



Silica-supported Karstedt-type catalyst for hydrosilylation reactions

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Abstract

The preparation, properties, catalytic kinetics and use as a hydrosilylation catalyst of a silica-supported Karstedt (Pt)-type catalyst are reported. This type of catalyst has high catalytic activity at room temperature under an atmospheric pressure, and the catalyst can be reused five times without any appreciable loss in the catalytic activity.

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1. Introduction

Hydrosilylation is one of the most important Si–C bond formation reactions in organosilicon chemistry [1]. Many silicon monomers containing functional groups have been synthesized via this reaction. Polymer bound transition metal complexes for hydrosilylation have been studied since Haag first reported such a catalyst in the 1960s [2–6]. Karstedt's catalyst, $\text{Pt}_2\{[(\text{CH}_2=\text{CH})\text{Me}_2\text{Si}]_2\text{O}\}_3$, is a particularly efficient homogeneous catalyst for hydrosilylation [7].

Herein we report preparation of a heterogeneous catalyst which is modeled after the Karstedt catalyst. Vinylsiloxane groups have been bonded to the surface of fume silica by treatment with vinyltriethoxysilane. Further treatment of this

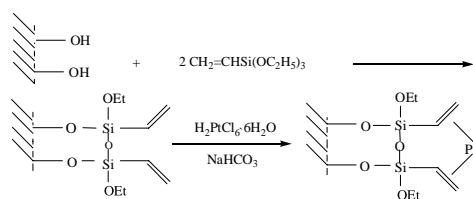
material with an aqueous solution of chloroplatinic acid leads to formation of a heterogeneous Karstedt like catalyst. The resulted silica-supported Karstedt-type catalyst is very effective for hydrosilylation reaction. Preparation of the silica support catalyst is outlined below (Scheme 1).

2. Experimental

Styrene, 1,3-divinyl-1,1,3,3-tetramethyldisiloxane, methyl methacrylate (MMA), Fume silica (surface area 150–200 m^2/g) and vinyltriethoxysilane were purchased from Shenyang Chemical Combination Factory and Hetou Petrochemical Factory, respectively. Vinyltriethoxysilane was redistilled prior to use. Vinyltrimethylphenylsilane was prepared by reaction of phenyl magnesium bromide with vinyltrimethylchlorosilane. Dimethylphenylsilane was prepared by reaction of magne-

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Scheme 1.

sium bromide with a twofold excess of dimethyldichlorosilane to form phenyldimethylchlorosilane. Phenyldimethylchlorosilane was purified by fractional distillation through a 15 cm vacuum jacketed Vigreux column. Reduction with lithium aluminum hydride gave the desired phenyldimethylsilane. ^1H NMR spectra were performed on AVANCE DMX500 instrument. Disappearance of starting materials and formation of products were recorded by gas liquid chromatograph on a SP-6800 A instrument equipped with capillary column (OV-17, 0.03 mm \times 30 m) and a TCD detector. The content of platinum in catalyst was detected on HITACHI 185-50 atomic absorption spectrophotometer (AAS).

Fume silica (6 g) was placed in toluene (140 ml) containing vinyltriethoxysilane (4 ml). The mixture was stirred and refluxed for 48 h, and then 30 ml of water was added. The aqueous reactant was stirred for another 48 h. The solution was then cooled to room temperature, and filtered. The solid was dried under vacuum (120 $^\circ\text{C}$, 26 Pa) for 3 h. It was then washed with 3 \times 60 ml of acetone, and dried under high vacuum. The silica, a white powder, 6.6 g (**1**) was obtained.

A mixture of sodium bicarbonate (0.006 g), $\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$ (0.02 g), **1** (0.4 g) and ethanol (30 ml) were mixed and stirred for 24 h at room temperature. The solution was then decanted from the fume silica and the silica was washed with 5 \times 20 ml of aqueous ethanol. It was then dried under vacuum (70 $^\circ\text{C}$, 26 Pa) to yield the desired silica bonded Karstedt-type Pt complex (**2**). The content of platinum in catalyst was 1.9% by AAS detection.

Dimethylphenylsilane (3 mmol), styrene (3 mmol) and **2** (0.02 g) were mixed and stirred in vessel (5 ml) at 30 $^\circ\text{C}$. Hydrosilylation products were obtained by fractional distillation. Gas chromatograph was employed to follow the course of the reaction by both the appearance of product and the disappearance of starting materials. The reaction was stopped when

the peak area of the products did not increase. The structures of desired product was confirmed by ^1H NMR of CDCl_3 solutions. Similar reactions were carried out at 0, 10, 20 and 30 $^\circ\text{C}$ in order to determine the effect of temperature on the reaction rates.

Similar reactions with dimethylphenylsilane were carried out with vinyl dimethylphenylsilane, 1,3-divinyl-1,1,3,3-tetramethyldisiloxane, MMA and allylepoxypropylether which were used instead of styrene. In these olefins, methyl methacrylate was the least active.

3. Results and discussions

Regioselective addition products (α -addition product and β -addition product) might be obtained for terminal alkenes when dimethylphenylsilane reacted with styrene. Based on the ^1H NMR data, it was found that the main product was β -addition product and there were rarely α -addition product. This is due to steric effects of the reactants. The highly regioselective result indicated that the silica-supported Karstedt catalyst have good selectivity.

Catalytic kinetics of hydrosilylation of Me_2PhSiH with styrene was studied. Curve of conversion versus reaction time at different temperature was shown in Fig. 1. Reaction rate was increased while reaction temperature increased. Based on Fig. 1, a chart of $1/1 - P$ versus t (Fig. 2) was made. From the Fig. 2, it clearly shows this is a second-order reaction. The second-order rate coefficients were listed in Table 1. Fig. 3 shows $\ln k$ versus $1/T$, the activation energy of this was calculated to 93.32 kJ/mol.

Result based on various olefins with Me_2PhSiH were shown in Fig. 4. We found the activity of styrene is higher than that of others and over 90% conversion was obtained within 70 min at 20 $^\circ\text{C}$. On the other

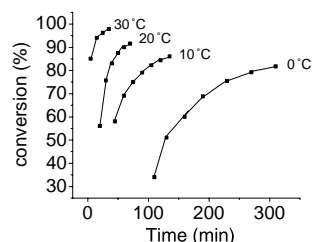


Fig. 1. Time versus conversion in the hydrosilylation of Me_2PhSiH with St.

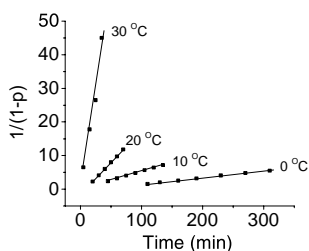


Fig. 2. Time versus $1/(1-P)$ in the hydrosilylation of Me_2PhSiH with St.

Table 1
The second-order rate coefficients

Temperature (°C)	k ($\text{mol l}^{-1} \text{s}^{-1}$)
0	0.67×10^{-4}
10	1.80×10^{-4}
20	7.07×10^{-4}
30	3.93×10^{-3}

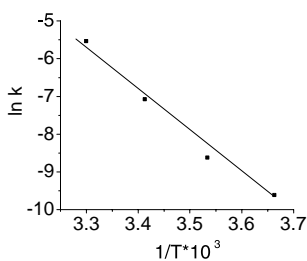


Fig. 3. $\ln k$ versus $1/T$.

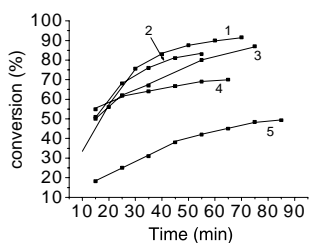


Fig. 4. The hydrosilylation results of various olefins with Me_2PhSiH . 1, styrene; 2, vinyl dimethylphenylsilane; 3, 1,3-divinyl-1,1,3,3-tetramethyldisiloxane; 4, allylepoxypropylether; 5, MMA. Reaction temperature of methyl methacrylate is 70 °C, others are 20 °C.

hand, 49% conversion was obtained within 85 min at 70 °C in the hydrosilylation of methyl methacrylate with Me_2PhSiH . 87% conversion was obtained within 75 min at 20 °C in the hydrosilylation of 1,3-divinyl-1,1,3,3-tetramethyldisiloxane with Me_2PhSiH . 70% and 83% conversion were reached in

Table 2
Result of the reuse test

Reuse cycles	Conversion
1	92.5
2	92.0
3	91.0
4	93.0
5	91.5

the hydrosilylation of allylepoxypropylether and vinyl dimethylphenylsilane with Me_2PhSiH , respectively. Styrene is most active towards the hydrosilylation reaction while MMA is the least active.

A reuse test of the catalyst was made in the hydrosilylation of styrene with dimethylphenylsilane at 20 °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 reactions were recharged, and the next cycle started. Catalyst activity of silica-supported Karstedt catalyst remained after five cycles. Result of reuse test was listed in Table 2.

4. Conclusion

A hydrosilylation catalyst of a silica-supported Karstedt (Pt)-type catalyst are prepared. Results demonstrate that this type of catalyst has high catalytic activity at room temperature under an atmospheric pressure, and the catalyst can be reused five times without any appreciable loss in the catalytic activity. $\text{H}_2\text{PtO}_6 \cdot 6\text{H}_2\text{O}$ is a useful catalyst for hydrosilylation in industry, but it cannot be reused. So the silica-supported Karstedt (Pt)-type catalyst will have good application in industry.

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