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Preparation of NO-doped β-MoO_3 and its methanol oxidation property

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HIGHLIGHTS

- NO-doped β-MoO_3 was synthesized by a facile and effective method.
- Its structure was confirmed by XRD, Raman and XPS analysis.
- X_{MeOH} and S_{HCHO} were stabilized at 98% and 99%, respectively, for the first 30 h.

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ABSTRACT

The major drawback of the industrial iron molybdate catalysts which is their deactivation problem has driven the study of alternative catalysts for formaldehyde production from methanol. In this paper, NO-doped β-MoO_3 was successfully synthesized from the commercial molybdic acid powder (H_2MoO_4) and characterized by differential thermal analysis (DTA), X-ray Diffraction (XRD), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). Results obtained from XRD and Raman spectroscopy indicated that the synthesized sample has all features of the well-known β-MoO_3 except for the presence of a new small peak. The curve-fitting of XPS spectra revealed that nitrogen-containing species may be present in the form of negatively charged nitrogen oxide in the prepared sample. Due to its metastable nature, NO-doped β-MoO_3 may be transformed into the thermally stable α-MoO_3 at temperature higher than 400 °C as pointed out by DTA study. However, when the reaction temperature was as low as 300 °C, the catalyst was stable for partial methanol oxidation with no significant change in activity during 30 h of catalytic study. Methanol conversion and formaldehyde selectivity were maintained at about 98% and 99%, respectively.

1. Introduction

Formaldehyde is one of the most important industrial chemicals due to its large demand for many industries. Manufacture of formaldehyde is partly done by the catalytic oxidation of methanol using an iron molybdate-based catalysts which are composed of not only $Fe_2(MoO_4)$ but also a large excess of MoO_3 [1]. It was well agreed that an isotropic $Fe_2(MoO_4)_3$ is much more active than an anisotropic MoO_3 due to its larger density of exposed catalytic active sites [2,3] but the role of these phases in selective methanol oxidation is still controversial. For many years, $Fe_2(MoO_4)_3$ was believed to be the only active phase [4–6] but with evidence from recent studies, it has been revealed that MoO_x species are the active surface in iron molybdate catalysts and a Mo-rich surface is critically important to ensure high selectivity and life-time of iron molybdate catalysts [7–10]. Thus, another MoO_3 3D-structure such as β-MoO_3 which possesses higher number of active sites than a layered structure of α-MoO_3 could be a promising candidate as an alternative catalyst for formaldehyde production [11–13]. However, this prospect has not been shown till now because of its complicated and ineffective synthesis method which used the blue molybdic acid solution obtained via cation exchange of Na_2MoO_4 solution [11,14–17]. Some efforts were made to synthesize β-MoO_3 from other molybdenum sources [12,18,19] but the undesired stable phase was usually detected in the final product.

Recently, a green metastable MoO_3 was produced from a simple synthesis method employing some cheap, commercial materials such as commercial molybdic acid, HCl and HNO_3 solution, which was created by Phuc *et al.* [20]. Stable α-MoO_3 can also be transformed to the green metastable one using this facile method [21].

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At first, a triclinic structure was predicted based on the similarity of the results obtained from XRD and Raman measurements between the new found MoO_3 and the well-known triclinic WO_3. Nitric acid which can be used as a nitrogen source for nitrogen doping into titanium dioxide [22] was involved in the synthesis process, however, the possibility of formation of a nitrogen-doped MoO_3 was omitted. Therefore, in this paper, it was considered and then proved by XRD, Raman and XPS analysis. In addition, its catalytic property on selective methanol oxidation to formaldehyde has also been investigated.

2. Experimental

2.1. Synthesis of green metastable MoO_3

The green metastable MoO_3 was synthesized according to the method described in our previous study [23] with a slight change in starting material. Briefly, H_2MoO_4 powder (4 g, Wako > 80% MoO_3) was dissolved in concentrated HCl (36 ml, Merck). Then, concentrated HNO_3 (3 ml, Merck) was added and the resulting solution was sealed and aged at 90 °C for 30 min. Afterwards, it was evaporated at this temperature for 30 min and 150 °C for 1 h in vacuum. To obtain the green MoO_3, the as-received powder was then calcined in static air at 300 °C for 2 h.

2.2. Characterization

Differential thermal analysis (DTA) curves of the prepared samples were recorded with TG 8120 (Rigaku) in 20 ml min^{-1} of air flow with heating rate of 20 K min^{-1} from room temperature to 500 °C with α-Al_2O_3 as standard material. The BET surface areas of the catalyst samples were measured by nitrogen adsorption–desorption in flowing N_2 at 77 K using a Micromeritics ASAP 2020.

X-ray photoelectron spectroscopy (XPS) was performed on a PHI Quantera SXM scanning X-ray microprobe (ULVAC-Phi Inc.) using an Al anode ($h\nu = 1486.6$ eV) under a base pressure of 5×10^{-9} Torr and an X-ray source with 100 W power, 26.0 eV pass energy, and 45° take-off angle. CasaXPS software was used to process the XPS data. The C1s binding energy of 284.6 eV was considered as the reference for charge correction [24,25]. Linear background subtraction was used for quantification of C1s, O1s and N1s spectra [26,27], while a Shirley background subtraction was applied to Mo3d spectra [28,29]. Curve-fitting of the Mo spectra was performed using asymmetric, Lorentzian-based, peak shapes (LF) [29,30] whereas mixture of Gaussian/Lorentzian peaks (GL) was used to fit N1s spectra [31,32]. Despite of Mo valence state, the peak area ratio and peak splitting required for Mo3d spin-orbit doublets were kept constant and equal to the value of 3/2 and 3.15 eV, respectively.

Temperature programmed heating (TPH) of the prepared MoO_3 was performed a closed circulation system. This allows the desorbed products to accumulate for sufficient detection. A known amount of sample was placed in a U-shaped quartz reactor which was then inserted in a programmable furnace. Before closing the system, the sample was outgassed at room temperature for 30 min in a flow of helium (50 ml.min^{-1}). Subsequently the sample was heated up to 600 °C at a rate of 5 °C.min^{-1} and kept at this temperature for a while. During the experiment, the internal gases were circulated using a piston-type pump at a flow rate of 250 ml.min^{-1}. The NO-TPH profile was derived from an in-line AlphaSense nitric oxide sensor (model NO-AE).

Powder X-ray diffraction (XRD) patterns were obtained by a powder X-ray diffractometer (ULTIMA IV, Rigaku) with CuKα radiation operating at 30 kV and 20 mA from 10° to 60° with a scanning speed of 2°.min^{-1} and scanning step of 0.02°. Raman measurements were carried out at ambient condition using a JASCO NRS-3100 spectrometer. A 532 nm green laser beam was focused using an objective lens (20X) with laser power less than 5 mW and 0.5 cm^{-1} of resolution. The system was calibrated with SiO_2/Si wafer with peak at 520 ± 0.5 cm^{-1}. The morphology and particle size of the samples were characterized using a Field Emission Scanning Electron Microscopy (FE-SEM, JSM-5700F, JEOL) operating at 50 kV and a Transmission Electron Microscopy (TEM, JEM-1400, JEOL) operating at 100 kV.

2.3. Catalytic performance

The oxidation of methanol was carried out using a fixed bed quartz reactor (500 mm length and 10 mm inner diameter) at atmospheric pressure to determine the catalytic activity and selectivity of the prepared and commercial MoO_3 (Sigma Aldrich, > 99.5%). The detailed experimental procedure is provided elsewhere [23].

3. Results and discussion

3.1. Catalyst characterization

The differential thermal analysis was firstly used to study the thermal behavior of the prepared sample. An exothermic peak centered at 435 °C was observed in the DTA curve attributed to the phase transformation of the prepared MoO_3. This is in the range of the phase transformation temperature of the known beta MoO_3, which was reported from 350 to 450 °C [11,14,15]. However, the known beta MoO_3 is yellow as described in the previous studies [11,14–16] while the prepared sample is green powder. Kühn *et al.* [33] synthesized a molybdenum oxide nitride from the commercial α-MoO_3 and observed that nitrogen-doping in α-MoO_3 can make its color change from light-grey to dark-blue. Although changes in particle size can cause color change, such structure modification should be considered as a possible cause for the color difference between our prepared MoO_3 and the yellow one.

Further information regarding the surface chemistry of the prepared sample was obtained by XPS study. High-resolution XPS spectra of the Mo3d, N1s, O1s and Cl2p regions are shown in Fig. 1. The results proved that no chlorine compounds were left on the sample surface as no chlorine signal was detected by XPS (Fig. 1a). The curve-fitting of the Mo3d signal (Fig. 1b) showed the presence of two well-resolved peaks at 232.7 and 235.9 eV which were assigned to the $Mo3d_{5/2}$ and $Mo3d_{3/2}$ spin-orbit of MoO_3, respectively [25,34,35]. Further, no peaks related to other chemical states of Mo was detected using the second derivative technique [36], which confirms the single phase of the prepared sample.

The overlap between the $Mo3p_{3/2}$ and N1s regions make it difficult to acquire an accurate curve-fitting. However, as shown in Fig. 1c, the spectrum is obviously asymmetrical with a small shoulder on the higher BE side which may indicate the presence of nitrogen-containing species. Therefore, the curve-fitting of the Mo3p spectra was first performed by constraining the peak area ratio of Mo 3p spin-orbit doublets to be 2/1. As a result, one peak was observed at 398.6 eV which can be assigned to Mo(VI) [34,37]. In order to complete the curve fit, two other peaks with the same full width at half maximum (FWHM) corresponding to the nitrogen related species need to be added at 401.9 and 404.5 eV. None of these peaks can be assigned to N–Mo because it is much higher than the 399.2 eV, which is the highest reported value for this bond [38–42]. Instead, it is supposed that there is a coexistence of surface nitrosyl and ammonium in the prepared sample due to their presence in the reaction. The former specie was believed to be

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