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FULL PAPER

Oxido-peroxido W(VI)-histidine–MgAl-layered double hydroxide composite as an efficient catalyst in sulfide oxidation

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Oxido-peroxido W(VI)-histidine–MgAl-layered double hydroxide composite was prepared by using MgAl-layered double hydroxide as a host and oxido-peroxido W(VI)-histidine complex as a guest. The composite was characterized by XRD, IR, EDX,SEM and TEM techniques. This composite is tested for catalytic selective sulfoxidation reactions using hydrogen peroxide as oxidant showing good to moderate conversion along with high selectivity.

KEYWORDS
LDH, oxidation, oxido-peroxido, sulfide, tungsten

1 | INTRODUCTION

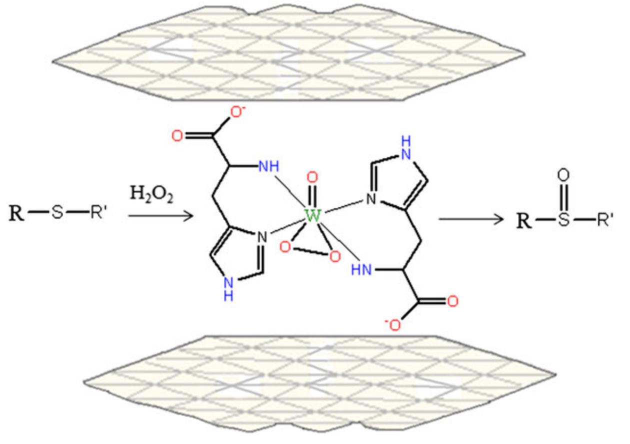
Sulfoxides are important intermediates in many industrial reactions owing to biological and pharmaceutical activities. Efficient and selective oxidation of sulfides to sulfoxides is an essential part of synthetic design in modern pharmaceutical processes.[1–7] The application of oxido–peroxido tungsten (VI) complexes are exciting due to tungsten centers activating peroxido groups for oxidation of a variety of organic substrates.[8–15]

Layered double hydroxides (LDHs) as a class of anionic clays with features such as large surface area, high anion exchange capacity, good thermal stability and low toxicity have been extensively applied as intercalation hosts for metal complexes for recyclable catalysts in varied organic reactions.[16–20] Herein, an oxido-peroxido W(VI)-histidine–MgAl-layered double hydroxide (**1**) was prepared by using MgAl-layered double hydroxide as host and oxido-peroxido W(VI)-histidine complex as guest. The composite was used as a catalyst for sulfide oxidation with hydrogen peroxide (H_2O_2) as an oxidant under ambient conditions (Scheme 1).

2 | EXPERIMENTAL

2.1 | Materials

All chemicals and solvents were obtained from Merck and Fluka Inc. and were used without further purification. Layered double hydroxide (LDH) with $Mg_{1-x}Al_x(OH)_2(Cl)_x.zH_2O$ composition and WO_3 were synthesized described in previous reported procedures.[21,22]



SCHEME 1 Sulfide oxidation in the presence of oxido-peroxido oxido-peroxido W(VI)-histidine- LDH composite

2.2 | Preparation of histidine- LDH

LDH (0.3 g) was suspended in a solution of ethanol-water (1:1) (20 ml) and L-histidine (0.39 g) was added to mix. The pH of the solution was adjusted to 8 by adding dropwise 0.5 M NaOH solution and stirred for 24 h at room temperature. The white solid was filtered, washed with ethanol and deionized water and dried at ambient.

2.3 | Preparation of oxido-peroxido W(VI)-histidine–MgAl-layered double hydroxide (1)

Freshly prepared $WO_3{\cdot}nH_2O$ (0.08 g) was dissolved in H_2O_2 (0.3 ml) and stirred until a clear solution is obtained. Histidine- LDH (0.2 g) was suspended in ethanol- water (1:1) (15 ml) and then the tungsten oxide solution was added to the suspension. Then two drops of trimethylamine was added to the solution and mixed for 24 h. The resultant precipitate was filtered, washed three times with ethanol and distilled water and air-dried.

2.4 | Oxidation of sulfides

A round bottom flask containing a mixture of sulfide (1.0 mmol), oxido-peroxido W(VI)-histidine–LDH (1 mg) and H_2O_2 (1.5 mmol) in methanol (1 ml) was kept on under continuous stirring at 65 °C. Then, progress of sulfide oxidation and conversion were determined by GC analysis.

3 | RESULTS AND DISCUSSION

3.1 | Catalyst characterization

The XRD patterns of histidine- LDH and oxido-peroxido W- histidine- LDH are shown in Figure 1. The main diffraction peaks of the histidine- LDH and oxido-peroxido W- histidine- LDH were in conformance with LDH XRD patterns. The interlayer distance of oxido-peroxido W-histidine- LDH was at 0.77 nm.

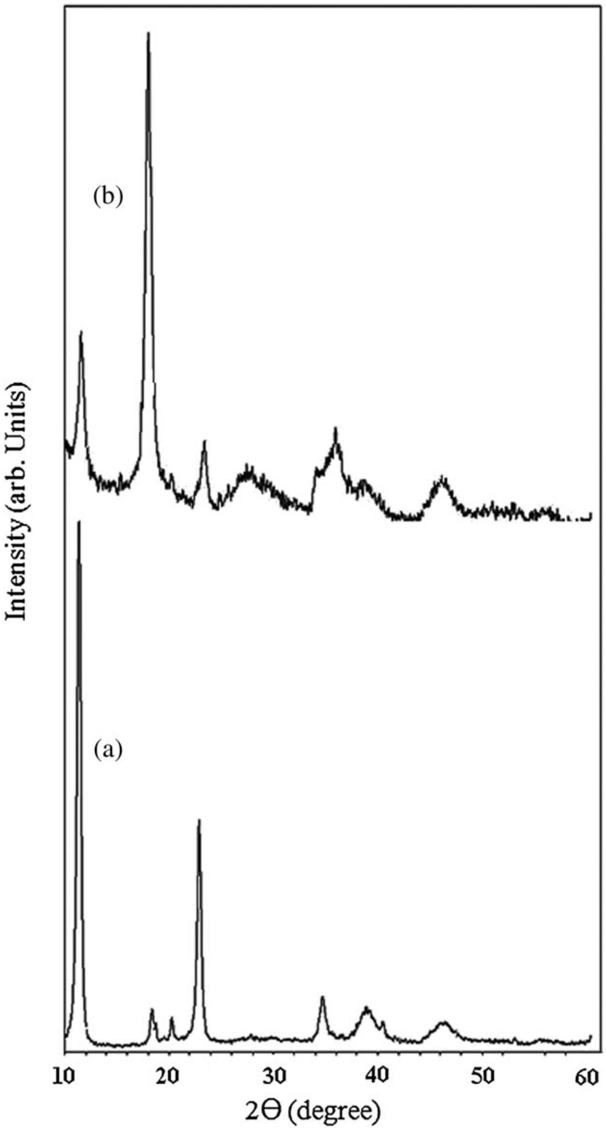


FIGURE 1 XRD pattern of histidine- LDH (A) and oxido-peroxidoW- histidine- LDH (B)

The SEM images of LDH, histidine- LDH and oxido-peroxido W- histidine- LDH are shown in Figure 2. SEM image shows that LDH crystals in all samples have a plate- like morphology and intermittent plate- plate stacking. Histidine- LDH and W- histidine- LDH are similar in plate as of LDH, and do not break the layers (2c,d and 2e, f). These demonstrate that histidine and W- histidine complex successfully intercalate into the interlayers of LDH.[23]

The TEM images for sample oxido-peroxido W- histidine- LDH are displayed in Figure 3. oxido-peroxido W-histidine- LDH particles showed hexagonal shape with a length of 60–80 nm.

EDX analysis shows presence of magnesium, aluminum, tungsten and oxygen as elements in the oxido-

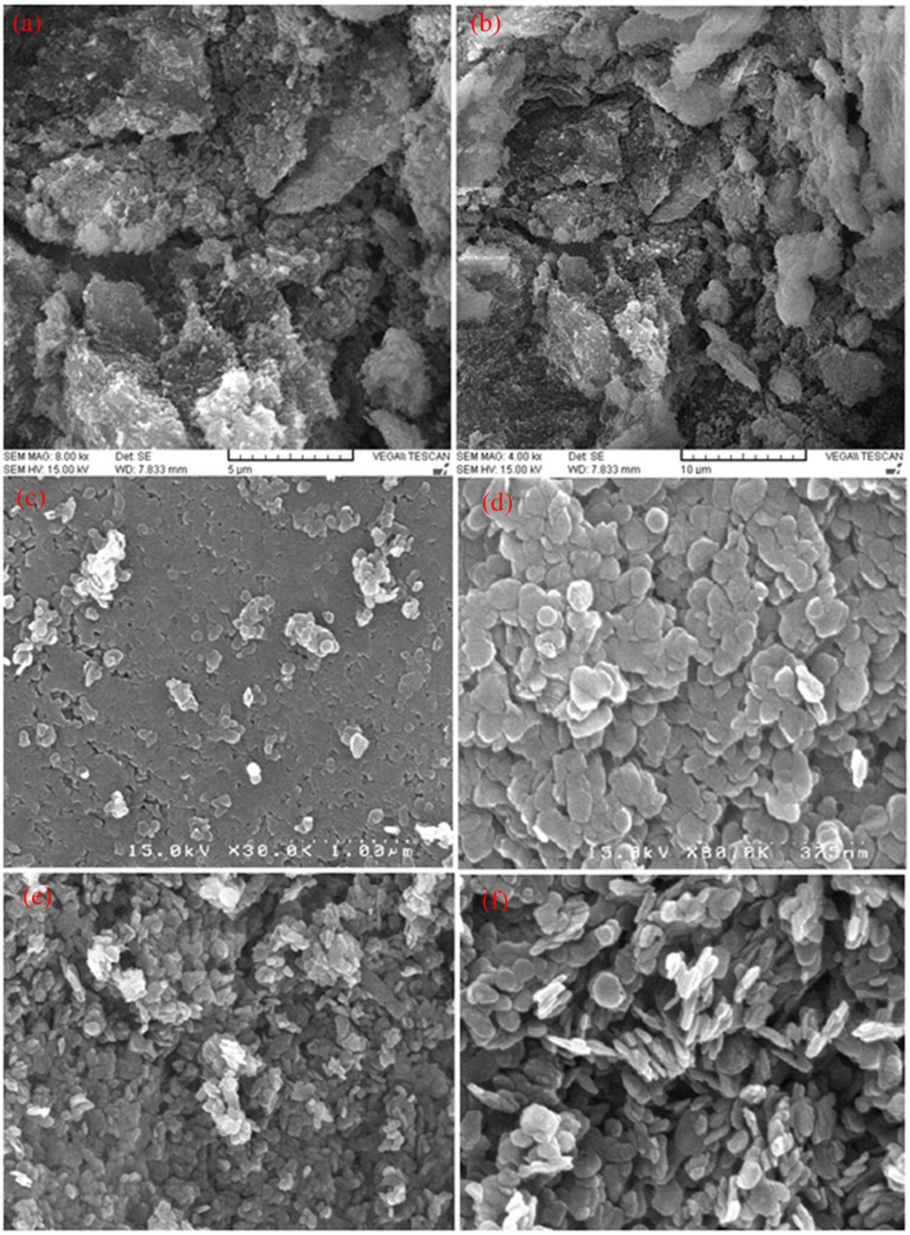


FIGURE 2 The SEM images of the (a,b) LDH, (c,d) histidine- LDH and (e,f) oxido-peroxido W- histidine-LDH

peroxido W- histidine- LDH nanoparticles. The tungsten in the composite **1** constitute about 4.9% (atomic %).

The FT-IR spectra of the LDH, histidine- LDH samples and **1** are shown at Figure 4. All three spectra contain a broad absorption band in the range of 3000–3600 cm^{-1} corresponding to the O-H stretching vibrations of the hydroxide groups in the LDH sheets and interlayer water.[24] The absorption band around 1620 cm^{-1} is attributed to bending vibrations of the interlayer water molecules and the hydroxide groups in the LDH layers.[25] The absorption peaks in the low frequency region (400–1000 cm^{-1}) of the spectra is related to the lattice vibration modes of M–O and O–M–O in the LDH sheets.

3.2 | Catalytic effects

Catalytic activities of W- histidine- LDH were studied in the sulfide oxidation reaction. First the influence of reaction solvent, temperature and time on the conversion and selectivity of the oxidation reaction of methyl phenyl sulfide (MPS) as a model reaction were studied (Table 1). For all oxidation reactions, minimum weighable amount of catalyst (1 mg) in the presence of H_2O_2 as oxidant was used. A control experiment in the absence of catalyst or in the presence of MgAl-LDH or histidine- LDH afforded low yields of the sulfoxide without sulfone (entries 1–3). The MPS oxidation reaction was studied

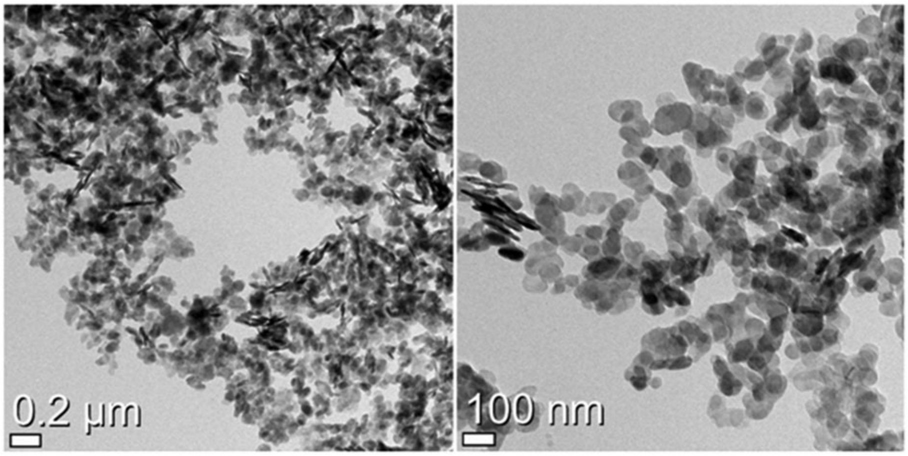


FIGURE 3 TEM image of oxido-peroxido W- histidine- LDH

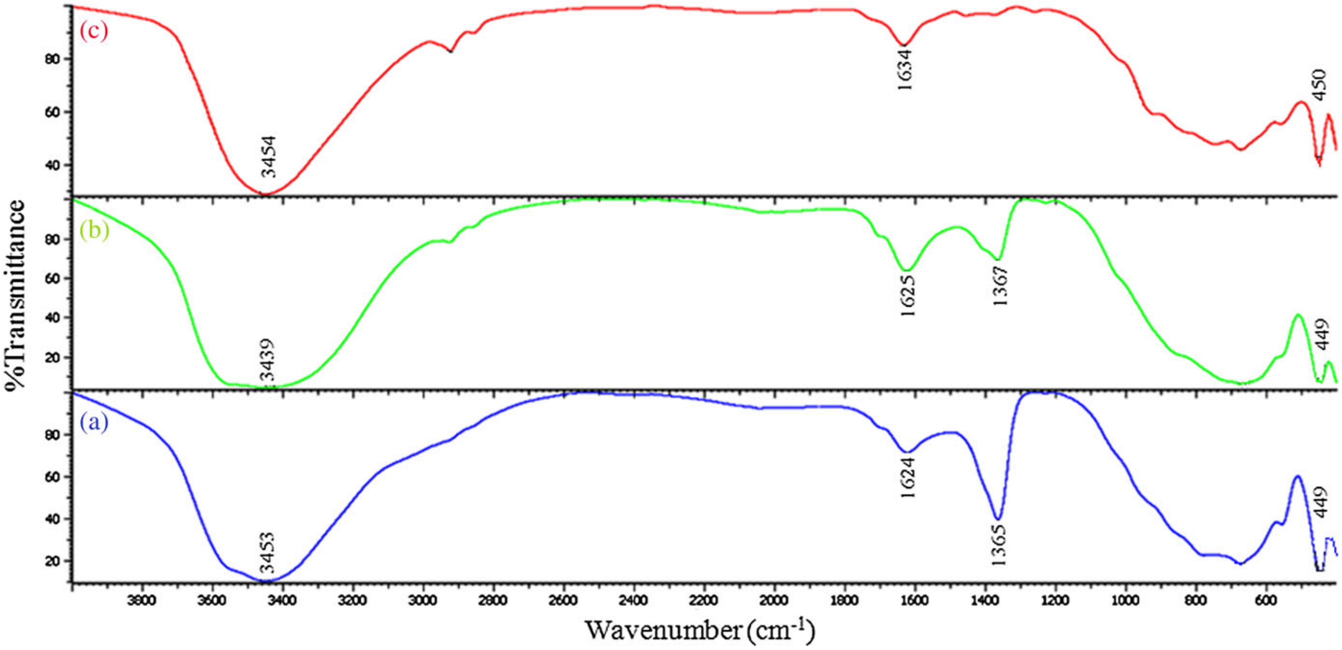


FIGURE 4 IR spectra of (a) LDH, (b) histidine- LDH and (c) oxido-peroxido W- histidine- LDH

using various solvents to carry out the reaction at room temperature. The results listed in Table 1 show that the reaction results depends on the nature of solvent (entries 4–8). Yields of 63% and 59% were obtained using methanol and dichloromethane (entries 6 and 8) but poor conversion was obtained in other solvents such as water, acetonitrile and ethylactate (entries 4, 5 and 7). Reactions in methanol had the best conversion rate and all other reactions were carried out in this solvent. To obtain a complete transformation of MPS, reaction temperature was increased to 65 °C, and result showed that the oxidation of MPS is highly selective (89%) to sulfoxide with 100% conversion of the substrate at a reaction time of 105 min (entry 13). It is noteworthy that the oxidation of MPS using H_2O as a solvent under identical reaction conditions, afforded the almost complete conversion (97%), but with low selectivity (64%) to the sulfoxide (entry 14). It can be observed that the conversion of MPS increased to 100% with the reaction time of 105 min (entry 13). The selectivity to sulfoxide was excellent (higher than 89%). A control experiment without W- histidine- LDH afforded the sulfoxide in only 11% yields without sulfone.

To study the scope of reaction, the oxidation of a variety of aromatic and aliphatic substrates was studied (Table 2). A series of substrates, aryl-alkyl (entry 1), diaryl (entry 2), benzyl–aryl (entry 3), dibenzyl (entry 4) and

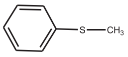
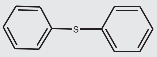
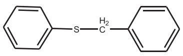
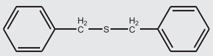
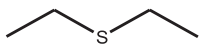
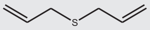
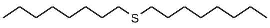
TABLE 1 The results for various conditions on the oxidation of sulfides[a]

Entry	catalyst	Solvent (1 ml)	Temperature (°C)	Time (min)	Conversion (%)[b]	Selectivity (%)[c]
1	-	CH_3OH	65	120	11	100
2	MgAl- LDH	CH_3OH	65	120	14	100
3	Histidine-LDH	CH_3OH	65	120	13	100
4	1	H_2O	r.t.	120	48	56
5	1	EtOAc	r.t.	120	42	68
6	1	CH_2Cl_2	r.t.	120	59	82
7	1	CH_3CN	r.t.	120	40	78
8	1	CH_3OH	r.t.	120	63	89
9	1	CH_3OH	65	120	100	87
10	1	CH_3OH	65	30	65	92
11	1	CH_3OH	65	60	89	90
12	1	CH_3OH	65	90	98	88
13	1	CH_3OH	65	105	100	89
14	1	H_2O	65	105	97	64

[a] Reaction conditions: 1 ml of solvent; 1 mmol of methylphenylsulfide; 1.5 mmol H_2O_2.

[b] Determined by GC on the crude reaction mixture. [c] Selectivity to sulfoxide = (sulfoxide%/ (sulfoxide% + sulfone%)) × 100.

TABLE 2 Oxidation of various sulfides in the presence of **1**

Entry	Substrate	Conversion (%)	Selectivity (%)
1		100	89
2		83	86
3		94	90
4		92	85
5		69	100
6		99	100
7		58	100

[a] Reaction conditions: 1 mmol of sulfide; 1.5 mmol H_2O_2; 1 mg of **1**; 1 ml of MeOH. [b] Determined by GC. [c] Selectivity to sulfoxide = (sulfoxide%/ (sulfoxide% + sulfone%)) × 100.

dialkyl sulfides (entries 5–7), are selectively oxidized to the corresponding sulfoxides in high yields and purity. The reactivity and conversion were dependent on the nature of the substituents. Dialkyl sulfides, diethyl sulfide and dioctyl sulfide, were mildly reactive affording the corresponding sulfoxide without over oxidation to the sulfone (entries 5, 7). In the case of diallyl sulfide, no oxidation was observed at the carbon–carbon double bond (entry 6).

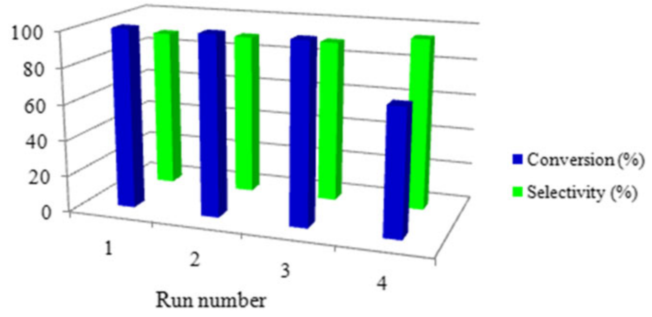
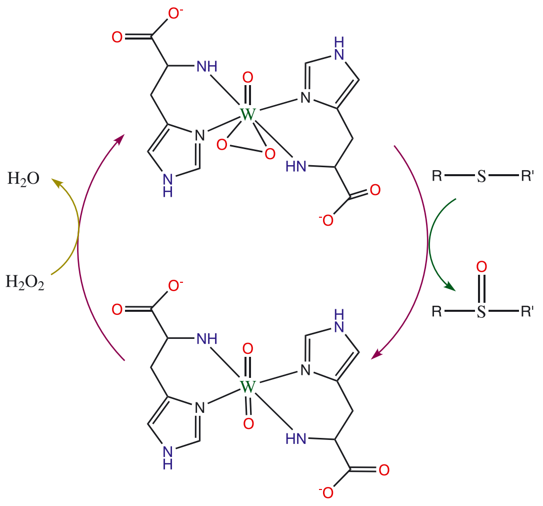


FIGURE 5 Recycling studies of 1 in the oxidation reaction



SCHEME 2 Mechanism of sulfide oxidation in the presence of **1**

TABLE 3 Comparison of the catalytic activity of **1** with some oxido-peroxido W/ Mo catalysts

Entry	Catalyst	Reaction Condition	Conversion (selectivity to sulfoxide) %	References
1	**1**	$H_2O_2/PhSCH_3/CH_3OH$/65 °C/ 105 min	100 (89)	Present work
2	$[WO(O_2)(CPHA)_2]$	$H_2O_2/CH_3SCH_3/CH_2Cl_2$/ 40 °C/60 min	100 (6%)	[28]
3	$[PPh_4][MoO(O_2)_2(QO)]$	$H_2O_2/CH_3SCH_3/CH_2Cl_2$/ 40 °C/60 min	18 (82)	[29]
4	$PPh_4[WO(O_2)_2(HPEOH)]$	$H_2O_2/CH_3SCH_3/CH_3CN$/reflux/ 60 min	100 (4%)	[30]
5	$[MoO(O_2)(phox)_2]$	$TBHP/CH_3CN$/rt/ 30 min	99 (100)	[2]

The recoverability and reusability of the oxido-peroxido W- histidine- LDH was investigated in the consecutive reaction of MPS oxidation (Figure 5). At the end of each run the catalyst was filtered and removed from reaction and after washing with ethanol and acetone, dried and then reused. The results of these studies showed that the oxido-peroxido W-histidine- LDH composite preserved its activity after three runs without any significant loss of catalytic activity. The reduction of the catalytic efficiency after three cycles is mainly due to loss of catalyst during the filtration and separation processes.

The mechanism of sulfide oxidation to sulfoxide is well studied using oxido-peroxido molybdenum (VI) or tungsten (VI)- containing catalyst.[26,27] In this mechanism, the oxidation reaction starts with nucleophilic attack of sulfide on one of the oxygen atoms of the peroxido ligand, providing sulfoxide and generating the related dioxido tungsten (VI)- LDH complex. Then the primary catalyst, oxido-peroxido W- histidine- LDH, is obtained with reaction of dioxido intermediate and H_2O_2 oxidant, which restarts the cycle (Scheme 2). Particularly, Calhadro et al. have shown by using DFT studies that this transformation by oxido-peroxido Mo(VI) complex takes place with the same mechanism.[3]

Comparison of the catalytic activity of **1** in oxidation of sulfides with reported oxido-peroxido W(VI) /Mo (VI) catalysts is summarized in Table 3. According to recoverability and reusability of catalyst (entries 1–5), high selectivity to sulfoxide (1–4) and using a green oxidant (entry 5), the oxido-peroxido W-histidine- LDH is effective and more efficient than other oxido-peroxido W/Mo catalytic systems.

4 | CONCLUSION

This work represents the first successful preparation and application of oxido-peroxido W(VI)-histidine–MgAl-layered double hydroxide catalyzed selective oxidation of sulfides to sulfoxides. The mild oxidizing conditions provides good to excellent transformation to sulfoxides. Also the catalyst is recovered by filtration and reused for four cycles in oxidation reaction with no significant loss in catalytic activity.

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REFERENCES

[1] F. Batigalhia, M. Zaldini-Hernandes, A. G. Ferreira, I. Malvestiti, Q. B. Cass, *Tetrahedron* **2001**, *57*, 9669.

[2] M. Bagherzadeh, M. M. Haghdoost, M. Amini, P. G. Derakhshandeh, *Catal Commun* **2012**, *23*, 14.

[3] L. F. Veiros, C. A. Gamelas, M. J. Calhorda, C. C. Romão, *Organometallics* **2011**, *30*, 1454.

[4] A. L. Nuzhdin, D. N. Dybtsev, V. P. Fedin, G. A. Bukhtiyarova, *Dalton Trans* **2009**, *2009*, 10481.

[5] M. Amini, H. Naslhajian, S. M. F. Farnia, M. Hołyn'ska, *Eur. J. Inorg. Chem.* **2015**, 3873.

[6] R. Frenzel, D. Morales, G. Romanelli, G. Sathicq, M. Blanco, L. Pizzio, *J. Mol. Catal. A: Chem.* **2016**, (420), 124.

[7] N. Baig, V. K. Madduluri, A. K. Sah, *RSC Adv* **2016**, *6*, 28015.

[8] M. Amini, M. M. Haghdoost, M. Bagherzadeh, *Coord Chem Rev* **2014**, *268*, 83.

[9] V. Vrdoljak, J. Pisk, D. Agustin, P. Novak, J. P. Vuković, D. Matković-Čalogović, *New J Chem* **2014**, *38*, 6176.

[10] G. Lyashenko, G. Saischek, M. E. Judmaier, M. Volpe, J. Baumgartner, F. Belaj, V. Jancik, R. Herbst-Irmer, N. C. Mösch-Zanetti, *Dalton Trans* **2009**, 5655.

[11] J. M. Brégeault, M. Vennat, L. Salles, J. Y. Piquemal, Y. Mahha, E. Briot, P. C. Bakala, A. Atlamsani, R. Thouvenot, *J. Mol. Catal. A: Chem.* **2006**, (250), 177.

[12] K. Vassilev, R. Stamenova, C. Tsvetanov, *React Funct Polym* **2000**, *46*, 165.

[13] B. Eftekhari-Sis, M. Akbari, M. Amini, F. Ashouri, M. Bagherzadeh, *J Coord Chem* **2017**, *70*, 328.

[14] B. S. Lane, M. Vogt, V. J. DeRose, K. Burgess, *J. Am. Chem. Soc.* **2002**, *124*, 11946.

[15] K. Kamata, S. Kuzuya, K. Uehara, S. Yamaguchi, N. Mizuno, *Inorg Chem* **2007**, *46*, 3768.

[16] M. R. Mahmoud, M. A. Soliman, G. M. Rashad, *Chem Eng J* **2017**, *326*, 781.

[17] G. Varga, S. Ziegenheim, S. Muráth, Z. Csendes, Á. Kukovecz, Z. Kónya, S. Carlson, L. Korecz, E. Varga, P. Pusztai, P. Sipos, I. Pálinkó, *J Mol Catal A Chem* **2016**, *423*, 49.

[18] M.-Z. Wang, Y. Li, J.-J. Ji, G.-L. Huang, X. Zhang, S.-H. Li, X.-J. Yang, *Chinese Chem Let* **2013**, *24*, 593.

[19] B. Monteiro, S. Gago, S. S. Balula, A. A. Valente, I. S. Gonçalves, M. Pillinger, *J Mol Catal A Chem* **2009**, *312*, 23.

[20] M. X. Reinholdt, R. J. Kirkpatrick, *Chem Mater* **2006**, *18*, 2567.

[21] M. Amini, M. Nikkhoo, S. M. F. Farnia, *Appl. Organomet. Chem. 2017*(31), e3710.

[22] M. Amini, M. Bagherzadeh, B. Eftekhari-Sis, A. Ellern, L. K. Woo, *J Coord Chem* **2013**, *66*, 1897.

[23] X. Zhang, J. Liu, W. Hou, J. Tong, L. Ren, G. Sun, Y. Sun, *Ind Eng Chem Res* **2016**, *55*, 1550.

[24] S. Aisawa, S. Takahashi, W. Ogasawara, Y. Umetsu, E. Narita, *J Solid State Chem* **2001**, *162*, 52.

[25] C. J. Wang, D. O'Hare, *J Mat Chem* **2012**, *22*, 23064.

[26] M. Amini, M. Bagherzadeh, B. Atabaki, P. G. Derakhshandeh, A. Ellern, L. K. Woo, *J Coord Chem* **2014**, *67*, 1429.

[27] M. Amini, M. M. Haghdoost, M. Bagherzadeh, *Coord Chem Rev* **2013**, *257*, 1093.

[28] S. K. Maiti, S. Dinda, S. Banerjee, A. K. Mukherjee, R. Bhattacharyya, *Eur. J. Inorg. Chem.* **2008**, *2008*, 2038.

[29] S. K. Maiti, S. Banerjee, A. K. Mukharjee, K. M. A. Malik, R. Bhattacharyya, *New J Chem* **2005**, *29*, 554.

[30] N. Gharah, S. Chakraborty, A. K. Mukherjee, R. Bhattacharyy, *Inorg Chim Acta* **2009**, *362*, 1089.

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