Synthesis, characterization and catalytic epoxidation of styrene using molecular oxygen over "neat" and host–guest nanocomposite materials

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Abstract

The complexes of Fe(II) were synthesized with the azamacrocyclic ligands; [12]aneN$_4$: 1,4,7,10-tetraazacyclododecane-2,3,8,9-tetraone; [14]aneN$_4$: 1,4,8,11-tetraazacyclotetradecane-2,3,9,10-tetraone; Bzo$_2$[12]aneN$_4$: dibenzo-1,4,7,10-tetraazacyclododecane-2,3,8,9-tetraone and Bzo$_2$[14]aneN$_4$: dibenzo-1,4,8,11-tetraazacyclotetradecane-2,3,9,10-tetraone. Iron(II) complexes with azamacrocyclic ligand were entrapped in the nanocavity of zeolite-Y by a two-step process in the liquid phase: (i) adsorption of bis(diamine)iron(II); in the supercages of the zeolite, and (ii) in situ condensation of the iron(II) precursor complex with diethyloxalate. The new nanocomposite materials were characterized by several techniques: chemical analysis, spectroscopic methods (DRS, BET, FTIR and UV/vis). Analysis of the data indicated that the Fe(II) complexes were encapsulated in the nanodimensional pores of zeolite-Y and exhibited different from those of the free complexes, which can arise from distortions caused by steric effects due to the presence of sodium cations, or from interactions with the zeolite matrix. The encapsulated nanomaterials are active catalyst for the epoxidation of styrene using molecular oxygen as an oxidant. By comparing the performance of the heterogeneous system with the free complex in the oxidation of styrene using O$_2$, protection effect of the matrix over the active center was evidenced by a higher conversion and yield of products.
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1. Introduction

The term nanoporous materials have been used for those porous materials with pore diameters of less than 100 nm. Many kinds of crystallines and amorphous nanoporous materials such as framework silicates and metal oxides, zeolites, pillared clays, nanoporous silicon, carbon nanotubes and related porous carbons have been described lately in the literature [1].

Nanopores encapsulated metal complexes are mostly used as heterogeneous and redox catalysts in petroleum industry and in the production of chemicals for various types of shape-selective conversion and separation reactions [2]. They form the basis of new environment-friendly technologies, involving cheaper, more efficient and more environment-friendly ways for carrying out chemical reactions. Transition metal-modified nanoporous molecular sieves with aluminosilicate frameworks catalyse a wide variety of synthetically useful oxidative transformations with clean oxidants such as hydrogen peroxide or oxygen under relatively mild conditions with the advantage of facile recovering and recycling, if compared to homogeneous liquid phase catalyst, like sulfuric acid [3–7].

The encapsulation of iron is widely used to modify the original properties of porous catalyst hosts in nanoporous structures. Both the acidity and redox properties can be modified by inserting iron into supercage of zeolite. Iron-containing nanoporous catalysts have been attracted considerable attention due to their remarkable activity in the reduction of nitrous oxides, oxidation of cyclohexane, oxidation of benzene to phenol, and the selective oxidation of methane [8–10]. In this paper, we have reported the synthesis and characterization of iron(II) complexes of 12- and 14-membered tetraaza macrocyclic ligands; [12]aneN$_4$: 1,4,7,10-tetraazacyclododecane-2,3,8,9-tetraone; [14]aneN$_4$: 1,4,8,11-tetraazacyclotetradecane-2,3,9,10-tetraone; Bzo$_2$[12]aneN$_4$: dibenzo-1,4,7,10-tetraazacyclododecane-2,3,8,9-tetraone and Bzo$_2$[14]aneN$_4$: dibenzo-1,4,8,11-tetraazacyclotetra-

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[12]aneN$_4$ [14]aneN$_4$

Bzo$_2$[12]aneN$_4$ Bzo$_2$[14]aneN$_4$
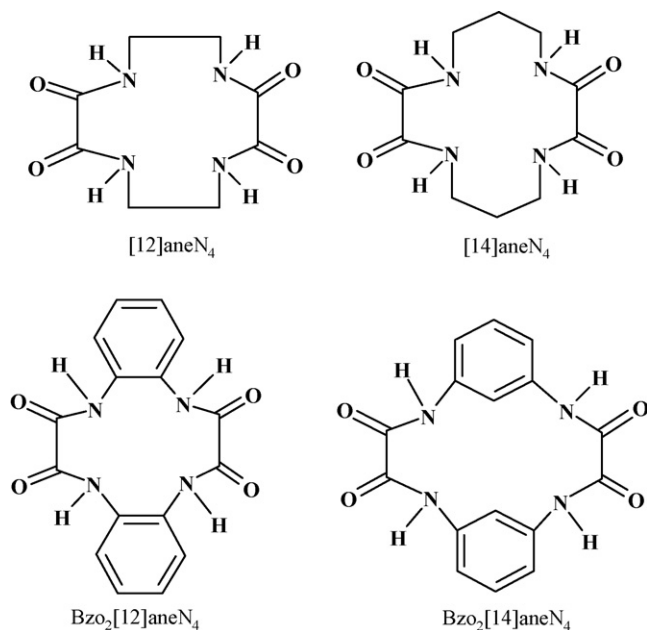
Scheme 1.

decane-2,3,9,10-tetraone; encapsulated within the nanopores of zeolite-Y by the one pot template condensation of diethyloxalate and diamine; [Fe([12]aneN$_4$)]$^{2+}$-NaY, [Fe([14]aneN$_4$)]$^{2+}$-NaY; [Fe(Bzo$_2$[12]aneN$_4$)]$^{2+}$-NaY; [Fe(Bzo$_2$[14]aneN$_4$)]$^{2+}$-NaY; shown in Schemes 1 and 2. Their catalytic activities have been tested for the epoxidation of styrene with molecular oxygen as oxygen donor.

2. Experimental

2.1. Materials and physical measurements

All the solvents were purchased from Merck (pro analysis) and were distilled and dried using molecular sieves (Linda 4 Å). Styrene was distilled under nitrogen and stored over molecular sieves (4 Å). NaY with the Si:Al ratio of 2.53 was purchased from Aldrich (Lot No. 67812). XRD patterns were recorded by a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu Kα radiation. Elemental analysis was obtained from Carlo ERBA Model EA 1108 analyzer. The iron contents of the samples were measured by Atomic Absorption Spectrophotometer (AAS-Perkin-Elmer 4100–1319) using a flame approach. After completely destroying the zeolitic framework with hot and concentrated HCl, sodium, aluminum and iron were analyzed by AAS and SiO$_2$ was determined by gravimetric analysis. The products were analyzed by GC-MS, using a Philips Pu 4400 Chromatograph (capillary column: DB5MS, 30 m), Varian 3400 Chromatograph (15 m capillary column of HP-5; FID) coupled with a QP Finnegan MAT INCOF 50, 70 eV. Diffuse reflectance spectra (DRS) were registered on a Shimadzu UV/3101 PC spectrophotometer the range 1500–200 nm, using MgO as reference. The stability of the supported catalyst was checked after the reaction by UV–vis and possible leaching of the complex was investigated by UV–vis in the reaction solution after filtration

of the encapsulated zeolite. Nitrogen adsorption measurements were performed at 77 K using a Coulter Omnisorb 100CX instrument. Micropore volumes were determined by the *t*-method; a "monolayer equivalent area" was calculated from the micropore volume [11,12].

2.2. Synthesis of azamacrocyclic ligand

Azamacrocyclic ligand ([12]aneN$_4$, [14]aneN$_4$, Bzo$_2$[12]-aneN$_4$ and Bzo$_2$[14]aneN$_4$) was prepared by following the procedures reported in Ref. [13]. The hot ethanolic solution (20 ml), of diethyloxalate (2.9228 g, 0.02 mol), and a hot ethanolic solution (20 ml) of diamine (0.02 mol); 1,2-diaminoethane (1.20 g), 1,3-diaminopropane (1.48 g), 1,2-diaminobenzene (2.16 g), 1,3-diaminobenzene (2.16 g); were mixed slowly with constant stirring. This mixture was refluxed for 7 h in the presence of few drops of concentrated hydrochloric acid. On cooling a solid precipitate was formed, which was filtered, washed with cold ethanol, and dried under vacuum over P$_4$O$_{10}$.

2.3. Synthesis of [Fe(azamac.)(CH$_3$CN)$_2$](PF$_6$)$_2$

Nitrogen was bubbled through methanol (150 ml) for 30 min and then iron powder (3.0 g, 0.053 mol, excess) was added. The stream of nitrogen was maintained throughout the following procedure. Anhydrous FeCl$_3$ (8.62 g, 0.053 mol) was added and the mixture was brought to gentle boil. SnCl$_2$·2H$_2$O (1.0 g, 0.004 mol) was added and the solution (now ∼0.08 M iron(II)) was allowed to cool. Under a blanket of nitrogen, the iron solution was filtered into a dropping funnel, and then added dropwise to the ligand solution (approximately 2 drop/S). Immediately after the start of the addition, dry potassium acetate (15.6 g, 0.16 mol) was added as a solid. Then nitrogen was bubbled through the solution for 30 min. The opaque blue reaction mixture was slowly warmed to about 35 °C over 8 h. After a total time of 12 h the solution was cooled to 10 °C. Acetonitrile (25 ml, 0.472 mol) was added, and the nitrogen atmosphere was no longer maintained. The resulting burgundy red mixture was filtered with suction and a yellow solid was discarded. A solution of NH$_4$PF$_6$ (10 g, 0.061 mol) in 100 ml of H$_2$O was added to the filtrate, causing the precipitation of a burgundy red solid. The product was collected immediately by suction filtration, washed with absolute ethanol until the filtrate became clear, then washed with diethyl ether, and dried under a stream of dry air: yield ≈ 30%.

2.4. Synthesis of Fe(II)-NaY

Ferrous ions (Fe^{2+}) were introduced into the NaY zeolite by an ion exchange in aqueous solution [14]. At first NaY was added to water and the pH value of the mixture was adjusted to 4.5 with diluted sulfuric acid, and then FeSO$_4$·7H$_2$O was added to the mixture under argon atmosphere. After stirring for 4 h to allow the ion exchange between zeolite and Fe^{+2} at room temperature in the argon atmosphere, the sample was recovered by filtration, followed by washing with diluted sulfuric acid and then with deionized water. Finally, the solid sample was dried
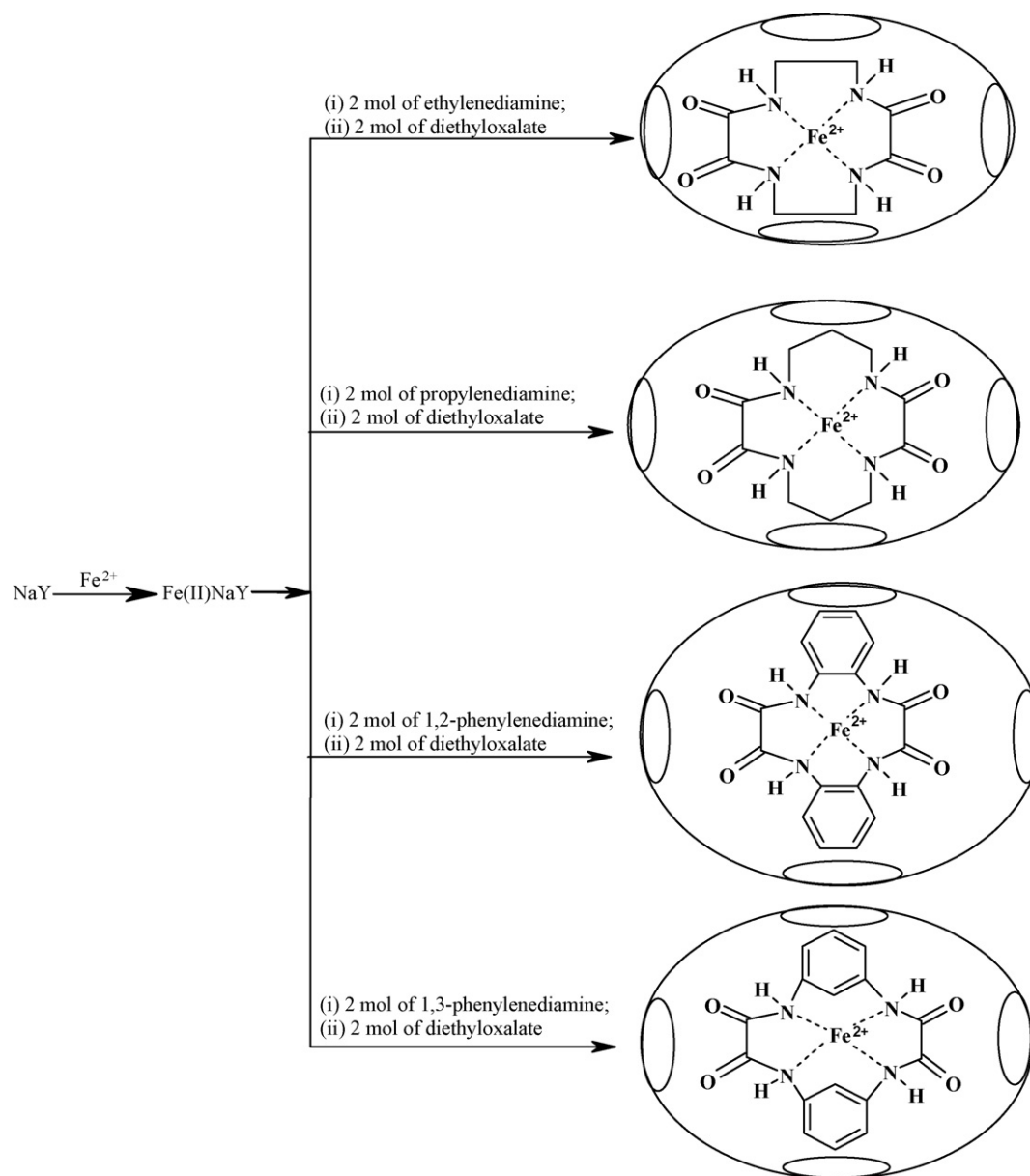
Scheme 2.

at 393 K in vacuum for 24 h. The dried powdery samples were used as catalysts, unless otherwise stated.

2.5. Preparation of [Fe(azamac.)]$^{2+}$-NaY

Nitrogen was bubbled through ethanol (100 ml) for 30 min and then Fe(II)-NaY (4 g) was added. The stream of nitrogen was maintained throughout the following procedure. Twofold diamine (in 25 ml of ethanol) was added to a stirred ethanol solution of Fe(II)-NaY and then refluxed for 8 h. The colored solid samples obtained were denoted as [Fe(N-N)$_2$]$^{2+}$-NaY where (N-N) represents the ligands; 1,2-diaminoethane, 1,3-diaminopropane, 1,2-diaminobenzene, 1,3-diaminobenzene; was collected by filtration, washed with cold ethanol (20 ml) and then dried at 60 °C under vacuum for 8 h. [Fe(N-N)$_2$]$^{2+}$-NaY (2 g) was refluxed with a threefold excess of diethyloxalate in

C$_2$H$_5$OH. After a 3 h reflux, the solid samples, [Fe(azamac.)]$^{2+}$-NaY, were filtered and the resulting zeolites were purified by Soxhlet extraction with *N,N*-dimethylformamide (for 8 h) and then with ethanol (for 4 h) to remove excess diethyloxalate and any iron(II) complexes adsorbed onto the external surface of the zeolite crystallites. The resulting solids were dried at 70 °C under vacuum for 10 h.

2.6. Catalytic activity

The epoxidation of styrene was performed using a batch-type reactor operated under atmospheric pressure. Typically, *N,N*-dimethylformamide (DMF) was used as a solvent, and molecular oxygen was bubbling into the liquid mixture containing styrene and the solvent. Molecular oxygen was pressured into the reactor and typically the reaction was allowed to proceed for 24 h. After

each reaction, the catalyst was filtered off, and the liquid organic products were quantified by a gas chromatograph using toluene as an internal standard.

3. Results and discussion

The bands corresponding to free –C=O and –NH$_2$ groups are not observed in the IR spectra of the complexes. It confirms complete condensation between amino ligands and diethyloxalate. Typically for [14]aneN$_4$ some new bands appear at 1651, 1518, 1226 and 762 cm^{-1} corresponding new groups [15]. A single sharp band observed at 3298 cm^{-1}, maybe due to ν(N–H) of the secondary amino group [16]. In the IR spectra of complexes a new band at 468–480 cm^{-1} is appeared. It may be formation of ν(Fe–N) bond. It supports the involvement of nitrogen in coordination. IR spectra indicated that the ligands act as tetradentate coordination through nitrogen [N$_4$].

The chemical compositions confirmed the purity and stoichiometry of the neat and encapsulated complexes. The chemical analyses of the samples revealed the presence of organic matter with a C/N ratio roughly similar to that for the neat complexes. The percentage of iron(II) contents were estimated before and after encapsulation by atomic absorption spectroscopy. The iron(II) ion contents estimated after encapsulation are only due to the presence of iron(II) complexes in nanopores of zeolite-Y. The Si and Al contents in Fe(II)-NaY and the zeolite complexes are almost in the same ratio as in the parent zeolite. This indicates few changes in the zeolite framework due to the absence of dealumination in metal ion exchange. The parent NaY zeolite has Si/Al molar in the ratio of 2.53 which corresponds to a unit cell formula Na$_{56}$[(AlO$_2$)$_{56}$(SiO$_2$)$_{136}$]. The unit cell formula of metal-exchanged zeolites show a iron dispersion of 11.4 moles per unit cell (Na$_{33.8}$Fe$_{11.4}$[(AlO$_2$)$_{56}$(SiO$_2$)$_{136}$]·nH$_2$O). The analytical data of each complex indicates Fe:C:N molar ratios almost close to those calculated for the mononuclear structure. Elemental analysis and spectroscopic data's (Tables 1 and 2) show that all of the neat complexes have octet coordinated structure with two CH$_3$CN at trans situation, but in encapsulated two CH$_3$CN at trans situations have been replaced with two oxygen of lattice. The IR bands of zeolite-encapsulated iron(II) complexes occur at frequencies shifted within ~3–5 cm^{-1} from those of the free complex; furthermore, some changes in band intensities can be observed in the region of the C=O stretching vibration. These observations not only confirm the presence of iron(II) complex of azamacrocycle in the zeolite, but also suggest that its structure is not identical to that of the neat complex, thus, it is stereochemically induced that the distortion of the complex, chemical ligation of the zeolite framework (NaY can act as a strong ligand), or some host–guest interactions (electrostatic) with the zeolite, cannot be ruled out. Comparable IR spectral patterns of fresh and used encapsulated catalysts suggest that these can be used further for catalytic study.

The X-ray diffraction patterns of zeolite contained azamacrocycle complexes are similar to Fe(II)-NaY and the parent NaY zeolite. The zeolite crystallinity is retained in encapsulating complexes. The crystalline phase of free metal ions or encapsulation ligand complexes were not detected in any of the patterns

Table 1
Elemental analysis, vibrations parameters and some physical properties for ligands and azamacrocyclic iron(II) complexes

Complex	Found (calculated)					$\Lambda_M{}^a$, Ω^{-1} cm^2 mol^{-1}	μ_{eff} (MB)	IR (KBr, cm^{-1})			d↔d (cm^{-1})^b
	%C	%H	%N	C/N	%Fe			ν(C=O)	ν(N–H)	ν(Fe–N)	
[12]aneN$_4$	42.11 (41.92)	5.30 (5.18)	24.54 (24.66)	1.72 (1.70)	–	–	–	1663	3314	–	–
[Fe([12]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$	21.97 (21.78)	2.77 (2.62)	12.81 (12.99)	1.72 (1.68)	8.51 (8.40)	240	−0.011	1660	3310	470	15,200
[14]aneN$_4$	46.87 (46.67)	6.29 (6.13)	21.85 (21.99)	2.14 (2.12)	–	–	–	1651	3298	–	–
[Fe([14]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$	24.58 (24.40)	3.24 (3.11)	12.28 (12.39)	2.00 (1.97)	8.16 (8.01)	236	−0.016	1647	3294	468	15,100
Bzo$_2$[12]aneN$_4$	59.26 (59.04)	3.73 (3.52)	17.27 (17.39)	3.43 (3.40)	–	–	–	1678	3325	–	–
[Fe(Bzo$_2$[12]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$	31.94 (31.75)	2.41 (2.30)	11.17 (11.29)	2.86 (2.81)	7.43 (7.29)	230	−0.028	1675	3320	480	15,400
Bzo$_2$[14]aneN$_4$	59.26 (59.00)	3.73 (3.48)	17.27 (17.41)	3.43 (3.39)	–	–	–	1675	3318	–	–
[Fe(Bzo$_2$[14]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$	31.94 (31.70)	2.41 (2.33)	11.17 (11.36)	2.86 (2.79)	7.43 (7.25)	235	−0.030	1670	3315	475	15,350

^{a} In methanol solution.
^{b} In acetonitrile solutions.

Table 2
Chemical composition, DRS absorption data and IR stretching frequencies (as KBr pellets) of zeolite-encapsulated azamacrocyclic iron(II) complexes

Sample	C (%)	H (%)	N (%)	C/N	Si (%)	Al (%)	Na (%)	Fe (%)	Si/Al	$\upsilon_{C=O}$ (cm^{-1})	υ_{N-H} (cm^{-1})	d ↔ d (cm^{-1})
NaY	–	–	–	–	21.76	8.60	7.50	–	2.53	–	–	–
Fe(II)-NaY	–	–	–	–	21.48	8.49	3.40	3.67	2.53	–	–	–
[Fe([12]aneN$_4$)]$^{2+}$-NaY	3.78	1.42	2.35	1.61	21.16	8.36	5.26	2.73	2.53	1662	3312	15,150
[Fe([14]aneN$_4$)]$^{2+}$-NaY	3.83	1.46	1.82	2.11	21.14	8.36	5.24	2.68	2.53	1653	3300	15,000
[Fe(Bzo$_2$[12]aneN$_4$)]$^{2+}$-NaY	4.12	1.38	1.22	3.38	21.12	8.34	5.23	2.66	2.53	1678	3324	15,340
[Fe(Bzo$_2$[14]aneN$_4$)]$^{2+}$-NaY	4.14	1.36	1.24	3.35	21.12	8.35	5.24	2.65	2.53	1673	3318	15,300

as their fine dispersion in zeolite might have been rendered them non-detectable by XRD.

The stability of the encapsulated catalyst was checked after the reaction by X-ray diffraction and DRS and possible leaching of the complex was investigated by UV–vis in the reaction solution after filtration of the catalyst. Moreover, iron was not detectable in the liquid filtrate after the epoxidation reaction with the [Fe(azamac.)]$^{2+}$-NaY. The use of liquid filtrate after the treating of the [Fe(azamac.)]$^{2+}$-NaY with the solvent in the flow of O$_2$ at 373 K instead of solid catalyst for reaction did not show significant styrene conversion. This is much different with many H$_2$O$_2$-oxidized liquid-phase oxidation catalysts based on molecular sieves, where the leaching of the active component (redox center) in H$_2$O$_2$ is regarded as a serious problem probably because H$_2$O$_2$ has high ability to dissolve redox component such as vanadium or chromium [17]. Thus, the use of O$_2$ as the oxidant in our system also possesses advantages to increase the stability against leaching for the molecular sieve-based heterogeneous catalysts and may thus be a promising direction.

The surface area and pore volume of the catalysts are presented in Table 3. The encapsulation of [Fe(azamac.)]$^{2+}$ complexes in zeolite reduced the adsorption capacity and the surface area of the zeolite. The lowering of the pore volume and surface area clearly prove the [Fe(azamac.)]$^{2+}$ complexes have been assembled inside the zeolite.

The selectivity and activity results of zeolite encapsulated and homogeneous catalysts on the epoxidation of styrene with O$_2$ have been given in Tables 4 and 5. Comparing between neat and [Fe(azamac.)]$^{2+}$-NaY as catalyst evidence that zeolite encapsulated catalysts gave higher conversion of styrene than their corresponding neat complexes. The higher activity of supported complexes is because of site isolation of the complexes (Tables 4 and 5).

Table 3
Surface area and pore volume data of azamacrocyclic iron(II) complexes encapsulated in nanopores of zeolite Y

Sample	Surface area[a] (m^2/g)	Pore volume[b] (ml/g)
NaY	545	0.31
Fe(II)-NaY	538	0.30
[Fe([12]aneN$_4$)]$^{2+}$-NaY	493	0.26
[Fe([14]aneN$_4$)]$^{2+}$-NaY	480	0.25
[Fe(Bzo$_2$[12]aneN$_4$)]$^{2+}$-NaY	465	0.23
[Fe(Bzo$_2$[14]aneN$_4$)]$^{2+}$-NaY	462	0.22

[a] Surface area is the "monolayer equivalent area" calculated as explained in the Refs. [11,12].
[b] Calculated by the *t*-method.

Table 4
Epoxidation of styrene with molecular oxygen over azamacrocyclic iron(II) complexes[a]

Catalyst	Conversion (%)	Epoxide
[Fe([12]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$	18.9	74.1
[Fe([14]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$	17.4	76.5
[Fe(Bzo$_2$[12]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$	25.7	72.7
[Fe(Bzo$_2$[12]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$[b]	8.9	67.9
[Fe(Bzo$_2$[12]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$[c]	19.6	71.3
[Fe(Bzo$_2$[12]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$[d]	22.4	70.5
[Fe(Bzo$_2$[12]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$[e]	13.5	64.2
[Fe(Bzo$_2$[14]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$	21.9	73.6
Fe(SO$_4$)$_2$	3.50	–

[a] Reaction conditions: catalyst, 0.3 mmol; temperature, 373 K; styrene, 10 mmol; DMF, 20 ml; flow rate of O$_2$, 3 ml/min.
[b] 0.1 mmol.
[c] 0.2 mmol.
[d] 0.4 mmol.
[e] 0.5 mmol.

The activity of the Fe(II)-NaY was higher than of Fe(III)-NaY. As shown in Table 5, the iron(III)-containing heterogeneous compound (Fe(III)-NaY) shows low activity for epoxidation of styrene with molecular oxygen. However, the Fe(II)-containing heterogeneous compounds tested here, exhibit

Table 5
Epoxidation of styrene with molecular oxygen over azamacrocyclic iron(II) complexes encapsulated in nanopores of zeolite-Y[a]

Catalyst	Solvent	Conversion (%)	Epoxide
[Fe([12]aneN$_4$)]$^{2+}$-NaY	DMF	57.4	72.4
[Fe([14]aneN$_4$)]$^{2+}$-NaY	DMF	53.8	74.5
[Fe(Bzo$_2$[12]aneN$_4$)]$^{2+}$-NaY	DMF	68.5	70.6
[Fe(Bzo$_2$[12]aneN$_4$)]$^{2+}$-NaY[b]	DMF	67.7	70.2
[Fe(Bzo$_2$[12]aneN$_4$)]$^{2+}$-NaY[c]	DMF	67.1	68.6
[Fe(Bzo$_2$[12]aneN$_4$)]$^{2+}$-NaY[d]	DMF	66.0	88.1
[Fe(Bzo$_2$[14]aneN$_4$)]$^{2+}$-NaY	DMF	61.9	71.3
[Fe(Bzo$_2$[12]aneN$_4$)]$^{2+}$-NaY	DMA	72.3	30.5
[Fe(Bzo$_2$[12]aneN$_4$)]$^{2+}$-NaY	DEF	50.9	35.1
[Fe(Bzo$_2$[12]aneN$_4$)]$^{2+}$-NaY	DBF	52.7	36.5
NaY	DMF	0.2	42.0
Fe(II)-NaY	DMF	38.6	61.4
Fe(III)-NaY	DMF	27.9	56.5

N,N-dimethylacetamide (DMA); *N,N*-diethylformamide (DEF); *N,N*-dibutylformamide (DBF); *N,N*-dimethylformamide (DMF).
[a] Reaction conditions: catalyst, 0.3 mmol; temperature, 373 K; styrene, 10 mmol; solvent, 20 ml; flow rate of O$_2$, 3 ml/min.
[b] First reuse.
[c] Second reuse.
[d] Third reuse.

high styrene conversion and styrene oxide selectivity in epoxidation of styrene by O_2. Thus, Fe(II) in the neat and encapsulated complexes might be function as the active sites for the epoxidation of styrene by O_2.

The color change of the Fe(II)-NaY from pale green to yellowish green after the reaction was observed, that is related to iron oxidation state from Fe(II) to Fe(III). However, the repeated run utilizing the recovered Fe(II)-NaY did not show significant decrease in catalytic performances. This may indicate that a part of Fe(II) ions still remain after the reaction.

The neat complexes, [Fe(azamac.)]$^{2+}$, showed some activity for the epoxidation of styrene, but both styrene conversion and styrene oxide selectivity were much less than the respective encapsulated ones. Therefore, the epoxidation reactions observed for the [Fe(azamac.)]$^{2+}$-NaY catalysts are heterogeneous in nature. Moreover, iron was not detectable in the liquid filtrate after the epoxidation reaction with the [Fe(azamac.)]$^{2+}$-NaY. The use of liquid filtrate after the treating of the [Fe(azamacrocycle)]$^{2+}$-NaY with the solvent in the flow of molecular oxygen at 373 K instead of solid catalyst for reaction did not show significant styrene conversion.

It is worthy mentioning that the appropriate amount for the heterogeneous Fe(II)-containing compound used in the reaction is a key factor for obtaining high catalytic performances. As shown in Table 4, in the case of [Fe(Bzo$_2$[12]aneN$_4$)]$^{2+}$-NaY, styrene conversion increased with increasing the amount of the catalyst up to 0.3 mmol, and a sharp decrease in styrene conversion was observed with further increase in the amount of the neat catalyst. Therefore, an amount of 0.3 mmol catalysts may be consider as appropriate to obtain the maximum conversion of styrene.

The effect of various solvents for the oxidation of styrene with [Fe(Bzo$_2$[12]aneN$_4$)]$^{2+}$-NaY catalyst was also studied (Table 5). It has been clarified that the solvent played important roles in the epoxidation of styrene. Several kinds of solvents have been tested for the epoxidation of styrene with O_2 at atmospheric pressure catalysed by the [Fe(Bzo$_2$[12]aneN$_4$)]$^{2+}$-NaY. Both the epoxide selectivity and the effect of reaction conditions on the catalyst performance were similar to those reported previously for other solid catalysts [18]. The solvent played a crucial role in the epoxidation of styrene, as shown in Table 5. Better than 30% epoxide yield was obtained only in alkyl formamides, and even within this class, DMF seems to be outstanding. On the other hand, no reaction was detectable in several solvents, such as 1,2-dichloroethane, hexane, ethyl acetate, and *tert*-butyl alcohol. No correlation between the epoxide yield and the typical characteristics of the solvents (polarity, acidity, or basicity) could be found. It is very probable that the outstanding yields in DMF indicate a special role of the solvent in the epoxidation process. Similar unusual solvent effects have been noted in several oxidation reactions [19,20].

At the end of the first catalytic cycle, there was no color change of the solution or catalysts, it shows that no decomposition of the complexes took place during the reaction. The materials were easily separated from the reaction medium, and the observation that no further styrene conversion occurred upon removal of the heterogeneous catalyst from the reaction medium

subsequent to 24 h of reaction indicates that styrene oxidation is catalysed essentially by the encapsulated metal complexes, and that no leaching of the active species have occurred during the catalytic cycle (Table 5). No appreciable loss in catalytic activity suggests that the complex is still present in the cavity of the zeolite-Y.

The results clearly suggest that [Fe(Bzo$_2$[12]aneN$_4$)]$^{2+}$-NaY efficiently catalyses conversion of styrene to styrene oxide with 70.6% selectivity. The more activity of Bzo$_2$[12]aneN$_4$ system has clearly arisen from the existence of electron donating ligand which facilitate the electron transfer rate, a process that has previously observed by us in other oxidation reactions [21–24]. All conversions efficiency with high selectivity obtained in this study is significantly higher than that obtained using metal containing porous and nonporous materials [25–30].

The detailed reaction mechanism is still not known, but the epoxidation may proceed via an active oxygen species with radical nature. The addition of radical scavengers such as hydroquinone and butyl hydroxy toluene to the reactant mixture remarkably inhibited the conversion of styrene. Further investigations of reaction mechanism are under way in our laboratory.

4. Conclusions

Synthesis and encapsulation of iron(II) complexes of azamacrocyclic ligands in the nanocavity of zeolite-Y by in situ template condensation method with preservation of the zeolite crystalline and morphology. [Fe(azamac.)]$^{+2}$ and [Fe(azamac.)]$^{+2}$-Y have been used as catalyst for the oxidation of styrene under molecular oxygen as the oxygene source under mild conditions. It is concluded from the catalytic information and conversion yield that [Fe(azamac.)]$^{+2}$-Y are better catalyst than the [Fe(azamac.)]$^{+2}$, neat complexes ones. These catalysts are used after third reused, and don't show any appreciable loss in catalytic activity.

Acknowledgments

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