Ultrasonication-Driven Downscaling and Formation of Lewis Acid–Base Sites in Hydrogen-Bonded Co Metal-Organic Framework Trigger Exceptional Catalytic Performance for Knoevenagel Condensation Reaction

Zhida Liu[a,b,c], Yan Zhou[c], Zheng Chen[c], Meng Zheng[b], Wenxiao Chen[b], Haiqing Ma[b], Xiaoyu Chen[b,*], Jin Wang[b,c,*]

[a] State Key Laboratory of Biobased Fiber Manufacturing Technology, Tianjin University of Science and Technology, Tianjin, 300457, China

[b] College of Materials Science and Engineering, Shenzhen University, Shenzhen 518071, China

[c] School of Chemistry and Materials Sciences, University of Science and Technology of China, Hefei, Anhui 230026, China

* Corresponding authors: Xiaoyu Chen: chxysh@126.com

Jin Wang: wangjin19@szu.edu.cn, wangjinchem@ahnu.edu.cn

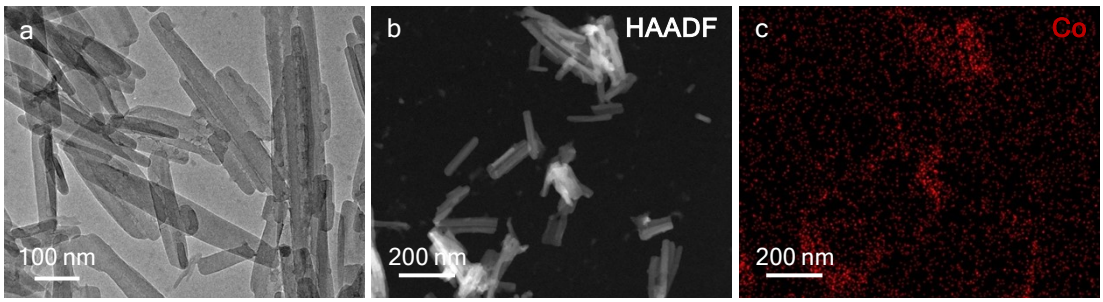

Figure S1. The TEM image of CoMOF-NR(a). TEM-mapping of CoMOF-NR. HRTEM dark field image (b) and Co element (c).

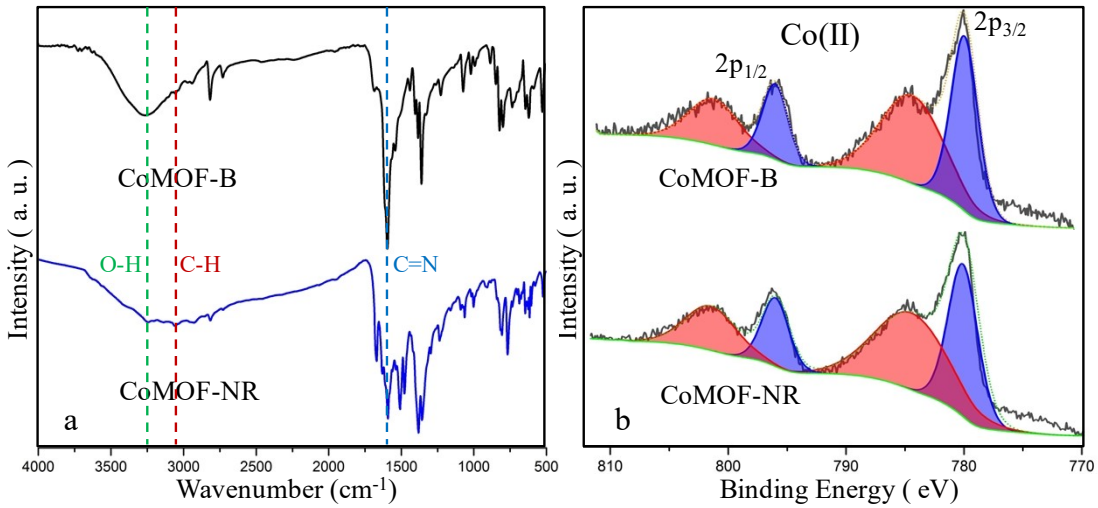

Figure S2. Infrared spectra of CoMOF-B (black) and CoMOF-NR (blue) (a). XPS for Co $2p_{3/2}$ and $2p_{1/2}$ of CoMOF-B and CoMOF-NR (b).

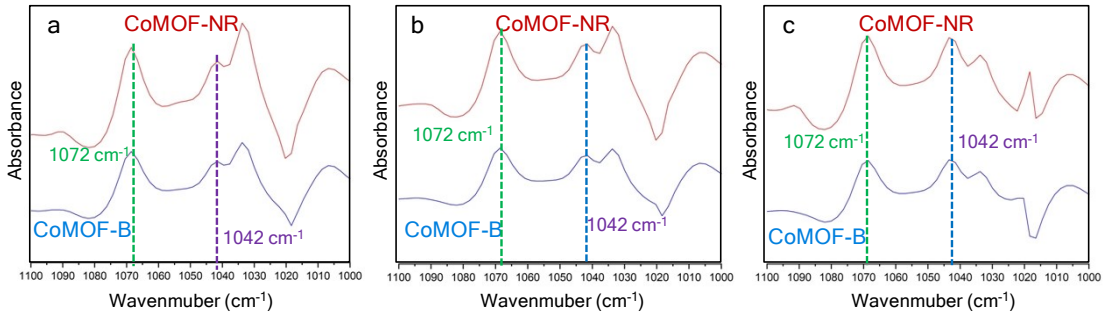

Figure S3. Py-FTIR spectra of CoMOF-B and CoMOF-NR at 25 ℃ (a), 80 ℃ (b) and 120 ℃ (c).

Table S1. Element content comparison of CoMOF-B and CoMOF-NR. (C, N, and H content were determined by Organic Elemental Analyzer (EA) and Co content were determined by ICP-OES.)

Elements/Samples	CoMOF-B(%)	CoMOF-NR(%)	Theoretical (%)
C	53.20	53.52	53.30
N	11.01	11.32	11.31
H	4.39	3.86	4.04
O	21.23	18.92	19.38
Co	11.65	12.18	11.91

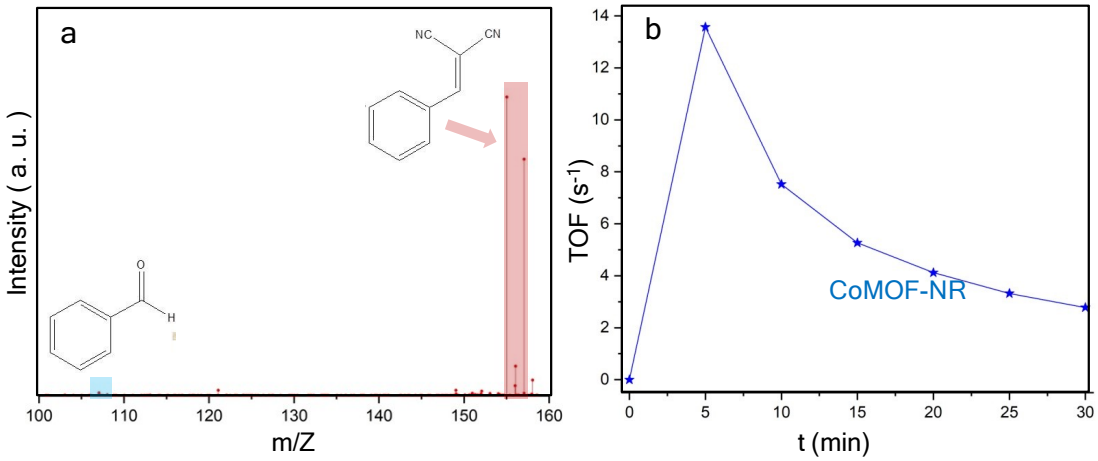

Figure S4. Mass spectrum of the reaction solution after 30 min (reaction condition: benzaldehyde 2 mmol, malononitrile 2.2 mmol, CoMOF-NR 2mol%, room temperature, ethanol 10mL) (a). The TOF (s^{-1}) of CoMOF-NR in Knoevenagel Condensation Reaction of benzaldehyde at different reaction time(b).

Table S2. Comparison of different catalytic performance of Knoevenagel Condensation Reaction of benzaldehyde.

Entry	Catalyst	Time(min)	T(℃)	Solvent	Yield(%)	TOF(s^{-1})	Ref.
1	PSM of $[Co(pytpy)(AIP)\cdot H_2O]_n$	30	40	methanol	79.0	3.51	1
2	NUC-70a	150	55	methanol	100	0.27	2
3	NUC-65Br	720	rt	ethanol	99	0.55	3
4	NUC-62	240	63	methanol	97	2.02	4
5	$C_{26}H_{30}N_2O_{17}Mn_2$	80	25	ethanol	>99	1.67	5
6	$H_{21}K_9\{[Cu(en)_2]_9(H_2O)_8\}[Cd_3O_6(SiNb_{18}O_{54})_3]\cdot 58H_2O$	120	60	ethanol	99	5.50	6
7	UiO-66-NH_2	60	25	DMF	70.8	/	7
8	Mg_1/NC	120	80	toluene	<96	0.01	8
9	NiXero	240	27	water	97	0.28	9
10	$Zn_3Sb_4O_6F_6$	300	60	/	99	/	10
11	CoMOF-NR	5	rt	ethanol	81.4	13.57	This work
12	CoMOF-NR	30	rt	ethanol	>99	2.78	This work

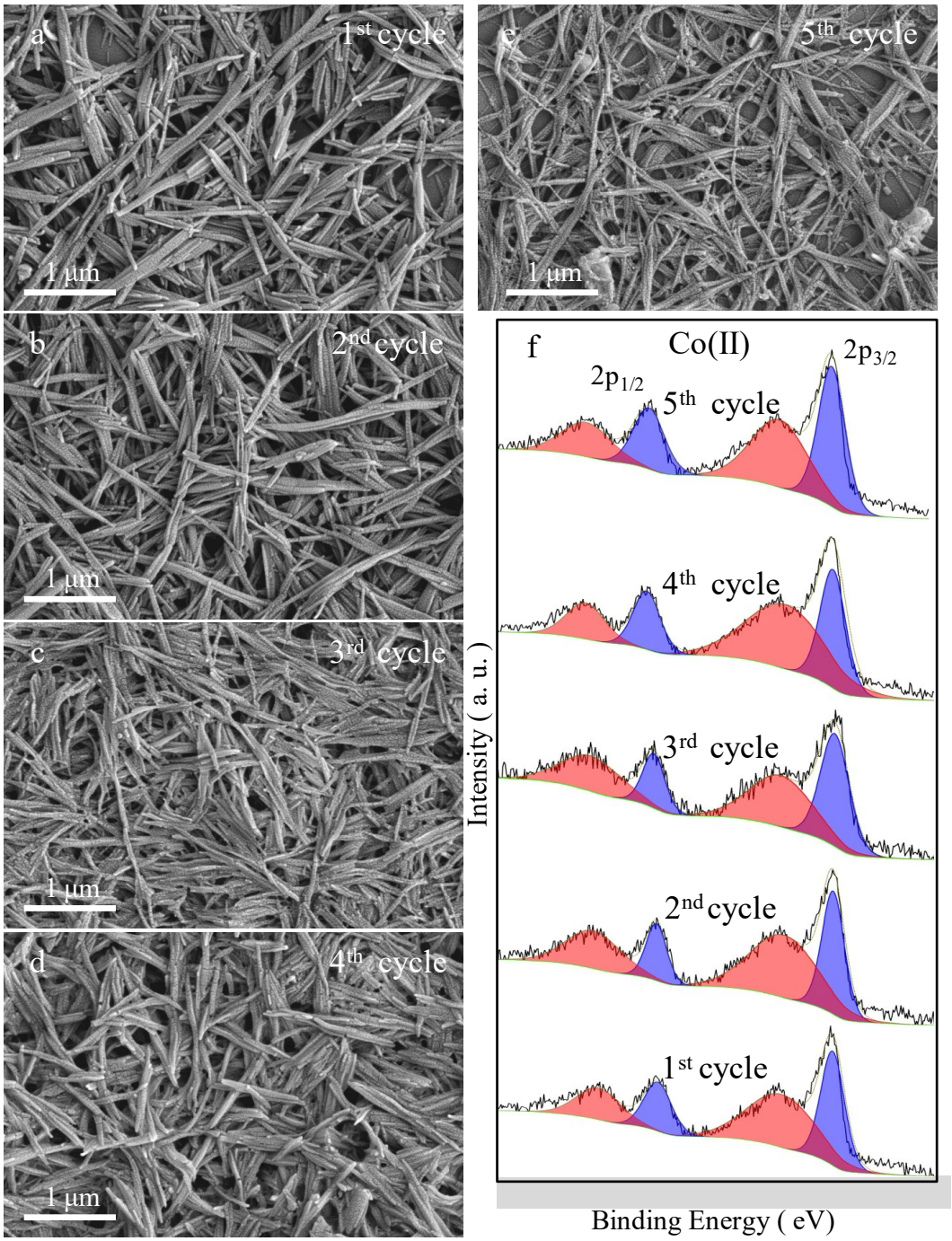

Figure S5. SEM images of CoMOF-NR after Knoevenagel Condensation Reaction for 1 cycle (a), 2 cycles (b), 3 cycles (c), 4 cycles (d) and 5 cycles (e). XPS for Co $2p_{3/2}$ and $2p_{1/2}$ of CoMOF-NR after Knoevenagel Condensation Reaction (f).

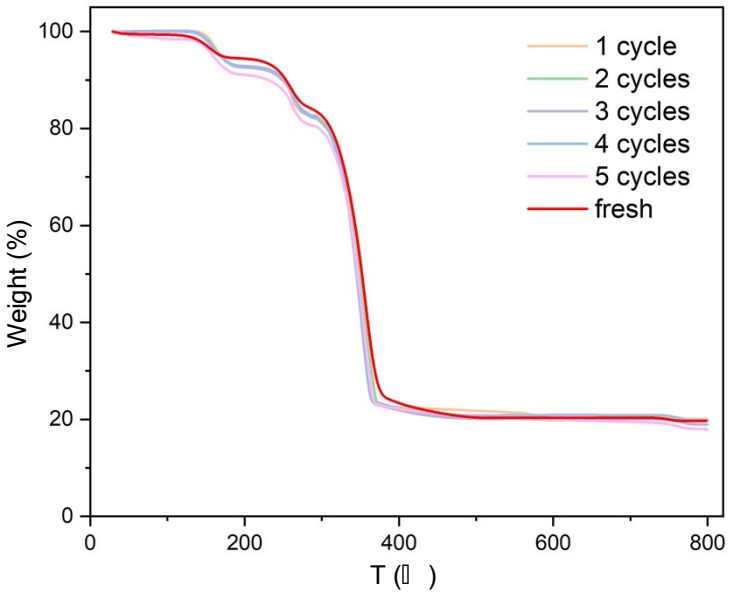

Figure S6. TGA curves of CoMOF-NR before and after Knoevenagel Condensation Reaction.

References for supporting information

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