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MOFs-derived Co@CN Bi-functional Catalysts for Selective Transfer Hydrogenation of α,β-unsaturated Aldehyde without Using the Base Additives

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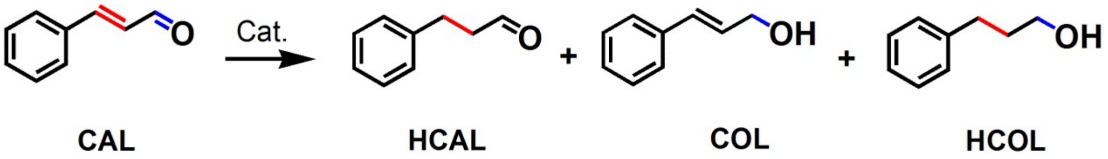
Contents

1. Characterizations

Powder X-ray diffraction patterns of the Co-MOF ([Co(TPA)(ted)$_{0.5}$]) and Co@CN catalysts were measured on a Rigaku diffractometer (D/MAX-IIIA) equipped with a Cu Kα radiation (40kV, 30mA, 0.1543nm). The surface appearances of Co@CN samples were investigated by Scanning Electron Microscope (ZEISS, MERLIN) and Transmission Electron Microscope (JEOL, JEM-2010HR) assembled with energy-dispersive X-ray spectroscopy (EDS) analysis. X-ray Photoelectron Spectroscopy (XPS) tests were conducted on a Kratos Axis Ultra DLD system with a base pressure of 10^{-9}Torr. BET surface areas and pore sizes were obtained from N_2 physisorption at 77K (Micromeritics ASAP 2020M). The mass of Co in the Co@CN samples were measured by atomic absorption spectroscopy (AAS, Hitachi, Z-2000). CO_2-TPD measured on a Micromeritics AutoChem II 2920 instrument. Typically, 200mg of activated sample was heated at 900°C for 2h under a He flow (50mL.min^{-1}) to remove the adsorption gases from the catalyst, and then cooling down to 50^{o}C. After adsorption of CO_2 at 50°C for 1h, the catalyst was purged with the He flow for 1h to remove the weakly adsorbed species. The TPD data were collected from 100°C to 900°C at a heating rate of 20°C min^{-1} in a flow of He.

2. Results of experiments

Table S1. Representative literature results for the hydrogenation of cinnamaldehyde over some catalysts.



Entry	Cat.	Sol.	Additives	T (°C)	**P (MPa)**	t (h)	Con. (%)	Sel. (%)			Ref.
								HCAL	COL	HCOL	
1	Au/PZnO	*i*-PrOH	-	110	**2**	0.5	**88.1**	3.7	**74.3**	22	1
2	Au/Fe_2O_3	*i*-PrOH	-	110	**2**	1.5	**94.6**	0.9	**89.1**	10	1
3	Au/MA	EtOH	-	120	**1**	6	**96**	42	**40**	15	2
4	Pt/C	*i*-PrOH	-	25	0.1	3	**3.5**	70.5	**10.8**	18.7	3
6	Pt/MIL-101	THF	-	25	0.1	3	**48.6**	87.6	**8.2**	4.2	3
5	Pt NCs	MeOH	-	25	**4**	44	**98.7**	2.5	**91.7**	4	4
7	0.5%Pt/GRA	EtOH	-	70	**2**	1.5	**83.6**	39.7	**28**	7.2	5,6
8	37%Co/Al_2O_3	EtOH	-	50	**0.98**	2	**55**	0	**99.3**	0	7
9	Ni−Co/MWCNT	EtOH	-	150	**0.5**	8.0	**62.6**	37.9	**62.1**	0	8
10	Ni−Co/AC	EtOH	-	150	**0.5**	9.5	**63.2**	50.5	**46.9**	2.6	8
11	Ni−Co/GRA	EtOH	-	150	**0.5**	5.0	**29.8**	44.7	**55.3**	0	8
12	Au/SiC	*i*-PrOH	KOH	20	-	2	**100**	-	**100**		9
13	Cobalt complex	*i*-PrOH	P-ligands	80	-	24	**96**	-	**-**	**98**	10
14	Fe complex	*i*-PrOH	P-ligands KO*t*Bu	24	-	2	**70**	-	**68**		11
15	MgAl doxide	*i*-PrOH	Hydrotalcites	80	-	5	**75**	-	**92**		12

Table S2. The contents of Co, C and N of some samples.

Entry	Samples	Co contents (%)[a]	C contents (%)[b]	N contents (%)[b]
1	Co-MOF	21.0	46.9	9.6
2	Co@CN-600	37.1	58.5	2.6
3	Co@CN-700	37.7	57.3	2.2
4	Co@CN-800	37.6	57.9	2.1
5	Co@CN-900	38.7	57.8	1.9

[a] Measured by AAS.

[b] Measured by elemental analysis.

Figure S1. The illustration for the magnetic separation of catalysts after reaction.

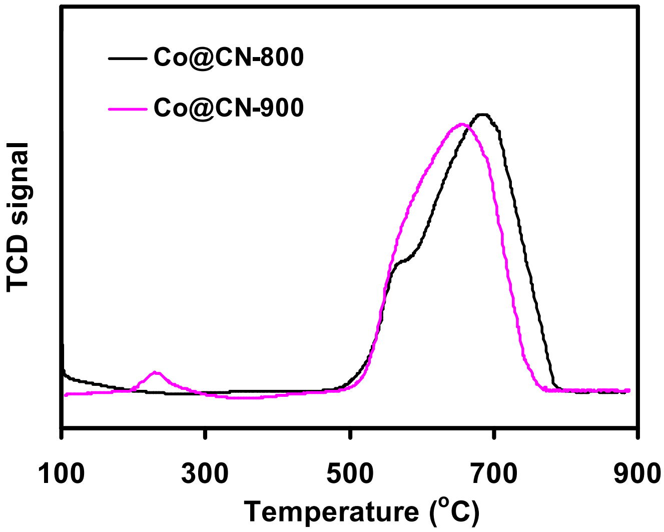


Figure S2. CO_2-TPD curves of Co@CN catalysts.

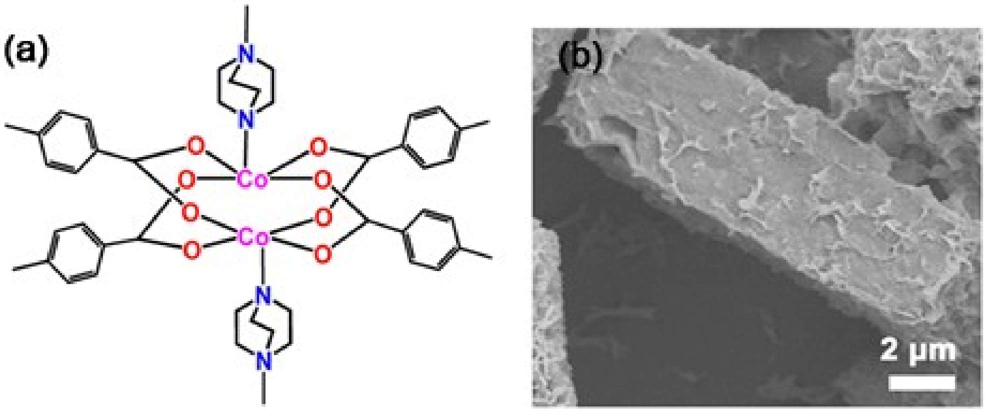


Figure S3. (a) The chemical structure of Co-MOF, (b) the typical SEM image of Co-MOF.

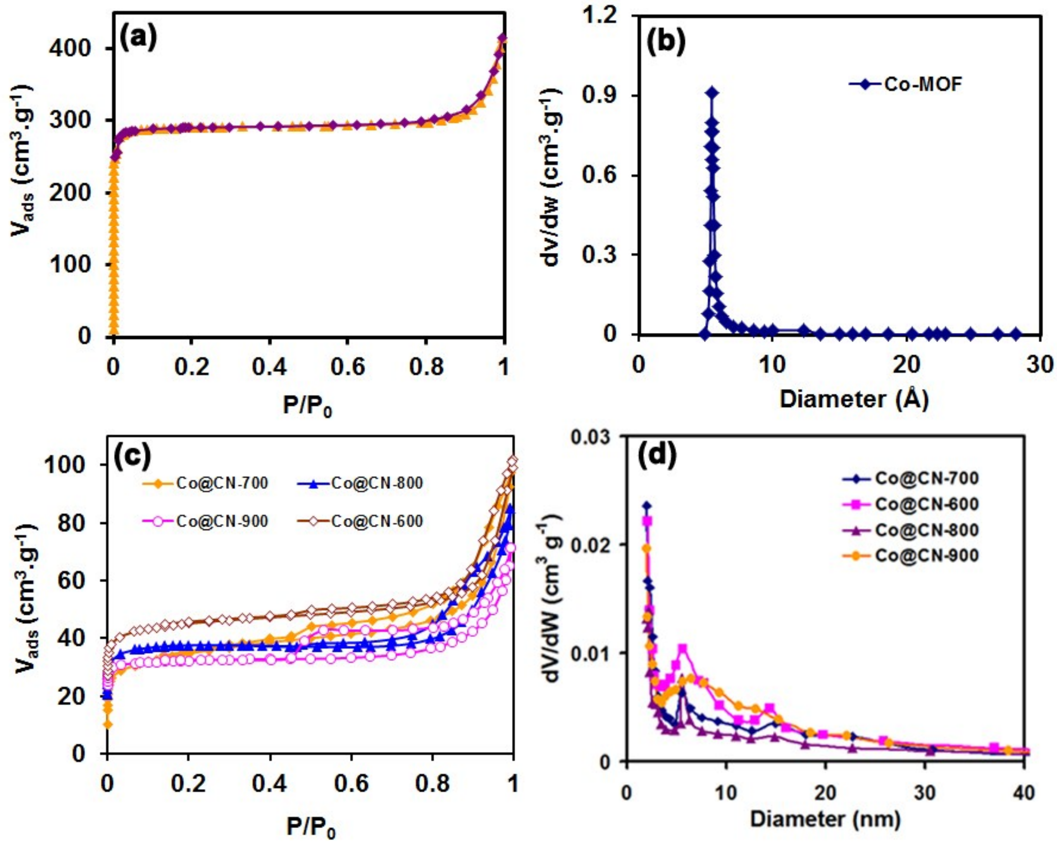


Figure S4. N_2 adsorption/desorption isotherms of Co-MOF (a) and the corresponding pore size distribution (b); the N_2 adsorption/desorption isotherms of Co@CN with different thermolysis temperatures (c), and the corresponding pore-distribution (d).

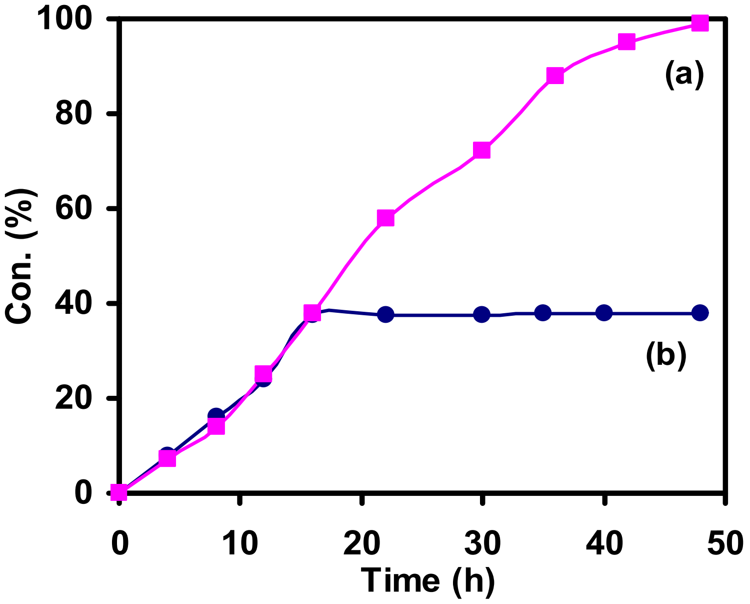


Figure S5. Cinnamaldehyde conversion as a function of time: 1mmol cinnamaldehyde, Co@CN-900 15mmol% catalyst, 2mL *n*-hexanol, 80^{o}C. (a)

Conversion of cinnamaldehyde, (b) cinnamaldehyde conversion after removal of catalyst at 16h.

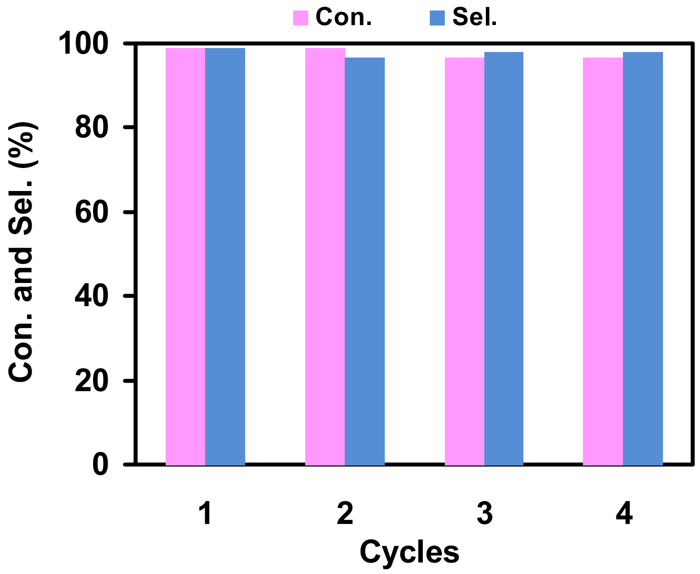


Figure S6. Reuses of Co@CN-900 catalyst in selective transfer hydrogenation of CAL to COL at the optimal conditions.

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