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Article

Diaquabis(*L*-phenylalaninato)nickel(II) Encapsulated in Zeolite: An Efficient Heterogeneous Catalyst System for the Oxidation of Cyclohexene, Toluene and Ethyl Benzene

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L-Fenilalanina reage com zeólita Y submetida a uma troca iônica com níquel(II) para formar diaquabis(*L*-fenilalaninato)níquel(II), o qual é encapsulado nos poros da zeólita. Nesta forma encapsulada, o complexo de níquel funciona como um catalisador eficiente quando ciclo-hexeno, tolueno e etilbenzeno são oxidados por peróxido de hidrogênio na presença de bicarbonato de sódio como cocatalisador. O catalisador foi facilmente recuperado da mistura de reação e foi reutilizado por três vezes sem perda observável de atividade. O catalisador heterogêneo apresentou atividade e seletividade significativamente mais altas quando comparado com o complexo diaquabis(*L*-fenilalaninato)níquel(II).

L-Phenylalanine reacts with nickel-exchanged zeolite Y to form diaquabis(*L*-phenylalaninato) nickel(II), which is encapsulated in the pores of the zeolite. In this zeolite-encapsulated form, the nickel derivative functions as an efficient catalyst when cyclohexene, toluene and ethyl benzene are oxidized by hydrogen peroxide in the presence of sodium bicarbonate (as co-catalyst). The catalyst was readily recovered from the reaction mixture, and it could be re-used for other three runs without noticeable loss of activity. The heterogeneous catalyst exhibited significantly higher activity and selectivity compared with diaquabis(*L*-phenylalaninato)nickel(II) itself.

Keywords: encapsulated catalyst, zeolite, heterogeneous, hydrogen peroxide, co-catalyst

Introduction

The conversion of hydrocarbons in the presence of peroxides as oxidants to oxygenated derivatives such as, for example, alcohols, aldehydes/ketones and carboxylic acids exemplifies a catalytic process that has been extensively studied owing to the importance of the products as reactants in industrial processes.[1] The efficiency of the conversion can be rated in terms of the recovery of the catalyst on completion of the reaction, and this, in turn, is related to the stability of the catalyst.[2] For heterogeneous catalysts in particular, one strategy for improving the stability involves encapsulation of the catalyst in zeolites; other strategies have the catalysts grafted onto polymers or bound onto MCM-41 silica.[3] Transition metal derivatives can be encapsulated in zeolites as encapsulation renders these complexes chemically stable; possibly, their stability allows for high activity so that the resulting catalytic system can selectively oxidize alkanes, alkenes and even alcohols because the molecules of the transition metal complexes themselves do not undergo reaction with themselves.[4] Detailed studies have not found any leaching if the transition metal complexes are confined to the pores of the zeolites.[5] Furthermore, such catalytic systems are also of interest in biomimetic chemistry since they serve as models of enzyme-active centers in which the zeolite framework would then be the rigid protein mantle itself.[6]

In continuation of our previous studies on the oxidation of a range of organic substrates catalyzed by transition metal complexes,[7-11] we report the use of diaquabis(*L*-phenylalaninato)nickel and diaquabis(*L*-phenylalaninato) nickel encapsulated in zeolite as catalyst systems for the oxidation of cyclohexene, toluene and ethyl benzene in the presence of hydrogen peroxide/sodium bicarbonate. The nickel complex is a compound that has already been characterized by crystal structure analysis.[12]

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Experimental

Materials and equipment

Chemicals and solvents were purchased from Merck. The exact concentration of the approximately 30% hydrogen peroxide (10.9 mol L^{-1}) was determined before use by titration with standard potassium permanganate. Elemental analyses were performed on a CHN Perkin-Elmer 2400 analyzer. Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer 597 spectrometer. The chemical composition of the nickel-exchanged zeolite was determined on an inductively coupled plasma atomic emission spectrometer (ICP-AES, Spectro Genesis) after treatment of a calculated quantity of the complex with concentrated hydrochloric acid (37%). X-Ray powder diffractograms were recorded on a Philips PW1130 X-ray diffractometer (XRD) with Cu-$K\alpha$ radiation (λ = 1.54 Å). Thermogravimetric analysis (TGA) was performed on an STA409PC Netzsch thermal analyzer in flowing N_2 (60 mL min^{-1}) at a heating rate of 10 °C min^{-1}. The reaction products of the oxidation were analyzed on an HP Agilent 6890 gas chromatograph (GC) equipped with an HP-5 capillary column (phenylmethylsiloxane 30 m × 320 μm × 0.25 μm) and a flame ionization detector.

Synthesis of the diaquabis(*L*-phenylalaninato)nickel, $[Ni(phe)_2(H_2O)_2]$

The complex was synthesized according to a literature procedure.[12] *L*-Phenylalanine (2 mmol) and sodium hydroxide (2 mmol) in methanol (10 mL) were added to a solution of nickel nitrate hexahydrate (1 mmol) in methanol (5 mL). The mixture was heated for 6 hours. Blue crystals of the compound were obtained upon the slow evaporation of the solvent over 5 days in 70% yield. Elemental analysis calcd.: C 51.10, H 5.72, N 6.62%; found: C 50.61, H 5.6, N 6.85%; IR (KBr) ν_{max}/cm^{-1} 3360 (br), 1645 (vs), 1609 (s), 1497 (s), 1404 (s, δ-NH_2), 555 (w), 575 (w), 467 (w).

Preparation of nickel-exchanged zeolite (Ni-Y)

Ni-Y was prepared by using an ion-exchange method.[13] NaY zeolite (1 g) was suspended in 25 mL aqueous nickel nitrate that contained 0.5 mmol nickel nitrate hexahydrate. The mixture was stirred for 24 h. The solid material was collected, washed with deionized water and dried at 100 °C to give Ni-Y. Analysis of the solution showed that approximately 2.5% of the ion had been exchanged. The Ni-Y product was characterized by FTIR spectroscopy, ICP and XRD. ICP results for Na-Y: Si 21.76, Na 7.5, Al 8.61%; Si/Al = 2.53. ICP results for Ni-Y: Si 21.46, Na 4.25, Al 8.46, Ni 2.46 %; Si/Al = 2.53.

Preparation of diaquabis(*L*-phenylalaninato) encapsulated in zeolite, $[Ni(phe)_2(H_2O)_2]$/Y

The metal complex was encapsulated in zeolite in several steps. The nickel-exchanged zeolite described earlier, along with a large excess of *L*-phenylalanine (1 mmol) were suspended in dichloromethane. The suspension was stirred for 24 hours under nitrogen. Unchanged ligand and any transition metal complex adsorbed on the external surface were removed by Soxhlet extraction with dichloromethane. The extracted product was further ion-exchanged with 0.1 mol L^{-1} sodium chloride to remove nickel ions. This was washed with deionized water until no chloride ions could be detected (by reaction with silver nitrate). The product was then dried in air before being further characterized by FTIR spectroscopy, ICP and XRD. The zeolite-encapsulated product is denoted as $[Ni(phe)_2(H_2O)_2]$/Y. ICP results for $[Ni(phe)_2(H_2O)_2]$/Y: Si 21.05, Na 5.31, Al 8.32, Ni 1.54%, i.e., encapsulated nickel complex corresponded to 0.26 mmol g^{-1} zeolite (or 1.54%); IR (KBr) ν_{max}/cm^{-1} 3640 (b), 3454 (b), 3370 (w), 3090 (w), 2929 (m), 2856 (m), 1646 (m), 1466 (w), 1410 (w), 1366 (w), 1224 (w), 1042 (vs), 795 (m), 607 (m), 468 (s); Elemental analysis calcd. for $[Ni(phe)_2(H_2O)_2]$/Y: C 5.66, H 0.72, N 0.73%, i.e., encapsulated organic ligand corresponded to 0.52 mmol g^{-1} zeolite (or 3.08%); found: C 6.28, H 0.82, N 0.80%, i.e., encapsulated ligand corresponded to 0.57 mmol g^{-1} zeolite (or 3.93%).

General oxidation procedure

The oxidation of the substrates (cyclohexene, ethyl benzene and toluene) with hydrogen peroxide was performed in a 25-mL round-bottom flask placed in an oil bath. In a typical reaction, the catalyst (4 mg), the solvent (2.0 mL) and cyclohexene (1.0 mmol) were stirred at 60 °C. Hydrogen peroxide was also added. At suitable intervals, aliquots were removed and the reaction products were quantified by gas chromatography by comparing their retention times with those of authentic samples. Yields are based on the added substrate and were determined by means of a calibration curve.

In order to examine the possibility of the formation of alkyl hydroperoxides in the $H_2O_2/[Ni(phe)_2(H_2O)_2]$ and $H_2O_2/[Ni(phe)_2(H_2O)_2]$/Y systems, the suspension of substrate/H_2O_2/$NaHCO_3$/catalyst [for which the catalyst is either $[Ni(phe)_2(H_2O)_2]$ (I) or $[Ni(phe)_2(H_2O)_2]$/Y (II)] was treated with excess triphenylphosphine for 2 hours. Chromatograms of the solution before and after the triphenylphosphine treatment were recorded. The solid catalyst (II) was separated from the mixture by centrifugation in order to investigate its activity in subsequent runs. It was washed with acetonitrile. The catalyst was then used in a subsequent reaction. In a separate experiment to examine the leaching of nickel, (II) was removed from the reaction after 2 hours. The supernatant was decanted and concentrated sulfuric acid added. The mixture was heated for 2 hours. The resulting solution was analyzed by atomic absorption spectrometry to detect the presence nickel ions.

Results and Discussion

The quantity of nickel in [Ni(phe)$_2$(H$_2$O)$_2$]/Y (II) was determined by ICP to be 1.54%; the transition metal complex, [Ni(phe)$_2$(H$_2$O)$_2$], is assumed to be entrenched within the pores of the zeolite. Excess *L*-phenylalanine reactant has already been removed by extraction with dichloromethane, which also removed any free [Ni(phe)$_2$(H$_2$O)$_2$] adsorbed on the zeolite. Furthermore, any free nickel ions in the zeolite had already been removed by exchanging them with sodium ions.

The TGA plots of Na/Y, Ni-Y and [Ni(phe)$_2$(H$_2$O)$_2$]/Y show different characteristics in the 25-800 °C temperature range (Figure 1).

The TGA plot of NaY displays a broad endotherm from 25-400 °C, which is attributed to water desorption,[14] and the plot shows a smooth mass loss corresponding to total mass of 10.17%. The TGA plot of Ni/Y is suggestive of the formation of Ni(OH)$^+$ because of the reaction of water with the nickel cations;[15] the cumulative weight loss is 38.5%. The derivative thermogravimetric analysis (DTG) thermogram of Ni/Y is much narrower, in contrast with that of Na/Y. The TGA plot of [Ni(phe)$_2$(H$_2$O)$_2$]/Y (II) shows an endothermic removal of 6.48% water occurring up to 150 °C, above which the endothermic weight loss of 3.37% is interpreted in terms of the elimination of intra-zeolite water from 150 to 350 °C. As the nickel complex itself exists as a diaqua-coordinated adduct, the removal of water is in accordance with the elimination of water from the coordination environment of nickel.[16] The third step includes the slow but exothermic weight loss of 3.93% arising from the decomposition of the metal complex. According to ICP measurements, the nickel complex amounted to 3.08% but according to the CHN and TGA measurements, the quantity should be 3.93%; the difference (0.85%) is attributed to the existence of free *L*-phenylalanine ligand in the zeolite cavities.[17]

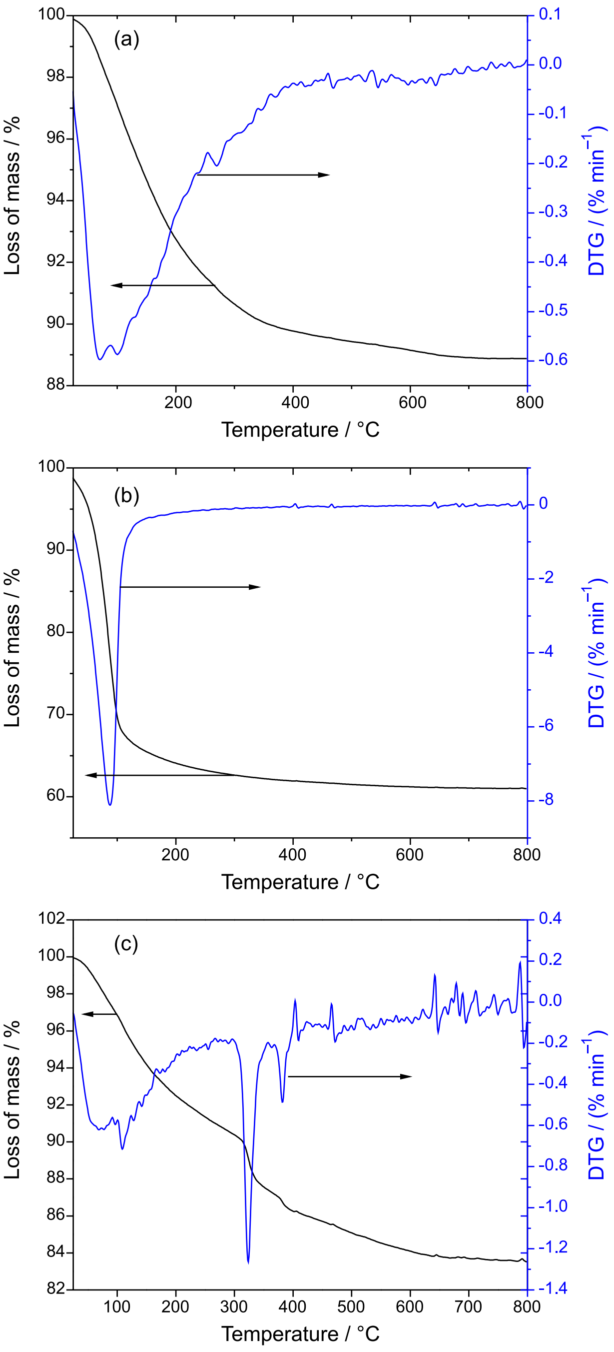


Figure 1. TGA profiles of (a) Na/Y; (b)Ni/Y and (c) [Ni(phen)$_2$(H$_2$O)$_2$]/Y.

Catalytic activity

Control experiments show that both catalyst and the oxidant are essential to the oxidation process, as seen from the experiments on the homogeneous catalyst [Ni(phe)$_2$(H$_2$O)$_2$] (I) in the oxidation of cyclohexene to 2-cyclohexene-1-ol at 60 °C; 30% aqueous hydrogen peroxide served as the oxidant and acetonitrile the solvent (Table 1).

Oxidation did not proceed in the absence of hydrogen peroxide, whereas in the absence of (I), the oxidation was

Table 1. Catalytic activity of [Ni(phe)$_2$(H$_2$O)$_2$] (I) in oxidation of cyclohexene[a]

entry	[H$_2$O$_2$]/[C$_6$H$_{10}$] molar ratio	NaHCO$_3$ / mmol	Conversion / %	Selectivity / %	
				A	B
1[b]	0	0	0	–	–
2[c]	1	0	6	27	73
3[d]	1	0	12	69	31
4[e]	1	0.5	41	78	22
5[e]	2	0.5	79	86	14
6[e]	3	0.5	100	98.28	1.72

[a]Reaction conditions: [Ni(phe)$_2$(H$_2$O)$_2$] 4 mg (0.009 mmol), temperature 60 °C, cyclohexene 1 mmol, acetonitrile 2 mL, reaction time 4 h; [b]NaHCO$_3$ (none), H$_2$O$_2$ (none); [c]catalyst (none), NaHCO$_3$ (none), H$_2$O$_2$ 1 mmol, reaction time 24 h; [d]NaHCO$_3$ (none); [e]NaHCO$_3$ 0.5 mmol. A: 2-cyclohexen-1-ol; B: cyclohexene epoxide.

only 6% complete after 24 hours.[7,18,19] The oxidation is poor, but the addition of a co-catalyst (sodium bicarbonate) increased the conversion from 12 to 41% after only 4 hours. The sluggish reaction in the absence of the co-catalyst is attributed to the strong binding nature of the hydroxide ion. However, the bicarbonate ion reacts with hydrogen peroxide to generate the peroxymonocarbonate (HCO$_4^-$) ion, which being a stronger nucleophile, is believed to enhance the rate of oxidation.[14] The conversion increased when more hydrogen peroxide was used. The nature of the solvent was found to have a marked effect (Table 2).

Table 2. Effect of solvents on oxidation of cyclohexene catalyzed by [Ni(phe)$_2$(H$_2$O)$_2$] (I)[a]

entry	Solvent	Conversion[b] / %	Selectivity / %	
			A	B
1	MeOH	68.5	81	19
2	CH$_3$CN	100	98	2
3	EtOH	63	72	28
4	CHCl$_3$	45	74	26
5	*n*-Hexane	0	–	–

[a]Reaction conditions: [Ni(phe)$_2$(H$_2$O)$_2$] 4 mg (0.009 mmol), temperature 60 °C, cyclohexene 1 mmol, solvent 2 mL, NaHCO$_3$ 0.5 mmol, H$_2$O$_2$ 3 mmol, time 4 h. A: 2-cyclohexen-1-ol; B: cyclohexene epoxide. [b]Conversions are based on the starting substrate.

The conversion was highest for acetonitrile, being 100% complete after 4 hours; acetonitrile was a better solvent medium than methanol, and *n*-hexane was associated with the lowest conversion. The difference is explained by the ready miscibility of acetonitrile with water, whereas both chloroform and *n*-hexane are immiscible. Temperature also had a noticeable effect in the 40 to 60 °C range, the conversion being higher at higher temperature (Table 3).

The reaction also produced cyclohexene oxide and the allylic oxidation product (2-cyclohexene-1-ol).[20] Allylic oxidation is believed to arise from the radical nature of the active oxidizing species.[21,22]

Table 3. Effect of temperature on oxidation of cyclohexene catalyzed by [Ni(phe)$_2$(H$_2$O)$_2$] (I)[a]

entry	Temperature / °C	Conversion[b] / %	Selectivity / %	
			A	B
1	40	48	85	15
2	60	100	98	2
3	80	95	80	2[c]

[a]Reaction conditions: ([Ni(phe)$_2$(H$_2$O)$_2$]) 4 mg (0.009 mmol), cyclohexene 1 mmol, solvent 2 mL, NaHCO$_3$ 0.5 mmol, H$_2$O$_2$ 3 mmol, time 4 h; [b]2-cyclohexen-1-one as the other product. A: 2-cyclohexen-1-ol; B: cyclohexene epoxide.

The activity of (I) is higher than those of other nickel compounds such as NiL^1 (where H$_2$L^1 is *N*,*N*'-bis-2-hydroxyphenyl(ethylenediimine)) and NiL^2 (where H$_2$L^2 is *N*-(2-hydroxyphenyl)acetylaldimine)-*N*'-(2-hydroxyphenylacetamide))[23] in the oxidation of cyclohexene by hydrogen peroxide.

In the oxidation of ethyl benzene, acetophenone is the major product and benzaldehyde and benzoic acid were obtained in small quantities (Table 4).

Evidently, oxidation occurred in the ethyl substituent, with the methylene unit being converted to a carbonyl unit. The conversion increased with increasing quantities of hydrogen peroxide to a maximum molar ratio of 4:1 (hydrogen peroxide:ethyl benzene); however with a higher ratio, selectivity is decreased; excess hydrogen peroxide is known to prevent non-selective hydroperoxide decomposition.[24] Acetophenone selectivity depended on the temperature, the conversion increasing with increasing temperature (Table 5). At higher temperatures, the selectivity to acetophenone was decreased whereas the selectivity to benzaldehyde and benzoic acid increased; this feature has been noted in a related study.[25]

The methyl substituent of toluene is oxidized (Table 6), and the selectivity to benzyl alcohol is higher than that

Table 4. Effect of oxidant/substrate molar ratio on oxidation of ethyl benzene catalyzed by [Ni(phe)$_2$(H$_2$O)$_2$] (I)[a]

entry	[H$_2$O$_2$]:[substrate] molar ratio	Conversion[b] / %	Selectivity / %		
			A	B	C
1	1:1	8	97	3	–
2	2:1	20	98	2	–
3	3:1	34	98	2	–
4	4:1	41	87	5	8

[a]Reaction conditions: [Ni(phe)$_2$(H$_2$O)$_2$] 4 mg (0.009 mmol), temperature 60 °C, ethyl benzene 1 mmol, acetonitrile 2 mL, NaHCO$_3$ 0.5 mmol, time 4 h; [b]conversions are based on the starting substrate. A: acetophenone; B: benzaldehyde; C: benzoic acid.

Table 5. Effect of temperature on oxidation of ethyl benzene catalyzed by [Ni(phe)$_2$(H$_2$O)$_2$] (I)[a]

entry	Temperature / °C	Conversion[b] / %	Selectivity / %		
			A	B	C
1	40	14	10	–	–
2	60	34	98	2	–
3	80	27	78	12	10

[a]Reaction conditions: [Ni(phe)$_2$(H$_2$O)$_2$] 4 mg (0.009 mmol), temperature 60 °C, ethyl benzene 1 mmol, acetonitrile 2 mL, NaHCO$_3$ 0.5 mmol, H$_2$O$_2$ 3 mmol, time 4 h. A: acetophenone; B: benzaldehyde; C: benzoic acid. [b]Conversions are based on the starting substrate.

to other products. The conversion rate is better than that found for a related manganese complex encapsulated in zeolite.[26]

A large difference is found in the oxidation of both ethyl benzene and toluene between catalyst (I) and zeolite-encapsulate (II) (Table 6). For both catalysts, toluene was oxidized to benzyl alcohol/benzaldehyde and ethyl benzene to acetophenone/benzaldehyde, but with different activities and selectivities. When encapsulated in the pores of zeolite, the nickel complex exists in a molecularly dispersed form so that self-degradation does not occur. In contrast, the yield is not noticeable for related cobalt and copper systems.[27]

When (II) is used in place of (I), the reaction time is decreased from 4 hours to only 2 hours. However, although catalysts such as Ni(salen),[28] [Ni(habenzil)]-Al$_2$O$_3$,[2] [Ni(mabenzil)]/Al$_2$O$_3$,[29] Ni(AAEMA),[27] [LMn(μ-O)$_3$MnL][PF$_6$]$_2$ and Ni(salen)/Y[28] have been used for the hydrogen peroxide oxidation of cyclohexene, the activity of (II) is significantly higher than the reported systems.

The hydrogen peroxide oxidation of hydrocarbons catalyzed by certain transition metal complexes is reported to yield hydroperoxides (ROOH) along with alcohols and ketones/aldehydes.[30] If a hydroperoxide is indeed formed, its presence can be confirmed by reaction with triphenylphosphine since this phosphine reduces it to an alcohol.[31] When toluene was oxidized in a reaction catalyzed by (II), the gas chromatogram showed an increase in amount of benzyl alcohol and a decrease in the amount of benzaldehyde. A similar result was found for cyclohexene and ethyl benzene (Table 7).

The formation of the hydroperoxide in the reaction of ethyl benzene probably proceeds by way of the following mechanism (Scheme 1).

The corresponding formation of cyclohex-2-enyl hydroperoxide from cyclohexene probably proceeds by a similar route (Scheme 2).[32] The hydroxyl radical attacks the allylic C–H bond to yield a radical that then reacts with oxygen to form another radical, which, in turn, ultimately yields the alcohol.

Table 6. Oxidation of hydrocarbons catalyzed by [Ni(phe)$_2$(H$_2$O)$_2$] (I) and [Ni(phe)$_2$(H$_2$O)$_2$]/Y (II)[a]

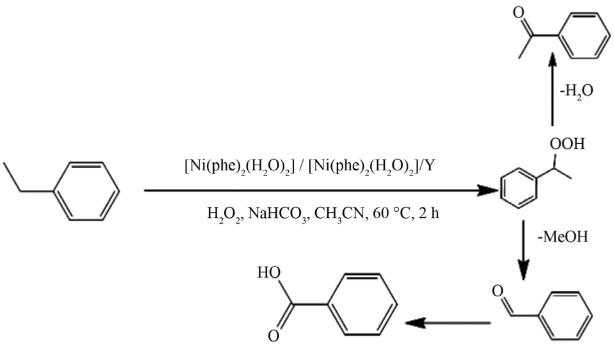
entry	Hydrocarbon	Conversion[b] / %, (I)/(II)	Selectivity / %, (I)/(II)		
			A	B	C
1	Ethyl benzene	35/45	2/0[c]	98/98[d]	0/2[e]
2	Toluene	20/31	26/59.7[c]	67.2/40.3[f]	6.8/0[e]
3	Cyclohexene	100/100	98/50[g]	2/50[h]	–

[a]Reaction conditions: [Ni(phe)$_2$(H$_2$O)$_2$] (I) 0.009 mmol, [Ni(phe)$_2$(H$_2$O)$_2$]/Y (II) 0.009 mmol, substrate 1.0 mmol, CH$_3$CN 2 mL, H$_2$O$_2$ 3 mmol, NaHCO$_3$ 0.5 mmol, temperature 60 ± 1 °C, time 4 h for (I) and 2 h for (II); [b]conversions are based on the starting substrate; [c]product is benzaldehyde; [d]product is acetophenone; [e]product is benzoic acid; [f]product is benzyl alcohol; [g]product is 2-cyclohexen-1-ol; [h]product is cyclohexene epoxide.

Table 7. Oxidation of hydrocarbons catalyzed by $[Ni(phe)_2(H_2O)_2]$ (I) and $[Ni(phe)_2(H_2O)_2]/Y$ (II)[a] in the presence of excess PPh_3

entry	Hydrocarbon	Conversion[b] / %, (I)/(II)	Selectivity / %, (I)/(II)		
			A	B	C
1	Ethyl benzene	35/45	2/0[c]	6/28[d]	92/72[e]
2	Toluene	20/31	2/8.4[c]	97.2/91.6[f]	0.8/0[g]
3	Cyclohexene	100/100	98/50[h]	2/50[i]	–

[a]Reaction conditions: $[Ni(phe)_2(H_2O)_2]$ (I) 0.009 mmol, $[Ni(phe)_2(H_2O)_2]/Y$ (II) 0.009 mmol, substrate 1.0 mmol, CH_3CN 2 mL, H_2O_2 3 mmol, $NaHCO_3$ 0.5 mmol, temperature 60 °C, time 4 h for (I) and 2 h for (II); [b]conversions are based on the starting substrate; [c]product is benzaldehyde; [d]product is acetophenone; [e]product is 1-phenylethanol; [f]product is benzyl alcohol; [g]product is benzoic acid; [h]product is 2-cyclohexen-1-ol; [i]product is cyclohexene epoxide.

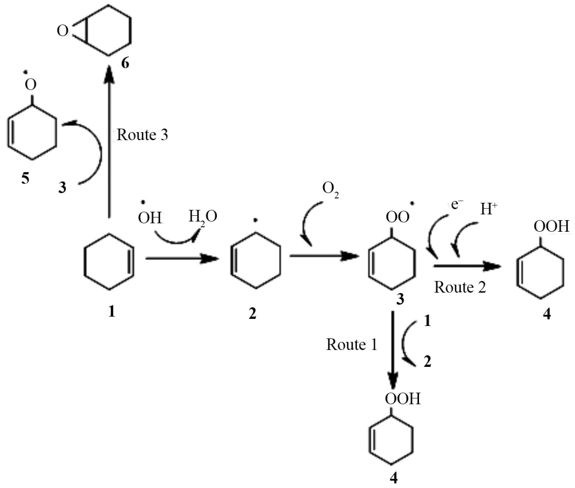


Scheme 1. Ethyl benzene oxidation pathway.

Table 8. Effect of catalyst recycling on the oxidation of cyclohexene[a]

Number of recycle	Conversion / %	Selectivity / %	
		A	B
Fresh	100	98	2
1	100	98	2
2	98	97	3
3	100	98	2

[a]Reaction conditions: $[Ni(phe)_2(H_2O)_2]/Y$ (II) 0.009 mmol, cyclohexene 1 mmol, solvent 2 mL, $NaHCO_3$ 0.5 mmol, H_2O_2 3 mmol, time 2 h. A: 2-cyclohexen-1-ol; B: cyclohexene epoxide.



Scheme 2. Cyclohexene oxidation pathway.

Catalyst recycling

The heterogeneous catalyst (II) could be used for a third run (Table 8) and noticeable decrease in activity was observed.

Catalyst stability

In the oxidation of cyclohexene by (II), the catalyst was separated by filtration after 1 hour (at which the conversion is 67%). GC analysis of the filtrate after the filtrate was set aside for another hour showed a conversion of 77%. The 10% difference increase in the conversion of cyclohexene relates to the oxidation in the absence of the catalyst, which had already been removed (Table 1). If the nickel complex was indeed leached,[33] then nickel should be detected by atomic absorption spectroscopy (AAS). However, the AAS results are inconsistent with leaching as the quantity was less than 0.1 ppm. The catalyst, when re-used in a subsequent run, displayed an identical FTIR spectrum compared with the one that had not been used (Figure 2).

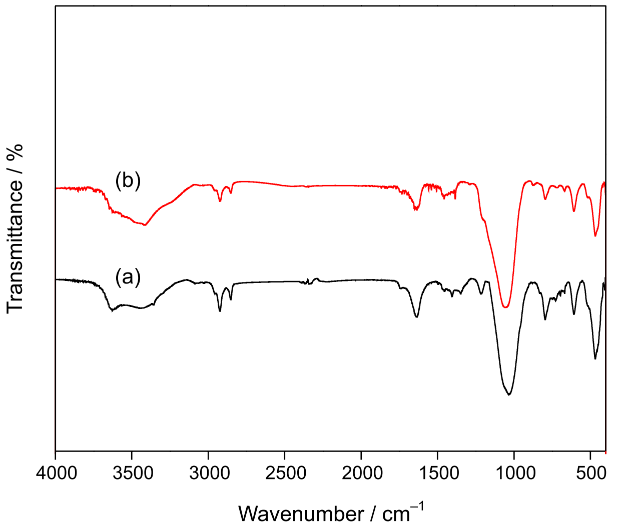


Figure 2. FTIR spectra of (a) fresh $[Ni(phe)_2(H_2O)_2]/Y$, (b) recycled ($[Ni(phe)_2(H_2O)_2]/Y$.

On the other hand, a (Cu-Fe)(salen)/Y complex used for the epoxidation of cyclohexene lost its activity by 45% after three consequent runs; the degradation of the catalyst was even noted from a change in color.[17] A manganese(III)-salen complex immobilized into pillared clays was found to be somewhat unstable.[34]

Supplementary Information

Supplementary information is available free of charge at http://jbcs.sbq.org.br as a PDF file.

Acknowledgements

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