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Short Communication

Graphite oxide-supported Karstedt catalyst for the hydrosilylation of olefins with triethoxysilane

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ABSTRACT

A graphite oxide-supported Karstedt heterogeneous catalyst was synthesized from vinyltriethoxysilane via immobilization on graphite oxide, followed by reacting with chloroplatinic acid. The samples were characterized by FT-IR, TGA, ICP-AES, XRD and TEM techniques. The catalyst was active for hydrosilylation of olefins with triethoxysilane and showed good recoverability without significant loss in activity and selectivity within successive runs.

1. Introduction

Hydrosilylation is an important organic transformation for the construction of Si–C bonds and plays a vital role in the synthesis of functional silanes and silicon polymers [1]. Generally, transition metal complexes are known to be efficient catalysts for the hydrosilylation reaction [2], in particular the Pt based catalysts; Karstedt's catalyst, characterized with C═C group coordination to Pt, is one of the most efficient homogeneous industrial catalysts [3]. However, the homogenous catalyst suffers from some drawbacks such as deactivation and difficult recovery and recycling of the catalyst. Consequently, development of efficient solid-based heterogeneous catalyst for hydrosilylation reaction is highly desirable due to its easy separation, reusability and environment-friendly. The solid immobile materials included silica [4–7], glass fiber [8], MCM-41 [9], and organic polymers [10–13]. Basically, the support has to be thermally and chemically stable during the reaction process and has to provide accessibility and a good dispersion of the active sites.

Graphite oxide (GO), one of the most important derivatives of graphene, is an inexpensive, stable and extraordinarily versatile carbon material [14]. Specifically, due to the various oxygen containing functional groups (hydroxyl, carboxyl, and epoxy groups) attached to carbons or at the edges of the layer [15], GO surface can be easily modified with compounds containing active groups [16–18]. Therefore, GO performs as an excellent supporting material for immobilizing homogenous catalysts. These suggest that immobilizing Karstedt's catalyst on GO might afford an efficient, reusable and environmentally benign catalyst for hydrosilylation.

Herein, we report the preparation and characterization of the intercalated GO composites modified with vinyltriethoxysilane (VTEO) to be used as host to further attach the catalytic Pt complex. The catalytic performance of the prepared hybrid catalysts was tested in the hydrosilylation of olefins with triethoxysilane.

2. Experiment

2.1. Preparation of the catalyst

2.1.1. Preparation of GO

GO was prepared by graphite powder based on a modified Hummers method [19]. Graphite powder (3 g, 8000 mesh) was added to an 80 °C solution containing concentrated H_2SO_4 (12 mL), $K_2S_2O_8$ (2.5 g), and P_2O_5 (2.5 g), stirred at 80 °C for 6 h, and then diluted with ultrapure water (500 mL). The mixture was filtered and washed with ultrapure water, and dried at 50 °C overnight. This pre-oxidized graphite was put into cold concentrated H_2SO_4 (120 mL), and then $KMnO_4$ (15 g) was added gradually under stirring, and kept to be below 20 °C by cooling. Successively, the mixture was stirred at 35 °C for 2 h, and then diluted with 250 mL of ultrapure water (below 50 °C). The mixture was stirred for another 2 h, and then additional ultrapure water (750 mL) was added. 30% H_2O_2 (20 mL) was added to the mixture, after which the color of mixture changed into brilliant yellow. The mixture was filtered and washed with 1:10 HCl aqueous solution (1 L) to remove metal ions followed by abundant water to remove the acid. The product was dried at 40 °C overnight under vacuum.

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2.1.2. Preparation of functionalized GO with VTEO (GO-VTEO)

GO (3 g) was dispersed in N-methylpyrrolidone (300 mL) under ultrasonication for 1 h. After further addition of VTEO (3 mL), the mixture was stirred at 110 °C for 24 h. The product was purified gradually by centrifugation in methanol, water, and acetone, and finally dried at 80 °C overnight under vacuum.

2.1.3. Preparation of GO-Karstedt catalyst

GO-VTEO (2 g) was added to a solution containing $NaHCO_3$ (0.032 g), $H_2PtCl_6 \cdot H_2O$ (0.05 g) and ethanol (120 mL), stirred at 40 °C for 24 h, filtered, washed with 6 × 40 mL of ethanol, and dried at 70 °C overnight under vacuum. The content of platinum in catalyst was 0.89% by ICP-AES detection. For comparison, the chloroplatinic acid was directly supported on the rGO which was prepared by directly reducing GO (Supplementary data), denoted as rGO-Pt catalyst.

2.2. Characterization techniques

FT-IR spectra were recorded on a Nicolet 5700 spectrometer, with samples being dispersed on KBr disks. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis was conducted on a PerkinElmer OPTIMA 5300DV emission spectrometer. Thermogravimetric analysis (TGA) was carried out on a SDT Q600 instrument with a heating rate of 10 $°C \cdot min^{-1}$ under nitrogen atmosphere. Powder X-ray diffraction (XRD) was conducted on a TD-3500 diffractometer with filtered Cu Kα radiation ($\lambda = 1.5406$ Å) at 40 kV and 30 mA. Transmission electron microscopic (TEM) studies were obtained on a JEOL JEM-2100 transmission electron microscope.

2.3. Catalytic tests

Typical hydrosilylation reaction procedures were as follows: GO-Karstedt catalyst (0.83×10^{-3} mmol Pt) was added to a 10 mL round bottomed flask equipped with a magnetic stirrer, and the olefin (5.0 mmol) and triethoxysilane (5.0 mmol) were then added. The reaction mixture was then stirred at 60 °C for 180 min. Hydrosilylation products were separated from the catalyst by decantation and the conversion of olefin and the selectivity were determined by GC–MS using a 25 m × 0.32 mm × 0.5 μm column.

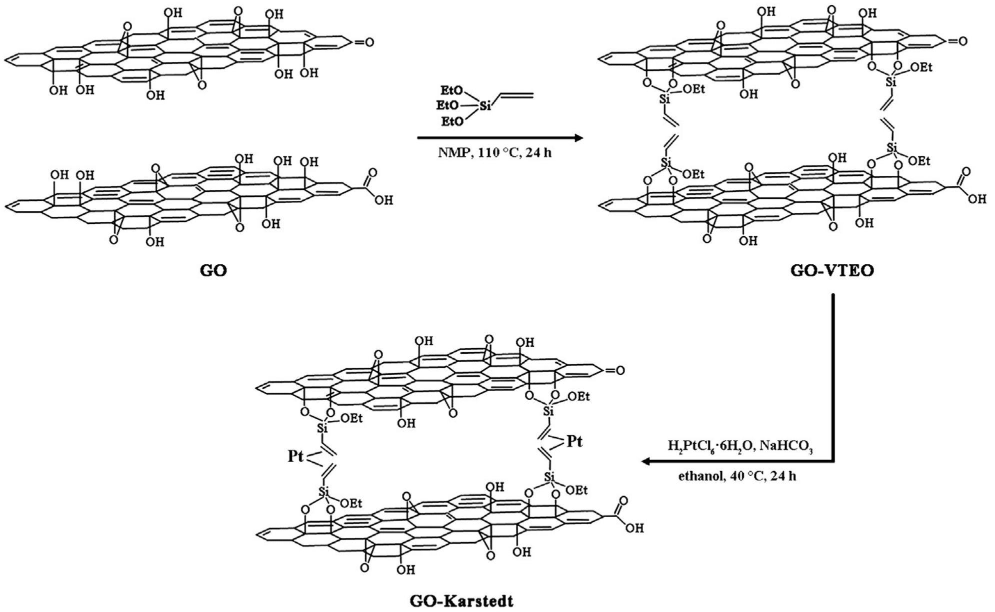
3. Result and discussion

3.1. Characterization

Scheme 1 displays the design and synthesis process of the GO-Karstedt catalyst. The reaction of GO with the organosilane is likely to take place through hydrolysis/condensation of the carboxyl and surface hydroxyl functional groups of GO and the hydrolyzed ethoxy groups of VTEO, and the vinyl groups of VTEO are the anchoring sites for Pt complexes.

First of all, the chemical changes occurring upon the treatment of VTEO can be observed by FT-IR spectra (Fig. 1A). The most characteristic features in the FT-IR spectra of GO are the O–H stretching at 3372 cm^{-1} and deformation vibration at 1404 cm^{-1}, the C═O carbonyl stretching at 1727 cm^{-1}, and the C–OH or the C–O stretching at 1221 and 1047 cm^{-1}. The resonance at 1615 cm^{-1} can be assigned to the vibrations of the adsorbed water molecules [20]. Upon treatment with VTEO, the condensation between the organosilane and the surface hydroxyl groups as seen by the changes in the 1250–1000 cm^{-1} region where contribution of both Si–O–C and Si–O from the silanol groups is observed. The new band at 1578 cm^{-1} can be assigned to stretching vibration of C═C bonds in VTEO moieties [21]. For GO-Karstedt, due to the complex interaction between Pt and vinyl group of VTEO, stretching vibration of C═C bonds causes a low-field shift (1560 cm^{-1}) [22]. Moreover, the content of platinum in catalyst was 0.89% by ICP-AES analysis. These results indicate the successful introduction of Pt.

Fig. 1B illustrates TGA curves for GO-Karstedt catalyst and intermediate products under nitrogen atmosphere. GO shows about 15% weight loss near 100 °C, evidently owing to evaporation of water molecules which are held in the material. Two other significant mass losses are observed in the range of 150–280 and 500–750 °C, corresponding to the removal of the labile oxygen-containing functional groups and pyrolysis of the carbon skeleton of GO, respectively [16,23]. Compared to the GO curve, the weight loss of GO-VTEO and GO-Karstedt catalysts around 100 °C is much lower, indicating that graphene oxide sheets exhibit high hydrophobicity upon silanization of VTEO [8]. Moreover, GO-VTEO and GO-Karstedt catalysts show another two obvious weight losses. The first loss is in the range of 150–220 °C attributed to the decomposition of undigested oxygen carrying functionalities which have not participated in interaction with VTEO. The other major mass loss



Scheme 1. Proposed view for the construction of GO-Karstedt.

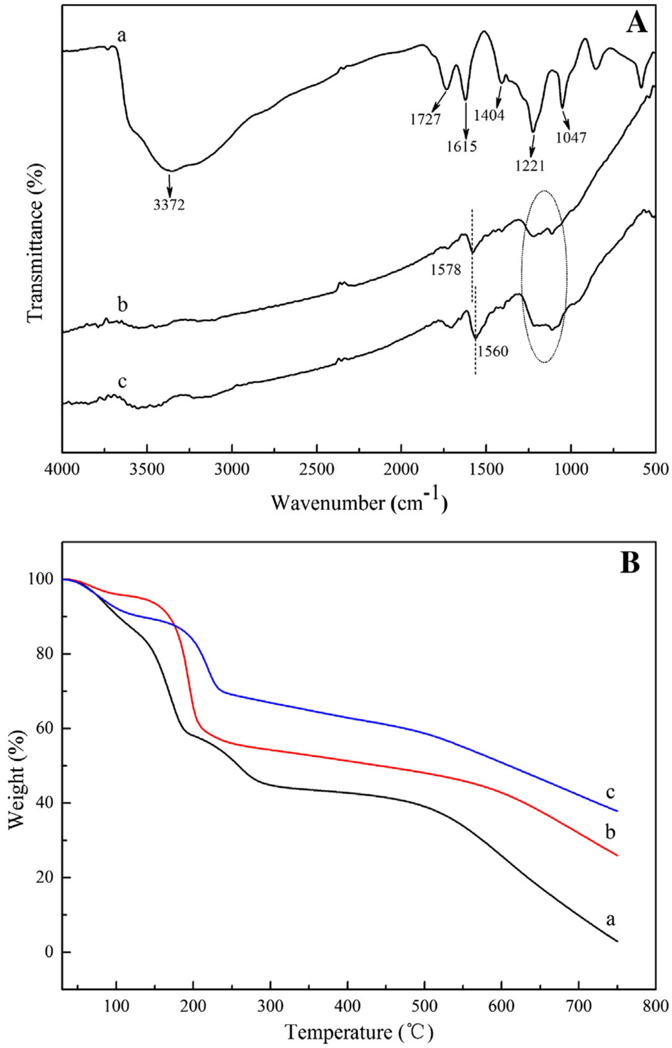


Fig. 1. (A) FT-IR spectra and (B) TGA curves for (a) GO, (b) GO-VTEO and (c) GO-Karstedt.

is in the range of 220–580 °C resulting from the pyrolysis of VTEO moieties [23].

The X-ray diffraction patterns of pristine graphite, GO, GO-VTEO and GO-Karstedt are shown in Fig. 2A. Pristine graphite exhibits a typical sharp (002) peak at $2\theta = 26.5°$ with a d spacing of 0.34 nm. The GO pattern shows a characteristic peak at $2\theta = 9.0°$, with a corresponding d spacing of 0.98 nm, attributed to the interlayer space between typical graphene oxide sheets needed to accommodate the water molecules trapped between oxygen-containing functional groups on graphene oxide sheets. Compared to the starting GO, the diffraction peak of GO-VTEO shifts to a higher angle ($2\theta = 10.0°$) corresponding to smaller interlayer distance (0.88 nm), which is due to the less hydrophilicity after functionalization [16]. The GO-Karstedt pattern exhibits a peak at $2\theta = 11.1°$, which asserts for a further decrease of the interlayer distance (0.80 nm). We suggest that the introduction of Pt into GO-VTEO narrowed the distance of graphene oxide sheets by the coordination between Pt and the C=C bonds of VTEO moieties.

Fig. 2B shows the TEM images of GO and GO-Karstedt. GO appears partially transparent with typical large crumpled thin flakes. GO-Karstedt shows that the immobilized complexes of Pt catalyst have a layered structure. It can be seen that the crumpled nanosheets are in an agglomerated phase [24].

3.2. Catalytic experiments

The prepared GO-Karstedt catalyst was tested in the hydrosilylation of olefins with triethoxysilane. Initially, we studied the catalytic activity at different temperatures using the hydrosilylation of 1-octene with triethoxysilane as the model reaction (Fig. 3). It was found that GO-Karstedt catalyst exhibited high catalytic activity; over 90% yield in favor of β-adduct could be obtained from 40 to 70 °C within 120 min, and the reaction rate raised with the increasing of temperature. Noticeably, when the reaction was carried out at 60 °C, octyltriethoxysilane was obtained in 90.4% yield after 60 min. Catalyst leaching experiments of GO-Karstedt have been performed by hot filtration of the reaction mixture and subsequent testing of the catalytic activity of the filtrate for hydrosilylation without addition of a catalyst, and no further reaction was observed for the solution following filtration. Also, a control experiment was conducted using a rGO-Pt catalyst, and only 74.9% yield of

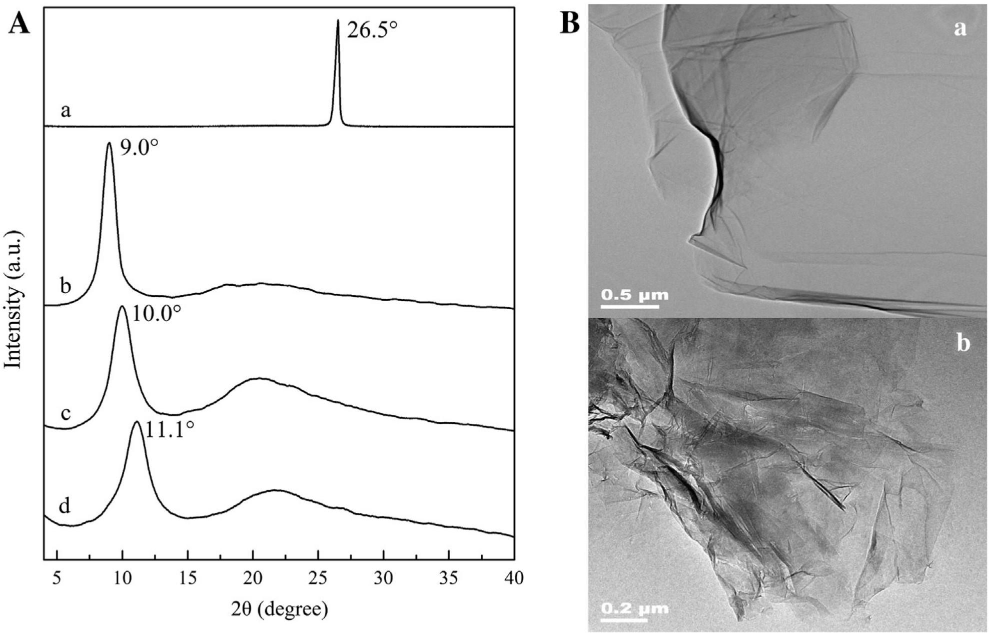


Fig. 2. (A) XRD patterns for (a) graphite, (b) GO, (c) GO-VTEO and (d) GO-Karstedt; (B) TEM images for (a) GO and (b) GO-Karstedt.

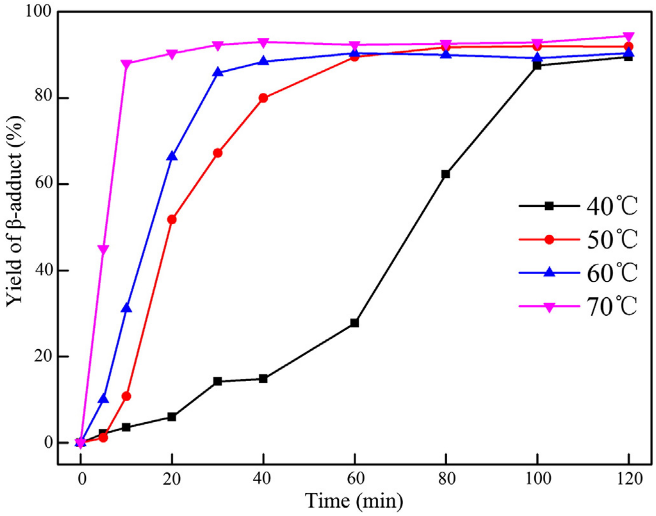


Fig. 3. Effect of reaction temperature on the yield of octyltriethoxysilane. Reaction conditions: 1-octene = 5.0 mmol, triethoxysilane = 5.0 mmol, catalyst = 0.83×10^{-3} mmol Pt.

octyltriethoxysilane was obtained after 180 min (Supplementary data), which shows that the rGO-Pt catalyst was not so effective for the hydrosilylation of olefins with triethoxysilane. The results indicate that vinyl groups of GO-Karstedt catalyst may play an important role to convert H_2PtCl_6 to Pt(0)-olefin complexes, which make GO-Karstedt catalyst more active [25].

To examine the substrate scope of GO-Karstedt catalyst, the hydrosilylation reaction was extended to several substituted olefins with triethoxysilane, and the catalytic results are listed in Table 1. In all cases, GO-Karstedt catalyst exhibits positive catalytic activity, and the substituted olefins were smoothly converted to their corresponding products. For the aliphatic olefins (entries 1–3), excellent conversion (over 97.8%) and selectivity (over 92.4%) were attained in all cases, indicating that the catalyst has a high activity for the hydrosilylation reaction. Unfortunately, when aromatic olefins were used as the substrates (entries 4–6), the β-adduct selectivity decreased significantly, although the catalyst exhibited high conversion of olefins, which results from the steric hindrance of substituted olefins [26].

The stability of the catalyst is an important aspect of any industrial application. Therefore we tested the reusability of GO-Karstedt catalyst in the hydrosilylation of 1-octene with triethoxysilane at 60 °C. For each cycle of the test, solution was decanted completely, leaving the catalyst powder on the bottom of the reaction vessel. The same amounts of the substrates were recharged, and the next cycle started. As shown in Fig. 4, GO-Karstedt catalyst exhibited a high operational stability with no dramatic loss of catalytic activity and selectivity even after seven successive times. When using rGO-Pt as catalyst, the catalytic activity decreased significantly, and almost no reaction for the hydrosilylation of 1-octene with triethoxysilane after four cycles (Fig. S1).

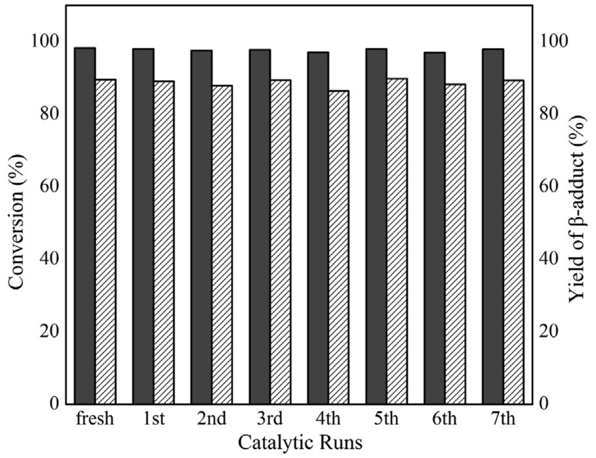


Fig. 4. Catalyst activity of reused GO-Karstedt catalyst for the hydrosilylation of 1-octene with triethoxysilane. ■: Conversion of 1-octene; ▨: Yield of octyltriethoxysilane.

4. Conclusion

Graphite oxide has been studied for the first time as a support of Karstedt catalyst and applied in hydrosilylation reaction. The results show that the catalyst was active for hydrosilylation of olefins with triethoxysilane, in particular for the aliphatic with triethoxysilane. Furthermore, the catalyst shows a good recoverability and can be recycled seven times without significant loss of catalytic activity and selectivity. These results imply that GO is a superior support for immobilizing complex catalysts.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2013.10.043.

Table 1
Catalytic activity of GO-Karstedt for the hydrosilylation reaction of olefins with triethoxysilane.[a]

Entry	Olefin	Time (min)	Conv.[b] (%)	Selectivity (%)			TOF (h^{-1})
				β	α	Alkane, etc.	
1	1-Hexene	90	100	92.5	Trace	7.5	10340
2	1-Octene	60	97.8	92.4	Trace	7.6	9875
3	1-Decene	60	98.0	92.4	Trace	7.6	9968
4	Styrene	100	94.9	67.2	28.9	3.9	8757
5	p-Methylstyrene	120	79.3	58.9	36.0	5.1	4098
6	p-Chlorostyrene	120	97.8	53.1	41.9	5.0	4844

[a] Reaction conditions: olefin = 5.0 mmol, triethoxysilane = 5.0 mmol, catalyst = 0.83×10^{-3} mmol Pt, and temperature = 60 °C.
[b] No increase in conversion with increasing reaction time.

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