

## Multi-walled Carbon Nanotubes as a Ligand in Nickel $\alpha$ -Diimine Based Ethylene Polymerization

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**Abstract** Two novel heterogeneous nickel  $\alpha$ -diimine based polymerization catalysts, containing MWCNT as the main ligand, were synthesized by novel *in situ* catalyst preparation technique. The *in situ* synthesis was performed by covalent attachment of the acenaphthene ligand core to amine functionalized MWCNT ligand arms through diimine bonding and further nickel dibromide chelation. The prepared catalysts were fully characterized and their structures and supporting efficiencies were determined. Single or double introduction of the MWCNTs through their ends or sidewall(s) in the catalytic system, as a ligand, influenced the catalytic performance, microstructure and morphology of obtained polyethylenes. MWCNT sidewall bonding to para-aryl position of the tetramethylphenyl moiety performed as more electron-donating ligand than MWCNT ends linked to the imine bond and protected the catalytic system to retain its activity. This character resulted in the maintenance of the resulting polymer topology at elevated temperatures so that the catalytic activity and the obtained polymer melting points remained around 110 g PE·mmol<sup>-1</sup> Ni·h<sup>-1</sup> and 123 °C in all polymerization temperatures respectively. In polymerization trials, molecular weight fall against temperature was not as sharp as what had been observed in sequentially prepared catalysts insofar as the molecular weight of resultant polymer at 60 °C reached to 310000 g·mol<sup>-1</sup> which was close to the highest value had been reported at 30 °C for sequentially prepared catalysts. TEM observations showed the presence of the stopped-growth polymer chains due to geometrical constraints or ligand debonding for both catalytic systems.

**Keywords:**  $\alpha$ -Diiminonickel catalyst; Ligand; Multi-walled carbon nanotubes; Ethylene polymerization; *In situ* catalyst preparation.

### INTRODUCTION

Since the Brookhart's creative discovery of nickel and palladium aryl-substituted  $\alpha$ -diimine catalysts for olefin polymerization, late transitional metal catalysts have been a matter of significant interest because they can make polymers with good tolerance against functional groups<sup>[1–5]</sup>, and controlled topology<sup>[6, 7]</sup>. As well known, the catalyst activity and the polymer properties are mainly dependent on the reaction conditions and ligand structures. The effect of the steric hindrance of the ligands with *ortho*-aryl position<sup>[8–10]</sup>, and *para*-aryl position substituents<sup>[11–13]</sup>, on the catalytic activity of  $\alpha$ -diiminonickel complexes and the microstructures of resultant polymers has been studied in detail by researchers.

The immobilization of late transition metal catalysts including the ones based on  $\alpha$ -diimine ligands on heterogeneous supports has been a renewed interest in late transition metal based catalysis. Immobilizing  $\alpha$ -diiminonickel complexes on inorganic carriers such as silica, alumina, zeolite, magnesium compounds, and bi-supports has been reported in the literature, and some researchers reported maintained activities without reactor fouling<sup>[14–19]</sup>.

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Carbon nanotubes show good electron mobility and have a very large steric bulkiness which makes them a proper candidate as an ancillary or a main ligand that tunes the reactivity of metal catalyzed reactions electronically and sterically<sup>[20]</sup>. Review of recent progress in heterogenization of late transitional metal complexes with diimine ligands<sup>[21, 22]</sup> reveals that researches concerning immobilization of  $\alpha$ -diiminonickel complexes on MWCNT<sup>[23, 24]</sup>, are rare. So the concept of introducing multi-walled carbon nanotubes (MWCNTs) as the ancillary or the main ligand in the late transition metal based catalysts, such as  $\alpha$ -diiminonickel complexes, can be considered as a novel feature in this matter.

The reported method for applying MWCNT as an ancillary ligand for transitional metals is a sequential technique based on synthesis of the catalyst complex and immobilizing the complex on the MWCNT ancillary ligand. The sequential technique is mainly divided into two categories: (a) covalent bonding of the functionalized MWCNT to the catalyst main ligand with or without a linker<sup>[24]</sup> and (b) physisorption of the complex onto the MWCNT surface by  $\pi$ - $\pi$  stacking, van der Waals or electrostatic interactions<sup>[25–31]</sup>. These methods are devoted *in situ* nanocomposite preparation mostly by metallocene-catalyzed polymerization reaction or investigation on how the catalyst immobilization influences the catalytic behavior.

In our previous work<sup>[24]</sup>, with the help of sequential catalyst preparation technique, we used MWCNT as an ancillary ligand for two  $\alpha$ -diiminonickel complexes comprising 4-bis(2,6-diisopropylphenylimino)acenaphthene nickel(II) dibromide and bis(4-amino-2,3,5,6-tetramethylphenylimino)acenaphthene nickel(II) dibromide and studied the effect of this heterogenization on catalytic activity and resultant polymer microstructure. However, to the best of our knowledge, there is no report on utilizing *in situ* technique for applying MWCNT as the main ligand in the nickel  $\alpha$ -diimine-based catalyst system and on how this method can affect the catalytic behavior of these systems for ethylene polymerization.

In this regard, herein, with the help of novel *in situ* catalyst preparation techniques, two novel heterogeneous nickel  $\alpha$ -diimine based polymerization catalysts, containing MWCNT as the main ligand, were synthesized and characterized. Furthermore, the influence of MWCNTs ligand and their sidewall or both ends introduction effects on the catalytic performance, microstructure and morphology of the resultant polyethylenes have been investigated in comparison to the previous results of the sequential catalyst preparation method<sup>[24]</sup> in different slurry polymerization conditions.

## EXPERIMENTAL

### Materials

Methanol (MeOH), sodium nitrite (NaNO<sub>2</sub>), hydrochloric acid (HCl), formic acid (HCOOH), nickel(II) dibromide-ethyleneglycol dimethyl ether complex (NiBr<sub>2</sub>(DME)), dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), 2,3,5,6-tetramethyl-phenylene1,4-diamine, hexane, dimethylformamide (DMF), acetone, tetrahydrofuran (THF), butylated hydroxy toluene (BHT), xylene and methylaluminoxane (MAO) were purchased from Aldrich Company, Germany. The MAO was used as a 100 mg·mL<sup>-1</sup> fresh prepared solution in dry toluene. Acenaphthenequinone was obtained from Merck Chemical Company, Germany. Polymerization grade ethylene was supplied by a local petrochemical complex. OH functionalized multi-walled carbon nanotube, MWCNT-OH, (average outer diameter > 50 nm, length: 10–20  $\mu$ m, purity > 95 wt%, OH content: 0.70 wt%, produced by chemical vapor deposition process) and NH<sub>2</sub> functionalized multi-walled carbon nanotube, MWCNT-NH<sub>2</sub>, (average outer diameter: 13–18 nm, length: 1–12  $\mu$ m, purity > 99 wt%, NH<sub>2</sub> content: 7 wt%, developed out of natural graphite source material by the split plasma process, primary functionality: NH<sub>2</sub> (primary amine), other functionalities: O=C–NH<sub>2</sub> (primary amide), N–H (secondary amine), C=N (substituted imines)) were purchased from Cheap Tubes, USA.

### General Methods

Manipulations of air and moisture sensitive materials were carried out under a dry nitrogen atmosphere using Schlenk or glove-box techniques. For moisture and oxygen removal, solvents for catalyst synthesis and polymerization were distilled after being reacted by sodium wire. Elemental analysis was performed on an

American Varian SpectrAA-10/20 atom adsorption spectrometer (AAS). Gel permeation chromatography was carried out with an American Waters Alliance GPC/V 2000 system equipped with Waters Millennium32 GPC/V software, a refractive index detector, viscometric detector and a set of three Styragel type columns in 1,2,4 tri-chlorobenzene at 140 °C. Firstly, Samples were heated in xylene in the presence of BHT at 145 °C and then filtered by Teflon filter over fritted glass funnel to remove attached polyethylene from the MWCNT surface prior to GPC analysis. Branching frequencies (the number of branches per 1000 carbon atoms) of the resulting polymers were calculated by Waters Millennium32 GPC/V software based on the intrinsic viscosity ( $[\eta]$ ) data of polymers at each molecular weight increase (*i.e.* slice) determined by RI/Viscometer followed by the calculation of branched to linear intrinsic viscosity ratio ( $[\eta]/[\eta]_{lin}$ ) in the viscosity law ( $\lg[\eta]$  versus  $\lg M$ ) plot. Melting temperatures,  $T_m$ , were determined by differential scanning calorimetry (DSC) with a DSC 821 E (Mettler-Toledo, Switzerland) at a heating rate of 10 K·min<sup>-1</sup>. Fourier transform infrared spectroscopy (FTIR) analysis was done by a Japanese Shimadzu 8900 equipment over the range of 400–4000 cm<sup>-1</sup> in a KBr disc matrix. Because of the high absorbance character of MWCNTs, very small amounts of MWCNT-based catalysts were used for preparing KBr discs. X-ray photoelectron spectroscopy (XPS) was performed on an 8025 Bes Tec German device with twin anode XR3E2 X-Ray source system. Samples were investigated using transmission electron microscopy (TEM) analysis with the Zeiss-EM10C-80 KV German microscope on the Formvar carbon coated grid. Thermogravimetry analysis (TGA) was carried out with a TG/DTA Perkinelmer American instrument under nitrogen atmosphere with a heating rate of 10 K·min<sup>-1</sup> in a temperature range of 30–620 °C.

#### **General Procedure for Applying MWCNT as the Main Ligand in the Nickel $\alpha$ -Diimine-Based Catalyst System**

##### *In situ catalyst synthesis by applying MWCNT-NH<sub>2</sub>*

Two hundred fifty milligrams of dried MWCNT-NH<sub>2</sub> was sonicated (ampl. 20 W, *t*: 30 min) in the mixture of 5 mL methanol and 0.5 mL formic acid. After that 20 mL of methanol was added and the suspension was ultrasonically separated again (ampl. 20 W, *t*: 45 min). Then 45 mg of acenaphthenequinone suspended in 45 mL methanol was added to the suspension and the mixture was heated to reflux for 3 days and water by-product was constantly removed by water and methanol azeotrope. The mixture was filtered by Teflon filter over fritted glass funnel, washed with methanol and dried in oven under nitrogen purge. In the next step, the dried product was ultrasonically separated (ampl. 20 W, *t*: 45 min) in 30 mL dichloromethane and added to a solution of 125 mg NiBr<sub>2</sub> (DME) in 10 mL dichloromethane. The mixture was stirred for 3 days at room temperature, filtered by Teflon filter over fritted glass funnel, washed with dichloromethane and dried in oven under nitrogen purge. By this novel procedure about 250 mg of the first MWCNT-based  $\alpha$ -diiminonickel catalyst (NC1) was prepared.

##### *In situ catalyst synthesis by applying aryl amine modified MWCNT*

In the first step, 250 mg of dried MWCNT-OH was suspended in 50 mL demineralized water in an ultrasonic bath (ampl. 20 W, *t*: 45 min), then added 8.2 mg 2,3,5,6-tetramethyl-phenylene1,4-diamine, 3.45 mg sodium nitrite and 5 mL of concentrated hydrochloric acid following with stirring for one night under reflux at 60 °C. The suspension was filtered by Teflon filter over fritted glass funnel, washed with successive aliquots of demineralized water, MeOH and acetone. To neutralize the acidic residue, the resulting filtered powder was added to 20 mL DMF and sonicated (ampl. 20 W, *t*: 30 min) following with filtration. To remove remaining salts and extra DMF, the filtered powder was suspended in 20 mL THF in an ultrasonic bath (ampl. 20 W, *t*: 30 min), filtered by Teflon filter over fritted glass funnel and dried in oven under nitrogen purge. By this procedure, aryl amine modified MWCNT-OH was prepared.

In the second step, 250 mg of dried aryl amine modified MWCNT-OH, prepared in the first step, was sonicated (ampl. 20 W, *t*: 30 min) in the mixture of 5 mL methanol and 0.5 mL formic acid. After that 20 mL of methanol was added and the suspension was ultrasonically separated again (ampl. 20 W, *t*: 45 min). Then 45 mg of acenaphthenequinone suspended in 45 mL methanol was added to the suspension and the mixture was heated to reflux for 3 days and water by-product was constantly removed by water and methanol azeotrope. The mixture was filtered by Teflon filter over fritted glass funnel, washed with methanol and dried in oven under nitrogen

purge. In the next step, the dried product was ultrasonically separated (ampl. 20 W,  $t$ : 45 min) in 30 mL dichloromethane and added to the solution of 125 mg  $\text{NiBr}_2(\text{DME})$  in 10 mL dichloromethane. The mixture was stirred for 3 days at room temperature, filtered by Teflon filter over fritted glass funnel, washed with dichloromethane and dried in oven under nitrogen purge. By this novel procedure about 250 mg of the second MWCNT-based  $\alpha$ -diiminonickel catalyst (NC2) was prepared.

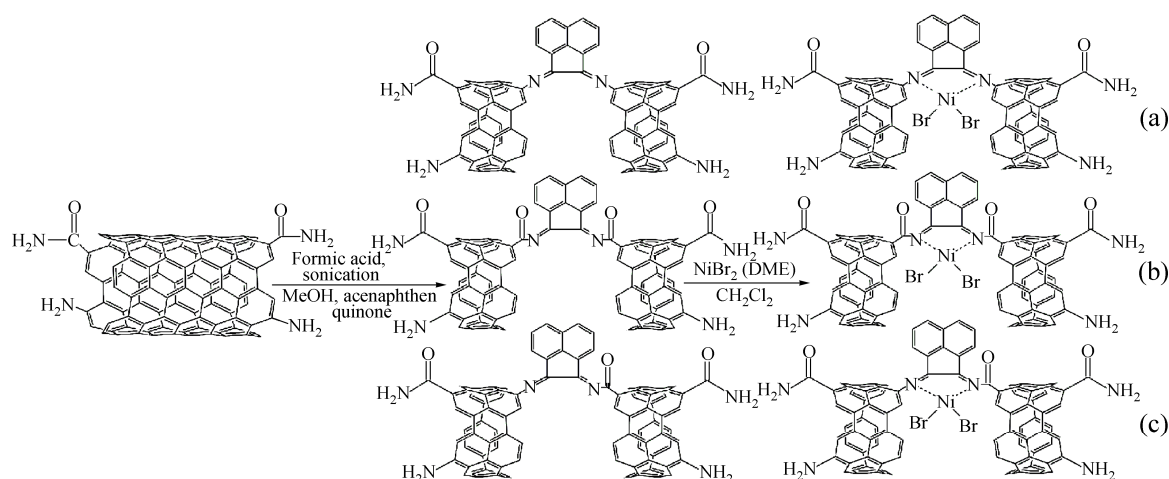
#### General Procedure for Slurry Ethylene Polymerization

Each batch of ethylene polymerization was carried out in a 1 L Buchi reactor. The reactor was heated and purged to remove poisonous elements for 2 h. The reactor was then cooled down to room temperature and charged with 400 mL of dried hexane as a solvent under nitrogen atmosphere. A desired amount of MAO as co-catalyst was added into the reactor by a syringe. Reactor stirrer was turned on for 5 min while all lines to reactor were closed. The MWCNT-based  $\alpha$ -diiminonickel catalysts (NC1 and NC2) were weighed and ultrasonically (ampl. 20 W,  $t$ : 45 min) suspended in hexane for each experimental run. The catalyst suspensions were injected into the reactor by syringe. The reactor was pressurized by ethylene at 1 MPa followed by warming up to desired temperatures with the help of controlled bath circulator. Then agitator was started at the speed of  $900 \text{ r} \cdot \text{min}^{-1}$ . After 30 min, the reactor was cooled to room temperature and vented. The polymerization was terminated by injection of 2% acidified ethanol solution into the reactor. The polymer solution or slurry was filtered, dried in vacuum oven at  $70^\circ\text{C}$ , weighed carefully, and characterized.

## RESULTS AND DISCUSSION

#### Characterization

The most probable structures and the proposed synthetic routes for *in situ* preparing of NC1 and NC2 catalysts through applying MWCNT- $\text{NH}_2$  and aryl amine modified MWCNT as the main ligands are illustrated in Scheme 1 and Scheme 2 respectively. As seen, in both  $\alpha$ -diimine-based catalyst systems, acenaphthenic rings act as the ligand core while MWCNTs are considered as the main ligand arms.

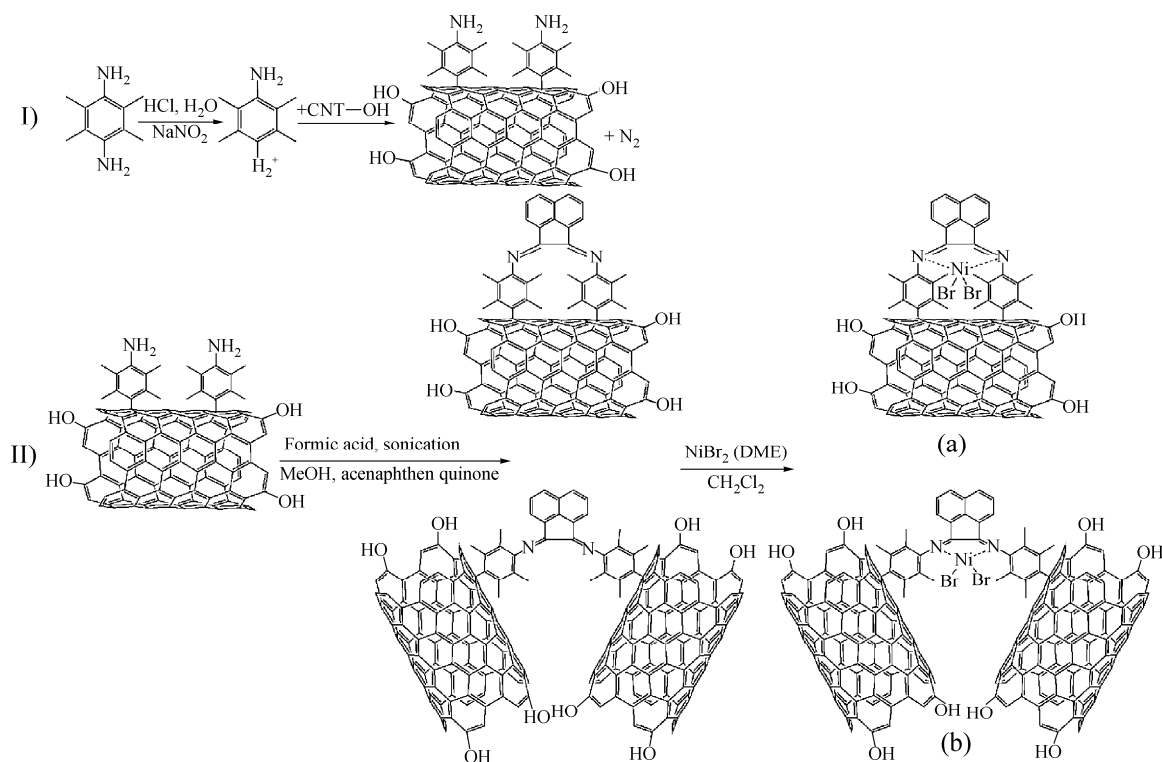


**Scheme 1** Synthetic route for the preparation of NC1 catalyst through applying MWCNT- $\text{NH}_2$  as the main ligand in the nickel  $\alpha$ -diimine-based catalyst system

As illustrated schematically in Scheme 1, NC1 may theoretically be synthesized in three forms (a), (b), and (c). Although primary amine, secondary amine, primary amide and substituted imine groups are present in the structure of MWCNT- $\text{NH}_2$  because of its synthetic procedure, just primary amine and amide functionalities are considered as the reacting agents in the condensation reaction with acenaphthenequinone and formation of the imine bonds. The dominant NC1 form is the form (a) because firstly  $\text{NH}_2$  is the primary functionality and secondly has more nucleophilic nitrogen non-bonding electrons than  $\text{O}=\text{C}-\text{NH}_2$  which accelerate the

condensation reaction with the diketone in the ligand synthesis process and boost Ni coordination in Ni chelation reaction. In  $\text{O}=\text{C}-\text{NH}_2$  groups, the electron withdrawing behavior of  $\text{O}=\text{C}$  bond attenuates the efficiency of the nucleophile nitrogen non-bonding electrons in condensation and chelation reactions. Since the length size of MWCNT- $\text{NH}_2$  particles is rather small (1–12  $\mu\text{m}$ ), the probable location of the functional groups on MWCNT- $\text{NH}_2$ , is the both ends of nanotubes rather than their sidewalls. On the other hand, smaller outer diameter of MWCNT- $\text{NH}_2$  (average outer diameter: 13–18 nm) and consequently the resulting sterical hindrance, presumably restricts diimine formation on the same end of one carbon nanotube and increases the probability that two distinct nanotubes act as the ligand arms in this nickel  $\alpha$ -diimine-based catalyst system as illustrated in Scheme 1.

In Scheme 2, In the step (I), aryl amine modified MWCNT is obtained through the reduction of *in situ* generated diazonium cations by MWCNT-OH surface. These cations are generated through the reaction of sodium nitrite with 2,3,5,6-tetramethyl-phenylene1,4-diamine and coupled with MWCNT-OH sidewall surfaces as the most probable terminals for grafting through reduction reactions. The reason that we chose MWCNT-OH rather than pristine or carboxyl functionalized multi-walled carbon nanotubes, is its phenolic electron donating characteristic that facilitates diazonium cations reduction. According to the previously reported results in the literature, with the similar procedures, about 7 wt% of aryl amine groups is estimated to be grafted on the MWCNT-OH sidewall surfaces<sup>[32, 33]</sup>. In the step (II) of Scheme 2, from the theoretical point of view, the condensation reaction and further Ni coordination may produce NC2 catalyst in two forms (a) and (b) depending on the sidewall introduction of unique or pair carbon nanotubes to the  $\alpha$ -diimine-based catalyst system.



**Scheme 2** Synthetic route for the preparation of NC2 catalyst through applying aryl amine modified MWCNT as the main ligand in the nickel  $\alpha$ -diimine-based catalyst system

Because of its very weak Van der Waals interaction compared to covalent interactions present in these two  $\alpha$ -diimine-based catalyst systems,  $\pi$ - $\pi$  stacking of the aromatic framework of acenaphthenequinone on the multi-walled carbon nanotube surfaces cannot be considered as an effective feature for bonding in the NC1 and NC2 catalyst systems.

Figure 1 shows the FTIR spectra of the nickel  $\alpha$ -diimine-based catalysts (NC1, NC2), their original multi-walled carbon nanotubes bases (MWCNT-NH<sub>2</sub>, MWCNT-OH) and part of the acenaphthenequinone peaks and bands (due to its large scale for layouting). For acenaphthenequinone FTIR spectra, bands of the peaks at 700–720 cm<sup>-1</sup> are associated with its structure while the bands for the peaks at 1439–1579 cm<sup>-1</sup> are referred to stretching modes of C=C in benzene and acenaphthenic rings. The bands of the sharp peak at 1720 cm<sup>-1</sup> indicates C=O stretching of ketones as well. Residual moisture in acenaphthenequinone may cause the appearance of the peak at 3420 cm<sup>-1</sup>.

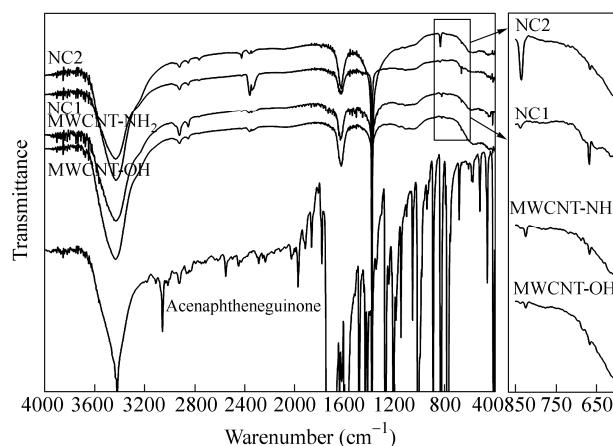


**Fig. 1** FTIR spectra of the nickel  $\alpha$ -diimine-based catalysts, NC1, NC2, their multi-walled carbon nanotube bases, MWCNT-NH<sub>2</sub>, MWCNT-OH, and acenaphthenequinone

For the catalysts and multi-walled carbon nanotubes, as previously reported<sup>[24, 34]</sup>, the peaks at 3431–3435 cm<sup>-1</sup> can be assigned to the O–H stretching in the C–OH groups and N–H stretching in primary amine or amide groups on the MWCNT surface. The peak at 1630 cm<sup>-1</sup> can be associated with the stretching of carbon nanotube backbone. The wave number of C=N stretching in Ni complexes normally appears from 1610–1650 cm<sup>-1</sup> in FTIR spectra, but in catalysts FTIR spectra shown in Fig. 1, it overlaps or convolutes with sharp peak of 1630 cm<sup>-1</sup> of carbon nanotube backbone stretching and therefore can not be traced. The sharp peak at 1385 cm<sup>-1</sup> can be attributed to C=C aromatic stretching of nanotube backbone. The rather small peaks at 2700–2933 cm<sup>-1</sup> can be referred to stretching modes of C–H attached to oxygen or nitrogen. Twin peaks at 2343 cm<sup>-1</sup> are related to retained air in KBr discs. The rather broad peaks at 1015–1200 cm<sup>-1</sup> can be attributed to C–O or C–N stretching modes of the alcoholic or primary amine groups respectively.

The considerable feature in FTIR spectra is the very small peaks appeared around 650 cm<sup>-1</sup> to 850 cm<sup>-1</sup>. Small peaks at 820–840 cm<sup>-1</sup>, as we introduced in our previous work<sup>[24]</sup>, may be referred to C–H out of plane deformation in benzene substituted rings which show the functionality of MWCNTs. In NC2 spectra, this peak is sharper indicating the presence of the grafting bulky 2,3,5,6-tetramethyl-phenylene1-amine groups. A more in-depth investigation on the FTIR spectra also reveals very small peaks around 670–680 cm<sup>-1</sup> which may indicate OH out-of-plane deformation in phenols and N–H wagging in primary and secondary amines.

X-ray photoelectron spectra of NC1 and NC2 catalysts, MWCNT-NH<sub>2</sub> and NiBr<sub>2</sub>(DME) are shown in Fig. 2. The sharp photoelectric peaks appear at 285 eV in all spectra are attributed to C 1s of C–H and C–C bonds. The intensity of C 1s in NC1, NC2, and MWCNT-NH<sub>2</sub> XPS spectra is higher compared to that in NiBr<sub>2</sub>(DME) due to their carbon nanotube backbones. In NiBr<sub>2</sub>(DME) XPS spectrum, peaks at 69.69 eV, 183.3 eV and 856.25 eV are associated with Br 3d<sub>5/2</sub>, Br 3p<sub>3/2</sub> and Ni 2p<sub>3/2</sub> respectively.

In all spectra, the sharp peaks at 533.23 eV and relatively broad peaks at 983 eV are related to O 1s and O KLL binding energies resulted from oxygen atoms in amide bonds in MWCNT-NH<sub>2</sub> and its resulting  $\alpha$ -diimine-based catalyst (NC1), oxygen atoms of the hydroxyl groups in NC2 originated from its MWCNT-OH base, and oxygen atoms in twin ether bonds in NiBr<sub>2</sub>(DME).

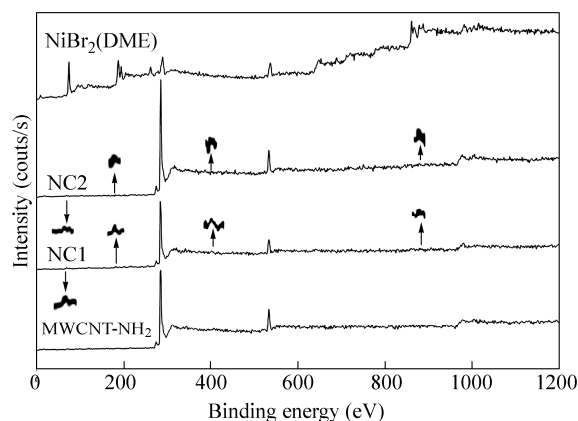


**Fig. 2** XPS spectra of NC1 and NC2 catalysts, MWCNT-NH<sub>2</sub> and NiBr<sub>2</sub>(DME)

The small convoluted shoulder peaks at 288 eV which have been appearing close to sharp peaks of 285 eV (C 1s of C—H and C—C bonds) may correspond to the C 1s binding energy of amine and amide bonds in NC1, NC2, and MWCNT-NH<sub>2</sub>. Noisy low intensity photoelectric peaks at 863.73 eV for Ni 2p<sub>3/2</sub>, 400.26 eV for N 1s<sub>1/2</sub>, 69.69 eV for Br 3d<sub>5/2</sub>, and 183.3 eV for Br 3p<sub>3/2</sub> are seen in NC1 and NC2 XPS spectra because of the less in-depth surface sensitivity of the XPS technique and the very low concentration of these elements in these catalysts.

To investigate the bonding strength between acenaphthenic ring ligand core and MWCNT ligand arms as well as the Ni chelation strength in synthesized  $\alpha$ -diimine-based catalysts, TGA has been carried out. TGA can provide the stability of the synthesized catalysts in terms of weight loss at pre-determined elevated temperature. Figure 3 shows the weight loss of NC1 and NC2 catalysts in the presence of their related MWCNT ligand bases versus temperature (37 °C to 610 °C). For omitting the effect of weight loss due to MWCNT ligand degradation, the weight loss of each catalyst can be subtracted from its MWCNT base weight loss. So it is found that the relative weight loss of catalysts at 610 °C is about 2.47% for NC2 and 2.99% for NC1. These values are set outside the lower weight loss limits of the  $\alpha$ -diimine-based/MWCNT catalysts synthesized by sequential technique in our previous research<sup>[24]</sup>. In that work covalent bonding *via* the reaction of amino para-aryl position functionality of the  $\alpha$ -diimine nickel catalyst (bis(4-amino-2,3,5,6-tetramethylphenylimino)acenaphthene nickel(II) dibromide) with acyl chloride functionality of MWCNT-COCl resulted in strongest linkage and showed 3.54% relative weight loss, while electrostatic immobilization of the other  $\alpha$ -diimine nickel catalyst (4-bis(2,6-diisopropylphenylimino)acenaphthene nickel(II) dibromide) on MWCNT-COOH *via* MAO linkage exhibited the weakest attachment with the relative weight loss of 14.01% at 610 °C. This indicates the *in situ* catalyst preparation technique can be considered as the determinant factor in boosting the thermal stability of heterogenized  $\alpha$ -diiminonickel catalyst.

Weaker thermal stability of NC1 compared to NC2 may be mainly attributed to the presence of O=C—NH<sub>2</sub> groups on MWCNT-NH<sub>2</sub> which create weaker imine bonds in the condensation reaction with diketone in ligand synthesis process and attenuate Ni coordination strength in Ni chelation reaction. The electron withdrawing behavior of O=C bond in amide groups attenuates the efficiency of the nucleophile nitrogen non-bonding electrons in condensation and chelation steps. The other reason could be the difference in the geometrical preserving effect of the MWCNT ends compared to MWCNT sidewall. The sidewall introduction of MWCNT into  $\alpha$ -diiminonickel catalytic system provides more stacking geometrical covering by the MWCNTs on the imine bonds and chelated NiBr<sub>2</sub> which results in the more thermal stability of the catalytic system. Presumably the MWCNT side wall introduction has more influence on restricting the motion and rotation of the ligand arms which is one of the factors responsible in catalyst thermal degradation.

Table 1 summarizes both the components and supporting efficiency results of the both synthesized  $\alpha$ -diimine-based catalysts. Since theoretically every two amine bonds on the MWCNTs surface can be considered as the site of condensation reaction with acenaphthenequinone and further chelation of  $\text{NiBr}_2$ , supporting efficiency is expressed as the ratio of Ni moles in the catalysts measured by AAS to Ni moles needed for 100% coverage of every pairs of the amine groups existing on the applied MWCNT surface.

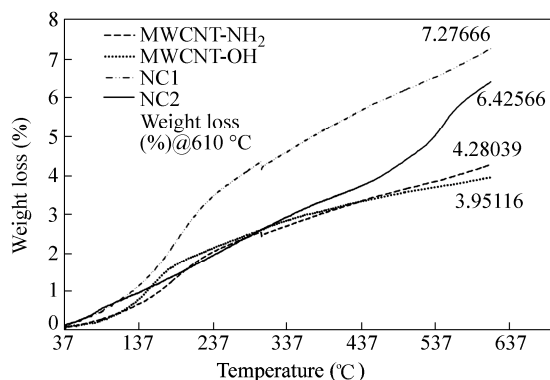


**Fig. 3** Weight loss of synthesized  $\alpha$ -diimine-based catalysts and their MWCNT main ligands versus temperature obtained from TGA

**Table 1.** Description of immobilized  $\alpha$ -diiminonickel catalysts

| Cat. name | Components            |                        |                             | Ni <sup>a</sup> | Supporting efficiency <sup>b</sup> (%) |
|-----------|-----------------------|------------------------|-----------------------------|-----------------|----------------------------------------|
|           | MWCNT functionality   | Functionality location | Functionality content (wt%) |                 |                                        |
| NC1       | —NH <sub>2</sub>      | Ends                   | 7                           | 0.0706          | 3.21                                   |
| NC2       | —aryl—NH <sub>2</sub> | Sidewall               | 7                           | 0.1112          | 5.05                                   |

<sup>a</sup> Based on atomic absorption spectrometry results in ( $\text{mmol}\cdot\text{g}^{-1}$  cat.);

<sup>b</sup> Ratio of Ni moles in the catalysts measured by AAS to theoretical Ni moles needed for 100% coverage of every pair of amine groups existing on the applied MWCNT surface

As seen in Table 1, although the functional content of the both MWCNTs is the same, the Ni content and its supporting efficiency in NC2 are considerably higher. The tendency of primary aryl-amine groups grafted on the sidewall of the carbon nanotubes for condensation and chelation reactions is higher than that of direct —NH<sub>2</sub> and O=C—NH<sub>2</sub> groups located at the MWCNTs ends. This may be originated from the electron donating character of the tetramethylphenyl moiety in the grafted aryl-amines, which boosts the nucleophilic efficiency of the nitrogen non-bonding electrons. This phenomenon facilitates supporting efficiency for NC2 despite the restriction of the amine pair units' availability for diimine bonding and sterical hindrance exists for  $\text{NiBr}_2$  chelation in the form (a) illustrated in Scheme 2. Contrary to its higher Ni content, NC2 showed a very low weight loss in TGA analysis (Fig. 3) which proves firstly the strong imine bonding and Ni coordination and secondly the more preserving effect of the MWCNT sidewall introduction in this catalyst compared to NC1.

NC1 nickel content locates in the range of results previously reported<sup>[24]</sup>, regarding  $\alpha$ -diimine-based/MWCNT catalysts prepared by sequential technique. The NC2 catalyst shows a considerable improvement in Ni content. Still, its rather low supporting efficiency indicates it is the high level of the functionality not the preparation method that increases the Ni content in this catalyst. In our previous research<sup>[24]</sup>, we prepared catalyst with  $0.0766 \text{ mmol}\cdot\text{g}^{-1}$  Ni content and 70% Ni supporting efficiency with just 0.7 wt% of acyl chloride functionality on the MWCNT surface by the sequential preparation technique.

Figure 4 demonstrates the TEM images of the NC1 and NC2 catalysts. TEM study of the catalysts reveals the successful condensation reaction with acenaphthenequinone and further chelation of the nickel complexes on the MWCNT surface. Figures 4(a) and 4(b) show it is mainly the ends of two adjacent carbon nanotubes that

form the ligand arms of NC1 catalyst. The introduction of two adjacent MWCNT in this catalytic system by *in situ* technique can be called punching phenomena expressing the linkage of the two adjoining MWCNTs by acenaphthenic ring *via* imine bonds. Punching phenomena observed in Figs. 4(a) and 4(b), confirms the illustration presented in Scheme 1 for NC1 catalyst. In NC1 catalytic system, the rather small length size (1–12  $\mu\text{m}$ ) and small outer diameter (13–18 nm) of the MWCNT-NH<sub>2</sub> resonate the punched structure compared with the other possible structure (one unique MWCNT end for both imine bond formation) during *in situ* preparation technique. In Figs. 4(c) and 4(d), Ni complexes mainly decorated on the unique MWCNT sidewall are seen. Figure 4(d) also shows the presence of punching phenomena for two adjacent MWCNTs *via* sidewall linkage. Therefore the proposed structures for NC2 catalyst in Scheme 2 is substantiated by TEM study.

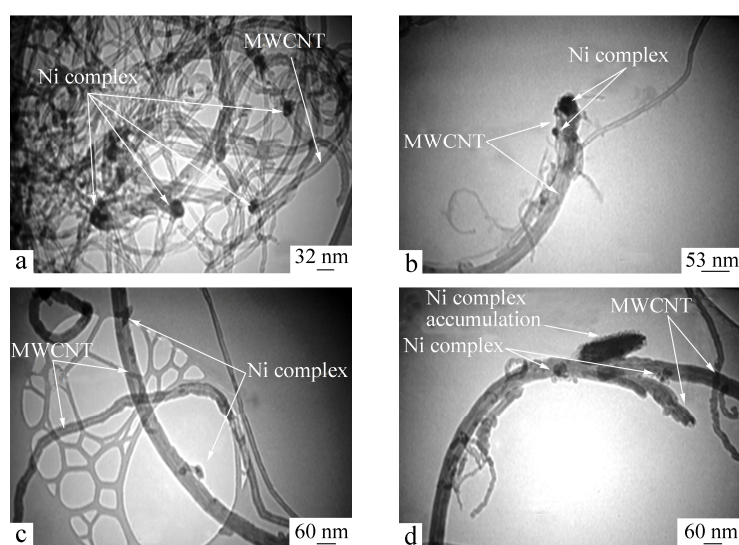


**Fig. 4** TEM images of (a, b) NC1 and (c, d) NC2 catalysts in different magnification scales. Ni complexes and MWCNTs introduced by their ends (a, b NC1) or sidewalls (c, d NC2) are observed.

A noteworthy feature in Fig. 4(d) is the accumulation of Ni complexes in case of punched structure. According to previously reported in the literature, the size of a single crystal of the Brookhart-type complex is around 1.3 nm<sup>[35]</sup>. However it seems that the sidewall introduction of two neighbor MWCNTs brings about more adjacent amine bonds for diimine bonding and consequently Ni chelation. As seen in Fig. 4(d), this may make Ni complex be accumulated bulkier even with the size of 180 nm, while for unique MWCNT sidewall introduction the size of Ni complex bulk reaches to around 30 nm.

#### Ethylene Polymerization Results Using Heterogeneous Catalysts

The results of ethylene polymerization runs using NC1 and NC2 catalysts are shown in Table 2. Compared to the ethylene polymerization results with homogenous  $\alpha$ -diiminonickel catalysts, a drastic reduction in activities, higher molecular weights, higher molecular weight distributions, higher melting temperatures, and lower branching frequencies are observed<sup>[13, 24]</sup>. As was expected,  $\alpha$ -diiminonickel complexes linked to the MWCNT surface show the lower activity caused by significant hindrance and electron donating interface of bulky carbon nanotube surface. The MWCNT ligand can act as an electron donating group and decreases the electrophilic properties of nickel centers, which, as a result, leads to fading of the catalytic activity.

Zhang and coworkers has described ethylene polymerization by aryliminoethylpyridine nickel complexes in the presence of MWCNT and suggests that  $\pi$ - $\pi$  stacking interactions are responsible for physisorption of bulky aromatic frameworks of nickel complexes on carbon nanostructures<sup>[23]</sup>. Although the ligand has been aryliminoethylpyridine, which is more bulkier than our ligands and creates more Van der Waals interactions between the Ni complex and MWCNT surface, and as a consequence imposes more surface sterical hindrance,

the observed catalytic activities are 30 times higher than our reported activities which indicates that in our system the interaction is stronger than physisorption. In our previous work<sup>[24]</sup>, the polymerization of homogenous catalyst, bis(4-amino-2,3,5,6-tetramethylphenylimino)acenaphthene nickel(II) dibromide, which has a similar structure to the  $\alpha$ -diimine complex bearing an aniline moiety as the one shown in Scheme 2(b), showed very high activity around 17000 g PE mmol<sup>-1</sup>·Ni·h<sup>-1</sup>. So this great reduction in catalytic activity could be reasonably attributed to MWCNT ligand covalently linked to the  $\alpha$ -diimine moiety.

**Table 2.** Ethylene polymerization results using heterogeneous catalysts

| Run | Polymerization Conditions |                    |        |                       | Results             |                                       |                                |                 |                      |
|-----|---------------------------|--------------------|--------|-----------------------|---------------------|---------------------------------------|--------------------------------|-----------------|----------------------|
|     | Cat. name                 | Al/Ni <sup>a</sup> | T (°C) | Activity <sup>b</sup> | T <sub>m</sub> (°C) | M <sub>w</sub> (g·mol <sup>-1</sup> ) | M <sub>w</sub> /M <sub>n</sub> | BF <sup>c</sup> | CNT in polymer (wt%) |
| 1   | NC1                       | 660                | 30     | 201                   | 121.8               | 300000                                | 5.3                            | 0.453           | 14.1                 |
| 2   | NC1                       | 660                | 40     | 169                   | 120.2               | 270000                                | 6.1                            | 0.472           | 16.7                 |
| 3   | NC1                       | 660                | 60     | 145                   | 111                 | 230000                                | 7.1                            | 0.991           | 19.5                 |
| 4   | NC2                       | 700                | 30     | 114                   | 123                 | 374000                                | 9.35                           | 0.440           | 15.6                 |
| 5   | NC2                       | 700                | 40     | 110                   | 122.8               | 350000                                | 12.1                           | 0.441           | 16.2                 |
| 6   | NC2                       | 700                | 60     | 100                   | 122.7               | 310000                                | 16.3                           | 0.442           | 17.9                 |

Polymerization conditions: catalysts: 25 mg, co-catalyst: MAO: 0.6 mL (runs 1–3) or 1 mL (runs 4–5), solvent: 400 mL hexane, ethylene pressure: 1 MPa, time: 30 min. Molecular weight, polydispersity and branching frequency (BF) were determined by GPC. Melting temperature was determined by DSC.

<sup>a</sup> in molar ratio

<sup>b</sup> in (g PE·mmol<sup>-1</sup> Ni·h<sup>-1</sup>)

<sup>c</sup> The number of branches per 1000 carbon atoms calculated by Millennium<sup>32</sup> GPC/V software

The steric effects between the MWCNT and the catalyst coordination site along with the electron donating atmosphere of MWCNT ligand, depress chain walking rates, producing chains with lower branching frequencies and higher melting temperatures<sup>[24]</sup>. The growth in molecular weights of polymers obtained from these catalytic systems in comparison with the homogenous catalyst results is attributed to steric hindrance of bulky MWCNT ligand that limits chain transfer at coordination sites. In other words, too bulky MWCNT ligand structure in these  $\alpha$ -diimine-based catalysts increases insertion reaction rates in comparison with chain transfer reaction rates and produces polymers with higher molecular weight, while the strong electron donating character of MWCNT ligand stabilizes the agostic catalytic intermediate<sup>[11, 12]</sup>, inhibiting  $\beta$ -hydride elimination and subsequent chain walking which leads to lower branching frequencies and higher melting points in resulting polymers.

Steric hindrance heterogeneity, caused by MWCNT surface, varies ethylene entrance-ability to the coordination site and hence increases molecular weight distribution. This active site variation (for ethylene insertion) derived from diffusion inhibition variances, produces polymers with different chain lengths and hence increases polydispersities. Although the very bulky structure of MWCNT ligand restricts ligand motion and rotation at the coordination site and decreases active site heterogeneity from this point of view, the controlling factor is the steric hindrance diversity generated by the MWCNT surface in this case.

The effect of temperature on the polymerization results is a consequential feature in Table 2. The catalytic activity of the  $\alpha$ -diiminonickel catalysts depends on both the inherent activity (accelerated by temperature) and catalyst thermal stability. According to the Brookhart deactivation theory, C–H bond activation of the ortho alkyl substituents, which is accelerated at higher temperatures because of the aryl ring motion and rotation, reduces the active centers<sup>[36]</sup>. From this point of view, the electron-donating MWCNT ligand may decrease the favorability of C–H activation by perturbing the close approach of the metal center to ligand axial moieties<sup>[11, 12]</sup>. But the geometry of MWCNT ligand is itself too bulky to be perturbed to limit the close approach of the metal center. Thus, unlike the activity increase trend versus temperature that was found for bis(4-amino-2,3,5,6-tetramethylphenylimino)acenaphthene nickel(II) dibromide immobilized on MWCNT by sequential technique in our previous study, NC1 and NC2 catalysts show activity fading versus temperature<sup>[24]</sup>.

As a common feature in homogenous and heterogeneous  $\alpha$ -diiminonickel polymerization trials reported in the literature<sup>[13, 19, 24]</sup>, NC1 and NC2 exhibit lower polymer molecular weights with higher polydispersities at

higher polymerization temperatures. Decrease in resulting polymer molecular weights can be referred to rotation and motion of the ligand at the axial catalyst coordination site at elevated temperatures which increases chain transfer rates against ethylene insertion rates. Broadening of the molecular weight distribution versus temperature rising has been observed in polymerization trials of the homogenous  $\alpha$ -diiminonickel complexes with electron-donating functionality at *para*-aryl position and heterogeneous  $\alpha$ -diimine-based catalysts<sup>[11, 13, 24]</sup>. This observation may be affiliated with several factors such as: the diversification of active sites versus temperature originated from ligand rotation and motion at elevated temperatures, electron-rich characteristic of the ligand or support, support surface effects, catalyst pulling-out and the deactivation rate attenuation resulted from the MWCNT ligand protective effect. Increasing polymerization temperature promotes chain walking in  $\alpha$ -diimine-based catalysts and results in polymers with higher branching frequencies and lower melting points.

Table 2 shows higher catalytic activity for NC1 catalyst while the polymers obtained from NC2 catalyst have higher molecular weights, higher polydispersities, higher melting points, and lower branching frequencies. In spite of the higher thermal stability of NC2 compared to NC1 reported in TGA analysis (Fig. 3) and its higher Ni content (Table 2), contrary to what was seen for  $\alpha$ -diimine-based catalysts prepared by sequential technique<sup>[24]</sup>, NC2 shows lower catalytic activity. This observation may be affiliated to smaller scales for ethylene insertions at the catalytic site existing in NC2 structure.

Remarkable hindrance resulted from sidewall introduction of bulky MWCNT in NC2 catalyst, especially the form (a) in Scheme 2, causes retarding in chain transfer rates versus insertion rates which automatically increases resulting NC2 polymer molecular weights. Active site diversity in NC2 catalyst can be considered as the reason of the molecular weight distribution broadening in NC2 polymers. This active site variety is derived from MWCNT ligand sidewall surface effects, active site-MWCNT surface imminence (specifically in the form (a) in Scheme 2), and the presence of the two different structures confirmed by TEM study (Fig. 4d).

Investigating of the obtained polymer melting points and branching frequencies reveals that chain walking rates has been retarded in NC2 polymerization runs. A more electron-donating ligand may better stabilize the transition state for monomer insertion than for chain walking, which should result in higher  $k_{\text{ins}}/k_{\text{walking}}$  ratio and afford more linear polymer<sup>[12]</sup>. It seems that, in this context, the rather electron-donating MWCNT sidewall attached to *para*-aryl position of the tetramethylphenyl moiety in NC2  $\alpha$ -diimine-based structure (Scheme 2) acts as more electron-donating ligand than MWCNT end linked to imine bond in the NC1 structure (Scheme 1) and retard chain walking rates efficiently. This character has presumably made the catalyst retain its activity and maintains resultant polymer topology at elevated temperatures. In this regard, the catalytic activity and resulting polymer melting points of NC2 catalyst remain around 110 g PE·mmol<sup>-1</sup>Ni·h<sup>-1</sup> and 123 °C in all polymerization of all used temperatures respectively.

For more in-depth investigation and comparing the polymerization results of NC1 and NC2 catalysts to the catalysts prepared by the sequential method in our previous research with the same polymerization conditions<sup>[24]</sup>, comparative bar charts in Fig. 5 can be referred. C1 and C3 catalysts were prepared by the electrostatic immobilization of 4-bis(2,6-diisopropylphenylimino) acenaphthene nickel(II) on the MWCNT-COOH and MWCNT-OH *via* MAO linker and C2, C4 and C5 were synthesized by covalent immobilization of bis(4-amino-2,3,5,6-tetramethylphenylimino) acenaphthene nickel(II) on MWCNT-COOH, MWCNT-OH and MWCNT-COCl<sub>2</sub> *via* MAO linker (C2 and C4) or amide linkage (C5) respectively<sup>[24]</sup>.

As seen in Fig. 5(a),  $\alpha$ -diimine-based catalysts prepared by *in situ* technique (NC1 and NC2) produce polyethylenes with higher molecular weights than the catalysts synthesized through sequential technique (C1–C5). Applying MWCNT as the main ligand in  $\alpha$ -diimine-based catalytic systems with the help of *in situ* technique imposes more ligand sterical hindrance on catalyst coordination site and, as a result, attenuates chain transfer rates. Decreasing molecular weight versus temperature is not as sharp as what was observed in sequentially prepared catalysts insofar as the molecular weight of NC2 polymer at 60 °C reaches to 310000 g·mol<sup>-1</sup> which is close to the highest value reported at 30 °C for sequentially prepared catalysts<sup>[24]</sup>.

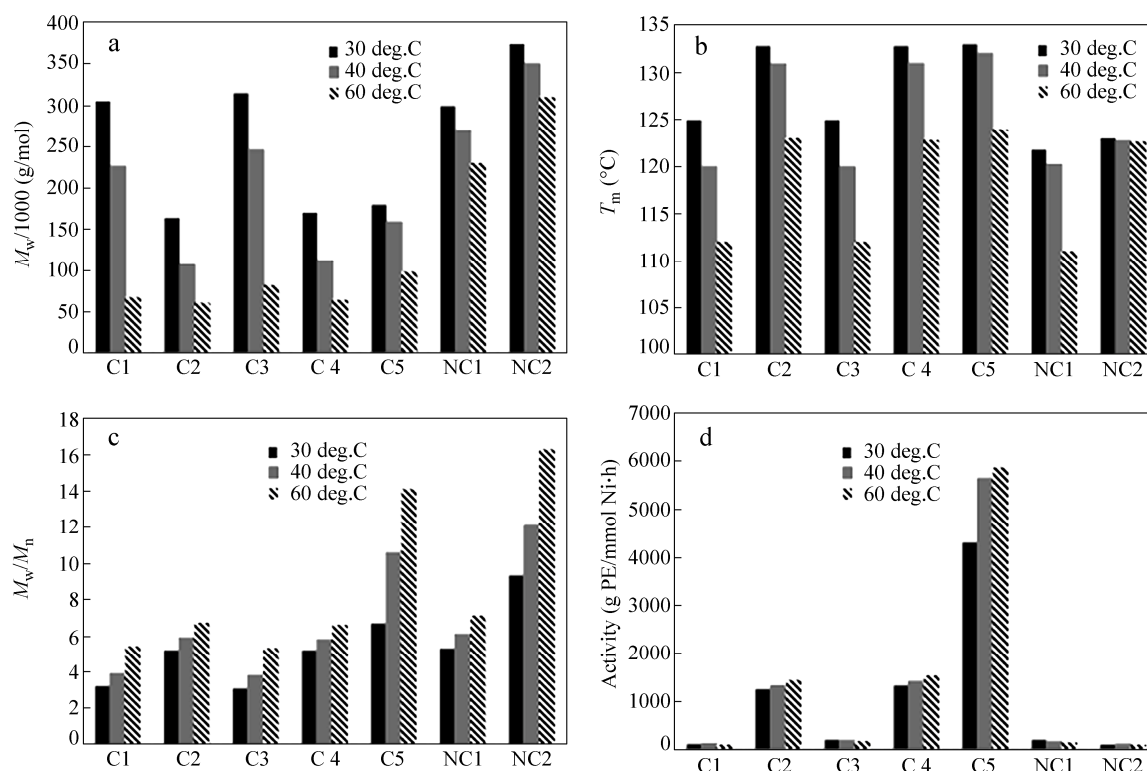


**Fig. 5** Comparison of the polymerization results of NC1 and NC2 catalysts to the catalysts C1, C2, C3, C4 and C5, prepared by the sequential method in our previous research with the same polymerization conditions<sup>[17]</sup> in different polymerization temperatures: (a) molecular weights, (b) melting temperatures, (c) molecular weight distributions, and (d) catalytic activities

As seen in Fig. 5(b), similar to sequentially prepared catalyst polymerization results, the melting points of NC1 and NC2 polymers decrease versus temperature. Reference to Fig. 5(a), the lower molecular weight polymers have a more branched microstructure as previously reported. The considerable feature in Fig. 5(b) is the rather lower values of melting temperatures of NC1 and NC2 polymers compared to C1–C5 polymers. Although it was expected that the bulky and rather electron-rich MWCNT main ligand would retard chain walking rates more efficiently, what has been observed is different. It seems that in *in situ* catalyst preparation method the MWCNT ligand is placed much closer to coordination site so that the access of the too bulky MWCNT ligand structure to the metal center is increased which in turn attenuates the stable state of the agostic intermediate complexes and consequently boosts chain walking rates. So chain walking rates is not as retarded as chain transfer rates in *in situ* prepared catalyst polymerization and hence high molecular weight polymers show rather higher branching frequencies. NC2 polymers also show a precipitous decrease in melting point (more branched structure) at 60 °C. We may deduce that presumably accelerated MWCNT-NH<sub>2</sub> ligand arm motion, rotation and debonding around 60 °C, is the main reason for chain walking increase observed at this temperature.

According to Fig. 5(c), the polydispersities of NC1 polymer are relatively higher than C1, C2, C3, and C4 polymer molecular weight distribution values. This testifies that the active site variety in NC1 is increased as an outcome of surface effects caused by coordination site-ligand surface imminence derived from *in situ* applying of MWCNT ends as the main ligand. The differences in NC1 possible structures, as show in the 3 forms in Scheme 1, can also promote active site diversification compared to the sequentially-prepared catalysts: C1, C2, C3, and C4. The exception is C5 which, despite of its sequential preparation technique, produces polymer with broader molecular weight distribution than NC1. This can be related to short and strong amide linkage between the diimine complex and the MWCNT surface in C5 that resonates sterical hindrance variance caused by

MWCNT surface *via* active site-MWCNT surface imminence and preserve active sites from degradation in temperature rising. NC2 polymers show the highest polydispersities among values represented in Fig. 5(c). This confirms that the *in situ* sidewall introduction of MWCNT ligand in NC2 synthesis causes more sterical hindrance diversity derived from MWCNT sidewall surface effects and hence more heterogeneous active sites. The other factors can be the existence of the two different NC2 forms observed in TEM study (Fig. 4d) and its remarkable thermal stability reported in TGA analysis (Fig. 3) that preserves active sites at elevated temperatures.

As seen in Fig. 5(d), the catalytic activities of NC1 and NC2 catalysts are in the range of activities reported for electrostatic immobilized catalysts C1 and C3. Although NC1 and NC2 have been synthesized by *in situ* technique *via* covalent interactions, they show very lower catalytic activity than covalently immobilized catalysts C2, C4, and C5 prepared by sequential technique. This observation reveals a considerable finding that strong covalent bonding, by itself, is not the sufficient condition for preparing high activity  $\alpha$ -diiminonickel/MWCNT catalytic system. This necessitates that preparation technique should be considered as the other remarkable factor in evaluating catalytic activity in this matter. NC2 catalyst with its very high thermal stability and strong covalent interaction, even higher and stronger than C5 thermal stability and interaction, shows about two percent of C5 catalytic activity because of very high ligand sterical hindrances imposed by its preparation technique.

Reduction in NC1 and NC2 catalytic activities can also be associated with insufficient catalyst-cocatalyst interaction as reported by Caruthers<sup>[37]</sup>. The catalyst-cocatalyst interaction is merely structural in nature than electronic. Hence, although MAO has been widely used as an alkylation agent, its long polymeric structure might not be able to interact sufficiently with the catalysts bearing too bulky ligands such as NC1 and NC2 and results in the generation of the lower number of active cationic sites and consequently lower activities.

To characterize the morphology of the polymers obtained from the polymerization of the  $\alpha$ -diiminonickel/MWCNT catalysts prepared by *in situ* technique at 60 °C, TEM observations have been carried out and the results are demonstrated in Fig. 6.

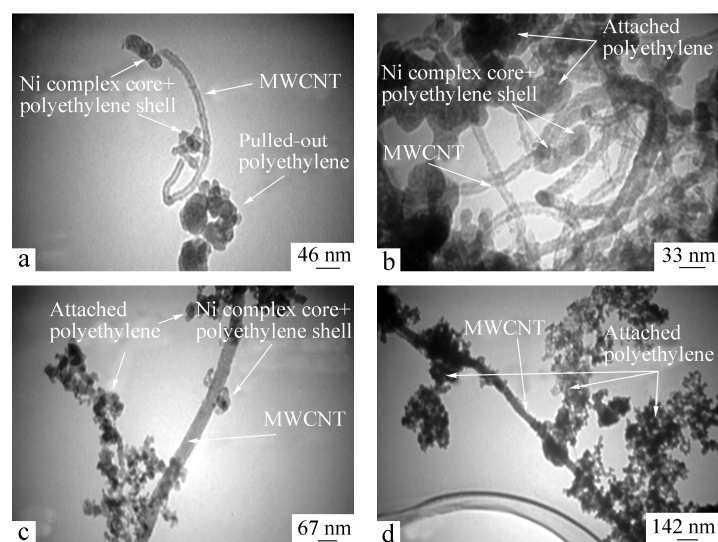


**Fig. 6** TEM images of polymers obtained from the polymerization of (a, b) NC1 and (c, d) NC2 catalysts in different magnification scales at 60 °C. The main morphology is semi covered MWCNTs with pulled-out polyethylene for (a, b) and botryoidally attached polyethylene for (c, d).

TEM images in Figs. 6(a) and 6(b) represent polyethylene coated on MWCNTs, mostly at the carbon nanotube ends, with the thickness of 20–70 nm and the pulled-out polymers as observed in our previous work<sup>[24]</sup>, for Van der Waals immobilized catalysts. Pulled-out polyethylene and high amount of the unpunched MWCNTs

versus punched ones covered by polymer at the ends, indicates MWCNT-NH<sub>2</sub> ligand arm debonding during NC1 polymerization caused by catalyst weak thermal stability and hydraulic pressure of growing polymer chain. Figures 6(c) and 6(d) show the attached polyethylene with botryoidal morphology as observed in our previous work<sup>[24]</sup>, for covalently attached catalysts. Polymer TEM observations in Figs. 6(c) and 6(d) confirm that the prevailing structure of NC2 catalyst is the form (a) as illustrated in Scheme 2. In NC2 catalyst, the active sites located on MWCNT sidewall face different diffusional constraints caused by sidewall surface effects and site-MWCNT surface imminence. These geometrical constrains are so determinant that polymer chain can be stopped from growth at the early steps of its propagation as seen in Fig. 6(c).

## CONCLUSIONS

By applying amine functionalized MWCNT as the main ligand, through novel *in situ* catalyst preparation technique, two novel nickel  $\alpha$ -diimine-based catalysts were synthesized and characterized. The sidewall introduction of MWCNT ligand into  $\alpha$ -diiminonickel catalyst system provided more supportive effect on preserving the imine bonds and chelated NiBr<sub>2</sub> compared to MWCNT-end-introduced configuration and resulted in the more thermal stability. The tetramethylphenyl moiety of the aryl-amine groups grafted on the sidewall of MWCNT-OH boosted the nucleophilic efficiency of the nitrogen non-bonding electrons and facilitated catalyst Ni supporting efficiency. TEM study of the prepared catalysts showed the presence of punching phenomena as a result of applying *in situ* synthesis method in both catalysts.

Polymerization trials using these catalysts exhibited low catalytic activities. The steric effects between the MWCNT and the catalyst coordination site, which were resonated by *in situ* preparation method and electron donating atmosphere of MWCNT ligand, decreased catalytic activity, increased insertion reaction rates in comparison with chain transfer reaction rates and depressed chain walking rates. Sidewall introduction of MWCNT as a ligand in the catalytic system imposed more sterical hindrance and as a result showed lower activity, higher molecular weights, higher polydispersities, higher melting points, and lower branching frequencies of the resultant polymers. Despite very high thermal stability of the MWCNT-sidewall-introduced configuration compared to MWCNT-end-introduced configuration and unlike what was seen for  $\alpha$ -diimine-based catalysts prepared by sequential technique, this catalytic system showed lower catalytic activity due to its smaller coordination scale for ethylene insertions. This implies that preparation technique should be considered as the other remarkable factor in evaluating catalytic activity. Polymerization of the *in situ* prepared catalyst exhibited that chain walking rates were not as retarded as chain transfer rates. In these catalytic systems, the MWCNT ligand is located much closer to coordination site so that the access of the too bulky MWCNT ligand structure to the metal center is increased which in turn attenuates the stable state of the agostic intermediate complexes and consequently boosts chain walking rates. TEM observations revealed high amount of the unpunched MWCNTs versus punched ones covered by polymer at the ends or sidewalls and presence of the stopped-growth polymer chains due to geometrical constrains or ligand debonding for both catalytic systems.

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