ASEC 2024 Conference

The 5th International Electronic Conference on Applied Sciences

04–06 December 2024 | Online

MDPI

Structural Insights into Molybdenum Schiff Base Complexes: Impedance Spectroscopy and Coordination Behavior

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INTRODUCTION

Molybdenum, a transition metal recognized for its diverse oxidation states and ability to form complex compounds, plays a significant role in various applications. Molybdenum Schiff base complexes, formed by coordinating molybdenum with ligands derived from primary amines and carbonyl compounds, exhibit remarkable catalytic and chemical properties.[1,2]

In industry, molybdenum-based complexes are highly valued for their catalytic functions in key processes such as oxidation, hydrogenation, and olefin metathesis, all of which are essential to chemical synthesis.[2,3] Additionally, these complexes are gaining prominence in materials science, where they contribute to the development of advanced materials with unique structures and electronic characteristics. These materials are crucial for energy conversion technologies and environmental protection efforts.[2,4]

METHODOLOGY

The ligand was synthesized via the reaction of oxalyldihydrazide with salicylaldehyde, followed by coordination with $[MoO_2(acac)_2]$ in methanol, resulting in a dinuclear complex, $[Mo_2O_4(L)(MeOH)_2]\cdot 2\ H_2O$. The obtained complex was subjected to various alcohol and water vapours, and its responses were analyzed using solid-state impedance spectroscopy (ss-IS) to evaluate its sensor properties. Additionally, the catalytic performance of the complex was investigated by employing it as a catalyst for the oxidation of benzyl alcohol, using *tert*-butyl hydroperoxide (TBHP) as the oxidant in an aqueous medium. This study seeks to explore the material's dual potential in sensing and catalytic applications.

RESULTS

Table 1. Conductivity after exposure of the dinuclear complex $[Mo_2O_4(L)(MeOH)_2]\cdot 2\ H_2O$ to methanol, ethanol, propanol and water vapours.

Solvent Vapours	1st cycling (Ω cm)$^{-1}$	2nd vapours (Ω cm)$^{-1}$
MeOH	6.73×10^{-7}	2.21×10^{-6}
EtOH	5.60×10^{-7}	8.85×10^{-8}
PrOH	2.52×10^{-8}	1.15×10^{-9}
H_2O	3.85×10^{-10}	1.75×10^{-9}

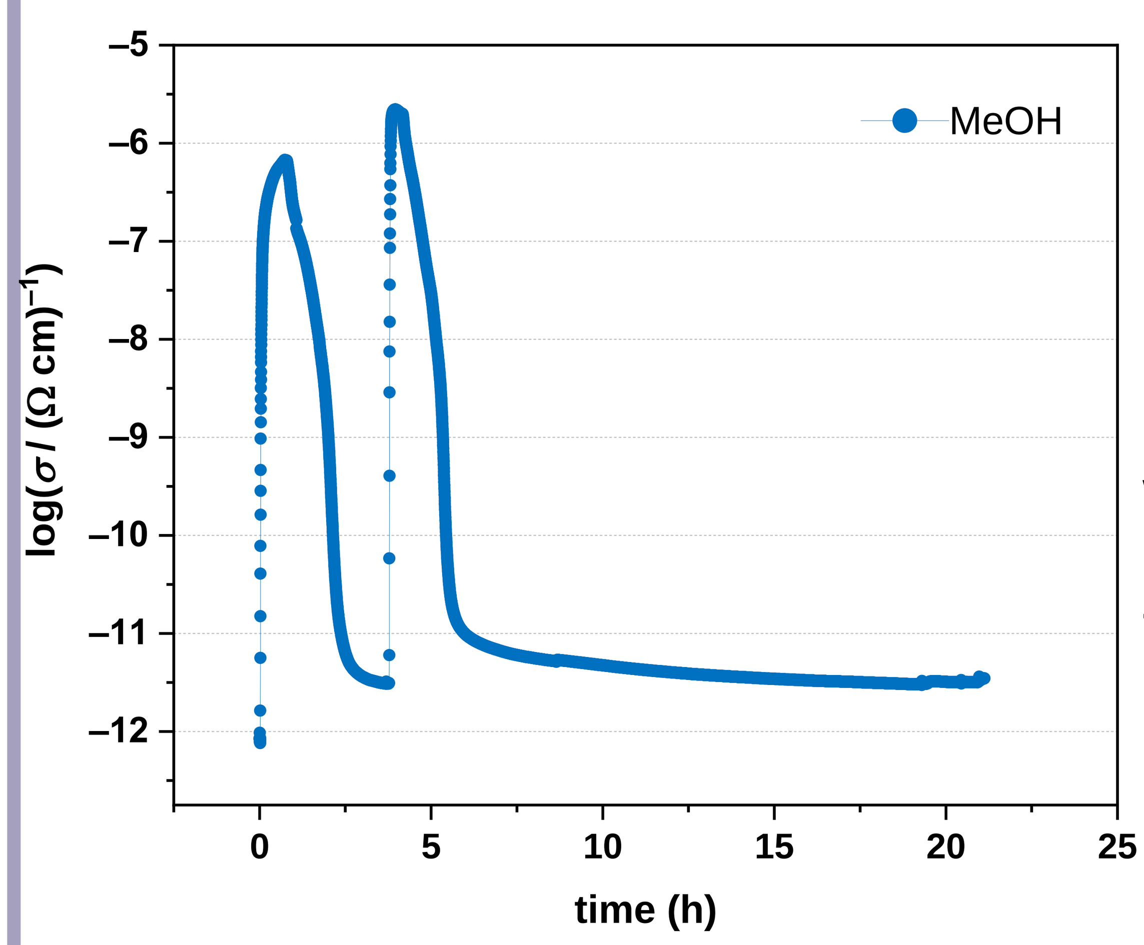

Figure 1. Conductivity after exposure of the dinuclear complex $[Mo_2O_4(L)(MeOH)_2]\cdot 2\ H_2O$ to MeOH vapours. After the initial exposure, the sample was left in the air to relax before being re-exposed to the MeOH vapours. All measurements were carried out at a frequency of 1 Hz.

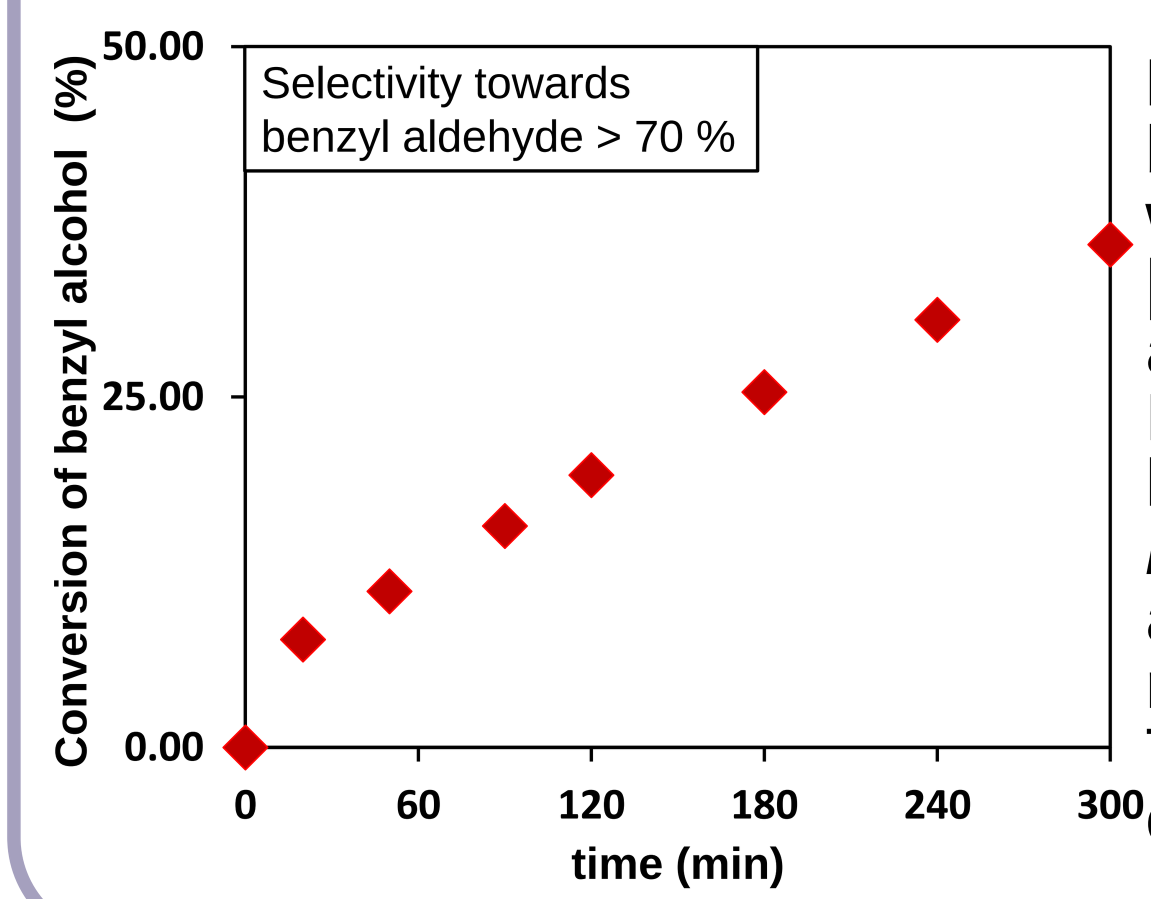

Figure 2. Kinetic profile of benzyl alcohol conversion with dinuclear complex $[Mo_2O_4(L)(MeOH)_2]\cdot 2\ H_2O$ as catalyst.
Reaction conditions: time, 5 h; temperature, 80 °C; *n*(catalyst):*n*(benzyl alcohol):*n*(oxidant) = 5 mmol/20 mmol/40 mmol. TBHP in water was used as oxidizing agent.

CONCLUSION

The dinuclear complex $[Mo_2O_4(L)(MeOH)_2]\cdot 2\ H_2O$ demonstrated remarkable performance in both sensor and catalytic applications. It exhibited a pronounced response to all tested alcohol and water vapours, with the strongest response observed for MeOH vapours. Conductivity increased dramatically, from approximately 10^{-12} (Ω·cm)$^{-1}$ under ambient conditions to 10^{-6} (Ω·cm)$^{-1}$ when exposed to MeOH vapors, representing an enhancement of six orders of magnitude. Importantly, the complex reverted to its original structure, $[Mo_2O_4(L)(MeOH)_2]\cdot 2\ H_2O$, after exposure, highlighting the sensor material's reversibility and stability. In catalytic testing, the complex achieved a benzyl alcohol conversion rate of approximately 30%, with a notable selectivity of around 70%. These findings underscore the potential of $[Mo_2O_4(L)(MeOH)_2]\cdot 2\ H_2O$ as a robust and selective catalyst.

REFERENCES

[1] V.K. Juyal; A. Pathak; M. Panwar; S.C. Thakuri; O. Prakash; A. Agrwal; V. Nand. *J. Organomet. Chem.* **999** (2023) 122825.

[2] J. Sarjanović; E. Topić; M. Rubčić; L. Androš Dubraja; L. Pavić; J. Pisk. *J. Mater. Chem. C* **12** (2024) 4013-4025.

[3] M. Xue; Z. Peng; K. Tao; J. Jia; D. Song; C.–H. Tung; W. Wang. *Nat. Commun.* **15** (2024) 797.

[4] J. Sarjanović; M. Cader; E. Topić; M. Razum; D. Agustin; M. Rubčić; L. Pavić; J. Pisk. *Mater. Adv.* **5** (2024) 9391-9402.