New approach on the catalytic oxidation of methanol to formaldehyde over MoO$_3$ supported on nano hydroxyapatite catalysts

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Abstract: Molybdenum oxide (20 wt. %) supported on nano hydroxyapatite mixed was prepared by impregnation method and calcined at 400°C, 500°C, 600°C and 700°C in static air atmosphere. The catalysts were characterized by thermogravimetry (TG), differential thermal analysis (DTA), X-ray diffraction (XRD), Transmission Electron Microscope (TEM) and nitrogen sorption measurements. The gas–phase oxidation of methanol to formaldehyde was carried out in a conventional fixed flow bed reactor. The obtained results clearly revealed that the formation of CaMoO$_4$ spinel nano particles was active and selective catalyst towards the formation of formaldehyde. The maximum yield of formaldehyde was 97% on the catalyst calcined at 400 °C. Moreover, the yield of formaldehyde was found unaffected by increasing the calcination temperature up to 700°C.

Keywords: MoO$_3$; nano hydroxyapatite support; structure; surface area; oxidation; methanol.

1. Introduction
Hydroxyapatite (HAP) has attracted the attention of researchers to biomaterials field in recent years [1]. HAP is a highly non-stoichiometric calcium phosphate compound with a Ca/P molar ratio ranging from 1.5 to 1.67. Moreover, HAP also is known [2] to have the character of both acidic and a basic catalyst when its Ca/P ratio is between 1.5 and 1.67. On the other hand, formaldehyde is obtained from oxidative dehydrogenation of methanol by two commercial processes; (i) On iron-molybdate based catalysts and (ii) On silver based catalysts. In both processes, a conversion of about 99 % and 92 % selectivity respectively are obtained the temperature of reaction is about 400°C in the first and 650°C in the second process. The silver process has high operating costs due to steam consumption. Moreover, the selective oxidation of methanol to formaldehyde takes place on MoO$_3$ mixed oxide catalysts [3,4]. However, the catalytic gas oxidation of methanol to formaldehyde over MoO$_3$ supported on nano hydroxyapatite to our knowledge has not yet been reported. Therefore, the main objective of the present work is synthesis of formaldehyde by oxidative dehydrogenation of methanol over MoO$_3$ (20 wt %) supported on n-HAP as a competitive catalyst with previous applied industrial catalysts.

2. Experimental
2.1. Materials
Methyl alcohol, citric acid, calcium nitrate, diammonium hydrogen phosphate and ammonium hydroxide were obtained as pure reagents and were used without further purification. Ammonium heptamolybdate (AHM) was obtained from Merck, (Darmstadt, Germany).

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2.2. Synthesis of nano hydroxyapatite by sol-gel method
The citric acid sol–gel method [5] has been used for the synthesis of nanocrystalline hydroxyapatite (nHAP) powder from calcium nitrate, diammonium hydrogen phosphate and citric acid. The pH of solution was adjusted by ammonia solution.

2.3. Preparation of nHAP-supported 20 wt. % MoO₃ catalyst
Nano hydroxyapatite supported with 20 % MoO₃ (wt./wt.) was prepared by the impregnation method. The sample produced was dried in an oven at 100°C for 24 h before being calcined at 400°, 500°, 600° and 700° C for 4 h in static air atmosphere, then quenched to room temperature. The prepared catalyst is donated by nHAP20Mo.

2.4. Apparatus and techniques

   **Thermal analysis**
Thermogravimetry (TG) and differential thermal analysis (DTA) thermogravimetry for pure nHAP and AHM supported on HAP were recorded upon heating up to 600°C at 10 °C min⁻¹ and a 40 ml min⁻¹ flow of air atmosphere, using a Shimadzu Thermal Analyzer TA60 Apparatus (Japan).

   **X-ray diffraction (XRD)**
XRD analysis of the catalysts was performed with a Philips diffractometer (Model PW 2103), (The Netherlands) λ = 1.5418 Å, 35 kV and 20 mA with a source of CuKα radiation (Ni filtered). Average particle sizes were estimated from X-ray line width broadening using the Scherrer equation [6].

   **Nitrogen gas adsorption**
Nitrogen gas adsorption-desorption isotherms were measured at -196°C using a Nova 3200 (Quantachrom Instrument Corporation, USA).

   **Catalytic activity measurements**
The catalytic activity of the catalysts for the gas-phase oxidation of methanol was carried out at the reaction temperature of 400° C in a conventional fixed–bed flow type reactor at atmospheric pressure using dry nitrogen as carrier gas. A mixture of methanol and nitrogen was introduced into the reactor after nitrogen was bubbled through methyl alcohol saturator. The total flow rate was fixed at 100 ml min⁻¹ in the gas feed. The gases after reaction were chromatographically analyzed by FID with a Unicam ProGC using a DNP glass column (2m) for analysis of the reaction products of methanol on the tested catalysts.

3. Results and discussion

3.1. Thermal analysis
TG and DTA curves of original catalyst are shown in Fig. (1).The results show that the weight loss can be differentiated into three regions such as (1) 30°–150° C, (2) 150°–250° C and (3) 400°–500° C. In the first region which accompanied with endothermic peak at 120° C, the weight loss is attributed to the removal of physically adsorbed water. The second stage of the weight loss from 150°-250° C which associated with sharp exothermic peak maximized at 190° C is due to the removal of structural water or decomposition of organic constituents. The third stage of the weight loss from 400°-500° C which accompanied with sharp exothermic peak maximized at 475° C, may be corresponded to the CaMoO₄ formation [7].
3.2. X-ray diffraction (XRD)
X-ray diffraction patterns of the powder calcined at 400°C in air atmosphere for 4h were carried out and presented in Fig. (2). Phase analysis was done using PDF card no. 85-0585 for the catalyst n-HAP20Mo, which provide information in the 2θ range of 4°– 80°. The diffractogram of the sample calcined at 400°C shows new peaks are appeared. These peaks may be attributed to the formation of new phase nanocrystalline CaMoO₄. The intensity of peaks of CaMoO₄ is due to planes around (101), (112), (004), (200), (211), (114), (123), (220), (312) and (224).

3.3. Surface area measurements
The specific surface area \( S_{\text{BET}} \) was obtained by applying the BET equation in its normal range of applicability (0.05-0.30 p/p°) and the values are cited in Table (1). From Table (1), it seems that, raising the calcination temperature from 400° up to 700°C led to a continuous decrease in \( S_{\text{BET}} \) values of pure HAP whereas, a sharp decrease in \( S_{\text{BET}} \) value of n-HAP20Mo on calcination at 500°C. This behavior may due to the complete formation of CaMoO₄ which exhibits low surface area. Moreover, from the above, Tables it important to mention here that the sharp reduction in \( S_{\text{BET}} \) value of the n-HAP20Mo calcined at 500°C may be attributed to a remarkable decrease in the total pore volume by 460 % compared to the sample calcined at 400°C. These results are in agreement with the results of thermal analysis in which the formation of CaMoO₄ was found between 400°-500°C.

3.4. Crystallite size determination
The average grain sizes of the catalysts calcined at 400 °C were calculated from XRD line broadening method and specific surface area (S\text{BET}) and TEM. Table (2) shows the average crystallite sizes for the calcination of n-HAP20Mo powders calculated by the above three methods.

Table (1): Texture data variation of S\text{BET} and S\text{t} of n-HAP and n-HAP20Mo catalysts calcined at different temperatures in air atmosphere for 4h.

| Temperature (°C) | S\text{BET} (m² g⁻¹) n-HAP | S\text{BET} (m² g⁻¹) n-HAP20Mo | S\text{t} (m² g⁻¹) n-HAP | S\text{t} (m² g⁻¹) n-HAP20Mo |
|------------------|-----------------------------|-------------------------------|--------------------------|-----------------------------|
| 400              | 56.1                        | 32.1                          | 55.2                     | 31.9                        |
| 500              | 47.3                        | 5.71                          | 47.2                     | 5.61                        |
| 600              | 22.5                        | 4.61                          | 22.4                     | 4.51                        |
| 700              | 19.4                        | 3.22                          | 0.21                     | 3.22                        |

Fig. (2): X-ray diffraction patterns of pure nHAP, nHAP20Mo and pure MoO₃ calcined at 400 °C in a static air atmosphere for 4 h.
3.5. Catalytic activity

The catalytic oxidation of methyl alcohol on n-HAP20Mo calcined at 400°, 500°, 600° and 700° C was carried out at the reaction temperature of 400° C and the results are shown in Fig. (3). It shows that nHAP20Mo is highly active and selective catalyst towards the formation of formaldehyde (major ≈ 97%) and formic acid (minor ≈ 3%) for all calcined catalysts. These results are very interesting not only for the high selectivity of the catalyst towards the formation of formaldehyde but also the capacity of the catalyst unaffected by increasing the calcination temperature, up to 700° C. In addition the selectivity of the catalyst is also, unaffected by the sharp decrease in the surface area as indicated in Table (1). Moreover, it is important to mention here that the formation of CaMoO$_4$ spinel resulted from the interaction between MoO$_3$ and nHAP is accompanying with existence of high oxidation state of molybdenum Mo$^{6+}$. These results are value added to the advantages of our prepared catalyst.

Table (2): Calculated average crystallite size of nHAP20Mo calcined at 400°C.

| Temperature (°C) | Average crystallite size (nm) |
|-----------------|-----------------------------|
|                 | XRD | $S_{BET}$ | TEM |
| 400             | 17.05 | 18.41 | 17.06 |

Fig. (3): Catalytic oxidation of methanol over nHAP20Mo at 400°C at different calcination temperatures.
Conclusions
From the results presented and the discussion above, it can be concluded that:

- nHAP20Mo calcined from 400° up to 700 °C acts as active and selective catalysts towards the formation of formaldehyde. The maximum yield of formaldehyde (≈97%) with low yield of formic acid (≈3%) as a side reaction was obtained.
- The activity and selectivity of nHAP20Mo are unaffected by increasing the calcination temperature up to 700°C.

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