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SYNTHESIS, CHARACTERIZATION, AND CATALYTIC OXIDATION PROPERTIES OF POLYMER-BOUND NICKEL COMPLEXES

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Key Words: Nickel Complexes, Cyclohexene, Catalytic Oxidation, Polymer-Bound Catalyst

ABSTRACT

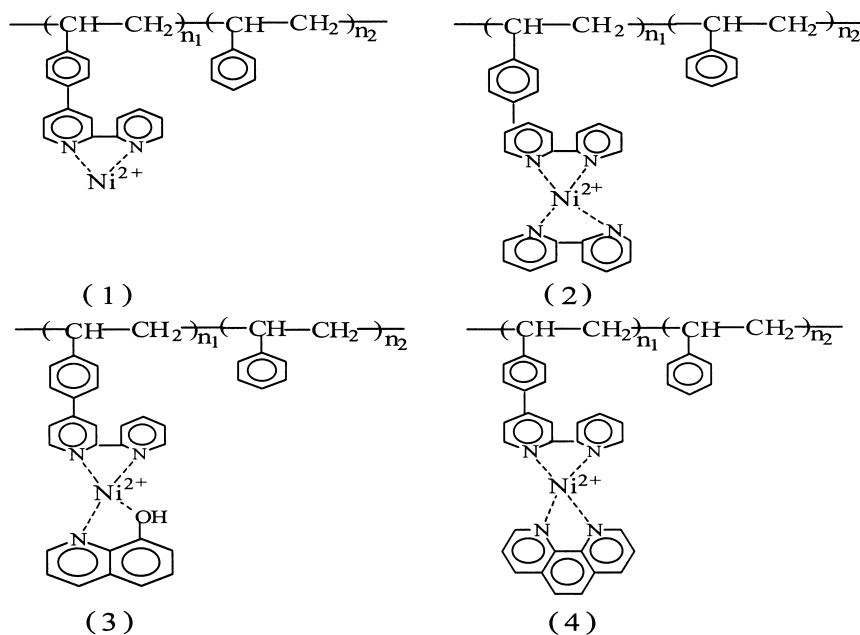
Polystyrene-bound-2,2'-bipyridine-nickel-L (where L = 2,2'-bipyridine, oxine and 1,10-phenanthroline) complexes were synthesized and characterized by IR, X-ray photoelectron spectroscopy, TG-DTA, ICP and routine elemental analysis. The complexes have been shown to catalytically oxidize cyclohexene in the presence of molecular oxygen and in the absence of solvent at 70°C, without the use of any special oxidant or coreductant. When cyclohexene is oxidized, 2-cyclohexen-1-ol, 2-cyclohexen-1-one and 2-oxygen-heterodicyclo[4.1.0]heptane were produced.

INTRODUCTION

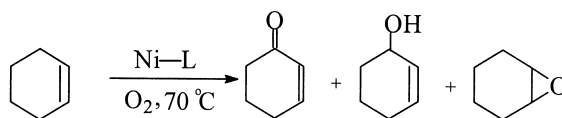
Cyclohexene was oxidized in the presence of a series of transition metal catalysts such as Cobalt-Schiff base complexes [1, 2], metal porphyrins [3-6],

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metal-acetylacetonate complexes [7] and metal salts [8-11]. Many of the cited investigations need special oxidants such as peroxide, iodosylbenzene and ozone, or need coreductants such as NaBH_4 , cyclic ketones, alcohols, and aldehydes, which results in the difficulty in analyzing and separating the products, or need 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 have previously reported the oxidation of cyclohexene catalyzed by polymer-bound copper complexes [12]. We report here the synthesis, characterization and catalytic oxidation properties of polystyrene-bound-2,2'-bipyridine-nickel(II) complexes PBPY-Ni (where PBPY=polystyrene-bound-2,2'-bipyridine), PBPY-Ni-bipy (where bipy=2,2'-bipyridine), PBPY-Ni-oxine and PBPY-Ni-phen (where phen=1,10-phenanthroline) (Schemes 1 and 2). The oxidation was performed under 1 atm of molecular oxygen in the presence of nickel complexes and in the absence of solvent at 70°C , without the use of any special oxidant or coreductant, affording 2-cyclohexen-1-ol, 2-cyclohexen-1-one and 2-oxygen-heterodicyclo[4.1.0] heptane.



Scheme 1. Suggested structure of PBPY-Ni(1), PBPY-Ni-bipy(2), PBPY-Ni-oxine(3) and PBPY-Ni-phen(4).



Scheme 2.

EXPERIMENTAL

Materials

Polymer-bound-2,2'-bipyridine (PBPY) was prepared according to the literature procedure [13, 14] using linear polystyrene (MW 130000-150000) as the supporter. The nitrogen content in PBPY is 7.4%. Nickel chloride NiCl₂·6H₂O obtained from Shanghai Chemical Reagent Company is of AR grade. 1,10-Phenanthroline was purified by literature method [15]. Cyclohexene was distilled and stored over molecular sieves. All other reagents and solvents were purchased from commercial sources and used as received unless noted otherwise.

Instrumentation

IR spectra were obtained on an Alpha-Centauri FT-IR spectrophotometer (KBr disks). X-ray photoelectron spectroscopic (XPS) analysis was performed under vacuum (1×10^{-8} Torr) at room temperature on a PHI-500 ESCA/SAM spectrometer using Mg K α radiation ($h\nu = 1254\text{eV}$). The typical X-ray power was 320W. The spectra were obtained with powdered samples pressed into a self-supporting disk. All XPS spectra were energy-referenced to the C1s photoemission peak at 284.6eV. Based on the handbook (C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder, *Handbook of X-ray Electronphoto Spectroscopy*, G. E. Muilenberg (Editor), Perkin-Elmer Corporation, Physical Electronics Division, 6509 Flying Cloud Drive, Eden Prairie, Minnesota 55344, 1978 P₈₀), the assignment of peaks in XPS spectra was made. Thermogravimetry-differential thermal analysis (TG-DTA) was carried out using a Shimadzu DT-40 thermal analyzer at a heating rate of 15°C·min⁻¹. Nickel content in complexes was analyzed by inductively coupled plasma atomic emission spectrometry using a Shimadzu ICP-1000s model. All samples were treated with concentrated nitric acid at 45°C for 24 hours. Elemental analysis data were obtained from a Carbo-

Erba 1106 model elemental analyzer. The oxidation products were analyzed on a Shimadzu QP-1000A GC/MS system.

Preparation of Polymer-Bound Nickel(II) Complexes

Polymer-bound-2,2'-bipyridine (0.3 g) was added to 40 mL of absolute ethanol and soaked for 24 hours. Nickel(II) chloride $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.24 g, 1.00 mmol), and the ligands L [where (1) L = 0; (2) L = 2,2'-bipyridine, 0.15 g, 0.96 mmol; (3) L = oxine, 0.26 g, 1.79 mmol; (4) L = 1,10-phenanthroline, 0.19 g, 0.95 mmol] were added to the mixture, refluxed in an argon atmosphere for 24 hours, and then cooled. The resulting polymer-bound nickel(II) complexes were isolated by filtration and washed with ethanol until the filtrate becomes colorless, and finally dried in vacuum at room temperature for 48h. The amount of nickel in complexes (1-4) was 1.49%, 0.43%, 4.32%, and 7.90%, respectively analyzed by ICP and the results are shown in Table 1.

Oxidation Procedure and Products Analysis

Generally, 3 mg of polymer-bound complex and 5 mL of cyclohexene were added to a glass reactor with a gas inlet tube which connected to a glass burette and an oxygen storage bottle, a reflux condenser and a gas outlet tube which could be opened to the air and used to adjust the initial oxygen pressure. The mixture was heated to 70°C in water bath and stirred with a magnetic stirring bar. The volume of oxygen absorbed was measured from the burette. The products in the reacted solution were analyzed on a Shimadzu QP-1000A GC/MS system with a 3m × 3mm OV-17 column. Column temperature: 60-300°C, at 5°C/min.

TABLE 1. Elemental Analysis Data of the Complexes and Ligand (Wt%)

Compound	C	H	N	Ni
PBPY	78.53	6.59	7.40	0.00
PBPY-Ni	84.70	6.21	5.22	1.49
PBPY- Ni - bipy	83.60	6.39	4.96	0.43
PBPY- Ni - oxine	72.00	5.05	6.40	4.32
PBPY- Ni -phen	61.90	5.49	3.17	7.90

RESULTS AND DISCUSSION

Characterization of the Polymer-Bound Nickel Complexes

The Ni($2p_{3/2}$) binding energy (Eb) is 857.5 in complex (1), 857.7eV in complex (2), 857.4eV in complex (3), 857.4eV in complex (4), and 856.3eV in nickel(II) chloride (Table 2 and Figure 1). The Ni($2p_{3/2}$) binding energy of the complexes (1-4) was increased 1.2eV, 1.4eV, 1.1eV, and 1.1eV, respectively compared with that of the nickel(II) chloride. The result indicates that the charge on the nickel atoms is decreased when complexes formed. The XPS spectra of N1s of the complexes are shown in Figure 2 and the corresponding Eb data are provided in Table 2. The N1s binding energy is 398.6eV in complex (1), 399.1eV in complex (2), 399.6eV in complex (3), 398.9eV in complex (4), and 399.3eV in PBPY. Compared with that of PBPY, the N1s binding energy of complex (1, 2, and 4) decreased 0.7eV, 0.2eV, and 0.4eV, respectively, while that of complex (3) increases 0.3eV. The resolved N1s XPS spectrum (Figure 2b) of complex (3) shows three N1s XPS peaks which correspond to three components of nitrogen. The low energy (397.3eV) component belongs to the coordinated nitrogen of the polymer ligands, the middle energy (399.6eV) component belongs to the uncoordinated nitrogen of the polymer ligands, while the high energy (401eV) component may belong to the coordinated nitrogen of oxine. The resolved N1s XPS spectrum (Figure 2c) of complex (2) shows two N1s peaks. The low energy

TABLE 2. XPS Data for Polymer-bipy, NiCl₂ and the Complexes (1-4)

Compound	XPS peak	binding energy Eb(eV)	ΔEb(eV)
NiCl ₂	Ni($2p_{3/2}$)	856.3	0.0
PBPY	N(1s)	399.3	0.0
PBPY-Ni	Ni($2p_{3/2}$)	857.5	+1.2
	N(1s)	398.6	-0.7
PBPY-Ni-bipy	Ni($2p_{3/2}$)	857.7	+1.4
	N(1s)	399.1	-0.2
		400.4	+1.1
PBPY-Ni-oxine	Ni($2p_{3/2}$)	857.4	+1.1
	N(1s)	397.3	-1.0
		399.6	+0.3
		401.0	+1.7
PBPY-Ni-phen	Ni($2p_{3/2}$)	857.4	+1.1
	N(1s)	398.9	-0.4

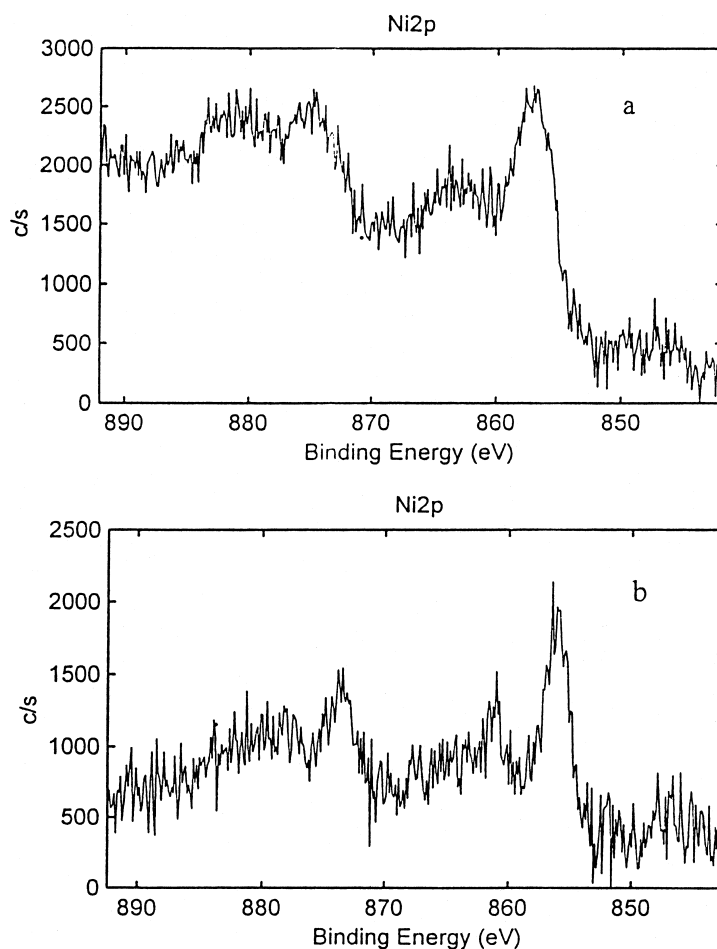


Figure 1. a. Ni($2p_{3/2}$) XPS spectrum of PBPY-Ni-phen, b. Ni($2p_{3/2}$) XPS spectrum of PBPY-Ni-oxine.

(399.1) band may belong to the nitrogen of the polymer-bound ligands(both coordinated and free), while the high energy band (400.4) may belong to the nitrogen of bipy. The change of both Ni ($2p_{3/2}$) and N1s binding energy of the complexes suggest that the charge on the nickel atoms is decreased while that on nitrogen atoms is increased when complexes were formed. The results suggest that the back-donation from nickel atoms to the (π - anti bond orbitals of the bipyridine rings of the polymer-bound ligands exceeds the donation from nitrogen atoms or bipyridine π orbitals) to d orbitals (or hybridized orbitals) of the

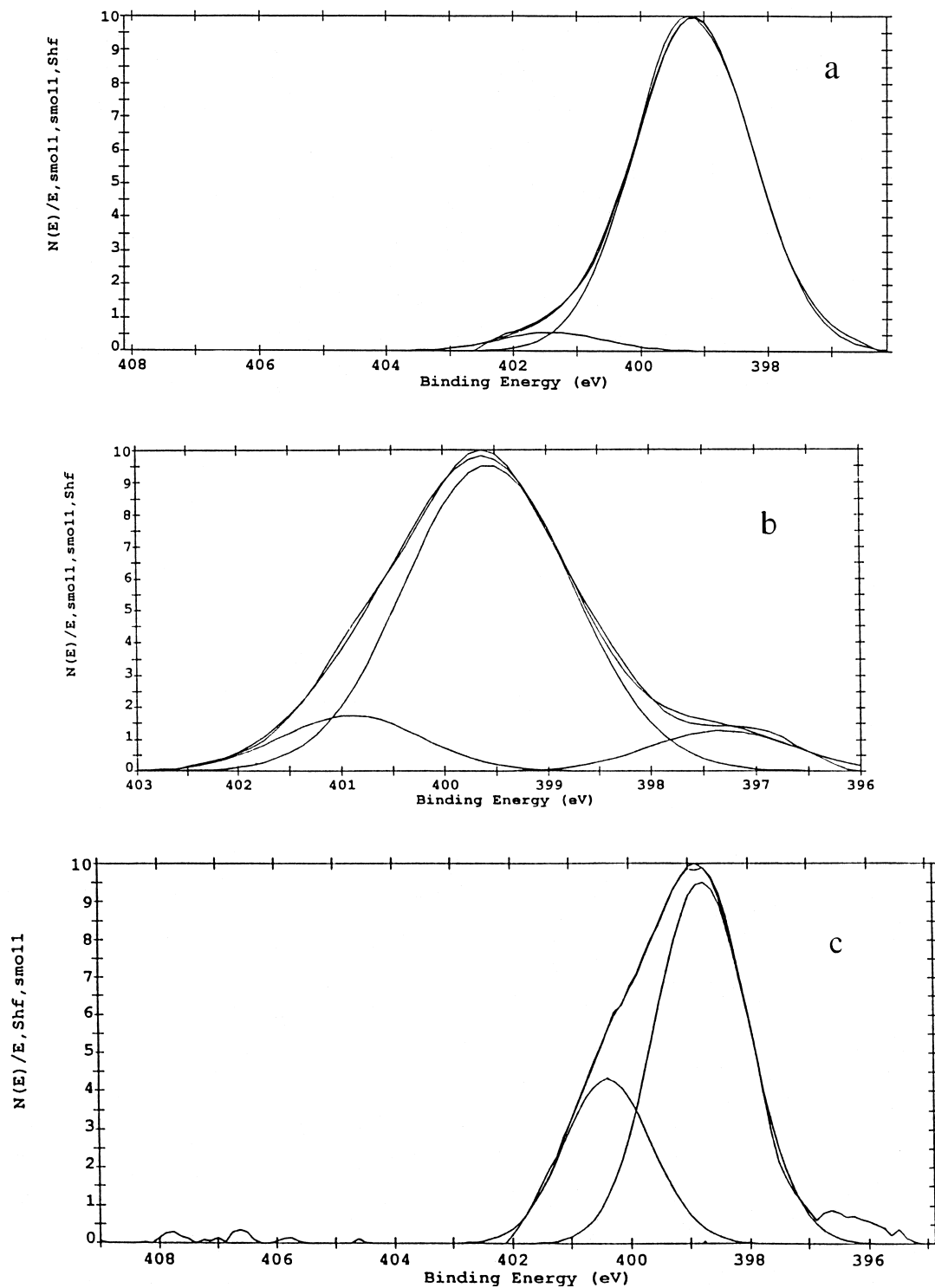


Figure 2. a. Resolved N 1s XPS spectrum of PBPY, b. Resolved N 1s XPS spectrum of PBPY-Ni-oxine, c. Resolved N 1s XPS spectrum of PBPY-Ni-bipy.

nickel ions. This is interesting as 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 [14].

The IR spectra of the nickel complexes (1, 4) are shown in Figure 3. The polymer chelate (PBPY) and the complexes (1, 4) exhibited C=N stretching at

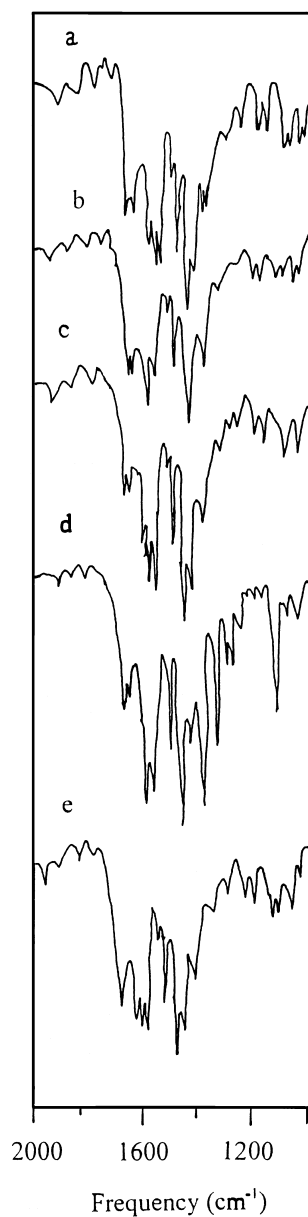


Figure 3. Infrared spectra of PBPY (a), PBPY-Ni (b), PBPY-Ni-bipy (c), PBPY-Ni-oxine (d), and PBPY-Ni-phen (e).

1653, 1632, 1634, and 1637 cm^{-1} . The C=N stretching frequencies were shifted to lower region (1621 cm^{-1}) when complexes formed. This result is in accordance with the XPS analysis. Compared with the IR spectrum of polymer ligand PBPY, new N-Ni stretching appears at 539 cm^{-1} , 540 cm^{-1} , 504 cm^{-1} and 541 cm^{-1} in the IR spectra of the complexes (1, 4) respectively. This also indicates that complexes were formed. Both Ni-N bond formation and the back-donation from nickel atoms to the π -anti bond orbitals of the ligands weaken carbon-nitrogen (C=N) bonds and hence leads to the C=N stretching frequencies in the IR spectra of the complexes shifted to lower values.

TG-DTA curves for complexes (1-4) revealed weight losses in the temperature range of 247 to 646°C, 290 to 589°C, 244 to 406°C, and 260 to 576°C, respectively. The results are shown in Figure 4. The corresponding weight losses for complexes (1-4) in the above temperature range was 89%, 87%, 83%, and 89%, respectively. This indicates that the polymer complexes (1-4) are stable below 249, 290, 244, and 260°C, respectively.

Catalytic Properties

The oxidation reactions were carried out under atmospheric pressure of molecular oxygen in the presence of the polymer-bound nickel(II) complexes in the absence of solvent at 70°C, providing 2-cyclohexen-1-ol, 2-cyclohexen-1-one and 2-oxygen-heterodicyclo [4.1.0] heptane as the major products. Typically, 3 mg nickel(II) catalyst and 5 mL of cyclohexene (the mole ratios of metal to cyclohexene are 1.5×10^{-5} , 4.4×10^{-6} , 4.5×10^{-5} , and 8.2×10^{-5} , respectively using complexes (1-4) as catalysts) were added to a glass reactor containing a magnetic stirring bar and equipped with a reflux condenser. The resulting catalytic activity and product selectivity of nickel(II) complexes used as catalysts are shown in Table 3.

All of the polymer-bound nickel(II) complexes studied catalyze the oxidation of cyclohexene with the reaction rate in the range of $8.57 \times 10^4 \text{ mL}\cdot\text{mol}^{-1}\cdot\text{min}^{-1}$ to $1.18 \times 10^6 \text{ mL}\cdot\text{mol}^{-1}\cdot\text{min}^{-1}$ and with the selectivity to total 2-cyclohexen-1-ol, 2-cyclohexen-1-one and 2-oxygen-heter-dicyclo[4.1.0]hep-tane of 93.2% to 98.5 %, without the use of any special oxidant or coreductant.

CONCLUSION

Polymer-bound nickel(II) complexes PBPY-Ni, PBPY-Ni-bipy, PBPY-Ni-oxine and PBPY-Ni-phen were synthesized and investigated by XPS, IR, ICP,

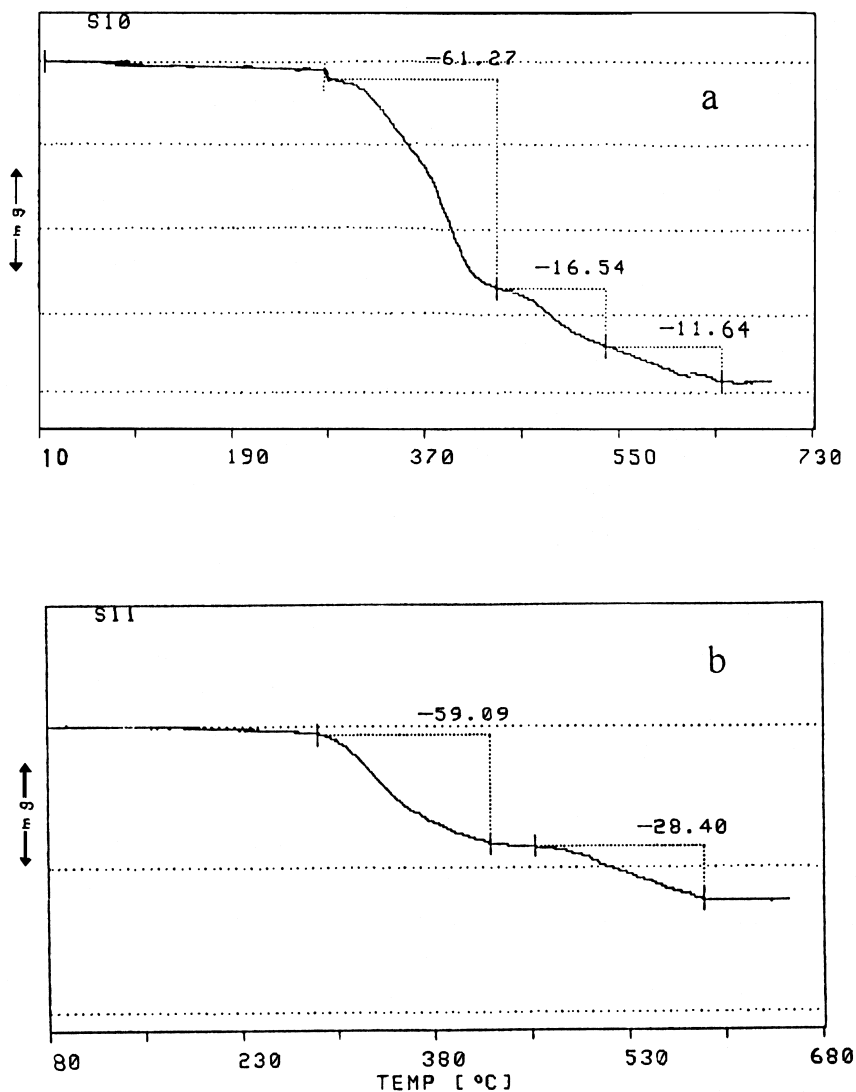


Figure 4. TG-DTA curves of PBPY-Ni (a), PBPY-Ni-bipy (b), PBPY-Ni-oxine (c), and PBPY-Ni-phen (d).

TG-DTA and routine elemental analysis. XPS result suggests that both coordinated and free ligands exist in the polymer-bound nickel(II) complexes. The change of charge on both nickel atoms and nitrogen atoms indicates that the back-donation from d orbitals (or hybridized orbitals) to π -anti bond orbitals of π -conjugated ligands surpasses the donation from nitrogen atoms to metal ions.

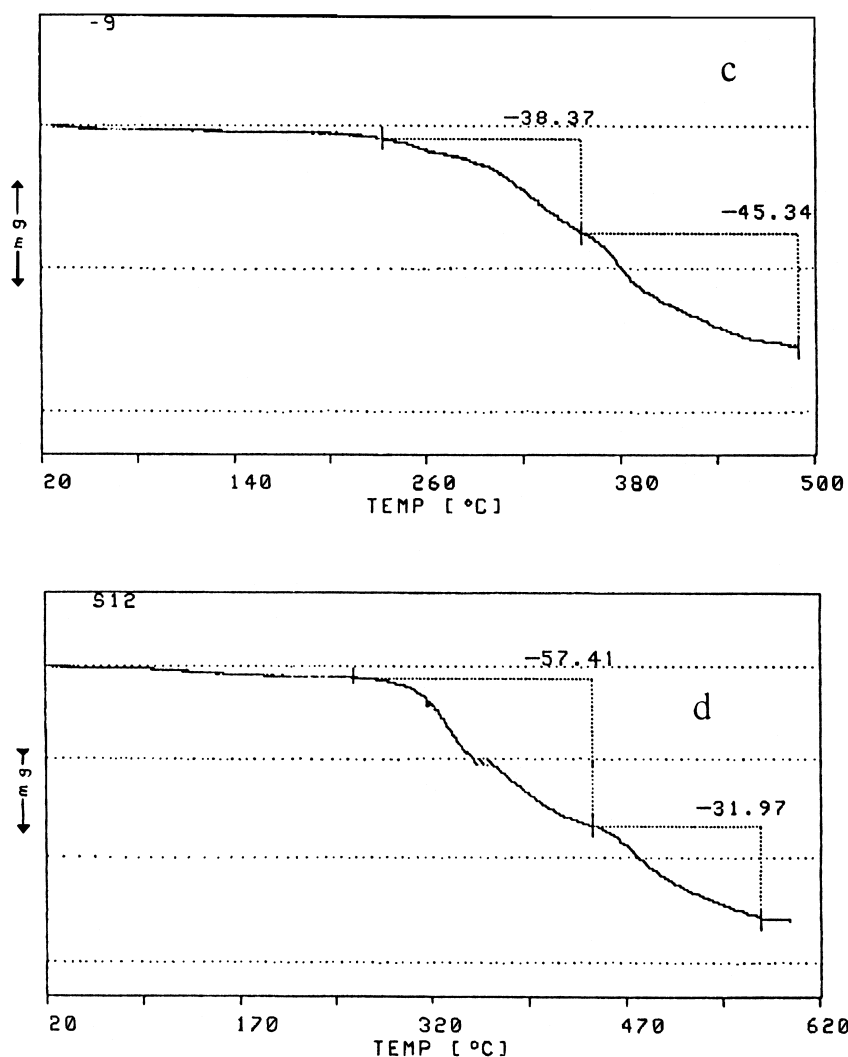





Figure 4. Continued.

TABLE 3. Effect of Different Catalysts on the Reactivity and Product Selectivity

Catalysts	Rate(mL·min ⁻¹ ·mol ⁻¹)	Product distribution		
				
PBPY-Ni	3.15×10^5	26.4	53.3	13.5
PBPY-Ni-bipy	1.18×10^6	27.2	56.3	11.2
PBPY-Ni-oxine	1.74×10^5	23.5	63.7	10.2
PBPY-Ni-phen	8.57×10^4	27.2	59.6	11.7

Reaction conditions: temperature 70°C; 1 atm.of O₂; time,8h; Cat.(3), 3mg;
substrate, cyclohexene 5mL

The complexes have been found to be active catalysts for the oxidation of cyclohexene.

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