# FULL PAPER

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# Highly efficient oxidative cleavage of alkenes and cyanosilylation of aldehydes catalysed by magnetically recoverable MIL-101

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Shahram Tangestaninejad, Majid Moghadam and Valiollah Mirkhani, Department of Chemistry, Catalysis Division, University of Isfahan, Isfahan 81746-73441, Iran. Email: stanges@sci.ui.ac.ir; moghadamm@sci.ui.ac.ir; mirkhani@sci. ui.ac.ir The catalytic activity of magnetically recoverable MIL-101 was investigated in the oxidation of alkenes to carboxylic acids and cyanosilylation of aldehydes. MIL-101 was treated with  $Fe_3O_4$  and the prepared catalyst was characterized using Fourier transform infrared spectroscopy, X-ray diffraction, N<sub>2</sub> adsorption measurements, field emission scanning electron microscopy, energy-dispersive X-ray spectroscopy and inductively coupled plasma analysis. The catalytic active sites in this heterogeneous catalyst are  $Cr^{3+}$  nodes of the MIL-101 framework. This heterogeneous catalyst has the advantages of excellent yields, short reaction times and reusability several times without significant decrease in its initial activity and stability in both oxidation and cyanosilylation reactions. Its magnetic property allows its easy separation using an external magnetic field.

### **KEYWORDS**

cyanosilylation, magnetization, metal-organic frameworks, MIL-101, oxidation

# **1** | INTRODUCTION

Metal–organic frameworks (MOFs) are a new class of hybrid materials that possesses crystalline lattices consisting of metal ions coordinated by organic ligands. These porous solids have high surface area, good thermal stability and modifiable pores and tunnels.<sup>[1–3]</sup>

These materials have received much attention because of their unique characteristics which make them an ideal class of materials for various applications in analytical chemistry,<sup>[4]</sup> gas adsorption and separation processes,<sup>[5]</sup> heterogeneous catalysis,<sup>[6–13]</sup> optoelectronics,<sup>[14]</sup> drug delivery systems<sup>[15,16]</sup> and sensor technology.<sup>[17–19]</sup>

In 2005 Férey *et al.* reported a porous chromium terephthalate MOF, MIL-101 ( $Cr_3X(H_2O)_2O(bdc)_3$ ; X = F, OH; bdc = benzene-1,4-dicarboxylate), with large pores.<sup>[20]</sup> MIL-101 has outstanding features including hierarchical pore structure, mesoporous cages, numerous unsaturated chromium(III) sites and high hydrothermal and chemical stability which make it a promising material for a wide range of applications. Especially, the pores of MIL-101 and chromium nodes lead to specific catalytic applications such as in the production of carboxylic acids and ketones by catalytic oxidation of alkenes,<sup>[21]</sup> cyanosilylation of aldehydes,<sup>[22]</sup> benzylic oxidation of tetralin,<sup>[23,24]</sup> sulfoxidation of thioethers with  $H_2O_2^{[25]}$ and allylic oxidation of alkenes with *tert*-butyl hydroperoxide.<sup>[26]</sup>

Catalyst recovery and reuse are very important features in many catalytic processes. Nowadays, magnetic nanoparticles (MNPs) have received much attention in catalytic systems because they provide much easier and faster separation of a catalyst from reaction media using an external magnetic field instead of performing tedious centrifugation and filtration steps.<sup>[27,28]</sup> The use of MNPs for enhancing the separation of MOFs from reaction media has been reported by various research groups.<sup>[29-33]</sup> Magnetite (Fe<sub>3</sub>O<sub>4</sub>) is one of the main representatives of MNPs that is synthesized using three different pathways: physical, wet chemical and microbial methods. Also, the use of surface coating materials during the synthesis of MNPs stabilizes the newly formed surfaces and prevents aggregation of the particles.<sup>[34-36]</sup> A silica coating on the outside surface of Fe<sub>3</sub>O<sub>4</sub> MNPs can be effective in preventing the magnetite particles from aggregation, oxidation, corrosion, chemical degradation and leaching under harsh conditions.<sup>[37,38]</sup>

Zhang *et al.* reported a facile method for the synthesis of MIL-100(Fe) at low temperatures and atmospheric pressure from the reaction of trimesic acid and ferric nitrate under HF-free conditions.<sup>[39]</sup> The synthesized MIL-100(Fe) was utilized as a catalyst in the liquid-phase acetalization of various aldehydes with diols. Recently Hu *et al.* synthesized a magnetic MIL-100(Fe)@SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub> catalyst with a novel core–shell structure via a facile *in situ* self-assembly method and applied it in the liquid-phase acetalization of benzaldehyde and glycol.<sup>[40]</sup>

In this paper, we report the preparation of magnetically recoverable MIL-101 (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-MIL-101) by mixing silica-coated iron nanoparticles and MIL-101 under sonication using a slight modification of the method reported by Huo and Yan.<sup>[41]</sup> The resulting heterogeneous catalyst was characterized using various methods. The catalytic activity of this hybrid material was investigated in the direct oxidation of alkenes to carboxylic acids in the presence of H<sub>2</sub>O<sub>2</sub> and cyanosilylation of aldehydes in the presence of trimethylsilylcyanide (Scheme 1).

# 2 | EXPERIMENTAL

# 2.1 | Reagents and methods

All materials were of commercial reagent grade. The alkenes and aldehydes were obtained from Merck or



Fluka. FT-IR spectra were obtained using potassium bromide pellets in the range 400-4000  $\text{cm}^{-1}$  with a JASCO 6300 spectrophotometer. Field emission scanning electron microscopy (FE-SEM) images were obtained with a Hitachi S-4700 instrument. X-ray diffraction (XRD) patterns were recorded using a Bruker  $D_8$ Advance X-ray diffractometer equipped with nickel monochromatized Cu  $K_{\alpha}$  radiation ( $\lambda = 1.5406$  Å). Specific surface area was determined using N2 gas adsorption-desorption measurements at 77 K with a Micromeritics ASAP 2000 instrument. Inductively coupled plasma (ICP) analyses were carried out with a PerkinElmer Optima 7300 DV spectrometer. GC experiments were performed with a Shimadzu GC-16A instrument using a 2 m column packed with silicon DC-200 or Carbowax 20 M. In the GC experiments, n-decane was used as the internal standard. The MNPs (Fe<sub>3</sub>O<sub>4</sub>) were synthesized and coated with silica as reported in the literature.<sup>[42]</sup> MIL-101 was synthesized according to the procedure reported previously.[20,43]

# 2.2 | Magnetization of MIL-101 (Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>@MIL-101)

Fe<sub>3</sub>O<sub>4</sub>–SiO<sub>2</sub>@MIL-101 was prepared according to the method of Huo and Yan<sup>[41]</sup> with some modification. MIL-101 (60 mg) and Fe<sub>3</sub>O<sub>4</sub>–SiO<sub>2</sub> (100 mg) were placed in a 25 ml glass vial, and dispersed in methanol under ultrasonic irradiation for 1.5 h to form Fe<sub>3</sub>O<sub>4</sub>–SiO<sub>2</sub>@MIL-101. The magnetic MIL-101 was separated using an external magnet from methanol and dried overnight in an oven at 75 °C.

### 2.3 | Catalytic experiments

# 2.3.1 | General procedure for direct oxidation of alkenes to carboxylic acids catalysed by Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>@MIL-101

Alkene (0.5 mmol),  $Fe_3O_4$ @SiO<sub>2</sub>-MIL-101 (20 mg),  $H_2O_2$  (30%, 500 µl, 5 mmol) and CH<sub>3</sub>CN (3 ml) were mixed in a 25 ml round-bottom flask and refluxed. The progress of the reaction was monitored by GC. At the end of the reaction, the catalyst was separated using an external magnet and washed with CH<sub>3</sub>CN (10 ml). The solvent was evaporated and the pure products were obtained by chromatography using a short silica gel column. All the products were characterized using <sup>1</sup>H NMR, FT-IR and mass spectral analyses (supporting information).

# 2.3.2 | General procedure for cyanosilylation of aldehydes catalysed by Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>@MIL-101

Aldehyde (1 mmol), trimethylsilylcyanide (TMSCN; 198.5 mg, 2 mmol) and Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>@MIL-101 (20 mg, 0.0053 mmol) were mixed in heptane (5 ml). The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by GC. Purification of the products was as described above. The products were characterized using <sup>1</sup>H NMR, FT-IR and <sup>13</sup>C NMR spectral analyses (supporting information).

# 2.4 | Recycling tests

The oxidation of cyclooctene was chosen as a model substrate for investigating the reusability of Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>@MIL-101. After each run the catalyst was separated from the reaction mixture, washed with acetonitrile and dried before being used in the next run. The same procedure was repeated for other runs. After the reaction was completed, the catalyst was filtered and the filtrate was dissolved in strong acidic solution (HNO<sub>3</sub>-HCl, 1:3). Then, the amount of Cr leached was determined using ICP analysis.

The reusability of the catalyst was also investigated in the cyanosilylation of benzaldehyde using the same procedure. After each run, the catalyst was separated easily using an external magnet, washed with heptane and dried before being used in subsequent runs.

#### 3 **RESULTS AND DISCUSSION**

# 3.1 | Characterization of Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>@MIL-101 catalyst

The XRD pattern (Figure 1a) and FT-IR spectrum (Figure 2b) of synthesized MIL-101 match well with those reported previously.<sup>[20,44]</sup> The main diffraction peaks at  $2\theta$  $(^{\circ}) = 5.1, 8.4, 9.0, 16.5$  were as same as the standard data for MIL-101.<sup>[20,45]</sup> As it is obvious from Figure 1c that the crystallinity of MIL-101 is maintained after magnetization with Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>. The additional peak in Figure 1 (c) corresponds to  $Fe_3O_4$ -SiO<sub>2</sub> as shown in Figure 1(b). According to these patterns, the synthesis of Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>@MIL-101 was successful.

As shown in Figure 2(c), the structure of the framework is preserved after magnetization and the characteristic vibrational bands of the framework -(O-C-O)groups around 1550 and 1400 cm<sup>-1</sup> confirm this point<sup>[46,47]</sup> and the catalyst C=O vibrations appear at 1708 and 1628 cm<sup>-1</sup>. Also, the FT-IR spectrum of Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub> (Figure 2a) exhibits characteristic bands at



FIGURE 1 XRD patterns of: (a) MIL-101, (b) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>, (c) Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>@MIL-101 and (d) recovered catalyst



FIGURE 2 FT-IR spectra of (a) Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>, (b) MIL-101, (c) Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>@MIL-101 and (d) recovered catalyst

580 cm<sup>-1</sup> (Fe–O), 950 cm<sup>-1</sup> (Si–OH) and 1091 cm<sup>-1</sup> (Si-O-Si), added to the MIL-101 spectrum (Figure 2b) after magnetization, which prove the synthesis of Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>@MIL-101.

The FE-SEM images in Figure 3 show that MIL-101 retains its nature and is not altered during modification and magnetization. Also, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> MNPs were found to be homogeneously assembled onto the external surface of MIL-101 crystals.<sup>[41,48]</sup>

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FIGURE 3 FE-SEM images of (a) MIL-101 and (b)  ${\rm Fe_3O_4-SiO_2@MIL-101}$ 



FIGURE 4 SEM-EDX spectrum of Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>@MIL-101

The energy dispersive X-ray (EDX) results, obtained from SEM analysis, for the magnetic MIL-101 in Figure 4 clearly show the presence of Fe, Si and Cr in  $Fe_3O_4$ -SiO<sub>2</sub>@MIL-101.

The specific surface area and pore volume of MIL-101 and Fe<sub>3</sub>O<sub>4</sub>–SiO<sub>2</sub>@MIL-101 were determined using nitrogen physisorption measurements at low temperature. There is a predictable decrease in pore volume from 1.35 to 0.602 cm<sup>3</sup> g<sup>-1</sup>. The BET surface area decreased from 2729 to 886 m<sup>2</sup> g<sup>-1</sup> (Figure 5).



**FIGURE 5**  $N_2$  adsorption-desorption isotherms of (a) MIL-101 and (b) Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>@MIL-101 (open circles, adsorption; filled circles, desorption)

The magnetization curves of  $Fe_3O_4$ ,  $Fe_3O_4$ -SiO<sub>2</sub> and  $Fe_3O_4$ -SiO<sub>2</sub>@MIL-101 are shown in Figure 6. The saturation magnetization value of 10 emu g<sup>-1</sup> for  $Fe_3O_4$ -SiO<sub>2</sub>@MIL-101 makes it susceptible to magnetic fields and easy to isolate from reaction media.

# 3.2 | Catalytic experiments

The catalytic activity of the  $Fe_3O_4$ -SiO<sub>2</sub>@MIL-101 was evaluated in both the oxidation of alkenes with  $H_2O_2$  and cyanosilylation of aldehydes with TMSCN.

# 3.2.1 | Catalytic activity of Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>@MIL-101 in direct oxidation of alkenes to carboxylic acids

At first, the effect of amount of catalyst on the oxidation of cyclooctene was investigated using various amounts of  $Fe_3O_4$ -SiO<sub>2</sub>@MIL-101 in acetonitrile under reflux condition. As evident from Table 1, the best result was obtained with 20 mg (0.0053 mmol) of the catalyst; no corresponding diacid was obtained in the absence of the catalyst. It is noteworthy that in the presence of  $Fe_3O_4$ -SiO<sub>2</sub> a yield of only 15% of suberic acid was obtained.

The effect of amount of oxidant  $(H_2O_2)$  on the oxidation of cyclooctene catalysed by  $Fe_3O_4$ -SiO<sub>2</sub>@MIL-101 was investigated. The results, obtained under reflux conditions, are summarized in Table 2 and show that 5 mmol of  $H_2O_2$  is the best amount.



**FIGURE 6** Magnetic hysteresis curves of (a)  $Fe_3O_4$ , (b)  $Fe_3O_4$ -SiO<sub>2</sub> and (c)  $Fe_3O_4$ -SiO<sub>2</sub>@MIL-101



 $\label{eq:table_to_alpha} \begin{array}{ll} \textbf{TABLE 1} & \mbox{Effect of Fe}_3O_4\mbox{-SiO}_2@\mbox{MIL-101} amount on oxidation of cyclooctene at 70 \mbox{°C}^a \end{array}$ 

Entry	Amount of catalyst (mg)	Yield (%) <sup>b</sup> after 4 h
1	Without catalyst	0
2	Fe <sub>3</sub> O <sub>4</sub> -SiO <sub>2</sub>	15
3	10	80
4	20	95
5	25	95
6	30	95

 $^{a}\text{Reaction}$  conditions: cyclooctene (0.5 mmol),  $\text{H}_{2}\text{O}_{2}$  (5 mmol), acetonitrile (3 ml).

<sup>b</sup>GC yield based on starting alkene.

**TABLE 2** Optimization of  $H_2O_2$  amount in oxidation ofcyclooctene catalysed by  $Fe_3O_4$ -SiO\_2@MIL-101 at  $70^{\circ}C^{a}$ 

Entry	$H_2O_2$ (mmol)	Yield (%) <sup>b</sup> after 4 h
1	4	90
2	5	95
3	10	95

<sup>a</sup>Reaction conditions: cyclooctene (0.5 mmol), catalyst (20 mg), acetonitrile (3 ml).

<sup>b</sup>GC yield based on starting alkene.

The kind of solvent was also optimized for this reaction. Among various solvents such as methanol, dichloromethane and 1,2-dichloroethane, acetonitrile was selected as best solvent (Table 3).

The optimized reaction parameters used for the oxidation of cyclooctene were catalyst, oxidant and substrate in a molar ratio of 0.0053:5:0.5. Under these conditions, various alkenes were oxidized with  $H_2O_2$  (Table 4). In this catalytic system, cyclooctene was cleaved readily under the reaction conditions and produced suberic acid in 95% yield. In the case of cyclohexene, the major product was adipic acid (89%) and cyclohexene oxide was obtained as a minor product (11%). Both adipic and suberic acids are industrially

**TABLE 3** Effect of solvent on oxidation of cyclooctene catalysed by  $Fe_3O_4$ -SiO<sub>2</sub>@MIL-101 at 70°C<sup>a</sup>

Entry	Solvent	Yield (%) <sup>b</sup> after 4 h
1	CH <sub>3</sub> OH	36
2	$CH_2Cl_2$	2
3	CH <sub>3</sub> CN	95
4	$C_2H_4Cl_2$	1

 $^{a}\text{Reaction}$  conditions: cyclooctene (0.5 mmol), catalyst (20 mg),  $\text{H}_{2}\text{O}_{2}$  (5 mmol), solvent (3 ml).

<sup>b</sup>GC yield based on starting alkene.

**TABLE 4** Oxidation of alkenes with  $H_2O_2$  catalysed by  $Fe_3O_4$ -SiO<sub>2</sub>@MIL-101 refluxing in acetonitrile<sup>a</sup>

Entry	Alkene	Yield (%) <sup>b</sup>	Time (h)	TOF $(h^{-1})$
1	Cyclooctene	95	4	22.40
2	Cyclohexene	89	8	10.49
3	Indene	90	3	28.30
4	1-Octene	80	8	9.43
5	1-Decene	77	8	9.08
6	1-Dodecene	80	5	15.09

 $^{\rm a}Reaction$  conditions: alkene (0.5 mmol),  $\rm H_2O_2$  (5 mmol), catalyst (20 mg), CH\_3CN (3 ml).

<sup>b</sup>GC yield based on starting alkene.

very important. Linear alkenes, such as 1-octene, 1decene and 1-dodecene, were easily converted into their corresponding alkanoic acids in 77–80% yields (Table 4, entries 4–6). Also, indene (Table 4, entry 3) was converted to 2-(carboxymethyl)benzoic acid (homophthalic acid) in 90% yield.

# 3.2.2 | Catalytic activity of Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>@MIL-101 in cyanosilylation of aldehydes

As evident from Table 5, the effect of amount of catalyst on the cyanosilylation of benzaldehyde was investigated using various amounts of  $Fe_3O_4@SiO_2-MIL-101$  in *n*-heptane at room temperature, the best result being obtained with 20 mg (0.0053 mmol) of the catalyst. Also a blank experiment in the absence of catalyst under the same experimental conditions was carried out and the corresponding product was obtained in a yield of only 5%, while in the presence of  $Fe_3O_4-SiO_2$  the corresponding silyl ether was produced in a yield of only 10%.

The effect of amount of TMSCN on the cyanosilylation of benzaldehyde was also investigated. The results in Table 6 show that 2 mmol of TMSCN was the optimum amount.

**TABLE 5** Effect of  $Fe_3O_4$ -SiO\_2@MIL-101 amount oncyanosilylation of benzaldehyde at room temperature<sup>a</sup>

Entry	Amount of catalyst (mg)	Yield (%) <sup>b</sup> after 4 h
1	Without catalyst	5
2	Fe <sub>3</sub> O <sub>4</sub> -SiO <sub>2</sub> (20)	10
3	15	93
4	20	100
5	30	100

<sup>a</sup>Reaction conditions: aldehyde (1 mmol), TMSCN (2 mmol), n-heptane (5 ml).

<sup>b</sup>GC yield based on starting aldehyde.

**TABLE 6** Effect of TMSCN amount on cyanosilylation of benz-<br/>aldehyde catalysed by  $Fe_3O_4$ -SiO\_2@MIL-101 at room temperature<sup>a</sup>

Entry	TMSCN (mmol)	Yield (%) <sup>b</sup> after 4 h
1	1	94
2	2	100
3	4	98

<sup>a</sup>Reaction conditions: aldehyde (1 mmol), catalyst (20 mg), *n*-heptane (5 ml). <sup>b</sup>GC yield based on starting aldehyde.

Also, the effect of solvent was investigated in the model reaction and it is clear that *n*-heptane was the best solvent (Table 7).

The optimized reaction parameters used for the cyanosilylation of benzaldehyde were catalyst, TMSCN and substrate in a molar ratio of 0.0053:2:1. Table 8 summarizes the results obtained for cyanosilylation of various aldehydes which were converted to their corresponding cyanohydrin trimethylsilyl ethers. Using this catalytic system, a variety of aromatic aldehydes such as benzaldehyde, 4-methylbenzaldehyde, 2-chlorobenzaldehyde, 2,4-dichlorobenzaldehyde, 3-nitrobenzaldehyde, nitrobenzaldehyde and 2-nitrobenzaldehyde were easily converted to their corresponding cyanohydrin trimethylsilyl ethers in 75-100% yields (Table 8, entries 1-7). Also, evident from Table 8, bulkier aromatic aldehyde (2-naphthaldehyde) was converted to trimethylsilyloxy-2-(2-naphthyl)acetonitrile in 75% yield (entry 8).

# 3.3 | Catalyst reuse and stability

For economical and synthetic purposes, the reusability of a heterogeneous catalyst is very important. Thus, for completion of our study, the reusability of  $Fe_3O_4$ –SiO<sub>2</sub>@MIL-101 was investigated in multiple sequential oxidation and cyanosilylation reactions. The oxidation of cyclooctene was chosen as a model substrate for investigating the reusability of  $Fe_3O_4$ –SiO<sub>2</sub>@MIL-101. As evident from Table 9, in the oxidation of cyclooctene the product yield was 95% in the first run after 4 h. In the second, third and fourth runs the product yield decreased to 92, 89 and 80%

**TABLE 7**Effect of solvent on cyanosilylation of benzaldehydecatalysed by  $Fe_3O_4$ -SiO\_2@MIL-101 at room temperature<sup>a</sup>

Entry	Solvent	Yield (%) <sup>b</sup> after 3 h
1	PhCH <sub>3</sub>	17
2	$n-C_6H_{14}$	35
3	CH <sub>3</sub> CN	28
4	n-C <sub>7</sub> H <sub>16</sub>	100

<sup>a</sup>Reaction conditions: aldehyde (1 mmol), TMSCN (2 mmol), catalyst (20 mg).
<sup>b</sup>GC yield based on starting aldehyde.

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TABLE 8 Cyanosilylation of aldehydes catalysed by Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>@MIL-101 with TMSCN at room temperature<sup>a</sup>

Entry	Aldehyde	Yield (%) <sup>b</sup>	Time (h)	TOF $(h^{-1})$
1	Benzaldehyde	100	3	62.89
2	4-Methylbenzaldehyde	85	4	40.09
3	2-Chlorobenzaldehyde	95	4	44.81
4	2,4-Dichlorobenzaldehyde	91	4.5	38.16
5	3-Nitrobenzaldehyde	88	4	41.51
6	4-Nitrobenzaldehyde	88	4.5	36.9
7	2-Nitrobenzaldehyde	75	5	28.3
8	2-Naphthaldehyde	75	7	20.22

<sup>a</sup>Reaction conditions: alkene (0.5 mmol),  $H_2O_2$  (5 mmol), catalyst (20 mg),  $CH_3CN$  (3 ml). <sup>b</sup>GC yield based on starting alkene.

TABLE 9	Recyclability	of Fe <sub>3</sub> O <sub>4</sub> -SiO <sub>2</sub> @MIL-101	in oxidation of cyclooctene <sup>4</sup>
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Run	Yield (%) <sup>b</sup> before activation	Cr leached (%) <sup>c</sup>	Yield (%) <sup>b</sup> after activation	Cr leached (%) <sup>c</sup>	Fe leached (%) <sup>c</sup> (both steps)
1	95	5.8	97	2.2	0
2	92	4.5	95	1.5	0
3	89	4.1	92	0.89	0
4	80	3.9	92	0	0
5	_	_	90	0	0
6	_	—	90	0	0

 $^aReaction$  conditions: cyclooctene (0.5 mmol),  $\rm H_2O_2$  (5 mmol), catalyst (20 mg), CH\_3CN (3 ml).

<sup>b</sup>GC yield based on starting alkene.

<sup>c</sup>Determined by ICP analysis.

TABLE 10	Recyclability of Fe <sub>3</sub> O <sub>4</sub> -SiO <sub>2</sub> @MIL-101 in
cyanosilylatio	on of benzaldehyde <sup>a</sup>

Run	Yield (%) <sup>b</sup>	Cr leached (%) <sup>c</sup>	Fe leached (%) <sup>c</sup>
1	100	4.3	0
2	97	2.1	0
3	94	3.1	0
4	84	1.8	0

<sup>a</sup>Reaction conditions: benzaldehyde (1 mmol), TMSCN (2 mmol), catalyst (20 mg), *n*-heptane (5 ml).

<sup>b</sup>GC yield based on starting alkene.

<sup>c</sup>Determined by ICP analysis.

respectively. The amount of Cr leached to the reaction mixture was measured using the ICP method.

As XRD analysis confirms that the catalyst maintains its stability even after the last run, it seems that the leached Cr is not the Cr which is positioned in the nodes of the framework. So this leaching is likely due to remaining Cr in the pores, which is not removed during washing of the framework. To decrease the catalyst leaching, microwave irradiation was used before recycling tests.<sup>[49]</sup> As evident from Table 9, after activation of the catalyst, the leaching of Cr decreased and the product yield and the catalyst reusability improved.

Also the recyclability of the catalyst was investigated in the cyanosilylation of benzaldehyde. The results are summarized in Table 10. At the end of the reaction, the catalyst was separated easily using an external magnet, washed with heptane and dried before using in subsequent runs. The amount of Cr leached in the four runs is about 11.3% of the initial Cr content, which is in accordance to the decreasing of the product yield from 100% in the first run to 84% in the fourth run.

# 4 | CONCLUSIONS

We have successfully synthesized and characterized a magnetically recoverable heterogeneous catalyst (Fe<sub>3</sub>O<sub>4</sub>– SiO<sub>2</sub>@MIL-101). The catalytic activity of this new catalyst

was evaluated in oxidation of alkenes to carboxylic acids and cyanosilylation of aldehydes, and showed excellent yields and noticeable reusability in both reactions. Easy workup, mild reaction conditions and separation of the catalyst using an external magnetic field are other unique features of this catalyst.

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### SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

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