

Tungsten- and Molybdenum-Based Coordination Polymer-Catalyzed *N*-Oxidation of Primary Aromatic Amines with Aqueous Hydrogen Peroxide

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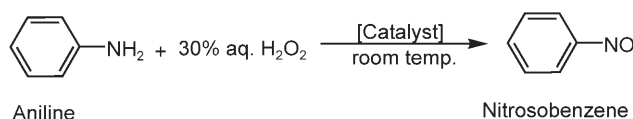
Abstract: Recyclable tungsten- and molybdenum-based coordination polymers efficiently catalyzed the oxidation of primary aromatic amines to the corresponding nitroso derivatives with 30 % aqueous hydrogen peroxide in high yields at room temperature.

Keywords: coordination polymers; hydrogen peroxide; oxidation; primary aromatic amines; recyclable catalyst

Oxidative biotransformation is amongst the most useful of all identified biologically mediated conversions. Environmentally friendly technologies acceptable with efficient formation of the desired products and with negligible waste and recyclability of the catalyst systems are the major aspects which must be considered when designing a new catalyst for selective oxidation reactions. One of the most attractive approaches is the catalytic oxidation reaction by heterogeneous means.^[1–3] Oxidation of amines is widespread in the area of biological science, reflecting the diverse roles for amine compounds. Amine compounds play important roles in neurotransmission,^[4] cell growth and differentiation,^[5] and neoplastic cell proliferation.^[6,7] On the other hand, the oxidation of amines is a fundamentally important reaction for industrial applications, particularly for the synthesis of oxygenated derivatives such as hydroxylamine, nitroso, nitro, oxime, azo and azoxy compounds. Among these, the preparations of nitro, oxime and azoxy compounds have assumed special importance as synthetically useful intermediates. Nitroso derivatives hold a key position in the chemistry of heterocycles offering functional group manipulation and structural modification possibilities that are not accessible by any other methods.^[8] Aromatic nitroso compounds are

used in the vulcanization of rubber, stabilization of halogenated materials and as antioxidants in lubricating oil.^[9]

Few homogeneous metal-catalyzed methods reported in the literature are able to yield aromatic nitroso compounds.^[10] These include the use of Caro's acid, 3-chloroperoxybenzoic acid (MCPBA), potassium permanganate, peracetic acid, peroxyformic acid, peroxybenzoic acid, oxaziridinium salts, oxygen difluoride, nitrous acid, trifluoroperacetic acid and, more recently, molybdic peroxo complexes. Catalytic methods using H₂O₂ or *tert*-butyl hydroperoxide as oxidant and sodium tungstate, oxomolybdate complexes, phosphotungstate, phosphomolybdate and zirconate salts were published later. Dimeric products due to condensation reactions such as azo or azoxy derivatives as well as over-oxidation to the nitro compounds are often observed as by-products or sometimes as main products. Some methods for the direct oxidation of aromatic amines to nitro derivatives with peracids were described and, more recently dioxirane, *tert*-butyl hydroperoxide and H₂O₂ have been used as oxidants whereas metal peroxo complexes, FeCl₃, Pb(AcO)₄ and chromium silicalite have been employed as catalysts.^[11] Nitroso compounds can also be produced by the direct reduction of nitro compounds with Mn₃O₄.^[12] But organic synthetic methods have not yet provided an easy and mild path to obtain the aromatic nitroso compounds. Our earlier report shows that [(*n*-Bu₃Sn)₂MO₄], (M = Mo and W) is able to transfer one peroxidic oxygen atom to an olefin to yield epoxides.^[13] Hence, to the best of our knowledge we present here for the first time a heterogeneous catalytic system based on tungsten and molybdenum coordination polymers [(*n*-Bu₃Sn)₂MO₄] for the selective oxidation of primary aromatic amines to the corresponding nitroso derivatives with 30 % aqueous H₂O₂ as oxidant at ambient conditions such as room temperature and under an air atmosphere (Scheme 1). This is a simple and clean process where the desired com-



Scheme 1. Oxidation of aniline.

pounds are formed free from any contamination with by-products.

The organometallic coordination polymers $[(n\text{-Bu}_3\text{Sn})_2\text{MO}_4]$, with $M=\text{Mo}$ and W were obtained in analytically pure form as colorless precipitates by the addition of a saturated aqueous solution of $\text{Na}_2\text{MO}_4 \cdot 2\text{H}_2\text{O}$ to a saturated solution of $n\text{-Bu}_3\text{SnCl}$ at room temperature. The products were recovered by filtration, washed with water, and air-dried at 100°C for several hours.^[14] The good crystallinity of $[(n\text{-Bu}_3\text{Sn})_2\text{MoO}_4]$ and $[(n\text{-Bu}_3\text{Sn})_2\text{WO}_4]$ could be seen by their powder XRD patterns. The powder XRD patterns of $[(n\text{-Bu}_3\text{Sn})_2\text{MoO}_4]$, and $[(n\text{-Bu}_3\text{Sn})_2\text{WO}_4]$ showed characteristic peaks of MoO_4 and WO_4 of the materials in the range of 20, 22 and 28, which are similar to the data reported in the literature. By fitting various peaks to Scherrer equation and taking into account the instrumental broadening, the average crystallite sizes were found to be 200 nm. N_2 sorption studies show that the surface area and pore volume of the materials are quite low. FT-IR and FT-Raman spectra of $[(n\text{-Bu}_3\text{Sn})_2\text{MoO}_4]$, and $[(n\text{-Bu}_3\text{Sn})_2\text{WO}_4]$ show all characteristic bands of organic and metal organic functionalities present in the coordination polymers. ^{119}Sn MAS NMR spectra of $[(\text{Bu}_3\text{Sn})_2\text{MoO}_4]$ show a tetrameric structure in which each Sn atom has a trigonal bipyramidal coordination geometry. Four main signals in ^{13}C CP MAS NMR were observed for the four methyl groups, two peaks each for the beta and gamma carbons, however, for the alpha carbon, the signal is clearly the sum of two components. The two small broad signals at 24 and 17 ppm are probably related to the coupling between ^{13}C and ^{117}Sn . The endothermic peaks around 240°C and 269°C , respectively for $[(n\text{-Bu}_3\text{Sn})_2\text{WO}_4]$ and $[(n\text{-Bu}_3\text{Sn})_2\text{MoO}_4]$ in the DTA curve indicate the decomposition of the coordination polymers. The typical average particle size estimated by SEM for both the catalysts is around 500 nm.^[17,18]

The catalysts $[(n\text{-Bu}_3\text{Sn})_2\text{MO}_4]$, ($M=\text{Mo}$ and W) were then investigated for the oxidation of aniline in the presence of 30% aqueous H_2O_2 . We were pleased to find that the oxidation occurred to afford nitrosobenzene in quantitative yield when the reaction mixture (4 mmol of aniline and 8 mmol of 30% aqueous H_2O_2) was allowed to stir in the presence of 0.4 mmol of catalyst, at room temperature and under atmospheric air for 1 h in acetone. A blank experiment showed that no oxidation occurred in the absence of catalyst and the amine remained unchanged. The cat-

alytic activity of $[(n\text{-Bu}_3\text{Sn})_2\text{WO}_4]$ and $[(n\text{-Bu}_3\text{Sn})_2\text{MoO}_4]$ catalysts in the oxidation of aniline shows that both the catalysts have almost similar activity (Table 1). However, Na_2WO_4 and Na_2MoO_4 catalysts show approximately half the activity compared to their corresponding polymers while Bu_3SnCl does not show any activity in the oxidation of aniline. Hence, we can conclude that the reaction was promoted mainly by tungsten and molybdenum species, and that tin enhances the activity.

To study the scope of the above catalysts for general applications, the oxidation of other amines were studied with $[(n\text{-Bu}_3\text{Sn})_2\text{WO}_4]$ catalysts (Table 2). Aniline was oxidized to the corresponding nitrosobenzene in high yield. Similarly, 4-methylaniline, 2,4-dimethylaniline, 2,4,6-trimethylaniline, 4-ethylaniline, 2-ethyl-6-methylaniline, isopropylaniline, 4-*tert*-butylaniline, 4-methoxyaniline, 1-naphthylamine could be oxidized to the respective nitroso compounds. Amines containing electron-withdrawing ring substituents, such as 2-bromoaniline, 4-bromoaniline, 2-chloroaniline, 4-chloroaniline, 2-nitro aniline, 4-nitroaniline are less reactive. These results clearly reveal that the present method could be applied for the oxidation of a variety of aromatic primary amines with 30% aqueous H_2O_2 by heterogeneous means. The products were detected by gas chromatography-mass spectrometry and quantified with FT-IR and ^1H NMR after work-up of the solutions and separation by flash chromatography. In order to obtain the highest yields of the nitroso derivatives, it is necessary to avoid the possible subsequent oxidation to the corresponding nitro derivatives, by frequent checking of the reaction profile, and by stopping the reaction immediately after the complete consumption of amine. The results given in the Table 2 represent the conditions for obtaining the best yields. The nitroso derivatives obtained in this way are monomeric and the FT-IR spec-

Table 1. Oxidation of aniline with different catalysts.^[a]

Entry	Catalyst	Substrate	Product	Yield [%] ^[b]
1	Na_2WO_4	Aniline	Nitrosobenzene	38
2	Na_2MoO_4	Aniline	Nitrosobenzene	31
3	$[(n\text{-Bu}_3\text{Sn})_2\text{WO}_4]$	Aniline	Nitrosobenzene	82
4	$[(n\text{-Bu}_3\text{Sn})_2\text{MoO}_4]$	Aniline	Nitrosobenzene	77
5	Bu_3SnCl	Aniline	-	No reaction
6	Without catalyst	Aniline	-	No reaction

^[a] Reaction conditions: amine (4 mmol), catalyst (0.4 mmol) and 30% aqueous H_2O_2 (8 mmol) were stirred in acetone (7 mL) at room temperature; reaction time = 1 h.

^[b] Yield [%] = actual yield/expected yield $\times 100\%$.

Table 2. Oxidation of primary amines using 30 % H₂O₂ catalyzed by [(*n*-Bu₃Sn)₂WO₄].^[a]

Entry	Substrates	Product	Yield [%] ^[b]
1	Aniline	Nitrosobenzene	82
2	4-Methylaniline	4-Methylnitrosobenzene	86
3	2,4-Dimethylaniline	2,4-Dimethylnitrosobenzene	90
4	2,4,6-Trimethylaniline	2,4,6-Trimethylnitrosobenzene	92
5	4-Ethylaniline	4-Ethyl nitrosobenzene	89
6	2-Ethyl-6-methylaniline	2-Ethyl-6-methylnitrosobenzene	83
7	Isopropylaniline	Isopropyl nitrosobenzene	81
8	4- <i>tert</i> -Butylaniline	4- <i>tert</i> -Butylnitrosobenzene	85
9	4-Methoxyaniline	4-Methoxynitrosobenzene	87
10	2-Bromoaniline	2-Bromonitrosobenzene	70
11	2-Chloroaniline	2-Chloronitrosobenzene	74
12	4-Bromoaniline	4-Bromonitrosobenzene	63
13	4-Chloroaniline	4-Chloronitrosobenzene	68
14	2-Nitroaniline	2-Nitronitrosoaniline	35
15	4-Nitroaniline	4-Nitronitrosoaniline	20
16	1-Naphthylamine	1-Naphthyl nitrosobenzene	72

^[a] Reaction conditions: amine (4 mmol), catalyst: [(*n*-Bu₃Sn)₂WO₄] (0.4 mmol) and 30 % aqueous H₂O₂ (8 mmol) were stirred in acetone (7 mL) at room temperature; reaction time = 1 h.

^[b] Yield [%] = actual yield/expected yield × 100 %.

tra in KBr showed a weak band close to 1500 cm⁻¹, attributable to the stretching mode of the N=O bond of the monomer. These assignments are in good agreement with reported values.^[15] The oxidation path of this reaction could follow the steps from amine to hydroxylamine and then to nitrosoamine. The oxygenation of the nitrogen atom of the substrate is accomplished by the formation of an oxo-tungsten complex, originating from nucleophilic attack of the amine onto peroxidic oxygen or SET processes.^[16] Early literature reports and a recent communication on this subject support this hypothesis.^[17]

The catalyst could be filtered and recycled without a loss of activity. After completion of the reaction, the catalyst was filtered, washed with acetone, dried at 100 °C and reused in the oxidation of aniline with fresh 30 % aqueous H₂O₂ for four runs. No loss of activity was observed and the corresponding nitrosobenzene was obtained in high yield. In another experiment, the filtrate was used for the oxidation of aniline in the presence of 8 mmol of 30 % aqueous H₂O₂ and no reaction was observed. This indicates that the active ingredient has not leached out of the solid catalyst during the reaction.

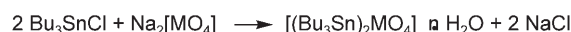
In conclusion, the *N*-oxidation of primary aromatic amines is described using tungsten- and molybdenum-based coordination polymers (heterogeneous catalyst) in the presence of 30 % aqueous H₂O₂ at room temperature and atmospheric air to give the corresponding nitroso derivatives in high yield. It is a clean process and the catalyst is recyclable without any loss of activity.

Experimental Section

Preparation of Catalysts

[(*n*-Bu₃Sn)₂MoO₄]: *n*-Bu₃SnCl (3.25 g, 10 mmol) was dissolved in a mixture of water (6 mL) and acetone (27 mL). A saturated aqueous solution of Na₂MoO₄·2H₂O (1.21 g, 5 mmol in 8 mL of H₂O) was added dropwise with magnetic stirring to *n*-Bu₃SnCl solution. A white precipitate was formed immediately and stirring was continued for 5 min. The precipitate was filtered, washed thoroughly with water, and dried in air at 100 °C for 6 h to give (*n*-Bu₃Sn)₂MoO₄; yield: 90 %.

[(*n*-Bu₃Sn)₂WO₄]: This material was prepared as described above using Na₂WO₄·2H₂O instead of Na₂MoO₄·2H₂O. The general reaction for the preparation of the organotin-oxometalate coordination polymer is as shown below:



M = Mo or W, Bu = butyl group

Elemental analysis confirmed that the above materials are as per the stoichiometric composition of the coordination polymers [(*n*-Bu₃Sn)₂MoO₄] and [(*n*-Bu₃Sn)₂WO₄].

Typical Procedure for Oxidation

Amine (4 mmol), catalyst (0.4 mmol) and 30 % aqueous H₂O₂ (8 mmol) were stirred in acetone (7 mL) at room temperature for the appropriate time (Table 1). After the completion of the reaction, the catalyst was filtered and the filtrate was subjected to reduced pressure to remove the solvent. Then 10 mL of CH₂Cl₂ were added and the mixture was washed with 10 mL of distilled water and brine. The organic layer was separated and dried over anhydrous Na₂SO₄. The mixture was again filtered and concentrated under reduced pressure to afford a residue, which was purified by flash chromatography over silica (*n*-hexane:CH₂Cl₂, 4:6). The catalyst could be recycled without a loss of activity. All compounds were analyzed by GC, GCMS, IR and ¹H NMR.

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