Catalytic Partial Oxidation of Propylene to Acrolein: The Activity of Bismuth Molybdate Catalysts under Oxygen-Rich Conditions

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The effect of Bi/Mo ratio, varied between 1:3 and 2:1, on the activity of bismuth molybdate catalysts, prepared by precipitation method, for partial oxidation of propylene has been investigated. X-ray diffraction analysis revealed that the catalysts contained a mixture of $\alpha$-Bi$_2$Mo$_3$O$_{12}$ and molybdite (MoO$_3$) for Bi/Mo = 1:3, pure $\alpha$-Bi$_2$Mo$_3$O$_{12}$ for Bi/Mo = 2:3, a mixture of $\beta$-Bi$_2$Mo$_2$O$_9$ and $\alpha$-Bi$_2$Mo$_3$O$_{12}$ for Bi/Mo = 1:1, and pure $\gamma$-Bi$_2$MoO$_6$ for Bi/Mo = 2:1. The catalytic activity tests showing that the catalysts achieved up to 56% conversion of C$_3$H$_6$ with up to 91% selectivity towards C$_3$H$_4$O production. The relative reactivity of the catalysts follow the order of Bi/Mo 2:3 ≈ Bi/Mo 2:1 > Bi/Mo1:3 > Bi/Mo 1:1.

Introduction

Catalysts for propylene oxidation to acrolein comprise a number of multiple oxide systems. Among several types of well-known multi-component metal oxide catalysts, Bismuth-Molybdate (Bi-Mo) is one of the most studied catalysts, and displays very good activity and selectivity.

The selectivity and activity of Bi-Mo catalysts are influenced by the ratio of Bi/Mo. It has been shown that the superior catalysts are those whose ratios of Bi to Mo are within the range of 2:3 and 2:1, namely $\alpha$-Bi$_2$Mo$_3$O$_{12}$, $\beta$-Bi$_2$Mo$_2$O$_9$, and $\gamma$-Bi$_2$MoO$_6$. However, which one gives the best activity and selectivity is still debatable.

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There are at least three opinions about the order of activity among $\alpha$, $\beta$, and $\gamma$. For example, Gorshkov et al.\textsuperscript{1} and Beres et al.\textsuperscript{2} found that the $\beta$-phase is most active and selective, followed by $\alpha$ and $\gamma$. However, Batist et al.\textsuperscript{3} observed that $\gamma$ phase was equally good. More recent studies by Agaqseinova et al. (in Cullis and Hucknall \textsuperscript{4}) observed that the order was $\alpha>\beta>\gamma$. In addition, Monnier and Keulks (in Cullis and Hucknall \textsuperscript{4}) found that the order of activity was $\beta>\alpha>\gamma$. Millet et al.\textsuperscript{5} also support the finding by Monnier and Keulks.

Fattore et al.\textsuperscript{6} investigated propylene oxidation over bismuth molybdate in the absence of gaseous oxygen. They found that the catalysts can use the lattice oxygen for partially oxidation of propylene to acrolein. On the other hand, Krenzke and Keulks \textsuperscript{7} found that the reaction order of propylene and oxygen on partial oxidation of propylene to acrolein on $\gamma$-Bi$_2$MoO$_6$ and Bi$_3$FeMo$_2$O$_{12}$ were different at different reaction temperatures. Kremenic et al.\textsuperscript{8} studied the kinetic and adsorption of propene and oxygen on a modified bismuth molybdate with praseodymium as an additive. They found that the adsorption of propylene on the pre-adsorption of oxygen on the catalyst surface was 25% lower than the clean surface. They also found that although the kinetics of propylene oxidation to acrolein fit with a model based on non-dissociative oxygen adsorption, the adsorbed oxygen did dissociate on the catalyst surface. These findings show that oxygen plays an important role in the partial oxidation of propylene to acrolein on bismuth molybdate catalysts.

This paper presents the preliminary findings of the catalysts’ activity under oxygen-rich conditions as a part of kinetics and reaction mechanisms study of propylene oxidation to acrolein over bismuth molybdate.

Experimental Methods

(i) Catalyst Preparation

The catalysts were prepared using the so-called co-precipitation method based on the literature\textsuperscript{5,6,9,10}. Bismuthyl nitrate, Bi(NO$_3$)$_3$.5H$_2$O and ammonium hepta-molybdate, (NH$_4$)$_6$Mo$_7$O$_{24}$.4H$_2$O were dissolved separately in hot water (70°C). The bismuthyl nitrate solution was then dropped slowly into the vigorously stirred ammonium hepta-
molybdate solution, producing a yellowish suspension. The suspension was kept in the water bath at 70°C and stirred well to evaporate the liquid slowly until it became a paste. The paste was then put into an oven at 120°C for 20 hours in air. The dried paste was then crushed into small pieces and then calcined at 250°C for 2 hours in an air oven. The catalysts were then ground to a powder and calcined for 20 hours at 480°C for catalysts with 2:1, 2:3, and 1:3 Bi/Mo ratios and 760°C for 1:1 Bi/Mo ratio.

(ii) Catalyst Characterisation

Structural phase of the catalysts were characterised using powder x-ray diffraction (XRD Siemens D500 Bragg-Brentano diffractometer employing Cu Kα radiation). All catalysts were grinded before being mounted onto the sample holder using the "knocking" method. The diffractograms were recorded at room temperature with 0.04° (2θ) step size over the angular of 5° to 80° (2θ). The current and voltage applied during analysis was 30 mA and 40 kV, respectively. Crystalline phases were compared with references from the data base software (Jade™ XRD version 5.0).

Figure 1. A schematic of the reactor configuration for catalyst activity scanning

Catalyst activity was measured in a single pass-fixed-bed-stainless steel reactor (10mm ID) as shown schematically in Figure 1. The catalyst powder (ca 1.9 gram) was sandwiched between two glass wool pads in the reactor. A type J thermocouple was fitted at the end of the catalyst bed. The outlet of the reactor was connected to a scrubber, which contains a sodium hydroxide solution with pH 11 to convert all
acrolein being produced to polyacrolein, preventing the harmful acrolein from being released.

The feed gasses used were industrial-grade O\textsubscript{2} and He, and polymer-grade propylene from BOC Australia without further purification. Total flow-rate was 120 cm\textsuperscript{3} min\textsuperscript{-1}, regulated with three MKS mass-flow controllers. The composition of the reactant gas was 85% He, 10% O\textsubscript{2}, and 5% C\textsubscript{3}H\textsubscript{6}. A gas chromatograph (Varian 3400CX) was used to analyse gas composition of the reactant and product streams. The GC was fitted with a molecular sieve 13X for separating O\textsubscript{2}, in series with a Porapak N for separating Propylene, Acrolein, CO\textsubscript{2}, and acetaldehyde. The gas analysis results were then used to calculate propylene conversion (\(X\)) and acrolein selectivity (\(S\)) which are defined as:

\[
X = \left(1 - \frac{\text{Mole}_{C,H_{inlet}}}{\text{Mole}_{C,H_{outlet}}}\right) \times 100\% \quad \ldots(1)
\]

\[
S = \left(\frac{\text{Mole}_{C,H_{O, outlet}}}{\text{Mole}_{C,H_{inlet}} - \text{Mole}_{C,H_{outlet}}}\right) \times 100\% \quad \ldots(2)
\]

Results and Discussion

The catalyst preparation procedure was designed to synthesise \(\alpha\)-Bi\textsubscript{2}Mo\textsubscript{3}O\textsubscript{12}, \(\beta\)-Bi\textsubscript{2}Mo\textsubscript{2}O\textsubscript{9}, \(\gamma\)-Bi\textsubscript{2}MoO\textsubscript{6}, and a mixture of \(\alpha\)-Bi\textsubscript{2}Mo\textsubscript{3}O\textsubscript{12} and MoO\textsubscript{3}. The first three are well known as selective catalysts for partial oxidation of propylene to acrolein. The fourth catalyst was designed to provide excess molybdenum oxide on \(\alpha\)-Bi\textsubscript{2}Mo\textsubscript{3}O\textsubscript{12}, which, according to the literature\textsuperscript{4,10}, could improve the activity of the catalyst.

The x-ray analysis result (Figure 2) shows that all four bismuth molybdates have very good crystalline structures. A search and match procedure of the x-ray peaks using Jade\textsuperscript{\textregistered} software showed clearly that \(\alpha\)-Bi\textsubscript{2}Mo\textsubscript{3}O\textsubscript{12} (scheelite structure) and \(\gamma\)-Bi\textsubscript{2}MoO\textsubscript{6} (koechlinite structure) were the only products from bismuth molybdate prepared with Bi/Mo ratios of 2:3 and 2:1, respectively. However, Bismuth
molybdates, which are prepared with Bi/Mo ratio 1:3 and 1:1, were not single phase materials.

In the catalysts with a Bi/Mo ratio of 1:3, $\alpha$-Bi$_2$Mo$_3$O$_{12}$ was the main phase with some molybdite (MoO$_3$) appearing on the x-ray diffractogram. The appearance of molybdite is believed to be due to excess molybdenum in the mixture. $\beta$-Bi$_2$Mo$_2$O$_6$ was the main product for the catalyst with a Bi/Mo ratio of 1:1, together with $\alpha$-Bi$_2$Mo$_3$O$_{12}$. The appearance of alpha phase in this catalyst suggests that some molybdite might also be formed due to incomplete reaction as well as heterogeneous precipitation during preparation. A series of quantitative x-ray diffraction studies as well as improvement of the preparation procedure are being carried out to investigate the phenomena.

Although the preparation of $\beta$-Bi$_2$Mo$_2$O$_9$ was not very successful, this result indicates that the preparation procedure was appropriate for preparing the bismuth molybdate catalysts for this study. It also indicates that the material of the catalysts were comparable with those reported in the literature$^{3,4,7,9,16}$.

A comparison of the activities of $\alpha$-Bi$_2$Mo$_3$O$_{12}$, $\beta$-Bi$_2$Mo$_2$O$_6$, $\gamma$-Bi$_2$MoO$_6$, and the mixture of $\alpha$-Bi$_2$Mo$_3$O$_{12}$ and MoO$_3$ (in this report is labelled as BiMo 1:3) is presented in Figures 3 and 4. As the reaction temperature increases, the propylene conversion over all catalysts increases with a maximum at 56% for $\gamma$-Bi$_2$MoO$_6$, except for BiMo 1:3 at 450°C, which did not increase the propylene conversion further. Below 450°C, the BiMo 1:3 always shows higher propylene conversions then $\alpha$-Bi$_2$Mo$_3$O$_{12}$. This agrees well with the literature$^{10,14,15}$ that excess molybdenum oxide does appear to improve the activity of $\alpha$-Bi$_2$Mo$_3$O$_{12}$. The activity of $\gamma$-Bi$_2$MoO$_6$ was about the same as those of both $\alpha$-Bi$_2$Mo$_3$O$_{12}$ and BiMo 1:3 while $\beta$-Bi$_2$Mo$_2$O$_6$ was the least active catalyst in this series.
Figure 2. Diffraction pattern of Bismuth Molybdates
Below 450 °C, γ-Bi$_2$MoO$_6$ was the best catalyst and the selectivity of α-Bi$_2$Mo$_3$O$_{12}$ was better than BiMo 1:3. However, at higher temperatures, α-Bi$_2$Mo$_3$O$_{12}$
overtook $\gamma$-$\text{Bi}_2\text{MoO}_6$ and BiMo 1:3 to show a better selectivity of acrolein, while the selectivity of the last two started to decrease.

It is interesting to compare the activities of $\alpha$, $\beta$ and $\gamma$ bismuth molybdates. Under the same conditions, the catalytic activity as indicated by propylene conversion decreased in the order of $\gamma$-$\text{Bi}_2\text{MoO}_6 > \alpha$-$\text{Bi}_2\text{Mo}_3\text{O}_{12} > \beta$-$\text{Bi}_2\text{Mo}_2\text{O}_9$ whereas the acrolein selectivity of the catalysts below 450°C decreased in the same order. However, at 450°C the selectivity decreased in the order of $\alpha$-$\text{Bi}_2\text{Mo}_3\text{O}_{12} > \gamma$-$\text{Bi}_2\text{MoO}_6 > \beta$-$\text{Bi}_2\text{Mo}_2\text{O}_9$. This finding is in contrast with previously reported results$^{2,3,4,7,9}$, where the selectivity as well as the activity of $\beta$-$\text{Bi}_2\text{Mo}_2\text{O}_9$ was never lower than the $\alpha$ and $\gamma$ bismuth molybdate.

There are three possibilities that could lead to the differences. The first might be due to the difference in the unit of the catalyst activity. In our study, the unit was in per mass unit of the catalyst. This might give rise to the great difference in catalytic activity if their density as well as their surface area is different. The second reason might be the different ratios of oxygen and propylene in the reactant gas mixtures. Some kinetic studies$^{7,8,16}$ showed that the reaction order of oxygen was different at different temperatures. This means that the oxygen concentration can affect the reaction rate. In order to prove this, further experiments to determine the kinetics of propylene oxidation to acrolein on the catalysts are underway. The other possibility might be related to the high propylene conversion achieved in this study, while literature reported results normally fall in very low conversion levels.

**Conclusions**

Three bismuth molybdate catalysts, namely $\alpha$, $\beta$, $\gamma$ and BiMo 1:3 bismuth molybdates were successfully prepared using the co-precipitation method from bismuthyl nitrate and ammonium hepta-molybdate solutions.

Below 450°C, the catalysts activity showed by propylene conversion was in the order of $\gamma$-$\text{Bi}_2\text{MoO}_6 \approx \text{BiMo} \ 1:3 \approx \alpha$-$\text{Bi}_2\text{Mo}_3\text{O}_{12} > \beta$-$\text{Bi}_2\text{Mo}_2\text{O}_9$ and the acrolein selectivity was in the order of $\gamma$-$\text{Bi}_2\text{MoO}_6 > \alpha$-$\text{Bi}_2\text{Mo}_3\text{O}_{12} \approx \text{BiMo} \ 1:3 > \beta$-$\text{Bi}_2\text{Mo}_2\text{O}_9$.

At higher temperature, the selectivity of $\alpha$-$\text{Bi}_2\text{Mo}_3\text{O}_{12}$ overtook $\gamma$-$\text{Bi}_2\text{MoO}_6$ and BiMo.
The results showed that the excess molybdite in $\alpha$-Bi$_2$Mo$_3$O$_{12}$ does improve its activity at lower temperatures. This means that the excess molybdite could lower the reaction temperature required to convert propylene to acrolein.

The catalyst activity and selectivity orders in this experiment were different from those reported in the literature. In this experiment, the activity as well as the selectivity of $\beta$-Bi$_2$Mo$_2$O$_9$ was always lower than $\alpha$-Bi$_2$Mo$_3$O$_{12}$ and $\gamma$-Bi$_2$MoO$_6$, while the literature reported the opposite. The difference might be due to the difference in the unit of the catalyst activity, ratios between oxygen and propylene, and high propylene conversion. Further experiments need to be done to clarify these findings.

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References