ONE-STEP SYNTHESIS OF THERMALLY STABLE SOLID MOLYBDENUM BLUE USING BORON PHOSPHATE

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ABSTRACT

For the first time, thermally stable ‘molybdenum blue’ was prepared in a single step, using boron phosphate. Even though molybdenum blue was discovered more than a century ago, it has not been studied extensively due to its instability. Presence of variable oxidation states of molybdenum makes it more suitable for catalytic transformations, but fewer reports are available, since, they were generally prepared in solutions. The present investigation reports the preparation of stabilized molybdenum blue powder using boron phosphate. The sample was evaluated for its catalytic activity on the transformation of diphenyl sulfide to sulfoxide selectively, and results were compared with MoO₃ impregnated analog.

Keywords: Molybdenum Blue, BPO₄ Stabilized, Polymolybdates, Selective Sulfoxidation.

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INTRODUCTION

Polyoxomolybdates are molecules containing molybdenum in high oxidation state, linked by oxygen atoms forming Keggin type structure¹. In the presence of hetero atoms like P, Si, As, etc., they form a big-sphere type structure containing Mo₁₃₂ or big-wheel type structure containing Mo₁₅₄ or lemon-shaped cluster (Mo₃₆₈). They appear as blue due to partial reduction of Mo^{VI} to Mo^V as first observed by Scheele in 1778^{1,2} to be amorphous. The structure of the molybdenum blue allows change of coordination number on side chain at Mo sites and made up of Mo-O-Mo bond with moderate strength containing terminal – Mo=O sites. In spite of the above said advantages, very less literature is available for exploring catalytic activity of molybdenum blue⁷. Generally, molybdenum blue was prepared by partial reduction of an acidified solution containing molybdates³. Other preparation methods include exfoliation of MoS₂ nanotube⁴, using reducing agents⁵ and microorganisms⁶. Most of the preparation methods reported in the above literature lead to molybdenum blue solution, where the catalytic applications are limited. Recently, the preparation of solid molybdenum blue powder has been achieved by evaporating the aqueous solution containing the same⁷; another method involved the electrochemical reduction of sodium molybdate solution using graphite/platinum electrodes⁸. The drawbacks of the above process are either they involve high temperature or time-consuming process or not viable for large scale synthesis of solid molybdenum blue.

EXPERIMENTAL

The preparation of the stabilized molybdenum blue by BPO₄ involved mixing of required quantities of boric acid (99.5%) and ammonium heptamolybdate (99.5%) thoroughly with the help of mortar-pestle, in presence of 25 ml of 2-propanol. After drying at room temperature, the powder was transferred into a glass beaker and blended well with calculated quantities of phosphoric acid (85%) to form a paste. The contents were dried at 120°C for 4 h and the dried mass was powdered and calcined between 150°C and 500°C for 2 h. The deep-blue colored powder sample was labeled as MB(10)BP (number in parenthesis represents weight % of Mo as MoO₃) and Table-1 gives the composition and identification of the samples. The appearance of the MB(10)BP is shown in Fig.-1.

The synthesis of the impregnated sample involved mixing boric acid and phosphoric acid in the mole ratio of 1:1 in presence of 25 ml of 2-propanol followed by drying in an oven at 120°C for 4 h.

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The resultant solid mass was crushed, powdered and calcined between 150°C and 500°C for 2 h to form BPO_4 . In the second step, the calcined BPO_4 was powdered and mixed with calculated quantities of ammonium heptamolybdate in presence of 25 ml of 2-propanol. The paste was dried at room temperature and again calcined at 500°C for 2h. The resulting pale green sample was labeled as Mo(10)BP-Imp and the composition is given in Table-1. Similarly, impregnated samples were prepared on silica and alumina support for comparison.

Fig.-1: Appearance of MB(10)BP calcined at 500°C.

Table-1: Composition and Identification of Samples

S. No.	Sample ID	Color	Mole Ratio			Weight %	
			B_2O_3	P_2O_5	As MoO_3	Support	As MoO_3
1.	BPO_4 (support)	White	0.5	0.5	--	100	--
2.	Mo(10)BP-Imp	Pale green	0.5	0.5	0.08	90.2	9.8
3.	MB(10)BP	Deep-blue	0.5	0.5	0.08	90.2	9.8
4.	MB(10)BP(1.1)	Deep-blue	0.5	0.55	0.08	90.8	9.2
5.	Mo(10) Al_2O_3	Pale green	-	-	0.08	90.1	9.9
6.	Mo(10) SiO_2	Pale green	-	-	0.08	90.1	9.9

The powder X-ray diffraction patterns of all samples were recorded in PANalytical X-PERT3 instrument, with $\text{Cu K}\alpha$ of 1.54Å, continuous scan in the 2θ range of 5-60°. The Scanning Electron Micrograph was captured using JEOL JSM-7401F instrument and the FTIR spectra were recorded in Perkin Elmer (Model: Spectrum RXi) by forming pellets with KBr. The UV-Visible spectra were recorded in Systronics Type 2202 spectrophotometer.

Oxidation is one of the most fundamental reactions in organic synthesis. The controlled oxidation of sulfides to sulfoxides without forming sulfones, yet remains a challenge. The stabilized molybdenum blue from the present investigation was tested for its catalytic activity for oxidation of diphenylsulfide using hydrogen peroxide as the oxidant. The reaction was conducted in a batch reactor, where, the diphenylsulfide (98%, 50 mg) was dissolved in a 2 ml of a suitable solvent (methanol or ethanol or 1:1 methanol/dichloromethane). The catalyst was charged (5 mg) under stirring followed by the addition of 28µl hydrogen peroxide (30%) at room temperature (27°C-30°C). The progress of the reaction was monitored using TLC and HPLC.

RESULTS AND DISCUSSION

In the preparation of stabilized molybdenum blue, the order of adding the components play a vital role. When phosphoric acid was added to a mixture of boric acid and ammonium heptamolybdate, it resulted in the formation of molybdenum blue, while such a phenomenon was not observed when the first phosphoric acid was added to boric acid, followed by addition of ammonium heptamolybdate. Thus, it was inferred that formation of BPO_4 and molybdenum blue takes place simultaneously. In the second method of addition, since, all phosphates are consumed for the formation of boron phosphate, free phosphates were not available for the formation of molybdenum blue.

The XRD patterns of boron phosphate calcined at 150°C showed distinct peaks corresponding to the formation of BPO_4 phase (JCPDS No.74-1169) (Fig.-2). Additional peaks at $2\theta = 14.5, 14.97, 28$ (100%)

indicates presence of unreacted boric acid (JCPDS No.73-2158). With the increase in calcination temperature to 350°C, the peaks corresponding to unreacted boric acid disappeared and on further increasing to 500°C, pure boron phosphate phase with increased crystallinity was formed. The XRD pattern of molybdenum impregnated sample (Mo(10)BP-imp) showed presence on MoO₃ phase (JCPDS PDF No.89-5108) and BPO₄ phase. Similarly, the XRD patterns of molybdenum impregnated silica confirmed the formation of MoO₃ phase, while that impregnated over alumina (neutral) showed an amorphous phase.

The XRD patterns of BPO₄ stabilized molybdenum blue sample (MB(10)BP) calcined at 150°C indicate peaks corresponding to boron phosphate and unreacted boric acid (Fig.-3). The additional peaks corresponding to $2\theta = 9.6, 12.19$ (100%) can be assigned to unreacted ammonium heptamolybdate (JCPDS No.70-1707) and the peaks at $2\theta = 12.19, 14.08$ can be assigned to the presence of (NH₄)₂Mo₂O₇ (JCPDS No.70-1706). With the increase in calcination temperature to 350°C, the intensity of peaks corresponding to unreacted ammonium heptamolybdate and (NH₄)₂Mo₂O₇ decreased, while the excess boric acid was converted to B₂O₃ confirmed by the peak at $2\theta=28$ (JCPDS PDF No.06-0297). With the increase in calcination temperature to 500°C, the crystallinity of BPO₄ increased.

The BPO₄ phase was formed reacting equimolar ratio of borate and phosphate. When the molybdenum was added in the reaction mixture during the preparation of MB(10)BP, it reacts with phosphates to form molybdenum blue, leaving excess borate in the mixture. This excess boric acid was converted to B₂O₃ at high temperatures, which was reflected in the corresponding XRD pattern (Fig.-3). To verify the inference, a sample was prepared using excess phosphoric acid (B₂O₃:P₂O₅ = 1:1.1; MB(10)BP(1.1)), which, showed absence of the peak at $2\theta=28$, exhibiting the presence of pure BPO₄ phase. The molybdenum blue was observed to be amorphous as reported by earlier workers.^{1,2,8}

Fig.-2: XRD Patterns of BPO₄ calcined at Different Temperatures and MoO₃ impregnated on BPO₄, SiO₂ and Al₂O₃.

The FTIR spectra of BPO₄ calcined at 500°C (Fig.-4) exhibited O-B-O bending vibration at 550 cm⁻¹ and tetrahedral B-O symmetrical stretching⁹ at 600 cm⁻¹. The asymmetric tetrahedral B-O stretching was observed at 900 cm⁻¹. The MB(10)BP calcined at 150°C showed additional absorption (other than BPO₄) at 709 cm⁻¹ due to ν-Mo-O vibration and Mo-O-Mo vibration at 885 cm⁻¹ corresponding to Mo⁶⁺ species¹⁰. The residual NH₄⁺ showed vibration¹¹ at 3173 cm⁻¹ and 1400 cm⁻¹. The intensity of these peaks decreased on increasing the calcination temperature to 500°C due to the decomposition of ammonium species.

The SEM of BPO_4 (Fig.-5A) shows flower-like morphology, having clusters of the size 1.5 – 2 microns, made of boron phosphate plates of the size around 100 nm $\times$ 300 nm. The morphology of the MB(10)BP (Fig.-5B) was completely different from that of BPO_4 and showed agglomerates of the size 500 nm, containing nanoparticles of molybdenum species.

Fig.-3: XRD patterns of Molybdenum Blue (MB(10)BP) calcined at 150°C, 350°C and 500°C; MB(10)BP(1.1).

Fig.-4: FTIR Spectra of Boron Phosphate calcined at 500°C; BPO_4 stabilized Molybdenum Blue calcined at 150°C and 500°C

The UV-visible spectra of the samples are shown in the Fig.-6. The BPO_4 did not show any characteristic absorption, while the MB(10)BP showed absorption at 600 nm and MB(10)BP(1.1) showed absorption at 610 nm as reported by earlier workers⁸.

The transformations of sulfides to sulfoxides over different catalysts were studied and the results are presented in Fig.-7. The blank support did not show any appreciable activity, while MoO_3 impregnated silica showed better activity and that impregnated over alumina and BPO_4 exhibited considerable activities. A maximum conversion of around 80% was observed at 120 min of reaction time. The MB(10)BP catalyst showed nearly 85% conversion within 30 min of reaction time and reached 90% conversion at 60 min.

The MB(10)BP calcined at different temperatures were tested for their catalytic activities and the results are presented in Fig.-8.

Fig.-5: SEM Images of (A) BPO_4 and (B) MB(10)BP-500 Samples

Fig.-6: UV-Visible Spectra of BPO_4 , MB(10)BP and MB(10)BP(1.1) Samples

Fig.-7: Oxidation of Diphenylsulfide to Diphenylsulfoxide Over Different Catalysts.

The initial activities of the catalysts were found to increase with calcination temperature but attained equilibrium activity after 60 min of reaction time. The MB(10)BP(1.1) catalyst exhibited very high activity of around 97% within 30 min of reaction time and the reactants were not detected in the reaction mixture after 35 min.

Table-2 compares the activities of the catalysts and that reported in the literature by earlier workers. The TON was calculate assuming all molybdenum species in the sample are participating in the reaction. The MoO₃ impregnated BPO₄ and Al₂O₃ exhibited TON of 28 and 21, respectively, with the formation of sulfones. The MB(10)BP showed TON of 67 and that of MB(10)BP(1.1) was calculated to be 69.

Fig.-8: Oxidation of Diphenylsulfide to Diphenylsulfoxide over MB(10)BP Catalysts calcined at Different Temperatures.

Earlier workers have reported nearly 100% conversion of sulphides, but the quantity of catalyst used was quite high (TON – 0.55 and 1). The Mojtaba Bagherzadeh *et al.* has reported 98% conversion of sulfides and formation of 2% sulfones with relatively less equivalence of catalyst (TON-28), but reaction time was 120 min¹⁴.

The influence of catalyst content (MB(10)BP-500) over the conversion of sulfide was studied in the range 1 mg to 5 mg for 50 mg of the substrate with 28 μ l of oxidant (H₂O₂) at room temperature (Fig.-9). The reaction reached maximum conversion with 2 mg of the catalyst at a reaction time of around 30 min.

Fig.-9: Influence of Catalyst (MB(10)BP-500) Content on Oxidation of Sulfide.

Table-2: Catalytic Transformation of Diphenylsulfide over Different Catalysts at Room Temperature

Catalyst	Substrate equivalence (mmol)	Catalyst equivalence (mmol as MoO ₃ content)	Oxidant (H ₂ O ₂) equivalence (mmol)	Time (min)	TON*	Yield % (Sulfoxide)	Yield % (Sulfone)	References
Mo(10)BP-imp	1	0.014	1	30	28	40	5	-
MB(10)BP	1	0.014	1	30	67	94	-	-

MB(10)BP(1.1)	1	0.014	1	30	69	98	-	-
Mo(10)Al ₂ O ₃	1	0.014	1	30	21	30	9	-
Mo(10)SiO ₂	1	0.014	1	30	2	3	-	-
Fe ₃ O ₄ @SiO ₂ -NH ₂ -Mo	1	1.8	1.1	30	0.55	99	-	¹²
CpMoO ₂ Cl	1	1.0	1	15	1	99	-	¹³
Schiff's Base complex	1	0.035	1	120	28	98	2	¹⁴

*TON calculated assuming that all molybdenum is involved in the reaction.

CONCLUSION

Solid molybdenum blue powder stabilized with BPO₄ has been prepared by a simple one-step synthesis procedure. The XRD analysis proved that the MB(10)BP was thermally stable upto 500°C containing BPO₄ phase, while molybdenum blue was found to be amorphous. The FTIR spectra of MB(10)BP showed vibrations of molybdenum corresponding to polymolybdates. The SEM image showed agglomerates of molybdenum blue nanoparticles. The present sample (MB(10)BP(1.1)) exhibited a high yield of nearly 97% sulfoxide, without forming sulfones within 30 minutes of the reaction time. On the other hand, the MoO₃ impregnated BPO₄ (Mo(10)BP-Imp) exhibited 40% selectivity of sulfoxide after 30 minutes of the reaction time, while the BPO₄ exhibited negligible reactivity.

REFERENCES

1. A. Müller, S. Roy, *Coordination Chemistry Reviews*, **245**, 153(2003), DOI:10.1016/S0010-8545(03)00110-3.
2. A. Müller, J. Meyer, E. Krickemeyer and E. Diemann, *Angewandte Chemie International Edition*, **35**, 1206(1996), DOI:10.1002/anie.199612061.
3. Ippei Nakamura, Haralampos N. Miras, Aya Fujiwara, Masaru Fujibayashi, Yu-Fei Song, Leroy Cronin and Ryo Tsunashima, *Journal of American Chemical Society*, **137**, 6524(2015), DOI: 10.1021/ja512758j.
4. M. KlanjsekGunde, J. Kovaca, I. Iskra, J. Jelenca, M. Remskara, *Material Research Bulletin*, **48(2)**, 802 (2013), DOI:10.1016/j.materresbull.2012.11.062.
5. José Escobar, María C. Barrera, Ana W. Gutiérrez, María A. Cortés-Jacome, Carlos Angeles-Chávez, José A. Toledo, Dora A. Solís-Casados, *Applied Catalysis B: Environmental*, **237**, 708(2018), DOI:10.1016/j.apcatb.2018.06.034.
6. Yunus Shukor, Hamzah Adam, Khalid Ithnin, Ibrahim Yunus, Nor Aripin Shamaan and Mohd. Arif Syed, *Journal of Biosciences*, **7**, 1448(2007), DOI:10.3923/jbs.2007.1448.1452.
7. Xi Liu, Marco Conte, Weihao Weng, Qian He, Robert L. Jenkins, Masashi Watanabe, David J. Morgan, David W. Knight, Damien M. Murphy, Keith Whiston, Christopher J. Kiely and Graham J. Hutchings, *Catalysis Science & Technology*, **5**, 217(2015), DOI:10.1039/c4cy01213e.
8. Ozge Koyun, Semih Gorduk, Melih Besir Arvas, Yucel Sahin, *Synthetic Metals*, **233**, 111(2017), DOI:10.1016/j.synthmet.2017.09.009.
9. M. Mamlouk, K. Scott, *Journal of Power Sources*, **286**, 290(2015), DOI:10.1016/j.jpowsour.2015.03.169.
10. Tzu Hsuan Chiang and Hung Che Yeh, *Materials*, **6**, 4609(2013), DOI:10.3390/ma6104609.
11. Jia Li, Fung-luen Kwong, Dickon H. L. Ng, *Journal of American Ceramic Society*, **91**, 1350(2008), DOI:10.1111/j.1551-2916.2008.02276.x.
12. Yasuhiro Uozumi, Makoto Nagaosa, *Synfacts*, **11**, 1117(2015), DOI:10.1055/s-0035-1560283.
13. Carla A. Gamelas, Tiago Lourenço, André Pontes da Costa, Ana L. Simplicio, Beatriz Royo, Carlos C. Romão, *Tetrahedron Letters*, **49**, 4708(2008), DOI:10.1016/j.tetlet.2008.05.126.
14. Mojtaba Bagherzadeh, Hooman Karimi and Mojtaba Amini, *Journal of Coordination Chemistry*, **70**, 2986(2017), DOI:10.1080/00958972.2017.1383603

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