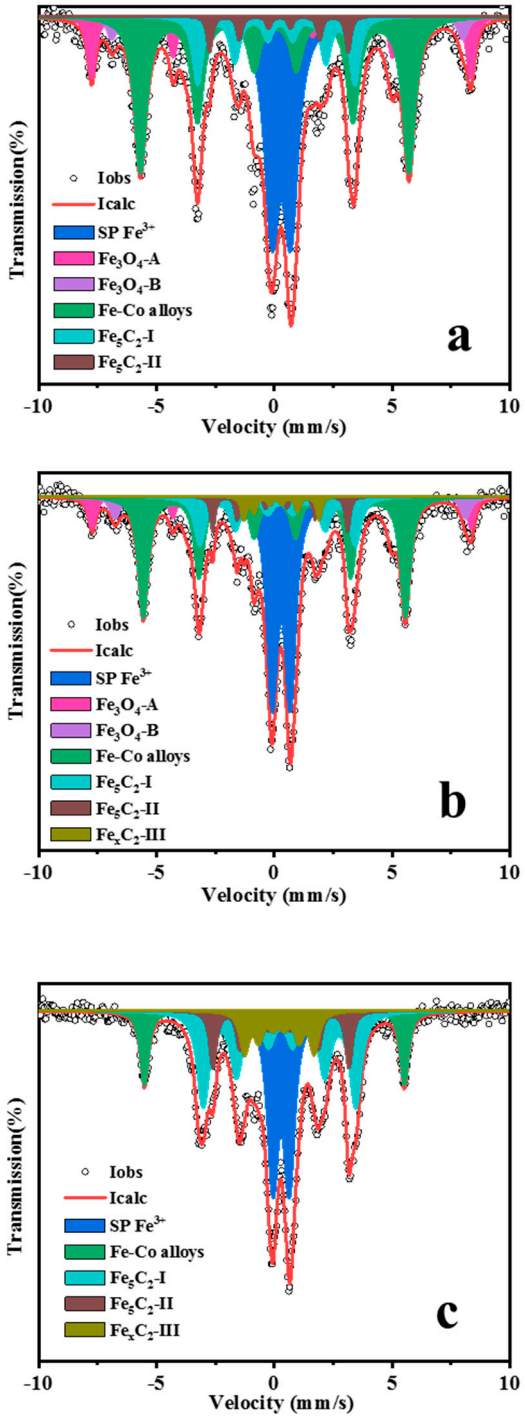

Figure S3. ^{57}Fe Mössbauer spectra recorded at room temperature : (a) FeCo/NC-400 (b) FeCo/NC-500 (c) FeCo/NC-700

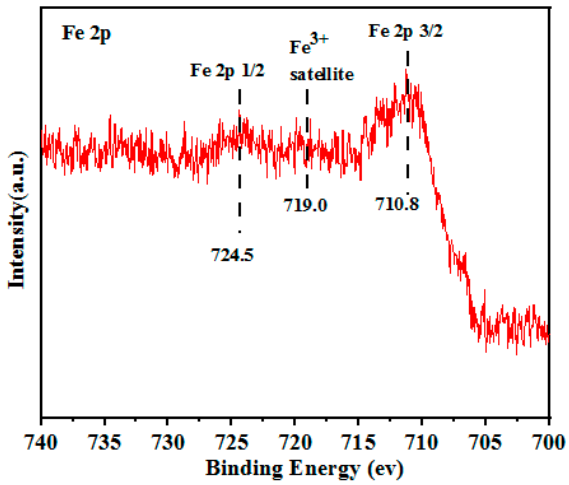

Figure S4. XPS spectra of FeCo/NC-600

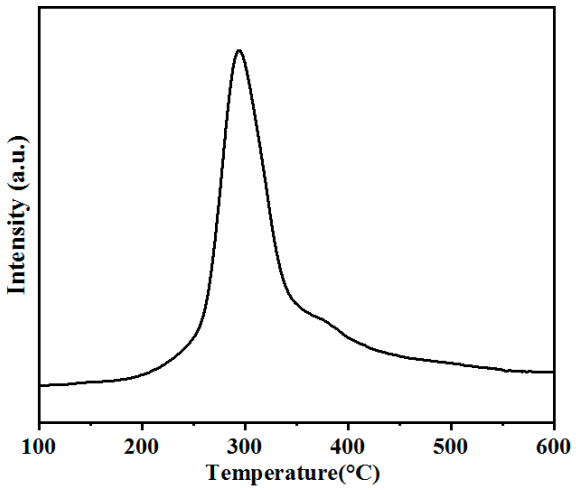

Figure S5. H_2-TPR spectra of FeCo/NC-600

The result of H_2-TPR is shown in supporting FigS5. Taking FeCo/NC-600 as an example, first of all, it can be seen from the XPS spectra of Fe 2p peak (FigS4) that although the pyrolyzed iron mainly exists in the form of iron-cobalt alloy, there is still a small amount of iron oxide. The two main peaks at 710.8 eV and 724.5 eV correspond to Fe 2p 3/2 and Fe 2p1/2, indicating the presence of Fe^{3+}, while the satellite peak at 719.0ev confirms the phase of Fe_2O_3. Typically, Fe_3O_4 is the main active phase of the RWGS reaction. It can be seen from H_2-TPR that there is a main peak around 300 °C, which is generally attributed to the process of reduction of Fe_2O_3 to Fe_3O_4. Therefore, H_2 gas is used to reduce the catalyst at 400 °C before the reaction to obtain the best reactivity.

Table S3. The physical properties of $FeCo/Al_2O_3$ sample.

Sample	Metal content(wt%)[a]			S_{BET}	S_{micro}	S_{meso}	V_{micro}	V_{meso}
	Fe	Co	Fe/Co	(m^2g^{-1})	(m^2g^{-1})	(m^2g^{-1})	($cm^{-3}g^{-1}$)	($cm^{-3}g^{-1}$)
$FeCo/Al_2O_3$	17.5	34.5	0.51	63.7	7.6	56.1	0.003	0.150

a: Measured by ICP-OES

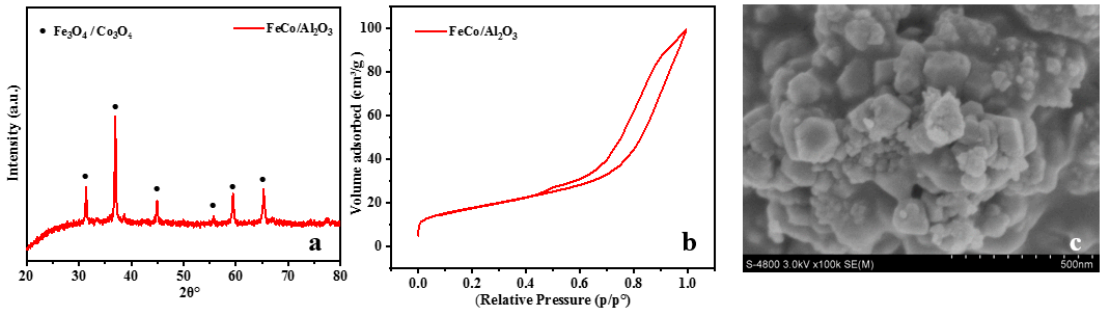

Figure S6. The basic properties of $FeCo/Al_2O_3$ sample.

(a) XRD image of $FeCo/Al_2O_3$ sample; (b): N_2 adsorption–desorption isotherms of $FeCo/Al_2O_3$ sample; (c): SEM image of $FeCo/Al_2O_3$ sample.