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Epoxidation of styrene over Fe(Cr)-MIL-101 metal–organic frameworks

Jian Sun,[a] Guangli Yu,[b] Qisheng Huo,[b] Qiubin Kan[a] and Jingqi Guan*[a]

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Epoxidation of styrene is one of the key reactions in organic synthesis. In this paper, we investigated the effect of different metal ions in MIL-101 metal–organic framework on styrene epoxidation using various oxidants such as air, H_2O_2 and TBHP. For the aerobic epoxidation of styrene, Fe-MIL-101 and Cr-MIL-101 presented good styrene conversion (87.2 *vs.* 65.5%) and epoxide selectivity (54.4% *vs.* 37.7%) using air as the oxidant. The styrene epoxidation activity for the different oxidants over Fe-MIL-101 was as follows: air > TBHP > H_2O_2, while that over Cr-MIL-101 showed a different trend: H_2O_2 > air > TBHP. Moreover, the selectivity to styrene oxide for the different oxidants was similar over the two catalysts: TBHP > air > H_2O_2. The study of the effect of various solvents revealed that CH_3CN is the optimal solvent for the aerobic epoxidation of styrene. Furthermore, the catalysts could be reused three times without any significant loss in catalytic activity.

Introduction

The catalytic epoxidation of styrene is vitally important in modern chemical industry because the obtained epoxide is an indispensable intermediate in the synthesis of both fine chemicals and pharmaceuticals.[1,2] Traditionally, homogeneous catalytic systems (*e.g.* metal-salen complexes, and chiral metalloporphyrins) or hazardous stoichiometric oxidants (*e.g.* organic peracids, PHIO, TBHP) have been employed to accomplish the epoxidation reaction.[3,4] Unfortunately, these procedures have considerable drawbacks, such as difficulty in catalyst separation and regenerability, utilization of unsafe and expensive oxidants, resulting in serious environmental pollution and industrial loss of interest. With the ever-increasing economic and environmental concerns, the development of heterogeneous catalytic system that can operate with air in place of traditional oxidants has drawn tremendous interest.

Metal–organic frameworks (MOFs) are a rapidly emerging class of porous organic–inorganic hybrid materials synthesized by the self-assembly of metal ions with organic ligands.[5] They display outstanding properties, including large specific surface area, tunable pores, diverse structure and chemical functionality, which make them potentially useful for applications in drug delivery, hydrogen storage, catalysis, separation, nonlinear optics and chemical sensors.[6–11] For catalysis, the most valuable preponderance of MOF is the large concentration of uniform accessible metal centers and coordination unsaturation.[12,13] In comparison with other organic–inorganic hybrid heterogeneous catalysts,[14–16] MOFs do not require cumbersome multistep grafting procedures to achieve the heterogenization of homogeneous catalysts. The zeotype crystal structure of Cr-MIL-101 and Fe-MIL-101 consist of trimeric chromium(III) or iron(III) octahedral clusters interconnected by 1,4-benzenedicarboxylate anions. After the removal of terminal water molecules from MIL-101 framework by heating in vacuum,[17] the formed active coordinatively unsaturated sites can provide accessible sites for guest molecules, playing a role as Lewis acid sites or catalytically active sites.[18,19] On the other hand, the robust MOFs of MIL-101 family are not only easy to synthesize but also present good resistance to water steam, common solvents, and possess relatively high thermal stability (especially Cr-MIL-101, which is even stable up to 300 °C).[20] Therefore, MIL-101 metal–organic framework as heterogeneous catalysts have been widely applied in several organic reactions.

Recently, Kholdeeva and co-workers found that Fe-MIL-101 and Cr-MIL-101 showed efficient catalytic performance in the selective oxidation of alkenes and cyclohexane to unsaturated ketones with molecular oxygen as oxidant and TBHP as initiator.[21,22] Férey *et al.* used Cr-MIL-101 as catalyst for the selective sulfoxidation of aryl sulfides with H_2O_2 as oxidant and obtained satisfactory catalytic results.[23] Moghadam and co-workers found that Cr-MIL-101 was efficient for the direct oxidation of alkenes to carboxylic acids with H_2O_2 as oxidant.[24] Cr-MIL-101 also exhibited good catalytic activity and selectivity in the oxidation of tetralin with TBHP as oxidant.[17] However, to best of our knowledge, there are no detailed reports on styrene epoxidation over MIL-101 family.

In the present study, we explored the catalytic performance of Fe-MIL-101 and Cr-MIL-10 in the aerobic epoxidation of

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[a] *College of Chemistry, Jilin University, Changchun, 130023, P.R. China. E-mail: guanjq@jlu.edu.cn; Tel: +86 431 88499140*

[b] *State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P.R. China*

styrene. The structure of M-MIL-101 (M = Fe or Cr) can be seen in Fig. 1. The effects of different oxidants and solvents have been investigated. Both the catalysts show high conversion and epoxide selectivity for aerobic epoxidation of styrene, and the catalysts can be reused three times without any significant loss in catalytic activity.

Experimental

Materials and methods

Terephthalic acid (H_2BDC, 99%), fluorhydric acid (HF, 40%), ferric chloride hexahydrate ($FeCl_3\cdot 6H_2O$, 99%), chromium(III) nitrate nonahydrate ($Cr(NO_3)_3\cdot 9H_2O$, 99%), ethanol (99.5%), *N*,*N*-dimethylformamide (DMF, 99.9%), styrene (98%), isobutylaldehyde (98%) and acetonitrile (99.8%) were used for synthesis. All the organic solvents were of analytical grade.

The powder X-ray diffraction (XRD) measurements were performed on a Rigaku D/MAX 2550 diffractometer with Cu-Kα radiation ($\lambda = 1.5418$ Å) and operating at 50 kV and 200 mA. The infrared spectra of the materials were recorded on a Nicolet 6700 instrument in the range of 500–2000 cm^{-1} using the KBr pellet technique. The morphology of the samples was obtained with JEOS JSM 6700F filed-emission scanning electron microscope. N_2 adsorption–desorption experiments were carried out at 77 K by an Autosorb iQ2 adsorptometer, Quantachrome Instrument. Prior to analysis, the samples were degassed at 423 K overnight under vacuum. Specific surface areas values of Cr-MIL-101 were calculated by the Brunauer–Emmett–Teller (BET) equation; and the pore volumes and pore size distributions were determined by applying *t*-plot, and non-local density functional theory (NL-DFT) methods, respectively.

Synthesis of Fe-MIL-101

Fe-MIL-101 was prepared *via* a reported solvothermal route.[25] Briefly, $FeCl_3\cdot 6H_2O$ (4.9 mol) and H_2BDC (2.5 mmol) were dissolved in DMF (30 mL) under vigorous stirring to form a clear solution. Then, the resulting solution was transferred into a Teflon-lined stainless-steel autoclave and heated at 110 °C for 20 h. After cooling to room temperature, the obtained brown powder was filtered to remove organic species trapped in the pores. The product was activated by boiling in ethanol overnight and then dried under vacuum.

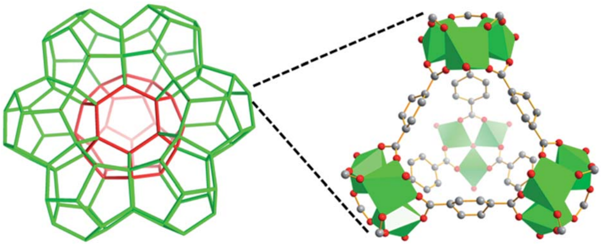


Fig. 1 Left: zeotype crystalline structure of M-MIL-101 (M = Fe or Cr). Right: trimeric Fe or Cr(III)-cluster in MIL-101, the octahedral represent the Fe or Cr ions (in green), oxygen and carbon atoms are represented in red and light grey, respectively.

Synthesis of Cr-MIL-101

Cr-MIL-101 was synthesized based on the procedure described by Férey *et al.*[20] Typically, a mixture of H_2BDC (6 mol), $Cr(NO_3)_3\cdot 9H_2O$ (6 mmol), 1.2 mL of 5 M HF (6 mmol) in 30 mL H_2O was heated at 220 °C for 8 h in a Teflon-lined stainless-steel autoclave. After cooling to room temperature, the obtained green powder was filtered under vacuum to remove organic species trapped in the pores. The product was activated by boiling in DMF and methanol several times, and then dried under vacuum.

Catalytic epoxidation of styrene

The aerobic epoxidation of styrene was performed in a 50 mL two-necked flask equipped with a liquid condenser and an air pump. In a typical run, styrene (10 mmol), catalyst (50 mg) and isobutyraldehyde (25 mmol) as reductant were added to 10 mL of acetonitrile (CH_3CN). Then, the mixture was refluxed at 80 °C for 8 h, and air was introduced at a stable flowing rate of 80 mL min^{-1}. After completion of the reaction, the solid catalyst was centrifuged, washed with acetonitrile and ethanol, dried in vacuum and reused without further purification. The products of the epoxidation reaction were quantified and monitored using a gas chromatograph (Shimadzu, GC-8A) equipped with a HP-5 capillary column and a FID detector. The aerobic epoxidation of styrene with other solvents (DMF, toluene or MeOH) was performed under identical reaction conditions. The epoxidation of styrene with other oxidants (H_2O_2 or TBHP) was performed in a similar manner, except that 30 mmol of oxidant was added into the reactor instead of reductant and air.

Results and discussion

Structure and morphology characterization

To confirm the successful synthesis of Fe-MIL-101 and Cr-MIL-101, XRD and FT-IR characterization have been used, and the results are shown in Fig. 2 and 3, respectively. The XRD patterns of the initial samples are similar to the previously reported pattern of MIL-101 family.[26] FT-IR characterization revealed the presence of the asymmetrical and symmetrical stretching modes of the framework O–C–O in the region from 1400 to 1600

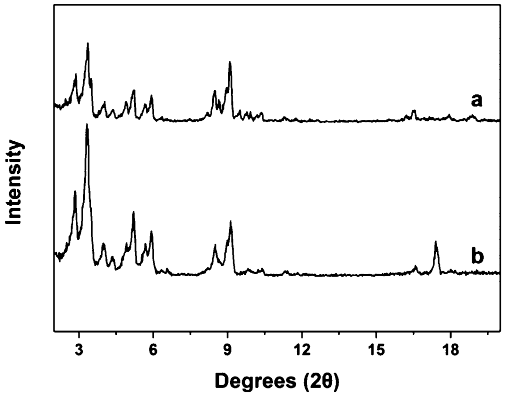


Fig. 2 XRD patterns of (a) Fe-MIL-101 and (b) Cr-MIL-101.

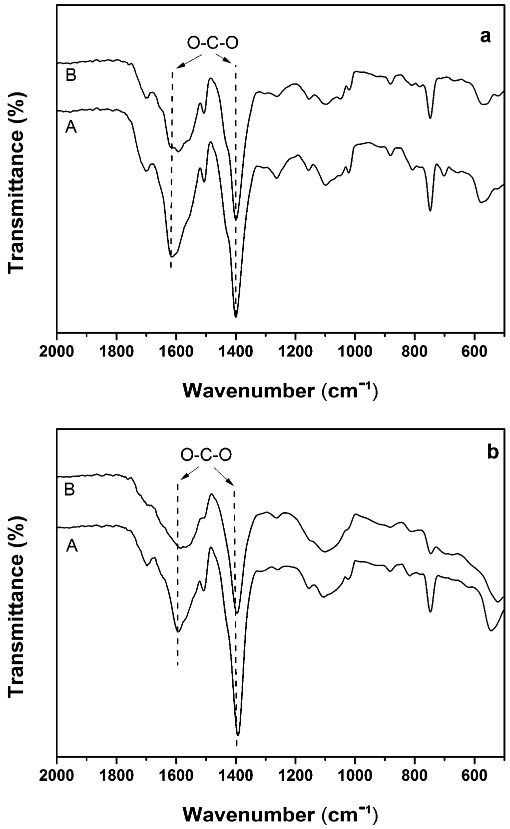


Fig. 3 FT-IR spectra of (a) Fe-MIL-101 and (b) Cr-MIL-101: fresh catalyst (A) and the reused catalyst after 3 cycles (B).

cm^{-1}, which are the typical characteristic bands of MIL-101 metal–organic framework.[27] We can clearly see characteristic bands both in the fresh and the recovered catalysts. Furthermore, SEM was performed to compare the morphology of the fresh and recycled catalysts, as shown in Fig. 4. Both the catalysts are octahedral in shape. No noticeable difference is observed for the initial materials and the reused catalysts. The specific surface areas and porosity of the fresh and reused Cr-MIL-101 catalysts were measured by N_2 adsorption–desorption experiments, and the results are presented in Fig. 5. The BET surface and pore volume of fresh Cr-MIL-101 are 2987 $m^2\ g^{-1}$ and 1.68 $cm^3\ g^{-1}$, respectively. The pore sizes of MIL-101 mainly range from 8.1 to 25 Å. After being used three times in the aerobic epoxidation of styrene, the BET surface area of Cr-MIL-101 decreased from 2987 to 1848 $m^2\ g^{-1}$. The pore volume of Cr-MIL-101 reduced from 1.68 to 0.72 $cm^3\ g^{-1}$. The pore size distribution shows no obvious difference. The decrease in the BET surface and pore volume might be because of the incomplete removal of reactant and product in the pores and/or a partial damage of the structure of Cr-MIL-101 after reusing several times.

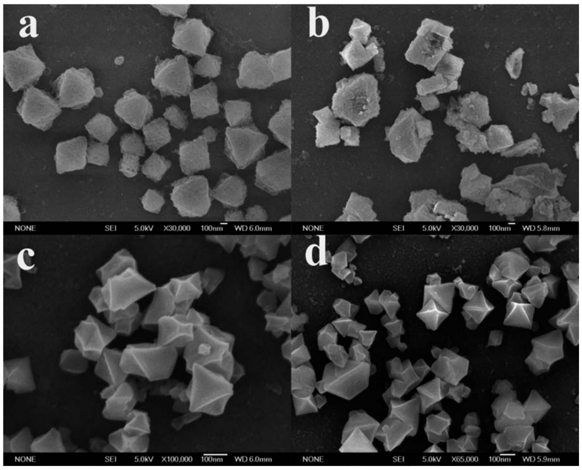


Fig. 4 SEM images of (a) the fresh catalyst Fe-MIL-101, (b) the recovered catalyst Fe-MIL-101 after 3 cycles, (c) the fresh catalyst Cr-MIL-101, and (d) the recovered catalyst Cr-MIL-101 after 3 cycles.

Catalytic properties

The catalytic activity of Fe-MIL-101 and Cr-MIL-101 in the epoxidation of styrene with various oxidants under identical conditions was investigated. The catalytic results are summarized in Table 1. The blank reaction was performed in the absence of catalyst for the aerobic epoxidation of styrene, suggesting very low styrene conversion (entry 1). When we used air as the oxidant and isobutyraldehyde as the reductant, Fe-MIL-101 showed good styrene conversion (87.2%) and epoxide

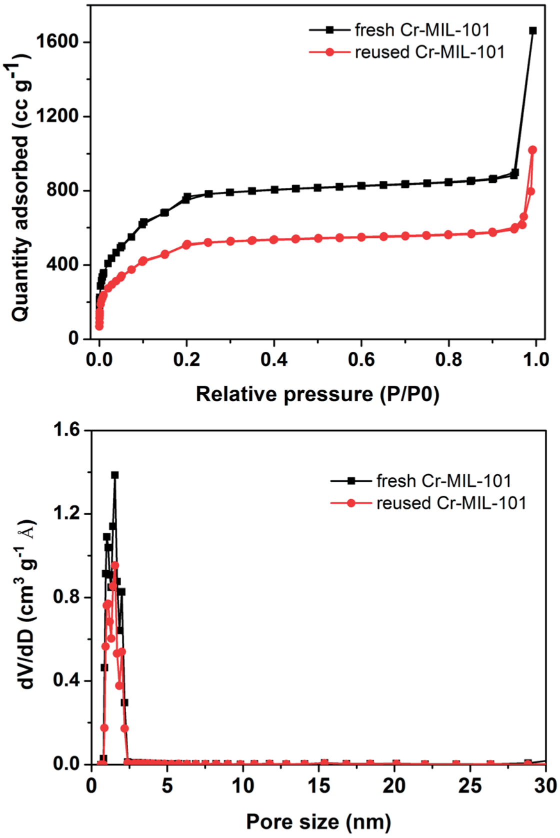


Fig. 5 N_2 adsorption–desorption isotherms and pore size distribution of the fresh and reused Cr-MIL-101.

Table 1 Styrene epoxidation using different oxidants over the Fe-MIL-101 and Cr-MIL-101 catalyst

					Product selectivity (mol%)			
Entry	Catalyst	Oxidant	Time (h)	Conversion (%)	Epoxide	Benzaldehyde	Others[d]	References
1[a]	No catalyst	Air	8	4.1	34.3	65.7	0	Herein
2[a]	Fe-MIL-101	Air	8	87.2	54.4	39.1	6.5	Herein
3[a]	FeQ_3–Y	Air	8	83.4	24.5	58.2	17.3	28
4[a]	Fe–salen–GO	Air	8	76.5	49.8	46.4	3.8	29
5[a]	Fe–salen–SBA	Air	8	80.9	59.7	32.8	7.5	30
6[b]	Fe-MIL-101	H_2O_2	1	32.8	1.9	96.8	1.3	Herein
7[b]	Fe-MIL-101	H_2O_2	4	36.5	2.1	96.5	1.4	Herein
8[b]	Fe-MIL-101	H_2O_2	8	37.3	2.5	93.2	4.3	Herein
9[c]	Fe-MIL-101	TBHP	1	8.5	93.2	6.8	0	Herein
10[c]	Fe-MIL-101	TBHP	4	37.4	91.7	7.5	0.8	Herein
11[c]	Fe-MIL-101	TBHP	8	52.1	92.2	6.6	1.2	Herein
12[a]	Cr-MIL-101	Air	8	65.5	37.7	58.0	4.3	Herein
13[b]	Cr-MIL-101	H_2O_2	1	73.2	2.7	95.4	1.9	Herein
14[b]	Cr-MIL-101	H_2O_2	4	96.3	6.3	91.1	2.6	Herein
15[b]	Cr-MIL-101	H_2O_2	8	97.6	5.7	88.2	6.1	Herein
16[c]	Cr-MIL-101	TBHP	1	3.4	92.0	8.0	0	Herein
17[c]	Cr-MIL-101	TBHP	4	21.4	88.7	9.8	1.5	Herein
18[c]	Cr-MIL-101	TBHP	8	35.4	82.6	15.7	1.7	Herein

[a] Reaction conditions: catalyst 50 mg, styrene 1.14 mL (10 mmol), CH_3CN 10 mL, flow of air 80 mL min^{-1}, isobutyraldehyde (25 mmol), temperature 80 °C and time 8 h. [b] H_2O_2 (30 mmol). [c] TBHP (30 mmol). [d] Others: including phenylacetaldehyde and benzoic acid.

selectivity (54.4%) after reaction for 8 h. In comparison to the traditional Fe-containing heterogeneous catalysts (*e.g.* FeQ3–Y, Fe-salen–GO, Fe-salen–SBA),[28–30] Fe-MIL-101 exhibited either higher conversion or epoxide selectivity in the aerobic epoxidation of styrene. The satisfactory catalytic results can be attributed to the following reason: MIL-101 possesses abundant coordinatively unsaturated sites (CUS) that play a role as catalytically active sites.[31,32] Because of the regular arrangement and well-understood surrounding environments of metal centers in the pore channels, MIL-101 with CUS could be used to induce regioselectivity and shape or size selectivity toward guest molecules or reaction intermediates.[33] Furthermore, the large pore windows and pore volumes of MIL-101 are efficient for guest molecules diffusing in and the product moving out, thus improving reaction efficiency.[34] Cr-MIL-101 shows lower styrene conversion (65.5%) and epoxide selectivity (37.7%) under the same experimental conditions. When H_2O_2 is used as an oxidant, the Fe-MIL-101 achieves a relatively low styrene conversion (37.3%), which may be caused by the rapid decomposition of H_2O_2 into O_2 in the initial stage.[35] Very high styrene conversion (97.6%) is acquired by Cr-MIL-101 using H_2O_2 as oxidant but the epoxide selectivity is very poor (only 5.7%). A similar situation involving benzaldehyde as a dominant product in styrene epoxidation, with H_2O_2 as oxidant and CH_3CN as solvent can be found in many earlier reports.[36–38] A reasonable explanation for this phenomenon is that a nucleophilic attack of H_2O_2 on epoxide occurs, followed by the cleavage of C=C bond to form benzaldehyde.[39] The effect of TBHP as an oxidant on styrene epoxidation was also investigated. Although epoxide selectivity far exceeded 80% when TBHP was used, the styrene conversion over Fe-MIL-101 is lower compared to that achieved using air as the oxidant. In addition, TBHP is expensive and unfriendly to environment. Thus, air is a suitable oxidant in the epoxidation of styrene over Fe-MIL-101.

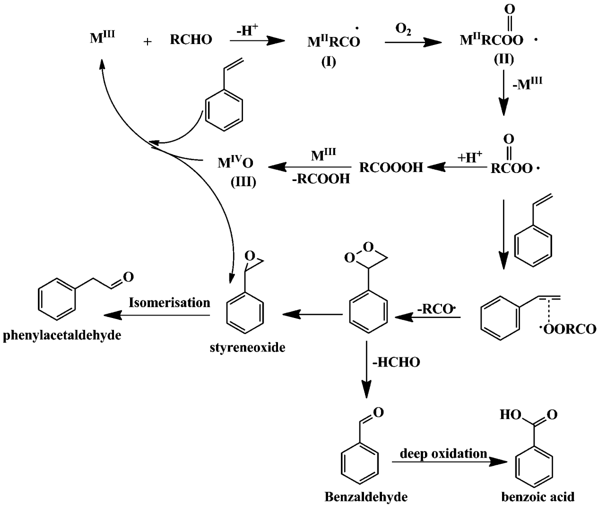
The effect of different solvents on the aerobic epoxidation of styrene over MIL-101 was studied and the results are shown in Table 2. The styrene conversion for different solvents over Fe-MIL-101 follows this trend: CH_3CN > Toluene > DMF > MeOH, while the styrene conversion for different solvents over Cr-MIL-101 follows another trend: CH_3CN > DMF > toluene > MeOH. In all the investigated cases, CH_3CN was observed to be the best solvent in terms of styrene conversion for aerobic epoxidation. Although the highest epoxide selectivity (64.2% for Fe-MIL-101 and 57.4% for Cr-MIL-101) is achieved when DMF is used as the solvent, styrene conversion is relatively low compared with CH_3CN as the solvent. Islam *et al.* proposed that CH_3CN is a polar solvent with high dielectric constant and dissolves a wide range of chemical compounds, which are favorable to high activity and selectivity for styrene oxide.[40] These results indicate that CH_3CN is the most suitable solvent for aerobic epoxidation styrene.

Based on the in-depth study of experimental results and relevant literature,[41–43] a tentative reaction mechanism for the aerobic epoxidation of styrene, in the presence of isobutyraldehyde as a sacrificial co-oxidant over M-MIL-101 (M = Cr or Fe) metal–organic framework, is proposed in Scheme 1. Coordinatively unsaturated sites M^{III} in M-MIL-101 interacts with isobutyraldehyde (RCHO) to generate intermediate species (I) and then activates molecular oxygen, resulting in the formation of species (II). M^{III} is regenerated by species (II) and the acylperoxy radical is released, following which the reaction may proceed through two routes. One is that acylperoxy radical directly attacks the C=C double bond of styrene molecule to form styrene epoxide. Another pathway is that metal-peroxy

Table 2 Aerobic epoxidation of styrene in different solvents over MIL-101[a]

				Product selectivity (%)		
Entry	Catalyst	Solvent	Conversion (%)	Epoxide	Benzaldehyde	Others[b]
1	Fe-MIL-101	CH_3CN	87.2	54.4	39.1	6.5
2	Fe-MIL-101	Toluene	63.7	32.6	63.9	3.5
3	Fe-MIL-101	DMF	19.7	64.2	26.7	9.1
4	Fe-MIL-101	MeOH	17.6	3.5	87.8	8.7
5	Cr-MIL-101	CH_3CN	65.5	37.7	58.0	4.3
6	Cr-MIL-101	DMF	21.9	57.4	32.1	10.5
7	Cr-MIL-101	Toluene	18.3	5.3	78.8	15.9
8	Cr-MIL-101	MeOH	1.5	21.3	78.7	0

[a] Reaction conditions: catalyst 50 mg, styrene 1.14 mL (10 mmol), solvent 10 mL, flow of air 80 mL min^{-1}, isobutyraldehyde (25 mmol), temperature 80 °C and time 8 h. [b] Others: including phenylacetaldehyde and benzoic acid.



Scheme 1 Tentative reaction mechanism for the epoxidation of styrene with air in the presence of isobutyraldehyde over M-MIL-101 (M = Cr or Fe).

active species (III) interacts with substrate to form styrene epoxide, regenerating the catalytic active species M^{III}. The formation of phenylacetaldehyde may be caused by the isomerisation of styrene oxide.[44] Lewis acid sites in the MOF most likely promote the epoxide-opening and rearrangement.[45] In addition, benzoic acid may be formed by the deep oxidation of benzaldehyde.

The reusability and stability of the heterogeneous catalysts are of significant importance in terms of practical application and green chemistry. To address the concern, recycling experiments were performed over the Fe-MIL-101 and Cr-MIL-101 using styrene as the substrate, and the results are presented in Fig. 6. After each reaction, the catalyst was centrifuged, washed thoroughly with acetonitrile and ethanol, dried under vacuum and reused for the subsequent cycles. In a series of three consecutive runs, Cr-MIL-101 exhibits basically stable catalytic activity and selectivity (63.7–65.5% conversion and 36.5–37.7% epoxide selectivity). In addition, the reused Fe-MIL-101 showed good epoxide selectivity (*ca.* 53.6%) but a slight decrease in styrene conversion from 87.2% to 82.4% after recycling three times. When we promoted the reaction cycles to four times, the catalytic activity of both the catalysts showed an obvious decrease. Fe-MIL-101 and Cr-MIL-101 presented a low styrene conversion (52.4 *vs.* 47.5%), which may be caused by partial structure collapse upon using three times. Thus, the MIL-101 catalyst can efficiently be reused three times. To further evaluate the stability of Fe-MIL-101 and Cr-MIL-101 during the catalytic process, the leaching test was carried out and the results are shown in Fig. 7. The aerobic epoxidation reaction was suspended after 3 hours. Subsequently, the

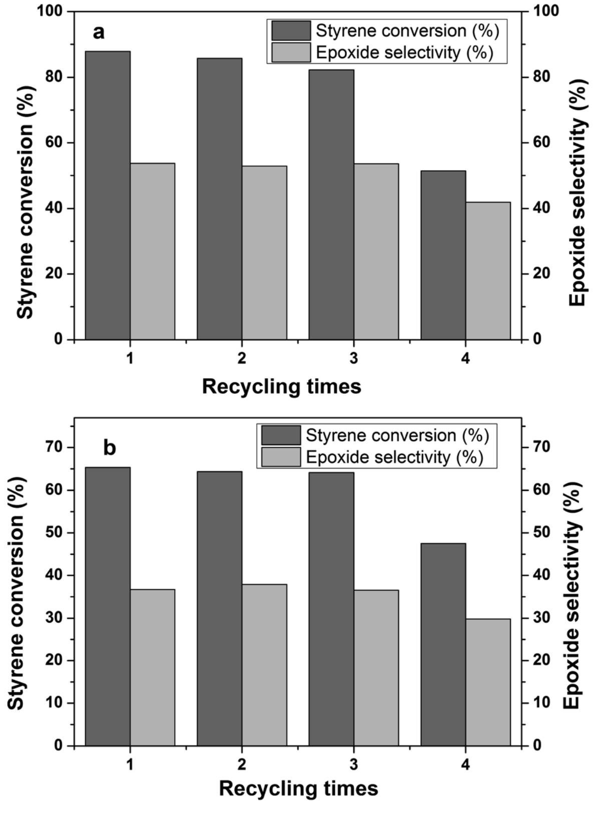


Fig. 6 Recycling experiments of (a) Fe-MIL-101 and (b) Cr-MIL-101 for aerobic epoxidation of styrene.

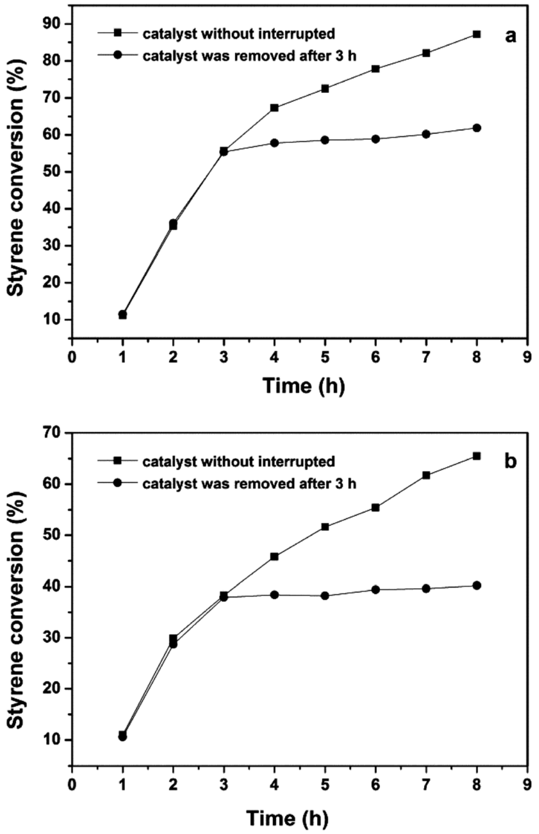


Fig. 7 Leaching experiments of (a) Fe-MIL-101 and (b) Cr-MIL-101 for aerobic epoxidation of styrene.

catalyst was centrifuged under hot conditions, and the resulting clear solution was stirred at 80 °C for another 5 h. However, no obvious improvement in styrene conversion could be observed after catalysts were removed. After completion of the reaction, the solution was analyzed by inductively coupled plasma analysis techniques, suggesting almost no detectable metal ions. These results indicate that Fe-MIL-101 and Cr-MIL-101 are rather stable in the catalytic process because no metal leaching occurs.

Conclusions

This research demonstrates that Fe-MIL-101 and Cr-MIL-101 are efficient heterogeneous catalysts for the epoxidation of styrene with air as an oxidant and isobutyraldehyde as a reductant in CH_3CN. Fe-MIL-101 and Cr-MIL-101 presented good styrene conversion (87.2% *vs.* 65.5%) and epoxide selectivity (54.4% *vs.* 37.7%). The effects of various oxidants for styrene epoxidation have been investigated. Over Fe-MIL-101, the conversion with air is higher than that with TBHP and H_2O_2, while over Cr-MIL-101, the conversion with H_2O_2 is better than air and TBHP. Moreover, the selectivity to styrene oxide for the different oxidants is similar over the two catalysts: TBHP > air > H_2O_2. The influence of various solvents can conclude that CH_3CN is the optimum solvent for aerobic epoxidation of styrene over Fe-MIL-101 and Cr- MIL-101. Both the catalysts can be reused three times with insignificant loss in catalytic activity and epoxide selectivity. The leaching experiments further indicate that the MIL-101 family are truly heterogeneous catalysts.

Acknowledgements

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