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Dual activity of durable chiral hydroxyl-rich MOF for asymmetric catalytic reactions

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ABSTRACT

The quest to prepare of asymmetric heterogeneous catalysts with both effective Brønsted acid sites (BASs) and Lewis acid sites is very significant challenge. Herein, we report the construction of a chiral metal-organic framework with two kinds of catalytic active sites (Lewis acid/Brønsted acid). It contains coordinative unsaturation metal centers and chiral functional groups that have cooperation in the catalytic activity. In the synthesized CMOF, the chiral decoration of metal node was performed through the practical method: anions exchange hypothesis (post-synthetic exchange). For this aim, the elimination of framework fluorides happened by using the enantiopure auxiliary anions (L-(+)-tartrate anion (tart⁻)) that led to a chiral cationic MOF with eventual chemical formula [Cr₃tart(H₂O)₂O(bdc)₃]. XRD, BET, ¹H NMR, SEM and EDX were employed to characterize of the present CMIL. Despite the chiral tartrate anions generate a chiral environment, they have main role in the activating of epoxide ring due to hydrogen-bonding interaction. Experiments show that the enantiopure tartrate-functionalized MIL-101 (Cr) as a green asymmetric catalyst has the considerable performance in the enantioselective reactions due to chiral modified surface without remarkable loss in activity.

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1. Introduction

Chirality as an important geometric property is one of the fundamental features in the nature especially in the biological structures and drug industry, so the designing of the new chiral systems has been considered [1]. The chiral compounds have useful potential applications in different areas therefore; the asymmetric catalytic reactions are one of the mandatory processes to make of them [2–4]. These reactions are better performed in the presence of the various chiral catalysts, homogeneous and heterogeneous, such as chiral metal salen complexes [5,6], chiral ketonederived organocatalysts [7], chiral metallo-porphyrin [8] and chiral magnetite manganese-porphyrin [9]. But, the chiral porous systems as the fascinating platforms can reveal striking properties, performance and unique characteristics. Among them, the chiral metal-organic frameworks (CMOFs) with the different morphologies can be ideal candidates in asymmetric catalysis with adjustable components like linkers, nodes, functional groups [10]. The designing of MOFs is very valuable specially the creation of CMOFs, with the various stereotype components, is a new open window toward more different applications as catalysis [11], pharmaceutical technology [12], proton conductivity [13], gas sensing and storage [14,15]. The CMOFs are synthesized via well-established methods with three classifications: Direct synthesis, Chiraltemplate synthesis and Post-synthesis [16,17]. Sometimes the chiral agents are not necessarily to synthesize of CMOFs. For example, in 1999, Aoyama and co-workers introduced a synthesized MOF with achiral linker that its chirality was due to helical array [18]. But, the using of the chiral molecules is more effective way than the inherent chiralization of the framework due to the complex topology. In the first state, the starting organic linker can be chiral that this procedure is difficult due to uncontrollable conditions and diverse complexities. Also, the achiral linker can be chiralized with functional groups as NH₂ via post-synthetic modification (PSM) method. Recently, five kinds of chiral MIL-101(Al)-NH₂ were generated by using five various chiral compounds through PSM approach [19]. However, CMOFs were constructed by using the organic linkers that have chiral multifunctions [17,20]. Metal nodes of MOFs can be also modified by the chiral species [16]. It is concluded that the accessible positions on the surface or inside pores of the achiral frameworks in the porous systems can be chiralized by pre- and post-synthesis strategy [21]. Postmodification is a simple and straight pathway to product the chiral functional materials. This general method can be applied to construct of CMOFs that have numerous catalytic chiral sites and they are







employed in the asymmetric transformations. Even, the chiral molecular catalysts can be also heterogenized by MOFs for the facile recovery and reuse in the catalytic reactions [22]. Totally, in the catalytic asymmetric transformations, designing, porosity, functional groups, the accessible catalytic active sites, stability in catalyst have a significant role in the generation of enantioselective product [23]. These factors affect on the interaction between solid catalyst and reactant.

Herein, we report the formation of a chiral MIL-101(Cr) as a asymmetric heterogeneous catalyst (MIL-101(Cr)-tart: Cr₃O (BDC)₃tart) via PSM for the enantioselective catalysis. There are two separate catalytic active centers (Scheme 1), Brønsted and Lewis acid which show catalytic activity for proceeding of the enantioselective epoxidation and methanolysis reactions. Open metal sites (Cr) as Lewis acid centers are generated from the removing of the adsorbed solvent molecules by activation process that MIL framework is not damaged during activation conditions. The Brønsted acid centers (tartrate anion) are found in the different ligands with the various functional groups like -OH and -SO₃H that they can attach to the open metal sites. To functionalize of the open metal nodes with chiral ligand, we used tartrate anion because it has been derived from tartaric acid which is as the foundation of the various asymmetric organocatalysts. The synergistic effect of coordinated chiral functional groups and open Cr sites of MIL framework in the catalytic experiments was observed. These centers can activate substrates in the asymmetric epoxidation/ methanolysis reactions. The Cr metals show a high activity as Lewis acid centers in the oxidation of olefins. Unlike the unsaturated metal sites, the functional groups of tartrate as Brønsted acid display a high acidic activity in the asymmetric methanolysis since they are more acidic [24]. Our aim was to chiralize a nonfunctionalized MIL-101(Cr) as an acidic solid catalyst with mixing of the catalytic active sites, Brønsted and Lewis acidity. These kinds of MOFs have rarely been reported [25]. The findings showed that not only the framework provides the accessible catalytic sites but also the manipulation of them (surface or pore) with different functional groups, can prepare new opportunities of catalytical units. Several MOFs with Lewis acid centers were synthesized and used in the various reactions but the preparing of MOFs with Brønsted acidity sites is more complicated [26,27]. In comparison to the previous reported structures, this kind of chiral MOF has not been presented until now.

2. Results and discussion

2.1. Synthesis of MIL-101(Cr)-tart

Chemicals and characterization methods have been reported in S1. The MIL-101(Cr) was constructed according to reported hydrothermal method [28]. Without additional explanations, the mixture of H₂BDC (164 mg), Cr(NO₃)₃·9H₂O (400 mg), HF (1 mmol) and D.I·H₂O (4.8 mL) was transferred into a 25 mL autoclave and heated in an oven under optimized condition (220 °C/8h). The filtered crystalline powder was washed by hot ethanol and NH₄F solution to eliminate of the unreacted components, metal and organic linker. At the end, MIL-101(Cr)-tart was synthesized by placing of the MIL-101(Cr)-F in the concentrated silver tartrate solution over 20 h at 90 °C, then the obtained solid was repeatedly washed with a certain amount of water, ethanol and, it was placed in an oven under vacuum to be dried.

2.2. General procedure of asymmetric epoxidation, methanolysis and reusing catalyst

The catalytic epoxidation experiments were carried out with 2 mmol styrene as a model substrate, 5 mmol isobutyraldehyde, 0.05 g catalyst, oxygen and 5 mL acetonitrile. Then this reaction mixture was constantly stirred at 80 °C for 8 h. During catalytic reaction, conversion, selectivity of products and enantiomeric excess were investigated via injection to the chiral GC and finally ¹H NMR was employed to corroborate of the generated products. The methanolysis reaction was performed with 1 mmol styrene oxide in 10 mL MeOH with 0.05 g catalyst for 9 h at 40 °C and 500 rpm in air atmosphere. The final reaction mixture was cooled to room temperature and after removing the catalyst, it was analyzed by chiral GC and ¹H NMR, too. To investigate of the reusability of MIL-101(Cr)-tart in both of catalytic reactions, after the finishing the reaction, the catalyst was separated from the reaction



Scheme 1. Synthetic route of chiral heterogeneous catalyst [MIL-101(Cr)-tart].

mixture, washed with the specific solvents (acetonitrile and methanol in the epoxidation and methanolysis, respectively) and dried in oven at 80 °C. Then, the used MIL-101(Cr)-tart was repeatedly employed in new similar catalytic reaction with fresh substrate under the optimized conditions. At the end, solutions of catalytic reactions were injected to chiral GC.

2.3. Structural characterization of MIL-101(Cr)-tart

Before the catalytic investigations, the structure of MIL-101(Cr)tart as a new chiral heterogeneous catalyst was studied. To remove of the first anions of framework (bonded F to Cr), the anions displacement process was performed. To accomplish this aim, the synthesized MIL-101(Cr) was soaked in the concentrated silver tartrate solution. The inclusion of the tartrate anion to the framework structure was observed (bonded tartrate to Cr) (post-synthetic modification via ion-exchange: F with tartrate). According to our suggestion in the preparation process of MIL-101(Cr)-tart, the special interactions can be considered. There is an electrostatic attraction in the silver tartrate salt that has been synthesized from L-(+)-tartaric acid and AgNO₃. In the first step, to convert the neutral framework of MIL-101(Cr) into cationic framework, the stripping of F⁻ anion was performed by using the concentrated silver tartrate. The advantage of this method is the using of a simple chiral salt to eliminate of the F anion on Cr as a monovalent anion. The non-covalent acid-base interaction between Ag and F goes toward the formation of a new chiral MOF (Scheme 2). It has been reported which the functionalized porous materials such MOFs can be used as ion exchangers. Due to their chemical structure, they can be cation or anion exchangers.

The prepared sample was characterized by several techniques that the results have been shown as follows. Normally, a routine method to confirm PSM or the incorporation of a new ligand is IR spectra. For comparing the MIL-101(Cr) versus MIL-101(Cr)-tart and displaying of L-(+)-tartrate anion in the prepared CMOF, FT-

Anatomy of the interactions

Electrostatic attraction:

The synthesis of silver tartrate salt from the acidic chiral source, L-tartaric acid. The ionic bond between two ions with opposite

charge (O^- with Ag⁺).

(1) Electrostatic interaction:

This interaction is as a non-covelent interaction. It can happen between molecules or within a molecule.

(2) Ion-exchange:

It is an exchange of ions between two different ionic components. MIL-101(Cr) as a functionalized porous polymer can be used as a ion-exchange resin.

IR of chiral MOF has been shown. (S2 in the Supporting Information (SI)). The intense band at about 1700 cm⁻¹ is related to the L-(+)-tartrate anion (tart⁻) [29]. The other absorption bands can be assigned to: Cr–O vibration (566 cm⁻¹), C–H deformation (734, 887, 950, 1124 cm⁻¹), symmetric vibrations of O–C–O (1425 cm⁻¹), C=C (1512 cm⁻¹), $v_{s(COO)}$ and $v_{as(COO)}$ (1300–1700 cm⁻¹) [30].

Both PXRD pattern and SEM image of MIL-101(Cr)-tart have been showed in Fig. 4a, that the perceptible changes were not specified. Therefore, MIL-101(Cr)-tart clearly retained their crystalline structure and cubic morphology than parent MOF after postmodification by chiral component. Hence, the chiral post-modification step not only did not change the structural features of MIL-101 (Cr) but also modified achiral MIL surface. To demonstrate of the chemical composition of MIL-101(Cr)-tart and the degree of the incorporated tartrate into achiral framework. ¹H NMR spectroscopy of the digested CMOF (by D_2SO_4) was investigated (S3). This technique is a useful characterization to detect of the chiral ligand protons in CMOF. In addition to the hydrogens signal of the linker, a new signal revealed at about 4.8 ppm that could be assigned to chiral species. The ratio of tartrate to Cr was estimated by ¹H NMR: 1.16:3. To confirm the replacement of F by tartrate, EDXs before and after modification have been studied (Fig. 1). The decrease and increase of F and O peaks intensity at about 0.50 and 0.25 keV, respectively, show that the anion exchange happened in the concentrated silver tartrate solution. So these changes indicated that the incorporation of tartrate anions has successfully occurred with the formation of silver(I) fluoride.

The porosity of chiral MIL was determined by the N₂ adsorption at 77 K (S4). BET surface area and total pore volume of MIL-101 (Cr)-tart were 1760 m² g⁻¹ and 1.52 cm³ g⁻¹, respectively. Whereas, these parameters in MIL-101(Cr) are: BET surface area: 3133 m² g⁻¹, pore volume: 1.68 cm³ g⁻¹. It is clear that the postsynthetic modification has easily happened without changes in the porosity of the synthesized CMIL. Additionally, Fig. 4a is a

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Scheme 2. Anatomy of the interactions in the synthesis of [MIL-101(Cr)-tart].



Fig. 1. EDX spectra of MIL-101(Cr) structure. (a) before and (b) after chiral modification.

powerful reason to show the maintenance of MIL morphology after chiral postmodification. Thereby, ion-exchange happened: $\{[MIL-101(Cr)]^+-[F]^- \text{ converted to } [MIL-101(Cr)]^+-[tart]^-\}$ by L-(+)-tartrate as a simple chiral organic compound without complexity. It seems that in addition to the Cr centers as acidic catalysts, the functional groups in tartrate anions have catalytic activity in the methanolysis *via* hydrogen bonding.

So the catalytic behavior of this chiral catalyst was investigated in enantioselective epoxidation of olefins and methanolysis of styrene epoxide that the evaluated results reported as follows.

2.4. Evaluation of enantioselective catalytic reactions under various conditions

(i) Epoxidation by using H₂O₂ and TBHP

MIL-101 can be utilized as acidic catalyst in the different reactions like oxidation reactions that are important processes in the chemical transformations [31–33]. Some examples are the benzylic oxidation of hydrocarbons [34], the conversion of methane to

Table 1

Control experiments for enantioselective epoxidation of styrene.^a



Entry Catalyst Catalytic conditions Conv. (%)b Epoxide selectivity (%) Ee (%) (Conf.)⁶ IBA/O₂/CH₃CN/80 °C/8 h [MIL-101(Cr)-tart] 87 70 89(S) 1 2 [MIL-101(Cr)-tart] H2O2/CH3CN/80 °C/6 h 100 16 68 (S) [MIL-101(Cr)-tart] TBHP/CH₃CN/80 °C/8 h 65 (S) 3 46 81 N.R. 4 [MIL-101(Cr)-tart] No co-catalyst/O₂/ CH3CN/80 °C/8 h 5 [MIL-101(Cr)-tart] IBA/O2/n-hexane/80 °C/8 h 28 23 44 (S) 6 [MIL-101(Cr)-tart] IBA/O2/EtOAc/80 °C/8 h 49 37 61 (S) IBA/O₂/CH₃OH/80 °C/8 h 7 [MIL-101(Cr)-tart] 6 17 34 (S) 8 [MIL-101(Cr)] without L-tartrate ion IBA/O2/CH3CN/80 °C/8 h 79 68 9 [MIL-101(Cr)-tart] IBA/O2/CH3CN/40 °C/8 h 42 24 61(S)

^a Reaction conditions: catalyst 50.0 mg, ratio of ⁱPrCHO/styrene: 3 mmol, solvents (CH₃CN, DMF, Toluene and CH3OH) 5 mL, molecular oxygen1 atm, 80 °C.

^b Conversions are based on the starting substrate and determined by GC.

^c Enantiomeric excess (Ee%) was determined by GC on a chiral SGE-CYDEX-B capillary column·H₂O₂ 6 mmol. TBHP 6 mmol.

methanol and ethane to ethanol [35], sulfoxidation of aryl sulphides [36]. So, MIL-101(Cr)-tart was used in the enantioselective epoxidation of a series of olefins. Styrene was employed as model substrate to determine the optimized conditions with three different oxidants (Table 1). In the control experiments, the oxidation of styrene was performed in H_2O_2 which the reaction was completed with enantiomeric excess (ee) 68% ((S)-enantiomer) and epoxide selectivity about 20% (Table 1, entry 2). The poor epoxide selectivity can be assigned to the generation of aldehyde products due to the cleavage of epoxide bond (the most: benzaldehyde, the least: phenylacetaldehyde).

In spite of these results, the oxidation styrene was also investigated in presence of TBHP as oxidant, that the conversion diminished (46%) and ee 65% obtained (the major isomer is (S)-enantiomer) (Table 1, entry 3). Since, *tert*-Butyl hydroperoxide is expensive and unfriendly environmentally, MIL-101(Cr)-tart activity was evaluated in the presence of molecular dioxygen as an available oxidant, cheap and safe [37,38].

(ii) Epoxidation by using IBA/O₂

In comparing to the other oxidants, under identical conditions (solvent, temperature and time) MIL-101(Cr)-tart showed better catalytic activity in the styrene epoxidation by using O_2 and isobutyraldehyde (IBA) with conversion 87% and ee 89% to (S)-enantiomer (Table 1, entry 1, TOF 167 h⁻¹).

In point of catalysis, two parameters of epoxide selectivity/ee in the catalytic reaction with H₂O₂ and conversion/ee in the catalytic reaction with TBHP were lower than IBA/O₂. So, we investigated the preliminary reactions under aerobic condition with O2 as terminal oxidant and isobutyraldehyde (Table 1). The asymmetric epoxidation of styrene was performed in the absence of catalyst which the negligible conversion was observed (conversion < 6%). This reaction was performed to show the effect of catalyst nature. The effect of co-catalyst and solvent was investigated in the progress of the reaction, too (entries 4–7). In the absence of IBA, MIL-101(Cr)-tart did not catalyze the reaction because the activation of oxygen as essential factor did not happen (entry 4). In fact, the used aldehyde is as a co-oxidant that has the activating role of O₂ with the producing of the acylperoxy radical. We used the common solvents of chemical reactions to indicate the polarity effect of solvents in catalytic reaction: acetonitrile, ethylacetate, n-hexane and methanol (entries 1, 5-7). According to the obtained evidences,

acetonitrile with higher polarity and lower coordinating ability provide the appropriate medium for the catalyst performance compared to other solvents [9]. MIL-101(Cr) activity was also studied without any chiral agent and as expected, the enantioselectivity was not observed (entry 8). However, the reaction was not completed at 80°, but we did the oxidation of styrene at 40 °C that the reaction was not completed (cnov. 42%, epoxide selectivity 24% and ee 61% to S-enantiomer). As well as, the MIL-101(Cr) ability was surveyed before the water exiting from structure (nonactivated catalyst) which it did not show the catalytic activity (conversion<10%) (not displayed in Table 1). In order to understand the catalyst efficiency, the enantioselective epoxidation of a few unfunctionalized olefins were examined (Table 2). In the styrene oxidation, benzaldehyde (BA) and 2phenylacetaldehyde (PAA) as side-products were identified (Table 1, entry 1).

Also, the oxidation of the styrene derivative, α -methyl styrene was checked after 8 h with the conversion 83% and ee 85% (S) (Table 2, entry 1, TOF 159 h⁻¹). Probably the decreasing of epoxide and enantioselectivity in this reaction than styrene is related to the steric effect of alkyl group around double bond. MIL-101(Cr)-tart was served to catalyze 1-phenyl-1-cyclohexene oxidation, which

 Table 2

 Enantioselective epoxidation of several olefins.^{a.}

Entry	Substrate	Converdion (%) ^b /Time (h)	Epoxide selectivity (%)	Ee (%) (Conf.) ^c
1	α-methyl styrene	83/8	68	85 (S)
2	1-Phenyl-1-cyclohexene	79/8	100	78 (R,R)
3	1-Octene	77/8	100	100 (R or S)
4	1-Decene	69/8	100	91 (R)
5	trans-stilbene	100/30 min	100	75 (R,R)
2.2				

^a Reaction conditions: catalyst 50.0 mg (0.0013 mmol Cr/g catalyst), ⁱPrCHO/substrate 3 mmol, CH₃CN 5 mL, molecular oxygen1 atm. b and c was mentioned in Table 1.



(R or S)-epoxide, 100% ee

(R)-epoxide, 91% ee (R,R)-trans epoxide, 75% ee

Fig. 2. Enantioselective epoxidation of the unfunctionalized olefins in the controlled stirring speed (500 rpm) with the acquired enantiomeric excess values by chiral-GC.

both epoxide selectivity and ee were 100% and 78%, separately (entry 2, TOF 151 $h^{-1}).$

In the epoxidaion of two aliphatic hydrocarbons, 1-octene and 1-decene, a decrease was observed in the conversions (77% and 69%, entries 3 and 4, TOF 148 and 132 h⁻¹ respectively). It is interesting that in both of them, the high epoxide selectivity and enantiomeric excess were seen after 8 h. Since, 1-decene is longer than 1-octene in term of the length, so the steric effect affects on the results, certainly. The oxidation of *trans*-stilbene as an organic compound with (*E*) stereochemistry was performed that the *trans*-stilbene epoxide obtained with selectivity 100%. In this oxidative reaction, (R,R)-*trans* stilbene epoxide enantiomer appeared with ee 75% after 30 min without the additional products (diol or benzaldehyde) (entry 5, TOF 769 h⁻¹). Fig. 2 demonstrates the gained ee values and the effect of L-tartrate anion as chiral agent on the sterogenic centre configuration of the produced epoxids.

The possible mechanism was suggested in S6a. Table 1 in S5 presents data of the carbon balance calculation in some of the alkenes epoxidation. The percentage of carbon from the initial time of the reaction to final time has been shown. The recyclability of MIL-101(Cr)-tart in the successive reactions of the styrene epoxidation was also studied. Conversion and ee were almost constant to the fourth step, but they decreased in the next step (76% and 82%, respectively, Fig. 3).

The lack of Cr in recycle solutions to the fourth step was proved by ICP. PXRD measurement revealed that the crystalline structure of chiral MIL-101(Cr)-tart is retained after 4 cycles with closely matching to PXRD pattern of fresh MIL-101(Cr)-tart (Fig. 4b). Also, SEM image of MIL-101(Cr)-tart after four recycles showed that the particles size of the used catalyst changed somewhat than fresh catalyst (Fig. 4).

(iii) Methanolysis of styrene oxide

Several MOFs as acidic catalysts were presented in the previous reports with Brønsted acidity (BA), Lewis acidity (LA) or both of them as active sites. They have been investigated in the different chemical reactions such as ring-opening of the epoxide [39], condensation of aldehydes with alcohols [40] and alcoholysis of styrene oxide [41]. Even, this capability (both of BA/LA) can be used in the tandem reactions like the use of Hf-NU-1000 in the tandem epoxidation and then the epoxide opening [42]. From comparative



Fig. 3. MIL-101(Cr)-tart recyclability investigation for model substrate in the asymmetric epoxidatin.





Fig. 4. The investigation of MIL-101(Cr)-tart structure. (a) and (b) PXRD patterns and SEM images (a) before and (b) after asymmetric epoxidatin catalysis.

study with the other works, we expected that this chiral MOF to show catalytic behavior in the asymmetric methanolysis due to the density of the chiral functional groups (as Brønsted acid). According to the constructed CMOF features, we focused on asymmetric methanolysis of styrene epoxide. The experiments confirmed our assumption whereas the affinity between CMOF and styrene epoxide was correct; the results showed that the epoxidation of styrene over MIL-101(Cr)-tart in MeOH was negligible because the Cr³⁺ nodes lost their performance. Solvent molecules as nucleophile coordinated to unsaturated metal centers and almost they turned off. But the chiral groups showed stronger effect in compared to Cr sites in methanolysis of styrene epoxide. The asymmetric methanolysis of styrene epoxide was done over achiral MIL-101(Cr) at 40 °C with low conversion (Conv.%<20%) for 48 h. But the present CMOF (combination of tartrate and Cr^{3+}) demonstrated the high conversion and enantioselectivity values (100% and 90% to S-enantiomer, TOF 221 h^{-1}) for 9 h (Table 3, entries 1 and 2). The methanolysis of styrene oxide at room temperature was also investigated that the conversion was not completed (cnov. 41% and ee 53% to S-enantiomer for 9 h). Separately, the catalytic activity of the tartrate was also studied and it showed the high conversion close to 100%, ee 89% and enantioselectivity 62% (main enantiomer: 2-methoxy-2-phenylethanol) than MIL-101(Cr)-tart (it has not been shown in Table 3).

The ideal asymmetric induction has originated from the tartrate anions with two chiral hydroxyl centers. These results show that the product enantioselectivity is very sensitive to the pore/surface surrounding of the catalysts [29]. To us, the host-guest interactions can happen due to the proper porosity and available content of the chiral group in the present chiral porous solid as host and styrene epoxide as guest. In the crystal structure of MIL-101(Cr)-tart, tartrate anions have two different kinds of functional groups. They can generate intermolecular hydrogen bonds toward epoxide ring Table 3



^a Reaction conditions: catalyst 50.0 mg, styrene oxide 1 mmol, MeOH 10 mL, 40 °C. b and c was mentioned in Table 1.

of the reactant (tartrate O-H...O epoxide). In fact, the present acidic centers can facilitate the ring opening of the SO due to: 1) hydrogen bonding and 2) the proton transfer to the oxygen of the epoxide ring. In the rich agreement with the mentioned hypothesis, MIL-101(Cr)-tart is like the rest of the hydrogenbonding-based catalysts: probably, the formation of the 2methoxy-2-phenylethanol can be assigned to the "functional groups-assisted" methanolysis due to hydrogen-bonds association. Herein, it can be concluded that the non-covalent interactions can affect on the improvement of the catalyst capability. These kinds of interactions are very important particularly in drug delivery like the electrostatic interactions between the functional groups of the mesoporous structures and target molecules [43]. Thereby, it should be noted that the combination of two abilities in the chiral functional groups, as active centers and creation of the asymmetric environment is an advantage for better asymmetric catalysis. Carbon balance was calculated in the enantioselective methanolysis of styrene epoxide, too. In initial time of reaction, the carbon percent was 79.97% and after 9 h, the reaction completed. In final time, the carbon percentages were 75.97% and 4.00% related to (S)- and (R)enantiomer products, respectively.

It is worth that MIL-101(Cr)-tart can be recycled from reaction mixture and reused in the same new catalytic reaction up to five times without significant changes in the results and no detectable Cr is seen by ICP. At the sixth step, the reduction of the conversion and ee was observed to 89% and 86%, separately (Fig. 5).



Fig. 5. MIL-101(Cr)-tart recyclability investigation for model substrate in the asymmetric methanolysis.

To show of the maintenance of the recycled catalyst structure and morphology, PXRD and SEM were used. As shown in Fig. 6, the appeared changes were not sensible in the reused catalyst than pristine MIL-101(Cr). These characterizations disclose that MIL-101(Cr)-tart has remarkable stability. The methanolysis mechanism has been shown in S6b.

Also, hot filtration test (HFT) as a general technique was performed to indicate the catalyst effect in the progress of two studied catalytic reactions (S7). In the epoxidation reaction of styrene after 2 h and methanolysis of styrene oxide after 3 h, the chiral catalyst was removed from the catalytic reactions. Then, the obtained solutions were stirred to optimized time at the determined temperature. The results showed that the reactions without the presence of catalyst did not proceed, considerably. Therefore, this experiment is a good procedure to find the heterogeneity. Of course, the catalytic behavior of the present catalyst was compared to several chiral heterogeneous catalysts in both of asymmetric catalytic reactions: olefin epoxidation and ring-opening (S8 and S9).





Fig. 6. The investigation of MIL-101(Cr)-tart structure. PXRD pattern and SEM image after asymmetric methanolysis at the fifth cycle.

Notably, the findings prove that our chiral catalyst can be used as a cost-effective asymmetric heterogeneous catalyst with satisfactory results. About chirality induction in both catalytic reactions, it can be assumed that the substrates with pro-S face or R-face can approach to the catalytic sites and then the asymmetric induction occurs through the H-bond interaction between the substrates and OH functional groups of the tartrate [44–48].

3. Conclusions

In summary, we reported an asymmetric cationic functional MOF that has been fabricated by chiral post-synthetic modification: incorporation of tartrate anions into the Cr³⁺ node of the neutral framework with F⁻ stripping. Chiral MIL with Lewis acids (Cr³⁺) and the existent hydrophilic functional groups as Brønsted acids has an important role in the enantioselective epoxidation of olefins and better catalytic behavior in the enantioselective methanolysis. The oxidative performance of MIL-101(Cr)-tart was investigated by employing various oxidants: H₂O₂, TBHP and IBA/ O2. IBA/O2 was selected because better enantiomeric excess was obtained. Interestingly, the functional groups of tartrate as Brønsted acid sites can simultaneously activate the epoxide ring through the hydrogen-bonding interactions. They are accessible by reactants and can induce chirality to methanolysis product with enantiomeric excess 90%. These features together, Lewis acid/ Brønsted acid and chirality induction show the effective and positive aspects of chiral MIL-101(Cr)-tart. Surely, the reactivity of the adjacent chiral functional groups in tartrate anions can be useful for a wide range of the asymmetric catalytic reactions through the generating of hydrogen bonding. Truly, MOFs components as secondary building units composition (metal ions or clusters). coordinatively unsaturated metal sites nature, organic linkers and functional groups can be efficient on the MOFs abilities. This work demonstrates that such chiral functional porous MOF can be successfully constructed from a potent starting MOF like MIL-101(Cr) with more accessible catalytic active sites along with the abundant chiral centers. It can be used in the recycle experiments without any damaging of the structure. In the future, we will develop new chiral MOFs for different applications especially in the asymmetric catalysis and enantioselective separation.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2019.08.015.

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