Catalysis Communications 17 (2012) 18–22

Contents lists available at SciVerse ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

MIL-101 metal–organic framework: A highly efficient heterogeneous catalyst for oxidative cleavage of alkenes with H_2O_2

Zahra Saedi, Shahram Tangestaninejad *, Majid Moghadam *,
Valiollah Mirkhani, Iraj Mohammadpoor-Baltork

Department of Chemistry, Catalysis Division, University of Isfahan, Isfahan 81746-73441, Iran

ARTICLE INFO

Article history:
Received 12 June 2011
Received in revised form 30 September 2011
Accepted 4 October 2011
Available online 12 October 2011

Keywords:
Metal–organic framework
MIL-101
Hydrogen peroxide
Oxidation
Carboxylic acid

ABSTRACT

In the present work, a new and efficient method for direct oxidation of alkenes to carboxylic acids with H_2O_2 catalyzed by metal–organic framework MIL-101 is reported. In this transformation, the MIL-101 catalyzes the oxidation reactions by framework nodes and acts as a heterogeneous and reusable catalyst. The structure of MIL-101 was stable after three catalytic cycles.

1. Introduction

Metal–organic frameworks (MOFs), as a new class of porous solids, have received considerable attention because of their potential applications in gas adsorption and separation processes [1,2], catalysis [3–6], ion exchange [7], optoelectronics [8,9], and sensor technology [10]. Three decades before the birth of metal–organic frameworks (MOFs), Tomic reported the materials which nowadays are known as MOFs, metal–organic polymers or supramolecular structures [11]. The interest in this field was developed by the Yaghi's group, which reported the MOF-5 as an exceptionally stable and highly porous metal–organic framework in 1999 [12]. Some structural properties of MOF such as their high internal surface area and microporosity are comparable to zeolites and for the most new MOF structures are higher than zeolites [13]. So, based on these similarities, these frameworks can be used as solid catalysts Pd-MOF [14], Al_2 (BDC)$_3$[15], $Cu_3(BTC)_2$[16], [Zn_2(bdc)(l-lac)(dmf)]·(DMF) [17], Cu(bpy)(H_2O)$_2$(BF_4)$_2$(bpy) [18], Mn_3(atpa)$_3$(dmf)$_2$and Mn_2(tpa)$_2$(dmf)$_2$[19], and Cu(2-pymo)$_2$ and Co(PhIM)$_2$[20]. First time in 2005, Ferey and co-workers reported the synthesis and characterization of the metal–organic framework MIL-101 [($Cr_3X(H_2O)_2O$(bdc)$_3$; X = F, OH; bdc = benzene-1,4-dicarboxylate)] [21] (Fig. 1). Due to the large pores and high surface area of the MIL-101, this compound is a good candidate in catalysis. Kaskel et al. reported the catalytic activity of MIL-101 in the efficient cyanosilylation of aldehydes [22]. Recently, the catalytic activity of MIL-101 has been reported in the oxidation of tetralin [23,24].

Catalytic oxidation of alkenes to carboxylic acids and ketones is a valuable reaction in organic synthesis [25] and several oxidation pathways have been reported in the literatures [25–33]. During the last few decades, numerous efforts have been made to devise safer alternatives for these useful reactions. Therefore, in order to develop a mild oxidative method, we decided to investigate the catalytic activity of MIL-101 in the direct oxidation of alkenes to carboxylic acids (Scheme 1).

2. Experimental

2.1. Synthesis of MIL-101

MIL-101 was synthesized based on procedure reported by Férey et al. [21]. In a typical procedure, a mixture of $Cr(NO_3)_3 \cdot 9H_2O$ (1.2 g, 3 mmol), terephthalic acid (H_2bdc, 500 mg, 3 mmol), and HF (5 M, 0.6 mL, 3 mmol) in H_2O (15 mL) was heated in a Teflon-lined stainless steel autoclave at 220 °C for 8 h. The resulting green solid was passed through a coarse glass filter to remove the unreacted colorless crystals of H_2bdc and then, the green solid materials were filtered on a dense paper filter. The green raw product was washed with hot DMF (100 °C, 8 h, 2 times) and with hot EtOH (80 °C, 8 h, 2 times), filtered off, and dried overnight in an oven at 75 °C.

---

* Corresponding author. Tel.:+98 311 7932710; fax: +98 311 6689732.
E-mail addresses: stanges@sci.ui.ac.ir (S. Tangestaninejad), moghadamm@sci.ui.ac.ir (M. Moghadam).

1566-7367/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.catcom.2011.10.005

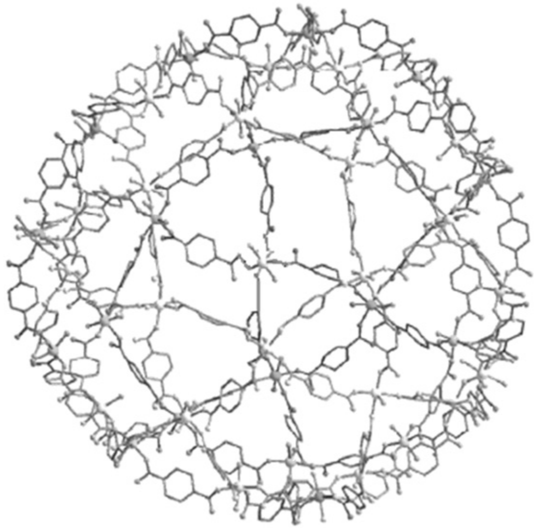


Fig. 1. Structure of MIL-101.

2.2. Physico-chemial measurements

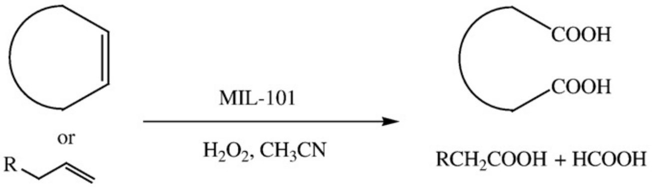
Specific surface area was measured by adsorption–desorption of N_2 gas at 77 K with ASAP 2000 micromeritics instrument. FT-IR spectra were recorded using potassium bromide pellets (MOF: KBr, 5: 95) in the range of 400–4000 cm^{-1} by a Jasco FT/IR-6300 instrument. X-ray diffraction (XRD) analysis was carried on a D_8 Advanced Bruker anode X-ray Diffractometer with Cu Kα (λ = 1.5406 Å) radiation. Thermogravimetric analysis (TGA) was performed on a mettler TA 4000 instrument at a heating rate of 5 K min^{-1}. The ICP analyses were carried out by a Perkin-Elmer optima 7300 DV spectrometer. GC analyses were performed using a Shimadzu GC-16A gas chromatograph equipped with a flame ionization detector and a 2 m column packed with silicon DC-200 or Carbowax 20 m. In GC experiments, *n*-decane was used as internal standard.

2.3. Catalytic experiments

All reactions were performed in a 25 mL round-bottom flask equipped with a condenser and a magnetic stirrer bar. The MIL-101 (5 mg, 0.0066 mmol) was added to a solution of alkene (0.5 mmol) in CH_3CN (3 mL). Then, H_2O_2 (30%, 500 μL, 5 mmol) was added to the mixture and refluxed. The progress of the reaction was monitored by GC. At the end of the reaction, the catalyst was filtered and washed with CH_3CN (10 mL). The solvent was evaporated and the pure products were obtained by chromatography on a short column of silica gel. The products were characterized by ^{1}H NMR, FT-IR spectroscopy and mass spectrometry.

2.4. Recycling test

The oxidation of indene was chosen as a model substrate for checking the reusability of MIL-101. After each run the catalyst was separated from reaction mixture, washed with acetonitrile and dried carefully before using in the next run. The same procedure was repeated for other runs. The amount of Cr leached to the reaction mixture was measured by inductively coupled plasma. After the reaction was completed, the catalyst was filtered. The filtrate was dissolved in strong acidic solution (HNO_3:HCl, 1:3). Then, the amount of Cr leached was determined by ICP analysis.



Scheme. 1. Oxidative cleavage of alkenes with MIL-101.

2.5. Spectral data of the corresponding carboxylic acids

Heptanoic acid ($C_6H_{13}COOH$):
Mass (m/e): 130.1
FT-IR (KBr, υ (C m^{-1})): 3215.72 (O–H), 1711.51 (C=O), 1282.43 (C–O)
^{1}H-NMR (CDCl$_3$, 400 MHz): 0.85 (t, 2H, J = 7.03 Hz), 1.28 (m, 6H), 1.53 (t, 2H, J = 7.13 Hz),
2.16 (t, 2H, J = 7.5 Hz)

Nonanoic acid ($C_8H_{17}COOH$):
Mass (m/e): 158.13
FT-IR (KBr, υ (C m^{-1})): 3419.17(O–H), 1719.23 (C=O), 1200.47 (C–O)
^{1}H-NMR (CDCl$_3$, 400 MHz): 0.85 (d, 1H, J = 14 Hz), 1.28 (s, 10H), 1.53 (t, 1H, J = 7.27 Hz),
2.16 (t, 2H, J = 7.4 Hz)

Undecanoic acid ($C_{10}H_{21}COOH$):
Mass (m/e): 186.16
FT-IR (KBr, υ (C m^{-1})): 3501.13 (O–H), 1714.41 (C=O), 1277.61 (C–O).
^{1}H-NMR (CDCl$_3$, 400 MHz): 0.85 (t, 3H, J = 6.78 Hz), 1.28 (br s, 14H), 1.53 (t, 2H, J = 7.08 Hz),
2.16 (t, 2H, J = 7.48 Hz).

Glutaric acid ($C_5H_8O_4$):
Mass (m/e): 132.97
FT-IR (KBr, υ (C m^{-1})): 3425.92 (O–H), 1731.76 (C=O), 1208.18 (C–O).
^{1}H-NMR (CDCl$_3$, 400 MHz): 2.37 (t, 4H, J = 7.48 Hz), 1.88 (m(q), 2H, J = 7.45 Hz).

Adipic acid ($C_6H_{10}O_4$):
Mass (m/e): 146.75
FT-IR (KBr, υ (C m^{-1})): 3425.92 (O–H), 1714.41 (C=O), 1220.72 (C–O).
^{1}H-NMR (CDCl$_3$, 400 MHz): 1.53 (m, 4H), 2.2 (m, 4H).

Suberic acid ($C_8H_{14}O_4$):
Mass (m/e): 174.84
FT-IR (KBr, υ (C m^{-1})): 3440.39 (O–H), 1732.73 (C=O), 1211.07 (C–O).
^{1}H-NMR (CDCl$_3$, 400 MHz): 2.16 (t, 4H, J = 7.51 Hz), 1.54 (t, 4H, J = 7.14 Hz), 1.29 (m, 4H).

2-(Carboxymethyl)benzoic acid or Homophthalic acid ($C_9H_8O_4$):
Mass (m/e): 180.93
FT-IR (KBr, υ (C m^{-1})): 3079.76(O–H), 1684.52(C=O), 1277 (C–O).
^{1}H-NMR (CDCl$_3$,400 MHz) : 3.4 (s, 2H), 7.15 (m, 2H), 7.25 (t, 1H, J = 7.4 Hz), 7.9 (d, 1H, J = 7.11 Hz).

3. Results and discussion

MIL-101 was synthesized by hydrothermal method. Figs. 2B and 3B show the X-ray diffraction patterns and FT-IR spectra of the resulted green powder which are as same as reported previously [34]. These observations confirmed the synthesis of MIL-101. The specific surface area of the obtained porous materials was determined using nitrogen physisorption measurements at low temperature and was obtained about 2125 m^2 g^{-1} (Fig. 4A).

Thermal stability of the MIL-101 was measured by TGA method (Fig. 5). Analysis of these thermograms strongly proposed that MIL-

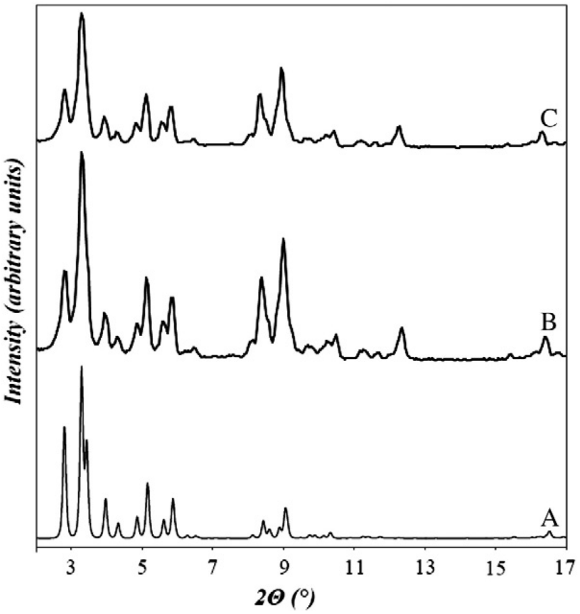


Fig. 2. XRD patterns of MIL-101: (A) calculated one; (B) synthesized MIL-101 and (C) recovered catalyst.

101 structure was stable and no further weight loss occurs below 350 °C. At temperatures higher than 350 °C, the framework structure was decomposed.

The catalytic activity of the MIL-101 was evaluated in the oxidation of alkenes with H_2O_2, in acetonitrile, under reflux conditions. Table 1 presents the results of the oxidation of alkenes by MIL-101. Cyclic alkenes such as cyclopentene, cyclohexene, and cyclooctene were cleaved readily under the reaction conditions and generated the glutaric acid (75%), adipic acid (90%) and suberic acid (98%), respectively (Table 1, entries 1–3). Both adipic and suberic acids are industrially very important. Even-numbered acyclic α-olefins such as 1-octene, 1-decene, and 1-dodecene were easily converted into their corresponding odd-numbered alkanoic acids of one less carbon in 80–90% yields (Table 1, entries 5–7). The substituted cyclic olefin, indene (Table 1, entry 4) was converted to 2-(carboxymethyl)benzoic acid (homophthalic acid) in 100% yield. The catalytic activity of $CrCl_3$ was investigated in the oxidation of indene under the same conditions for MIL–101. The results showed that the product was epoxide and the yield was about 17%. In the absence of catalyst only 15% of its corresponding epoxide was produced in the oxidation of indene and no diacid was detected.

For a more complete study, the reusability of MIL-101 was also investigated in the oxidation of indene. As mentioned before, the product yield was 100% in the first run after 3 h. In the second and third runs, the product yields decrease to 94% and 81%, respectively (Table 2). In addition, a decrease in the reaction rate is observed from the first to the third run as can be seen from Fig. 6. This is due to the some catalyst leaching during the catalytic experiments. Despite decreasing in the reaction rate and yield, the catalyst reserve

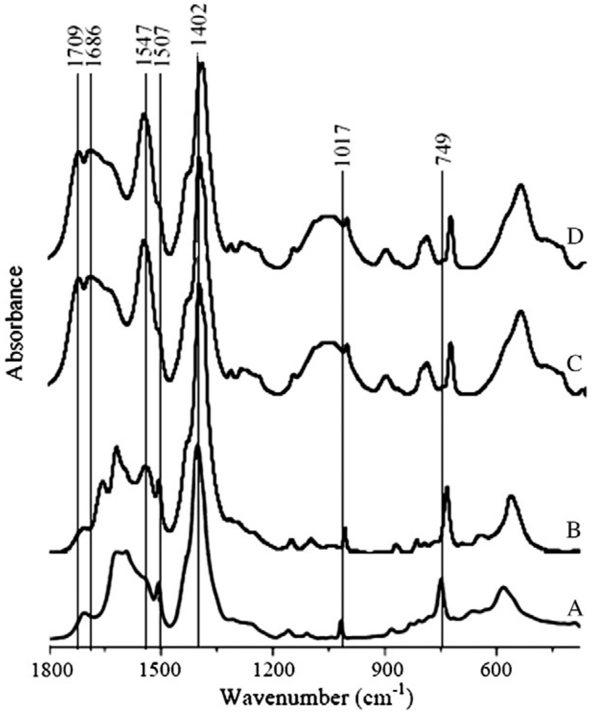


Fig. 3. FT-IR spectrum of MIL-101: (A) reported in 34; (B) before catalytic activity; (C) recovered catalyst and (D) treatment with H_2O_2.

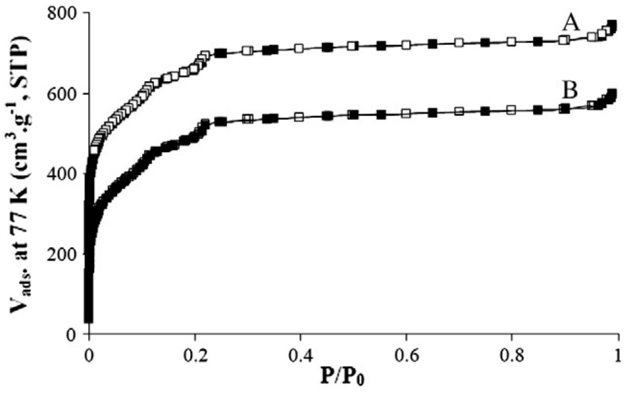


Fig. 4. N_2 isotherms of: (A) fresh MIL-101, (B) recovered catalyst (■ Adsorption, □ Desorption).

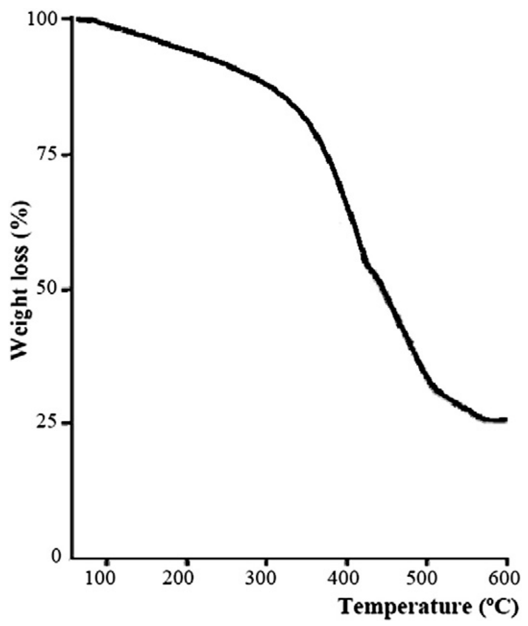
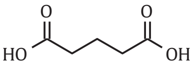
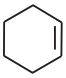
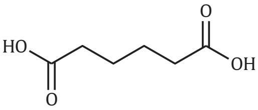
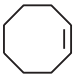
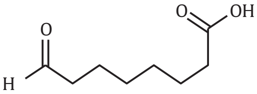
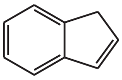
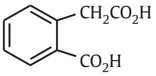


Fig. 5. Thermogram of MIL-101.

Table 1
Oxidation of alkenes with H_2O_2 catalyzed by MIL-101 refluxing in acetonitrile [a].

Entry	Alkene	Product	Yield (%)[b]	Time (h)	TOF (h^{-1})
1			75	8	7.10
2			90	8	8.52
3			98	4	18.56
4			100	3	25.25
5	1-octene	$CH_3(CH_2)_5COOH$	90	8	8.52
6	1-decene	$CH_3(CH_2)_7COOH$	80	8	7.57
7	1-dodecene	$CH_3(CH_2)_9COOH$	85	5	12.88

[a] Reaction conditions: alkene (0.5 mmol), H_2O_2 (5 mmol), MIL-101 (5 mg, 0.0066 mmol), acetonitrile (3 mL).
[b] GC yield based on the starting alkene.

Table 2
Recyclability of MIL-101 in the oxidation of indene[a].

Cr leached (mmol)	TOF (h^{-1})	Yield (%)[b]	Run
0.002	25.25	100	1
0.001	23.74	94	2
0.0006	20.45	81	3

[a] Reaction conditions: indene (0.5 mmol), H_2O_2 (5 mmol), MIL-101 (5 mg, 0.0066 mmol), acetonitrile (3 mL).
[b] GC yield based on the starting alkene.

81% of its initial activity. The amounts of Cr leached were measured by ICP technique and are shown in Table 2. As can be seen in Table 2, the amount of Cr leached in the three runs is about 18% of the initial Cr, which is in accordance to the decreasing of the product yield from 100% in the first run to 81% in the third run. The nature of the recovered MIL-101 was studied by FT-IR spectroscopy and XRD analysis. The presence of new bands in 1500–1800 cm^{-1} is due to the oxidative degradation of the MIL-101 structure. The presence of bands corresponding to the carboxylic groups of terephthalic acid in the spectral region of 1500–1800 cm^{-1} is an evidence for this observation (Fig. 3C). Moreover, new bands corresponding to stretching C=O vibrations appeared at 1709 and 1686 cm^{-1}. To check this point, a sample of catalyst was stirred with H_2O_2 in the absence of substrate and the same results were observed (Fig. 3D).

Also, the XRD pattern of the recovered catalyst is as same as the fresh catalyst but the peaks intensity has been decreased (Fig. 2C). The N_2 isotherm of the recovered catalyst is shown in Fig. 4B. It is clear that the surface area of the MIL-101 decreased to 1790 $m^2\,g^{-1}$.

To check the heterogeneity of MIL-101 catalyst in liquid phase oxidation indene, a hot filtering experiment (separation of catalyst at the reaction temperature) and recycling runs over the spent catalysts were carried out at a fixed temperature (70 °C). In this case, the catalyst was filtered off after 30 min reaction and the filtrate mixture was then stirred at 70 °C for duration of up to 360 min (Fig. 7). The results showed that no further progress was observed than in the presence of catalyst. The low catalytic activity of Cr leached (and also $CrCl_3$) shows that the catalyst active sites are the framework nodes not metals nodes [6].

In order to investigate the reaction mechanism, a series of oxidation reactions were carried out using cyclohexene, cyclohexene oxide and *trans*-1,2-cyclohexanediol. The results showed that all these compounds were efficiently converted to adipic acid. As can be seen in Scheme 2, the reaction times for oxidation of cyclohexene,

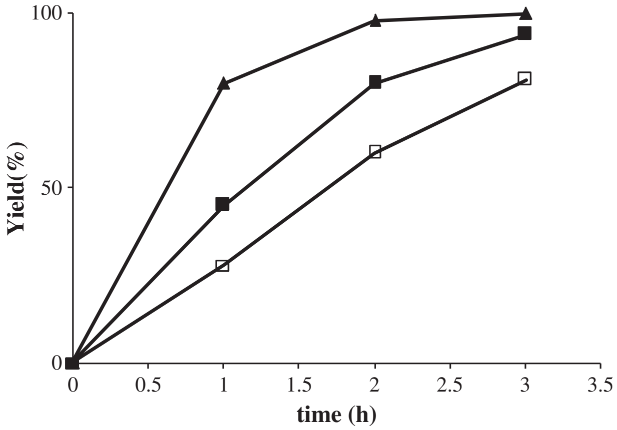


Fig. 6. Product conversion for MIL-101 catalyzed oxidation of indene; ▲ run 1, ■ run 2, □ run 3.

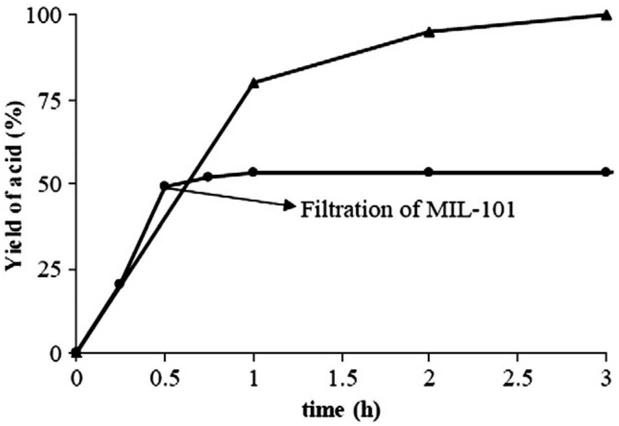
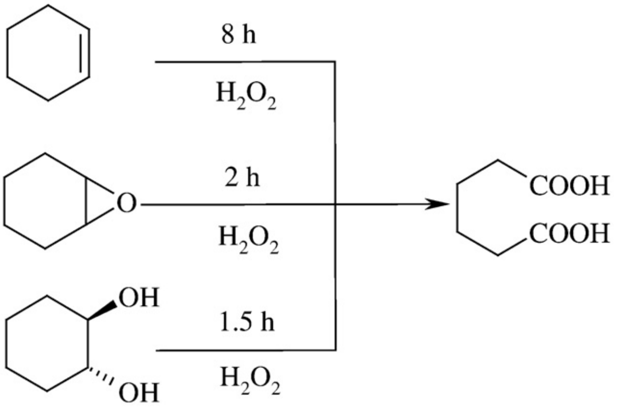


Fig. 7. Indene oxidation after 3 h: ● Filtration test, and ▲ MIL-101.



Scheme 2. Catalytic oxidation of cyclohexene, cyclohexene oxide and *trans*-1,2-cyclohexandiol to adipic acid.

Table 3
Comparison of the results obtained for the oxidation of cyclooctene catalyzed by MIL-101 with those obtained by the recently reported catalysts.

Catalyst	Oxidant	T (°C)	TOF (h^{-1})	Ref.
$InCl_3$	*t*-BuOOH (70%)	90	0.58	[25]
OsO_4	Oxone	rt	27.33	[27]
$[(n\text{-Octyl})_3NCH_3]_3\{PO_4[W(O)(O_2)_2]_4\}$	H_2O_2 (30%)	85	5.71	[28]
$RuCl_3$	$NaIO_4$	rt	20.45	[31]
MIL-101	H_2O_2 (30%)	70	18.56	Present work

cyclohexene oxide and *trans*-1,2-cyclohexanediol were 8, 2 and 1.5 h, respectively. These observations clearly prove that the alkene first is converted to epoxide and then, upon epoxide ring-opening a diol is produced which finally oxidized to diacid [35]. These results well described that the rate determination step (RDS) is conversion of alkene to epoxide step, then other steps take place fast.

In comparison with previously reported methods for oxidation of alkenes to carboxylic acids, the presented method is more efficient and more acceptable. For example, although ozonolysis is a very reliable method, ozone gas is highly toxic and damaging to human health and its generation requires special instrumentation. On the other hand, OsO_4 is highly volatile and toxic and is not environmentally benign which restrict its use for large-scale applications in industry [27]. Ruthenium compounds are very expensive [31]. $InCl_3$[25] and $[(n\text{-Octyl})_3NCH_3]_3\{PO_4[W(O)(O_2)_2]_4\}$ [28] have low TOF. Thus, in comparison with these methods, aqueous H_2O_2, which is a clean and green oxidant, in the presence of MIL-101 is an efficient method for oxidation of alkenes to acids especially if the oxidation reaction is achieved with a H_2O_2 concentration of <60% (Table 3).

4. Conclusion

Summary, in this work, a new route for conversion of alkenes to their corresponding carboxylic acids is reported based on catalytic properties of MIL-101 metal–organic framework. Comparison with other systems that reported for oxidative cleavage of C-C double bond in alkenes, this catalytic system has the following advantages: i) using H_2O_2 as a clean and green oxidant, ii) no need to phase transfer catalyst, iii) high to excellent yield, and iv) MIL-101 is a heterogeneous and reusable catalyst.

Acknowledgment

We are thankful to the Center of Excellence of Chemistry of the University of Isfahan for financial support of this work.

References

[1] J.R. Li, R.J. Kuppler, H.C. Zhou, Chemical Society Reviews 38 (2009) 1477–1504.
[2] Z. Chang, D.-S. Zhang, T.-L. Hu, X.-H. Bu, Inorganic Chemistry Communications 14 (2011) 1082–1085.
[3] M.H. Alkordi, Y. Liu, R.W. Larsen, J.F. Eubank, M. Eddaoudi, Journal of the American Chemical Society 130 (2008) 12639–12641.
[4] D. Jiang, T. Mallat, F. Krumeich, A. Baiker, Journal of Catalysis 257 (2008) 390–395.
[5] S. Horike, M. Dinc , K. Tamaki, J.R. Long, Journal of the American Chemical Society 130 (2008) 5854–5855.
[6] J.-Y. Lee, O.K. Farha, J. Roberts, K.A. Scheidt, S.T. Nguyen, J.T. Hupp, Chemical Society Reviews 38 (2009) 1450–1459.
[7] K.S. Min, M.P. Suh, Journal of the American Chemical Society 122 (2000) 6834–6840.
[8] A. Schaate, M. Schulte, M. Wiebcke, A. Godt, P. Behrens, Inorganica Chimica Acta 362 (2009) 3600–3606.
[9] L. Jiang, Z.-X. Li, Y. Wang, G.-D. Feng, W.-X. Zhao, K.-Z. Shao, C.-Y. Sun, L.-J. Li, Z.-M. Su, Inorganic Chemistry Communications 14 (2011) 1077–1081.
[10] G. Lu, J.T. Hupp, Journal of the American Chemical Society 132 (2010) 7832–7833.
[11] E.A. Tomic, Journal of Applied Polymer Science 9 (1965) 3745–3752.
[12] H. Li, M. Eddaoudi, M. O'Keeffe, O.M. Yaghi, Nature 402 (1999) 276–279.
[13] S.-H. Cho, B. Ma, S.T. Nguyen, J.T. Hupp, T.E. Albrecht-Schmitt, Chemical Communications (2006) 2563–2565.
[14] F.X. Llabrés i Xamena, A. Abad, A. Corma, H. Garcia, Journal of Catalysis 250 (2007) 294–298.
[15] A. Dhakshinamoorthy, M. Alvaro, H. Garcia, Advanced Synthesis and Catalysis 351 (2009) 2271–2276.
[16] E. Pérez-Mayoral, J. Čejka, ChemCatChem 2 (2010) 1–3.
[17] D.N. Dybtsev, A.L. Nuzhdin, H. Chun, K.P. Bryliakov, E.P. Talsi, V.P. Fedin, K. Kim, Angewandte Chemie International Edition 45 (2006) 916–920.
[18] D. Jiang, T. Mallat, F. Krumeich, A. Baiker, Journal of Catalysis 257 (2008) 390–395.
[19] T. Ladrak, S. Smulders, O. Roubeau, S.J. Teat, P. Gamez, J. Reedijk, European Journal of Inorganic Chemistry (2010) 3804–3812.
[20] F.X. Llabrés i Xamena, O. Casanova, R.G. Tailleur, H. Garcia, A. Corma, Journal of Catalysis 255 (2008) 220–227.
[21] G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surble´, I. Margiolaki, Science 309 (2005) 2040–2042.
[22] A. Henschel, K. Gedrich, R. Kraehnert, S. Kaskel, Chemical Communications (2008) 4192–4194.
[23] J. Kim, S. Bhattacharjee, K.-E. Jeong, S.-Y. Jeong, W.-S. Ahn, Chemical Communications (2009) 3904–3906.
[24] E.V. Ramos-Fernandez, M. Garcia-Domingos, J. Juan-Alcãniz, J. Gascon, F. Kapteijn, Applied Catalysis A: General 391 (2011) 261–267.
[25] B.C. Ranu, S. Bhadra, L. Adak, Tetrahedron Letters 49 (2008) 2588–2591.
[26] S.-K. Lee, R. Raja, K.D.M. Harris, J.M. Thomas, B.F.G. Johnson, G. Sankar, Angewandte Chemie International Edition 42 (2003) 1520–1523.
[27] B.R. Travis, R.S. Narayan, B. Borhan, Journal of the American Chemical Society 124 (2002) 3824–3825.
[28] E. Antonelli, R. D'Aloisio, M. Gambaro, T. Fiorani, C. Venturello, Journal of Organic Chemistry 63 (1998) 7190–7206.
[29] T.A. Foglia, P.A. Barr, A.J. Malloy, Journal of the American Oil Chemists' Society 54 (1977) 858A–861A.
[30] H. Sokumoto, K. Ohtsuka, S. Banjoya, Synlett (2007) 3201–3207.
[31] F. Zimmermann, E. Meux, J.-L. Mieloszynski, J.-M. Lecuire, N. Oget, Tetrahedron Letters 46 (2005) 3201–3203.
[32] D. Xing, B. Guan, G. Cai, Z. Fang, L. Yang, Z. Shi, Organic Letters 8 (2006) 693–696.
[33] P.P. Thottumkara, T.K. Vinod, Organic Letters 12 (2010) 5460–5463.
[34] N.V. Maksimchuk, M.N. Timofeeva, M.S. Melgunov, A.N. Shmakov, Y.A. Chesalov, D.N. Dybtsev, V.P. Fedin, O.A. Kholdeeva, Journal of Catalysis 257 (2008) 315–323.
[35] K. Sato, M. Aoki, R. Noyori, Science 281 (1998) 1646–1647.