

Synthesis of $\text{Fe}_2(\text{MoO}_4)_3/\text{MoO}_3$ Nanocatalysts by Solution Combustion Approach and Their Catalytic Performance for the Selective Oxidation of Methanol

Ji Hun Ri¹, Jong Hyok Kim^{2*}, Hyon A Ri³, Kwang Son Pak⁴, Jun Ho Kim⁵

Abstract

The $\text{Fe}_2(\text{MoO}_4)_3/\text{MoO}_3$ nanocatalysts comprising $\text{Fe}_2(\text{MoO}_4)_3$ nanoparticles supported on MoO_3 nanorods were synthesized via two-step solution combustion approach and their catalytic performance for the selective oxidation of methanol were evaluated. The materials have been characterised using electron microscopy, powder X-ray diffraction and Raman spectroscopy. First, MoO_3 nanoparticles were prepared by solution combustion reaction employing ammonium nitrate as oxidant, and ammonium molybdate as fuel and Mo source. The synthesized MoO_3 nanoparticles were found to have orthorhombic crystal structure and rod-like shape with width and thickness of 50-200 nm and length of 0.2-1 μm . Then, the MoO_3 nanorods were dispersed in aqueous solution of the ferric nitrate as oxidant and glycine as fuel, and combustion was performed to prepare $\text{MoFeO}_x/\text{MoO}_3$ precursor particles. To investigate the formation process of $\text{Fe}_2(\text{MoO}_4)_3$ phases on MoO_3 nanorods, the precursors were calcined at different temperatures of 300-500°C for 2h. The $\text{Fe}_2(\text{MoO}_4)_3$ phases were not formed on MoO_3 nanorods in samples calcined at 300 and 400°C. The XRD patterns of the samples calcined at 300 and 400°C were consistent with that of the uncalcined sample. The $\text{Fe}_2(\text{MoO}_4)_3/\text{MoO}_3$ nanocatalysts comprising $\text{Fe}_2(\text{MoO}_4)_3$ nanoparticles supported on MoO_3 nanorods were synthesized when the precursor particles were calcined at 500°C for 2h. The size of $\text{Fe}_2(\text{MoO}_4)_3$ phases formed on MoO_3 nanorods was less than 40nm. The catalytic performance of the synthesized $\text{Fe}_2(\text{MoO}_4)_3/\text{MoO}_3$ nanocatalysts for the selective oxidation of methanol to formaldehyde were compared with commercial catalysts. Selectivity to formaldehyde of the synthesized $\text{Fe}_2(\text{MoO}_4)_3/\text{MoO}_3$ nanocatalyst was higher than that of the commercial catalyst.

Keywords: Iron molybdate, Solution combustion, Molybdenum trioxide, Formaldehyde

INTRODUCTION

Formaldehyde is a major raw material widely used in many industrial chemical products such as resins, 1,4-butylene glycol (BDO) and pesticides. In recent years, the annual demand for formaldehyde has exceeded 30 megatons, and the growth of formaldehyde production has been remarkably steady. There are two typical industrial processes for the production of formaldehyde, that is, the dehydrogenation of methanol over silver catalysts and the partial oxidation of methanol over Fe-Mo oxide catalysts. The lower operating temperature and excellent catalytic performance has made the Fe-Mo oxide process more economically viable compared with the silver process [1].

The Fe-Mo oxide catalysts are composed of crystalline $\text{Fe}_2(\text{MoO}_4)_3$ and MoO_3 . MoO_3 has high

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selectivity, low activity, and $\text{Fe}_2(\text{MoO}_4)_3$ has high activity but lower selectivity than MoO_3 . The catalyst consisting of $\text{Fe}_2(\text{MoO}_4)_3$ and MoO_3 exhibits the same activity as pure $\text{Fe}_2(\text{MoO}_4)_3$, and selectivity as pure MoO_3 . Each oxide in the catalyst plays its own specific role, MoO_3 dissociates molecular oxygen into atomic oxygen and $\text{Fe}_2(\text{MoO}_4)_3$ utilizes this atomic oxygen to oxidize methanol to formaldehyde. On the other hand, during the reaction, the Mo component is volatilized forming compounds with methanol, resulting in the formation of Fe_2O_3 with high selectivity to carbon dioxide. In order to prevent loss of MoO_3 , excess MoO_3 phase must be present in the catalyst [2-6].

The demand for formaldehyde has been increasing annually and the catalyst is important in the process, so the research for catalysts continues. In particular, various synthetic methods have been investigated to improve the catalytic performance, to prepare the catalyst more easily and to minimize the environmental pollution during catalyst preparation.

Commercial catalysts are synthesized industrially by coprecipitation method. The coprecipitation method is the most well-studied synthesis method of catalyst. The atomic ratio of Mo and Fe in industrial catalysts synthesized by coprecipitation method is 3 [6-10].

The synthesis of catalysts by sol-gel method has been studied. Generally, the specific surface area of the catalyst prepared by sol-gel method is larger than that of the catalyst by coprecipitation. And the catalyst by sol-gel method can better disperse excess MoO_3 in the $\text{Fe}_2(\text{MoO}_4)_3$ lattice, preventing Mo sublimation and enhancing the stability and selectivity of the catalyst. However, the catalyst by sol-gel method was less active than the catalyst by coprecipitation due to irreversible surface reduction during calcination [11, 12].

The catalysts were also synthesized by hydrothermal method. In the catalysts prepared by other methods, the excess MoO_3 was present as a thermodynamically stable orthorhombic α - MoO_3 phase, whereas in the catalysts produced by hydrothermal process it was present as a metastable hexagonal h- MoO_3 phase. The h- MoO_3 had a smaller specific surface area where the sublimation of molybdenum occurred than α - MoO_3 , and therefore a higher stability [13, 14].

The synthesis of supported catalysts has also been studied. In the synthesis of supported catalysts, the impregnation method was generally used, and the sol-gel method was also used. However, the supported catalyst showed lower catalytic activity compared to the unsupported catalyst due to the interaction between the support and the active site of the catalyst [15, 16].

Guojie Jin and co-workers synthesized the $\text{Fe}_2(\text{MoO}_4)_3/\text{MoO}_3$ nanostructured catalyst by hydrothermal and impregnation processes, assuming that small $\text{Fe}_2(\text{MoO}_4)_3$ particles supported on bulk MoO_3 would be the ideal configuration for a methanol oxidation catalyst [17].

The above mentioned preparation processes based on liquid phase method leads to the consumption of lots of solvent water and simultaneously produces large amount of industrial wastewater containing ferric, molybdenum and ammonium salt, which are environmentally unfavorable. In addition, the physicochemical properties of catalyst are dramatically influenced by multiple preparation factors such as pH and concentration of the solution. To overcome these drawbacks, mechanochemical methods have been investigated. The mechanochemical method is solvent-free and simplified, thus can easily be implemented in industrial-scale applications [18-22].

The solution combustion is an effective method for synthesis of nano-size materials. The solution combustion method is a very economical method to synthesize nanopowders easily and rapidly with simple equipment. No wastewater is produced in this method [23-27].

However, there are few reports on the synthesis of Fe-Mo oxide catalysts by solution combustion. Synthesis of the $\text{Fe}_2(\text{MoO}_4)_3$ as a photocatalyst and a battery material by solution combustion method were reported in the literature [28] and [29].

Hence, the aim in this paper is to investigate a novel synthesis method of Fe-Mo oxide catalyst based on solution combustion. In this study, we synthesized $\text{Fe}_2(\text{MoO}_4)_3/\text{MoO}_3$ nanocatalysts comprising $\text{Fe}_2(\text{MoO}_4)_3$ nanoparticles supported on MoO_3 nanorods via two-step solution combustion approach and tested their catalytic performance for the selective oxidation of methanol.

EXPERIMENTAL

Catalyst Synthesis

Synthesis of MoO_3 Nanorods

MoO_3 nanorods were synthesized by solution combustion method. Ammonium molybdate ($(\text{NH}_4)_2\text{MoO}_4$) was used as the fuel and Mo source, and ammonium nitrate (NH_4NO_3) was used as the oxidant.

All reagents used in the experiments were of analytical grade and used without further purification.

7.2 g of MoO_3 was dissolved in 80 mL of 5wt.% ammonia water at 60 °C under stirring to prepare ammonium molybdate solution. 12 g of ammonium nitrate was dissolved in 20 mL of distilled water and mixed with ammonium molybdate solution. The quartz beaker with this mixed solution was heated using a hot plate kept at 400 °C. Once the majority of the water was evaporated, instantaneous combustion occurred with generation of a large amount of smoke, resulting in formation of grey MoO_3 nanopowders.

Synthesis of $\text{Fe}_2(\text{MoO}_4)_3/\text{MoO}_3$ Nanocatalysts

The $\text{Fe}_2(\text{MoO}_4)_3/\text{MoO}_3$ nanocatalysts comprising $\text{Fe}_2(\text{MoO}_4)_3$ nanoparticles supported on MoO_3 nanorods were synthesized via the following procedures.

According to Mo/Fe molar ratio=3, weigh MoO_3 nanopowders and ferric nitrate hydrate($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$). Then, the amount of glycine($\text{CH}_2\text{NH}_2\text{CO}_2\text{H}$) that could be equivalently reacted with ferric nitrate was weighed. Ferric nitrate and glycine were dissolved in appropriate amount of distilled water and, then MoO_3 nanopowders were added and dispersed in the solution. The obtained suspension was transferred to a quartz beaker and then heated using a hot plate kept at 400 °C. Soon water evaporated and the combustion reaction occurred, resulting in the formation of precursor. The resultant precursor was then calcined in air to form the $\text{Fe}_2(\text{MoO}_4)_3$ phase via solid-state reaction between the MoO_3 support and the Fe component. The temperature and time of the calcination step were systematically varied to investigate the influence of these parameters on the $\text{Fe}_2(\text{MoO}_4)_3$ formation. The powder calcined at 500 °C for 2h was light green-yellow color.

Catalyst Characterisation

The XRD, Raman spectroscopy and SEM were performed to obtain composition, morphology and structural information of the synthesized samples.

XRD patterns of all samples were collected with X-ray diffractometer RINT-2000 using $\text{CuK}\alpha$ ($\lambda=1.54056\text{\AA}$) according to the Joint Committee on Powder Diffraction Standards(JCPDS) card. SEM and Raman spectroscopy were performed using scanning electron microscope JSM-6610A and raman spectrometer LRS-5 using a green laser ($\lambda=532\text{ nm}$) as an excitation source.

Catalyst Testing

The catalysts were tested for the oxidation of methanol to formaldehyde in a fixed-bed micro-reactor at atmospheric pressure [18-20].

The catalyst was pressed before being sieved to yield particles between 150 and 250 μm . Typically, 0.5 g of catalyst was placed in a quartz U type reactor tube (I.D = 8 mm) held between plugs of quartz

wool. The reactor was placed in a tubular furnace and the temperature of the reactor was controlled and measured using the thermocouple fixed in the middle of the catalyst bed. The total feed flow rate was fixed at 100 mL/min, the flow rates of nitrogen, oxygen and methanol vapor were 85, 10 and 5 mL/min, respectively. The stainless steel pipe line between the reactor and the gas absorber was heated using temperature-controlled resistance wire to prevent any condensation of methanol and the products. The catalytic performances of all catalysts were tested under 285 °C. The outlet gas mixture was firstly absorbed by the given mass deionized water, and then the methanol content was analyzed by GC-14B gas chromatograph. The formaldehyde content in this reaction was determined by the bisulfite method. Measurements of the conversion were recorded after 4 h from the initial introduction of methanol into the reactor.

The methanol conversion of catalyst was evaluated by the molar ratio of the consumed methanol to supplied methanol, and the selectivity to formaldehyde was determined by the molar ratio of the produced formaldehyde to consumed methanol.

RESULTS AND DISCUSSION

MoO₃ Nanorods

(NH₄)₂MoO₄ is a water-soluble metal compound and has a reducing valency of +6. It contains H and N elements in composition that can be burned to release a large amount of heat and gas, and when heated it produce NH₃ which ignite with NO_x. These are some important criteria for fuel in solution combustion reactions [23]. Therefore, ammonium molybdate can be used as Mo source and fuel in solution combustion reaction to synthesize nano molybdenum oxide. In this case, ammonium nitrate can be selected as oxidant. The stoichiometric combustion equation between ammonium nitrate and ammonium molybdate can be written as



XRD, Raman spectroscopy and SEM results show that MoO₃ nanoparticles were successfully synthesized by the solution combustion reaction.

Figure 1 shows the XRD pattern of the synthesized MoO₃ nanoparticles. The obtained pattern is well matched with standard data file of α-MoO₃ (JCPDS:05-0508). It has been confirmed that the MoO₃ nanoparticles are having orthorhombic crystal structure. From the strong and sharp diffraction peaks, it can be seen that the prepared powders have high crystallinity. In particular, the peaks of the (0 k 0) planes show stronger intensities compared to the other (h k l) planes, indicating that the synthesized α-MoO₃ nanoparticles have a higher anisotropy.

The Raman spectra of the synthesized MoO₃ nanoparticles is shown in Figure 2. Raman spectroscopy also confirm that the nanoparticles are α-MoO₃. The Raman peak at 995cm⁻¹ is assigned to the stretching mode of terminal oxygen (Mo=O). The presence of Raman peak at 820cm⁻¹ indicates the stretching mode of doubly coordinated oxygen (Mo-O-Mo). The peak at 665cm⁻¹ corresponds to the stretching mode of triply coordinated oxygen (Mo₃-O), where the edge-shared oxygens are in common to three MoO₆ octahedra. These peaks are considered as the fingerprints of the α-MoO₃ phase. The bending and scissoring modes of Mo₃-O are observed at 337 and 378cm⁻¹, respectively. The peak at 287cm⁻¹ is related to double bond O=Mo=O and the peak at 168cm⁻¹ is related to lattice vibrations [30, 31].

Figure 3 shows the SEM micrograph images of synthesized MoO₃ nanoparticles. It reveals that the MoO₃ nanoparticles have rod-like structure with roughly uneven size with width and thickness of 50–200nm, and length of 0.2–1μm.

Generally, MoO₃ nanoparticles are synthesized by precipitation and hydrothermal methods. The MoO₃ nanoparticles prepared by these methods are also rod-like. Their width and thickness are varying between 300nm and 2μm, and length is varying between 1 and 40μm [30-33].

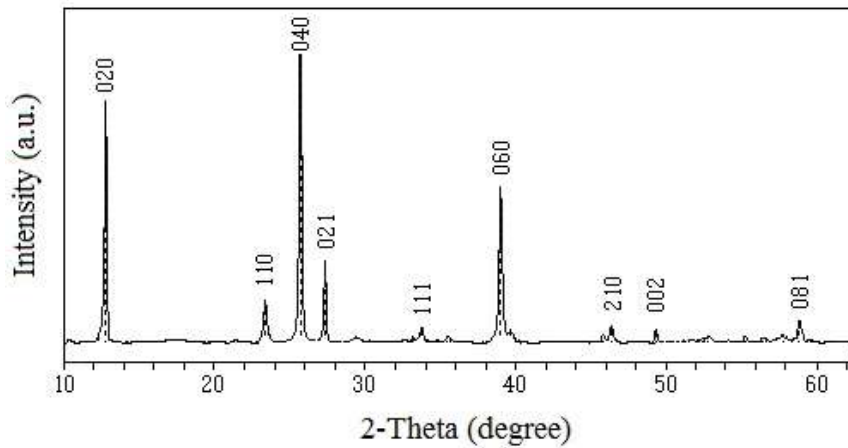


Figure 1. XRD pattern of MoO₃ nanoparticles.

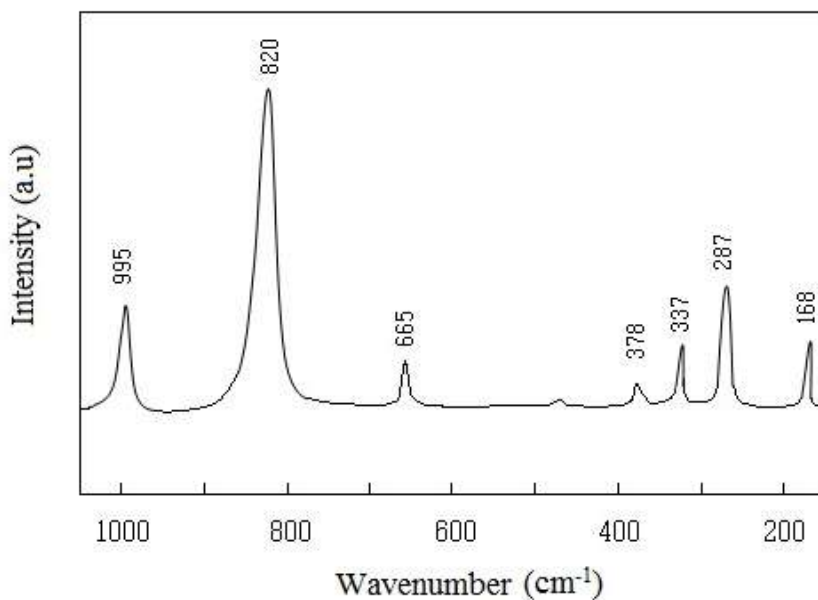


Figure 2. Raman spectra of MoO₃ nanoparticles.

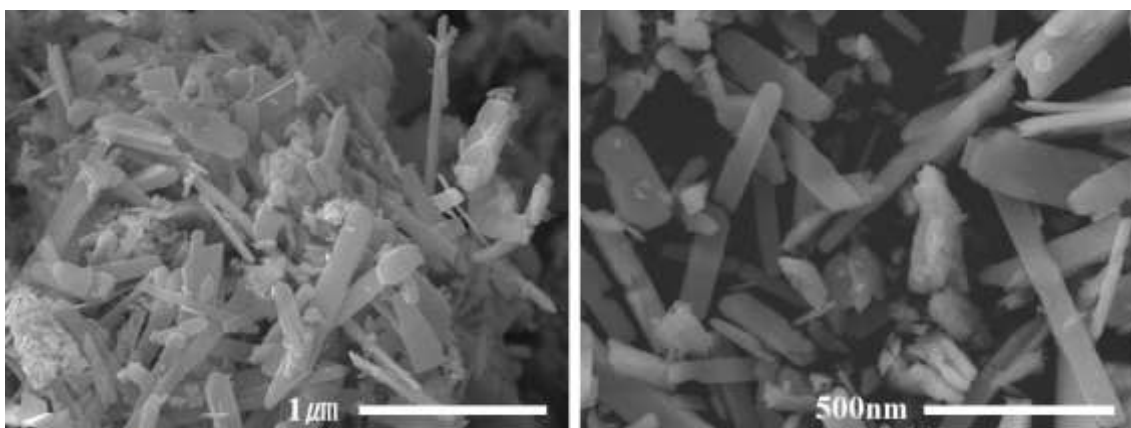


Figure 3. SEM image of MoO₃ nanoparticles.

The novel synthesis method of MoO₃ nanoparticles based on solution combustion reaction is very simple in the process and the size of the synthesized particles is smaller compared to the precipitation and hydrothermal methods.

$\text{Fe}_2(\text{MoO}_4)_3/\text{MoO}_3$ nanocatalysts

XRD analysis for precursor prepared by combustion reaction of mixing solution of the ferric nitrate and glycine dispersed MoO_3 nanorods was performed.

Figure 4a shows the XRD pattern of the precursor powders. The combustion product between ferric nitrate and glycine is Fe_2O_3 [26, 27]. Thus, it was expected that the precursor would consist of molybdenum oxide and iron oxide phases. However, unlike the prediction, only MoO_3 phase was observed and no iron oxide phase was observed in the XRD pattern. Of course, the XRD pattern of the precursor is different from that of the pure MoO_3 . Compared with Figure 1, the peak intensity of the (0 k 0) planes decreased and the peak intensity of other planes increased. After the solution combustion reaction, the peak positions were unchanged and the peak intensities changed in the XRD pattern of MoO_3 powders, indicating that the iron component interacts with MoO_3 phase to form a solid solution. When the solution combustion reaction between ferric nitrate and glycine occurs, the temperature of the reaction system increases instantaneously to about 1 500°C. At such high temperature, the MoFeO_x solid solution could be formed by the interaction between MoO_3 phase and iron compounds. That is, the precursor consists of the MoFeO_x solid solution supported on the MoO_3 nanorods.

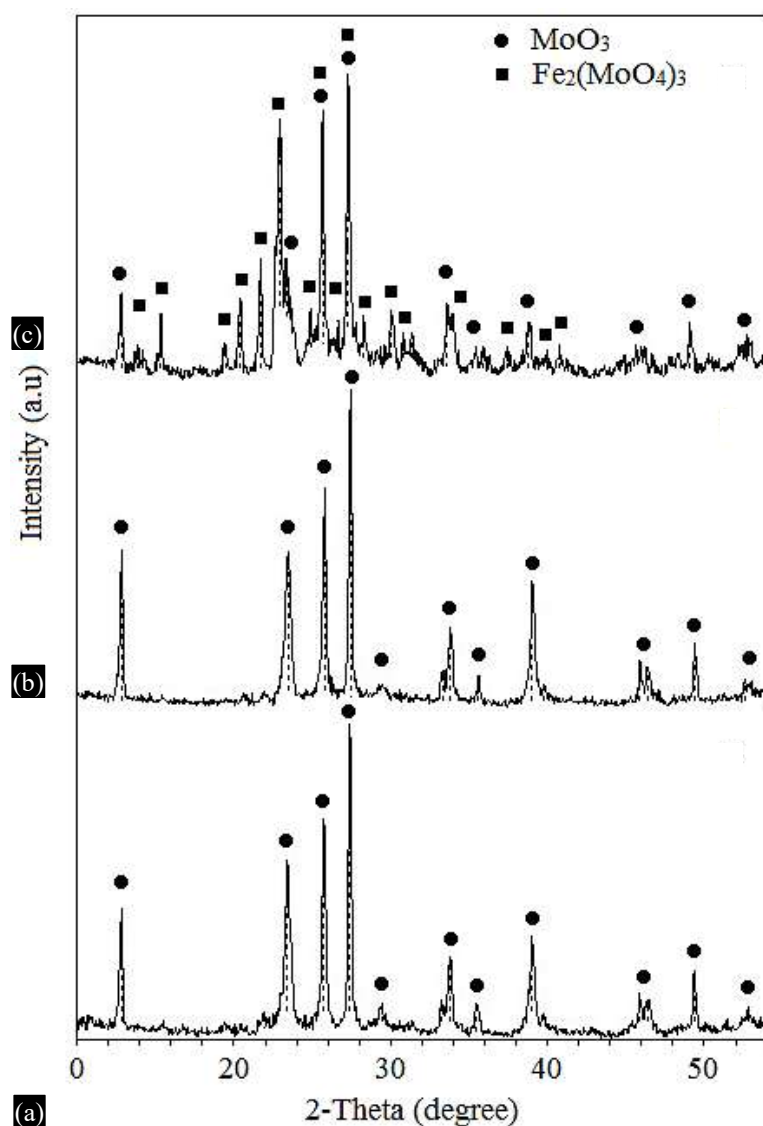


Figure 4. XRD patterns of samples calcined at different temperatures for 2h: (a) uncalcined sample; (b) 400°C; (c) 500°C

To investigate the formation process of $\text{Fe}_2(\text{MoO}_4)_3$ phases on MoO_3 nanorods, the precursors were calcined at different temperatures of 300-500 °C for 2h. After calcination, the samples were analysed by the XRD.

The XRD patterns of the samples calcined at 300 and 400 °C were consistent with that of the uncalcined sample. The XRD pattern of the sample calcined at 400 °C is shown in Fig. 4b. It states that no $\text{Fe}_2(\text{MoO}_4)_3$ phase is formed and MoFeO_x solid solution still exists on MoO_3 nanorods even at 400 °C. Figure 4c shows the XRD pattern of the sample calcined at 500 °C. The XRD pattern of this sample is consistent with the standard data of α - MoO_3 (JCPDS:05-0508) and standard data of $\text{Fe}_2(\text{MoO}_4)_3$ (JCPDS:31-0642). It indicates that the MoFeO_x solid solution is transformed into the $\text{Fe}_2(\text{MoO}_4)_3$ phase on the MoO_3 nanorods at 500°C.

Next, after calcination of precursors at 400 °C for different times of 3~48h, calcined samples were analysed by the XRD. The XRD patterns of samples calcined for less than 18h revealed only peaks of MoO_3 phase as in Figure 4b. On the other hand, the XRD patterns of the samples calcined for more than 24h revealed peaks of MoO_3 and $\text{Fe}_2(\text{MoO}_4)_3$ phases as in Figure 4c. It suggests that the MoFeO_x solid solution formed on the MoO_3 nanorods is gradually transformed into the $\text{Fe}_2(\text{MoO}_4)_3$ phase with increasing calcination time.

As can be seen from the XRD analysis results, the precursors should be calcined at 400 °C for 24h or at 500 °C for 2h to form $\text{Fe}_2(\text{MoO}_4)_3$ phase on MoO_3 nanorods. The calcination condition was chosen to be 500 °C and 2h, because the calcination time was too long at 400°C.

Figure 5 shows the Raman spectra of the sample calcined at 500 °C for 2h. The Raman spectra indicates that $\text{Fe}_2(\text{MoO}_4)_3$ phases were successfully formed on MoO_3 nanorods. As discussed above, the Raman peaks at 995, 820, 665, 378, 337, 287, and 168 cm^{-1} are the peaks are related to α - MoO_3 . And the Raman peaks at 968 and 783 cm^{-1} are associated with $\text{Fe}_2(\text{MoO}_4)_3$. The Raman peak at 968 cm^{-1} is assigned to the stretching mode of the terminal Mo=O bond within the $\text{Fe}_2(\text{MoO}_4)_3$ phase, and the peak at 783 cm^{-1} to stretching mode of the Mo-O-Mo bond within the $\text{Fe}_2(\text{MoO}_4)_3$ phase [19, 20].

Figure 6 shows the SEM micrograph images of the sample calcined at 500 °C for 2h. As can be seen from images, the small islands were formed on the MoO_3 nanorods. The XRD and Raman spectroscopy analysis indicate that these islands are just $\text{Fe}_2(\text{MoO}_4)_3$ phases. The size of the $\text{Fe}_2(\text{MoO}_4)_3$ phases is less than 40nm.

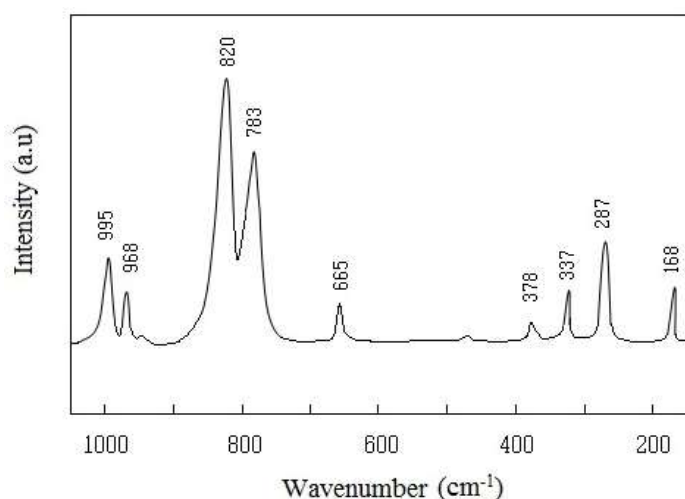


Figure 5. Raman spectra of $\text{Fe}_2(\text{MoO}_4)_3/\text{MoO}_3$ nanocatalysts.

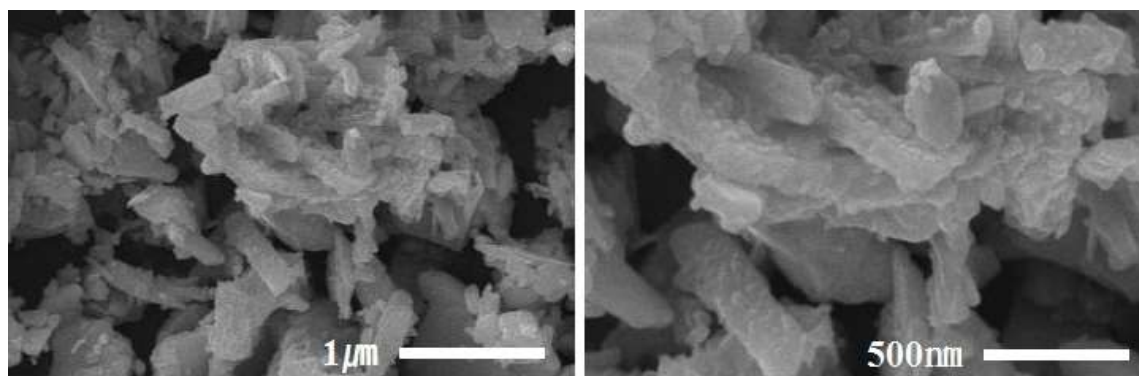


Figure 6. SEM image of $\text{Fe}_2(\text{MoO}_4)_3/\text{MoO}_3$ nanocatalysts.

Table 1. Methanol conversion and formaldehyde selectivity of catalysts.

Catalysts	Methanol conversion (%)	Formaldehyde selectivity (%)
Catalyst prepared by uncalcined precursor ($\text{MoFeO}_x/\text{MoO}_3$)	71.30	82.05
Catalyst prepared by calcined powders ($\text{Fe}_2(\text{MoO}_4)_3/\text{MoO}_3$)	100	97.82
Commercial catalyst ($\text{Fe}_2(\text{MoO}_4)_3\text{-MoO}_3$)	100	94.86

The performance of Fe-Mo oxide catalysts for the oxidation of methanol to formaldehyde is greatly affected by the atomic ratio between Mo and Fe. Regardless of the preparation methods, the catalysts with an Mo:Fe atomic ratio of 2.2~2.6:1 showed the best catalytic performance [7, 17, 19, 21]. However, catalysts with Mo/Fe = 3 are used in industry to increase the catalyst lifetime [10, 11, 16].

Hence, in this study, $\text{Fe}_2(\text{MoO}_4)_3/\text{MoO}_3$ nanocatalysts with Mo/Fe = 3 were prepared and their performance were compared with commercial catalysts. The results of catalytic tests are given in Table 1.

The conversion and selectivity of the catalyst prepared by the uncalcined precursor are low. The reason is that $\text{Fe}_2(\text{MoO}_4)_3$ phase which is the main active phase was not formed in the catalyst. On the other hand, the performance of $\text{Fe}_2(\text{MoO}_4)_3/\text{MoO}_3$ nanocatalyst prepared by solution combustion approach is better than that of commercial catalyst. The methanol conversion was 100% for both catalysts. But the formaldehyde selectivity of the prepared catalyst was higher than that of the commercial catalyst. The higher selectivity of the $\text{Fe}_2(\text{MoO}_4)_3/\text{MoO}_3$ nanocatalyst is attributed to its structural character. In $\text{Fe}_2(\text{MoO}_4)_3\text{-MoO}_3$ catalysts prepared by coprecipitation, sol-gel, hydrothermal and mechanochemical methods, the $\text{Fe}_2(\text{MoO}_4)_3$ and MoO_3 phases are dispersed mutually. It can be seen from the SEM images of these catalysts [6, 11, 13, 18]. However, in the $\text{Fe}_2(\text{MoO}_4)_3/\text{MoO}_3$ nanocatalyst prepared in this study, the $\text{Fe}_2(\text{MoO}_4)_3$ phases were formed on the MoO_3 particles. Therefore, close contact between the surface $\text{Fe}_2(\text{MoO}_4)_3$ phases and MoO_3 support particles is achieved, and thus the synergistic effect between the two phases can be pronounced. In the literature [17], it was also claimed that highly dispersed, small $\text{Fe}_2(\text{MoO}_4)_3$ particles supported on bulk MoO_3 would be the ideal configuration for a methanol oxidation catalyst, because this structure would maximise both the iron molybdate surface area and the size of the interface between MoO_3 and $\text{Fe}_2(\text{MoO}_4)_3$ phases, which are thought to be key parameters influencing catalyst performance.

In this study, $\text{Fe}_2(\text{MoO}_4)_3/\text{MoO}_3$ nanocatalysts with ideal configuration for the oxidation of methanol to formaldehyde were prepared relatively easily by solution combustion approach. The formation process of the $\text{Fe}_2(\text{MoO}_4)_3/\text{MoO}_3$ nanocatalysts via two-step solution combustion reactions and calcination is shown in Figure 7.

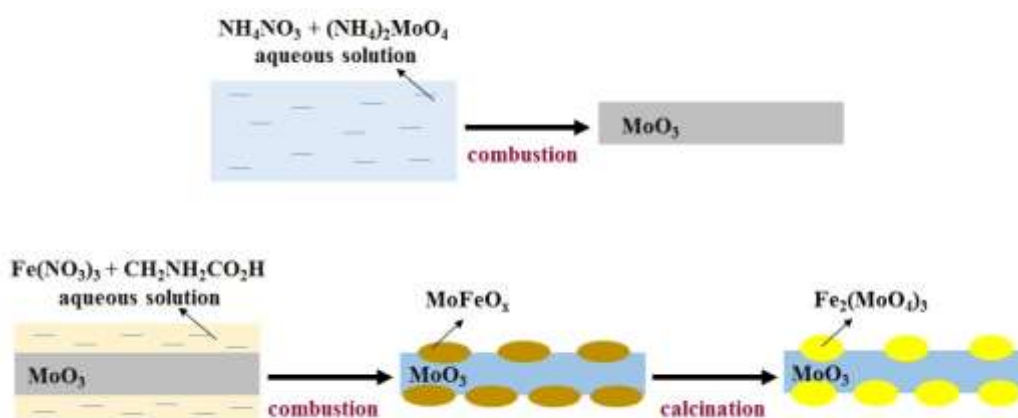


Figure 7. Schematic diagram depicting the formation sequence of Fe₂(MoO₄)₃/MoO₃ nanocatalysts.

CONCLUSION

The Fe₂(MoO₄)₃/MoO₃ nanocatalysts were synthesized via two-step solution combustion approach and their catalytic performance were tested for the selective oxidation of methanol. In the first stage of solution combustion, MoO₃ nanoparticles were synthesized using ammonium nitrate as oxidant and ammonium molybdate as fuel. The morphology of the synthesized MoO₃ nanoparticles are rod-like, their width and thickness are varying between 50 and 200 nm, and length is varying between 0.2 and 1 μm.

In the second stage, MoO₃ nanorods were dispersed in aqueous solution of the ferric nitrate (oxidant) and glycine (fuel), and combustion was performed to prepare MoFeO_x/MoO₃ precursor particles. These precursor particles were then calcined. During calcination at 500 °C for 2h, the MoFeO_x solid solution phase was transformed into the Fe₂(MoO₄)₃ phase.

The XRD, Raman spectroscopy and SEM analysis showed that the Fe₂(MoO₄)₃/MoO₃ nanocatalysts comprising Fe₂(MoO₄)₃ nanoparticles supported on MoO₃ nanorods were successfully synthesized. The size of Fe₂(MoO₄)₃ phases formed on MoO₃ nanorods was less than 40 nm.

The prepared Fe₂(MoO₄)₃/MoO₃ nanocatalyst had better catalytic performance than the commercial catalyst. The synthesis method of Fe₂(MoO₄)₃/MoO₃ nanocatalysts based on solution combustion approach could be easily applied to the production of industrial Fe-Mo oxide catalysts due to simplicity of the process and good performance of the synthesized catalyst.

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