Solvent-Free Heterogeneous Catalysis for Cyanosilylation in a Dynamic Cobalt-MOF

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The butterfly-like tetranuclear cobalt cluster based 3D MOF $[Me_2NH_2][Co_2(bptc)(\mu_3\text{-}OH)(H_2O)_2]$ (**1**) underwent a reversible thermally triggered single-crystal-to-single-crystal transformation *via* Co-O_{water} weakened intermediate **1a** to produce partly dehydrated phase $[Me_2NH_2][Co_2(bptc)(\mu_3\text{-}OH)(H_2O)]\cdot$(**2**), which was confirmed by single-crystal X-ray diffraction, powder X-ray diffraction, thermogravimetric analysis, and IR spectroscopy. During dehydration course, the local coordination environment of one Co^{2+} ion was changed from saturated octahedron to coordinately unsaturated square-pyramid, accompanied with crystal color change from red to purple. Compared with pristine hydrated **1**, dehydrated **2** exhibits highly efficient and recyclable catalytic activity for cyanosilylation of carbonyl compounds with lower catalyst loading of 0.1 mol% Co at room temperature under solvent-free conditions, which due to the opened Co^{2+} sites as catalytic activated sites played a significant role in heterogeneous catalytic process.

Introduction

The cyanosilylation of carbonyl compounds with trimethylsilyl cyanide (TMSCN), as a direct and efficient method for the formation C-C bond in organic synthesis, has recently received tremendous attention, due to cyanohydrins are key intermediates in the synthesis of biologically important compounds such as α-hydroxy acids, α-hydroxyl ketones andα-amino acids.[1-5] Majority of these studies have revealed that the reaction is catalyzed by homogeneous catalysts i.e. metallic Lewis acids/ bases, inorganic solid acids/bases, and nonmetallic organic molecules,[6-8] whose performance is still limited with large difficulty in separation and recyclable use. From the view of economy, the strong industrial preference for heterogenous catalysts arises from their inherent stability and ease of recovery, allowing for more efficient separation and recycling.[9-11] HKUST-1 features weakly axially coordinating Cu^{2+} sites was reported to heterogeneous catalyze cyanosilylation reaction of aldehydes in moderate yield (70%) after 48 h by higher catalyst loading of 5 mol%.[12] Recently, Cr-MIL-101, UiO-66, and biphenol-based MOF remarkably accelerated the cyanosilylation of various aldehydes and ketones, even in excellent yield (98%), but the rate depended on the type of organic solvent.[13-16] However, from the point of green chemistry, it is a pressing challenge to seek efficient heterogeneous catalyst under environmentally friendly conditions.

Metal-organic frameworks (MOFs) have recently attracted the interest of material scientists due to their friendly catalysis features such as large surface areas and porosity, high catalyst loadings, more accessible and identifiable catalytic centers.[17-20] Furthermore, compared with other heterogeneous catalysts, the ordered nature of MOFs allows for precise characterization of catalytic sites through X-ray diffraction studies. The catalytic active sites can be implemented at the organic or inorganic component of framework by direct synthesis or post-synthetic modification.[21-23] For example, the axial ligand of paddlewheel-typed copper dimer[3] can be removed by heating to create opened metal sites as Lewis acid catalytic active centers. Therefore, structural information of catalytic centers is critical for the systematic elucidation of activity-structure relationships. However, through post-synthetic metalation, or light, heat, pressure *etc* external stimuli, the framework will produce defects, even complete collapse,[24-26] which makes it difficult to obtain intact single crystal data to further explore catalytic mechanisms. Therefore, few dynamic single-crystal-to-single-crystal (SCSC) transformations have been documented, especially creation of coordinately unsaturated metal centers.

We have been pursuing porous magnet materials by using paramagnetic metal cobalt cluster/chain-based magnets and have presented significant solvomagnetic effect in a dynamic SCSC fashion by removing water molecules of the channels.[27] Co^{2+} ions is a good candidate not only for dynamic porous magnets, but also for catalytic materials, because it can adopt flexible, diverse coordination geometries and may coordinated by solvent molecules, which makes it possible to engineer coordinatively unsaturated catalytic centers. In our ongoing investigation on heterogeneous catalyst for cyanosilylation reaction by a modified sodalite-type copper-MOF with opened metal centers,[28] a cobalt cluster based MOFs in our group coordinated by terminal water

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† Electronic Supplementary Information (ESI) available: Crystallographic data, PXRD patterns, IR and TGA plots of **1-2**. CCDC 1059844-1059846. For ESI and crystallographic data in CIF see DOI: 10.1039/x0xx00000x

molecule[29] inspired us to explore heterogeneous catalytic activity. Herein, the tetranuclear cobalt cluster based MOFs (**1**) was dynamic transformed to dehydrated phase $[Me_2NH_2][Co_2(bptc)(\mu_3\text{-}OH)(H_2O)]$ (**2**) *via* Co-O$_{water}$ bond weakened intermediate **1a** by *in situ* SCSC dehydration. Partly dehydrated **2** exhibits efficient, stable, recyclable heterogeneous catalytic activity for cyanosilylation of carbonyl compounds under solvent-free conditions, while hydrated **1** and **1a** don't show catalytic activity, due to all Co^{2+} ions are coordinately saturated octahedron and less Lewis acid.

Experimental section

Materials and physical measurements

All chemicals were analytically pure from commercial sources and used without further purification. Elemental analyses were performed on a Vario EL-II analyzer. FTIR spectra were recorded from KBr pellets in the range 4000-400 cm^{-1} on a Perkin Elmer Spectrum BX FTIR spectrometer. Powder X-ray diffraction (PXRD) and temperature dependent PXRD data were collected in a Rigaku Ultima IV diffractometer. The thermogravimetric analyses (TGA) were carried out in N_2 atmosphere using SETARAM LABSYS equipment at a heating rate of 10 °C/min.

$[Me_2NH_2][Co_2(bptc)(\mu_3\text{-}OH)(H_2O)_2]$ (1):

The synthetic method has been improved to increase the yield of **1** (from our previously reported 62.3 % to 83.2%), by using triethylamine instead of KOH to adjust the solution pH value, which guarantees enough quantity of the material for catalytic tests. PXRD analysis of the samples revealed that the material is phase-pure (Fig. **S1**).

Intermediate $[Me_2NH_2][Co_2(bptc)(\mu_3\text{-}OH)(H_2O)_2]$ (1a) and dehydrated phase $[Me_2NH_2][Co_2(bptc)(\mu_3\text{-}OH)(H_2O)]$ (2):

The purple rice-like crystals of **1a** with weakened Co-O$_{water}$ bonds and dehydrated phase **2** were obtained by heating **1** to 160 °C and 170 °C in dry air, respectively (Fig. 1). The diffraction data for them were collected in dry air in the diffractometer at room temperature. Many attempts to obtain a crystal of fully dehydrated suitable single crystal analysis *via* enhancing temperaure or prolonging heat time, failed.

X-ray Crystallography

Data The diffraction data were collected using an Agilent Gemini EOS diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at room temperature. The program CrysAlisPro was used for absorption correction. All the structures were solved by direct methods and refined by full-matrix least-squares analysis with SHELXL-97 software.[30] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of organic ligand were generated theoretically onto the specific carbon and nitrogen atoms, and refined isotropically with fixed thermal factors. Further details for structural analysis are summarized in Table 1, corresponding bond lengths and bond angles are shown in Table S1.

The heterogeneous Catalytic Cyanosilylation Tests

The catalyst of **2** 5 mg (0.1 mol %), aldehyde (1 mmol) and trimethylsilyl cyanide (TMSCN 2.0 mmol) were placed into a Pyrex-glass screw cap vial (volume *ca* 5 mL), which was vigorously stirred at room temperature under nitrogen atmosphere. The reaction progress was monitored by GC analysis, which performed using Agilent 7820 GC with a cross-linked (95%)-dimethyl-(5%)-diphenylpolysiloxane column (HP-5, 30 m×0.32 mm×0.25 μm), injector temperature 250 °C, FID detector temperature 300 °C, and oven temperature program 45 °C (3 min) -20 °C/min - 280 °C (2 min). All products (cyanohydrin trimethylsilyl ethers) were identified by comparison of their GC retention times, GC/MS spectra.

Table 1. Crystallographic data and dtructure definement of **1, 1a** and **2**.

Compound	**1**	**1a**	**2**
Formula	$C_{18}H_{18}Co_2NO_{11}$	$C_{18}H_{17}Co_2NO_{10.13}$	$C_{18}H_{18}Co_2NO_{10}$
Fw	542.20	524.28	524.20
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/c	P2(1)/c	P2(1)/c
a (Å)	13.5820(4)	13.5497(7)	13.4701(13)
b (Å)	10.8173(3)	10.8567(4)	10.8298(6)
c (Å)	14.7037(5)	14.6263(7)	14.6883(11)
α(°)	90	90	90
β (°)	110.6280(10)	109.784(6)	109.830(10)
γ(°)	90	90	90
V (Å^3)	2021.77(11)	2024.60(16)	2015.7(3)
Z	4	4	4
$\rho_{calc,}$(g cm^{-3})	1.775	1.719	1.681
μ (mm^{-1})	1.704	1.696	1.699
F(000)	1096.0	1161.0	1031.0
Reflections	11035/4101	7999/4147	8111/4112
Size (mm)	0.26 × 0.20 × 0.16		
T_{max}/T_{min}	0.772/0.666	0.773/0.667	0.773/0.666
R_{int}	0.0164	0.0260	0.0295
Data/parameters	4101/0/293	4147/5/299	4112/9/291
S	1.057	1.292	1.264
$R_1{}^a$, $wR_2{}^b$[I>2σ(I)]	0.0299/0.0782	0.0557/0.1299	0.0657/0.1518
R_1, wR_2 (all data)	0.0330/0.0809	0.0767/0.1595	0.0790/0.1573
$\Delta\rho_{max}/\Delta\rho_{min}$(eA^{-3})	0.716/-0.357	1.20/-0.89	1.340/-0.514

$^aR_1 = \sum||F_o|-|F_c||/\sum|F_o|$. $^bwR_2 = [\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$

Results and Discussion

SCSC transformation analyzed by various techniques

As shown in Fig. S1, the temperature dependent PXRD experiments for **1** recorded in the temperature range of 50−200°C suggested that coordinated water molecules might be removed around 160−180°C, which was well accord with the TGA of the first weight loss in the temperature range of 130−210 °C (Fig. S2). But the temperature dependent PXRD patterns also showed that the structural transformation was gradual with no clear transition and none of the complex patterns could be indexed to a single phase, which may indicate that the 3D framework is still retained only slight change in the structure. Comparison of the IR spectra of complexes **1** and **2**, two strong signals at 3500–3100 cm^{-1} in **1** indicate the presence of hydrogen-bonded OH groups, but only one strong signal at 3440 cm^{-1} in **2** is attributed to the O-H stretching vibration of H_2O molecule (Fig. S3). Furthermore, the different frequency numbers and shapes in the range of 1400-1430 and 1550–1650 cm^{-1}, which are assigned to the ǔ$_s$(COO$^-$) and ǔ$_{as}$(COO$^-$) modes, respectively, indicate the different coordination modes of the carboxylic groups in **1** and **2**.[31,32]

Similar behaviors are observed in the TG analysis. For **1, 1a** and **2**, the initial weight loss in the range of 30-270°C corresponding to the removal of whole or partly coordinated water molecules. It also provides a further evidence for the existence of a potential weak bond during the dehydration process, according to the nearly same TGA plots of **1** and **1a**. After "gently" heating the single crystal of **1** at 160 °C for 4 hours or at 170 °C two hours, crystal color changed from red to purple. we fortunately obtained crystals **1a** and **2**, characterized them by the single-crystal X-ray diffraction method. However, it is unsuccessful to attempt to dehydrate the second coordinated water molecule by heating, may be due to shorter bond length of Co(2)-O(2w) (table 2), larger steric hindrance and stronger hydrogen bond interaction than that of Co(1)-O(1w). Moreover, dehydrated phase **2** is exposed to moisture air for a few days, the purple crystals return to red without loss of single-crystallinity (Fig. 1). The phenomenon is similar to those materials, such as silica gel and bluestone, which can rapidly display a color change when in contact with water. Therefore, **1** may be the appropriate candidate as a new-fashioned water indicator.[33]

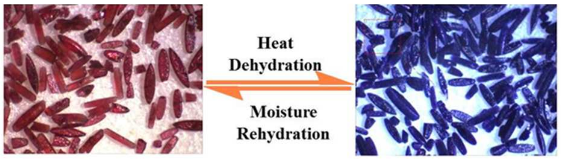

Fig. 1 Crystal photographs of *in situ* reversible SCSC transformations between **1** and **2**.

Crystal structures

For the sake of understanding catalytic mechanism, a detailed structure analysis of **1, 1a** and **2** are necessary. Single-crystal X-ray diffraction analysis reveals that complex **1** undergoes thermally driven SCSC transformation to produce intermediate **1a** with weakened Co-O$_{water}$ bond and partly dehydrated **2**, which all crystallizes in the monoclinic $P2_1/c$ space group (Table 1). As shown in Fig. 2, complex **1** consists of two unique Co^{2+} ions, one bptc ligand, one μ_3-OH group, two coordinated water molecules and one cation $[Me_2NH_2]^+$ in the asymmetric unit. Both Co^{2+} ions are hexa-coordinated showing distorted octahedral geometries. Edge-sharing Co(1) and Co(1a) dimer is bridged to Co(2) and Co(2a) by μ_3-OH, forming a butterfly-like tetranuclear cobalt cluster $[Co_4(\mu_3\text{-}OH)_2]$ in which Co(1) and Co(2) can function as "body" and "wing" of butterfly, respectively. As shown in Fig. 3, each bptc ligand is linked to four butterfly-like $[Co_4(OH)_2]$ clusters and each butterfly-like $[Co_4(OH)_2]$ cluster is connected to eight bptc groups, thus form a rare (4,8)-connected 3D *scu* topoloy anionic open framework with 7.97 × 9.04 Å pore, which are filled by organic cations $[Me_2NH_2]^+$ for charge-compensation and space-filling. Calculation with *PLATON* software reveals that the free volume of the channels is 448.3 Ǻ^3 per unit cell, or 22.5 % of the total volume.

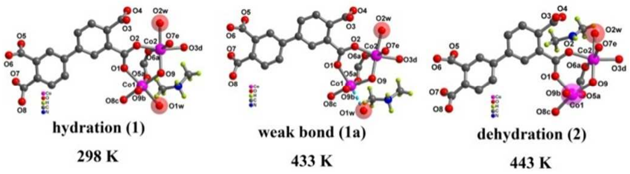

Fig. 2 View of coordination environment of Co^{2+} ions and organic $[Me_2NH_2]^+$ cation in **1, 1a** and **2**.

Table 2. Distance (Å) between cobalt and oxygen atoms of water molecule.

Bond	1	1a	2
Co(1)-O(1w)	2.267	2.433	H_2O removed
Co(2)-O(2w)	2.184	2.162	2.211

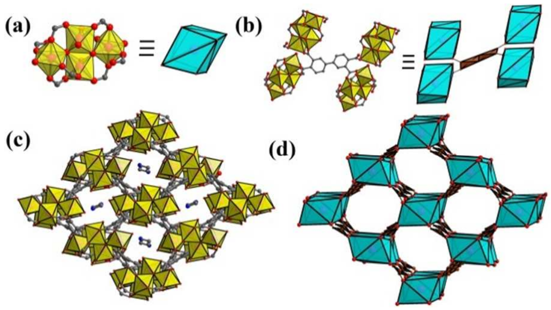

Fig. 3 (a) View of tetranuclear $[Co_4(OH)(RCO_2)_8]$ cluster SBUs, (b) each bptc linked by four Co_4 clusters, (c) 3D open anionic framework $[Co_2(bptc)(OH)(H_2O)_2]^-$ along the *a*-axis, filled with organic $[Me_2NH_2]^+$ cations in the pores, (d) the 3D (4,8)-connected *scu* net along the *a*-axis in **1**. For clarity, organic $[Me_2NH_2]^+$ cations have been omitted in (d).

Compared with complex **1**, three significant structural changes occur after SCSC transformation, although the (4,8)-connected 3D *scu* topology framework is still retained. Firstly, as the rise of the temperature, the distance between Co(1) and oxygen atom of water molecule increase from 2.2678(18) Ǻ to 2.433Ǻ, then the bond cleaved (Fig. 2 and Table 2) and produce UMCs, which may as the potential catalytic active sites. Secondly, local coordination environment of Co(1) atom changed from octahedron to coordinated unsaturated square-pyramid, accompanied by a color change from red to purple rice-like crystals. The basal positions of the square pyramid are occupied by the two carboxylate oxygen atoms and two μ_3-OH oxygen atoms, whereas the O1 atom locates

Fig. 4 View dynamic process of dehydration in tetranuclear $[Co_4(OH)(CO_2)_8]$ cluster.

in the apical position. Thirdly, the Co···Co distances of the butterfly-like [$Co_4(\mu_3\text{-}OH)_2$] cluster decrease (Fig. 4), from 3.1350(1) to 3.1279(1) Å for Co_{body}-Co_{body}, from 3.3802(1) and 3.5218(1) Å to 3.3296(2) and 3.5051(2) Å for Co_{body}-Co_{wing}, respectively in **1**and **2** (Table S3).

Catalytic Studies

Considering that complex **2** has large channels and coordinatively unsaturated metal centers (UMCs) which might serve as potential Lewis acid catalyst, the cyanosilylation reaction of carbonyl compounds was carried out to test its catalytic property. Our model experiment was tested with benzaldehyde as the standard molecule and varying the amount of catalyst and temperature under solvent-free conditions. As shown in Table S2, complex **2** demonstrated excellent catalytic activity, affording 98% conversion of benzaldehyde in 12 h at room temperature with lower catalyst loading of 0.1 mol % Co, which is only one-fifteenth amount of the reported Cr-MIL-101 (1.5 mol% Cr-active site) with the highest catalytic activity to date in the cyanosilylation reaction.[10] Furthermore, with Co-MOF as catalyst, does not need dichloromethane organic solvent, but catalyst Cr-MIL-101 does. Removal of **2** by filtration after only two hours completely cease the reaction, affording only 45% total conversion upon standing for 15 h, which demonstrates that no homogeneous catalyst species exists in the reaction solution and Co-MOF **2** is true heterogeneous catalyst.

Under the optimized conditions (2 eq TMSCN, 0.1 mol % catalyst, room temperature), nine carbonyl substrates, including aromatic, aliphatic aldehydes, and cyclic ketone were subjected to cyanosilylation reaction. The results were summarized in Table 3, which showed that the reaction has broad tolerance for various substrates. Under standard conditions, the corresponding products were obtained in excellent yields (above 90%) after 9-12 hours, when aromatic aldehyde with the electronic effect substituents (electron-donating CH_3, electron-withdrawing NO_2) or the position of substituents was employed. But aliphatic aldehyde and ketone typically give lower catalytic efficiency than aromatic aldehydes under standard conditions. due to their innate reduced reactivity. The conversion of cyclobutanone only reached 83% for the cyanosilylation reaction after prolonged reaction time (48 h). To investigate and explain the excellent catalytic activity of the open Co^{2+} sites, **1** and **1a** were tested under the same reaction conditions as well, 38.2% and 40.3% conversion of the cyanosilylation reaction were obtained (Table. S2), respectively, which was close to that of without catalyst, probably due to saturated octahedron geometry of all Co^{2+} ions in **1** and **1a**. It also indicated that coordinately unsaturated Co^{2+} sites in **2** have played a significant role in catalytic process. The pores of cobalt MOFs act as a "microreactor" to provide a favorable environment for the cyanosilylation reaction. The unsaturated Co^{2+} sites as Lewis acidity could lead to a preference for the adsorption of aromatic substrates thus enhance the reactivity of catalyst **2**.

To further explore activation of the carbonyl species occurs inside the pores or on the surface of the solid catalyst, substrates of increasing dimension were tested. As shown in table 3, a significant size-selectivity effect is observed with **2** catalyst, when the substrate was 1-naphthaldehyde with dimensions 9.7×8.4 Å^2, the conversion was reduced to 76% even prolong the reaction time (40 h). When a larger substrate 9-Anthraldehyde was used, no product was obtained though the temperature was raised to 50°C. The comparable results suggest that the pore systems of **2** are too small to readily accommodate the transition state geometry required for activating larger substrates, thus the cyanosilylation reaction takes place in the pore of catalyst **2**.

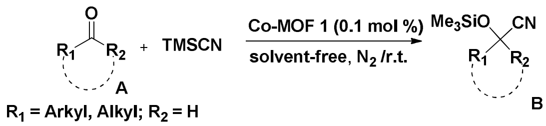

Table 3. The cyanosilylation of various carbonyl compounds with TMSCN[a]

Entry		R_1	R_2	Time (h)	Conv. (%)[b]		TOF (h^{-1})[c]
1	**A1**	Ph	H	12	**B1**	98	82.5
2	**A2**	2- $CH_3C_6H_4$	H	12	**B2**	93	99.0
3	**A3**	4-$CH_3C_6H_4$	H	12	**B3**	94	81.7
4	**A4**	4-$NO_2C_6H_4$	H	9	**B4**	99	106.6
5	**A5**	*n*-propyl	H	30	**B5**	90	63.4
6	**A6**	2-furyl	H	34	**B6**	95	33.0
7	**A7**	$(CH_2)_4$		40	**B7**	83	27.9
8	**A8**	1-nathphyl	H	40	**B8**	76	17.3
9	**A9**	9-anthryl	H	48	**B9**	0	--

[a] Reaction conditions: Me_3SiCN (1.0 mmol), aldehyde/ketone (0.5 mmol), 2 (0.003 g, 0.1 mol%), room temperature, under N_2 atmosphere; [b] Determined by GC based on the carbonyl substrate; [c] TOF calculated as [mol(substrates) × Conv.%]/[mol(catalyst) × (reaction time)]

Recycle Experiment

We also carried out experiments to demonstrate the recyclability of the MOFs catalyst. After the reaction was completed, the catalyst was easily separated from the reaction solution by centrifugation, washed with ethanol. It was dried at 150 °C under vacuum for 5 hours, which was regenerated for catalysis. As shown in Fig. 5, catalyst **2** can be reused at least five times without significant decreases in catalytic activity for the cyanosilylation reaction under the optimized conditions. The PXRD pattern of the reused catalyst was similar to that of the fresh catalyst **2** (Fig. S1), showed that the framework of **2** was well maintained after the catalytic reaction.

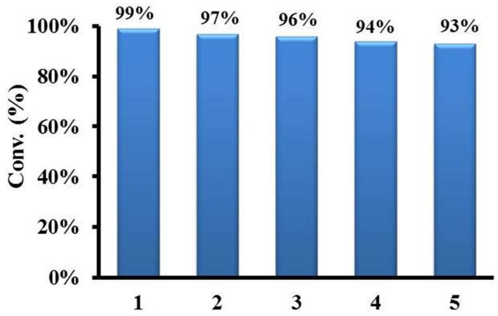

Fig. 5 Recycling tests with catalyst **2** for cyanosilylation reaction.

Conclusions

In summary, terminal coordinated water molecule has been successfully removed *via* dynamic Co-O$_{water}$ weakened intermediate **1a** in a butterfly-like tetranuclear cobalt cluster based 3D metal-carboxylate frameworks by SCSC transformation. Interestingly, the partly dehydrated MOF with UMCs Co^{2+} as strong Lewis acid can efficiently heterogeneous catalyze cyanosilylation of aldehydes and exhibit size-selectivity effect at room temperature under solvent-free conditions. Our finding will help to understand the structure–activity relations of a catalyst. Further studies will focus on modifying MOFs toward enantio-selective versions of cyanosilylation reactions, as well as on investigating the differences arising upon exchange of Co^{2+} for other reactive metal centers.

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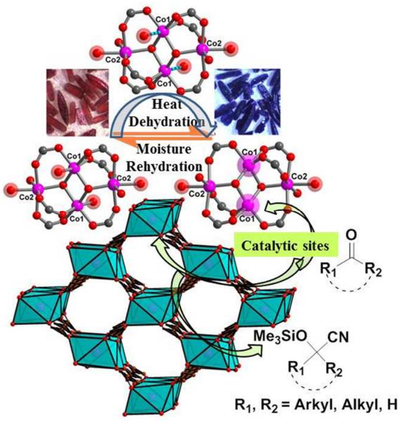
Table of Contents Graphic and Synopsis



Terminal coordinated water molecule has been successfully removed in a butterfly-like cobalt cluster based 3D frameworks by SCSC transformation. Interestingly, dehydrated phase with opened Co^{2+} sites as strong Lewis acid can efficiently heterogeneous catalyze cyanosilylation of aldehydes and exhibit size-selectivity effect at room temperature under solvent-free conditions, which will help understand the structure–activity relations of catalyst.