

Intercalation of $[\text{Mo}^{\text{VI}}\text{O}_2(\text{O}_2\text{CC}(\text{S})\text{Ph}_2)_2]^{2-}$ in a Zn(II)–Al(III) Layered Double Hydroxide Host: A Strategy for the Heterogeneous Catalysis of the Air Oxidation of Thiols

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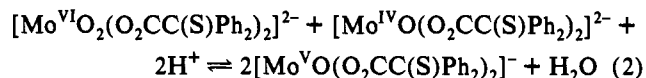
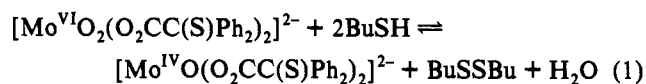
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We previously reported the synthesis of $[\text{Mo}^{\text{VI}}\text{O}_2(\text{O}_2\text{CC}(\text{S})\text{Ph}_2)_2]^{2-}$ (I), ($[\text{O}_2\text{CC}(\text{S})\text{Ph}_2]^{2-}$ being the sterically hindered 2,2-diphenyl-2-mercaptoethanoate ligand), which is the first dioxomolybdenum(VI) complex capable of oxidizing aliphatic thiols under homogeneous conditions.¹ We first demonstrated this capacity in the reaction of I with its own free ligand in excess. Such a reaction led to oxidation of thiobenzilic acid to the disulfide $(\text{O}_2\text{CCPh}_2\text{S})_2^{2-}$, while I was reduced to the monomeric complex, $[\text{Mo}^{\text{VO}}(\text{O}_2\text{CC}(\text{S})\text{Ph}_2)_2]^{-}$ (II). Both complexes, I^a and II,^{1b} contain two coordinated carboxylate groups each, as revealed by single-crystal X-ray structural studies. Atomic parameters for I and II correlate well with those determined from EXAFS data for Mo enzyme systems in the oxidized and reduced forms, respectively.²

Compared to other *cis*-dioxo Mo(VI) complexes previously reported as potential catalysts for the oxidation of the aromatic thiol PhSH by Me_2SO ,³ complex I has several unique features: (i) it has anionic character; (ii) it has a proven capacity to oxidize aliphatic thiols; (iii) the product is a monomeric, anionic Mo^{VO} complex instead of the neutral, monomeric Mo^{IVO} complex always given by all other reported systems; and (iv) complexes I and II are stable in slightly acidic media, as well as in the presence of excess thiol and/or moderate amounts of water, while all the other reported complexes decompose under such conditions. The third feature, which is reminiscent of enzymatic systems undergoing reduction to Mo(V), implies, however, an important limitation to the catalytic activity of I. Such a limitation stems from the well-known difficulty of reoxidizing Mo(V) to Mo(VI). Thus, contrary to all Mo^{IVO} complexes tested so far, our Mo^{VO} complex II shows no reducing capacity on dialkyl *S*-oxides or amine *N*-oxides. Consequently, formation of II prevents the use of common oxidants such as Me_2SO to the design of catalytic cycles.

Yet, we must point out that, apparently, Mo^{VO} is not formed directly from Mo^{IVO}_2 , but *via* intermediate Mo^{IVO} species, according to eqs 1 and 2.⁴



On the basis of the above considerations, we herein propose and demonstrate the potential of a novel strategy to facilitate the catalytic activity of I, consisting in its intercalation within a layered double hydroxide (LDH) system^{5,6} to prevent the formation of a Mo^{VO} species such as II. To our knowledge, interlayered systems of this type containing oxo-transfer molybdenum complexes have not been reported previously. We herein describe the synthesis of this unique material, I-LDH, as well as the catalytic heterogeneous oxygenation of thiols performed by it.

Intercalation of I is achieved by stirring a methanolic solution of complex I with a nitrate Zn(II)–Al(III) LDH, as a result of the partial substitution of intercalated NO_3^- by I.⁷ The material obtained, which seems to be indefinitely stable in air, was characterized by powder X-ray diffraction, Fourier-transform IR, diffuse reflectance, and thermogravimetric analysis. Its X-ray powder pattern is typical of a layered material, similar to that of the starting NO_3^- -LDH except for the (001) peaks which are shifted to higher basal space, from 8.9 Å to 17.6 Å. Assuming a thickness of the Zn(II)–Al(III) hydroxide layer of *ca.* 4.7 Å, this result indicates that the interlayer spacing generated in I-LDH is close to 13 Å. This, in turn, probably indicates that the anionic complex I intercalates with its C_2 axis parallel to the metal hydroxide layers, as shown in Figure 1. The strong band observed at 1367 cm^{-1} in the IR spectrum of NO_3^- -LDH is considerably diminished upon reaction with I, indicating that most interlayered nitrate ions are indeed displaced by I. Moreover, the appearance of new bands at 900 cm^{-1} ($\text{Mo}=\text{O}$) and 1600 cm^{-1} (CO_2^-) constitutes additional evidence of intercalation of I into the Zn(II)–Al(III) LDH. The elemental analysis of I-LDH is consistent with the formulation $[\text{Zn}_{1-x}\text{Al}_x(\text{OH})_6][(\text{NO}_3)_{x-y}\text{I}_{y/2} \cdot \text{H}_2\text{O}]$ ($x=0.25$).

I-LDH induces oxidation of EtSH or PhSH in excess to the corresponding disulfide by either Me_2SO or air. Unfortunately, this catalytic reaction is too slow (*ca.* 50 turnovers in 2 weeks) due to the initial sluggish rate of reduction of I by thiols.^{3b} Yet, we were able to observe that in the presence of a protonic zeolite or amberlite IR-120(H) the thiol reduction rate increased considerably.⁸ Thus, we undertook a ¹H- and ¹³C-NMR study of a reaction system consisting of an air-free methanolic solution of EtSH, Me_2SO , and I-LDH (18:18:1 initial molar ratio), to which 0.1% by weight of amberlite IR-120(H) had been added. ¹³C-NMR spectra show that both EtSH (signals at 19.55, 18.82

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(6) Increased interest in layered double hydroxides (LDH) system stems from their potential as catalysts. Thus, the interlayered cobalt(II) phthalocyaninetetrasulfonate complex $[\text{Mg}_5\text{Al}_2(\text{OH})_{14}][\text{CoPcTs}]_{0.5} \cdot 6\text{H}_2\text{O}$ has been prepared and used to catalyze the oxidation of aqueous solutions of 1-decanethiol by O_2 at alkaline pH (9.25). Pérez-Bernal, M. E.; Ruano-Casero, R.; Pinnavaia, T. J. *Catal. Lett.* 1991, 55.

(7) A Zn–Al LDH nitrate was prepared by coprecipitation, using deionized and decarbonated water throughout, according to the following procedure. A solution prepared by dissolving 94 g of $\text{Zn}(\text{NO}_3)_2$ (0.36 mol) and 45 g of $\text{Al}(\text{NO}_3)_3$ (0.12 mol) in 180 mL of water was added dropwise to a second solution prepared by dissolving 30.4 g of NaOH (0.76 mol) and 54.4 g of NaNO_3 (0.64 mol) in 235 mL of water. The resulting slurry had a pH of 8. The thick slurry was transferred to a stainless-steel autoclave, in which crystallization took place under autogeneous pressure at 80 °C. Partial substitution of intercalated nitrate ions by I was achieved by addition of 24 g of the LDH-nitrate precursor to 20.8 g of Na_2I (29.2 mmol) in 2 L of a glycol–methanol–water (1:1:1) mixture, followed by stirring at room temperature for 48 h. The resulting yellowish solid was then washed with methanol and dried in the oven at 340 K for 18 h, giving 26 g of I-LDH.

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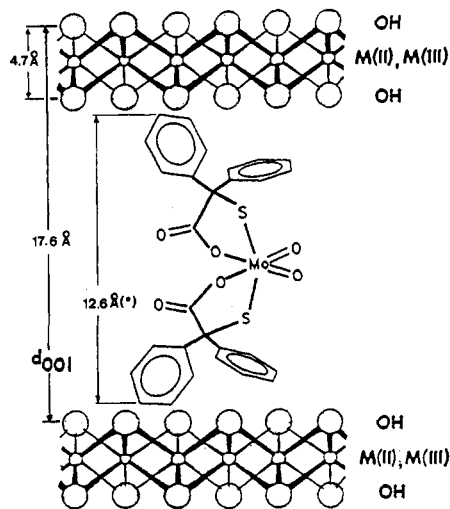


Figure 1. Schematic illustration of the orientation of I intercalated in LDH. The value marked with an asterisk (*) was calculated from the molecular structure of I which was previously established by X-ray crystallography.^{1a}

ppm) and Me_2SO (signal at 39.80 ppm) were completely consumed over a 72-h period, while Et_2S_2 (signals at 32.86, 14.23 ppm) and Me_2S (signal at 17.36 ppm) were progressively generated. Integrated areas indicate complete conversion, which is in agreement with the observation of no other signals during the period of time studied. In a control experiment, NO_3^- -LDH showed no reaction activity.

Molecular oxygen was alternatively used as the oxidant. In a typical experiment, 250 mg of I-LDH (0.1 mmol of intercalated complex I) and a 450-fold excess of PhSH (4.0 g) were stirred in ethanol under an O_2 atmosphere for 60 h at 80 °C. The progress of the reaction was monitored by gas chromatography. Time-concentration curves (see Figure 2) indicate that the reaction is first order with respect to the concentration of thiol, with no deterioration of the catalyst during at least 50 h (ca. 90 turnovers).

To our knowledge, this study constitutes the first report of a molybdenum-based catalyst for the oxidation of thiols by molecular oxygen. For this reason, it is worth comparing our results with those reported for other neutral amino thiol or dithiocarbamate dioxo-Mo(VI) complexes previously studied⁹ as homogeneous catalysts for the air oxidation of tertiary phosphines or benzoin. These latter systems, unlike the one reported herein, yield inert μ -oxo dimers which are responsible for deactivation of the catalyst within the first 20 min, as reported, for example, for $[\text{MoO}_2(\text{S}_2\text{CNET}_2)_2]$.^{9a}

The bulk of our results concerning the catalytic activity of I-LDH with Me_2SO or O_2 as oxidants are consistent with I being the active oxidant and a transient $\text{Mo}^{\text{IV}}\text{O}$ species the active reductant. Formation of a mononuclear Mo^{VO} species such as that previously observed under homogeneous conditions (eq 2) can be ruled out since complex II has been found to be completely

(8) The catalytic effect of protons, which presumably promote protonation of a $\text{Mo}=\text{O}$ moiety, has been previously studied under homogeneous conditions by adding acetic acid to a solution containing BuSH and I.⁴ In the present system, however, acetic acid cannot be used because acetate ions can replace I in LDH. Because of the heterogeneous nature of this reaction system, the reaction rate is also dependent on particle size, solution volume, and stirring rate.

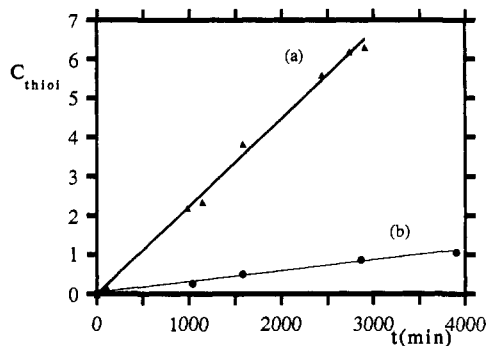


Figure 2. Concentration ($\times 10 \text{ mol kg}^{-1}$) of $\text{C}_6\text{H}_5\text{SH}$ oxidized by O_2 ($P_{\text{O}_2} = 1 \text{ atm}$) vs time at $T = 353 \text{ K}$ in EtOH (20 mL). The initial concentration of $\text{C}_6\text{H}_5\text{SH}$ is 4 g (36.3 mmol) in (a) I-LDH (250 mg, 24% in I) plus protonic amberlite IR-120(H) (250 mg) or (b) NO_3^- -LDH (250 mg) plus protonic amberlite IR-120(H) (250 mg).

inactive with respect to the oxidation by Me_2SO and decomposes immediately in air.^{1b}

Our results demonstrate the potential of intercalation into LDH as a new strategy to prevent the formation of monomeric and dimeric $\text{Mo}(\text{V})$ species. Such a strategy is probably of general applicability to anionic complexes as an alternative to the use of sterically-hindered bulky ligands.¹⁰ An important advantage of the intercalation strategy consists in the fact that water can be used as a solvent. To our knowledge, all $\text{Mo}^{\text{VI}}\text{O}_2$ catalytic systems previously studied require the use of aprotic solvents, and even then, the water generated during the oxidation of thiols (reaction 1) or benzoin precipitates and/or decomposes the molybdenum catalyst. Much in contrast to these previous findings, addition of water to ethanolic solutions of PhSH considerably increases the rate of the oxidation reaction catalyzed by our intercalated complex I. Such a rate increase is probably associated to the greater extent of dissociation of the acidic amberlite in the presence of water.

In conclusion, the chemical properties shown by I-LDH make it a unique, promising material of direct application to the elimination of contaminant thiols under ambient conditions.

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Supplementary Material Available: Powder diffraction X-ray and IR spectra of exchanged and nonexchanged material (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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