Electronic Supporting Information

Solvent-Free Heterogeneous Catalysis for Cyanosilylation in Modified Sodalite-typed Cu(II)-MOF

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Table S1. Crystal data and structure refinement for complex **1**.

Complex **1**	
Empirical formula	$C_{24}H_{16}Cl_{0.31}Cu_4N_{32}O_{4.69}$
Formula weight	1092.90
Temperature	293(2)K
Crystal system	cubic
Space group	Pm-3m
a (Å)	18.6233(12)
b (Å)	18.6233(12)
c (Å)	18.6233(12)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
V (Å^3)	6459.1(7)
Z	3
ρ_{calc}, (g cm^{-3})	0.843
μ, (mm^{-1})	1.022
F(000)	1628.0
Size (mm)	0.22×0.22×0.20
θ(°)	5.36 to 52.7°
Reflections/unique	6572

T_{max} /T_{min}	0.8065/0.8218
Data/restraints/parameters	1366/0/48
S	1.056
R_1	0.0705
wR_2	0.2205
$\Delta\rho_{max}/\Delta\rho_{min}$(eÅ^{-3})	-0.730/1.157

[a]$R_1 = F_o\text{-}F_c/F_o$, [b]$wR_2 = [w(F_o^2\text{-}F_c^2)^2/w(F_o^2)^2]^{1/2}$

Table S2. Bond lengths [Å] for complex **1**

complex **1**					
Cu1	N2	2.018(3)	N2	N2^4	1.341(6)
Cu1	N2^1	2.018(3)	C1	C2^5	1.397(4)
Cu1	N2^2	2.018(3)	C1	C2	1.397(4)
Cu1	N2^3	2.018(3)	C2	C1^6	1.397(4)
Cu1	O2	2.396(9)	C2	C3	1.480(7)
N1	N2	1.349(4)	C3	N1^4	1.346(4)
N1	C3	1.346(4)			

Symmetry codes: (1) +X,+Y,-Z; (2) 1-X,+Y,-Z; (3) 1-X,+Y,+Z; (4) +X,+Z,+Y; (5) +Z,+X,+Y; (6) +Y,+Z,+X.

Table S3. Angles [deg] for complex **1**

complexe **1**							
N2^1	Cu1	N2	91.78(15)	N1	N2	Cu1	128.7(2)
N2^1	Cu1	N2^2	177.13(16)	N2^4	N2	Cu1	121.70(8)
N2	Cu1	N2^2	88.15(15)	N2^4	N2	N1	109.63(17)
N2^1	Cu1	N2^3	88.15(15)	C2^5	C1	C2	119.8(5)
N2	Cu1	N2^3	177.13(16)	C1^6	C2	C1	120.2(5)

N2[2]	Cu1	N2[3]	91.78(15)	C1[6]	C2	C3	119.9(3)
N2	Cu1	O2	91.44(8)	C1	C2	C3	119.9(3)
N2[1]	Cu1	O2	91.44(8)	N1	C3	N1[4]	113.3(4)
N2[3]	Cu1	O2	91.44(8)	N1	C3	C2	123.4(2)
N2[2]	Cu1	O2	91.44(8)	N1[4]	C3	C2	123.4(2)
C3	N1	N2	103.7(3)				

Symmetry codes: 1) +X,+Y,-Z; 2) 1-X,+Y,+Z; 3) 1-X,+Y,-Z; 4) +X,+Z,+Y; 5) +Z,+X,+Y; 6)+Y,+Z,+X

Table S4. The optimization of reaction condition.

Entry	Cat. mol %	TMSCN	Temp.(℃)	Conv.(%)[a]
1	0	3 eq.	r.t.	60
2	2	3 eq.	r.t.	76
3	2	3 eq.	40	98
4	1	3 eq.	40	98
5	0.5	3 eq.	40	84
6	*1*	***2 eq.***	***40***	***96***

[a] Determined by GC based on the carbonyl substrate.

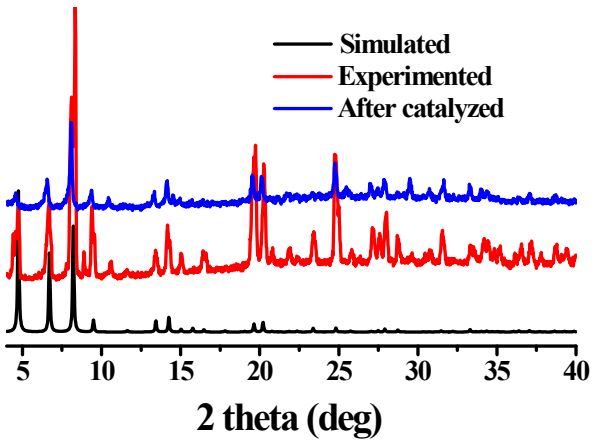


Fig. S1 The PXRD patterns of simulated, experimented and after catalyzed for **1**.

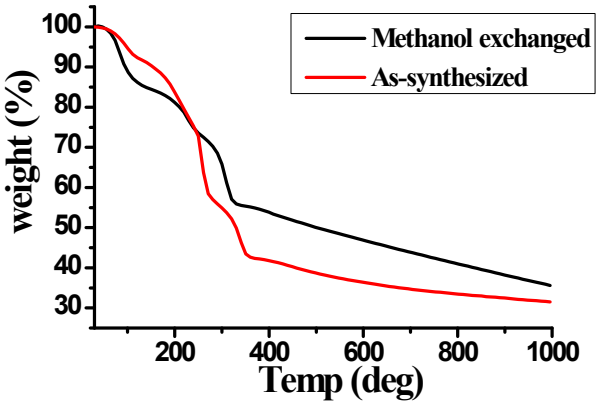


Fig. S2 The TGA plots of as-synthesized and methanol exchanged **1** at a heating rate of 10°C min^{-1} in air.

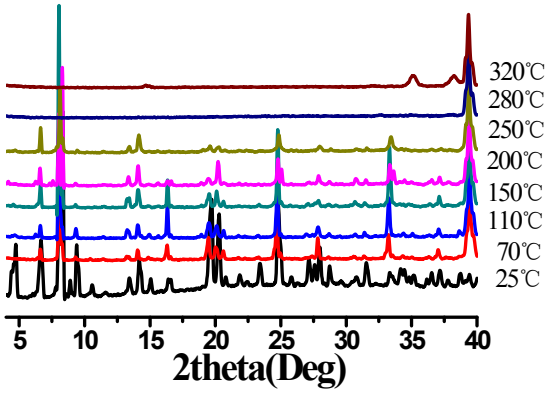
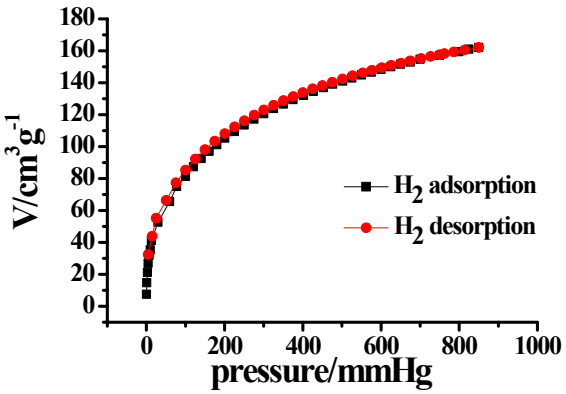
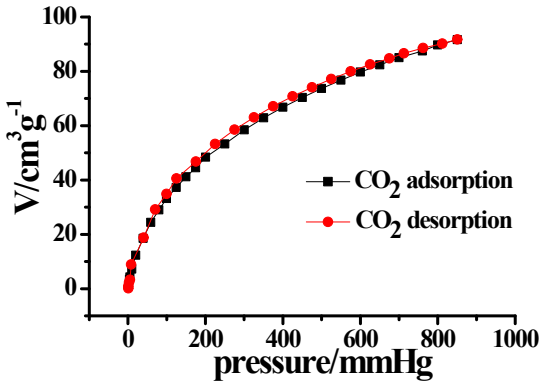


Fig. S3 The temperature-dependent X-ray diffraction patterns of **1**.



(a)



(b)

Fig. S4 Adsorption isotherms in **1** for the uptake of H_2 at 77 K (a) and CO_2 at 273 K (b).

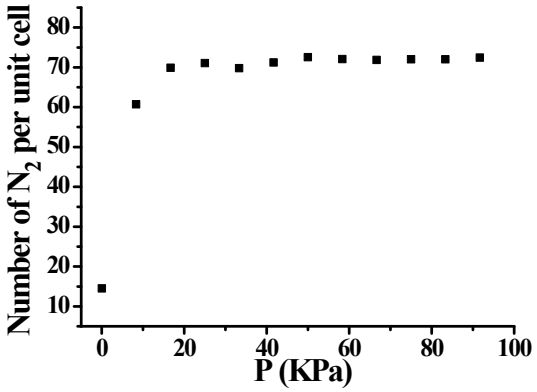


Fig. S5 Grand canonical Monte Carlo (GCMC) simualted N_2 adsorption isotherms of **1** were employed at 77 K**.**

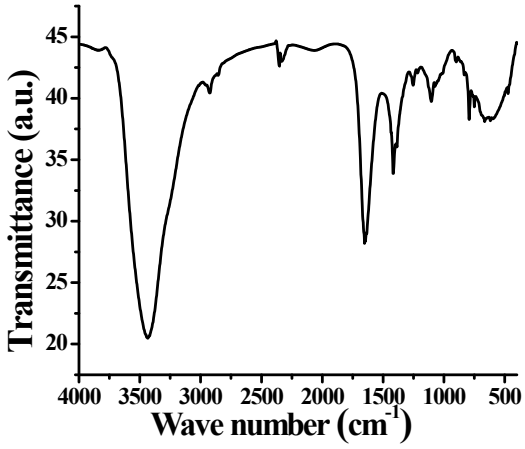


Fig. S6 Infrared spectra of **1** in KBr pellet.

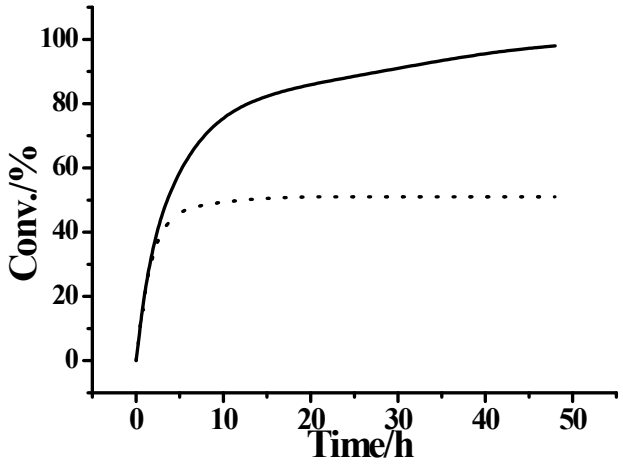


Fig. S7 The conversion of the cyanosilylation of benzaldehyde determined by GC: dashed line indicate the conversion after filtration of solid **1′** at 2 h.