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Kinetic Study of 2-Propranol Oxidation by Using of Nano Catalysts MoO_3, $Na_2MoO_4.2H2O$, $(NH_4)_6Mo_7O_{24}.4H_2O$

F. Ashrafi[*§], A. A. Khodadadi[†], M. Afsharpour[†], A. Safarpour Malakroudi[§]

[§] *Payame Noor University, Faculty of Sciences, Tehran, Iran*
[†]*Tehran University, Faculty of Technology, Tehran, Iran*

ABSTRACT

New nano structures of molybdenum oxide based on carbon nanotubes (CNTs) as MoO_5, $Na_2MoO_4.2H_2O$ and $(NH_4)_6Mo_7O_{24}.4H_2O$ have prepared in presence of water by reflex and hydrothermal method. The structures and morphologies of these nano – catalysts, also, have confirmed by IR, SEM, TEM, TGA and XRD. In this investigation kinetics of reaction of 2-propanol in presence of hydrogen peroxide as oxidant, n- dodecane as intern standard and CH_2Cl_2 as solvent, was studied. Between these three nano – catalysts for transformation of 2-propanol to 2-propanone, $(NH_4)_6Mo_7O_{24}$- MWNT disposed better yield than the two others. The selectivity of these reactions is total, because of single product. The constant of rate of oxidation reaction of 2- propanol by using $(NH_4)_6Mo_7O_{24}$- CNT nano – catalyst, is greater than the others one. Experimental data for these reactions show that they follow a kinetic of second order. The kinetic relation of oxidation reaction of 2- propanol in presence of nano – catalyst was studied by a proposed mechanism. By using two methods, approximation for rate limiting stage and stationary state approximation, r = [2- propanol] $[H_2O_2]$ was obtained.

Keywords: MoO_5, $Na_2MoO_4.2H_2O$ and $(NH_4)_6Mo_7O_{24}.4H_2O$, nano – catalyst, 2- propanol, constant of rate, stationary state approximation.

INTODUCION

Metal oxides, in particular, transition metal oxides are well known for their physical, chemical, surface and catalytic properties [1-3]. MoO_3 oxide which is the basis of three nano – catalysts which were used in this approach, have two morphological structures.

α- MoO_3 thermodynamically stable and has an orthorhombic structure [4] and β- MoO_3 semi – stable and has a monoclinic structure [5-8].

α- MoO_3 has a layer structure which has octahedral MoO_6 in this layer. MoO_3 layers are parallel to (100) crystalline planes which have the week intra – layer interaction. Therefore, present (100)

crystalline planes are thermodynamically stable and in this case only oxygen atoms lay on the surface [4]. β- MoO_3 has a structure similar to WO_3 one [5].

Molybdenum oxide and molybdates have investigated for their technological uses in a vast range [9 -12], for example, their uses in gas sensors [11], electrochromic elements [13], cathode in lithium micro – cells [14 -16]. Moreover, one of the largest applications of molybdenum oxide is its usage as catalyst [17]. Applicability of molybdenum oxide achieve by a series of dynamic processes on its surface [18].

Carbon nanotube (CNT) hazardously have discovered by Iigima et al[19]. Carbon nanotubes have a vacuous structure of single layer of graphen which have enveloped in cylindrical form. Two forms of CNTs are remarkable, multi - wall carbon nanotubes (MWNT) [19] and single - wall carbon nanotubes (SWNT)[20].

Nano particles of transition metal oxides on the basis of carbon nanotubes may form nano – catalysts. In this study nano – catalysts of MoO_5, $Na_2MoO_4.2H_2O$ and $(NH_4)_6Mo_7O_{24}.4H_2O$ on the basis of multi - wall carbon nanotube have synthesized. Obtained nano – catalysts were contributed in oxidation reaction of 2- propanol.

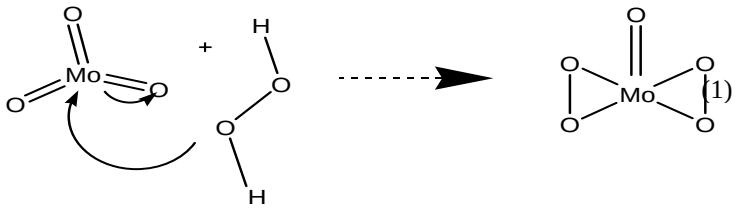
Kinetic of reaction was studied and the order of reaction was obtained experimentally. Finally, with respect to experimental data and evidences a mechanism for this reaction was proposed.

MATERIALS AND METHODS

1- Catalysts synthesis method

(a) MoO_5 synthesis

This catalyst was processed in two stages. In First stage, MoO_5 was provided by MoO_3 oxidizing with H_2O_2. In second stage, MoO_5 under oxo-diperoxo form was added to carbon nanotube and MoO_5 – MWNT have obtained by reflex in 100°C.



(1)

(b) Na_2MoO_4 – MWNT

This catalyst was prepared by adding carbon nanotube to saturated solution of sodium molybdate and treating in an oven in 180°C.

(c) $(NH_4)_6Mo_7O_{24}$ – MWNT

This catalyst was prepared by adding carbon nanotube to saturated solution of ammonium hepta molybdate and has treated in an oven in 180°C.

All catalysts were tested and identified by IR, SEM, TEM, TGA, and XRD.

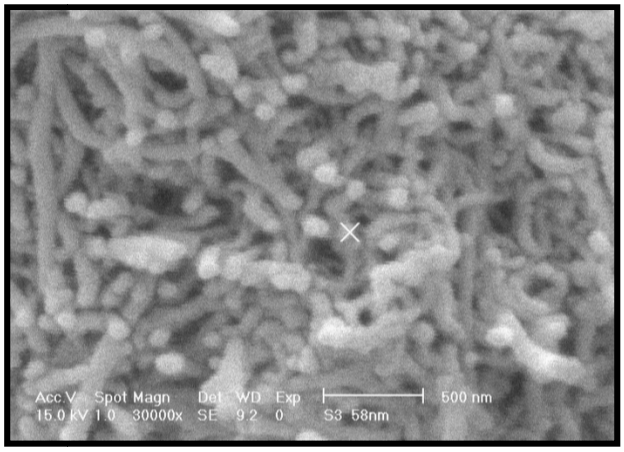


Figure 1. SEM image of MoO_5-MWNT nano-catalyst

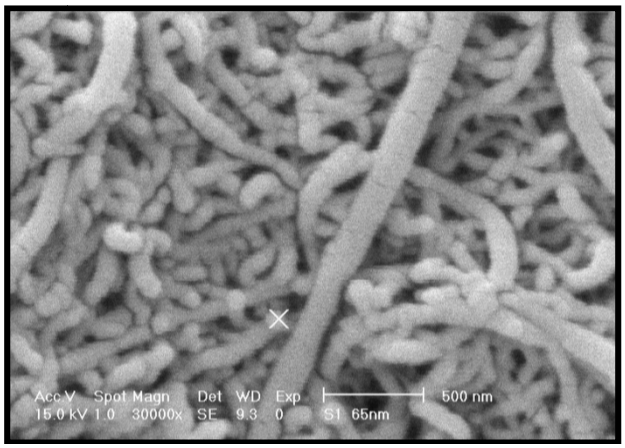


Figure 2. SEM image of Na_2MoO_4-MWNT nano-catalyst

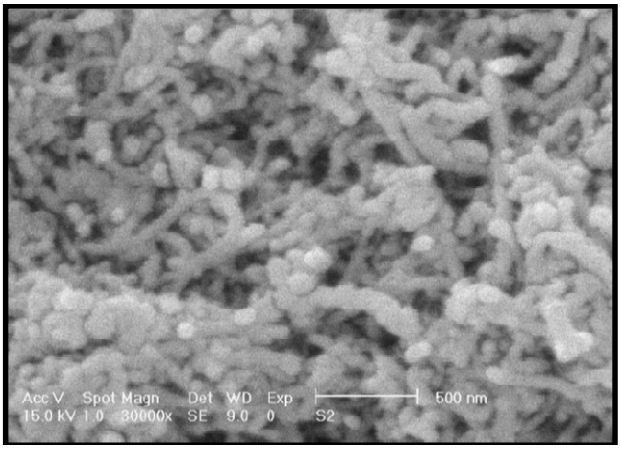


Figure 3. SEM image of $(NH_4)_6Mo_7O_{24}$-MWNT nano-catalyst

RESULTS AND ISCUSSION

The results obtained by SEM were shown that in MoO_5-MWNT case, nano - particles are aggregated over the ends of nanotube. In Na_2MoO_4-MWNT case nano – particles are coated on the surface of nanotube and in $(NH_4)_6Mo_7O_{24}$-MWNT case nano – particles are dispersed over MWNT filaments. SEM images of these 3 catalysts were shown in figures 1, 2 and 3.

1- Catalytic testes

These catalysts were used for catalytic oxidation of 2-propanol with H_2O_2 in CH_2Cl_2 solvent and n-Dodecane as internal standard. The general reaction is as following.

$$2-\text{propanol} \xrightarrow[CH_2Cl_2,\text{n-dodecane}]{\text{Nano-catalyst},H_2O_2} 2-\text{propanone} \qquad (2)$$

By kinetic study of reactions the order of reaction and the constant of rate are determined. A mechanism was proposed on the basis of reaction evidences.

2- Kinetic study of oxidation off 2-propanol by using MoO_5-MWNT as nano catalyst

The reaction was performed and the results of conversion of 2-propanol to 2-propanone are indicated in table 1 and figure 4. The result of this oxidation is a single product; therefore the selectivity of reaction is 100%.

$$2-\text{propanol} \xrightarrow[CH_2Cl_2,\text{n-dodecane}]{MoO_5-\text{MWNT},H_2O_2} 2-\text{propanone} \qquad (3)$$

The plots 5 and 6 show that the reaction may be accepted as a second order one.

Table 1. The yield of conversion of 2-propanol to 2-propanone by using MoO_5-MWNT as catalyst

Conversion (wt %)	Time (min)
0	00.00
10	82.00
20	81.50
30	83.38
40	81.89
50	83.21
60	83.70

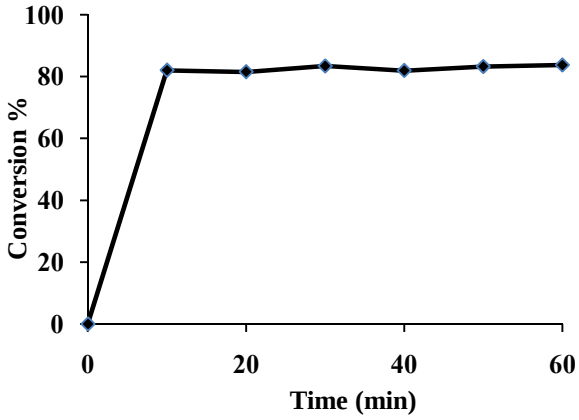


Figure 4. Yield of conversion plot indicated in table 1

3- Kinetic study of oxidation off 2-propanol by using Na_2MoO_4-MWNT as nano catalyst

The reaction was performed and the results of conversion of 2-propanol to 2-propanone are indicated in table 1 and figure 7.The result of this oxidation is a single product; therefore the selectivity of reaction is 100%.

$$2-\text{propanol} \xrightarrow[CH_2Cl_2,\,n-\text{dodecane}]{Na_2MoO_4-MWNT,\,H_2O_2} 2-\text{propanone} \qquad (4)$$

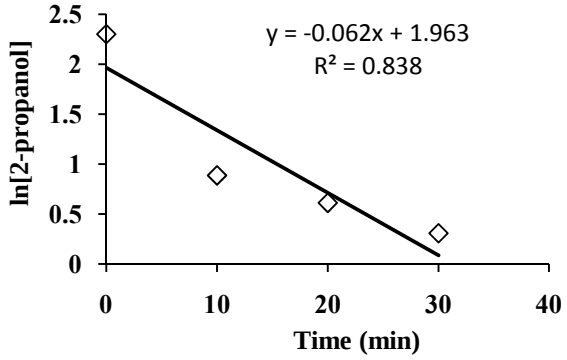


Figure 5. The plot of ln[2-propanol] against time for first order reaction

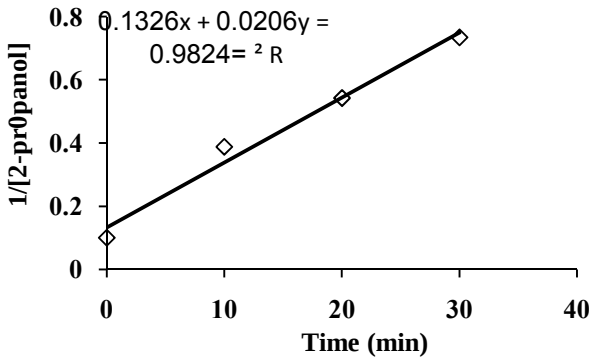


Figure 6. The plot of 1/ [2- propanol] against time for second order reaction

3- Kinetic study of oxidation off 2-propanol by using Na_2MoO_4-MWNT as nano catalyst

The reaction was performed and the results of conversion of 2-propanol to 2-propanone are indicated in table 1 and figure 7.The result of this oxidation is a single product; therefore the selectivity of reaction is 100%.

$$2-\text{propanol} \xrightarrow[CH_2Cl_2,\,n-\text{dodecane}]{Na_2MoO_4-MWNT,\,H_2O_2} 2-\text{propanone} \qquad (4)$$

Table 2. The yield of conversion of 2-propanol to 2-propanone by using Na_2MoO_4-MWNT as catalyst

Conversion (wt %)	Time (min)
0	00.00
10	81.89
20	83.27
30	81.26
40	81.63
50	83.58
60	81.70

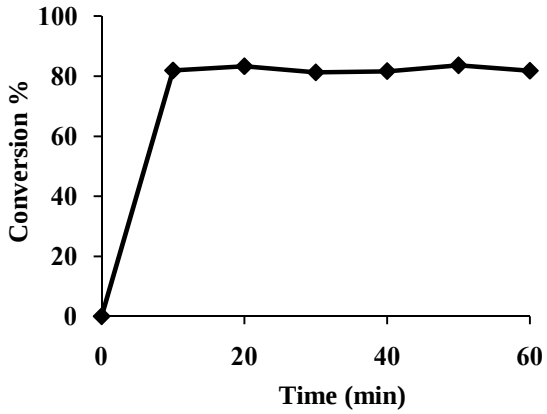


Figure 7. Yield of conversion plot indicated in table 2

Determining the order of reaction the charts of zero, first and second order have plotted, also, for this nano catalytic reaction. Below the plots of first and second order are shown in figures 8 and 9. The charts are plotted up to 30 minutes, because after 25 minutes the reaction reaches to equilibrium. The plot dependent to reaction of zero order have neglected because the values were inconsequential. The plots were shown that the reaction of oxidation of 2-propanol conform to second order.

Therefore, it may be deduced from the plots 8 and 9 that the reaction is rather a second order reaction.

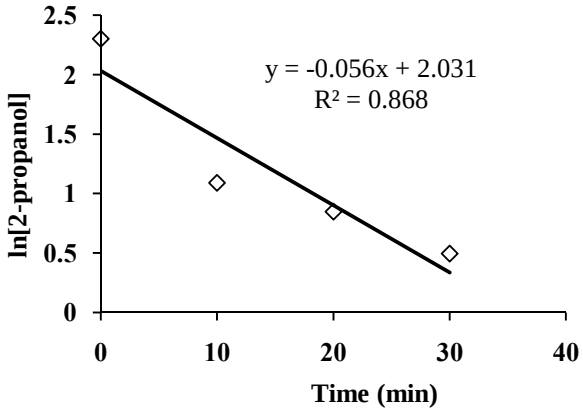


Figure 8. The plot of ln[2-propanol] against time for second order reaction

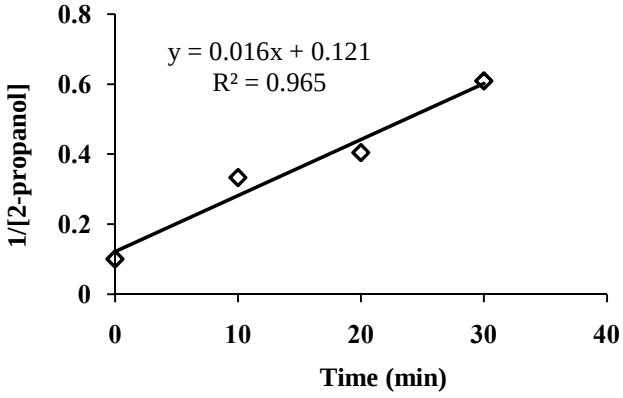


Figure 9. The plot of 1/[2-propanol] against time for time for first order reaction

4- Kinetic study of oxidation off 2-propanol by using $(NH_4)_6Mo_7O_{24}$-MWNT as nano catalyst

The oxidation reaction of 2-propanol by using $(NH_4)_6Mo_7O_{24}$-MWNT was studied as two precedent reactions. The yield of conversion is indicated in table 3 and figure 10. Selectivity of reaction because of single product is always 100 %.

$$2-\text{propanol} \xrightarrow[CH_2Cl_2,\text{n-dodecane}]{(NH_4)_6Mo_7O_{24}-MWNT,H_2O_2} 2-\text{propanone} \qquad (5)$$

Table 3. The yield of conversion of 2-propanol to 2-propanone by using Na_2MoO_4-MWNT as catalyst

Conversion (wt %)	Time (min)
0	00.00
10	88.53
20	93.24
30	95.02
40	92.44
50	88.49
60	69.09

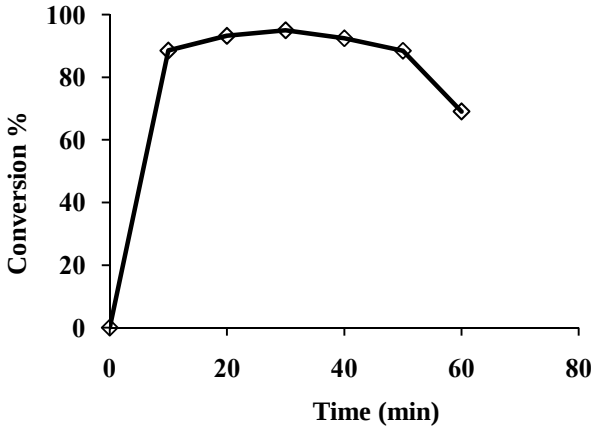


Figure 10. Yield of conversion plot indicated in table 3

Diminution of conversion value above 40 minute probably was due to reversibility of reaction. Determining the order of reaction the chart of zero, first and second order has plotted similar to precedent nano catalytic reactions. As the precedent reactions, the plots are more convenient with a second order reaction. Below the plots of first and second order reactions are shown in figures 11 and 12.

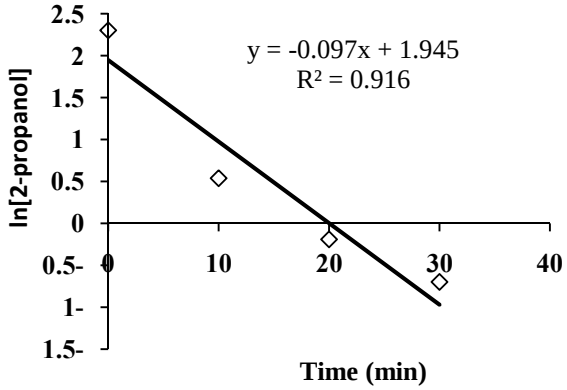


Figure 11. The plot of ln[2-propanol] against time for first order reaction

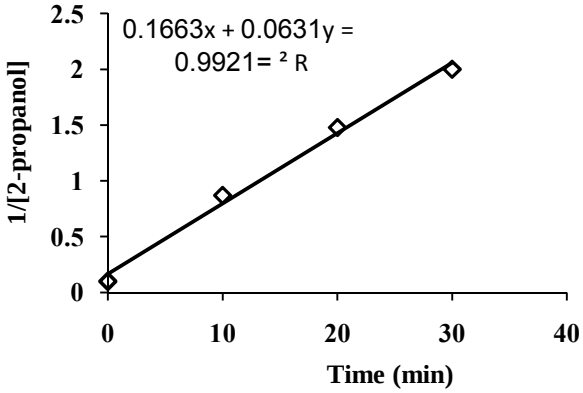


Figure 12. The plot of 1/ [2-propanol] against time for second order reaction

Comparing the results obtained from all plots, it may be deduced that all of these catalytic reactions are of second order and the yield of conversion of 2-propanol to 2-propanone reaction by using $(NH_4)_6Mo_7O_{24}$-MWNT nano catalyst is greater than the others. Table 4 shows the average values of yields of conversion for the reactions using these 3 nano catalysts. Constant of rates of 3 mentioned reactions in presence of 3 different nano catalysts were compared in table 5.

Table 4. The average value of conversion for 3 mentioned cases

Nano catalyst	Conversion (average wt. %)
$(NH_4)_6Mo_7O_{24}$-MWNT	88.53
MoO_5-MWNT	82.00
Na_2MoO_4-MWNT	81.89

Table 5. Comparing the value of constant of rates

Nano catalyst	K (min^{-1})
$(NH_4)_6Mo_7O_{24}$-MWNT	6.3×10^{-2}
MoO_5-MWNT	2.4×10^{-2}
Na_2MoO_4-MWNT	1.8×10^{-2}

Experimental data show that molecularity of oxidation reaction of 2-propanol to 2-propanone in presence of nano catalysts is 2 and on basis of these data proposed relation for rate of reaction is as following:

$$r = k[2-propanol][H_2O_2] \quad (6)$$

Proposed mechanism must be convenient with above relation for reaction rate. Two methods were used for this approach: rate determining-step approximation and steady-state approximation.

5- Determining the equation of rate by using rate determining-step approximation

This approximation assume that the reaction contain one or several reversible reactions which are almost rapid. This follows by a slow reaction which is determining step. Then this step follows by one or several rapid reactions.

Following mechanism may be propose for oxidation reaction of 2-propanol by using MoO_5 – MWNT.

$$MoO_3 - MWNT_{(s)} + H_2O_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} MoO_5 - MWNT \ \text{(Rapid)} \quad (7)$$

$$MoO_5 - MWNT + C_3H_7OH \xrightarrow{K_2} MoO_3 - MWNT + C_3H_6CO + H_2O \ \text{(Slow)} \quad (8)$$

Since second reaction is determining step, thus the relation of reaction rate will be as following:

$$r = k_2[MoO_5 - MWNT][C_3H_7OH] \quad (9)$$

Therefore, the relation (6) must be deducted from relation (9) for proposed mechanism. The constant of equilibrium of equilibrium (7) may be obtained as following.

$$K_{e,1} = \frac{k_1}{k_{-1}} = \frac{[MoO_5 - MWNT]}{[H_2O_2]} \quad (10)$$

And,

$$[MoO_5 - MWNT] = \frac{k_1}{k_{-1}}[H_2O_2] \quad (11)$$

By replacing the relation (11) in relation (9) the relation of reaction rate will be obtain.

$$r = k_2 \frac{k_1}{k_{-1}}[H_2O_2][C_3H_7OH] \quad (12)$$

$$r = k_{obs}[H_2O_2][C_3H_7OH] \quad (13)$$

Then the relation (13) is same as relation (6).

6- Determining the equation of rate by using steady-state approximation

The approximation assumes that formation rate of an intermediate is equal to its expending rate, as its steady-state concentration preserved relatively constant. The supposed reaction has the same rate which indicated in relation (9). Thus in steady-state following relation may be established.

$$\frac{d[MoO_5 - MWNT]}{dt} = k_1[H_2O_2] - k_{-1}[MoO_5 - MWNT] - k_2[MoO_5 - MWNT][CH_3OH] \quad (14)$$

And then,

$$[MoO_5 - MWNT] = \frac{k_1[H_2O_2]}{k_{-1} + k_2[CH_3OH]} \quad (15)$$

By replacing equation (15) in equation (9) the following relation will obtain.

$$r = k_2 \frac{k_1[H_2O_2]}{k_{-1} + k_2[CH_3OH]}[CH_3OH] \quad (16)$$

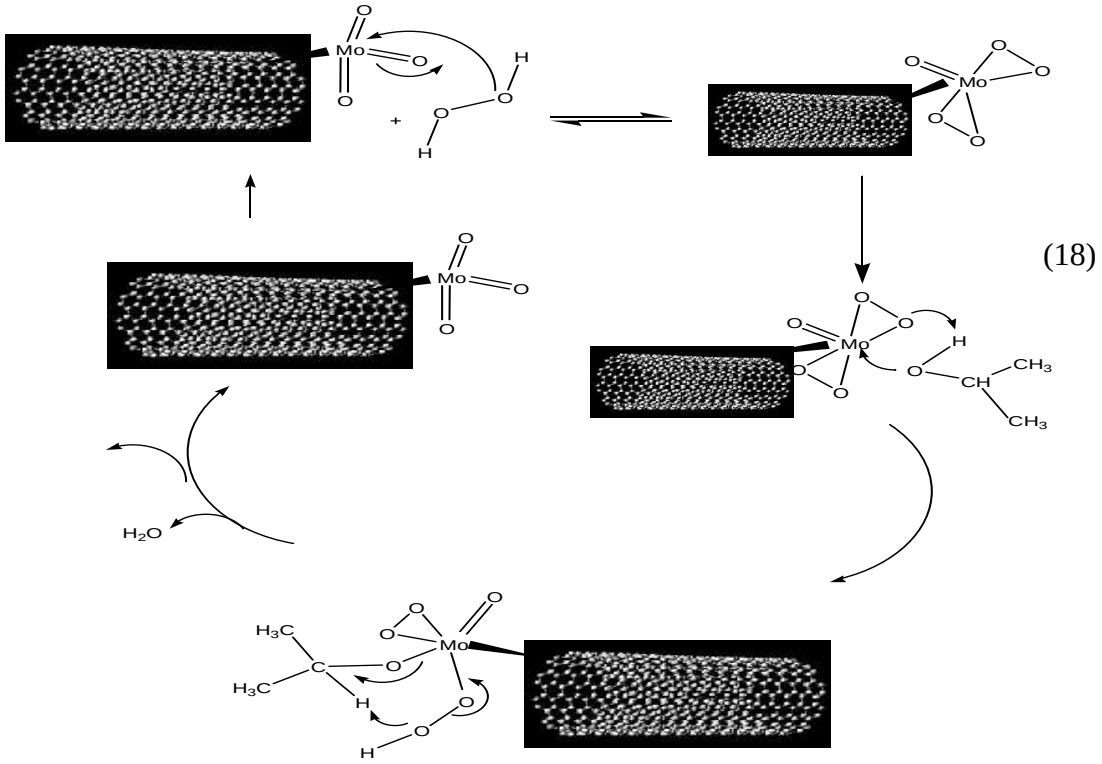
Assuming $k_{-1} >> k_2[C_3H_7OH]$, relation (6) will be obtain.

For example, the rate of reaction catalyzed by $(NH_4)_6Mo_7O_{24}$-MWNT may be calculated as following.

$$r = 0.063(min^{-1}) \times 0.01(mol.L^{-1}) \times 0.03(mol.L^{-1}) = 1.89 \times 10^{-5}(mol.L^{-1}.min^{-1}) \quad (17)$$

7- Proposal of a mechanism on the basis of experimental evidence

Following mechanism may be proposed for catalytic reaction by using MoO_5-MWNT catalyst.



(18)

CONCLUSION

As experimental results show $(NH_4)_6Mo_7O_{24}$-MWNT nano catalyst has better catalytic behavior (88.53% conversion) in comparing with both MoO_5-MWNT and Na_2MoO_4-MWNT nano catalysts. This characteristic may be interpreted as following:

(a) The structure of hepta molybdate has the more Mo-O and Mo=O bindings which increase its catalytic behavior.

(b) Comparing SEM images of these three catalysts, $(NH_4)_6Mo_7O_{24}$ can be well dispersed over MWNT surface, thus this effect gives better catalytic characteristic to $(NH_4)_6Mo_7O_{24}$-MWNT.

Moreover, the reaction of oxidation of 2-propanol by H_2O_2 by using all three nano catalysts has a kinetic of second order. Demonstrating that the above reaction has the molecularity 2, a mechanism proposed by two different approximations, rate determining-step approximation and steady-state approximation. By both approximations the rate equation r = k[2-prppanol][H_2O_2] is the best confirmation of proposed mechanism.

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