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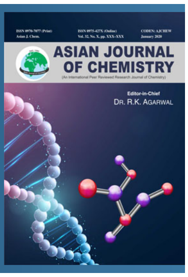

Selective Catalytic Oxidation of Organic Sulfides to Sulfoxides without Forming Sulfones over Solid Molybdenum Blue: Kinetic and Thermodynamic Studies

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The present investigation reports studies on the selective catalytic oxidation of organic sulfide substrates over molybdenum blue catalyst supported on boron phosphate. The catalyst was synthesized through partial precipitation method and characterized by XRD, FTIR and SEM techniques. The sulfoxidation was carried out in a batch reactor using benzyl phenyl sulfide as the substrate over the present catalyst and the reaction parameters were varied and optimized. The results were compared with the MoO_3 impregnated boron phosphate. The catalyst was also studied for its performance over other sulfide substrates and the results were compared with available studies in literature. The reaction followed pseudo first-order kinetics and rate of the reaction under optimized condition was 10.1×10^{-3} min^{-1}, with energy of activation of 29.3 kJ/mol. The Mo-O-Mo bridging and -Mo=O bonds present in molybdenum blue were participating in the reaction and possible mechanism has been proposed. The 100% selectivity of the product towards sulfoxide has been attributed to the big-wheel structure of molybdenum blue as it sterically hinders further reaction of sulfoxides formed to sulfones.

Keywords: Molybdenum blue catalyst, Boron phosphate, Sulfoxidation, Thermodynamic studies.

INTRODUCTION

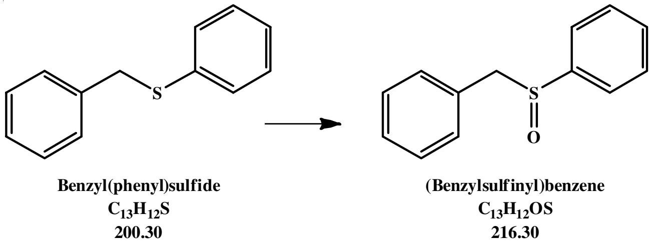
Oxidation of organic sulfides to respective sulfoxides is an industrially important reaction [1]. Sulfoxides are used in fundamental research [2-8], active ingredients in the preparation of drugs [9], valuable intermediates in the preparation of chemicals and medication [10,11], antifungals [12,13], food and cosmetics [14]. Conventionally, the oxidation of sulfides is catalyzed by peracids as catalyst and halogen derivatives [15]. However, these processes are always associated with the formation of byproducts, which are not environmentally safe. Selective oxidation of sulfides to sulfoxides is always a challenge, as any oxidation catalyst, generally lead to complete oxidation of substrate forming sulfones. Various transition metals were evaluated for the oxidation of sulfides [16-18]. Among the transition metals, molybdenum based catalysts were widely used by different research groups. MoO_3 was used as the catalyst for oxidation of various sulfides using H_2O_2 as oxidant in ethanol, which resulted in formation of both sulfoxides and sulfones with nearly 98% conversion in 12 min of reaction time [19]. Subsequently, Mo(VI) salt was used for the oxidation with 1.05 equivalent of oxidant, 1.5 equivalent of catalyst leading to the formation of sulfoxide and by taking 4 equivalents of oxidant and 15 equivalents of the catalyst, the process resulted in the formation of sulfones [20]. Gamelas *et al.* [21] got sulfoxides by using 1 equivalent of H_2O_2 and sulfones by using 2 equivalents of H_2O_2 [21]. Mo(VI) complex anchored on ferrous ferric oxide supported silica exhibited controlled oxidation to form sulfoxides from phenyl methyl sulfide with substrate to catalyst ratio of 1:1.8 using urea-H_2O_2 oxidant in dichloromethane-methanol solvent [22]. The yield obtained was 79% within 30 min of reaction time. A recent report on using Mo(VI) Schiff base complex supported on ferrous ferric oxide nanoparticles under solvent free conditions showed 100% conversion of sulfides within 3 min of reaction time with nearly 80% selectivity of sulfoxide [23]. In the present work, molybdenum blue is made up of Mo154 big-wheel with Mo-O-Mo bridging and terminal -Mo=O bonds containing Mo^{6+} and Mo^{5+} in the ratio of 5:1 [24]. The uniform distribution of bridging molybdenum allows flipping of oxidation states, which makes it as an efficient catalyst. Thus, the oxidation behavior of molybdenum blue catalyst over various organic sulfides has been studied and the results were discussed. The reaction parameters were varied and studied in order to find the kinetics and thermodynamics of the reaction.

EXPERIMENTAL

Molybdenum blue (MB) catalyst was prepared by adopting the procedure reported in literature [25]. The typical procedure involves mixing calcium carbonate and ammonium hepta molybdate in the ratio of CaO:MoO$_3$ = 1:0.08, followed by addition of phosphoric acid in the ratio of CaO:P$_2$O$_5$ = 1:1.1 and mixed thoroughly. The contents were dried, calcined at 500 ºC for 4 h and labeled as MB-BP. MoO$_3$ impregnated with borophosphate was prepared by taking ammonium heptamolybdate and boron phosphate in the weight ratio MoO$_3$:BPO$_4$ of 1:10, mixing thoroughly in presence of acetone, followed by drying, calcination at 500 ºC for 4 h and labeled as MoO$_3$-BP.

The PANalytical X-PERT3 instrument was used to collect XRD patterns for powders, the SEM images were captured using JEOL JSM-7401F instrument. The FTIR spectra were recorded in Perkin-Elmer, Spectrum RXi instrument.

The reaction was carried out in a batch reactor by taking substrate (benzyl phenyl sulfide, 50 mg) in 2 mL of a suitable solvent. A 5 mg of catalyst was added along with hydrogen peroxide as oxidant (30%, 1 equivalence) and stirred at room temperature. The reaction was monitored by analyzing the formation of product (**Scheme-I**) as well as the decrease of substrate in the reaction mixture using TLC and HPLC . The formation of product (sulfoxide) was further confirmed by recording mass spectra.



Scheme-I: Oxidation of sulfide to sulfoxide

RESULTS AND DISCUSSION

The XRD patterns of molybdenum blue and molybdenum oxide impregnated samples are given in Fig.1. The molybdenum blue has been reported as amorphous [26] and hence, no characteristic phases were observed in the XRD analysis. The MB-BP showed presence of pure boron phosphate phase (PDF No. 741169, Fig.1a) and the XRD pattern of MoO$_3$-BP showed presence of molybdenum oxide (PDF No. 895108, Fig. 1b) and boron phosphate phases in the sample. FTIR spectra of MB-BP showed absorptions at around 720 and 900 cm^{-1} corresponding to -Mo-O and Mo-O-Mo vibrations, respectively [25] (Fig.2). The SEM image of MB-BP showed the deposition of molybdenum blue particles over boron phosphate matrix (Fig. 3).

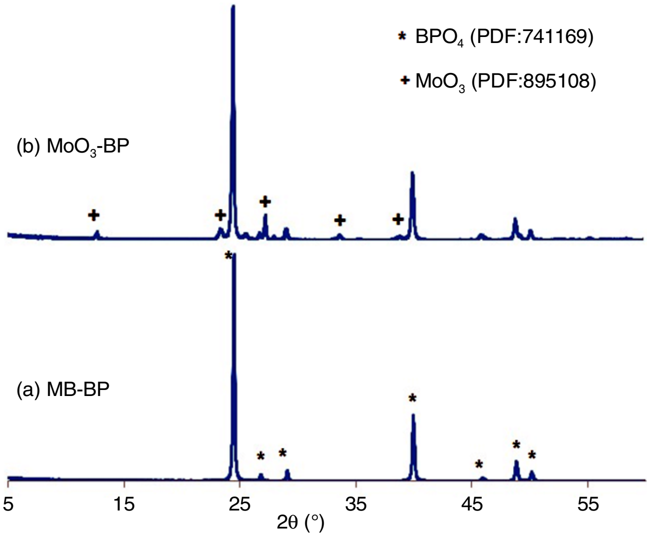


Fig. 1. XRD patterns of (a) MB-BP catalyst and (b) MoO$_3$-BP impregnated catalyst

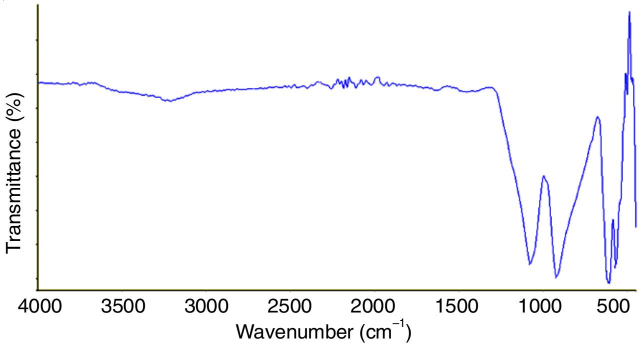


Fig. 2. FTIR spectra of MB-BP catalyst

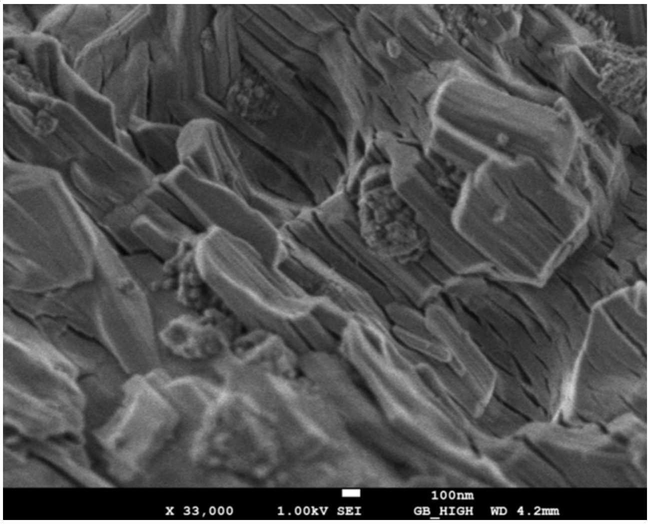


Fig. 3. SEM image of MB-BP catalyst

The oxidation of sulfoxide involves activation of hydrogen peroxide as the first step. The cleavage of peroxide linkage in H$_2$O$_2$ can take place via two types; either by formation of HO$^\bullet$ radicals through homolytic fission or by formation of water oxide by elimination of proton, which reacts with sulfide to form sulfoxide [27]. Efficiency of the reaction depends on the activation of peroxide.

Table-1 presents the initial studies over different catalyst, by varying solvent and reaction time. The conversion of the substrate is presented along with selectivity towards sulfoxide.

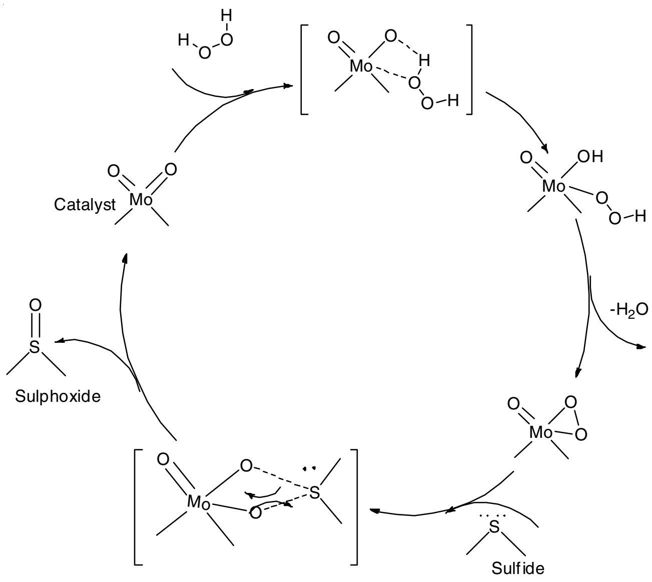
TABLE-1

INITIAL STUDIES ON THE CATALYST FOR OPTIMIZING THE REACTION CONDITIONS

Solvent	Catalyst (mg)	H_2O_2 equivalence	Time (min)	Conversion (%)	Selectivity (sulfoxide %)
Methanol	MB-BP	1	30	95.36	100
Methanol	MB-BP	1	120	98.00	100
Ethanol	MB-BP	1	30	94.96	100
Dichloromethane	MB-BP	1	120	4.50	100
Dichloromethane/methanol (1:1)	MB-BP	1	30	94.74	100
Acetonitrile	MB-BP	1	120	9.60	100
Acetone	MB-BP	1	120	11.20	100
Hexane	MB-BP	1	120	0.80	100
Toluene	MB-BP	1	120	1.40	100
Methanol	MoO_3-BP	1	30	40.00	80
Methanol	MoO_3-BP	1	120	58.00	55
Methanol	Boron phosphate (blank)	1	180	5.00	90

Substrate - Benzyl phenyl sulfide – 50 mg; Solvent – 2 mL; Catalyst – 5 mg.

The MB-BP catalyst exhibited 95% conversion within 30 min of reaction time using methanol and ethanol as solvent. On using dichloromethane, acetonitrile, hexane, toluene and acetone as the solvents, the oxidation was poor with very low conversion even after 120 min of reaction time. When, a mixture of dichloromethane and methanol was used as the solvent, again it showed good activity. This proves that the reaction requires protonated solvent, which favours sulfoxidation through water oxide mechanism. The plausible mechanism for the oxidation of sulfide by MB-BP catalyst is shown in **Scheme-II**.



Scheme-II: Mechanism of sulfoxidation by MB-BP catalyst

In the literature, the formation of sulfones was observed with the increase in oxidant equivalence, where sulfoxide formed in the Step-I reacted again with the catalyst to form sulfone in Step-II. In the presence catalyst, cluster of molybdenum blue does not favour further reaction of sulfoxide due to steric hindrance. This can be inferred by the fact that irrespective of oxidant equivalence or with reaction time, no sulfone was formed (entries 1 & 2, Table-1), while the impregnated sample (MoO_3-BP) showed 80% selectivity towards sulfoxide, which decreased with the increase in reaction time (entries 10 & 11, Table-1). The performance of the above two catalysts were studied by varying reaction parameters.

Influence of catalyst content: Catalyst content with respect to the substrate plays an important role in accelerating the reaction. In certain cases, it decides the nature of product formed, as reported by Kandasamy *et al*. [20] that with 10-fold increase of catalyst leads to formation of 95% selectivity of sulfones, which was 96% sulfoxide otherwise. In the present MB-BP catalyst, when the catalyst content was changed from 0.5 mg to 5 mg, the conversion was found to increase, with 100% selectivity towards sulfoxide (Fig. 4). However, beyond 2 mg of catalyst content, the reactivity was found to be nearly same. The reaction reached steady state at 30 min, beyond which time; the conversion did not change appreciably. The reactivity of impregnated catalyst was found to be very low as compared to that of MB-BP catalysts.

Oxidant content in the reaction mixture plays a vital role. Relatively, less quantity of oxidant lead to incomplete reaction and higher quantity lead to pollution to the environment, if unreacted oxidant is released as such without treatment. In addition, there are reports available that the oxidant content alters the selectivity of the product. Generally, the conversion increases with the increase in the oxidant concentration. In order to study the influence of oxidant concentration, the catalyst content was fixed as 1 mg; since, 5 mg catalyst generally leads to completion of reaction within few minutes of reaction time. The conversion was very low for 0.25 equivalence of H_2O_2 over MB-BP catalyst, which increased with the increase in oxidant and reached steady state at 60 min of reaction time (Fig. 5). The important observation made in the study was the selectivity of sulfoxide was retained in spite of increasing oxidant concentration. The impregnated sample showed low activity.

Kinetics studies: The rate of the reaction is given by decrease in concentration of sulfide or increase in concentration of sulfoxide with respect to time. The reaction takes place between sulfide and H_2O_2 and hence, expected to follow second order kinetics.

The second order rate equation can be given as:

$$-\frac{d[\text{sulfide}]}{dt} = k[\text{sulfide}][\text{oxidant}]$$

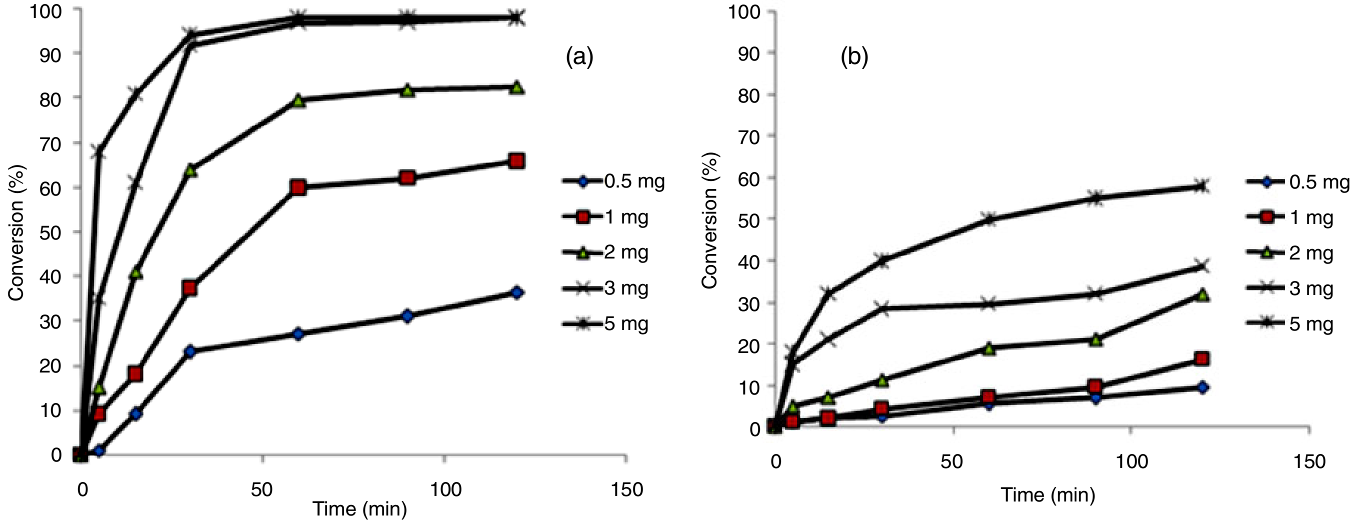


Fig. 4. Oxidation of benzyl phenyl sulfide: influence of catalyst content over (a) MB-BP catalyst (b) MoO_3-BP catalyst

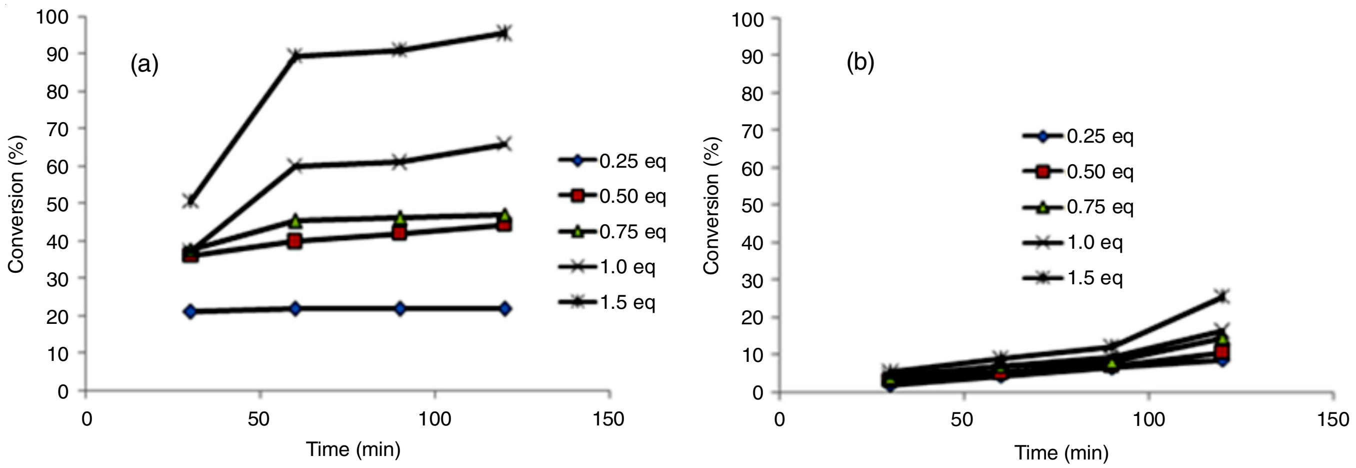


Fig. 5. Oxidation of benzyl phenyl sulfide: influence of oxidant content over (a) MB-BP catalyst and (b) MoO_3-BP catalyst

which yields

$$\frac{1}{[\text{sulfide}]} = \frac{1}{[\text{sulfide}]_o} + kt$$

A plot of $1/[\text{sulfide}]_t$ *vs.* time 't' should give a straight line. But, when the data were fitted, straight line was not obtained, which infers that the reaction do not proceed through second order kinetics, which might be due to fact that activation of H_2O_2 being the rate determining step, the reaction may follow pseudo first-order kinetics and the equation can be given as follows:

$$-\frac{d[\text{sulfide}]}{dt} = k[\text{sulfide}]$$

which yields

$$\ln\,[\text{sulfide}]_t = \ln\,[\text{sulfide}]_0 - kt$$

A plot of $\ln[\text{sulfide}]_t$ *vs.* 't' should give a straight line and the same was obtained for MB-BP catalyst. Fig. 6 shows the first

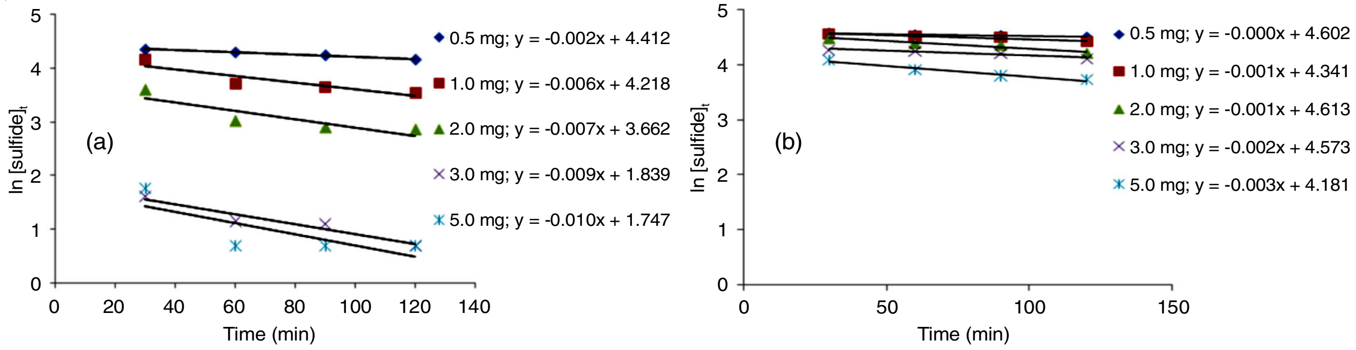


Fig. 6. Pseudo first order kinetics graph at different catalyst content for (a) MB-BP catalyst (b) MoO_3-BP catalyst

order kinetics plot of the catalyst with different concentrations and the rate was calculated from the slope.

The rate of the reaction was calculated from slope of the straight line for different catalyst content and is given in Table-2. The rate of the reaction was found to increase with the increase in MB-BP and MoO_3-BP catalysts (Fig.7). However, the rate of the reaction was found to be linear beyond 1 mg of catalyst content for MB-BP and the performance was around 4 times faster than the impregnated catalyst.

TABLE-2
RATE OF REACTION WITH VARYING CATALYST CONTENT

Cat. wt. (mg)	Rate × 10^{-3} (min^{-1})	
	MB-BP	MoO_3-BP
0.5	2.1	0.11
1.0	6.2	1.20
2.0	7.1	1.50
3.0	9.0	2.40
5.0	10.1	3.50

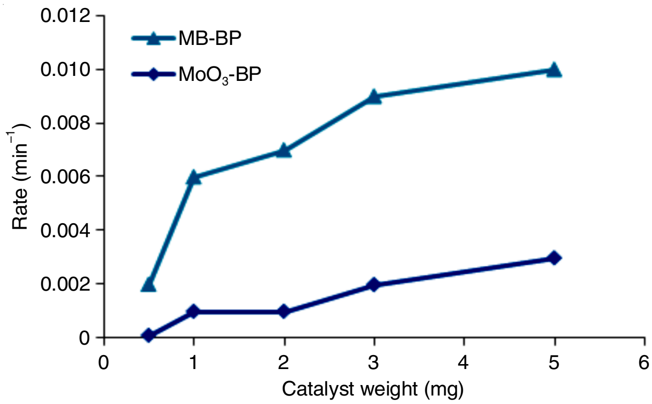


Fig. 7. Variation of rate of the reaction with catalyst content

Influence of oxidant content over the rate of the reaction was studied by varying oxidant equivalents to substrate from 0.25 to 1.5 over MB-BP catalyst and the plot of substrate content with respect to time allows us to calculate the rate of the reaction (Fig. 8) and the same is presented in Table-3. A plot of rate *vs.* oxidant content shows that upto 0.75 equivalence of H_2O_2 content, the rate did not change appreciably, but on further increase in H_2O_2 content, an exponential increase in the rate was observed (Fig. 9). The impregnated catalyst showed a liner increase in the rate with respect to oxidant content.

TABLE-3
RATE OF REACTION WITH VARYING OXIDANT (H_2O_2) EQUIVALENCE

H_2O_2 (equivalence)	Rate × 10^{-3} (min^{-1})	
	MB-BP	MoO_3-BP
0.25	0.1	0.09
0.50	1.1	0.09
0.75	1.6	1.30
1.00	6.2	1.40
1.50	24.1	2.10

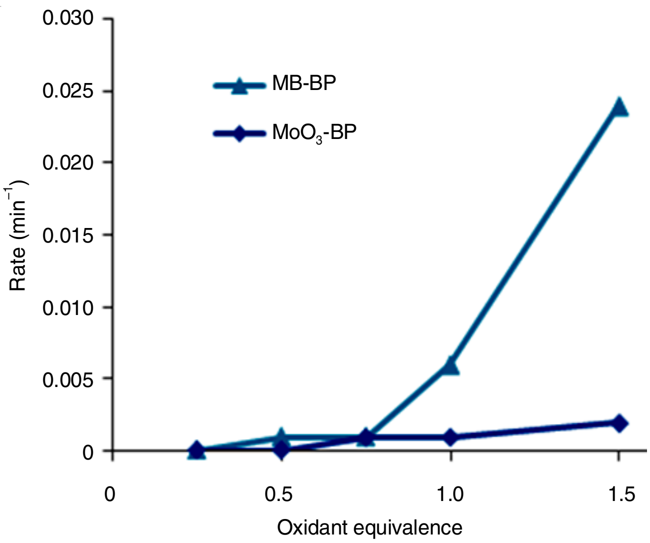


Fig. 9. Variation of rate with respect to oxidation equivalence over (a) MB-BP catalyst and (b) MoO_3 catalyst

Thermodynamic studies: In general, with the increase in temperature, the rate of the reaction and conversion tends to increase. The influence of temperature on the oxidation of sulfide over MB-BP catalyst was studied between 5 ºC and 60 ºC (catalyst wt. = 1 mg; H_2O_2: 1 eq.). With an increase in the temperature, the conversion increased and steady state was attained at 60 min of reaction time, except of the reaction that was carried out at 60 ºC, where the conversion was found to increase linearly (Fig. 10a).

The rate of the reaction at different temperatures was calculated by substituting the data in first order rate equation (Table-4) (Fig. 10b), to find the thermodynamic parameters of catalyst. A linear increase in the rate of the reaction with temperature was observed (Fig. 11).

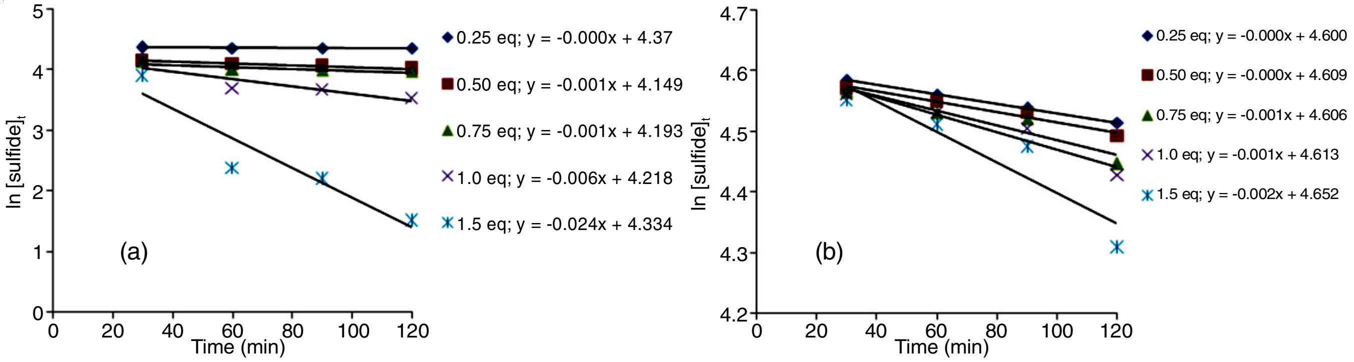


Fig. 8. First order kinetics: variation of oxidant over (a) MB-BP catalyst and (b) MoO_3-BP catalyst

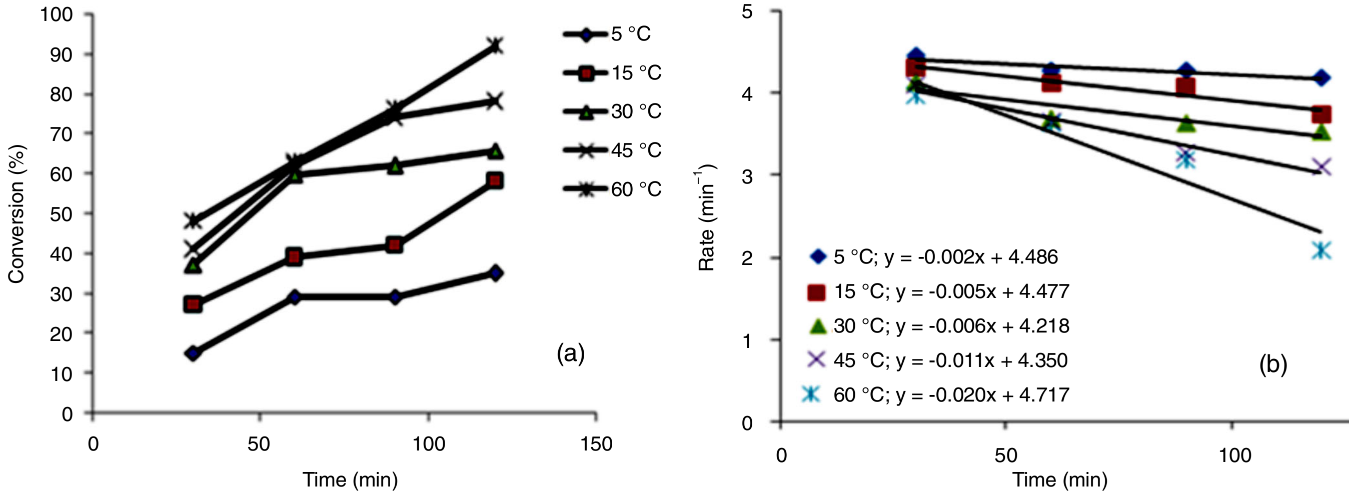


Fig. 10. Oxidation of sulfides over MB-BP catalyst (a) influence of temperature (b) first order kinetics plot

TABLE-4
RATE OF THE SULFOXIDATION OVER MB-BP
CATALYST AT DIFFERENT TEMPERATURES

Temp. (°C)	Rate × 10^{-3} (min^{-1}) MB-BP
5	2.2
15	5.3
30	6.2
45	11.1
60	20.2

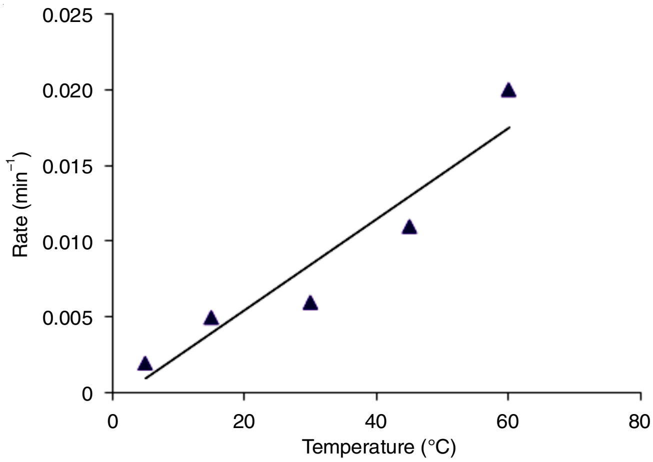


Fig. 11. Oxidation of sulfides over MB-BP catalyst: variation of rate with temperature

The energy of activation for the reaction was obtained by plotting rate of the reaction with 1/T according to the following Arrhenius equation:

$$\ln(k) = \ln(A) - \frac{Ea}{RT}$$

A slope of the straight line of the activation energy (ΔG^+) of catalyst for reaction was determined (Fig.12a). By plotting ln (k/T) *vs.* 1/T, a straight line was obtained and from the slope, H^+ for the reaction was determined [28] (Fig.12b). By substituting values of ΔG^+ and ΔH^+, the value of ΔG^+ for the reaction was obtained.

The energy of activation was found to be 29.3 kJ/mol, the H^+ for the catalyst was 26.77 kJ/mol and the entropy change ΔS^+ of the catalyst was 8.48 J K^{-1}. For the oxidation of various sulfides to sulfoxdes, the activation energy was reported in the range of around 40-80 kJ/mol [27]. The presence catalyst was very much efficient in bringing down the activation energy to around 29.3 kJ/mol.

Finally, the reactivity of MB-BP catalyst was evaluated for various substrates and the results were compared with other catalyst reported in literature. A report on the reaction conditions along with the conversions are presented in Table-5. It is evident from the above substrate studies that MB-BP catalyst, effectively converts most of the organic sulfides to their respective sulfoxides, without forming sulfones.

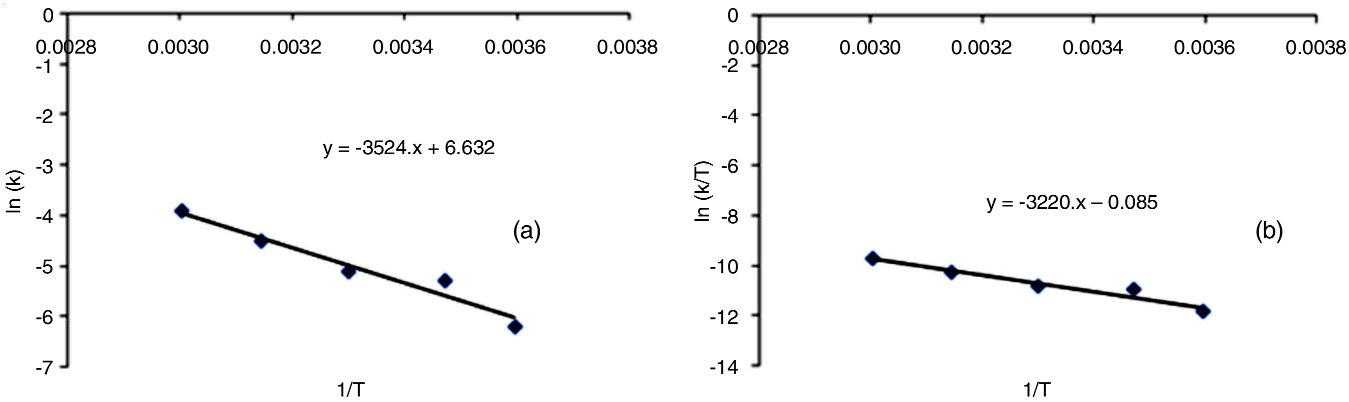
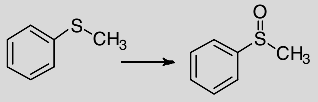
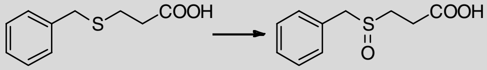
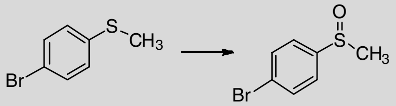
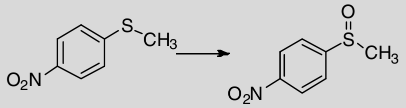
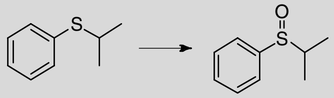
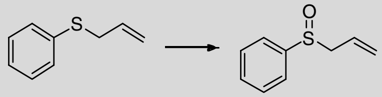


Fig. 12. Oxidation of sulfide over MB-BP catalyst, (a) Arrhenius plot and (b) ln (k/T) *vs.* 1/T plot

TABLE-5
OXIDATION OF VARIOUS SULFIDE SUBSTRATES OVER DIFFERENT CATALYSTS

Reaction	Catalyst	Oxidant equivalence	Time (min)	Conv. (%)	Selectivity of sulfoxde (%)	Ref.
 Thioanisole	MB-BP	1	30	99	100	–
	TaC/NbC	1	165	99	>80	[29]
 3-(Benzylthio)propanoic acid	MB-BP	1	30	99	100	–
 (4-Bomophenyl)(methyl)sulfide	MB-BP	1	60	99	100	–
	Rh(II) complex	1	>180	99	99	[30]
 Methyl(4-nitrophenyl)sulfide	MB-BP	1.1	60	99	100	–
	Mo complex	1	>180	75	75	[21]
 *iso*-Propyl(phenyl)sulfide	MB-BP	1.2	60	99	100	–
	WO_4-SiO_2	3	>150	75	75	[31]
 Allyl(phenyl)sulfide	MB-BP	1.1	60	99	100	–
	MoO_3	1	45	94	6	[19]

Conclusion

Oxidation of benzyl phenyl sulfide was studied over solid molybdenum blue deposited over boron phosphate. The Mo-O-Mo bridging bonds and terminal Mo=O bonds bought the reaction. It is found that the presence of Mo^{6+} and Mo^{5+} oxidation states in molybdenum blue favours the oxidation process. Moreover, the activation of H_2O_2 is the crucial step for the oxidation process. The selectivity of the product namely, sulfoxide was 100%, irrespective of the oxidant and catalyst concentration, which was mainly due to the structure of Mo clusters in molybdenum blue. The catalyst could oxidize various other sulfide substrates to respective sulfoxides in a maximum time of 60 min at room temperature.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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