

Ammonia Decomposition over Ni Supported on Multi-Wall Carbon Nanotubes: Effect of Surface Functional Groups

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ABSTRACT

Graphene, single-wall carbon nanotubes (SWCNTs) and three types of commercial MWCNTs with different functional surface groups (MWCNTs-COOH, MWCNTs-OH, MWCNTs-NH₂) and non-functionalized multiwall carbon nanotubes (MWCNTs) were used as supports to prepare nickel based catalysts. All catalysts were prepared by the incipient wetness method. Catalysts were characterized by using powder X-ray diffraction (XRD), Temperature programmed reduction (TPR), and X-ray Photoelectron Spectrometry (XPS). Ammonia decomposition (AD) reaction was carried out in a fixed bed quartz microreactor at atmospheric pressure and reaction temperatures from 400-500 °C. The gas hourly space velocity (GHSV) was varied between 6000 to 24000 h⁻¹.

Activity tests revealed that both Ni/Graphene and Ni/SWCNTs are essentially inactive with NH₃ conversions not exceeding 1.0% at 500°C and GHSV of 6000 h⁻¹. Ni supported on MWCNTs with different surface functional groups showed that the Ni/MWCNTs-COOH catalyst was most active with ammonia conversion as high as 25.4 % at 500 °C and 6000 h⁻¹. Comparable conversions were obtained with Ni/MWCNTs-OH (23.5%) and Ni/MWCNTs-NH₂ (24.6%). Non-functionalized, Ni/MWCNTs exhibited a much lower conversion of ammonia (13.2%) compared to Ni supported on functionalized MWCNTs. It was demonstrated that the presence of the attached surface functional groups on MWCNTs is essential for preparation of active Ni catalyst. The NiO crystallites sizes obtained from XRD diffraction of calcined catalysts were similar in size for both functionalized and non-functionalized supports. XPS measurements did not show significant difference in binding energies (Ni2p_{3/2} peaks of NiO), however, in agreement with XRD results, it showed that NiO was the major surface phase for all catalysts. TPR measurements indicated the presence of two reduction peaks in the temperature intervals from 100–500 °C and 500–700 °C. The first peak could be assigned to the reduction of the NiO particles to Ni. The TPR measurements indicated that the functionalized MWCNTs are much easier to reduce which could partially explain their higher activity in AD reaction.

Keywords: Ni catalyst, ammonia decomposition, hydrogen, multi walls carbon nanotubes, graphene.

1 INTRODUCTION

Multi-Wall Carbon Nanotubes (MWCNTs) have specific pore structure and good thermal stability, which makes them suitable to design nano-structured catalysts [1, 2]. However, the carbon hydrophobic properties restricted their extensive applications as catalysts support. Attachment of different functional groups to the surface of carbon nanotubes during the process of their production can help to overcome this disadvantage. Functional groups on the MWCNTs surface play an important role in anchoring metal ions [3, 4]. Transition metals such as Fe, Co, Ni supported on MWCNTs with surface carboxyl groups have demonstrated an excellent catalytic activity for ammonia decomposition [5-7].

The aim of this work is to study the ammonia decomposition reaction using Ni supported on MWCNTs and to elucidate the role of surface functional groups on the MWCNTs support and its effect on the activity of such catalysts.

2 EXPERIMENTAL

To realize the objectives of this study, several types of commercial MWCNTs, graphene, and single-wall carbon nanotubes (SWCNTs) were selected to be used as support of Ni based catalyst. The MWCNTs (Product code: TNMC1), graphene (Product code: TNRGO) and SWCNTs (Product code: TNST) were purchased from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences, China. Three types of MWCNTs with -OH, -COOH and -NH₂ surface groups were selected for this study and they are designated as MWCNTs-OH, MWCNTs-COOH and MWCNTs-NH₂, respectively. In addition a MWCNTs without attached surface group was also used and it is denoted as MWCNTs. The textural properties of the commercial carbon nanotubes used in this study are listed in Table 1.

2.1 Catalyst Preparation

All catalyst samples were prepared by incipient wetness impregnation method. An amount of support which was previously dried at 90 °C for 1 hour is introduced into an aqueous solution of nickel nitrate such that a metal loading of 5% Ni is obtained. After impregnation, the catalyst samples were dried in

an oven overnight at 90 °C. Dried catalysts were further calcined in nitrogen atmosphere at 450 °C for 5 hours. Calcination was performed by placing the catalysts into a tubular oven and the temperature was ramped to 450 °C at a rate of 2 °C/min. The supported nickel based catalysts were denoted as Ni/MWCNTs-OH, Ni/MWCNTs-COOH, Ni/MWCNTs-NH₂, Ni/MWCNTs, Ni/SWCNTs and Ni/Graphene respectively.

2.2 Catalyst Characterization

Powder X-ray diffraction analysis was conducted on an EQUINOX 1000 (Inel, France) with Cu (K α) radiation ($\lambda=0.154056$ nm) at a setting of 30 kV and 30 mA.

Temperature programmed reduction (TPR) experiments were performed using the Quantachrome Pulsar automated chemisorption analyzer. Prior to TPR measurements, 50 mg sample was loaded into reactor and pretreated with helium gas flow at 120 °C for 60 min to remove the adsorbed water. After cooling down to 50 °C, the flow of He was switching to flow of 5% H₂ in N₂ with a flow rate of 30 ml/min. The temperature of reactor was increasing linearly from 100 to 700 °C at a ramping rate of 10 °C.min⁻¹. A thermal conductivity detector (TCD) analyzed the effluent stream.

The X-ray Photoelectron Spectrometry (XPS) measurements were carried out in an ultrahigh vacuum multi-technique surface analysis system (SPECS GmbH, Germany). A standard X-ray source SPECS XR-50 (AlK α = 1486.6 eV) was used to irradiate the sample surface with 13.5 kV, 150W X-ray power and a take-off-angle for electrons at 90° relative to sample surface plane. The analysis chamber was maintained at 5 \times 10⁻⁹ bar during all measurements. As the standard practice accepted in XPS studies, the adventitious hydrocarbon C1s line (284.6 eV) corresponding to C-C bond has been used as binding energy reference for charge correction.

Support	Surface area (m ² /g)	Length (μ m)	O.D (nm)	Functional Group wt. %	Purity (%)
MWCNTs-COOH	233	50	8-15	2.56	95
MWCNTs-OH	233	50	8-15	3.70	95
MWCNTs-NH ₂	233	50	8-15	0.45	95
MWCNTs	233	50	8-15	-	95

Table 1: Textural properties of support and chemical composition of nickel based catalysts

2.3 Activity measurements

NH₃ decomposition was carried out in a fixed bed quartz microreactor (PID Eng&Tech, Spain) at atmospheric pressure using 100 mg sample of the catalyst which was previously reduced (25% H₂ in N₂) in situ at 500 °C. Pure NH₃ gas was introduced into the reactor at temperatures between 400-500 °C and NH₃ GHSV of 6000 to 24000 h⁻¹.

NH₃ conversion in a blank quartz reactor at 500 °C and NH₃ GHSV of 6000 h⁻¹ was below 0.5 %.

The analysis of the effluent from reactor was performed by using on-line gas chromatograph (GC-450, Varian, USA) equipped with a TCD and a Poropak Q column.

3 RESULTS AND DISCUSSIONS

Activity measurements for AD using Ni/Graphene and Ni/SWCNTs catalysts have shown that both catalysts exhibited very low activities. NH₃ conversions less than 1.0% was obtained at 500 °C and NH₃ GHSV of 6000 h⁻¹.

The results of testing of catalytic activity of the other catalysts supported on Ni/MWCNTs carriers with different surface functional groups are illustrated in Figure 1. The top figure in Figure 1 shows the effect of reaction temperature at GHSV = 6000 h⁻¹ on ammonia conversion. It is clear from this figure that NH₃ conversion increased with reaction temperature, while it was decreasing with increasing GHSV (bottom). However, the effect of GHSV was much smaller compared to the effect of temperature.

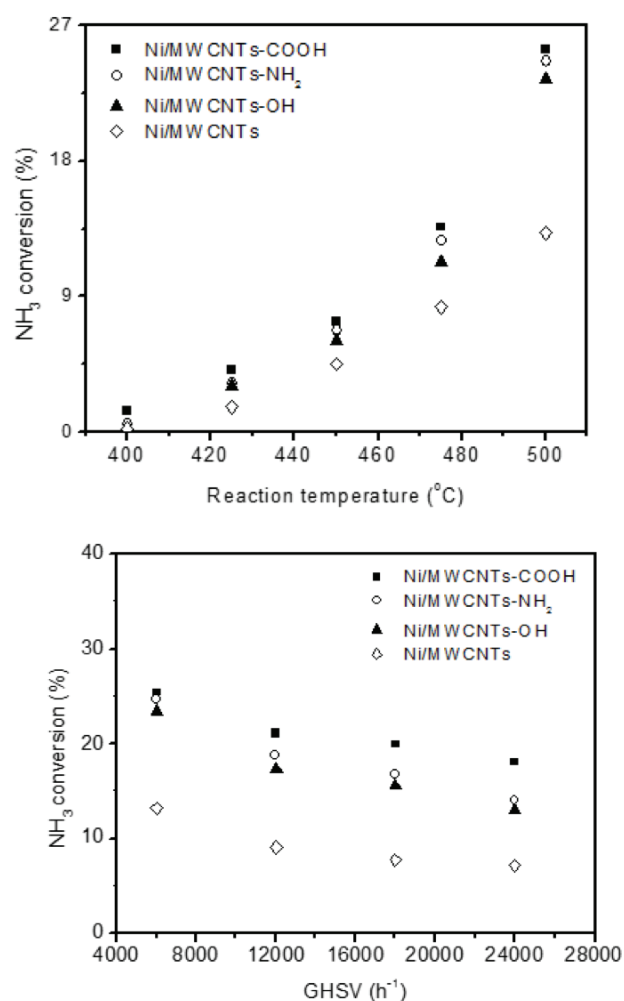


Figure 1: Effect of reaction temperature at GHSV = 6000 h⁻¹ on ammonia conversion (top) Effect of GHSV on ammonia conversion at 500 °C (bottom).

From the presented activity data (Figure 1) it is clear that the Ni/MWCNTs-COOH catalyst was the most active in ammonia decomposition reaction where ammonia conversion of 25.4 % is achieved at 500 °C and 6000 h⁻¹. Comparable conversions were obtained with the three functionalized catalysts Ni/MWCNTs-COOH (25.4%), Ni/MWCNTs-OH (23.5%) and Ni/MWCNTs-NH₂ (24.6%). On the other hand the non-functionalized, Ni/MWCNTs catalyst exhibited a much lower activity with conversion of ammonia of only 13.2% at the same conditions. Although the presence of the attached surface functional groups on MWCNTs is essential for preparation of active catalyst, it seems that the nature of the surface functional group have small effect on the activity of the obtained catalysts.

The XRD patterns of Ni/MWCNTs catalysts are presented in Figure 2. The characteristic peak of NiO was present in the diffractograms of all calcined catalysts. The NiO crystallite sizes were calculated from the widths of XRD peaks using the Debye-Scherrer equation at $2\theta = 75.9^\circ$ [8]. The NiO crystallite sizes of Ni/MWCNTs, Ni/MWCNTs-OH, Ni/MWCNTs-NH₂, Ni/MWCNTs-COOH were 9.2 nm, 10.3 nm, 8.2 nm and 8.1 nm (see Table 2), respectively. The different functional groups on CNTs have no significant influence on the supported nickel oxide particles size. In our previous works [1, 9], it was found that the metal particles sizes supported on CNTs was mostly affected by chemical interactions that occurred during the decomposition of catalyst precursor.

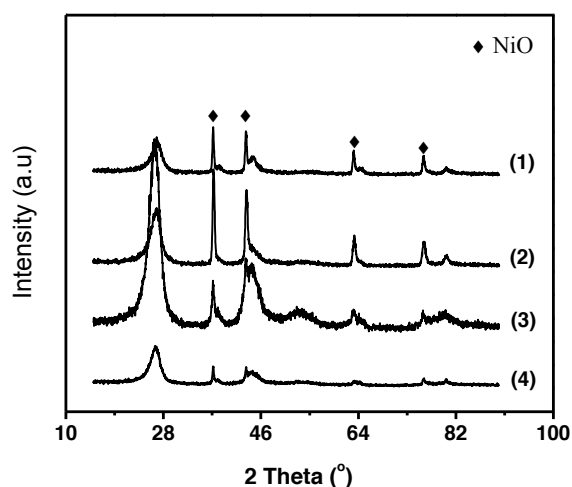


Figure 2: XRD patterns of Ni/MWCNTs catalysts: (1) Ni/MWCNTs; (2) Ni/MWCNTs-OH; (3) Ni/MWCNTs-NH₂; (4) Ni/MWCNTs-COOH

XPS technique is a valuable characterization tool based on the electron binding energy. It can also provides information about chemical composition of catalyst surface [10]. XPS Ni2p spectrum of nickel catalysts are shown in Figure 3. The observed Ni2p3/2 peaks of NiO with binding energy of Ni/MWCNTs, Ni/MWCNTs-OH, Ni/MWCNTs-NH₂ and Ni/MWCNTs-COOH were 855.1 eV, 855.1 eV, 854.8 eV and 855.6 eV, respectively. In agreement with XRD results, it was found that NiO was major surface phase in calcined Ni/MWCNTs catalysts. Ni2p3/2 binding energy

of NiO in Ni/MWCNTs-COOH was slightly higher than for other three samples which may indicate a stronger interaction between the Ni and the support for this catalyst.

XPS data were used to quantify the surface elemental compositions of Ni catalysts prepared on MWCNTs carriers with different functional groups. The surface nickel concentration (mass %) for the four catalysts, Ni/MWCNTs, Ni/MWCNTs-OH, Ni/MWCNTs-NH₂ and Ni/MWCNTs-COOH were 2.16 %, 2.28 %, 1.26 % and 2.45 %, respectively as shown in Table 2.

Catalyst	Surface elements composition (mass %)			Binding Energy at Ni2p3/2 (eV)	Crystallite size, NiO, nm by XRD
	Ni	O	C		
Ni/MWCNTs	2.16	2.74	95.10	855.1	9.2
Ni/MWCNTs-OH	2.28	5.31	92.41	855.1	10.3
Ni/MWCNTs-NH ₂	1.26	3.10	95.65	854.8	8.2
Ni/MWCNTs-COOH	2.45	5.14	92.41	855.6	8.1

Table 2: summary of XPS measurements

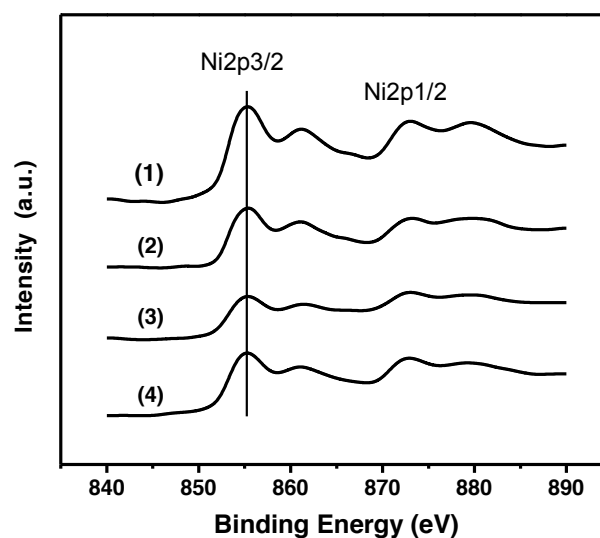


Figure 3: Ni2p XPS spectra of Ni/CNTs with different surface groups. (1) Ni/MWCNTs; (2) Ni/MWCNTs-OH; (3) Ni/MWCNTs-NH₂; (4) Ni/MWCNTs-COOH

Ni reducibility of calcined Ni/MWCNTs catalysts with different functional groups were studied by TPR as shown in Figure 4. It can be seen from this figure that two reduction peaks were obtained one at a relatively low temperature from 100–500 °C and a high temperature peak from 500–700 °C. The first peaks could be assigned to the reduction of the NiO particles to Ni. Another broad reduction peak at temperatures higher than 500 °C is also observed for the four catalysts and it is attributed to the gasification of carbon. For functionalized MWCNTs, the first TPR peak usually has a maximum below 400 °C while for the non-functionalized MWCNTs catalyst this peak has a maximum at 425°C. Thus it is clear from this TPR measurements that the

functionalized MWCNTs are much easier to reduce than the non-functionalized one which could partially explain their higher activity in AD reaction.

Studied catalysts thus can be divided into two groups according to their catalytic activity. The first group are the Ni catalysts with high catalytic activity. These are catalysts prepared by using MWCNTs with attached different functional groups. Catalysts prepared by using MWCNTs with -COOH functional group has demonstrated the highest catalytic activity. The other group are catalysts prepared by using carbon supports without attached functional groups such as graphene, SWCNTs and MWCNTs. In general the catalysts prepared using these supports exhibited very low activity. Further investigation are required to clarify the role of surface functional groups in the activity of these catalysts.

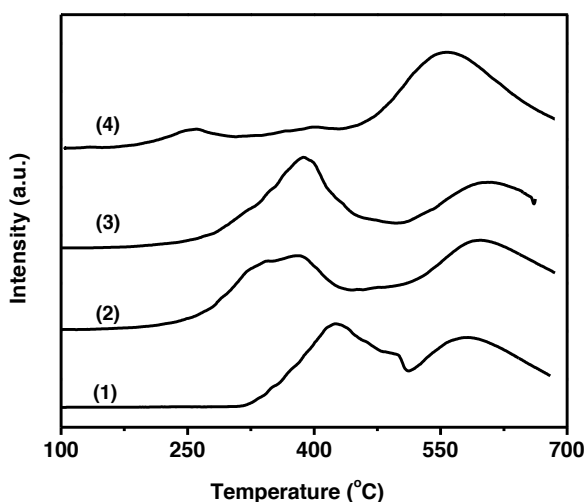


Figure 4: H₂-TPR patterns of Ni/MWCNTs: (1) Ni/MWCNTs; (2) Ni/MWCNTs-NH₂; (3) Ni/MWCNTs-OH; (4) Ni/MWCNTs-COOH

4 CONCLUSIONS

The presence of the attached surface functional groups on MWCNTs is vital precondition for preparation of active Ni supported catalyst for NH₃ decomposition.

MWCNTs with attached different surface functional groups used as nickel catalysts carrier did not affect Ni phase composition. NiO specie was the major phase in the calcined Ni/MWCNTs catalysts and the obtained nickel particles are similar in size as indicated by XRD measurements.

Catalysts activity tests in reaction of ammonia decomposition have shown that catalysts supported on carbon nanotubes with different functional groups have essentially the same activity per gram of catalyst. The TPR measurements show that the functionalized MWCNTs are much easier to reduce which could partially explain their higher activity in AD reaction compared to catalyst prepared using non-functionalized MWCNTs. Further work, however, is required to better elucidate the role of surface functional groups on the activity of such catalysts.

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6. References

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