

# Nanoscale microreactor-encapsulation 14-membered nickel(II) hexamethyl tetraaza: synthesis, characterization and catalytic activity

Masoud Salavati-Niasari\*

*Institute of Nano Science and Nano Technology, University of Kashan, Kashan, P.O. Box 87317-51167, Iran*

Received 20 September 2004; received in revised form 16 November 2004; accepted 20 November 2004

Available online 1 January 2005

## Abstract

Nanoscale microreactor containing (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-4,11-diene)nickel(II) were successfully have been prepared by the template condensation of tris(ethylenediamine)nickel(II) complex with acetone within the nanodimensional pores of zeolite Y. This complex were entrapped in the supercage of zeolite Y by a two-step process in the liquid phase (i) inclusion of a nickel(II) precursor complex  $[\text{Ni}(\text{en})_3]^{2+}\text{-NaY}$  and (ii) in situ template reaction of the nickel(II) precursor complex with the acetone. The new material  $[\text{Ni}(\text{Me}_6[14]\text{ane N}_4)]^{2+}\text{-NaY}$  characterized by several techniques: chemical analysis and spectroscopic methods (FT-IR, UV-vis, XPS, XRD, BET, DRS). Analysis of the data indicates that the nickel(II) complex are encapsulated in the nanodimensional pores zeolite and exhibit different from the free this of complex, which can arise from distortions caused steric effects due to the presence of sodium cations, or from interactions with the zeolite matrix. The host-guest nanoscale tetraaza macrocycle was found catalytic activity. Cyclohexene was catalytically oxidized in the presence of molecular oxygen and  $[\text{Ni}(\text{Me}_6[14]\text{ane N}_4)]^{2+}\text{-NaY}$  in the absence of solvent at 70 °C, affording 2-cyclohexene-1-ol and 2-cyclohexene-1-one. The effect of temperature, and the amount of  $[\text{Ni}(\text{Me}_6[14]\text{ane N}_4)]^{2+}\text{-NaY}$  used on the catalytic activity and product selectivity were discussed.

© 2004 Elsevier B.V. All rights reserved.

**Keywords:** Microreactor; Nanoscale; Nickel(II); 14-Membered macrocycle; Tetraaza; Oxidation; Cyclohexene

## 1. Introduction

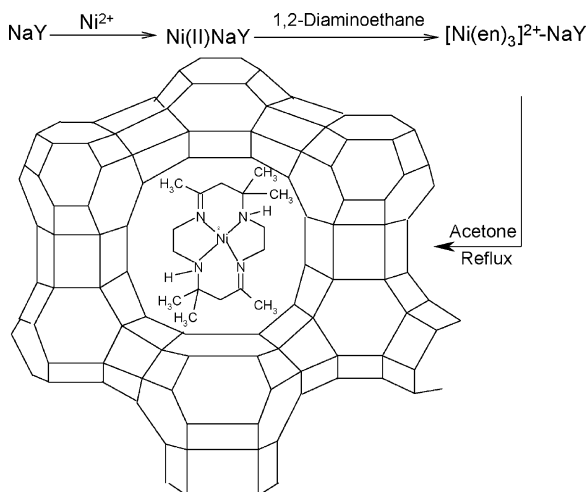
Oxidation is an important reaction in organic chemistry. An attractive oxidant in these oxidation reactions is molecular oxygen because it is an inexpensive and environmentally friendly reactant. Many processes based on molecular oxygen, however, require elevated temperatures. As a consequence, there is a demand for mild and selective aerobic oxidation processes. Macrocyclic metal complexes have recently attracted attention as dioxygen activation catalysts in oxidation reactions. The catalytic ability of nickel(II) macrocyclic complexes towards hydrocarbon oxidation has been well documented in [1–6]. Some square-planar nickel(II) complexes of macrocyclic ligands such as cyclam and Schiff-base have been shown to act as catalysts for epoxidation of alkenes

when PhIO [1,2] or NaOCl [3,8–11] was used as a terminal oxidant. However, catalytic efficiency of these complexes remains inexplicable with regards to the general consideration of the systematic of the metal redox as a function of coordination environment and the nature of terminal oxidants. The full capacity of these oxidation reactions, however, can be realized only if the metal complexes can be made stable towards self-oxidation and degradation and can be used in subsequent catalytic cycles.

Metal macrocycles encapsulated in nanoscale microreactors such as zeolites seem to be a solution to overcome the above-mentioned problems. In these catalysts the large, electrostatic metals macrocycle species is held in the zeolite cavities topologically rather than electroneutrally. These combine successfully the advantages of homogeneous catalysts, especially their selectivity and controllability, with the ease of separation and stability of heterogeneous catalysts.

\* Tel.: +98 361 555 333; fax: +98 361 552 930.

E-mail address: [salavati@kashanu.ac.ir](mailto:salavati@kashanu.ac.ir).



In this paper, we report the synthesis and characterization of nickel(II) complex of 14-membered tetraaza macrocyclic ligand “5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienenickel(II)”, encapsulated within the nanodimensional pores of zeolite Y by template reaction of tris(ethylenediamine)nickel(II) complex with acetone, “[Ni(Me<sub>6</sub>[14]ane N<sub>4</sub>)<sup>2+</sup>-NaY (Scheme 1). In continue we report here the oxidation of cyclohexene catalyzed by [Ni(Me<sub>6</sub>[14]ane N<sub>4</sub>)<sup>2+</sup>-NaY. The reaction was performed in the presence of atmospheric pressure of molecular oxygen in the absence of solvent at 70 °C, without the use of any special oxidant or conductant. Under these reaction conditions, 2-cyclohexene-1-ol and 2-cyclohexene-1-one were product. The effect of temperature and the amount of catalyst used on the reactivity and product selectivity were discussed.

## 2. Experimental

### 2.1. Materials

All other reagents and solvent were purchased from Merck (pro-analysis) and was dried using molecular sieves (Linda 4 Å). NaY with the Si:Al ratio of 2.53 was purchased from Aldrich (Lot No. 67812). Cyclohexene was distilled before use. Cyclohexanone was used as an internal standard for the quantitative analysis of the product using gas chromatography. 2-Cyclohexene-1-ol and 2-cyclohexene-1-one were identified by comparisons of their retention times with those of pure compounds (obtained from Merck). The acid salt of the ligand (Me<sub>6</sub>[14]ane N<sub>4</sub>)-2HClO<sub>4</sub> was prepared by the method of Curtis et al. [12].

### 2.2. Physical measurements

After completely destroying the zeolitic framework with hot and concentrated HCl, sodium, aluminum and nickel were

analyzed by atomic absorption spectrophotometer (AAS, Perkin-Elmer 4100-1319) and SiO<sub>2</sub> was determined by gravimetric analysis. FT-IR spectra were recorded on 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 the range 1500–200 nm, using MgO as reference. The elemental analysis (carbon, hydrogen and nitrogen) of the materials was obtained from Carlo ERBA Model EA 1108 analyzer. XRD patterns were recorded by a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu K $\alpha$  radiation. Nitrogen adsorption measurements were performed at 77 K using a Coulter Omnisorb 100CX instrument. The samples were degassed at 150 °C until a vacuum better than 10<sup>-3</sup> Pa was obtained. Micropore volumes were determined by the *t*-methanol [20]; a “monolayer equivalent area” was calculated from the micropore volume [20]. 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 catalyst. The products were analyzed by GC-MS, using a Philips Pu 4400 Chromatograph (1.5 m, 3% OV-17 Column), Varian 3400 Chromatograph (25 m, DB-5 Column) coupled with a QP Finnegan MAT INCOF 50, 70 eV. X-ray photoelectron spectroscopy (XPS) analysis was performed at room temperature on a PHI-500 ESCA/SAM spectrometer with the use of Mg K $\alpha$  radiation ( $h\nu = 1254$  eV). The typical X-ray powder was 320 W. All XPS spectra were energy referenced to the C 1s photoemission peak at 284.6 eV.

### 2.3. Preparation of neat complex

The [Ni(Me<sub>6</sub>[14]ane N<sub>4</sub>)](ClO<sub>4</sub>)<sub>2</sub> was prepared by heating 50 ml of a 1:1 methanol-water mixture with an excess of nickel(II) carbonate and 2 g of [Me<sub>6</sub>[14]ane N<sub>4</sub>]-2HClO<sub>4</sub> on a steam bath for 5–10 min. The yellow solution thus formed was filtered from the unreacted nickel(II) carbonate and evaporated to a small volume. On cooling the concentrated solution the yellow nickel(II) complex crystallized. The product was recrystallized from hot water [12].

### 2.4. Preparation of Ni(II)-NaY

A 2 g NaY zeolite was suspended in 100 ml distilled water, which contained nickel(II) nitrate (0.025 M). The mixture was then heated while stirring at 90 °C for 24 h. The solid was filtered, washed with hot distilled water till the filtrate was free from any nickel(II) ion (by AAS of filtrate) content and dried for 10 h at 80 °C under vacuum. The ionic exchange degree was determined by atomic absorption spectrophotometer.

### 2.5. Preparation of [Ni(en)<sub>3</sub>]<sup>2+</sup>-NaY

A solution of three-fold excess ethylenediamine in dry methanol was added to a suspension of dry Ni(II)-NaY

in CH<sub>3</sub>OH. The resulting suspension was stirred at 50 °C under Ar atmosphere. The light yellow solid was filtered, washed with CH<sub>3</sub>OH. The samples were Soxhlet-extracted with ethanol for 8 h to remove excess ethylenediamine and Ni(II) complexes from the external surface of zeolite crystalline. The resulting light yellow solid [Ni(en)<sub>3</sub>]<sup>2+</sup>-NaY, was dried at 90 °C for 24 h. The remaining uncomplexed nickel(II) ions were removed by exchanging with aqueous 0.1 M NaNO<sub>3</sub> solutions.

### 2.6. Preparation of [Ni(Me<sub>6</sub>[14]ane N<sub>4</sub>)<sup>2+</sup>-NaY

[Ni(en)<sub>3</sub>]<sup>2+</sup>-NaY (2 g) was mixed in acetone (200 ml) and the suspension kept at reflux and after 24 h reflux the solid changed color to light orange. The samples were Soxhlet-extracted with ethanol for 12 h to remove nickel(II) complexes from the external surface of zeolite crystallites. The resulting light orange solid [Ni(Me<sub>6</sub>[14]ane N<sub>4</sub>)<sup>2+</sup>-NaY, was dried at 60 °C for 10 h.

## 3. Results and discussion

### 3.1. Characterization of [Ni(Me<sub>6</sub>[14]ane N<sub>4</sub>)<sup>2+</sup>-NaY

Refluxing of the [Ni(en)<sub>3</sub>]<sup>2+</sup>-NaY with acetone for about 24 h effected template formation of the 14-membered tetraaza macrocyclic in the cavity followed by complex formation with metal ion (Scheme 1). The crude mass was finally purified by Soxhlet-extraction method. The remaining tris(ethylenediamine)nickel(II) ions in nanodimensional pores of zeolite Y were removed by exchanging with aqueous 0.1 M NaNO<sub>3</sub> solution. The flexible ligand synthesis lead to the encapsulation of Ni(II) complexes of tetraaza ligand inside the zeolite pore. The results of chemical analyses of the samples are given in Table 1. The parent NaY zeolite has Si/Al molar ratio of 2.53 which corresponds to a unit cell formula Na<sub>56</sub>[(AlO<sub>2</sub>)<sub>56</sub>(SiO<sub>2</sub>)<sub>136</sub>]. Metal ion exchange at 39% leads to a metal loading 3.8% in zeolite. The unit cell formula of metal-exchanged zeolites show a nickel dispersion of 11.1 moles per unit cell (Na<sub>33.8</sub>Ni<sub>11.1</sub>[(AlO<sub>2</sub>)<sub>56</sub>(SiO<sub>2</sub>)<sub>136</sub>].*n*H<sub>2</sub>O). The analytical data of each complex indicate Ni:C:N molar ratios almost close to those calculated for the mononuclear structure. However, the presence of minute traces of free [Ni(en)<sub>3</sub>]<sup>2+</sup> in the lattice could be assumed as the [Ni(en)<sub>3</sub>]<sup>2+</sup>

Table 2  
DRS absorption and IR stretching frequencies of ligand, complexes and nanoscale microreactor-encapsulated of 14-membered nickel(II) complexes

Sample	IR (KBr, cm <sup>-1</sup> )				d-d (cm <sup>-1</sup> )
	ν <sub>N-H</sub>	ν <sub>NH<sub>2</sub></sub>	ν <sub>C=N</sub>	ν <sub>C-H</sub>	
[Me <sub>6</sub> [14]aneN <sub>4</sub> ]-2HClO <sub>4</sub>	3145	1544	1670	2910	–
[Ni(Me <sub>6</sub> [14]aneN <sub>4</sub> )(ClO <sub>4</sub> ) <sub>2</sub> NaY	3170	–	1662	2932	2320 <sup>a</sup>
Ni(II)-NaY	–	–	–	–	–
[Ni(en) <sub>3</sub> ] <sup>2+</sup> -NaY	–	–	–	–	25300
[Ni(en) <sub>3</sub> ] <sup>2+</sup> -NaY	–	1537	–	2925	29000
[Ni(Me <sub>6</sub> [14]ane N <sub>4</sub> ) <sup>2+</sup> -NaY	3158	–	1658	2936	23400

<sup>a</sup> In aqueous solutions at 25 °C as never specified.

content is slightly higher than the stoichiometric requirement only a portion of [Ni(en)<sub>3</sub>]<sup>2+</sup> in exchanged zeolite has undergone complexation and the rest is expected to be removed on re-exchange with sodium nitrate solution.

The chemical compositions (Table 1) confirmed the purity and stoichiometry of the neat and zeolite-encapsulated complexes. The chemical analyses of the samples reveal the presence of organic matter with a C/N ratio roughly similar to that for neat complexes. In Table 1 the mol ratios Si/Al obtained by chemical analysis for zeolites are presented. The Si and Al contents in NiNaY and the zeolite complexes are almost in the same ratio as in the parent zeolite. This indicates little changes in the zeolite framework due to the absence of de-alumination in metal ion exchange. The X-ray diffraction patterns of zeolite contained tetraaza complexes are similar to those of NiNaY and the parent NaY zeolite. The zeolite crystallinity is retained on encapsulating complexes. Crystalline phase of free metal ions or encapsulation ligand complexes were not detected in any of the patterns as their fine dispersion in zeolite might have rendered them non-detectable by XRD.

IR spectroscopy can provide information on the encapsulated metal complexes and on the crystallinity of the host zeolite. The spectra of all samples are dominated by bands due to the zeolite [13] (surface hydroxyl groups, ν<sub>OH</sub>, in the range 3700–3300 cm<sup>-1</sup>; lattice vibrations in the range 1300–450 cm<sup>-1</sup>), even though the presence of nickel(II) complexes can be detected (Table 2). No significant dealumination or expansion of the cavities took place, as the zeolite structure-sensitive vibrations (e.g. the asymmetric stretch at 1130 cm<sup>-1</sup> and the symmetric stretch at 810 cm<sup>-1</sup>) did not shift or broaden significantly upon inclusion of the complexes. This result supports the observation that the encapsu-

Table 1

Chemical composition of ligand, complexes and nanoscale microreactor-encapsulated of 14-membered nickel(II) complexes (calculated values are given in parentheses)

Sample	C (%)	H (%)	N (%)	C/N	Si (%)	Al (%)	Na (%)	Ni (%)	Si/Al
[Me <sub>6</sub> [14]aneN <sub>4</sub> ]-2HClO <sub>4</sub>	40.01 (39.11)	7.10 (6.86)	11.71 (11.93)	3.42 (3.28)	–	–	–	–	–
[Ni(Me <sub>6</sub> [14]aneN <sub>4</sub> )(ClO <sub>4</sub> ) <sub>2</sub> NaY	35.71 (35.11)	5.99 (5.70)	10.40 (10.51)	3.43 (3.34)	–	–	–	10.91 (10.78)	–
NaY	–	–	–	–	21.76	8.60	7.50	–	2.53
Ni(II)-NaY	–	–	–	–	21.79	8.62	3.28	3.72	2.53
[Ni(en) <sub>3</sub> ] <sup>2+</sup> -NaY	2.27	2.16	2.64	0.86	19.84	7.84	5.29	1.85	2.53
[Ni(Me <sub>6</sub> [14]aneN <sub>4</sub> ) <sup>2+</sup> -NaY	3.45	2.24	1.04	3.31	19.83	7.83	5.28	1.16	2.53

lation process does not modify the zeolite framework. The bands due to the complexes are weaker (due to a low concentration of the complexes) and thus can only be observed in the regions where the zeolite matrix does not absorb, i.e. from 1200–1620  $\text{cm}^{-1}$ . The IR bands of zeolite-encapsulated nickel(II) complexes occur at frequencies shifted within  $\sim 10 \text{ cm}^{-1}$  from those of the free complex; furthermore, some changes in band intensities can be observed in the region of the N–H stretching vibration. These observations not only confirm the presence of nickel(II) complex of 14-membered tetraaza macrocycle in the zeolite, but also suggest that its structure is not identical to that of the neat complex, thus, stereochemically induced 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, can not be ruled out [14,15]. The entrapped tetraaza complex exhibit very similar IR spectra with bands at all regions that are shifted  $\sim 10 \text{ cm}^{-1}$  relative to those of the corresponding free complex (Table 2). These vibrations in band frequency can also be attributed to (i) distortions of the complexes, or to (ii) interactions with the zeolite matrix (by electrostatic effects or coordination—the higher negative charge of the zeolite host makes it a strong ligand) (Table 2).

Electronic data for neat and encapsulated nickel(II) complex within the nanodimensional pores of zeolite Y are summarized in Table 2. Bands due to  $[\text{Ni}(\text{Me}_6[14]\text{ane N}_4)]^{2+}\text{-NaY}$  appear at  $23,400 \text{ cm}^{-1}$ , and charge transfer bands appear in the near-UV region (at  $46,800$ ,  $\epsilon = 17,000$ ); these values are very similar to those obtained for the discrete complex (Table 2). Electronic spectra of the encapsulated 14-membered tetraaza macrocycle complex are very similar and show  $d \leftrightarrow d$  bands in the visible region: again, they are also similar to those obtained for the corresponding discrete complexes and to those of other  $\text{N}_4$  macrocycle nickel(II) complexes [12,16,17].

Surface area and pore volume values estimated by the low-temperature nitrogen adsorption at relative pressures ( $P/P_0$ ) in the range 0.05–0.9 are given in Table 3. There is a drastic reduction of surface area and pore volume of zeolites on encapsulating the nickel(II) complexes. Since the zeolite framework structure is not affected by encapsulation as shown by the XRD pattern, the reduction of surface area and pore volume provides direct evidence for the presence of complexes in the cavities [18].

Table 3  
Nitrogen adsorption isotherm data for parent zeolite and nickel modified zeolites

Sample	Surface area <sup>a</sup> ( $\text{m}^2/\text{g}$ )	Pore volume <sup>b</sup> ( $\text{ml}/\text{g}$ )
NaY	545	0.31
NiNaY	528	0.31
$[\text{Ni}(\text{en})_3]^{2+}\text{-NaY}$	415	0.24
$[\text{Ni}(\text{Me}_6[14]\text{ane N}_4)]^{2+}\text{-NaY}$	390	0.23

<sup>a</sup> Surface area is the “monolayer equivalent area” calculated as explained in Ref. [20].

<sup>b</sup> Calculated by the *t*-method.

XPS have shown the Ni ( $2p_{3/2}$ ) binding energy ( $E_b$ ) is 859.2 in the  $[\text{Ni}(\text{Me}_6[14]\text{ane N}_4)]^{2+}\text{-NaY}$  and 856.3 eV in  $\text{NiCl}_2$ . The Ni ( $2p_{3/2}$ ) binding energy of the tetraaza complex was increased 2.9 eV compared with that of the Ni(II) chloride. The results indicate that the charge on the nickel atoms is decreased when complex was formed. The N 1s binding energy is 400.3 eV in complex and 399.6 eV in  $[\text{Me}_6[14]\text{ane N}_4]\cdot 2\text{HClO}_4$ . Compared with that of  $[\text{Me}_6[14]\text{ane N}_4]\cdot 2\text{HClO}_4$ , the N 1s bonding energy of complex is increased 0.7 eV. The resolved N 1s XPS spectrum of the tetraaza complex shows two N 1s XPS peak that correspond to the one component of the nitrogen. The low energy (394.5 eV) component belongs to the coordinate nitrogen of the N–H bonds, and the high energy (400.3 eV) component may belong to the coordinated nitrogen of imines. The change of both Ni ( $2p_{3/2}$ ) and N 1s binding energy of the tetraaza macrocycle complex suggests that the charge on the nickel atoms is decreased while that on nitrogen atoms is increased when the complex was formed. The result suggests that the back-donation from the nickel atoms to the anti- $\pi$  orbitals of the 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-4-11-diene rings prevails over the donation from the nitrogen atoms to the d orbitals of the nickel ions. We tentatively suggest that for a metal ions rich in d-electrons such as nickel(II) ions ( $3d^8$ ), the back donation from metal ions to the anti- $\pi$  orbitals of the conjugated system prevails over the donation from the coordinated atoms such as nitrogen to d orbitals or hybridized orbitals of the metal ions.

### 3.2. Catalytic activity

One of the major drawbacks of homogeneous metal complexes as catalysts is their irreversible deactivation due to formation of  $\mu$ -oxo and  $\mu$ -peroxo dimeric and other polymeric species especially when using oxidant. Since the formation of these bulky dimeric/polymeric species is sterically impossible when the monomeric complex is encapsulated and physical confined within the nanodimensional pores of zeolite Y, it was anticipated that encapsulated catalysts would be more rugged and can be recycled for use. The data in Table 5 support the above hypothesis. As mentioned earlier, the neat complexes could not be recycled even once as they lost their catalytic activity after use. By contrast, the encapsulated, solid catalysts could be filtered, washed with a solvent and reused without major loss in activity (Table 4) [19].

In our recent publications, we reported the role of some transition metals and their complexes included within zeolite Y and supported on alumina as catalysts in the activation of C–H bond [19]. In both cases, it was observed that these catalysts were able to transfer oxygen from TBHP to substrate and hydroxylate the hydrocarbons.

Results of Table 5 show the catalytic activity of homogeneous catalysts. Comparing between neat and zeolite encapsulated complexes as catalyst evidence that zeolite-encapsulated catalysts gave higher conversion of cyclohexene

Table 4  
Effect of temperature on the reactivity and product selectivity

Temperature	Conversion (%)	Selectivity (%)	
		2-Cyclohexene-1-ol	2-Cyclohexene-1-one
50	4.8	60.2	39.8
60	10.6	62.6	37.4
70	61.6	65.5	34.5
70 <sup>a</sup>	61.2	65.2	34.8
70 <sup>b</sup>	60.9	64.6	35.4
70 <sup>c</sup>	60.6	62.5	37.5
80	20.6	68.6	31.4

Reaction condition: 1 atm of O<sub>2</sub>; time 8 h; catalyst 10 mg; substrate, cyclohexene 10 ml.

<sup>a</sup> First reuse.

<sup>b</sup> Second reuse.

<sup>c</sup> Third reuse.

than their corresponding neat complexes. The higher activity of encapsulated complexes is because of site isolation of the complexes.

The selectivity and activity of this zeolite-encapsulated catalyst on the oxidation of cyclohexene with O<sub>2</sub> are given in Tables 4 and 5. At the end of reaction, the catalyst was separated by filtrations, thoroughly washed with solvent and reused under similar conditions by atomic absorption spectroscopy showed no reduction in the amount of copper; they exhibited slightly lower catalytic activities (0.80%).

### 3.2.1. Effect of temperature on the reactivity and product selectivity

Generally, 10 ml of cyclohexene and 10 mg of heterogeneous catalyst were added to a glass reactor with a gas inlet tube connected to a gas burette and an oxygen storage bottle. The mixture was heated to 70 °C in water bath and stirred with a magnetic stirring bar. The oxidation reactions were performed under atmospheric pressure of molecular oxygen in the absence of solvent, giving 2-cyclohexene-1-ol and 2-cyclohexene-1-one as the major products. To investigate

Table 5  
Effect of the amount of heterogeneous catalyst used on the reactivity

Amount of catalyst (mg)	Conversion (%)	Selectivity (%)	
		2-Cyclohexene-1-ol	2-Cyclohexene-1-one
5	53.2	53.6	46.4
6	54.5	55.4	44.6
7	56.3	57.6	42.4
8	57.4	59.4	40.6
9	59.6	61.3	38.7
10	61.6	65.5	34.5
11	59.1	60.6	39.4
12	58.3	51.4	48.6
1 <sup>a</sup>	51.6	53.2	36.8
2 <sup>a</sup>	53.9	54.7	35.3
3 <sup>a</sup>	46.7	60.5	29.7
4 <sup>a</sup>	44.8	64.3	21.8

Reaction condition: 1 atm of O<sub>2</sub>; time 8 h; substrate, cyclohexene 10 ml at 70 °C.

<sup>a</sup> Reaction condition: 1 atm of O<sub>2</sub>; time 8 h; cyclohexene 10 ml; homogeneous catalyst.

the effect of temperature on the reactivity and product selectivity of catalyst, the oxidations were carried out only at temperatures >50 °C. The results are shown in Table 4. At temperatures ranging from 50 to 80 °C, the reactivity and product selectivity of the complex varies with the temperature. At 70 °C the conversion is 61.6% and the selectivity to 2-cyclohexene-1-ol and 2-cyclohexene-2-one is 65.5% and 34.5%, respectively, while at 50 °C. The conversion is 4.8% and the selectivity to 2-cyclohexene-1-ol and 2-cyclohexene-1-one is 60.2% and 39.8%, respectively. The typical trend shows that reactivity and the selectivity to 2-cyclohexene-1-ol are increased with the temperature in the range of 50–70 °C.

### 3.2.2. Effect of the amount of catalyst used on the reactivity

To investigate the effect of catalyst used on the reaction, the oxidation were carried out at 70 °C by varying the amount of catalyst; [Ni(Me<sub>6</sub>[14]ane N<sub>4</sub>)]<sup>2+</sup>-NaY; while holding the amount of cyclohexene constant. The results are shown in Table 5. The catalytic conversion was found to be related to the amount of catalyst used is 10 mg in 10 ml cyclohexene. Although the amount of catalyst used obviously influenced the reactivity of the catalyst, it showed a relatively small effect on the product distribution.

## 4. Conclusion

The results show that [Ni(Me<sub>6</sub>[14]ane N<sub>6</sub>)]<sup>2+</sup> can be encapsulated in the nanodimensional pores of zeolite NaY by in situ template condensation between pre-entrapped Ni(en)<sub>3</sub><sup>2+</sup> complexes and acetone. This strategy appears to be effective for the encapsulated of metal complexes with 14-membered tetraaza macrocycle ligands derived from [Ni(en)<sub>3</sub>]<sup>2+</sup>-NaY, as in situ one-pot template condensation in the supercage is still possible and no unreacted [Ni(en)<sub>3</sub>]<sup>2+</sup> ions was detected. Furthermore, the spectroscopic data suggest that the encapsulated complexes do not experience extensive distortions in the supercage and that chemical ligation to the zeolitic surface is minimal. Cyclohexene was catalytically oxidized in the presence of molecular oxygen and host-guest nanocatalyst in the absence of solvent at 70 °C, affording 2-cyclohexene-1-ol and 2-cyclohexene-1-one. The effect of temperature, and the amount of nanocatalyst used on the catalytic activity and product selectivity were discussed.

## References

- [1] J.D. Koola, J.K. Kochi, *Inorg. Chem.* 26 (1987) 908.
- [2] J.F. Kinnary, T.R. Wagler, C.J. Burrows, *Tetrahedron Lett.* 29 (1988) 877.
- [3] H. Yoon, C.J. Burrows, *J. Am. Chem. Soc.* 110 (1988) 4087.
- [4] D. Chatterjee, H.C. Bajaj, S.B. Halligudi, K.N. Bhatt, *J. Mol. Catal.* 84 (1993) 1.
- [5] D. Chatterjee, S. Mukherjee, A. Mitra, *J. Mol. Catal.* 154 (2000) 5.
- [6] D. Lee, H. Bang, M.P. Suh, *J. Mol. Catal.* 51 (2000) 71.

- [8] M. Yamada, S. Ochi, H. Suzuki, A. Hisazumi, S. Kuroda, I. Shima, K. Araki, *J. Mol. Catal.* 87 (1994) 195.
- [9] H. Yoon, T.R. Wagler, K.J. O'connor, C.J. Burrows, *J. Am. Chem. Soc.* 112 (1990) 4568.
- [10] T.R. Wagler, Y. Fang, C.J. Burrows, *J. Org. Chem.* 54 (1989) 1584.
- [11] T.R. Wagler, C.J. Burrows, *Tetrahedron Lett.* 40 (1988) 5091.
- [12] N.F. Curtis, Y.M. Curtis, H.K.J. Powell, *J. Chem. Soc. A* (1966) 1015;  
N.F. Curtis, *J. Chem. Soc.* (1960) 4409;  
M.M. Blight, N.F. Curtis, *J. Chem. Soc.* (1962) 1204;  
N. Sadasivan, J.F. Endicott, *J. Am. Chem. Soc.* 88 (1966) 5468.
- [13] B. Imelik, J.V. Vadrine, *Catalyst Characterization, Physical Techniques for Solid Materials*, Plenum Press, New York, 1994.
- [14] L. Fruncka, H. Kosslick, *J. Mol. Catal. A: Chem.* 123 (1997) 179.
- [15] B.Z. Zhan, X.Y. Li, *Chem. Commun.* (1998) 349.
- [16] A.B.P. Lever, J. Lewis, R.S. Nyholm, *J. Chem. Soc.* (1963) 2552.
- [17] (a) M. Salavati-Niasari, H. Najafian, *Polyhedron* 22 (2003) 2633;  
(b) M. Salavati-Niasari, M. Rezai-Adaryani, *Polyhedron* 23 (2004) 1325;  
(c) M. Salavati-Niasari, *Inorg. Chem. Comm.* 7 (2004) 698;  
(d) S.G. Kang, M.S. Kim, K. Ryu, *Polyhedron* 15 (1996) 1835;  
(e) B. Korybut-Daszkiwicz, *J. Coord. Chem.* 19 (1988) 101;  
(f) R.W. Hay, M.P. Pujari, B. Korybut-Dasz-Kiewicz, G. Ferguson, B. Ruhl, *J. Chem. Soc., Dalton Trans.* (1989) 85;  
(g) B. Korybut-Daszkiwicz, *J. Chem. Soc., Dalton Trans.* (1992) 1673;  
(h) G.A. Lawrence, M.A. O'Leary, *Polyherdon* 6 (1987) 1291;  
(i) M.P. Suh, W. Shin, D. Kim, S. Kim, *Inorg. Chem.* 23 (1984) 618;  
M.P. Suh, D. Kim, S. Kim, *Inorg. Chem.* 24 (1985) 3712;  
M.P. Suh, W. Shin, H. Kim, C.H. Koo, *Inorg. Chem.* 26 (1987) 1846;  
M.P. Suh, S.-G. Kang, *Inorg. Chem.* 27 (1988) 2544;  
M.P. Suh, W. Shin, S.-G. Kang, M.S. Lah, T.-M. Chung, *Inorg. Chem.* 28 (1989) 1602;  
S.-K. Jung, S.-G. Kang, M.P. Suh, *Bull. Korean Chem. Soc.* 10 (1989) 362;  
M.P. Suh, S.-G. Kang, V.L. Goedken, S.-H. Park, *Inorg. Chem.* 30 (1991) 365;  
M.P. Suh, D. Kim, *Inorg. Chem.* 24 (1985) 3712;  
M.P. Suh, W. Shin, H. Kim, C.H. Koo, *Inorg. Chem.* 26 (1987) 1846.
- [18] K.J. Balkus, A.G. Gabrielov, *J. Inclu. Phenom. Mol. Recognition Chem.* 21 (1995) 159.
- [19] (a) M. Salavati-Niasari, *J. Mol. Catal. A* 217 (2004) 87;  
(b) M. Salavati-Niasari, S.H. Banitaba, *J. Mol. Catal. A* 201 (2003) 43;  
(c) M. Salavati-Niasari, F. Farzaneh, M. Ghandi, L. Turkian, *J. Mol. Catal. A* 148 (2000) 183;  
(d) M. Salavati-Niasari, J. Hasanalian, H. Najafian, *J. Mol. Catal. A: Chem.* 209 (2004) 209;  
(e) M. Salavati-Niasari, M.R. Elzami, M.R. Mansournia, S. Hydarzadeh, *J. Mol. Catal. A* 221 (2004) 169.
- [20] S.W. Wang, H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquerol, T. Siemieniowska, *Pure Appl. Chem.* 57 (1985) 603;  
A. Lineares-Solano, Textural characterization of porous carbons by physical adsorption of gases, in: J.L. Figueiredo, J.A. Moulijn (Eds.), *Carbon and Coal Gasification*, Martinus Nijhoff, Dordrecht, MA, 1986, p. 137.

### Further reading

- [7] J.F. Kinneary, J.S. Albert, C.J. Burrows, *J. Am. Chem. Soc.* 110 (1988) 6124.