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Heterogeneous Gif Oxidation of Cyclohexane Using Fe^{3+}-PicolinateComplex Encapsulated within Zeolites

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Abstract: A series of catalysts containing the Fe^{3+}-picolinate (Fe–PA) complex inside the micropores of zeolite Y and mordenite has been synthesized by treating pre–exchanged Fe^{3+} zeolites with a solution with picolinic acid in dichloromethane. The Fe^{3+}–content of the solids was purposely low to avoid the presence of uncomplexed, free Fe^{3+} ions that could decrease the selectivity of the catalysts. Formation of the Fe–PA complex was ascertained by diffuse–reflectance UV–vis (characteristic absorption at 340 nm), FT–IR (vibrations at 1705 and 1480 cm^{-1}) and luminescence (emission at 540 nm) spectroscopies. These solids have been found to act as heterogeneous catalysts for the oxidation of cyclohexane by H_2O_2 with a similar selectivity to that reported in the literature as much higher conversion for the same complex in solution. The beneficial influence of a high PA/Fe^{3+} ratio in the solid reflects the need to use a large excess of PA to ensure the absence of uncomplexed Fe^{3+} ions. In addition, mordenite (channels, 0.74 nm) was found more efficient(93% selectivity at 49.1% of the maximum conversion) as a support than the more open Y zeolite (spherical cavities, 1.3 nm diameter). © 1999 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Oxidation of alkanes to the corresponding alkanols and alkanones constitutes one of the most important reactions from a fundamental and applied point of view.[1] In an extensive series of articles, Barton and co–workers have developed and optimized different catalytic systems, commonly known as Gif systems, to perform the oxidation of alkanes using hydrogen peroxide or organic hydroperoxides.[2-6] Thus, the complex of Fe(III) with picolinic acid (PA) working in a mixture of acetonitrile-pyridine as solvent and hydrogen peroxide as oxidizing reagent has been found to be one of the most efficient systems to effect the oxidation of simple aliphatic alkanes.[7] All the different Gif varieties studied so far have in common that they operate in homogeneous solution.

Heterogenization of an homogeneous catalyst by supporting it on or within an inorganic support is a general strategy to improve the efficiency of the process allowing easy separation of the reaction mixture, provided that the activity and selectivity of the catalyst are maintained after incorporation in the support.[8] In the present work, we have carried out the (ship-in-a-bottle) synthesis of the Fe(III)–picolinate (Fe-PA) complex inside the micropores of large pore sized zeolites Y and mordenite. The resulting embedded complex exhibits an activity for cyclohexane oxidation comparable to that reported by Barton for the same complex in solution.[7] Furthermore, the activity and selectivity of the Fe-PA complex is clearly modulated by the characteristics of the zeolite host.

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Related to our work is the use of Fe^{3+}–exchanged Y zeolite as heterogeneous catalyst for the oxidation of cyclohexane reported by Herron in the 80s.[9] More recently, a vanadyl picolinate complex has been prepared inside Y zeolite and used as catalyst for hydrocarbon oxidation.[10] In this case working under strictly anhydrous conditions (dried solvents and anhydrous urea-hydrogen peroxide adduct) the reported cyclohexane oxidation selectivity was around 30 %. In addition, silica gel-supported iron oxides[11] has also been used for cyclohexane oxidation with low selectivity.

RESULTS AND DISCUSSION

Preparation and Characterization of Fe^{3+}-PA complex incorporated inside zeolites.

Fe^{3+}-PA complex was prepared inside the zeolite micropores by a stepwise assembly procedure consisting of the chelation of the ligand to previously exchanged Fe^{3+}-zeolites.

For the present work, two large pore sized zeolites differing in the chemical composition and the geometry of the voids, namely Y and mordenite zeolites, were used. Zeolite Y encompasses almost spherical large cavities of 1.3 nm of diameter interconnected tetrahedrally through smaller windows of 0.74 nm.[12] In addition, the Si/Al ratio is among the lowest possible for a zeolite. In contrast, the structure of mordenite is formed by an array of parallel channels of 0.74 nm of diameter[12] and the Si/Al ratio is comparatively higher. The remarkable difference between these two zeolites in terms of the Si/Al ratio (that determines the number of counter–cations present within the pores, higher for Y zeolite, see Table 1) and the dimensions and polarity of the reaction cavities where the Fe-PA complex would be hosted provide us with the opportunity to achieve a certain degree of control on the activity and selectivity of the embedded Fe–PA complex as oxidizing catalyst.

Thus, starting from the commercial Na^+-form of the Y and mordenite zeolites, Fe^{3+} was introduced by ion exchange from diluted $Fe(NO_3)_3$ aqueous solutions. Before the ion exchange the initial pH of the solution was adjusted to 3.0 to avoid the presence of undesired $Fe(OH)^{2+}$ and $Fe(OH)_2^+$ hydroxy species that would make uncertain the nature of the ions introduced by exchange and would interfere in the subsequent formation of the complex.[13] The percentage of Fe^{3+} exchange was purposely kept low to minimize the population of free Fe^{3+} that could be present in the solid. In view of the reported activity of Fe^{3+}–Y zeolite (10-15 % selectivity for alkane oxidation)[9] and the homogeneous Fe–PA complex (total selectivity at 35 % H_2O_2 conversion)[2] it was anticipated that residual, free Fe^{3+} would lower the selectivity of the solid towards cyclohexane oxidation. Again to favor the complexation of Fe^{3+}, some of the samples contain a large excess of PA, much higher than the Fe^{3+}–PA stoichiometric value used to form the complex in solution.[14,7] The composition of the samples prepared in the present work is summarized in Table 1.

Formation of the Fe-PA complex inside zeolites was confirmed by comparing the FT-IR spectra of the self-supported wafers of zeolite Y/PA sample (no Fe^{3+}) with those of the Fe-zeolite/PA samples (See Figure 1A). The excess of PA in the wafers could be removed by degassing the sample at 100 °C under 10^{-2} Pa for 1 h. Two new bands at 1705 and 1480 cm^{-1} not present for zeolite/PA (spectrum a) clearly appears in the FT-IR spectrum of Fe-zeolite/PA (plots b and c, Figure 1A). The 1705 cm^{-1} band can be safely assigned to the C=O stretching vibration of the PA carboxylate group co-ordinated to the electron withdrawing Fe^{3+} ions. On the other hand, the band appearing at 1480 cm^{-1} can also be taken as a spectroscopic evidence for the formation of the Fe-PA complex based on related IR data for Lewis adducts of pyridines inside zeolites. These studies have shown a band around 1450 cm^{-1} as the most characteristic peak for these adducts. In fact pyridines are routinely used as probe molecules in spectroscopic characterization tests due to the presence of specific IR bands to distinguish between Brönsted and Lewis sites.[15]

Faujasite Mordenite

Chart 1. Geometry of the internal micropores of the two zeolites used as solid supports in the present work. In the case of faujasite the three known locations for countercations in the structure have been indicated.

Table. 1. Nomenclature and analytical data of the zeolites used in this work.

Zeolite	Unit Cell Composition
FeY/PA-1	$Fe_{0.4}Na_{51.8}Al_{53}Si_{139}O_{384}\cdot 141H_2O\cdot 0.1PA$
FeY/PA-2	$Fe_{0.3}Na_{52.1}Al_{53}Si_{139}O_{384}\cdot 142H_2O\cdot 0.4PA$
FeY/PA-3	$Fe_{0.4}Na_{51.8}Al_{53}Si_{139}O_{384}\cdot 141H_2O\cdot 3.1PA$
FeY/PA-4	$Fe_1Na_{49}Al_{53}Si_{139}O_{384}\cdot 141H_2O\cdot 14PA$
FeY/PA-5	$Fe_{0.4}Na_{51.8}Al_{53}Si_{139}O_{384}\cdot 141H_2O\cdot 21PA$
FeMor/PA	$Fe_{0.1}Na_{3.7}Al_4Si_{40}O_{96}\cdot 17H_2O\cdot 1.2PA$

Diffuse reflectance UV-Vis spectra for the Fe-zeolite/PA samples show a band at 340 nm (Figure 1B). This absorption band is characteristic of the Fe-PA complex and it is also observed in the transmission UV-Vis spectra of an aqueous solution of the Fe-PA complex (prepared by addition of PA to an aqueous solution of $Fe(NO_3)_3$), (Figure 1C). The variation in λ_{max} from 320 nm for aqueous Fe-PA complex to 340 nm for Fe-zeolite/PA can be explained as a reflection of the encapsulation of the Fe-PA complex inside zeolites.

Emission spectroscopy also provides a firm piece of evidence for the formation of the Fe-PA complex supported within the inorganic zeolite matrix. Thus, upon excitation at 320 nm an aqueous solution of the Fe-PA complex exhibits a broad emission band with λ_{max} at 440 nm. The excitation spectrum monitoring the intensity of light emitted at 440 nm coincides with the most characteristic absorption band of the Fe-PA complex in water (Figure 2). Importantly, none of the components of the complex, either hydrated Fe^{3+} ions [from $Fe(NO_3)_3$] or PA, show luminescence, proving that this 440 nm emission is a specific property of the complex. Analogous behavior was observed when emission and excitation spectra of the zeolite samples containing embedded Fe-PA complex were recorded (Figure 2). The main differences in the luminescence measurements between the samples in solution and those within zeolites is the shift in the λ_{max} of emission and excitation towards longer wavelengths and a significantly larger Stokes gap between excitation and emission energies. As can be anticipated taking into account the lower PA content (see Table 1) and the reduced micropore dimensions of mordenite that imposes steric restrictions to the formation of the complex, the intensity of the emission for Fe–Mor/PA is significantly weaker than that recorded for the Fe–Y/PA samples.

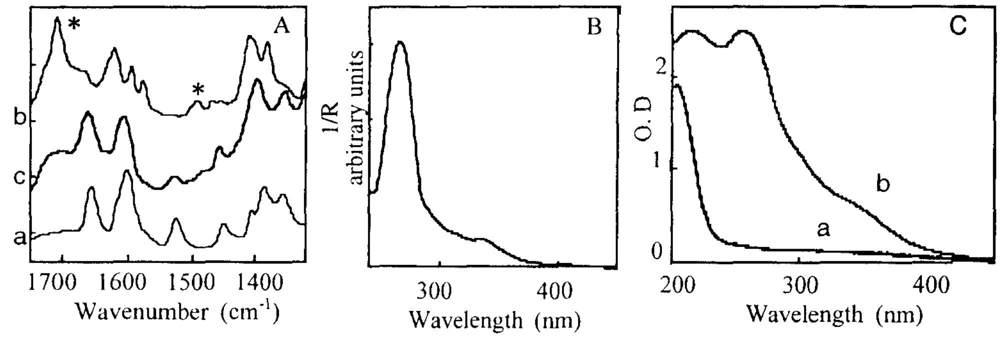


Figure 1. A: Aromatic region of the FT-IR spectra of (a) Y/PA, (b) FeY/PA-5 (after outgassing the sample at 200 °C under 10^{-2} Pa for 1 h) and (c) FeY/PA-5 (same sample as before without any pretreatment). The two most characteristic bands of the Fe-PA complex are indicated by asterisks. B: Diffuse reflectance (plotted as the inverse of the reflectance, R) UV/Vis spectrum of FeMor/PA. C: Transmission UV/Vis spectra of a solution of a 6 x 10^{-5} M aqueous solution of $Fe(NO_3)_3$ before (a) and after (b) adding PA (3 x 10^{-4} M).

Embedded Fe-PA complex as Heterogeneous Oxidation Catalyst.

When taken together, the spectroscopic information combined with the analytical data clearly proves that some Fe-PA complex has been assembled inside the zeolite. However, the presence of an excess of PA is evidenced by the low Fe–to–PA molar ratio and by IR spectroscopy (see Figure 1A). This large excess of ligand was purposely adsorbed on the zeolites, to avoid the presence of a residual population of uncomplexed Fe^{3+} ions. The reason for this is that while PA is not expected to have any negative influence on the performance of the catalyst (in fact the reaction is carried out using pyridine as co–solvent), it is obvious, comparing the reported catalytic activities of FeY and homogeneous Fe-PA complex that free or hydrated Fe^{3+} should decrease the selectivity of the catalyst. However, even for those samples containing the lowest Fe^{3+}/PA ratio the fact that a fraction of uncomplexed Fe^{3+} could still be present at certain sites of the zeolite cannot be ruled out. Particularly for faujasite Y zeolite there are two sites inside the hexagonal prism and sodalite (sites type I and II) where cations can be accommodated and solvated by the zeolite oxygens, but they cannot participate in the formation of Fe^{3+}-PA complexes due to steric constraints. Only those Fe^{3+} located inside the supercages (sites III) are available to interact with PA, forming the complex.

Since it is known that sites I and II are less prone to be exchanged,[16] the Fe^{3+}–ion exchange percentage was purposely maintained very low in the hope that the catalytic performance of the resulting material would be optimum.

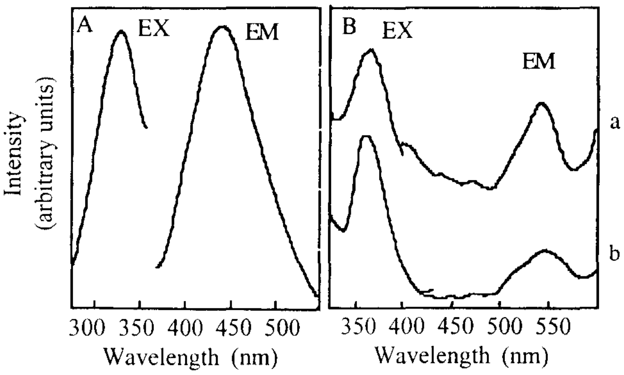
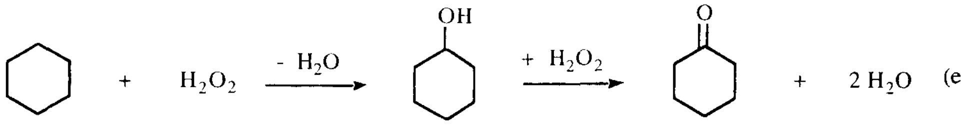


Figure 2. Excitation (EX) and Emission (EM) spectra of Fe^{3+}-PA complex in H_2O (A) and those recorded for FeY/PA-5 (curve a) and FeMor/PA (B, plot b).

The Fe-PA complex inside zeolites was used as heterogeneous catalyst in the oxidation of cyclohexane to cyclohexanol and cyclohexanone under Gif conditions, using a mixture of acetonitrile and pyridine as solvent and H_2O_2 as oxidant. The employed conditions in terms of ratios of reagents and solvents are directly comparable to those previously reported for the same process in the homogeneous phase.[7] In all cases the only products observed were cylohexanol and cyclohexanone, the latter always being the predominant reaction product. The results achieved are collected in Table 2. To calculate the selectivity of H_2O_2 towards oxidation it is assumed that according to eq.1 the formation of cyclohexanol and cyclohexanone consumes one and two equivalents of H_2O_2, respectively.



(eq. 1)

From the results shown in Table 2 it can be concluded that there is an influence of the Fe^{3+}/PA ratio of the catalyst and the nature of the zeolite host in the activity of the solid as oxidizing catalyst. Thus, increasing the amount of PA clearly improves the performance of the solid (runs 1 to 5). When this ratio is not sufficiently high other decomposition processes besides those leading to the formation of cyclohexanol and cyclohexanone are favored for H_2O_2. This fact seems to indicate that a large excess of PA is required to avoid the presence of uncomplexed Fe^{3+} that could react with H_2O_2 without leading to cyclohexane oxidation.

Importantly, the geometry of the internal voids of the zeolite plays also a role in the activity of the solid as catalyst. Thus, the highest cyclohexane conversion and H_2O_2 selectivity was achieved using the Fe/PA complex hosted within mordenite. The corresponding values (run 6, Table 2) compare favorably with those achieved by Barton and Lee in homogeneous phase under similar conditions whereby a quantitative yield at 30 % conversion was reported. Molecular modeling clearly shows that there is not enough room inside these channels to accommodate a Fe/PA complex with a stoichiometry of 1:2 and with a square planar configuration. This leads us to suggest that the stoichiometry of the complex inside mordenite is more likely to be 1:1, with the zeolite framework oxygens occupying other coordination positions around Fe^{3+}. Since multi–ligand complexation is known to be a stepwise equilibrium, it should be possible to impede higher ligand–to–metal ion stoichiometries by restricting the space available to the complex. Related precedents of a reduced stoichiometry for a Eu^{3+} complex inside the channels of mordenite have been reported in the literature.[17] It has to be noted that the activity of a complex as heterogeneous catalyst is not necessarily related to its stoichiometry, but rather to the electron density at the metal ion that determines the ability to adequately bind substrates and reagents.

Table 2. Results of the heterogeneous Gif oxidation at room temperature (except run 1, see footnote b) of cyclohexane (0.56 ml) (except run 7, see footnote c) in CH_3CN (7 ml)/pyridine (7 ml) catalyzed by zeolite (1.00 g) using H_2O_2 (0.15 ml, 30%) as oxidizing reagent after almost complete consumption of H_2O_2. The cycloalkane/H_2O_2 molar ratio is 4.

Run	Catalyst	Reaction Time (h)	MaximumCycloalkane Conversion [a] (%)	Selectivity[b] (%)		
				H_2O_2[c]	Cycloalkanol	Cycloalkanone
1[d]	FeY/PA-1	24	1.00	1.7	29.70	70.30
2	FeY/PA-2	24	7.31	13.7	12.22	87.78
3	FeY/PA-3	91	22.86	42	17.07	82.93
4	FeY/PA-4	121	23.82	45	11.68	88.32
5	FeY/PA-5	120	44.83	85	11.07	88.93
6	FeMor/PA	96	49.10	93	6.93	93.07
7[e]	FeMor/PA	118	0.02	0[f]	-	-

[a] Given the four-fold molar excess of cycloalkane respect to H_2O_2, the maximum possible cycloalkane conversion is 25% of the initial amount; [b] Moles of product divided by the moles of reacted cyclohexane; [c] Selectivity of H_2O_2 towards cycloalkane oxidation at total H_2O_2 conversion; [d] reaction temperature 100 °C; [e] adamantane as substrate; [f] The conversion of H_2O_2 was 45 %.

Furthermore, in agreement with the reduced dimensions of the reaction cavity surrounding the Fe–PA complex and a more restricted diffusion of reagents and products through the pores of mordenite, cyclohexane oxidation takes significantly longer using Fe-Mor/PA than the Fe-Y/PA samples (note the complete consumption of H_2O_2 at 24 h for entries 1 and 2). A representative time conversion plot is shown in Figure 3.

A point of final concern that has to be carefully addressed in heterogeneous catalysis when the active sites are supposedly embedded inside a solid support is the possibility that the observed activity could be partly or totally due to the leaching of some sites out of the solid into the solution. To rule out this possibility, the H_2O_2 oxidation of adamantane using Fe–Mor/PA as catalyst was attempted. It is known that adamantane is far more reactive than cyclohexane under the conditions of the Gif oxidation.[2] However, in spite of its intrinsic higher reactivity the relatively large molecular size of adamantane should preclude this molecule to diffuse inside the 0.74 nm voids of mordenite. Therefore, if the reaction takes place inside the micropores of the catalyst, adamantane oxidation should not occur, even for prolonged reaction times. This was in fact observed (see entry 7 in Table 2) and clearly proves that the catalytic process is taking place inside the zeolite pores.

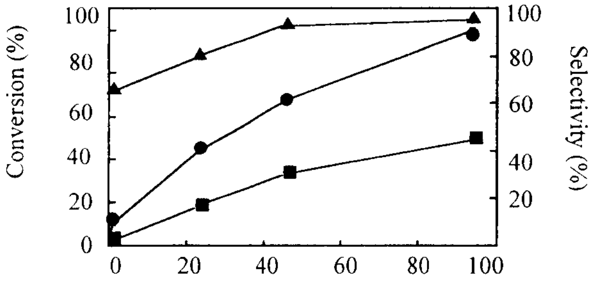


Figure 3. Time-conversion for the r.t. oxidation of cyclohexane (0.56 ml) by H_2O_2 (0.15 ml, 30 %) using FeMor/PA-1 (1 g) as catalyst: ■ percentage of cyclohexane with respect to the maximum stoichiometric yield (25%); • H_2O_2 conversion; ▲ selectivity of reacted H_2O_2 towards cyclohexanol+cyclohexanone (right axis).

In conclusion, by immobilizing the Fe^{3+}–PA complex inside the micropores of zeolites a heterogeneous Gif catalyst exhibiting similar activity and selectivity than those reported for homogeneous complex has been obtained. The main advantage of the zeolite encapsulated complex is the ease of separation from the reaction mixture by simple filtration of the solid. Although reuse of the encapsulated Fe^{3+}-PA complex could be possible, further studies are necessary to determine the deactivation profile of these solids and possible treatments to recover the initial catalytic activity.

EXPERIMENTAL

Preparation of Fe-Zeolite/PA Catalysts. NaY (Si/Al 2.6) and NaMor (Si/Al 10) were commercial samples (P.Q. Industries). Fe^{3+}-to-Na^+ ion exchange was carried out by stirring at room temperature for 5 h a suspension of the corresponding zeolite in its Na^+ form (10 g) in an aqueous solution of $Fe(NO_3)_3$ using a liquid-to-solid weight ratio of 10:1. The concentration of the aqueous solution of $Fe(NO_3)_3$ was 4.62 x 10^{-3} M and 4.95 x 10^{-4} M for zeolite Y and mordenite, respectively. The initial pH of the solution was adjusted to 3 by adding a few drops of concentrated HNO_3 After exchange the solid was filtered and dried at 100 °C for 2 h. A solution of picolinic acid (PA, 2.28 g and 0.48 g for zeolite Y and mordenite, respectively) in CH_2Cl_2 (80 ml) was added to the dry, partially-exchanged Fe-zeolite and the suspension stirred at reflux temperature for 5 h. Then the solid was filtered and washed with a

2 x 10^{-5} M solution of NaOH to remove adventitious Fe species from the zeolite external surface. The final Fe content was determined by quantitative atomic absorption spectroscopy after dissolving the solid in a mixture of HF/HNO_3. The loading of PA was measured by combustion analysis (C, N) (Neztch thermobalance operating under air stream using Kaolin as standard). The water content was determined by thermogravimetry. The main analytical data of the samples prepared were summarized in Table 1.

IR spectra of self-supported compressed pellets (10 mg) were carried out in a greaseless IR quartz cell fitted with CaF_2 windows using a Nicolet 710 FT-IR spectrophotometer. The IR spectra were recorded at room temperature after outgassing under reduced pressure (10^{-2} Pa) at increasing temperatures for periods of 1 h. Diffuse reflectance UV-Vis spectra were recorded with a Shimadzu UV-2101/3101 PC scanning spectrophotometer adapted with an integrating sphere and using $BaSO_4$ as reference Fluorescence spectra were recorded using an Edinburgh spectrofluorimeter with a front-face attachment for solids. Molecular modeling was performed at the semiempirical level using the Insight II program from Biosym and a Silicon Graphics workstation.

Heterogeneous Gif oxidation. Fe-zeolite/PA (1 g) is added to a mixture of cyclohexane (0.56 ml), H_2O_2 (0.15 ml, 30% vol), CH_3CN (5.5 ml) and pyridine (5.5 ml). The suspension was stirred at room temperature. The system was sealed to avoid cyclohexane losses by evaporation. The course of the reaction was periodically followed by GC (product distribution) and iodimetric titrations after filtration of the samples to separate the solid catalyst from the reaction mixture. Quantification of the reaction products was accomplished by GC using a 25 m capillary column of 5 % crosslinked phenylmethylsilicone and using naphthalene as internal standard. The temperature program followed in the runs was: 35 °C (3 min); 10 °C x min^{-1}; 140 °C.

The H_2O_2 plus hydroperoxide content of the samples was determined by titrating a solution which contains the sample (0.1–0.2 g), H_2SO_4 4N (10 ml) and KI (1 g), with a standard solution of $Na_2S_2O_3$ (0.01 M) using starch as indicator.

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REFERENCES AND NOTES

1. Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995,** *28*, 154-162.
2. Barton, D. H. R. *Tetrahedron* **1998,** *54*, 5805-5817.
3. Perkins, M. J. *Chem. Soc. Rev.* **1996,** *25*, 229-236.
4. Barton, D. H. R.; Hu, B. *Pure Appl. Chem.* **1997,** *69*, 1941-1950.
5. Barton, D. H. R. *Chem. Soc. Rev.* **1996,** *25*, 237-239.
6. Barton, D. H. R.; Doller, D. *Acc. Chem. Res.* **1992,** *25*, 504-512.
7. Barton, D. H. R.; Tingsheng, L. *Tetrahedron* **1998,** *54*, 1735-1744.
8. Weitkamp, J.; Karge, H. G.; Pfeifer, H.; Hölderich, W. Eds. Zeolites and Related Microporous Materials: State of the Art 1994; Elsevier: Amsterdam, 1994.
9. Herron, N. *New J. Chem.* **1989,** *13*, 761-766.
10. Kozlov, A.; Kozlova, A.; Asakura, K.; Iwasawa, Y. *J. Mol. Catal. A: Chem.* **1999,** *137*, 223-237.
11. Lee, K. W.; Kim, S. B.; Jun, K. W.; Shim, E. K. *New J. Chem.* **1993,** *17*, 409-411.
12. Meier, W. M.; Olson, D. H.; Baerlocher, C. *Zeolites* **1996,** *17*, 1-229.
13. Skoog, D. A.; West, D. M.; Holler, F. J. Fundamentals of Analytical Chemistry, Sixth Edition; Trans. Reverté: Barcelona.
14. The PA/Fe^{3+} molar ratio employed as Gif oxidation catalyst is 4.
15. Corma, A. *Chem. Rev.* **1995,** *95*, 559-614.
16. Breck, D. W. Zeolite Molecular Sieves: Structure, Chemistry and Use; John Wiley and Sons: New York, 1974.
17. Alvaro, M.; Fornés, V.; García, S.; García, H.; Scaiano, J. C. *J. Phys. Chem. B.* **1998,** *102*, 8744-8750.