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Highly efficient and metal-free oxidation of olefins by molecular oxygen under mild conditions

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Abstract—Highly efficient and metal-free aerobic oxidations of cyclohexene and styrene were successfully performed under mild conditions in the presence of 1,4-diamino-2,3-dichloro-anthraquinone and *N*-hydroxyphthalimide. When cyclohexene was oxidized, an 89% conversion and 71% selectivity for 2-cyclohexen-1-one was obtained under 0.3 MPa at 80 °C for 5 h. In the oxidation of styrene, a 77% conversion and 69% selectivity for benzaldehyde was obtained for 10 h. Furthermore, more olefins were efficiently oxidized to corresponding oxygenated products under mild conditions. All kinds of factors that affected cyclohexene oxidation were well investigated, and the possible reaction mechanism was provided.

1. Introduction

Selective oxidation process plays an important role in modern organic chemistry. Thereinto, the oxidation of olefin is a crucial transformation, which is utilized in natural product synthesis and production of fine chemicals.[1–3] For example, the oxygenated products of cyclohexene and their derivatives are very important in organic synthesis owing to the existence of a highly reactive α,β-unsaturated carbonyl group, which are extensively used in the preparation of a range of chemical intermediates and products. Traditionally, some inorganic oxidants containing chromium were employed for the oxidation of cyclohexene.[4,5] However, when chromium compounds were used, there existed several obvious disadvantages, for example, the typical separation problem of products, disposal of toxic solid and liquid wastes, etc. In recent years, a variety of studies on the direct oxidation of cyclohexene have been reported which employed the peroxide (such as *tert*-butylhydroperoxide or hydrogen peroxide, etc.) or molecular oxygen as terminal oxidant for both economical and environmental benefits. These oxidation processes were mainly catalyzed by metallic compounds. These metallic catalysts generally contained iron,[6] manganese,[7–10] ruthenium,[11] vanadium,[12,13] chromium,[14] copper,[15] nickel and cobalt element,[16–19] etc., which were extensively used in homogenous or heterogenous catalytic systems. With these catalytic systems, cyclohexene was generally oxidized to 2-cyclohexen-1-one, 2-cyclohexen-1-ol, and cyclohexene oxide. Besides, in the oxidation of styrene, benzaldehyde and styrene epoxide are desirable and valuable products in fine chemicals. Recently, some efficient catalysts containing transition metal have also been reported for the oxidation of styrene.[20–29] Furthermore, the catalytic system containing *N*-hydroxyphthalimide (NHPI) and metal compound was especially attractive because of its high efficiency and mild reaction conditions in the aerobic oxidation,[30,31] which was also used in oxidation of some olefins.[32]

Although these catalyst systems containing metal element could improve the oxidation of olefin, these systems suffered from relatively harsh conditions or poor conversion and selectivity. On the other hand, the disadvantage of metallic toxicity and the high expense could not be avoided. Thus, metal-free and more efficient catalytic systems for oxidation of olefin with molecular oxygen become particularly desirable.

Catalysis with organic molecules is a significant research orientation in modern catalytic chemistry.[33,34] Our research group has reported several organocatalytic systems for efficient oxidation of aromatic hydrocarbons.[35–38] Herein, extending the former work, we report an efficient and metal-free catalytic process for oxidations of cyclohexene and styrene by molecular oxygen in the presence of NHPI and 1,4-diamino-2,3-dichloro-anthraquinone (DADCAQ). The promising conversions and selectivities are obtained.

Keywords: Metal-free; Oxidation; Cyclohexene; Styrene; *N*-Hydroxyphthalimide.
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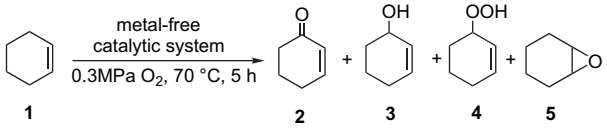
2. Results and discussion

2.1. Oxidation of cyclohexene

Cyclohexene (**1**) was efficiently oxidized by dioxygen under mild conditions in the presence of NHPI and anthraquinone (AQ) or derivates (shown in Scheme 1). Based on GC and GC–MS analysis, the major product was 2-cyclohexen-1-one (**2**). In most cases, the by-products were 2-cyclohexen-1-ol (**3**), 2-cyclohexen-1-hydroperoxide (**4**), and cyclohexene oxide (**5**).



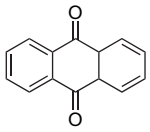
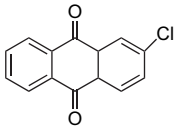
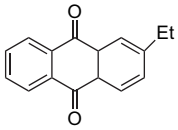
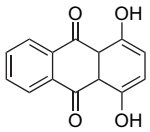
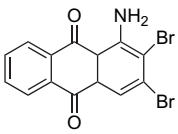
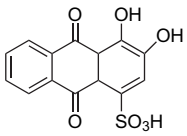
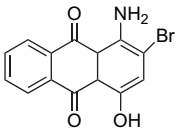
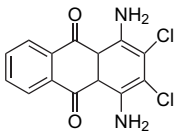
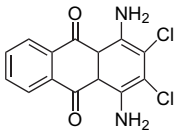
Scheme 1. Oxidation of cyclohexene by molecular oxygen.

2.1.1. The investigation of catalyst combinations. The oxidation of cyclohexene was investigated with the catalyst combination of different anthraquinone compounds and NHPI. The reaction results are summarized in Table 1. It could be seen that 75% conversion of **1** and 57% selectivity of **2** were obtained when anthraquinone (AQ) and NHPI were employed; especially, selectivity of **4** also reached 18%. Then, different substituted AQ compound, which was substituted by chlorine, bromine, hydroxyl, sulfonic group, amino or their combination, was investigated. As a result, it was found that the combination of 1,4-diamino-2,3-dichloro-anthraquinone (DADCAQ) and NHPI was most efficient and highly selective. Under 0.3 MPa at 75 °C, an 83% conversion and 67% selectivity for **2** were obtained for 5 h (entry 8). Here, it was indicated that the amino and chlorine groups could promote the decomposition of hydroperoxide through the electron effect and molecular structure functioning.[39] Otherwise, it was found that **1** was just oxidized with 25% conversion without any catalyst (entry 9), and only 29% conversion or 47% conversion of **1** was, respectively, obtained in the absence of NHPI or DADCAQ (entries 10 and 11). It was also seen that compound **4** was the major product instead of compound **2** when oxidation of **1** was carried out without any catalyst or in the presence of only NHPI (entries 9 and 11). This phenomenon was probably explained that the existence of AQ could facilitate the decomposition of cyclohexene hydroperoxide and have a notable effect upon the product distribution.

Then the effects of different catalyst contents were investigated, and it was found that the oxidation of cyclohexene could efficiently and selectively proceed when the content of NHPI–DADCAQ was 4.0–1.0 mol %.

2.1.2. Effect of temperature. The effect of temperature on oxidation of **1** was investigated and summarized in Table 2. It was shown that the conversion was increased and the selectivity for **2** was first increased then decreased along with the increase of temperature from 60 °C to 90 °C. When the temperature was 80 °C, an 87% conversion and 68% selectivity for **2** were obtained in the presence of 4.0 mol % NHPI and 1.0 mol % DADCAQ.

Table 1. Oxidation of cyclohexene by different catalyst combinations[a]

Entry	Anthraquinone (derivatives)	Conversion[b] (%)	Product distribution (%)				
			2	**3**	**4**	**5**	Others
1		75	57	9	18	4	12
2		76	61	10	12	4	13
3		50	43	18	15	1	11
4		52	39	11	19	1	17
5		71	63	11	10	4	12
6		79	61	8	11	5	15
7		69	65	8	10	5	12
8		83	67	8	7	7	11
9[c]	No	25	21	18	45	5	11
10[c]		29	65	11	7	7	10
11	No	47	33	12	38	4	13

[a] Reaction conditions: cyclohexene was performed on a 2 mL scale, in the presence of NHPI (5.0 mol %), anthraquinone (or derivatives) (1.25 mol %), in 10 mL CH_3CN, pressure=0.3 MPa, time=5 h, temperature=75 °C.

[b] The data were obtained by GC and GC–MS analysis using toluene as an internal standard.

[c] Oxidation was performed in the absence of NHPI.

2.1.3. Effect of reaction time. The effect of reaction time was investigated and outlined in Figure 1. It was indicated that the selectivity of **2** almost kept unchanged and the conversion gradually increased during the oxidation of cyclohexene from 30 min to 300 min. The reaction speed sharply increased during 150–180 min, which matched with the chain propagation process in the radical oxidation.

Table 2. The effect of reaction temperature on oxidation of cyclohexene[a]

Entry	Temperature (°C)	Conversion[b] (%)	Product distribution (%)				
			2	**3**	**4**	**5**	Others
1	60	44	53	14	3	19	11
2	70	80	65	10	5	9	11
3	80	87	68	9	5	7	11
4	90	91	64	8	9	7	12

[a] Reaction conditions: cyclohexene was performed on a 2 mL scale, in the presence of NHPI (4.0 mol %), DADCAQ (1.0 mol %), in 10 mL CH_3CN, pressure=0.3 MPa, time=5 h.
[b] The data were obtained by GC and GC–MS analysis using toluene as an internal standard.

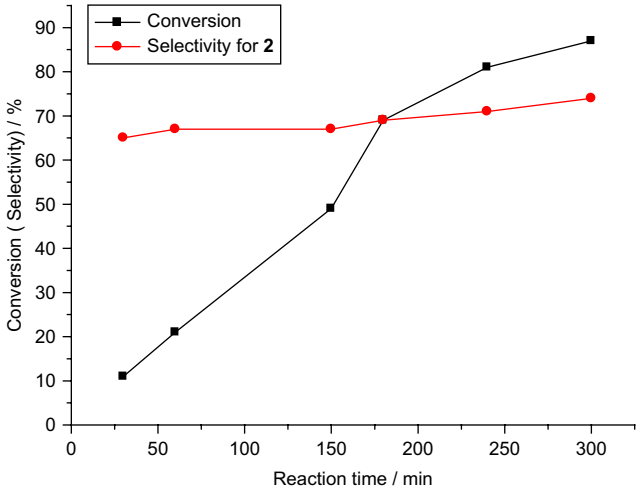


Figure 1. The effect of reaction time in oxidation of cyclohexene (Reaction conditions: 4.0 mol % NHPI, 1.0 mol % DADCAQ, temperature=80 °C, pressure=0.3 MPa).

Moreover, it should be mentioned that the conversion hardly increased and the selectivity gradually decreased if the oxidation was continuingly preceded to 330 min or longer reaction time, so 300 min is considered as a preferable reaction time.

2.1.4. Effect of additive. The reaction exhibited an interesting effect after an additive was added. In Table 3, it could be clearly seen that acidic additives could improve the selectivity of **2** and conversion was appreciably decreased (entries 1 and 2); thereinto, 89% conversion and 71% selectivity for **2** were obtained when acetic acid was used as an additive. However, the addition of pyridine made the conversion lessen sharply (entry 3) and only 34% conversion of **1** was obtained.

Table 3. The effect of additive in the oxidation of cyclohexene[a]

Entry	Additive	Conversion[b] (%)	Product distribution (%)				
			2	**3**	**4**	**5**	Others
1	Acetic acid	89	71	11	4	5	9
2	Acetic anhydride	85	71	12	4	3	10
3	Pyridine	34	75	10	2	5	8

[a] Reaction conditions: cyclohexene was performed on a 2 mL scale, in the presence of NHPI (4.0 mol %), DADCAQ (1.0 mol %), and the additive (1 mL), in 10 mL CH_3CN, temperature=80 °C, pressure=0.3 MPa, time=5 h.
[b] The data were obtained by GC and GC–MS analysis using toluene as an internal standard.

Table 4. The effect of solvent in the oxidation of cyclohexene[a]

Entry	Solvent	Conversion[b] (%)	Product distribution (%)				
			2	**3**	**4**	**5**	Others
1	$PhCF_3$	71	61	15	3	11	10
2	CCl_4	81	63	12	4	10	11
3	DMAc	84	69	14	5	4	8

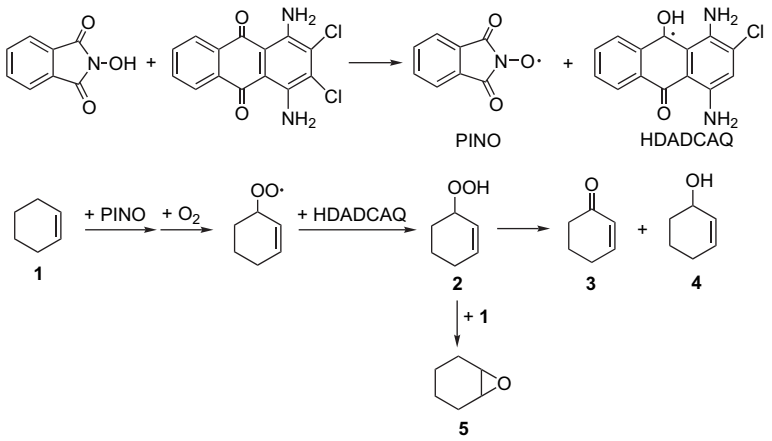
[a] Reaction conditions: cyclohexene was performed on a 2 mL scale, in the presence of NHPI (4.0 mol %), DADCAQ (1.0 mol %), in 10 mL solvent, temperature=80 °C, pressure=0.3 MPa, time=5 h.
[b] The data were obtained by GC and GC–MS analysis using toluene as an internal standard.

2.1.5. Effect of solvent. Different solvents, including polar (CH_3CN, DMAc) and apolar ones (CCl_4, $PhCF_3$), were employed on the oxidation of cyclohexene (entry 3 in Tables 2 and 4). Here, 89% conversion or 84% conversion with CH_3CN or DMAc as a solvent was superior to 71% conversion or 81% conversion with $PhCF_3$ or CCl_4 as a solvent. So, it was shown that polar solvent was more suitable to this reaction system, which could be attributed to better solubility of catalyst in the polar one.

2.1.6. Mechanism of oxidation of cyclohexene. Here, a possible reaction mechanism was proposed for cyclohexene oxidation (Scheme 2). Firstly, NHPI can be converted to phthalimide *N*-oxyl radical (PINO) through electron and proton transfer with the assistance of DADCAQ in the beginning of the reaction (step 1). The following step involves the hydrogen atom abstraction from cyclohexene by PINO, and the resulting cyclohexene radical being trapped by molecular oxygen provides peroxy radical, which is eventually converted into products through cyclohexene hydroperoxide (step 2). Furthermore, the better result was obtained when acetic acid or acetic anhydride was added as an additive probably because hydrogen bonding between NHPI and this additive increased the O–H bond dissociation energy,[40] and the conversion sharply fell after a little pyridine was added probably because pyridine could accelerate decay of PINO in acetonitrile.[41] Further investigation about reaction mechanism, especially including more direct information of cyclohexene radical and peroxy radical in the oxidation, is underway.

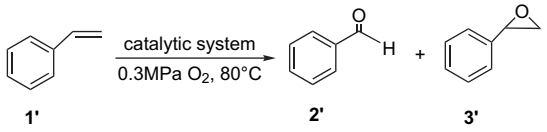
2.2. Oxidation of styrene and other olefins

It could be seen from Table 5 that styrene was mainly oxidized to benzaldehyde and styrene epoxide with this catalytic system. When NHPI and AQ were employed as a catalyst combination, a 51% conversion and 71% selectivity for benzaldehyde were obtained (entry 1). Similarly, a 55% conversion and 72% selectivity for benzaldehyde were obtained when AQ was replaced by DADCAQ (entry 2). Further investigations indicated that the conversion of styrene could be increased and the selectivity was decreased little along with the increase of reaction time. When styrene was oxidized for 10 h, the conversion was increased to 77% and the selectivity for benzaldehyde was 69% (entry 3). To our surprise, when 1 mL acetic acid was added as an additive, the selectivity for benzaldehyde was improved, but the conversion was acutely decreased (entry 4). It was also found that a 19% conversion of styrene and 78% selectivity for benzaldehyde were obtained in the absence of any



Scheme 2. Proposed reaction mechanism for cyclohexene oxidation.

Table 5. Oxidation of styrene by different catalyst combination[a]



Entry	Catalyst	Reaction time (h)	Conversion[b] (%)	Product distribution (%)		
				2′	3′	Others
1	NHPI+AQ	5	51	71	12	17
2	NHPI+DADCAQ	5	55	72	13	15
3	NHPI+DADCAQ	10	77	69	13	18
4[c]	NHPI+DADCAQ	10	25	89	1	10
5	No	5	19	78	5	17
6	NHPI	5	32	74	11	15
7	DADCAQ	5	21	79	7	14

[a] Reaction conditions: styrene was performed on a 2 mL scale, in the presence of NHPI (4.0 mol %), AQ or DADCAQ (1.0 mol %), in 10 mL CH_3CN, temperature=80 °C, pressure=0.3 MPa.
[b] The data were obtained by GC and GC–MS analysis using toluene as an internal standard.
[c] 1 mL acetic acid was added as an additive.

catalyst (entry 5), and the conversion was, respectively, 32% or 21% in the presence of only NHPI or DADCAQ (entries 6 and 7). These results indicated that oxidation of styrene could be possibly different from oxidation of cyclohexene, and oxidation of styrene could be performed through the addition and decomposition processes of radicals.

In addition, oxidations of other olefins were investigated and the results are shown in Table 6. It was found that an 89% conversion and 67% selectivity for 4-methoxybenzadehyde were obtained when 4-methoxystyrene was oxidized; 4-chlorostyrene was oxidized with 69% conversion and 73% selectivity for 4-chlorobenzadehyde in the presence of NHPI and DADCAQ. Moreover, when 3-methylstyrene was oxidized, 51% conversion and 69% selectivity for 3-methylbenzaldehyde were obtained. All these results showed that the oxidation efficiency was relative with the structure of olefins. On the other hand, we also investigated the oxidation of aliphatic chain olefins; however, the products were various and the selectivity was low. For example, when 1-octene was oxidized, the oxygenated products were hexanal, 2-hexyloxirane, oct-1-en-3-one, hept-2-enal, etc. So, it could be concluded that this metal-free catalytic system was more favorable to the oxidation of alicyclic and aromatic olefins.

Table 6. Oxidation of some olefins by the combination of NHPI and DADCAQ[a]

Entry	Substrate	Conversion[b] (%)	Product distribution (%)		
			Aldehyde[c]	Epoxide[d]	Others
1	4-Methoxystyrene	85	67	11	22
2	4-Chlorostyrene	69	73	14	13
3	3-Methylstyrene	51	69	14	17

[a] Reaction conditions: substrates were performed on a 1 mL scale, in the presence of NHPI (4.0 mol %), DADCAQ (1.0 mol %), in 10 mL CH_3CN, temperature=80 °C, pressure=0.3 MPa, time=10 h.
[b] The data were obtained by GC and GC–MS analysis using 1,2-dichlorobenzene as an internal standard.
[c] The ordinal aldehydes were 4-methoxybenzaldehyde, 4-cholorobenzaldehyde, and 3-methylbenzaldehyde.
[d] The ordinal epoxides were 4-methoxystyrene oxide, 4-chlorostyrene oxide, and 3-methylstyrene oxide.

3. Conclusion

It was demonstrated that various alicyclic and aromatic olefins could be efficiently oxidized by molecular oxygen under mild conditions in the presence of DADCAQ and NHPI. Thereinto, when cyclohexene was oxidized, an 89% conversion and 71% selectivity for 2-cyclohexen-1-one

were obtained under 0.3 MPa at 80 °C for 5 h. In oxidation of styrene, a 77% conversion and 69% selectivity for benzaldehyde were obtained under 0.3 MPa at 80 °C for 10 h. The detailed investigations about reaction mechanisms and radical intermediates are underway.

4. Experimental

4.1. Reagents and equipments

NHPI, anthraquinone (AQ), and anthraquinone derivates were purchased from commercial source and purified before they were employed.

Cyclohexene, styrene, and other olefins were rectified before they were used as reaction substrates.

All of the solvents including CH_3CN, CCl_4, $PhCF_3$, and DMAc (*N*,*N*′-dimethylacetamide) were analytical reagents.

The products of oxidation were determined by an Agilent 6890N GC/5973 MS detector and analyzed by an Agilent 4890D gas chromatography.

4.2. Oxidation of olefins

4.2.1. General procedure for the oxidation of olefins. All oxidation experiments were performed in a closed Teflon-lined stainless steel autoclave equipped with magnetic stirring and automatic temperature control. Typical procedure for cyclohexene oxidation was as follows: acetonitrile (10 mL) solution of the freshly distilled **1** (2.0 mL), NHPI (5.0 mol %), and DADCAQ (1.25 mol%) were charged into the reactor. The atmosphere inside was replaced with oxygen before the reactor was airproofed. Under stirring, the autoclave was preheated to 75 °C and then oxygen was charged to 0.3 MPa and kept for 5 h. After the reaction, the autoclave was cooled and excess gas was purged. The products were analyzed with internal standard technique by Agilent 4890D gas chromatography (OV-1701 capillary column) with a flame ionization detector (all products were determined on GC-MC with Agilent 6890N GC/5973 MS detector).

4.2.2. Special analysis procedure for the oxidation of olefins. The analysis procedure for oxidation of cyclohexene: after **1** was oxidized, the **4** could decompose to **2** when the oxidized mixture was injected into gas chromatography; hereby, to quantify the selectivity of the different products in the oxidation of **1**, the reaction mixture was treated with excess Ph_3P for 1 h after the first GC measurement and was analyzed again. Here, Ph_3P could reduce quantitatively the **4** to **3** at room temperature, so the selectivity of the oxygenated products could be accurately attained after a second GC measurement.

Acknowledgements

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Supplementary data

It contains general procedure for the detailed GC measurement conditions, explanation to several phenomena, and GC–MS diagrams for all the products. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.05.038.

References and notes

1. Cainelli, G.; Cardillo, G. *Chromium Oxidation in Organic Chemistry*; Springer: Berlin, 1984.
2. Hudlicky, M. *Oxidations in Organic Chemistry*; ACS Monographs 186; American Chemical Society: Washington, DC, 1990.
3. Trost, B. M. *Comprehensive Organic Synthesis (Oxidation)*; Pergamon: New York, NY, 1991.
4. Smith, A. B.; Konopelski, J. P. *J. Org. Chem.* **1984**, *49*, 4094–4095.
5. Muzart, J. *Chem. Rev.* **1992**, *92*, 113–140.
6. Medina, J. C.; Gabriunas, N.; Pfiez-Mozo, E. *J. Mol. Catal. A: Chem.* **1997**, *115*, 233–239.
7. Niassary, M. S.; Farzaneh, F.; Ghandi, M.; Turkian, L. *J. Mol. Catal. A: Chem.* **2000**, *157*, 183–188.
8. Połtowicz, J.; Serwicka, E. M.; Bastardo-Gonzalez, E.; Jones, W.; Mokaya, R. *Appl. Catal. A: Gen.* **2001**, *218*, 211–217.
9. Salavati-Niasari, M.; Farzaneh, F.; Ghandi, M. *J. Mol. Catal. A: Chem.* **2002**, *186*, 101–107.
10. Tong, J.; Zhang, Y.; Li, Z.; Xia, C. *J. Mol. Catal. A: Chem.* **2006**, *249*, 47–52.
11. Lei, Z. *React. Funct. Polym.* **2000**, *43*, 139–143.
12. Boghaei, D. M.; Mohebi, S. *Tetrahedron* **2002**, *58*, 5357–5366.
13. Maurya, M. R.; Kumar, A. *J. Mol. Catal. A: Chem.* **2006**, *250*, 190–198.
14. Sakthivel, A.; Dapurkar, S. E.; Selvam, P. *Appl. Catal. A: Gen.* **2003**, *246*, 283–293.
15. Mukherjee, S.; Samanta, S.; Chandra Roy, B.; Bhaumik, A. *Appl. Catal. A: Gen.* **2006**, *301*, 79–88.
16. Salavati-Niasari, M.; Banitaba, S. H. *J. Mol. Catal. A: Chem.* **2003**, *201*, 43–54.
17. Serwicka, E. M.; Połtowicz, J.; Bahranowski, K.; Olejniczak, Z.; Jones, W. *Appl. Catal. A: Gen.* **2004**, *275*, 9–14.
18. Salavati-Niasari, M.; Salemi, P.; Davar, F. *J. Mol. Catal. A: Chem.* **2005**, *238*, 215–222.
19. Salavati-Niasari, M.; Hassani-Kabutarkhani, M.; Davar, F. *Catal. Commun.* **2006**, *7*, 955–962.
20. Kim, S.; Zhang, W.; Pinnavaia, T. J. *Catal. Lett.* **1997**, *43*, 149–154.
21. Nickerson, D. P.; Harford-Cross, C. F.; Fulcher, S. R.; Wong, L. L. *FEBS Lett.* **1997**, *405*, 153–159.
22. Zsigmond, Á.; Horváth, A.; Notheisz, F. *J. Mol. Catal. A: Chem.* **2001**, *171*, 95–102.
23. Liu, J.; Li, X.; Li, Y.; Chang, W.; Huang, A. *J. Mol. Catal. A: Chem.* **2002**, *187*, 163–167.
24. Freitag, J.; Nüchter, M.; Ondruschka, B. *Green Chem.* **2003**, *5*, 291–295.
25. Kurek, S. S.; Michorczyk, P.; Balisz, A. *J. Mol. Catal. A: Chem.* **2003**, *194*, 237–248.

26. Ma, N.; Yue, Y.; Hua, W.; Gao, Z. *Appl. Catal. A: Gen.* **2003**, *251*, 39–47.
27. Hulea, V.; Dumitriu, E. *Appl. Catal. A: Gen.* **2004**, *277*, 99–106.
28. Gao, D.; Gao, G. *Microporous Mesoporous Mater.* **2005**, *85*, 365–373.
29. Gómez, S.; Garces, L. J.; Villegas, J.; Ghosh, R.; Giraldo, O.; Suib, S. L. *J. Catal.* **2005**, *233*, 60–67.
30. Ishii, Y.; Sakaguchi, S.; Iwahama, T. *Adv. Synth. Catal.* **2001**, *343*, 393–427.
31. Sheldon, R. A.; Arends, I. W. C. E. *Adv. Synth. Catal.* **2004**, *346*, 1051–1071.
32. Sheldon, R. A.; Arends, I. C. W. E.; Dijksman, A. *Catal. Today* **2000**, *57*, 157–166.
33. Bolm, C. *Adv. Synth. Catal.* **2004**, *346*, 1021.
34. List, B. *Adv. Synth. Catal.* **2004**, *346*, 1022.
35. Yang, G.; Ma, Y.; Xu, J. *J. Am. Chem. Soc.* **2004**, *126*, 10542–10543.
36. Yang, G.; Zhang, Q.; Miao, H.; Tong, X.; Xu, J. *Org. Lett.* **2005**, *7*, 263–266.
37. Tong, X.; Xu, J.; Miao, H. *Adv. Synth. Catal.* **2005**, *347*, 1953–1957.
38. Tong, X.; Xu, J.; Miao, H.; Gao, J. *Tetrahedron Lett.* **2006**, *47*, 1763–1766.
39. Swern, D. *Organic Peroxides*; Wiley-Interscience, A Division of John Wiley and Sons: New York, NY, 1971; Vol. II, Chapter I, pp 60–151.
40. Koshino, N.; Cai, Y.; Espenson, J. H. *J. Phys. Chem. A* **2003**, *107*, 4262–4267.
41. Koshino, N.; Saha, B.; Espenson, J. H. *J. Org. Chem.* **2003**, *68*, 9364–9370.