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Short communication

Immobilization of molybdenum-based complexes on dendrimer-functionalized graphene oxide and their catalytic activity for the epoxidation of alkenes

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ARTICLE INFO	A B S T R A C T			
Keywords: Molybdenum Graphene oxide Dendrimer Epoxidation Alkenes	Two novel molybdenum-based heterogeneous catalysts immobilized on dendrimer-functionalized graphene oxide via electrostatic interactions (Mo-1) or covalent bonding (Mo-2) are reported. The catalysts show excellent catalysis in epoxidation of alkenes with high conversion, better selectivity and good recyclability. The characteristics were identified by SEM, TEM (EDS-mapping), FT-IR, XRD, and XPS. The cause of the difference between the two catalysts is supported by DFT calculations.			

1. Introduction

Epoxides are important precursors for the production of fine chemicals, such as nanomaterials, surfactants, food additives, cosmetics and epoxyresins. They are vital intermediates in organic synthesis and are important to achieve structural and functional versatility. In recent years, the epoxidation of alkenes has been the main route to produce epoxides. In this process, metal-based catalysis has played an important role because of the high selectivity and activities of the catalysts [1–4]. Molybdenum, an abundant and nonnoble metal, has naturally attracted much attention from researchers [5].

The historic progress of molybdenum-based catalysts for epoxidation of alkenes can be traced back to the 1960s. Originally, molybdenum complexes as homogeneous catalysts were widely used, including Mo (CO)₆, MoO₂-phthalocyanine, MoO₂(trans-cyclohexane-1,2-diol)₂ [6,7] and MoO₂(acac)₂ [8]. Moreover, molybdenum complexes with various kinds of ligands, such as Schiff-base ligands [9–11], 1,2,4-triazole(trz) ligands [12], salen ligands [13], etc., have also been certified as efficient homogeneous catalysts. Unfortunately, although homogeneous catalysts have high catalytic activity, their non-recyclability and difficulty of separation have seriously limited their application. Therefore, innovative effort has been made to design and prepare heterogeneous catalysts to overcome the drawbacks of homogeneous catalysts. Support materials with chemical and thermal stability, large specific surface

areas, and hierarchical structures have been widely used. Polyoxometalate (POM), an anionic transition metal oxygen clusters, can be used not only as an efficient catalyst in epoxidation directly [14], but also as modificatory materials these have better stability and could be easily reused without distinct loss in both mass and activity [15-17]. In addition, Polyoxometalate-based catalysts immobilized on proper materials have also exhibited unexpected catalytic activity [18]. Graphene oxide (GO), as an efficient support for heterogeneous catalytic reactions, has been widely studied because of its abundant oxygen-containing functional groups, superior mechanical strength and considerable specific surface area. Surface-functionalized GO, which was coordinated with MoO₂(acac)₂ [19] or Sali-cylaldehydoethylenediamine (salen)-Mocomplexes [20-22] has high conversion, good selectivity and excellent reusability, and the major difference among them are the coupler and the type of interaction. Furthermore, many other stable materials have also been used as supports, such as dendrimer-functionalized magnetic nanoparticles [23], porous silica materials [24] and photocatalyzed epoxidation catalysts [25]. Overall, exploiting innovative molybdenumbased heterogeneous catalysts for epoxidation of alkenes is inevitable to overcome the problems with separation and recycling and improve their properties and commercial value.

Herein, we report two novel molybdenum-based heterogeneous catalysts for epoxidation of alkenes, that have been immobilized onto dendrimer-functionalized GO via covalent bonding or electrostatic

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interactions [26,27] under mild conditions using *tert*-butyl hydroperoxide (TBHP) as an oxidant with good activity, high selectivity and sufficient stability and reusability.

2. Experimental

2.1. Materials

All reactants and solvents were directly obtained from commercial sources (Energy Chemical, Shanghai, China) and used without further purification, such as graphite powder (crystalline, -325 mesh, 99%), PAMAM-G1 (M.W = 516.38, 98%), H₃PO₄·12MoO₃ (M.W = 1825.48 g/ mol, 98%), MoO₂(acac)₂ (98%), silica gel (100-200, 200-300 mesh). Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) were obtained by Q45-XFlash 6-30 (FEI-BRUKER, Shanghai, China) and JEM2100F (JEOL, Tokyo, Japan). The Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) was measured by Optima 8000 (PerkinElmer, Saint Paul, USA). Fourier Transform Infrared Spectroscopy (FT-IR) were measured by a Nicolet IS5 (Thermo Fisher, Waltham, USA). X-Ray Powder Diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) patterns were obtained by X'Pert3PowderX (PANalytical, Almelo, Holland) and ESCALAB250Xi (Thermo Fisher, Waltham, USA). The Density Functional Theory (DFT) calculations were carried out at the b3lyp level, and the standard LanL2DZ basis set was employed to represent the H, C, O, P, S and Mo atoms to optimize these structural fragments, as implemented in the Gaussian09 program. The conversion and selectivity of the substrates and products were determined by Gas Chromatography-Mass Spectrometer (GC-MS) with internal standard curve method (Inert mass selective datevtor: 5975, Network GC system: 6890 N, chromatographic column: HP-5MS 19091S-433, 30.0 m*250 μm*0.25 μm, dodecane as an internal standard) ¹H and ¹³C NMR spectra were recorded with Bruker Avance-III 600 spectrometers and referenced to DMSO-d₆.

2.2. Catalysts synthesis

2.2.1. Synthesis of graphene oxide (GO)

In a typical experiment, graphite powder (6.0 g), H₂SO₄ (60 ml), K₂S₂O₈ (7.5 g), and P₂O₅ (7.5 g) were mixed in a 500 ml round-bottom flask. The solution was heated to 80 $^\circ$ C and stirred for 12 h. Next, after cooling to room temperature, the solution was diluted with 300 ml of deionized (DI) water. After that, the mixture was filtered and washed with 500 ml of deionized water. The product was dried at 60 $^\circ \rm C$ under vacuum for 12 h. The pretreated graphite powder was then stirred in concentrated H₂SO₄ (150 ml) for 12 h. Afterwards, NaNO₃ (3.0 g) was added into the mixture, and then KMnO₄ (30 g) was added slowly while stirring at 0 °C. The mixture was then heated to 35 °C for 0.5 h, and later, it was slowly diluted with DI water (1 L) to keep the temperature below 40 °C. Next, the mixture was heated to 90 °C and transferred to ambient conditions after 15 min. After that, DI water (300 ml) was added quickly. Afterward, 30% H₂O₂ (60 ml) was gradually added to the mixture. After the oxidation process, the mixture was centrifuged and washed three times with 5 wt% HCl to remove metal ions and then washed with large amounts of deionized water and ethanol. The prepared dark-brown product was dried in an oven at 40 °C for 24 h to afford graphene oxide (black solid, 8.5 g).

2.2.2. Synthesis of GO-PAMAM-G1

GO (3.0 g) was dispersed in 100 ml of deionized water by sonication for 30 min. Then, 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI) (520 mg) and *N*-hydroxysuccinimide (NHS) (150 mg) were added to the solution and stirred for 15 min to activate the carbonyl group on GO. Finally, Polyamide-amine dendritic polymer-G1 (PAMAM-G1) (3 g) in 20 ml DI water was added dropwise to the system, and the reaction was allowed to proceed at 25 °C for 24 h. The suspension was filtered and washed with water and ethanol. The product was dried at 60 °C under vacuum for 12 h. The resulting dark-brown precipitates of the modified GO-PAMAM-G1 were ready to use (5.1 g).

2.2.3. Synthesis of Mo-1

 H_3PO_4 ·12MoO₃ (HPMo) (2.5 g) was added to a liquid suspension of



Fig. 1. The probable structures of catalysts.

GO-PAMAM-G1 (2.5 g) in water. The mixture was stirred for 48 h at room temperature. The black precipitate was collected and washed with water and diethyl ether to yield a black solid (3.7 g).

2.2.4. Synthesis of GO-PAMAM-G1-salen

A solution of salicylaldehyde (0.52 ml, 5 mmol) in methanol (10 ml) was added to GO-PAMAM-G1 (2.5 g), dispersed in 100 ml methanol in a 250 ml round bottom flask and refluxed for 12 h. The mixture was cooled, filtered and dried at room temperature to obtain a black solid (3.0 g).

2.2.5. Synthesis of Mo-2

A solution of $MoO_2(acac)_2$ (0.98 g, 3.0 mmol) in methanol was added to a suspension of GO-PAMAM-G1-salen (3.0 g) in methanol. The mixture was refluxed for 24 h, and the black precipitate was collected and washed with methanol and diethyl ether to yield a black solid (3.5 g).

2.3. Evaluation of catalytic performance

2.3.1. General procedure for epoxidation of alkenes catalyzed by Mo-1 and Mo-2 $\,$

In a typical procedure, the epoxidation reaction was carried out as follows: 6 mmol TBHP (80% in di-tertiary butyl peroxide), as an oxidant, was added to a mixture of catalyst (Mo-1, 50 mg or Mo-2, 50 mg) and olefin (1 mmol) in toluene (20 ml), after the mixture had been stirred for 15 min. The mixture was then refluxed for an appropriate time, and the final products were quantified by GC–MS with dodecane as an internal standard, and the spectra of the products are given in the supporting information.

2.3.2. Synthesis of synephrine

Acetic anhydride (2 mmol, 0.189 ml), triethylamine (2 mmol, 0.278 ml) and 4-dimethylaminopyridine (0.2 mmol, 24.4 mg) were added to a mixture of 4-hydroxystyrene (in 10% butanediol solution, 1 mmol) in 20 ml dichloromethane (DCM). Then, the mixture was stirred for 1 h at room temperature. The mixture was extracted by DCM, washed with saturated sodium chloride aqueous solution, and dried with anhydrous sodium sulfate. The organic layer was removed in vacuo. The residue was purified by silica gel column chromatography (petroleum ether: ethyl acetate =10:1) to afford the compound: 4-acetoxy-styrene. Then, the epoxidation of 4-acetoxy-styrene was performed via the general procedure to obtain the corresponding epoxide. Finally, the epoxide (1 mmol) was dissolved in 10 ml methylamine (40% in water), and refluxed for 2 h. The solvent was removed in vacuo, and the remaining product was purified by silica gel column chromatography (dichloromethane: methanol =10:1) to afford synephrine (yield: Mo-1, 91.2%; Mo-2, 80.2%), the spectra of the synephrine are given in the supporting information.

3. Results and discussion

3.1. Preparation and characterization of catalysts

GO was prepared by following Hummers' method [28]. Dendrimerfunctionalized GO was obtained following the procedure described by Tarahomi et al. [27], whereby HPMo was immobilized as a molybdenum complex to obtain Mo-1 (Fig. 1, and Scheme S1a, see Supporting Information). Analogously, Mo-2 was prepared via condensation with dendrimer-functionalized GO and salicylaldehyde to obtain a salen ligand, followed by covalent bonding with MoO₂(acac)₂ (Fig. 1, and Scheme S1b).

The characteristics of the catalysts were identified and characterized by morphological and spectroscopic analysis.

The morphologies of the catalysts are shown in Fig. S1. Fig. S1a-S1b displays the SEM images of the catalysts, which indicated that there





Fig. 3. XRD patterns of the catalysts.

were slight differences in particle size between the two kinds of catalysts, but both of them were granular and the sheet structure of GO was not destroyed through the modification. TEM and element mapping characterization are shown in Fig. S1c-S1d. There were marked differences between them. Mo was uniformly distributed in both of the catalysts but with a difference in quantity. The catalysts were also evaluated by ICP-OES to accurately measure the content of Mo, which was calculated by mass ratio (Mo-1: 23.88%, Mo-2: 7.12%).

The optical properties were analysed by FTIR spectroscopy, as shown in Fig. 2. In GO-PAMAMA-G1, the peaks at 3053 cm⁻¹ could be ascribed to bending vibrations of nitrogen hydrogen bond($-NH_2$); the peaks at 3448 cm⁻¹ could be ascribed to bending vibrations of the amido bonds, the corresponding signals appeared at 3405 cm⁻¹ in GO [19] and 3279 cm⁻¹ in PAMAM-G1 [29], which indicated that GO was functionalized by dendrimers. But the peaks at 3053 cm⁻¹ was disappeared in the other solids, which meaned amino interacted with salicylaldehyde or Mocomplexes. The peaks at 948 cm⁻¹ and 793 cm⁻¹ in catalyst Mo-1 could be assigned to the interaction of Mo with the supports compared with 1064 cm⁻¹(P–O) and 964 cm⁻¹(Mo=O) in HPMo. 900 cm⁻¹ and 762 cm⁻¹ in catalyst Mo-2 is characteristic of the presence of MoO₂ group [22].

Fig. 3 shows the XRD patterns of the catalysts. As we know, the XRD pattern of GO shows the characteristic diffraction peak at $2\theta \approx 10^{\circ}$, as well as the HPMo at $2\theta \approx 26^{\circ}$ [22].The samples show a distinct broad



Fig. 4. XPS spectra (a) and N 1 s peak in the XPS spectra (b) of the catalysts.

diffraction peak between 20° and 30°, which indicates that the GO was complexed with Mo after functionalization by PAMAM-G1. And the diffraction peak at $2\theta \approx 10^{\circ}$ does not disappear, suggesting that the structure of graphene oxide is not destroyed during sample preparation.

XPS analysis was conducted to further verify the formation of the catalysts, and the elemental composition and valences of the various elements, as shown in Fig. 4a. Fig. 4b shows the high-resolution XPS

spectrum of N 1 s. The bands at approximately 398, 400, and 401 eV can be assigned to the bonds of CH_2-N , -CH=N, and MO, and -C-NH. The above results show that the type of interaction of the catalysts are different(compared with the GO-PAMAM-G1 and GO-

Table 1					
The epoxidation for alkene under optimun	n condition with	1 catalysts	of Mo-1	and I	Mo-2 ^a .

Entry	Substrate	Product	Catalyst	Conversion ^b (%)	Selectivity ^b (%)
1		⊂ ∼ ⁰	Mo-1	43.8	55.6
2			Mo-2	21.8	73.4
3	\sim	ò	Mo-1	60.1	72.3
4			Mo-2	30.4	78.6
5	\sim	<u>_</u> 9	Mo-1	99.7	93.7
6	\bigvee		Mo-2	99.5	76.3
7	A A 4	\sim	Mo-1	89.0	12.2
8		$\sim \sim <$	Mo-2	90.1	13.5
9		-0	Mo-1	87.5	89.2
10			Mo-2	94.6	66.1
11		\sim	Mo-1	50.6	34.1
12	(/3	(/3)	Mo-2	45.3	28.4
13	\sim	_ Q	Mo-1	99.9	50.5
14			Mo-2	99.9	66.4
15	I		Mo-1	97.2	76.4
16			Mo-2	92.1	54.6
17	\sim	Q	Mo-1	81.1	71.2
18			Mo-2	79.9	56.1
	UI UI	ci			
19	Ph	Ph	Mo-1	99.4	98.8
20		FII	Mo-2	99.0	86.1
	~	Ľ			

^a Reaction conditions: alkene (1 mmol), toluene (20 ml), TBHP (6 mmol), catalyst (Mo-1, 50 mg, Mo-2, 50 mg), 24 h.

^b Determined by GC–MS.



Fig. 5. Study of the catalysts' recyclability for the epoxidation of cyclohexene.

PAMAM-G1-salen, as shown in Fig. S2).

3.2. Evaluation of catalytic performance

We chose cyclohexene as a model compound and TBHP as an oxidant to investigate the performance of the catalysts in toluene at 80 °C, and the results are shown in Table S1. Under the same conditions, Mo-1 and Mo-2 exhibited better catalytic activity in the order of Mo-1 > Mo-2 in comparison to the intermediates and a previously reported catalyst, which named PAMAMA-G1-Mo, a dendritic phosphomolybdate hybrid by composite based on PAMAM-G1 and HPMo.

Subsequently, we chose Mo-1 as the catalyst to optimize the conditions for the epoxidation of cyclohexene as compiled in Table S2. First, the effects of the oxidant in the catalyzed reaction system were investigated. The conversions were very low, less than 5%, as was the selectivity, when we chose different oxidants, such as air, 30% H₂O₂, NaClO or PhIO; all the reactions were performed under the same conditions except that of TBHP (Table S2, entries 1-5). After that, we screened several solvents, viz., DCM, EtOH, 95% EtOH, THF, and acetonitrile (Table S2, entries 6-10), as reaction media, but all the above solvents showed poor results both in conversion and selectivity, except for acetonitrile, which showed a conversion of 55.4%. Homogeneously, catalyzing the epoxidation of cyclohexene in different solvents with 30% H₂O₂ and NaClO was also investigated (Table S2, entries 11-20), but we observed that all the results were unsatisfactory. Ultimately, the epoxidation of alkenes was carried out in 20 ml toluene at 110 °C using 6 eq. TBHP as the oxidant and 50 mg catalyst.

By keeping these facts in mind and based on our past knowledge and experience, a diverse range of alkenes was chosen to confirm the application scope of this methodology, as shown in Table 1. All of the alkenes were converted to the corresponding epoxide both in better conversion and selectivity under the optimum conditions; likewise, the order of active activity was Mo-1 > Mo-2. The alkene structure played an important role in the catalytic activity. The cyclic olefins were more reactive than the linear olefins (Table 1, entries 1–12), the aromatic alkene showed the best activity, and the substituted groups and steric hindrance had little effect on the results (Table 1, entries 13–20). The types of byproducts mainly include aldehyde or ketone compound, alcohol compound and diol compounds.

Encouraged by the overall results of the epoxidation of alkenes in terms of conversion and selectivity, for the first time, we evaluated the synthetic potential of this protocol for the preparation of synephrine, an α 1-receptor agonist, that can be synthesized via an epoxidation intermediate (Scheme S2). Synephrine was obtained in high yields, all greater than 80%, under mild reaction conditions and with convenient post-processing. Mo-1 had a higher yield at 91.2%. The results provide a new method for the synthesis of amino alcohol compounds.

To study the recyclability of the catalysts, we chose cyclohexene as a

model substrate, TBHP as oxidant and reaction 24 h similarly. The catalysts were easily recovered by filtration and vacuum drying at 60 °C. After recycling for 5 runs, the catalytic activity (conversion) and selectivity of the catalysts were maintained with minor loss, as shown in Fig. 5. In addition, there were no obvious differences between the fresh and reused catalysts (named R-Mo-1 and R-Mo-2) both in morphology and spectroscopy (Fig. S3-S5).

3.3. DFT calculations

All the morphologic and spectroscopic analysis revealed that the new catalysts had tiny differences in morphology, molybdenum content and distribution, but there were some differences between them in catalytic activity. To further study the cause of the different catalytic properties, a DFT study was conducted. In the reaction, the molybdenum complex first reacts with the oxidant to form the peroxymolybdenum complex, and then the alkene interacts with the oxygen atom of the peroxygen complex by nucleophilic attack to obtain the epoxidized products, as shown in Fig. S6 [30]. Therefore, the natural population analysis (NPA) charge of each of the optimized structures was calculated using the same basis set to illustrate the charge value, explain the activity of the Mo-1 and Mo-2 by comparing the NPA charge of oxygen atoms.

To simplify the calculation, representative key structural fragments of the two peroxygen complexes were selected because of the relatively complex structures of the two catalysts. Due to the steric hindrance of the surrounding atoms, the O2 atoms of the catalysts do not easily combine with alkenes. Therefore, the charge of the O1 atom was used for comparison, as shown in Fig. S7. In a comparison of the charges of the oxygen atoms in the two catalyst peroxygen complexes, the values in decreasing order was Mo-1 (-0.290e) < Mo-2 (-0.301e). Because this reaction is a nucleophilic reaction, the order of catalyst activity was Mo-1 > Mo-2, which was consistent with the experimental results (Mo-1 > Mo-2). In conclusion, the reaction activity of the catalysts may be related to the charge of the peroxygen atom of the catalystic peroxygen complex, which increased with the decrease in the charge of the oxygen atom.

4. Conclusion

In summary, we synthesized two new catalysts by immobilizing Mobased complex onto dendrimer-functionalized graphene oxide, and the structures were confirmed and characterized by SEM, TEM(ESDmapping), FT-IR, XRD and XPS. The catalysts can be applied to the epoxidation of alkenes under mild conditions using TBHP as an oxidant with favourable conversion and selectivity, and the catalysts can be easily reused at least five runs with no obvious loss in catalytic activity. The activity differences of the catalysts were calculated via DFT, which indicated that the decrease in the charge of the peroxygen atom of the catalystic peroxygen complex was beneficial for improving the reaction activity of the catalysts. The catalysts could also be employed to synthetize medicines containing epoxide intermediates (such as synephrine, which had yields of up to 91.2%). These catalysts will have broad prospects in the field of catalytic oxidation.

Credit author statement

Dr. Maosheng Cheng and Dr. Yang Liu supervised the whole experiment and provided technical guidance. Zhanfang Fan designed and synthesized all of novel catalysts and evaluated their catalytic activity. Dr. Bin Lin supervised and carried out calculation via DFT. Yongqing Liu assisted in the synthetic research.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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