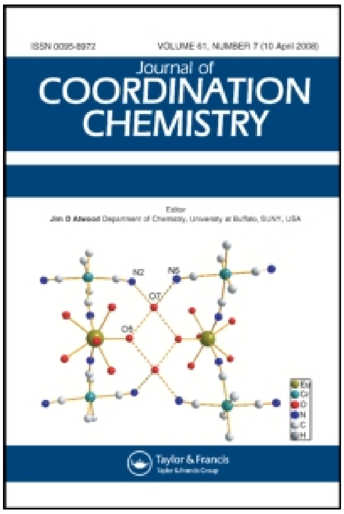

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Host (nanopores of zeolite-Y)/guest (Co(II)-azamacrocyclic complexes) nanocomposite materials: synthesis, characterization and catalytic epoxidation of styrene with molecular oxygen

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A series of Co(II) azamacrocyclic complexes, [12]aneN_4, [14]aneN_4, Bzo_2[12]aneN_4 and Bzo_2[14]aneN_4, have been encapsulated in the nanocavity of zeolite-Y by a one pot template condensation reaction. Co(II) complexes with azamacrocyclic ligands were entrapped in the nanocavity of zeolite-Y by a two-step process in the liquid phase: (i) adsorption of [bis(diamine)cobalt(II)], [Co(N–N)$_2$]-NaY, in the supercages of the zeolite, and (ii) *in situ* condensation of the cobalt(II) precursor complex with diethyloxalate. The new host/guest nanocomposite materials (HGNM) have been characterized by FTIR, DRS and UV-Vis spectroscopic techniques, XRD and elemental analysis, as well as nitrogen adsorption. These complexes (neat and HGNM) were used for epoxidation of styrene with O_2 as oxidant in different solvents. Electronic spectra of the reaction mixture indicated oxidation proceeds through a free radical mechanism.

Keywords: Nanocomposite materials; Zeolite encapsulation; Epoxidation of styrene; Cobalt(II); Azamacrocycle

1. Introduction

Encapsulation of transition metal complexes inside nanoporous supports has emerged as a general technique to increase and control selectivity of catalysts [1]. In addition, the confinement of guest molecules leads to higher stability by reducing dimerization of active sites. Nanopores of zeolites are attractive supports for encapsulation as they combine high thermal and chemical stability with a regular, crystalline framework. Zeolite complexes possess a number of structural similarities to metalloenzymes and

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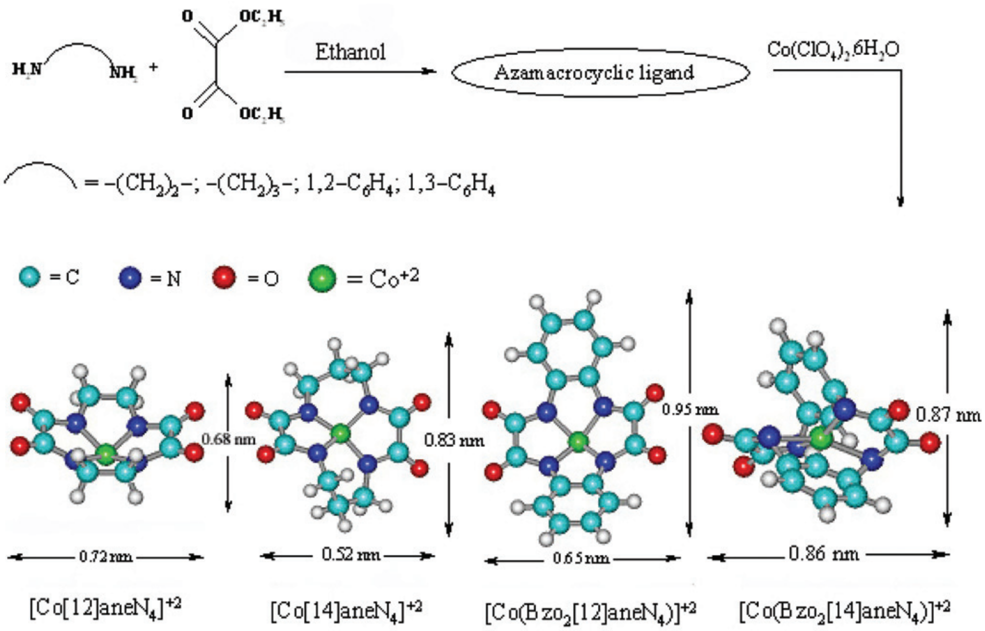
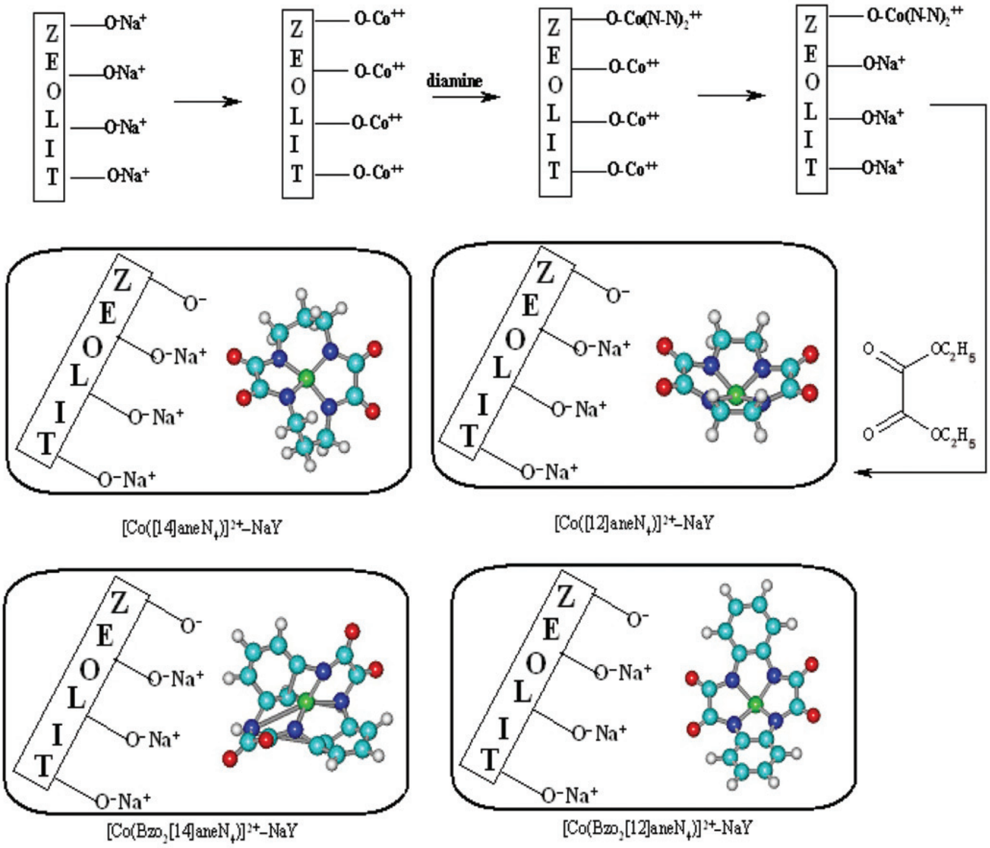


Scheme 1.

therefore are expected to mimic enzyme active sites for the catalytic reaction. Zeolites are excellent candidates for reaction such as oxidation [2, 3], hydrogenation [4] and dehalogenation [5] etc.

Transition metal complexes have been used for homogeneous epoxidation of organic substrates such as styrene with high selectivity under mild reaction conditions, but the difficult recovery of the catalyst, degradation of ligand, dimerization of transition metal complexes and formation of inactive oxox, peroxo dimeric and other polymeric species, limit their reuse. Increasing interest has been generated for preparation of heterogeneous catalysts [6–16]. Heterogenization is achieved by two different processes, encapsulating the metal complex inside the nanopores of zeolites and anchoring or tethering them to inert supports [7]. The grafting and tethering refer to directly or through space covalent attachment of the metal complex, respectively. The encapsulation (ship-in-a-bottle) is an ideal approach because the complex formed inside the cages of the zeolite is not only too large to diffuse out but also not lost into the liquid phase during the reaction. Since these composite materials mimic biological enzymes, they are also called ''zeozymes'' (acronym for zeolite mimics of enzymes). The metal complex may lose some of its degrees of freedom because of confinement in the zeolite matrix; so, it adopts unusual geometries which are stabilized by coordination to the zeolite-surface functional groups. In a general sense, the encapsulated complexes mimic enzyme systems in which the porous inorganic mantle (similar to the protein mantle in enzymes) provides (hopefully) the right steric requirement for the metal complex and imposes certain requirements (based on size and shape) to access of the active site by the substrate molecules (substrate selectivity). However, many porous materials have been used; among them zeolites are the best nanopore because of the crystalline structure and the size of nanocavity (1.2 nm diameter).



Scheme 2.

Metalloporphyrins and their analogues such as phthalocyanines and Schiff bases have been encapsulated inside the cage of zeolite [17–19]. They have been extensively studied as biomimetic catalysts for alkene epoxidation and alkane hydroxylation with a variety of oxidants including hydrogen peroxide, *tert*-butylhydroperoxide (TBHP), iodosylbenzene and hypochlorite [20]. There are only a few papers on oxidation of hydrocarbons with molecular oxygen in the presence of zeolite-encapsulated metallocomplexes as catalysts [21, 22]. The present article describes the synthesis, characterization and catalytic activity in the aerobic oxidation of styrene of various azamacrocyclic complexes encapsulated in the nanocavity of zeolite-Y by the flexible ligand method (schemes 1 and 2).

2. Experimental

2.1. *Materials and physical measurements*

Safety note: Cobalt perchlorate salt with organic ligands is often explosive and should be handled with caution. All other reagents and solvents were purchased from Merck (pro-analysis) and dried using molecular sieves (Linde 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). FT-IR spectra were recorded on a Shimadzu Varian 4300 spectrophotometer in KBr pellets. The electronic spectra of the neat complexes were taken on a Shimadzu UV-Vis scanning spectrometer (Model 2101 PC). Diffuse reflectance spectra (DRS) were registered on a Shimadzu UV/3101 PC spectrophotometer over the range 1500–200 nm using MgO as reference. Elemental analyses (CHN) of the materials were obtained from a Carlo ERBA Model EA 1108 analyzer. XRD patterns were recorded by a Rigaku D-max C III X-ray diffractometer using Ni-filtered Cu-Kα radiation. Nitrogen adsorption measurements were performed at 77 K using a Coulter Ofeisorb 100CX instrument. The samples were degassed at 150°C until a vacuum more than 10^{-3} Pa was obtained. Micropore volumes were determined by the *t*-method, a "monolayer equivalent area" was calculated from the micropore volume [23, 24]. The stability of the encapsulated 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 zeolite. The amounts of metallocomplexes encapsulated in zeolite matrix were determined by elemental analysis and followed by subtracting the amount of metallocomplex left from the solutions after synthesis of the catalysts as determined by UV-Vis spectroscopy, from the amount taken for the synthesis. Atomic absorption spectra (AAS) were recorded on a Perkin-Elmer 4100–1319 spectrophotometer using a flame approach, after acid (HF) dissolves known amounts of the zeolitic material. SiO_2 was determined by gravimetric analysis. Magnetic moments were calculated from magnetic susceptibility data obtained using a Johnson Matthey MK-1 magnetic susceptibility balance and conductance measurements with a Metrohm Herisau conductometer E 518.

2.2. *Synthesis of azamacrocyclic ligand*

Azamacrocyclic ligands ([12]aneN_4, [14]aneN_4, Bzo$_2$[12]aneN_4 or Bzo$_2$[14]aneN_4) were prepared by the procedures reported [25]. 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 a few drops of concentrated hydrochloric acid. On cooling a precipitate formed, was filtered, washed with cold ethanol and dried under vacuum over P_4O_{10}.

2.3. *Preparation of [Co(azamac.)](ClO$_4$)$_2$*

Cobalt(II) perchlorate hexahydrate (3.66 g, 0.01 mol) dissolved in ethanol (20 mL) was reacted with an ethanolic (20 mL) solution of azamacrocyclic ligands ([12]aneN_4, [14]aneN_4, Bzo$_2$[12]aneN_4 or Bzo$_2$[14]aneN_4) (0.01 mol) by refluxing for 1 h under nitrogen. The mixture was heated at reflux for 6 h resulting in an orange solution. The solution was cooled to room temperature and filtered to remove cobalt hydroxide. Excess lithium perchlorate dissolved in methanol was added to the filtrate, and the mixture was kept in the refrigerator until orange solid formed. The solids were filtered, washed thoroughly with cold ethanol and dried in vacuum.

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

A 2 g NaY zeolite was suspended in 100 mL distilled water, which contained cobalt(II) nitrate (0.025 M). The mixture was heated while stirring at 90°C for 24 h. The solid was filtered, washed with hot distilled water until the filtrate was free from any cobalt(II) ion (by AAS of filtrate) and dried for 10 h at 80°C under vacuum. The ionic exchange degree was determined by AAS. To a stirred methanol solution of Co(II)–NaY (4 g) were added 0.37 g of diamine (1,2-diaminopropane, 1,3-diaminopropane, 1,2-diaminobenzene or 1,3-diaminobenzene) suspended in 100 mL of methanol and then refluxed for 8 h under N_2 atmosphere. The light orange solid consisting of $[Co(N{-}N)_2]^{2+}$ denoted as $[Co(N{-}N)_2]^{2+}$-NaY was collected by filtration and washed with ethanol. The resulted zeolites were Soxhlet extracted with *N*,*N*′-dimethylformamide (for 4 h) and then with ethanol (for 3 h) to remove excess unreacted diamine and any Co(II) complexes adsorbed onto the external surface of the zeolite crystallines. The resulting light orange solids were dried at 60°C under vacuum for 24 h. To a stirred methanol suspension (100 mL) of $[Co(N{-}N)_2]^{2+}$-NaY (2 g) was slowly added diethyloxalate (under N_2). The mixture was heated under reflux for 24 h until a pale orange suspension resulted. The solution was filtered and the resulting zeolites were Soxhlet extracted with *N*,*N*′-dimethylformamide (for 6 h) and then with ethanol (for 5 h) to remove excess unreacted products from amine-ester condensation and any cobalt(II) complexes adsorbed onto the external surface of the zeolite crystallines. The resulting pale orange solids were dried at 70°C under vacuum for 12 h. The remaining [bis(diamine)cobalt(II)] ions in zeolite were removed by exchanging with aqueous 0.1 M $NaNO_3$ solutions. The stability of the encapsulated 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 zeolite. The amount of cobalt(II) complexes encapsulated in zeolite matrix were determined by elemental analysis and subtracting the amount of Co(II) complex left from the solutions after the synthesis of the catalysts, is determined by UV-Vis spectroscopy, from the amount taken for the synthesis.

2.5. Catalytic reactions

The epoxidation of styrene with molecular oxygen was carried out with a round-bottomed glass flask reactor. In a typical run, a measured amount of catalyst was added to the reactor, which was precharged with the desired amount of reactant and solvent, typically *N*,*N*-dimethylformamide (DMF), at the desired temperature. The reaction started off under bubbling O_2, or O_2 diluted with N_2, into the liquid. The reactant mixture was stirred vigorously during the reaction. After the reaction, the catalyst was filtered off, and the organic products were quantified with a gas chromatograph with toluene as an internal standard. Styrene oxide and benzaldehyde were obtained as the two main products.

3. Results and discussion

The ligand synthesis scheme leads to encapsulation of Co(II) complexes of azamacrocyclic ligands ([12]aneN_4, [14]aneN_4, Bzo_2[14]aneN_4 and Bzo_2[12]aneN_4)

inside the nanopores of zeolite. Chemical analyses of the samples are given in table 1. The parent NaY zeolite has Si/Al molar ratio of 2.4 which corresponds to a unit cell formula $Na_{56}[(AlO_2)_{56}(SiO_2)_{136}]$. The unit cell formula of metal-exchanged zeolite shows 11 moles of cobalt dispersion per unit cell ($Na_{34}Co_{11}[(AlO_2)_{56}(SiO_2)_{136}] \cdot nH_2O$). Metal ion exchange at around 34% leads to 2.70–3.70% metal loading in zeolite.

The CHN analyses of the neat cobalt complexes showed similarity to the theoretical values. The cobalt contents of the zeolite encapsulated catalysts were estimated by dissolving known amounts of the catalyst in concentric HCl and using AAS. Analytical data of each complex indicate molar ratios of metal : C : H close to those calculated for the mononuclear structure (table 1). However, traces of free metal ions in the lattice could be assumed as the metal content is slightly higher than the stoichiometric requirement. Only a portion of the metal ions in metal-exchanged zeolite undergo complexation and the rest are removed on re-exchange with sodium nitrate solution. Some of these cation sites in the zeolite lattice might be blocked from solution access by the encapsulated complexes. This shielding effect is probable in the present case since complex loading is higher than that reported previously [26]. The remaining traces of free metal ions in the zeolite do not show interference in the behavior of the encapsulated complexes [27].

The Si and Al content in the metal-exchanged zeolites and the zeolite complexes are almost the same ratio as in the parent zeolite, indicating little change in the zeolite framework due to absence of dealumination in metal ion exchange. The X-ray diffraction patterns of zeolite-containing azamacrocyclic complexes are similar to those of metal-exchanged zeolites and the parent NaY zeolite (figure 1). Zeolite crystallinity is retained on encapsulating azamacrocyclic complexes. The crystalline phases of free metal ions or the encapsulated azamacrocyclic complexes were not detected in any of the patterns because their fine dispersion in zeolite is non-detectable by XRD. The SEM photographs of the samples taken before Soxhlet extraction show deposition of complexes on the external surface. However, the absence of extraneous materials in the SEM photographs of finished products indicates complete removal of complexes on the surface after extended extraction.

The molar conductance values ($\sim 240\,\Omega^{-1}\,\text{mol}^{-1}\,\text{cm}^2$) measured for tetraaza macrocyclic complexes correspond to 1 : 2 electrolytes. Comparing the obtained magnetic measurement at room temperature and the results of electronic spectra (table 1) of metal complexes with square-planar Co(II) tetraaza macrocycle complexes indicate that the tetraaza tetraone ligands of this study do not differ significantly from tetraaza ligands in ligand field strength. Bands due to zeolite encapsulated Co(II) complex appeared in the visible, and charge transfer bands appeared in the near-UV region, similar to the discrete complex [28–31].

IR spectra of the ligands do not exhibit any band corresponding to free primary diamine and ketone. Four new bands in the spectrum of ligand [32] in the regions 1651, 1518, 1226 and 762 cm^{-1} are assignable to amide-I ν(C=O), amide-II [ν(C–N) + δ(N–H)], amide-III [δ(N–H)] and amide-IV [ρ(C=O)] bands, respectively, supporting the macrocyclic nature of the ligand. A single sharp band observed at 3300 cm^{-1} may be due to ν(N–H) of the secondary amino group [33]. The complexation process leads to shifting of ν(N–H) to lower frequency compared to the macrocyclic ligand; a new medium intensity band at $\sim$470 cm^{-1} attributed to ν(Co–N) provides strong evidence for the involvement of nitrogen in coordination. IR spectra of neat as well as encapsulated complexes presented in table 1 gave information about the stretching

Table 1. Chemical composition, magnetic and conductance data, UV-Vis and DRS absorption, and IR stretching frequencies of neat and zeolite-encapsulated.[a]

										IR/(KBr, cm^{-1})[c]				
Sample	C%	H%	N%	M%	C/N	Si%	Al%	Na%	Si/Al	$\upsilon_{C=N}$	υ_{N-H}	μ_B	$\Lambda_M{}^b\,(\Omega^{-1}cm^{-2}M)$	$d \leftrightarrow d\ (cm^{-1})$
NaY	–	–	–	–	–	21.76	8.60	7.50	2.53	–	–	–	–	–
CoNaY	–	–	–	3.71	–	21.53	8.53	3.36	2.53	–	–	–	–	–
[12]aneN_4	42.11 (41.92)	5.30 (5.18)	24.54 (24.66)	–	1.72 (1.70)	–	–	–	–	1663	3314	–	–	–
[Co([12]aneN_4)] $(ClO_4)_2$	19.76 (19.59)	2.47 (2.32)	11.53 (11.66)	12.13 (12.01)	1.71 (1.68)	–	–	–	–	1658	3307	1.73	243	21505
[Co([12] aneN_4)]$^{2+}$-NaY	3.69	1.50	2.77	2.78	1.49	21.09	8.34	5.32	2.53	1661	3309	–	–	21710
[14]aneN_4	46.87 (46.67)	6.29 (6.13)	21.85 (21.99)	–	2.14 (2.12)	–	–	–	–	1651	3298	–	–	–
[Co([14]aneN_4)] $(ClO_4)_2$	23.34 (23.21)	3.11 (3.02)	10.90 (10.99)	11.47 (11.30)	2.14 (2.11)	–	–	–	–	1645	3292	1.74	240	21380
[Co([14] aneN_4)]$^{2+}$-NaY	3.64	1.52	1.90	2.75	1.92	21.07	8.33	5.30	2.53	1649	3296	–	–	21500
Bzo_2[12]aneN_4	59.26 (59.04)	3.73 (3.52)	17.27 (17.39)	–	3.43 (3.40)	–	–	–	–	1678	3325	–	–	–
[Co(Bzo_2[12] aneN_4)] $(ClO_4)_2$	33.00 (32.81)	2.06 (1.89)	9.63 (9.80)	10.13 (10.01)	3.43 (3.35)	–	–	–	–	1672	3320	1.73	237	21800
[Co(Bzo_2[12] aneN_4)]$^{2+}$-NaY	3.61	1.53	1.33	2.71	3.19	21.03	8.31	5.28	2.53	1675	3323	–	–	21890
Bzo_2[14]aneN_4	59.26 (59.00)	3.73 (3.48)	17.27 (17.41)	–	3.43 (3.39)	–	–	–	–	1675	3318	–	–	–
[Co(Bzo_2[14] aneN_4)] $(ClO_4)_2$	33.00 (32.76)	2.06 (1.85)	9.63 (9.84)	10.13 (9.92)	3.43 (3.33)	–	–	–	–	1670	3312	1.75	234	21600
[Co(Bzo_2[14] aneN_4)]$^{2+}$-NaY	3.60	1.54	1.14	2.70	3.17	21.02	8.31	5.27	2.53	1674	3316	–	–	21680

[a] Estimated values are given in parentheses.
[b] In nitromethane solutions at 25°C unless otherwise specified.
[c] Vibrational stretching of coordinated C=N.

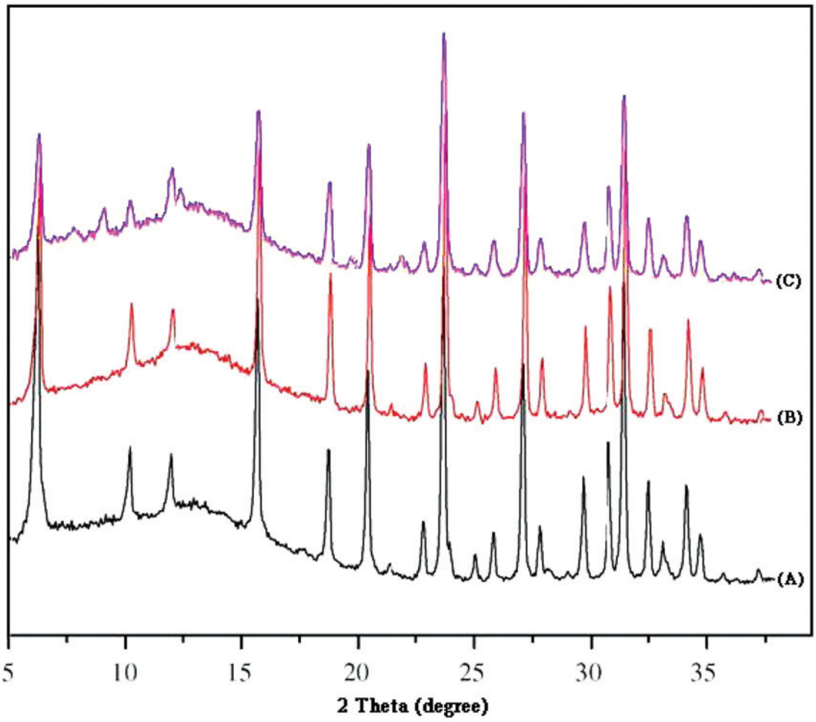


Figure 1. XRD pattern of (A) Na–Y, (B) CoNa–Y, (C) $[Co(Bzo_2[12]aneN_4)]^{2+}$-NaY.

vibrations of the functional groups, the environment of the complex and the crystallinity of the zeolite. The IR bands of all encapsulated complexes are weak compared with the neat complexes due to their low concentrations in nanocavities of zeolite.

The surface area and nanopore volume of the used catalysts in the oxidation reaction are presented in table 2. The encapsulation of cobalt ions and cobalt azamacrocyclic complexes reduced the surface area and adsorption capacity of zeolite. The lowering of the nanopore volume and surface area supported the fact that Co(II)-azamacrocyclic complexes are present within the zeolite cages and not on the external surface. The XRD of Co(II)-azamacrocyclic-NaY were studied. All samples exhibit patterns which can be indexed to NaY and not to the complex, indicating the crystallinity and morphology of zeolite were preserved during encapsulation.

As shown in table 3, the Co ($2p_{3/2}$) binding energy (E_b) is 857.7 and 856.3 eV in the Co complex in cobalt(II) chloride, respectively. The Co ($2p_{3/2}$) binding energy of the cobalt(II) complex increases 1.4 eV compared with that of the cobalt(II) chloride, indicating that the charge on Co decreases when complexes form. The encapsulated complexes are referenced to the binding energy of 102.7 eV for the Si 2p core level due to extensive use of this binding energy in the NaY system [34–37]. However, the neat complexes are referenced to the binding energy of 292.7 eV for the K $2p_{3/2}$ core level. Table 3 shows the Co 2p core levels of the neat and the encapsulated complexes. Cobalt remains in the +2 oxidation state in both the neat and the encapsulated complexes matching well with reported values for similar systems [37]. There is a high increase in

Table 2. Surface area and pore volume data of azamacrocyclic Co(II) complexes encapsulated in nanoporous of zeolite-Y.

Sample	Surface area[a] ($m^2 g^{-1}$)	Pore volume[b] ($mL g^{-1}$)
NaY	545	0.31
Co(II)–NaY	532	0.30
$[Co([12]aneN_4)]^{2+}$-NaY	495	0.27
$[Co([14]aneN_4)]^{2+}$-NaY	482	0.26
$[Co(Bzo_2[12]aneN_4)]^{2+}$-NaY	467	0.23
$[Co(Bzo_2[14]aneN_4)]^{2+}$-NaY	463	0.22

[a] Surface area is the "monolayer equivalent area" calculated as explained in references [23] and [24].
[b] Calculated by the *t*-method.

Table 3. XPS data of neat and nanopores of zeolite-Y cobalt(II) azamacrocyclic complexes.

Sample	BE, Co $2p_{3/2}$ (eV)	$2p_{3/2}$ and $2p_{1/2}$ separation (eV)
$[Co([12]aneN_4)](ClO_4)_2$	781.8	15.5
$[Co([12]aneN_4)]^{2+}$-NaY	782.6	16.2
$[Co([14]aneN_4)](ClO_4)_2$	781.6	15.4
$[Co([14]aneN_4)]^{2+}$-NaY	782.3	16.1
$[Co(Bzo_2[12]aneN_4)](ClO_4)_2$	782.2	15.8
$[Co(Bzo_2[12]aneN_4)]^{2+}$-NaY	782.9	16.9
$[Co(Bzo_2[14]aneN_4)](ClO_4)_2$	782.0	15.6
$[Co(Bzo_2[14]aneN_4)]^{2+}$-NaY	782.5	16.0

satellite intensity for Co 2p levels and a large energy gap (~16.9 eV) in the encapsulated complex which show the higher catalytic activity than the neat complex.

Table 4 shows the catalytic activity; comparing between the neat and the host guest nanocomposite materials (table 5 and figures 2 and 3) as catalysts, suggest that HGNM gave higher conversion of styrene than corresponding neat complexes. The higher activity of supported complexes is due to site isolation of the complexes. One of the major drawbacks of homogeneous metal complexes as catalysts is their irreversible deactivation due to formation of μ-oxo and μ-peroxo dimeric and other polymeric species especially when using an oxidant. This problem may be avoided by isolating the metal azamacrocyclic complexes from each other by encapsulation in the nanopores of a molecular sieve. The conversion increases by several orders of magnitude when the cobalt(II) complexes were isolated from each other by encapsulation within the nanocavity of the faujasite zeolites (scheme 2). Since the formation of these bulky dimeric and polymeric species is impossible when the monomeric complex was encapsulated within the nanopores of zeolite, the encapsulated catalysts should be more rugged and recycled. The data in table 5 support the above hypothesis.

The catalytic oxidation of styrene was studied with zeolite azamacrocyclic complexes using O_2 as the oxidant. Blank reactions performed over NaY zeolite under identical conditions show only negligible conversion indicating that the zeolite host is inactive for oxidation (table 5). Furthermore, O_2 alone is unable to oxidize the substrates in the absence of any catalyst. In representative tests, zeolite complex was filtered out and the filtrate was analyzed for metal content using atomic absorption spectrophotometry.

Table 4. Epoxidation of styrene with molecular oxygen catalyzed by a variety of catalysts based on cobalt(II) azamacrocyclic complexes.[a]

Catalyst	Styrene conversion (%)	Epoxide selectivity (%)
$[Co(Bzo_2[12]aneN_4)](ClO_4)_2$	41.9	47.6
$[Co(Bzo_2[12]aneN_4)](ClO_4)_2$[b]	26.5	49.6
$[Co(Bzo_2[12]aneN_4)](ClO_4)_2$[c]	38.9	44.8
$[Co(Bzo_2[12]aneN_4)](ClO_4)_2$[d]	31.7	38.3
$[Co(Bzo_2[14]aneN_4)](ClO_4)_2$	35.2	48.1
$[Co([12]aneN_4)](ClO_4)_2$	30.7	44.9
$[Co([14]aneN_4)](ClO_4)_2$	28.9	45.2
$CoCl_2$	16.1	30.2

[a] Reaction conditions: amount of cobalt(II) azamacrocycle complex as catalyst: 1.30 mmol; reaction temperature, 373 K; styrene, 10 mmol; DMF, 20 mL; reaction time, 6 h.
[b] catalyst = 0.65 mmol.
[c] catalyst = 2.60 mmol.
[d] catalyst = 3.90 mmol.

Table 5. Epoxidation of styrene with molecular oxygen catalyzed by various catalysts based on host/guest nanocomposite materials.[a]

Catalyst	Solvent	Temperature (K)	Styrene conversion (%)	Epoxide selectivity (%)
$[Co(Bzo_2[12]aneN_4)]^{2+}$-NaY	DMF	373	65.2	86.5
$[Co(Bzo_2[12]aneN_4)]^{2+}$-NaY[b]	DMF	373	64.8	85.9
$[Co(Bzo_2[12]aneN_4)]^{2+}$-NaY[c]	DMF	373	64.0	85.1
$[Co(Bzo_2[12]aneN_4)]^{2+}$-NaY[d]	DMF	373	63.2	84.7
$[Co(Bzo_2[12]aneN_4)]^{2+}$-NaY	DMF	353	26.7	52.5
$[Co(Bzo_2[12]aneN_4)]^{2+}$-NaY	DMF	363	48.2	60.3
$[Co(Bzo_2[12]aneN_4)]^{2+}$-NaY	DMA	373	67.5	89.3
$[Co(Bzo_2[12]aneN_4)]^{2+}$-NaY	DMSO	373	53.6	3.7
$[Co(Bzo_2[12]aneN_4)]^{2+}$-NaY	py	373	–	–
$[Co(Bzo_2[12]aneN_4)]^{2+}$-NaY	monochlorobenzene	373	–	–
$[Co(Bzo_2[12]aneN_4)]^{2+}$-NaY	*tert*-butyl alcohol	373	–	–
$[Co(Bzo_2[14]aneN_4)]^{2+}$-NaY	DMF	373	61.4	87.9
$[Co([12]aneN_4)]^{2+}$-NaY	DMF	373	55.7	82.7
$[Co([14]aneN_4)]^{2+}$-NaY	DMF	373	51.5	83.9
Co(II)–NaY	DMF	373	48.2	60.1

[a] Reaction conditions: the amount of transition metal ions in catalysts was fixed at 1.30 mmol; styrene, 10 mmol; DMF, 20 mL; reaction time, 6 h.
[b] First reuse.
[c] Second reuse.
[d] Third reuse.
DMF: *N*,*N*-dimethylformamide.DMA: N,N-dimethylacetamide.DMSO: dimethylsulfoxide.

The absence of metal ions in solution phase indicates that no leaching of complexes occurs during reaction when they are in the pores. These observations suggest that the oxidations occur due to the catalytic nature of the encapsulated azamacrocyclic complexes with no significant role by either the zeolite support or free complexes.

Transition metal complex-based soluble catalysts are more prone to deactivation by dimerization, which is expected to be reduced by encapsulating them in zeolites. HGNM were recycled for the oxidation of styrene with molecular oxygen with a view to establish the effect of encapsulation on stability. The initial run shows a conversion of 65.2% and it is only marginally reduced to 64.8% on recycling the catalyst, indicating

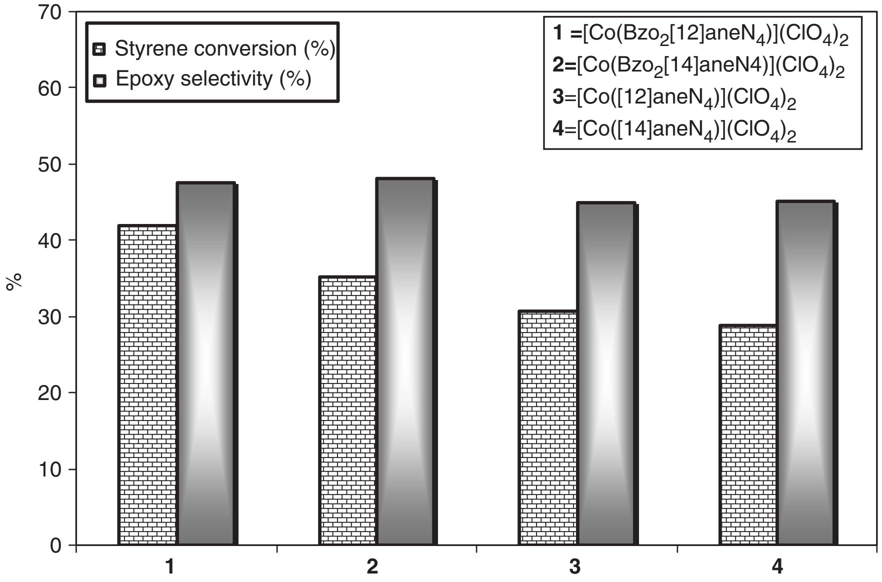


Figure 2. Bar diagram showing styrene conversion and epoxide selectivity in DMF for various azamacrocyclic cobalt(II) complexes. (Reaction conditions: amount of cobalt(II) azamacrocycle complex as catalyst: 1.30 mmol; reaction temperature, 373 K; styrene, 10 mmol; DMF, 20 mL; reaction time, 6 h.)

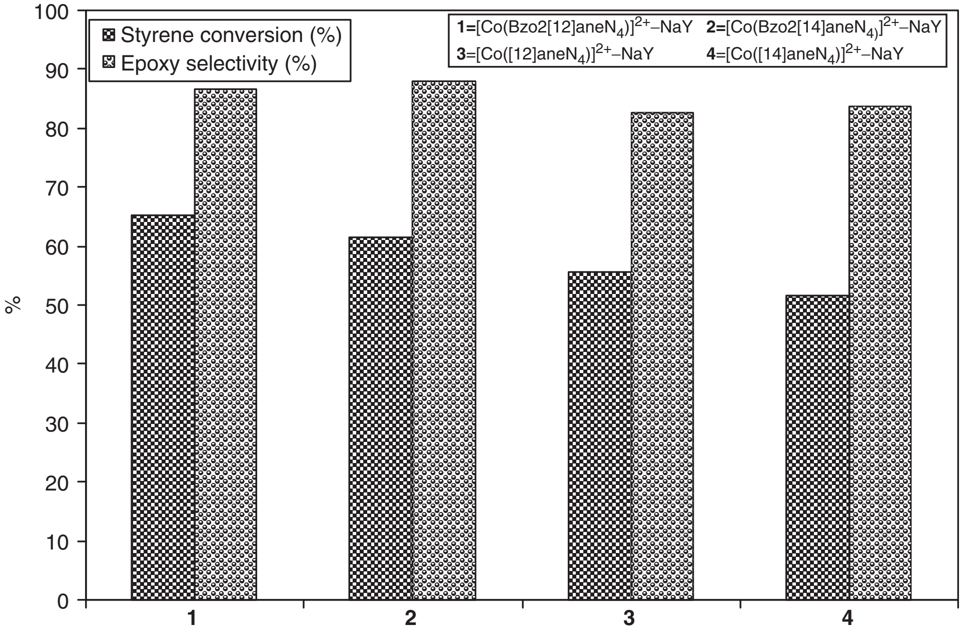


Figure 3. Bar diagram showing styrene conversion and epoxide selectivity in DMF for various azamacrocyclic cobalt(II) complexes encapsulated in zeolite. (Reaction conditions: the amount of transition metal ions in catalysts was fixed at 1.30 mmol; reaction temperature, 373 K; styrene, 10 mmol; DMF, 20 mL; reaction time, 6 h.)

that the HGNM can be recycled for the oxidation of styrene without loss in activity. Thus, encapsulation of complexes in nanopores of zeolites increases the life of the catalyst by reducing dimerization. IR spectrum of the recycled sample is quite similar to the fresh sample indicating little change in coordination of the azamacrocyclic after the oxidation reactions.

Repeated runs of the recovered $[Co(Bzo_2[12]aneN_4)]^{2+}$-NaY for the epoxidation of styrene have been carried out (table 5). Neither styrene conversion nor epoxide selectivity changed significantly in the repeated runs. After the reaction the liquid filtrate was subjected to atomic absorption spectroscopic analysis, and no cobalt could be detected. When the liquid filtrate was used in the reaction instead of the solid catalyst, no significant conversion of styrene was observed. Moreover, $CoCl_2$ or $[Co([12]aneN_4)](ClO_4)_2$, $[Co(Bzo_2[14]aneN_4)](ClO_4)_2$, $[Co(Bzo_2[12]aneN_4)](ClO_4)_2$ and $[Co([14]aneN_4)](ClO_4)_2$ are poor homogeneous epoxidation catalysts, as shown in table 4. Epoxidation probably proceeds heterogeneously over the $[Co([12 \text{ or } 14]aneN_4)]^{2+}$-, $[Co([12 \text{ or } 14]aneN_4)]^{2+}$-faujasite zeolite. Leaching of the active component (redox center) from molecular sieve-based catalysts is a serious problem when hydrogen peroxide or organic hydroperoxide is used as the oxidant for epoxidation. Evidently, hydrogen peroxide or organic hydroperoxide has a marked ability to dissolve the redox component from molecular sieves into the liquid phase [38]. Therefore, molecular oxygen as the oxidant in this system has increased stability against leaching for zeolite based heterogeneous catalysts and may provide another opportunity to exploit the redox molecular sieves for liquid phase-selective oxidation reactions.

Table 5 shows the effect of reaction temperature on the catalytic performance of $[Co(Bzo_2[12]aneN_4)]^{2+}$-NaY. At temperatures lower than 363 K, styrene conversion and styrene oxide selectivity decreased markedly with reaction temperature (table 5). The selectivities for styrene oxide and benzaldehyde remained almost unchanged with reaction time, indicating that benzaldehyde is formed in parallel with styrene oxide.

Various solvents with relatively low volatility (b.p. $>$ 373 K) have been tested for epoxidation of styrene by molecular oxygen over the $[Co(Bzo_2[12]aneN_4)]^{2+}$-NaY catalyst; the results are summarized in table 5. The acylamides, including dimethylformamide (DMF) and dimethylacetamide (DMA), are particularly efficient in providing both high styrene conversion and high epoxide selectivity. Although high styrene conversion could be obtained when dimethylsulfoxide (DMSO) was used, the selectivity for styrene oxide was low. No reaction occurred when nitrogen- or chloro-containing solvents such as pyridine and monochlorobenzene were used. It should be noted that *tert*butyl alcohol, a potential co-reductant for the activation of molecular oxygen [39], did not work here. The use of DMF (or DMA) as the solvent suggests several possible roles, such as coordination with cobalt sites to form the true active sites during the reaction and/or acting as a co-reductant.

Table 6 shows the catalytic performances for the epoxidation of styrene with different oxidants over the $[Co(Bzo_2[12]aneN_4)]^{2+}$-NaY catalyst. No styrene conversion was observed when the reaction was carried out under Ar or a pure N_2 atmosphere without any oxidants. In the case of molecular oxygen, styrene oxide and benzaldehyde were produced. Very low activity was obtained with NaClO; although styrene conversion was high with TBHP, styrene oxide selectivity was very low. In addition to

Table 6. Epoxidation of styrene with various oxidants over the $[Co(Bzo_2[12]aneN_4)]^{2+}$-NaY (Co, 1.30 mmol).[a]

Oxidant	Styrene conversion (%)	Epoxide selectivity (%)
None[b]	–	–
O_2	65.2	86.5
H_2O_2	42.6	82.3
TBHP	85.3	20.2
NaClO	5.2	93.3

[a] Reaction conditions: reaction temperature, 373 K; styrene, 10 mmol; DMF, 20 mL; reaction time, 6 h.
[b] The reaction was carried out under nitrogen atmosphere without adding an oxidant.

benzaldehyde (38%), polymeric products were among the by-products for TBHP, indicating free radical reactions. Hydrogen peroxide gave reasonably good performance for the epoxidation of styrene, but styrene conversion was lower compared to molecular oxygen. Rapid decomposition of hydrogen peroxide into molecular oxygen over the catalyst initially could be the reason for lower activity. Therefore, the current Co-based catalysts are very specific in the activation of molecular oxygen for the epoxidation of alkenes.

Many cobalt(II) complexes bind and activate molecular oxygen to form complexes comprising cobalt(III)-(O^{2-}) [40]. It was supposed that this research has a similar binding of molecular oxygen to cobalt(II) located in the molecular sieves. The formed Co(III)-(O^{2-}) species might undergo further reactions to generate an active radical oxygen species responsible for the epoxidation. It is known that cobalt (III) ions catalyze the formation of an acylperoxy radical from benzaldehyde by molecular oxygen [41]. The acylperoxy radical may epoxidize alkenes to epoxides and benzoic acid. In this system, although benzaldehyde was formed as a by-product, formation of a significant amount of benzoic acid was not observed. Moreover, the epoxidation was not significantly enhanced when excess benzaldehyde was added to the reactant mixture, excluding the possibility that benzaldehyde acts as the co-reductant. However, DMF itself may act as a co-reductant in the formation of active oxygen species. To clarify this point, the influence of the addition of a radical scavenger, butyl hydroxy toluene, on catalytic performance has been investigated. The results reveal that with $[Co(Bzo_2[12]aneN_4)]^{2+}$-NaY catalyst, styrene conversion decreased to almost zero after addition of a small amount of butyl hydroxy toluene, confirming the radical nature of the active oxygen species formed by molecular oxygen with cobalt(II).

The activity of styrene oxidation decreases $[Co(azamac.)](ClO_4)_2 > CoCl_2$ with the trend observed in tables 4 and 5 and figures 2 and 3 explained by the donor ability of ligand. As Wang and co-workers have pointed out recently, the key point in the conversion of olefin to product is the reduction of L–Co^{3+} to L–Co^{2+}, which is facilitated with the ligands [42]. As mentioned before [43–46], higher activity of $[Co(Bzo_2[12]aneN_4)]^{2+}$-NaY may be attributed to higher activity of aromatic ligand and its more active cation radical intermediate with respect to the aliphatic ligand system ethylenediamine. Lower activity of $[Co([14]aneN_4)]^{2+}$-NaY can be accounted by the substantial steric hindrance of propylene groups that prevent the approaching oxidant toward the cobalt.

4. Conclusions

The cobalt(II) azamacrocycle encapsulated in nanopores of faujasite catalyze the epoxidation of styrene by molecular oxygen with higher efficiency than cobalt(II) azamacrocycle in the liquid phase. Oxygen is a better oxidant for epoxidation than H_2O_2, TBHP, and NaClO over $[Co(Bzo_2[12]aneN_4)]^{2+}$-NaY. An oxygen species with radical nature has been proposed for the epoxidation. These catalyst systems offer structural integrity by uniform distribution of the cobalt complex in the nanopore structure of the support. The zeolite framework keeps the guest complexes dispersed and prevents their dimerization thus retaining catalytic activity. Future work on this system will examine industrial applications for partial oxidation.

References

[1] P.K. Dutta. *J. Inclus. Phenom. Mol. Recognition Chem.*, **21**, 215 (1995).
[2] I.F.J. Vankelecom, R.F. Parton, M.J.A. Casselman, J.B. Uytterhoeven, P.A. Jacobs. *J. Catal.*, **163**, 457 (1996).
[3] N. Herron. *J. Coord. Chem.*, **19**, 25 (1988).
[4] D. Chatterjee, H.C. Bajaj, A. Das, K. Bhatt. *J. Mol. Catal. A: Chem.*, **92**, L235 (1994).
[5] R. Raja, P. Ratnasamy. *J. Catal.*, **170**, 244 (1997).
[6] C.R. Jacobs, S.P. Varkey, P. Ratnasamy. *Micropor. Mesopor. Mater.*, **33**, 465 (1998).
[7] K.J. Balkus Jr., A.G. Gabrielov. *J. Incl. Phenom. Mol. Recog. Chem.*, **21**, 159 (1995).
[8] M. Salavati-Niasari. *J. Mol. Catal. A: Chem.*, **245**, 192 (2006).
[9] M. Salavati-Niasari, F. Davar. *Inorg. Chem. Commun.*, **9**, 175 (2006).
[10] M. Salavati-Niasari, P. Salemi, F. Davar. *J. Mol. Catal. A: Chem.*, **238**, 215 (2005).
[11] J.J.E. Moreau, M.W.C. Man. *Coord. Chem. Rev.*, **178–180**, 1073 (1998).
[12] D. Brunel, N. Bellocq, P. Sutra, A. Cauvel, M. Lasperas, P. Moreau, F. Di Renzo, A. Galarneau, F. Fajula. *Coord. Chem. Rev.*, **178–180**, 1085 (1998).
[13] M.R. Maurya, S.J.J. Titinchi, S. Chand. *J. Mol. Catal. A: Chem.*, **214**, 257 (2004).
[14] D.E. De Vos, M. Dams, B.F. Sels, P.A. Jacobs. *Chem. Rev.*, **102**, 3615 (2002).
[15] M. Salavati-Niasari. *Inorg. Chem. Commun.*, **9**, 268 (2006).
[16] M. Salavati-Niasari. *Inorg. Chem. Commun.*, **8**, 174 (2005).
[17] K.J. Balkus, A.A. Welch, E.B. Gnade. *Zeolites*, **10**, 722 (1990).
[18] C. Bowers, K.P. Dutta. *J. Catal.*, **122**, 271 (1990).
[19] S. Nakagaki, C.R. Xawier, A.J. Wosniak, A.S. Mangrich, F. Wypych, M.P. Cantao, I. Denicolo, L.T. Kubota. *Colloids Surf. A*, **168**, 261 (2000).
[20] K.J. Balkus Jr., A.K. Khanmamedowa, K.M. Dixon, F. Bedioui. *Appl. Catal. A: Gen.*, **143**, 159 (1996).
[21] I.L. Viana Rosa, C.M.C.P. Manso, O.A. Serra, Y. Yamamoto. *J. Mol. Catal. A: Chem.*, **160**, 199 (2000).
[22] S.P. Varkey, C. Ratnasamy, P. Ratnasamy. *J. Mol. Catal. A: Chem.*, **135**, 295 (1998).
[23] S.W. Wang, H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquerol, T. Siemieniewska. *Pure Appl. Chem.*, **57**, 603 (1985).
[24] A. Lineares-Solano. Textural characterization of porous carbons by physical adsorption of gases. In *Carbon and Coal Gasification*, J.L. Figueiredo, J.A. Moulijn (Eds), M. Nijhoff, Dordrecht (1986).
[25] S. Chandra, L.K. Gupta. *Spectrochim. Acta A*, **61**, 2139 (2005).
[26] N. Herron, G.D. Stucky, C.A. Tolman. *J. Chem. Soc., Chem. Commun.*, 1521 (1986).
[27] H. Diegruber, P.J. Plath, G. Schulz-Ekloff, M. Mohl. *J. Mol. Catal. A: Chem.*, **24**, 115 (1984).
[28] A.B. Lever. Edn. *Inorganic Electronic Spectroscopy*, 2nd Edn, Elsevier, New York (1968).
[29] M. Salavati-Niasari. *Chem. Lett.*, **34**, 244 (2005).
[30] M. Salavati-Niasari. *Chem. Lett.*, **34**, 1444 (2005).
[31] M. Salavati-Niasari, M. Shaterian, M.R. Ganjali, P. Norouzi. *J. Mol. Catal. A: Chem.*, **261**, 147 (2007).
[32] M. Shakir, O.S.M. Nasman, A.K. Mohamed, S.P. Varkey. *Ind. J. Chem.*, **35A**, 770 (1996).
[33] U.K. Pandey, S.K. Sengupta, S.C. Tripathi. *Polyhedron*, **6**, 1611 (1987).
[34] E.E. Mercer, R.R. Buckley. *Inorg. Chem.*, **4**, 1692 (1981).
[35] L.A. Pederson, J.H. Lunsford. *J. Catal.*, **61**, 39 (1980).
[36] T.L. Barr, D. Briggs, M.P. Seah. *Practical Surface Analysis*, Wiley, New York (1980).

[37] L. Guczi, R. Sundararajan, Zs. Koppany, Z. Zsoldos, Z. Schay, F. Mizukami, S. Niwa. *J. Catal.*, **167**, 482 (1997).
[38] R.A. Sheldon, M. Wallau, I.W.C.E. Arends, U. Schuchardt. *Acc. Chem. Res.*, **31**, 485 (1998).
[39] Y.H. Lin, I.D. Williams, P. Li. *Appl. Catal. A*, **150**, 221 (1997).
[40] R.D. Jones, D.A. Summerville, F. Basolo. *Chem. Rev.*, **79**, 139 (1979).
[41] R. Raja, G. Sankar, J.M. Thomas. *Chem. Commun.*, 829 (1999).
[42] M. Wang, C.J. Hao, Y.P. Wang, S.B. Li. *J. Mol. Catal. A: Chem.*, **147**, 173 (1999).
[43] M. Salavati-Niasari, H. Banitaba. *J. Mol. Catal. A: Chem.*, **201**, 43 (2003).
[44] M. Salavati-Niasari, A. Amiri. *Appl. Catal. A: Gen.*, **290**, 46 (2005).
[45] M. Salavati-Niasari, S.N. Mirsattari. *J. Mol. Catal. A: Chem.*, **268**, 50 (2007).
[46] M. Salavati-Niasari, S. Hydarzadeh. *J. Mol. Catal. A: Chem.*, **237**, 254 (2005).