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View Article Online
DOI: 10.1039/C5CY01099C

Journal Name

ARTICLE

Co(II) complexes loaded into metal organic framework as an efficient heterogeneous catalyst for aerobic epoxidation of olefins

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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A series of efficient cobalt(II) anchored Cr-MOF (Cr-MIL-101-NH_2) catalysts, such as Co(II)@Cr-MIL-101-Sal, Co(II)@Cr-MIL-101-P2I and Co(II)@Cr-MIL-101-P3I, have been successfully synthesized by one-pot modifying terminal amino group with salicylaldehyde, pyridine-2-aldehyde or pyridine-3-aldehyde and anchoring Co(II) ions into mesoporous Cr-MOFs support. The Co(II)@Cr-MIL-101-P2I catalyst exhibited high catalytic performance for epoxidation of olefins with air as oxidant due to nitrogen atom in pyridine ring as a strong electron-withdrawing substituent, high dispersion of Co(II) species and high surface area for sufficient contact between substrate and active sites. The strong coordination interaction between Co(II) ions and chelating groups in Co(II)@Cr-MIL-101-P2I catalyst guaranteed the excellent recycled performance. Furthermore, the synthesized Co(II)@Cr-MIL-101-P2I catalyst realized general applicability towards varied olefins, such as cyclic olefins, tri-substituted olefins, aliphatic olefins and aromatic olefins.

Introduction

Metal organic frameworks (MOFs) are crystalline hybrid inorganic/organic solids with extended structures which can be utilized in many fields, such as gas separation and storage, sensors, drug delivery.[1-3] Especially, MOFs used for heterogeneous catalysis materials have sparked numerous interesting due to their high crystallinity with well-defined pore properties, high specific surface area and tailorable structure.[4-7] However, established MOFs have relatively low catalytic activity due to their limited selections of metals and organic ligands.[8] In order to further enhance the catalytic activity, the postsynthetic modification (PSM), defined as chemical derivatization of MOFs after their formation, becomes a practical and powerful tool to generate MOF-based heterogeneous catalysts with improved catalytic performance.[9,10]

MIL-101 discovered by Férey et al. shows a rigid zeotype cubic structure, which defines nano cages of about 2.9 and 3.4 nm with windows of 1.2 and 1.6 nm, respectively.[11] MIL-101-NH_2 maintains features of MIL-101 and introduces amino groups to the organic frames of the MOF lattice.[12] Cr-MIL-101-NH_2 can be a good candidate for PSM due to its large pores, good thermal stability as well as excellent chemical stability to water and common organic solvents.[13] Moreover, the reactive amino groups existed on the surface of Cr-MIL-101-NH_2 pores can provide great opportunities to covalently attach functional species. Tremendous efforts of the PSM strategy of Cr-MIL-101-NH_2, such as urea derived MIL-101 by introducing ethyl isocyanate[14,15] and photo-switchable MIL-101 by installing an azo functionality,[12] have been achieved successfully. However, the PSM strategy of Cr-MIL-101-NH_2 in catalytic oxidation reaction received much less attention.

Cobalt(II)-based organometallics, as efficient and selective homogeneous catalysts, have been applied in the epoxidation of olefin.[16,17] However, the main drawback of these catalysts is the catalyst recycling and product separation. To overcome these problems, various supports, such as polymer,[18,19] zeolite,[20] and silica,[21,22] have been used to load the homogeneous complex. Nevertheless, these heterogeneous catalysts typically involve some problems, such as trivial preparation, low chemical stability, non-uniform structure and low efficiency. Therefore, how to obtain an accessible, reusable and novel heterogeneous cobalt(II)-based catalyst which shows high activity of homogeneous catalyst and good re-usability of heterogeneous catalyst remains a challenge.

In this paper, a novel system for aerobic oxidation of olefins under air atmosphere employing metal organic framework-anchored cobalt(II) catalyst has been developed. Co(II)-based complex were immobilized into mesoporous Cr-MIL-101-NH_2 in one-pot method using salicylaldehyde, pyridine-2-aldehyde or pyridine-3-aldehyde as linker agent (Scheme 1). The amino group of Cr-MIL-101-NH_2 upon condensation with salicylaldehyde, pyridine-2-aldehyde or pyridine-3-aldehyde afforded a Schiff base moiety in the porous matrix. The Schiff base moieties as chelating groups can anchor the Co(II) ions. The Cr-MIL-101-NH_2 MOFs with high surface area were used as

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† Electronic Supplementary Information (ESI) available: [FTIR, ^{1}HNMR, diffuse reflectance UV-vis spectra and TGA the samples. Proposed reaction mechanism. XRD, FTIR and SEM of the recovered catalyst. Internal standard calibration.] See DOI: 10.1039/x0xx00000x

support to improve the dispersion of Co(II) ions. The uniform and big pores of MOFs guarantee sufficient contact between the catalytic active sites and the substrate. The strong coordination interaction between Co(II) ions and chelating groups in Co(II)@Cr-MIL-101-P2I catalyst enhances the re-usability of catalyst after the reaction. The developed cobalt(II)-based solid catalysts showed high catalytic activity, easy recovery, excellent recycling stability for the epoxidation of olefin in mild reaction condition.

Experimental

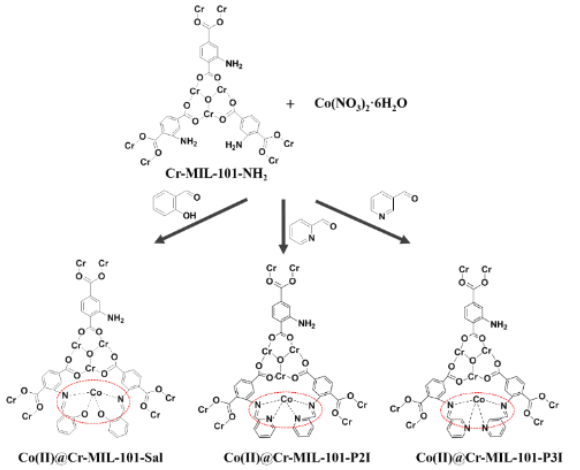
Synthesis of Cr-MIL-101-NH_2

Cr-MIL-101-NH_2 was prepared by a hydrothermal synthesis method according to the literature.[23] In a typical process, chromic nitrate hydrate (6.40 g, 16 mmol), 2-aminoterephthalic acid (2.88 g, 16 mmol) and sodium hydroxide (1.60 g, 40 mmol) were dissolved into deionized water (120 mL) under stirring, then the solution was transferred to a 200 mL Teflon-lined stainless steel autoclave and kept at 150 °C for 12 h. The autoclave was left to cool down to room temperature. The green precipitate was collected by centrifugation, and washed with deionized water, DMF and methanol, respectively. Finally, the products were dried under vacuum at 40 °C for overnight.

Preparation of cobalt(II)-based solid catalyst

In order to ensure that sufficient Co(II) moiety could be immobilized in the MOFs pores, the molar ratio of terminal amino group of MOFs, modifying aldehyde group and Co(II) was set at 1:4:1 during the synthesis of three kinds of catalysts.

To modify Cr-MIL-101-NH_2 with salicylaldehyde and load Co(II) ions, 0.40 g Cr-MIL-101-NH_2 were first dispersed into 30 mL methanol at a flask under ultrasond, and 0.62 mL salicylaldehyde and 0.43 g cobalt nitrate hexahydrate was added into the mixture, and then the solution refluxed at 85 °C for 10 h. Afterward, the precipitate was washed with abundant ethanol for three times and dried under vacuum at 40 °C overnight. The obtained product was labeled as Co(II)@Cr-MIL-101-Sal.



Scheme 1 Schematic illustration of the preparation of Co(II) complexes loaded into Cr-MIL-101-NH_2.

The synthesis procedure of modifying pyridine-2-aldehyde or pyridine-3-aldehyde and loading cobalt(II) on Cr-MIL-101-NH_2 was same as that of Co(II)@Cr-MIL-101-Sal but replace salicylaldehyde with pyridine-2-aldehyde or pyridine-3-aldehyde, respectively. The obtained product was accordingly named as Co(II)@Cr-MIL-101-P2I or Co(II)@Cr-MIL-101-P3I.

Catalytic epoxidation reactions

The catalytic epoxidation reaction was carried out in the liquid phase in a 25 mL two-neck flask. Olefin (1 mmol), catalyst (0.6 mol% cobalt) and isobutyraldehyde (2 mmol) were added into acetonitrile (5 mL). The reaction mixture was stirred at 35 °C for 5 h under air atmosphere. After the reaction, nitrobenzene (0.2 mmol) as an internal standard was added into the mixture for the determination of yield and selectivity. The filtrate was analyzed by Agilent 7890/5975C-GC/MS.

For catalyst recycling, the catalyst was filtered from the reaction solution, washed with acetonitrile and dried for the next run. The dried catalyst was reused for the epoxidation of *cis*-cyclooctene in acetonitrile under the same reaction conditions.

The hot filtration test was performed by separating the catalyst at 1 h from the reaction mixture, and the filtrate was stirred for a further 4 h. The reaction progress was monitored by GC/MS.

Characterization

Field-emission scanning electron microscope (FESEM) images were observed by a ZEISS SUPRA55 operated at the accelerating voltages of 10 kV. Fourier transform infrared (FTIR) spectra were obtained by a Nicolet 6700 using the potassium bromide (KBr) pellet technique. Diffuse reflectance UV-vis spectra were recorded on a UV-2550 spectrometer equipped with a diffuse reflectance integrating sphere coated with $BaSO_4$, which also served as a standard. Powder X-ray diffraction (XRD) patterns were recorded by a M21X diffractometer (MAC Science Co. Ltd., Japan) using a Cu Karadiation (k = 1.541 Å) source at 40 kV and 200 mA. The chemical compositions were analysed with inductively coupled plasma-atomic emission spectrometry (ICP-AES, Vavian 715-ES) and an X-ray photoelectron spectrometer (XPS, ESCALAB 250Xi). C 1s line at 284.8 eV from adventitious carbon was used as the reference for binding energy. The thermal gravimetric analysis (TGA) was used to investigate the thermal decomposition behavior of the samples using Netzsch STA449F3 instrument at a heating rate of 10 °C min^{-1} under an air flow. Nitrogen adsorption-desorption isotherms were measured at 77 K with a Micromeritics ASAP 2420 adsorption analyzer. The specific surface area was calculated with the Brunauer-Emmett-Teller (BET) method. The pore size distributions were derived from the adsorption branches of isotherms by using the Barrett-Joyner-Halenda (BJH) model. The catalytic results were analyzed with a gas chromatography-mass spectrum (GC-MS, Agilent7890/5975C-GC/MSD), and nitrobenzene was used as an internal standard.

Results and discussion

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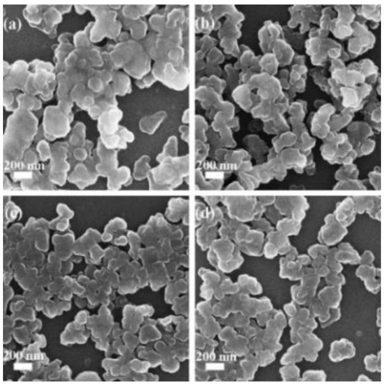

Fig. 1 SEM images of (a) Cr-MIL-101-NH$_2$, (b) Co(II)@Cr-MIL-101-Sal, (c) Co(II)@Cr-MIL-101-P2I and (d) Co(II)@Cr-MIL-101-P3I.

Catalyst characterization

Typical morphologies of Cr-MIL-101-NH$_2$, Co(II)@Cr-MIL-101-Sal, Co(II)@Cr-MIL-101-P2I and Co(II)@Cr-MIL-101-P3I samples were shown in Fig. 1. SEM images of Cr-MIL-101-NH$_2$ (Fig. 1a) showed that the as-prepared MOFs was particles and the particle size was around 50-300 nm, which was similar to the previous reports.[23] After modifying with salicylaldehyde, pyridine-2-aldehyde or pyridine-3-aldehyde followed by anchoring of Co(II) ions, the morphology and size of Co(II)@Cr-MIL-101-Sal (Fig. 1b), Co(II)@Cr-MIL-101-P2I (Fig. 1c) and Co(II)@Cr-MIL-101-P3I (Fig. 1d) were similar to those of Cr-MIL-101-NH$_2$, indicating the strong chemical stability of Cr-MIL-101-NH$_2$ support during the aldehyde group modification and Co(II) ions anchoring procedure.

XRD patterns of Cr-MIL-101-NH$_2$, Co(II)@Cr-MIL-101-Sal, Co(II)@Cr-MIL-101-P2I and Co(II)@Cr-MIL-101-P3I samples were shown in Fig. 2. The XRD pattern of Cr-MIL-101-NH$_2$ sample corresponded well with the literature data, which indicated that the desired MOFs support was obtained.[14,23] Co(II)@Cr-MIL-101-Sal, Co(II)@Cr-MIL-101-P2I and Co(II)@Cr-MIL-101-P3I samples showed similar diffraction patterns to that of Cr-MIL-101-NH$_2$, which clearly suggested that the framework structure of Cr-MIL-101-NH$_2$ remained intact during the modifying and loading procedure. Moreover, comparing with Cr-MIL-101-NH$_2$, a decrease at the peak intensity $2\theta = 3.2$ of the Co(II)@Cr-MIL-101-Sal, Co(II)@Cr-MIL-101-P2I and Co(II)@Cr-MIL-101-P3I samples was observed, which was attributed to the modifying complexes inside the pores.[24]

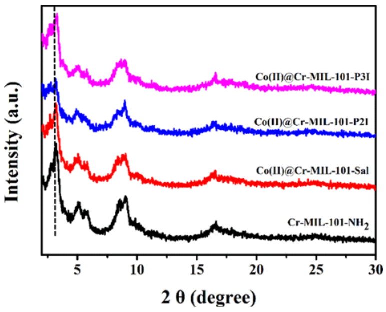

Fig. 2 Powder XRD patterns of Cr-MIL-101-NH$_2$, Co(II)@Cr-MIL-101-Sal, Co(II)@Cr-MIL-101-P2I and Co(II)@Cr-MIL-101-P3I.

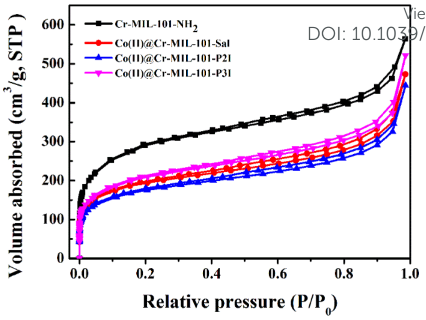

Fig. 3 Nitrogen adsorption-desorption isotherms of Cr-MIL-101-NH$_2$, Co(II)@Cr-MIL-101-Sal, Co(II)@Cr-MIL-101-P2I and Co(II)@Cr-MIL-101-P3I.

In order to evaluate the surface area, pore volume and pore structure of the samples, nitrogen adsorption-desorption isotherms were performed and shown in Fig 3. All the samples featured same type IV isotherm, which further indicated that the pore structure was well retained after functionalization of the linker and anchoring of Co(II) ions. The surface area of the samples was calculated with the Brunauer-Emmett-Teller (BET) method. The total pore volume was obtained from the volume of N_2 adsorption at P/P0 = 0.985. The BET surface area and the total pore volume of the Cr-MIL-101-NH$_2$ sample were 1039.2 m^2 g^{-1} and 1.56 cm^3 g^{-1}, respectively. An obvious decrease in the BET surface area as well as the total pore volume was observed in the Co(II)@Cr-MIL-101-Sal, Co(II)@Cr-MIL-101-P2I and Co(II)@Cr-MIL-101-P3I sample, which demonstrated that the pores of Cr-MIL-101-NH$_2$ were occupied by Co(II) complexes.[21,24] FTIR (Fig. S1†) and ^{1}H NMR (Fig. S2†) and diffuse reflectance UV-vis spectra (Fig. S3a†) results also confirmed the successful modifying of Cr-MIL-101-NH$_2$. The Co(II)@Cr-MIL-101-P2I sample had the lowest BET surface area and total pore volume, which could be ascribed to its high content of the anchored Co(II) complex. The content of cobalt measured by ICP-AES in the Co(II)@Cr-MIL-101-Sal, Co(II)@Cr-MIL-101-P2I and Co(II)@Cr-MIL-101-P3I sample (Table 1) was 0.12 mmol g^{-1}, 0.29 mmol g^{-1} and 0.03 mmol g^{-1}, respectively. Under the same synthesis procedure and the same molar ratio of raw material, the varied loading content of cobalt in these samples should be due to the different coordination environment of Co(II) ions.

In order to gain deeper insight into the surface constitution of the catalysts, the XPS spectrum of the Co(II)@Cr-MIL-101-P2I sample was investigated. As shown in Fig. 4a, the sample contained C, O, Cr, N and Co elements. The Cr 2p1/2 and Cr 2p3/2 signals showed two peaks at 586.8 eV and 577.2 eV (Fig. 4b), respectively. Both peaks corresponded to typical binding

Table 1 The BET surface area, the pore volume and ICP analysis result of Cr-MIL-101-NH$_2$, Co(II)@Cr-MIL-101-Sal, Co(II)@Cr-MIL-101-P2I and Co(II)@Cr-MIL-101-P3I.

Samples	S_{BET} (m^2 g^{-1})	Total Pore Volume (cm^3 g^{-1})	ICP (Co mmol g^{-1})
Cr-MIL-101-NH$_2$	1039.2	1.56	-
Co(II)@Cr-MIL-101-Sal	702.5	0.73	0.12
Co(II)@Cr-MIL-101-P2I	632.2	0.69	0.29
Co(II)@Cr-MIL-101-P3I	757.1	0.81	0.03

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DOI: 10.1039/C5CY01099C

energies for Cr^{3+}.[25] No other oxidation states of chromium were observed, which indicated the chromium trimers were chemically stable during functionalization of the linker and anchoring of cobalt precursor. The peak-fitted N1s core-line spectrum of Co(II)@Cr-MIL-101-P2I (Fig 4c) showed three resolved peaks at 400.4 eV, 399.7 eV and 398.9 eV, corresponding to imine (-C=N-) groups[26] amino ($-NH_2$) groups [27] and pyridine N,[28] respectively. Additionally, the peak at 406.7 eV was due to the existence of the N in NO^{3-} group.[29] The Co $2p_{3/2}$ and Co $2p_{1/2}$ core level peak was at a binding energy of 781.7 eV and 796.9 eV, respectively (Fig 4d). The Co $2p_{1/2}$ and Co $2p_{3/2}$ separation of 15.2 eV for tethered cobalt catalyst was identical to the value reported for Co(salen) $\cdot 1/2H_2O$.[30] Additionally, the presence of satellite lines at a binding energy of 803.4 eV and 786.4 eV was furthermore indicative of a high-spin Co^{2+} center in the Co(II)@Cr-MIL-101-P2I sample.[31]

TGA curves of the Cr-MIL-101-NH_2, Co(II)@Cr-MIL-101-Sal, Co(II)@Cr-MIL-101-P2I and Co(II)@Cr-MIL-101-P3I sample were shown in Fig. S4†. The total weight loss of the Cr-MIL-101-NH_2 sample occurred by two weight-loss steps. The initial weight loss of 9.8 % in the range 40-230 °C was assigned to the loss of free guest water in the pores. The subsequent weight loss of 56.6% in the range 230-330 °C was due to the decomposition of the organic framework. It was noteworthy that the weight-loss of Co(II)@Cr-MIL-101-Sal, Co(II)@Cr-MIL-101-P2I and Co(II)@Cr-MIL-101-P3I sample were similar to that of Cr-MIL-101-NH_2. The cobalt(II)-based solid catalysts showed a higher decomposed temperature and were more stable than Cr-MIL-101-NH_2 attributed to the rigid structure of the formed coordinated Co(II) complexes.[24]

Catalytic study

The catalytic activity of cobalt(II)-based solid catalyst was studied by catalyzing olefin epoxidation with 1 atm air and isobutyraldehyde in acetonitrile. Epoxidation of *cis*-cyclooctene was carried out as a model reaction to identify the optimal reaction conditions. Initially, a blank control experiment was performed, and the conversion of *cis*-cyclooctene was only 20% in 5 h (Table 2, entry 1), which agreed with previous report.[32] No change of the conversion of *cis*-cyclooctene was observed by employing Cr-MIL-101-NH_2 as the catalyst (Table 2, entry 2). Interestingly, when 0.6 mol% $Co(NO_3)_2 \cdot 6H_2O$ was used as the catalyst, the conversion was about 99% (Table 2, entry 3). The conversion of *cis*-cyclooctene was only 47% when 0.3 mol% $Co(NO_3)_2 \cdot 6H_2O$ was applied as the catalyst (Entry 4, Table 2). The conversion of *cis*-cyclooctene was not improved when the mixture of $Co(NO_3)_2 \cdot 6H_2O$ and diaminocyclohexane (Entry 5, Table 2) or the mixture of $Co(NO_3)_2 \cdot 6H_2O$ and 2-aminoterephthalic acid (Entry 6, Table 2) were used as the homogeneous catalyst, which indicated that the homogeneous organic aminos did not contribute to the catalytic activity and Co(II) ions played a significant role in the epoxidation of *cis*-cyclooctene. However, the homogeneous system leads to difficult for product separation and catalyst recycling. When Cr-MIL-101-NH_2-anchored cobalt(II) complex including Co(II)@Cr-MIL-101-Sal, Co(II)@Cr-MIL-101-P2I and Co(II)@Cr-MIL-101-P3I sample were used as the catalyst, the conversion of *cis*-cyclooctene was 78% (Table 2, entry 7), 99% (Table 2, entry 8) and 92% (Table 2, entry 9), respectively. The TOFs for *cis*-cyclooctene epoxidation catalysed by Co(II)@Cr-MIL-101-Sal, Co(II)@Cr-MIL-101-P2I and Co(II)@Cr-MIL-101-P3I catalyst were calculated to be 25.74 h-1, 32.67 h-1 and 30.36 h-1, respectively, which were higher than the Co6-CP-

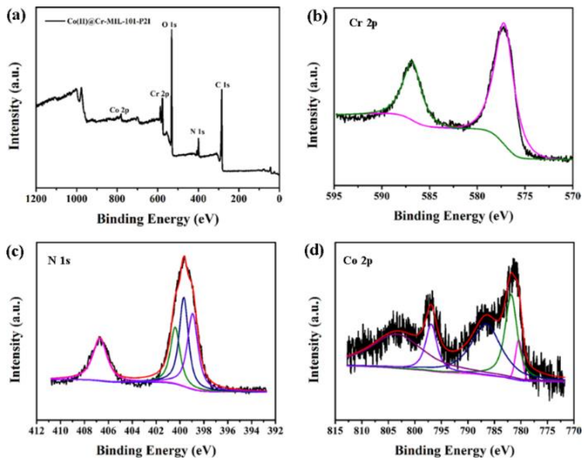
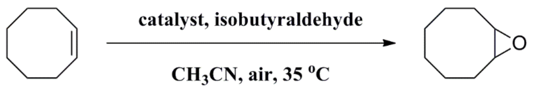


Fig. 4 X-ray photoelectron spectrum of (a) the Co(II)@Cr-MIL-101-P2I sample, (b) Cr 2p, (c) N 1s and (d) Co 2p.

Table 2 Catalyst screening in the epoxidation of *cis*-cyclooctene[a]



Entry	Catalyst	Conv. (%)[b]	Sel. (%)[b]	TOF$_{epo}$ (h^{-1})
1	No	20	>99	-
2[c]	Cr-MIL-101-NH_2	21	>99	-
3[d]	$Co(NO_3)_2 \cdot 6H_2O$	>99	>99	54.45
4[e]	$Co(NO_3)_2 \cdot 6H_2O$	47	>99	-
5[f]	$Co(NO_3)_2 \cdot 6H_2O$ + diaminocyclohexane	48	>99	-
6[g]	$Co(NO_3)_2 \cdot 6H_2O$ + 2-aminoterephthalic acid	51	>99	-
4[h]	Co(II)@Cr-MIL-101-Sal	78	>99	25.74
5[h]	Co(II)@Cr-MIL-101-P2I	>99	>99	32.67
6[h]	Co(II)@Cr-MIL-101-P3I	92	>99	30.36
7[i]	Co(II)@Cr-MIL-101-Sal	76	>99	-
8[i]	Co(II)@Cr-MIL-101-P2I	>99	>99	-
9[i]	Co(II)@Cr-MIL-101-P3I	57	>99	-

[a] Reaction conditions: *cis*-cyclooctene (1.0 mmol), catalyst, isobutyraldehyde (2 mmol), acetonitrile (5.0 mL), at 35 °C under air atmosphere stirring for 5 h.
[b] Conversion and selectivity were determined by GC/MS using nitrobenzene as internal standard.
[c] Reaction was performed using 20 mg MOF.
[d] Reaction was stirring for 3 h.
[e] 0.3 mol% Co(II), reaction was stirring for 3 h..
[f] 0.3 mol% Co(II) + diaminocyclohexane, reaction was stirring for 3 h.
[g] 0.3 mol% Co(II) + 2-aminoterephthalic acid, reaction was stirring for 3 h.
[h] Fresh catalyst, 0.6 mol% Co(II) based on the amount of cobalt in sample.
[i] 2 cycle catalyst.

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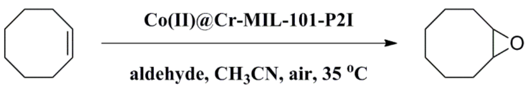
DOI: 10.1039/C5CY01099C

catalysed *cis*-cyclooctene epoxidation with a TOF of 3.72 h^{-1} at 120 ^{o}C. [33] Although the TOF of the solid catalysts were lower than that of $Co(NO_3)_2 \bullet 6H_2O$ with a TOF of 54.45 h^{-1}, they could be recollected and reused. The enhanced catalytic efficiency for the epoxidation of *cis*-cyclooctene was due to the high dispersion of active catalytic sites at the pore walls of MOFs. Importantly, the conversion of *cis*-cyclooctene with Co(II)@Cr-MIL-101-Sal catalyst was lower than that of Co(II)@Cr-MIL-101-P2I and Co(II)@Cr-MIL-101-P3I catalyst, which could be due to the nitrogen atom in pyridine ring is a π electron acceptor.[34,35] It can be regarded as a strong electron-withdrawing substituent which could be conducive to electrophilic attack of the Co-peroxy species and then accelerated the rate of epoxidation (Fig. S5†). However, the conversion of *cis*-cyclooctene was significantly decreased after re-collected Co(II)@Cr-MIL-101-P3I sample was used as the catalyst again (Table 2, entry 9), which can be ascribed to the relatively weakly coordination ability of the chelating groups. The XRD patterns of Co(II)@Cr-MIL-101-Sal, Co(II)@Cr-MIL-101-P2I and Co(II)@Cr-MIL-101-P3I catalysts after 2 cycles reaction were shown in Fig. S6†. No obvious change can be observed comparing the powder XRD of the fresh and reused catalyst. Furthermore, the cobalt content of the reused Co(II)@Cr-MIL-101-Sal and Co(II)@Cr-MIL-101-P2I catalyst determined by ICP-AES analysis also showed almost no obvious reduction. However, the cobalt content of the reused Co(II)@Cr-MIL-101-P3I catalyst was reduced to 0.018 mmol g^{-1} from 0.03 mmol g^{-1}, ICP-AES analysis of the reaction solution after one cycle of epoxidation for Co(II)@Cr-MIL-101-P3I catalyst showed the presence of 0.34 ppm of the cobalt in reaction solution, which further indicated that Co(II) ions were chelated relatively weakly in Co(II)@Cr-MIL-101-P3I sample. Therefore, among three kinds of heterogeneous cobalt(II)-based catalysts, Co(II)@Cr-MIL-101-P2I was chosen as optimized catalyst for the epoxidation of *cis*-cyclooctene.

Table 3 Aldehyde screening in the oxidation of *cis*-cyclooctene[a]

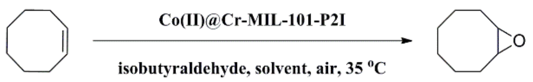


Entry	Aldehyde (mmol)	Conv. (%)[b]	Sel. (%)[b]
1	-	-	-
2	Isobutyraldehyde (2 mmol)	>99	>99
3	Cyclohexanecarboxaldehyde (2 mmol)	86	>99
4	Heptaldehyde (2 mmol)	71	>99
5	Benzaldehyde (2 mmol)	<5	>99
6	Isobutyraldehyde (1 mmol)	44	>99
7	Isobutyraldehyde (0.5 mmol)	18	>99

[a] Reaction conditions: *cis*-cyclooctene (1.0 mmol), Co(II)@Cr-MIL-101-P2I catalyst (0.6 mol% cobalt), aldehyde, acetonitrile (5.0 mL), at 35 ^{o}C under air atmosphere stirring for 5 h.

[b] Conversion and selectivity were determined by GC/MS using nitrobenzene as internal standard.

Table 4 Oxidation of *cis*-cyclooctene in different solvents over Co(II)@Cr-MIL-101-P2I catalyst[a]



Entry	Solvent	Conv. (%)[b]	Sel. (%)[b]
1	acetonitrile	>99	>99
2	acetone	82	>99
3	ethyl acetate	59	>99
4	dichloromethane	48	>99
5	n-Hexane	25	>99
6	ethyl alcohol	0	-

[a] Reaction conditions: *cis*-cyclooctene (1.0 mmol), Co(II)@Cr-MIL-101-P2I catalyst (0.6 mol% cobalt), isobutyraldehyde (2.0 mmol), solvent (5.0 mL), at 35 ^{o}C under air atmosphere stirring for 5 h.

[b] Conversion and selectivity were determined by GC/MS using nitrobenzene as internal standard.

Aldehyde acted as a sacrificial co-reductant, could be transformed in situ to a carboxylperoxo radical which facilitated oxygen transfer to aerobic epoxidation of olefins.[36,37] Several aldehydes were evaluated as additive for the epoxidation of *cis*-cyclooctene in the presence of Co(II)@Cr-MIL-101-P2I catalyst. The blank control experiment showed no reactivity for the formation of 1,2-Epoxycyclooctane (Table 3, entry 1), which indicated aldehyde was an critical additive for aerobic epoxidation. The yield of 1,2-Epoxycyclooctane was reached up to 99% when isobutyraldehyde was used as the additive (Table 3, entry 2), which was higher than that of the cyclic cyclohexanecarboxaldehyde (86%, Table 3, entry 3), aliphatic heptaldehyde (71%, Table 3, entry 4) and aromatic benzaldehyde (<5%, Table 3, entry 5). The distinctly different yields further suggested the steric and electronic effects of the aldehyde were vital for dioxygen activation in the epoxidation of olefins. Moreover, it gave compromised yield of 1,2-Epoxycyclooctane using lower amounts of isobutyraldehyde (Table 3, entry 6-7).

Solvents play a crucial role in epoxidation reactions. The selected model reaction was performed in different solvents and the results were summarized in Table 4. The yield of 1,2-Epoxycyclooctane was 99%, 82%, 59%, 48% and 25% when acetonitrile, acetone, ethyl acetate, dichloromethane and n-Hexane were employed as the solvent, respectively (Table 4, entry 1-5), which revealed that the solvent with greater polarity was beneficial to the enhancing of the conversion of *cis*-cyclooctene. This can be due to that the greater polarity of the solvent facilitated the dispersion and collision of the catalyst, the substrate and the oxygen source.[38] However, no 1,2-Epoxycyclooctane was observed when ethyl alcohol was used as solvent owing to the coordination with Co(II) ions and competing oxidation reaction.[5,27]

The evolution of the conversion of *cis*-cyclooctene as reaction time using the fresh Co(II)@Cr-MIL-101-P2I catalyst was explored and shown in Fig. 5 (curve a). The conversion was increased linearly as the reaction time and reached 77% at 2 h.

Then, the conversion was increased gradually and *cis*-cyclooctene was completely converted to 1,2-Epoxycyclooctane at 5 h. Additionally, the selectivity of desired product maintained 99% during the whole reaction process. Therefore, the optimized catalytic condition involved 1 mmol substrate, 0.6 mol% Co(II)@Cr-MIL-101-P2I catalyst based on cobalt, 2 mmol isobutyraldehyde as an additive under 1 atm air atmosphere at 35 °C stirring for 5 hours. Such catalytic system is more efficient and eco-friendly than the cobalt(II)-based zeolites X catalyst at 100 °C[39] and cobalt(II)-based MCM-41 catalyst at 110 °C.[21]

To confirm that the Co(II)@Cr-MIL-101-P2I catalyst was heterogeneous for the epoxidation reaction, a hot filtration test was carried out. The solid catalyst was separated by centrifugation at 1 h in the first cycle, and the residual liquid phase was transferred into a clean reactor vessel and stirred for another 4 h under the same reaction condition. In absence of catalyst (Fig 5b), GC results showed that the conversion of *cis*-cyclooctene was increased to 51% from 44%, which was caused by isobutyraldehyde (Fig. S7†). Furthermore, ICP-AES analysis of the filtrate showed almost no presence of the cobalt in the solution.

In order to evaluate the reusability of Co(II)@Cr-MIL-101-P2I catalyst, the epoxidation of *cis*-cyclooctene was performed using recovered catalyst under the optimized catalytic condition. After each reaction, the catalyst was recovered by simple centrifugation and washed with acetonitrile for the next reaction run. The catalyst remained active during each recycle and retained 95% of conversion, 93% of selectivity even after 5 recycles (Fig. 6). XRD and FTIR results (Fig. S8†) of fresh and recovered Co(II)@Cr-MIL-101-P2I catalyst showed that the composition of the catalyst had no obvious change after reaction. While the SEM images (Fig. S8†) showed that the structure of the catalyst was slightly aggregated. ICP-AES analysis indicated the cobalt content was reduced from 0.29 mmol g^{-1} to 0.26 mmol g^{-1}. This may lead to the slight reduction in the conversion and selectivity of the epoxidation of *cis*-cyclooctene.

The general applicability of the epoxidation in the presence of air over Co(II)@Cr-MIL-101-P2I catalyst was demonstrated in Table 5. Varied cyclic olefins, such as cyclopentene, cyclohexene, cycloheptene and norbornene, were transformed to the corresponding epoxides with high conversion and selectivity (Table 5, entry 1-4). The relatively bulky cyclic olefin of cyclododecene showed lower catalytic activity than *cis*-cyclooctene under the same reaction condition because of more difficult electrophilic attack of the Co-peroxy species (Table 5, entry 5). The epoxidation of 1,5-cyclooctadene occurred only at one double bond with compromised yield and the main product was 9-oxabicyclo [6.1.0]non-4-ene (Table 5, entry 6). The tri-substituted olefin, such as *α*-pinene, was converted to the corresponding epoxide with excellent conversion (>99%) and selectivity (>99%) (Table 5, entry 7). Moreover, aliphatic olefin, generally considered as inactive towards epoxidation, such as 1-

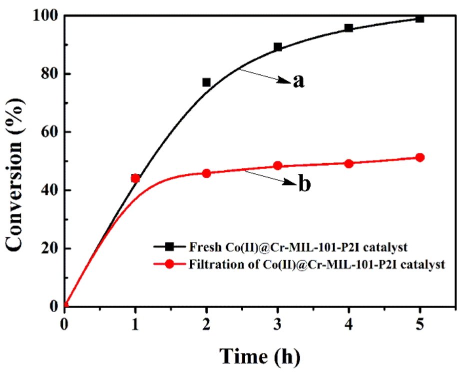


Fig. 5 Curve (a): change of conversion over the reaction time for model reaction catalyzed by fresh Co(II)@Cr-MIL-101-P2I catalyst, curve (b): leaching test.

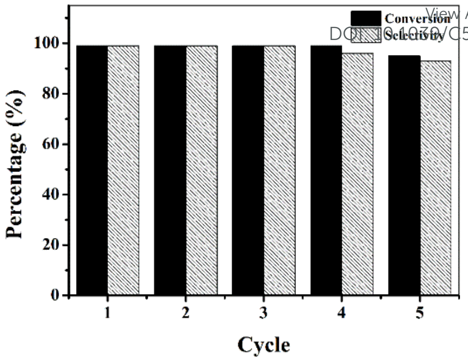
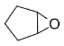
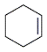
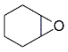
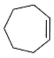
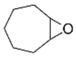
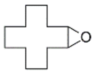
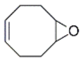
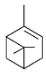
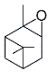
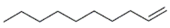
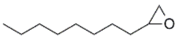
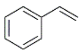
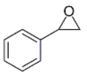
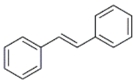
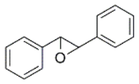
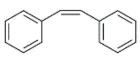
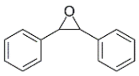


Fig. 6 The reusability of the Co(II)@Cr-MIL-101-P2I catalyst for the epoxidation of *cis*-cyclooctene.

Table 5 Scope in the epoxidation of olefins catalyzed by Co(II)@Cr-MIL-101-P2I catalyst[a]

Entry	Substrate	Product	Time (h)	Conv. (%)[b]	Sel. (%)[b]	TOF$_{epo}$ (h^{-1})
1			5	>99	82	27.06
2			5	>99	74	24.42
3			5	>99	94	31.02
4			5	>99	>99	33.00
5			5	69	>99	22.77
6			5	46	97	14.87
7			5	>99	>99	33.00
8			12	62	>99	8.53
9			24	80	59	3.28
10			24	91	>99	6.26
11			24	45	>99	3.09

[a] Reaction conditions: subatrate (1.0 mmol), Co(II)@Cr-MIL-101-P2I catalyst (0.6 mol% cobalt), isobutyraldehyde (2.0 mmol), solvent (5.0 mL), at 35 °C under air atmosphere.

[b] Conversion and selectivity were determined by GC/MS using nitrobenzene as internal standard.

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decene, was oxidized to 1,2-epoxydecane in decent conversion and high selectivity (Table 5, entry 8). The aromatic olefins, such as styrene, *trans*-stilbene and *cis*-stilbene, were also catalytically epoxidized. Interestingly, the epoxidation of *trans*-stilbene proceeded more smoothly than that of styrene and *cis*-stilbene due to the steric hindrance effect (Table 5, entry 9-11).[40] The epoxidation of styrene proceeded in low yield along with the formation of benzaldehyde byproduct. *Trans*-stilbene showed remarkable conversion over 91% of epoxide as the sole product while *cis*-stilbene only gave 45% yield of epoxide.

Conclusions

In summary, highly effective and recyclable cobalt(II)-based solid catalysts have been successfully synthesized and applied for epoxidation of olefins with air as the oxidant and isobutyraldehyde as a sacrificial co-reductant. In Co(II)@Cr-MIL-101-P2I catalyst, nitrogen atom in pyridine ring as a strong electron-withdrawing substituent ensured high activity, and the strong coordination interaction between Co(II) ions and chelating groups guaranteed the excellent recycled performance. The high dispersion of Co(II) species promoted the sufficient contact between substrate and active sites. The catalyst showed good general applicability towards varied olefins, such as cyclic olefins, tri-substituted olefins, aliphatic olefins and aromatic olefins. The Co(II) incorporation strategy provides a highly efficient, low-cost and simple approach for the synthesis of heterogeneous catalyst and can be extended to the structure design of other MOF-based nanohybrid catalysts.

Acknowledgements

We thank the National High Technology Research and Development Program of China (863 program) (No. 2013AA031702) and Co-building Special Project of Beijing Municipal Education.

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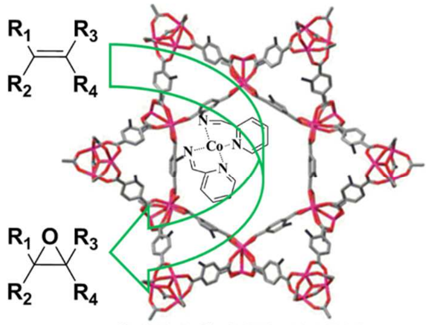
Co(II) complexes loaded into metal organic framework as an efficient heterogeneous catalyst for aerobic epoxidation of olefins

Efficient cobalt(II) anchored Cr-MOF (Cr-MIL-101-NH_2) catalyst, Co(II)@Cr-MIL-101-P2I, have been successfully synthesized by one-pot modifying terminal amino group with pyridine-2-aldehyde and anchoring Co(II) ions into mesoporous Cr-MOFs support. Nitrogen atom in pyridine ring as a strong electron-withdrawing substituent ensured high catalytic performance, and strong coordination interaction between Co(II) ions and chelating groups guaranteed the good re-usability.



Co(II)@Cr-MIL-101-P2I