Manganese Schiff Base Immobilized on Graphene Oxide Complex and Its Catalysis for Epoxidation of Styrene

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Summary: Immobilization of metal complexes on solid supports is an efficient approach to circumvent the drawbacks of homogeneous catalysis. In this paper, using graphene oxide as carrier, manganese Schiff base supported on graphene oxide (Salen Mn-GO) was prepared through aminosilane covalent modification as well as salicylaldehyde condensation and coordination reaction. The structures and properties of the composite were examined by FT-IR, XRD, XPS, TEM, TG techniques, and the catalytic performance of Salen Mn-GO in styrene epoxidation was explored. The effects of catalyst and styrene amount as well as that of reaction time on the performance of the catalyst were investigated. The results showed that Salen Mn-GO has excellent catalytic activity and reusability for epoxidation of styrene in the presence of hydrogen peroxide. Finally, the mechanism of styrene epoxidation catalyzed by Salen Mn-GO has been preliminarily discussed.

Keywords: Graphene oxide; Schiff base; Manganese; Styrene; Epoxidation; Heterogeneous catalyst.

Introduction

Epoxides are widely used as intermediates for the production of fine chemicals, pharmaceuticals and perfumes, and much attention has been given to their generation [1-3]. The oxidizing agents commonly used in the preparation of epoxides are peracetic acid, t-butyl hydroperoxide (TBHP), sodium hypochlorite, high concentration hydrogen peroxide, etc. [4]. They are highly explosive and are applied in high concentration, leading to high safety requirements, product complication and poor selectivity to target product. These shortcomings restrict their industrial production, which is also a reason for the high prices of related pharmaceuticals and spices. In recent years, the use of hydrogen peroxide for olefin epoxidation has become a hot spot. With high effective oxygen content, it can be applied in concentration lower than that of strong oxidants such as oxyacetic acid and TBHP. It is ideal for epoxide synthesis because the requirements for equipment safety are not high. Furthermore, it is a green oxidant, and water is the only by-product [5-7]. To make the process economical and environmentally benign, it is necessary to design catalysts that can facilitate high selectivity to target product under green and safe conditions. It is a global desire to obtain stable catalysts of efficacy that can be facilely generated to catalyze the epoxidation of olefins using hydrogen peroxide as green oxidant.

In the search of oxidation processes that have application prospect, the use M-Salen complexes (M=Ti, Zr, Fe, Mn, Ni, Cu, Co, Zn, Al, etc) has come to the attention of researchers [8, 9]. Salen is a chelate Schiff base which can be used as ligand for the formation of metal complexes. It was reported that M-Salen exhibits good catalytic activity in photochemical synthesis [10], stereoselective epoxidation [11], cyclopropanation reaction [12], Diels-Alder addition [13], and polymerization [14]. As for the epoxidation of olefins, M-Salen complexes with simple structures were reported in recent years to show good catalytic activity, especially in catalytic asymmetric epoxidation. However, the M-Salen complexes were mainly applied in homogeneous reactions, and their application is somehow limited. Recently, the immobilization of Mn (III) salen complexes on insoluble solid carriers such as mesoporous materials, polymers, zeolites, clays, organic polymer inorganic hybrid materials has been extensively investigated [15-19]. As a new type of carbon material, graphene has received much attention in catalysis due to its good dispersibility, high specific surface area and stability in chemical environments. Moreover, it can be easily functionalized, and the surface of graphene oxide (GO) is usually rich with oxygen-containing groups (such as carboxyl, hydroxyl, and epoxy groups). With such functionalities, GO can be modified to a variety of composite materials. By anchoring organic or inorganic molecules onto its surface, GO properties can be diversified. The consequence is enlargement of application prospect of graphene-based materials in catalysis [20-25]. Su et al. reported transition metal Schiff base complexes immobilized on graphene as efficient and recyclable catalysts for epoxidation of styrene [26]. Zarnegaryan et al. prepared GO-supported copper(salen) complex for epoxidation of alkenes [27].

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Allahresani et al. reported the covalent bonding of Ni (II) Schiff base complex onto GO sheets for the oxidation of alcohols [28].

In this paper, a functionalized graphene composite catalyst was prepared by using GO as support for the immobilization of Salen Mn catalyst by means of covalent bonding. The catalytic activity of the anchored catalyst was investigated in the epoxidation of olefins using a low concentration of hydrogen peroxide. The structure of the composite was analyzed by FT-IR, XRD, XPS, Raman and TG techniques. The reaction mechanism of the related reaction was discussed.

**Experimental**

**Experimental reagents**

Graphite, sulfuric acid, potassium permanganate, acetonitrile, 3-aminopropyltrimethoxysiloxane (APTMS), ethanol, salicylaldehyde, styrene, chlorobenzene, H2O2, and NaHCO3 of analytical grade were purchased from Shanghai Aladdin Chemical Reagent Co., Ltd., and were used without purification. Distilled water prepared in our laboratory was used in all the experiments.

**Catalyst preparation**

Synthesis of amino-functionalized graphene oxide (NH2-GO): Graphene oxide was prepared by a modified Hummers process [29]. The graphene oxide was ultrasonically dispersed in an ethanol solution to obtain a 0.5 mg mL−1 brownish yellow graphene oxide ethanol solution. Then 360 mL of the graphene oxide ethanol dispersion was placed in a three-necked flask. After the mixture was subject to 30 min of ultrasonication, an excess amount of 6.0 mmol APTMS in ethanol was added, and the reaction solution was refluxed for 6 h with stirring. After the reaction, the solid substance was filtered out and washed with a large amount of ethanol, and then dried under vacuum at 60 °C for 3 h to obtain amino-functionalized graphene oxide (NH2-GO) which was brown in color.

Preparation of M-salen Complex anchored on GO: First 0.5 g of the prepared NH2-GO was dispersed in 30 mL of methanol, and excess salicylaldehyde (1.22 g, 10.0 mmol) was added to the suspension, and the resulted mixture was subject to reflux for 3 h. Afterward, the solid product was filtered out and washed with methanol three times to remove unreacted salicylaldehyde. After vacuum drying, the obtained powder was separately added with a certain amount of Mn(CH3COO)2·4H2O and an appropriate amount of methanol, and the mixture was stirred at room temperature for 12 h. The resulting solid substance was filtered out and washed with methanol several times to remove excess uncoordinated metal manganese ions, followed by vacuum drying at 60 °C for 2 h to obtain a graphene complex of “graphene oxide-loaded central metal Mn”, which is herein named as Salen Mn-GO.

Characterization. Powder X-ray diffraction (XRD) analysis was performed on a Bruker D8 A25 diffractometer with a Cu Kα source (λ = 0.154 184 nm) at voltage of 40 kV and current of 40 mA. Infrared spectra were recorded on a Shimadzu IR Prestige-21 type Fourier transform infrared spectrophotometer with a wavenumber range of 400–4000 cm−1, adopting the KBr pellet approach. TEM images were obtained from a Tecnai G20 transmission electron microscope with a CCD imaging system at an acceleration voltage of 200 kV. Raman spectra were recorded by using excitation from the 514.5 nm line of an Ar-ion laser (Renishaw, RM 1000). XPS analysis was conducted on a PHI Quantera SXM with Al Kα = 1486.6 eV excitation source. Thermogravimetric analysis (TGA) was performed using a thermogravimetric analyzer (TG 209 F3, Netzsch, Germany) under a flow of nitrogen.

Catalytic performance. Styrene epoxidation using CH3CN as solvent and H2O2 as oxidizing agent was carried out in a round bottom flask at 50 °C. First 100 mg of catalyst, 10 mmol of styrene, and 4 mL of CH3CN were added to a 25 mL single-neck round bottom glass vial. Then, a mixture of 1.36 g (12 mmol) of 30% H2O2 and NaHCO3 (0.2 mol/L, 4 mL) was added dropwise to the above solution under continuous stirring in a period of 0.5 h. After reacting at 50°C for 2 h, the reaction was terminated. The reaction solution after filtering off the catalyst through a membrane was analyzed by an Agilent 6890 N chromatograph equipped with Agilent DB-1 (30 m *0.25 mm* 0.25 μm) column and a flame ionization detector (FID). The chromatographic conditions were as follows: heating program 80°C for 2 min, 10°C /min to reach 200°C and then maintained for 5 min. As for injector and detector temperatures, they were 220°C. The solid catalyst was filtered off, washed thoroughly with acetone and dried at 60°C for 3 h for recycling without purification. Chlorobenzene was used as an internal standard to quantify components. Styrene conversion and styrene oxide selectivity are calculated according to the following formula:

\[
\text{Styrene conversion} = \frac{\text{Amount of styrene before reaction} - \text{Amount of residual styrene}}{\text{Amount of styrene before reaction}} \times 100\%
\]

\[
\text{Styrene oxide selectivity} = \frac{\text{Amount of styrene oxide produced}}{\text{Amount of styrene before reaction}} \times 100\%
\]
Results and Discussion

Material characterization

Fig 1 shows the X-ray diffraction patterns of graphite, GO, NH2-GO, and Salen Mn-GO. As shown in Fig 1, graphite has a sharp diffraction peak at 26.5° (layer spacing \(d=0.335\) nm) according to the Bragg equation \(2\sin(\theta)=\lambda\). Upon oxidation of graphite, the diffraction peak of GO at 10.8° (layer spacing \(d=0.79\) nm) can be ascribed to the reflection of GO (001) plane, indicating that a large number of oxygen-containing groups have been introduced between the graphite layers, and the outcome is enlargement of interlayer spacing. After the loading of Salen complex, the characteristic peak of GO at 10.8° weakens but still exists, indicating that the modification does not destroy the sheet structure of graphene oxide. In the meantime, NH2-GO and Salen Mn-GO show a wide and weak peak at 20°=20–25°, which is the diffraction peak of amorphous silicon derived from 3-aminopropyltrimethoxysiloxane.

![Graphite, GO, NH2-GO, and Salen Mn-GO XRD](image)

Fig. 1: XRD of graphite, GO, NH2-GO and Salen Mn-GO.

Fig 2 shows the FT-IR spectra of GO, NH2-GO and Salen Mn-GO. The broad band of GO spectrum at 3400 cm\(^{-1}\) is ascribable to hydroxyl groups. The absorption at 1724 cm\(^{-1}\) and 1626 cm\(^{-1}\) is correspond to the stretching vibration of C=O and C=C double bond, while that at 1050 cm\(^{-1}\) and 1217 cm\(^{-1}\) to C-O and C-OH single bond, respectively, which are consistent with the characteristic peaks of GO [30]. Compared to the FT-IR spectrum of GO, there are changes upon modification with silane coupling agent and salicylaldehyde. The NH2-GO sample obtained after GO silanization exhibits significant signal enhancement at 1105 cm\(^{-1}\) and 1045 cm\(^{-1}\), which is attributed to the absorption of Si-O-Si and Si-O-C

![FTIR spectra of GO, NH2-GO and Salen Mn-GO](image)

Fig. 2: FTIR spectra of GO, NH2-GO and Salen Mn-GO.

Raman spectroscopy is often used to characterize the ordered and disordered structure of carbon materials (e.g., graphite, graphene, GO, etc.). Shown in Fig 3 are the Raman spectra of GO, NH2-GO, and Mn-Salen-GO. The Raman plots of GO, NH2-GO, and Mn-Salen-GO show two distinct bands at about 1334 cm\(^{-1}\) and 1596 cm\(^{-1}\), commonly referred to as D and G bands, respectively. The G band is characteristic of carbon with \(sp^2\) hybrid structure, which reflects the symmetry and crystallinity of graphene materials. As for the D band, it signifies the existence of defects in graphite [31]. The intensity ratio of D and G band, viz. ID/IG, is a unique parameter to indicate the graphitization level of graphite materials [31]. The ID/IG value of GO is ca. 1.1, while that of NH2-GO and Mn-Salen-GO is ca. 1.19 and 1.21, respectively. The results indicate that the grafting of silane coupling agent and salicylaldehyde onto GO causes defects and/or deoxygenation [32]. It is observed that compared to the G band of GO at 1587 cm\(^{-1}\), that of NH2-GO and Mn-Salen-GO blue shifts to 1593 cm\(^{-1}\) and 1596 cm\(^{-1}\), respectively, plausibly due to local stress caused by the increase of covalent bond chains.
Fig. 3: Raman spectra of GO, NH$_2$-GO and Salen Mn-GO.

Fig. 4 shows the results of XPS analysis performed over GO, NH$_2$-GO and Salen Mn-GO. After silanization of GO, characteristic Si and N peaks can be observed in the NH$_2$-GO spectrum. Upon coordination with manganese acetate, Mn2p signals can be observed over the Salen Mn-GO sample. The results indicate successful immobilization of Salen Mn on GO. Fig 5(a) shows the deconvolution results of the C1s spectrum of GO, and the signals at ca. 284.8, 286.5, and 288.5 eV can be attributed to C-C, C=C, and C=O species, respectively. Fig 5(b) shows the C1s spectrum of NH$_2$-GO, and one can see decrease of C1s intensity at 286.5 eV, reflecting the involvement of hydroxyl groups during silylation of GO. Fig. 5(c) and Fig. 5(d) show the N1s spectra of NH$_2$-GO and Salen Mn-GO. After the condensation reaction of NH$_2$-GO with salicylaldehyde, most of the N-H bonds are converted to C-N bonds (399 eV). Furthermore, the binding energy of the C-N peak shifts from 399.6 to 399.9 eV, and that of NH$^+$ from 401.4 to 401.7 eV, which should be due to interaction between nitrogen atoms and Mn ions. In Fig. 6(a), the deconvolution of the Si 2p profile of NH$_2$-GO suggests two valence states corresponding to Si-O-Si and Si-O-C. The presence of Si-O-Si is due to self-polymerization of certain amount of silane coupling agent, and its presence cannot be eliminated by subsequent washing. The large presence of Si-O-C indicates the involvement of hydroxyl groups on GO is substantial during silylation. The Mn2p spectrum of Salen Mn-GO (Fig. 6(b)) shows Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$ peaks at 641.8 eV and 653.5 eV, respectively, which are characteristic of divalent Mn [33]. Considering that the XPS technique is surface sensitive, the total manganese content was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES), and was found to be 0.96 wt% (i.e., 0.17 mmol·g$^{-1}$).
Fig. 6: (a) Si 2p spectrum of NH$_2$-GO and (b) Mn 2p spectrum of Salen Mn-GO.

Fig. 7 shows the thermogravimetric (TG) curves of GO and Salen Mn-GO. The TG curve of GO shows two significant weight losses in the range of 25–700 °C which belongs to the loss of physisorbed water and/or the decomposition of oxygen-containing functional groups [34]. Compared with GO, Salen Mn-GO shows a thermogravimetric curve that is relatively flat, and the mass loss in the interval of 100 to 150 °C is mainly caused by water loss; as for the mass loss at 150–300 °C, it is caused by the loss of undecomposed oxygen-containing groups. The mass loss above 300 °C is caused by the decomposition of metal Schiff base. According to the calculation based on Salen Mn-GO weight loss, the loading of Schiff base ligand Salen was about 0.35 mmol/g. As mentioned above, the Mn content based on ICP-AES analysis was 0.17 mmol/g. Hence, the ligand-to-metal molar ratio of Salen Mn-GO is close to 2:1. The above results indicate that the organometallic group has been successfully loaded onto GO.

Transmission electron microscopy (TEM) images reveal the microstructure and morphology of the GO, NH$_2$-GO and Salen Mn-GO samples (Fig. 8a-c). Compared to the two-dimensional plane of GO, despite NH$_2$-GO and Salen Mn-GO still maintain a sheet-like structure, and they have more folds due to chemical modification. Without the destruction of the two-dimensional GO structure, the reaction sites of the supported catalyst are highly exposed to the reaction medium, and the GO surface serves as a platform for the entry of reactants and departure of products.

**Catalytic epoxidation of styrene**

For comparison, we have also studied the catalytic performance of homogeneous complex catalysts. When acetonitrile was used as solvent and H$_2$O$_2$ as oxidant for styrene oxidation, the conversion of cyclooctene was 74.3% after 2 h of homogeneous reaction over the Mn-Salen catalyst, which is significantly lower than that of Mn-Salen-GO (99.5%). The results indicate that the catalytic active sites are Mn ions, and the Mn sites of the supported catalyst are isolated from one another.
Fig. 8: TEM images of (a) GO; (b) NH$_2$-GO and (c) Salen Mn-GO.

Fig. 9: Effect of (a) catalyst amount, (b) styrene amount, and (c) reaction time on styrene epoxidation over Salen Mn-GO, and (d) effect of H$_2$O$_2$-to-styrene molar ratio on the performance of Salen Mn-GO catalyst.

Fig 9 (a) shows the effect of the amount of Salen Mn-GO catalyst on styrene conversion and epoxy product selectivity. The amount of catalyst has a great influence on the conversion of styrene but has little effect on epoxide selectivity. With the other reaction parameters kept unchanged and the amount of catalyst increased from 20 to 120 mg, the conversion of styrene increased drastically from 44.5% to 99.5%, while epoxide selectivity decreased slightly from 81.5% to 79.4%. At a catalyst amount of 100 mg, the
conversion of styrene is the highest. Fig 9 (b) shows the effect of styrene amount on the epoxidation reaction. It was observed that the selectivity to epoxide is insensitive to the change of styrene amount, which stayed at about 80% with a change of styrene amount from 3 to 20 mmol. As for styrene conversion, it was ca. 99.5% during the change of styrene amount from 3 to 10 mmol. However, when the amount of styrene was increased from 15 to 20 mmol, styrene conversion decreased from 79.3% to 64.7%. Fig 9(c) illustrates the effect of reaction time on the epoxidation of styrene. When the reaction time increased from 0.5 to 2 h, the conversion of styrene increased from 64.6% to 99.5%, and there was slight decrease of epoxide selectivity from 83.5% to 80.4%. Further prolong of reaction had little effect on styrene conversion but resulted in slight decrease of selectivity. At reaction time of 2.5 h, styrene conversion was 99.4% and styrene oxide selectivity was 78.2%. When H2O2 is used as oxygen source, the H2O2-to-styrene molar ratio has a great influence on reaction activity. It can be seen from Fig 9(d) that the amount of H2O2 affects styrene conversion but has little effect on styrene oxide selectivity. When H2O2-to-styrene molar ratio increased from 0.8 to 1.4, the conversion of styrene gradually increased from 72.6% to 99.3% and remained unchanged with further increase of hydrogen peroxide. Therefore, the optimum H2O2-to-styrene molar ratio is 1.4.

In practical applications, the lifetime and reusability of the supported catalyst are important factors. We investigated the lifetime of the catalyst under the adopted reaction conditions. The specific method comprises the following steps: An appropriate amount of n-hexane was added to the system at the end of the reaction to extract reaction product. The reaction solution is statically layered, and the catalyst is dispersed in the aqueous phase. The organic phase and the aqueous phase were separated using a separation funnel. The aqueous phase was subject to filtration, washed with n-hexane and methanol, and dried in vacuo for repeat use. The results of activity change are shown in Fig. 10(a). Across five runs, styrene conversion and styrene oxide selectivity remain at a superior level, and there is no significant decrease of catalyst activity. Meanwhile, from the XRD patterns of fresh and recycled samples in Fig. 10 (b), there is no distinct difference in terms of crystal phase structure.

The results show that the Salen Mn-GO catalyst has good stability in the epoxidation of styrene and could be reused for many times.

![Fig. 10](image-url)

**Fig. 10:** (a) The reusability test of Salen Mn-GO catalyst; (b) XRD patterns of Salen Mn-GO catalyst before and after use.

The heterogeneous properties of Salen Mn-GO catalyst were studied by hot filtration experiment. In the same reaction system, when the conversion of styrene was about 40%, the reaction solution was subject to filtration at 50 °C to remove the catalyst, and the filtrate allowed to react under the same reaction conditions. It was found that there was no further increase of styrene conversion in the filtrate after the thermal filtration. Also, no manganese was detected in the solution by ICP-AES, confirming no leaching of manganese into the solution. These results indicate that the Salen Mn-GO catalyst is stable during the reaction and the observed catalysis is heterogeneous in nature.

### Table-1: Comparison of the efficiency of Salen Mn-GO with different heterogeneous Schiff base catalyst.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Time (h)</th>
<th>Oxidant</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Salen Mn-GO</td>
<td>2</td>
<td>H2O2</td>
<td>99.5</td>
<td>80.2</td>
<td>This study</td>
</tr>
<tr>
<td>2</td>
<td>Salen-GO</td>
<td>8</td>
<td>O2</td>
<td>46.5</td>
<td>64.7</td>
<td>[38]</td>
</tr>
<tr>
<td>3</td>
<td>Cu(salen)-f-GO</td>
<td>12</td>
<td>TPHP</td>
<td>52.8</td>
<td>43.6</td>
<td>[39]</td>
</tr>
<tr>
<td>4</td>
<td>Salen Ni-GO</td>
<td>3</td>
<td>TPHP</td>
<td>91</td>
<td>99</td>
<td>[40]</td>
</tr>
<tr>
<td>5</td>
<td>PGO-salen-Co</td>
<td>6</td>
<td>H2O2</td>
<td>21</td>
<td>55.9</td>
<td>[41]</td>
</tr>
<tr>
<td>6</td>
<td>VO-salen-GO</td>
<td>8</td>
<td>O2</td>
<td>89</td>
<td>74.5</td>
<td>[37]</td>
</tr>
<tr>
<td>7</td>
<td>Fe-salen-GO</td>
<td>8</td>
<td>O2</td>
<td>77.5</td>
<td>90.2</td>
<td>[37]</td>
</tr>
</tbody>
</table>
Despite the mechanism of olefin epoxidation by Schiff base complex is still uncertain, we conduct discussion on the catalytic epoxidation of olefins according to related literature [35-36]. In the reaction system, two kinds of catalyst assistants, viz. hydrogen carbonate and acetonitrile, react with hydrogen peroxide to produce two active intermediates:

\[ \text{HCO}_3^- + \text{H}_2\text{O}_2 \rightleftharpoons \text{HCO}_4^- + \text{H}_2\text{O} \]

\[ \text{CH}_3\text{CN} + \text{H}_2\text{O}_2 \rightleftharpoons \text{NH}_3 \]

The two reactive intermediates are oxidizing agents which should interact with the olefinic substrate or first with the catalyst and then with the olefinic substrate. According to relevant literature [37] and referring to the reaction system, the following mechanism hypothesis is proposed as illustrated in Scheme-2: First, both bicarbonate and acetonitrile interact with \( \text{H}_2\text{O}_2 \) to form two oxidatively active intermediates. With themselves reduced, the two active intermediates oxidize Salen Mn-GO to form a reactive metal-oxide-containing peroxometal compound. Finally, the reactive oxygen-species-containing peroxometalate catalyst transfers the reactive oxygen atom to the alpha-pinene double bond. While the double bond is oxidized to an epoxy bond, the supported reactive intermediate is reduced and continues to react with the two reactive intermediates until the end of reaction. The specific mechanism is shown in Scheme-1. From the structure of Salen Mn, the benzene ring is conjugated with C=N to form an approximately planar bond. The raw material styrene is affected by the \( \pi \) bond and tends to approach Salen Mn in a planar manner, thus producing mainly the epoxidized products.

Also, the results obtained using Salen Mn-GO in the epoxidation reaction was compared with the results reported for some other heterogeneous Schiff base catalysts. As can be seen, our reported method is superior in terms of reaction times, oxidant, yields or selectivity (Table-1).

**Conclusion**

In this paper, we prepared the heterogeneous catalyst Salen Mn-GO by means of stepwise grafting. The results of XRD, TEM, HR-TEM, FT-IR, Raman, XPS and TG characterization directly or indirectly confirmed the successful preparation of the target catalyst as well as the maintenance of the support structure during the grafting processes. The Salen Mn-GO catalyst was used in the epoxidation of styrene. It was observed that the supported catalyst has higher catalytic activity than the unsupported one, probably
due to the separation of the active centers in the former. In addition, the effects of catalyst and styrene amount as well as that of reaction time on the performance of the catalyst were investigated. In the reusability test, Salen Mn-GO did not significantly reduce in catalytic performance after repeated runs of styrene oxidation, indicating that the catalyst is stable and there is almost no loss of active sites during the reaction.

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References


26 H. Su, Z. Li, Q. Huo, J. Guan and Q. Kan, Immobilization of Transition Metal (Fe$^{3+}$, Co$^{3+}$, V$^{5+}$ or Cu$^{2+}$) Schiff Base Complexes onto Graphene Oxide as Efficient and Recyclable Catalysts for Epoxidation of Styrene, *RSC Adv.*, **4**, 9990 (2014).


