

Effect of temperature and additives on the reactivity and product selectivity of polymer-bound nickel(II) complex

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Abstract

Cyclohexene was catalytically oxidized in the presence of molecular oxygen and polymer-bound nickel(II) complex PS-bipy–Ni(II)–oxine (where PS-bipy = polystyrene, bipy = 2,2'-bipyridine) in the absence of solvent at 70°C, affording 2-cyclohexen-1-ol, 2-cyclohexen-1-one and dicyclo[4.1.0]-2-oxygen-heterocycloheptane in 27.5% yield. The effect of temperature, additives and the amount of catalyst used on the catalytic activity and product selectivity were discussed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Nickel complexes; Cyclohexene; Polymer-bound catalyst; Catalytic oxidation

1. Introduction

Oxidation of cyclohexene catalyzed by transition metal complexes is a topic of current research [1–6]. Some of the cited researches have been reported where oxidation of cyclohexene occurs with high yield, but the procedure needs special oxidants such as peroxide and iodosylbenzene, or conductants such as aldehydes or NaBH₄, which results in the difficulty in analyzing and separating the products, or needs to be carried out in aqueous solution which, from the point of view of synthetic utility, suffers from the drawback of low solubility of most organic substrates. We reported here the oxidation of cyclohexene catalyzed by polystyrene-bound-2,2'-bipyridine–nickel(II)–oxime complex. 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-cyclohexen-1-ol, 2-cyclohexen-1-one and dicyclo[4.1.0]-2-oxygen-heterocycloheptane were produced in 27.5% yield. The selectivity to 2-cyclohexen-1-ol, 2-cyclohexen-1-one and dicyclo[4.1.0]-2-oxygen-heterocycloheptane was 63.7, 23.5 and 10.2%, respectively. The total selectivity mounted to 97.4%. The effect of temperature, additives and the amount of catalyst used on the reactivity and product selectivity were discussed (Schemes 1 and 2).

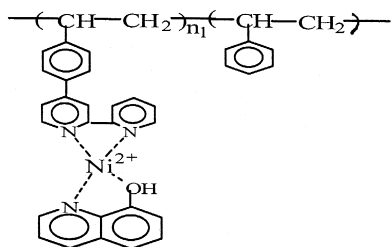
2. Experimental

2.1. Materials and instrumentation

Cyclohexene was distilled before use. All other reagents and solvents were purchased from

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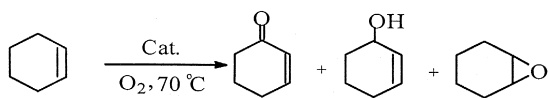


Scheme 1. Suggested structure of PBPY-Ni-oxime.

commercial sources and used as received unless noted otherwise. Polymer-bound-2,2'-bipyridine(PS-bipy) was prepared in the general procedure based on the method described in the literatures [7,8]. The content of nitrogen in PS-bipy is 7.4%. The preparation and investigation of the polymer-bound complex PS-bipy-Ni(II)-oxime will be published elsewhere. Nickel content of PS-bipy-Ni(II)-oxime is 4.32%, which was analyzed by inductively coupled plasma atomic emission spectrometry using an ICP-1000S model. Oxidation products were analyzed on a Shimadzu QP-1000A GC/MS system. X-ray photoelectron spectroscopy (XPS) analysis was performed at room temperature on a PHI-500 ESCA/SAM spectrometer with the use of Mg K α radiation ($h\nu = 1254$ eV). The typical X-ray power was 320 W. All XPS spectra were energy referenced to the C 1s photoemission peak at 284.6 eV.

2.2. Preparation of the polystyrene-bound-2,2'-bipyridine-nickel-oxime

Polymer-bound-2,2'-bipyridine(0.3 g) was added to 40 ml of absolute ethanol and soaked for 24 h. Nickel(II) chloride NiCl₂ · 6H₂O (0.24 g, 1.00 mmol), and low molecular ligand (oxime, 0.26 g, N, 1.79 mmol) was added to the mixture, refluxed in argon atmosphere for 24 h and then cooled down. The resulting poly-



Scheme 2.

mer-bound nickel(II) complex was isolated by filtration and washed with ethanol until the filtration becomes colorless, dried in vacuum at room temperature for 48 h. The amount of C, H, N and Ni in complex was 72.00%, 5.05%, 6.40% and 4.32%, respectively, analyzed by ICP.

3. Results and discussion

3.1. Characterization of the polystyrene-bound-2,2'-bipyridine-nickel-oxime

As shown in Table 1, the Ni (2p_{3/2}) binding energy (Eb) is 857.4 in the nickel complex and 856.3 eV in nickel(II) chloride. The Ni (2p_{3/2}) binding energy of the complex was increased 1.1 eV compared with that of the nickel(II) chloride. The result indicates that the charge on the nickel atoms is decreased when complexes were formed. The corresponding Eb data are shown in Table 1. The N 1s binding energy is 399.6 eV in complex and 399.3 eV in PBPY. Compared with that of PBPY, the N 1s binding energy of complex is increased 0.3 eV. The resolved N 1s XPS spectrum of the complex shows three N 1s XPS peaks that correspond to the three components of the nitrogen. The low energy (397.3 eV) component belongs to the coordinated nitrogen of the polymer ligands, the middle energy (399.6 eV) component belongs to the uncoordinated nitrogen of the polymer ligands, while the high energy (401 eV) compo-

Table 1
XPS Data for polymer-bipy, NiCl₂ and the nickel complex

Compound	XPS peak	Binding energy Eb (eV)	Δ Eb (eV)
NiCl ₂	Ni(2p _{3/2})	856.3	0.0
PBPY	N(1s)	399.3	0.0
PBPY-Ni-oxime	Ni(2p _{3/2})	857.4	+1.1
	N(1s)	397.3	-1.0
		399.6	+0.3
		401.0	+1.7

Table 2

Effect of temperature on the reactivity and product selectivity
Reaction conditions: 1 atm of O₂; time 8 h; cat. 3 mg; substrate, cyclohexene 5 m

Temp.	Conversion (%)	Selectivity (%)	
		2-cyclohexen-1-ol	2-cyclohexen-1-one
50	0.5	58.8	27.6
60	5.0	59.7	26.5
70	27.5	63.7	23.5
80	18.1	65.6	21.9

ment may belong to the coordinated nitrogen of oxime. The change of both Ni ($2p_{3/2}$) and N 1s binding energy of the complexes suggests that the charge on the nickel atoms is decreased while that on nitrogen atoms is increased when the complex was formed. The results suggest that the back-donation from the nickel atoms to the anti- π orbitals of the bipyridine rings of the polymer-bound ligands prevails over the donation from the nitrogen atoms (or bipyridine π orbitals) to the d orbitals (or hybridized orbitals) of the nickel ions. This is interesting for it is different from our previously reported results of the corresponding iron and ruthenium complexes in which the charge is transferred from nitrogen atoms to the metal ions. We tentatively suggest that for a metal ion rich in d-electrons such as nickel(II) ion ($3d^8$), the back-donation from metal ions to the anti- π orbitals of the π -conjugated systems prevails over the donation from the coordinated atoms such as nitrogen to d orbitals or hybridized orbitals of the metal ions. On the contrary, for a metal ion not so much rich in d-electrons such as iron(III) ion ($3d^5$), the donation from the coordinated atoms to the d orbitals (or hybridized orbitals) of the metal ions surpasses the back-donation.

3.2. Effect of temperature on the reactivity and product selectivity

Generally, 5 ml of cyclohexene and 3 mg of PS-bipy-Ni(II)-oxime 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-cyclohexen-1-ol, 2-cyclohexen-1-one and dicyclo[4.1.0]-2-oxygen-heterocycloheptane as the major products. To investigate the effect of temperature on the reactivity and product selectivity of PS-bipy-Ni(II)-oxime, the oxidations were carried out only at temperatures $\geq 50^\circ\text{C}$. The results are shown in Table 2.

At temperatures ranging from 50°C to 80°C, the reactivity and product selectivity of the complex varies with the temperature. At 70°C, the conversion is 27.5% and the selectivity to 2-cyclohexen-1-ol and 2-cyclohexen-1-one is 63.7% and 23.5%, respectively, while at 50°C, the conversion is 0.5% and the selectivity to 2-cyclohexen-1-ol and 2-cyclohexen-1-one is 58.8% and 27.6%, respectively. The typical trend shows that the reactivity and the selectivity to 2-cyclohexen-1-ol are increased with the temperature in the range of 50°C to 70°C.

3.3. Effect of additives on the reactivity and product selectivity

The experiments for determining the influence of additives on the reactivity and product selectivity of PS-bipy-Ni(II)-oxime were performed at a temperature of 70°C, using 3 mg of

Table 3

Effect of additives on the reactivity and product selectivity
Reaction conditions: 1 atm of O₂; time 8 h; cat. 3 mg; substrate, cyclohexene 5 ml, at 70°C.

Additives	Conversion (%)	Selectivity (%)	
		2-cyclohexen-1-ol	2-cyclohexen-1-one
–	27.5	63.7	23.5
phen (1 mg)	20.5	55.4	32.1
bipy (1 mg)	23.8	46.4	41.2
HAc (0.1 ml)	5.1	67.1	20.2
Py (0.1 ml)	14.1	48.9	39.2

Table 4

Effect of the amount of catalyst used on the reactivity

Reaction conditions: 1 atm of O₂; time 8 h; substrate, cyclohexene 5 ml, at 70°C.

Amount of catalyst (mg)	Conversion (%)	Selectivity (%)	
		2-cyclohexen-1-ol	2-cyclohexen-1-one
2	23.1	50.0	32.6
2.5	24.1	55.2	28.8
3.0	27.5	63.7	23.5
3.5	22.7	49.1	30.6
4.0	21.2	53.2	29.1

PS-bipy–Ni(II)–oxime and 5 ml of cyclohexene. The results are shown in Table 3. The addition of all additives leads to the decrease of conversion. It also results in the variation of product distribution. The addition of acetic acid, for example, reduces the conversion from 27.5% to 5.1%. Although the addition of 2,2'-bipyridine, 1,10-phenanthroline and pyridine decreases the reactivity, it increases the selectivity to 2-cyclohexen-1-one. With the addition of 1 mg of bipyridine, for instance, the selectivity to 2-cyclohexen-1-one is increased from 23.5% to 41.3%.

3.4. Effect of the amount of catalyst used on the reactivity

To investigate the effect of catalyst used on the reaction, the oxidations were carried out at 70°C by varying the amount of catalyst PS-

bipy–Ni(II)–oxime while holding the amount of cyclohexene constant. The results are shown in Table 4. The catalytic conversion was found to be related to the amount of catalyst used. The optimum amount of catalyst used is 3 mg in 5 ml of cyclohexene. Although the amount of catalyst used obviously influenced the reactivity of the catalyst, it showed a relatively small effect on the product distribution.

Acknowledgements

We thank the Natural Science Foundation of Gansu Province for financial support (grant no. ZQ-97004).

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