Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

Boosting catalytic performance of Co-N-C derived from ZIF-67 by mesoporous silica encapsulation for chemoselective hydrogenation of furfural

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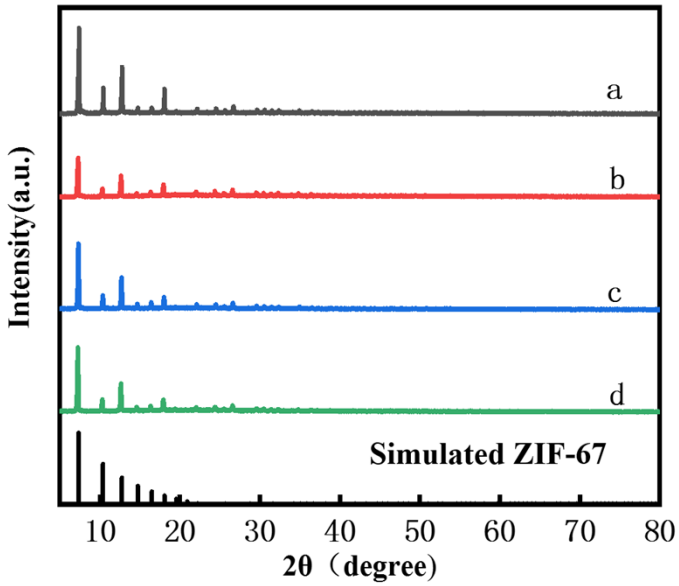

Fig. S1. XRD patterns of ZIF-67 and ZIF-67@SiO_2: (a) ZIF-67, (b) ZIF-67@SiO_2-20, (c) ZIF-67@SiO_2-50, (d) ZIF-67@SiO_2-100.

Figure S1 showed the peaks at 7.5°, 10.6°, 12.9° and 18.3°, in good agreement with the simulated characteristic peaks of ZIF-67, showing the successful formation of ZIF-67. The XRD pattern of ZIF-67@SiO_2 showed the typical peaks of pure ZIF-67, suggesting that the crystallinity of ZIF-67 was maintained after the coating of silica from hydrolysis of TEOS.

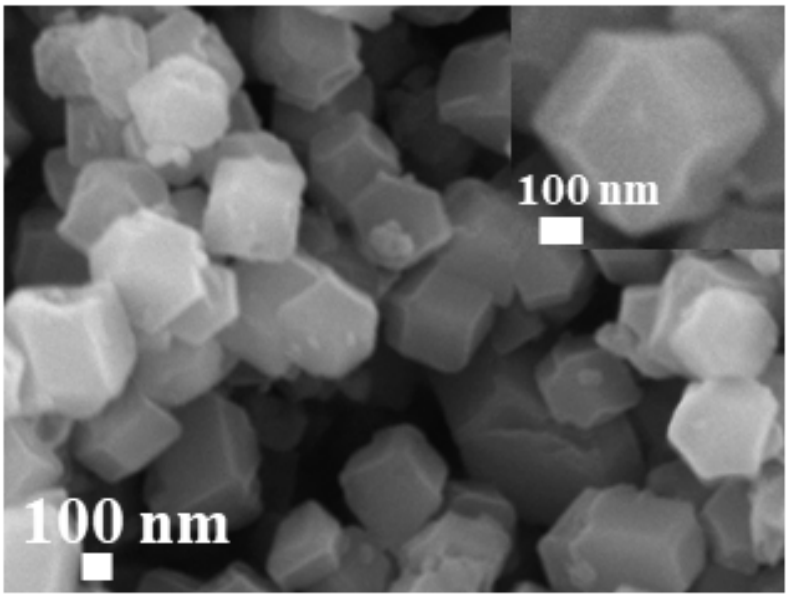

Fig. S2. SEM image of ZIF-67.

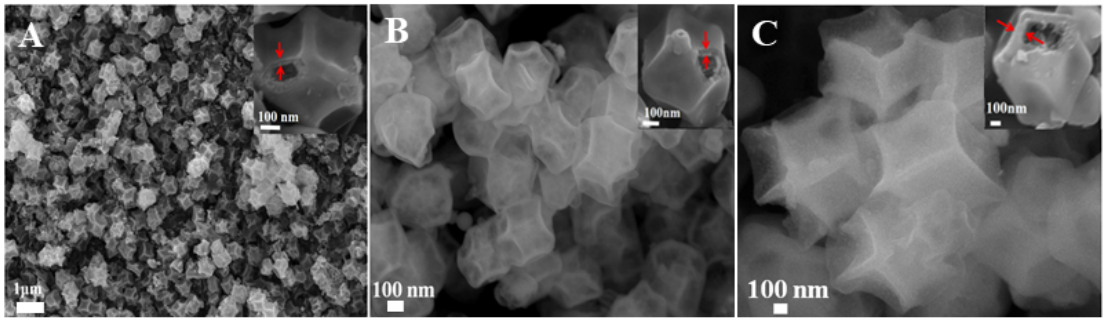

Fig. S3. SEM images: (A) Co-N-C@mSiO_2-20-600, (B) Co-N-C@mSiO_2-50-600, and (C) Co-N-C@mSiO_2-100-600.

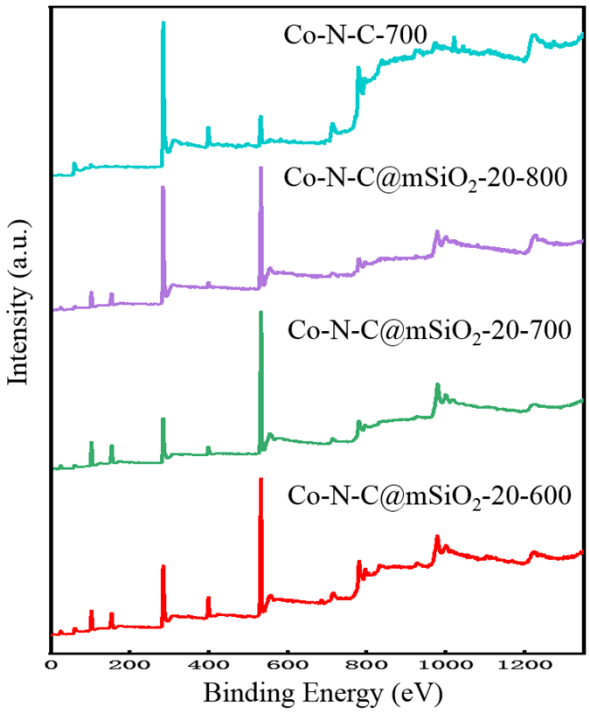

Fig. S4. Full XPS survey spectra of samples.

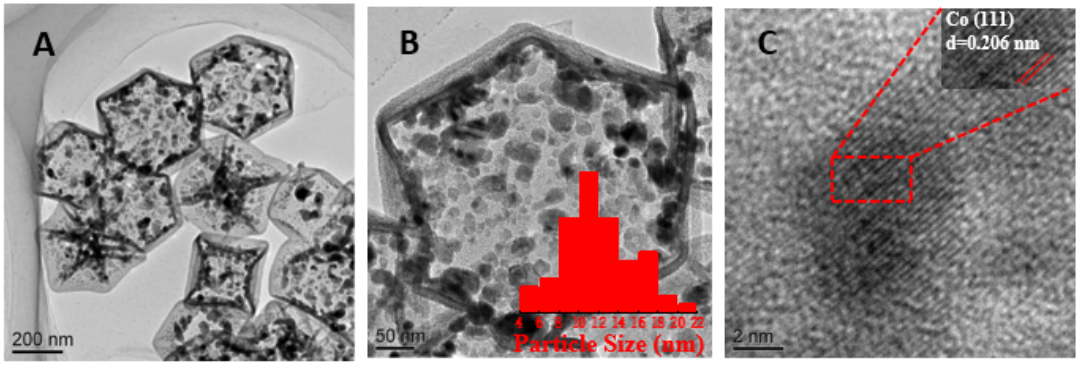

Fig. S5. Co@mSiO$_2$-20: (A,B) TEM images and (C) HRTEM image.

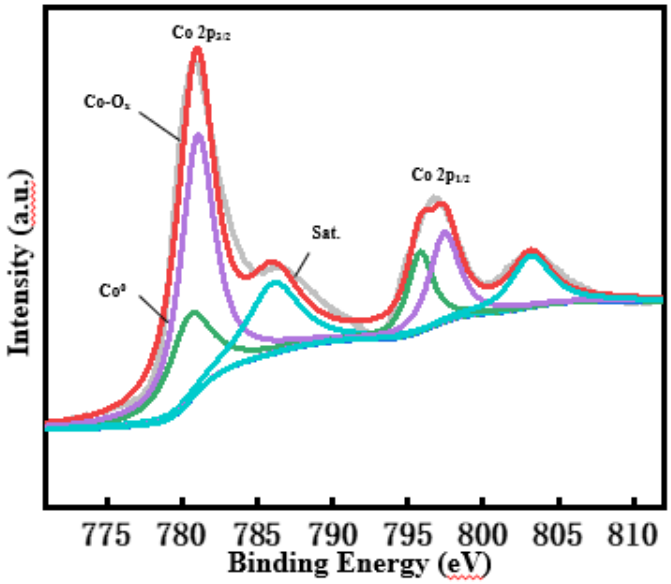

Fig. S6. Co 2p XPS spectra of Co@mSiO$_2$-20. The deconvolved peaks in Co 2p spectra were ascribed to metallic Co^0, Co-O$_x$, and satellite peak, respectively. No Co-N$_x$ species was found.

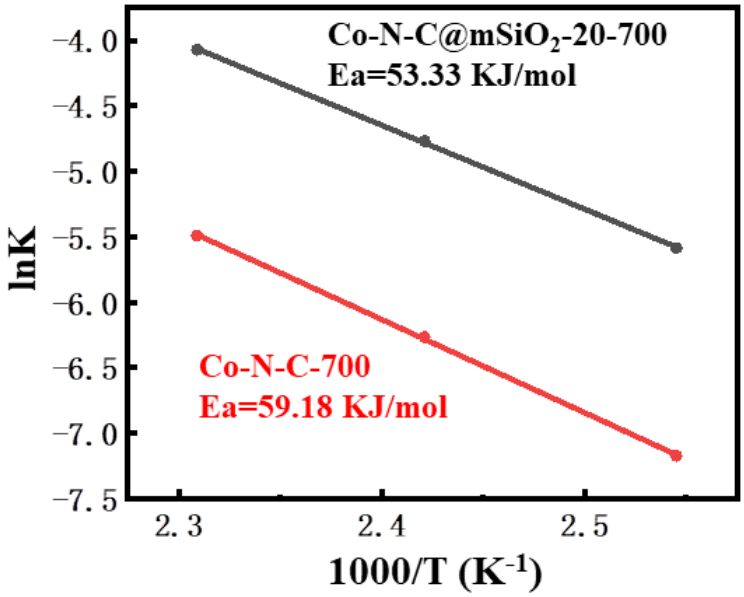

Fig. S7. Arrhenius plots for furfural hydrogenation over CoN$_x$-C@mSiO$_2$-20-700 and Co@N-C-700 catalysts. Other reaction conditions: furfural, 1 mmol; 2-Propanol, 3 mL; catalyst, 0.005 g; stirring speed, 500 rpm.

Spent catalysts

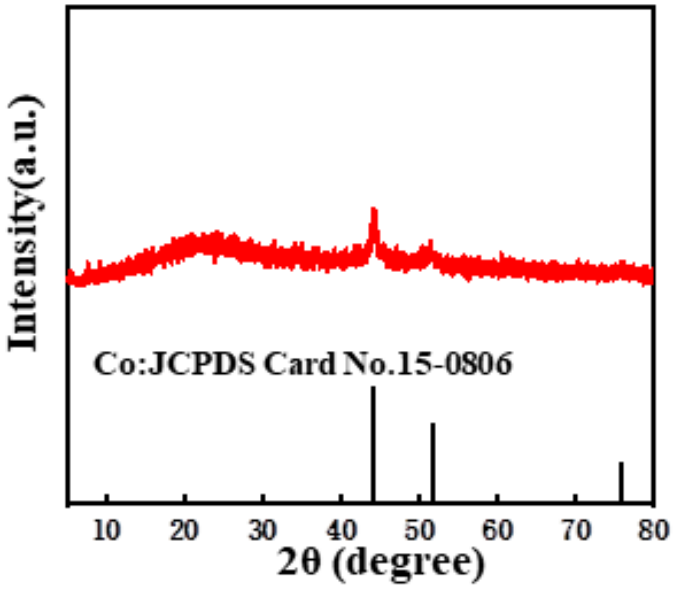

Fig. S8. XRD patterns of spent CoN_x-C@mSiO_2-20-700.

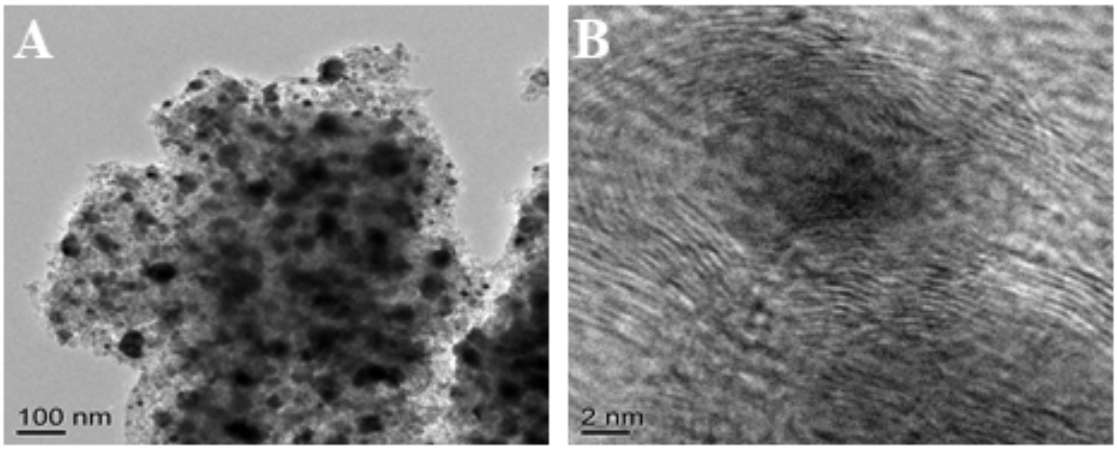

Fig. S9. TEM images of spent CoN_x-C@mSiO_2-20-700.

Table S1. The Co valence and content of Co catalysts were determined by XPS.

Catalysts	Co^0 (%)	Co-O_x (%)	Co-N_x (%)
Co@N-C-700	42.6	34.1	23.3
Co-N-C@mSiO_2-20-600	38.9	37.1	24.0
Co-N-C@mSiO_2-20-700	27.2	41.8	31.0
Co-N-C@mSiO_2-20-800	32.8	39.4	27.8

Table S2. The specific surface area and pore volume of Co catalysts were determined by BET.

Catalysts	BET Surface Area (cm^2/g)	Pore Volume (cm^3/g)	pore size (nm)
Co@N-C-700	174.2	0.15	3.83
Co-N-C@mSiO_2-20-600	207.2	0.35	3.88
Co-N-C@mSiO_2-20-700	296.2	0.37	3.94
Co-N-C@mSiO_2-20-800	291.9	0.35	3.90

Table S3. Comparison of catalytic performance over non-precious metal catalysts in the hydrogenation of furfural to furfuryl alcohol.

Entry	Catalyst	T/ ^{o}C	P_{H2} /MPa	Solvent	Con. /%	Sel. /%	TOF /h^{-1}	Ref.
1	Co/SBA-15	150	2	ethanol	92	96	1.0	[1]
2	Cu-Co/SBA-15	170	2	2-propanol	99	80	7.6	[2]
3	Co/NC-400-6	180	2	2-propanol	99	22	---	[3]
4	NiCoZn@NC-600	160	2	THF	86	>99	---	[4]
5	$CuCo_{0.4}$/C-873	140	3	ethanol	99	98	--	[5]
6	2%Ni-5%Cu/SiO_2	100	2	methanol	94	64	1.3	[6]
7	Cu-Cr	110	1	2-propanol	48	100	1.3	[7]
8	CuNi/MgAlO	100	4	methanol	99	99	15	[8]
9	Ni_3Fe_1/SiO_2	140	3.4	methanol	100	96	49	[9]
10	Co-N-C@mSiO_2-20-700	140	1	2-propanol	95	89	13	This work

Table S4. TOFs of metal Co and CoN_x active sites.

Catalysts	d_{TEM}[a]/nm	Con.[b]/%	TOF[c]/h^{-1}	X_{CoNx}[d]/%	TOF_{Co}/h^{-1}	$TOF_{Co\text{-}Nx}$/h^{-1}
$Co@SiO_2$	11.3	2.3	1.2	-	1.2	--
Co-N-C@$mSiO_2$-20-700	9.0	20.5	12.9	31.0	1.2	39

[a] Co particle size was determined by TEM. [b] Conversion of furfural (Con.) was tested by GC. [c] Conversion of furfuralwas tested by GC. [d]X_{CoNx} was the proportion of CoNx calculated by XPS.

Here TOF_{CoNP} of metal Co was assumed to be equal for $Co@SiO_2$ and CoN_x-C@$mSiO_2$-20-700. The TOF of Co-N-C@$mSiO_2$-20-700 was defined as the total activity of metal Co and Co-N_x species. The TOF of Co-N_x species was obtained as follows:

$$TOF_{CoNx} = \frac{TOF\text{-}TOF_{CoNP} \times (1 - X_{CoNx})}{X_{CoNx}}$$

Reference

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