Synthesis of Nickel/ Molybdenum Oxide Bimetallic Nanoparticles via Microwave Irradiation Technique

Faeze Tari[1], Mehrdad Manteghian[2,*] and Sudeh Tazarv[2]

[1]Synthesis of chemical, polymeric and petrochemical Department, Research Institute of Petroleum Industry, Tehran, Iran.
[2]Department of Chemical engineering, Tarbiat Modares University, Tehran, Iran.

(*) Corresponding author: manteghi@modares.ac.ir

Abstract
Nickel-molybdenum oxide bimetallic nanoparticles were synthesized in ethylene glycol using the microwave irradiation technique. According to the results, successive reduction of nickel and molybdenum ions, followed by thermal treatment of obtained nanoparticles led to formation of core-shell structured nickel-molybdenum oxide nanoparticles. According to the results, the thickness of the shell and core were 5 and 40 nm, respectively. The structure and composition of nanoparticles were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), UV-vis spectroscopy, scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).
Keywords: Core-shell nanoparticles, Nickel-Molybdenum oxide, Microwave polyol.

1. INRODUCTION

Today, nanoparticles play an important role in changing the traditional applications in industrial and experimental processes [1]. Given the structure of nanoparticles, they can be composed of a single or multiple components [2]. Bimetallic nanoparticles have significant applications in the fields of catalysis [3-5], solar cell [6, 7], environmental [8, 9], biomedical [10] and etc. These types of nanostructures can be prepared via different routes including: chemical reduction [11] reverse microemulsions [12], anion coordination [13], sonochemical reduction [14, 15], microwave irradiation [16, 17] and so on. It is generally accepted that simultaneous or successive reduction of different types of metal ions may lead to formation of alloy and core-shell nanostructures, respectively [18]. Usually stepwise reduction of one metal over the nuclei of another metal leads to formation of core-shell nanoparticles. Also, scholars believe

that incorporation of a shell on a metallic core changes the electronic structure of both elements, especially the shell component and alters its affinity and reactivity toward chemical reactions [4].

In this paper, we report on the synthesis of nickel-molybdenum oxide core-shell nanoparticles by successive reduction of relevant ions using the microwave assisted polyol method. Polyol approach is based on reduction or stabilization by alcohols such as ethylene glycol. But scholars have found that combination of microwave radiation and polyol approach can significantly improve the synthesis output for preparation of metal nanoparticles. This method was firstly applied by Komareni [19] for preparation of metal nanopowders.

Nickel and molybdenum particles together with their oxide or sulfide phases are among the components frequently used as catalyst in different processes including hydroprocessing [20], hydrogenation of dimethyl oxalate [21], oxidation of

methanol [22], methane reforming [23], dehydrogenation of hydrazine borane [3] and etc. Bimetallic nanostructures containing nickel or molybdenum such as core-shell structures of Ni-Silica [23], Fe-Ni [24], Pd-Ni [25], carbon-Ni_3S_2-MoS_2 [26], MoO_3-Fe_2O_3 [22] and etc., have been synthesized in different ways. However, synthesis of bimetallic nickel-molybdenum oxide nanoparticles under microwave irradiation is an interesting subject that has not been investigated so far. The microwave assisted polyol synthesis of nickel nanoparticles was reported by Li [27] and Xu [28]. More importantly, researchers have shown that combination of Ni and Mo in the structure of a catalyst coated in some substrates such as alumina increased the activity of resulting catalyst toward some reactions such as hydrodesulfurization of dibenzothiophene [29], thiophene HDS reaction [30] and hydrotreatment [31]. Although the Ni/Mo phase in so mentioned catalysts was a combination of mixed oxide or not specified exactly, it would be possible to examine the application of core-shell Ni/Mo oxide particles on the catalytic activity in future practices. In this paper, we applied the same method for successive reduction of nickel and molybdenum ions. According to the results, final nanoparticles have a core-shell structure and reaction completion time is quite short.

2. EXPERIMENTAL
2.1. Materials

All of the reagents were obtained from Merck (Darmstadt). Nickel Chloride Hexahydrate($NiCl_2.6H_2O$), polyvinyl pyrrolidone (PVP), ethylene glycol (EG), Hydrazinium hydroxide ($N_2H_4.H_2O$, 99%), sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH) and molybdatophosphoric acid hydrate ($H_3PMo_{12}O_{40}$). All of the reagents were of the highest commercially available purity.

2.2. Apparatus

The XRD patterns of the products were recorded with a Philips X'Pert MPD X-ray diffractometer (using Cu Kα λ=1.78897Å radiation). The transmission electron micrographs (TEM) were imaged on a Ziess W.Germany 900 EM microscope, using an 80 kV accelerating voltage. Samples for TEM were prepared by placing a drop of the sample suspension on a copper grid coated with a carbon film. The grid was then air-dried. SEM images were recorded by an AL30 Philips using a 17 kV accelerating voltage. For EDAX, the attached function was linked to a scanning electron microscopy (SEM). The samples for SEM and EDAX analysis were prepared by placing a little amount of nanoparticles sedimentary on a glass plate. The UV-Vis spectra were recorded with samples in 1 cm^3 quartz cells using a Varian Carry 100 (UV-Vis) Spectrophotometer in the spectral range of 190–1100 nm.

The microwave-assisted reaction was carried out in a Panasonic MX21WF Spectra- 900 W domestic microwave oven, with 2.45 GHz of working frequency.

2.3. Synthesis of Nickel nanoparticles

Nickel nanoparticles were synthesized according to the Xu et al. [28]. Briefly, 5 ml of 0.02M nickel chloride solution, 1 ml of 0.1M Na_2CO_3 solution, 4 ml of 0.1M PVP solution, 0.2 ml of 0.1M NaOH solution and 0.6 ml of 0.87M $N_2H_4 \cdot H_2O$ solution were added in a flask. EG was then added to keep the volume of the mixture fixed at 20 ml. The mixture solution was then put under microwave irradiation in an oven for 60 seconds. When the black colloids of nickel were observed in the solution, heating was stopped and obtained nanoparticles were transferred to an ice-bath to prevent further agglomeration.

2.4. Synthesis of Molybdenum Oxide Nanoparticles

Synthesis procedure of molybdenum oxide nanoparticles is reported in our

previous publication [32]. Briefly, a calculated amount of $H_3PMo_{12}O_{40}$ (based on the desired composition of final nanoparticles) was dissolved in EG. After addition of 2ml of $N_2H_4 \cdot H_2O$ solution, the total mixture was heated in a domestic microwave oven for 50s.

2.5. Synthesis of Bimetallic Nanoparticles

For the preparation of bimetallic nanoparticles, the above nickel nanoparticles were recovered and re-dispersed into fresh ethylene glycol ([Ni]=0.1 mM). Then, a solutions containing $H_3PMo_{12}O_{40}$ dissolved in EG ([Mo]/[Ni]=1) with 2ml of Hydrazinium hydroxide was put in the oven to start the reaction. Irradiation temperature was fixed at 195°C in the microwave oven. After about 60-70 seconds, the dark color of the solution (pertinent to nickel nanoparticles) was turned to brown. This point was considered as the end of the reaction. Final product was filtered, washed, dried and calcinated at 500°C for 1 hour.

2. RESULTS and DISCUSSIONS

Size, structure and composition of nickel and bimetallic nanoparticles were investigated by TEM, SEM, XRD and EDS analyses. Figure 1 shows the EDS spectrums of nickel nanoparticles. It should be mentioned that because of placing the sedimentary on a glass plate, the spectrums of glass components are existed in the spectrometry results.
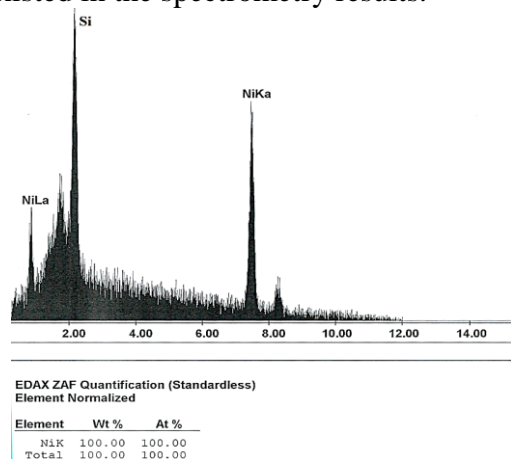

Figure 1. EDS spectrums of nickel nanoparticles.

SEM image of obtained nanoparticles is shown in Figure 2. Accordingly, the nanoparticles are spherical with the average size of about 38nm.
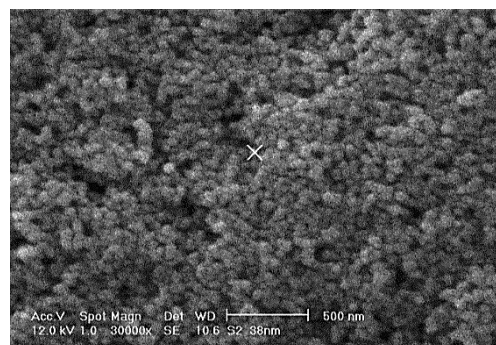
Figure 2. SEM image of nickel nanoparticles. The final diameter seems to be about 38 nm.

For more information about the shape and size of synthesized product, TEM micrographs of nanoparticles were also obtained. As shown in Figure 3, it is clear that nanoparticles have a semi-spherical flower shape with a diameter of about 10-40 nm. So we can come into conclusion that SEM and TEM results are compatible.
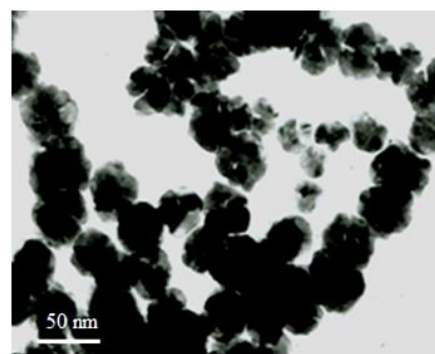

Figure 3. TEM micrograph of 1:1 nickel nanoparticles.

As noted above, synthesis procedure and analytical results of molybdenum oxide nanoparticles are reported elsewhere [32]. The XRD patterns of nickel-molybdenum oxide nanoparticles are presented in Figure 4. It is obvious that product obtained under microwave irradiation was nanocrystalline as evidenced from the XRD patterns.

Using the Debye–Sherrer equation, crystallite size was detected as about 30 nm. The XRD results also confirm that nickel nanoparticles were not formed in the bulk phase, because no characteristics peak pertaining to nickel, shown by Xu et al., [28], was detected. So it can be estimated that molybdenum oxide particles have covered the nickel cores. The obtained data are compatible with ASTM data file for MoO_3 (18-0844 standard) and Ni (04-0850 standard).
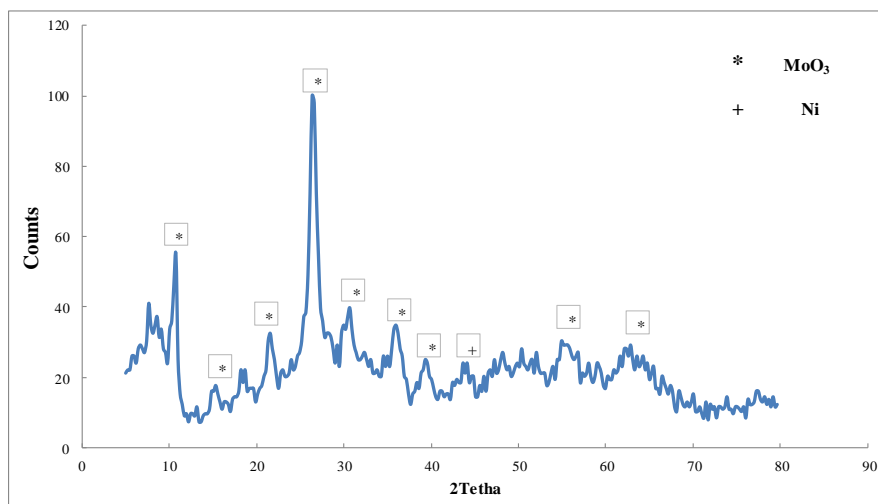
Figure 4. XRD patterns of 1:1 bimetallic nanoparticles.

According to Figure 4, the majority of detected peaks are corresponded to MoO_3 phase. However a small peak of Ni is also existed in the spectrum, which may refer to the detection of Ni core in the particles or existence of some monometallic particles in the mixture. Therefore, more analyses are required to get hints about this phenomenon. In the next step, comparison of TEM image of nickel nanoparticles (Figure 3) with that of bimetallic nanoparticles shown in Figure 5, also suggest that the final nickel nanoparticles with a diameter of about 40 nm were coating by molybdenum oxide shell. In order to study the effect of increase of concentration on the thickness of the shell, bimetallic nanoparticles with composition ratio of core: shell=1:3 were also prepared. Maybe it could be inferred from the comparison of the left and right images that increase of concentration of molybdenum solution, led to formation of a thicker shell. As shown in the TEM images, in the case of 1:1 bimetallic nanoparticles, thickness of the shell was about 5 nm, which increased somehow irregularly by concentration of shell (molybdenum) precursor in 1:3 nanoparticles. Since TEM micrographs have been taken in special points of a smell droplet of whole solution, these results could be helpful for more investigations. Therefore, it is essential to take other analyses such as SEM and EDS for more information.
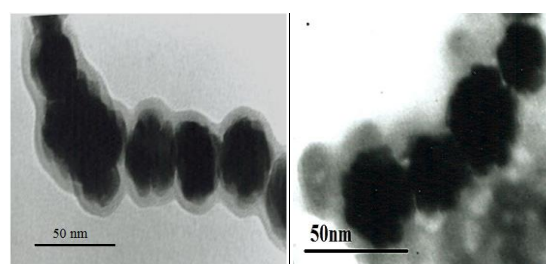
Figure 5. *TEM images of 1:1 (left) and 1:3 (right) nickel-molybdenum oxide bimetallic nanoparticles*

According to the Figure 6, increasing the concentration of molybdenum solution from ratio of 1 to 3 led to increase of final size of nanoparticles from 48nm to 58nm. This point may refer to the positive

relationship between increase of shell thickness and concentration of molybdenum salt solution. This point is very important and affects the final application of nanoparticles in chemical processes including catalysis. As Yang et al. [33] tuned the catalytic activity of core-shell nanoparticles by changing the thickness of shell. This way, it was proved that the number of atoms in shell monolayers or thickness of monolayer have changed the kinetic parameters in chemical reaction systems.
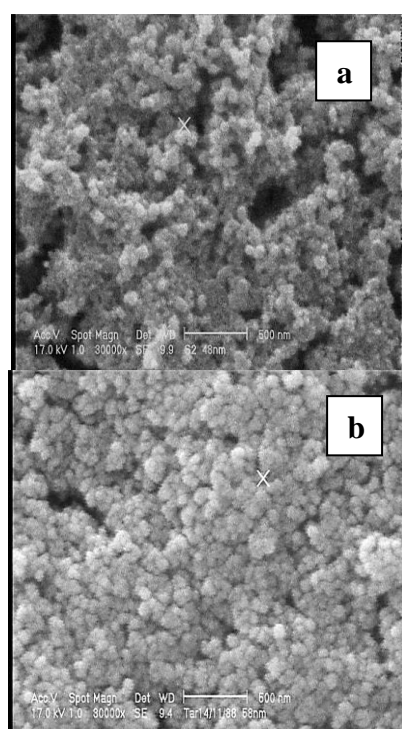
Figure 6. *SEM images of 1:1(a) and 1:3 (b) bimetallic nanoparticles with a mean diameter about 48 nm and 58nm, respectively.*

Also, as reported by Hota et al [34], addition of shell layers may reduce the intensity of EDS peaks pertinent to the core nanoparticles. Similarly, as shown in Figure 7, the EDS spectrum of nickel element in the bimetallic nickel-molybdenum oxide nanoparticles (both 1:1 and 1:3 compositions) is dramatically decreased, compared to the EDS spectrum of monometallic nickel nanoparticles shown in the Figure 1. On the contrary, the

EDS peak of molybdenum is sharp and clearly obvious in the structure of bimetallic nanoparticles. Besides, it should be noted that reduction of intensity of nickel EDS peak was more sensible in the case of 1:3 than 1:1 composition ratio. This point is also consistent with previous results, because increase of the concentration of shell solution may lead to formation of a thicker shell layer which inhibits the detection of core element.
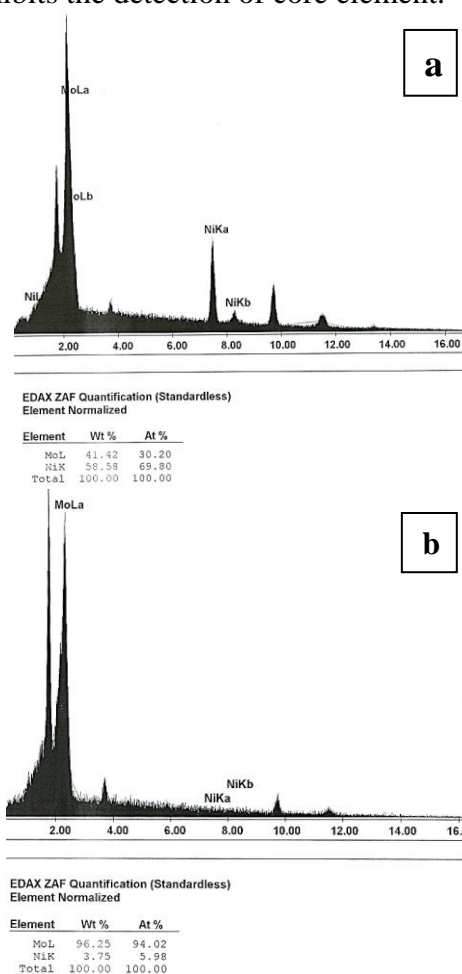
Figure 7. *EDS spectrums of 1:1 (a) and 1:3 (b) bimetallic nanoparticles.*

In continue, UV–Vis absorption spectra of nickel, molybdenum oxide and bimetallic nanoparticles were also recorded to have a better understanding about the core-shell structure of final nanoparticles. In this way, Figure 8 shows the absorption spectra of reaction solutions obtained at [Ni]=0.1 mM and various [Ni]/[Mo] ratios. Obviously, the magnetic nickel nanoparticles did not show any distinct

peak in their characteristic absorption band which can be due to their magnetic forces that causes them to precipitate. On the contrary, molybdenum oxide nanoparticles showed an obvious peak at about 300 nm. For bimetallic nanoparticles, the characteristic absorption band occurred at 250-300 nm and the peak intensity increased by increasing the concentration of molybdatophosphoric acid hydrate.
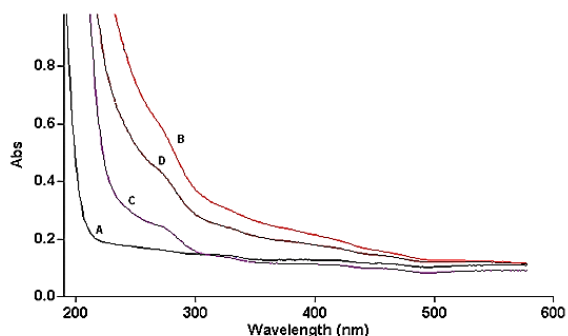
Figure 8. *UV–vis absorption spectra of nickel(A); molybdenum oxide (B); Ni:Mo= 1:1 (C); and Ni:Mo= 1:3 (D).*

Overall speaking, the general information obtained by XRD, SEM, TEM, EDS and UV-vis analyses suggests that the microwave-assisted prepared bimetallic nanoparticles could be composed of a nickel core and molybdenum oxide shell. However, the possibility of formation of intermediate phases could not be ignored, as it is somehow expected in synthesis of bimetallic nanoparticles. In this article the general analyses suggests that the majority of solution is composed of core-shell structure.

3. CONCLUSION

In summary, it could be said that due to the unique promotion effects of Ni and Molybdenum elements in catalysis reactions, here bimetallic nickel-molybdenum oxide nanoparticles have been synthesized the via a fast and facile route. The results of analyses indicated that successive reduction of nickel and molybdenum ions resulted in formation of nanoparticles with core-shell structure. This was examined by tracing the increase of nanoparticles diameter in TEM and SEM images and also reduction of intensity of Ni element peak in EDS analysis. Similarly, Intensity of adsorption peak in UV-Vis analysis was consistent with the other results, as increase of shell precursor concentration led to emergence of Molybdenum oxide peaks in relation to the pure Ni nanoparticles. So it could be inferred that this approach is suitable for tailoring the shell thickness, which highlights the future application of prepared bimetallic nanoparticles in catalysis reactions. Actually, the nature of fast and uniform heating of microwaves caused a homogeneous nucleation and growth in the reaction solution. Some of the advantages of the described process are including the simplicity, short reaction time and homogeneous heating of the reaction media.

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