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HYDROSILYLATION CATALYZED BY POLYSILOXANE-BOUND PLATINUM COMPLEXES

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ABSTRACT

A series of polysiloxane-bound platinum complexes was prepared by the reaction of chloroplatinic acid with silica-supported polysiloxane ligands containing S (A), $\begin{matrix} -S \\ \diagdown \\ \text{CHC}_6\text{H}_4\text{N}(\text{CH}_3)_2 \\ \diagup \\ -S \end{matrix}$ (B), $-\text{N}(\text{COCH}_3)_2$ (C), and $-\text{COOH}$ (D) groups. These were tested as catalysts for the hydrosilylation of acetylene and olefins with functional groups, with the aim of synthesizing organosilicon monomers and silane coupling agents. It was found that supported platinum Catalyst A was an active catalyst for the hydrosilylation of acetylene and allyl chloride by dichloromethylsilane or trichlorosilane. By these catalytic reactions, several useful organosilicon monomers, such as dichloromethylvinylsilane and 3-chloropropyl-trichlorosilane, were obtained in good yield. Supported platinum Catalysts B, C, and D proved to be effective for the hydrosilylation of allyl glycidyl ether by trimethoxysilane to yield an important silane coupling agent, 3-glycidoxypropyltrimethoxysilane. The stability of supported Catalyst A is reported.

These polysiloxane-bound platinum complexes have been tested as catalysts for the hydrosilylation of acetylene and several functional olefins, aiming at the synthesis of organosilicon monomers and silane coupling agents. In this paper we report the preparation of the polysiloxane-bound platinum complexes and their catalytic properties for hydrosilylation.

EXPERIMENTAL

Materials

Dichloromethylsilane and trichlorosilane were supplied by Beijing Chemical Works. Trimethoxysilane, 3-chloropropyltriethoxysilane, and 3-mercaptopropyltriethoxysilane were obtained from Gaixian Chemical Works. 3,3'-Bis-(triethoxysilyl)dipropyl thioether was prepared by the literature procedure [16]. Chloroplatinic acid, heptene-1, dodecene-1, allyl chloride, allyl acetate, diallyl ether, methyl methacrylate, styrene, and allyl glycidyl ether were commercial products and were dried over Molecular Sieves. Fumed silica of surface area 370 m²/g was used.

Equipment and Analytical Measurements

Infrared spectra were recorded on a Perkin-Elmer Model-180 spectrophotometer, and ¹H-NMR spectra on a Cameca TSN-250 spectrometer with TMS as an internal standard. XPS spectra were recorded on a Kratos ES-300 spectrometer. Gas chromatographic analyses were carried out on a Beijing PS-2305 instrument, equipped with a thermal-conductivity detector and steel columns packed with 10% SE-30 on Chromosorb. Other physicochemical as well as elemental analytical data were determined by commonly used methods.

Preparation of Supports Containing Functional Groups

Support A: 3,3'-Bis(triethoxysilyl)dipropyl thioether, 13.3 g (30.0 mmol), was added to a suspension of 10.0 g silica in 250 mL toluene. A solution of 8.0 mL water, 1.0 mL 15% HCl, and 20 mL ethanol was added with stirring. The mixture was refluxed for 8 h and filtered, washed with toluene and ethanol, and dried *in vacuo* to give silica-supported sulfur-containing polysiloxane Ligand A. Analysis found: S, 2.6%.

Supports B, C, and D were prepared by the following route: First three silane coupling agents, 3-mercaptopropyltriethoxysilane, 3-aminopropyltri-

TABLE 1. Analytical Data for Supported Platinum Catalysts^a

Catalyst	Pt	S	N	O	L/Pt ^b
A	6.71	2.20			1.99
B	7.92	2.60			2.00
C	9.33		2.68	5.95	3.89
D	8.53			5.60	4.02

^aAll in wt%.^bMolar ratio.

ethoxysilane, and 2-cyanoethyltriethoxysilane, were hydrolyzed and condensed in the presence of silica to produce silica-supported polysiloxanes containing SH, NH₂, and CN groups, which were then converted to Supports B, C, and D by the following procedures: 1) Poly-3-mercaptopropylsiloxane was reacted with *p*-dimethylaminobenzaldehyde to give Support B. 2) Poly-3-aminopropylsiloxane was acetylated by acetic anhydride to produce Support C. 3) Poly-2-cyanoethylsiloxane was hydrolyzed to form Support D. The details of the preparation for Supports B, C, and D have been given elsewhere [17].

Preparation of Supported Catalysts

The preparation of Catalyst A is described as an example; the other catalysts were prepared similarly. Support A (1.0 g) was suspended in 20 mL ethanol, and 210.0 mg chloroplatinic acid (0.40 mmol) was added. The mixture was refluxed for 10 h under nitrogen and cooled to room temperature. The reaction mixture was filtered, washed with ethanol, and dried *in vacuo* to give polysiloxane-bound platinum Catalyst A. All the analytical data of the supported catalysts are summarized in Table 1. The atomic ratio of S to Pt in this catalyst was 2.

Hydrosilylation of Acetylene

The reaction was carried out under 1 atm of acetylene in the absence of solvent. Catalyst A (0.58 g) was weighed into a reaction vessel equipped with a manometer, a gas burette, a magnetic stirrer, and an oil bath with automatic temperature control. Acetylene from the pressure cylinder was passed through concentrated sulfuric acid, potassium hydroxide, and Molecular Sieves and in-

roduced into the reaction system. The system was flushed three times with the dry acetylene. Dichloromethylsilane (23.0 g, 0.2 mol) was then introduced into the reaction vessel by hypodermic syringe. The reaction mixture was monitored by GLC at regular intervals.

Hydrosilylation of Olefins

All experiments were carried out in a 100-mL flask equipped with a magnetic stirrer and a cooled condenser (-30°C). The reaction conditions are given in Table 2. Olefin and silicon hydride were used in equimolar amounts without solvent, except that the molar ratio of silicon hydride to diallyl ether was 2. The catalysts were added in such amounts that the concentration of platinum was the same in all experiments. The molar ratio of olefin to platinum was $1:5 \times 10^{-4}$. The products were isolated, and their structure was confirmed by IR and NMR. The yields of reaction products were determined by GLC.

A reuse test of supported platinum Catalyst A was made in the hydrosilylation of allyl acetate by dichloromethylsilane in subsequent runs. For each use the reaction vessel was cooled, the solution decanted, and equimolar amounts of the substrates added. This procedure was repeated 20 times.

RESULTS AND DISCUSSION

In principle, the preparation of the polysiloxane supports containing

S (A), $\begin{matrix} -\text{S} \\ \diagdown \\ \text{CHC}_6\text{H}_4\text{N}(\text{CH}_3)_2 \\ \diagup \\ -\text{S} \end{matrix}$ (B), $-\text{N}(\text{COCH}_3)_2$ (C), and $-\text{COOH}$ (D) groups

was based on Allum's method [18]. An improvement of this method was achieved by use of an acid or base to catalyze the hydrolysis and condensation of a suitable silane coupling agent in the presence of silica. In this way, not only the reaction between SiOR groups of the silane with the surface hydroxyl groups of silica became easier, but self-condensation of the silane occurred. The polysiloxane supports so formed contained a higher content of ligand groups.

Polysiloxane-bound platinum complexes were prepared easily by the reaction of these polysiloxane supports with chloroplatinic acid in ethanol. By varying the amounts of polysiloxane ligands and chloroplatinic acid, polysiloxane-bound platinum complexes with different ratios of L/Pt were obtained (Table 1).

These supported platinum complex catalysts were characterized by x-ray

TABLE 2. Reaction Products and Yields for Hydrosilylation of Various Olefins by Dichloromethylsilane or Trimethoxysilane Catalyzed by Supported Platinum Catalysts

Olefin	Catalyst	Temperature, °C	Time, min	Reaction product	Yield, %
<u>Dichloromethylsilane</u>					
Heptene-1	A	60	10	$\text{CH}_3(\text{CH}_2)_6\text{SiCH}_3\text{Cl}_2$	91
Dodecene-1	A	60	10	$\text{CH}_3(\text{CH}_2)_{11}\text{SiCH}_3\text{Cl}_2$	93
Allyl chloride	A	70	30	$\text{ClCH}_2\text{CH}_2\text{CH}_2\text{SiCH}_3\text{Cl}_2$	69
Allyl acetate	A	70	10	$\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_2\text{SiCH}_3\text{Cl}_2$	95
Diallyl ether	A	70	30	$(\text{Cl}_2\text{CH}_2\text{SiCH}_2\text{CH}_2\text{CH}_2)_2\text{O}$	87
Methyl methacrylate	A	70	60	$\text{CH}_3\text{OOC}(\text{CH}_3)\text{CHCH}_2\text{SiCH}_3\text{Cl}_2$	79
Styrene	A	60	10	$\left\{ \begin{array}{l} \text{C}_6\text{H}_5(\text{CH}_3)\text{CHSiCH}_3\text{Cl}_2 \\ \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{SiCH}_3\text{Cl}_2 \end{array} \right.$	24
					52
<u>Trimethoxysilane</u>					
Allyl glycidyl ether	B	80	30	$\text{CH}_2-\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$	96
	C	80	30	$\left\{ \begin{array}{l} \text{O} \\ \text{O} \end{array} \right.$	98
	D	80	30		72

TABLE 3. XPS Data for Supported Platinum Catalysts, Supports, and H_2PtCl_6

Compound	Binding energy, eV				
	Pt(4f)	S(2p)	N(1s)	Cl(2p)	O(1s)
Catalyst A	73.5	164.6		199.0	533.0
Support A		163.3			533.0
Catalyst B	73.3	164.5	398.7	198.4	
Support B		163.5	398.8		
Catalyst C	73.0		401.9	198.4	534.6
Support C			399.8		532.4
Catalyst D	73.5			198.5	534.8
Support D					532.5
H_2PtCl_6	75.3			198.5	

photoelectron spectroscopy (XPS) (Table 3). In order to compare with the corresponding supports and chloroplatinic acid, the XPS data of the supports and chloroplatinic acid are included. It has been found that the binding energies of Pt(4f_{7/2}) in all the supported catalysts are between 73.0 and 73.5 eV, which is about 2.0 eV less than that in chloroplatinic acid (75.3 eV), whereas Cl(2p) binding energies change little. The decrease of the Pt(4f_{7/2}) binding energy in these catalysts means a reduction of its oxidation state or an increase of its electron density. On the other hand, S(2p) binding energy in Catalysts A and B is 1.3 and 1.0 eV more, respectively, than that in the corresponding support. The electronic state of the sulfur atoms in the supported catalysts is of lower electron density and, therefore, the electrons on the sulfur atom may flow into the platinum atom to form an S→Pt coordination bond. Similarly, the increase of N(1s) and O(1s) binding energy in Catalysts C and D, compared with those in the corresponding Supports C and D, shows that coordination structures of N→Pt and O→Pt are present in Catalysts C and D. As parts of the Cl groups in [PtCl₆]²⁻ are displaced by S, N, or O ligand groups, Pt^(IV) is reduced to lower valency. In view of the similarity of the platinum binding energy, we measured for Pt^(II) complex with that reported in the literature [19]. These supported platinum catalysts are most likely divalent platinum complexes.

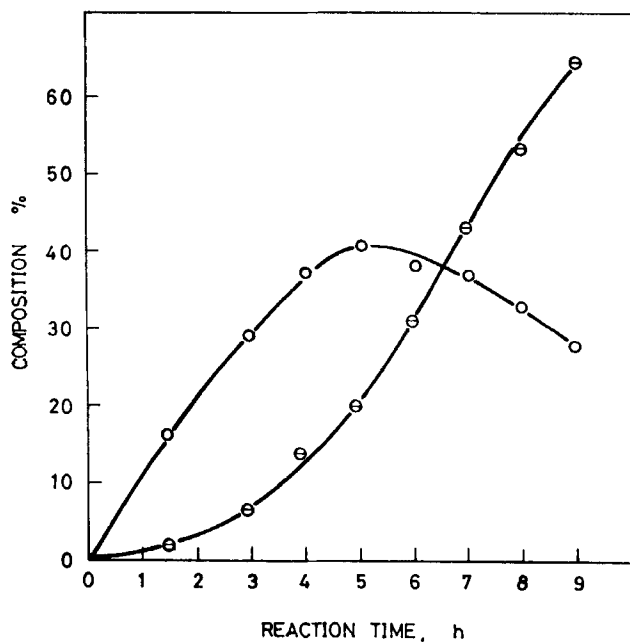


FIG. 1. Composition of reaction products during the hydrosilylation of acetylene by dichloromethylsilane: (O) dichloromethylvinylsilane, (⊖) 1,2-bis(dichloromethylsilyl)ethane.

The supported Catalyst A was used to catalyze the hydrosilylation of acetylene by dichloromethylsilane in order to prepare an organosilicon monomer, dichloromethylvinylsilane. The experiment demonstrated that the supported catalyst was active for hydrosilylation. At ambient temperature and under 1 atm of acetylene, the reaction resulted in two products, dichloromethylvinylsilane (1) and 1,2-bis(dichloromethylsilyl)ethane (2). The composition of the products during the reaction course is shown in Fig. 1.

It is clear that this reaction consists of two consecutive steps: addition of dichloromethylsilane to acetylene forms dichloromethylvinylsilane, which then reacts further with dichloromethylsilane to give 1,2-bis(dichloromethylsilyl)ethane. When the reaction was carried out for 5 h, the yield of 1 reached a maximum (40%). Longer reaction time led to an increase in 2.

The total conversion of dichloromethylsilane was affected by the atomic ratio of S/Pt in the supported Catalyst A. Figure 2 shows the relationship be-

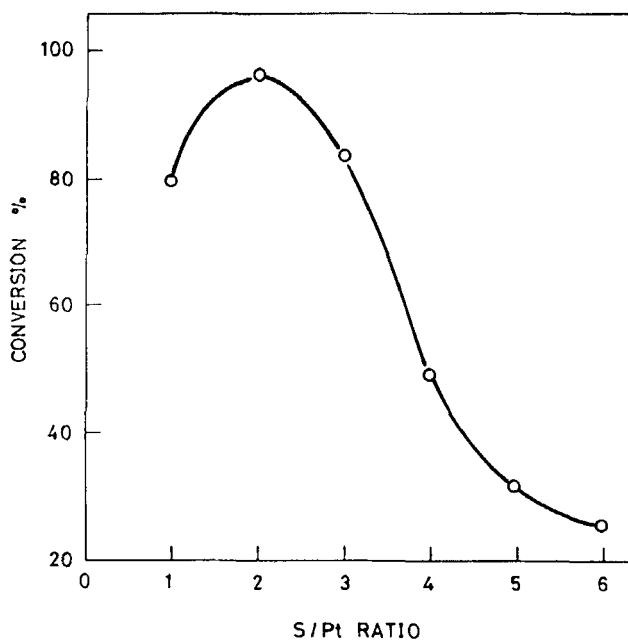


FIG. 2. Relationship between the conversion of dichloromethylsilane and the S/Pt ratio in supported Catalyst A.

tween the conversion of dichloromethylsilane and the atomic ratio S/Pt. The highest conversion of dichloromethylsilane (98%) was obtained when the atomic ratio S/Pt was 2.

Tests of the hydrosilylation of allyl chloride by trichlorosilane at 70°C proved that Catalyst A was very effective for this reaction, which occurred rapidly and produced 3-chloropropyltrichlorosilane in 84% yield. In contrast, the reaction catalyzed by chloroplatinic acid gave only 60% yield. Figure 3 shows that there is an induction period for the reaction catalyzed by chloroplatinic acid. This induction period has been studied by Speier [20], who indicates that an active catalytic species is formed during this period, and that its formation requires reduction of chloroplatinic acid. This induction period can sometimes last for a relatively long time, even hours. However, when supported Catalyst A with lower valent platinum was used, the reaction occurred immediately without an induction period and gave a higher yield within 1 h than the reaction catalyzed by chloroplatinic acid.

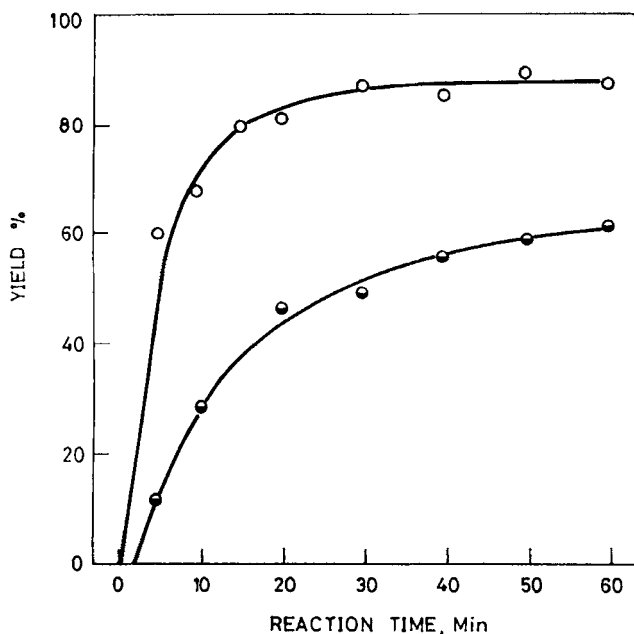


FIG. 3. Yield of 3-chloropropyltrichlorosilane vs reaction time: (○) supported Catalyst A, (●) chloroplatinic acid.

Furthermore, supported Catalyst A was found to be active for the addition of dichloromethylsilane to other olefins such as heptene-1, dodecene-1, allyl chloride, allyl acetate, diallyl ether, methyl methacrylate, and styrene. The products formed in these reactions were confirmed by ^1H NMR, and the yields were determined by GLC. These results are summarized in Table 2.

Supported Catalysts B, C, and D were tested to catalyze the hydrosilylation of allyl glycidyl ether by trimethoxysilane, with the aim of preparing a silane coupling agent, 3-glycidoxypropyltrimethoxysilane. It was found that the three supported catalysts were all active for the hydrosilylation; however, they showed some difference in catalytic activity. When Catalyst B or C was used, the reaction occurred rapidly at 80°C and was nearly completed within 30 min. Analysis of the reaction products by NMR and GLC indicated that only one product, 3-glycidoxypropyltrimethoxysilane, was formed in each case. The product yield was 96 and 98%, respectively. In the case of Catalyst D, the reaction rate was not as rapid as that by Catalyst B or C, and the product yield was

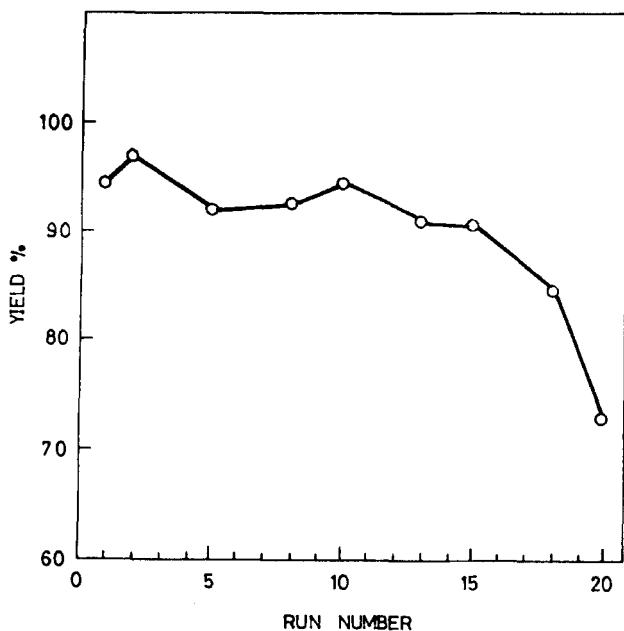


FIG. 4. Yield of 3-acetoxypropyldichloromethylsilane for reuse of supported Catalyst A.

only 72%. The difference of catalytic activity between Catalysts B, C, and D might be due to the effect of different ligand groups attached to the platinum atom [15]. These results are summarized in Table 2.

The reuse experiment of supported Catalyst A was carried out in the hydrosilylation of allyl acetate by dichloromethylsilane. Figure 4 shows the relationship between the product yield and run number. It can be seen that the reaction yield increases somewhat after the first run, and there is no subsequent change in yield until Catalyst A is recycled 15 times. When Catalyst A is recycled more than 15 times, the yellow catalyst darkens and turns a brown-black. This indicates that the divalent platinum complex is reduced to platinum metal. Therefore, the reaction yield after 15 recycles of Catalyst A decreases abruptly.

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