THE EFFECT OF PHOSPHORUS ADDITION ON THE ACTIVITY OF BISMUTH MOLYBDATE CATALYST FOR PARTIAL OXIDATION OF PROPYLENE TO ACROLEIN

Hamzah Fansuri[1,*], Gia Hung Pham[2], Sandra Wibawanta[2], and Dong-ke Zhang[3]

[1]*Department of Chemistry, Institut Teknologi Sepuluh Nopember (ITS), Kampus ITS Sukolilo, Surabaya 60111*

[2]*Department of Chemical Engineering, Curtin University of Technology, Kent St Bentley WA 6102, Australia*

[3]*UWA Centre for Energy, University of Western Australia, 35 Stirling Highway, Crawley WA 6009, Australia*

ABSTRACT

In order to examine the effect of phosphorus addition on the activity and selectivity of bismuth molybdate catalysts for partial oxidation of propylene to acrolein, three modes of phosphorus addition were performed. The three modes of Preparation were performed by (1) adding phosphorus into α-$Bi_2Mo_3O_{12}$ to obtain $Bi_2P_xMo_3O_y$, (2) inserting phosphorus on bismuth sites to obtain $Bi_{2-x}P_xMo_3O_y$, and (3) inserting phosphorus on molybdenum sites to obtain $Bi_2P_xMo_{3-x}O_y$. Four major phases of bismuth phosphomolybdate were detected as the result of the phosphorus addition, namely α-$Bi_2Mo_3O_{12}$, $Bi_9PMo_{12}O_{52}$, MoO_3, and $BiPO_4$. Experimental results showed that the catalysts solely containing $BiPO_4$ and/or MoO_3 have very low activities for partial oxidation of propylene to acrolein. Meanwhile, catalysts containing α-$Bi_2Mo_3O_{12}$ and $Bi_9PMo_{12}O_{52}$, together with either MoO_3 or $BiPO_4$ showed on average the same activities as α-$Bi_2Mo_3O_{12}$ and one of them (combination of α-$Bi_2Mo_3O_{12}$, $Bi_9PMo_{12}O_{52}$ and MoO_3) has better performance than α-$Bi_2Mo_3O_{12}$ at lower temperatures. The presence of the oxygen donor phase, i.e. $BiPO_4$ and MoO_3, are believed to play a key role for the high activities of bismuth-phosphomolybdate catalysts. However, at higher temperatures, the presence of oxygen donor reduces the catalyst selectivity to acrolein.

Keywords: *Propylene, Acrolein, Bismuth Molybdate, Partial oxidation*

INTRODUCTION

Phosphorus has long been used as an additive for bismuth molybdate catalysts for propylene to acrolein conversion. The first phosphorus containing bismuth molybdate catalyst for this purpose was developed by Sohio in 1957 in the form of $Bi_9PMo_{12}O_{52}$ supported on SiO_2 [1]. Since then, phosphorus has become an essential additive for bismuth molybdate-based commercial catalysts.

There are numerous reports on the role of phosphorus in bismuth molybdate catalysts for selective oxidation of hydrocarbon. Chang et al. [2] reported that phosphorus additive increases the acidity of molybdate leading to promotion of O^{2-} as the product of O_2 dissociation. The increased acid/base ratio in phosphorus added bismuth molybdate catalysts was also reported by Kaddouri et al. [3].

The increase in acidity of bismuth molybdate catalysts plays an important role in enhancing the catalyst activity because the acid site is the place where the hydrocarbon species were adsorbed by the catalyst. The acid sites, then, capture one hydrogen atom from the gaseous reactant to produce, in the case of propylene partial oxidation, allyl groups. This process is believed to be the rate-determining step in the partial

oxidation of propylene to acrolein over the bismuth molybdate catalysts [4-7].

Meanwhile, Qiu et al. [8] reported that the phosphorus additive in the form of $BiPO_4$ improved the performance of $ZnFe_2O_4$ catalyst for butene dehydrogenation to butadiene. They found that $BiPO_4$ protects the catalysts against deactivation, which was then proved by Weng and co-workers in 1992 [9].

In our previous work, we reported that the action of bismuth molybdate catalysts (α-$Bi_2Mo_3O_{12}$, b-$Bi_2Mo_2O_9$, and g-Bi_2MoO_6) in catalysing selective partial oxidation of propylene to acrolein was influenced by their lattice oxygen [10]. This paper discusses the effect of phosphorus addition in alpha-Bismuth molybdate (α-$Bi_2Mo_3O_{12}$) and its effect on the catalyst activities and selectivities to the formation of acrolein from propylene.

EXPERIMENTAL SECTION

Materials

All chemicals used in this research are analytical grade. The source of bismuth, molybdenum and phosphorous were $Bi(NO_3)_3.5H_2O$, $(NH_4)_6Mo_7O_{24}.4H_2O$ and H_3PO_4, respectively. All gasses were High Purity (HP)

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* Corresponding author. Tel/Fax : +62-31-5943353/5928314
Email address : h.fansuri@chem.its.ac.id

Table 1. The catalyst formula and chemical composition in the catalyst preparation

Catalyst Formula	Bismuth nitrate (g)	Ammonium hepta molybdate (g)	H_3PO_4 (mL)	H_2O (mL)
$Bi_2PMo_3O_x$	21.6341	11.8107	1.30	19.5
$Bi_2P_3Mo_3O_x$	21.6341	11.8107	3.90	19.5
$Bi_2P_{0.5}Mo_{2.5}O_x$	21.6341	9.8519	0.76	17.5
$Bi_2PMo_2O_x$	21.6341	7.8744	1.52	14.0
$Bi_2P_{1.5}Mo_{1.5}O_x$	21.6341	5.9058	2.29	12.5
$Bi_{1.5}P_{0.5}Mo_3O_x$	16.2500	11.8112	0.76	16.5
$BiPMo_3O_x$	10.8171	11.8112	1.52	15.0
$Bi_{0.5}P_{1.5}Mo_3O_x$	5.3843	11.8112	2.29	13.0
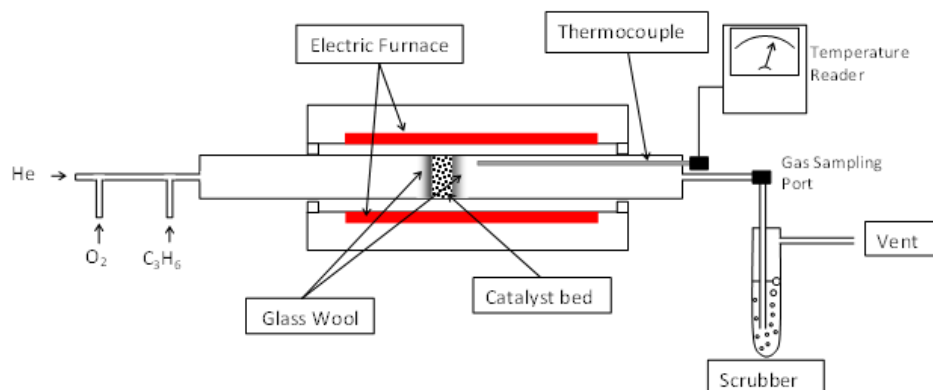
Fig 1. Schematic of the reactor configuration for catalyst activity scanning (Adapted from [10])

grade from BOC gas, Australia. Micromat-14[TM] (Grace, Cat. No. 19792) was used as standard gas for GC calibration.

Instrumentation

A Siemens D500 X-ray Diffractometer was used in all diffraction analysis. Meanwhile, A Varian 3400 CX Gas Chromatography was used to analyse gas composition.

Procedure

Catalyst Preparation and Characterisation

The catalysts were prepared using the so-called co-precipitation method based on the preparation of α-$Bi_2Mo_3O_{12}$ [10]. Powders of $Bi(NO_3)_3.5H_2O$ and $(NH_4)_6Mo_7O_{24}.4H_2O$ were dissolved separately in warm water (70 °C). Phosphoric acid, H_3PO_4, was then added into the bismuthyl nitrate solution. The mixture was 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 h in air. The dried cake, that was formed, was crushed and heated at 250 °C for 2 h in an

air oven. The catalyst was then ground to powder and calcined for 20 h at 480 °C. The final catalysts formula and the composition of the ingredients in the catalyst preparation are listed in Table 1.

All catalysts were characterised by X-ray diffraction using Cu Kα source without any filter. The diffractograms were taken from 5° to 70° (2θ), step size 0.02°, and scan speed 2.4°min[-1]. The phase analysis was carried out by JADE ver. 6.0 software available at Applied Physics Department, Curtin University of Technology.

Activity and Selectivity tests

Catalyst activity was measured in a single pass fixed-bed stainless steel reactor (10mm ID). The catalyst powder (ca 1.9 g) 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 to the environment. The arrangement of the reactor is given in Fig. 1.

The feed gases used were industrial-grade O_2, high purity He, and polymer-grade propylene from BOC Australia without further purification. The total flow-rate

was 120 cm^3 min^{-1}. The flow-rate was regulated with three MKS mass-flow controllers. The composition of the reactant gas was set to 85% He, 10% O_2 and 5% C_3H_6. A gas chromatograph was used to analyse gas composition of the reactant and product streams. The GC was fitted with a molecular sieve in series with a Porapak N and equipped with a TCD and FID detectors. Micromat-14^{TM} containing 5% CO, 5% CO_2, 4% CH_4, 4% H_2, 5% O_2 and 5% N_2 in Helium, were used as standard gas for calibration. A mixture of 5% Propylene, 5% acrolein and 5% acetaldehyde were freshly made prior to calibration which was carried in regular basis. Typical GC analysis results of the calibration gasses and retention time of each component are given in Table 2 and Fig. 2.

The gas analysis results were then used to calculate propylene conversion (X), acrolein selectivity (S) and acrolein yield (Y) which was defined in Equations 1–3.

Table 2. The retention time of reactants and products of activity-selectivity analysis using the GC method

Component	Retention time (min)	Detector
CO_2	1.49	TCD
O_2	2.20	TCD
CO	2.56	TCD
C_3H_6	4.54	FID
C_2H_4O	8.87	FID
C_3H_4O	13.30	FID
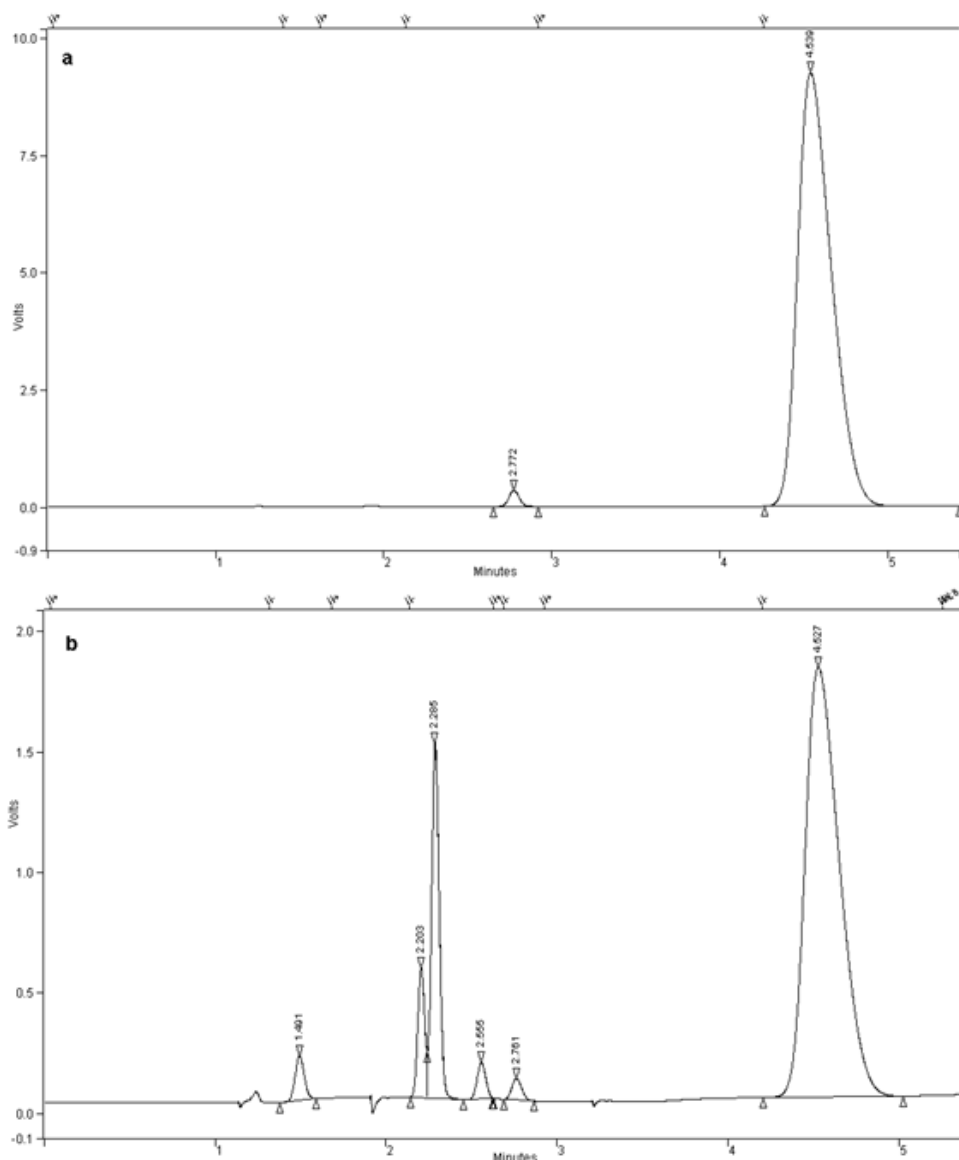
Fig 2. Qualitative chromatogram of standard Micromat-14 gas containing CO_2, O_2, N_2, CO, and CH_4 mixed with C_3H_6 detected by a) FID and b) TCD [11]

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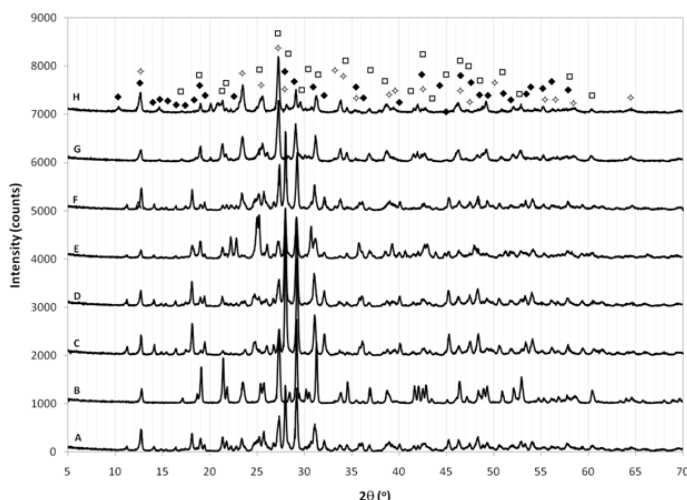
Fig 3. X-ray diffractograms of bismuth-phosphomolybdates. $\diamondsuit$ = MoO_3, $\blacklozenge$ = $Bi_2Mo_3O_{12}$ and $\square$ = $BiPO_4$

Table 3. Symmetry and cell parameters of phases found from the diffraction analysis

Cell Parameters	α-$Bi_2Mo_3O_{12}$	MoO_3	$BiPO_4$
Symmetry/Point Group	$P1\ 2_1/C1$ (monoclinic)	$Pbnm$ (orthorhombic)	$P2_1/n$ (*monoclinic*)
a (Å)	7.71	3.96	6.75
b (Å)	11.53	13.86	6.93
c (Å)	11.98	3.70	6.47
α	115.28°	90°	90°
β	115.28°	90°	103.7°
γ	115.28°	90°	90°
Volume (Å^3)	962.89	202.99	294.16

$$X = \left[1 - \frac{Mole_{C_3H_6 outlet}}{Mole_{C_3H_6 inlet}} \right] \times 100\% \qquad (1)$$

$$S = \left[\frac{Mole_{C_3H_4O, outlet}}{Mole_{C_3H_6 inlet} - Mole_{C_3H_6 outlet}} \right] \times 100\% \qquad (2)$$

$$Y = X * S \qquad (3)$$

The performance of all bismuth phospho-molybdate catalysts was compared to the performance of α-$Bi_2Mo_3O_{12}$ from our previous work [11].

RESULT AND DISCUSSION

Fig. 3 shows the XRD patterns obtained for the bismuth-phosphomolybdate catalysts on which major phases are marked. There are three major phases found from the XRD analysis, namely α-$Bi_2Mo_3O_{12}$, MoO_3 and $BiPO_4$ in the catalysts. Symmetry and cell parameters of each phase are given in Table 3. No evident is found on the formation of phosphorous substituted α-$Bi_2Mo_3O_{12}$ from the diffraction patterns. If the phase exist, it crystal size might be too small or the concentration is too low so X-ray diffraction can not detect it. Other phase of

bismuth molybdates such as β-$Bi_2Mo_2O_9$ and γ-Bi_2MoO_6, and Bi_2O_3 might also be formed as there are several peaks on the diffractograms which can not be identified due to their very low intensities.

The unit cell of α-$Bi_2Mo_3O_{12}$ is closely resembles van den Elzen and Rieck [12] model with slightly larger unit cell volume. The slight difference of the prepared structure with the van den Elzen model is believed to be caused by different preparation method. The structure of van den Elzen model was derived from the single crystalline form of alpha bismuth molybdate. Crystallisation of alpha phase has to be carried out at high temperature, i.e. at its melting point (670 °C). In contrast, the powder form in this report was prepared at low temperature (480 °C). As a result, the powder structure is more relaxed than the single crystalline one and thus resulting larger unit cell volume.

Crystal structure of MoO_3 is indexed to orthorhombic phase (JC-PDF2 Card No. 05-0508). The structure resembles those reported by Galy et al. [13]. In this structure, Mo^{6+} ion is surrounded by oxygen atoms in the form of distorted octahedral symmetry. The octahedra associate by edge-sharing along [010] to form $(MoO_3)_n$ double layers.

$BiPO_4$ crystal structure can be indexed to the monoclinic phase (JC-PDF2 Card No. 15-0767) rather than the low temperature, hexagonal phase (JC-PDF2 Card No. 15-0766). The structure is similar to those reported by Xue et al. [14] for nano-cocoons and nanorods $BiPO_4$, prepared by solvothermal method.

The results of diffraction analysis do not show any $Bi_9PMo_{12}O_{52}$ phase which, according to the literature [1], is the most active phase of bismuth phosphomolybdate catalyst. According to the empirical formulae, $Bi_9PMo_{12}O_{52}$ shall contain a combination between BiO^+ and phosphomolybdate ions as in the heteropolyacid $P_2O_5.24MoO_3.30H_2O$. The combination is resulting a very good acid catalyst that can enhance the activity of bismuth molybdate catalyst when both phases are coexisted. However, Batist et al. [15] revealed that $Bi_9PMo_{12}O_{52}$ was actually a mixture between $BiPO_4$ and α-$Bi_2Mo_3O_{12}$. Therefore, the catalyst that contains both $BiPO_4$ and α-$Bi_2Mo_3O_{12}$ will have higher activity than those that do not contain both phase.

Phase distribution of α-$Bi_2Mo_3O_{12}$, MoO_3, and $BiPO_4$ depends on the composition of bismuth, molybdenum and phosphorous in the reaction mixture. Table 4 shows the distribution of the phases among the bismuth-phophomolybdates based on their X-ray diffraction's Relative Intensity Ratio (RIR). The results reveal that the ratio of Bi:P:Mo determines which phases will be formed in the catalyst preparation. The table also shows that the main products from the catalyst preparation are α-$Bi_2Mo_3O_{12}$ and $BiPO_4$. $BiPO_4$

Table 4. The phase composition of all bismuth-phosphomolybdates

Index	Catalysts	Composition		
		$Bi_2Mo_3O_{12}$	MoO_3	$BiPO_4$
A	$Bi_2PMo_3O_x$	xxx	x	x
B	$Bi_2P_3Mo_3O_x$	-	x	xxx
C	$Bi_2P_{0.5}Mo_{2.5}O_x$	xxx	-	-
D	$Bi_2PMo_2O_x$	xxx	-	x
E	$Bi_2P_{1.5}Mo_{1.5}O_x$	xx	-	xxx
F	$Bi_{1.5}P_{0.5}Mo_3O_x$	xxx	x	
G	$BiPMo_3O_x$	-	xx	xxx
H	$Bi_{0.5}P_{1.5}Mo_3O_x$	-	xx	xx
I	$Bi_2Mo_3O_{12}$	xxx	-	-

"x" mark a rough composition of each phase
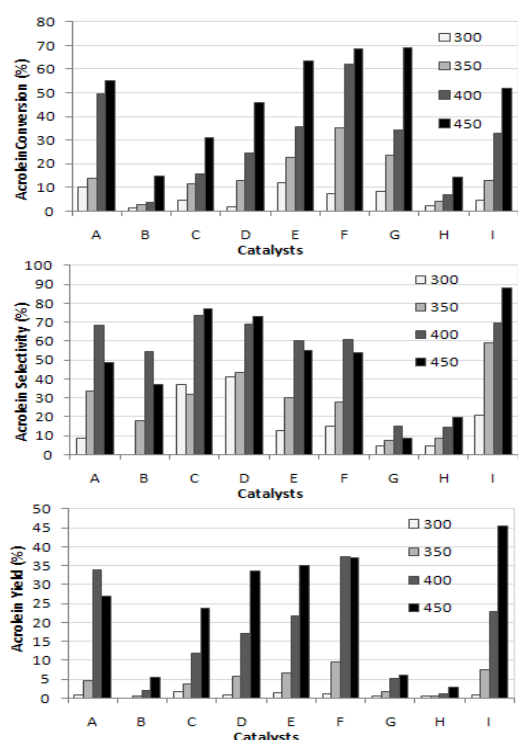
Figure 4. The bismuth-phosphomolybdate performance on the partial oxidation of propylene to acrolein
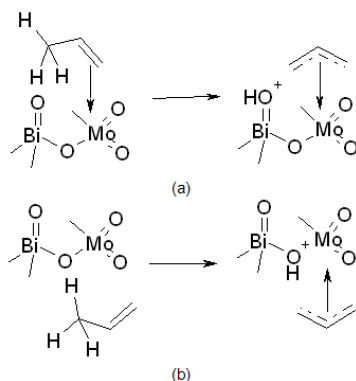
Fig 5. Allyl formation on bismuth-phosphomolybdate catalyst. a) Hydrogen ion is captured by a carbonyl oxygen and b) Hydrogen ion is captured by the bridge oxygen [18]

is detected when the ratio of Bi:P≥0.5. At lower ratio, the phase is not detected may be due to its very low concentration or poor crystallinity. MoO_3 is more likely to be formed if there are elements not reacted to form α-$Bi_2Mo_3O_{12}$ or $BiPO_4$.

Study on the catalyst activity and selectivity on the conversion of propylene to acrolein shows that the phase composition of each bismuth phosphomolybdate seems to have little effects. Fig. 4 shows the propylene conversion, selectivity of acrolein, and acrolein yields as a function of the catalyst phase composition.

Catalysts α-$Bi_2Mo_3O_{12}$ in its mixture with $BiPO_4$ and MoO_3 exhibit a higher activity and selectivity than the mixture of just $BiPO_4$ and MoO_3. The catalysts, which only consist of $BiPO_4$ and MoO_3 (catalyst B, G and H), have a very poor activity to the formation of acrolein from propylene.

The low activity of the catalysts consisting of only $BiPO_4$ and MoO_3 is consistent with those reported in literatures [16-17]. According to the literatures, there are two steps involved in the partial oxidation of propylene to acrolein, i.e., allyl formation and oxygen insertion. The allyl formation, as depicted by Fig. 5, requires the existence of bismuth-oxide groups on the catalyst surface while the Mo-O groups supply the oxygen to oxidise the allyl. Catalyst B, G and H do not have a bismuth oxide group adjacent to molybdenum oxide to facilitate those activation reactions. Due to this reason, the absence of Bi-O groups in catalysts B, G and H is believed as the major cause of the poor activities of those catalysts, although one of them (catalyst G) showed a high conversion of propylene.

An interesting trend of activities is shown by catalysts C, D, E and F. Fig. 3 shows that the catalysts, which contain $Bi_2Mo_3O_{12}$ and $Bi_9PMo_{12}O_{52}$, are more active than those which do not contain them. Based on this information, the coexistence of $Bi_2Mo_3O_{12}$ together with $Bi_9PMo_{12}O_{52}$ is most probably a factor responsible for the high activities of catalysts C, D, E, and F. Fig. 3 and Table 2 also shows the influence of coexistence of a third additive, namely MoO_3 or $BiPO_4$. The existence of both phases makes the catalysts D, E, and F have higher activity than catalysts C.

All above information proves that both $BiPO_4$ and MoO_3, although on their own have very low activity toward the acrolein formation, are able to improve the activity of the main catalysts ($Bi_2MO_3O_{12}$ and $Bi_9PMo_{12}O_{52}$). Some literature believes that either MoO_3 or $BiPO_4$ improves the catalyst activity by acting as an oxygen source for rapid re-oxidation of the active site [8,16-17,19]. The MoO_3 provides oxygen for the reaction by reducing the oxidation number of Mo^{6+}, to Mo^{5+} and/or Mo^{4+}. On the other hand, phosphorus has unstable pπ-pπ bonds, weak to moderate dπ-pπ bonds, and valence expansions. These properties make

phosphorus oxide, which has a pπ-pπ bond between phosphorus and oxygen, to easily donate its oxygen for the reaction. Phosphorus could also perform multiple bonding and, as a result, improve the stability of the complexes with transition elements in the catalysts [20].

CONCLUSION

Phosphorus addition in the preparation of α-Bi$_2$Mo$_3$O$_{12}$ precursor produced four major phases of bismuth phosphomolybdate under the preparation condition mentioned in the experimental method, namely α-Bi$_2$Mo$_3$O$_{12}$, Bi$_9$PMo$_{12}$O$_{52}$, MoO$_3$, and BiPO$_4$. The BiPO$_4$ was formed when the Bi:P $\geq$ 0.5 while other phases will be formed if there were elements not reacted to form either α-Bi$_2$Mo$_3$O$_{12}$ or BiPO$_4$. The catalysts activity and selectivity test show that those that solely containing BiPO$_4$ and MoO$_3$ have very low activities for partial oxidation of propylene to acrolein. Meanwhile, catalysts containing α-Bi$_2$Mo$_3$O$_{12}$ and Bi$_9$PMo$_{12}$O$_{52}$, together with either MoO$_3$ or BiPO$_4$ showed on average the same activities as α-Bi$_2$Mo$_3$O$_{12}$. One of the catalysts which contain a combination of α-Bi$_2$Mo$_3$O$_{12}$, Bi$_9$PMo$_{12}$O$_{52}$ and MoO$_3$ has even better performance than α-Bi$_2$Mo$_3$O$_{12}$ at lower temperatures. The presence of the oxygen donor phase, i.e. BiPO$_4$ and MoO$_3$, are believed to play a key role for the high activities of bismuth-phosphomolybdate catalysts. However, at higher temperatures, the presence of the oxygen donor reduces the catalyst selectivity to acrolein.

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