Journal of Catalysis 289 (2012) 259-265

Contents lists available at SciVerse ScienceDirect

Journal of Catalysis

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

# Aerobic oxidation of cycloalkenes catalyzed by iron metal organic framework containing N-hydroxyphthalimide

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#### ARTICLE INFO

Article history: Received 27 November 2011 Revised 19 February 2012 Accepted 23 February 2012 Available online 30 March 2012

Keywords: Aerobic oxidation Epoxidation of cycloalkenes Metal organic frameworks as solid Catalysts N-hydroxyphthalimide

# ABSTRACT

Iron metal organic framework [Fe(BTC)] loaded with N-hydroxyphthalimide (NHPI) promotes the aerobic oxidation of (cyclo)alkenes to give variable percentages of allylic oxidation products and the corresponding epoxide, dependidng on the nature of the substrate. In the case of cyclopentene and cyclohexene, aerobic oxidation catalyzed by NHPI/Fe(BTC) renders their corresponding unsaturated cyclic alcohol and ketone with 97% selectivity in 5 h at 6% and 12% conversion, respectively. Under the same experimental conditions, cyclooctene exhibited 95% selectivity toward the formation of cyclooctene oxide with 2% of cyclooctenol/one at 4 h. Cycloheptene as substrate exhibits an intermediate behavior, and the aerobic oxidation catalyzed by NHPI/Fe(BTC) leads to the formation of cycloheptenol/cycloheptenoe with 77% selectivity, accompanied by 23% of cycloheptene oxide at 4 h. Further experiments with non-symmetric olefins exhibited also a mixture of products including epoxides and allyic products. A mechanism to explain these experimental results has been proposed.

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JOURNAL OF CATALYSIS

# 1. Introduction

Oxygen is the ideal oxidizing agent from the environmental point of view since it is free, forms water as the only by-product, and contains the maximum oxidizing weight percentage [1]. While there has been in recent years a considerable progress on the aerobic oxidation of alcohols, particularly using noble metal nanoparticles as catalysts [2], there are still many oxygenation reactions in which a general catalyst has yet to be found. Although ethylene oxide is produced by the reaction of ethylene and oxygen using a silver catalyst [3], an analogous process for aerobic epoxidation of other (cyclo)alkenes has not been yet possible. Limited progress in this field has been achieved by using supported gold catalysts in combination with alkanes that can form in situ hydroperoxides that then will act as oxygen transfer intermediates in the formation of the epoxide [4]. Also recently, Iglesia and Haruta have reported the epoxidation of propene using supported gold catalysts but the conversions were less than 1% in order to keep high the selectivity toward the target epoxide [5,6]. The target for propene epoxidation will be to achieve conversions higher than 5% with very high selectivity toward epoxide. In general, selective epoxidation of alkenes using molecular oxygen instead of peracids or peroxides still remains a challenge in catalysis and green chemistry. Although epoxidation of alkenes having allylic positions is the main challenge, allylic oxidations [7] are also of industrial relevance in the fragrance industry and the synthesis of fine chemicals.

Metal organic frameworks (MOFs), also called as porous coordination polymers (PCPs) [8], are attracting much current interest as heterogeneous catalysts because they combine a large surface area and porosity with a high percentage of active sites [9–12]. While MOFs are micro-/mesoporous crystalline solids that have many similarities in their use as solid catalysts with zeolites and related periodic structured silicas and related materials, MOFs have the advantage of a much larger percentage of transition metal content that are in crystallographic well-defined positions with strictly regular surroundings. Thus, MOFs can be considered as solid catalysts that contain a single type of site, this being reflected in the possibility to achieve the largest possible turn over numbers. In addition, MOFs are very versatile in the structure of organic linker and nature of the transition metal that can be present in their composition.

In the present case, the MOF that has been used, Fe(BTC) (iron content 25%) (BTC: 1,3,5-benzenetricarboxylate) contains Fe(III) as metal and tripodal BTC as ligand. Although the crystal structure of a Fe(BTC) corresponding to MIL-100 has been determined by X-ray diffraction methods, the exact crystal structure of the commercial Fe(BTC) sample used in the present work provided by BASF is still unresolved. Commercial BASF Fe(BTC) exhibits XRD with broad diffraction peaks frequently found in PCPs rather than in MOFs, a high surface area (840 m<sup>2</sup> g<sup>-1</sup>) and average pore diameter (21.7 Å) which are the characteristic features of MOFs, but the crystal cell is not yet known.

We have shown that commercially available BASF Fe(BTC) could be conveniently used as heterogeneous catalysts in various reactions [13–17]. In addition, it has been demonstrated that MIL-100(Fe) exhibited high selectivity and conversion in p-xylene



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acylation with benzoyl chloride [18]. Oxidation of cyclohexene to cyclohexene oxide, 2-cyclohexenone, and 2-cyclohexenol has been reported using Co [19] and V [20] containing MOFs as catalysts in the presence of *tert*-butylhydroperoxide (TBHP) as oxidant. In contrast, allylic oxidation of cyclohexene with molecular oxygen has also been reported using copper-based MOFs [21]. Recently, a new heterogeneous catalyst for epoxidation of cyclohexene, cyclooctene, and styrene was reported using IRMOF-3 post-functionalized with a manganese(II) acetylacetonate complex using molecular oxygen under mild reaction conditions [22].

Although MOFs have been used as heterogeneous catalysts for many organic reactions, and in particular epoxidation of olefins using TBHP as oxidant, developing a protocol where molecular oxygen is used as oxidant for olefin epoxidation is a challenging and attractive methodology. In the present work, we report that an iron containing MOF including N-hydroxyphthalimide (NHPI 20 wt.% loading) as cocatalyst is able to affect the aerobic allylic oxidation of cyclopentene and cyclohexene and, more remarkably, the epoxidation of cyclooctene at conversions higher than 10% with almost complete selectivity toward the corresponding epoxide. Cycloheptene exhibits an intermediate behavior giving mixtures of allylic oxidation and epoxidation. Scheme 1 summarizes the catalytic activity observed for the aerobic oxidation of cycloalkenes promoted by NHPI containing Fe(BTC). Besides activity and selectivity, one additional advantage of our catalyst is that it contains a base metal rather than precious metals.

# 2. Experimental methods

#### 2.1. Materials

Basolite F300 [Fe(BTC)] and other MOFs used in the present study were purchased from Sigma Aldrich and used as received. NHPI, various substrates and solvents used in the present study were purchased from Sigma Aldrich.

### 2.2. Characterization techniques

The percentage conversion, purity, and relative yields of the final products were determined using Hewlett Packard 5890 series II gas chromatograph with FID detector and high purity helium as carrier gas. The products were identified by comparing their retention times in GC with authentic samples and with GC-MS Hewlett Packard 6890 series. Powder XRD diffraction patterns were recorded in the refraction mode using a Philips X'Pert diffractometer using the Cu K $\alpha$  radiation ( $\lambda$  = 1.54178 Å) as the incident beam, PW3050/60  $(2\theta)$  as Goniometer, PW 1774 spinner as sample stage, PW 3011 as detector, incident mask fixed with 10 mm. PW3123/10 for Cu was used as a monochromator. PW3373/00 Cu LFF was used as Xray tube with power scanning of 45 kV and 40 mA current. The sample powder was loaded into a holder and levelled with a glass slide before mounting it on the sample chamber. The specimens were scanned between 2° and 70° with the scan rate of 0.02 s<sup>-1</sup>. ESR spectra were recorded using a Bruker EMX, with the typical settings: frequency 9.80 GHz, sweep width 30.6 G, time constant 80 ms, modulation frequency 100 kHz, modulation width 0.2G, microwave power 200 mW. Benzonitrile (2 mL) containing 75 mg of NHPI/ Fe(BTC) was stirred under oxygen atmosphere at 120 °C for 2 h. The air in the ESR tube was replaced by nitrogen gas by means of



external purging method. Blank experiment was performed under identical conditions but under nitrogen atmosphere. Nitrogen adsorption isotherms were measured at 77 K on a Micromeritics ASAP 2000 volumetric adsorption analyser. Before the measurements, the samples were out gassed for 4 h at 473 K. The specific surface area was calculated by applying the BET model to the nitrogen adsorption data. Chemical composition was determined by atomic absorption in a Varian SpectrAA-10 Plus and elemental analysis in a Fisons EA1108CHN-S. IR spectra of Fe(BTC) and NHPI/ Fe(BTC) were recorded within KBr pellets in a Nicolet 710 FT spectrophotometer. FT-Raman spectra of Fe(BTC) and NHPI/Fe(BTC) were recorded with a Bio-Rad FT-Raman II spectrophotometer. Nd:YAG laser was used for excitation along with a germanium detector cooled at liquid nitrogen temperature using high-quality quartz tubes as cells.

#### 2.3. Experimental procedure

In a typical reaction, 0.5 mL of cycloalkene was placed into the flask (10 mL capacity) together with the appropriate amount of catalyst (75 mg). These mixtures were stirred at 100 °C under molecular oxygen atmosphere for the required time. For cyclopentene and cyclohexene, the reactions were carried out in closed reinforced glass vessels that can stand pressure. After the reaction time, the catalyst was filtered and extracted with acetonitrile, and the reaction mixture analyzed by GC. Nitrobenzene was always used as an external standard for the determination of conversion level. The products were identified by GC and GC-MS. A preparative scale experiment using 5 mL of cyclooctene was carried out under the same conditions. When the conversion was 5%, the reaction mixture was filtered to remove the catalysts, concentrated under vacuum, and submitted to flash chromatography to isolate cyclooctene oxide in 4.5% vield. The reusability of the catalyst was tested for the oxidation of cyclooctene. After the reaction time, the reaction mixture was diluted with acetonitrile, filtered, dried at 70 °C for 2 h, and reused directly without further treatment for a subsequent run with fresh cyclooctene. The mass balance in all the runs was higher than 90%. The absence of active species leached from the solid to the solution was assured by the Sheldon's hot filtration test. In this case, the reaction was initiated under the typical oxidation conditions indicated above and the solid catalyst filtered at the reaction temperature at a cyclooctene conversion of 4%. Then, the clear solution was allowed to react further at 100 °C in the absence of any solid. No further cyclooctene conversion was observed after filtration of the catalyst.

A series of three control experiments was performed using 60 mg of Fe(BTC) with 12 mg of NHPI or 145 mg of iron nitrate nonahydrate with 30 mg of NHPI or 115 mg of Fe(acac)<sub>3</sub> with 23 mg of NHPI for the unsupported NHPI-catalyzed aerobic oxidation of cyclooctene at 100 °C adopting the above-mentioned reaction procedure.

### 2.4. Experimental procedure for silylation

The reaction was performed as indicated in the manuscript under the same reaction conditions. After 4 h, unreacted cyclooctene was removed, and 1 mL of N,O-(trimethylsilyl)trifluoroacetamide containing trimethylchlorosilane was added and stirred at 80 °C for 8 h. This reaction mixture was analyzed by GC–MS. A control using commercial octanedioic acid showed that over 95% can be silylated with this procedure.

# 2.5. Preparation of NHPI/Fe(BTC)

NHPI (200 mg, 1.22 mmol) was dissolved in 7 mL of dichloromethane and 3 mL of methanol. To this solution, 1 g of [Fe(BTC)] (3.8 mmol) was added and the resulting suspension was heated at 40 °C for 4 h. After the required time, the mixture was cooled and the solvent was removed by rotary evaporation. The resulting NHPI/Fe(BTC) was dried at 80 °C for 2 h and used. The NHPI/Fe wt. and molar ratios were 1/1.06 and 1/3.1, respectively. As an average, the number of NHPI molecules per surface area unit is  $1.4 \,\mu\text{mol}\,\text{m}^{-2}$ .

# 3. Results and discussion

# 3.1. Characterization of Fe(BTC)

Surface area, pore volume, and pore size distribution of the solid samples (200 mg) were calculated by the BET method by carrying out liquid nitrogen adsorption experiment at 77 K in a Micromeritics Flowsorb apparatus. Prior to this experiment, the solid was treated at 200 °C for 2 h to desorb the water molecules. This treatment is common for most of the gas adsorption studies in MOFs [23] due to the thermal unstability of the organic linker, and the fact that the hydration of the adsorbed water can be performed at mild temperatures.

BET surface area (m <sup>2</sup> /g)	840
Total pore volume	0.457 cm <sup>3</sup> /g
Average pore diameter	21.7 Å

Chemical composition was determined by atomic absorption in a Varian SpectrAA-10 Plus and elemental analysis in a Fisons EA1108CHN-S. The iron content in Fe(BTC) was measured to be 25%.

The EPR spectra shown in Fig. 1 demonstrate the existence of Fe(III). The values for parameter G corresponding to the main signal on the spectra are in the range of 2.01. In order to quantify the signal from Fe(BTC) spectra, we have used  $Cu(SO_4)_2$ ·12H<sub>2</sub>O as reference material. The spectra of known weights of both solids were recorded under the same conditions and the area of the signals determined. These values have led to estimate the percentage of Fe(III) in Fe(BTC) as 28%.

# 3.2. Characterization of NHPI/Fe(BTC)

N-hydroxyphthalimide was incorporated onto Fe(BTC) by adsorption from a dichloromethane solution as described in the experimental section, and the resulting NHPI/Fe(BTC) material was characterized by IR and Raman spectra. As it can be seen in Figs. 2 and 3, the presence of NHPI at the small loading used in this work and the high intensity of the IR and Raman bands due to the



Fig. 1. EPR spectrum recorded for Fe(BTC) in solid state at room temperature.

tricarboxylate linker in Fe(BTC) precluded to observe any major spectroscopic changes after NHPI inclusion.

Considering the molecular size of NHPI (around 6.5 Å of kinetic diameter) and pore dimension presumed for Fe(BTC), it is reasonable to assume that the NHPI will be accommodated inside Fe(BTC) intracrystalline space. One evidence in supporting this internal location of NHPI inside the MOF is the significant reduction of BET surface area of Fe(BTC) after incorporation of NHPI that goes from 840 to 24  $m^2/g$  (see experimental section). The paramagnetic property of Fe(BTC) precludes the study of NHPI/Fe(BTC) by both in solid and in liquid state <sup>1</sup>H NMR spectroscopy. The complete lack of solubility of NHPI in cycloalkenes makes unlikely the migration of NHPI outside the pores under the reaction conditions. To provide further evidence that no NHPI migrates to the solution due to its remarkable insolubility, we performed a control in which NHPI/ Fe(BTC) was extracted with cyclooctene at 100 °C for 5 h and then the solid filtered while hot. This presumed extracted NHPI/Fe(BTC) was used as catalyst for cyclooctene oxidation observing the same performance as the one that was not submitted to solid liquid extraction.

# 3.3. Aerobic oxidation of cyclooctene

The main objective of the present study is to oxidize cyclic, aliphatic olefins to their epoxides with high selectivity in the presence of oxygen. To achieve this target, we have made use of NHPI/Fe(BTC) (1:5) as catalyst whose catalytic activity in styrene oxidation has already been reported elsewhere [24]. The reactivity of styrene versus aerobic oxidation is different to that of aliphatic (cyclo)alkenes due to the reactivity of the benzylic positions, this explaining the formation of benzaldehyde as the major product under various reaction conditions.

NHPI in combination with Co salts [25] has been extensively used as homogeneous catalyst for the functionalization of hydrocarbons [26,27] in the presence of acetic acid as solvent. In these systems, the role of Co salts is to generate the first N-oxyl radical from NHPI by electron transfer. This radical generated from NHPI initiates a radical chain mechanism with alkene and oxygen leading to the products. It would be anticipated that Fe(III) present in Fe(BTC) can play the role of Co salts as promoter of NHPI, leading to the formation of NHPI-derived radical that will initiate hydrocarbon oxidations. Here, we wish to report the results obtained with NHPI/Fe(BTC) as catalyst for the aerobic oxidation of olefins in the absence of any solvent, particularly acetic acid that is not compatible with Fe(BTC).

Initially, epoxidation of cyclooctene resulted in no conversion with oxygen in the absence or presence of Fe(BTC) as catalyst. However, NHPI adsorbed onto Fe(BTC) [NHPI/Fe(BTC)] resulted in an active heterogeneous catalyst in the presence of oxygen at



Fig. 2. FTIR spectra of (a) Fe(BTC) and (b) NHPI/Fe(BTC) recorded at room temperature.



Fig. 3. Raman spectra of (a) Fe(BTC) and NHPI/Fe(BTC).

100 °C, and 3.6% of cyclooctene was converted to cyclooctene oxide with 99% selectivity in 2 h in the absence of any cosolvent. Table 1 lists the results obtained for the epoxidation of cyclooctene by oxygen using NHPI/Fe(BTC) as solid catalysts.

Increasing the time, gradually increases cyclooctene conversion to reach in 6 h 13% conversion with 90% selectivity toward the formation of cyclooctene oxide (Fig. 1). The formation of a very low amount of hydroperoxides and peroxides in the reaction mixture was confirmed by adding triphenylphosphine to the reaction mixture and observing the formation of very little amount of triphenvlphosphine oxide as well as a slight increase in the yield of ol/one. This test indicated that the combined selectivity of hydroperoxides and peroxides is 0.27% at 9% conversion of cyclooctene. Additionally, the formation of trace amounts (<0.2%) of octanedioic acid derived from the oxidative cleavage of C=C double bond was determined by silvlation of the residue after concentration of the reaction mixture with N,O-(trimethylsilyl)trifluoroacetamide containing trimethylchlorosilane and observing only detectable amounts of corresponding octanedioc acid disilyl derivative. Control experiments performing the same derivatisation protocol with authentic samples of octanedioic acid showed that complete silylation occurs under our experimental conditions. As expected based

Table 1

Aerobic oxidation of cyclooctene using NHPI/Fe(BTC) as heterogeneous catalyst.<sup>a</sup>

Run	Catalyst	Time (h)	Con. (%)	Selectivity (%)	
				Epoxide	Enol + enone
1	-	2	-	-	-
2	Fe(BTC)	2	-	-	-
3	Silica/NHPI	5	-	-	-
4	NHPI/Fe(BTC)	1	0.8	98 (1)	1
5	NHPI/Fe(BTC)	2	3.6	97 (2)	1
6	NHPI/Fe(BTC)	3	6.6	97 (2)	1
7	NHPI/Fe(BTC)	4	9.2 <sup>b</sup>	95 (3)	2
8	NHPI/Fe(BTC)	5	13	87 (4)	9
9	NHPI/Fe(BTC)	4	8.6 <sup>c</sup>	95	2
10	NHPI/Fe(BTC)	4	9.0 <sup>d</sup>	93	3
11	NHPI/Fe(BTC)	5	29 <sup>e</sup>	88	12
12	NHPI/Fe(BTC)	7	33 <sup>e</sup>	84	16
13	NHPI/Fe(BTC)	5	48 <sup>f</sup>	85	9
14	NHPI/Fe(BTC) <sup>g</sup>	5	<0.4	-	-
15	NHPI+Fe(BTC)	4	18	72 (6)	22
16	NHPI+Fe(NO3)3.9H2O	4	27	52 (8)	9
17	NHPI+Fe(acac) <sub>3</sub>	4	4	64 (5)	31

<sup>a</sup> Reaction conditions: cyclooctene (0.5 mL), NHPI/Fe(BTC) (75 mg), 100 °C, oxygen purged through balloon. The values in brackets correspond to peroxides determined by reaction with PPh<sub>3</sub>.

<sup>b</sup> TON is calculated by mmol of cyclooctene converted to epoxide/mmol of NHPI. TON is 4 and 1 based on NHPI and Fe, respectively, at 4 h.

<sup>c</sup> First reuse.

d Second reuse

<sup>e</sup> Reaction temperature 110 °C.

<sup>f</sup> Reaction temperature 120 °C.

g With 50 mg of TEMPO.

on the general inverse relationship between alkene conversion and epoxide selectivity, the selectivity of epoxide decreased gradually as the conversion increases. The occurrence of cyclooctene allylic oxidation resulting in the formation 2-cyclooctenol and 2-cyclooctenone is observed at higher conversions (Table 1). Increasing the temperature to 110 and 120 °C increases cyclooctene conversion to 33% and 48% with a selectivity toward epoxide still over 80%.

In order to confirm the analytical data obtained by GC analysis, we performed the aerobic oxidation of cyclooctene (5 mL) and proceeded to the isolation of cyclooctene oxide. When the cyclooctene conversion was 5%, this large-scale reaction allowed us to isolate cyclooctene oxide with high purity as confirmed by <sup>1</sup>H NMR with 4.5% yield. These results are outstanding and without equivalent for any aerobic oxidation of neat cycloalkenes in the liquid phase. For instance, van Sickle and coworkers reported that treatment of cyclooctene with oxygen forms the corresponding cyclooctene oxide with 39.9% selectivity [28]. Also, recent reports from Hermans' group about autooxidation of  $\alpha$ -pinene have led to complex mixtures in which the epoxide is accompanied by many other products [29,30]. To evaluate the performance of NHPI/Fe(BTC) as catalyst for aerobic oxidation of cyclooctene, turnover numbers (TONs) for epoxide formation both with respect to NHPI and Fe were calculated. The data (see footnote "b" in Table 1) indicated that about four molecules of epoxides are formed per NHPI molecule. To put this TON into context in a related precedent using a Co(II)-containing MOF as catalyst and *t*-butylhydropeoxide (TBHP) as oxidant reagent, the estimated TON for epoxide formation was around 5 [19] that is similar as the one achieved here using oxygen as oxidant. Similarly, V-MIL-47 exhibits for cyclohexene oxidation using TBHP as reagent a turnover frequency of 43 h<sup>-1</sup> [20], while NHPI/Fe(BTC) inspite of the induction period (see Fig. 4) and the use of oxygen exhibits a turnover frequency of 5  $h^{-1}$ .

Based on the presented evidence (reduction of BET surface area upon incorporation of NHPI and the lack of solubility of NHPI in cycloalkenes), we believe that the loaded NHPI on Fe(BTC) should be located in and around of Fe(BTC) crystals, and it will not undergo extraction or relocation under the reaction conditions.

In order to determine the prevailing advantages of NHPI/Fe(BTC) in cyclooctene epoxidation, a control experiment was performed using a physical mixture of Fe(BTC) and NHPI in 5:1 ratio as solid catalyst, whereby a 18% conversion with 72% of epoxide selectivity accompanied by 22% enol/enone was measured at 4 h. The observed results clearly show that NHPI/Fe(BTC) exhibited higher selectivity of epoxide compared with the NHPI and Fe(BTC) mechanical mixture. This better performance of NHPI/Fe(BTC) over its mixture could be attributed to the following two reasons: (i) confinement of the radical intermediates generated during the course of the reaction inside Fe(BTC) pores leading to preferential in-cage recombination resulting in higher epoxide selectivity as compared to the situation



**Fig. 4.** Time conversion plot and leaching test as evidence for heterogeneity in the catalysis of epoxidation of cyclooctene with oxygen (a) in the presence of NHPI/ Fe(BTC) or (b) after filtration of the solid at about 4% conversion.

3.5. Reusability

where no confinement occurs, and (ii) control of the reactivity and transition states formed inside the pores of NHPI/Fe(BTC) due to steric restrictions inside the cage. On the other hand, it has been reported that Fe/MgO in combination with NHPI can also catalyze C—H oxidation in benzylic compounds [31].

To provide a qualitative assessment of the catalytic performance of NHPI/Fe(BTC) with respect to analogous, unsupported catalysts, we have also performed two additional experiments with iron(III) salts in combination with NHPI (5:1) having the same total iron amount as that of NHPI/Fe(BTC) catalyst. Fig. 5 summarizes the results obtained using unsupported NHPI compared with the performance of NHPI loaded on Fe(BTC). The reaction with iron nitrate nonahydrate with NHPI resulted in 27% conversion with 52% of epoxide and 9% of enol/enone in 4 h. In addition, some unidentified products were also formed which reduce significantly the selectivity of desired epoxide. On the other hand, iron acetylacetonate with NHPI exhibited 4% conversion with 64% epoxide and 31% enol/enone selectivities in 4 h. These control experiments clearly demonstrate the prevailing advantages of NHPI/Fe(BTC) in achieving higher selectivity of epoxide, reducing the formation of other side by-products by performing the reaction in the confined environment. In other words, selectivity of the aerobic oxidation will be modified by the fact that the process taken place is mostly in a restricted reaction cavity where the concentration of substrate, oxygen, and products is different from that in the liquid phase. This diffusion limitation typically increases selectivity by minimizing secondary reactions of the primary products and also by favouring preferential reaction pathways. Similar rationalization as the one provided here based on the confinement effect in NHPI/Fe(BTC) has been already proposed to explain the synergistic effects observed for the encapsulation of metal phthalocyanine complexes on MIL-101 in the aerobic oxidation of tetralin [32].

# 3.4. Hot filtration test

To verify whether the catalysis of NHPI/Fe(BTC) is truly heterogeneous or the catalytic activity is due, at least in part, to some leached iron species present in the liquid phase, the reaction was carried out under optimized conditions (footnote "a" in Table 1 for reaction conditions) and the NHPI/Fe(BTC) solid catalyst was filtered out of the reaction mixture at 4% formation of cyclooctene oxide under the reaction temperature using nylon filter. After removal of the NHPI/Fe(BTC) catalyst, the solution in the absence of solid was again stirred. After 4 h, no further product formation was observed in the absence of solid (see Fig. 4). Hence, it can be concluded that the catalysis occurs due to the presence of the solid phase and the process is truly heterogeneous.

without further treatment. Only minor changes in the conversion and no noticeable variations in the epoxide selectivity were observed for cyclooctene oxidation upon two consecutive reuses. After three consecutive uses, the stability of MOF crystal structure was confirmed by comparison of the XRD patterns of the fresh and two times reused NHPI/Fe(BTC) (Fig. 6). In addition, Fig. 6 shows that inclusion of NHPI on Fe(BTC) does not change the diffraction pattern of the PCPs. The results of these reusability tests are in agreement with the previous experiment in which extraction with cvclooctene of NHPI was not observed.

The reusability of NHPI/Fe(BTC) for the epoxidation of cyclooc-

tene using molecular oxygen was investigated under identical con-

ditions as described in Table 1. After the required time, the reaction

mixture was stirred with acetonitrile and the catalyst filtered and dried. The recovered solid was used for another consecutive run

In order to have some insights onto the reaction mechanism, a control experiment for aerobic oxidation of cyclooctene under the condition described in Table 1 was performed with TEMPO as radical guencher. Interestingly, TEMPO completely guenches the reaction (see Table 1, entry 14). This indicates that the reaction proceeds through carbon-centered radicals. The induction period observed in the time-conversion plot shown in Fig. 4 can be interpreted as the time needed for the generation of these C-centered radicals.

# 3.6. Aerobic oxidation cycloalkenes

In view of the excellent results achieved for the selective epoxidation of cyclooctene in the absence of solvent, the scope of the NHPI/Fe(BTC) aerobic oxidation was studied for other cycloalkenes (Table 2). Thus, when NHPI/Fe(BTC) was used as catalyst for aerobic oxidation of cyclopentene and cyclohexene under identical conditions as those used for cyclooctene, three main products namely the epoxide, 2-cycloalkanol, and 2-cycloalkanone were identified at short reaction times. At 5 h, the selectivity toward 2-cycloalkanone increased significantly, while the percentage of epoxide present in the reaction mixture was very low.

The aerobic oxidation was also inhibited by the presence of TEMPO indicating that the reaction mechanism for the three products is a C-centered radical autooxidation. Interestingly, in the case of cycloheptene, the epoxide selectivity is maintained fairly constant over the course of the reaction to a value about 20%. In contrast, we observe that for cyclopentene and cyclohexene, the selectivity of epoxide decreases significantly with reaction time (see Table 2, entries 1, 2 and 3, 4). For cycloheptene, 23% of epoxide was observed in 13% conversion at 4 h, while the epoxide selectivity is 3% for cyclopentene and cyclohexene at 5 h. This



Fig. 5. Comparison of conversion and epoxide selectivity achieved for the aerobic oxidation of cyclooctene with different catalysts: (1) NHPI/Fe(BTC); (2) NHPI+-Fe(BTC); (3) Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O+NHPI; and (4) Fe(acac)<sub>3</sub>+NHPI.



Fig. 6. Powder XRD pattern of (a) Fe(BTC), (b) NHPI/Fe(BTC), and (c) two times reused NHPI/Fe(BTC) (see footnote "a" in Table 1 for reaction conditions). The asterisk indicates the peak due to the sample cell holder.

Table 2

	Aerobic oxidation of o	cvcloalkenes	using NHPI/I	Fe(BTC) a	s heterogeneous	catalysts <sup>a</sup> .
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$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Run	Cycloalkene	Time (h)	Con. (%) <sup>b</sup>	Selectivity (%) <sup>b</sup>		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$					Epoxide	Enol	Enone
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1 <sup>c</sup>		1	1.1	9	27	64
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2 <sup>c</sup>	~	5	6	3	5	92
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3 <sup>c</sup>		2	9	20	33	47
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	4 <sup>c</sup>	~	5	12	3	38	59
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	5 <sup>d</sup>		5	1.5	-	40	60
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	6		1	1.5	20	30	50
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	7	5	2	6	21	32	47
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	8		3	10	22	28	50
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	9		4	13	23	27	50
11 5 3.3 <sup>f</sup> 17 39 44	10		3	2 <sup>e</sup>	-	35	65
	11		5	3.3 <sup>f</sup>	17	39	44

<sup>a</sup> Reaction conditions: cycloalkene (0.5 mL), NHPI/Fe(BTC) (75 mg), 100 °C, oxygen purged with balloon.

- <sup>b</sup> Determined by GC. TON values calculated based on NHPI for cyclopentene (5 h), cyclohexene (5 h) and cycloheptene (4 h) are 13, 25, 24, respectively.
- <sup>c</sup> Reaction was carried out with 5 bar of oxygen in a sealed reactor.
- <sup>d</sup> Reaction was carried out with 5 bar of oxygen and 50 mg of TEMPO in a sealed reactor.
- e With 50 mg of TEMPO.
- <sup>f</sup> With 10 mg of  $\beta$ -carotene.

decrease in selectivity could indicate that in the case of cyclopentene and cyclohexene, the corresponding epoxides are not stable under the reaction conditions decomposing during the course of the reaction.

With respect to the reaction mechanism, we observe that the aerobic oxidation of cycloheptene in the presence of radical quenchers, namely TEMPO and β-carotene, also retards the percentage conversion. Comparison of the results shown in Tables 1 and 2 establishes two different reactivity patterns for the aerobic oxidation promoted by NHPI/Fe(BTC), that is, either epoxidation or allylic oxidation. The later predominates for cyclopentene and cyclohexene, while cycloheptene presents a transition toward the high epoxide selectivity found for cyclooctene at low or moderate conversions. In fact, in the case of cyclooctene, formation of cyclooctene oxide dominates with very high selectivity even up to conversions close to 50%. Previous reports in the literature have found that the order of reactivity of cyclic olefins increases in the order, cyclohexene < cycloheptene < cyclooctene [33,34]. The conversion and selectivity toward epoxides are mainly dependent on cycloalkene conformation, the bond angle strain, torsional strain, ring size, and electronic nature of cyclic olefin which as it has been observed in earlier precedents [33,34]. We propose that this

Tabl	e 3
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Aerobic oxidation of various alkenes catalyzed by NHPI/Fe(BTC)<sup>a</sup>.



<sup>a</sup> All the reactions were performed in oxygen atmosphere.

<sup>b</sup> Percentage selectivity was determined by GC and products were identified by GC-MS.

<sup>c</sup> Various isomers of ol/one products at different allylic positions.

<sup>d</sup> Epoxide selectivity corresponds to cis and trans.



**Scheme 2.** Proposed mechanism for the aerobic oxidation of C=C double bonds catalyzed by NHPI/Fe(BTC). This mechanism is favored for highly reactive C=C double bonds.



**Fig. 7.** ESR spectrum of phthalimide N-oxyl radical generated *in situ* by exposing a NHPI/Fe(BTC) suspension in benzonitrile to oxygen at 120 °C.

difference in reactivity of the C=C double bond as a function of the ring size previously observed is also responsible for the higher tendency of cyclooctene to undergo epoxidation rather than allylic oxidation, while the less reactive smaller cycloalkenes containing less reactive C=C double bond prefer allylic oxidation.

#### 3.7. Scope of NHPI/Fe(BTC)

To further extend the scope of NHPI/Fe(BTC), 1-methylcyclohexene (0.5 mL) was also used as substrate. 16% selectivity to epoxide at 6% conversion was observed for the reaction carried out at 80 °C with 25 mg of catalyst. Increasing the catalyst amount to 75 mg at 100 °C resulted in 22% conversion with 13% selectivity to epoxide. In addition to the epoxide, we also observed the formation of different ol/one isomers of 1-methylcyclohexene at various allylic positions. Similarly, (S)- $\alpha$ -pinene (0.5 mL) undergoes oxidation in the presence of NHPI/Fe(BTC) giving the corresponding epoxide with a maximum selectivity of 31% at 5% conversion. In this case, we observed the formation of products derived from epoxide rearrangement (see Table 3). This data show the general catalytic activity of NHPI/Fe(BTC) for aerobic oxidation and the selectivity toward the epoxide depending on the substrate and the conversion. Finally, (S)-limonene (0.5 mL) resulted in 15% conversion with 33% selectivity of *cis*- and *trans*-epoxide with 75 mg of catalyst at 100 °C in 2 h.

Besides oxidation of cyclic alkenes, we were also interested to oxidation of aliphatic olefins. It was found that 1-octene undergoes in the presence of NHPI/Fe(BTC) under the optimal conditions indicated in footnote of Table 1 1% conversion, mostly in allylic positions.

# 3.8. Mechanism

Concerning the reaction mechanism and in view of the product distribution and the precedents in the use of NHPI as organocatalyst for aerobic oxidations [35], it is reasonable to consider that all the products arise from autooxidation. The generation of the first carbon-centered radical will arise from phthalimide N-oxyl radical derived from NHPI. Evidence for this has been obtained by EPR. Allylic oxidation will arise from the interception of allylic radicals by oxygen and will predominate for 5 and 6 membered cycloalkenes. Concerning the formation of cyclooctene oxide, this compound will result of the higher reactivity of C=C bond for this large cycloalkene. In this case, the initial 2-cyclooctene peroxyl radical would add to the C=C double bond of another cyclooctene leading eventually to the epoxide as the product by elimination of 2-cyclooctene oxyl radical (Scheme 2). This mechanism is in agreement with those previously reported in the literature [28–30].

C-centered radicals will be generated from NHPI after formation of the corresponding N-oxyl radical. To confirm the formation of phthalimide N-oxyl radicals promoted by NHPI/Fe(BTC) in the presence of oxygen, electron spin resonance (ESR) spectra were recorded [17]. A control test did not detect the presence of any radical in powder NHPI/Fe(BTC). When a benzonitrile solution of NHPI/Fe(BTC) was exposed to dioxygen at 120 °C for 2 h, an ESR spectrum attributable to phthalimide N-oxyl radicals (Fig. 7) was recorded as a triplet signal. The *g*-value and hfs constant observed for NHPI/Fe(BTC) were coincident with those reported for phthalimide N-oxyl in solution (g = 2.0073,  $a_{\rm N}$  = 0.423 mT) [36].

#### 4. Conclusion

We have shown that Fe(BTC) containing NHPI could be used as heterogeneous catalyst for the aerobic oxidation of cycloalkenes. Two different types of products, namely, epoxidation and allylic oxidation have been observed in the absence of cosolvents at moderate conversions depending on the ring size. Very high selectivity for the aerobic epoxidation was achieved with cyclooctene, while decreasing the ring size favors allylic oxidation. In general, the present study highlights the use of commercially available Fe(BTC) as heterogeneous catalysts in aerobic oxidation of cycloalkenes and no additional solvent was used.

# Acknowledgments

Financial support by the Spanish DGI (CTQ-2010-18671 and CTQ2007-67805) and European Commission Integrated Project (MACADEMIA) is gratefully acknowledged.

# References

- [1] G. ten Brink, I.W.C.E. Arends, R.A. Sheldon, Science 287 (2000) 1636-1639.
- [2] A. Corma, H. Garcia, Chem. Soc. Rev. 37 (2008) 2096-2126
- [3] M. Olus Özbek, I. Önal, R.A.V. Santen, ChemCatChem 3 (2011) 150-153.
- [4] C. Aprile, A. Corma, M.E. Domine, H. Garcia, C. Mitchell, J. Catal. 264 (2009) 44.
- [5] M. Ojeda, E. Iglesia, Chem. Commun. (2009) 352-354.
- [6] J. Huang, T. Akita, J. Faye, T. Fujitani, T. Takei, M. Haruta, Angew. Chem. Int. Ed. 48 (2009) 7862–7866.
- [7] N.V. Maksimchuk, K.A. Kovalenko, V.P. Fedin, O.A. Kholdeeva, Adv. Synth. Catal. 352 (2010) 2943-2948.
- [8] S. Kitagawa, R. Kitaura, S.-I. Noro, Angew. Chem. Int. Ed. 43 (2004) 2334-2375.
- [9] A. Corma, H. Garcia, F.X. Llabres i Xamena, Chem. Rev. 110 (2010) 4606.
- [10] D. Farrusseng, S. Aguado, C. Pinel, Angew. Chem. Int. Ed. 48 (2009) 7502.
- [11] J.Y. Lee, O.K. Farha, J. Roberts, K.A. Scheidt, S.T. Nguyen, J.T. Hupp, Chem. Soc. Rev. 38 (2009) 1450.
- [12] G. Ferey, Chem. Soc. Rev. 37 (2009) 191.
- [13] A. Dhakshinamoorthy, M. Alvaro, H. Garcia, J. Catal. 267 (2009) 1.
- [14] A. Dhakshinamoorthy, M. Alvaro, H. Garcia, Adv. Synth. Catal. 352 (2010) 711– 717.
- [15] A. Dhakshinamoorthy, M. Alvaro, H. Garcia, Chem. Eur. J. 16 (2010) 8530– 8536.
- [16] A. Dhakshinamoorthy, M. Alvaro, H. Garcia, Chem. Commun. 46 (2010) 6476– 6478.
- [17] A. Dhakshinamoorthy, M. Alvaro, H. Garcia, ChemCatChem 2 (2010) 1438.
  [18] L. Kurfirtova, Y.-K. Seo, Y.K. Hwang, J.-S. Chang, J. Cejka, Catal. Today 179 (2012) 85–90.
- [19] M. Tonigold, Y. Lu, B. Bredenkotter, B. Rieger, S. Bahnmuller, J. Hitzbleck, G. Langstein, D. Volkmer, Angew. Chem. Int. Ed. 48 (2009) 7546.
- [20] K. Leus, I. Muylaert, M. Vandichel, G.B. Marin, M. Waroquier, V.V. Speybroeck, P.V.D. Voort, Chem. Commun. 46 (2010) 5085.
- [21] D. Jiang, T. Mallat, D.M. Meier, A. Urakawa, A. Baiker, J. Catal. 270 (2010) 26– 33.
- [22] S. Bhattacharjee, D.-A. Yang, W.-S. Ahn, Chem. Commun. 47 (2011) 3637– 3639.
- [23] P. Horcajada, S. Surble, C. Serre, D.-Y. Hong, Y.-K. Seo, J.-S. Chang, J.-M. Greneche, I. Margiolaki, G. Ferey, Chem. Commun. (2007) 2820–2822.
- [24] A. Dhakshinamoorthy, M. Alvaro, H. Garcia, ACS Catal. 1 (2011) 836-840.
- [25] Y. Ishii, S. Sakaguchi, in: J.E. Backvall (Ed.), Modern Oxidation Methods, Wiley, 2004 (Chapter 5, and the other chapters described in this book).
- [26] Y. Ishii, S. Sakaguchi, T. Iwahama, Adv. Synth. Catal. 343 (2001) 393-427.
- [27] I. Hermans, J.V. Deun, K. Houthoofd, J. Peeters, P.A. Jacobs, J. Catal. 251 (2007) 204-212.
- [28] D.E. Van Sickle, F.R. Mayo, R.M. Arluck, J. Am. Chem. Soc. 87 (1965) 4824.
- [29] U. Neuenschwander, F. Guignard, I. Hermans, ChemSusChem 3 (2010) 75.
- [30] U. Neuenschwander, I. Hermans, Phys. Chem. Chem. Phys. 12 (2010) 10542.
- [31] S.-H. Cho, M.-S. Cheong, K.-D. Jung, C.-S. Kim, S.-H. Han, Appl. Catal. A: Gen. 267 (2004) 241-244
- [32] E. Kockrick, T. Lescouet, E.V. Kudrik, A.B. Sorokin, D. Farrusseng, Chem. Commun. 47 (2011) 1562–1564.
- [33] T.-J. Wang, Y.-Y. Yan, M.-Y. Huang, Y.-Y. Jiang, React. Funct. Polym. 29 (1996) 145–149.
- [34] K.M. Jinka, J. Sebastian, R.V. Jasra, J. Mol. Catal. A: Chem. 274 (2007) 33-41.
- [35] R.A. Sheldon, I.W.C.E. Arends, Adv. Synth. Catal. 346 (2004) 1051.
- [36] A. Mackor, T.A.J.W. Wajer, T.J. de Boer, Tetrahedron 24 (1968) 1623-1631.