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Dioxomolybdenum(VI) complex covalently attached to amino-modified graphene oxide: heterogeneous catalyst for the epoxidation of alkenes

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Transition metal salen complex MoO_2 -salen was successfully tethered onto amino-functionalized graphene oxide (designated as MoO_2 -salen-GO), which was tested in the epoxidation of various alkenes using *tert*-butylhydroperoxide or H_2O_2 as oxidant. Characterization results showed that dioxomolybdenum(VI) complex was successfully grafted onto the amino-functionalized graphene oxide and the structure of the graphene oxide was well preserved after several stepwise synthesis procedures. Catalytic tests showed that heterogeneous catalyst MoO_2 -salen-GO was more active than its homogeneous analogue MoO_2 -salen in the epoxidation of cyclooctene due to site isolation. In addition, the MoO_2 -salen-GO catalyst could be reused three times without significant loss of activity. Copyright © 2014 John Wiley & Sons, Ltd.

Keywords: epoxidation; dioxomolybdenum complex; alkene; graphene oxide

Introduction

The epoxidation of alkenes has attained much attention recently because the corresponding epoxides are significant raw materials in the production of many fine chemicals and pharmaceuticals.^[1,2] Various transition metal compounds (Fe, V, Mn, Mo, Co, etc.) were used in a variety of catalytic reactions and showed excellent catalytic activity and selectivity for the homogeneous oxidation of alkenes.^[3] Many countermeasures have been taken to heterogenize these homogeneous catalysts onto insoluble supports such as SBA-15,^[4] montmorillonite,^[5] ZSM-5,^[6] polymer,^[7] zeolite-X^[8] and zeolite-Y^[9] because heterogeneous catalysis provides easy recovery of the catalyst and reaction products, which is preferred in most industrial applications.^[3] Therefore, covalent attachment transition metal Schiff complexes onto insoluble supports received much attention in the past decade. For example, Masteri-Farahani et al.^[10] reported that MCM-41 containing molybdenum catalyst (MoO₂(salpr)/Si-MCM-41) showed high selectivity, high turnover frequencies and good stability for the oxidation of 1-hexene, 1-octene, cyclohexene and cyclooctene using tert-butylhydroperoxide (TBHP) to produce the corresponding epoxides.

Compared with conventional mesoporous silicates such as MCM-41 and SBA-15, graphene is a fascinating two dimensional carbon-based material with interesting physical properties such as excellent thermal and mechanical stability.^[11] As is well known, the graphene can be prepared from natural graphite, a low-cost material. Therefore, graphene and its derivatives have aroused general attention. As a member of graphene derivatives, graphene oxide (GO) possesses a unique nanostructure (a monolayer or just a few stacked layers), ample oxygen-carrying functionalities and excellent mechanical strength.^[12,13] In the

meantime, graphene oxide has been extensively applied to such fields as composite materials, catalysis, optoelectronics, supercapacitors, memory devices and drug delivery.^[13–18] It has been reported that GO can be prepared by the oxidation of graphite into graphite oxide, followed by the exfoliation of this graphitic oxide into GO.^[12,19] Mungse *et al.*^[13] reported that grafting of oxo-vanadium Schiff base onto graphene nanosheets exhibited high catalytic activity for the oxidation of various alcohols, diols and α -hydroxyketones to carbonyl compounds using TBHP as an oxidant. Meanwhile, the immobilized catalyst could be reused for several runs without significant loss in its catalytic activity. Our group found that the tethered dioxomolybdenum (VI) catalyst shows higher catalytic activity in the epoxidation of styrene with TBHP as the oxidant and CHCl₃ as the solvent than its homogeneous analogue.^[20]

Herein, we report the design and characterization of dioxomolybdenum(VI) salen complex grafted onto the amino-

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modified graphene oxide (NH₂–GO) via a stepwise procedure. The catalytic properties in the epoxidation of various alkenes using TBHP or H_2O_2 as oxidant and CH₃CN or CHCl₃ as solvent were also investigated.

Experimental

Materials

Graphite powder, H₂SO₄, KMnO₄, 30% H₂O₂, hydrochloric acid, salicylaldehyde (99%), ZnCl₂, diethyl ether, petroleum ether, MgSO₄, NaHCO₃, 3-aminopropyltriethoxysilane (3-APTES), MoO₃, DMF and all organic solvents were AR grade. Na/diphenylketone ketyl was used to dry toluene, and toluene was distilled under N₂ atmosphere and stored over 4Å molecular sieves.

Synthetic Procedures (Scheme 1)

The procedure for the covalent attachment of salen complex of molybdenum dioxide (VI) onto GO via a stepwise procedure is depicted in Scheme 1 and is described as follows.

Synthesis of graphene oxide

GO was synthesized as follows. Graphite powder and concentrated H_2SO_4 were added to a 250 ml three-necked flask and the mixture was stirred in an ice bath for 120 min. Then, 6.0 g KMnO₄



Scheme 1. Schematic outlines of syntheses of (a) GO, (b) CM–salen and (c) dioxomolybdenum(VI) complex covalently attached on amino-modified GO.

was added to the mixture gradually under vigorous stirring and the reaction mixture was stirred at room temperature for 30 min. Afterwards, the mixture was stirred at 35°C for 120 min and 92 ml deionized water was added under vigorous stirring. The resulting mixture was heated to 95°C, stirred for 15 min and transferred to a 1000 ml beaker; this was followed by addition of 30% H_2O_2 solution and distilled water to the mixture. Finally, the resulting oxidized product was collected by filtering, washing abundantly with 5% HCl solution and deionized water and drying. The sample obtained was denoted as GO.

Synthesis of amino-functionalized graphene oxide (NH_2 -GO)

 $\rm NH_2-GO$ was synthesized according to our earlier work, with slight modification. $^{[21]}$ Typically, 10 ml dry THF and 20 ml dry toluene were added to a 50 ml two-necked flask and then 1.0 g GO was dispersed by ultrasound. Then, 2.3 mmol 3-APTES was added to the stirred solution and the mixture was allowed to reflux at 110°C under N₂ atmosphere for 24 h. Finally, the resulting sample was filtered, washed with absolute toluene, extracted with CH₂Cl₂ and then dried. The obtained sample was denoted as NH₂–GO.

Synthesis of MoO₂Cl₂(dmf)₂

 $MoO_2CI_2(dmf)_2$ was synthesized and characterized as described in our earlier work.^[22] A mixture of 1.0 g MoO_3 and 10 ml (6 M) HCl was heated to boiling until most of the MoO_3 dissolved, and then cooled immediately to room temperature. Finally, the clear solution was collected by filtration. 2.5 ml DMF was added to the clear solution and the mixture was stirred for 2 h. The white solid was collected by filtration, washed and dried.

Synthesis of GO-tethered N,N'-bis(5-chloromethyl-salicylidene) ethylenediamine (CM–salenH₂) metal complexes

5-Chloromethyl-2-hydroxybenzaldehyde was synthesized and characterized as described in our earlier work.^[21] Typically, a mixture of 80 mmol salicylaldehyde, 12 ml 38% aqueous formal-dehyde and 0.6 g ZnCl₂ was introduced into a three-necked flask. Then, 50 ml concentrated HCl was slowly added under N₂ atmosphere. Finally, the mixture was stirred moderately at room temperature under N₂ atmosphere for 24 h. The solution was filtered and 5-chloromethyl-2-hydroxybenzaldehyde was recovered by crystallization.

N,*N*'-Bis(5-chloromethyl-salicylidene)ethylenediamine was also synthesized and characterized as described in our earlier work.^[21] In brief, a solution of 5-chloromethyl-2-hydroxybenzaldehyde (10 mmol, 10 ml) was added to a solution of ethylenediamine (5 mmol, 10 ml) in CH₂Cl₂. Afterwards, the resulting mixture was stirred at room temperature under N₂ atmosphere for 24 h. The solvent was removed under vacuum. The sample was designated as CM–salenH₂.

GO-tethered CM-salenH₂ was synthesized by nucleophilic reaction between the chloromethyl modified salen and the aminopropyl-functionalized GO. The general procedure was as follows. 1.15 mmol CM-salenH₂ was added to the above prepared NH₂-GO in 20 ml toluene and then the mixture was refluxed under N₂ atmosphere for 24 h. The solution was filtered and the resultant solid was washed with toluene and dried. Uncomplexed ligands were removed by full Soxhlet extraction with CH₂Cl₂. The solid material was denoted as salenH₂-GO.

Mo-salen complexes M-salen-GO (M = Mo) were prepared by adding a certain amount of $MoO_2CI_2(dmf)_2$ to a CHCI₃ solution containing SalenH₂-GO, which was stirred at room temperature

for 24 h. The resulting material was filtered, washed with large quantities of $CHCl_3$, Soxhlet-extracted with CH_2Cl_2 for 24 h and then dried.

Synthesis of pure dioxomolybdenum(VI) salen complex

Dioxomolybdenum(VI) salen complex was synthesized and characterized as described in our earlier work.^[20] In brief, 2.0 mmol salen ligand and 2.0 mmol $MoO_2Cl_2(dmf)_2$ were added to a round-bottomed flask containing 20 ml CH_2Cl_2 and the mixture was stirred at room temperature for 24 h. The mixture was then filtered and the obtained sample was denoted as MoO_2 -salen.

Characterization

Powder X-ray diffraction (XRD) patterns of the samples were recorded with a Shimadzu XRD-6000 diffractometer using Nifiltered Cu- K_{α} radiation scanning from 5 to 40° (2 θ). FT-IR spectra were recorded as KBr pellets in the range $400-4000 \text{ cm}^{-1}$ using the NICOLET impact 410 spectrometer. Diffuse reflectance UV-visible spectra of the solid samples were performed from 200 to 800 nm on a Shimadzu UV-3600 spectrophotometer with an integrating sphere using $BaSO_4$ as standard. N₂ adsorption-desorption isotherms were measured with a Micromeritics ASAP 2020 system at liquid N₂ temperature. Before measurements, the sample was outgassed at 130°C for 6 h. The surface area was calculated using the Barrett-Emmett-Teller (BET) method. The metal contents of the catalysts were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis conducted on a PerkinElmer emission spectrometer. TGA was carried out on a Shimadzu DTA-60 instrument working in an N₂ stream with a heating rate of 10°C min⁻¹. Transmission electron microscopy (TEM) was performed using a TECNAI F20 transmission electron microscope with an acceleration voltage of 200 kV. Raman spectra were recorded on a Renishaw Raman system model 1000 spectrometer with an excitation wavelength of 514 nm. X-ray photoelectron spectra were obtained on an ESCALAB 250 X-ray electron spectrometer using Al- K_{α} radiation.

Catalytic Tests

The epoxidation of various alkenes (cyclooctene, styrene, geraniol or 1-octene), with TBHP or H_2O_2 as the oxidant plus CH_3CN or $CHCl_3$ as the solvent, was carried out in a round-bottomed flask at 70°C under magnetic stirring, using substrate (5 mmol), solvent (5 ml), dodecane (2.5 mmol, internal standard), catalyst (50 mg) and oxidant (5 mmol). The filter liquor was analyzed by GC with a Shimadzu GC-8A (Japan) instrument equipped using an HJ-5 capillary column and flame ionization detector. At the end of the reaction the catalyst was filtered off, washed with copious solvent and dried. The catalyst was then reused in the next reaction without further purification.

Results and Discussion

Structural Integrity Studies

Figure 1 exhibits the wide-angle X-ray diffraction patterns of GO, salen–GO and MoO₂–salen–GO. GO shows an obvious peak at $2\theta = 10.9^{\circ}$ (Fig. 1a), which can be ascribed to the (001) reflection of graphite oxide, suggesting that graphite powder was oxidized to graphite oxide.^[13] Nevertheless, the diffraction peak becomes



Figure 1. XRD patterns of (a) GO, (b) salen–GO and (c) MoO₂–salen–GO.

very weak and broad after the introduction of the organometallic group (Fig. 1b), indicating that the salen complex was successfully tethered onto the GO. Meanwhile, a very weak and broad diffraction peak centered at around 25.0° emerged for salen–GO, indicating that a part of the graphite oxide was changed into graphene^[23] (Fig. 1b). A similar pattern was found for MoO₂– salen–GO (Fig. 1c).

TEM and high-resolution (HR)-TEM images of MoO₂-salen-GO are shown in Fig. 2. It is evident from Fig. 2(a) that the immobilized catalyst has a layer structure (monolayers or just a few layers). Additionally, the crumpled nanosheets can also be seen due to an agglomerated phase (Fig. 2a). As is shown in Fig. 2 (b), the d-spacing value of 0.485 nm is calculated according to the spacing of the (002) plane, which is larger than that of graphite $(d_{002} = 0.34 \text{ nm}).^{[24]}$

The N₂ adsorption–desorption isotherm of MoO₂–salen–GO is shown in Fig. 3. It exhibits typical type IV sorption isotherms with a hysteresis loop at a relative pressure of $0.4 < p/p_0 < 1.0$, suggesting that MoO₂–salen–GO is a kind of mesoporous material.^[25] In addition, the BET specific surface area is $18.0 \text{ m}^2 \text{ g}^{-1}$ for MoO₂–salen–GO.

Spectroscopic Characterization

GO and MoO₂-salen–GO were characterized by FT-IR. As shown in Fig. 4(a), the FT-IR spectrum of GO exhibited characteristic IR bands at ~3400, 1729, 1621, 1376, 1220, and 1048 cm⁻¹, which are associated with the stretching mode of O—H, CO, C—C, C—OH, C—O—C and C—O, respectively.^[12] Comparing the FT-IR spectrum of MoO₂-salen–GO with that of GO, some new weak peaks in the range 1600–1200 cm⁻¹ were observed, which can be ascribed to C—O, C—N and aromatic ring vibrations.^[20] In addition, there were new bands at ~942 and 906 cm⁻¹, which could be due to the characteristic bands of Mo O. The FT-IR results suggest that dioxomolybdenum(VI) salen has been successfully immobilized onto the GO. Moreover, ICP-AES analysis of MoO₂salen–GO also suggests the successful introduction of metal ion.

Raman spectroscopy is a non-destructive way to characterize graphitic materials (e.g. graphite, graphene and GO), in particular to decide ordered and disordered crystal structures of these





Figure 2. TEM and HR-TEM images of MoO₂-salen-GO.



Figure 3. N₂ adsorption–desorption isotherms profile of MoO₂–salen–GO.



Figure 4. FT-IR spectra of (a) GO and (b) MoO₂-salen-GO.

carbon materials.^[24] The Raman spectra of GO and MoO₂–salen–GO are shown in Fig. 5. Both of the catalysts exhibit peaks at ~1581 and 1331 cm⁻¹, which are generally attributed to the G band (the graphitic lattice) and D band (defects in the graphitic domain), respectively.^[26] However, I_D/I_G (the Raman intensity ratio of D and G bands) is a little different. Compared with GO (1.10), MoO₂–salen–GO gives a slightly high ratio of I_D/I_G (1.13), indicating that the size of the in-plane sp² domains decreases and the covalent attachment of dioxomolybdenum(VI) salen to GO by a stepwise procedure causes some defects or deoxygenation.^[27,28]

TG Studies

The TG curves of GO and MoO₂-salen-GO are shown in Fig. 6. The TG curve of GO shows two obvious weight losses in the temperature range 25-700°C (Fig. 6a), which are assigned to the loss of the physically adsorbed water and the decomposition of oxygen-carrying functionalities.^[13] In contrast, the TG curve of MoO₂-salen-GO shows three-step weight loss in the range 25-700°C. The first loss below 250°C was attributed to the physically adsorbed water and the decomposition of undigested oxygen-carrying functionalities, which do not interact with 3-aminopropyl-trimethoxysilane.^[13] The second loss at temperatures between 250 and 450°C corresponds to the combustion of amine. The third loss of ~9.0% in the range 450-700°C is probably attributed to the decomposition of salen ligand. Therefore, the loading of salen ligand is ~ 0.33 mmol g⁻¹ based on the weight loss for the MoO₂-salen-GO catalyst. In the meantime, the content of molybdenum is 0.16 mmol g^{-1} , as estimated by ICP-AES. Therefore, the molar ratio of ligand/metal is close to 2/1, which indicates that all metal ions have coordinated to ligand.

X-ray Photoelectron Spectroscopy (XPS) Studies

Figure 7 shows the X-ray photoelectron spectra of GO and MoO_2 -salen–GO. Compared with GO, XPS of MoO_2 -salen–GO gives signals mainly associated with N 1s, Cl 2p, Si 2p and Mo 3d, confirming the presence of dioxomolybdenum(VI) salen complex in MoO_2 -salen–GO, in good agreement with the above characterization results. The high-resolution C 1s X-ray photoelectron



Figure 5. Raman spectra of (a) GO and (b) MoO₂-salen-GO.



Figure 6. TG curves of (a) GO and (b) MoO₂-salen-GO.





Figure 7. X-ray photoelectron spectra of (a) GO and (b) MoO₂-salen-GO.

spectrum (Fig. 8a,b) shows peaks at ~284.2, 285.3, 287.4 and 289.3 eV, which are attributed to C C, C—OH, C—O—C and O—C O groups, respectively, indicating that GO has been successfully synthesized.^[29] Obviously, the relative intensity of C—OH signal for MoO₂—salen—GO decreases compared with the pure support GO, suggesting that dioxomolybdenum(VI) salen complex has been successfully introduced onto GO. The Mo 3d spectrum of the MoO₂–salen–GO catalyst (Fig. 8) shows two peaks centered at ~232.9 eV and 236.1 eV in the 3d orbits, which could be due to Mo 3d_{5/2} and Mo 3d_{3/2}, respectively, suggesting that the molybdenum species with such a binding energy could be assigned to Mo(VI).^[30]

Catalytic Tests

The catalytic activity and epoxide yield over the catalysts were explored for the epoxidation of various substrates (cyclooctene, geraniol, styrene and 1-octene) using TBHP or H₂O₂ as oxidant plus (CHCl₃ or CH₃CN) as the solvent system. The results are summarized in Table 1. Notably, the listed catalysts are active and remarkably selective for the epoxidation of the vast majority of substrates. When CHCl₃ was used as solvent and TBHP as oxidant, the freshly prepared MoO₂-salen-GO catalyst shows 91.7% conversion of cyclooctene, with a turnover frequency (TOF) of $69.5 h^{-1}$ and 91.7% yield of the cyclooctene epoxide after 8 h. However, it only exhibits 12.5% conversion of cyclooctene with a TOF of 9.5 h^{-1} and 12.5% yield of the corresponding epoxide after 8 h when TBHP was used as the oxidant plus CH₃CN as the solvent. Furthermore, it shows 44.3% conversion of cyclooctene with a TOF of $33.6 \, h^{-1}$ and 44.3% yield of the corresponding epoxide after 8 h when H_2O_2 was used as the oxidant plus CH_3CN as the solvent. In addition, it only shows 5.6% conversion of cyclooctene with a TOF of 4.2 h⁻¹ and 5.6% yield of the corresponding epoxide after 8 h when H₂O₂ was used as the oxidant plus CHCl₃ as the solvent. It seems obvious that the MoO₂salen-GO catalyst performs well with TBHP as the oxidant in CHCl₃, which is in accordance with the findings reported in the literature and our earlier work.^[20,31]





Figure 8. High-resolution C1s spectrum of (a) GO and (b) MoO₂-salen-GO, and Mo3d spectrum of MoO₂-salen-GO.

57.3	57.4	1.6	58.6		>99	>99	
90.6	58.8	6.6	58.6	I	54.3	18.2	ire 70°C.
0.165	0.165	0.165	0.165	0.165	2.538	2.538	mol, duration 8 h, temperatu
Geraniol	Styrene	Styrene	1-Octene	1-Octene	Cyclooctene	Cyclooctene	ıl, solvent 5 ml, oxidant 5 m on per hour.
-	-	-	-	-	-	-	trate 5 mmc 10le metal i
CH ₃ CN	CHCI ₃	CH ₃ CN	CHCI ₃	CH ₃ CN	CHCI ₃	CH₃CN	at catalyst), subs converted per n
H_2O_2	TBHP	H_2O_2	TBHP	H_2O_2	TBHP	H_2O_2	g (5.0 mg for ne. oles of substrate
MoO ₂ –salen–GO	MoO ₂ -salen-GO	MoO ₂ –salen–GO	MoO ₂ –salen–GO	MoO ₂ -salen-GO	MoO ₂ salen	MoO ₂ salen	1 conditions: catalyst 50 m (turnover frequency), mo
6	10	11	12	13	14	15	^a Reaction ^b TOF, h ⁻¹

26.7 9.0

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Entry

8 7 6 5 4 3 2 1

For comparison, the catalytic properties of neat complex were also investigated and the results are listed in Table 1. The MOO_2 -salen catalyst shows 54.3% conversion of cyclooctene with a TOF of 26.7 h⁻¹ after 8 h when using TBHP as the solvent in CHCl₃, which is much lower than the corresponding heterogeneous catalyst MoO_2 -salen-GO. A similar result is observed when using H₂O₂ as the solvent in CH₃CN. A blank experiment performed over SalenH₂-GO showed only 2.8% conversion of cyclooctene. These results suggest that the active sites are the transition metal ions and the supported catalyst could effectively isolate the active species and prevent formation of μ -oxo and μ -peroxo dimeric or other polymeric species.

Furthermore, the results of the epoxidation of various substrates (cyclooctene, geraniol, styrene and 1-octene) using different oxidants over the MoO₂-salen-GO catalyst were also investigated (Table 1). It is obvious that the heterogeneous catalyst showed comparable or even higher conversions in oxidation of cyclooctene, geraniol, styrene and 1-octene using TBHP as oxidant in CHCl₃ than those achieved using H₂O₂ as oxidant in CH₃CN, which might be attributed to the decomposition of H₂O₂ into molecular oxygen and water.^[32] Moreover, the conversion of cyclooctene is highest, followed by geraniol and then 1octene using TBHP as oxidant in CHCl₃ (Table 1), which may be due to electron density.^[31]

To assess the long-term stability and reusability of the supported dioxomolybdenum(VI) salen complex catalyst, cyclooctene was used as substrate, and the recycling experiments were carried out with 0.05 g MoO₂-salen-GO. The results of the recovered catalyst after three recycling experiments are listed in Table 1. It is clear that the MoO₂-salen-GO catalyst could be successfully recycled three times without significant loss of activity and selectivity in the same manner as that of the fresh catalyst.

Conclusions

The covalent attachment of dioxomolybdenum(VI) salen complex onto monolayer GO was prepared via a stepwise procedure and screened as heterogeneous catalyst for the epoxidation of alkenes. The structures of the support GO and the tethered catalyst, successful immobilization of the organometallic complex, and loading of metal ion and organic ligand were characterized by various techniques such as XRD, N₂ adsorption–desorption, TEM, HR-TEM, FT-IR, Raman, ICP-AES, XPS and TG. It was found that heterogeneous catalyst was active and selective for the epoxidation of various alkenes. In addition, the catalyst showed good recoverability without significant loss in activity and selectivity within successive runs.

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