

Allylic oxidation of cyclohexene over silica immobilized iron tetrasulfophthalocyanine

Lina M. González,^a Aída L. Villa de P.,^{a,*} Consuelo Montes de C.^a
and Alexander Sorokin^b

^a*Environmental Catalysis Research Group, Universidad de Antioquia, Sede de Investigación Universitaria – SIU, A.A. 1226, Calle 62 # 52-59, Medellín, Colombia*

^b*Institut de Recherche sur la Catalyse, CNRS, 2 Avenue A. Einstein, 69626 Villeurbanne Cedex, France*

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Abstract—Iron tetrasulfophthalocyanine was immobilized on silica (FePcS–SiO₂) and its activity examined on the allylic oxidation of cyclohexene using TBHP as oxidant. Under our reaction conditions, attack of the activated C–H bond was preferred instead of the epoxidation of C=C bond, yielding 2-cyclohexen-1-one as the main product. μ -Oxo dimeric (d-FePcS) appears to be the active species for this reaction.

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Synthetic iron porphyrin complexes have been extensively investigated as models for the catalytic action of the enzyme Cytochrome P-450 in oxidation reactions. However, porphyrins often degrade under reaction conditions. Metallophthalocyanine (MePc) complexes have been used as alternative catalysts, because they have a similar structure to porphyrins and are cheaper and more stable to degradation.¹ The immobilization of MePc on solid supports is highly desirable to synthesize heterogeneous catalysts.² Iron tetrasulfophthalocyanines (FePc) have been immobilized on zeolites,³ activated carbon⁴ and siliceous materials such as MCM-41 and silica.² Iron tetrasulfophthalocyanines immobilized on siliceous materials in a dimeric form, d-FePcS–SiO₂, are active catalysts for the oxidation of 2,3,6-trimethylphenol with *tert*-butyl hydroperoxide (TBHP) as oxidant to obtain 1,4-trimethylbenzoquinone (yield higher than 80% to quinone), which is a vitamin E precursor.⁵

The homogeneous oxidation of cyclohexene on Mn(III), Co(II), and Fe(II) tetra-*tert*-butylphthalocyanines, in the presence of isobutylaldehyde as a reducing agent, resulted in the formation of cyclohexene oxide and

2-cyclohexene-1-one.⁶ Here, we report on the activity of FePcS–SiO₂ for the allylic oxidation of cyclohexene with TBHP. The effect of oxidant/cyclohexene ratio, amount of catalyst, temperature, and the type of solvent on cyclohexenone yield was examined.

All chemicals were of the highest commercially available grade and were used as received. First, iron tetrasulfophthalocyanine (FePc) samples were modified to obtain tetrachloro-sulfonylphthalocyanine, FePc(SO₂Cl)₄, by the treatment with SOCl₂ in the presence of traces of DMF.² Then, amorphous SiO₂ was functionalized with 3-aminopropyltriethoxysilane (3-APTES) and the modified complex supported on functionalized silica.⁷ Catalyst samples were characterized by elemental analyses, BET, UV–vis, IR, and TGA/DTG.

Oxidation reactions were carried out in a three-necked flask under reflux. In a typical procedure a catalyst sample (0.5–2 mol %) was added to a cyclohexene solution; then, dry TBHP ($C_{\text{TBHP}} = 3.5 \text{ M}$ in CH₂Cl₂) was added and the reaction mixture heated under stirring at the desired temperature for 24 h. Reaction products were separated from the catalyst with a filter syringe and analyzed in a Varian Star 3400 gas chromatograph equipped with a flame ionization detector and a capillary DB-1 column (length: 50 m, film thickness: 1.2 μm , diameter: 0.32 mm; J&W Scientific). Methylbenzoate was used as internal standard. At the end of

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* Corresponding author. Tel.: +57 4 2105595; fax: +57 4 2106609; e-mail: alvilla@udea.edu.co

the reaction, the catalyst was recovered by filtration, thoroughly washed with acetonitrile, acetone, and water, dried under vacuum at 40 °C overnight and re-used under similar conditions. The standard error by variance analysis using Statgraphics 5.1 software was 2.9% for sample analyses.

DTG profiles of FePcS and FePcS–SiO₂ are shown in Figure 1. The first peak, around 90 °C in DTG of FePcS, is ascribed to the desorption of water molecules.^{8,9} Peaks at 560 and 730 °C are associated with complex decomposition.⁹ The DTG profile of immobilized complex, FePcS–SiO₂, shows a weight loss of 0.42 wt % around 80 °C due to the evolution of physisorbed water. A peak around 425 °C is assigned to the decomposition of 3-APTES.¹⁰ A shoulder around 520 °C may be due to immobilized complex.⁹ From TGA, a total weight loss of 4.6 wt % is assigned to ligand and complex decomposition.

Linkage of FePcS complex to the silica surface was evidenced by different characterization techniques. The iron content of FePcS–SiO₂ was 36.7 μmol Fe/g; the specific surface area of silica (244 m²/g) decreased to 203 m²/g after phthalocyanine complex incorporation, indicating the successful modification of SiO₂. The blue color of the catalyst and UV–vis bands at 345 nm and 659 nm in Figure 2 denote the presence of the μ-oxo dimeric species.^{2,5} As shown in Figure 3b and d it was not possible to detect new FTIR bands after supporting FePcS on SiO₂ because of strong bands at 1100 cm⁻¹ and 800 cm⁻¹ attributed to Si–O–Si vibrational modes¹¹ that overlapped phthalocyanine bands. However, the FTIR spectrum of FePcS–SiO₂ (Fig. 3b) shows a band at 730 cm⁻¹ due to C–H bond vibration in the phthalocyanine molecule.⁸ Furthermore, the increased band intensity at 960 cm⁻¹ may be attributed to silanol groups, due to the presence of the phthalocyanine complex which has vibration modes at 956 cm⁻¹ assigned to benzene.¹²

Table 1 shows that immobilization of the iron phthalocyanine complex improves 2-cyclohexen-1-one yield, especially for short reaction times. Due to the high yield of allylic oxidation products, 2-cyclohexen-1-one and 2-cyclohexen-1-ol, compared to that of epoxide, preferen-

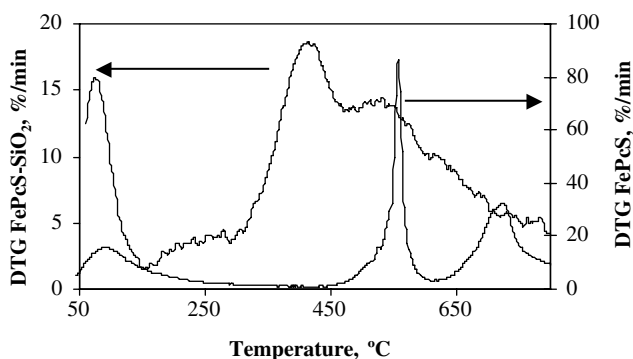


Figure 1. DTG profile: (a) FePcS–SiO₂ catalyst and (b) FePcS complex.

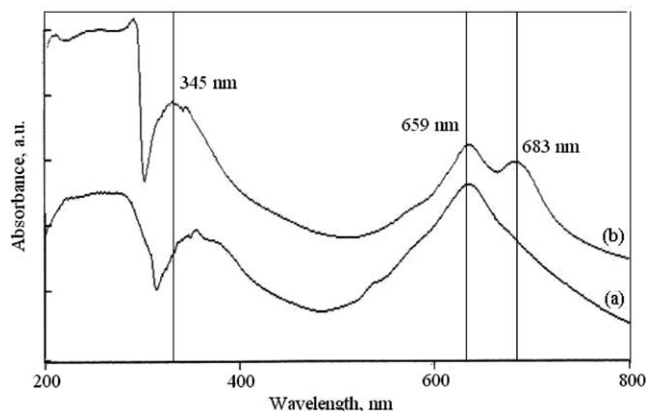


Figure 2. UV–vis spectra of phthalocyanine catalyst samples: (a) fresh FePcS–SiO₂ and (b) FePcS–SiO₂ after the reaction.

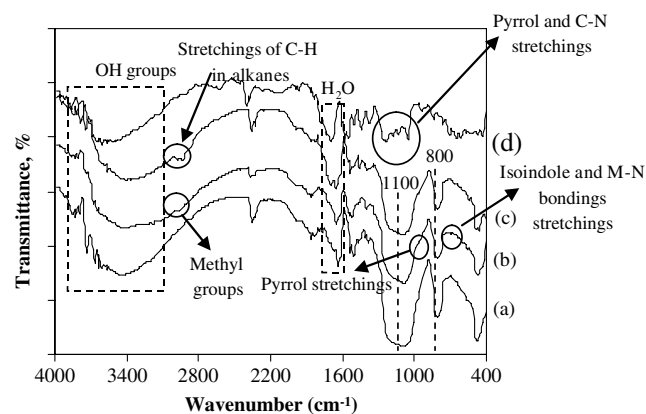


Figure 3. FTIR spectra of: (a) SiO₂, (b) FePcS–SiO₂, (c) FePcS–SiO₂ after the reaction, and (d) FePcS.

tial attack of the activated C–H bond over the C=C bond appears to occur under our reaction conditions. 2-Cyclohexen-1-one yield increased with TBHP/cyclohexene molar ratio up to about 2.6 and it was approximately constant (33%) between 2.6 and 5.2.

Reactions were carried out with both polar and non-polar solvents (Table 2) and catalytic activity was analyzed based on the electron donor number (DN) and dielectric constant (ϵ) of solvent. The DN is a dimensionless and more accurate polarity scale,^{13,14} directly related to the trend toward complex formation with a metal center, which can retard or avoid the formation of oxometal complexes (active oxidation species).¹⁵ As can be observed in Table 2, 2-cyclohexen-1-one yield increases as DN¹⁶ decreases and, in general, ϵ increases: acetonitrile (DN: 14.1, ϵ : 37.5, entry 2) > acetone (DN: 17, ϵ : 20.7, entry 14) > ethyl acetate (DN: 17.1, ϵ : 6.02, entry 12) > THF (DN: 20, ϵ : 7.58, entry 13). Although the highest ketone yield was expected with toluene (entry 11) due to its low DN value of 0.1, its polarity (ϵ : 2.38) appears to be also important.

The highest yield of alcohol and the lowest one of 2-cyclohexen-1-one has been observed with THF (Table

Table 1. Catalytic activity of FePcS and FePcS–SiO₂^a

Catalyst	Yield ^b (%)								
	3 h			5 h			24 h		
	E	OL	ONE	E	OL	ONE	E	OL	ONE
None	<1	1	<1	1	1	1	1	2	8
FePcS	1	3	8	1	5	14	4	12	41
FePcS–SiO ₂	1	4	30	1	6	38	2	5	57

^a Reaction conditions: 4 mL of 0.125 M cyclohexene in CH₃CN, 0.5 mol % catalyst, 1.3 mmol TBHP in CH₂Cl₂ (3.5 M), 40 °C, 24 h.

^b Yield (%): mole of products/initial moles of cyclohexene. E: cyclohexene oxide, OL: 2-cyclohexen-1-ol, ONE: 2-cyclohexen-1-one.

Table 2. Product yield in the allylic oxidation of cyclohexene with TBHP over FePcS–SiO₂^a

Entry	Catalyst (mol %)	Solvent	TBHP (mmol)	Temperature (°C)	Yield ^b (%)		
					E	OL	ONE
1	0.25	CH ₃ CN	1.3	40	2	6	25
2	0.5	CH ₃ CN	1.3	40	1	4	30 ^d
3	1.0	CH ₃ CN	1.3	40	2	7	43
4	0.5	CH ₃ CN	1.3	25	2	4	25
5	0.5	CH ₃ CN	1.3	60	0	3	28
6	0.5	CH ₃ CN	1.3	70	1	5	25
7	2.0	CH ₃ CN/CH ₂ Cl ₂ (1:1)	2.6	40	1	4	40
8	2.0	CH ₃ CN	2.6	60	1	2	35
9	0.5	CH ₃ CN	2.6	60	2	6	28
10 ^c	2.0	Ethanol	2.6	60	2	6	15
11	0.5	Toluene	1.3	40	4	5	14
12	0.5	Ethyl acetate	1.3	40	1	3	18
13	0.5	THF	1.3	40	2	11	2
14	0.5	Acetone	1.3	40	1	4	22

^a Reaction conditions: 4 mL of 0.125 M cyclohexene in CH₃CN, TBHP in CH₂Cl₂ (3.5 M), 3 h.

^b Yield (%): mole of products/initial moles of cyclohexene.

^c 24 h.

^d 38% at 6 h and 57% at 24 h. E: cyclohexene oxide, OL: 2-cyclohexen-1-ol, ONE: 2-cyclohexen-1-one.

2, entry 13). The use of dichloromethane as co-solvent favored 2-cyclohexen-1-one yield (Table 2, entry 7); this effect has been associated with its noncoordinating nature.^{17,18} When the catalyst amount was increased (Table 2, entries 1–3), 2-cyclohexen-1-one yield increased probably due to an increase of the amount of active species. It was found that the ketone yield did not depend appreciably on temperature (Table 2, entries 2, 4–6); however, there is a trend to decrease at high temperatures probably because of oxidant decomposition.

According to the UV–vis spectra (Fig. 2a) dimeric species are present in fresh catalyst. Although traditionally dimeric μ -oxo species had been considered as catalytically inactive forms,¹⁸ our catalyst was active for the allylic oxidation of cyclohexene. Also, a dimeric iron phthalocyanine catalyst was more active and selective than the monomeric one in the liquid phase oxidation of 2-methylnaphthalene and 2,3,6-trimethylphenol with TBHP over FePcS–MCM-41 and FePcS–SiO₂ catalysts.^{2,7}

After reaction, the presence of monomeric species in FePcS–SiO₂ was evidenced⁷ by its green color and the appearance of a UV–vis band at 683 nm (Fig. 2b). No catalyst activity was observed over reused FePcS–SiO₂ suggesting catalyst deactivation through the formation of monomeric species. Additionally, by thermogravimetric analyses total 6.3–7.2 wt % weight lost in used cata-

lyst samples between 100 °C and 800 °C may be linked to entrapped organic species from the reaction mixture not removed by catalyst washing. This is confirmed by FTIR since new bands around 1640 cm⁻¹, 2960 cm⁻¹ and 2928 cm⁻¹ due to the presence of C–H bands in saturated chains are observed in Figure 3c.¹⁹

In summary, the main product of the allylic oxidation of cyclohexene with TBHP over FePcS–SiO₂ when acetonitrile, acetone, and ethyl acetate are used as solvents is the allylic ketone, 2-cyclohexen-1-one. Under the reaction conditions of this study, μ -oxo dimeric species seem to be the active species. The extent of catalyst deactivation is currently underway in our laboratories.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.06.137.

References and notes

1. Sehlotho, N.; Nyokong, T. *J. Mol. Catal. A* **2002**, *179*, 113.
2. Sorokin, A. B.; Tuel, A. *Catal. Today* **2000**, *57*, 45.
3. Parton, R. E.; Peere, G. J.; Neys, P. E.; Jacobs, P. A.; Claessens, R.; Baron, G. V. *J. Mol. Catal. A* **1996**, *113*, 445.
4. Parton, R. E.; Neys, P. E.; Jacobs, P. A.; Sosa, R. C.; Rouxhet, P. G. *J. Catal.* **1996**, *164*, 341.
5. Sorokin, A. B.; Mangematin, S.; Pergrale, C. *J. Mol. Catal. A* **2002**, *182–183*, 267.
6. Kasuga, K.; Tsubai, K.; Handa, M.; Sugimori, T.; Sagabe, K. *Inorg. Chem. Commun.* **1999**, *2*, 507.
7. Sorokin, A. B.; Tuel, A. *New J. Chem.* **1999**, *23*, 473.
8. Vinod, M. P.; Das, T. Kr.; Chandwadkar, A. J.; Vijayamohanan, K.; Chandwadkar, J. G. *Mater. Chem. Phys.* **1999**, *58*, 37.
9. Niño-Gómez, M. E. PhD. Thesis, Universidad Industrial de Santander, 2002.
10. Chong, A. S. M.; Zhao, X. S.; Kustedjo, A. T.; Qiao, S. Z. *Micropor. Mesopor. Mater.* **2004**, *72*, 33.
11. Liu, X.; Chang, F.; Xu, L.; Yang, Y.; Tiang, P.; Qu, Z. *Micropor. Mesopor. Mater.* **2005**, *79*, 269.
12. Zhang, X.; Zhang, Y.; Jiang, J. *Spectrochim. Acta A* **2004**, *60*, 2195.
13. Cilli, E. M.; Oliveira, E.; Marchetto, R.; Nakaie, C. R. *J. Org. Chem.* **1996**, *61*, 8992.
14. Malavolta, L.; Oliveira, E.; Cilli, E. M.; Nakaie, C. R. *Tetrahedron* **2002**, *58*, 4383.
15. Farzaneh, F.; Majidian, M.; Ghandi, M. *J. Mol. Catal. A* **1999**, *148*, 227.
16. Reichardt, C. *Solvent Effects in Organic Chemistry*; Verlag Chemie: New York, 1979; pp 270–272.
17. Salavati-Niasari, M.; Elzami, M. R.; Mansournia, M. R.; Hydarzadeh, S. *J. Mol. Catal. A* **2004**, *221*, 169.
18. Salavati-Niasari, M.; Salemi, P.; Davar, F. *J. Mol. Catal. A* **2005**, *23*, 215.
19. Morrison, R. T.; Boyd, R. N. *Química Orgánica*; Pearson Educación: México, 1998; pp 608–609.