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AN ACTIVE AND STABLE HYDROSILYLATION CATALYST: A SILICA-SUPPORTED POLY-γ-MERCAPTOPROPYLSILOXANE-PLATINUM COMPLEX

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Summary

A silica-supported poly-γ-mercaptopropylsiloxane-platinum complex was prepared and used as hydrosilylation catalyst with 1-hexene and acetylene. When it was used as the catalyst for addition of triethoxysilane to 1-hexene at 80°C or room temperature, the product was n-hexyltriethoxysilane only, and the catalyst could be reused over twenty times (turnover numbers achieved were about 10.000) without any appreciable loss in the catalytic activity. The addition of triethoxysilane to acetylene by this catalyst at 80°C or room temperature under an atmospheric pressure gave vinyltriethoxysilane and bis(triethoxysilyl)ethane in good yields.

Introduction

Polymer-supported metal complexes are currently attracting great interest because they combine the advantages of homogeneous and heterogeneous catalysed processes [1,2]. Čapka and his coworkers [3,4] have reported that the Pt or Rh complex of polystyrene, polyallyl chloride or polymethacrylate with diphenylphosphino, dimethylamino or cyano groups can be used as the heterogeneous hydrosilylation catalyst of olefins. Among these catalysts, the Pt complexes of polystyrene with diphenylphosphino groups and polymethacrylate with dimethylamino groups were relatively active for the addition of triethoxysilane to 1-hexene and could be reused twice [4]. However, we can not further evaluate the useful lives of these catalysts because of the lack of data in the paper [4]. From the point of view of practical application perhaps the most important feature of the polymer catalysts is the fact that they can be easily recovered and reused many times. We have found that the Pt complex of silica-supported poly-γ-aminopropylsiloxane (abbreviated as "Si"–NH_2–Pt) is an active catalyst for hydrosilylation of olefins and can be reused several times [5].

In this paper, we wish to report the preparation of silica-supported poly-γ-mercaptopropylsiloxane-Pt complex ("Si"–SH–Pt) and its catalytic properties in the

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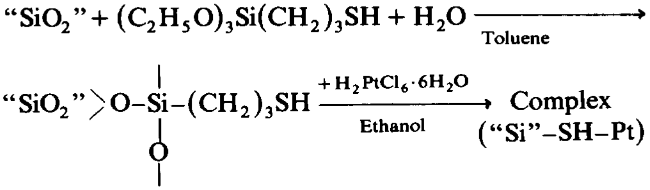
addition of triethoxysilane to 1-hexene and acetylene. This complex was prepared as follows:



$$\text{“SiO}_2\text{”} + (C_2H_5O)_3Si(CH_2)_3SH + H_2O \xrightarrow[\text{Toluene}]{} \text{“SiO}_2\text{”} > O\text{-}\overset{|}{\underset{\overset{|}{O}}{Si}}\text{-}(CH_2)_3SH \xrightarrow[\text{Ethanol}]{+H_2PtCl_6\cdot 6H_2O} \underset{(\text{“Si”-SH-Pt})}{\text{Complex}} \qquad (1)$$

Silica gel was treated with γ-mercaptopropyltriethoxysilane and water to give silica-supported poly-γ-mercaptopropylsiloxane, then it was treated with chloroplatinic acid to form the complex. This complex can catalyze the addition of triethoxysilane to 1-hexene in over 90% yield at 80°C or room temperature and can be reused 20 times without any appreciable loss in the catalytic activity.

$$CH_3(CH_2)_3CH{=}CH_2 + HSi(OC_2H_5)_3 \rightarrow CH_3(CH_2)_5Si(OC_2H_5)_3 \qquad (2)$$

The addition of triethoxysilane to acetylene can also be catalyzed by this catalyst at 80°C or room temperature to give vinyltriethoxysilane and 1,2-bis(triethoxysilyl)ethane in 50% and 50% yields, respectively, or 60% and 20% yields, respectively.

$$CH{\equiv}CH + HSi(OC_2H_5)_3 \rightarrow CH_2{=}CHSi(OC_2H_5)_3 + [(C_2H_5O)_3SiCH_2]_2 \qquad (3)$$

This reaction was also catalyzed by Pt/C to give the same products [6], but this catalyst requires higher temperature, e.g., 130°C, to promote the reaction. Thus, "Si"-SH-Pt is probably a more suitable catalyst for preparing vinyltriethoxysilane, which is an important silane coupling agent in industry [7].

Expermental

A. Preparation of silica-supported poly-γ-mercaptopropylsiloxane ("Si"-SH)

Allum and his coworkers [8] have prepared "Si"-SH by the condensation of silica gel with γ-mercaptopropyltriethoxysilane. However, the sulfur content of the product was only 0.6 wt%, because the OH group content on silica gel was generally very small. We have shown that if an excess carbon-functional organotriethoxysilane and water are mixed with silica gel, the hydrolysis and condensation of the ethoxysilane itself also occur on silica gel, and the ligand element content in silica-supported polyorganosiloxane can be increased, which is favorable for increasing the activity of silica-supported polyorganosiloxane-metal complex catalyst [9,10]. Therefore, we have prepared "Si"-SH by the following method:

Toluene (150 ml) and 7.2 g of fumed silica (surface area 370 m^2/g) were placed in a flask equipped with a mechanical stirrer, dropping funnel, and reflux condenser. After stirring for 10 min, 7 g of γ-mercaptopropyltriethoxysilane was added, then 8 ml of ethanol solution containing 2 ml of water and 0.2 ml of 10% hydrochloric acid was added slowly, and the mixture was heated to reflux. During refluxing the white mixture became colorless and transparent. After refluxing for 4 h the product was allowed to cool, then filtered, dried in vacuo. Extraction with toluene was followed by drying. The sulfur content was determined to be 2.8 wt% by elemental analysis.

B. Preparation of silica-supported poly-γ-mercaptopropylsiloxane-Pt complex "Si"-SH-Pt)

Some "Si"-SH-Pt complexes with different S/Pt atomic ratio were prepared. For example, 0.423 g (0.37 mg atom of S) of "Si"-SH, 30 ml of ethanol and 1 ml of ethanol solution containing 0.0319 g (0.0615 mmol) of $H_2PtCl_6 \cdot 6H_2O$ were placed in a three-necked flask (50 ml) equipped with a mechanical stirrer, reflux condenser and gas inlet tube. The mixture was refluxed under nitrogen for 12 h. The solid particles became golden in color, and the solution became colorless and transparent. The product was filtered, and dried in vacuo. The atomic ratio of S/P of the product was 6.

Table 1 shows the XPS data for "Si"-SH-Pt, "Si"-SH and H_2PtCl_6 [11]. It can be seen that the binding energies of Si(2*p*) and O(1*s*) of "Si"-SH-Pt are similar to those of "Si"-SH, and the binding energy of Cl(2*p*) of "Si"-SH-Pt is similar to that of H_2PtCl_6. However the difference of S(2*p*) binding energies between "Si"-SH-Pt and "Si"-SH is 1.1 eV. The difference of Pt(4*f*) binding energies between "Si"-SH-Pt and H_2PtCl_6 is 2.2 eV. These results show that a dative bond is formed between the sulfur and platinum atom in the complex.

C. Preparation of silica-supported poly-γ-mercaptopropylsiloxane-Pd and -Rh complexes, and silica-supported poly-γ-aminopropylsiloxane-Pt complex [5]

These complexes were prepared from the corresponding siloxane and $PdCl_2 \cdot 2H_2O$, $RhCl_3 \cdot 3H_2O$ or $H_2PtCl_6 \cdot 6H_2O$, respectively, in a similar way to that mentioned above.

D. Addition of triethoxysilane to 1-hexene

0.19 g (0.026 mg atom of Pt) of "Si"-SH-Pt, 2.5 ml (13.6 mmol) of triethoxysilane and 2.2 ml (17.9 mmol) of 1-hexene were placed in a three-necked flask (50 ml) equipped with a mechanical stirrer, reflux condenser and gas inlet tube, and stirred under nitrogen at 80°C for 2 h or at room temperature for 8 h. The product was filtered and distilled to give n-hexyltriethoxysilane; b.p. 121–124°C/10 mmHg (200–205°C/760 mmHg [12]). (Found: C, 57.59; H, 11.30 Calcd. for $C_{12}H_{28}O_3Si$: C, 58.06; H, 11.29%.). NMR (CCl_4): δ 0.51 (2H, t, Si-CH_2-), 0.89 (3H, t, -C-CH_3), 1.19 (9H, t, -(OC-CH_3)$_3$), 1.29 (OH, s, -(CH_2)$_5$), 3.72 (6H,q, (OCH_2-)$_3$). The yields were determined by GLC.

E. Addition of triethoxysilane to acetylene

0.15 g (0.02 mg atom of Pt) of "Si"-SH-Pt and 6.4 ml (34.7 mmol) of triethoxysilane were placed in a three-necked flask (50 ml) equipped with a mechanical stirrer, reflux condenser and gas inlet tube. The mixture was stirred, and

TABLE 1. XPS DATA FOR "Si"-SH-Pt, "Si"-SH AND H_2PtCl_6 (IN eV)

XPS peak	"Si"-SH-Pt	"Si"-SH	H_2PtCl_6
Pt(4*f*)	73.4		75.1
S(2*p*)	164.8	163.7	
Cl(2*p*)	199.0		199.3
Si(2*p*)	103.5	103.7	
O(1*s*)	533.1	533.3	

TABLE 2

ADDITION OF TRIETHOXYSILANE TO 1-HEXENE CATALYZED BY DIFFERENT METAL COMPLEXES OF "Si"-SH [a]

Metal in the Complex	Yield of n-hexyltriethoxysilane (%)
Pt	96
Rh	61
Pd	41

[a] Complex: S/metal atomic ratio, 4; metal content, 0.026 mg atom; triethoxysilane, 13.6 mmol; 1-hexene, 17.9 mmol; 80°C, 2 h.

acetylene was introduced at the rate of about 8 ml/min at 80°C or room temperature. The product was filtered, and fractionated to give vinyltriethoxysilane, b.p. 63°C/24 mmHg (62.5–63°C/20 mmHg [13]), and 1,2-bis(triethoxysilyl)ethane, b.p. 124°C/16 mmHg n_D^{20} 1.4062 (102–103°C/5 mmHg; n_D^{20} 1.4052 [14]). The yields were determined by GLC.

Results and discussion

Pt, Rh and Pd complexes of "Si"-SH were used as catalysts for addition of triethoxysilane to 1-hexene. The results are shown in Table 2. As can be seen, the Pt complex was the most active catalyst for this reaction.

The relationship between the atomic ratio of S/Pt in the complex and the yield of n-hexyltriethoxysilane is shown in Fig. 1. An increase in the atomic ratio of S/Pt in the complex decreases the yield of n-hexyltriethoxysilane in the range of 4 to 12 S/Pt atomic ratio. In other words, a decrease of the S/Pt atomic ratio increases the catalytic activity of the complex. However, another experiment showed that the complex was unstable during the hydrosilylation when the S/Pt atomic ratio was less than 4.

If the reaction was carried out at 80°C for 2 h, over 90% yield was obtained. However, the reaction was also carried out at room temperature as shown in Fig. 2.

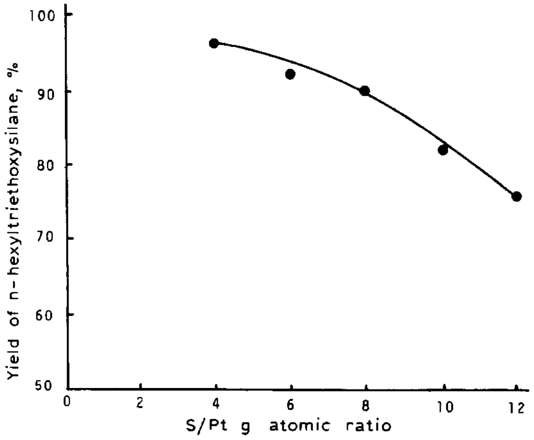


Fig. 1. The relationship between the atomic ratio of S/Pt in "Si"-SH-Pt and the yield of n-hexyl-triethoxysilane. Pt, 0.0026 mg atom; triethoxysilane, 13.6 mmol; 1-hexene, 17.9 mmol; 80°C, 2h.

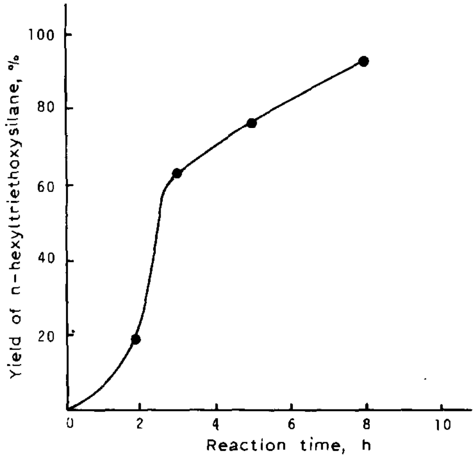


Fig. 2. Addition of triethoxysilane to 1-hexene at room temperature. S/Pt atomic ratio in "Si"-SH-Pt, 6; Pt, 0.026 mg atom; triethoxysilane, 13.6 mmol; 1-hexene, 17.9 mmol.

Over 90% yield was also obtained after 8 h.

The stabilities of "Si"-NH_2-Pt and "Si"-SH-Pt in the addition reaction of triethoxysilane to 1-hexene are shown in Fig. 3. The former was reused five times (turnover numbers achieved were about 2,000). However, the catalytic activity decreased remarkably when it was reused six times. The latter was reused 20 times (turnover numbers achieved were about 10,000) without any appreciable loss in the catalytic activity.

From the point of view of practical application, the stability of polymer-supported metal catalyst is a very important problem. However, as far as we know, there are no satisfactory data on this problem. Thus, our above experimental results may offer some promise for obtaining stable polymer-supported metal catalyst for use in industry.

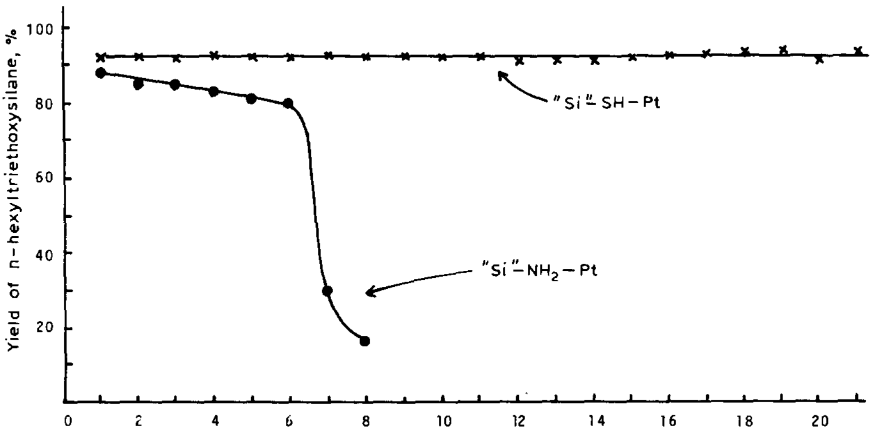


Fig. 3. The stabilities of "Si"-SH-Pt and "Si"-NH_2-Pt in the addition reaction of triethoxysilane to 1-hexene. Pt, 0.026 mg atom; triethoxysilane, 13.6 mmol; 1-hexene, 17.9 mmol; 80°C, 2h.

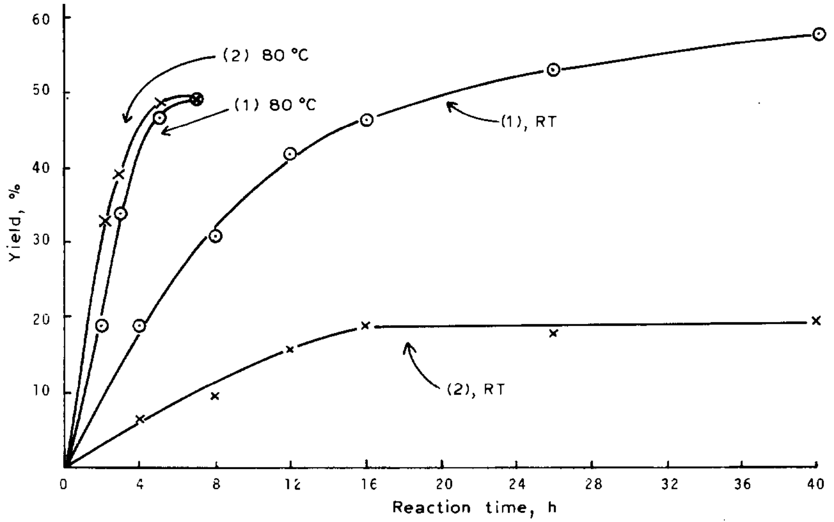


Fig. 4. Addition of triethoxysilane to acetylene catalyzed by "Si"-SH-Pt. (1) $CH_2{=}CHSi(OC_2H_5)_3$, (2) $((C_2H_5O)_3SiCH_2)_2$. S/Pt, 6; Pt, 0.026 mg atom; triethoxysilane, 34.7 mmol.

The results on the addition of triethoxysilane to acetylene are shown in Fig. 4. When the reaction was carried out at 80°C, vinyltriethoxysilane and bis(triethoxysilyl)ethane were obtained in 50% and 50% yields, respectively, in 7 h. At room temperature, vinyltriethoxysilane was obtained in ca. 60% yield in 40 h. However, the yield of bis(triethoxysilyl)ethane was only 20%. In other words, at room temperature the reaction proceeded slowly, but the yield of the main product, vinyltriethoxysilane, was somewhat higher, and the yield of byproduct, bis(triethoxysilyl)ethane, was lower.

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