The Synergy Effect in TiO₂ Supported Bi-Mo Catalysts for Facile and Environmentally-Friendly Synthesis of Pyridylaldehydes from Oxidation of Picolines

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Abstract—The oxidation of picolines to pyridlaldehydes was studied over bismuth molybdate catalysts supported on TiO₂. The research results showed that α -Bi₂Mo₃O₁₂ was superior to β -Bi₂Mo₂O₉ and γ -Bi₂MoO₆ in terms of reactivity. Further doping MoO₃ to α -Bi₂Mo₃O₁₂/TiO₂ gave rise to increased catalytic performance, which was due to the synergy effect of α -Bi₂Mo₃O₁₂ and MoO₃. The effect was on one hand manifested in the intimate relationship between α -Bi₂Mo₃O₁₂ and MoO₃ in stabilizing the crystallographic structure of catalysts and thereafter maintaining the surface area of the catalyst, as indicated by the BET surface area and XRD analysis. Moreover, NH₃-TPD analysis demonstrated the effect in modifying the surface acidity of the catalysts, and thus facilitating the substrate adsorption as the picolines are alkaline substances. Additionally, the effect between α -Bi₂Mo₃O₁₂ and MoO₃ rendered the modification of the electronic properties and thereafter the oxygen desorption properties and reducible properties of the catalysts, as evidenced in the H₂-TPR and O₂-TPD analysis.

Keywords: picoline, pyridylaldehyde, oxidation, bismuth molybdate, synergy **DOI:** 10.1134/S0965544120020061

INTRODUCTION

Pyridylaldehydes as synthetic intermediates are of paramount significance in chemistry because of their widespread application in the fields of pharmaceuticals, agrochemicals, chiral catalysts, functional polymers and as well as others [1-5]. Therefore, intensive study for their preparation turns out to be meaningful. Molecular oxygen as a green oxidant is preferably involved in oxidative processes [6] since it is environmentally benign, especially for bulk chemical industries. Meanwhile, water as a nontoxic, economical and environmentally friendly medium is of widespread interest in organic synthesis [7]. Based on these, it is extremely desirable to achieve the green synthesis of pyridylaldehydes from picolines via heterogeneous catalysis employing oxygen as terminal oxidant and water as reaction medium. As for the catalysts reported, vanadia based catalysts [8-10] were the most commonly used, however, the yield was relatively low and dissatisfying. Thus, to develop an effective and highly efficient catalyst is still a challenge.

Generally, the synergetic effect of two metal active components may result in a surprising catalytic activity in oxidation reactions, such as Cu-Ce [11], Fe-V [12] and Bi-Mo [13]. The Bi-Mo system is wellknown owing to its good catalytic performance in hydrocarbon oxidative reactions since 1960s [14–16], especially propylene oxidation to acrolein [17] that has been industrialized successfully, and researches of this system are ongoing in discovering new properties and applications [18–20]. Till now, research work concerning the oxidation of picolines to pyrdiylaldehydes over this system has been rarely reported, we envisioned that the Bi-Mo catalyst could be an effective candidate in the oxidation of picolines in that they have similar unsaturated structures and active hydrogen atoms with propylene. Our previous study [21] by using 2-picoline as probe molecular showed that α -Bi₂Mo₃O₁₂ and MoO₃ supported onto titania in cooperative catalysis gave outstanding performances better than that of V_2O_5 and MoO_3 also supported onto titania [22]. However, the reasons accounting for the cooperative catalysis between α -Bi₂Mo₃O₁₂ and MoO₃ haven't been understood well yet.

Therefore, in the present work, the synergy effect between α -Bi₂Mo₃O₁₂ and MoO₃ was uncovered. Besides, by taking into consideration process integrity, the catalytic behaviors of three phases of bismuth molybdates as well as the performances of titania supported α -Bi₂Mo₃O₁₂ and MoO₃ catalysts in oxidation reactions of picolines were also investigated in detail.

EXPERIMENTAL

Catalyst Preparation. Catalysts were prepared using the co-precipitation method. Commercially available chemical reagents were used without any further purification. $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ was dissolved in deionized water and heated to 70°C with stirring, then a solution of 1M Bi $(NO_3)_3 \cdot 5H_2O$ in 2M HNO₃ was dropwise added. Subsequently, a certain amount of TiO₂ (anatase) was added, the resulting slurry was stirred for 3 h and water was removed by a rotary evaporator, the residue was then extruded with the size of 2 mm in diameter and 2.5 mm in length, dried at 80°C for 2 h, and calcined at 550°C for 10 h.

Catalyst Characterization. The BET surface areas were determined by nitrogen adsorption at 77K employing a Micromeritics TriStar II 3020 instrument.

X-ray diffraction (XRD) patterns were collected on a Rigaku D/max-2550pc diffractometer using Cu $K\alpha$ radiation (40 kV, 250 mA) at diffraction angles (20) from 20° to 90°.

Temperature-programmed desorption of ammonia (NH₃-TPD) was determined by a PX200 adsorption instrument. The sample (100 mg) was pretreated at 500°C for 1 h in helium atmosphere, cooled to 40°C, filled with 4% NH₃/He mixed gas for half an hour, and then switched to pure helium (30 mL min⁻¹) for 1 h to remove weakly adsorbed ammonia, and finally heated to 500°C at 10°C min⁻¹ in pure He (30 mL min⁻¹).

Temperature-programmed reduction (TPR) was carried out on a Micromeritics AutoChem II 2920 instrument, and the samples of the catalyst (100 mg) were crushed into 60 meshes and preheated under argon atmosphere at 400°C for 1 h, then cooled down to 80°C and reduced with a 10% H₂/Ar mixed gas (30 mL min⁻¹) from 80 to 800°C at a heating rate of 15° C min⁻¹.

Temperature-programmed desorption of oxygen (O₂-TPD) was performed with a GC1690 instrument, and the samples of the catalyst (100 mg) were treated with a 5% O₂/Ar mixed gas (30 mL min⁻¹) at 300°C for 1 h, then cooled down to 50°C, and heated to 900°C at 20°C min⁻¹ in pure He (40 mL min⁻¹).

Catalytic Tests. The catalytic tests were carried out in a fixed-bed stainless tube reactor with 10 mm ID of 600 mm length under atmospheric pressure. The temperature in the catalyst zone was kept constant and measured using a thermocouple, after the temperature reached the set point and stabilized, oxygen regulated by a flowmeter was fed in for one hour, then deionized water was introduced into the system using a pulseless pump for one hour, after that, the picoline in water was used in place of pure water. Crude products were collected and analyzed using an Agilent 6820 GC instrument. The conversion of picolines and the selectivity to pyridylaldehydes were calculated based on their peak areas in gas chromatograph (external standard method).

RESULTS AND DISCUSSION

Our initial efforts then focused on screening of three bismuth molybdates, namely, $Bi_2Mo_3O_{12}(\alpha)$, $Bi_2Mo_2O_9(\beta)$, and $Bi_2MoO_6(\gamma)$, by using 2-picoline as the probe molecule. Catalytic test results were summarized in Table 1. As shown, all the three phases can be readily prepared at 600° C (Entry 1–3 and 6–8), while at 550°C (Entry 5 and 10), the β phase was unstable, and thus decomposed into α and γ phases [23], irrespective of whether loaded into titania or not. It is obvious that catalysts with pure α or β phase exhibited similar reactivity, both better than that of the γ phase (e.g. Entry 6, 7 to Entry 8), and the existence of the γ phase in the catalyst caused a decline in conversion of 2-picoline and selectivity to 2-pyridylaldehyde (Entry 5 and 10). In addition, for α and β phases, the conversion nearly doubled when supported on titania, while the selectivity only slightly changed with a difference not exceeding 7%, exemplified in the case of MB32/550 (α , conv. 15.5%, sel. 87.3%) and MB32T550 (α, conv. 29.5%, sel. 81.3%).

Based on the above, the α phase supported on titania (MB32T550) was subsequently used for further research on account of its stability as well as the superior catalytic performance over others. The reaction temperature was an important parameter in terms of the reactivity. With other conditions remaining unchanged as in Table 1, when the reaction was carried out at 290°C, an increase of the conversion to 45.2% followed by a decrease of the selectivity to 70.3% was observed, further increasing the temperature to 310°C provided an improvement of the conversion to 57.2% but also led to a downturn of the selectivity to 61.0%. In terms of atom economy and as well as product yield, a temperature of 290°C was assumed as a reasonable and expedient value for follow-up experiments.

In the previous research, in order to pursue better catalytic performance, we had found that by introducing an extra amount of MoO₃ into the α -Bi₂Mo₃O₁₂/TiO₂ catalyst, the reactivity was significantly improved. Therefore, five catalyst samples were prepared (Table 2) and catalytic tests were carried out accordingly (Table 3) [21]. It was shown that the conversion for MB32T and MT each with only one active component was much lower than that for the other

Entry	Catalysts ^b	Active phase	Conversion of 2-picoline, %	Selectivity to 2-pyridylaldehyde, %
1	MB32/600	α	8.6	94.1
2	MB11/600	β	9.9	93.2
3	MB12/600 ^c	γ	N.a.	N.a.
4	MB32/550	α	15.5	87.3
5	MB11/550	α and γ	12.2	78.5
6	MB32T600	α	17.7	87.2
7	MB11T600	β	19.1	86.6
8	MB12T600	γ	13.1	63.5
9	MB32T550	α	29.5	81.3
10	MB11T550	α , β , and γ	19.7	68.1
11	MB12T550	γ	16.0	52.1

Table 1. Bi-Mo catalysts screening for oxidation of 2-picoline^a

^a Reaction conditions: 4 g catalyst, 270°C, flow rate of 10% 2-picoline aqueous solution 0.5 mL min⁻¹, oxygen flow rate 0.1 L min⁻¹. ^b Catalysts MBxy/z were unsupported and MBxyTz were those loaded into TiO₂, M = Mo, B = Bi, xy = molar ratio of Mo/Bi, and z = calcination temperature.

^c Catalyst inapplicable for activity test due to its poor mechanical strength.

Table 2. Detailed information of various Bi-Mo catalysts^a supported on TiO_2

Catalyst	Catalysts composition			Hydrogen consumption
	α phase/MoO ₃ , mol/mol	MoO ₃ content, %	Surface area, $m^2 g^{-1}$	in TPR, mmol g_{cat}^{-1}
MT	0:1	15	4.1	1.56
MB32T	∞	0	3.1	1.77
MB21T	1:1	2.1	4.0	1.96
MB74T	2:1	1.1	4.0	1.98
MB85T	5:1	0.5	3.9	1.96

^a Catalysts MBxyT were with 15% load amount supported on TiO₂ and calcined at 550°C, M = Mo, B = Bi, xy = molar ratio of Mo/Bi.

three catalysts with two active components, and the similar trend for the selectivity. Moreover, catalyst MB21T with a 1/1 molar ratio of α -Bi₂Mo₃O₁₂/MoO₃ gave the best performance. By these, it might be considered the outstanding performance of MoO₃ doped α -Bi₂Mo₃O₁₂/TiO₂ catalysts was owing to the synergy effect between α -Bi₂Mo₃O₁₂ and MoO₃.

To interpret this synergy effect, BET analysis (Table 2) and XRD analysis (Fig. 1) were carried out in the first place. In some sense, the much lower reactivity of MB32T can be perceived partly in terms of its reduced BET surface area ($3.0 \text{ m}^2 \text{ g}^{-1}$) by about 25% compared with others ($4.0 \text{ m}^2 \text{ g}^{-1}$ or so), which may as a result generate much less active sites. It can be seen in Fig. 2 that catalyst MT bears MoO₃ and anatase TiO₂, and the other four Bi-containing samples consist of α -Bi₂Mo₃O₁₂ and anatase TiO₂. According to the literature [23], catalysts with Bi/Mo molar ratios lower than 2/3 consisted of both α -Bi₂Mo₃O₁₂ and

 Table 3. Influence of various Bi-Mo catalysts on oxidation of 2-picoline^a

Entry	Catalysts	Conversion of 2-picoline, %	Selectivity to 2-pyridylaldehyde, %
1	MT	51.8	78.1
2	MB32T	45.2	70.3
3	MB21T	70.9	83.1
4	MB74T	63.6	80.3
5	MB85T	61.0	81.7

^a Reaction conditions: 4 g catalyst, 290°C, flow rate of 10% 2-picoline aqueous solution 0.5 mL min⁻¹, oxygen flow rate 0.1 L min⁻¹.

 MoO_3 , whereas MoO_3 in the Bi-containing catalysts was not detected by XRD analysis because its quantity was too small, but it was observed by SEM analysis [21]. At the same time, the analysis shows that rutile



Fig. 1. XRD analysis of MT, MB32T, MB21T, MB74T and MB85T, (a) anatase TiO_2 , (a*) rutile TiO_2 , (b) MoO_3 and (c) α -Bi₂Mo₃O₁₂.

TiO₂, which was not found in the other three Bi-containing samples, had comparable intensity with anatase TiO₂ in MB32T. On the other hand, Bond G. C. reported that anatase wouldn't transform into rutile TiO_2 lower than 600°C in pure samples [24], so the coexistence of anatase and rutile TiO₂ in MB32T calcined at 550°C implies that α -Bi₂Mo₃O₁₂ facilitated the transformation from anatase to rutile, which reduced the surface area of the catalyst by 25% compared with others as shown in Table 2, but this transformation effect was inhibited by MoO₃ as there was no formation of rutile in the other three Bi-containing catalysts with excess MoO₃. It may be concluded that the existence of Mo retarded the association between α -Bi₂Mo₃O₁₂ and TiO₂, thus delaying the change of crystallographic structure of TiO₂. In other words, this synergy effect was on one hand interpreted by the active components in stabilizing the crystallographic structure of catalysts and thereafter maintaining the surface area.

Oxidation reactions of hydrocarbons in heterogeneous catalysis is a process that follows Mars-van Krevelen mechanism [25, 26] which includes many steps: (1) chemisorption of hydrocarbon on the surface of the catalyst and abstraction of an α -hydrogen to form an intermediate; (2) insertion of lattice oxygen into the intermediate to form product; and (3) replenishment of lattice oxygen removed from the surface of the catalyst during the second step in order to reconstitute the active site. The generally accepted approach for propylene oxidation is proceeded through the formation of an allyl intermediate by α -hydrogen abstraction [27]. Bi was considered the α -hydrogen abstraction center to generate allyl species, while Mo was the chemisorption and oxygen insertion center,



Fig. 2. NH₃-TPD analysis of the catalysts.

and the relative reactivity of α -Bi₂Mo₃O₁₂ was much better than that of MoO₃ as MoO₃ had no α -hydrogen abstracting sites [28]. Based on the explanation above, the formation of a picolinic intermediate via α -hydrogen abstraction during the oxidation of 2-picoline to 2-pyridylaldehyde was proposed. However, in the case of oxidation of 2-picoline to 2-pyridylaldehyde, the fact that the reactivity of MT was better than that of MB32T proves MoO₃ does have α -hydrogen abstracting sites. A plausible explanation for this is that picoline is an alkaline substance, so that the acidity of the catalyst is favourable for its adsorption and the interaction with the catalysts accordingly, and thereafter possibly α -hydrogen abstraction. NH₃-TPD was performed to determine the acidity of the catalysts, as shown in Fig. 2. It is seen that week acidic sites existed in all samples. Integration of the desorption peaks showed the surface acidic sites density followed the order of MB21T > MT > MB74T > MB85T > MB32T, implying that the surface acidity of those catalysts containing α -Bi₂Mo₃O₁₂ increased with the addition amount of MoO₃. Moreover, the slightly higher density of MB21T than that of MT demonstrates the synergy effect of α -Bi₂Mo₃O₁₂ and MoO₃ in modifying the surface acidity of the catalysts.

Additionally, α -hydrogen abstraction of picolines was easy to take place because the picolinic intermediate should be much more easily and steadily formed than the allyl intermediate in that the electron of the picolinic radical is delocalized by a conjugated heterocycle after α -hydrogen abstraction while that of the allyl radical is delocalized merely by a double bond. Moreover, the N atom at which the converging of the electrons takes place due to its strong negativity may further stabilize the picolinic radical.

Literature shows that lattice oxygen mobility plays a key role in determining the reactivity of the bismuth molybdate catalysts [29], and addition of a small amount of conductive metal oxide can promote the



Fig. 3. O₂-TPD analysis of the catalysts.

transfer of the lattice oxygen in the bismuth molybdate catalysts [30], and hence the improvement of the reactivity of the catalysts accordingly. MoO_3 is a conductive metal oxide [31] in this case, though the connection between conductivity and catalytic activity was not the objective of the present research.

In H_2 -TPR analysis (Table 2), the fact that the hydrogen consumption amount of MB21T, MB74T, MB85T were almost the same and higher than that of MT and MB32T implied that α -Bi₂Mo₃O₁₂ and MoO₃ in synergy could enhance the lattice oxygen mobility of the catalyst and thus its reducibility, which was further evidenced in the O₂-TPD analysis results, as shown in Fig. 3. There was one apparent desorption peak at around 500°C with a shoulder and a weak desorption peak at around 800°C for MT, two weak broad desorption peaks at around 500 and 750°C for MB32T, and one apparent desorption peak at around 500°C with a shoulder and one apparent desorption peak at around 850°C all for MB21T, MB74T, and MB85T. It is also seen that the overall intensities of the desorption peaks for MB21T, MB74T and MB85T were stronger than that of MB32T and MT, and among which, the one for MB21T was the strongest.

Table 4. Oxidation of picolines over the catalyst MB21T^a

Entry	Substrate	Conversion of picoline, %	Selectivity to pyridylaldehyde, %
1	2-Picoline	70.9	83.1
2	3-Picoline ^b	18.9	93.7
3	4-Picoline	73.1	80.3

^a Reaction conditions: 4 g catalyst, 290°C, flow rate of 10% picoline aqueous solution 0.5 mL min⁻¹, oxygen flow rate 0.1 L min⁻¹.
 ^b 16 g catalyst.

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This was an indication that the α -Bi₂Mo₃O₁₂ and MoO₃ cooperated in synergy and enhanced the lattice oxygen mobility of the catalyst.

The synergy effect can be due to either the formation of a new phase or the "remote control mechanism" where there is no generation of new phases [32]. Since the XRD analysis gave no indication of formation of a new phase, the increase in the intrinsic reactivity of MoO₃ doped α -Bi₂Mo₃O₁₂/TiO₂ catalysts can be interpreted in terms of the "remote control mechanism" in which activated "spillover oxygen" by a "donor phase" migrates to an "acceptor phase" where new active catalytic sites are created [33]. Previous research revealed that Bi facilitates the dissociation of gaseous oxygen into lattice oxygen and its subsequent diffusion into the active sites [34]. The mobility of lattice oxygen in MoO_3 is very high [35], thus the lattice oxygen facilitated by α -Bi₂Mo₃O₁₂ should be able to easily diffuse into MoO₃ where new active catalytic sites are created, resulting in increased reactivity. It can be inferred that the intimate relationship between α -Bi₂Mo₃O₁₂ and MoO₃ led to the modification of the electronic properties and thereafter the oxygen desorption properties and reducible properties of the catalysts, giving rise to its increased catalytic performance.

Catalyst MB21T was also used for catalytic test for the other two isomers of picoline, and as it was shown in Table 4, the catalyst was also effective when used in 4-picoline oxidation. Nevertheless, the low conversion of 3-picoline with access use of catalyst amount was mainly because the methyl at *meta*-position of N would have higher electron density than that at *ortho*and *para*-positions, which was unfavorable for deprotonation of the methyl.

CONCLUSIONS

In the present work, oxidation of picolines to pyridylaldehydes over TiO₂ supported bismuth molybdate catalysts was studied. The research results showed that $\alpha\text{-}Bi_2Mo_3O_{12}$ was superior to $\beta\text{-}Bi_2Mo_2O_9$ and γ -Bi₂MoO₆ in terms of reactivity. Further doping MoO₃ to α -Bi₂Mo₃O₁₂/TiO₂ gave rise to increased catalytic performance, which was due to the synergy effect of α -Bi₂Mo₃O₁₂ and MoO₃. Catalyst with 1 : 1 molar ratio of $\alpha\text{-}Bi_2Mo_3O_{12}$ and MoO_3 gave the best performance. 2-picoline and 4-picoline could be readily oxidized to 2-pyridylaldehyde and 4-pyridylaldehyde, respectively. The much lower conversion of 3-picoline was mainly because the methyl at metaposition of N would have higher electron density than that at ortho- and para-positions, which was unfavorable for deprotonation of the methyl. Further research on the Bi-Mo catalyst system as well as catalyst adaptability to a variety of picoline derivatives and other related substrates is now being carried out in our laboratories.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

SUPPLEMENTARY MATERIALS

Supplementary materials are available for this article at https://doi.org/10.1134/S0965544120020061 and are accessible for authorized users.

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