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ARTICLE

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

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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, H₂O₂ and TBHP. For 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%) by using air as the oxidant. The styrene epoxidation activity for the different oxidants over Fe-MIL-101 was as follows: air > TBHP > H₂O₂, while it over Cr-MIL-101 showed a different trend: H₂O₂ > air > TBHP. Moreover, the selectivity to styrene oxide for the different oxidants was similar over the two catalysts: TBHP > air > H₂O₂. The influence of various solvent can conclude that CH₃CN might be the optimum solvent for aerobic epoxidation of styrene. Furthermore, the catalysts could be reused three times without significant loss in catalytic activity.

Introduction

The catalytic epoxidation of styrene is vitally important in modern chemical industry, since the obtained epoxide is 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) were employed to accomplish the epoxidation reaction.^{3,4} Unfortunately, these procedures have considerable drawbacks such as difficulty in the catalyst separation and regenerability, utilization of unsafety and expensive oxidants, resulting in seriously environmental pollution and industrial interest loss. 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 rapidly emerging class of porous organic-inorganic hybrid materials synthesized by self-assembly of metal ions with organic ligands.⁵ Due to their outstanding properties including large specific surface area, tunable pores, diverse structure and chemical functionality, which make MOF potential 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 MOF does not need cumbersome multi-step grafting procedure to achieve heterogenization of homogeneous catalysts. The zeotype crystal structure of Cr-MIL-101 and Fe-MIL-101 was consisted of trimeric chromium(III) or iron(III) octahedral clusters interconnected by 1,4-benzenedicarboxylate anions. After 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 MOF of MIL-101 family not only is easy to be synthesized, but also presents a good resistance to water steam, common solvents, and a relatively high thermal stability (especially Cr-MIL-101 is even stable up to 300°C).²⁰ Therefore MIL-101 metal organic framework as heterogeneous catalysts was widely applied in many organic reactions.

Recently, Kholdeeva and co-workers found that Fe-MIL-101 and Cr-MIL-101 showed efficiently 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 selective sulfoxidation of aryl sulfides with H₂O₂ as oxidant and obtained satisfied catalytic results.²³ Moghadam and co-workers found that Cr-MIL-101 was efficient for direct oxidation of alkenes to carboxylic acids with H₂O₂ as oxidant.²⁴ Cr-MIL-101 also exhibited good catalytic activity and selectivity in the oxidation of tetralin with TBHP as oxidant.¹⁷

Nevertheless, to best of our knowledge, there are no detail reports on styrene epoxidation over MIL-101 family.

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

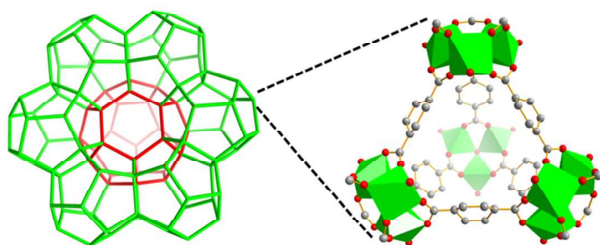


Fig.1. Left: the zeotype crystalline structure of M-MIL-101 (M=Fe or Cr). Right: trimeric Fe or Cr(III)-cluster in MIL-101, the octahedral represent the Fe or Cr ions (in green), oxygen and carbon atoms are represented in red and light grey, respectively.

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%), acetonitrile (99.8%). All organic solvents are analytical grade.

The powder X-ray diffraction (XRD) measurements were performed on a Rigaku D/MAX 2550 diffractometer with $Cu-K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) and operating at 50 KV and 200 mA. The infrared spectra of the materials were conducted on a Nicolet 6700 instrument in the range of $500\text{--}2000 \text{ cm}^{-1}$ using 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 (30ml) under vigorous stir to form a clear solution. Then the resulting solution was transferred into a Teflon-lined stainless-steel autoclave and heated at $110 \text{ }^\circ\text{C}$ for

20 h. After cooled to room temperature, the obtained brown powder was filtered to remove organic species trapped in the pores. The product was activated by boiling ethanol overnight and dried under vacuum.

Synthesis of Cr-MIL-101

Cr-MIL-101 was synthesized based on the procedure described by Férey et al.¹⁷ 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 $220 \text{ }^\circ\text{C}$ for 8 h in a Teflon-lined stainless-steel autoclave. After cooled 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 DMF and methanol several times, and 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 isobutylaldehyde (25 mmol) as reductant were added into 10 ml of acetonitrile (CH_3CN). Then, the mixture was refluxed at 80°C for 8 h, and air was introduced with a stable flowing rate of $80 \text{ ml}\cdot\text{min}^{-1}$. 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 solvent (DMF, toluene or MeOH) was performed under identical reaction condition. The epoxidation of styrene with other oxidants (H_2O_2 or TBHP) was performed in a similar way except that 30 mmol of oxidant was added into the reactor instead of reductant and air.

Results and discussion

Structure and morphology characterization

In order 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 depicted in Fig. 2 and Fig. 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 existence of the asymmetrical and symmetrical stretching modes of the framework O–C–O in the region from 1400 to 1600 cm^{-1} , which are the typical characteristic bands of MIL-101 metal–organic framework.²⁷ We can clearly see the characteristic bands both in the fresh catalysts and the recovered catalysts. Furthermore, SEM was performed to compare the morphology of the fresh and recycled catalysts as shown in Fig. 4. Both of 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 N₂ adsorption–desorption experiments and the results are presented in Fig. 5. The BET surface and pore volume of fresh Cr-MIL-101 are 2987 m²g⁻¹ and 1.68 cm³g⁻¹, respectively. Pore sizes of MIL-101 mainly range from 8.1 to 25 Å. After using three times in the aerobic epoxidation styrene, the BET surface area of Cr-MIL-101 decreased from 2987 to 1848 m²g⁻¹. The pore volume of Cr-MIL-101 reduced from 1.68 to 0.72 cm³g⁻¹. The pore size distribution shows no obvious difference. The decrease in BET surface and pore volume might be due to the incomplete removal of reactant and product in the pores and/or a partial damage of structure of Cr-MIL-101 after using many times.

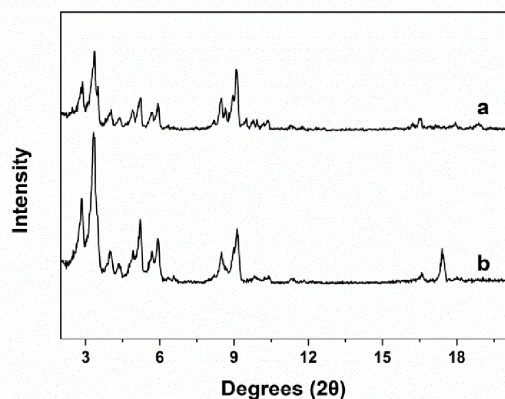


Fig.2. XRD patterns of (a) Fe-MIL-101 and (b) Cr-MIL-101.

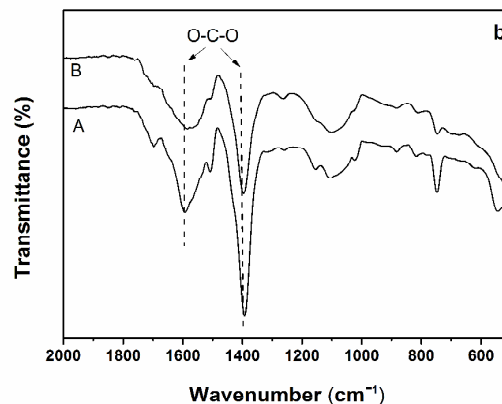
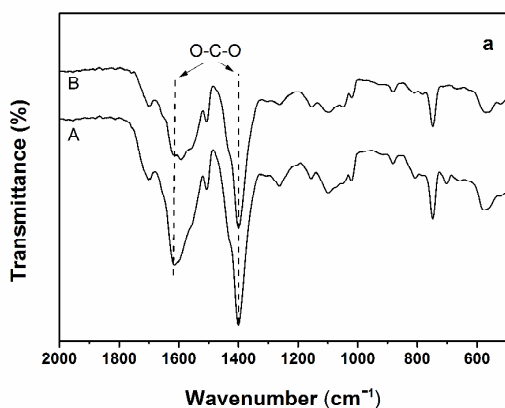


Fig.3. FT-IR spectra of (a) Fe-MIL-101 and (b) Cr-MIL-101: fresh catalyst (A) and the reused catalyst after 3 cycles (B).

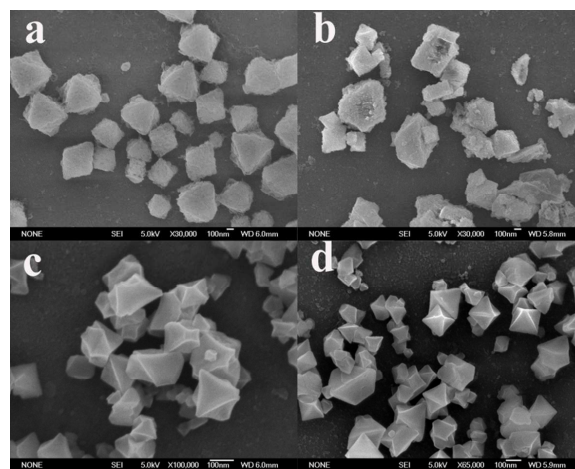
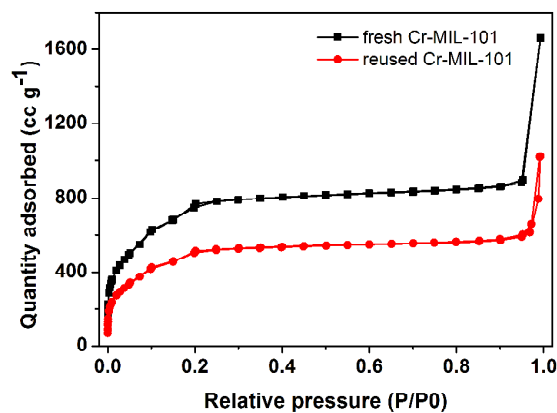


Fig.4 SEM images of (a) the fresh catalyst Fe-MIL-101, (b) the recovered catalyst Fe-MIL-101 after 3cycles, (c) the fresh catalyst Cr-MIL-101, and (d) the recovered catalyst Cr-MIL-101 after 3cycles



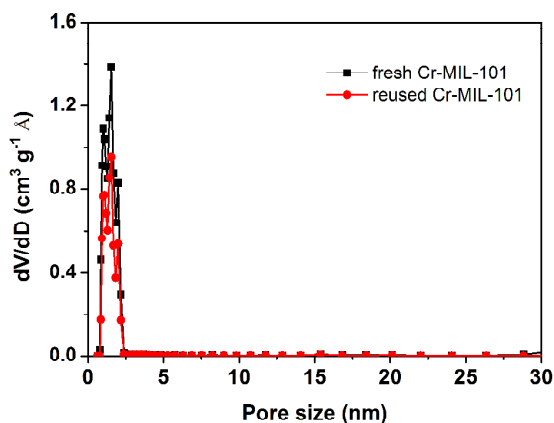


Fig.5 N₂ adsorption/desorption isotherms and pore size distribution of the fresh and reused Cr-MIL-101

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 aerobic epoxidation styrene, suggesting very low styrene conversion (entry 1). When we used air as the oxidant and isobutyraldehyde as the reductant, Fe-MIL-101 shows good styrene conversion (87.2%) and epoxide 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 exhibits either higher conversion or epoxide selectivity in aerobic epoxidation styrene. The satisfactory catalytic results can be attributed to the following reason: MIL-

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

Entry	Catalyst	Oxidant	Time (h)	Conversion (%)	Product selectivity (mol %)			References
					Epoxide	Benzaldehyde	Others ^d	
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 ₂ O ₂	1	32.8	1.9	96.8	1.3	Herein
7 ^b	Fe-MIL-101	H ₂ O ₂	4	36.5	2.1	96.5	1.4	Herein
8 ^b	Fe-MIL-101	H ₂ O 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 ₂ O ₂	1	73.2	2.7	95.4	1.9	Herein
14 ^b	Cr-MIL-101	H ₂ O ₂	4	96.3	6.3	91.1	2.6	Herein

101 possesses abundant coordinatively unsaturated sites (CUS) that play a role as catalytically active sites.^{31, 32} Due to 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 towards guest molecules or reaction intermediates.³³ Furthermore, the large pore windows and pore volumes of MIL-101 are efficient for guest molecule diffusing and 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 we used H₂O₂ as oxidant, the Fe-MIL-101 achieves a relatively low styrene conversion (37.3%), which may be caused by the rapid decomposition of H₂O₂ into O₂ in the initial stage.³⁵ Very high styrene conversion (97.6%) is acquired by Cr-MIL-101 using H₂O₂ as oxidant, but the epoxide selectivity is quietly poor (only 5.7%). The similar situation of benzaldehyde as dominant product in styrene epoxidation with H₂O₂ as oxidant and CH₃CN as solvent can be found in many earlier reports.³⁶⁻³⁸ A reasonable explanation for this phenomenon is the nucleophilic attack of H₂O₂ on epoxide, following via the cleavage of C=C bond to form benzaldehyde.³⁹ The effect of TBHP as oxidant on styrene epoxidation has also been studied. Though 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 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.

15 ^b	Cr-MIL-101	H ₂ O 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), CH₃CN 10 mL, flow of air 80 mL/min, isobutyraldehyde (25 mmol), temperature 80 °C and time 8 h. ^b H₂O₂ (30 mmol). ^c TBHP (30 mmol). ^d Others: including phenylacetaldehyde and benzoic acid.

Table 2 aerobic epoxidation of styrene in different solvents over MIL-101^a

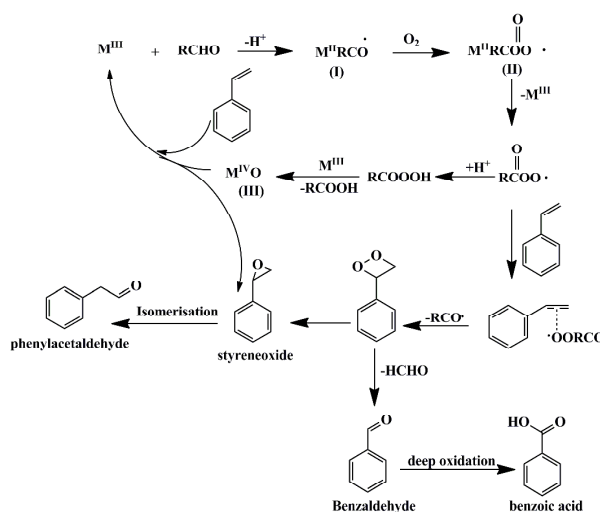
Entry	Catalyst	Solvent	Conversion. (%)	Product selectivity (%)		
				Epoxide	Benzaldehyde	Others ^b
1	Fe-MIL-101	CH ₃ CN	87.2	54.4	39.1	6.5
2	Fe-MIL-101	Toluene	63.7	32.6	63.9	3.5
3	Fe-MIL-101	DMF	19.7	64.2	26.7	9.1
4	Fe-MIL-101	MeOH	17.6	3.5	87.8	8.7
5	Cr-MIL-101	CH ₃ CN	65.5	37.7	58.0	4.3
6	Cr-MIL-101	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, isobutyraldehyde (25 mmol), temperature 80 °C and time 8 h.

The influence of different solvents on the aerobic epoxidation of styrene over MIL-101 was studied in Table 2. The styrene conversion for different solvents over Fe-MIL-101 is in this trend: CH₃CN > Toluene > DMF > MeOH, while the styrene conversion for different solvents over Cr-MIL-101 is in another trend: CH₃CN > DMF > Toluene > MeOH. In all the studied cases, CH₃CN is the best solvent in terms of styrene conversion for aerobic epoxidation. Though the highest epoxide selectivity (64.2% for Fe-MIL-101 and 57.4% for Cr-MIL-101) is achieved when DMF is used as solvent, the styrene conversion is relatively low compared with CH₃CN as solvent. Islam et al. proposed that CH₃CN 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 CH₃CN 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 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 interacted with isobutyraldehyde (RCHO) to generate intermediate species (I) and then activated the molecular oxygen resulting in the formation of species (II). M^{III} was regenerated by species (II) and released acylperoxy radical, following that the reaction may proceed through two routes. One is that acylperoxy radical directly attacked the C=C double

bond of styrene molecule to form styrene epoxide. Another pathway is that metal-peroxy active species (III) interacted with substrate to form styrene epoxide meanwhile 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 promoted epoxide-opening and rearrangement.⁴⁵ In addition, benzoic acid may be formed by deep oxidation of benzaldehyde.



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

The reusability and stability of the heterogeneous catalysts are of great 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 slightly decrease in styrene conversion from 87.2 % to 82.4% after recycling for three times. When we promoted the reaction cycles to four times, the catalytic activity of both catalysts has 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 after using three times. Thus, MIL-101 catalyst can efficiently be reused three times. In order 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 catalyst was centrifuged under hot conditions, and the resulting clear solution was stirred at 80 °C for another 5 h. Nevertheless, no obvious improvement in styrene conversion can 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 seriously metal leaching happens.

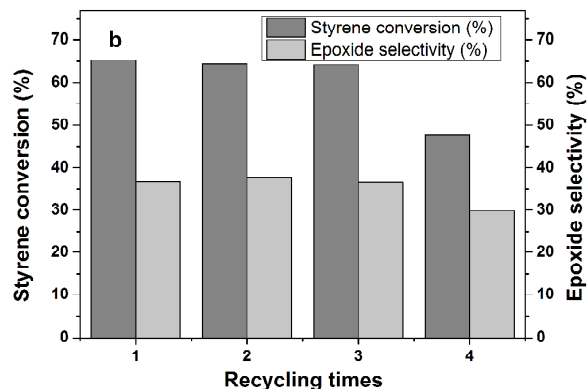


Fig.6 Recycling experiments of (a) Fe-MIL-101 and (b) Cr-MIL-101 for aerobic epoxidation of styrene

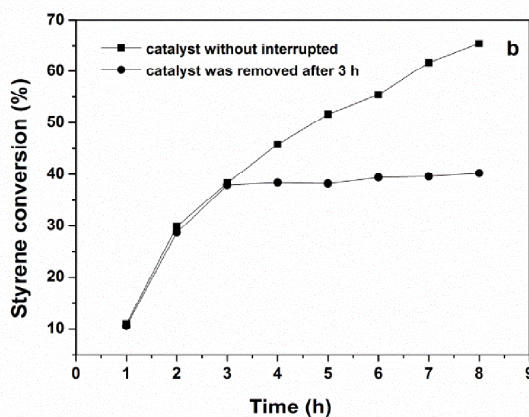
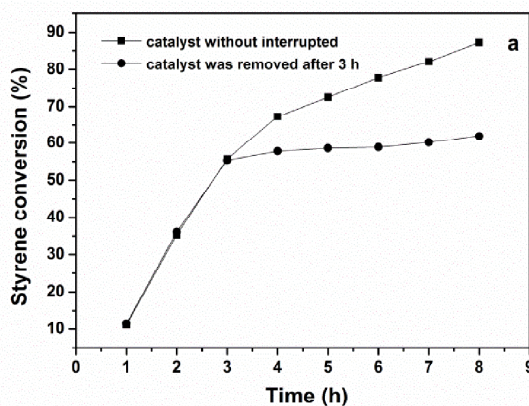
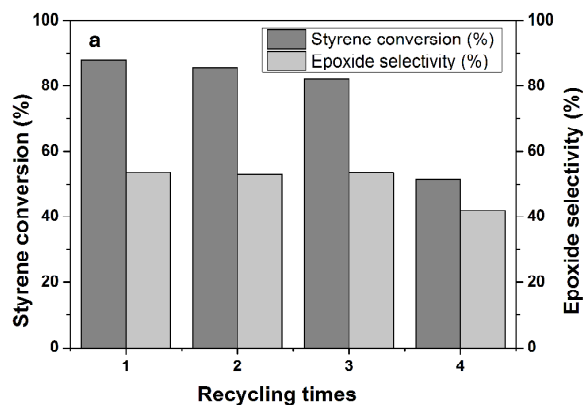


Fig.7. Leaching experiments of (a) Fe-MIL-101 and (b) Cr-MIL-101 for aerobic epoxidation of styrene.



Conclusions

This research demonstrates that Fe-MIL-101 and Cr-MIL-101 are efficient heterogeneous catalysts for epoxidation of styrene with air as oxidant and isobutyraldehyde as 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 H₂O₂, while over Cr-MIL-101, the conversion with H₂O₂ is better than air and TBHP. Moreover, the selectivity to styrene oxide for the different oxidants is similar over the two catalysts: TBHP > air > H₂O₂. The influence of various solvent can conclude that CH₃CN is the optimum solvent for aerobic epoxidation styrene over Fe-MIL-101 and Cr-MIL-101. Both of the catalysts can be reused three times with insignificantly loss in catalytic activity and epoxide selectivity. The leaching experiments further indicate that MIL-101 family is truly heterogeneous catalysts.

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Notes and references

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- S. A. Hauser, M. Cokoja and F. E. Kühn, *Catal. Sci. Technol.*, 2013, **3**, 552-561.
- V. R. Choudhary, R. Jha and P. Jana, *Green Chem.*, 2006, **8**, 689-690.
- E. M. McGarrigle and D. G. Gilheany, *Chem. Rev.*, 2005, **105**, 1563-1602.
- J. R. L. Smith and G. Reginato, *Org. biomol. chem.*, 2003, **1**, 2543-2549.
- A. Corma, H. Garcia and F. Llabrés i Xamena, *Chem. Rev.*, 2010, **110**, 4606-4655.
- A. Dhakshinamoorthy, M. Alvaro and H. Garcia, *Catal. Sci. Technol.*, 2011, **1**, 856-867.
- C. Wang, T. Zhang and W. Lin, *Chem. Rev.*, 2012, **112**, 1084-1104.
- M. P. Suh, H. J. Park, T. K. Prasad and D. W. Lim, *Chem. Rev.*, 2012, **112**, 782-835.
- J. R. Li, J. Sculley and H. C. Zhou, *Chem. Rev.*, 2012, **112**, 869-932.
- L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.*, 2012, **112**, 1105-1125.
- P. Horcajada, T. Chalati, C. Serre, B. Gillet, C. Sebrie, T. Baati, J. F. Eubank, D. Heurtaux, P. Clayette, C. Kreuz, J. S. Chang, Y. K. Hwang, V. Marsaud, P. N. Bories, L. Cynober, S. Gil, G. Férey, P. Couvreur and R. Gref, *Nat. Mater.*, 2010, **9**, 172-178.
- J. Zhang, A. V. Biradar, S. Pramanik, T. J. Emge, T. Asefa and J. Li, *Chem. Commun.*, 2012, **48**, 6541-6543.
- A. Dhakshinamoorthy, M. Alvaro and H. Garcia, *J. Catal.*, 2012, **289**, 259-265.
- J. Sun, Q. Kan, Z. Li, G. Yu, H. Liu, X. Yang, Q. Huo and J. Guan, *RSC Adv.*, 2014, **4**, 2310-2317.
- L. Ma, F. Su, X. Zhang, D. Song, Y. Guo and J. Hu, *Microporous and Mesoporous Mater.*, 2014, **184**, 37-46.
- A. R. Silva, K. Wilson, A. C. Whitwood, J. H. Clark and C. Freire, *Eur. J. Inorg. Chem.*, 2006, **2006**, 1275-1283.
- J. Kim, S. Bhattacharjee, K. E. Jeong, S. Y. Jeong and W. S. Ahn, *Chem. Commun.*, 2009, 3904-3906.
- L. Alaerts, E. Seguin, H. Poelman, F. Thibault-Starzyk, P. A. Jacobs and D. E. De Vos, *Eur. J. Chem.*, 2006, **12**, 7353-7363.
- P. Horcajada, S. Surblé, C. Serre, D. Y. Hong, Y. K. Seo, J. S. Chang, J. M. Greneche, I. Margiolaki and G. Férey, *Chem. Commun.*, 2007, 2820-2822.
- G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé and I. Margiolaki, *Science*, 2005, **309**, 2040-2042.
- N. V. Maksimchuk, K. A. Kovalenko, V. P. Fedin and O. A. Kholdeeva, *Chem. Commun.*, 2012, **48**, 6812-6814.
- O. A. Kholdeeva, I. Y. Skobelev, I. D. Ivanchikova, K. A. Kovalenko, V. P. Fedin and A. B. Sorokin, *Catal. Today*, 2014.
- Y. K. Hwang, D.-Y. Hong, J.-S. Chang, H. Seo, M. Yoon, J. Kim, S. H. Jung, C. Serre and G. Férey, *Appl. Catal., A*, 2009, **358**, 249-253.
- Z. Saedi, S. Tangestaninejad, M. Moghadam, V. Mirkhani and I. Mohammadpoor-Baltork, *Catal. Commun.*, 2012, **17**, 18-22.
- K. M. Taylor-Pashow, J. D. Rocca, Z. Xie, S. Tran and W. Lin, *J. Chem. Soc.*, 2009, **131**, 14261-14263.
- I. Y. Skobelev, A. B. Sorokin, K. A. Kovalenko, V. P. Fedin and O. A. Kholdeeva, *J. Catal.*, 2013, **298**, 61-69.
- R. B. Ferreira, P. M. Scheetz and A. L. B. Formiga, *RSC Adv.*, 2013, **3**, 10181-10184.
- Y. Yang, H. Ding, S. Hao, Y. Zhang and Q. Kan, *Appl. Organomet. Chem.*, 2011, **25**, 262-269.
- Z. Li, S. Wu, H. Ding, H. Lu, J. Liu, Q. Huo, J. Guan and Q. Kan, *New J. Chem.*, 2013, **37**, 4220.
- Y. Yang, Y. Zhang, S. Hao and Q. Kan, *Chem. Eng. J.*, 2011, **171**, 1356-1366.
- A. Vimont, J.-M. Goupil, J.-C. Lavalley, M. Daturi, S. Surblé, C. Serre, F. Millange, G. Férey and N. Audebrand, *J. Am. Chem. Soc.*, 2006, **128**, 3218-3227.
- A. Vimont, H. Leclerc, F. Maugé, M. Daturi, J.-C. Lavalley, S. Surblé, C. Serre and G. Férey, *J. Phys. Chem. C*, 2007, **111**, 383-388.
- D. Y. Hong, Y. K. Hwang, C. Serre, G. Férey and J. S. Chang, *Adv. Fun. Mater.*, 2009, **19**, 1537-1552.
- A. Henschel, K. Gedrich, R. Kraehnert and S. Kaskel, *Chem. Commun.*, 2008, 4192-4194.
- H. Cui, Y. Zhang, L. Zhao and Y. Zhu, *Catal. Commun.*, 2011, **12**, 417-420.
- W. Tanglumlert, T. Imae, T. J. White and S. Wongkasemjit, *Catal. Commun.*, 2009, **10**, 1070-1073.
- J. Hu, K. Li, W. Li, F. Ma and Y. Guo, *Appl. Catal., A*, 2009, **364**, 211-220.
- S. Jana, B. Dutta, R. Bera and S. Koner, *Langmuir*, 2007, **23**, 2492-2496.
- V. Hulea and E. Dumitriu, *Appl. Catal., A*, 2004, **277**, 99-106.
- S. M. Islam, A. S. Roy, P. Mondal, M. Mobarok, B. Roy, N. Salam, S. Paul and S. Mondal, *Monatsh. Chem.*, 2011, **143**, 815-823.
- L. Hamidipour, F. Farzaneh and M. Ghandi, *React. Kinet., Mech. Catal.*, 2012, **107**, 421-433.
- E. Angelescu, R. Ionescu, O. D. Pavel, R. Zăvoianu, R. Bîrjega, C. R. Luculescu, M. Florea and R. Olar, *J. Mol. Catal. A: Chem.*, 2010, **315**, 178-186.
- A. Zhang, L. Li, J. Li, Y. Zhang and S. Gao, *Catal. Commun.*, 2011, **12**, 1183-1187.
- P. Cancino, V. Paredes-García, P. Aguirre and E. Spodine, *Catal. Sci. Technol.*, 2014, **4**, 2599-2607.
- A. Dhakshinamoorthy, M. Alvaro and H. Garcia, *ACS Catal.*, 2011, **1**, 836-840.