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ORIGINAL PAPER

# Ru(III) complex anchored onto amino-functionalized MIL-101(Cr) framework via post-synthetic modification: an efficient heterogeneous catalyst for ring opening of epoxides

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## Abstract

In this work, the metallo Schiff base-functionalized metal–organic framework was prepared by post-synthetic method and used as an electron-deficient catalyst for the alcoholysis of epoxides. In this manner, the aminated MIL-101 was modified with 2-pyridine carboxaldehyde and then the prepared Schiff base reacted with $RuCl_3$. This new catalyst, MIL-101–$NH_2$–PC–Ru, was characterized by Fourier transform infrared, UV–Vis spectroscopic techniques, X-ray diffraction, BET, inductively coupled plasma atomic emission spectroscopy and field-emission scanning electron microscopy. In the presence of this heterogeneous catalyst, ring opening of epoxides was performed under mild condition to show the significant ability and successful applications of Lewis acid containing catalysts in corporation with metal–organic frameworks. The reusability of the catalyst was also investigated. No noticeable decrease in the catalytic activity was found after four consecutive times.

**Keywords** Metal–organic framework · Heterogeneous catalyst · Post-synthetic modification · Ring opening · Alcoholysis · Epoxides

## Introduction

Epoxide ring opening represents one of the most fundamentally important reactions in organic synthesis [1]. High regio- and stereoselectivity and specificity reactions of epoxides frequently constitute crucial process in the transformation of aliphatic compounds [2]. Epoxide ring-opening reactions generally proceed under basic or acidic conditions. In recent years, several catalysts have been used, which can promote ring opening of epoxides [3–8]. Although some of the reported catalysts suffer from disadvantages such as high acidity, long reaction times and inconvenient handling. As a result, the introduction of new methods for the ring opening of epoxides, which work under mild reaction conditions, is necessary in synthetic organic chemistry.

In recent years, the use of transition metal complexes in different synthesis protocols has rapidly increased. Spatially, Ru complexes known as versatile catalysts for organic synthesis and polymer chemistry because of the widest range of oxidation states of Ru compared with other elements in periodic table [9–12]. A number of homogeneous and heterogeneous ruthenium complexes have been prepared and extensively used in a variety of chemical transformations such as hydration [13–15], hydrogenation [16–21], epoxidation [22, 23], oxidation [24–28], isomerization [29, 30], decarbonylation [31–33], cyclopropanation [34], olefin metathesis [35], Diels–Alder reaction [36], Kharasch addition [37], atom transfer radical polymerization [38, 39] and enol-ester synthesis [40, 41].

Different ligands such as hydride, hydrate, carboxylalate, halide, phosphane, oxygen or nitrogen chelating groups, amine, Schiff bases, arenes and carbenes were used to achieve appropriate ruthenium complexes with particular structure and properties [42–49]. Among these ligands,

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Schiff bases have attracted increasing attention due to steric and electronic effects of them around the Ru core. Immobilization of Ru complexes bearing bidentate Schiff base is of great current interest in our group.

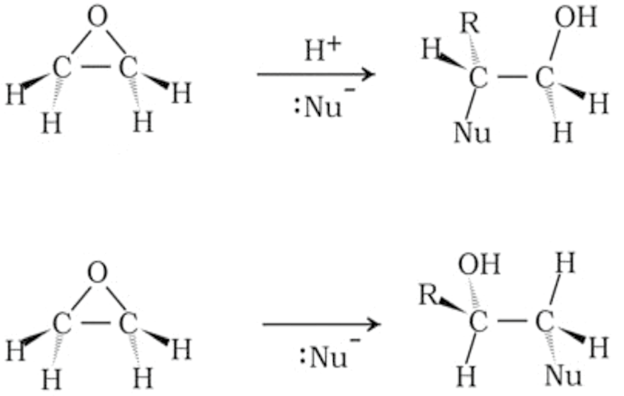
Metal–organic frameworks (MOFs) known as very interesting class of porous material are combination of inorganic and organic subunits [50]. Due to their outstanding properties such as flexible pore size, shape and structure, high surface area, porosity and thermo stability, they are prominent candidates for a wide range of applications from gas separation/storage [51, 52], sensing [53], magnetic imaging and drug delivery systems [54, 55] to catalysis [56–60].

Post-synthetic modification (PSM) is a very versatile way for producing MOF-based catalysts. In this way, the organic linkers of the framework can be functionalized and attached to the catalytically active sites. So different materials with various physical and chemical properties can be produced [61]. Usually metal–organic frameworks that undergo PSM have alcohol and amino groups such as IRMOF-3 (an amino MOF-5), $NH_2$–DMOF, $NH_2$–UiO-66 and $NH_2$–UMCM-1.

Bhattacharjee et al. reported the immobilization of manganese(II) acetylacetonate complex on IRMOF-3 via PSM [62]. Recently, Tangestaninejad et al. prepared metal–organic frameworks (MOFs) containing Mo–Schiff base complexes by post-synthesis method and applied as efficient catalysts in the epoxidation of alkenes with *tert*-BuOOH [57]. They have also succeeded in designing a novel catalyst by anchoring a Cu(II) Schiff base into UiO-66-$NH_2$ based on a post-synthetic strategy [63]. This new immobilized catalyst was successfully applied for synthesis of benzimidazoles and benzothiazoles.

The chromium terephthalate metal–organic framework, MIL-101(MIL = Matérial Institute Lavoisier), [($Cr_3X(H_2O)_2O(bdc)_3$; X = F, OH; and bdc = benzene-1,4-dicarboxylate)], first synthesized by Férey et al. [48] is a highly porous three-dimensional structure with high surface area, high chemical and hydrothermal stability and large pores which make it a suitable case for catalytic purposes [64]. If terephthalic acid replaced with amino-terephthalic acid as linker, amino-functionalized MIL-101 has been produced and it is easier to be functionalized.

Herein, we wish to report the preparation and characterization of a Ru-anchored metal organic framework. In this manner, MIL-101 reacted with 2-pyridine carboxaldehyde and a bidentate ligand was produced for coordination to Ru species. This new catalyst, MIL-101–$NH_2$–PC–Ru, was used as an efficient and highly active catalyst for ring-opening reactions of epoxides with methanol as nucleophile (Scheme 1).



**Scheme 1** Nucleophilic ring opening of epoxides

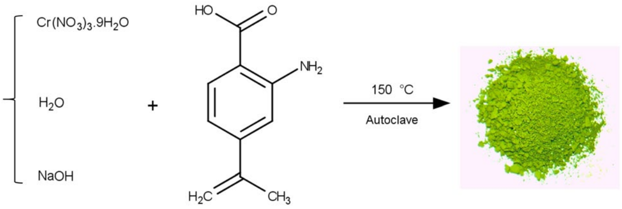
## Experimental

### Reagents and methods

Chemicals were purchased from Fluka and Merck chemical companies. The diffuse reflectance UV–Vis spectra were recorded by a JASCO V-670 UV–Vis spectrophotometer. Diffuse reflectance FTIR spectra were obtained with potassium bromide pellets in the range of 400–4000 $cm^{-1}$ with a JASCO 6300 spectrophotometer. The XRD patterns were recorded using a Bruker D8 ADVANCE X-ray diffractometer equipped with nickel monochromatized Cu $K_\alpha$ radiation ($\lambda$ = 1.5406 Å). The scanning electron micrographs were taken on a Hitachi S-4700 field-emission scanning electron microscope (FE-SEM). Specific surface area was measured by adsorption–desorption of $N_2$ gas at 77 K with ASAP 2000 Micromeritics instrument. The ICP analyses were carried out by a Jarrell Ash 1100 spectrometer. Gas chromatography experiments (GC) were performed with a Shimadzu GC-16A instrument using a 2 m column packed with silicon DC-200 or Carbowax 20 M. In the GC experiments, *n*-decane was used as the internal standard.

### Preparation of $NH_2$–MIL-101

$NH_2$–MIL-101(Cr) was synthesized and prepared according to the procedure reported by Lin et al. [65]. In brief, $Cr(NO_3)_3 \cdot 9H_2O$ (800 mg, 2 mmol), 2-amino-terephthalic acid (360 mg, 2 mmol) and sodium hydroxide (200 mg, 5 mmol) were dispersed in distilled water (15 ml) and stirred for 5 min, and then the solution was poured to a 50-ml Teflon-lined stainless steel autoclave and kept at 150 °C for 12 h. After that, autoclave was left to cool down to room temperature (Scheme 2). Subsequently, the green precipitate was collected by centrifugation and washed with abundant amounts of DMF at room temperature to remove the excess unreacted 2-amino-terephthalic acid. The precipitate



**Scheme 2** Synthesis of $NH_2$–MIL-101(Cr)

is washed afterward with hot alcohol at 100 °C for 24 h in an autoclave. Finally, the products were dried at 80 °C in air.

### Preparation of MIL-101–$NH_2$–PC

The Schiff base-grafted $NH_2$–MIL-101 was prepared as following: To the solution of $NH_2$–MIL-101 (0.4 g) in 30 ml toluene, 2-pyridine carboxaldehyde (0.4 ml) was added. The mixture was stirred for 6 days at room temperature [66–69], and afterward it was filtrated and washed several times with ethanol to drive out unreacted 2-pyridine carboxaldehyde. At last, the imine-functionalized MOF was dried at 353 K to become suitable for the metalation step.

### Preparation of MIL-101–$NH_2$–PC–Ru(III)

The Ru-grafted MIL-101–$NH_2$–PC was prepared as following: The imine-functionalized MOF (0.2 g) was dispersed in DMF (15 ml). Excess $RuCl_3$•$6H_2O$ (0.2 g) was dissolved in minimum amount of DMF, added dropwise to the mixture and refluxed at 343 K for 24 h. Finally, the mixture was filtrated and washed several times with ethanol and dried at 353 K under vacuum to gain the desired catalyst.

### General procedure for the methanolysis of epoxides

To a solution of epoxide (1 mmol) in methanol, the catalyst MIL-101–$NH_2$–PC–Ru(III) (50 mg) was added. The mixture was stirred for the appropriate time at room temperature according to Table 1. The progress of the reaction was monitored by GC.

### Recovery and reuse

The methanolysis of styrene oxide was chosen as a model reaction for checking the reusability of MIL-101–$NH_2$–PC–Ru(III). At the end of the reaction, the catalyst was recovered by filtration, washed with $Et_2O$ and dried. The catalyst was reused four times without any loss of activity. After each run, the catalyst was isolated from the reaction mixture, and the amount of Ru leaching was followed by ICP.

## Results and discussion

### Preparation and characterization of the catalyst, MIL-101–$NH_2$–PC–Ru(III)

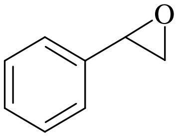
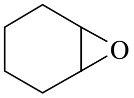
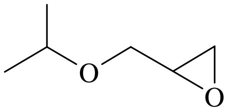
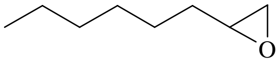
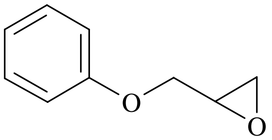
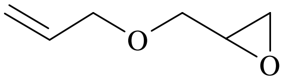
The amine groups in porous MOF, amino-MIL-101, are not involved in the framework backbone, so they were easily modified with 2-pyridine carboxaldehyde, and a bidentate Schiff base ligand containing nitrogen-donating atoms was prepared (Scheme 3).

The amount of Ru(III), determined by ICP analysis, was about 0.0173 mmol/g of catalyst. The prepared catalyst was also characterized by FTIR (Fig. 1). The characteristic stretching vibrational bands between 1300 and 1700 $cm^{-1}$ and bending vibrational bands between 400 and 700 $cm^{-1}$ refer to COO and C–C bonds and indicate the presence of dicarboxylate functional groups. The relatively narrow weak bands in 767 and 970 $cm^{-1}$ indicate $\delta$ and $\gamma$ vibrational bands of C–H in aromatic ring, and the presence of them in all spectra confirms the stability of the framework during post-synthetic modification [65] (Fig. 1a–c). Symmetric and asymmetric stretching vibrational bands which can be seen in 3370 $cm^{-1}$ and 3473 $cm^{-1}$ are related to $NH_2$ groups. These bands present in all four spectrums shows that converting of amine functional groups to imine is not 100% during the modification. The N–H bending vibrational bands of $NH_2$ and the C–N stretching vibrational bands of aromatic amines appear in 1620 and 1338 $cm^{-1}$, respectively (Fig. 1a). The C=N vibrational band of imine-functionalized framework appears in 1713 $cm^{-1}$ (Fig. 1b). An obvious thickening and a slight shift from 1713 to 1668 $cm^{-1}$ are seen after attachment of Ru(III) to the framework (Fig. 1c) which is an evidence of successful synthesis of the catalyst.

The X-ray diffraction patterns of samples are shown in Fig. 2. Comparison of the XRD pattern of $NH_2$–MIL-101, MIL-101–$NH_2$–PC and MIL-101–$NH_2$–PC–Ru clearly shows that the framework structure of amino-MIL-101 remained intact during the post-synthetic modification (Fig. 2). The main peaks in the patterns are in accordance with the reported patterns for $NH_2$–MIL-101 in the literature [65]. It is deduced from the UV–Vis spectrum of (A) and (B) that the exhibited peak at 502 nm can be attributed to metal–ligand charge transfer (Fig. 3).

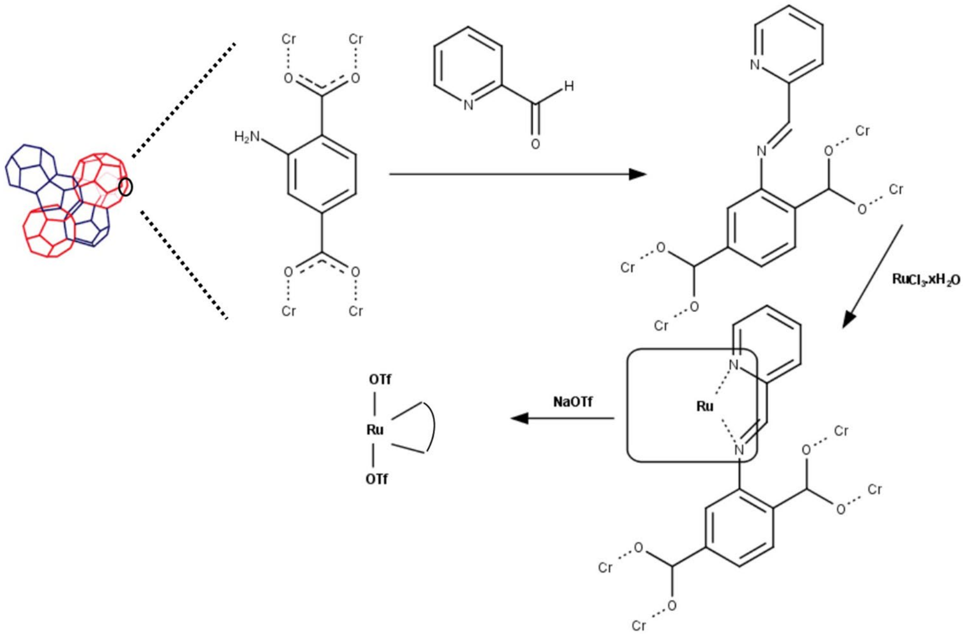
As shown in Fig. 4, from FE-SEM images of $NH_2$–MIL-101 and MIL-101–$NH_2$–PC–Ru(III), it is clear that there are no significant changes in the morphology of crystals during the preparation of the catalyst. Also, the energy-dispersive X-ray (EDX) results, obtained from SEM analysis, show the presence of Ru in the prepared catalyst (Fig. 4c).

**Table 1** Methanolysis of epoxides catalyzed by MIL-101-$NH_2$-PC-Ru(III)[a]

| Entry | Epoxide | Yield (%)[b] | Time (h) | TOF ($h^{-1}$) |
|---|---|---|---|---|
| 1 |  | 100 | 30 | 2325 |
| 2 |  | 100 | 45 | 1550 |
| 3 |  | 94 | 60 | 1093 |
| 4 |  | 98 | 50 | 1372 |
| 5 |  | 95 | 55 | 1205 |
| 6 |  | 96 | 75 | 895 |

[a] Reaction conditions: epoxide (1 mmol), $CH_3OH$ (4 ml) and catalyst (50 mg) at room temperature

[b] GC yield



**Scheme 3** Preparation of the catalyst

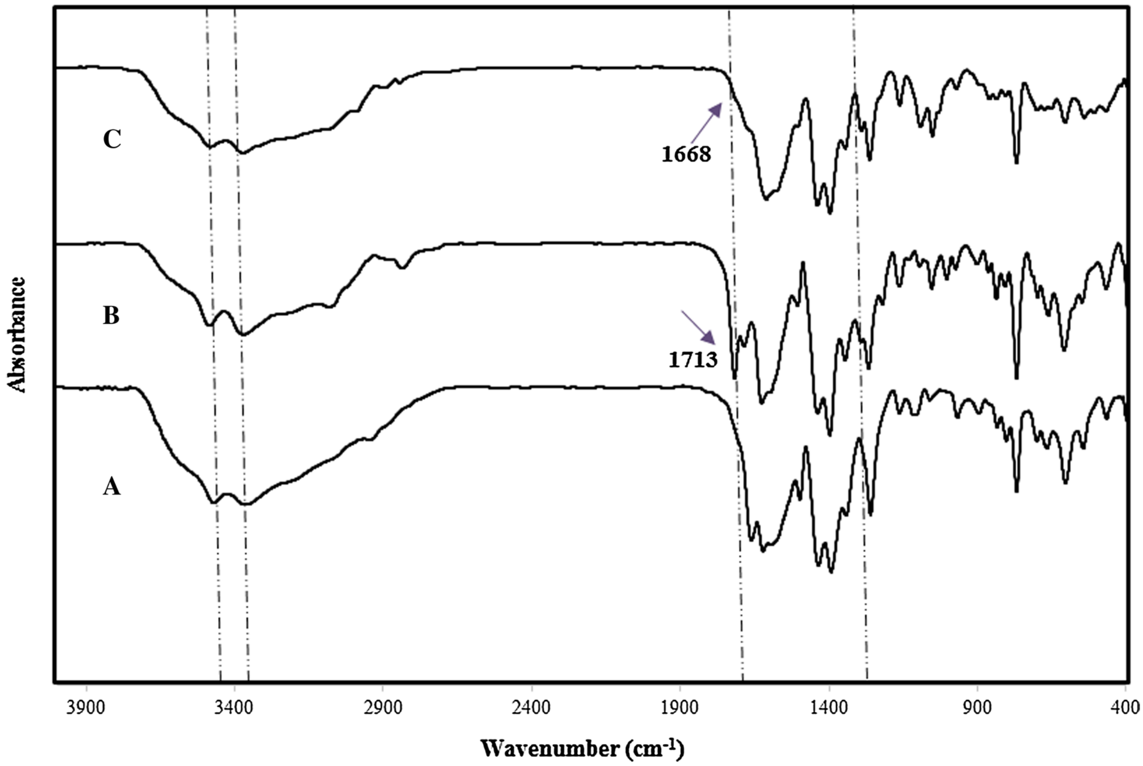


**Fig. 1** FTIR spectrum of: *A* $NH_2$–MIL-101, *B* imine-functionalized framework, *C* MIL-101–$NH_2$–PC–Ru(III)

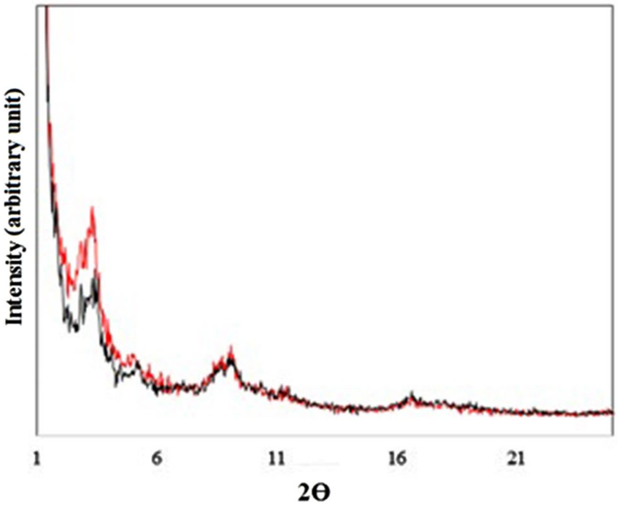


**Fig. 2** XRD pattern of: **a** $NH_2$–MIL-101, **b** MIL-101–$NH_2$–PC–Ru(III)

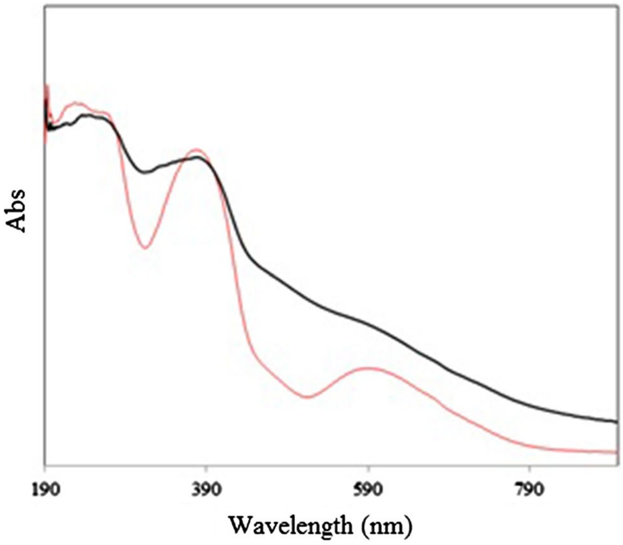


**Fig. 3** UV-Vis spectrum of: **a** $NH_2$–MIL-101, **b** MIL-101–$NH_2$–PC–Ru(III)

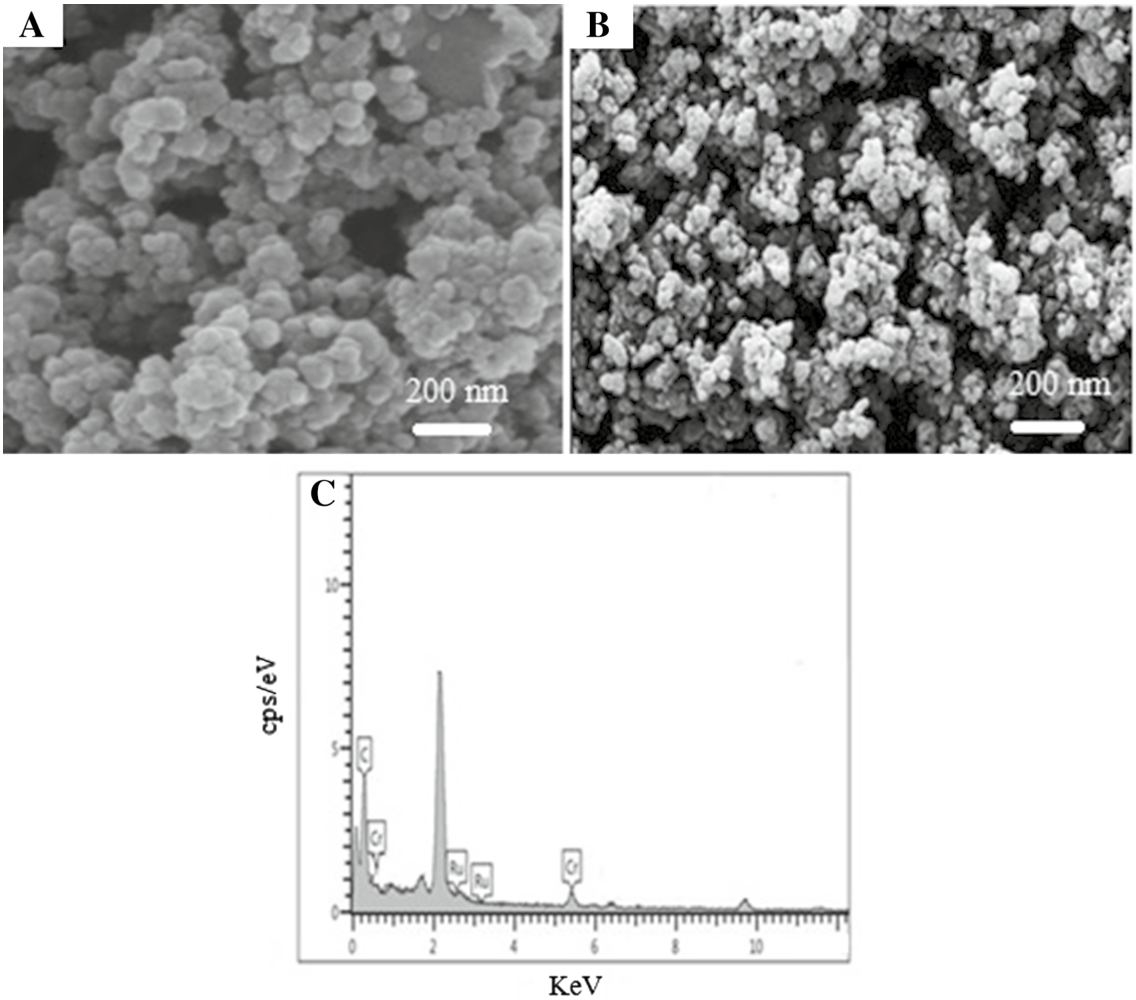


**Fig. 4** FE-SEM images of: **a** $NH_2$–MIL-101; **b** MIL-101–$NH_2$–PC–Ru(III) and **c** SEM–EDX spectrum of MIL-101–$NH_2$–PC–Ru(III)

The specific surface area and pore volume of MIL-101–$NH_2$ and MIL-101–$NH_2$–PC–Ru(III) were determined using nitrogen physisorption measurements (Fig. 5). It shows a predictable decrease in pore volume from 1.55 to 0.79 $cm^3\ g^{-1}$, and also BET surface area decreased from 1610 to 792 $m^2\ g^{-1}$ after complexation of MIL-101–$NH_2$ with Ru. This great decrease in surface area and pore volume after post-synthetic modification indicates that the cavities of MIL-101–$NH_2$ are occupied by Ru(III) complexes.

## Catalytic experiments

The ability of the prepared catalyst was investigated in the ring opening of styrene oxide with methanol as model reaction. First, the amount of catalyst was optimized. The best results were obtained with 50 mg of the catalyst at room temperature (Fig. 6).

In the similar conditions, a blank experiment in the presence of primary framework, $NH_2$–MIL-101 and methanol,

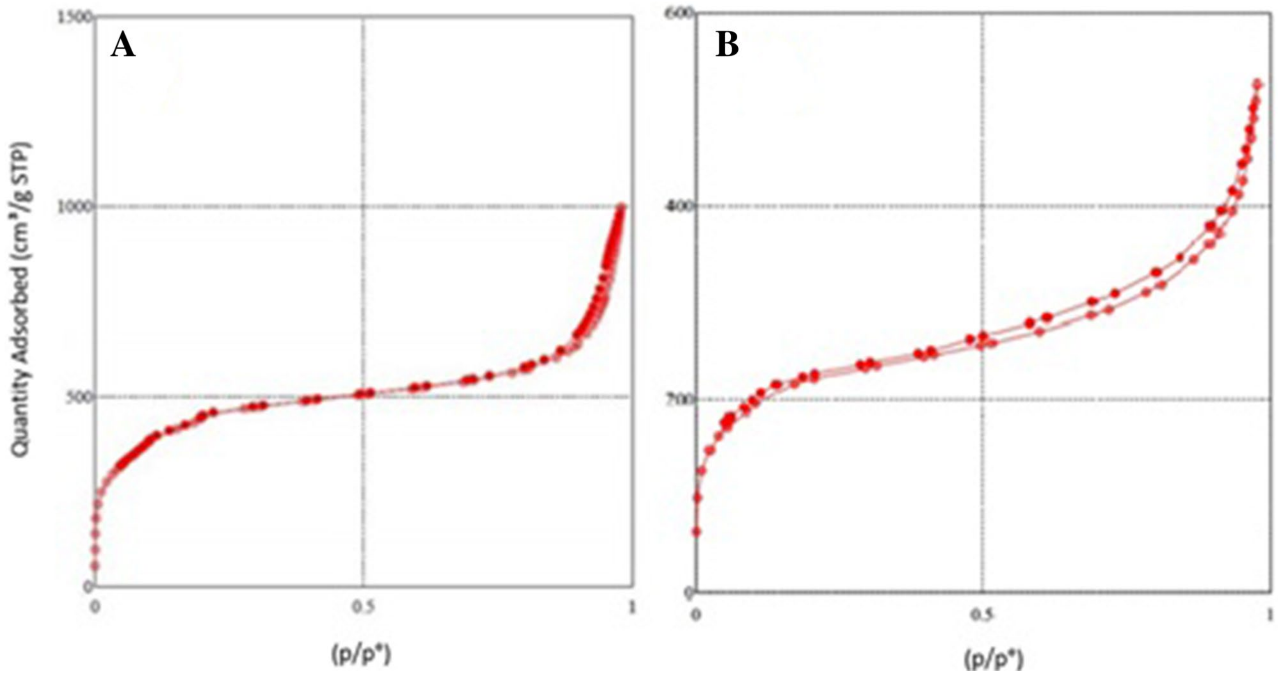


**Fig. 5** $N_2$ adsorption/desorption isotherm of: **a** $NH_2$–MIL-101 and **b** MIL-101–$NH_2$–PC–Ru(III)

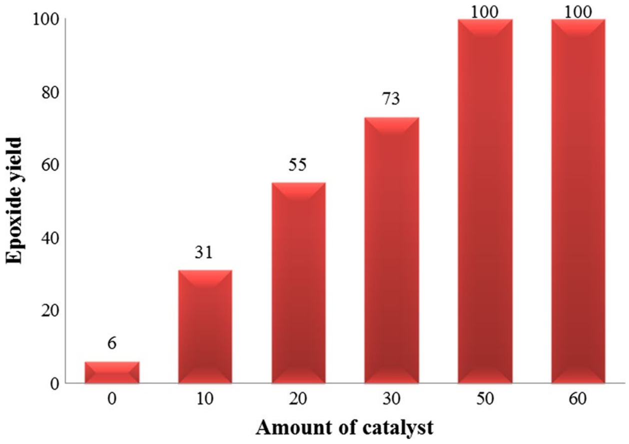


**Fig. 6** Optimization of the catalyst amount in the methanolysis of styrene oxide at room temperature in 45 min

was also done. The results from GC analysis showed that only 6% of styrene oxide was converted to the related alcohol after 24 h, so these experiments revealed that the active site of the catalyst is the intercalated Ru species. The reaction was performed in the presence of different epoxides, and the corresponding β-alkoxy alcohols were obtained. The results are summarized in Table 1. The actual mechanism is not clear at present. However, a plausible explanation is that epoxide is first activated by catalyst to afford 1. Alcohol attacks 1 to give 2 which in turn converts to the final product and releases the catalyst for the next catalytic cycle (Scheme 4).

## Catalyst reuse and stability

From economical point of view, the stability and reusability of a heterogeneous catalyst are very important. The reusability of the prepared catalyst was investigated using methanolysis of styrene oxide as model reaction. At the end of reaction, the catalyst was separated by simple filtration and washed several times with $Et_2O$ and dried in oven before using in the next run. The results showed that the catalyst could be reused for four consecutive cycles without substantial reduction in its activity (Table 2). The Ru(III) ion leaching was determined by analyzing the collected filtrates by ICP method. The results showed that only small amounts of Ru catalyst were leached (less than 1.3% in the two first runs). No Ru was detected after the second run in the reaction mixture. So it is clear that the catalyst is stable under the reaction conditions, can be recovered and reused. The nature of the recovered catalyst was monitored by FTIR and XRD analysis. The XRD patterns indicated that the basic lattice structure of MIL-101–$NH_2$–PC–Ru(III) was

**Scheme 4** Proposed mechanism for the ring opening of epoxides

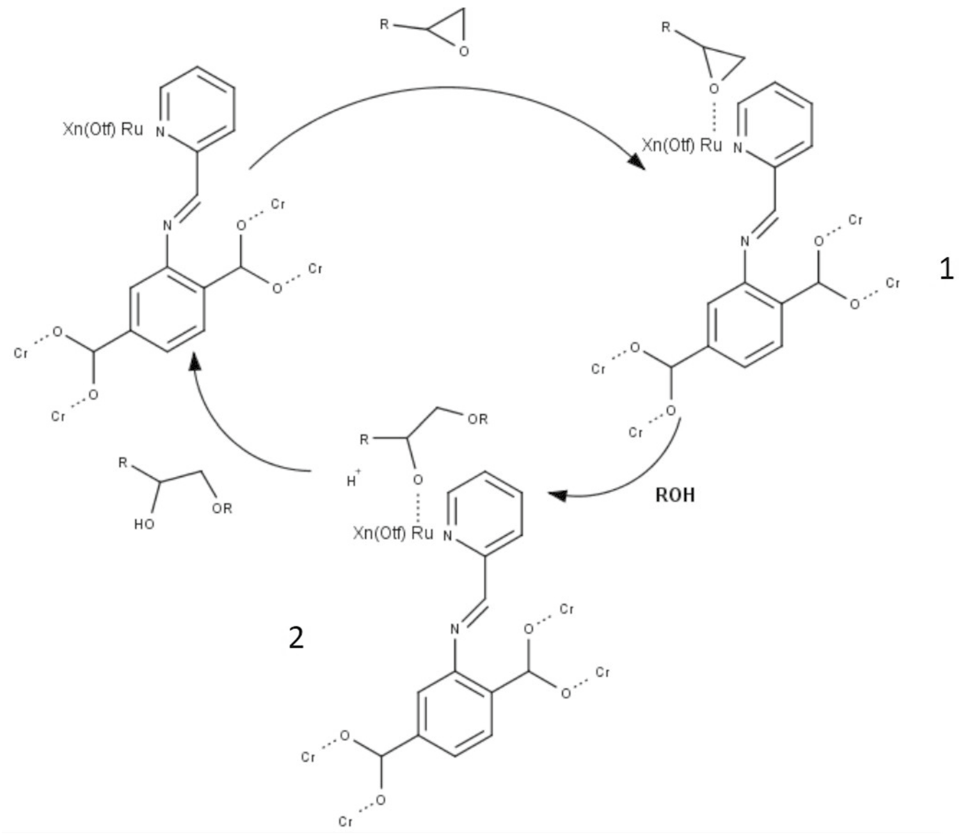


**Table 2** Recyclability of MIL-101–$NH_2$–PC–Ru(III) in methanolysis of styrene oxide

| run | Yield (%)[a] | Ru leached (%)[b] |
|---|---|---|
| 1 | 100 | 1.1 |
| 2 | 98 | 0.2 |
| 3 | 95 | 0 |
| 4 | 95 | 0 |

Reaction conditions: styrene oxide (1 mmol), $CH_3OH$ (4 ml) and catalyst (50 mg)

*T* room temperature

[a] GC yield based on the starting epoxide

[b] Determined by ICP

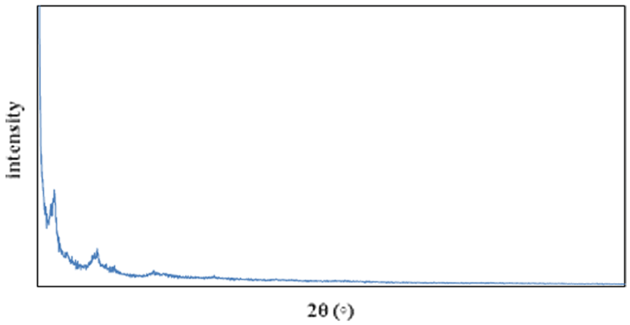


**Fig. 7** XRD pattern of the recovered catalyst

not altered after three cycles (Fig. 7). Also, by considering the FTIR spectra, it is proved that the catalyst has retained its nature during the reaction (Fig. 8).

## Conclusion

In conclusion, we have succeeded in designing a heterogeneous Ru(III) Schiff base catalytic system by post-synthetic modification of MIL-101–$NH_2$ metal organic framework via 2-pyridine carboxaldehyde as support. The prepared hybrid

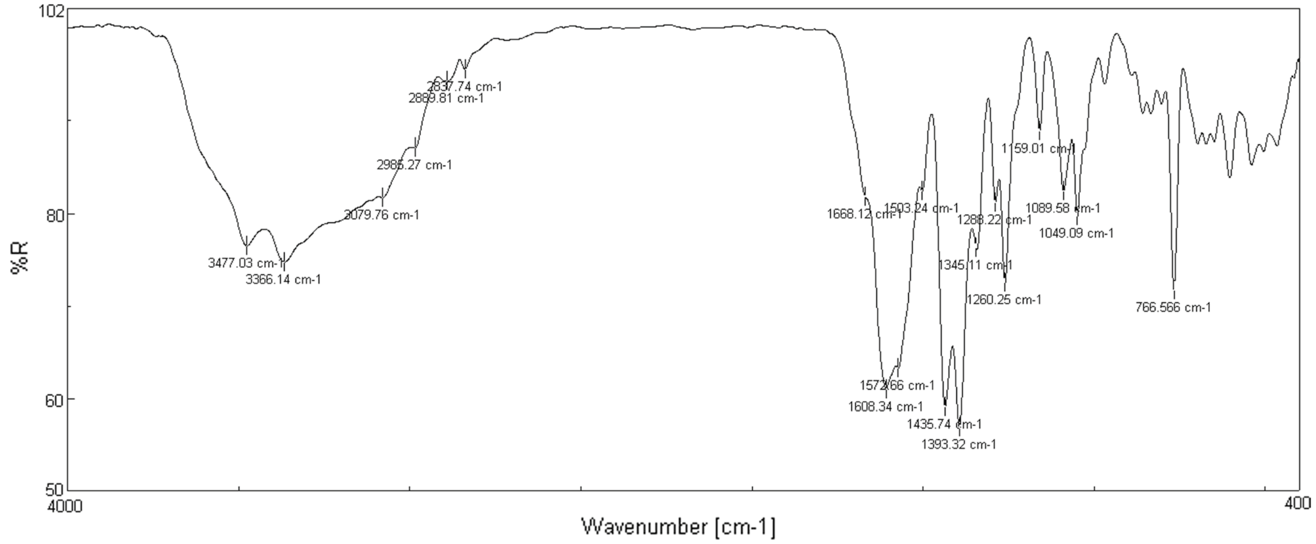


**Fig. 8** FTIR spectrum of the recovered catalyst

material was used as an efficient and highly active catalyst for ring-opening reactions of epoxides with methanol as nucleophile. This novel catalyst can be recovered and reused four consecutive times without significant loss of its initial activity and mass. High activity, selectivity, extremely mild reaction conditions and easy workup are other advantages of this new catalytic system.

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