



Defect-rich Mo/MoO₂ catalyst for efficient peroxymonosulfate activation and refractory pollutants degradation

Hongjun FANG, Hui GUO, Xinzhen FENG, Weijie JI*

Key Laboratory of Mesoscopic Chemistry, MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, China

*e-mail: jiwj@nju.edu.cn

Significance and Relevance

A Mo/MoO₂ catalyst fabricated *via* electro-explosive method comprises enriched oxygen vacancies, capable of rapid redox cycles among Mo⁴⁺/Mo⁵⁺/Mo⁶⁺ and accelerates electron transfer kinetics, more conducive to catalytic degradation of acid orange (AO7). A degradation of AO7 with a rate constant of 1.108 min⁻¹ was achieved on the Mo/MoO₂-10h/PMS system. Relative significance of AOSs in the current system was identified as ¹O₂ > [•]O₂⁻ > [•]OH > SO₄^{•-}. The detailed AO7 degradation pathways have been proposed in terms of the LC/MS analysis. This system also exhibited high performance for removal of a variety of pollutants including antibiotics and organic dyes.

Introduction and Motivations

Acid orange 7 (AO7) is frequently detected in textile wastewater and poses an ongoing impact on aquatic ecosystems because of its high ecotoxicity and water solubility.^{1,2} For effective AO7 removal, advanced oxidation processes (AOPs) have been taken into consideration. Among these AOPs, the sulfate radical-based AOP using peroxymonosulfate (PMS) as oxidant has the merits of stronger oxidation capacity, wider pH adaptability, and higher stability, thus more suitable for refractory pollutants removal (Yang et al., 2021a and 2022b). At present, various activation methods are applied to activate PMS, yielding active oxygen species for pollutants degradation. However, development of high-performance catalyst (high activity/durability) for PMS activation is still challenging.

Materials and Methods

The electro-synthesis of Mo and Mo/MoO₂ catalysts was operated on a commercially available apparatus (Thor Series Nano Metal Machine) with the Mo wire as raw material. This electric-explosion method is environmentally friendly and free of additional chemical reagents. The fresh sample was subjected to an oxidation exposure in air for different time (5 h, 10 h, and 20 h), and denoted as Mo/MoO₂-5 h, Mo/MoO₂-10 h, and Mo/MoO₂-20 h, respectively. Meanwhile, the reference sample MoO₂-H with deficient Vo was synthesized by hydrothermal method for comparison. The catalytic activity of each sample was evaluated by degradation of AO7 with PMS oxidant. The catalysts were characterized by various techniques and the DFT simulation was also performed to better understand the catalyst properties and the reaction details.

Results and Discussion

Defect engineering has been proven to alter the electron mobility of catalyst by generating high content of defects (i.e., Vo), thus favorable for electron transfer and providing more active sites for catalytic reactions. Integration of Mo⁰ and Vo into MoO₂ could significantly improve the activity of the resulting material. Notably, the traditional catalyst synthesis usually involved the use of various chemical reagents, which also poses additional negative impact on the environment. Therefore, a facile synthesis route without additional chemical input and easy to scale-up is highly desirable for practical application. This work reported a convenient electric explosion route to obtain the Vo-rich Mo/MoO₂ system using the Mo wire as raw source without employing any additional chemicals. Evidently, the Mo site of different oxidation states contributed to chemical activation of PMS, while the Vo favored the activation of PMS and the generation of non-radical ¹O₂ species. As a result, the Mo/MoO₂-10 h/PMS system delivered a complete removal of acid orange 7 (AO7) within 4 min, significantly exceeding the activity of Mo/PMS (16%), MoO₂-H/PMS (25%), and most of other PMS-based systems. Theoretical calculations revealed that the PMS dissociation is not a rate-determining step in the

involved system, while the activation efficiency of catalyst is largely related to the difference of its binding ability to PMS. Expectedly, the Vo-rich Mo/MoO₂ owned a stronger adsorption capacity of PMS and rapider electron transfer kinetics compared to that of Vo-deficient MoO₂, thereby accounting for an enhanced catalytic activity for the PMS-AOP. Quenching experiments and EPR analysis suggested that the ¹O₂ species was the dominated one for AO7 removal. Toxicity prediction analysis of the original, the intermediates, and the final products indicated that the degradation intermediates were less toxic to the environment. Moreover, the current system showed high potential for removal of different pollutants such as CIP, TC, RhB, and MB.

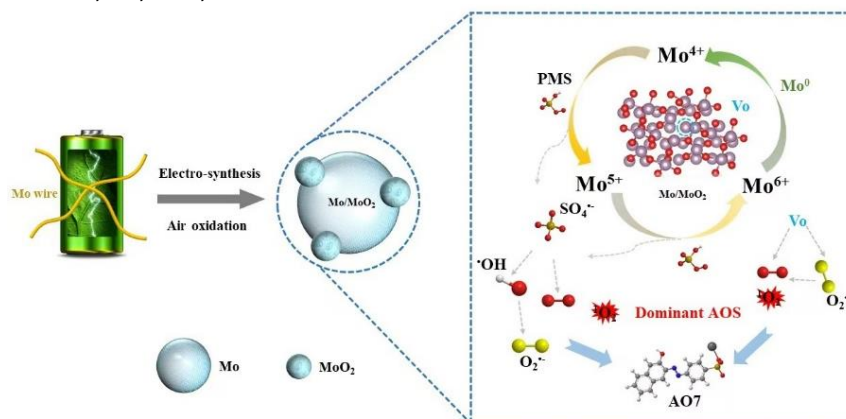


Figure 1 Schematic illustration of electro-explosive route to synthesize the oxygen vacancy enriched Mo/MoO₂ catalyst, the involved PMS activation, and the critical AOS of ¹O₂ formation.

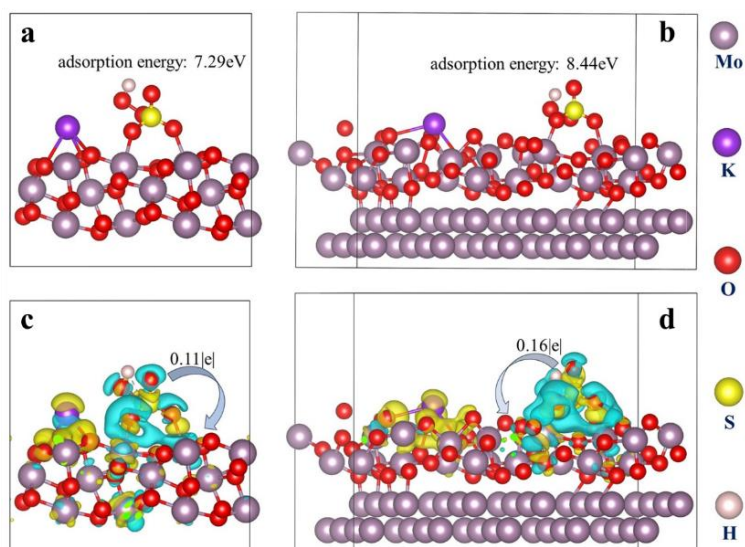


Figure 2. The calculated adsorption energy of (a) MoO₂ (-111) surface and (b) the Mo (110)/MoO₂ (-111) interface; the charge density difference of (c) MoO₂ (-111) surface and (d) the Mo (110)/MoO₂ (-111) interface.

References

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