[Supporting Information]

Olefin Epoxidation Reaction Promoted by Internal Oxygen Transfer: Research on Oxygen Transfer Mechanism Based on Mn(Salen)-POM System

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The current reports on Olefin Epoxidation Reaction based on POMs

Currently, various efficient catalytic systems based on polyoxometalates (POMs) for the epoxidation of olefins have been developed, covering multiple dimensions such as heterogeneous catalyst design, structural modification, and mechanistic investigation. In the construction of heterogeneous systems, Keggin-type heteropoly acids (e.g., $H_3PW_{12}O_{40}$) exhibited excellent performance in a multiphase system composed of isooctane/Aliquat 336/water, achieving 72% conversion and 70% selectivity in the epoxidation of cyclohexene, which was significantly superior to homogeneous or biphasic systems. Additionally, the decomposition of H_2O_2 was effectively suppressed (only 12% decomposition). Green metrics analysis further confirmed the enhanced environmental friendliness of this heterogeneous system.[1] In contrast, nanodice (NDs) with a tetrakisdecahedral structure, formed through the self-assembly of lacunary POMs (e.g., $[PW_{11}O_{39}]^{7-}$) and tetrabutylammonium bromide (TBAB), demonstrated outstanding performance in the epoxidation of cyclooctene, yielding 99.8% product—55.4 times higher than that of pure PW_{11}. Raman spectroscopy and DFT calculations indicated that hydroperoxy species, generated via H_2O_2 activation, are the key active intermediates. The lacunary structure was shown to reduce the energy barrier for H_2O_2 activation and enhance cyclooctene adsorption, thereby improving catalytic activity.[2]

In the design of inorganic-organic hybrid POMs, a vanadium-substituted Keggin-type POM-based coordination polymer (e.g., $[Co_2(H_2O)_4(BBTZ)_3]$ $[HPW_{10}V_2O_{40}]$) synthesized via a hydrothermal method achieved 97.6% conversion and >99% selectivity for cyclooctene within 4 hours using O_2 as the oxidant. The superior performance was attributed to the synergistic effect between the Co^{2+} metal centers and $PW_{10}V_2$, which collectively facilitated the generation of O_2^- active species from O_2. Moreover, the catalyst maintained over 95% conversion after five cycles with no significant change in its crystal structure.[3] Furthermore, a composite material, $PMo_{10}V_2$-ILs@MIL-100(Fe), was constructed by encapsulating ionic liquids (e.g., 1-octyl-3-methylimidazolium bromide) into a POM-based metal-organic framework (MOF). Leveraging the mesoporous structure of MIL-100(Fe), the strong acidity of $PMo_{10}V_2$, and the activating effect of ILs on POMs, this composite achieved 92% conversion and 93% selectivity in the epoxidation of cyclohexene. It could be reused for 12 cycles without significant loss of activity.[4]

Regarding reaction mechanisms, it was demonstrated that water-coordinated sandwich-type POMs (e.g., $WZnTM_2(H_2O)_{22}^{n-}$, TM = Rh^{2+}, Pd^{2+}, Pt^{2+}) catalyze the epoxidation of olefins with H_2O_2 via a two-step mechanism involving H_2O_2 activation and oxygen transfer. Two pathways—"stepwise" and "concerted"—were identified for H_2O_2 activation, with the concerted pathway being more favorable and serving as the rate-determining step. Rh-based POMs exhibited higher reactivity due to strong interactions between Rh and the peroxo unit. Analysis

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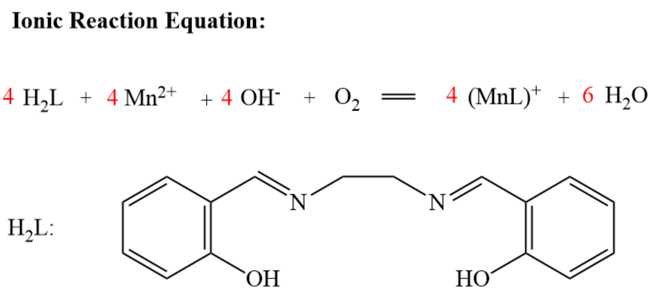
† Electronic supplementary information (ESI) available: Experimental details, procedures, FT-IR spectra, UV-vis spectra and TG acquisition data.

of active oxygen sites revealed that the O_{2m} site bonded to two metals was more advantageous owing to reduced steric hindrance. Additionally, explicit water molecules were found to further lower the energy barrier through hydrogen bonding.[5] These studies not only enrich the structural design strategies for POM-based catalysts but also provide important support for their application in green olefin epoxidation, promoting the functional diversification of inorganic-organic hybrid POMs.



Scheme S1[†] The chemical equation for the conversion of Mn^{2+} to Mn^{3+} by oxygen in the air during catalyst synthesis.

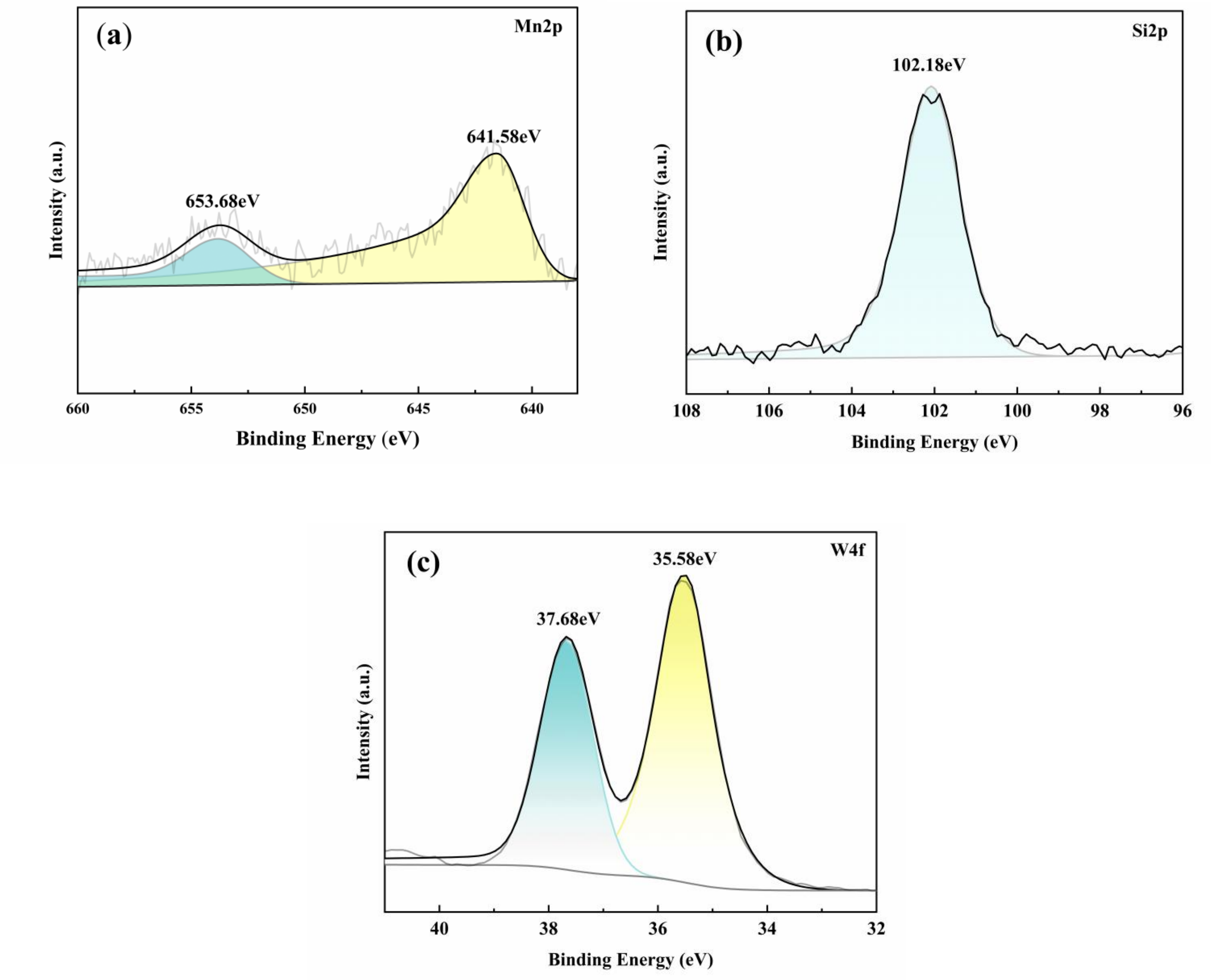


Fig. S1(a-c)[†] The high-resolution XPS spectra of Mn, Si, and W for compound **1**.

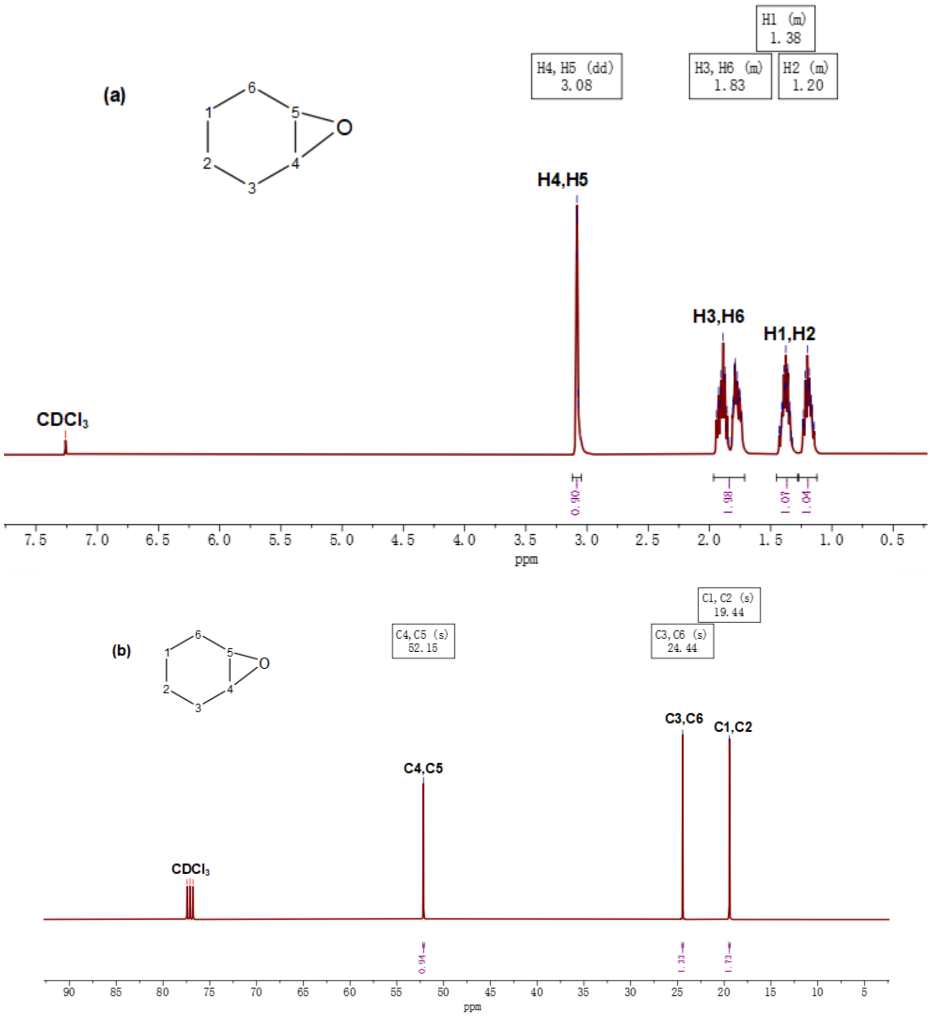


Fig. S2† ^{1}H and ^{13}C NMR spectra of cyclohexene epoxide deuterated chloroform as solvent at room temperature.

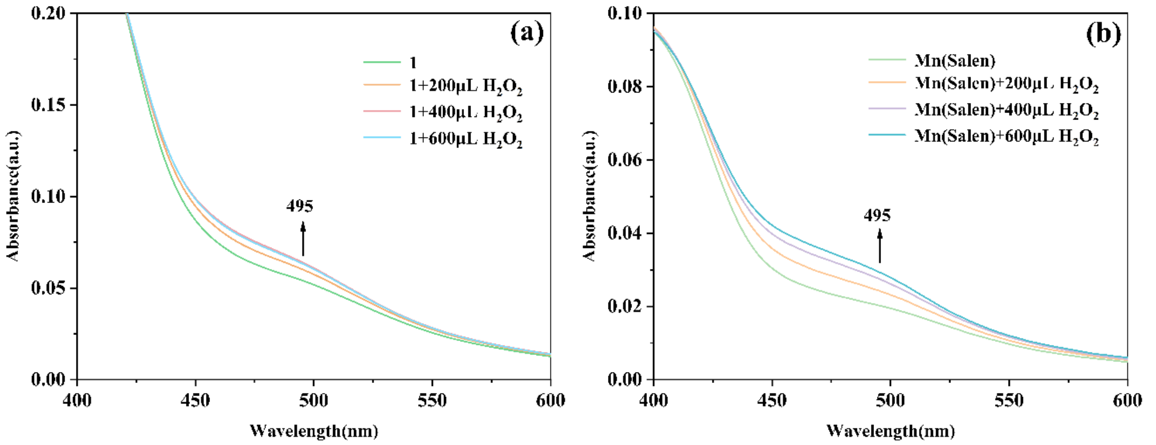


Fig. S3 (a)† The UV-vis spectra of compound **1** in acetonitrile solution upon gradual addition of H_2O_2. (b)† The UV-vis spectra of Mn(Salen) in acetonitrile solution upon gradual addition of H_2O_2.

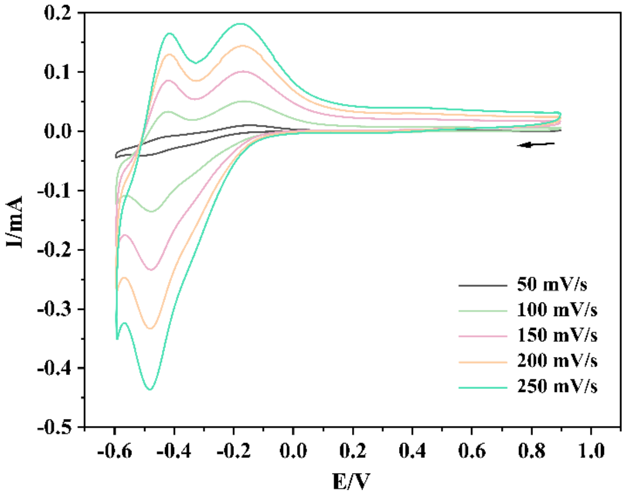


Fig. S4† CV curves of Compound **1** at different scan rates within the potential range of −0.6 to 0.9 V.

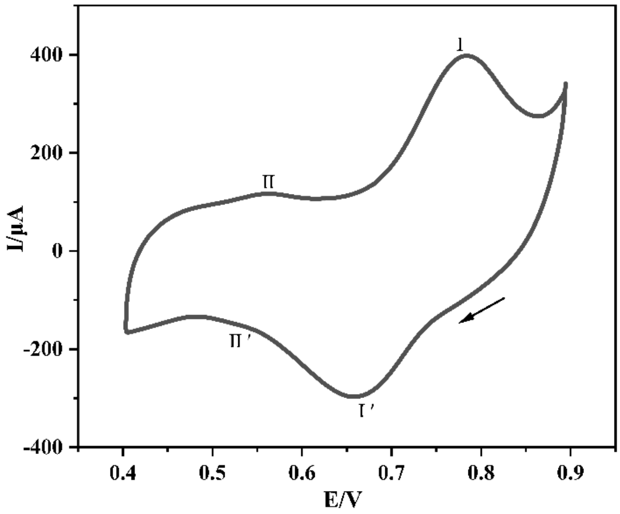


Fig.S5† The electrochemical behaviour of a carbon-paste electrode modified with **1** (1-CPE).

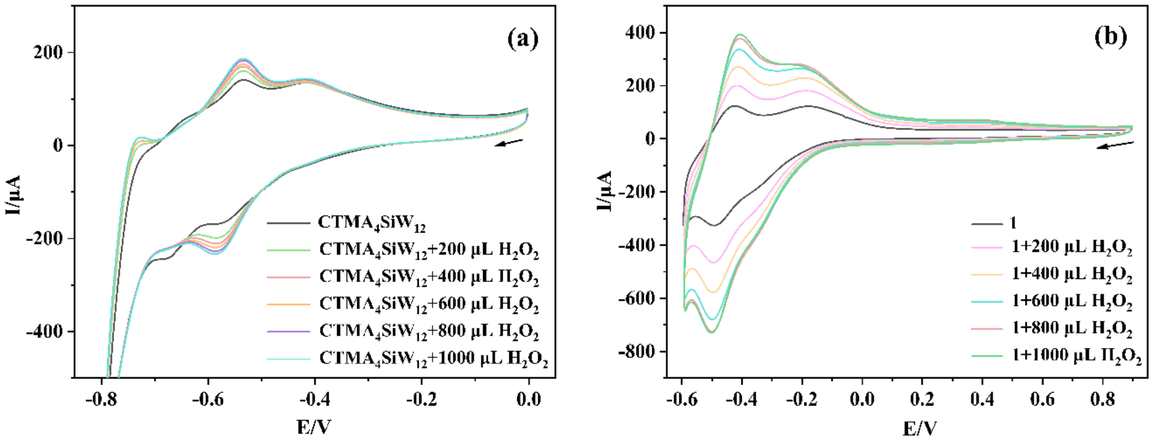


Fig. S6† CV curves of $[C_{16}H_{33}N(CH_3)_3]_4[SiW_{12}O_{40}]$ ($CTMA_4SiW_{12}$) (a) and Compound **1** (b) in 1 M H_2SO_4 with varying amounts of aqueous H_2O_2.

Notes and references

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