Facile method for synthesis of nanosized $\beta$–MoO$_3$ and their catalytic behavior for selective oxidation of methanol to formaldehyde

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Abstract

$\beta$-MoO$_3$ was successfully synthesized from all commercial materials using a fast, effective and simple method and characterized by differential scanning calorimetry, x-ray powder diffraction, field emission scanning electron microscopy, infrared and Raman spectroscopy. The prepared sample was highly active and selective to formaldehyde formation from methanol over a wide range of reaction temperatures. $\beta$-MoO$_3$ catalyst also exhibited stable methanol conversion and formaldehyde selectivity at around 84% and over 95% respectively for over 15 operating hours at 320 $^\circ$C. However, it may be deactivated at elevated reaction temperature due to transformation of metastable to stable phase. It was revealed that the prepared catalyst maintains its high selectivity to formaldehyde during deactivation. This can be considered as an advantage of the prepared MoO$_3$ catalyst in comparison with the industrial one.

Keywords: methanol oxidation, formaldehyde, molybdenum trioxide, monoclinic MoO$_3$

Classification numbers: 5.06

1. Introduction

Molybdenum trioxide is one of the most interesting transition metal oxides due to its outstanding catalytic properties in methanol selective oxidation [1–3], hydrocarbon selective oxidation [4] or photocatalyst [5–7]. Therefore it is the major component of many industrial catalysts such as iron molybdates based catalyst which are widely used for the industrial production of formaldehyde from methanol. Although Fe$_2$(MoO$_4$)$_3$ is found to be more active than MoO$_3$ for formaldehyde formation due to the larger density of exposed catalytic active sites of isotropic Fe$_2$(MoO$_4$)$_3$ than that of anisotropic MoO$_3$ [8, 9], the commercial catalysts always have a large excess of molybdenum [10]. The presence of MoO$_3$ phase in addition to Fe$_2$(MoO$_4$)$_3$ is always detected. However, the role of these phases in selective methanol oxidation is still controversial. Many authors consider that the active phase is stoichiometric iron molybdate and an excess MoO$_3$ is only required to prevent the catalyst deactivation due to sublimation of MoO$_3$ [11–13] while some recent studies reveal that surface MoO$_3$ species are the active sites in iron molybdate catalysts and a Mo excess is needed to replenish the sublimated ones [14–16]. Moreover, the presence of Fe in iron molybdate catalysts or in Fe$_2$O$_3$ which is used as a support material make these catalysts to be more easily deactivated [11–13] or less selective than unsupported MoO$_3$ [16]. Thus, study on an alternative for formaldehyde production from methanol is still of interests.

Generally, molybdenum trioxide has three well-known polymorphs: the thermodynamically stable orthohombic $\alpha$-MoO$_3$, metastable monoclinic $\beta$-MoO$_3$ [17, 18] and hexagonal h-MoO$_3$ [19–21]. Metastable phases have been reported to be superior to stable $\alpha$-MoO$_3$ in catalysis and electrochemical applications [22, 23]; however, producing
metastable materials is usually more complicated. Among these metastable phases, hexagonal MoO₃ seems to be thoroughly investigated [24] because it can be synthesized from many kinds of molybdenum-containing precursor, such as ammonium molybdate, molybdic acid, polyoxomolybdate. On the contrary, a limited study has been successful in synthesis of the metastable β-MoO₃ phase partly due to the difficulty in finding suitable molybdenum source [25]. Dehydration of blue molybdic acid solution which is obtained via cation exchange of Na₂MoO₄ solution has been used as the most common method to prepare β-MoO₃ since the first successful synthesis by McCarron [17] till now. However, this method consumes a lot of water and also has very low yield. Mizushima et al [23] reported that the Mo content in the final solution was only 3.3% of the initial value. Some research groups tried to synthesize β-MoO₃ from other molybdenum sources, such as peroxo-polyoxomolybdate [26], commercial α-MoO₃ [27] or sodium molybdate solution [28] but these efforts were unsuccessful since the stable α-MoO₃ was usually detected in the final product. Therefore, a metastable β-MoO₃ which has been reported to have high catalytic property in methanol oxidation to formaldehyde [23, 27, 29] due to the overall symmetry of this phase, may exhibit potential application for HCHO production. However, this prospect has not been shown till now because of the complicated and ineffective synthesis method as mentioned before.

In this study β-MoO₃ was successfully synthesized by a novel method from commercially available molybdic acid powder. The prepared sample exhibited excellent catalytic properties in partial oxidation of methanol to formaldehyde.

2. Experimental

2.1. Materials

Molybdic acid (H₂MoO₄, powder) and α-MoO₃ was supplied by Sigma-Aldrich; 37% HCl solution, 68% HNO₃ solution and high purity methanol (99.99%) were purchased from Merck. The entire chemicals were used as received without any further purification.

2.2. Catalysts preparation

4 g of commercial molybdic acid was dissolved in 36 ml of 37% HCl solution to prepare a yellowish transparent solution. 3 ml of 68% HNO₃ solution was then added and the received solution was aged at 90 °C for 30 min before evacuated at this temperature for 30 min and 150 °C for 1 h to eliminate HCl and water. The as-received powder was then transferred into a quartz reactor and subsequently calcined at 350 °C with a heating rate of 10 °C min⁻¹ for 2 h in an air flow of 25 ml min⁻¹ to get β-MoO₃.

2.3. Characterization

The samples were characterized with differential scanning calorimetry (DSC), x-ray powder diffraction (powder XRD), field emission scanning electron microscopy (FE-SEM), infrared (IR) and Raman spectroscopy. DSC measurement was carried out on a Setaram Labsys Evo in 20 ml min⁻¹ of air flow with heating rate of 10 °C min⁻¹ from room temperature to 500 °C.

Powder XRD patterns were obtained by a powder x-ray diffractometer (ULTIMA IV, Rigaku) with Cu-Kα radiation operating at 30 kV and 20 mA from 10° to 70° with a scanning speed of 2° min⁻¹ and scanning step of 0.03°. The morphologies and microstructures of the synthesized products were characterized using a FE-SEM (JSM-5700F, JEOL, Japan) operating at 20 kV.

Fourier transform infrared spectra were recorded on a Bruker Tensor 27 spectrometer (Germany) using KBr pellets in the 4000–400 cm⁻¹ region. Raman measurements were carried out at ambient condition using a Labram-HR (Horiba Jobin Yvon) spectrometer. Raman scattering was excited at 632.8 nm by means of a HeNe laser. The laser beam was focused using an objective lens (50×) with laser power less than 5 mW and 0.5 cm⁻¹ of resolution. The system was calibrated with SiO₂/Si wafer with peak at 520 ± 0.5 cm⁻¹.

2.4. Partial oxidation of methanol

The oxidation of methanol was carried out using a fixed bed quartz reactor (500 mm length and 10 mm inner diameter) at atmospheric pressure. Feed mixture of 6.2% (v/v) methanol in air was prepared by bubbling air into methanol at 5 °C. An amount of 0.15 g catalyst (0.25–0.5 mm) was mixed with quartz of the same size at ratio of 1/3 (v/v) and used for each run. The catalyst was activated at 350 °C for 1 h in air flow of 25 ml min⁻¹ and then evaluated at varying temperature and feed flow rate. The reaction was left to reach the steady state for 2 h before analyzing all products. CO and CO₂ were continuously recorded by a gas sensor (Senko); methanol, formaldehyde, methylformate (MF), dimethylether (DME) and dimethoxymethane were analyzed on a gas chromatography HP 5890 Series II equipped with a TCD detector and HP-Plot U capillary column (30 m × 0.32 mm × 10 μm) by ChemStation Software.

3. Results and discussion

3.1. Catalyst characterization

The DSC curve of the prepared β-MoO₃ was shown in figure 1. An exothermic peak at around 433 °C shows the phase transformation from metastable phase to stable α-MoO₃. This phase transformation temperature lies in the range of reported results. The highest known phase transition temperature from β to α-MoO₃ is 450 °C [17], and the lowest one is 387 °C [23]. Moreover, the existence of only one exothermic peak may be considered as a proof of pure metastable MoO₃ phase presented in our sample.

In order to study the crystalline structure of the prepared samples, an XRD measurement was carried out. Figure 2 shows the XRD patterns of commercial molybdic acid,
commercial $\alpha$-MoO$_3$ powder and the as-prepared molybdenum oxide powder. For comparative purposes, the XRD pattern of $\beta$-MoO$_3$ produced by Mizushima’s method [23] was also included. None of typical peaks of H$_2$MoO$_4$ precursor as well as stable phase was detected in XRD profile of the prepared sample. As can be seen in curve d of figure 2, the prepared $\beta$-MoO$_3$ exhibits two sharp peaks located at $2\theta = 22.9^\circ$ and $24.9^\circ$ which were assigned to the characteristic reflections from (011) and (200) planes of $\beta$-MoO$_3$ (JCPDS 47-1081), respectively. These peaks are also excellently fixed with the XRD patterns of the $\beta$-MoO$_3$ produced by Mizushima’s method (curve c in figure 2). The results shown that similar product which contains pure $\beta$-MoO$_3$ can be easily obtained by using a more simple and effective method.

Additional information regarding structure change during transformations of MoO$_3$ phases was obtained using Raman spectroscopy. Figure 3 presents the Raman spectra of the commercial H$_2$MoO$_4$, commercial $\alpha$-MoO$_3$, $\beta$-MoO$_3$ produced by Mizushima’s method [23] and the prepared MoO$_3$ sample. As cited in literature, there are three types of stretching vibrations that can be used to identify $\alpha$-MoO$_3$: (1) a sharp peak at 996 cm$^{-1}$ due to stretching vibration of Mo = O; (2) a very strong and well-defined peak at 820 cm$^{-1}$ originated from stretching vibrations of Mo–O–Mo groups; and (3) a couple of weak peaks at 666 and 472 cm$^{-1}$ is characteristic of the vibrations of Mo$_2$O$_2$ units formed by edge shared Mo$_6$ octahedra [30–34]. Three well-defined peaks centered at 991, 816, and 663 cm$^{-1}$ were detected in the case of commercial $\alpha$-MoO$_3$ powders as can be seen in curve b of figure 3; however, no Raman peak at around 990 cm$^{-1}$ and 400–700 cm$^{-1}$ was observed in the case of prepared $\beta$-MoO$_3$ (curve d in figure 3) due to the absence of Mo = O and Mo$_2$O$_2$ entities in this metastable phase. Moreover, the Raman peaks of the prepared $\beta$-MoO$_3$ which are located at 773, 848 and 905 cm$^{-1}$ are nearly similar to those of the $\beta$-MoO$_3$ produced by Mizushima’s method [23] (curve c in figure 3) and other reported results [30, 35]. It can be concluded that a pure $\beta$-MoO$_3$ powder was successfully produced by a more simple method than those reported in the literature.

Raman spectra of the prepared molybdenum trioxides after catalytic activity study at different reaction temperatures are demonstrated in figure 4. The reaction of methanol oxidation to formaldehyde is strongly exothermic; therefore, the catalyst was deactivated more rapidly with an increase in reaction temperature. Similarity of spectrum of the as-prepared $\beta$-MoO$_3$ (curve d of figure 3) and that of the used one after catalytic study at 320 °C (curve a in figure 4) indicates that the prepared catalyst was still stable in this reaction condition. The spectra of sample after catalytic test at 350 °C (curves b, c and d in figure 4) exhibit the presence of alpha MoO$_3$. Since the prepared sample only transfers into alpha MoO$_3$ at temperature above 420 °C as pointed out by DSC.
measurements, the formation of alpha MoO₃ during catalytic test at 350 °C may originate from the local overheating due to the considerable amount of heat released from reaction. It can be seen obviously that the longer time on stream, the more amount of alpha phase transformed during catalytic test.

IR spectroscopy was employed to additionally identify MoO₃ phases. Figure 5 presents the IR spectra of the prepared MoO₃ powders and commercial one. There are three main absorption patterns in the region of the stretching vibrations, between 1050 and 400 cm⁻¹ that can be used to identify α-MoO₃ (curve a in figure 5): (1) a narrow IR band at 990 cm⁻¹ due to the vibration of the Mo=O terminal bond; (2) an absorption pattern with two maxima at 876 and 818 cm⁻¹ coming from the vibration of Mo–O–Mo bridging bonds; and (3) a broad and complex band centered at about 600 cm⁻¹ is characteristic of the vibration of Mo₂O₂ units formed by edge shared MoO₆ octahedra [30, 36]. Therefore, the main difference between alpha and beta phases was found in the absorption regions around 600 cm⁻¹ and at 990 cm⁻¹. As can be seen in curve b of figure 5, no absorption bands at 990 cm⁻¹ and bands around 600 cm⁻¹ is observed due to the absence of Mo = O and Mo₂O₂ entities in this polymorph. Instead, the bands at 900 cm⁻¹ and 790 cm⁻¹ can be observed in the case of monoclinic MoO₃ [37, 38].

In order to further understand structure of the commercial and prepared MoO₃ before and after catalytic test at different conditions, SEM images of them were recorded and depicted in figure 6. It can be seen that the prepared β-MoO₃ was composed of small primary particles in the range 50–100 nm (figure 6(a)) and its morphology was dramatically changed after methanol oxidation at 350 °C for 15 h (figure 6(b)). The morphology similarity of the used β-MoO₃ and commercial α-MoO₃ (figure 6(c)) was observed as a proof of metastable phase transformation during reaction. Both of them were composed of micro blocks as can be seen in their SEM images.

3.2. Catalytic behavior

The major product was formaldehyde for all catalytic tests. Small amounts of MF and DME were observed as byproducts. CO₂ was not detected for all tested conditions. The carbon balance was within 99.5 ± 2% for all measurements.

The activity and the selectivity of the prepared MoO₃ samples were evaluated as a function of temperature. The reaction was left for 2 h before analyzing all products. As can be seen in figure 7, the conversion and selectivity increase with rising temperature. In the case of using the prepared β-MoO₃ as a catalyst, formaldehyde selectivity can reach up to 98.8% at about 99% methanol conversion. It is obviously more active and selective than the commercial α-MoO₃.

According to some authors [23, 27, 29], this significant difference is mainly due to the differences between their structures. Both of them are built from the same MoO₆ octahedra but in different ways. A layer structure of α-MoO₃ is formed from stacking many double-layered sheets composed of corner- and edge-shared MoO₆ octahedra along the (001) direction by week van der Waals interactions [39]. As a result, cleavage along the (010) direction without breaking any Mo–O bond is easier than other direction making coordinatively saturated Mo atoms become predominant in case of the bulk α-MoO₃ terminated. However, dissociative chemisorption of methanol was observed to be only occurred on the under-coordinated surface Mo sites [8, 40]. Therefore, an anisotropic structure of α-MoO₃ was considered as an important factor that limits its activity as a catalyst for methanol oxidation [29, 41]. In case of β-MoO₃, its structure is composed of corner-shared MoO₆ octahedra. Accordingly, its symmetric structure can be cleaved in any direction with breaking of the Mo–O bonds, resulting in a large amount of coordinatively unsaturated Mo atoms on the surface. It can attribute to a higher reactivity of β-MoO₃ compared to α-MoO₃.

The stability test of the prepared β-MoO₃ were performed at 320 °C and 350 °C for approximate 15 operating
hours. Figure 8(a) shows that the methanol conversion and HCHO selectivity catalyzed by the as-synthesized material at 320 °C do not change with time on stream. They are stabilized at around 84% and over 95% respectively for the first 15 h test. Unfortunately, as can be seen in figure 8(b), activity of the prepared β-MoO₃ was stable for only 2.5 h at 350 °C, then decreased with reaction time. After 150 min on stream, methanol conversion decreased sharply from 99% to 18% and then stayed constant for the rest of the reaction time. This deactivation is caused by transformation of β-MoO₃ to the stable phase as confirmed by Raman spectra of the spent catalyst (figure 4). The SEM images of the used β-MoO₃ and commercial α-MoO₃ showed a similarity in their morphology as can be seen in figures 6(b) and (c). As a result, their activity on methanol oxidation was found to be the same. However, the selectivity of the prepared sample changed insignificantly during deactivation whereas both activity and HCHO selectivity decreased considerably in the case of deactivation of iron molybdate [42, 43]. This can be considered as an

Figure 6. SEM images of the prepared β-MoO₃ before (a) and after catalytic test at 350 °C (b) and commercial α-MoO₃ (c).

Figure 7. Methanol conversion (■) and selectivity of formaldehyde (●) and DME (△) over the as-prepared β-MoO₃ (solid lines) and commercial α-MoO₃ (dot lines) versus reaction temperature at air flow rate of 60 ml min⁻¹.

Figure 8. Methanol conversion (□) and selectivity of formaldehyde (■) over the as-prepared β-MoO₃ at (a) 320 °C and (b) 350 °C with an airflow rate of 60 ml min⁻¹.
advantage of the pure MoO₃ catalyst in comparison with the industrial one.

4. Conclusion

In this paper a facile and effective synthesis process has been demonstrated for the producing nanosized β-MoO₃ powder from all commercial materials. As expected from literatures, β-MoO₃ showed much higher catalytic activity and selectivity to formaldehyde formation from methanol oxidation than α-MoO₃. The prepared catalyst also exhibited stable activity for over 15 operating hours at 320 °C. It has been demonstrated that the β-MoO₃ catalyst maintains its high selectivity to formaldehyde although its catalytic activity may be decreased under elevated temperature due to its metastable nature. This can be considered as an advantage of the prepared MoO₃ catalyst in comparison with the industrial one.

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