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Preparation of NiO Nanocatalyst Supported on MWCNTs and its Application in

Reduction of Nitrobenzene to Aniline in Liquid Phase

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Abstract

In this research NiO nanoparticles supported on multi-walled carbon nanotubes (MWCNTs) and activated carbon (AC) were prepared and applied as nanocatalyst in hydrogenation of nitrobenzene (NB) to aniline (AN). The nanocatalysts were prepared via homogenous deposition precipitation (HDP) from nickel nitrate hexahydrate using urea as reducing agent and polyvinyl alcohol (PVA) and polyvinyl pyrolidione (PVP) as dispersant agents in aqueous media. The nanocatalysts were characterized by FT-IR, SEM, XRD, TEM, TPR and BET. The results show that the yield of reduction reaction of nitrobenzene (NB) to aniline (AN) in $140\,^\circ C$ and hydrogen

pressure of 12 bars was 99.5% with 100% selectivity of aniline. Also the NiO/MWCNTs have more catalytic activity than NiO/AC in nitrobenzene hydrogenation.

Keywords

Hydrogenation, Carbon Nano Tubes (CNTs), Nickel, Nanocatalyst

1. Introduction

Aniline is an important substance for chemical industrial such as rubber process, dyes and pigments, pesticides, herbicides and production of Methylene Diphenyl Isocyanate (MDI). There are several methods for the synthesis of aniline using a variety of starting materials which nitrobenzene is the classical and the most frequently used feedstock. In the small scale, aniline can be produced by the chemical reduction of nitrobenzene with use of iron in the presence of HCl (Bechamp reaction) [1, 2].The major problem of iron-acid reduction is generation of large amounts of Fe-FeO sludge. Aniline is mostly produced via hydrogenation of nitrobenzene (about 85%) and electrochemical synthesizing method [3-5]. Hydrogenation of nitrobenzene was studied over Pd-B/SiO$_2$ amorphous catalyst [6], Pd/C [7], Pt/CNT [8] and1% Pd supported on hydrotalcite MgO and γ-Al$_2$O$_3$ at 225-300 °C [9]. Some of other researches on hydrogenation of nitrobenzene in liquid phase [10-20] are summarized in Table 1.

Carbon nanotubes (CNTs) which was synthesized by Ijima in 1991 [21,22] have been used as a novel catalyst support in both heterogeneous and electrocatalyst [23-25] as well as they are efficiently used as a support material of fuel cell catalysts like Pt and Pt-based alloys [26-35] which are essentially insoluble in most solvents. The small dimensions, good mechanical strength, high external surface area and the remarkable physical properties of these structures make them as a very unique material with a whole range of promising applications [36, 37]. Different CNTs supported catalysts such as Ru, Pt, Rh and Pd have shown good activity and selectivity in a variety of chemical reactions, which was generally attributed to the improved metal-support interaction and mass transfer [38-41].

In this research a simple method is reported to preparation of high loaded NiO nanoparticles on MWCNTs and activated carbon by reaction between acidic Ni precursor and urea as mild reducing agent. PVA and PVP were used as dispersant agent to prevent agglomeration. Finally, the resultant was calcinated and converted to NiO/MWCNTs and NiO/AC and used in nitrobenzene hydrogenation under mild and different conditions with high conversion and selectivity.

2. Experimental

2.1. Chemicals and equipment

All the reagents were obtained from commercial available purity. Multi-walled carbon nanotubes with purity more than 95% were purchased from Research Institute of Petroleum Industry (R.I.P.I) with surface area of 270 m^2/g, 10μm length and 10-30 nm diameter. The Transition Electron Microscopy (TEM) images were taken on a Philips ZEISS EM900 at an accelerating voltage of 100 KeV and SEMs were conducted with SEM-XL30- Philips instrument. Thermogravimetric analysis (TGA) were taken on a METTLER TOLEDO TGA SDTA 851e instrument at 30-800 °C with 10 °C/min. BET surface area of NiO/AC and supported NiO/MWCNTs were determined by QUANTASORB at 300 °C in the presence of N_2 and He. X-ray powder diffraction (XRD) analysis was conducted by Philips instrument with graphite monochromatic Cu Kα radiation (λ = 1.5418 Å) to verify the formation of products. The UV-Vis spectrum of reaction was recorded on a SINCO UV-Vis 1100 diode array in the range of 190-1100 nm. Temperature Programmed Reduction (TPR) of NiO/MWCNTs were recorded at the temperature range of 20-800 °C, at a heating rate of 10 °C/min using a Micrometrics 2900

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system. Gas chromatography (GC) was carried out by SRI 8022C instrument with FID detector and MXT-624 capillary column (0.53 mm in diameter and 30 m long).

2-3. Preparation of NiO nanoparticles in the presence of PVP and PVA as dispersant agents

For preparation of NiO nanoparticles, 2.9 g of nickel nitrate hexahydrate (10 mmol) and 0.5 g of PVA in 200 ml deionized water were heated to 90 °C and stirred until transparent solution was obtained, and then an aqueous solution (10 ml) containing 0.92 g (15 mmol) of urea was added to solution in 1 hour at the same temperature. The mixture was refluxed overnight, and then the resultant light-green precipitant was filtered and washed with deionized water for 5-10 times to remove any remained unreacted starting materials. The solid was dried at 150 °C for 2 h, heated to 250 °C for 2 hours; finally it was increased to 400 °C and remained at this temperature for 3 hours to obtain black green solid nickel oxide. Particle size of NiO was calculated by Scherrer Equation. Different nanoparticles with 5.3-9.6 were obtained in the presence of different amounts of PVA nd PVP as dispersant agent and results are illustrated in Table 2. It is found from these results that the amount and kind of dispersant agent can control the particle size of NiO nanoparticles.

2-2. Preparation of 58% NiO/MWCNT

The multi-walled carbon nanotubes was synthesized previously through a special chemical vapor deposition (CVD) method by decomposing of methane on Co-Mo/MgO catalyst at a temperature of 1000 °C [42,43]. The high purity MWCNTs were obtained through (I) acid treatment to dissolve remained metal catalysts impurities (II) oxidation to remove amorphous carbons. Initially, MWCNTs immersed in 18% HCl solution and stirred at 55 °C for 12 h, then

treated in 6M nitric acid (HNO_3) at 50 °C for 6 h and finally filtered and washed filtrate with distilled deionized water until pH reached neutral. The residue dried at 100 °C for 3 h, and then resultant MWCNTs were oxidized at 400 °C for 20 min to burn out all amorphous carbons.

Preparation of NiO on MWCNTs and AC carried out similar to NiO preparation in the presence of 0.5 g of PVA. To dispersing of supports in solution, the reaction sonicated for 10 min. Thermal decomposition and calcinations process was performed with purging of reactor under N_2 for 10 min to prevent support damaging The catalysts at loading of 20, 40 and 60% of NiO were prepared on supports.

2-3. Hydrogenation of Nitrobenzene

At first, 0.1 g of NiO/MWCNTs nanocatalyst was introduced to the 100 ml stainless steel autoclave reactor and reduced by 100 ml.min^{-1} of H_2 at 400 °C for 1 h. After gradual cooling to the room temperature, 1 ml of nitrobenzene and 10 ml of toluene as solvent were added to the reactor under N_2 Atmosphere. In order to remove any oxygen, the mixture purged with N_2 for 10 min. The reaction carried out in different pressure, temperature, time and loading of active catalyst. Yield of reaction was determined using gas chromatography (GC) with flame ionization detector (FID).

3. Resaults and discussion

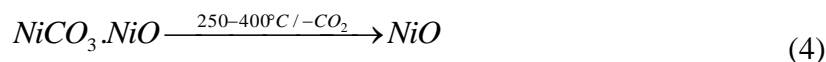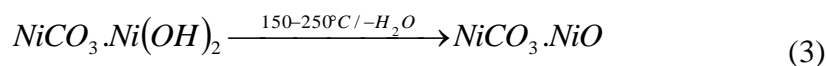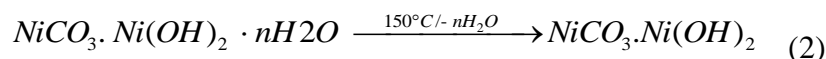*3-1. Synthesis of NiO nanocatalyst*

The catalysts were prepared via homogenous deposition precipitation (HDP) method by using of urea as precipitant agent. Urea hydrolyzed slowly at above 90 $°C$ in aqueous media as shown in below.

$$CO(NH_2)_2 + 3H_2O \xrightarrow{T \geq 90°C} CO_2 + 2NH_4OH \tag{1}$$

As slow formation of hydroxyl regarding to slow rate of urea decomposition in solution, Ni^{+2} ions are free to be dispersing by PVA and PVP then react slowly with hydroxyl ions to produce the bright green precipitates. The probably formula of the solid precipitate was identified as Nickel Carbonate Hydroxide Hydrate $NiCO_3 \cdot Ni(OH)_2 \cdot 4H_2O$ and it completely converted into NiO nanoparticles below 450 °C [44].

As illustrated in Figure 1, the end of the reaction was determined by Uv-Vis spectrum of solution that the peak of nickel ions was disappeared in 466.7 nm.

The bright green solid filtered and washed with water to remove any remained dispersant agent and impurities, then dried at oven for 4 h at 100 °C. Then NiO nanoparticles were prepared and Calinated simultaneously according to the following procedure. The solid precipitates were introduced to the reactor, heated to 150°C and hold for 1.5 hours. Then the mixture gradually heated to 250 °C over 30 minutes and hold for 2 hours and at last, temperature rose to 400 °C and remained for 3 hours. Preparation of NiO/MWCNTs has a similar protocol but at first, the reactor must be purged with N_2 for 10 minutes to prevent damaging of MWCNTs structure. Decomposition steps can be summarized as follows:

$$NiCO_3 . Ni(OH)_2 \cdot nH2O \xrightarrow{150°C/-nH_2O} NiCO_3 . Ni(OH)_2 \tag{2}$$

$$NiCO_3 . Ni(OH)_2 \xrightarrow{150-250°C/-H_2O} NiCO_3 . NiO \tag{3}$$

$$NiCO_3 . NiO \xrightarrow{250-400°C/-CO_2} NiO \tag{4}$$

3-2. FT-IR Analysis of the synthesized substances

The FT-IR spectra of the light green powder (dried at 105 °C for 2 h) are shown in Figure 2a.The broad absorption band at 3300-3650 cm^{-1} was attributed to the O–H bond stretching vibrations, and the peak near 1625 was assigned to H–O–H bending vibrations of H_2O in structure. This provided the evidence for the water of hydration in the structure, and it also implied the presence of hydroxyl in the structure. The wide absorption band around 1384 cm^{-1} indicated the existence of CO_3^{2-} ions, and the three bands appearing around 1290, 995, and 640 cm^{-1} were correlated with the stretching and bending vibrations of the intercalated C–O species in the substance. This confirmed the presence of CO_3^{2-} ions. The broad absorption bands at 2216 cm^{-1} indicated the existence of CO_2 which derived from the powder samples prepared in air [44]. Therefore, the synthesized precursor could be the nickel salt of hydrated basic carbonates as $Ni_2CO_3(OH)_{2.nH2O}$.

The FT-IR spectra of gray powder nickel oxide resulted from decomposition of nickel carbonate is shown in Figure 2(b). Remove the peaks at 3445 and 1620 cm^{-1} show that the elimination of H_2O and hydroxyl and the absence of three peaks at 1114, 833, and 620 cm^{-1} confirm the elimination of CO_3^{2-} ions in the structure of product. The strong absorption band around 410 cm^{-1} was assigned to Ni–O stretching vibration which indicates the NiO was produced. The FT-IR spectrum of NiO/MWCNTs and NiO/AC are shown in Figure 2c and 2d respectively.

3-3. X-ray powder diffraction (XRD)

The XRD pattern of pristine MWCNTs and synthesized NiO/MWCNTs in the range of 10-80° are shown in Figure 3a and 3b respectively. In Figure 4a the peak at 2θ = 26.08 can be assigned

to plane of MWCNTs. In Figure 4b three characteristic peaks of nickel compound (2θ=36.89, 43.04, 62.50) marked by Miller indices ((1,1,1), (2,0,0), (2,2,0) are in agreement with NiO structure based on comparison with standard spectrum (JCPDS, NO.4-835) [44].

The mean nickel particle sizes of various samples were calculated using Debye–Scherrer equation:

$$D(nm) = \frac{0.9\lambda}{\beta Cos\theta} \qquad (5)$$

Where D is the average particle size in nm, λ the wavelength of the X-ray (1.54056Å for CuK), θ the angle at the maximum of the peak, and $\beta_{2\theta}$ is the width of the peak at half-height. The peak of Ni (111) is used to calculation of NiO particle size in Scherrer equation for overlapping of (200) NiO peak with peak of pure MWCNTs. The NiO particle size calculated by Scherrer equation is shown in Table 2.

As shown in the Table 2, the NiO Nanoparticles were in the range of 5.3-9.6 nm in different media with use of two dispersant agents which is confirmed by TEM image. The best result was obtained when 0.5 g of PVA was used as dispersant agent. In the absence of dispersant agents (PVA and PVP) the particle size of NiO is 10.2 nm. This material reduces particles size thorough prevention of agglomeration. The excessive wideness of diffraction peaks is due to the very fine nature of metal particles.

3-4. BET Analysis of NiO Nanocatalyst and NiO/MWCNTs

The specific surface area of the NiO nanoproducts calculated by the BET method was 274.0,

182.7 and 503.67 m^2/g for NiO and NiO/MWCNTs and NiO/AC respectively. The smaller size of particles caused much higher external surface area of NiO nanoparticles. The larger external surface area of a catalyst and mesoporous structure of support, enhanced chance of hydrogen absorption, better mass transfer and lead to higher activity of NiO/MWCNTs in comparison with NiO/AC that has higher surface area (503.67 m^2/g). In overall, mesoporous structure of support (MWCNTs) and nanostructure of active metal (Ni), improved yield of reaction and caused the reaction carried out in mild conditions including temperature, pressure and time. Result of accelerated surface area and porosimetry (ASAP) of NiO/MWCNTs and NiO/AC are shown in Table 3.

3-5. Temperature-programmed reduction (TPR)

A TPR profile of NiO/MWCNTs is shown in Figure 4. The TPR was carried out in a quarts reactor, 100 mg of catalyst sample was filled into the reactor, heated from 25 to 830 °C at the rate of 10 °C.min^{-1}, and swept with 95% Ar-5% H$_2$ (by volume) stream at flow rate of 40 ml.min^{-1}. The hydrogen concentration was detected by the TCD detector. Reduction of NiO to Ni active species was happened at low temperature in 281.7 °C that can be attributed to high activity of NiO nanostructure while NiO generally reduce at 450-550 °C. TPR analysis results of synthesized NiO/MWCNTs nanocatalyst are shown in Table 4. From this results, the reduction carried out in two steps: first reduction is happened at 281.7 °C that attributed to NiO (81.53%) species and second reduction happened at 546 °C which can be assigned to remained unconverted nickel carbonate hydroxide (18.41 %) in thermal decomposition process. TPR results revealed that mostly of catalyst (81.5 %) is reduced at less than 300 °C.

3-6. TEM Analysis of synthesized Nano NiO/MWCNTs

TEM of the purified Multi-walled carbon nanotubes as a supported catalyst and NiO/MWCNTs are shown in Figure 5a and 5b respectively. Well dispersion and deposition of nanoparticles with weak agglomeration on MWCNTs surface is clear obvious in Figure 5b. The mean particle size of 5.3-9.6 nm in different conditions was calculated through XRD in agreement with TEM image. According to the TEM image, it could be concluded that this preparation method of the precursor obtained by homogeneous precipitation with use of dispersant agent had successfully overcome the problem of agglomeration to obtain the NiO nanoparticles below 10 nm.

3-7. TGA and DTG analysis of NiO/MWCNTs

Thermal decomposition behavior of synthesized nanocatalyst was determined using thermal gravimetric analyzer (TGA) in an inert atmosphere of nitrogen. In a typical experiment, 1.5 mg of the synthesized catalyst (NiO/MWCNTs) was placed in sample pan and the temperature was increased from 30-800 °C at a rate of 10 °C/min and weight changes were recorded as function of temperature. Figure 6 shows TGA and DTG curves. The results show that a little loss of weight happened at 50-100 °C due to lose of moisture in sample, and after that, there was no obvious weight lose with further increase in temperature until 600 °C. Most of weight lose happened upper 600 °C to 800 °C due to lose of amorphous carbon in nanotubes structure and at 800 °C about 83.16 % of MWCNTs structure remained. It is found that the catalyst is resistant to thermal decomposition until 600 °C and capable to use at ambient to 600 °C in both liquid and gas phase reactions.

3-7. Hydrogenation of nitrobenzene to aniline

Reduction of nitrobenzene to aniline proceeds according to scheme1.

3-7-1. Effect of pressure on the reaction

Reactions were carried out in 8, 10 and 12 bars of hydrogen pressure. According to the Table 5 with 60% NiO Loading, it is obvious that 4 bars $(8 \longrightarrow 12)$ increasing in the hydrogen pressure, provide increasing of 58% in the yield of the reaction. At first two bars from 8-10, 66% of reactions have increased higher than 50% while at last two bars 10-12, 33% of reactions have such increase in reaction yield. It is revealed that first increasing in pressure(8 to 10) has more effect on yield of reaction. Increasing in the yield is reasonable concerning to this fact that increasing of pressure lead to increase in solubility of hydrogen in toluene which provided larger molecular interaction of hydrogen with surface of the catalyst.

3-7-2. Effect of temperature on yield of reaction

Reactions were carried out in 100, 120 and 140 °C. Influence of temperature on yield and rate of reaction is listed in Table 5. As temperature is increased, the nitrobenzene conversion is found to increase in all the pressures. It is obvious that the increasing of temperature has more effects in shorter times (t = 60 min). Since the reaction was carried out in liquid phase and relatively low temperature, the Coke formation is not important but water generated during the reaction may be poised the catalyst meanwhile the hydrophobicity nature of MWCNTs aids to decrease these phenomena. As toluene has higher vapor pressure due to its phase diagram [46], the reaction in all conditions was carried out in liquid phase.

3-7-2. Activity of catalyst supported on MWCNTs and AC on the reaction

The liquid phase hydrogenation of nitrobenzene to aniline was carried out over NiO/MWCNTs and NiO/AC at 60% loading. Activity of NiO catalyst supported on MWCNTs with 182.7 m^2/g surface area and activated carbon with 503.7 m^2/g surface area at 60% loading are presented in

Table 6 and depicted in Figure 7. In spite of the NiO/AC have higher surface area than NiO/MWCNTs (more than 2.7 times), results revealed that yield of reaction with NiO supported on MWCNTs in all conditions almost three times higher than NiO supported on activated carbon under similar conditions that attributed to surface mesoporosity and better mass transfer of carbon nanotubes than activated carbon.

3-7-1. Reaction representation in mathematics

Operating conditions have widely effects on the reaction yield. Aniline yield of reaction has been represented in mathematical from through simplified estimating optimal transformations for multiple regressions [47] as:

$$Y_{Aniline}\% = AX^3 + BX^2 + CX + D$$
$$A = -0.000142$$
$$B = 0.0229817$$
$$C = -0.004947$$
$$D = 10$$
$$X = -175.287 + 0.9497 \; NiO \; Loading\% + 9.2647P + 0.4631T + 0.1813t$$

(7)

This equation can estimate aniline yield of reaction with good precision ($R^2 = 0.848$) and accuracy (AAD% = 17.32). The effects of parameters in equation 7 at average conditions (120 °C, 10 bar, 180 min) for NiO loading at 20, 40, and 60% are shown in Figure. 8. Results revealed that increasing of pressure, NiO loading and temperature lead to higher yield and conversion over shorter time. However, regarding to this figure and equation 7, it is clear that pressure has most important effect. NiO loading percent, temperature and time almost have the same effects.

Conclusion

In this research, we have demonstrated that the NiO/MWCNTs nanocatalyst is very efficient and active catalyst for reduction of nitrobenzene in liquid phase with a 99.5 % yield and selectivity toward aniline. The activity of catalyst depends on type of support so that the yield of reaction with NiO supported on MWCNTs in best conditions were three times more active than the catalyst supported on activated carbon. The MWCNTs due their mesopore structures perform better mass transfer than activated carbon with micropore structure. In comparison to other methods reported in the literature, our novel methodology in nanocatalyst preparation has mild conditions, high isolated yields and high conversion without any by products, clean reactions, easy workup and reusability of the used catalyst. All these features make this method as attractive and useful alternative in catalytic preparation of aniline.

Acknowledgments

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Table 1. Reduction of nitrobenzene to aniline using various catalysts in liquid phase

ttCatalyst	conditions	%Conv	% AN	Time	Ref
Pd	PMHS[a]/KF/THF, RT	90-100	50	0.5-12h	10
Pt	10 bar, RT-50 $^\circ C$	100	99	2h	11
Rh	RhCl(PPh3)$_3$, Toluene,TES[b]	90	86	2h	12
Re	ReIO$_2$(PPh$_3$)$_2$, PhMe$_2$SiH, Toluene, Reflux	80	100	4h	13
Pd or Pt	Pt/glass fiber 7×10^5 Pa, 50 $^\circ C$	100	100	50min	14
Pt/c	40 bar,35 $^\circ C$	73	56	30min	15
Sn	Sn/HCl, C$_2$H$_5$OH, Reflux	80	60	4 h	16
Mo	Mo(CO)$_6$, EtOH, Reflux	-	54	24 h	17
Ni/Al$_2$O$_3$	CO$_2$: 400bar, H$_2$:20-60 bar,EtOH, Reflux	13-73	62-99	20 min	18
Ni/TiO$_2$	20bar, 140 $^\circ C$	99	100	4h	19
Fe	Fe(acac)$_3$/N$_2$H$_4$/MeOH, Microwave, 150 $^\circ C$	80	99	10 min	20
NiO/MCNTs	Toluene, 12bar, 140 $^\circ C$	100	100	4h	This article

a: Polymethylhydrosiloxane

b: triethylsilane(Et$_3$SiH)

Table 2. Particle size of NiO in different media with use of 0.05 M of Ni $(NO_3)_2.6H_2O$

Run	Conc. of disp.agent as g/200 ml	PVA	PVP	Particle Size(nm)
1	-	-	-	10.2
2	0.5	+	-	5.3
3	1.0	+	-	5.6
4	2.0	+	-	6.3
5	0.5	-	+	8.6
6	1.0	-	+	9.1
7	2.0	-	+	9.6

Table 3. Accelerated surface area and porosimetry (ASAP) of synthesized catalysts

Catalyst	BET m^2/g	Pore Volum (cm^3/g)	A.P.D($A°$)	A.A.P.D ($A°$)	D.A.P.D($A°$)
NiO/MWCNTs	182.71	0.56	121.59	117.9	106.54
NiO/AC	503.67	0.35	37.79	71.8	66.24

A.P.D= Average Pore Diameter(4V/A by BET)

AAPD= Adsorption Average Pore Diameter(4V/A)

DAPD= Desorption Average Pore Diameter(4V/A)

Table 4. Results of TPR analysis

Peak	Area	Height	Temp(°C)	Time (sec)	Total Qty,Unit	Total Qty/g,Unit
1	6.930E+05	1923.4	281.7	1406	0.30 mmole H_2	5.58 mmole H_2/g
2	1.571E+05	1032.1	546.0	2756	0.12 mmole H_2	2.32 mmole H_2/g

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Table 5. Nitrobenzene hydrogenation with different loadings of NiO/MWCNTs

Entry	NiO/MWCNTs Loading %	Pressure(bar)	T($^\circ$C)	time(min)	Yield(Aniline) %
1	20	10	120	60	8.8
2	20	10	120	180	21.3
3	20	10	120	300	37.4
4	20	12	140	60	28.6
5	20	12	140	180	45.7
6	20	12	140	300	63.8
7	40	10	120	60	19.6
8	40	10	120	180	66.4
9	40	10	120	300	84.9
10	40	12	140	60	53.2
11	40	12	140	180	74.6
12	40	12	140	300	96.5
13	60	8	100	60	20.2
14	60	8	100	180	28.2
15	60	8	100	300	34.3
16	60	8	120	60	28.8
17	60	8	120	180	37.6
18	60	8	120	300	43.1
19	60	8	140	60	42.5
20	60	8	140	180	53.2
21	60	8	140	300	65.7
22	60	10	100	60	25.1
23	60	10	100	180	68.2
24	60	10	100	300	92.5
25	60	10	120	60	29.1
26	60	10	120	180	78.3
27	60	10	120	300	97.2
28	60	10	140	60	36.8
29	60	10	140	180	88.2
30	60	10	140	300	99.0
31	60	12	100	60	38.1
32	60	12	100	180	71.2
33	60	12	100	300	93.5
34	60	12	120	60	45.5
35	60	12	120	180	88.1
36	60	12	120	300	98.1

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37	60	12	140	60	63.4
38	60	12	140	180	98.5
39	60	12	140	300	99.5

Table 6. Nitrobenzene reduction using NiO suppoted MWCNTs and AC

Entry	T($^{\circ}$C)	t(min)	Yield(AN) % [a]	Yield(AN) % [b]
1	100	60	25.1	9.3
2	100	180	68.2	16.5
3	100	300	92.5	26.3
4	120	60	29.1	14.2
5	120	180	78.3	21.3
6	120	300	97.2	34.1
7	140	60	36.8	19.5
8	140	180	88.2	27.8
9	140	300	99.0	38.5

Conditions: 1gr NB, 10 ml toluene, 0.1 gr cat.60%, 12 bar H_2

a: NiO/ MWCNTs   b: NiO/AC   AN: Aniline
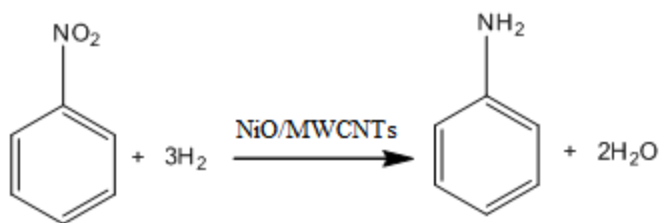
Scheme 1: In this reaction, three mole of hydrogen and one mole of nitrobenzene are consumed to produce one mole of aniline and two mole of water [45]. Reaction carried out in toluene as solvent in the presence of nanocatalyst with different loading of NiO on MWCNTs that overall results are shown in Table 5.
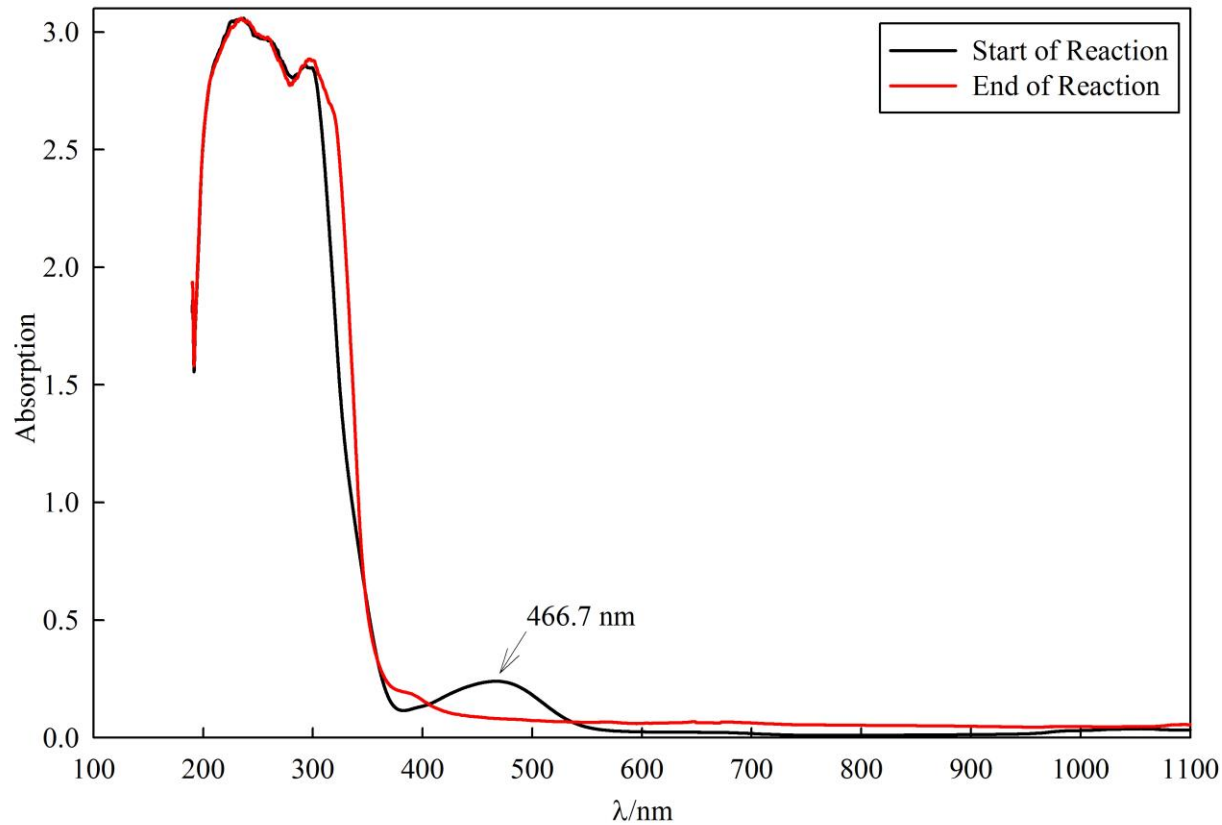
Figure 1. Uv-Vis spectrum of reaction.
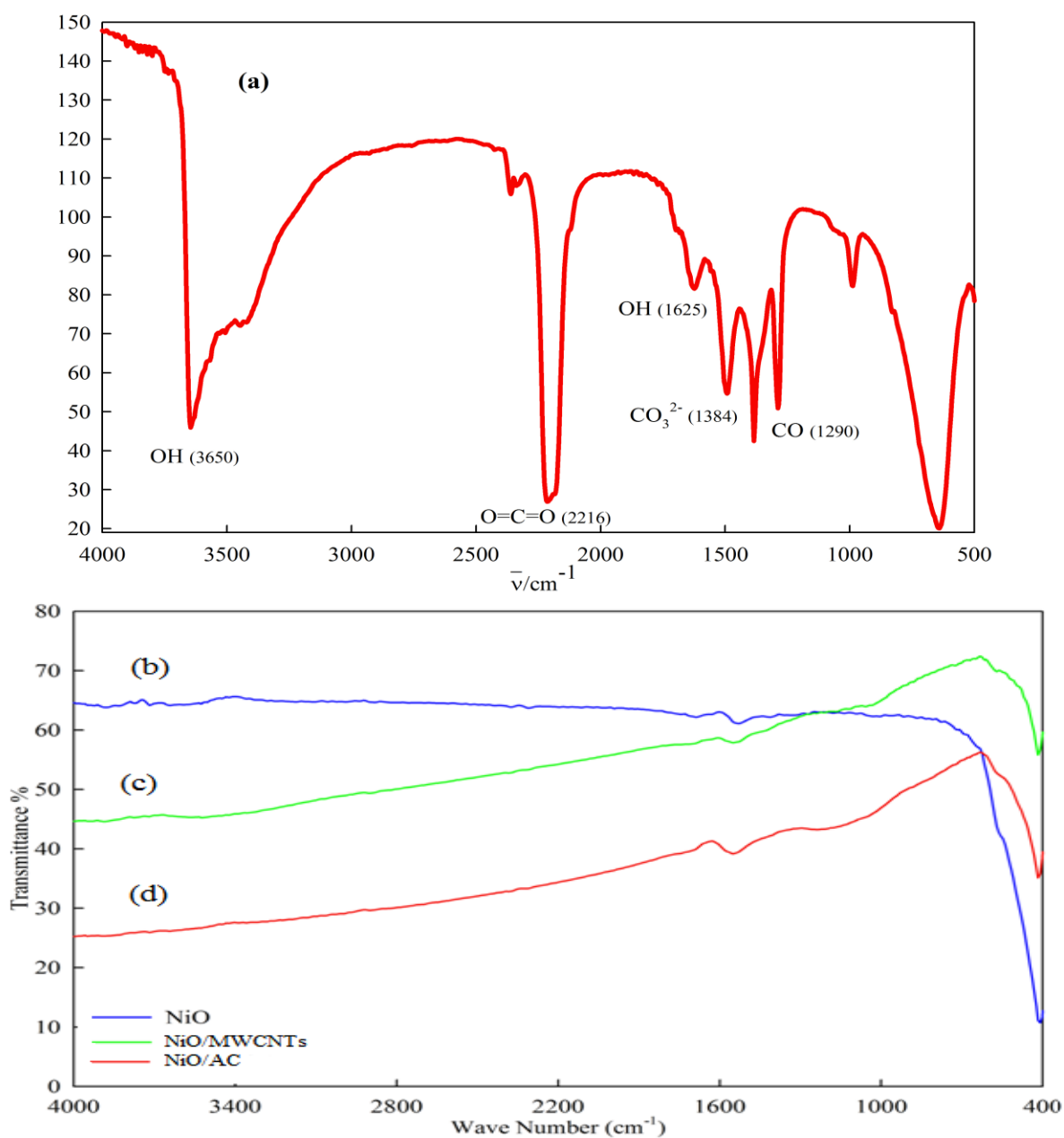
Figure 2. FT-IR Spectrum of (a) $NiCO_3$. Ni $(OH)_2.4H_2O$ (b) NiO (c) NiO/MWCNTs (d) NiO/AC.
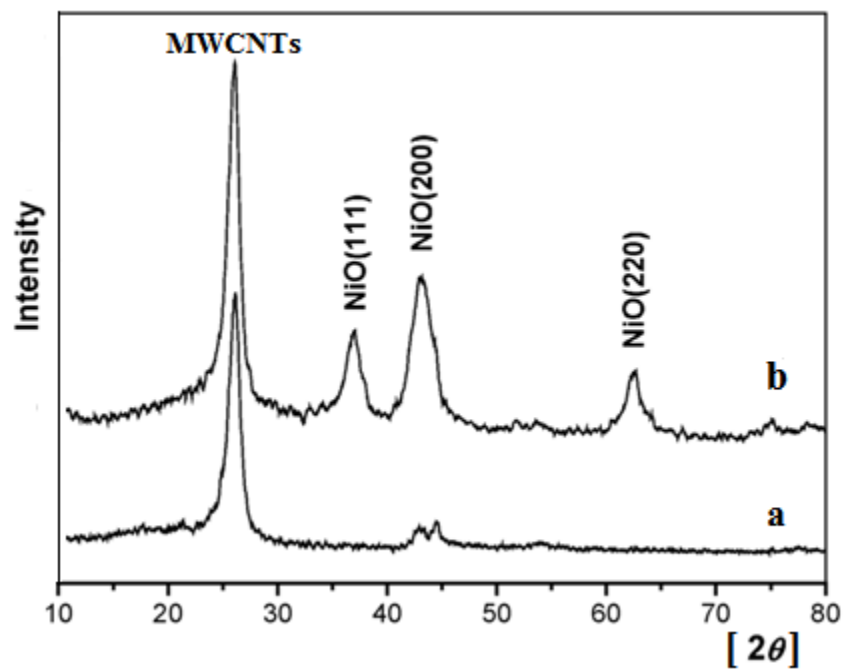
Figure 3. XRD-Spectrum of (a) MWCNTs (b) NiO/MWCNTs.
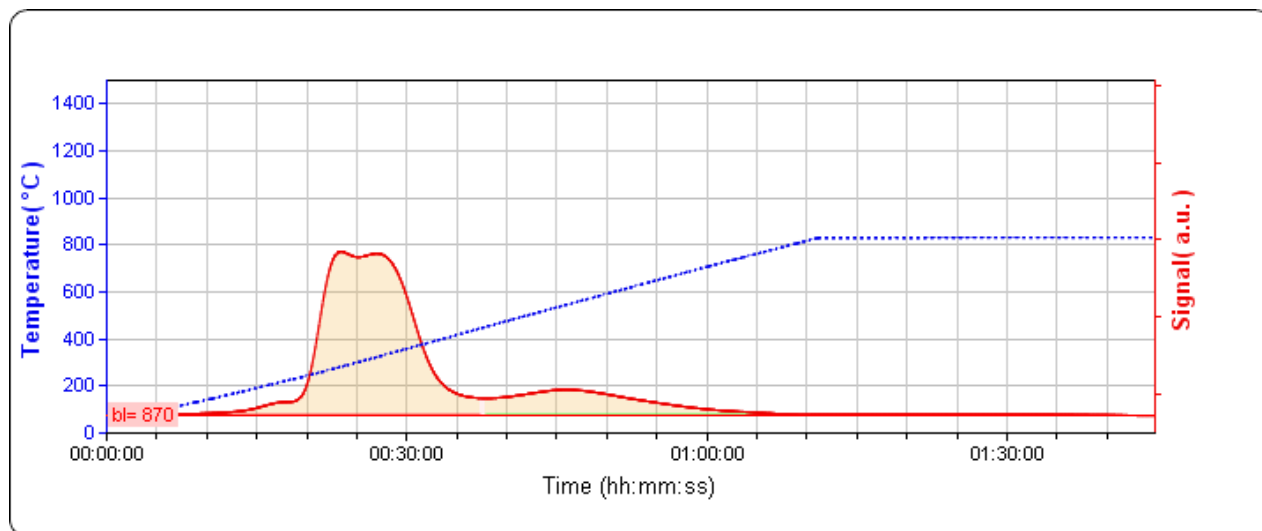
Figure 4. TPR analysis of NiO/MWCNTs.
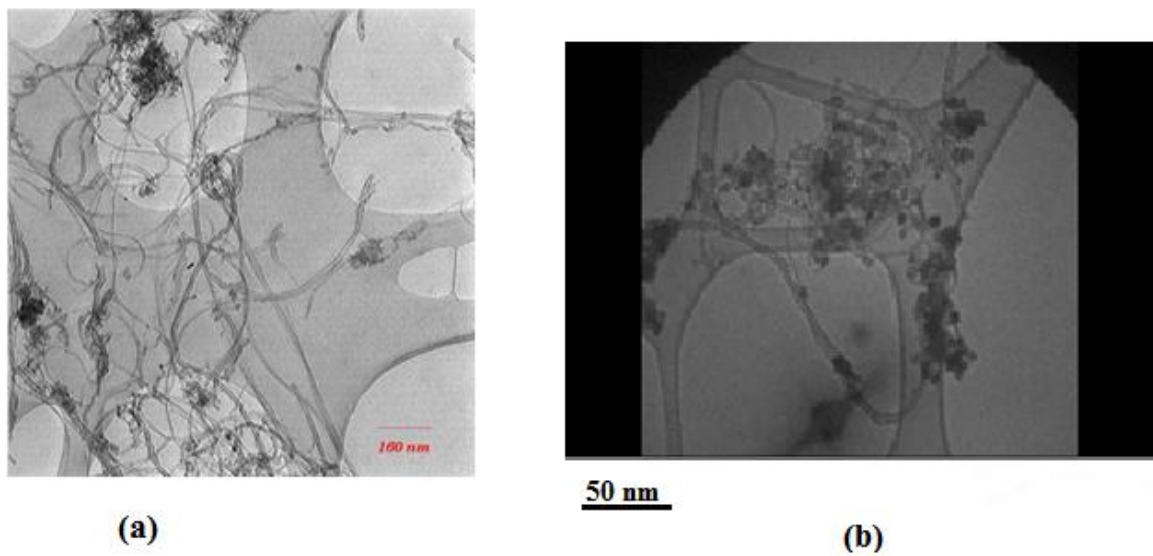
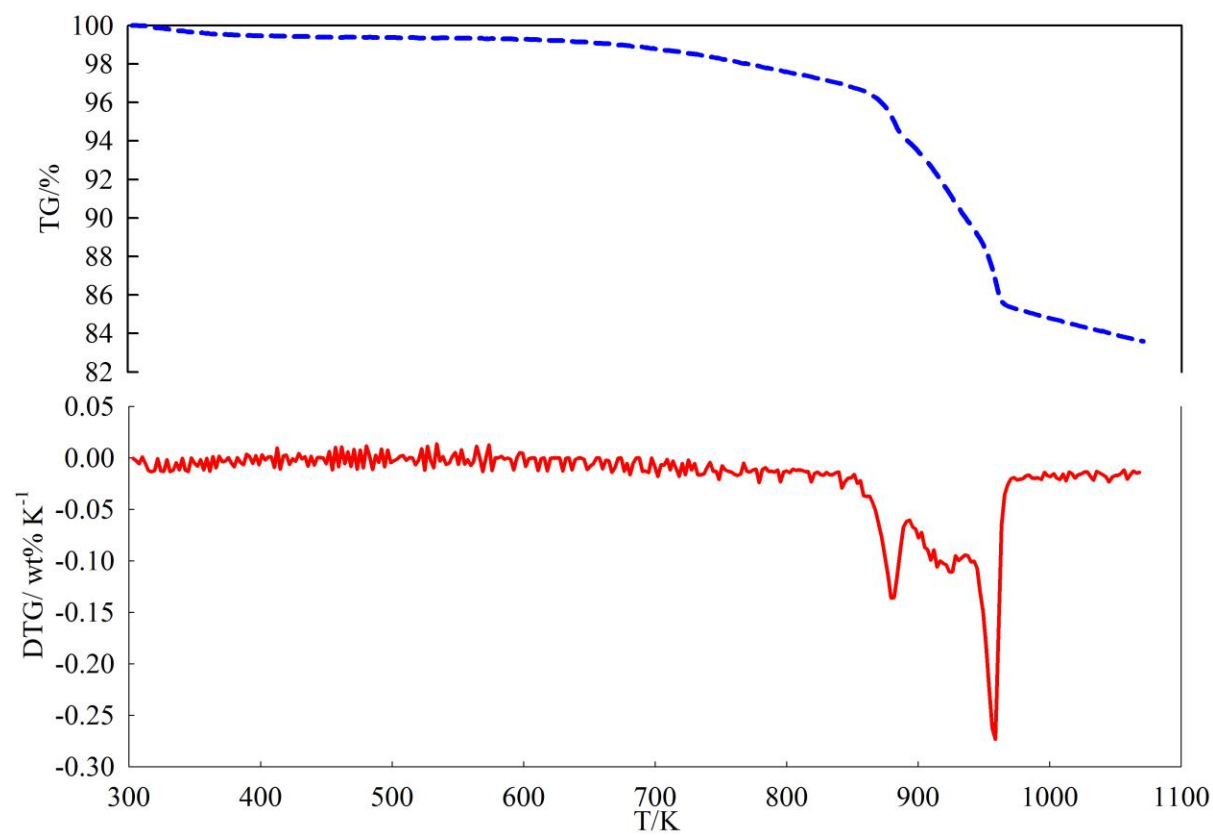Figure 5. TEM of (a) MWCNTs (b) NiO/MWCNTs.
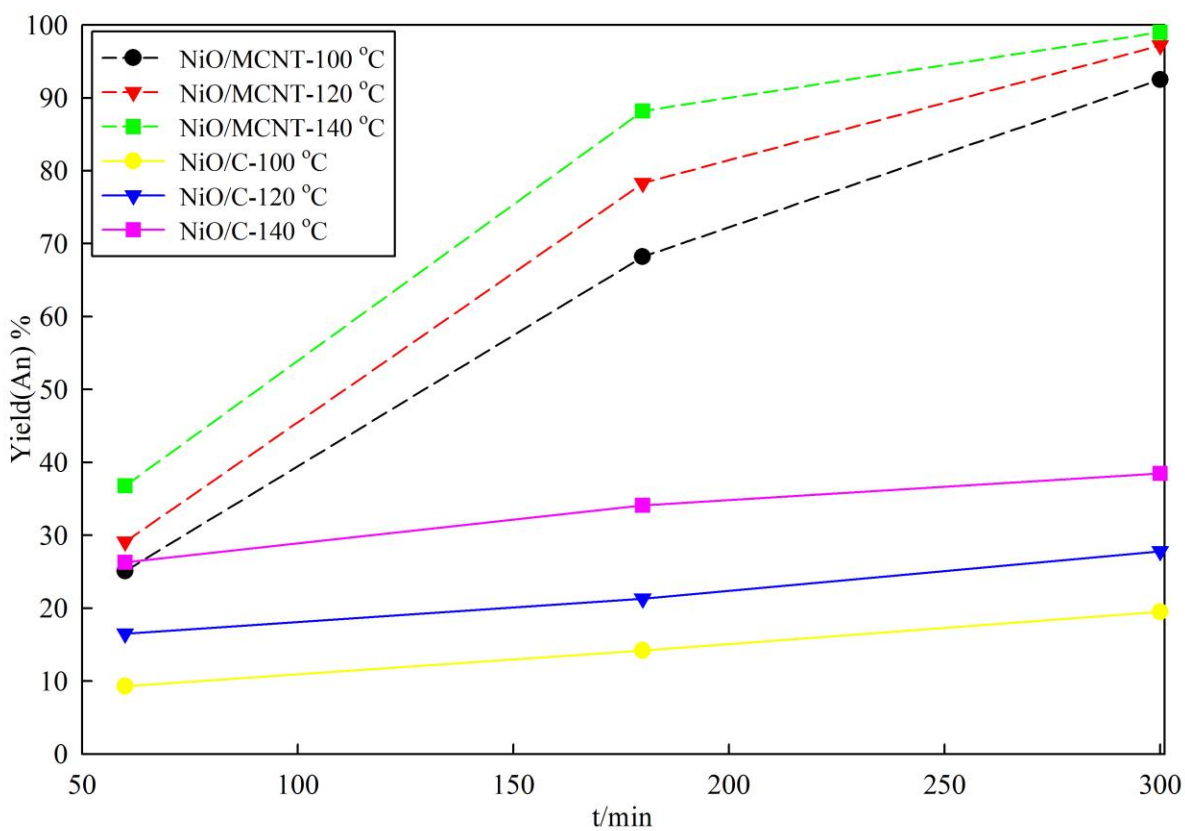
Figure 6. TGA and DTG of NiO/MWCNTs.

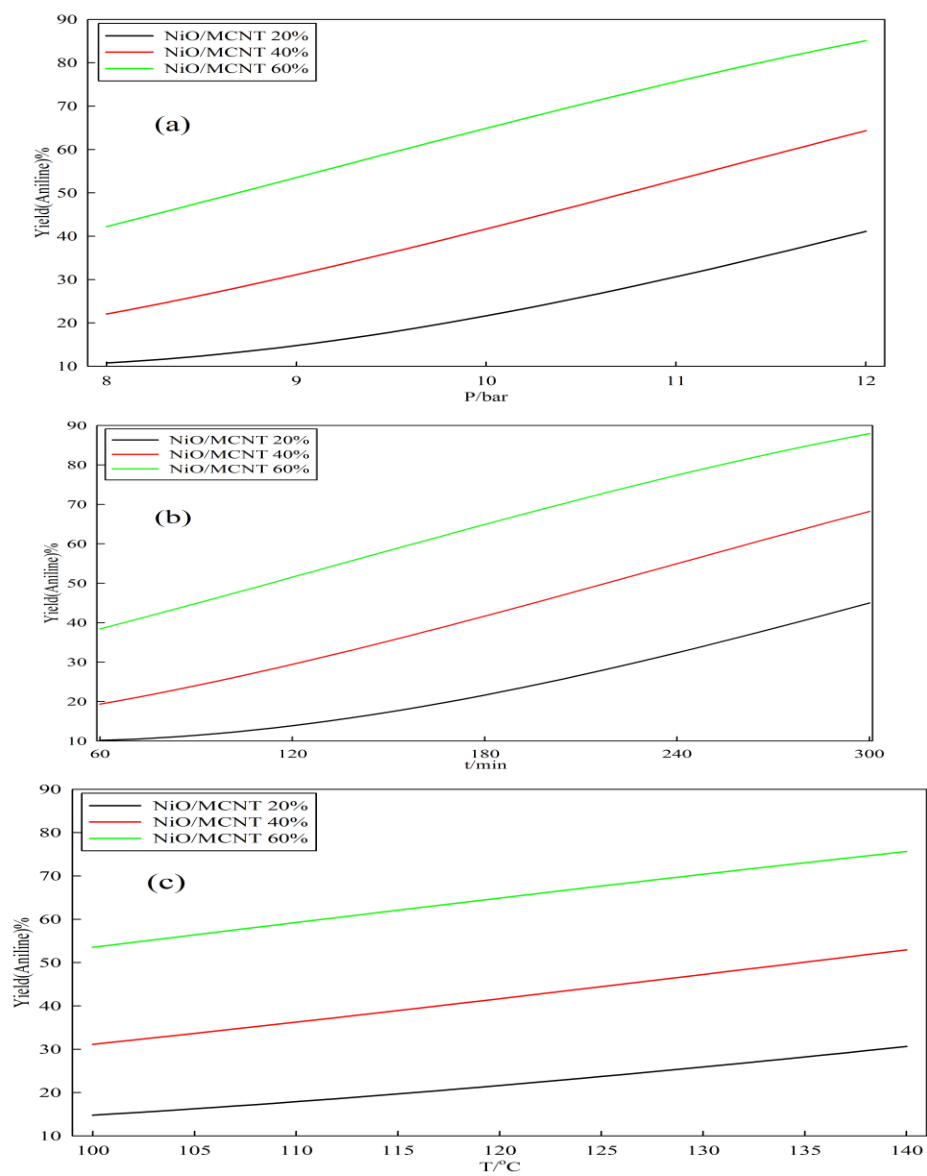Figure 7. Effect of supports (MWCNTs & AC) on yield of reaction.

Figure 8. Dependency of reaction using different loading of NiO/MCNTs to: (a) Pressure (b) time (c) Temperature

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