

# Effective heterogenization and catalytic use of active $C_5H_5NiLX$ complex for the hydrosilylation

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Received 9 August 2007; received in revised form 25 January 2008; accepted 20 February 2008

Available online 4 March 2008

## Abstract

An effective route was first developed to heterogenize active  $C_5H_5NiLX$  complex for the preparation of the solid catalyst  $\text{P}-CH_2C_5H_4NiPPh_3Cl$ . The attachment of the nickel complex onto the polymer was carefully characterized by IR, solid diffuse reflectance UV–vis,  $^{31}P$  CP MAS NMR spectra and ICP-OES elemental analysis, which proved that the present route was relatively simple and effective for the immobilization of active centers, and that the materials used was considerably cheap. Thus-prepared solid catalyst  $\text{P}-CH_2C_5H_4NiPPh_3Cl$  showed high activity, selectivity and an excellent recyclability for the hydrosilylation of alkenes with trichlorosilane at mild conditions, outstandingly overcoming the problem of homogeneous system. This is a key success to provide a new methodology for heterogenizing active homogeneous components.

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**Keywords:** Polystyrene beads; Immobilization; Heterogeneous solid nickel complex catalyst; Hydrosilylation

## 1. Introduction

The catalytic hydrosilylation applied to many industrial processes is the addition of Si–H across an unsaturated bond such as  $C \equiv C$ ,  $C=C$ ,  $C=O$  or  $C \equiv N$  promoted by transition-metal catalysts [1]. Although noble metal complexes (Pt, Pd, Ru, Rh, Ir and Os) are very active for the hydrosilylation [2], those are too expensive to be widely used in industry. Later, more attention was paid to cheaper transition metals, especially of nickel (Ni) complexes, which showed good activity and selectivity in some hydrosilylations. But, poor stability and easy loss of activity of those catalysts  $Ni(PR_3)_2Cl_2 + AlR_3$ ,  $CodNi(bipy)$  and  $(\eta^5-C_4H_7NiI)_2$  seriously limited their wide uses [3]. Since 1974, some relatively stable homogeneous nickel complexes with cyclopentadienyl ligand ( $C_5H_5NiLR$ ) have been synthesized [4].

Since the mid-1970s, the heterogenization of transition-metal complexes on solid supports has become a key challenge worldwide, because people believe the heterogenized catalyst can resolve the problem of homogeneous one in the separation and recycling. Pt-catalysts linked to inorganic or organic supports by using various functional groups were studied [5]. One report disclosed good activity, selectivity and stability of polystyrene resin-supported Pt-catalysts combined with nice recyclability in the solvent-free hydrosilylation of 1-octene with trichlorosilane [6]. Polysiloxane-supported ferrocenyl selenoether platinum was efficient for the hydrosilylation of olefins with triethoxysilane (TES) [7]. Immobilized analogues of Rh complexes catalyzed the hydrosilylation of TES with 1-hexene (>90% yield) [8]. Rh(I) complexes linked on polyamides containing a pyridine moiety were active for the hydrosilylation of phenylacetylene with TES [9]. Also, manganese complexes was immobilized for the hydrosilylation of terminal olefins, e.g. poly(siloxane)-linked decacarbonyl dimanganese catalyst [10]. Polymer anchored Ni(II) complex was

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synthesized by sequential attachment of *o*-phenylenediamine and nickel chloride to chloromethylated styrene-divinyl benzene copolymer with 6% cross-linking. The resulting catalyst was active for the oxidation of toluene to benzaldehyde [11]. Also, polystyrene supported nickel(II) carborane complexes were synthesized and used for the polymerization of olefins [12].

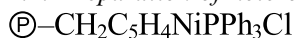
However, to date, no success has been reported on the immobilization of active nickel complex  $C_5H_5NiLX$  ( $L = PPh_3$ ,  $X = Cl$ ) onto the support for the hydrosilylation. Herein, we first described an efficient route to prepare an active heterogeneous  $\textcircled{P}-CH_2C_5H_4NiPPh_3Cl$  catalyst for the hydrosilylations at mild conditions. Thus-prepared solid catalyst could be easily recovered from the reaction mixture and reused without any appreciable loss of activity and selectivity.

## 2. Experimental

### 2.1. Materials

The main reagents used in the synthesis and catalytic reactions included chloromethylated polystyrene beads ( $\textcircled{P}-CH_2Cl$ , 17%Cl), dicyclopentadiene ( $C_{10}H_{12}$ , 99%),  $NaNH_2$  (99%), KOH (98%), triphenyl phosphine ( $PPh_3$ , 98%), glacial acetic acid (99%), nickelous chloride ( $NiCl_2 \cdot 6H_2O$ , 98%), methyl acrylate ( $CH_2=CHCOOCH_3$ , 99%), *n*-butyl acrylate ( $CH_2=CHCOOC_4H_9$ , 99%), styrene ( $PhCH=CH_2$ , 99%), cyclohexene ( $C_6H_{12}$ , 99%), trichlorosilane ( $Cl_3SiH$ , 98%, stored in a refrigerator), and some solvents like dry ethanol (>99.9%, pretreated with fresh CaO, then refluxed for 5 h together with Mg and  $I_2$  and redistilled), dry tetrahydrofuran (THF), dry *n*-hexane and dry benzene (pretreated with anhydrous  $MgSO_4$ , then refluxed for 5 days together with pure sodium threads and redistilled).

### 2.2. Preparation of heterogeneous solid catalyst



The synthetic route of heterogeneous catalyst is presented in Scheme 1, where all the syntheses were carried out in the presence of nitrogen or argon under anhydrous and oxygen-free conditions (unless specialized). Chlorome-

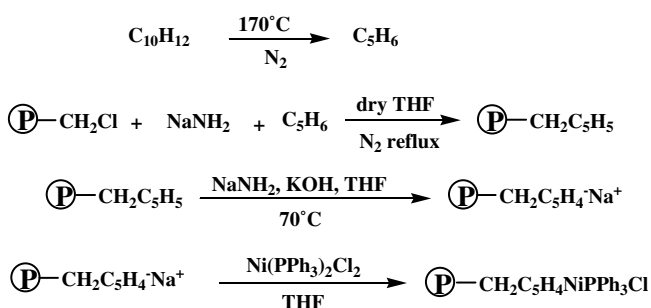
thylated polystyrene beads ( $\textcircled{P}-CH_2Cl$ , 17%Cl) were washed successively with 0.5 M sodium hydroxide solution (10%), 1 N hydrochloric acid solution, deionized water, ethanol and diethyl ether, and then dried to constant weight under reduced pressures. In a 250 ml four-necked flask mounted with a dripping funnel and a reflux condenser, 6 g (0.15 mol) of sodium amide and 5 g of chloromethylated beads (pretreated as stated above) were suspended in 100 ml of dry THF. Then was dropwise added with 15 ml (0.2 mol) of freshly-distilled cyclopentadiene at room temperature in nitrogen while magnetic stirring. The mixture was heated and refluxed for 4 days. Thereafter, the solution was filtered off, and the  $\textcircled{P}-CH_2C_5H_5$  beads were recovered. Subsequently, the latter underwent consecutive washing in a Soxhlet extractor with THF/water (4:1), ethanol, dry benzene, dry THF and drying in vacuo.

Six grams (25 mmol) of  $NiCl_2 \cdot 6H_2O$  were added to the mixed solution of 5 ml water and 125 ml glacial acetic acid under stirring, a light-green suspension was achieved. Then, was added with the solution of 13.1 g (50 mmol)  $PPh_3$  dissolved in 60 ml of glacial acetic acid under stirring, the dark-green precipitation occurred. The precipitate  $Ni(PPh_3)_2Cl_2$  was recovered by filtration, followed by washing with a little acetic acid and drying at 353 K under vacuum.

In a 50 ml three-necked flask with a reflux condenser, 5 g of  $\textcircled{P}-CH_2C_5H_5$  beads, 2 g of KOH and 2 g of  $NaNH_2$  were added into 40 ml of dry THF. The mixture were heated and refluxed for 4 days under argon atmosphere while stirring. Then,  $\textcircled{P}-CH_2C_5H_4Na^+$  was recovered by a careful separation under argon atmosphere, and subsequently washed three times with dry THF. Thereafter, the recovered solid was again suspended in 60 ml of dry THF under argon atmosphere and 8 g of  $Ni(PPh_3)_2Cl_2$  was carefully added. The stirring was continued for 4 days at room temperature under argon atmosphere. The  $\textcircled{P}-CH_2C_5H_4NiPPh_3Cl$  beads were recovered by filtration, washed several times with dry THF and dried in vacuo.

### 2.3. Characterization

Infrared/IR spectra were recorded on a Shimadzu IR Prestige-21 Fourier Transform Infrared spectrophotometer; the sample was ground with KBr and pressed into thin wafers. The scanning range was from 4000 to  $400\text{ cm}^{-1}$ , with a resolution of  $2\text{ cm}^{-1}$ . For the ultraviolet diffuse reflectance mode, the powdered solid sample was loaded into a quartz cell; UV-vis spectra of samples were recorded in the range of 800–190 nm referenced to  $BaSO_4$  on a Shimadzu UV-2550 spectrometer. The elemental analysis (nickel) was carried out by ICP-OES (inductively coupled plasma optical emission spectroscopy). Prior to determination, the sample was first calcined at 1073 K in air for decomposition, and then treated with concentrated nitric acid. The resulting solution was evaporated off, and the res-



Scheme 1. Synthetic route of heterogeneous solid catalyst.

idue was dissolved with deionized water to prepare a clear solution for ICP analysis. Thermal analysis was carried out on a Shimadzu DTG-60 thermogravimetric (TG) analyzer; the sample was heated to 1200 K with a heating rate of 20 K/min.  $^{31}\text{P}$  CP MASNMR was determined by an Inova-600 NMR spectrometer; the chemical shift (ppm) was referenced to 85%  $\text{H}_3\text{PO}_4$ .

#### 2.4. Catalytic hydrosilylations

The catalytic hydrosilylation of olefins with trichlorosilane was carried out in sealed Pyrex vials (5 ml), which were predried before use. In unspecialized cases, the reactions were carried out at 353 K for 6 h under optimal conditions (catalyst: 0.3 g, alkene: 3.72 mmol,  $\text{Cl}_3\text{SiH}$ :alkene = 1.2 (molar ratio)). The appropriate amount of catalysts was added into the vial under argon atmosphere, followed by adding freshly-distilled olefins, trichlorosilane and solvent. The vial was placed in a water bath and stirred for some time, then the solid catalyst was recovered by filtration, and the liquid products were analyzed by a GC-9800 gas chromatograph equipped with a packed column (SE-30, 2 m) and a TCD detector. Hydrogen was used as carrier gas, and toluene or chlorobenzene was used as internal standard to quantify the components. The conversion (mol%) of reactants and the selectivity of products were calculated accordingly.

### 3. Results and discussion

The synthesis was carried out according to the route as depicted in Scheme 1. Chlorine contents of the samples were determined by the method reported in the literature [10c,13]. Cyclopentadiene content could be obtained by comparing the difference of chlorine contents between the samples before and after the reaction. Thus, for  $\text{P}-\text{CH}_2\text{C}_5\text{H}_5$  the cyclopentadiene content was 3.83 mmol Cp/g. IR, UV-vis and  $^{31}\text{P}$  CP MASNMR spectra of all samples are illustrated

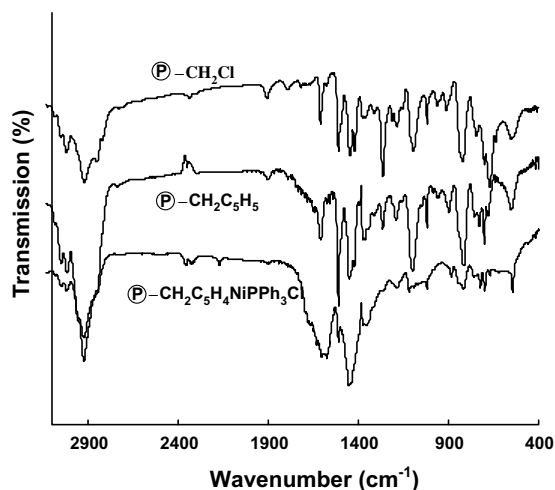


Fig. 1. Infrared spectra of support, intermediate and solid catalyst.

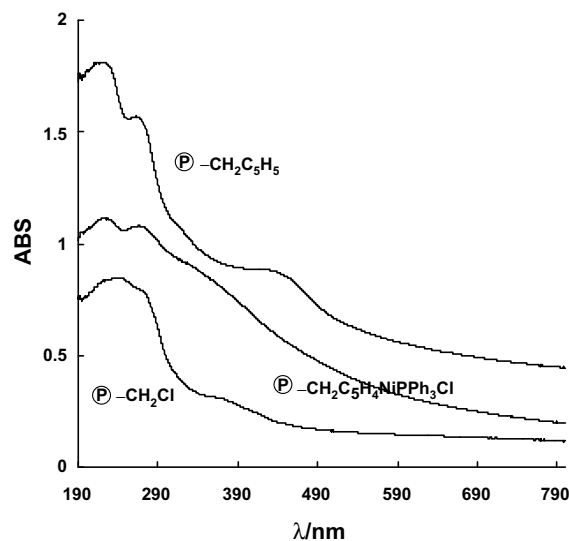


Fig. 2. UV-vis spectra of support, intermediate and solid catalyst.

in Figs. 1–3, which clearly show the success of immobilization by the present route. IR, UV-vis and  $^{31}\text{P}$  CP MASNMR spectral data of support, intermediates and solid catalysts are ascribed below.  $\text{P}-\text{CH}_2\text{Cl}$  IR (KBr) ( $\text{cm}^{-1}$ ): 2928.2  $\nu(\text{C}-\text{H})$ , 1612.8  $\nu(\text{C}=\text{C})$ , 1265.5, 672  $\nu(\text{C}-\text{Cl})$ ; UV-vis (nm): 250, 272, 385 (benzene ring);  $\text{P}-\text{CH}_2\text{C}_5\text{H}_5$  IR (KBr) ( $\text{cm}^{-1}$ ): 2928.2  $\nu(\text{C}-\text{H})$ , 1612.8  $\nu(\text{C}=\text{C})$ , 1265.5, 672  $\nu(\text{C}-\text{Cl})$ , nearly disappeared; UV-vis (nm): 230 (C=C), 270 (benzene ring), 475 (C=C);  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  UV-vis (nm): 209, 422 (Ni);  $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$  UV-vis (nm): 291 (benzene ring), 422 (Ni), 563;  $^{31}\text{P}$  CP MASNMR (ppm):  $-6.370$ ;  $\text{P}-\text{CH}_2\text{C}_5\text{H}_4\text{NiPPh}_3\text{Cl}$  IR (KBr) ( $\text{cm}^{-1}$ ): 2928.2  $\nu(\text{C}-\text{H})$ , 1608  $\nu(\text{C}=\text{C})$ , 1450  $\nu$  (benzene ring); UV-vis (nm): 225 (C=C), 267 (benzene ring), 340–430 (Ni);  $^{31}\text{P}$  CP MASNMR (ppm):  $-23.429$ ,  $-27.627$ . For  $\text{P}-\text{CH}_2\text{C}_5\text{H}_4\text{NiPPh}_3\text{Cl}$ ,  $^{31}\text{P}$  CP MASNMR contained two peaks emerging at  $-23.429$  ppm and  $-27.627$  ppm, showing that phosphorous was coordinated without the occurrence of oxidation but located in different chemical environments. The nickel content of  $\text{P}-\text{CH}_2\text{C}_5\text{H}_4\text{NiPPh}_3\text{Cl}$  was analyzed by ICP-OES to be  $8.35 \times 10^{-4}$  mol Ni/g. TG test in Fig. 4 showed good thermal stability of thus-prepared solid catalyst below 473 K, after which the weight loss was mainly concentrated between 500–900 K, while that of homogeneous  $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$  located in the range of 450–600 K. Note that our attempt to use benzene-Si PMO materials as supports suffered a failure due to the collapse of PMO structures acted with strong base  $\text{NaNH}_2$ .

We tested the catalytic activity of thus-prepared heterogeneous catalyst for the hydrosilylation of methyl acrylate with trichlorosilane with or without solvent at 338 K (suitable for all the solvents) for 6 h under identical conditions. When using toluene as the solvent, 69.3 mol% of methyl acrylate was converted, closely comparable to 69.4 mol% of conversion achieved by THF, slightly higher than 69.0 mol% of conversion in the case of either *n*-hexane as

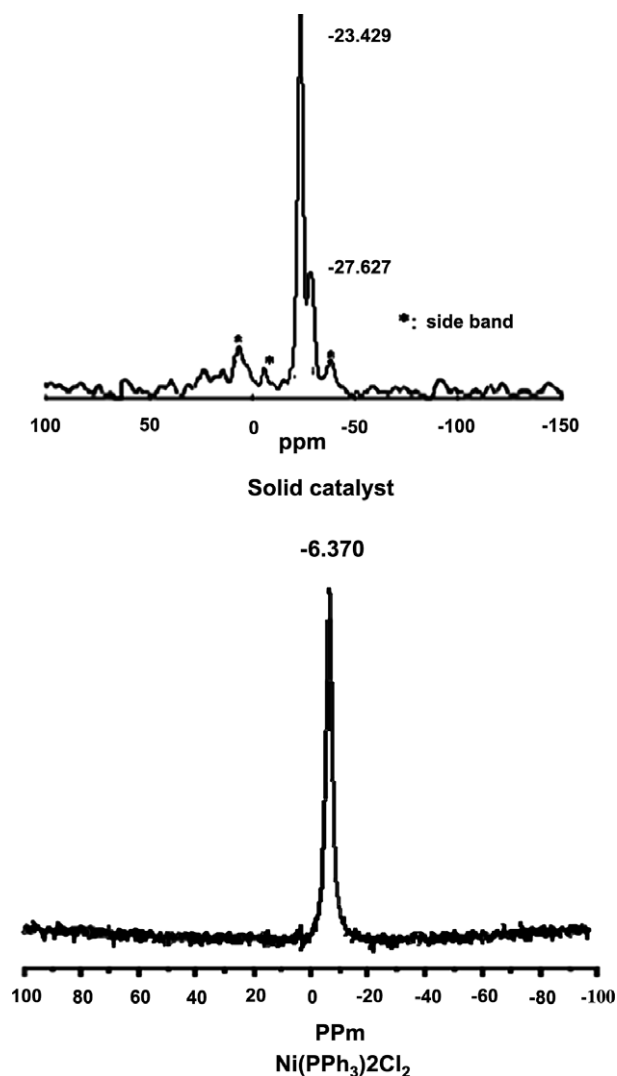


Fig. 3.  $^{31}\text{P}$  CP MAS NMR spectra of solid catalyst and  $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$ .

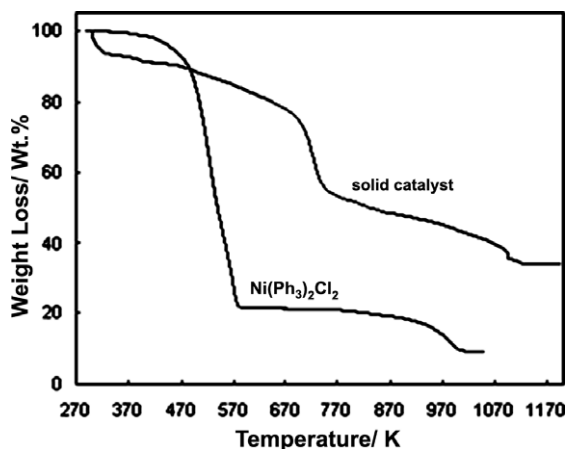


Fig. 4. TGA profiles of solid catalyst and  $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$ .

hydrosilylation could proceed very well without solvent; therefore, all the reactions were carried out in a green system without any solvent unless specialized. Actually, any solvent used in the hydrosilylation must undergo strict dehydration and degassing. Control experiments showed that both precursors  $\text{P}^{\ominus}\text{-CH}_2\text{Cl}$  and  $\text{P}^{\ominus}\text{-CH}_2\text{C}_5\text{H}_5$  were totally inactive for the hydrosilylation of methyl acrylate with trichlorosilane (353 K for 6 h), and that the catalytic activity of  $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$  was also extremely low (6.6 mol% conversion). However, the heterogenized solid catalyst  $\text{P}^{\ominus}\text{-CH}_2\text{C}_5\text{H}_4\text{NiPPh}_3\text{Cl}$  achieved a high conversion of 81.0 mol% under identical conditions, quite comparable to 85.3 mol% of homogeneous  $\text{C}_5\text{H}_5\text{NiPPh}_3\text{Cl}$  catalyst. Similarly, both catalysts selectively promoted the  $\alpha$ -addition product (methyl (3-trichlorosilyl-) propionate) with a selectivity of 100%. Compared with heterogeneous  $\text{P}^{\ominus}\text{-CH}_2\text{C}_5\text{H}_4\text{NiPPh}_3\text{Cl}$ , the synthesis of homogeneous analogue  $\text{C}_5\text{H}_5\text{NiPPh}_3\text{Cl}$  was quite difficult and one single route usually spent a time gap of 2–3 months. The main problem lied in difficult separation and purification of soluble components under anhydrous and oxygen-free conditions from a homogeneous system due to easy decomposition of intermediates [4].

When the molar ratio of  $\text{Cl}_3\text{SiH}$ : MA was 0.7, the conversion of methyl acrylate was only 50.1 mol%. Along with increasing the molar ratio of  $\text{Cl}_3\text{SiH}$ : MA from 0.7 to 1.2, the conversion gradually increased to 71.9 mol% (molar ratio = 1.0) and to 81.0 mol% (=1.2), respectively. Only  $\alpha$ -addition product (methyl (3-trichlorosilyl-) propionate) was detected with a selectivity of 100%. However, when the molar ratio of  $\text{Cl}_3\text{SiH}$ : MA was over 1.2, the conversion of methyl acrylate still kept a small increase to 81.4 mol% (molar ratio = 1.6) and to 81.7 mol% (=2.0), but the selectivity of  $\alpha$ -addition product stepwise decreased to about 98.7%. This is understandable that the increase of  $\text{Cl}_3\text{SiH}$  amount as one of both reactants enhanced the conversion of the other one, but meanwhile promoted the occurrence of  $\beta$ -addition. The effect of reaction temperature on the hydrosilylation of methyl acrylate with trichlorosilane (molar ratio = 1.2) was also studied. Distinctly, the reaction could not occur at 273 K at all. When the temperature increased from 313 to 353 K, the conversion of methyl acrylate exhibited an increase from 38.9 mol% (313 K) to 76.1 mol% (343 K) and to 81.0 mol% (353 K), respectively. In the temperature zone from 273 to 353 K, the selectivity of  $\alpha$ -addition product had kept at a level of 100%. Along with a continuous increase of temperature to 373 K, the conversion still showed a small increase to 81.9 mol% (363 K) and to 82.2 mol% (373 K), while the selectivity of  $\alpha$ -addition product slightly decreased to about 98.0% with 2.0% of  $\beta$ -addition product. We investigated the effect of reaction time on the hydrosilylation of methyl acrylate with trichlorosilane. The conversion of methyl acrylate showed a continuous increase from 49.1 mol% (2 h) to 75.9 mol% (4 h), and to 81.0 mol% (6 h). When the reaction time was prolonged to 8 h, the conversion merely increased to 81.4 mol%; however, the selectivity had kept at the level

the solvent or no solvent. In any case, GC detected only one product (methyl (3-trichlorosilyl-) propionate) with a selectivity of 100% without any by-product. Since the

Table 1  
The hydrosilylation of various alkenes with  $\text{Cl}_3\text{SiH}$

Substrates	Conversion (mol%)	Selectivity (%)	TON
Methyl acrylate	81.0	100	12.03
<i>n</i> -Butyl acrylate	63.1	100	9.38
Styrene	54.7	100	8.13
Cyclohexene	39.2	100	5.82

of 100% within 8 h. The hydrosilylation of methyl acrylate with trichlorosilane could not happen without the addition of catalyst, which confirmed the necessity of catalyst for the reaction. The use of 0.1 g of catalyst led to a low conversion of 29.7 mol%. When the amount of catalyst was increased to 0.2 g, the conversion was doubled to 59.8 mol%. Along with increasing the amount of catalyst

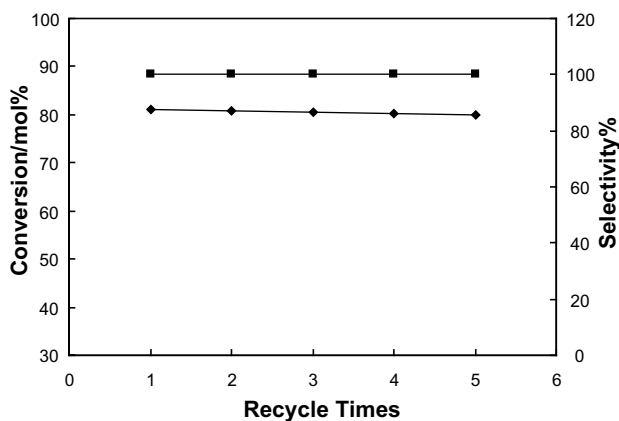
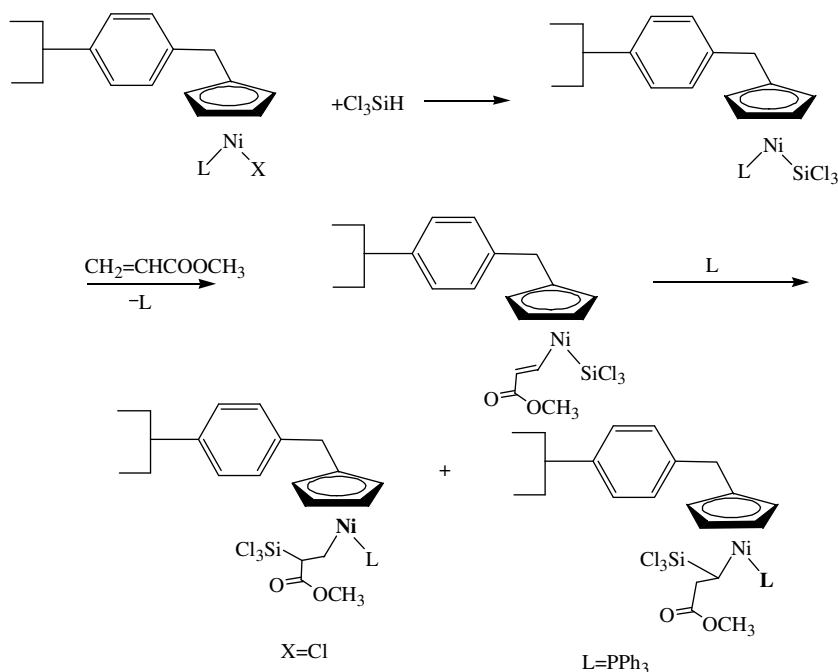


Fig. 5. Recycling experiments of thus-prepared catalyst. (353 K for 6 h, 0.3 g cat., molar ratio = 1.2; symbols ■: selectivity, ◆: conversion).

to 0.3 g, the conversion was notably increased to 81.0 mol%. Thereafter, even though the amount of catalyst was largely increased to 0.5 g, the conversion increased to only 81.3 mol%, in which the increment of 0.2 g catalyst resulted in a tiny increase of conversion of 0.3 mol%.

As presented in Table 1, the catalytic conversion of four substrates showed an order of methyl acrylate (81.0 mol%) > *n*-butyl acrylate (63.1 mol%) > styrene (54.7 mol%) > cyclohexene (39.2 mol%). Without exception GC detected only one product with 100% of selectivity, i.e. (1-trichlorosilyl-) ethyl benzene, trichlorosilyl cyclohexane, methyl (3-trichlorosilyl-) propionate and *n*-butyl (3-trichlorosilyl-) propionate. For 0.3 g of the catalyst, the number of active nickel centers equaled to 67.3 mmol Ni/mol alkene. Based on the actual conversions, the TON values were calculated to be 12.03 (methyl acrylate), 9.38 (*n*-butyl acrylate), 8.13 (styrene), and 5.82 (cyclohexene). Recycling experiments of the catalyst were carried out with repeated uses of the solid catalyst  $\text{P}^-\text{CH}_2\text{C}_5\text{H}_4\text{NiPPH}_3\text{Cl}$  in the hydrosilylation of methyl acrylate with trichlorosilane at 353 K for 6 h. After the catalyst was first used, it would be recovered by filtration under argon atmosphere, followed by washing several times with dry THF and drying at 353 K in a vacuum oven for 5 h before next use. Fig. 5 shows that the solid catalyst  $\text{P}^-\text{CH}_2\text{C}_5\text{H}_4\text{NiPPH}_3\text{Cl}$  was reused five times, the conversion of substrate varied merely in a small range of 80–81 mol% with a stable selectivity of 100% ( $\alpha$ -addition product), revealing an excellent recyclability of thus-prepared catalyst.

The catalyst was beneficial to the hydrosilylation of conjugate alkenes ( $\text{C}=\text{C}-\text{C}=\text{O}$ ) with silane, due to the fact that  $\text{C}=\text{C}$  bond linking with an electron-withdrawing  $\text{C}=\text{O}$  group is electron-deficient so that the neutrophilic



Scheme 2. Transition states of hydrosilylation on the solid catalyst.



addition occurs readily [1,2]. The mechanism of hydrosilylation catalyzed by the solid catalyst could be suggested to start from the heterolytic dissociation of  $\text{Cl}_3\text{SiH}$  into  $\text{Cl}_3\text{Si}^-$  and  $\text{H}^+$  acted on the active centers, then  $\text{Cl}_3\text{Si}^-$  would exert a neutrophilic attack to  $\text{C}=\text{C}$  bond of methyl acrylate to form two transition states (a) and (b) (in Scheme 2). The synergic cointeraction of electron-rich Ni–C bonding with electron-withdrawing  $-\text{COOCH}_3$  radical stabilized transition state (b) more than (a), i.e. the yield of  $\alpha$ -addition product dominated in certain a temperature range, quite maintaining the catalytic characteristics of homogeneous complex.

#### 4. Conclusions

In conclusion,  $\text{C}_5\text{H}_5\text{NiLX}$  ( $\text{L} = \text{PPh}_3$ ,  $\text{X} = \text{Cl}$ ) complex has been successfully immobilized to prepare a solid heterogeneous catalyst, in which the used materials were considerably cheap. The attachment of the nickel complex to the support was characterized by IR, solid UV–vis,  $^{31}\text{P}$  CP MASNMR spectra and ICP-OES elemental analysis. The supported solid catalyst showed high activity and selectivity for the hydrosilylation of olefins with trichlorosilane at mild conditions. Thus-prepared catalyst exhibited an excellent recyclability for the hydrosilylation of methyl acrylate with trichlorosilane at 353 K, overcoming the problem of homogeneous system. The hydrosilylation mechanism on the solid catalyst was suggested to start from the heterolytic dissociation of  $\text{Cl}_3\text{SiH}$  into  $\text{Cl}_3\text{Si}^-$  and  $\text{H}^+$  acted on the catalyst, then  $\text{Cl}_3\text{Si}^-$  would exert a neutrophilic attack to the substrate to form optimal product, which completely maintained the catalytic characteristics of homogeneous complex.

#### Acknowledgements

This work was supported by National Natural Science Foundation of China (no. 20673035), the 2007 excellent

mid-youth innovative team project of the Education Department of Hubei Province (no. T200701), and MOE Key Laboratory of Hubei University (no. 2006-KL-001).

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