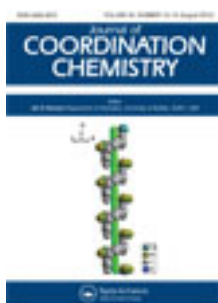


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### Multi-walled carbon nanotube bound nickel Schiff-base complexes as reusable catalysts for oxidation of alcohols

Ravindra Rajarao <sup>a</sup>, T.H. Kim <sup>b</sup> & Badekai Ramachandra Bhat <sup>a</sup>

<sup>a</sup> Department of Chemistry, Catalysis and Materials Laboratory, National Institute of Technology Karnataka, Surathkal, Mangalore - 575 025, Karnataka, India

<sup>b</sup> Energy Material Center, Korea Institute of Energy Research, 71-2 Jang-dong, Yuseong-gu, Daejeon 305-343, South Korea

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## Multi-walled carbon nanotube bound nickel Schiff-base complexes as reusable catalysts for oxidation of alcohols

RAVINDRA RAJARAO<sup>†</sup>, T.H. KIM<sup>‡</sup> and  
BADEKAI RAMACHANDRA BHAT<sup>\*†</sup>

<sup>†</sup>Department of Chemistry, Catalysis and Materials Laboratory, National Institute of Technology Karnataka, Surathkal, Mangalore – 575 025, Karnataka, India

<sup>‡</sup>Energy Material Center, Korea Institute of Energy Research, 71-2 Jang-dong, Yuseong-gu, Daejeon 305-343, South Korea

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Nickel salen and salophen complexes have been covalently anchored on multi-walled carbon nanotubes (MWNTs). The MWNT-supported nickel complexes have been characterized by inductive coupled plasma spectroscopy, FT-IR spectroscopy, UV-Vis spectrophotometry, transmission electron microscopy, and X-ray diffraction. The catalytic performance for the oxidation of primary and secondary alcohols was evaluated using periodic acid as oxidant. Reaction conditions have been optimized for MWNT-supported salen and salophen complexes by considering the effect of parameters such as solvent, reaction time, concentration of catalyst, amount of oxidant, etc. The catalytic activity was higher for supported catalysts than similar homogeneous ones. These supported catalysts were highly stable and reused several times without the loss of catalytic activity.

**Keywords:** Carbon nanotubes; Nickel salen complex; Nickel salophen complex; Oxidation of alcohols; Reusability

### 1. Introduction

Schiff-base transition metal complexes have been used as efficient and selective homogeneous catalysts in reactions such as epoxidation of olefins [1, 2], oxidation of alcohols [3], oxidation of phenols [4], reduction of ketones [5], polymerization [6, 7], decomposition of hydrogen peroxides [8], isomerization [9], and aldol condensation [10]. However, the main drawback of these catalysts is separation from the reaction mixture at the end of the reaction; design and synthesis of catalytically active supported metal complexes have received considerable interest. Supported catalysts offer advantages such as high catalytic activity and selectivity besides their easy recycling and metal recovery methodologies [11–13]. Different approaches have been used for the immobilization of complexes on inert supports such as alumina [14], polymers [15], silicates [16], MCM-41 [17], carbon [18], and zeolites [19].

\*Corresponding author. Email: chandpoorna@yahoo.com

High-surface-area carbons have been the catalyst supports of choice for many metals to convert a homogeneous into a heterogeneous process. A special type of carbon that is attracting current interest is carbon nanotubes (CNTs) due to their unique mechanical, structural, electronic, and thermal properties. High surface area and insolubility in most organic solvents indicate CNTs as promising catalyst support [20].

Salen and salophen have received much attention with extensive applications in catalysis [21, 22]. Oxidation of primary and secondary alcohols into carbonyl compounds is a pivotal functional group transformation in organic synthesis. In particular, oxidation of benzyl alcohol to benzaldehyde has applications in pharmaceutical and agrochemical industries.

Recently, Niasari *et al.* [23] used MWNT-supported cobalt Schiff-base complex as catalyst for the epoxidation of cyclohexene by air and Zakeri *et al.* [24] used MWNT-supported manganese porphyrin complex as catalyst for the epoxidation of alkenes by sodium periodate.

In this work, we have prepared homogeneous and immobilized MWNT-anchored nickel salen and salophen base complexes. The catalytic efficiency of the neat and MWNT-supported salen and salophen complexes were tested for the oxidation of alcohols under mild conditions using periodic acid as oxidant. MWNT-supported nickel catalysts showed excellent catalytic activity and reusability.

## 2. Experimental

### 2.1. Materials

All reagents were chemically pure and of analytical reagent grade. The solvents were dried and distilled before use following standard procedures [25]. All alcohols, periodic acid, and other chemicals were purchased from Sigma Aldrich and Merck.

### 2.2. Physical measurements

Melting points were determined by the open capillary method. Elemental analyses were performed on a Flash EA 1112 series CHNS–O Analyzer. IR spectra (in KBr pellets) were recorded on a Thermo Nicolet Avatar 330-FT-IR spectrophotometer.  $^1\text{H-NMR}$  spectra were recorded (DMSO- $d_6$ ) on a Bruker (400 MHz) spectrometer using TMS as an internal standard. Transmission electron microscopy (TEM) was performed on a CM200, Philips. Scanning electron microscopy (SEM) was performed on a SUPRA 40VP, Carl Zeiss. X-ray diffraction (XRD) patterns were obtained on a JEOL JDX 8P diffractometer with Cu-K $\alpha$  radiation,  $\lambda = 1.5418 \text{ \AA}$ . The amount of metal in supported catalysts was determined using ACROS Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). UV-Vis spectra were recorded on a SD 2000, Ocean optics.

### 2.3. Synthesis of salen (L1) and salophen (L2)

**2.3.1. Synthesis of N,N'-bis(4-hydroxysalicylidene)ethylene-1,2-diamine (L1).** Reaction mixture containing 4-hydroxysalicylaldehyde (0.02 mol) and 1,2-diaminoethane

(0.01 mol) in methanol was refluxed at 60°C for 4 h. The reaction mixture after cooling produced yellow crystals, which were filtered and recrystallized in methanol. Yield: 90%; yellowish orange solid; the ligand decomposes at  $230 \pm 2^\circ\text{C}$ ; IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{C}=\text{N}}$  1604.8;  $^1\text{H-NMR}$  (DMSO, ppm)  $\delta$  8.78 (s, 2H, CH=N); CHN found (Calcd) for  $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4$ , C: 63.84 (63.99), H: 5.22 (5.37), N: 9.42 (9.33), C/N: 6.77% (6.86%); UV-Vis:  $\lambda_{\text{max}}$  (nm) intraligand transitions: 320, 370.

**2.3.2. Synthesis of N,N'-bis(4-hydroxysalicylidene)phenylene-1,2-diamine (L2).** Reaction mixture containing 4-hydroxysalicylaldehyde (0.02 mol) and phenylene-1,2-diamine (0.01 mol) in methanol was refluxed at 60°C for 4 h. The reaction mixture after cooling produced yellow crystals, which were filtered and recrystallized in methanol. Yield: 90%; yellowish orange solid; the ligand decomposes at  $240 \pm 2^\circ\text{C}$ ; IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{C}=\text{N}}$  1611;  $^1\text{H-NMR}$  (DMSO, ppm)  $\delta$  8.52 (s, 2H, CH=N); CHN found (Calcd) for  $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_4$ , C: 68.86 (68.96), H: 4.52 (4.63), N: 8.08 (8.04), C/N: 8.25% (8.57%); UV-Vis:  $\lambda_{\text{max}}$  (nm) intraligand transitions: 280, 300.

#### 2.4. Synthesis of NiL1 and NiL2

L1 and L2 (0.01 mol) in the minimum quantity of methanol:acetone (3:1) was mixed with a methanolic solution of nickel(II) acetate tetrahydrate (0.01 mol). The resulting solutions were refluxed with stirring on a magnetic stirrer equipped at 80°C for 2 h. The bright red NiL1 and NiL2 separated out, were filtered, washed, and dried under vacuum [26].

NiL1 yield: 70%; red solid; the complex decomposes at  $260 \pm 2^\circ\text{C}$ ; IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{C}=\text{N}}$  1599; CHN found (Calcd) for  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{NiO}_4$ , C: 53.87 (53.83), H: 3.96 (3.95), N: 7.87 (7.85); UV-Vis:  $\lambda_{\text{max}}$  (nm) intraligand transitions: 320, 370, d  $\rightarrow$  d: 440.

NiL2 yield: 70%; red solid; the complex decomposes at  $270 \pm 2^\circ\text{C}$ ; IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{C}=\text{N}}$  1606;  $\text{C}_{20}\text{H}_{14}\text{N}_2\text{NiO}_4$ , C: 59.25 (59.31), H: 3.45 (3.48), N: 6.90 (6.92); UV-Vis:  $\lambda_{\text{max}}$  (nm) intraligand transitions: 280, 310, d  $\rightarrow$  d: 430.

#### 2.5. Multi-walled carbon nanotubes synthesis and purification

The multi-walled carbon nanotubes (MWNTs) prepared by the Ni/Co catalyst over  $\text{CaCO}_3$  support using chemical vapor deposition method were used in this study. The diameter of MWNTs obtained was 20–40 nm. The raw product was first immersed in an aqueous solution of HCl to remove  $\text{CaCO}_3$ , then filtered, washed with distilled water, and dried in an oven. The purity was up to 99%. The SEM micrograph of purified MWNT is shown in figure 1.

#### 2.6. Oxidation and chlorination of MWNTs

The purified MWNTs were refluxed in dilute  $\text{HNO}_3$  for 4 h. The resulting solid (MWNT-COOH) was then separated by filtration and washed with water and dried. The MWNT-COOH (5 g) previously dried was suspended in a solution of  $\text{SOCl}_2$

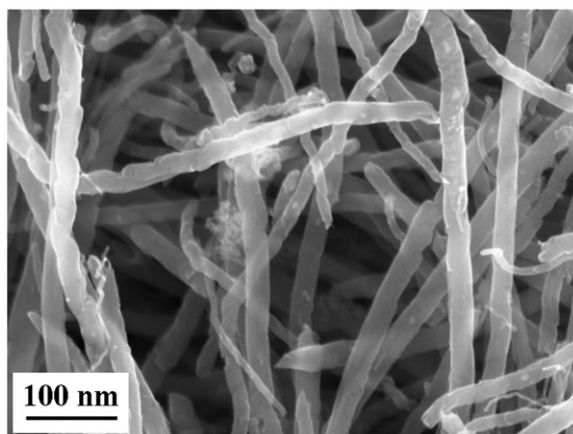


Figure 1. SEM image of purified MWNT.

(100 mL). The suspension was stirred at 65°C for 24 h under nitrogen. After that, the reaction mixture was cooled and  $\text{SOCl}_2$  was evaporated [27]. The resulting precipitate was chlorinated multi-walled carbon nanotubes (MWNT-COCl) (scheme 1).

### 2.7. Supporting nickel complexes on functionalized MWNT

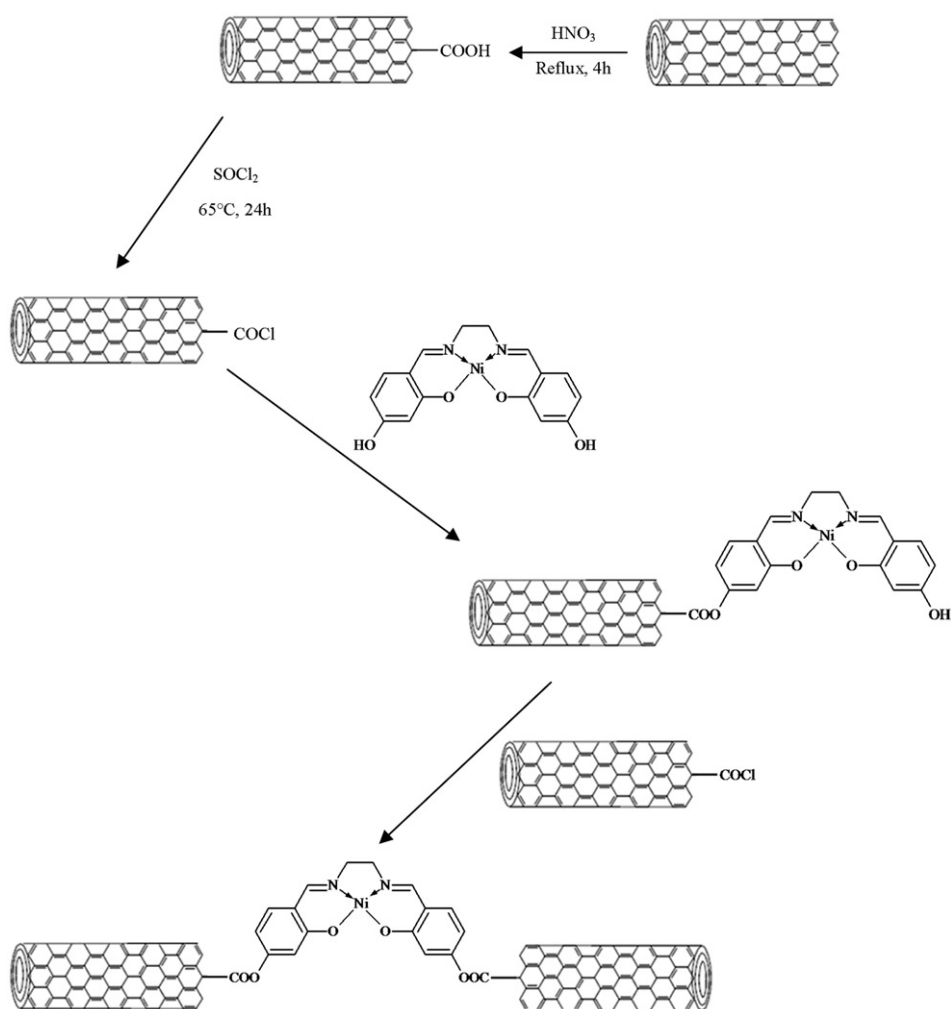
The MWNT-COCl was added (5 g) to a solution of nickel complex, i.e., NiL1 or NiL2 (1 g) in  $\text{CHCl}_3$ , and the suspension was stirred for 40 h under  $\text{N}_2$  at 70°C (scheme 1). The solid was then separated by filtration and washed with THF,  $\text{CH}_2\text{Cl}_2$ , and dried in vacuum.

### 2.8. General procedure for the oxidation of alcohols

Catalytic oxidation of primary and secondary alcohols to corresponding aldehydes and ketones by MWNT-supported nickel complexes was studied in acetonitrile ( $\text{CH}_3\text{CN}$ )–periodic acid ( $\text{H}_5\text{IO}_6$ ). The reaction conditions have also been optimized for the maximum oxidation of benzyl alcohol by varying different parameters. The reaction mixture was filtered and then analyzed by gas chromatography.

### 2.9. Catalyst reuse and stability

The reusability of supported catalysts was investigated in the multiple sequential oxidation of benzyl alcohol. At the end of each reaction, the catalyst was separated from the reaction mixture by simple filtration, washed with diethyl ether, and dried before using in the next run.



Scheme 1. Synthesis of MWNT-supported nickel complexes.

### 3. Results and discussion

#### 3.1. Characterization of MWNT-supported nickel salen complex

The synthesized MWNTs were functionalized by COOH groups by oxidation using nitric acid. In order to increase the reactivity, it was further converted to COCl by thionyl chloride. The MWNT-COCl was reacted with the nickel salen complex to obtain MWNT-supported catalyst. The prepared supported catalyst was characterized by ICP-AES, FT-IR, UV-Vis, TEM, and XRD. The nickel content in the supported catalysts NiL1 and NiL2 was 0.099 and 0.102 mmol  $\text{g}^{-1}$ , respectively, measured by ICP-AES.

More information about anchoring of NiL1 and NiL2 to MWNT was obtained by FT-IR spectroscopy. The intensity of the IR spectrum of MWNT-supported nickel

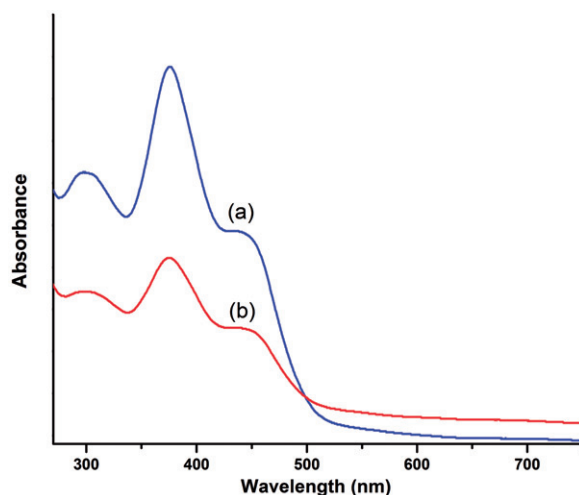


Figure 2. Electronic spectra of (a) NiL1 and (b) MWNT-NiL1.

complexes was weak due to the low concentration of the complex. The IR spectra of supported complexes are similar to those of neat complexes. The azomethine band (C=N) is observed at  $\sim 1600\text{ cm}^{-1}$  in supported catalysts when compared to its neat complexes at  $\sim 1605\text{ cm}^{-1}$  (Supplementary material). This observation clearly confirms the anchoring of NiL1 and NiL2 to MWNT.

The electronic spectra of neat and supported complexes were recorded. The electronic spectra of the neat and supported complexes were identical, indicative of no changes in the structural features before and after anchoring to MWNT (figures 2 and 3). The spectrum of MWNT did not show any peak, therefore, it is confirmed that complexes have been supported on MWNTs.

TEM images of clean MWNT and complexes supported on MWNT show further evidence for attachment to MWNTs. CNTs are neat, straight and long (figure 4a). Complexes (black dots) attached on the surfaces and tips of MWNTs were clearly observed from the supported MWNT TEM image (figure 4b and c).

X-ray diffraction studies were performed for all MWNT-anchored complexes. The diffraction pattern of MWNT-COOH was the same as raw CNT, clearly indicating that structural perfection was not altered after oxidation (figure 5). The XRD patterns of CNTs anchored by complexes also show similar patterns as raw MWNT, indicating that crystallinity and morphology were not altered after anchoring of complexes.

### 3.2. Catalytic activity

The prepared catalysts were used for the oxidation of primary and secondary alcohols using periodic acid as oxidant. The oxidation was studied in more detail to optimize reaction variables such as solvent, length of reaction time, alcohol/oxidant, and alcohol/catalyst molar ratio. We checked the activity of supported catalysts in different solvents (methanol, acetonitrile, and acetone) with periodic acid as the oxidant and the best conversion was observed in acetonitrile. The optimizations of other reaction conditions



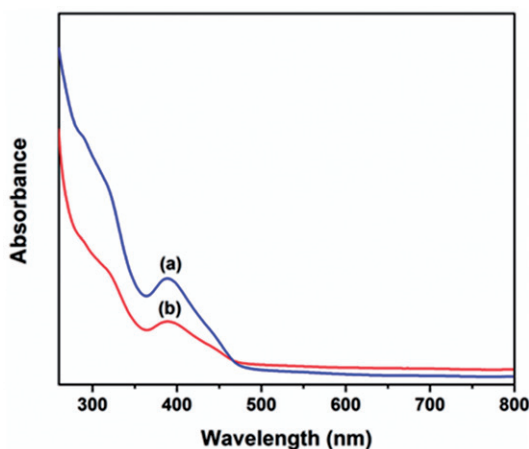


Figure 3. Electronic spectra of (a) NiL2 and (b) MWNT-NiL2.

were studied by taking benzyl alcohol as a substrate in the acetonitrile– $\text{H}_5\text{IO}_6$  system. The benzaldehyde formed was quantified by GC. The product analysis was done at regular intervals of time, under similar reaction conditions for supported catalyst. In the  $\text{CH}_3\text{CN}$ – $\text{H}_5\text{IO}_6$  system, the time required for maximum conversion of benzaldehyde to benzyl alcohol was 90 min.

In order to study the effect of the concentration of catalysts with respect to substrate, the reaction was studied at different substrate to catalyst ratios for supported catalysts. The reaction was also studied in the absence of catalyst and no conversion was observed (table 1). A 400 mg sample (0.04 mmol) of catalyst was sufficient for effective transformation of benzyl alcohol to benzaldehyde for both supported complexes. The reactions were studied at various substrate-to-oxidant ratios. A minimum quantity of 1 mmol of oxidant was sufficient for effective oxidation of benzyl alcohol to benzaldehyde by supported catalysts.

The supported catalysts exhibited high catalytic activity for the oxidation of various alcohols (table 2). Allylic alcohols, benzylic alcohols, and secondary alcohols gave high yields of the corresponding carbonyls. All benzylic primary and secondary alcohols studied were oxidized smoothly to give aldehydes and ketones, respectively. It is clear from the GC analysis that no side reaction took place during catalytic oxidation. The over oxidation to carboxylic acid was ruled out by a derivative test. All the experiments were carried out in air since there is no change in conversion if the reaction is carried out under argon. This indicates that air is not involved in the oxidation.

### 3.3. Influence of support

The anchoring of complexes on MWNT could result in a favorable combination of heterogeneous and homogeneous catalysis. The MWNT support can provide a stabilizing effect, since it can prevent catalyst deactivation by hindering the formation of peroxy- and  $\mu$ -oxo-bridged species. The  $\mu$ -oxo dimers can be formed easily with neat complexes during oxidation [28]. In order to demonstrate the effect of MWNT supporting on the catalytic activity of complexes in the oxidation of alcohols, we

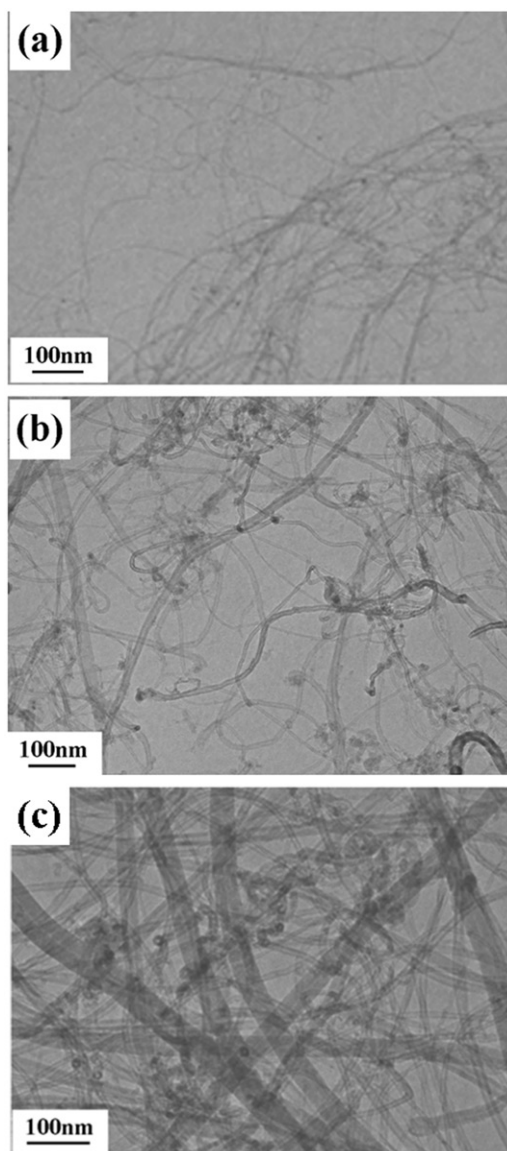


Figure 4. TEM images of (a) neat MWNT, (b) MWNT-NiL1, and (c) MWNT-NiL2.

repeated all reactions under the same reaction conditions with neat complexes. The catalytic activity was higher for supported catalysts than homogeneous. The higher activity is due to site isolation effect, suppressing the formation of peroxo- and  $\mu$ -oxo-bridged complexes.

### 3.4. Recycling and stability of catalyst

The recycling of catalysts is very important for industrial applications. After filtration and washing with diethyl ether, we supported catalysts for the oxidation of

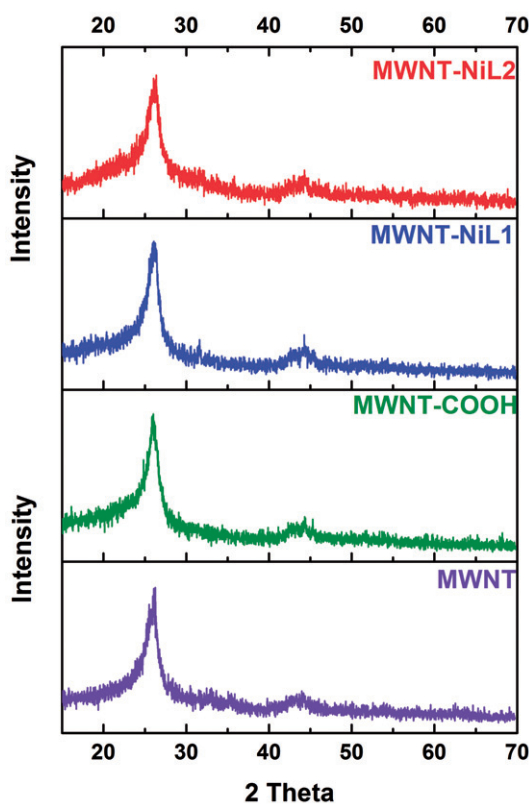


Figure 5. XRD pattern of MWNT, MWNT-COOH, MWNT-NiL1, and MWNT-NiL2.

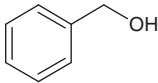
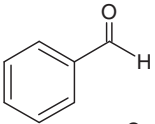
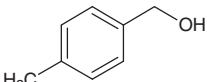
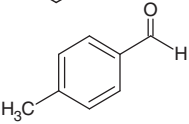
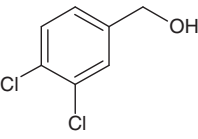
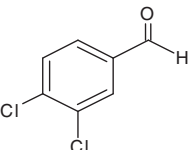
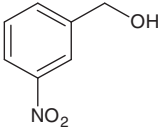
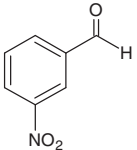
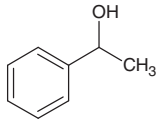
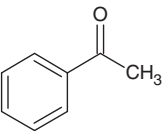
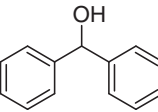
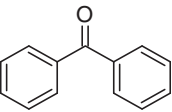
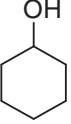
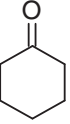
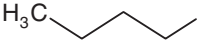
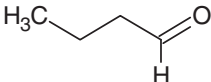
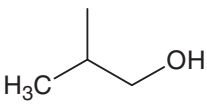
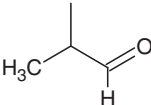
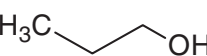
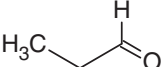
Table 1. Optimization of concentration of oxidant and catalyst for oxidizing benzyl alcohol to benzaldehyde by supported NiL1 and NiL2 complexes.<sup>a</sup>

Sl. No.	Amount of catalyst (mmol)	Amount of oxidant (mmol)	% Yield <sup>b</sup>	
			MWNT-NiL1	MWNT-NiL2
1	0	1.0	2.0	2.2
2	0.01	1.0	58.1	64.7
3	0.02	1.0	72.4	73.0
4	0.03	1.0	80.3	85.1
5	0.04	1.0	80.4	95.2
6	0.05	1.0	80.3	95.0
7	0.04	0	3.6	2.7
8	0.04	0.25	26.5	26.4
9	0.04	0.50	52.2	50.2
10	0.04	0.75	73.1	72.8
11	0.04	1.0	80.3	95.1
12	0.04	1.25	80.1	95.2

<sup>a</sup>1 mmol alcohol, 15 mL CH<sub>3</sub>CN, 90 min, stirring at 80°C.

<sup>b</sup>GC yield, average of three trials.

Table 2. Oxidation of alcohols catalyzed by neat and supported nickel complexes in  $\text{CH}_3\text{CN}-\text{H}_5\text{IO}_6^{\text{a}}$ 

Entries	Alcohols	Product	% Yield of carbonyl compound <sup>b</sup>			
			NiL1	MWNT-NiL1	NiL2	MWNT-NiL2
1			80.2	80.2	93.1	95.2
2			76.9	76.9	86.5	87.1
3			77.5	77.5	90.3	91.0
4			78.3	78.3	89.2	90.1
5			82.4	82.4	94.7	95.1
6			81.7	81.7	94.1	94.6
7			61.5	61.5	70.3	71.2
8			63.0	63.0	72.2	73.0
9			64.1	64.1	74.5	75.2
10			70.5	70.5	79.8	80.5

<sup>a</sup>1 mmol alcohol, 1 mmol  $\text{H}_5\text{IO}_6$ , 0.04 mmol complex, 15 mL  $\text{CH}_3\text{CN}$ , 90 min, stirring at  $80^\circ\text{C}$ .<sup>b</sup>Average of three trials.

benzyl alcohol. The oxidation was carried out five times under identical reaction conditions with the recycled MWNT-supported nickel salen and salophen catalysts. The yield of product was 80.2% in the first run. No significant decrease was observed in the yield of products. The catalyst stability and yield were good, indicating excellent reusability of the catalysts.

#### 4. Conclusions

We have successfully synthesized MWNT-supported nickel salen and salophen complexes. The heterogeneous catalysts show high catalytic activity in the oxidation of primary and secondary alcohols. The catalytic activity was evaluated in the presence of periodic acid as oxidant in acetonitrile at 80°C. The MWNT-supported nickel complexes were catalytically more active than unsupported complexes. The advantages of supported catalysts are high activity, stability, reusability, and avoidance of the deactivation of catalyst by site isolation.

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#### References

- [1] G.A. Morris, S.T. Nguyen, J.T. Hupp. *J. Mol. Catal. A: Chem.*, **174**, 15 (2001).
- [2] R.I. Kureshy, N.H. Khan, S.H.R. Abdi, S.T. Patel, P.K. Iyer, R.V. Jasra. *J. Catal.*, **209**, 99 (2002).
- [3] T.S. Reger, K.D. Janda. *J. Am. Chem. Soc.*, **122**, 6929 (2000).
- [4] K.C. Gupta, A.K. Sutar. *J. Mol. Catal. A: Chem.*, **280**, 173 (2007).
- [5] S.R. Cicco, M. Latronico, P. Mastrorilli, G.P. Suranna, C.F. Nobile. *J. Mol. Catal. A: Chem.*, **165**, 135 (2001).
- [6] P.T. Anastas, M.M. Kirchoff, T.C. Williamson. *Appl. Catal. A: Gen.*, **221**, 3 (2001).
- [7] B.M. Trost. *Acc. Chem. Res.*, **35**, 695 (2002).
- [8] J. Tong, Y. Zhang, Z. Li, C. Xia. *J. Mol. Catal. A: Chem.*, **249**, 47 (2006).
- [9] R. Irie, T. Hashihayata, T. Katsuki, M. Akita, Y. Morooka. *Chem. Lett.*, **24**, 1041 (1998).
- [10] F.C. Skrobot, A.A. Valente, G. Neves, I. Rosa, J. Rocha, J.A.S. Cavaleiro. *J. Mol. Catal. A: Chem.*, **201**, 211 (2003).
- [11] Y. Huang, V. Adeeva, W.M.H. Sachtler. *Appl. Catal. A*, **196**, 73 (2000).
- [12] B.M. Reddy, G.K. Reddy, K.N. Rao, A. Khan, I. Ganesh. *J. Mol. Catal. A: Chem.*, **265**, 276 (2007).
- [13] N. Madhavan, C.W. Jones, M. Weck. *Acc. Chem. Res.*, **41**, 1153 (2008).
- [14] A. Kuzusaka, R.F. Howe. *Mol. Catal.*, **9**, 199 (1980).
- [15] N.E. Leadbeater, M. Marco. *Chem. Rev.*, **102**, 3217 (2002).
- [16] Z. Ma, W.H. Sun, N. Zhu, Z. Li, C. Shao, Y. Hu. *Polym. Int.*, **51**, 349 (2002).
- [17] H. Zhao, L. Zha, M. Cai. *React. Kinet. Mech. Cat.*, **100**, 187 (2010).
- [18] D.E.D. Vos, F.T. Starzyk, P.P.K. Gerrits, R.F. Parton, P.A. Jacobs. *Macromol. Symp.*, **80**, 157 (1994).
- [19] A. Valente, C. Palma, I.M. Fonseca, A.M. Ramos, J. Vital. *Carbon*, **41**, 2793 (2003).
- [20] P. Serp, M. Corrias, P. Kalck. *Appl. Catal. A*, **253**, 337 (2003).
- [21] K. Gupta, A. Sutar. *Coord. Chem. Rev.*, **252**, 1420 (2008).
- [22] P.G. Cozzi. *Chem. Soc. Rev.*, **33**, 410 (2004).

- [23] M.S. Niasari, E. Esmaeili, H. Seyghalkar, M. Bazarganipour. *Inorg. Chim. Acta*, **375**, 1 (2011).
- [24] M. Zakeri, M. Moghadam, I.M. Baltork, S. Tangestaninejad, V. Mirkhani, A.R. Khosropour. *J. Coord. Chem.*, **65**, 7 (2012).
- [25] A.I. Vogel. *Text Book of Practical Organic Chemistry*, 5th Edn, Longman, London (1989).
- [26] S.D. Bell, I. Fragal, N. Leonardi, S. Sortino. *Inorg. Chim. Acta*, **357**, 3865 (2004).
- [27] I.D. Rosca, F. Watari, M. Uo, T. Akasaka. *Carbon*, **43**, 3124 (2005).
- [28] R. Belal, B. Meunier. *J. Mol. Catal.*, **44**, 187 (1988).