



Catalysis behavior of boehmite-supported iron tetraphenylporphyrins with nitro and methoxyl substituents for the aerobic oxidation of cyclohexane

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ABSTRACT

In this work, boehmite-supported iron tetraphenylporphyrins with *p*-substituted nitro and methoxyl groups on the phenyl ring were prepared and characterized by UV–vis, FT-IR and XRD techniques. The catalytic activity and efficiency of the two supported catalysts for the aerobic oxidation of cyclohexane were investigated and compared. From the experimental evidence we conclude that the differences in the catalysis behavior should be mainly attributed to the effect of the different *p*-substituents on the redox potential, and the differences in the promotion of activity by the boehmite support.

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1. Introduction

Metalloporphyrins are effective catalysts for both the hydroxylation of hydrocarbons and the epoxidation of olefins by a number of different oxidants [1,2]. This has attracted the attention of researchers from around the world. There has been much interest in the study of different metalloporphyrins and various oxygenation reactions of hydrocarbons under mild conditions [3–6]. It was found that these macrocyclic complexes, when used in homogeneous systems, lacked sufficient stability, making their recovery and reuse difficult. However, macrocyclic compounds immobilized on organic polymers [7–9] and inorganic materials [10–12] cannot only offer more efficient oxidation systems, but also have improved availability. Metalloporphyrins, either free or immobilized on inorganic supports, have been used as catalysts for the oxidation of hydrocarbons or olefins; with those substituted with electron-withdrawing groups being the most popular [13,14]. This has resulted in the availability of efficient and selective catalysts for the oxidation of hydrocarbons; with regard to tetraphenylporphyrins with strongly electron-withdrawing groups on the phenyl ring, this is due to the relatively higher positive oxidation and reduction potentials compared with those of normal tetraphenylporphyrins [15]. The matrix support can impose shape selectivity and pro-

mote a particular environmental favoring of the substrate for the active species [16]. In addition, the immobilization may prevent molecular aggregation or bimolecular self-destruction reactions, which lead to deactivation of catalytic metalloporphyrin species, and allow metalloporphyrins to be recycled easily. To our knowledge, there are few reports on the catalysis of metalloporphyrins substituted with electron-donating substituents for the oxidation of hydrocarbons and the epoxidation of alkenes, particularly regarding the differences in catalytic behavior between the two classes of metalloporphyrins (those with electron-withdrawing and electron-donating substituents on the benzene ring).

To explore the differences in performance of the catalysts having π electron-lacking and π electron-rich metalloporphyrins anchored on supports for the oxidation of cyclohexane with air, we report in this paper the immobilization of a second generation of iron porphyrins on boehmite (BM). These are 5,10,15,20-tetrakis(4-nitrophenyl)porphyrinate iron(III) [Fe TNPP] and 5,10,15,20-tetrakis(4-methoxyphenyl)porphyrinate iron(III) [Fe TMOPP]. In this work homogeneous and heterogeneous catalytic systems were investigated for the oxidation of cyclohexane using air as the oxidant, in the absence of co-reductants and solvents, to gain a better understanding of the reasons for the different behavior of the two classes of iron porphyrins.

2. Experimental

2.1. Materials

All reagents and solvents were of analytical grade and were obtained commercially. TMOPP, TNPP and their iron compounds,

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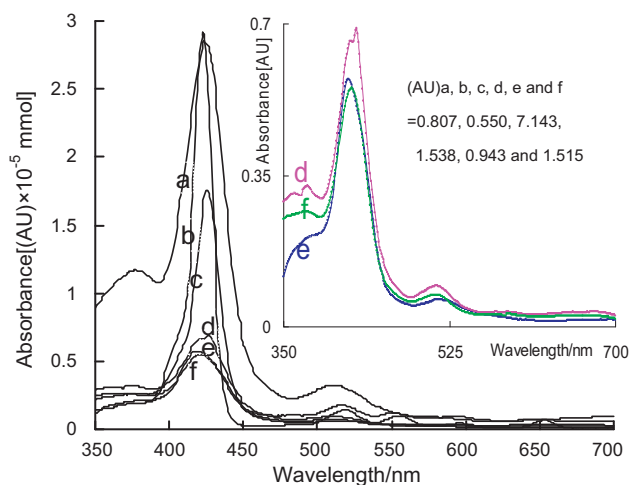


Fig. 1. UV-vis spectra at room temperature: benzene of Fe TMOPP (a), TMOPP (b) and TNPP(c), and in benzene suspension of Fe TMOPP/BM (e); dichloromethane of Fe TNPP(d) and in dichloromethane suspension of Fe TNPP/BM(f).

Fe TMOPP and Fe TNPP, were synthesized according to published procedures [17,18]. No impurities were found in the cyclohexane by GC analysis before use.

2.2. Preparation of boehmite-supported catalysts and measurement of the quantity of supported metalloporphyrins

Using a previously published procedure [19], the immobilization of Fe TMOPP and Fe TNPP on boehmite produced the two heterogeneous catalysts, Fe TMOPP/BM and Fe TNPP/BM, as described below.

Under stirring, 0.7 mol of NH₄OH diluted with distilled water was slowly added to 400 ml of a 0.5 M aluminum chloride solution. After holding the white aluminum hydroxide precipitate for 0.5 h, it was filtered and washed with distilled water. The precipitate was then added to 250 ml of ethanol in a three-neck flask with stirring at high speed for 0.5 h. Subsequently, 20 mg of Fe TMOPP (or Fe TNPP) dissolved in chloroform was slowly added to the suspension, and the mixture was heated to 60 °C with rapid stirring for 6 h. The suspension was filtered and washed with bulk distilled water and the cake was dried at 0.10 MPa and 170 °C for 6 h. The supported catalysts, Fe TMOPP/BM and Fe TNPP/BM, were thus obtained. The amounts of iron porphyrin supported per gram of boehmite were 1.84×10^{-6} mol and 1.72×10^{-6} mol, respectively, as determined by UV-vis spectrophotometry [20].

2.3. Characterization of the heterogeneous catalysts

UV-vis and FT-IR spectra of the two heterogeneous catalysts, Fe TMOPP/BM and Fe TNPP/BM, were obtained by UV-vis spectrophotometry, with a scan range of 280–850 nm and with a Perkin Elmer model 783 IR spectrophotometer in the range 4000–400 cm⁻¹ at a resolution of 2 cm⁻¹, respectively, using methods similar to those published [21,22]. The electronic spectra of the Fe TMOPP/BM and Fe TNPP/BM were measured as a benzene suspension in a quartz vessel. The UV-vis spectra of Fe TMOPP/BM or Fe TNPP/BM were compared with those of Fe TMOPP or Fe TNPP and similarly the corresponding UV-vis spectra of TMOPP or TNPP were compared with each other in the region 350–700 nm (Fig. 1). The benzene extraction from the superfine powder of the two heterogeneous catalysts was measured using UV-vis spectrophotometry (Fig. 1a and d). The electronic spectrum for the recovered Fe TMOPP/BM or Fe TNPP/BM, was the same as that of Fe TMOPP/BM or Fe TNPP/BM (Fig. 1e and f).

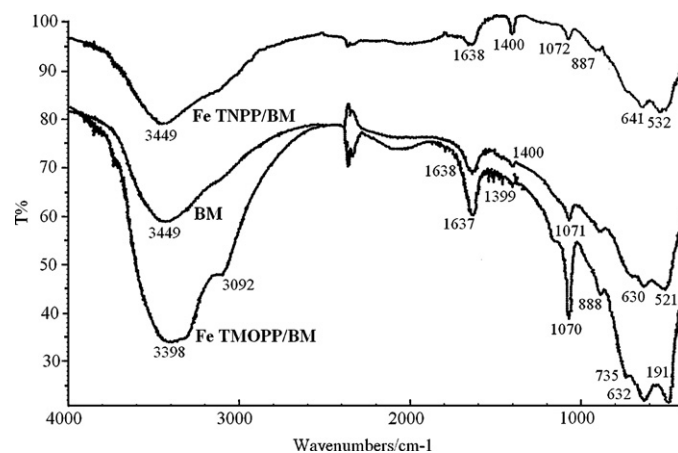


Fig. 2. FT-IR spectra of boehmite, iron tetra (*p*-nitrophenyl) porphyrin and iron tetra (*p*-methoxyphenyl) porphyrin supported on boehmite with an effective frequency range of 4000–400 cm⁻¹.

Dry BM, Fe TMOPP/BM and Fe TNPP/BM samples were ground into fine powders, mixed with KBr and pressed into thin pellets. These were placed in the sample holder of the spectrometer to record their spectra, with the results shown in Fig. 2.

X-ray diffraction (XRD) patterns for powder samples of BM, Fe TMOPP/BM and Fe TNPP/BM were collected on a Rigaku D/MAX RINT 2500 X-ray diffractometer with Cu K α radiation. Scans were performed from (2θ) 15° to 70° at a rate of 5° min⁻¹. The XRD patterns are presented in Fig. 3.

2.4. Cyclohexane oxidation catalyzed by the catalysts

Except where indicated, all cyclohexane oxidations were performed according to the following procedures.

Into a 250 ml autoclave reactor were added a measured amount of the catalysts (containing 1.1×10^{-6} mol of iron porphyrins) and 200 ml of cyclohexane. The mixture was stirred and heated to 145 °C. Afterwards, air was continuously pumped into the reaction system and the pressure was maintained at 0.9 MPa. The flow of air was measured with a rotameter and the oxygen concentration of the tail gas was determined with a CYS-1 digital oxygen detector. Samples of the reaction mixture were identified by GC-MS and were quantified by GC using chlorobenzene as the internal standard [23]. After the oxidation was terminated, i.e., when the reduction of oxygen content in the tail gases ceased, the supported catalyst was recovered by simple separation from the reaction mixture, was followed by washing with ethanol and air-drying, then used in subsequent cyclohexane oxidation reactions.

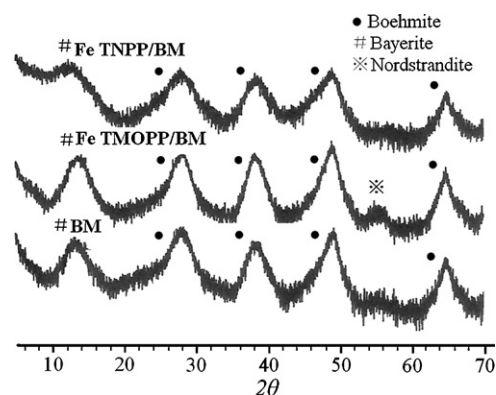


Fig. 3. XRD patterns of boehmite (BM), Fe TNPP/BM and Fe TMOPP/BM, respectively.

3. Results and discussion

3.1. Characterization of the catalysts

Nano-boehmite is an inorganic support with high surface energy and can be prepared easily [24]. In addition, it possesses an oxygen atom acting as an electron pair donor, thus providing an opportunity of coordination to the iron ion of the iron porphyrins. Consequently, the stably supported iron porphyrins on boehmite performed extremely well. In the immobilization procedure, all iron porphyrins were completely transferred to the BM gel and only a very small amount could be spectrometrically detected in solution by UV–vis analyses. The light grey solid materials obtained indicate the presence of iron porphyrins on the boehmite. Furthermore, Fig. 1 shows the different UV–vis spectra for the *p*-nitro- and methoxyl-substituted meso-tetraphenylporphines, the corresponding iron porphyrins and the boehmite-supported iron complexes. As far as the spectra for Fe TMOPP/BM and Fe TMOPP are concerned, there are two main peaks for the two catalysts present, at about 422 nm (Soret peak) and 512 nm (Q band). Similarly, the spectra for Fe TNPP/BM and Fe TNPP show main peaks at about 421 nm (Soret peak) and 511 nm (Q band), indicating that the porphyrin ring had not been modified during the anchoring procedure but was firmly anchored on the boehmite. Of course, there were some very weak peaks present at 550–700 nm for the unsupported iron porphyrins. The very weak peaks present at 569 nm, 661 nm and 697 nm for Fe TMOPP disappear after anchoring the iron porphyrin on BM. Although very weak peaks for Fe TNPP and the corresponding supported complex appear at 587 nm and 681 nm, and 588 nm and 672 nm, respectively, the former peaks are stronger than those of the latter. Therefore, we suggest that the disappearance or the weakening of these peaks all indicate the iron porphyrins to be well-anchored on boehmite, and moreover the data show Fe TMOPP to be more firmly anchored on BM because it has more π electrons on the porphyrin ring than Fe TNPP. The surplus or scarcity of π electrons directly relates to the stability of the iron porphyrin in an oxidation system. Fig. 1 also gives the spectra for the free bases, namely substituted tetraphenylporphyrins. The peaks of TMOPP appear at 422 nm (Soret peak), 518 nm, 554 nm, 596 nm and 653 nm (four Q bands), and the bands of TNPP are present at 426 nm (Soret band), 516 nm, 552 nm, 591 nm and 648 nm (four Q peaks). It is interesting that, comparing the UV–vis spectra of TNPP with those of TMOPP, the Soret peak wavelength for TNPP is slightly red shifted, while the wavelength of the corresponding Q bands are blue shifted. This is almost in accordance with a previous explanation of these modest wavelength shifts [25]. Studies of the intricate relationships between the redox potential, the molecular stability and the UV–vis spectra of the free bases and their metal complexes [15,25–27], imply that the more electron-donating groups substituted on a phenyl-substituted or an un-substituted conjugated porphine ring are present, the more negative the redox potentials of the free bases are. Consequently, these are not stable and easily oxidized by various oxidants, while the O_2 activating power of the corresponding metal complexes is weaker. Conversely, the more the electron-withdrawing groups are substituted on the conjugate ring, the more positive are the redox potentials for the free bases. These are then difficult to oxidize by various oxidants and are stable, while the power of activating O_2 for the corresponding metal complexes is stronger. The redoxidation of the conjugate ring and the corresponding metalloporphyrins can both occur in reaction conditions reported elsewhere [15] and in the practical oxidation of cyclohexane using our reaction conditions.

The FT-IR spectra (see Fig. 2) show the stretching vibration of OH for boehmite to be a very strong and broad band centered at 3449 cm^{-1} , for Fe TNPP/BM at 3449 cm^{-1} and for Fe TMOPP/BM at

3398 cm^{-1} . This also has a shoulder band at 3092 cm^{-1} , the presence of which implies that Fe TMOPP/BM was better crystallized than Fe TNPP/BM and BM [28]. This effect can also be monitored by the increase in the relative intensity of the IR bands at 1070 cm^{-1} . We suggest that the peak at about 1637 cm^{-1} may be the characteristic peak for bayerite, while the peak at about 1400 cm^{-1} is the deformation vibration of OH for boehmite, similar to the report in Ref. [29]. There still is a relatively strong peak at 888 cm^{-1} for the Fe TMOPP/BM compared with a weak peak at 887 cm^{-1} for the Fe TNPP/BM, but no corresponding peak is present for the BM shown in Fig. 2. This implies that the iron porphyrin was anchored on BM, with coordination bonds between them, i.e. Al–O–Fe, which would strengthen the stretching vibration frequency of the Al–O bond. In view of the relative intensity of the IR band, the coordination bonds in the Fe TMOPP/BM appear to be slightly stronger than those in Fe TNPP/BM. Besides, there were another two peaks at 630 cm^{-1} and 521 cm^{-1} for the mixture phase of BM; these are assigned to stretching vibrations of the Al–O bond, which generally appear as a broad band in the wave number range $750\text{--}480\text{ cm}^{-1}$ [30]. After the iron porphyrins were anchored on BM, the stretching vibrations of the Al–OFe bond for the Fe TMOPP/BM or the Fe TNPP/BM are, respectively, blue-shifted to 735 cm^{-1} and 632 cm^{-1} or to 641 cm^{-1} and 532 cm^{-1} , respectively. This indicates that the Fe TMOPPs are more strongly anchored on the support, due to the coordination of the rich π electrons on the TMOPP ring to the empty orbit of the Al ion in BM.

The XRD spectra exhibited broad peaks characteristic of the boehmite phase (see Fig. 3), which probably included a small quantity of the bayerite phase. These phenomena are similar to those observed in an earlier report [31]. It is interesting to note that when the iron porphyrins were anchored on the boehmite, compared to the 5 peaks for BM, the XRD spectra for Fe TMOPP/BM showed 5 slightly sharp peaks, while the XRD spectra for Fe TNPP/BM showed the 5 slightly blunt peaks. This indicates that the Fe TMOPP/BM was well-crystallized, as described above. Consequently, Fe TMOPP is more strongly adsorbed by BM than Fe TNPP.

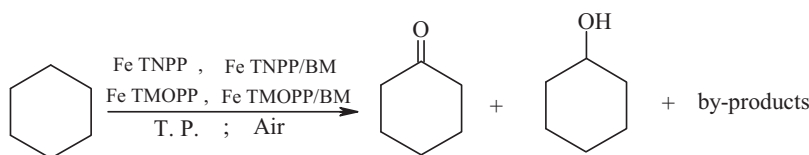
3.2. Catalysis of cyclohexane oxidation over the four catalysts

We have investigated the aerobic oxidation of cyclohexane over the four catalysts and BM, without the addition of any reductant or solvent. We found that the first four catalysts could selectively catalyze the aerobic oxidation of cyclohexane to cyclohexanone and cyclohexanol under our reaction conditions. However, the support, BM, could not. The catalytic aerobic oxidation of cyclohexane is described in Scheme 1.

The main oxidation products were cyclohexanone and cyclohexanol, with the by-products cyclohexyl hydrogen peroxide, hexanedioic acid and esters, as confirmed by GC–MS analysis.

Fig. 4 shows the changes in mole percent of the main products with reaction time for cyclohexane oxidation over Fe TMOPP and Fe TNPP, respectively. Obviously, the latter has stronger catalytic activity to convert cyclohexane to main products than the former, especially in the conversion of cyclohexane to cyclohexanone. The reason is that Fe TNPP shows stronger activation of O_2 , just as described above. In spite of having better catalytic activity and stability, Fe TNPP still cannot avoid the destruction of its molecular structure by O_2 . This situation is the same as for Fe TMOPP used in a homogenous oxidation system. The two catalysts are all exhausted in a single use.

The immobilization of metalloporphyrins on BM is a very good method for the maintenance and promotion of their catalytic activity for the oxidation of hydrocarbons. Fig. 5 presents the changes in mole percent of the main products with reaction time for cyclohexane oxidation catalyzed by Fe TMOPP/BM and Fe TNPP/BM,



Scheme 1. The cyclohexane oxidation catalyzed by the given catalysts with air.

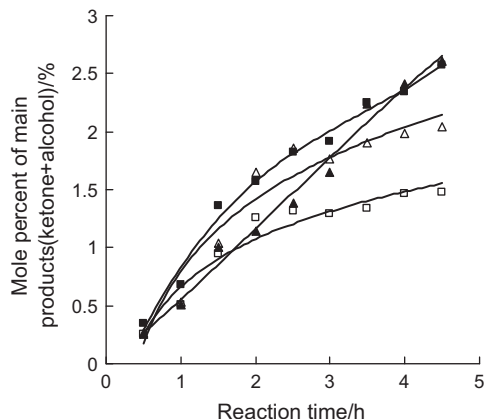


Fig. 4. Changes in mole percent of main products with reaction time for cyclohexane oxidation over Fe TMOPP(□) ketone; (△) alcohol) and Fe TNPP(■) ketone; (▲) alcohol). Reaction conditions: catalysts: 1.1×10^{-6} mol of iron porphyrins, 200 ml cyclohexane, 145 °C, 0.9 MPa, 0.020 m³/h airflow.

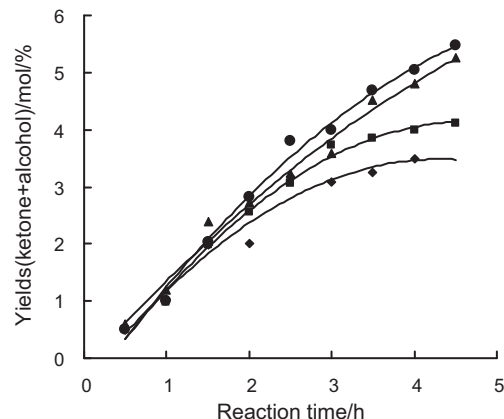


Fig. 6. Changes in molar yields of products (ketone + alcohol) with reaction time for cyclohexane oxidation over Fe TMOPP(□), Fe TNPP(▲), Fe TMOPP/BM(■) and Fe TNPP/BM(●). Reaction conditions: see Figs. 4 and 5.

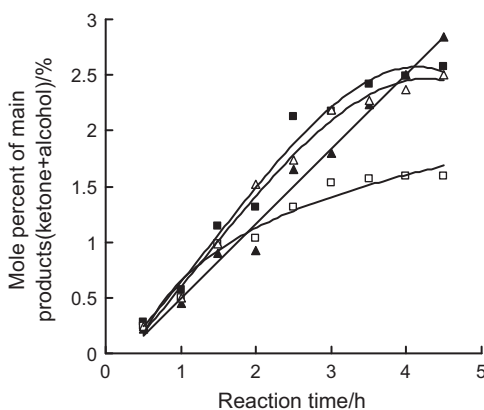


Fig. 5. Changes in mole percent of main products with reaction time for cyclohexane oxidation over Fe TMOPP/BM(□) ketone; (△) alcohol) and Fe TNPP/BM(■) ketone; (▲) alcohol). Reaction conditions: catalysts: containing 1.1×10^{-6} mol of iron porphyrins, 200 ml cyclohexane, 145 °C, 0.9 MPa, 0.020 m³/h airflow.

respectively. Clearly, the BM-supported catalysts show at least as good a catalytic performance compared with the corresponding unsupported catalysts. For instance, the BM-anchored Fe TNPP has a better performance for activating molecular oxygen than the BM-anchored Fe TMOPP. In addition, the conversion of cyclohexane to ketone for the Fe TNPP/BM catalyst is quite exceptional.

Fig. 6 presents the catalytic efficiency, i.e. molar yields of the main products per hour, for the four catalysts, Fe TMOPP, Fe TNPP, Fe TMOPP/BM and Fe TNPP/BM, for cyclohexane oxidation. After 2 h reaction, their catalytic efficiencies are quite different. Although boehmite-supported metalloporphyrin can raise the catalytic efficiency of metal porphyrin to a certain extent, for example, Fe TMOPP/BM vs. Fe TMOPP and Fe TNPP/BM vs. Fe TNPP, the amount of increase is not greater than that provided by *p*-substitution of the tetraphenylporphyrin by a nitro or methoxyl group, for instance, Fe TNPP vs. Fe TMOPP and Fe TNPP/BM vs. Fe TMOPP/BM. The upward trends of production of the main products with reaction time for Fe TNPP and Fe TNPP/BM are stronger than those for Fe TMOPP and Fe TMOPP/BM. This again indicates that the nitro groups have a more important role in the change of the redox potential for the iron tetraphenylporphyrin than the methoxyl groups, which should be “more negative” so that Fe TNPP and Fe TNPP/BM easily bind and activate molecular oxygen.

Table 1

Data for catalytic efficiency for Fe TNPP, Fe TMOPP, reused Fe TNPP/BM and Fe TMOPP/BM.

Catalysts	Run conversion yields of K/A oil		Catalysts	Run conversion yields of K/A oil			
		(%)		(mol%)	(%)	(mol%)	
Fe TMOPP	1	4.1	3.6	Fe TNPP	1	6.0	5.3
Fe TMOPP/BM	1	4.4	4.1	Fe TNPP/BM	1	6.0	5.5
	2	4.1	4.0		2	5.7	5.3
	3	4.0	3.9		3	5.8	5.4
	4	4.1	4.2		4	5.6	5.2
	5	4.6	4.4		5	5.5	5.0
	6	4.5	4.6		6	5.3	4.8
	Average	4.3	4.2		Average	5.7	5.2

Reaction conditions: see Figs. 4 and 5.

3.3. Reuse of the two supported catalysts for cyclohexane oxidation

The catalytic efficiency of the four catalysts for aerobic oxidation of cyclohexane was investigated, with the results shown in Table 1, from which we learn that the Fe TNPP catalyst shows better conversion of cyclohexane to the main products and higher yield of K/A oil than Fe TMOPP. However, in our homogenous catalytic system, both catalysts suffer the same fate of exhaustion after the oxidation. In contrast, the two supported catalysts could be efficiently reused 5 times at least for the oxidation under our reaction conditions. Compared with the Fe TMOPP/BM catalyst, we find that the trend of losing its catalytic activity and efficiency is greater for Fe TNPP/BM. We suggest that the reason is probably coordination of fewer macrocyclic π electrons to the aluminum ions of BM and formation of weaker AlO–Fe bonds for the latter than the former, resulting in slow leaching of Fe TNPP from BM, according to the results of the UV–vis, IR spectra and XRD pattern analysis above.

4. Conclusions

In conclusion, the catalytic activity and efficiency of the boehmite supported *p*-substituted tetraphenylporphyrins with nitro and methoxyl groups for the aerobic oxidation of cyclohexane depend on the electron-withdrawing or -donating group substituted on the phenyl ring and the performance of the support. The substituents directly affect the density of macrocyclic π electrons, and then affect the redox potentials of the tetraphenylporphyrin and its iron complexes, as well as the immobilization of the iron porphyrins. In addition, it is probably very important that boehmite provides some special aluminum ions that prefer to accept π electrons from the metal porphyrins, and some special oxygen atoms that prefer to donate an electron pair to the central ion of the metal porphyrins. These would all promote the immobilization and stability of the iron *p*-substituted tetraphenylporphyrins and an increase of catalytic activity and efficiency for the supported catalysts. Considerable experimental data on this subject await further study.

Acknowledgments

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