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Aerobic Oxidation of Styrenes Catalyzed by an Iron Metal Organic Framework

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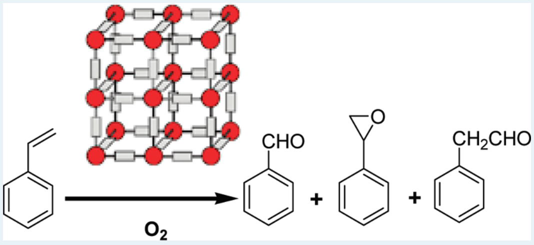
ABSTRACT: Aerobic oxidation of a series of styrenes to benzaldehyde, styrene oxide, and derivatives has been performed with *N*-hydroxyphthalimide loaded on Fe(BTC) (BTC: 1,3,5-benzenetricarboxylate) under different reaction conditions. A suitable mechanism based on peroxidation of the primary benzaldehyde has been proposed for the formation of styrene oxide based on the observed results.

KEYWORDS: aerobic oxidation, styrenes, iron metal organic framework, benzaldehyde, styrene oxide



INTRODUCTION

Oxidation of olefins is a fundamental reaction in organic chemistry that has also many industrial applications.[1] The array of products that can be derived from oxidation of olefin like epoxide and carbonylic compounds are frequently key starting materials for organic synthesis. Usually, this type of reaction is carried out using transition metals as catalysts in combination with peroxides, peracids, and other oxidizing reagents. In addition, these oxidizing agents are frequently used in over stoichiometric amounts. Because of the cost of the peroxides and the native byproduct derived from the oxidant, it is always advantageous from the environmental and economical points of view to use molecular oxygen as oxidant.

Metal–organic frameworks (MOFs) are crystalline solids, whose structure is constructed from metal ions or clusters coordinated to polytopic organic ligands.[2−5] The combination of large metal content and porosity make MOFs very attractive in the field of catalysis.[6−8] Although there are many types of MOFs differing in the nature of the metal and organic linkers,[9−15] the fact that recently some MOFs have become commercially available makes it of interest to explore the catalytic activity of these commercial MOFs in view of their wide availability. In particular, Basolite F300 is a Fe(BTC) (BTC: 1,3,5-benzenetricarboxylate), whose composition is the same as MIL-100, although its crystal structure is still unknown. In view of the composition, the structure of Fe(BTC) is expected to be not far from MIL-100 that is constituted of trimers of iron octahedra sharing a common vertex μ_3-O.[16] These octahedra are linked to the BTC linkers in such a way that this leads to two types of mesoporous cages of 25 and 29 Å, accessible through microporous windows of 5.5 and 8.6 Å. Eventhough Fe(BTC) possesses somewhat smaller surface area than MIL-100, the specific Brunauer–Emmett–Teller (BET) area of Fe(BTC) is still large (over 840 $m^2 \times g^{-1}$), and considering the common linkers and metal ions of both MOFs, it is reasonable to assume that Fe(BTC) should entail most of the characteristic features of MIL-100. In addition, IR spectroscopy using probes has shown that Fe(BTC) contains cordinatively unsaturated sites. In the case of MIL-100, the coordination sphere of nodal Fe(III) ions has one position occupied by a solvent molecule that is not compromised by the framework and can participate in a catalytic cycle. It is also likely that a similar situation occurs in commercial Fe(BTC). In our group, Fe(BTC) has been extensively used for benzylic oxidation using *t*-butylhydroperoxide (TBHP),[17] ring-opening of styrene oxide with methanol and aniline,[18] Claisen–Schmidt condensation reaction,[19] and aerobic oxidation of thiophenol to diphenyldisulfide.[20] Recently, *N*-hydroxyphthalimide (NHPI) supported on Fe(BTC) has been reported for aerobic oxidation of cyclooctane and benzylic compounds with very high selectivity[21] and aerobic oxidation of benzyl amine to imines.[22] NHPI is an organocatalyst that in combination with transition metal can act as initiator of radical chain oxidation of (cyclo)alkanes, alkanes, alcohols, and benzylic compounds.[23,24] Adsorption of NHPI inside the pores of MOFs could have advantages in terms of higher activity and selectivity and would allow the easy recovery of the catalyst after the reaction.

Concerning epoxidation of alkenes, it has been reported that MFU-1 as heterogeneous catalyst can perform the epoxidation of cyclohexene using TBHP as terminal oxidant.[25] Recently, a copper[26] and vanadium MOF[27] has also been employed for the epoxidation of cyclohexene using TBHP as oxidant. The use of MOFs as oxidation catalysts has been recently reviewed,[28] and it is interesting to note that up to now there are no reports concerning the use of oxygen as oxidant to perform epoxidation of alkenes catalyzed by MOFs. Hence, in the present study, we investigate the catalytic activity of MOFs in the aerobic oxidation of aromatic alkenes.

RESULTS AND DISCUSSION

Styrene was selected as model substrate to optimize the reaction conditions. Blank experiments in the absence of catalyst

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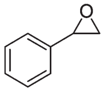
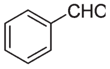
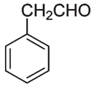
Table 1. Aerobic Oxidation of Styrene Using NHPI/Fe(BTC) As Heterogeneous Catalyst[d]

Run	Time (h)	Con. (%)	Selectivity (%)		
					
1[a]	1	3	20	66	14
2[a]	2	10	28	60	12
3[b]	1	1.8	-	99	-
4[b]	2	2.7	-	99	-
5[b]	3	3.5	-	99	-
6[b]	6	7	14	86	-
7[c]	1	0	-	-	-
8[c]	6	4	25	75	-

[a] Reaction conditions: styrene (1 mL), NHPI/Fe(BTC) (75 mg), oxygen purged through balloon, 100 °C. [b] Reaction conditions: styrene (0.250 mL), NHPI/Fe(BTC) (75 mg), toluene (4 mL), oxygen purged through balloon, 100 °C. [c] Reaction conditions as in footnote b but in the presence of β-carotene (25 mg). [d] Mass balances were in all cases above 90%.

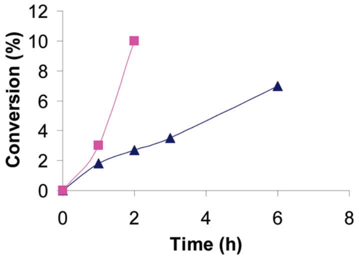
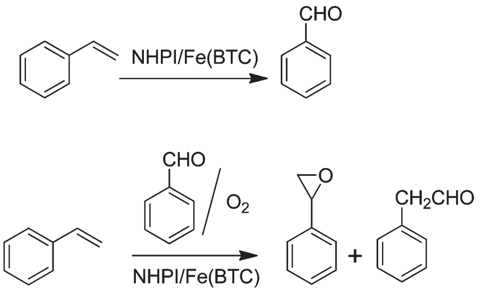


Figure 1. Temporal profile of styrene oxidation in the absence (square) and presence (triangle) of toluene with NHPI/Fe(BTC) (see footnotes "a" and "b" in Table 1 for reaction conditions).

Scheme 1. Aerobic Oxidation of Styrene in the Presence of NHPI/Fe(BTC) As Catalyst[a]



[a] Benzaldehyde (the primary product of the C=C oxidative degradation) can act as oxidant for the secondary oxidation of styrene to styrene oxide and phenylacetaldehyde.

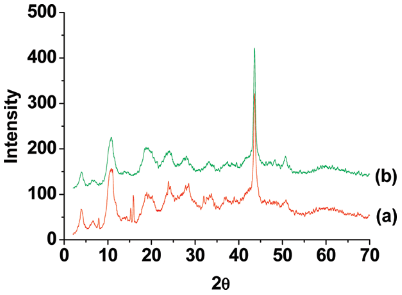


Figure 2. Powder XRD pattern of (a) fresh and (b) twice used NHPI/Fe(BTC).

or using Fe(BTC) without NHPI using oxygen resulted in no conversion of styrene. Two different conditions were tested for aerobic oxidation of styrene. In the first set, neat styrene was used as substrate without any solvent as described in Table 1 (footnote a).

Catalytic aerobic oxidation of styrene resulted in the formation of styrene epoxide, benzaldehyde, and phenylacetaldehyde. Conversion of styrene increases with time reaching 10% at 2 h with an increase in the selectivity toward epoxide. Figure 1 shows the time versus conversion plot for the aerobic oxidation of styrene under solventless conditions or using toluene as solvent. In contrast to the behavior of Fe(BTC), the use of $Fe(NO_3)_3$ resulted in the formation of unidentified polymeric material.

The product distribution shown in Table 1 can be interpreted considering the operation of two competing reaction mechanisms, that is, epoxidation followed by partial rearrangement to its derived product phenylacetaldehyde or oxidative C=C bond cleavage leading to benzaldehyde. In the second set of conditions (foot note b in Table 1), styrene was allowed to react with this catalyst using toluene as solvent, and the reaction becomes highly selective toward the formation of the product benzaldehyde until 3 h. It is interesting to note that in toluene, styrene oxide appears after a long induction period in which a build up of benzaldehyde concentration takes place suggesting that its formation requires the presence of benzaldehyde (Scheme 1).

In the literature, it has been reported that the system composing an aldehyde and a transition metal could effect the aerobic epoxidation of alkenes.[29] One typical example is the combination of pivalaldehyde and cobalt(II)acetylacetonate.[29] In principle, we propose that a similar pathway can be operating here when benzaldehyde is present in combination of Fe(III). This hypothesis was supported by performing styrene oxidation, adding at the initial time 1 mmol of benzaldehyde, and observing the formation of 1 and 3% of styrene oxide and phenylacetaldehyde, respectively, at 2 h reaction time. In an attempt to increase the selectivity toward epoxidation, additional experiments were performed using different solvents such as acetonitrile and chlorobenzene. In all cases high selectivity to benzaldehyde was observed. Similarly, using *t*-butyl hydroperoxide as oxidant in acetonitrile in combination with Fe(BTC) led to the conversion of styrene into benzaldehyde in high selectivity.

To gain some insight into the reaction mechanism, epoxidation was performed in toluene in the presence of a catalytic amount of β-carotene as a radical quencher. The rate of the reaction was decreased significantly because of the presence of carotene, and the selectivity to the styrene oxide at the same styrene conversion was increased substantially with respect to the experiments in the absence of of carotene. These quenching experiments suggest that the formation of benzaldehyde derives from carbon radicals that are intercepted by carotene.

Concerning the formation of phenylacetaldehyde, the most likely origin is rearrangement of styrene oxide. The occurrence of this rearrangement is supported by an independent control

Table 2. Aerobic Oxidation of Various Olefins Catalyzed by NHPI/Fe(BTC)[a]

				product disributions(%)[b]				
run	olefin	time (h)	con (%)	A	B	C	D	E
1	α-methylstyrene	10	12	75	18			7
2	4-fluorostyrene	10	60	63	5	10	11	11
3	4-chlorostyrene	10	58	72	5	12	6	5
4	4-methoxystyrene[d]	7	45[c]	68	17	3		8
5	3-nitrostyrene	3	2	99				

[a] Reaction conditions: styrene (0.250 mL), 75 mg of NHPI/Fe(BTC), 4 mL of toluene, oxygen purged, 100 °C. Mass balances were above 90%. [b] (A) Oxidative cleavage products; (B) rearranged products from epoxide; (C) epoxide; (D) carboxylic acids; (E) unidentified products. [c] Reaction conditions: styrene (0.5 mL), 75 mg of NHPI/Fe(BTC), oxygen purged, 100 °C. [d] 4-Methoxyacetophenone is formed in 4%.

experiment using styrene oxide as substrate in the presence of Fe(BTC) and observing the formation of phenylacetaldehyde. Lewis acid sites present in the MOF are the most likely sites responsible for this rearrangement.

The reusability of NHPI/Fe(BTC) was checked for the oxidation of styrene. The catalyst was reused two times without much variation in the temporal profiles of the percentage conversion and product distribution as compared to the first run. In addition the stability of Fe(BTC) under the reaction conditions was checked by characterizing the solid after its use as catalyst. Figure 2 shows the powder X-ray diffraction (XRD) pattern of fresh and twice used catalyst showing that the catalyst retains its crystallinity after three consecutive runs.

These results on the catalytic activity of NHPI/Fe(BTC) for the aerobic oxidation of styrene have prompted us to extend this catalytic system for other aromatic olefins with different substituents. Blank controls indicate that no reaction takes place for the time being considered under the reaction conditions in the absence of NHPI/Fe(BTC). α-Methylstyrene showed 12% conversion with 75% formation of acetophenone and 18% of propiophenone in 10 h. On the other hand, 4-fluorostyrene resulted in 60% conversion in 10 h with a product distribution wherein the major product was 4-fluorobenzaldehyde (63%), accompanied by 4-fluorophenylacetaldehyde, 4-fluorostyrene oxide, and 4-fluorobenzoic acid. 4-Chlorostyrene showed similar behavior to 4-fluorostyrene, and very high conversions were achieved with a product distribution comprising as major product 4-chlorobenzaldehyde accompained by 4-chlorophenylacetaldehyde, 4-chlorostyrene oxide, and 4-chlorobenzoic acid. On the other hand, 4-methoxystyrene showed 45% conversion in 7 h yielding 68% of 4-methoxybenzaldehyde accompained by 4-methoxyphenylacetaldehyde and 4-methoxyacetophenone. The conversion of 3-nitrostyrene resulted only in 2% to 3-nitrobenzaldehyde in 3 h. The influence of the substituents on the reactivity of the styrene clearly points out that the reaction mechanism involves an electrophilic radical attack to the C═C double bond, electron donating substituent exhibiting high reactivity. From the data of Table 2 it is remarkable that under solventless conditions and using molecular oxygen under atmospheric pressure, very high conversions of neat styrenes into aldehydes can be achieved when adequate substituents are present.

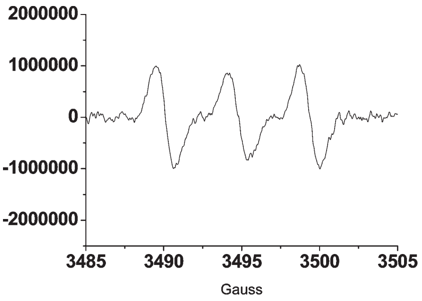


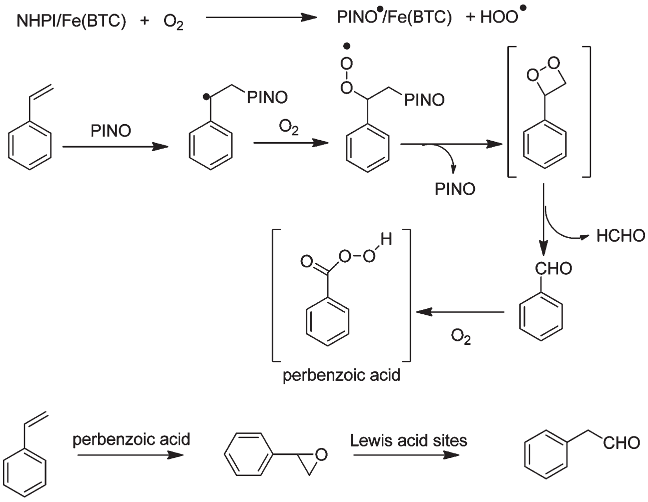
Figure 3. ESR spectrum corresponding to PINO radical generated upon exposure of NHPI/Fe(BTC) in benzonitrile suspension to air at 120 °C.

Concerning the reaction mechanism and in view of the precedents in the use of NHPI as organocatalyst for aerobic oxidations,[30,31] it is reasonable to assume the intermediacy of phthalimide *N*-oxyl radical (PINO) acting as precursor of C-centered radicals that would undergo autoxidation. To confirm the formation of PINO radicals in the present NHPI/Fe(BTC) catalyzed aerobic oxidation, electron spin resonance (ESR) spectra were recorded under different conditions. A control test did not detect the presence of any radical in solid NHPI/Fe(BTC). When a benzonitrile suspension of NHPI/Fe(BTC) was exposed to dioxygen at 120 °C for 2 h, an ESR spectrum attributable to PINO radicals was recorded as a triplet signal with the corresponding hyperfine splitting (hfs) due to the nitrogen atom ($g =$ 2.0073, $a_N = 0.460$ mT) (Figure 3). The *g*-value and hfs constant observed for PINO in NHPI/Fe(BTC) were consistent with those ($g = 2.0073$, $a_N = 0.423$ mT) reported by Mackor and co-workers for this *N*-oxyl radical in solution.[32]

Analogous measurements in the absence of oxygen or in its presence but in the absence of NHPI in Fe(BTC) failed to detect the same spectra. These spectra clearly support that in our case NHPI adsorbed in Fe(BTC) generates PINO. It is proposed that the weak interactions of NHPI with the nodal Fe(III) ions of the MOF are responsible for the activation of NHPI into its corresponding PINO radical. On the basis of this ESR evidence for PINO formation, it is proposed that the NHPI/Fe(BTC) system follows the general radical chain mechanism for the aerobic oxidation of styrene (Scheme 2), except that the reaction is taking place in a confined space. Thus, this primary PINO radical will in turn add electrophilically to the C═C double bond to generate a carbon centered radical. This is further trapped by molecular oxygen to give a peroxyl radical which attacks the neighboring carbon removing PINO and forming the corresponding dioxetane intermediate. [2 + 2] cyclo reversion of aryl dioxetane will give benzaldehyde. The radical chain mechanism will take place inside the constrained spaces of the Fe(BTC), restricting diffusion and mobility of the radicals. This confinement can lead to variations in the product distribution as it has been observed in the case of zeolites and other microporous solids.[33,34] On the other hand, a small amount of styrene oxide is also formed mostly from the aromatic aldehyde being transformed into the peracid. Finally, the formation of phenylacetaldehyde would be promoted by the Lewis acid sites from Fe(BTC). The Lewis acidity of Fe(BTC) was assessed by monitoring by IR the interaction of Fe(BTC) with acetonitrile and CO as probes and also by testing the activity of the solids in typical acid-catalyzed organic reactions.[35,36]

In conclusion, the utility of NHPI/Fe(BTC) as heterogeneous catalyst for aerobic oxidation of styrene to benzaldehyde accompanied by a small percentage of styrene oxide and phenylacetaldehyde has been studied. Electron donor substituents favor

Scheme 2. Proposed Mechanism for the Aerobic Oxidation of Styrene with NHPI/Fe(BTC) As Catalyst[a]



[a] Formation of perbenzoic acid from benzaldehyde triggers a second pathway in the oxidation of styrene leading to styrene oxide and pehenylacetaldehyde.

the process by increasing conversion. A suitable mechanism based on the intermediacy of the PINO radical is proposed for the formation of benzaldehyde based on its ESR spectroscopic characterization.

EXPERIMENTAL SECTION

All reagents, starting materials, and MOFs were obtained commercially from Aldrich and used as received, and styrenes were distilled. Elemental chemical analysis shows that the iron content of Fe(BTC) was 25%. The percentage conversion, purity, and relative yields of the final products were determined using a Hewlett-Packard 5890 series II gas chromatograph with FID detector and high purity helium as carrier gas. The products were identified by GC-MS using a Hewlett-Packard 6890 series spectrometer. Powder XRD patterns of fresh and reused Fe(BTC) were recorded in a Philips X'Pert diffractometer using the Cu K_α radiation at a scan rate of 0.2° min^{-1}. ESR spectra were recorded using a Bruker EMX, with the typical settings: frequency 9.476 GHz, sweep width 6900 G, time constant 5.12 ms, modulation frequency 100 kHz, modulation width 1 G, microwave power 19.93 mW.

TYPICAL OXIDATION PROCEDURE

In a 25 mL round bottomed flask, 0.250 mL of freshly distilled olefin was taken in 4 mL of toluene, and to this solution, 75 mg of NHPI/Fe(BTC) was added. This reaction mixture was purged with balloon with oxygen, and the whole content was stirred at 100 °C in a preheated bath for the required time. The sample was taken periodically to monitor the reaction. After the reaction, the reaction mixture was stirred with acetonitrile and filtered. The products were analyzed by GC and GC-MS.

A similar procedure was followed for the reusability tests. After the reaction, the reaction mixture was extracted with acetonitrile, and the catalyst was separated, dried, and reused for further runs. The detailed procedure for loading of NHPI/Fe(BTC) and its characterization have been reported in the ref 21.

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REFERENCES

(1) Trost, B. M. *Comprehensive Organic Synthesis*; Pergamon: New York, 1991.
(2) Corma, A.; Garcia, H.; Llabres i Xamena, F. X. *Chem. Rev.* **2010**, *110*, 4606.
(3) Eddaoudi, M.; Moler, D. B.; Li, H. L.; Chen, B. L.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319–330.
(4) Ferey, G. *Chem. Soc. Rev.* **2008**, *37*, 191–214.
(5) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334–2375.
(6) Wang, Z.; Chen, G.; Ding, K. *Chem. Rev.* **2009**, *109*, 322.
(7) Lee, J. Y.; Farha, O. K.; Roberts, J.; Scheidt, K. A.; Nguyen, S. T.; Hupp, J. T. *Chem. Soc. Rev* **2009**, *38*, 1450.
(8) Farrusseng, D.; Aguado, S.; Pinel, C. *Angew. Chem. Int. Ed.* **2009**, *48*, 7502.
(9) Bourrelly, S.; Llewellyn, P. L.; Serre, C.; Millange, F.; Loiseau, T.; Ferey, G. *J. Am. Chem. Soc.* **2005**, *127*, 13519–13521.
(10) Eddaoudi, M.; Kim, J.; Wachter, J. B.; Chae, H. K.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2001**, *123*, 4368–4369.
(11) Kaye, S. S.; Long, J. R. *J. Am. Chem. Soc.* **2005**, *127*, 6506–6507.
(12) Latroche, M.; Surble, S.; Serre, C.; Mellot-Draznieks, C.; Llewellyn, P. L.; Lee, J. H.; Chang, J. S.; Jhung, S. H.; Ferey, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 8227–8231.
(13) Loiseau, T.; Serre, C.; Huguenard, C.; Fink, G.; Taulelle, F.; Henry, M.; Bataille, T.; Ferey, G. *Chem.—Eur. J.* **2004**, *10*, 1373–1382.
(14) Tao, J.; Tong, M. L.; Chen, X. M. *J. Chem. Soc., Dalton Trans.s* **2000**, 3669–3674.
(15) Wang, B.; Cote, A. P.; Furukawa, H.; O'Keeffe, M.; Yaghi, O. M. *Nature* **2008**, *453*, 207–211.
(16) Horcajada, P.; Surblé, S.; Serre, C.; Hong, D.-Y.; Seo, Y.-K.; Chang, J.-S.; Grenèche, J.-M.; Margiolaki, I.; Férey, G. *Chem. Commun.* **2007**, 2820.
(17) Dhakshinamoorthy, A.; Alvaro, M.; Garcia, H. *J. Catal.* **2009**, *267*, 1.
(18) Dhakshinamoorthy, A.; Alvaro, M.; Garcia, H. *Chem.—Eur. J.* **2010**, *16*, 8530.
(19) Dhakshinamoorthy, A.; Alvaro, M.; Garcia, H. *Adv. Synth. Catal.* **2010**, *352*, 711.
(20) Dhakshinamoorthy, A.; Alvaro, M.; Garcia, H. *Chem. Commun.* **2010**, *46*, 6476.
(21) Dhakshinamoorthy, A.; Alvaro, M.; Garcia, H. *Chem.—Eur. J.* **2011**accepted for publication.
(22) Dhakshinamoorthy, A.; Alvaro, M.; Garcia, H. *ChemCatChem* **2010**, *2*, 1438.
(23) Ishii, Y.; Sakaguchi, S.; Iwahama, T. *Adv. Synth. Catal.* **2001**, *343*, 393–427.
(24) Sheldon, R. A.; Arends, I. *Adv. Synth. Catal.* **2004**, *346*, 1051–1071.
(25) Tonigold, M.; Lu, Y.; Bredenkotter, B.; Rieger, B.; Bahnmuller, S.; Hitzbleck, J.; Langstein, G.; Volkmer, D. *Angew. Chem., Int. Ed.* **2009**, *48*, 7546.
(26) Brown, K.; Zolezzi, S.; Aguirre, P.; Venegas-Yazigi, D.; Paredes-Garcia, V.; Baggio, R.; Novak., M. A.; Spodine, E. *Dalton Trans.* **2009**, 1422.
(27) Leus, K.; Muylaert, I.; Vandichel, M.; Marin, G. B.; Waroquier, M.; Speybroeck, V. V.; Der Voort, P. V. *Chem. Commun.* **2010**, *46*, 5085.

(28) Dhakshinamoorhty, A.; Alvaro, M.; Garcia, H. *Catal. Sci. Technol.* **2011**, *1*, DOI: 10.1039/c1cy00068c.

(29) Yamada, T.; Imagawa, K.; Mukaiyama, T. *Chem. Lett.* **1992**, 2109.

(30) Sheldon, R.; Arends, I. W. C. E. *Adv. Synth. Catal.* **2004**, *346*, 1051.

(31) Ishii, Y.; Sakaguchi, S. *Catal. Today* **2006**, *117*, 105–113.

(32) Mackor, A.; Wajer, T. A. J. W.; Boer, T. J. D. *Tetrahedron* **1968**, *24*, 1623.

(33) Scaiano, J. C.; García, H. *Acc. Chem. Res.* **1999**, *32*, 783–793.

(34) Turro, N. J.; Lei, X.; Cheng, C.-C. *J. Am. Chem. Soc.* **1985**, *107*, 5824–5826.

(35) Dhakshinamoorthy, A.; Alvaro, M.; Garcia, H. *Adv. Synth. Catal.* **2010**, *352*, 3022–3030.

(36) Dhakshinamoorthy, A.; Alvaro, M.; Garcia, H. *Adv. Synth. Catal.* **2010**, *352*, 711–717.