Available online at www.pelagiaresearchlibrary.com

Pelagia Research Library

Der Chemica Sinica, 2012, 3(4):974-983

Pelagia Research Library

ISSN: 0976-8505
CODEN (USA) CSHIA5

Synthesis of MoO_5, $Na_2MoO_4.2H_2O$ and $(NH_4)_6Mo_7O_{24}.4H_2O$ nano catalysts based on multi-walled carbon nanotube

A. Safarpour Malakroudi[1], *F. Ashrafi[1] and H. Sedighian Rad[2]

[1]*Dept. of Chem., Payame Noor University, PO BOX 19395-3697, Tehran, Iran*
[2]*Appl. Microbiology Res. Center, Baghiatallah Univ. of Med. Sci., Tehran, Iran*

ABSTRACT

In this study, 3 different molybdenum oxide nano catalysts based on carbon nanotubes were synthesized with the precursors of MoO_5, $Na_2MoO_4.2H_2O$ and $(NH_4)_6Mo_7O_{24}.4H_2O$, using reflex and hydrothermal methods. The structure and morphology of these nano catalysts were studied by FTIR, scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermal gravimetric analysis (TGA) and X-ray diffraction (XRD) spectra. FTIR spectra show that MoO_5 has the peaks more intense than both $Na_2MoO_4.2H_2O$ and $(NH_4)_6Mo_7O_{24}.4H_2O$ spectra peaks. XRD spectra also, show higher intensity for MoO_5-MWNT peaks than intensities of the others one. SEM and TEM spectra show that in MoO_5-MWNT catalyst, nano particles mostly were placed on the open end and interior of nanotubes. Whereas, the amounts of nano particles of molybdenum oxide, in Na_2MoO_4-MWNT and $(NH_4)_6Mo_7O_{24}$-MWNT catalysts, are low and are placed on the surface of nanotubes. TGA analysis show that the amount of MoO_5-MWNT catalyst lies over nanotube, in respect of the two others, was more considerable (57/06 wt %). Thereafter, catalytic ability of these nano catalysts was examined by oxidation of 2-propanol (in presence of H_2O_2 as oxidant, n-dodecanone as interior standard and CH_2Cl_2 as solvent). Studying the results show that, the transformation of 2-propanol to product, by $(NH_4)_6Mo_7O_{24}$-MWNT catalyst is more than the two others.

Keywords: molybdenum oxide, nano catalyst, spectrum peak, catalytic ability, 2-propanol.

INTRODUCTION

Adsorption ability of carbon nanotubes which is due to the nature, large surface area and cylindrical structure of these materials [1, 2 and 3], make them capable, in using as the base for metal oxides nano catalysts. Much more studies have performed over transition metals interactions with carbon nanotube and graphite which the results differ vastly [4], these phenomena were interpreted due to the differences in bonding places over carbon nanotube used as the base of nano catalysts.

Studies on metallic nickel were shown that it has more stable bond on the surface of single-walled carbon nanotube than on graphite matrix. This may be considered due to cylindrical structure of nanotube. Presence of nickel atoms over the walls of nanotube will cause transmission of charges from these atoms to nanotube and vice versa [4].

Reaction of ammoniac synthesis by ruthenium on MWNT matrix as a catalyst was compared with ruthenium on other matrixes such as graphite, fullerene and activated carbon. It was observed that ruthenium – MWNT catalyst progresses reaction much more than ruthenium – other matrixes.

This difference may be due to the large surface area of carbon nanotubes which causes better distribution of catalyst metal over it and electronic properties of carbon nanotubes, also, cause better transmission of electrons to ruthenium [5].

Molybdenum oxide was found in two crystalline forms, α-MoO_3 thermodynamically stable, and β- MoO_3 thermodynamically instable [6, 7, 8, 9 and10]. The layers of α-MoO_3 is parallel to (100) crystalline planes, which their inter layers interaction is weak, therefore (100) planes are disposable and thermodynamically stable; in this case only oxygen atoms are over the surface.

Molybdenum oxide, α-MoO_3, is widely used as a catalyst. For example, α-MoO_3 catalysts were used often in polymerization and dehydrogenation reactions and also, as dehydration catalyst [11, 12 and 13]. Moreover, Molybdenum oxide is one of the most important catalysts in oxidation of hydrocarbons and alcohols to form aldehydes and ketones. MoO_3 catalytic characteristics occur by a series of dynamic processes over their surfaces (surface rearrangement, and movement of oxygen species over surface), under catalytic conditions [14 and15].
Carbon nanotubes were discovered in 1991 by Iijima in a process of arc-discharge method [16]. There are two structures of carbon nanotubes which are remarkable they consist of multi-walled carbon nanotubes (MWNT) [16], and single-walled carbon nanotubes (SWNT) [17].

In this study we have synthesized three different types of nano catalysts MoO_5-MWNT, $Na_2MoO_4.2H_2O$-MWNT and $(NH_4)_6Mo_7O_{24}.4H_2O$-MWNT, and then catalytic characteristic of these catalysts in the case of oxidation reaction of 2-propanol, then obtained results were discussed.

MATERIALS AND METHODS

This study was performed in Payame Noor University, tehran, Iran, as a thesis project on molybdenum catalyst - MWNT properties in 2011.

2.1. Materials

All materials used in this investigation have been of analytical grade: 1- Multi-walled carbon nanotube (Shenzen Co.), 2- Molybdenum oxide (Merck Co.), 3- Sodium molybdate dihydrate (Merck Co.), 4- Ammonium molybdate hepta hydrate (Merck Co.), 5- Hydrogen peroxide, 2-popanol, dichloromethane, n-dodecane (Merck Co.).

2.2. Instruments

Following analytical instruments were used in this study: 1- Infra red spectroscopy (IR, Bruker, Equinox 55), 2- Scanning electron microscopy (SEM, XL30, Philips Co.), 3- Transmission electron microscopy (TEM, EM 900, ZEISS 80 KV), 4- Thermal gravimetric analysis (TGA, Perkin Elemer, Pyris Diamond), X – ray diffraction (XRD, X Pert MPD, Philips Co., Tube: Cu kα, 40 kV), Gas chromatography (GC, Varian).

2.3. Synthesis of MoO_5-MWNT

This process consists of two stages: Stage 1- synthesis of molybdenum pentoxide: 0.72 g MoO_3 was mixed with 5 mL H_2O_2 and agitated for 48 hours with a magnetic stirrer at 40^oC till insoluble MoO_3 transform to yellowish MoO_5 soluble in water. Stage 2- synthesis of MoO_5-MWNT: 100 mg carbon nanotube was added to MoO_5 provided in stage 1, and then this solution was agitated for 48 hours at 100 ^oC in a reflex system. Obtained precipitate was filtered and rinsed several times by deionized water and then dried in an oven. This synthesized substance have analyzed by IR, SEM, TEM, TGA and XRD.

2.4. Synthesis of Na_2MoO_4-MWNT

30 mL of saturated solution of sodium molybdate was prepared, and then 100 mg carbon nanotube was added to it and agitated for a few minutes. All obtained solution was transferred to an autoclave vessel which was sealed and placed for 48 hours in an oven at 180 ^oC. The precipitate was filtered, rinsed and dried, and then analyzed by IR, SEM, TEM, TGA and XRD.

2.5. Synthesis of $(NH_4)_6Mo_7O_{24}$-MWNT

100 mg carbon nanotube with10 mL deionized water and homogenized about 5 minutes by an ultrasonic system. Then 20 mL of saturated solution of ammonium molybdate hepta hydrate was prepared. Both prepared solutions was mixed and transferred to an autoclave vessel which was sealed and placed for 48 hours in an oven at 180 ^oC. The precipitate was filtered, rinsed and dried, and then analyzed by IR, SEM, TEM, TGA and XRD.

2.6. Catalytic tests

Catalytic tests were performed in the same condition for three catalysts synthesized above as will describe below. 10 m mol (0.6 g) 2-propanol with 0.03 g catalyst and 5 mL dichloromethane was transferred to a 25 mL balloon and it was agitated by a magnetic stirrer which is placed inside it. Every 10 minutes the reaction was stopped and one drop

of organic phase was injected into the GC for determining amount of oxidizing alcohol. The results will discuss later.

RESULTS AND DISCUSSION

In this section, firstly the results of synthesizing nano catalysts will be analyze and then Catalytic tests for oxidizing 2-propanol alcohol will be discussed.

3.1. Analyzing the results obtained for Synthesis of MoO_5-MWNT

MoO_3 is a heterogeneous catalyst and water insoluble. Oxidizing this catalyst by H_2O_2 transform oxo group to peroxo group and MoO_5 is water soluble and homogeneous catalyst. By binding this catalyst to carbon nanotube a nano catalyst will be obtain which is water insoluble.

IR spectrum of MoO5-MWNT (Fig. 1) shows three peaks in 612, 913 and 979 cm^{-1} which are related to tensional vibrations of different bonds between molybdenum and oxygen. The peak in 1608 cm-1 is due to binding between molybdenum metal and water. The peaks which appear in 3140 and 35109 cm^{-1} is due to symmetric and asymmetric vibrations of water molecule.

The peaks of molybdenum and oxygen bonds in MoO5 (Fig. 2), are placed in 918 and 942 cm^{-1}. The position of C = C bond in IR spectrum of MWNT is in 1494 cm^{-1} (Fig. 3). Comparing these three spectra, the peaks of MoO5-MWNT are shifted towards upper frequencies which confirm formation of covalence bond between MoO5 and MWNT.

Figure 1. IR spectrum of MoO_5-MWNT nano catalyst

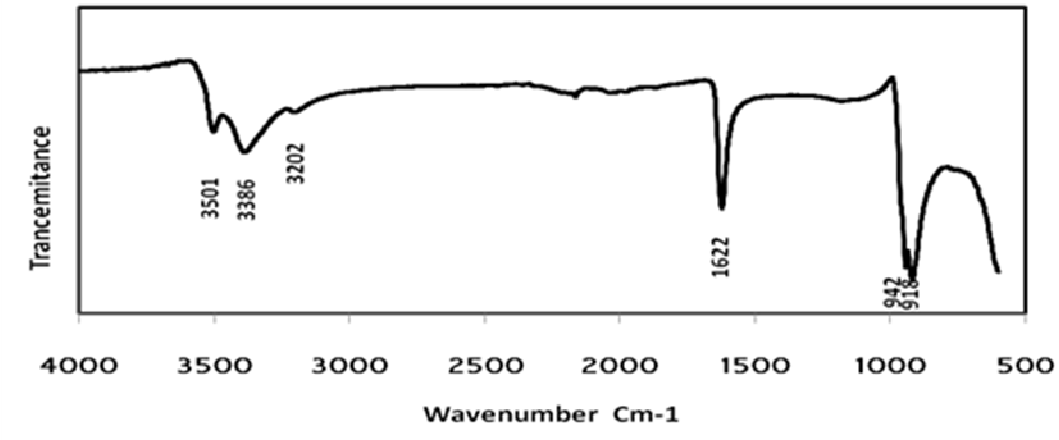

Figure 2. IR spectrum of MoO_5

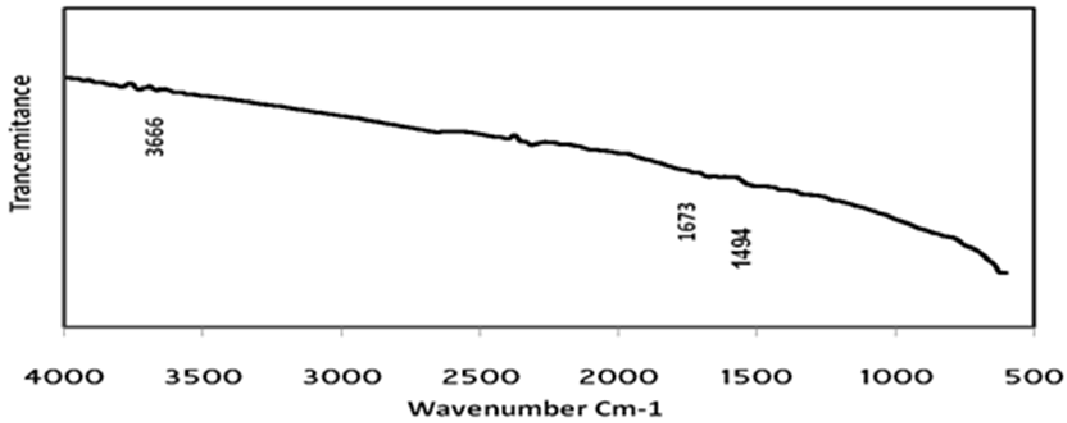

Figure 3. IR spectrum of MWNT

SEM image of MoO5-MWNT shows that the structure of nanotube was not disturbed by reaction. Assemblage of nano particles of MoO5 at the end of nanotubes clearly is observable (Fig. 4).
TEM image of MoO5-MWNT shows a precise illustration of reaction characteristic between MoO5 and MWNT. In TEM image it is observed that MoO5 is diffused inside of carbon nanotubes (Fig. 5).

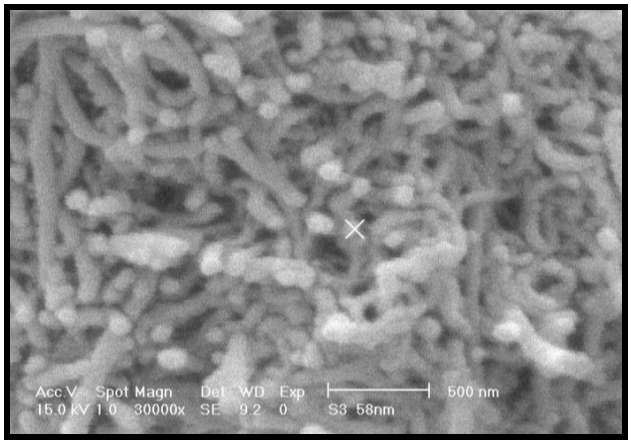

Figure 4. SEM image of MoO_5-MWNT

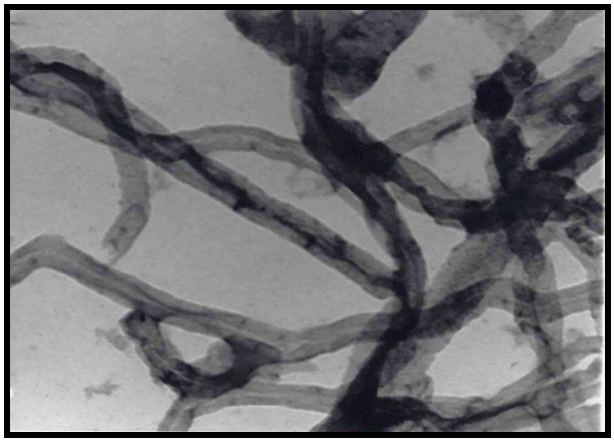

Figure 5. TEM image of MoO_5-MWNT

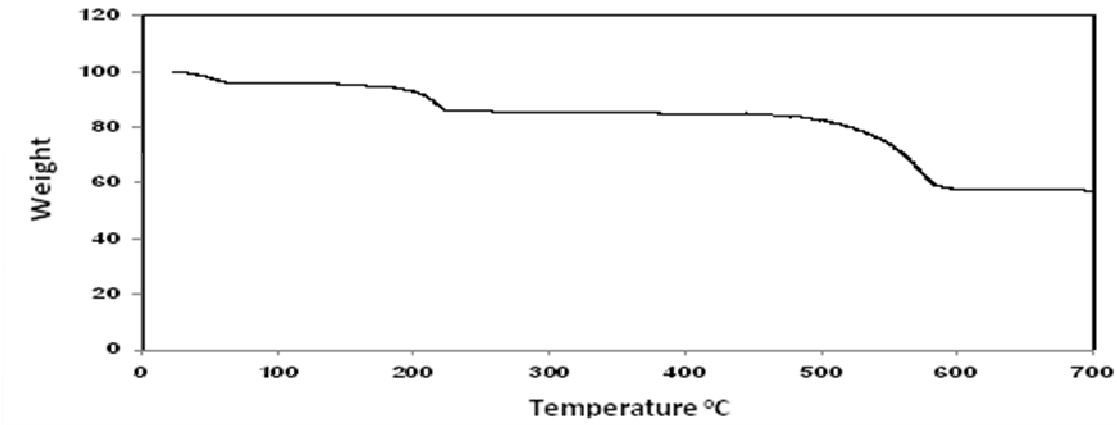

Figure 6. TGA diagram of MoO_5-MWNT nano catalyst

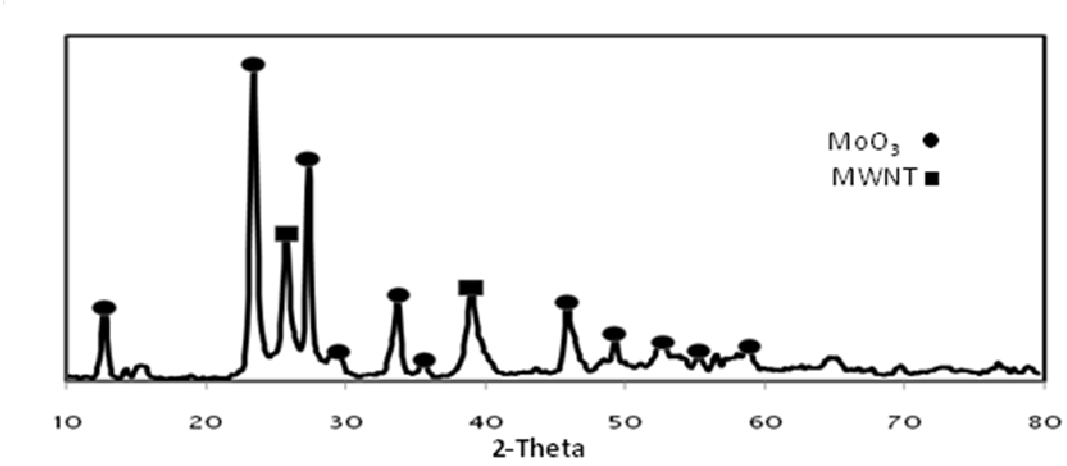

Figure 7. XRD spectrum of MoO_5-MWNT nano catalyst

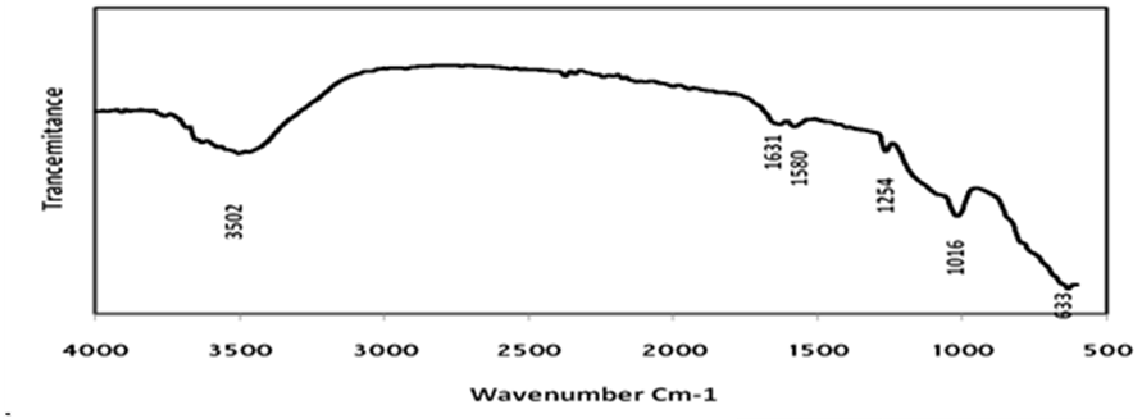

Figure 8. IR spectrum of Na_2MoO_4-MWNT nano catalyst

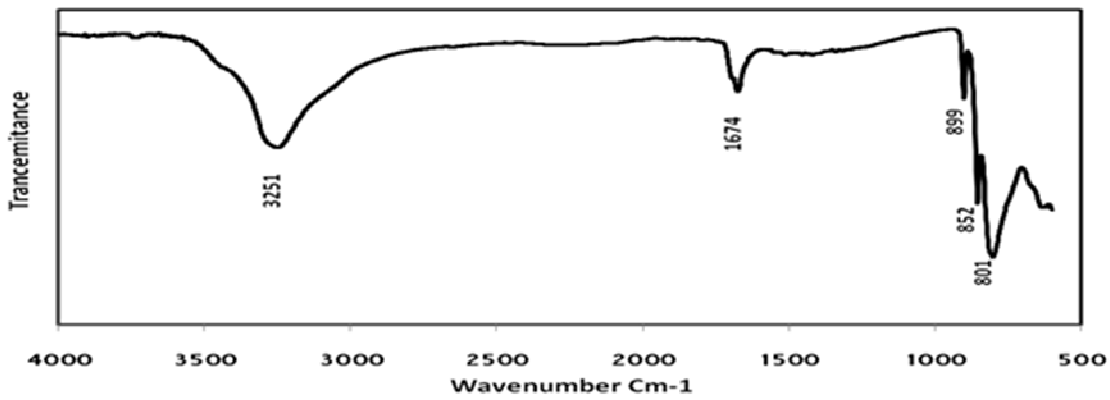

Figure 9. IR spectrum of Na_2MoO_4

TGA analyze of MoO_5-MWNT catalyst from room temperature to 700^{o}C was shown in Fig. 6. Blow 100 ^{o}C weight increasing is due to dehydration. The sample, at about 200 ^{o}C, losses its peroxo groups, and in the range of 500 to 600 ^{o}C the whole of nanotubes will be burn and at last, remaining residue is molybdenum oxide (57/06 wt %).

The obtained nano-fibers before analyzing by XRD, was exposed to a calcification at 350 ^{o}C about 1 hour for transforming its amorphous structure to crystalline one. Fig. 7 shows XRD spectrum of MoO_5-MWNT catalyst.

In this spectrum 12.77, 23.41, 27.33, 29.49, 33.73, 35.57, 45.89, 49.25, 52.77, 55.33 and 58.85 angles as well as in accordance with orthorhombic structure of MoO_3 which coincide with JCPDS No. 35-0609 and correspond with (020), (110), 021), (130), (111), (041), (200), (002), (211), (112) and (081) crystalline planes. The 25.73 and 39.01

angles also, show presence of carbon nanotube (MWNT) which coincide with JCPDS No. 41-1487 and correspond with (002) and (100) crystalline planes.

3.1. Analyzing the results obtained for Synthesis of Na_2MoO_4- MWNT

This nano catalyst was produced by hydrothermal process.

IR spectrum of Na_2MoO_4- MWNT nano catalyst is show on Fig. 8. The peaks in 633, 1016 and 1254 cm^{-1} are due to tensional vibration of bonds formed between molybdenum an oxygen (Mo – O – Mo and Mo = O). The peaks in 1580 and 1631cm^{-1} correspond with MWNT. These peaks are shifted towards upper frequencies, comparing with Na_2MoO_4 peaks (Fig. 9) and MWNT peaks (Fig. 3) which confirm formation of covalence bond between MoO5 and MWNT in Na_2MoO_4- MWNT nano catalyst.

SEM image of Na_2MoO_4-MWNT nano catalyst shows MWNT which nano particles of molybdenum oxide are coated its surface (Fig. 10). TEM image shows the same result, but the amount of coated nano particles is small (Fig. 11).
TGA analyze of Na_2MoO_4-MWNT catalyst from room temperature to 700^oC was shown in Fig. 12. The catalyst looses lightly its weight; about 530 ^oC nanotube begins to burn and at about 630 ^oC it burns completely. At last, molybdenum oxide remains as a residue (7.20 wt %).

XRD spectrum of Na_2MoO_4-MWNT was shown in Fig. 13. In this spectrum 26.13, 42.93 and 44.37 angles coincide with (002), (100) and (101) crystalline planes and show the presence of carbon nanotubes (JCPDS No. 41-1487).

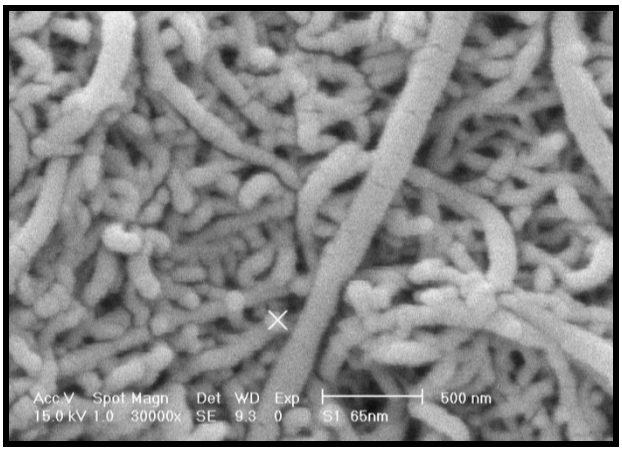

Figure 10. SEM image of Na_2MoO_4-MWNT

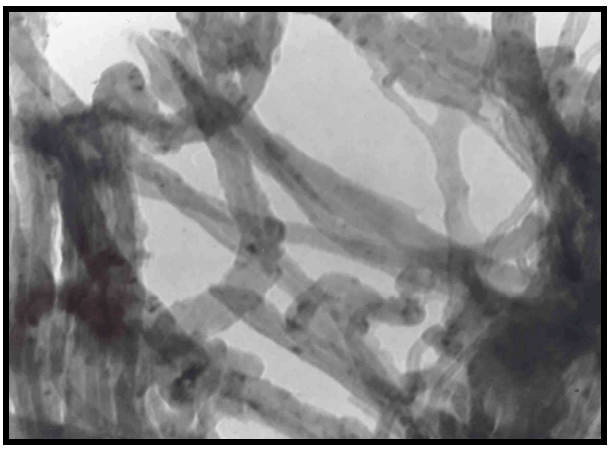

Figure 11. TEM image of Na_2MoO_4-MWNT

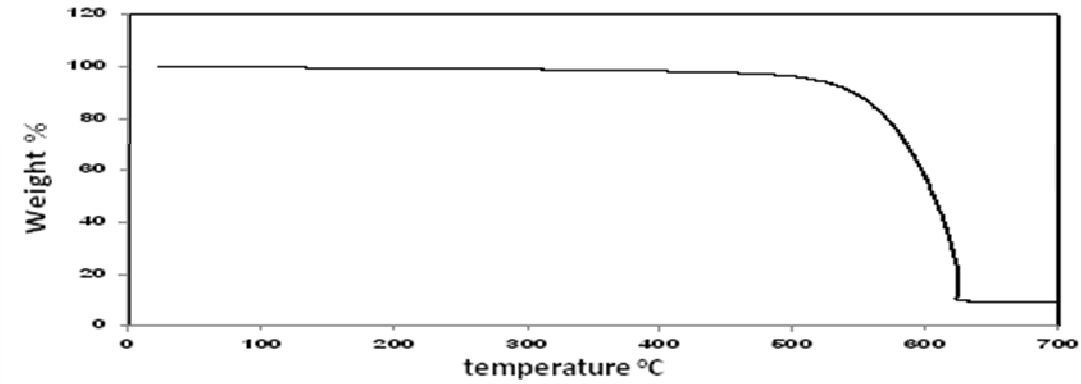

Figure 12. TGA diagram of Na_2MoO_4-MWNT nano catalyst

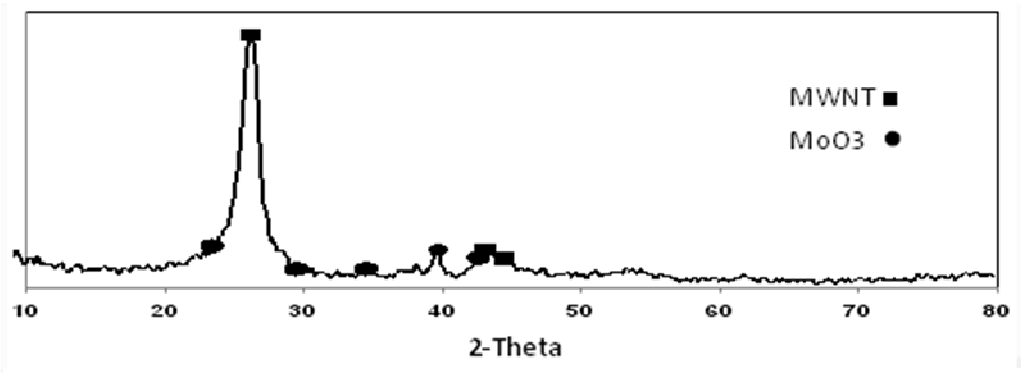

Figure 13. XRD spectrum of Na_2MoO_4-MWNT nano catalyst

23.33, 29.41.34.37, 39.57 and 42.53 angles are due to presence of molybdenum oxide and are in coincidence with (110), (130), (140), (150) and (141) crystalline planes which correspond to orthorhombic phase of MoO_3 which coincide with JCPDS No. 35-0609.

3.3. Analyzing the results obtained for Synthesis of $(NH_4)_6Mo_7O_{24}$- MWNT

This nano catalyst was produced by hydrothermal process as have described above. The peaks of IR spectrum of which $(NH_4)_6Mo_7O_{24}$- MWNT nano catalyst which was appear in 684, 762, 797, 905 and 947 cm^{-1} are related with different bonds between oxygen and molybdenum (Fig. 14) . The peaks placed in 1414, 1442 and 1560 cm^{-1} depend on carbon nanotube bindings. The peak in 1640 cm^{-1} depends on the bond between water and molybdenum. All these peaks comparing with the peaks in IR spectrum of $(NH_4)_6Mo_7O_{24}$ (Fig. 15) were shifted towards upper frequencies which are due to covalence bonds.

In SEM image of $(NH_4)_6Mo_7O_{24}$- MWNT we observe MoO_3 nano particles which were dispersed over MWNTs filament (Fig. 16).

In TEM image of $(NH_4)_6Mo_7O_{24}$- MWNT we observe MoO_3 nano particles in small quantities were dispersed over MWNTs (Fig. 17).

TGA analyze of $(NH_4)_6Mo_7O_{24}$ -MWNT nano catalyst from room temperature to 700^oC was shown in Fig. 17. The catalyst looses lightly its weight; about 550 ^oC nanotube begins to burn and at about 650 ^oC it burns completely. At last, molybdenum oxide remains as a residue (4.06 wt %).

XRD spectrum of this nano catalyst (Fig. 18) show that 26.29, 42.53, 44.21 and 54.53 angles are in relation with (002), (100), (101) and (004) crystalline planes of MWNTs and coincide with JCPDS No. 41-1487.

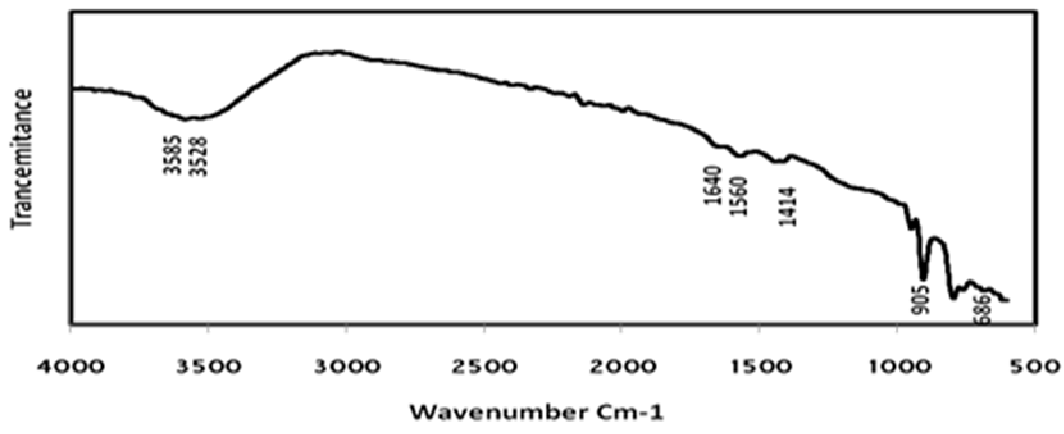

Figure 14. IR spectrum of $(NH_4)_6Mo_7O_{24}$-MWNT nano catalyst

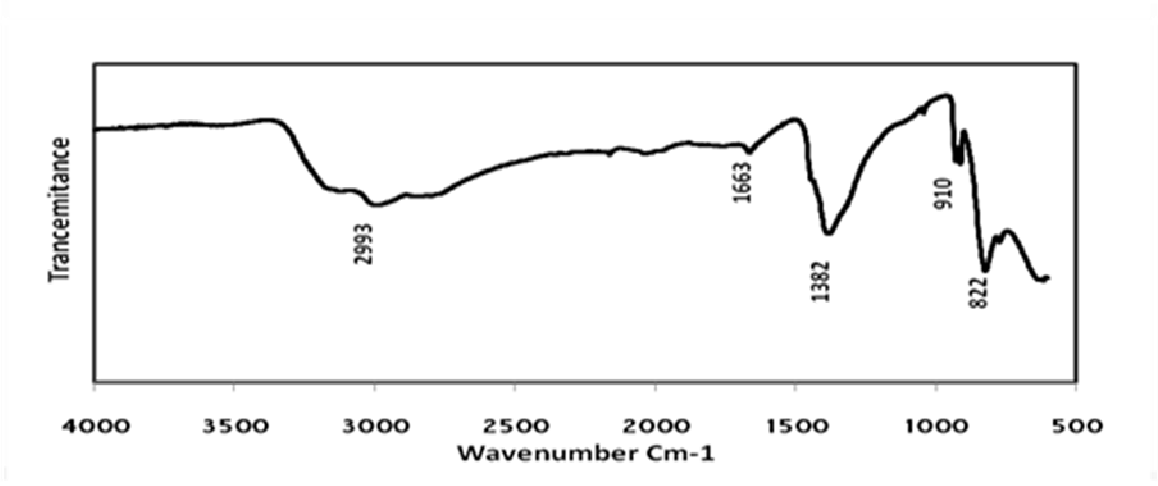

Figure 14. IR spectrum of $(NH_4)_6Mo_7O_{24}$

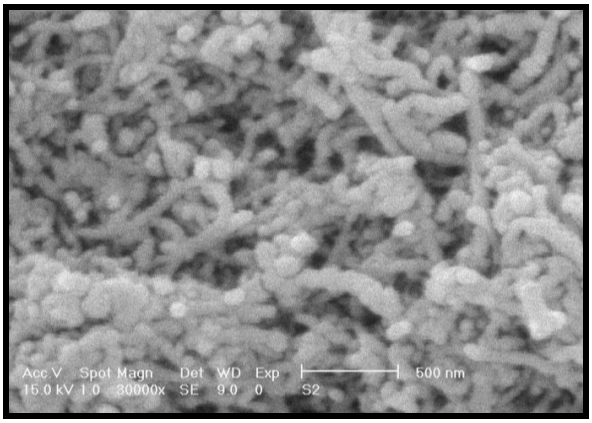

Figure 15. SEM image of $(NH_4)_6Mo_7O_{24}$ -MWNT

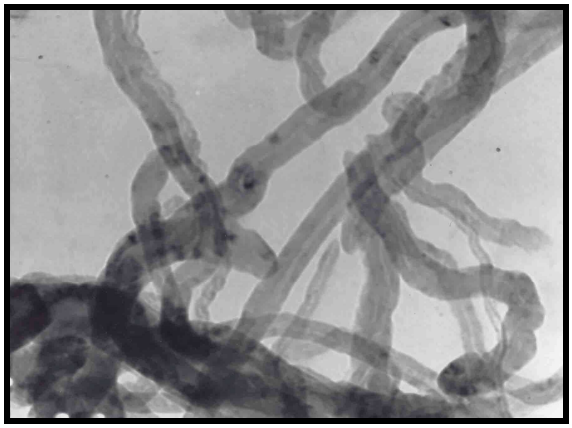

Figure 16. TEM image of $(NH_4)_6Mo_7O_{24}$-MWNT

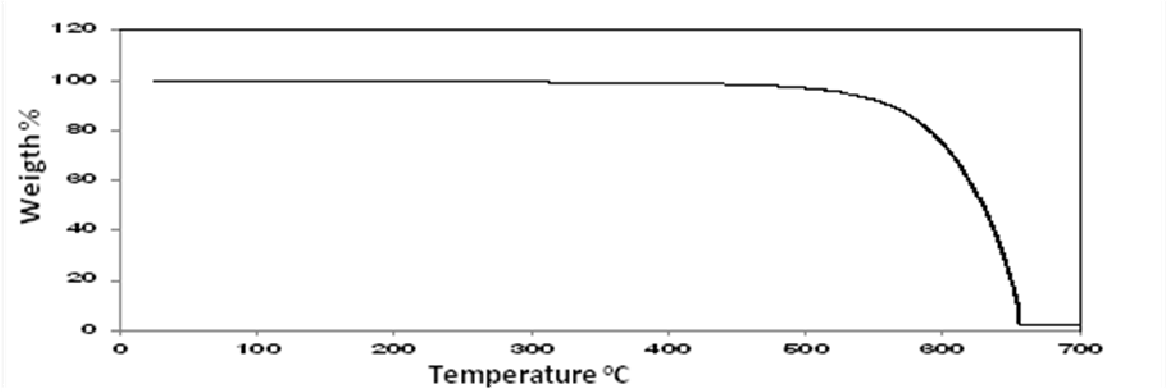

Figure 17. TGA diagram of $(NH_4)_6Mo_7O_{24}$ -MWNT nano catalyst

Presence of molybdenum oxide was presented by 23.41, 27.65, 29.65 and 33.01 angles which correspond to (110), (021), (130) and (101) orthorhombic phase of MoO_3 and coincide with JCPS No. 35-0609.

Analysis these three synthetic nano catalysts show that MoO_5-MWNT nano catalyst is in better compatibility with carbon nanotubes than two other. IR and XRD peaks of this nano catalyst have been higher intensity. But, SEM and TEM images of MoO_5-MWNT nano catalyst large amount of Molybdenum oxide have observed inside of nanotubes. Whereas, the amount of this oxide for two other nano catalyst is low, but was placed over their surfaces.

TGA Analysis shows that remaining residues due to MoO_5-MWNT, Na_2MoO_4-MWNT and $(NH_4)_6Mo_7O_{24}$ –MWNT nano catalysts burning are 57.06 %, 7.20 % and 4.06 %, respectively. At last, XRD spectra show covalence bonds between oxide and nanotube.

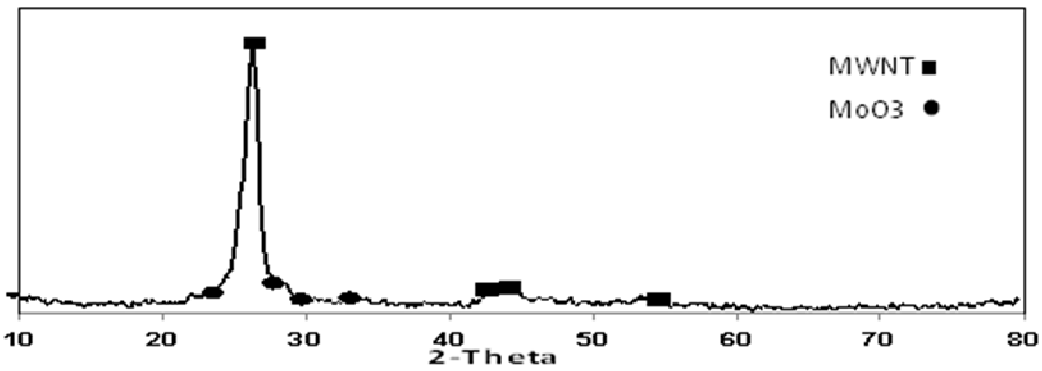

Figure 18. XRD spectrum of $(NH_4)_6Mo_7O_{24}$ -MWNT nano catalyst

Now we must examining catalytic reaction of oxidation of 2-propanol in presence of these three nano catalysts and comparing obtained results. As it was described further, we have stopped every 10 minute the reaction and its progress was determined. We have performed six measurements during 60 minutes and the calculation show that alcohol conversion yields of oxidizing reactions in presence of MoO_5-MWNT, Na_2MoO_4-MWNT and $(NH_4)_6Mo_7O_{24}$ –MWNT nano catalysts, are 83.87 %, 81.89%, and 88.53 %, respectively. The order of reactions in presence of any of these three nano catalysts have been determined to be 2 [18]. The rate of these catalytic reactions was given by following relation [18]:

$$r = k\,[2\text{-propanol}][H_2O_2] \qquad (1)$$

The constant of rates of oxidizing reactions in presence of MoO_5-MWNT, Na_2MoO_4-MWNT and $(NH_4)_6Mo_7O_{24}$ –MWNT nano catalysts were determined and are 1.8×10^{-2} min^{-1}, 2.4×10^{-2} min^{-1} and 6.3×10^{-2} min^{-1}, respectively. These results show that catalytic effect of $(NH_4)_6Mo_7O_{24}$ –MWNT nano catalyst is suitable than two other nano catalysts. $(NH_4)_6Mo_7O_{24}$ –MWNT nano catalyst nevertheless of its small amount of molybdenum oxide, has better catalytic effect and higher yield than both other nano catalysts. It may be interpreted as following: in MoO_5-MWNT nano catalyst molybdenum oxide placed inside of nanotubes and this may decrease its catalytic effect, whereas, in Na_2MoO_4-MWNT and $(NH_4)_6Mo_7O_{24}$ –MWNT nano catalysts molybdenum oxide was dispersed over the surface of carbon nanotubes. Otherwise, $(NH_4)_6Mo_7O_{24}$ –MWNT, has several types of Mo – O and Mo = O bonds and this make it capable to have more catalytic effect than Na_2MoO_4-MWNT.

CONCLUSION

We have synthesized three nano catalysts of molybdenum oxide on basis of carbon nanotubes (MWNTs) by using MoO_5, Na_2MoO_4 and Na_2MoO_4 compounds.

The peaks of IR and XRD spectra of MoO5-MWNT are more intense comparing with Na2MoO4-MWNT and $(NH_4)_6Mo_7O_{24}$ –MWNT peaks. All IR peaks of three nano catalysts were shifted towards upper frequencies which are due to covalent bonds between MoO5 and MWNT.

SEM and TEM images of three nano catalysts show that in MoO5-MWNT a large amount of molybdenum oxide was placed inside of carbon nanotubes, whereas in Na_2MoO_4-MWNT and $(NH_4)_6Mo_7O_{24}$ –MWNT, molybdenum oxide was placed over MWNTs surface.

TGA diagram shows that remaining residues after complete burning of nano catalysts are 57.06 %, 7.20 % and 4.06 % for MoO_5-MWNT, Na_2MoO_4-MWNT and $(NH_4)_6Mo_7O_{24}$ –MWNT nano catalysts, respectively. Nevertheless of its smallest amount of molybdenum oxide, $(NH_4)_6Mo_7O_{24}$ –MWNT nano catalyst have more compatible catalytic ability due to better dispersion of molybdenum oxide over the surface of MWNTs and several types of molybdenum oxygen bonds.

These nano catalysts were contributed in catalytic oxidation of 2-propanole and the conversion yields show that all these synthesized nano materials act as good catalysts.

The order of these catalytic oxidations was determined to be 2. Determined constants of rates of these catalytic oxidations, confirm more compatible catalytic ability of $(NH_4)_6Mo_7O_{24}$ –MWNT nano catalyst.

REFERENCES

[1] Yang Q.H., Hou P.X., Bai S., Wang M.Z., H.M. *Cheng, Chem. Phys. Lett*., (**2001**), 345, pp.18.
[2] Inoue S., Ichikumi N., Suzuki T., Uematsu T., Kaneko K., *J. Phys. Chem*., (**1998**), 102, pp. 4689.
[3] Eswaramoorthy M., Sen S., Rao C.N.R., *Chem. Phys. Lett*., (**1999**), 304, pp. 207.
[4] Menon M., Andriotis A.N., Froudakis G.E., *Chem. Phys. Lett*., (**2000**), 320, pp. 425.
[5] Chen H.B., Lin J.D., Cai Y., Wang X.Y., Wang J., Wei G., Lin Y.Z., Liao D.W., *Appl. Surf. Sci*., (**2001**), 180, pp. 328.
[6] Kihlborg L., *Arkiv Kemi*., (**1963**), 21, pp. 357.
[7] McCarron E.M., *J. Chem. Soc. Chem. Commun*., (**1986**), 198, pp. 336.
[8] Salje E., Gehlig R., *J. Solid State Chem*., (**1978**), 25, pp. 239.
[9] Parise J.B., McCarron E.M., Sleight A.W., *Mater. Res. Bull*., (**1987**), 22, pp. 803.
[10] Parise J.B., McCarron E.M., Von Dreele R., Goldstone J.A., *J Solid State Chem*., (**1991**), 93, pp. 193.
[11] Haber J., *Catal. Today*, (**1997**), 33, pp. 119.
[12] Zhou B., Machej T., Ruiz P., Delmon B., *J. Catal*.\, (**1991**), 132, pp. 183.
[13] Gaigneaux E.M., Naeye M.L., Dupont O., *DGMK Tagunsbericht*, (**1998**), 9803, pp. 181.
[14] Gaigneaux E.M., Naud J.C., Ruiz P., Delmon B.,, *Stud. Surf. Sci. Catal*., (**1997**), 110, pp. 185.
[15] Gaigneaux E.M., Abdel Dayem H.M., Godard E., Ruiz P., *Appl. Catal A: Gen*., (**2000**), 202, pp.265.
[16] Iijima S., *Nature*, (**1991**), 354, pp. 56.
[17] Iijima S. and Ichihashi T .,*Nature* , (**1993**), 363, pp. 603.
[18] Ashrafi F., Khodadadi A.A., Afsharpour M., Safarpour Malakroudi A., *Adv. Appl. Sci. Research*, (**2011**), 2, pp. 384.