Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

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

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In order to prove the successful formation of the covalent functionalized compound, FTIR spectra of samples were performed and shown in Fig S1. The double peaks at 3460 cm^{-1} and 3380 cm^{-1} of Cr-MIL-101-NH_2 were clearly observed, which were attributed to the asymmetrical and symmetrical stretching vibration adsorption of the amino groups. Additionally, the peak at 1660 cm^{-1} corresponded to the N-H bending vibration of primary amino. [S1] After anchoring of Co(II) complex, the relative intensities of peaks at 3460 cm^{-1} and 3380 cm^{-1} was decreased obviously and the peak at 1660 cm^{-1} was disappeared, which indicated the amino groups were transformed to the amino groups.

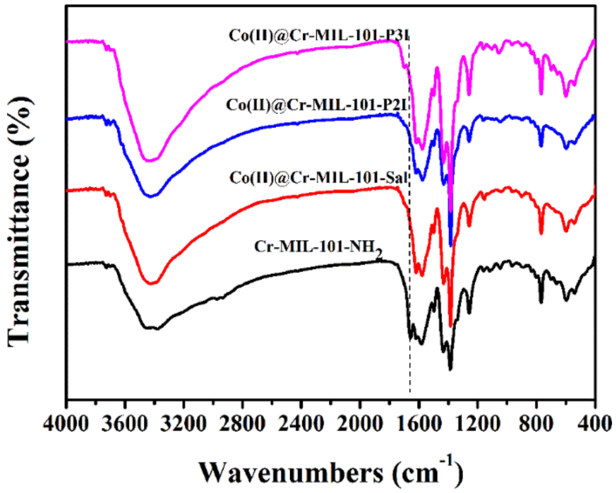

Fig. S1 FTIR spectra of the Cr-MIL-101-NH_2, Co(II)@Cr-MIL-101-Sal, Co(II)@Cr-MIL-101-P2I and Co(II)@Cr-MIL-101-P3I sample.

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 samples were decomposed by adding NaOH, respectively. After separation of $Cr(OH)_3$ by filtration and addition of HCl, an orange solid was obtained, respectively. The ^1H NMR spectra of these solids were shown in Fig S2. New proton peaks showed around 6.0-10.2 ppm corresponding to the salicylaldehyde, pyridine-2-aldehyde or pyridine-3-aldehyde modification of Cr-MIL-101-NH_2, which confirmed the successful modification.

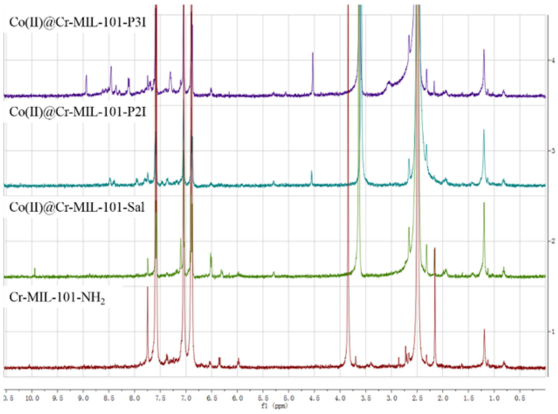

Fig. S2 ^{1}H NMR spectra of the Cr-MIL-101-NH$_2$, Co(II)@Cr-MIL-101-Sal, Co(II)@Cr-MIL-101-P2I and Co(II)@Cr-MIL-101-P3I sample.

The diffuse reflectance UV-vis spectra of the fresh 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 performed. As shown in Fig. S3a†, the bands in the high energy region of Cr-MIL-101-NH$_2$ and the solid catalysts could be assigned to the π-π* transition of the organic linker.[S2] The UV-vis spectrum of the solid catalysts showed a new band at 265 nm due to the charge transfer transition arising from π-electron interactions between the metal and ligand, which involves a ligand to metal electron transfer typical for a Co-Schiff base complex.[S3,S4] The UV-vis result along with the FTIR and XPS analysis confirmed the successful modifying of Cr-MIL-101-NH$_2$. Furthermore, the intensity of the band at 265 nm in the UV-vis spectra of reused Co(II)@Cr-MIL-101-P3I catalyst after 2 cycles reaction was slightly decreased(Fig. S3d†), which may be ascribed to the relatively weakly coordination ability of the chelating groups.

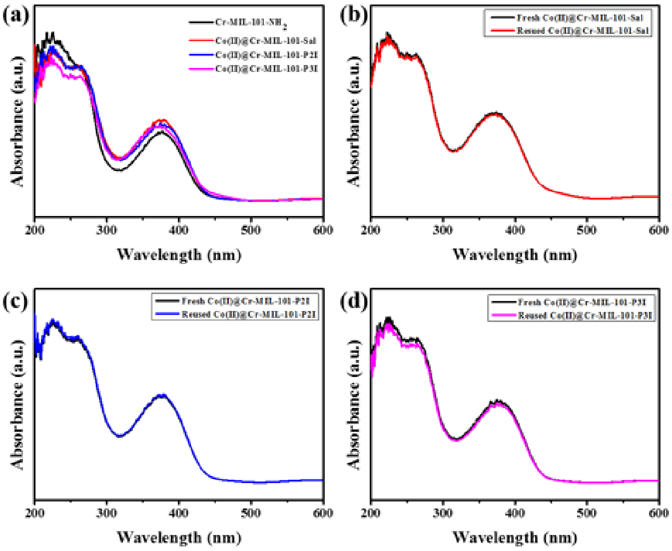

Fig. S3 The diffuse reflectance UV-vis spectra of (a) the fresh Cr-MIL-101-NH2, Co(II)@Cr-MIL-101-Sal, Co(II)@Cr-MIL-101-P2I and Co(II)@Cr-MIL-101-P3I sample, (b) reused Co(II)@Cr-MIL-101-Sal, (c) reused Co(II)@Cr-MIL-101-P2I and (d) reused Co(II)@Cr-MIL-101-P3I after 2 cycles reaction.

TGA curves showed that these solid catalysts were more stable than Cr-MIL-101-NH_2 MOFs and showed good thermal stability below 250 °C.

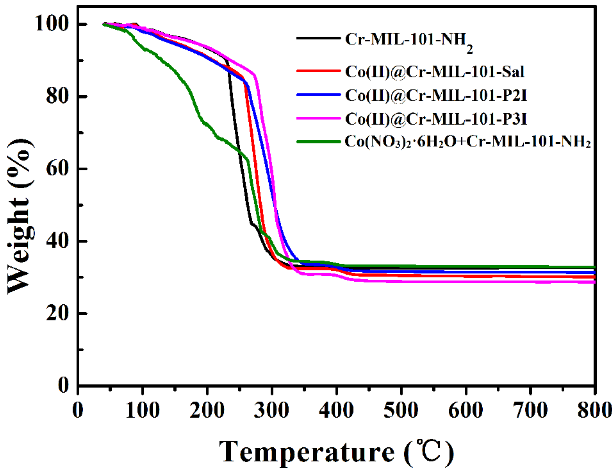

Fig. S4 TGA curves of the Cr-MIL-101-NH_2, Co(II)@Cr-MIL-101-Sal, Co(II)@Cr-MIL-101-P2I, Co(II)@Cr-MIL-101-P3I sample physical mixture of Cr-MIL-101-NH_2 and $Co(NO_3)_2$•$6H_2O$..

As shown in Fig. S5, the reaction mechanism for the epoxidation of *cis*-cyclooctene to 1,2-Epoxycyclooctane using Co(II)@Cr-MIL-101-P2I catalyst in the presence of isobutyraldehyde was proposed based on previous literature.[S5,S6] First, the Co-peroxy species were generated by reacting isobutyraldehyde with oxygen instituted by the Cr-MOF framework. Then, an electrophilic attack of the Co-peroxy species on *cis*-cyclooctene happeneds, along with a concerted oxygen transferred. Finally, the Co-O bond of Co-peroxy species ruptured, getting the epoxide of *cis*-cyclooctene and regenerating the catalyst. Therefore, a pyridine N as a strong electron-withdrawing substituent in Co(II)@Cr-MIL-101-P2I catalyst could be conducive to electrophilic attack of the Co-peroxy species.

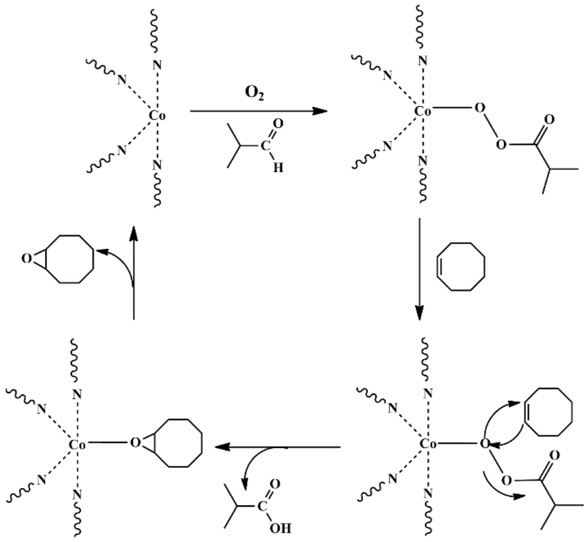

Fig. S5 Proposed reaction mechanism for the epoxidation of *cis*-cyclooctene to 1,2-Epoxycyclooctane using Co(II)@Cr-MIL-101-P2I catalyst in the presence of isobutyraldehyde.

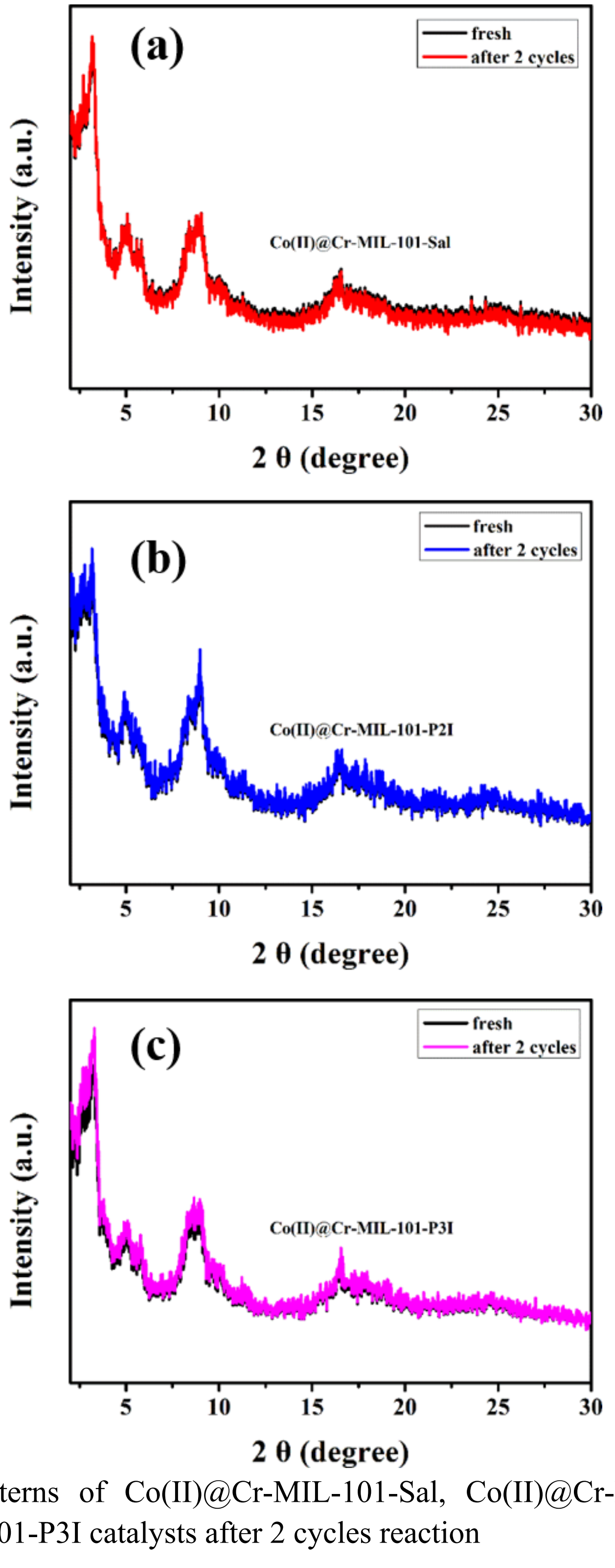

Fig. S6 XRD patterns of Co(II)@Cr-MIL-101-Sal, Co(II)@Cr-MIL-101-P2I and Co(II)@Cr-MIL-101-P3I catalysts after 2 cycles reaction

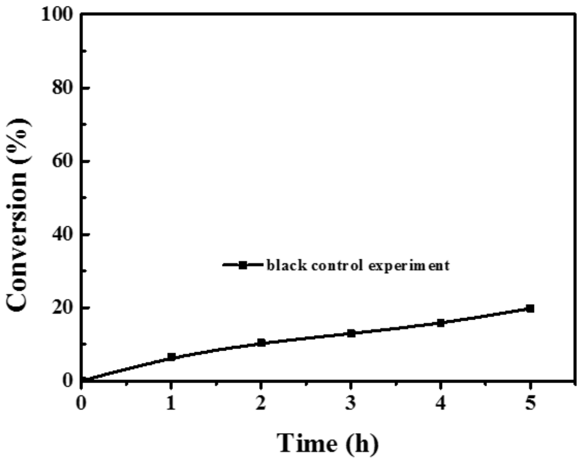

Fig. S7 Change of conversion over the reaction time for model reaction in absence of catalyst.

The fresh and recovered Co(II)@Cr-MIL-101-P2I catalyst after 5 cycles reaction was characterized by XRD, FTIR and SEM (Fig. S8). The powder XRD curves of the fresh and recovered catalyst (Fig. S8 a) revealed that the overall structure of the material remained intact after the catalytic experiments. The FTIR (Fig. S8 b) results of fresh and recovered catalyst showed that the composition of the catalyst had almost no obvious change after reaction. While the SEM images (Fig. S8 c) showed that the structure of the catalyst was slightly conglobatus.

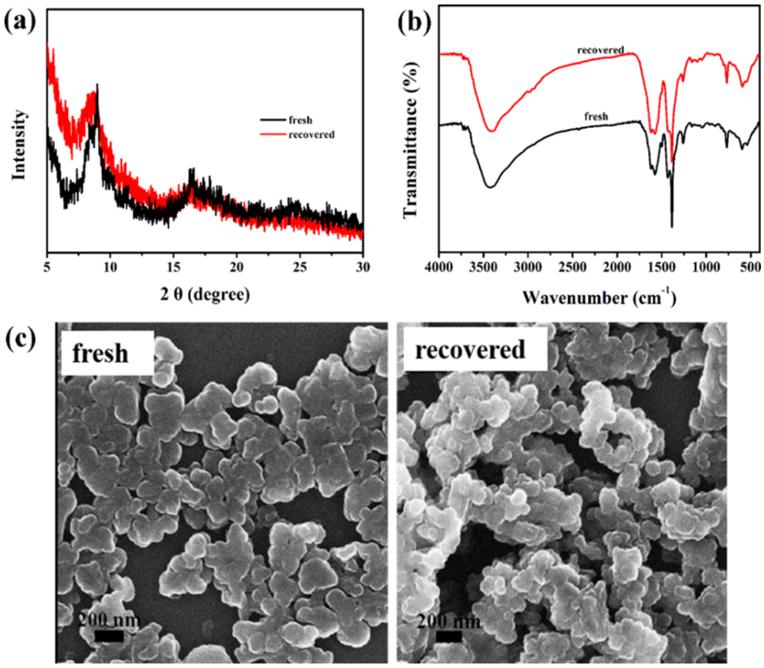

Fig. S8 Powder XRD patterns (a), FTIR spectra (b) and SEM images (c) of fresh and recovered Co(II)@Cr-MIL-101-P2I catalyst.

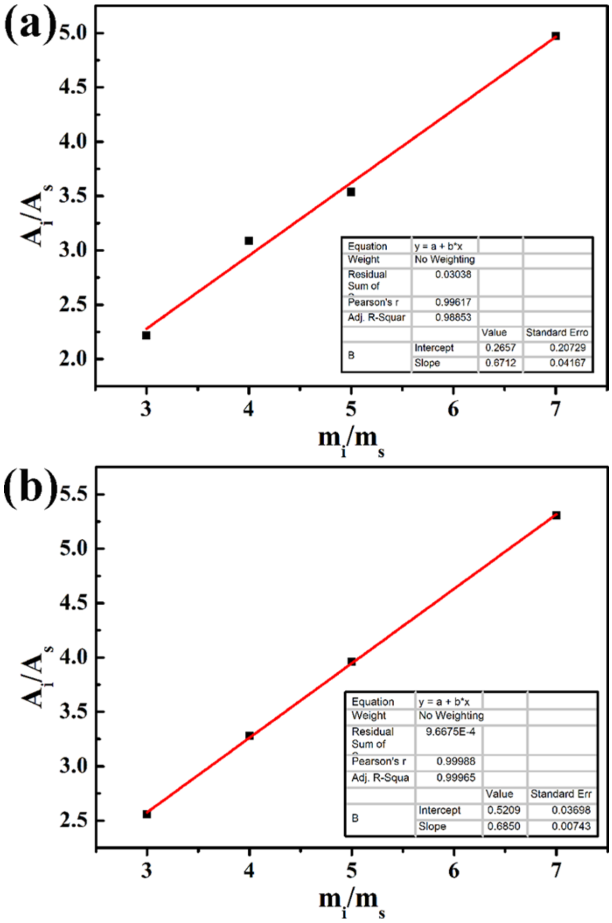

Fig. S9 (a) *cis*-cyclooctene and (b) 1,2-Epoxycyclooctane vs. nitrobenzene internal standard for GC/MS analysis.

Notes and references

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