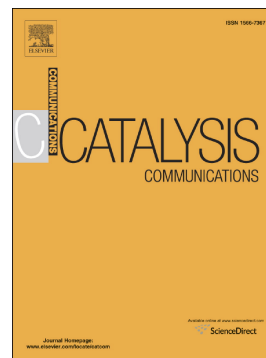


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**Mn-MIL-100 heterogeneous catalyst for the selective oxidative
cleavage of alkenes to aldehydes**

Ying Ha^a, Manman Mu^b, Qingling Liu^{a,c,*}, Na Ji^{a,c}, Chunfeng Song^{a,c}, Degang Ma^{a,c}

^aTianjin Key Laboratory of Indoor Air Environmental Quality Control, School of Environmental Science and Engineering, Tianjin University, No. 135, Yaguan Road, Haihe Education Park, Tianjin, 300350, China

^bSchool of Science, Tianjin University, No. 135, Yaguan Road, Haihe Education Park, Tianjin, 300350, China

^cState Key Laboratory of Engines, Tianjin University, No. 135, Yaguan Road, Haihe Education Park, Tianjin, 300350, China

Abstract

Four MIL metal organic framework materials with large surface area and high stability were utilized as heterogeneous catalysts in the selective oxidation of styrene with *tert*-butylhydroperoxide (70% aqueous) as an oxidant in acetonitrile. Mn-MIL-100 exhibits excellent styrene conversion (89%) and benzaldehyde selectivity (85%) under optimized conditions. Furthermore, Mn-MIL-100 displays superior catalytic activity in the selective oxidation of aryl-olefins and is reused at least three times without significant deactivation. It appears that this specific material would open up a new pathway for MOFs towards the selective catalytic oxidation of aryl-olefins to the corresponding aldehydes.

Keywords: MOFs; Mn-MIL-100; Selective oxidation; Styrene; Benzaldehyde.

1. Introduction

Benzaldehyde is one of the important chemical materials that can be widely applied in perfumes, pharmaceuticals, dyes and fine chemicals industry [1]. Traditionally, benzaldehyde is produced *via* toluene or benzoyl alcohol oxidation, benzoic acid hydrogenolysis and benzoyl chloride hydrolysis [2-4]. Owing to complex procedures, harsh conditions and toxic waste disposal, these methods are gradually eliminated and the selective oxidation of styrene is considered as a desirable process. Recently, a series of heterogeneous catalysts, such as metal oxides, transition metal coordination polymers and metal nanoparticles supported on porous materials (e.g., metal oxides or zeolites) [5-7], have been explored for the oxidation of styrene using *tert*-butylhydroperoxide as an oxidant. However, most of them have been studied for the selective oxidation of alkenes to epoxides and relative few studies were focused on the corresponding aldehydes as the main reaction product.

In recent years, metal-organic frameworks (MOFs) have been received considerable attention worldwide as a new class of porous materials built from metal nodes and organic ligands. Compared to the traditional porous materials (zeolite), MOFs are provided with certain predominant features, such as large surface area, controllable pore size and suitable functionalization, which render them ideal candidates for various applications, such as gas storage, chemical sensors, separation and catalysis [8-11]. Nevertheless, MOFs still exhibit some drawbacks such as low thermal and chemical stability, which restrict their applications in catalysis. Férey and co-workers [12] reported on the mesoporous chromium and iron terephthalates,

Cr-MIL-101 and Fe-MIL-101, which have a rigid zeotype crystal structure. These two kinds of MOFs revealed good resistance to air, water, common solvents and thermal treatments (e.g., Fe-MIL-101 is stable up to 150 °C while Cr-MIL-101 maintains its structure up to 300 °C). In addition, a crystalline iron trimesate (Fe-MIL-100) discovered by Férey and co-workers [13] also possess high chemical and thermal stability (up to 300 °C). In 2013, Reinsch and co-workers [14] have proposed the formation of Mn-MIL-100 that can be obtained in a methanolic solution of trimesic acid and manganese nitrate in short reaction times (2 h). The chemical stability of Mn-MIL-100 is analogous to that of other MIL materials, but its thermal stability is relatively higher (ca. stable up to 400 °C). Furthermore, after the removal of the terminal water molecules from MIL framework by heating in vacuum, coordinatively unsaturated sites are provided and can be utilized as catalytic active sites in various reactions [15]. So far, Fe-MIL-101 and Cr-MIL-101 have been employed in the selective oxidation of alkenes with oxygen, H₂O₂ and *tert*-butyl hydroperoxide (TBHP) as oxidants, respectively, but the main products obtained are epoxide compounds [16-18]. To the best of our knowledge, there are rare reports on the selective oxidative cleavage of styrene to benzaldehyde over MOFs.

Based on the above consideration, in the present work we describe four MIL materials (Mn-MIL-100, Fe-MIL-100, Fe-MIL-101, Cr-MIL-101) as catalysts for the selective oxidation of styrene to benzaldehyde using TBHP (70% aqueous) as an oxidant. In particular, the effects of solvents and reaction conditions: temperature, reaction time, catalyst dosage and mole ratio have been investigated. It was clearly

observed that Mn-MIL-100 exhibits excellent styrene conversion and benzaldehyde selectivity for this selective oxidation reaction. Finally, the selective oxidation of various alkenes over the Mn-MIL-100 catalysts and its recyclability were also tested.

2. Experimental

All chemicals and solvents were purchased from Tianjin Jiangtian Chemical Technology (China) Co. and used without further purification except for otherwise noted.

2.1 Catalysts preparation

All the MOFs materials were prepared by the solvothermal method. The Mn-MIL-100 was prepared according to the literature [14] with some modifications. An ethanolic solution of trimesic acid and manganese nitrate was heated in a Teflon-lined steel autoclave without stirring to produce Mn-MIL-100 in high yield. Zhang and co-workers [19] vaguely mentioned the similar synthetic method. It was eco-friendly for the synthetic process to use ethanol instead of methanol as solvent. Specifically, manganese nitrate ($\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 2 mmol) and trimesic acid (H_3BTC , 1.9 mmol) were dissolved in ethanol (18 ml) under ultrasonic conditions to form a clear solution. Then, the clear reaction solution was transferred into a Teflon-lined steel autoclave and heated at 125 °C for 2 h. After cooled down to room temperature, the brown product was obtained by centrifugation and washed with ethanol for three

times. Finally, the resulting solid was dried at 70 °C in vacuum overnight.

Fe-MIL-100, Fe-MIL-101 and Cr-MIL-101 were synthesized according to the methodology described in Huo et al. [20], Maksimchuk et al. [18] and Férey et al. [12], respectively.

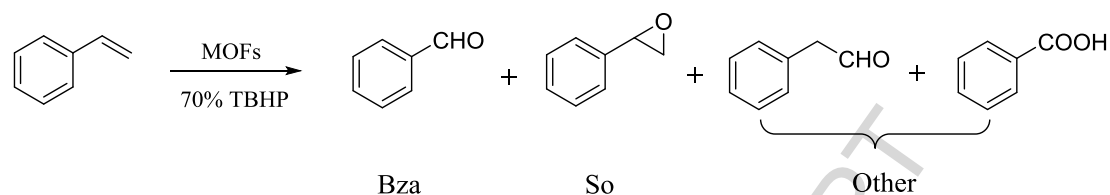
2.2 Catalysts characterization

Powder X-ray diffraction (XRD) patterns were measured on a D8-Focus X-ray diffractometer equipped with Cu K α radiation (1.54 Å) in the range of 3-30° 2theta. Scanning electron microscopy (SEM) images were obtained using a HitachiS-4800 scanning electron microscope. FT-IR spectra were collected on a Nicolet 22 AVATAR 370 FT-IR spectrometer in the 4000-550 cm⁻¹ region. Thermogravimetric analyses (TGA) were performed on an STA 409PC thermal analyzer at the heating rate of 10 °C min⁻¹ from room temperature to 800 °C. Nitrogen adsorption-desorption isotherms were measured at 77 K (liquid N₂) using a NOVA 2000e surface and porosity analyzer (Quantachrome, USA).

2.3 Selective oxidative cleavage of styrene

The selective oxidation of styrene to benzaldehyde was carried out in a 25 mL round bottom flask equipped with a magnetic stirrer and reflux condenser. Generally, styrene (1 mmol) and an appropriate amount of *tert*-BuOOH (TBHP, 70% aqueous) were dispersed in acetonitrile (1 mL) and an appropriate amount of catalyst (5 wt%) was then added in the solution. The resulting mixture was heated up to 70 °C and

stirred for 6 h. After cooled to room temperature, the mixture was filtered and the filtrate was analyzed by gas chromatography with an OV-1701 capillary column (30 m \times 0.25 mm, 0.2 μ m film thickness) and a flame ionization detector (FID).



Scheme 1. The synthetic route of selective oxidation of styrene.

3. Results and discussion

As it is well known, the selective oxidation of styrene mainly **generates** benzaldehyde (Bza), styrene oxide (So), benzoic acid and phenylacetaldehyde. Compared to traditional porous materials, MOFs containing metal ions as active sites may enhance the catalytic performance of this oxidation. Thus, in order to further investigate the influence of various metal sites or organic ligands, four different MOFs (e.g., Mn-MIL-100, Fe-MIL-100, Fe-MIL-101, Cr-MIL-101) were selected. Initially, a blank experiment in the absence of catalyst was performed. The oxidation reaction occurs at a low rate and only a low conversion of styrene was estimated. The catalytic performance of the selective oxidation of styrene over the four MOFs materials is presented in Table 1. It **is obviously** seen that the main product is benzaldehyde, resulting from the direct oxidative cleavage of the styrene side chain C=C bond. The results indicate that styrene conversion is higher but the selectivity of benzaldehyde is lower over Fe-MIL-101 compared to Cr-MIL-101. When Fe-MIL-100 linked with trimesic acid was used as catalyst, the styrene conversion and

the selectivity of benzaldehyde obtained are 73.87% and 76.31%, respectively. This demonstrates that Fe-MIL-101 exhibits superior styrene conversion but benzaldehyde selectivity is distinctly reduced. It is worth noting that styrene conversion and benzaldehyde selectivity obtained over Mn-MIL-101 are 72.52% and 81.81%, respectively. The catalytic performance results of the selective oxidation of styrene over four MOFs under different reaction conditions are presented in Table S2. When the reaction time is reduced to 4 h or reaction temperature is increased to 75 °C, the tendency in the catalytic activity behavior remains the same. Thus, it was concluded that Mn-MIL-100 with manganese as metal site and trimesic acid as organic ligand exhibits superior catalytic performance than the other three MOFs. Based on the above consideration, Mn-MIL-100 was selected as the optimum catalyst which was further investigated.

Table 1. The selective oxidation of styrene over four different MOFs.

Catalyst	Conversion (%)	Selectivity (%)		
		Benzaldehyde	Styrene oxide	Other
Mn-MIL-100	72.52	81.81	12.01	6.18
Fe-MIL-100	73.87	76.31	13.45	10.25
Fe-MIL-101	83.72	67.94	24.61	7.45
Cr-MIL-101	46.79	91.20	8.80	-

Reaction conditions: $n_{(70\% \text{ TBHP})} : n_{(\text{Styrene})} = 3:1$; reaction temperature = 70 °C; time = 6 h; catalyst dosage = 5 wt%; solvent: CH₃CN.

3.1 Characterization of materials

In order to verify the chemical structure of the four MIL MOFs, powder XRD, SEM and FT-IR techniques were used. The XRD patterns of Mn-MIL-100 and Fe-MIL-100 are illustrated in Fig S1. It is observed that the XRD patterns of the synthesized Fe-MIL-100 matches the simulated one, indicating that Fe-MIL-100 is successfully synthesized. The same result is also observed for the Mn-MIL-100 material. Furthermore, the XRD pattern of Mn-MIL-100 is similar to that of Fe-MIL-100, further indicating that the structures of Mn-MIL-100 and Fe-MIL-100 are analogous.

The SEM images obtained for the Mn-MIL-100 and Fe-MIL-100 solids are shown in Fig S2. It is observed that Mn-MIL-100 and Fe-MIL-100 both show cubic shape with an average secondary crystal size $\sim 0.5 \mu\text{m}$ [21, 22]. It can be also observed that the structure of Mn-MIL-100 is less regular than that of Fe-MIL-100. Thus, Mn-MIL-100 is expected to present more crystal defects than Fe-MIL-100.

To further prove the incorporation of trimesic acid into the framework, FT-IR spectra of Mn-MIL-100 and Fe-MIL-100 are presented in Fig S3. Strong absorption bands at ~ 1640 and 3400 cm^{-1} confirm the presence of water molecules within the frameworks. It is clearly shown that the presence of vibrational bands (O-C-O) at 1390 and 1470 cm^{-1} indicate the coordination of the tricarboxylate within two MOFs [23]. These results further verify that the two Mn-MIL-100 and Fe-MIL-100 MOFs materials were prepared.

Thermogravimetric analyses of Mn-MIL-100 and Fe-MIL-100 solids were

performed to study their thermal stability and results are presented in Fig. S4. The main weight loss can be observed at ~ 350 °C for the Fe-MIL-100 because of the collapse of the framework. In the case of Mn-MIL-100, the main weight loss occurred at 400 °C as the result of the collapse of the framework. Moreover, Fe-MIL-100 and Mn-MIL-100 were respectively calcinated in different temperatures (100, 200, 300, 350, 400 or 500°C) at the rate of 10°/min in a muffle furnace for 30 min. The obtained XRD patterns of these samples are shown in Fig. S5. It is found that the characteristic peaks of Fe-MIL-100 and Mn-MIL-100 are still preserved when the calcination temperature is below 300 °C. When Fe-MIL-100 is calcinated at 350°C, the characteristic peaks disappear, indicating that the framework of Fe-MIL-100 has collapsed. When Mn-MIL-100 is also calcinated at 350°C, the characteristic peaks still exist but the intensities become weaker. The framework of Mn-MIL-100 is destroyed once the calcination temperature is raised to 400°C. Based on these investigations, it could be concluded that Mn-MIL-100 is more stable than Fe-MIL-100.

The surface area and porosities of Mn-MIL-100 and Fe-MIL-100 solids are further examined by N₂ adsorption-desorption isotherms at 77 K (Table S1). It is found that the two MOFs present type-I isotherm. It is observed that the surface area and pore volume of Mn-MIL-100 are 1133 m²/g and 0.49 cm³/g, respectively. The synthesized Fe-MIL-100 gave larger BET surface area (1215 m²/g) and pore volume (0.64 cm³/g) than the Mn-MIL-100 solid.

3.2 Effect of solvent

As it is well known, the solvent has a significant influence on the yield and by-product formation in an oxidation reaction. . To examine the solvent's influence in the selective oxidation of styrene, polar and nonpolar solvents, such as acetonitrile (CH_3CN), 1,2-dichloromethane ($\text{CH}_2\text{ClCH}_2\text{Cl}$), carbon tetrachloride (CCl_4) and tetrahydrofuran (THF) were tested and experimental results are listed in Table 2. It is seen that the styrene conversion in other solvents are higher than that in CH_3CN . However, due to the excessive oxidation of benzaldehyde to benzoic acid, the benzaldehyde selectivity in the other solvents is relatively lower. When the reaction temperature was decreased, the benzaldehyde selectivity is still not high. Thus, CH_3CN is considered to be the optimum solvent.

Table 2. Effect of various solvents on the selective oxidation of styrene.

Solvent	Conversion (%)	Selectivity (%)		
		Benzaldehyde	Styrene oxide	Other
CH_3CN	72.52	81.81	12.01	6.18
$\text{CH}_2\text{ClCH}_2\text{Cl}$	98.78	50.92	18.30	30.78
CCl_4	100	48.79	-	51.11
THF	83.66	36.40	11.80	51.80

Reaction conditions: $n_{(70\% \text{ TBHP})} : n_{(\text{Styrene})} = 3:1$; reaction temperature = 70 °C; time = 6h; catalyst dosage = 5 wt%.

3.3 Effect of various reaction conditions

The effect of various reaction conditions, such as temperature, reaction time, catalyst dosage and mole ratio have been tested and results are presented in Fig 1. The effect of reaction temperature on the selective oxidation of styrene using 5 wt% Mn-MIL-100 as the catalyst and 3 equiv. TBHP (70 wt% aqueous) as the oxidant for 6 h is presented in Fig. 1A. It is clearly observed that styrene conversion rapidly increases but the benzaldehyde selectivity decreases with the increase of reaction temperature. Meanwhile, the amount of by-product benzoic acid also increases. Thus, the temperature of 70 °C was promising to be the optimum temperature. Figure 1B presents the effect of reaction time on selective oxidation at 70 °C. With increasing reaction time, the conversion apparently increases, while the selectivity to benzaldehyde remains unchanged after 6 h of reaction. The 88.99% conversion of styrene and 84.97% selectivity of benzaldehyde were obtained at t=10 h. Based on this, 10 h reaction time was selected as the optimum one. The effect of catalyst dosage on the selective oxidation using Mn-MIL-100 and TBHP at 6 h is also presented (Fig. 1C). When the amount of Mn-MIL-100 was raised from 2.5 to 5 wt%, the conversion of styrene increases from 55.89 to 72.52% and the reaction selectivity to benzaldehyde is also enhanced (from 75.99 to 81.81%). However, the amount of Mn-MIL-100 continues to increase, whereas the selectivity to benzaldehyde rapidly decreases. This behavior indicates that the addition of excess catalyst was not beneficial to the selective oxidation of styrene. Thus, 5 wt% was considered as the optimum catalyst dosage. Finally, Fig. 1D describes the effect of 70% TBHP/styrene

molar ratio on the selective oxidation of styrene. When the molar ratio of $n(70\% \text{ TBHP})/n(\text{styrene})$ was raised from 1:1 to 3:1, the styrene conversion increases from 68.45 to 72.52% and the selectivity to benzaldehyde increases from 59.44 to 81.81%. When the molar ratio was further increased to 5:1, the conversion suddenly declines to 48.21%. Thus, when the molar ratio of $n(70\% \text{ TBHP})/n(\text{styrene})$ is 3:1, maximum yield of benzaldehyde is attained.

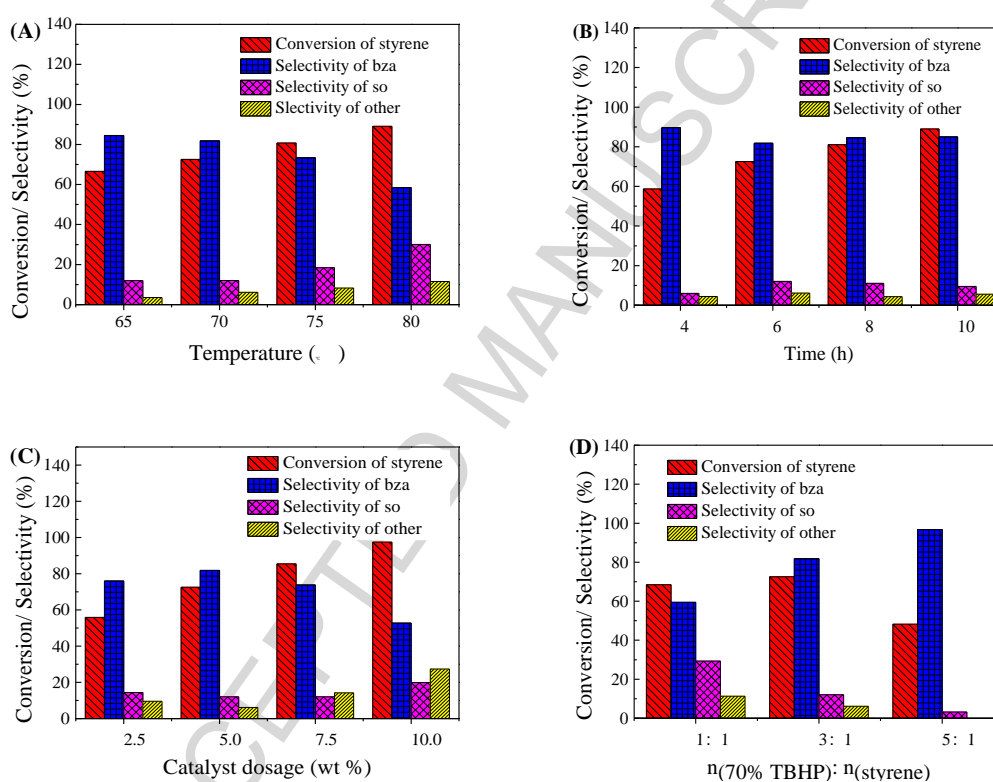


Fig. 1. Effect of (a) temperature, (b) reaction time, (c) catalyst dosage and (d) reactants molar ratio on the selective oxidation of styrene.

3.4 Possible mechanism of the selective oxidation of styrene

The possible mechanism of the selective oxidation of styrene over the present catalysts was investigated. A radical scavenger, butyl hydroxy toluene (BHT) was

added after the Mn-MIL-100-catalyzed reaction proceeded for 2 h. It was observed that the reaction terminated immediately with the addition of BHT, demonstrating that the reaction proceeded *via* radical intermediates [24]. Thus, the radical mechanism for the formation of benzaldehyde, styrene oxide and other products could be proposed (see Scheme S1), which is similar to that for Co(II)-MOF, Cu(II)-MOF [25] and CPO-27-Mn [26]. First, TBHP reacts with Mn-MIL-100 to form a Mn(III)-peroxy adduct by the removal of terminal water. Then, Mn(III)-peroxy adduct releases a *t*-butylperoxy radical and regenerates Mn-MIL-100. The *t*-butylperoxy radical reacts with styrene to generate a benzylic radical derivative, which further reacts with *t*-butylperoxy radical to afford benzaldehyde *via* C-C oxidative cleavage (route II). In addition, the benzylic radical derivative undergoes oxygen migration to form styrene oxide and *t*-BuOH product (route I). Benzaldehyde could be obtained through the ring-opening reaction of styrene oxide with TBHP followed by C-C oxidative cleavage (route III). Besides, phenylacetaldehyde and benzoic acid might be formed by the Lewis acid catalyzed ring-opening isomerization of styrene oxide (route IV) or over-oxidation of benzaldehyde (route V).

3.5 Catalytic selective oxidation of various alkenes

To determine the general scope of reaction, the selective oxidation of various alkenes such as α -styrene, diphenylethene, cyclohexene and cyclooctene over Mn-MIL-100 are performed under the optimum condition identified in the case of styrene and results are shown in Table S3. Apparently, phenyl-substituted olefins

underwent oxidative cleavage and efficiently produced aldehydes or ketones. It is also clearly observed from Table S3 that the reaction rate of cyclic olefins is lower than that of phenyl-substituted olefins. In the case of cyclic olefins, there is competition between oxidation of the allylic position and oxidation of the double bond. Cyclohexene was converted to the corresponding epoxide (59.07% yield) with no other product, whereas cyclooctene was converted to the corresponding epoxide with low yields (only 8.95%).

In addition, the catalytic properties of various materials [27] previously reported are shown in Table S4. Compared with a series of porous materials, such as Cr-ZSM-5, SBA-Fe(acac:salen), MoO₂(acac)-POM, hierarchical ZSM-5, [Cu₂(bipy)₂(btec)], MOF-525-Mn, MOF-74(Cu), MOF-74(Co) and MOF-74(Cu/Co), it is obvious that Mn-MIL-100 has an excellent conversion and benzaldehyde selectivity.

3.6 Recyclability of the catalyst

The recyclability of catalyst is one of the most important criteria for commercial applications. The recyclability of Mn-MIL-100 was tested towards the selective oxidation of styrene. This catalytic system could be easily recovered from the reaction mixture by centrifugation and it was ready for reuse after washing with acetonitrile twice. As summarized in Fig. S6, the styrene conversion was only slightly reduced (< 4%) but the benzaldehyde yield remained practically constant in three consecutive runs, implying high recyclability for the Mn-MIL-100 catalyst.

4. Conclusions

Mn-MIL-100 is synthesized by a modified solvothermal method and utilized as a heterogeneous catalyst for the selective oxidation of styrene. Compared to Fe-MIL-100, Fe-MIL-101 and Cr-MIL-101, Mn-MIL-100 exhibits excellent styrene conversion and benzaldehyde selectivity, which is probably due to the presence of manganese ion as metal sites. Moreover, the characterization results of XRD and TGA indicate that the structures of Fe-MIL-100 and Mn-MIL-100 are analogous but Mn-MIL-100 possesses higher thermal stability than Fe-MIL-100. An 88.99% conversion of styrene and 84.97% reaction selectivity to benzaldehyde were obtained using 5 wt% Mn-MIL-100 and 3:1 molar ratio of 70% TBHP/styrene at 70 °C for 10 h. Mn-MIL-100 not only has high chemical stability and recyclability but also exhibits superior catalytic activity in the selective oxidation of aryl-olefins. Thereby, this work provides a new pathway for the selective oxidation of aryl-olefins to the corresponding aldehydes.

Acknowledgements

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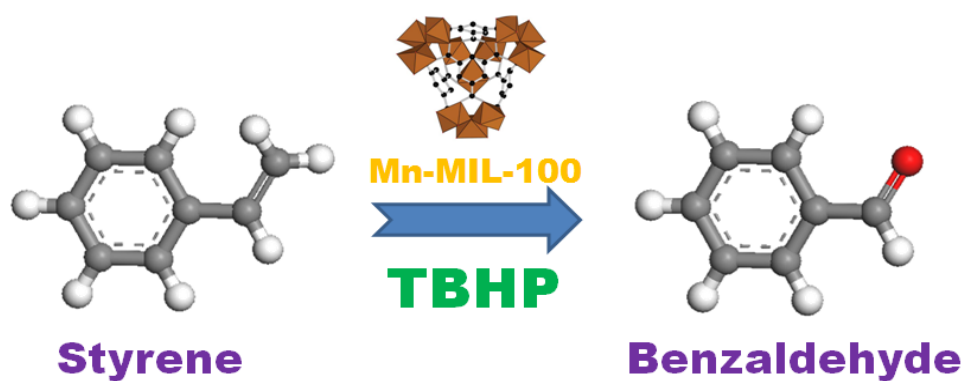
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Graphical Abstract



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Highlights

1. Mn-MIL-100 is synthesized by a modified solvothermal method.
2. Mn-MIL-100 exhibits excellent styrene conversion and benzaldehyde selectivity.
3. Mn-MIL-100 has superior catalytic activity in the selective oxidation of aryl-olefins.
4. Mn-MIL-100 exhibits high chemical stability and recyclability.

Keywords: MOFs, Mn-MIL-100, Selective oxidation, Styrene, Benzaldehyde

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