Catalysis Today xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

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

Hydrocarbon oxidation over Fe- and Cr-containing metal-organic frameworks MIL-100 and MIL-101–a comparative study

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ARTICLE INFO

Article history:
Received 1 December 2013
Accepted 14 January 2014
Available online xxx

Keywords:
MIL-101
MIL-100
Heterogeneous catalysis
Alkenes
Anthracene
Selective oxidation

ABSTRACT

Catalytic properties of Fe- and Cr-based metal-organic frameworks (MOFs) MIL-100 and MIL-101 have been assessed in two liquid-phase reactions: solvent-free allylic oxidation of alkenes (cyclohexene, α- and β-pinenes) with molecular oxygen and oxidation of anthracene (AN) with *tert*-butyl hydroperoxide (TBHP). In the oxidation of alkenes, the product selectivity strongly depends on the nature of metal (Fe or Cr) but, for the same metal, only slightly differs for the MIL-100 and MIL-101 structures. The Fe-containing MOFs afford the formation of unsaturated alcohols while Cr-based MOFs give mainly unsaturated ketones. Both Cr-MIL-100 and Cr-MIL-101 favor decomposition of cyclohexenyl hydroperoxide to produce 2-cyclohexen-1-one with 67–69% selectivity. Stability toward destruction reduced in the order Cr-MIL-101, Cr-MIL-100 > Fe-MIL-100 > Fe-MIL-101. In the oxidation of anthracene over both Cr-MOFs and Fe-MIL-101, the selectivity toward 9,10-anthraquinone (AQ) attained 100% at 92–100% AN conversion. The turnover frequency (TOF) decreased in the order Cr-MIL-101 > Fe-MIL-101 > Cr-MIL-100 > Fe-MIL-100. Cr-MIL-101 revealed superior catalytic performance in terms of AN conversion, AQ selectivity and TOF. Nearly quantitative yield of AQ was obtained after 1.5 h at 100 °C in chlorobenzene as solvent. No leaching of active metal occurred under optimal reaction conditions and the MOFs could be recycled several times without deterioration of the catalytic properties.

1. Introduction

Metal-organic frameworks (MOFs) have attracted considerable attention owing to a unique combination of properties, such as crystalline open structures, extremely high surface areas and pore volumes, tunable pore size and functionality. All these allow consideration of MOFs as prospective materials for molecular recognition, separation, gas storage and catalysis [1–10]. These materials potentially combine advantages of both homogeneous and heterogeneous catalysts because their structure consists of isolated metal clusters or atoms connected by polydentate organic ligands to form a rigid porous framework. The important feature of such framework is a high number of regularly distributed uniform metal centers that are accessible for reagents the size of which is comparable or smaller than the MOF cage entrances.

Until recently, low thermal, chemical and solvolytic stabilities (in comparison with inorganic zeolites) limited the application of MOFs in catalysis. In 2005, Férey and co-workers reported the synthesis of a mesoporous chromium terephthalate, Cr-MIL-101, which demonstrated a good resistance to air, water, common solvents and thermal treatment (up to 300 °C) [11]. Taylor-Pashow et al. synthesized an iron-containing analog, Fe-MIL-101 [12]. The MIL-101 material has a zeotype crystal structure consisting of two types of cages with a diameter of 34 and 29 Å (the corresponding windows are 16 and 12 Å). Coordinatively unsaturated metal sites (CUS) can be easily generated in the structure of MIL-101 by heating the material in vacuum [13]. Changing the linker molecule from 1,4-benzenedicarboxylic acid for 1,3,5-benzenetricarboxylic acid resulted in the formation of another MOF structure, MIL-100, which contains cages of 27 and 24 Å accessible through microporous windows of 9 and 6 Å, respectively. Both Cr-MIL-100 [14] and Fe-MIL-100 [15] have been reported by Férey's group. Schematic representation of the MIL-101 and MIL-100 structures is shown in Fig. 1.

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0920-5861/$ – see front matter
http://dx.doi.org/10.1016/j.cattod.2014.01.010

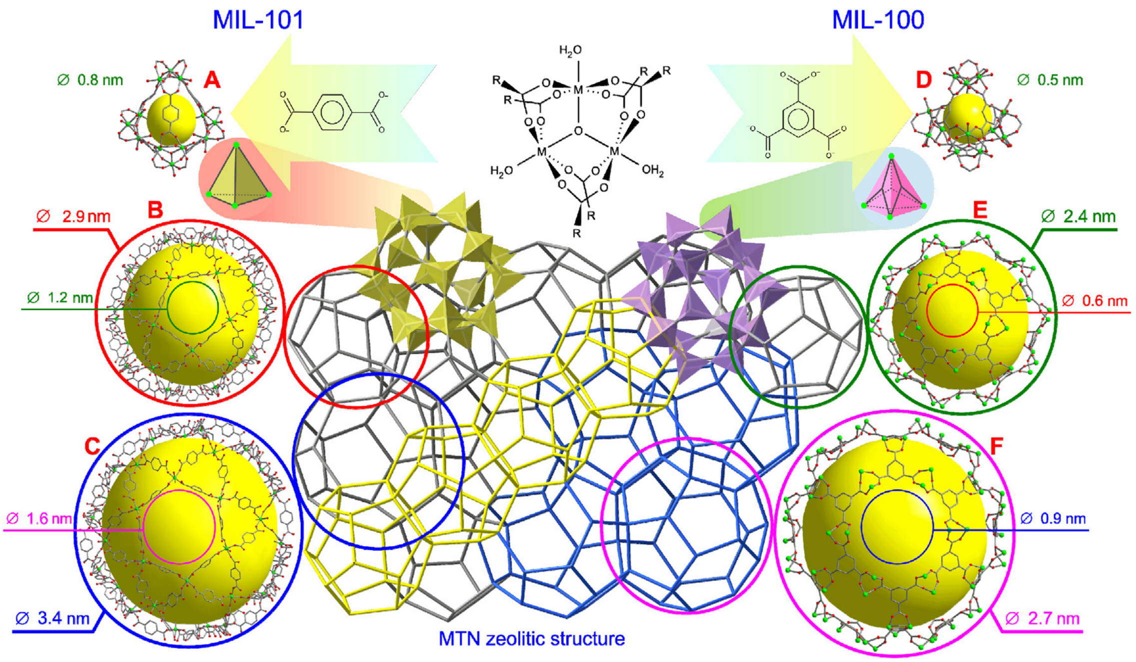

Fig. 1. Schematic representation of the MIL-101 and MIL-100 structures: M_3O-carboxylate trimer—primary building unit, A and D—supertetrahedra, secondary building units, B and E—small cages, C and F—large cages of MIL-101 and MIL-100, respectively.

Fe-MIL-100 revealed catalytic activity in the oxidation of diphenylmethane and triphenylmethane with *tert*-butyl hydroperoxide (TBHP) [16] and Friedel–Crafts benzylation of benzene [15]. Iron coordinated to 1,3,5-benzenetricarboxylate (BTC), the so-called [Fe(BTC)] metal-organic framework, has been commercialized by BASF under the trade name of Basolite F 300. Although the exact crystal structure of Fe(BTC) is still unknown, it is likely that it has a structure similar to that of Fe-MIL-100. [Fe(BTC)] is an effective catalyst for aerobic oxidation of cyclooctane [17] and styrene [18]. In turn, Cr-MIL-100 operates as effective Lewis acid catalyst in various organic transformations [19]. Cr-MIL-101 is able to catalyze cyanosilylation of benzaldehyde [20], carboxylation of epoxides [21], benzilyc oxidation of tetralin [22], sulfoxidation of thioethers with H_2O_2 [13], oxidation of cyclohexane [23] and allylic oxidation of alkenes with TBHP [24] or O_2 [25,26]. Recently, we reported the use of Fe-MIL-101 in the allylic oxidation of alkenes with molecular oxygen and found a product distribution significantly different from Cr-MIL-101 [25,26]. So far, no direct comparison of the catalytic behavior of MIL-100 and MIL-101 materials in selective oxidation reactions has been reported. In the present work, we assessed and compared catalytic properties of Fe- and Cr-based MIL-100 and MIL-101 in two liquid-phase reactions: solvent-free allylic oxidation of alkenes with molecular oxygen and oxidation of anthracene (AN) to 9,10-anthraquinone (AQ) using TBHP as oxidant.

2. Experimental

2.1. Materials

Cyclohexene (CyH), α- and β-pinene (Sigma-Aldrich or Alpha-Aesar) were purified prior to use by passing through a column filled with neutral alumina to remove traces of possible oxidation products. Anthracene (99%) and anthraquinone (99%) were purchased from Aldrich and used without additional purification. Chlorobenzene, toluene, dichloroethane and acetonitrile (Fluka) were dried and stored over activated 4 Å molecular sieves. All other reactants were obtained commercially and used without additional purification. TBHP was used as a solution in decane (4.7 M; Aldrich) or as a 70 wt% aqueous solution. Cyclohexenyl hydroperoxide was prepared according to the literature [27]. The exact concentration of hydroperoxides was determined iodometrically prior to use.

2.2. MOF synthesis and characterization

Cr-MIL-101 [11] and Fe-MIL-101 [12] were prepared by the solvothermal method following protocols reported elsewhere [25]. Fe-MIL-100 and Cr-MIL-100 were synthesized according to the literature [14,15] with some modifications. In a typical synthesis of Fe-MIL-100, 140 mg metal iron (2.5 mmol), 350 mg trimesic acid (1.65 mmol), 5 mL HF (5 mmol), 1.2 mL HNO_3 (1.2 mmol) and 13 mL H_2O were put into a Teflon-lined stainless steel bomb and heated up to 150 °C and then kept at this temperature for 24 h. The resulting orange solid was filtered off and washed with hot (*ca.* 80 °C) water for 3 h. Then, the material was dried at room temperature overnight. In a typical synthesis of Cr-MIL-100, 100 mg metal chromium (2 mmol), 300 mg trimesic acid (1.4 mmol), 1 mL HF (4 mmol) and 9 mL H_2O were placed into a Teflon-lined stainless steel bomb and heated with the rate of 20 °C/min up to 220 °C during 96 h. Cooling was performed with the rate of 10 °C/min. The resulting green solid was filtered off, washed with water and acetone and dried at room temperature.

The MOFs were characterized by X-ray diffraction (XRD) technique and low temperature N_2 adsorption measurements. XRD patterns of all the materials were in accordance with the literature [11,12,14,15]. The average size of crystallites was ca. 0.7 and 7 μm for the MIL-101 and MIL-100 materials, respectively. The specific BET surface areas were in the range of 3200–3400 (MIL-101) and 2000–2200 (MIL-100) m^2/g. The content of Cr (Fe) was *ca.* 23 and 26 wt% in activated MIL-101 and MIL-100, respectively.

2.3. Catalytic tests and product analysis

Catalytic oxidations of alkenes with O_2, product analysis and product adsorption measurements were performed as described

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Table 1
CyH oxidation with molecular oxygen over MIL-100 and MIL-101.

Entry	Catalyst (mg)	T (°C)	Selectivity (%)			CyH conversion (%)	Reference
			1	**2**	**3**		
1	Fe-MIL-100 (13)	50	21	36	43	10	This work
2	Fe-MIL-100 (13)	40	11	62	27	7	This work
3	Fe-MIL-100 (26)	40	14	60	26	8	This work
4	Fe-MIL-101 (13)	50	22	11	63	27	[25]
5	Fe-MIL-101 (13)	40	15	58	27	8	[25]
6	Fe-MIL-101 (26)	40	18	57	25	8	This work
7	Cr-MIL-100 (26)	60	52	31	17	12	This work
8	Cr-MIL-101 (26)	60	56	38	6	16	[25]

Reaction conditions: 1 mL CyH, 1 bar O_2, 0.02–0.03 mmol TBHP (as initiator), 16 h.

elsewhere [25,26]. Catalytic oxidations of AN were carried out in thermostated glass vessels under vigorous stirring (600 rpm). Reactions were started by the addition of TBHP to a mixture containing anthracene, MOF, internal standard (biphenyl) and solvent. Prior to use, MOFs were activated in vacuum: Cr-MIL-101–at 120 °C for 2 h and then 180 °C for 4 h, Fe-MIL-101—at 120 °C for 6 h and Cr(Fe)-MIL-100—at 150 °C for 6 h. Samples of the reaction mixture were withdrawn periodically during the reaction course by a syringe. The oxidation products were identified by GS–MS. Yields of AQ and conversions of AN were quantified by GC. Each experiment was reproduced 3–4 times. Turnover frequency (TOF) values were determined from initial rates of AN consumption. Catalyst reusability was studied in 4–6 time scaled experiments. Before reuse, catalysts were filtered off, washed with hot chlorobenzene (PhCl) and acetone, and dried in air at 30–40 °C for 1–2 h. The nature of catalysis was verified by hot filtration test [28].

2.4. Instrumentation

GC analyses were performed using a gas chromatograph Agilent 4890D equipped with a flame ionization detector and a 30 m × 0.25 mm VF-5 MS capillary column or gas chromatograph Chromos GC-1000 equipped with a flame ionization detector and a 30 m × 0.25 mm BPX-5 capillary column. GC–MS analyses were carried out using a gas chromatograph HP 6890 (a 50 m × 0.25 mm DB-5 MS capillary column) equipped with a mass-selective detector Agilent MSD 5973. XRD measurements were performed on Shimadzu XRD 7000S or DRON-3M. Nitrogen adsorption at 77 K was measured using an ASAP-2020 instrument (Micrometrics) or Autosorb iQ (Quantachrome) within a partial pressure range of 10^{-6}–1.0.

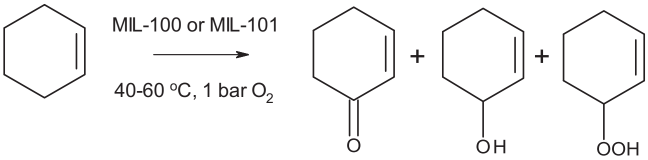
3. Results and discussion

3.1. Cyclohexene oxidation with molecular oxygen

Previously, we found that the presence of both MOF catalyst and initiator (TBHP) is required to accomplish CyH oxidation at mild reaction conditions, viz., 1 atm of O_2 and 60 °C [25]. Hence, in all catalytic experiments, we added small amounts of TBHP to initiate the reaction.

3.1.1. Fe-MIL-100 and MIL-101

Table 1 presents the results on solvent-free CyH oxidation with molecular oxygen over both Fe- and Cr-containing MIL-100 and MIL-101. The main oxidation products were 2-cyclohexen-1-one (**1**), 2-cyclohexen-1-ol (**2**) and cyclohexenyl hydroperoxide (**3**). Minor amounts of cyclohexene oxide were found in few experiments.



1 **2** **3**

In our previous work, we revealed that the product distribution in CyH oxidation over Fe-MIL-101 strongly depended on the reaction temperature, which, in turn, determined the nature of catalysis [25]. Thus at 50–60 °C, Fe-MIL-101 underwent iron leaching and Fe species in solution favor the formation of **3**. We did not investigate the structure and composition of the soluble iron species. It could be mono or di(polynuclear) complexes of Fe(III) with carboxylates (linker) or some other ligands (e.g. reaction products). On the contrary, the MOF was stable to leaching at 40 °C and produced **2** as the main oxidation product [25]. The same regularities turned out to operate with Fe-MIL-100. Indeed, when the reaction was performed at 50 °C, hydroperoxide **3** predominated for both Fe-MIL-100 (Table 1, entry 1) and Fe-MIL-101 (entry 4). While decreasing the reaction temperature down to 40 °C, cyclohexenol became the main product over both Fe–MOFs and formed with the selectivity of 58–62% at 7–8% conversion (entries 2 and 5). No further substrate conversion occurred upon increasing the reaction time. Enlarging the catalyst amount produced no significant changes in CyH conversion and product selectivity (Table 1, compare entries 2 and 3 or entries 5 and 6). Hot catalyst filtration test (Fig. 2a) proved that the catalysis over Fe-MIL-100 at 40 °C is truly heterogeneous. At such temperature, both Fe–MOFs can be used repeatedly without deterioration of the catalytic properties. Table 2 presents the results on CyH conversion and selectivity toward the main product **2** obtained in four consecutive reuses. Importantly, studies by XRD revealed that Fe-MIL-100 preserved its structure after four reuses (Fig. 3a). This differs significantly Fe-MIL-100 from Fe-MIL-101 that partially lost the regular structure under the same conditions [25]. Therefore, we may conclude that Fe-MIL-100 and Fe-MIL-101 demonstrate similar catalytic properties in CyH

Table 2
Recycling of MIL-101 and MIL-100 in CyH oxidation.

Catalyst	CyH conversion[a] (%)	Selectivity to **2** (%)
Fe-MIL-101 [25]	9 (8, 9, 8)	57 (55, 58, 56)
Fe-MIL-100	7 (8, 7, 7)	60 (63, 61, 62)
		Selectivity to **1** (%)
Cr-MIL-101 [25]	16 (15, 17, 16)	56 (58, 56, 57)
Cr-MIL-100	11 (13, 12, 11)	50 (53, 52, 51)

Reaction conditions: 1 mL CyH, 1 bar O_2, 0.02–0.03 mmol TBHP (as initiator), 16 h, 40 °C for Fe-MILs (13 mg) or 60 °C for Cr-MILs (26 mg).

[a] In parentheses, 2nd, 3rd and 4th reuses.

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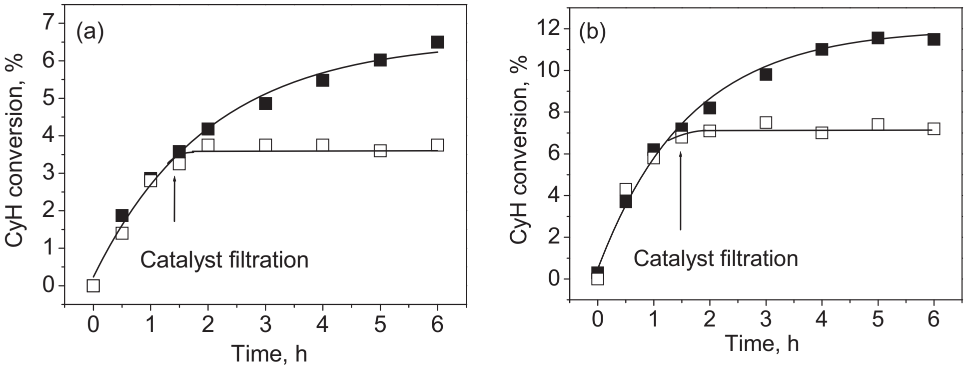


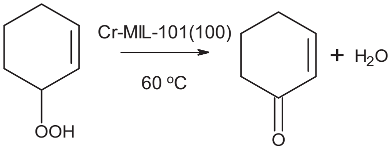
Fig. 2. Hot catalyst filtration test for (a) Fe-MIL-100 (40 °C) and (b) Cr-MIL-100 (60 °C). Reaction conditions as in Table 1, entries 2 and 7.

oxidation but the former has a higher stability toward degradation under the reaction conditions.

3.1.2. *Cr-MIL-100 and MIL-101*

In contrast to Fe-MIL-100, the main product of CyH oxidation over Cr-MIL-100 is α,β-unsaturated ketone **1**, which forms with the selectivity of 52% at 12% CyH conversion (Table 1, entry 7). The selectivity is close to that acquired with Cr-MIL-101 (entry 8) although the substrate conversion over MIL-101 is higher (16% versus 12%). Hence, again the product distribution is determined mostly by the nature of the transition metal in the MOF framework. Hot catalyst filtration test confirmed no leaching of active chromium species from Cr-MIL-100 at 60 °C (Fig. 2b), pointing out that Cr-MIL-100 is more stable toward metal leaching than the iron analog that can not survive at such temperature. Both Cr-MOFs could be used at least four times without loss of the catalytic properties (Table 2). XRD showed no degradation of the Cr-MIL-100 structure after four consecutive cycles (Fig. 3b). Previously, the structural integrity of Cr-MIL-101 was also corroborated by XRD [25]. Hence, in contrast to the Fe-MILs, no difference in stability of Cr-MIL-100 and Cr-MIL-101 has been found.

Thus the product selectivities found for CyH oxidation in the presence of Fe-MIL-100 and Cr-MIL-100 are similar to those obtained with Fe-MIL-101 and Cr-MIL-101 [25], thereby indicating that the nature of transition metal rather than the nature of the MOF linker determinates the oxidation mechanism. Like in the case of Fe-MIL-101 and Cr-MIL-101 [25], radical scavengers (ionol) impede the oxidation processes over both Fe-MIL-100 and Cr-MIL-100, indicating that radical chain steps are involved. To explain the difference in the product distribution in CyH oxidation over Fe-MIL-101 and Cr-MIL-101, we suggested different pathways for the transformation of the primary oxidation product, **3** [25,26]. The high selectivity toward **1** realized over Cr-MIL-101 was attributed to the ability of Cr centers to promote dehydration of **3**.



Earlier, Sheldon et al. demonstrated the possibility of such transformations for both cyclohexenyl hydroperoxide [27] and cyclohexyl hydroperoxide [29] over Cr-containing catalysts. Indeed, we found that both Cr-MIL-101 and Cr-MIL-100 catalyze decomposition of **3** to yield **1**. Fig. 4 shows plots of the accumulation of **1** versus time. Cyclohexenone selectivity remains constant during the decomposition process (67–69%). The only byproduct is **2** which might form along with **1** in the decomposition of **3** via >Haber–Weiss mechanism [30]. Similar values of cyclohexenone selectivity (65–74%) were reported by Sheldon et al. for various chromium catalysts, including $Cr(acac)_3$, Cr-APO5 and CrS-1 [27]. Possible routes leading to the preferable formation of unsaturated alcohols over Fe-MIL-101 have been suggested earlier [25]. Similar product distributions found for Fe-MIL-100 and Fe-MIL-101 imply that similar pathways might operate with Fe-MIL-100.

3.2. *Terpene oxidation with molecular oxygen*

Oxidation of two representative terpenes, α- and β-pinenes, was explored under the conditions at which all the MOF catalysts remain stable, i.e. 40 and 60 °C for Fe- and Cr-MILs, respectively. The results are presented in Table 3. In the oxidation of α-pinene, both Fe-MIL-100 and Fe-MIL-101 produced a significant amount of verbenol along with campholenic aldehyde, hydroperoxides and epoxide, but no verbenone was found in the reaction mixture

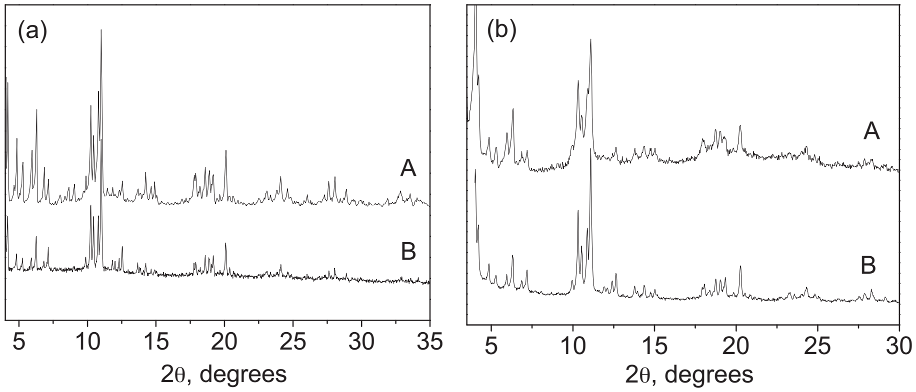


Fig. 3. XRD pattern of (a) Fe-MIL-100 and (b) Cr-MIL-100: initial sample (A) and after four catalytic cycles (B). Reaction conditions as in Table 2.

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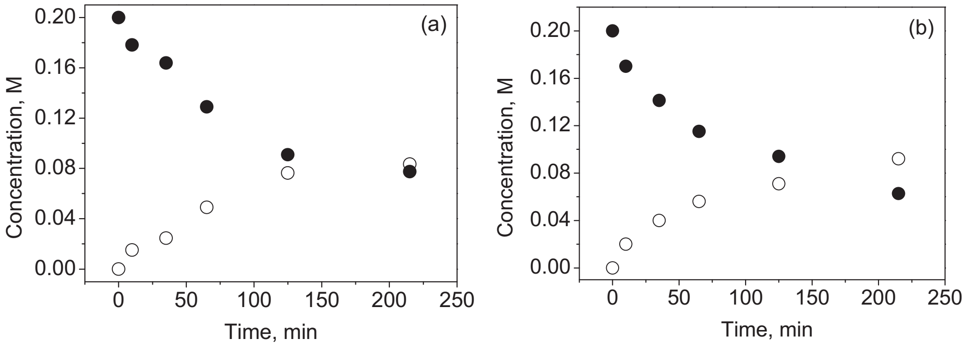
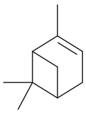
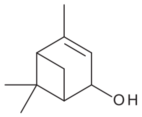
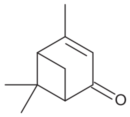
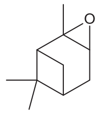
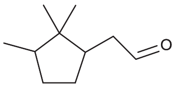
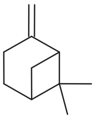
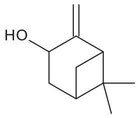
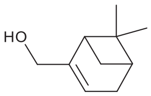
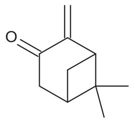
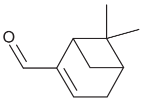


Fig. 4. Formation of cyclohexenone (○) in the course of decomposition of cyclohexenyl hydroperoxide **3** (●) over Cr-MIL-100 (a) and Cr-MIL-101 (b). Reaction conditions: 0.2 mmol of **3**, 26 mg MOF, 1 mL cyclohexane, 60 °C.

Table 3
Solvent-free oxidation of α- and β-pinenes with O_2 over MIL-101 and MIL-100.

Entry	Catalyst	Conversion (%)	Selectivity (%)				
							ROOH[a]
1	Fe-MIL-100	9	32	–	9	15	44
2	Cr-MIL-100	20	15	30	9	9	37
3	Fe-MIL-101 [26]	12	33	–	9	33	25
4	Cr-MIL-101 [26]	26	31	39	8	8	14
							ROOH[a]
7	Fe-MIL-100	12	64		–	10	26
8	Cr-MIL-100	18	20		2	33	45
9	Fe-MIL-101 [26]	13	57		–	–	43
10	Cr-MIL-101 [26]	22	32		23	27	18

Reaction conditions: 1.5 mL of alkene, 1 bar O_2, 0.02–0.03 mmol TBHP (initiator), 16 h, 40 °C for Fe-MILs (13 mg) or 60 °C for Cr-MILs (26 mg).
[a] Sum of hydroperoxides.

(Table 3, entries 1 and 3). The conversion of α-pinene was slightly lower for Fe-MIL-100 relative to Fe-MIL-101 (9% versus 12%). In β-pinene oxidation, both Fe-MILs gave two unsaturated alcohols (pinocarveol and myrtenol) along with hydroperoxides, but practically no ketones formed (Table 3, entries 7 and 9). The substrate conversion was close for both MOFs: 12% and 13% for Fe-MIL-100 and Fe-MIL-101, respectively.

Cr-containing MIL-100 and MIL-101 transformed α- and β-pinene mainly to hydroperoxides and unsaturated ketones and alcohols, with ketones predominating over alcohols (Table 3). Minor amounts of epoxide and campholenic aldehyde also formed in the reaction with α-pinene. Higher substrate conversions were attained for Cr-MIL-101 than for Cr-MIL-100 (26% versus 20% and 22% versus 18% for α- and β-pinene, respectively). Although the composition of products is more complicated in the oxidation of terpenes than in case of CyH, most likely, because of isomerization/rearrangement reactions typical of terpenoids, we may conclude that, in general, Fe-MILs favor the formation of unsaturated alcohols while Cr-MILs mediate the formation of unsaturated ketones.

3.3. Product adsorption studies

From the data presented in Tables 1 and 3, one can judge that the nature of metal strongly affects not only the product distribution but also the attainable substrate conversion that is considerably higher for Cr-containing MOFs than for the iron analogues. The organic linker nature produces less effect on the alkene conversion and product selectivity. Interstingly, the situation is different if we compare adsorption properties of the MOFs with regards to the CyH oxidation products. We evaluated the diffusion time and product (**1** and **2**) adsorption constants for Fe- and Cr-MIL-100 following the methodology reported in our previous work [25]. The results are presented in Table 4 in comparison with the results acquired ealier for the MIL-101 analogues. While the diffusion time does not exceed 1.5 min for all the MOFs, the adsorption constants are higher for MIL-100 than for MIL-101 and, surprisingly, do not depend on the nature of metal.

Previously we demonstrated that the addition of both **1** and **2** could stop CyH oxidation over Cr- and Fe-MIL-101 [25]. We found similar rate-retarding effects upon addition of these products to the reaction with Fe- and Cr-MIL-100 (Fig. 5a and b). Water, the product which forms in a stoichiometric amount along with **1**, can also act as an inhibitor of the alkene oxidation catalyzed by MOFs, as confirmed by the experiment with H_2O additives (Fig. 5b and

Table 4
Adsorption of cyclohexenone (**1**) and cyclohexenol (**2**) on MIL-100 and MIL-101.

Material	K_1 (M^{-1})	K_2, (M^{-1})	Diffusion time (min)
Fe-MIL-100	8 ± 2	8 ± 2	1
Fe-MIL-101 [25]	3 ± 1	1 ± 0.3	1.5
Cr-MIL-100	8 ± 2	8 ± 2	1.5
Cr-MIL-101 [25]	3 ± 1	1 ± 0.3	1.5

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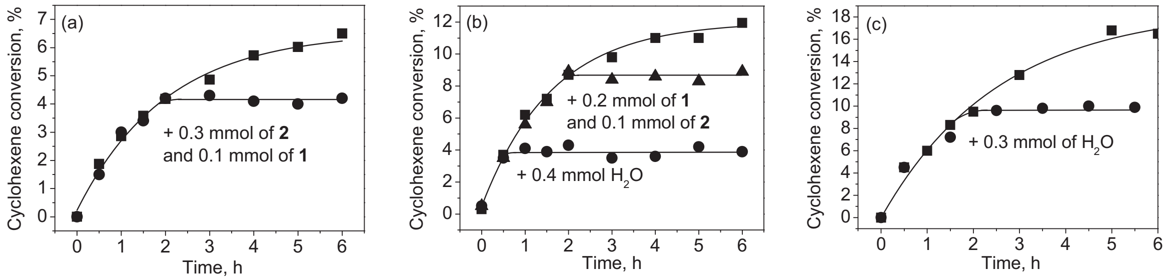
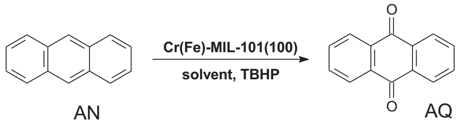


Fig. 5. Inhibition effects of oxidation products on CyH oxidation over (a) Fe-MIL-100, (b) Cr-MIL-100 and (c) Cr-MIL-101.

c). Hence, we believe that adsorption of the oxidation products is responsible for the rather low conversions of alkenes observed in oxidation over the MOF catalysts. Meanwhile, we should mention that solvent-free conditions ensure high volume yields of products even at low substrate conversions. Indeed, volume yields of the oxygenated products in the oxidation of CyH and pinenes attained 138 and 246 g/L for Fe- and Cr-MILs, respectively.

3.4. Anthracene oxidation with TBHP

The development of a truly heterogeneous catalyst for the selective oxidation of AN to AQ is a challenging goal, and various types of solids have been tested in this reaction [31–34]. Since the framework of both MIL-100 and MIL-101 has a strong affinity to aromatic hydrocarbons [35], we attempted to use these MOFs as catalytic materials for AN oxidation with nonaqueous TBHP as oxidant.



Because of the poor solubility of AN in most organic solvents, benzene is typically employed to perform AN oxidation under liquid phase conditions [31–33]. We studied AN oxidation over Cr-MIL-101 in a few organic solvents and found that chlorobenzene is the best choice in terms of AN conversion, AQ selectivity and TOF (Fig. 6). Therefore, this solvent was used in all other experiments.

Selvaraj at al. [31] reported that temperature around 80 °C was optimal for AN oxidation with TBHP in the presence of Cr-SBA-15 as catalyst. For Cr-MIL-101, we found that the increase of the reaction temperature from 80 to 100 °C allowed the reaction rate to be increased *ca.* 4 times without loss of the AQ selectivity (Fig. 7). Furthermore, the solubility of AN in chlorobenzene at 100 °C increases and a higher concentration (0.1 M) of the aromatic substrate can be employed to produce AQ with excellent selectivity (Table 5). While using 10 mol% excess of TBHP relative to AN (the stoichiometry of AN oxidation with TBHP to produce AQ is 1:3) the conversion of AN attained 95% (Table 5, entry 2). By increasing the amount of the oxidant, quantitative conversion of AN to AQ can be accomplished (Table 5, entry 4). The efficiency of the oxidant utilization was, therefore, in the range of 67–86%. The use of aqueous TBHP reactant instead of its nonaqueous solution in decane did not lead to deterioration of the product yield but decreased the reaction rate (Table 5, entry 5). This is not surprising if we remember that water can adsorb on the MOF active centers and compete with reactants for the adsorption sites. It is precedented in the literature that catalyst activation in vacuum enables improvement of the catalytic performance [13,23,24]. Indeed, nonactivated Cr-MIL-101 showed some reduction of the reaction rate in the oxidation of AN.

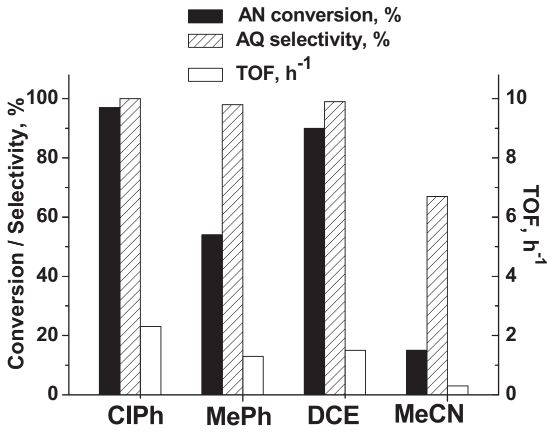


Fig. 6. Effect of solvent nature on AN oxidation with TBHP over Cr-MIL-101. Reaction conditions: AN 0.02 M, TBHP 0.09 M, Cr-MIL-101 2.5 mg, solvent 5 mL, 80 °C, 4–6 h.

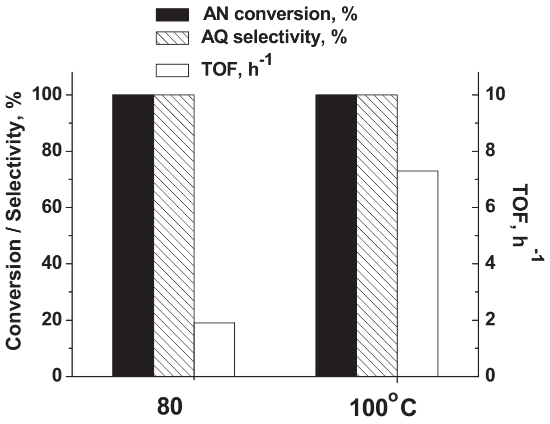


Fig. 7. Effect of temperature on AN oxidation with TBHP over Cr-MIL-101. Reaction conditions: AN 0.02 M, TBHP 0.09 M, Cr-MIL-101 1.5 mg, ClPh 2.5 mL.

Fig. 8 shows a comparison of different parameters in oxidation of AN over Cr- and Fe-containing MIL-101 and MIL-100. With Fe-MIL-101, the reaction was significantly slower than with the Cr analogue and 92% conversion of AN was reached after 6 h (compare with

Table 5
Oxidation of anthracene with TBHP over Cr-MIL-101.

Entry	Catalyst	[TBHP] (M)	Time (h)	Conversion AN (%)	Select. AQ (%)	TOF[a] (h^{-1})
1	no catalyst	0.45	3	5	100	–
2	Cr-MIL-101	0.33	2.5	95	100	12
3	Cr-MIL-101	0.38	1.5	98	100	22
4	Cr-MIL-101	0.45	1	100	100	24
5	Cr-MIL-101	0.45[b]	2.5	100	100	15

Reaction conditions: AN 0.1 M, MOF 3.2 mg, chlorobenzene 2 mL, 100 °C.
[a] TOF = (moles of AN consumed)/[(moles of Cr)·time]; determined from the initial rates.
[b] Aqueous TBHP (70 wt%) was used.

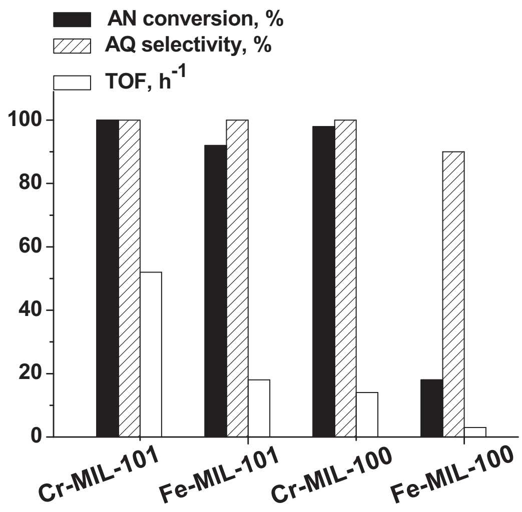


Fig. 8. AN oxidation with TBHP over Cr- and Fe-MIL-101 and MIL-100. Reaction conditions: AN 0.1 M, TBHP 0.45 M, MOF 1.6 mg, ClPh 5 mL, 100 °C, 1.5 (Cr-MIL-101) or 6 h (other MOFs).

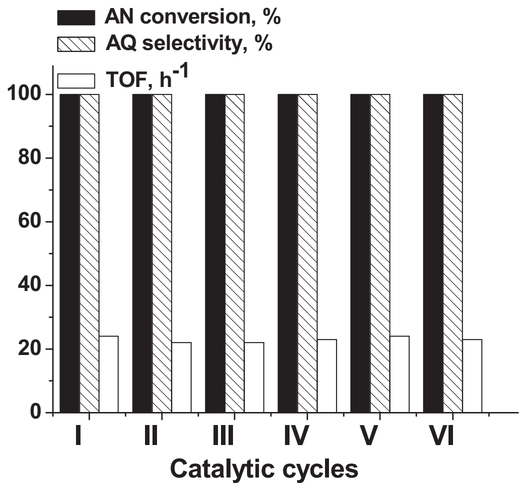


Fig. 9. Recycling of Cr-MIL-101 in oxidation of AN with TBHP. Reaction conditions as in Table 5 (entry 4).

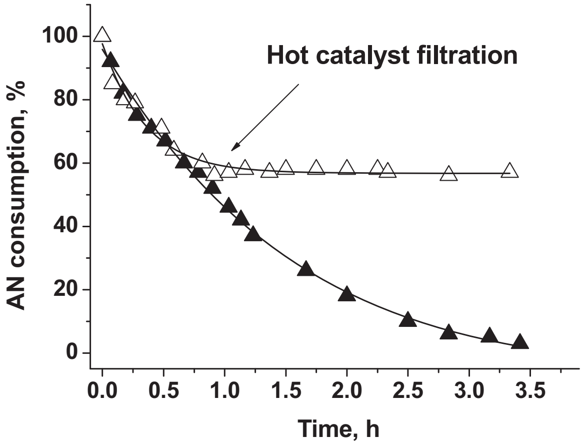


Fig. 10. Hot catalyst filtration test for AN oxidation with TBHP over Cr-MIL-101. Reaction conditions: AN 0.02 M, TBHP 0.09 M, Cr-MIL-101 1 mg, ClPh 2 mL, 100 °C.

100% conversion after 1.5 h for Cr-MIL-101). The selectivity toward AQ remained 100%. If we compare Cr-MIL-101 with Cr-MIL-100, we can see that the reaction rate expressed in TOFs decreases *ca.* 4 times for the latter, pointing out that diffusion limitation may take place for the bulky AN and AQ molecules within MIL-100 that possesses smaller cages and larger crystallites than MIL-101. Although both aromatic substrate and product molecules are flat, the size of AN molecule in two other dimensions is 9.2 × 5.0 Å while the size of AQ molecule is 9.3 × 5.4 Å. The size of the TBHP molecule is estimated as 4.4 × 3.7 × 4.0 Å. At the same time, the average diameter of cage entrances in MIL-100 is 9 and 6 Å for the large and small windows, respectively [14,15]. So, we may suppose that both AN and AQ molecules can diffuse only through the large windows. Given in mind that the cage entrances for MIL-101 are 12 and 16 Å, it is not surprising that this MOF is considerably more active than MIL-100 in the oxidation of AN. Among the MOFs studied, Fe-MIL-100 showed inferior catalytic properties (only 18% AN conversion after 6 h and 90% AQ selectivity), indicating the influence of both the MOF structure (determined by the nature of the organic linker) and the nature of transition metal (Fe versus Cr) on the oxidation process. The lower selectivity of Fe-MIL-100 relative to Fe-MIL-101 could be due to the lower substrate conversion (and, therefore, the presence of some intermediate products) over the former. Finally, we may conclude that Cr-MIL-101 revealed superior catalytic performance in terms of AN conversion, AQ yield and TOF in comparison with other catalysts. For example, mesostructured chromium-silicate Cr-SBA-15 catalyzed AN oxidation with TBHP to produce AQ with 100% selectivity at 90% AN conversion [31] while the attainable selectivity and conversion were 98% and 79%, respectively, with Cr-MCM-41 as catalyst [32]. Furthermore, the total reaction time was by order of magnitude greater with chromium-silicates than with Cr-MIL-101 (20 h versus 1.5 h), indicating much higher activity of the MOF catalyst.

Importantly, Cr-MIL-101 can be used repeatedly without loss of the catalytic activity and selectivity. Fig. 9 demonstrates the recycling behavior of this MOF in six consecutive runs. The catalyst was simply separated by filtration, washed, dried in air and used in the next run. No MOF reactivation was required between the catalytic runs, which makes the recycling a convenient and fast procedure. The hot catalyst filtration test (Fig. 10) proved heterogeneous nature of catalysis over Cr-MIL-101: after fast removal of the catalyst at *ca.* 45% conversion, the reaction in the filtrate stopped completely, indicating that no active chromium species had leached into solution during the oxidation process. Additionally, elemental analysis confirmed that no chromium species (≤0.1 ppm) were present in the filtrate. XRD patterns of Cr-MIL-101 before the catalytic reaction and after reuse are practically identical (Fig. 11),

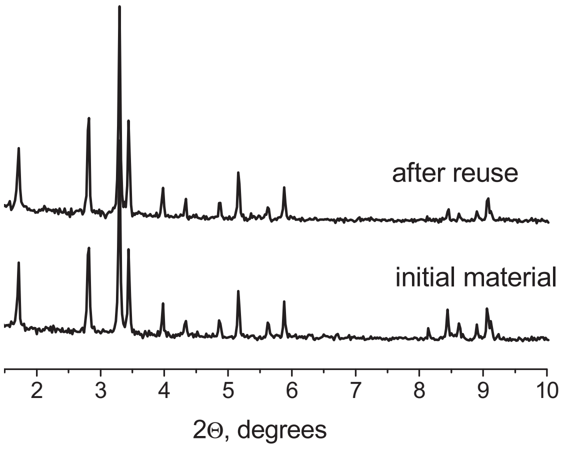


Fig. 11. XRD patterns for Cr-MIL-101: initial material and after reuse.

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which implies that no structural damage of the MOF occurred under the turnover conditions of AN oxidation with TBHP.

4. Conclusions

The iron- and chromium-containing MOFs of the MIL-100 and MIL-101 structure are efficient catalysts for both solvent-free alkene oxidation with molecular oxygen and AN oxidation to AQ with TBHP in chlorobenzene as solvent. Studies on cyclohexene oxidation revealed that the Cr-MILs are more stable than their iron analogs. While Cr-MIL-100 and Cr-MIL-101 were stable to metal leaching at 60 °C, both Fe-MIL-101 and Fe-MIL-100 could resist only 40 °C. According to XRD, Fe-MIL-100 preserved its structure after several reuses at 40 °C, which contrasts with Fe-MIL-101 that lost partially the structural integrity under the same conditions. Hence, the MOF stability increases in the sequence Fe-MIL-101 < Fe-MIL-100 < Cr-MIL-100, Cr-MIL-101. Whereas the MOF structure (MIL-101 versus MIL-100) just slightly affects the catalytic performance in the alkene oxidation, the nature of transition metal determines both the attainable substrate conversion and the reaction selectivity. In general, Fe-MILs favor the formation of unsaturated alcohols, while Cr-MILs afford the formation of unsaturated ketones. The high selectivity of the Cr-containing MOFs toward ketones is, most likely, due to the high activity of these materials in dehydration of corresponding hydroperoxides to produce unsaturated ketones. Adsorption of the oxidation products, including water, inhibits the oxidation process over the MOFs. The product (cyclohexenol and cyclohexenone) adsorption constants are higher for MIL-100 than for MIL-101 and do not depend on the nature of the metal.

In AN oxidation with TBHP, Cr- and Fe-MIL-101 are more active than their MIL-100 analogues, which indicates that diffusion of bulky AN molecules meets limitation within MIL-100 that has smaller cage entrances and larger crystallites than MIL-101. The nature of the metal also affects the catalytic performance. The catalytic activity decreases in the order Cr-MIL-101 > Fe-MIL-101 > Cr-MIL-100 > Fe-MIL-100. Cr-containing MIL-101 revealed superior catalytic performance in terms of AN conversion, AQ selectivity and TOF. No leaching of chromium into solution occurred and the MOF could be reused several times without loss of the catalytic properties.

Acknowledgment

The authors thank Dr. A. N. Shmakov and V. A. Utkin for some XRD and GC–MS measurements, respectively. The research was partially supported by the Russian Foundation for Basic Research (grant N 13-03-00413) and the Ministry of Education and Science of the Russian Federation. I.Y.S. acknowledges French Embassy in Moscow for the doctoral fellowship.

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