Journal of Molecular Catalysis A: Chemical 420 (2016) 254–263

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Preparation of efficient and environment-friendly silica-supported EDTA platinum catalyst and its applications in hydrosilylation of olefins and methyldichlorosilane

Futing Li, Youxin Li*

Tianjin Key Laboratory for Modern Drug Delivery and High-Efficiency, Collaborative Innovation Center of Chemical Science and Engineering, School of Pharmaceutical Science and Technology, Tianjin University, Tianjin 300072, China

ARTICLE INFO

Article history:
Received 31 January 2016
Received in revised form 2 April 2016
Accepted 18 April 2016
Available online 23 April 2016

Keywords:
Environment-friendly immobilized platinum
Hydrosilylation
Heterogeneous catalyst
Ethylenediaminetetraacetic acid

ABSTRACT

A novel catalyst by preparing silica supported ethylenediaminetetraacetic acid (EDTA) platinum complex was developed. The preparation conditions, such as heating temperature and solvent types, were optimized. The catalyst was phosphine-free and sulfur-free which was characterized by infrared spectroscopy (IR), energy dispersive X-ray spectrometer (EDS), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), ultraviolet spectroscopy (UV) and atomic absorption spectroscopy (AAS). Its catalytic activity was evaluated by catalyzing solventless hydrosilylation reactions. In the hydrosilylation reaction between 1-hexene and methyldicholosilane, the new catalyst showed a higher catalytic activity than that provided by Spiere's catalyst. Moreover, the new catalyst could be reused for 12 times without obvious loss of catalytic activity. To confirm its practical feasibility, catalyzing the hydrosilylation reaction between 1-octene and methyldichlorosilane was performed. Our results indicated that the new catalyst can efficiently catalyze the hydrosilylation reaction.

1. Introduction

Hydrosilylation of olefins is the key catalytic reaction for the production of industrially important organosilicon compounds such as organofunctional silanes and silicones [1,2]. Homogenous platinum catalysts, such as Speier's catalyst [3], Karstedt's catalyst [4] and various modified Karstedt's catalysts [5,6], are usually used to catalyze those hydrosilylation reactions which are between olefins and alkoxysilanes, or between olefins and chlorosilanes. However, there are some drawbacks for these homogenous platinum catalysts, such as deactivation caused by formation of black platinum colloid, high cost, environmental pollution, difficult recycling, and risk of reacting violently [7].

Consequently, immobilized platinum catalysts were developed over the past few decades. Many substances have been used as supported materials, such as cross-linked polymers (e.g. polyamides [8], polystyrene [9,10]), silica [11,12], glass [13], aluminum oxide [14], and carbon [15,16]. The supported materials are usually able to be anchored with a variety of functional groups and thermally and chemically stable during the reaction process. Yves Fort et al. [14] prepared alumina-supported phosphinate platinum catalyst, which showed excellent catalytic performance in hydrosilylation of 1-octene and dimethylphenylsilane. Hu et al. [17] immobilized platinum on MCM-41-supported material by mercapto group and proved the catalyst was simply, convenient, highly efficient through catalyzing the hydrosilylation reaction of olefins and triethoxysilane. Ye et al. [18] immobilized platinum on MCM-41-supported material by the mercapto and vinyl bi-groups. Compared with single vinyl group (MCM-41-vinyl-Pt) or mercapto group (MCM-41-SH-Pt), the bi-groups immobilized platinum has superior activity in hydrosilylation reaction.

Abbreviations: MCM-41-vinyl-Pt, MCM-41 supported vinyl platinum; MCM-41-SH-Pt, MCM-41 supported mercapto platinum; IR, Infrared Spectroscopy; EDS, Energy Dispersive X-ray Spectrometer; TEM, Transmission Electron Microscopy; HRTEM, High Resolution Transmission Electron Microscopy; XPS, X-ray Photoelectron Spectroscopy; UV, Ultraviolet Spectroscopy; AAS, Atomic Absorption Spectroscopy; NMR, Nuclear Magnetic Resonance; GC, Gas Chromatography; EDTA, Ethylenediaminetetraacetic Acid; EDTAD, Ethylenediaminetetraacetic Dianhydride; APTES, γ-aminopropyltriethoxysilane; APSG, Aminopropyl Silica Gel; SiO_2-EDTA, Silica-supported EDTA; SiO_2-EDTA-Pt, Immobilized Platinum on SiO_2-EDTA; TMS, Tetramethylsilane; TOF, Turnover Frequency.

* Corresponding author at: Room A606, Building 24, School of Pharmaceutical Science and Technology, Tianjin University, 92 Weijin Road, Nankai District, Tianjin 300072, China.

E-mail addresses: lyx@tju.edu.cn, liyouxin2008@163.com (Y. Li).

http://dx.doi.org/10.1016/j.molcata.2016.04.019
1381-1169/

Compared with polymers, functionalized inorganic supports without swelling phenomenon have attracted widespread attention for their rigid structures which could effectively prevent being deformed during the reaction. Among these inorganic supports, functionalized silica is known as a good supported material because of its large surface area, high mechanical strength, thermal and chemical stability. Many silica supported catalysts, silica-supported sulfide platinum [19], Karstedt (Pt)-type catalyst [12], phosphinate platinum [20,21], polyamidoamine dendrimers platinum, and nitrogenous platinum complex [22] were developed to catalyze hydrosilylation reactions. But they are still far away from practical applications for large-scale manufacture of organosilicon compounds. The stability and cost of those immobilized catalysts are the main reasons hampering their practical applications. The catalysts anchored by phosphine ligands or sulfur ligands were unstable at high temperatures [23,24]. The deciduous ligands may not only contaminate the product leading to lower repeatability and reliability of reaction results, but also have a negative impact on the environment and catalyst activity resulting from catalyst poisoning [25]. Therefore, it is highly required to develop a recyclable phosphine-free and sulfur-free silica supported catalyst. Ethylenediaminetetraacetic acid (EDTA), a hexadentate ligand containing both carboxylate and amine groups, is becoming attractive reagent in organic synthesis for its non-volatile, cheap, and non-toxic nature. Moreover, its properties can be tuned by modifying with functional groups. The commercially available and powerful complexing agent [26] was proved to be efficient in the complexation of a verity of metals [27,28]. To the best of our knowledge, however, silica modified by EDTA never was used as metal immobilization support until now.

In this work, we reported a new catalyst immobilizing platinum on silica modified by EDTA. Ethylenediaminetetraacetic acid (EDTA) is a hexadentate ligand containing both carboxylate and amine groups and is easy to be modified by functional groups [26–28]. The conditions of immobilizing platinum on silica were systematically investigated. The complex was then characterized by infrared spectroscopy (IR), energy dispersive X-ray spectrometer (EDS), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), ultraviolet spectroscopy (UV) and atomic absorption spectroscopy (AAS). Its catalytic ability was evaluated by catalyzing hydrosilylation reaction of methyldichlorosilane and 1-hexene or 1-octene. Under the optimization hydrosilylation conditions, the reaction product was identified by nuclear magnetic resonance (NMR) and quantified by gas chromatography (GC).

2. Experimental

2.1. Reagents and chemicals

Unless otherwise stated, all reagents were analytical reagent grade or better. Silica was purchased from Yantai Xinnuo Chemical Industry Co., Ltd. (Shandong, China). Methyldichlorosilane was purchased from Zhejiang Kaihua Synthetic Co., Ltd. (Zhejiang, China). 1-Hexene was from Shanghai Aladdin Biological Technology Co., Ltd. (Shanghai, China). 1-Octene was from J & K Scientific Ltd. (Beijing, China). 1-Hexyl-methyldichlorosilane was from CNW Technologies Co., Ltd. (Nordrhein Westfalen, Germany). 1-Octyl-methyldichlorosilane was from Alfa Aesar Co., Ltd. (Massachusetts, USA). γ-Aminopropyltriethoxysilane was from Qufu Chenguang Chemical Co., Ltd. (Shandong, China). $H_2PtCl_6{\cdot}6H_2O$ was from Shanghai Jiuyue Chemcial Engineering Co., Ltd. (Shanghai, China). Ethylenediaminetetraacetic acid, anhydrous pyridine, acetic anhydride, diethyl ether, HCl, toluene, acetone, ethanol, *n*-decane, *i*-propanol, *n*-butanol and *n*-hexanol were from Tianjin Jiangtian Scientific Co., Ltd. (Tianjin, China). Nitric acid (HNO_3) and hydrofluoric acid (HF) were from Sigma Aldrich Co., LLC (Missouri, USA). Platinum standard liquid was from Beijing Gangyan Nano Detection and Technology Co., Ltd. (Beijing, China). Distilled water was from Yongyuan Distilled Water Manufacturing Centre (Tianjin, China). $CDCl_3$ and DMSO were purchased from Beijing Coupling Technology Co. Ltd. (Beijing, China).

2.2. Instruments

All separation experiments were performed in GC 2020 with a flame ionization detector (Wuhan Trust Century Technology Co., Ltd., Hubei, China) and a 30m × 0.25mm × 0.25 μm capillary column (Lanzhou ATEO Analytical Technology Co., Ltd., Gansu, China). Data were collected and analyzed using ZB2020 Data System from Surwit Technology (Hangzhou) Co., Ltd. (Zhejiang, China). Bruker Advance 600 MHz spectrometer (Bruker, Germany) was used for analyzing of products using tetramethylsilane (TMS) as an internal standard and $CDCl_3$ or DMSO as solvent. ^1H NMR spectra were recorded using an IconNMR Data System (Bruker, Germany). Fourier transform infrared spectra were recorded on a Bruker TENSOR 27 spectrophotometer (Bruker, Germany). Energy dispersive X-ray spectrum was recorded on an ISRF-550i spectrophotometer (IXRF, Texas, USA). Ultraviolet–visible (UV–vis) absorption spectra were recorded on a Cary-300 Ultraviolet–visible Spectrophotometer (Agilent Technology, California, USA). The immobilization amounts of Pt were determined by a Thermo SOLAAR M6 Atomic Absorption Spectrophotometer (Thermo Fisher Scientific Inc., USA). All deionized water for Pt determination in atomic absorption spectrophotometer was prepared by a Milli-Q Deionizer (Millipore, Massachusetts, USA). Microwave dissolver for digesting immobilized Pt catalysts was from Milestone S.r.L. (Sorisole, Italy). Transmission Electron Microscopy (TEM) and High Resolution Transmission Electron Microscopy (HRTEM) were recorded on JEM-2100F (JEOL Ltd., Tokyo, Japan). The X-ray photoelectron spectroscopy (XPS) experiments were carried out in a Kratos Analytical Axis Ultra DLD instrument (Shimadzu, Tokyo, Japan).

2.3. Preparation of the immobilized platinum catalyst

2.3.1. Preparation of ethylenediaminetetraacetic dianhydride (EDTAD)

EDTAD was synthesized according to the method described [29]. A 20 g EDTA was suspended in 34 ml anhydrous pyridine and followed by adding 26 ml acetic anhydride. The mixture solution was stirred at 65 °C of external heating temperature for 24 h. Collection of raw product (EDTAD) was performed by filtration, following a washing step with diethyl ether. To purify the raw EDTAD, the solid product was re-dispersed in 55 ml acetic anhydride and stirred intermittently for 30 min. After filtration, solid EDTAD was then washed by acetic anhydride and diethyl ether. The product was dried at 65 °C in vacuum. The synthetic route was shown in Fig. 1 Step 1 and the prepared EDTAD was characterized using ^1H NMR spectroscopy, ^{13}C NMR spectroscopy and IR spectroscopy.

2.3.2. Preparation of silica-supported EDTA (SiO_2-EDTA)

Silica gel was pretreated by 6 M HCl at 60 °C of external heating temperature for 6 h. And it was washed by distilled water until pH neutral, followed by drying at 60 °C for 12 h and further drying at 130 °C for 3 h to remove residual water. To modify the silica gel, 5 g silica gel, 50 ml toluene and 7 ml γ-aminopropyltriethoxysilane (APTES) were added into 100 ml 3-neck boiling flask. The suspended solution was mechanically stirred at 300 rpm and the reaction was performed at 80 °C of external heating temperature for 24 h. The modified silica gel, Aminopropyl silica gel (APSG), was filtered and washed by toluene and acetone. It was then dried at 70 °C

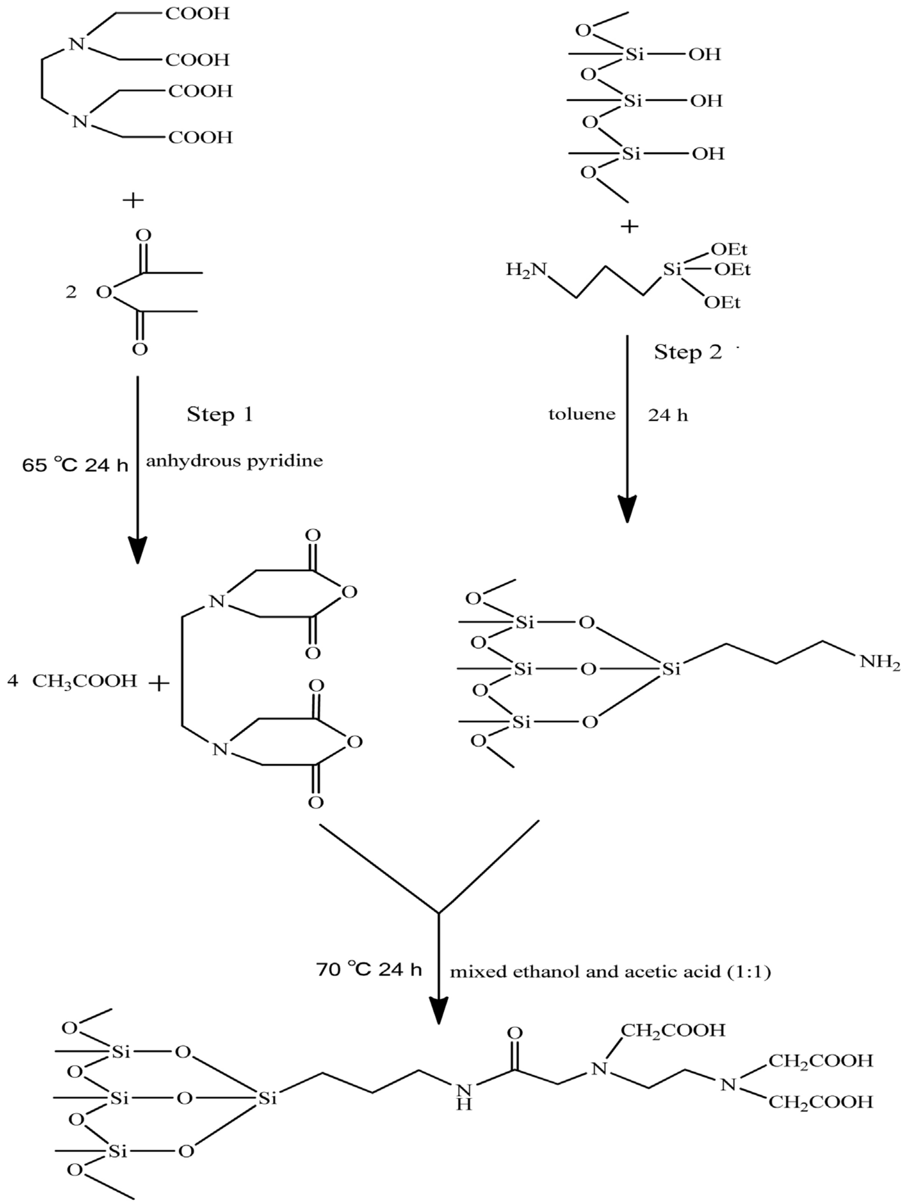


Fig. 1. The synthesis route of SiO_2-EDTA.

for 12 h. To prepare silica-supported EDTA, 2 g APSG, 4 g EDTAD and 50 ml mixture of ethanol and acetic acid (v/v, 1/1) were added into 100 ml 3-neck boiling flask and mechanically stirred at 300 rpm at 70 °C of external heating temperature for 24 h. After filtration, the product was washed by acetone and water respectively, and then dried at 70 °C [30]. The synthetic route was shown in Fig. 1 Steps 2 and 3.

2.3.3. Preparation of the immobilized platinum on SiO_2-EDTA (SiO_2-EDTA-Pt)

An i-propanl-H_2PtCl_6 solution (0.0386 mol/L) was prepared by dissolving 1.0 g $H_2PtCl_6 \cdot 6H_2O$ in 50 *i*-propanol. The reactants, 1.01 g SiO_2-EDTA, 80 ml ethanol and 10 ml *i*-propanl-H_2PtCl_6 solution, were added in a 250 ml 3-neck boiling flask. Under nitrogen protection, the suspended solution was mechanically stirred at 300 rpm and the reaction was carried out at 100 °C of external heating temperature for 9 h. After filtration, the solid product was washed by ethanol and acetone successively and dried in an oven at 70 °C for 12 h to obtain SiO_2-EDTA-Pt power.

2.4. Hydrosilylation reactions

The catalytic activity of SiO_2-EDTA-Pt was evaluated by catalyzing a model hydrosilylation reaction of 1-hexene and methyldichlorosilane. The reaction was carried out in a 50 ml flat-bottomed centrifuge tube with a magnetic stirrer and a homemade reflux condenser. A 10 mmol 1-hexene and SiO_2-EDTA-Pt containing 10.0×10^{-4} mmol Pt were added into the centrifuge tube and stirred at 60 °C of external heating temperature for 0.5 h before adding 18 mmol methyldichlorosilane. The mixture was magnetically stirred at 60 °C of external heating temperature for 3 h and then cooled to room temperature. The product was characterized by GC and ^1H NMR.

In order to evaluate the recyclable character of SiO_2-EDTA-Pt, the immobilized catalyst was repeatedly used 12 times. After each hydrosilylation reaction, the immobilized Pt was kept in the centrifuge tube by centrifuging the mixture and pouring out all of liquid. Fresh 1-hexene and methyldichlorosilane were added to perform the new reaction under the same conditions.

The feasibility of SiO_2-EDTA-Pt to catalyze hydrosilylation reactions was further confirmed in the reaction between 1-octene and methyldichlorosilane. The reaction was also carried out in a 50 ml flat-bottomed centrifuge tube with a magnetic stirrer and a home-made reflux condenser. A 10 mmol 1-octene and SiO_2-EDTA-Pt containing 10.0×10^{-4} mmol Pt were added into the centrifuge tube and stirred at 60 °C of external heating temperature for 0.5 h before adding 18 mmol methyldichlorosilane. The mixture was magnetically stirred at 60 °C of external heating temperature for 4 h and then cooled to room temperature. The product was characterized by GC and ^{1}H NMR.

2.5. Charactering methods

All middle products and products, EDTAD, SiO_2, SiO_2-EDTA, and SiO_2-EDTA-Pt were characterized by IR. The samples were dried in IR oven for 3 h and were then dispersed on KBr power at the ratio of 1:100 to prepare KBr tablets for IR measurement.

SiO_2-EDTA-Pt was characterized by EDS, SEM and XPS. The valance state of platinum in *i*-propanol-H_2PtCl_6 was characterized by scanning the sample by UV spectrometry from 200 nm to 400 nm. The different valance state of platinum causes the maximum wavelength change. The amount of immobilized platinum was determined by AAS with a working standard curve. A 0.1 g SiO_2-EDTA-Pt was added in 2 ml HF and 3 ml HNO_3 solution. The digestion was accelerated by a microwave dissolver. The microwave digestion procedures: 130 °C for 15 min, 160 °C for 5 min, 170 °C for 10 min, and then 180 °C for 20 min. After digestion, the residual acids were removed at 145 °C for 1 h. The activity of the immobilization platinum was evaluated by a model reaction, i.e. the hydrosilylation between 1-hexene and methyldichlorosilane and further applied to the hydrosilylation of 1-octene and methyldichlorosilane. The structures of the products were identified by NMR. ^{1}H NMR or ^{13}C NMR spectroscopies of EDTAD and hydrosilylation products were performed on 600 MHz NMR at 20 °C using tetramethylsilane (TMS) as an internal standard and DMSO or $CDCl_3$ as solvent. Qualitative and quantitative analysis of the reaction products were performed in GC, using *n*-decane as the internal standard. The programming of GC was as following: the injection volume was 0.8 μl, the split ratio was 30:1, the inlet temperature was 260 °C, the detection temperature was 260 °C, the column temperature was first 60 °C for 3 min, and then increased to 250 °C at the speed of 10 °C·min^{-1}, finally, 250 °C was maintained for 5 min.

3. Results and discussion

3.1. Characterization of products

3.1.1. Characterization of EDTAD

The two groups of splitting peaks in IR spectrum of EDTAD (Fig. 2(A)) were the preliminary evidence of the anhydride structure. The peaks in the high frequency region split at 1810, 1761 cm^{-1} with a gap of about 50 cm^{-1} between adjacent peaks. The low frequency groups split at 1127, 1072, and 1008 cm^{-1} with the same interval. Additionally, the bands at 1247 and 1423 cm^{-1} were related to C–O and C–N stretching respectively. ^{1}H NMR (600 MHz, DMSO, Fig. 2(B)): δ 3.71 (s, 8H, $O{=}CCH_2N$), 2.67 (s, 4H, N $(CH_2)_2N$), ^{13}C NMR (600 MHz, DMSO, Fig. 2(C)): δ 51.17 (N $(CH_2)_2N$), 52.24($O{=}CCH_2N$), 165.76 (C=O) which consisted with the characteristic peaks in the ideal product [31].

3.1.2. Characterization of SiO_2-EDTA-Pt

The prepared SiO_2-EDTA-Pt was firstly characterized by IR, EDS, SEM, XPS, UV, and AAS. The IR spectra of the silica, SiO_2-EDTA and SiO_2-EDTA-Pt were shown in Fig. 3(A). In the three spectra, there are two broad bands at 1110 cm^{-1} and 803 cm^{-1} arising from Si–O

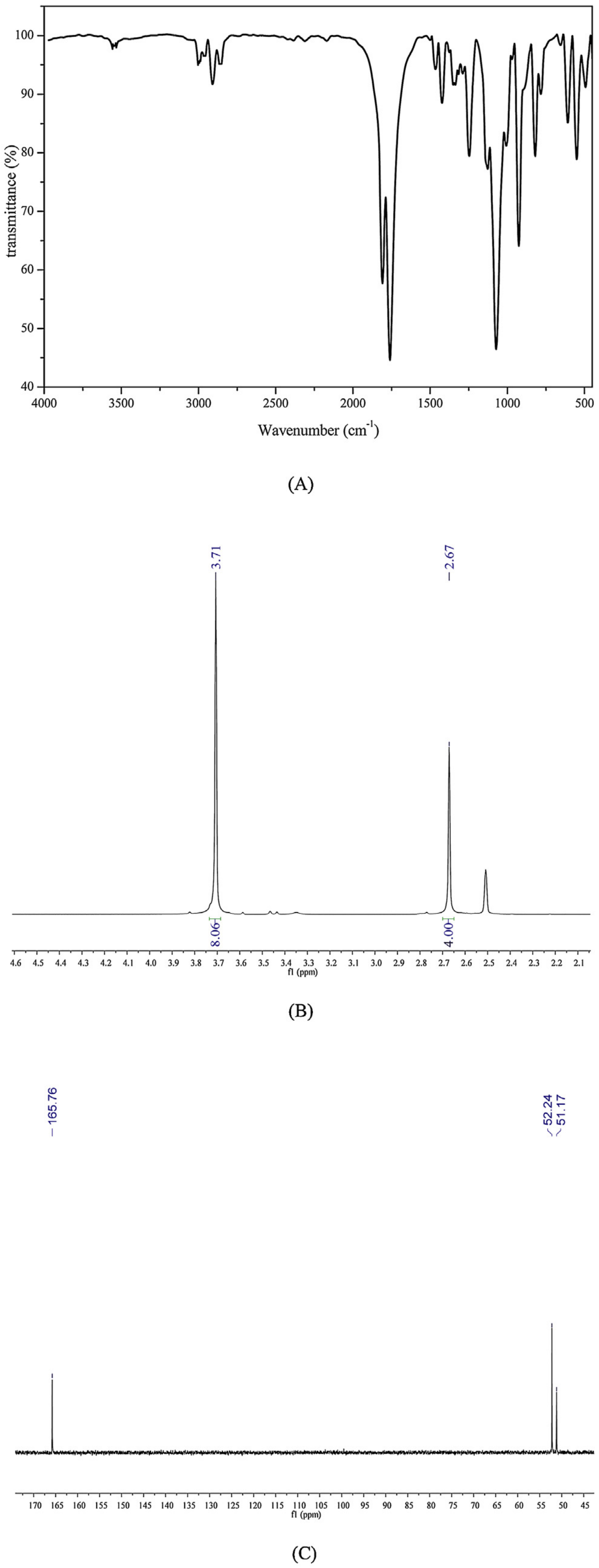
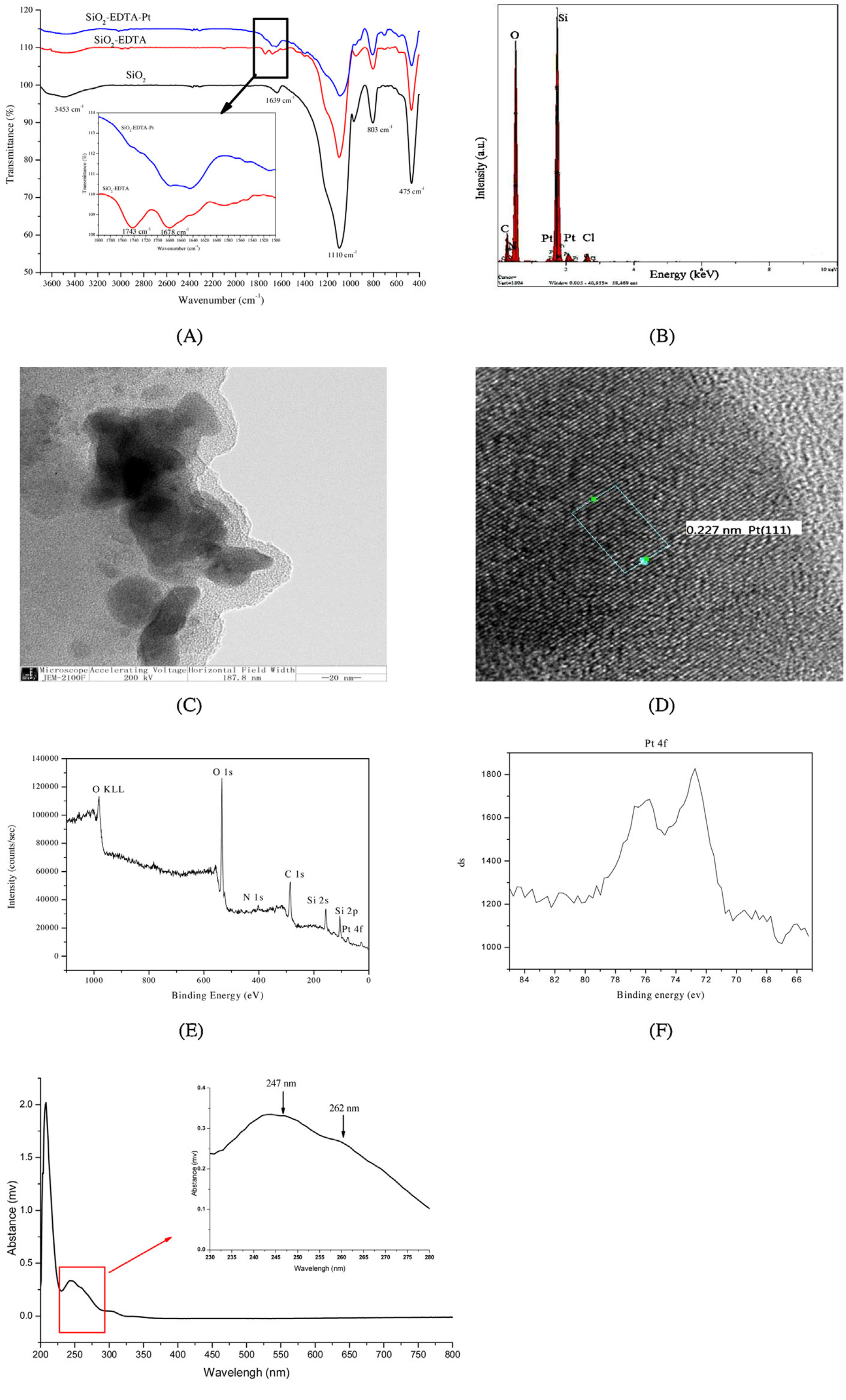


Fig. 2. (A) IR spectrum of EDTAD, (B) ^{1}H NMR spectrum of EDTAD and (C) ^{13}C NMR spectrum of EDTAD.



(A) (B) (C) (D) (E) (F) (G)

Fig. 3. (A) IR spectra of bare silica, SiO$_2$-EDTA and SiO$_2$-EDTA-Pt, (B) EDS image of SiO$_2$-EDTA-Pt, (C) The TEM of SiO$_2$-EDTA-Pt, (D) The HRTEM of SiO$_2$-EDTA-Pt, (E) The XPS entire spectrum scanning images of SiO$_2$-EDTA-Pt, (F) The XPS of SiO$_2$-EDTA-Pt in the region of Pt 4f5/2 and 4f7/2, and (G) UV/Vis absorption spectrum of SiO$_2$-EDTA-Pt prepared in 100 °C.

stretching, and a band at 475 cm^{-1} arising from O–Si–O bending [32]. In the SiO$_2$ spectrum, two bands at 1639 and 3453 cm^{-1} correspond to unassociated hydroxyl groups on the silica surface [33] and O–H vibrations respectively [34]. For the SiO$_2$-EDTA, two bands at 1678 and 1743 cm^{-1} were from carbonyl groups of amides and carboxylic groups, respectively [35]. However, the immobilization of Pt induced some changes of carbonyl groups, which might be resulted from interaction or charge transfer.

The energy dispersive X-ray spectrum was recorded by using an IXRF-550i instrument and the EDS analysis showed the elements present in the material. As shown in Fig. 3(B), the EDS analysis of fresh SiO_2-EDTA-Pt catalyst indicated the presence of Si, C, O, N, Pt, Cl elements.

The TEM and HRTEM of SiO_2-EDTA-Pt have been performed to observe the morphology and distribution of Pt and the results were shown in Fig. 3(C) and (D). From the TEM image, nanoparticles on the surface of SiO_2-EDTA can be observed. According to the lattice fringes analysis, the lattice fringes at (111) surface of nanoparticle was 0.227 nm, which was very consistent to the lattice fringes of platinum crystal.

X-ray photoelectron spectroscopy (XPS) was further performed to probe the electronic state of Pt in SiO_2-EDTA-Pt. The XPS survey spectra (Fig. 3(E)) also indicated the presence of elements Pt, Si, C, N and O as expected. The XPS spectrum of Pt 4f region was shown in Fig. 3(F). Compared with bulk Pt (71.2 eV) [17], the positive shift approximately +1.5 eV indicated charge transfer from Pt to coordination atoms of the ligand [36] which was consistent to the IR results.

According to the UV spectrum (Fig. 3(G)), maximum absorbance appeared at 247 nm and 262 nm in the residual i-propanol- H_2PtCl_6 solution when the external heating temperature of immobilization was 100 °C, which was consistent with reported data of reduced Pt particle and Pt (IV) [37,38]. It indicated that Pt may have been immobilized on the support material at different forms. Some researchers reported the reduced form Pt had the catalytic activity [39]. In order to evaluate the amount of Pt anchored on SiO_2-EDTA, the complex was analyzed by atomic absorption spectroscopy. The data indicated that the amount of platinum immobilized onto SiO_2-EDTA was 0.197 mmol/g or 3.84 wt%, which was higher than 1 wt% immobilized onto TiO_2 [40] and functionalized polyethylene glycol [38]. However, the immobilized platinum amount in the conditions was lower than 0.292 mmol/g [33] and 0.22 mmol/g [17].

3.1.3. Catalytic activity evaluation of SiO_2-EDTA-Pt

To evaluate the catalytic activity of immobilized Pt, hydrosilylation of 1-hexene with methyldichlorosilane was chosen as a model reaction catalyzed by SiO_2-EDTA-Pt. SiO_2-EDTA-Pt was prepared at 90 °C of external heating temperature. The other experimental conditions, including external heating temperature, time, additive sequence of reactants, the catalyst dosage, and the ratio of reactants, were systematically investigated. The results showed that the hydrosilylation of 1-hexene with methyldichlorosilane could be catalyzed by SiO_2-EDTA-Pt (Fig. 4(A)). In all GC analysis, there was only one product with the same retention time as the 1-hexyl-methyldichlorosilane standard substance. The hydrosilylation product of the model reaction was characterized by ^{1}HNMR. As shown in Fig. 4(B), the spectrum displayed six peaks, which were 0.77 (s, 3H, $CH_3{-}SiCl_2{-}$), 1.12 (t, 2H, $CH_3{-}SiCl_2{-}CH_2{-}$), 1.30 (m, 4H, $CH_3{-}SiCl_2{-}CH_2{-}CH_2{-}CH_2{-}(CH_2)_2{-}$), 1.38 (m, 2H, $CH_3{-}SiCl_2{-}CH_2{-}CH_2{-}CH_2{-}$), 1.50 (m, 2H, $CH_3{-}SiCl_2{-}CH_2{-}CH_2{-}$), 0.89 (t, 3H, CH_3-$SiCl_2{-}CH_2{-}CH_2{-}CH_2{-}(CH_2)_2{-}CH_3{-}$), respectively. Moreover, the spectral data matched with that of 1-hexyl-methyldichlorosilane standard.

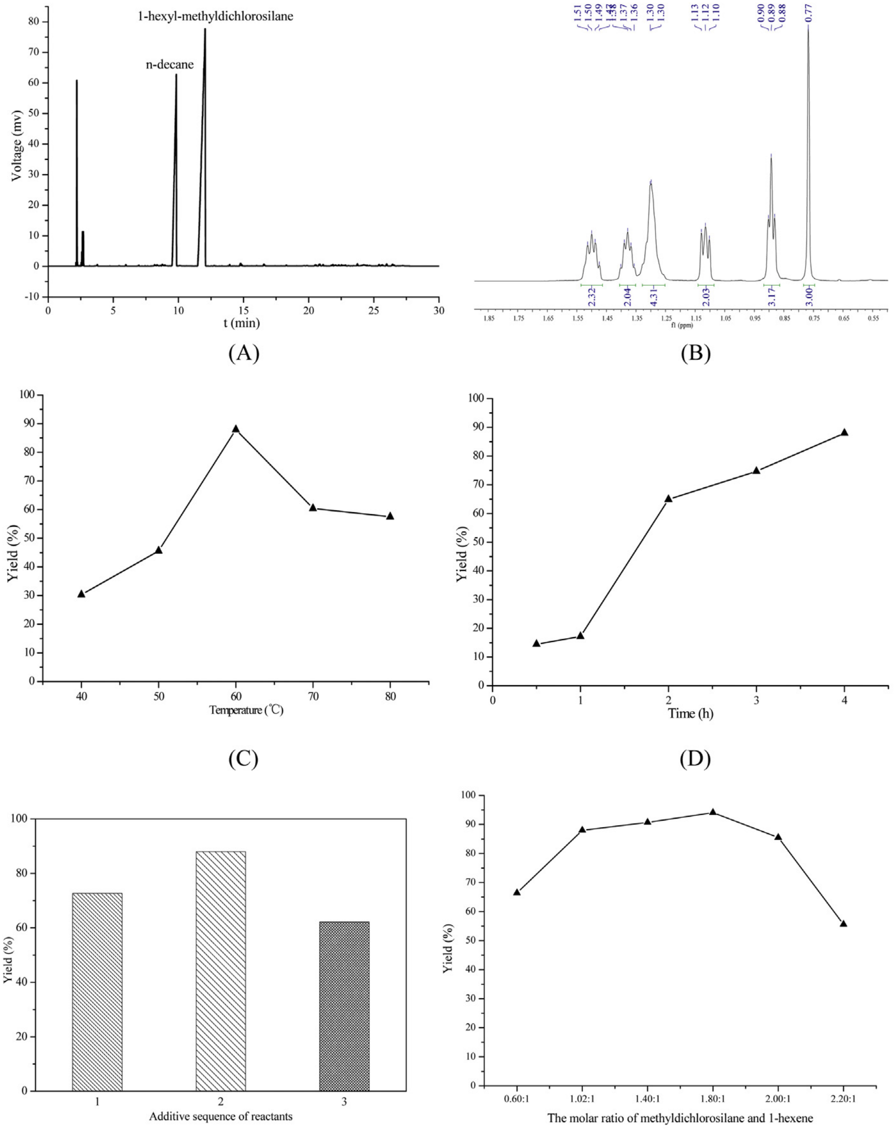
The hydrosilylation reaction of 1-octene with triethoxysilane was clearly faster at higher temperature and obtained higher turnover number within shorter time [41], which indicated that the reaction temperature had an important effect on the hydrosilylation. Therefore, the effect of external heating temperature from 40 °C to 80 °C on the yield of 1-hexyl-methyldichlorosilane was investigated. As shown in Fig. 4(C), maximum yield (about 90%) was obtained at 60 °C. When reaction temperature was lower than 60 °C, fewer yields was achieved in 4 h, i.e., 30% at 40 °C and 45% at 50 °C. It indicated that a high temperature may lead to a more efficient reaction. When reaction temperature was higher than 60 °C, the yield decreased to about 60% at 70/80 °C. The possible reason was that the reactants, especially methyldichlorosilane, dramatically evaporated during the reaction process. This caused an insufficient reaction. Based on the results, 60 °C was chosen as the heating temperature in the following experiments.

To achieve a sufficient reaction, a series of reaction time were investigated whilst keeping the other conditions constant. Namely, the reaction was performed in 0.5 h, 1 h, 2 h, 3 h, and 4 h, respectively. As shown in Fig. 4(D), the yield was lower than 20% in the first 1 h reaction. It indicated that there was an induction period of 1 h for this reaction. There was then a yield jump to 65% from 1 h to 2 h reaction. It indicated that the reaction was activated. The yield increased slowly after 2 h reaction and reached the maximum (87.97%) after 4 h reaction. During this period, the amount of reactants decreased and the amount of products increased. Thus, the reaction time of hydrosilylation was fixed at 4 h in the following experiments when SiO_2-EDTA-Pt prepared at 90 °C of external heating temperature was used.

The effect of additive sequence of reactants on the hydrosilylation reaction was also investigated and the results were shown in Fig. 4(E). It was found that the additive sequence was also an essential factor for this hydrosilylation. The yield of 1-hexyl-methyldichlorosilane was up to 88.0% when methyldichlorosilane was added to 1-hexene, whereas the yield reduced to 62.1% when 1-hexene was added to methyldichlorosilane and the yield was 72.6% when all reactants were added simultaneously. The results demonstrated that the activation of double bond maybe benefit to promotion on the activity of the active center Pt and the activation of catalyst which was might critical for improving catalytic properties. Thus, the order of methyldichlorosilane to 1-hexene was adapted in the following experiments.

The catalyst dosage was a key factor to estimate catalyst activity. Thus, the effect of the amount of the SiO_2-EDTA-Pt containing 0.25×10^{-3}, 1.0×10^{-3} or 4.0×10^{-3} mmol Pt on the hydrosilylation reaction was investigated. Results indicated the maximum yield of 1-hexyl-methyldichlorosilane was up to 88% when SiO_2-EDTA-Pt containing 1.0×10^{-3} mmol Pt was used. When SiO_2-EDTA-Pt containing 0.25×10^{-3} mmol Pt was used, the yield of 1-hexyl-methyldichlorosilane at 4 h was only 38.2%. A large number of the residual reactants proved the whole of reaction rate was apparently restricted by the limited amount of Pt catalyst, which may be the main reason of the low yield. Another reason may be the increase of by-product whose retention time was twice as much as 1-hexyl-methyldichlorosilane in GC. When SiO_2-EDTA-Pt containing 4.0×10^{-3} mmol Pt was used, the final yield of 1-hexyl-methyldichlorosilane was only 71.7%. As increasing the amount of the catalyst, the accelerated reaction rate and intensely heat-emission might lead to a rapid temperature rise in reactions, and therefore might lead to more by-products. This could be proved by the three peaks around 1-hexene and a peak whose retention time was twice as much as 1-hexyl-methyldichlorosilane. Thus, the amount of the SiO_2-EDTA-Pt should be controlled and fixed at 1.0×10^{-3} mmol to catalyze 10.0 mmol 1-hexene in this paper.

In the platinum-catalyzed hydrosilylation of trichlorosilane $HSiCl_3$ with allyl chloride, most experiments were carried out in an excess of $HSiCl_3$ which was reported to be the optimum ratio of these two reactants [42]. Therefore, the effect of ratio of methyldichlorosilane and 1-hexene including 0.60:1, 1.02:1, 1.40:1, 1.80:1, 2.00:1, and 2.20:1 was also investigated. The results were shown in Fig. 4(F). The data indicated the apparent 1-hexane was residual when the reactant ratio was 0.60:1. The limited amount methyldichlorosilane contributed to a low yield, 66.4%. When ratio of methyldichlorosilane and 1-hexene increased from 1.02:1 to 1.80:1, the yield of product arose from 88.0% to 94.1%. With the continuous increase of reactant ratio, the yields of 1-hexyl-methyldichlorosilane were dramatically dropped from



(A) (B)

(C) (D)

(E) (F)

Fig. 4. (A) Typical GC chromatogram of reaction catalyzed by SiO_2-EDTA-Pt, (B) The ^{1}H NMR spectrum of 1-hexyl-methyldichlorosilane, (C) Effect of external heating temperature on the yield of 1-hexyl-methyldichlorosilane, (D) Effect of reaction time on the yield of 1-hexyl-methyldichlorosilane, (E) Effect of additive sequence of reactants on the yield of 1-hexylmethyldichlorosilane, (F) Effect of reactant ratio on the yield of 1-hexyl-methyldichlorosilane.

Conditions: (A) Chromatographic column: SE-54 (30 m × 0.25 mm × 0.25 μm), internal standard: *n*-decane, injection volume: 0.8 μl, temperature programming: split ratio was 30:1, inlet temperature was set at 260 °C, detection temperature was 260 °C, column temperature was first 60 °C 3 min, and then was up to 250 °C at the speed of 10 °C min^{-1}, finally, 250 °C was maintained 5 min. (C) 1-Hexene: 10.0 mmol; methyldichlorosilane: 10.2 mmol; the amount of the catalyst: 10.0×10^{-4} mmol Pt; reaction temperature: 40, 50, 60, 70, and 80 °C; reaction time: 4 h; additive sequence: Methyldichlorosilane is added to 1-hexene. (D) Reaction temperature: 60 °C; reaction time: 0.5, 1, 2, 3, and 4 h. The other conditions were the same as (C). (E) Reaction time: 4 h 1: all materials are added simultaneously. 2: methyldichlorosilane is added to 1-hexene. 3: 1-hexene is added to methyldichlorosilane. The other conditions were the same as (D). (F) Additive sequence: Methyldichlorosilane is added to 1-hexene. Reactants ratio of methyldichlorosilane and 1-hexene was 0.60:1, 1.02:1, 1.40:1, 1.80:1, 2.00:1or 2.20:1. The other conditions were the same as (E).

85.5% to 55.6% and a large number of by-products were observed. Thus, the ratio of methyldichlorosilane and 1-hexene was fixed at 1.80:1.

3.2. Effect of immobilization conditions on SiO_2-EDTA-Pt

Alumina-supported platinum catalyst properties could be affected by conditions of immobilized catalyst [14]. As a result, after verifying the good catalytic effect of SiO_2-EDTA-Pt, the effects of immobilization conditions including temperature, platinum density and solvent were investigated.

3.2.1. Effect of the temperature on SiO_2-EDTA-Pt

SiO_2-EDTA-Pt was prepared at 30, 50, 70, 90, or 100 °C of external heating temperature in accordance with the experimental steps of Section 2.3.3 respectively. Their catalytic activities were shown in Table 1. The results indicated that the catalytic activity and immobilized amount of platinum were strongly dependent on the temperature and the catalytic activity was not completely correlated to the immobilized amount of platinum. With increase of heating temperature prepared SiO_2-EDTA-Pt, induction periods of the catalytic reaction were gradually shortened and reaction rates at the beginning of the model reaction were gradually accelerated. When the heating temperature was lower than 90 °C, such as 30 °C, 50 °C, 70 °C, although the immobilized amount of plat-

Table 1
Effect of the external heating temperature on Pt immobilization.

Catalyst		Yield (%)[a]					TOF[b] (s^{-1})
External heating temperature (°C)	Platinum content (mmol/g)	0.5 h	1.0 h	2.0 h	3.0 h	4.0 h	
30	0.243	7.5	9.3	60.7	75.7	81.3	0.42
50	0.251	10.3	30.2	80.4	81.8	82.5	0.57
70	0.269	15.5	71.7	79.5	84.9	86.3	0.86
90	0.210	66.7	83.9	88.1	90.9	94.1	3.71
100	0.197	87.7	88.7	96.8	99.1	–	4.87

[a] Conditions: 1-hexene: 10.0 mmol; methyldichlorosilane: 18.0 mmol; the amount of the catalyst: 10.0×10^{-4} mmol Pt; external heating temperature of hydrosilylation: 60 °C; additive sequence: Methyldichlorosilane is added to 1-hexene.

[b] Turnover frequency calculated after 0.5 h of reaction.

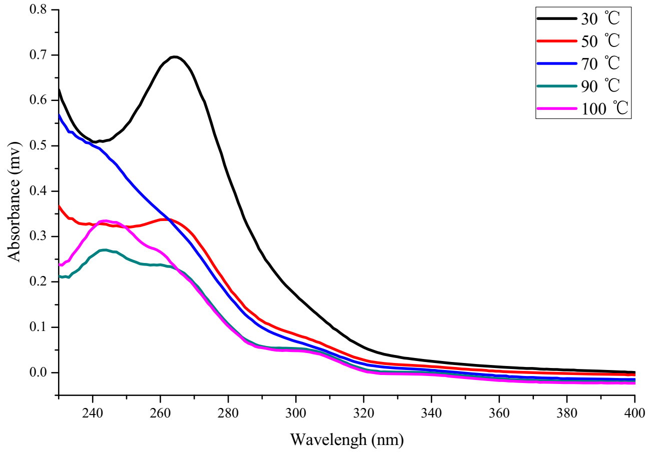


Fig. 5. UV/Vis absorption spectra of SiO_2-EDTA-Pt prepared at different external heating temperatures.

inum was increasing from 0.243 mmol/g to 0.269 mmol/g, the reaction was not finished until 4 h and the yield was only 81.3%, 82.5 and 86.3%, respectively. When the temperature increased from 90 °C to 100 °C, the immobilized amount of platinum was decreasing from 0.210 mmol/g to 0.197 mmol/g, but the catalytic activity of SiO_2-EDTA-Pt apparently increased. Using SiO_2-EDTA-Pt prepared at 100 °C of external heating temperature, the yield of 1-hexyl-methyldichlorosilane could reach the maximum 99.1% at 3 h. According to the above results, it could be hypothesized that the high temperature allowed the efficient reduction of Pt (IV) in active and stable low oxidation state platinum species and this assumption is consistent with the UV/Vis spectra. As shown in the Ref. [38] and Ref. [39], the absorbance of Pt (IV) and Pt particle is 262 nm, 247 nm respectively. As Fig. 5 shown, it could be observed that more and more Pt (IV) was reduced to Pt particle with the increase of the immobilized temperature. Thus, the external heating temperature immobilized Pt onto SiO_2-EDTA was chosen at 100 °C.

3.2.2. *Effect of the platinum loading amount on platinum catalytic activity*

Because the catalytic activity was not completely correlated to the platinum amount, it may be meaningful to investigate the effect of catalyst density on the activity of SiO_2-EDTA-Pt. As result, we prepared different immobilized Pt catalysts in accordance with the experimental steps of Section 2.3.3 respectively. The three kinds of SiO_2-EDTA-Pt catalysts containing equal total Pt amount but different platinum density of 0.073 mmol/g, 0.138 mmol/g and 0.197 mmol/g were used for hydrosilylation reaction between methyldichlorosilane and 1-hexene. The data were shown in Table 2. Results indicated that the reaction rate decreased with decrease of the platinum density. The highest yield still was obtained when Pt immobilization amount was 0.197 mmol/g.

Table 2
Effect of the immobilization catalyst loading amount.

Platinum content (mmol/g)	Yield (%)[a]				TOF[b] (s^{-1})
	0.5 h	1.0 h	2.0 h	3.0 h	
0.073	18.8	30.0	34.3	66.8	1.04
0.138	32.6	35.6	65.6	78.4	1.81
0.197	87.7	88.7	96.8	99.1	4.87

[a] Conditions: 1-hexene: 10.0 mmol; methyldichlorosilane: 18.0 mmol; the amount of the catalyst: 10.0×10^{-4} mmol Pt; external heating temperature of hydrosilylation: 60 °C; reaction time: 3 h; additive sequence: Methyldichlorosilane is added to 1-hexene.

[b] Turnover frequency calculated after 0.5 h of reaction.

Table 3
Effect of the solvent on Pt immobilization and activity.

Catalyst		Yield (%)[a]				TOF[b] (s^{-1})
Solvent of preparation	Platinum content(mmol/g)	0.5 h	1 h	2 h	3 h	
ethanol	0.197	87.7	88.7	96.8	99.1	4.87
i-propanol	0.153	8.8	77.2	78.0	86.4	0.49
n-butanol	0.166	62.6	74.6	75.0	95.1	3.48
n-hexanol	0.162	86.5	91.8	96.7	97.3	4.81

[a] Conditions: 1-hexene: 10.0 mmol; methyldichlorosilane: 18.0 mmol; the amount of the catalyst: 10.0×10^{-4} mmol Pt; external heating temperature of hydrosilylation: 60 °C; reaction time: 3 h; additive sequence: Methyldichlorosilane is added to 1-hexene.

[b] Turnover frequency calculated after 0.5 h of reaction.

3.2.3. *Effect of the solvent on Pt immobilization and activity*

The significant temperature effect encouraged us to investigate whether coordination solvent with higher reflux temperatures could cause a better catalytic activity. In accordance with the experimental steps of Section 2.3.3, we prepared SiO_2-EDTA-Pt at 100 °C of external heating temperature in ethanol, *i*-propanol, *n*-butanol and *n*-hexanol respectively. As shown in Table 3, the platinum content and the hydrosilylation activity were dependent on the solvent. Platinum content of SiO_2-EDTA-Pt prepared in ethanol, *i*-propanol, *n*-butanol and *n*-hexanol was decreased gradually. However, activity sequence was SiO_2-EDTA-Pt prepared in ethanol, *n*-hexanol, *n*-butanol and i-propanol when the reactions were added equal amount Pt. Finally, ethanol was chosen as solvent for further use.

3.3. *Comparison of SiO_2-EDTA-Pt and other Pt catalysts*

In order to further evaluate the SiO_2-EDTA-Pt, we also prepared immobilized platinum catalysts with bare SiO_2 and SiO_2-NH_2. The results showed that when a non-functionalized SiO_2 was submitted to a similar metal solution, the isolated solid contained merely 0.029% of Pt. Furthermore, the model hydrosilylation reaction was carried out using the homogeneous Spiere's catalyst at the above optimum reaction conditions, and using SiO_2-NH_2-Pt at the following conditions. (Conditions: 1-hexene: 10.0 mmol; methyldichlorosilane: 18.0 mmol; the amount of the catalyst:

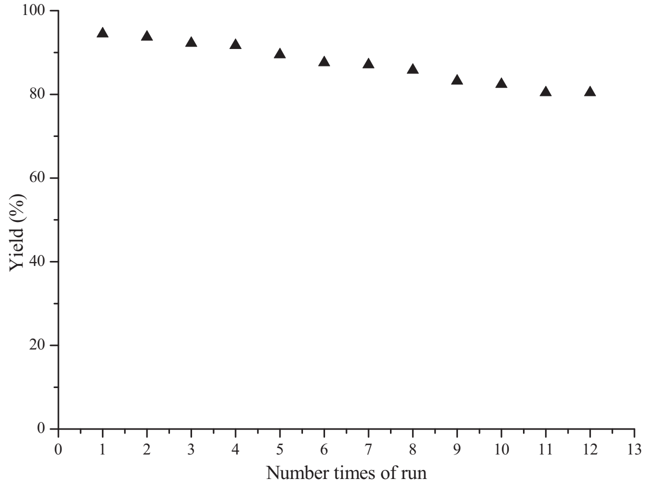


Fig. 6. The reusability of SiO_2-EDTA-Pt.
Conditions: GC chromatographic conditions were the same as Fig. 4A.

10.0×10^{-4} mmol Pt; external heating temperature: 60 °C; additive sequence: Methyldichlorosilane and 1-hexene were added simultaneously)

The yield of 1-hexyl-methyldichlorosilane reached the maximum (89.6%) at 2 h using an equal content of i-propanol-H_2PtCl_6. The turnover frequency (TOF), defined as the molar ratio of produced product to the amount of Pt immobilized on SiO_2-EDTA after 30 min of reaction, could reach 4.90. With SiO_2-NH_2-Pt, we found that the TOF is only 1.09 with 43.18% yield of the 1-hexyl-methyldichlorosilane at 3 h. The yield can reach 86.91% when the reaction was performed for 4 h, whilst the yield of 1-hexyl-methyldichlorosilane was up to 99.1% and the TOF was 4.87 when using SiO_2-EDTA-Pt. By comparison, the SiO_2-EDTA-Pt not only can ensure high catalytic activity, but also high selectivity.

3.4. *Reusability of SiO_2-EDTA-Pt*

To test the reusability of SiO_2-EDTA-Pt, hydrosilylation reaction between 1-hexene with methyldichlorosilane was performed 12 runs. After each run, the mixture solution of the reaction was centrifuged. The solid catalyst remained in the tube and liquid solution was removed. Fresh reactants were added in the tube and performed the reaction again. As shown in Fig. 6, SiO_2-EDTA-Pt could be recycled up to twelve consecutive runs and kept above 80% final yield of product. The little drop of activity may be because of the loss of SiO_2-EDTA-Pt in each pouring out liquid after reaction completion. By contrast, SiO_2-NH_2-Pt can effectively catalyze the reaction for 4 times.

3.5. *Application of SiO_2-EDTA-Pt*

1-Octene was hydrosilylated with methyldichlorosilane catalyzed by SiO_2-EDTA-Pt to investigate the catalytic scope of SiO_2-EDTA-Pt in other hydrosilylation reactions. The highest yield of 1-octyl-methyldichlorosilane (98.5%) could be obtained when SiO_2-EDTA-Pt was prepared at 100 °C of external heating temperature. The product of the reaction was characterized by ^1H NMR. The data was consistent with that of commercially available 1-octyl-methyldichlorosilane. In particular, 1-Octyl-methyldichlorosilane, ^1H NMR ($CDCl_3$) δ: 1.50 (m, 2H), 1.35(m, 10H), 1.11 (m, 2H), 0.88 (t, 3H), 0.77 (s, 3H). The spectrum was shown in Fig. 7. The result indicated the SiO_2-EDTA-Pt might have wide application prospect.

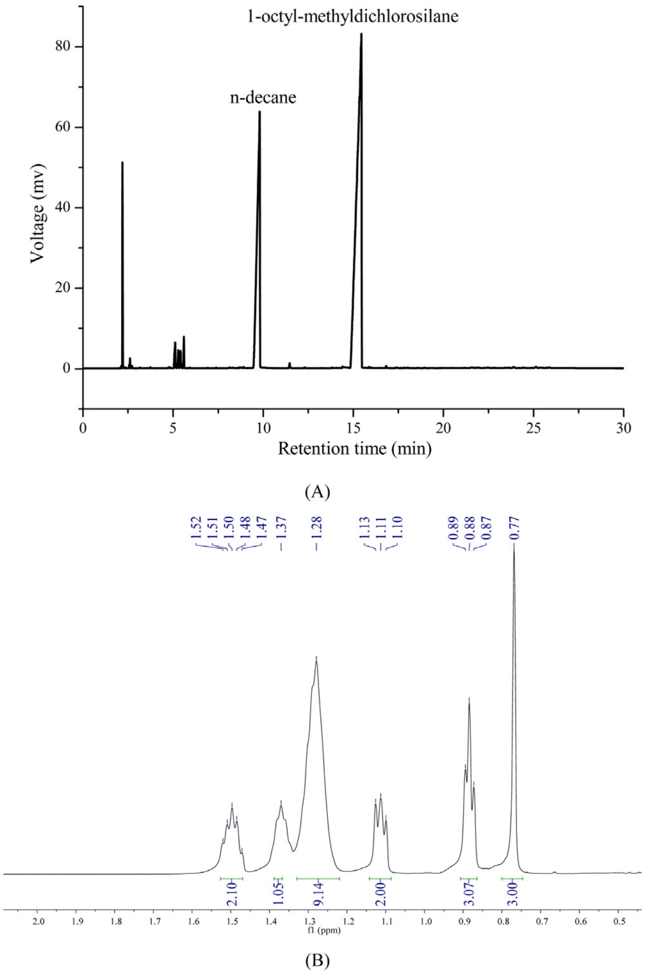


Fig. 7. (A) GC chromatogram of reaction system of 1-octene and methyldichlorosilane catalyzed by SiO_2-EDTA-Pt, (B) ^1H NMR of 1-octyl-methyldichlorosilane.
Conditions: (A) GC chromatographic conditions were the same as Fig. 4A except sample.

4. Conclusions

A new catalyst, silica supported platinum, has been successfully developed in this work. According to the optimization results, 100 °C of external heating temperature is the best immobilized temperature and ethanol is the best solvent for preparing SiO_2-EDTA-Pt. In the model solvent-less hydrosilylation of 1-hexene and methyldichlorosilane, our results indicates that the new catalyst has the advantages of high catalytic activity, environmentally friendly, easy handling, and recyclable. Application of SiO_2-EDTA-Pt in catalyzing the hydrosilylation of 1-octene and methyldichlorosilane indicates that the new catalyst may be potentially used in other hydrosilylation reactions. From an industrial point of view, the new catalyst is in accordance with the principle of green chemistry. This will bring it a good future both in laboratory and in industry.

Acknowledgements

The authors would like to appreciate the financial supports from the National Natural Science Foundation of China (No. 21375093), the Specialized Research Fund for the Doctoral Program of Higher Education (No. 20130032120081), Youth Fund of the Science and Technology Committee of Tianjin Municipal Government (No. 15JCQNJC43200) and the Independent innovation foundation of Tianjin University (No. 1102213).

References

[1] P.B. Glaser, T.D. Tilley, J. Am. Chem. Soc. 125 (2003) 13640–13641.
[2] A.K. Roy, Adv. Organomet. Chem. 55 (2007) 1–59.
[3] J. Speier, J. Webster, G. Barnes, J. Am. Chem. Soc. 79 (1957) 974–979.
[4] B.D. Karstedt, US: 3775452 (1973).
[5] B. Olivier, G. Berthon-Gelloz, S. Sterin, G. Mignani, Chem. Commun. 30 (2005) 3856–3858.
[6] J.Y. Li, C.B. Niu, J.J. Peng, Appl. Organomet. Chem. 28 (2014) 454–460.
[7] K. Kiyotomi, E. Kohki, Bull. Chem. Soc. Jpn. 79 (2006) 981–1016.
[8] Z.M. Michalska, K. Strzelec, J. Sobczak, J. Mol. Catal. A: Chem. 156 (2000) 91–102.
[9] B.R. Stranix, H.Q. Liu, G.D. Darling, J. Org. Chem. 62 (1997) 6183–6186.
[10] R. Drake, D.C. Sherrington, S.J. Thomson, React. Funct. Polym. 60 (2004) 65–75.
[11] Z.M. Michalska, K. Rozga-Wijas, J. Chojnowski, W. Fortuniak, J. Mol. Catal. A: Chem. 208 (2004) 187–194.
[12] Q.J. Miao, Z.P. Fang, G.P. Cai, Catal. Commun. 4 (2003) 637–639.
[13] H.T. Yang, Z.P. Fang, X.Y. Fu, L.F. Tong, Catal. Commun. 9 (2008) 1092–1095.
[14] Y. Fort, A. Silvestri, H. Graindorge, J. Mol. Catal. A: Chem. 112 (1996) 31l–316.
[15] M. Chauhan, B.J. Hauck, L.P. Keller, P. Boudjouk, J. Organomet. Chem. 645 (2002) l–13.
[16] B. Marciniec, H. Maciejewski, W. Duczmal, R. Fiedorow, D. Kitynski, Appl. Organomet. Chem. 17 (2003) 127–134.
[17] R.H. Hu, L.F. Zha, M.Z. Cai, Catal. Commun. 11 (2010) 563–566.
[18] Z.G. Ye, H.X. Shi, H.M. Shen, Phosphorus, Sulfur Silicon Relat. Elem. 190 (2015) 1621–1631.
[19] D.A. de Vekki, M.A. Il'ina, Russ. J. Gen. Chem. 84 (2014) 1580–1586.
[20] A.L. Prignano, W.C. Trogler, J. Amer. Chem. Soc. 109 (1987) 3586–3595.
[21] Z.M. Michalska, J. Mol. Catal. 3 (1977) 125–134.
[22] S. Dierick, E. Vercruysse, G. Berthon-Gelloz, Chem.-Eur. J 21 (2015) 1–7.
[23] J. Masllorens, M. Moreno-Manas, Synthesis 2002 (2002) 1903–1911.
[24] K.I. Shimizu, S. Koizumi, T. Hatamachi, H. Yoshida, S. Komai, T. Kodama, Y. Kitayama, J. Catal. 228 (2004) 141–151.
[25] D. Troegel, J. Stohrer, Coord. Chem. Rev. 255 (2011) 1440–1459.
[26] L.V.A. Gurgel, O.K. Junior, Bioresour. Technol. 99 (2008) 3077–3083.
[27] M. Sillanpaa, M. Orama, J. Ramo, Sci. Total Environ. 267 (2001) 23–31.
[28] E. Repo, J.K. Warchoł, A. Bhatnagar, J. Colloid Interface Sci. 358 (2011) 261–267.
[29] M. Tu, K.E. Geckeler, Polym. Int. 48 (1999) 909–914.
[30] Y. Shiraishi, G. Nishimura, Ind. Eng. Chem. Res. 41 (2002) 5065–5070.
[31] M. Mayor, R. Scheffold, Helv. Chim. Acta. 80 (1997) 1183–1189.
[32] E.R. Lippincott, A.V. Valkenburg, C.E. Weir, E.N. Bunting, J. Res. Natl. Bur. Stand. 61 (1958) 61–70.
[33] J. Li, C.H. Yang, L. Zhang, J. Organomet. Chem. 696 (2011) 1845–1849.
[34] M. Shahabi nejada, G. Ghasemi, J. Mol. Catal. A: Chem. 406 (2015) 118–126.
[35] S. Nagib, K. Inoue, T. Yamaguchi, Hydrometallurgy 51 (1999) 73–85.
[36] C. Liu, G. Li, D. Kauffman, J. Colloid Interface Sci. 423 (2014) 123–128.
[37] M. Luty-Blocho, M. Wojnicki, K. Pacławski, Chem. Eng. J. 226 (2013) 46–51.
[38] Y. Bai, S.F. Zhang, Y. Deng, J. Colloid Interface Sci. 394 (2013) 428–433.
[39] M. Pagliaro, R. Ciriminna, Eur. J. Org. Chem. 2013 (2013) 6227–6235.
[40] F. Alonso, R. Buitrago, Y. Moglie, J. Organomet. Chem. 696 (2011) 368–372.
[41] H.S. Hilal, M.A. Suleiman, J. Mol. Catal. A: Chem. Chem. 144 (1999) 47–59.
[42] B. Marciniec, H. Maciejewski, W. Duczmal, R. Fiedorow, D. Kitynski, Appl. Organomet. Chem. 17 (2003) 127–134.