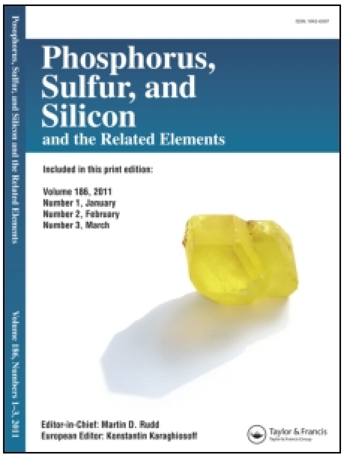

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Hydrosilylation Catalyzed with $Rh(PPh_3)_3Cl$/Ionic-Liquid-Functionalized SiO_2

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HYDROSILYLATION CATALYZED WITH $Rh(PPh_3)_3Cl$/IONIC-LIQUID–FUNCTIONALIZED SiO_2

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Ionic liquid–modified silica has been prepared by a "one-pot" reaction of activated silica, 3-chloropropyltriethoxysilane, and alkylimidazole or pyridine. It was found that the catalytic activity and β-adduct selectivity of the supported catalyst $Rh(PPh_3)_3Cl$/ionic-liquid–modified-SiO_2 for the hydrosilylation reaction of alkenes with triethoxysilane was significantly improved. Furthermore, the catalyst system could be recovered easily.

Keywords Hydrosilylation; ionic-liquid–functionalized SiO_2; recyclable; $Rh(PPh_3)_3Cl$

INTRODUCTION

Room temperature ionic liquids (ILs) have attracted considerable attention in recent years due to their special physical and chemical properties. Ionic liquids can give rise to a number of particular advantages over their molecular counterparts.[1,2] Although the application of ionic liquids in diverse areas has been well developed over the last two decades, some problems such as cost must be tackled, and better ways to recycle ionic liquids need to be found. Since 2001, many authors[3–5] have found that immobilization on solid materials such as SiO_2 can minimize the consumption of ionic liquids and facilitate the reuse of catalysts. Pyridium and imidazolium cation–based ionic liquid functionalized silica has been applied to several organic reactions, e.g., Kharasch addition,[6] Knovenagel condensation,[7] and hydroformylation,[8] as well as a new stationary phase for anion-exchange chromatography.[9]

Hydrosilylation is one of the most important reactions for Si—C bond formation in organosilicon chemistry.[10,11] Transition metal complexes have usually been applied as

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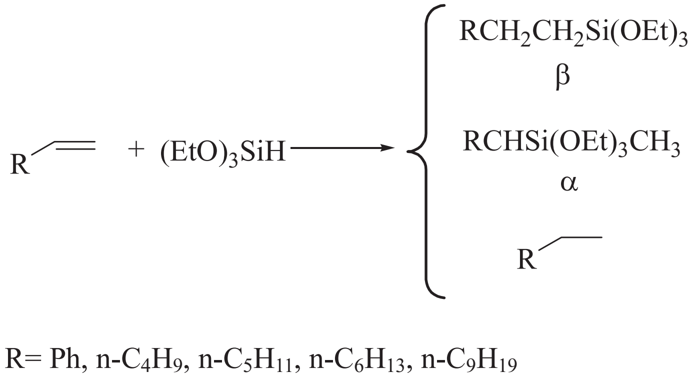
catalysts for hydrosilylation reactions. However, the types of hydrosilylation catalysts available are not beneficial for product separation and are expensive.[12,13] Very recently, Weyershausen et al.[14] reported that hydrosilylation reactions catalyzed with platinum complexes were remarkably improved by using ionic liquids as media. Also, hydrosilylation reactions catalyzed with $Rh(PPh_3)_3Cl$ in ionic liquids were studied in our laboratory.[15,16] Along with research to minimize the amount of ionic liquid and noble metal catalyst in hydrosilylation processes, we report in this article that IL-functionalized SiO_2 can be prepared by a one-step procedure. The $Rh(PPh_3)_3Cl$ was then supported on the IL-functionalized SiO_2 to obtain the $Rh(PPh_3)_3Cl$/IL-functionalized SiO_2 catalyst. Subsequently, the hydrosilylation of styrene and α-olefins with triethoxysilane catalyzed with this $Rh(PPh_3)_3Cl$/IL-functionalized SiO_2 catalyst was investigated (Scheme 1).



Scheme 1 Hydrosilylation of olefins with triethoxysilane.

RESULTS AND DISCUSSION

Infrared spectroscopy is a useful tool to confirm the chemical modifications proposed. Diffuse reflection infrared Fourier-transform spectra are shown in Figure 1 for silica before (**A**) and after the modification with *N,N′*-dialkylimidazolium chloride (**B**), *N,N′*-dialkylimidazolium hexafluorophosphate (**C**), *N*-alkylpyridinium chloride (**D**), and *N*-alkylpyridinium hexafluorophosphate (**E**).

Two new bands in the spectra of **B** and **C** at 1565 and 1160 cm^{-1} are assigned to the presence of the imidazolium ring. The new band in the spectra of **D** and **E** at 1490 cm^{-1} is assigned to the presence of the pyridinium ring. The new band in the spectra of **C** and **E** at 840 cm^{-1} is assigned to the presence of the hexafluorophosphate. These results demonstrate that the ILs were linked to the silica. Moreover, elemental analysis data and maximal theoretical values for IL-functionalized silica are in close agreement (Table I). The

Table I Elemental analysis data (%) of IL over silica supports

	C	H	N	IL/SiO_2 (wt.%)
B	5.35	0.66	1.69	9.60
C	4.11	0.61	1.05	9.60
D	6.67	0.53	0.85	9.55
E	4.04	0.41	0.60	10.84

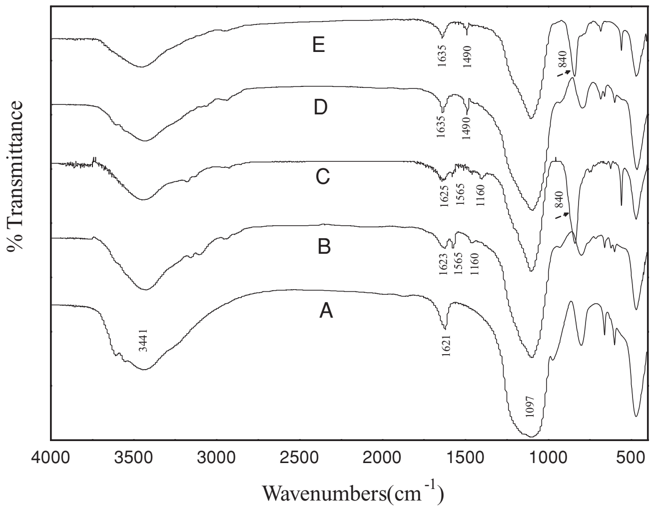
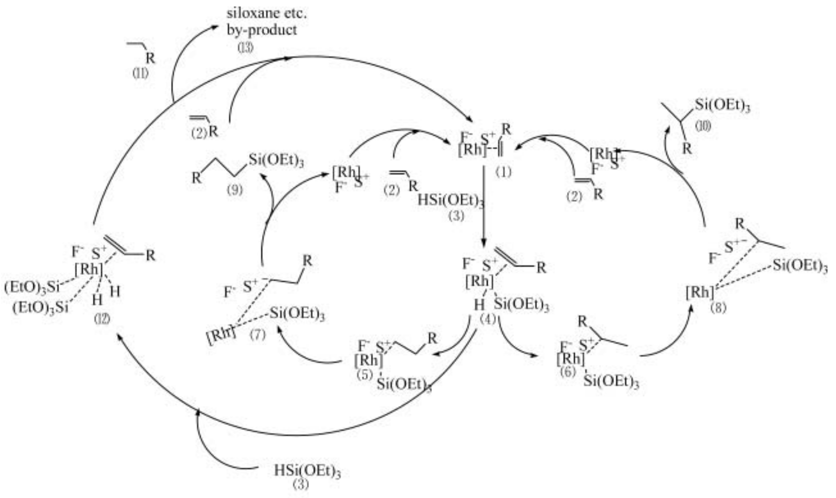


Figure 1 IR spectra of (**A**) unmodified silica; (**B**, **C**) methylimidazolium-functionalized silica; and (**D**, **E**) pyridinium-functionalized silica.

results prove that IL-functionalized silica material can be obtained by a one-pot reaction of silica, 3-chloropropyltriethoxysilane, and pyridine or *N*-methylimidazole.

Results on the hydrosilylation reaction of the alkenes with triethoxysilane catalyzed with $Rh(PPh_3)_3Cl/SiO_2$ are listed in Table II. These results indicate that the $Rh(PPh_3)_3Cl$/unmodified-SiO_2 catalyst alone exhibits only a low selectivity for the hydrosilylation of styrene. However, the $Rh(PPh_3)_3Cl$/modified-SiO_2 catalyst exhibits high catalytic activity and selectivity in alkene hydrosilylation reactions. Moreover, higher selectivity was obtained for hexafluorophosphate IL-functionalized silica. On the basis of these data, we propose the reaction mechanism shown in Scheme 2.



S$^+$: Pyridium and imidazolium cation-based ionic liquid functionalized silica
F$^-$: Cl$^-$, PF$_6^-$

Scheme 2 The reaction mechanism.

Table II Effect of unmodified silica and modified silica on the hydrosilylation reaction of styrene with triethoxysilane catalyzed with $Rh(PPh_3)_3Cl$

Entry	Amount of catalyst (g)	Conv. (%)	Selectivity (%) β	α	Alkane
1	$Rh(PPh_3)_3Cl$/A, 0.1	100	72.8	15.3	11.9
2	$Rh(PPh_3)_3Cl$/B, 0.1	100	86.8	2.4	10.8
3	$Rh(PPh_3)_3Cl$/C, 0.1	100	87.8	0.3	11.9
4	$Rh(PPh_3)_3Cl$/C, 0.05	92.4	87.6	0.3	12.1
5	$Rh(PPh_3)_3Cl$/C, 0.025	81.0	87.6	0.2	12.2
6	$Rh(PPh_3)_3Cl$/C, 0.01	60.8	87.6	0.2	12.2
7	$Rh(PPh_3)_3Cl$/D, 0.1	100	87.6	3.1	9.3
8	$Rh(PPh_3)_3Cl$/E, 0.1	100	91.3	0.5	8.2
9*	$Rh(PPh_3)_3Cl$/C, 0.1	100	87.7	0.4	11.9
10*	$Rh(PPh_3)_3Cl$/C, 0.1	100	87.7	0.4	11.9
11*	$Rh(PPh_3)_3Cl$/C, 0.1	100	87.8	0.4	11.8
12*	$Rh(PPh_3)_3Cl$/C, 0.1	100	87.8	0.3	11.9
13*	$Rh(PPh_3)_3Cl$/C, 0.1	100	87.7	0.3	12.0
14*	$Rh(PPh_3)_3Cl$/C, 0.1	100	87.7	0.4	11.9
15*	$Rh(PPh_3)_3Cl$/C, 0.1	100	87.7	0.3	12.0
16*	$Rh(PPh_3)_3Cl$/C, 0.1	100	87.7	0.4	11.9
17*	$Rh(PPh_3)_3Cl$/C, 0.1	99.9	87.7	0.4	11.9
18*	$Rh(PPh_3)_3Cl$/C, 0.1	99.5	87.7	0.4	11.9

Reaction conditions: styrene, 2.5 mmol; triethoxysilane, 3.0 mmol; 90°C, 2 h; Catalyst: 0.24% $Rh(PPh_3)_3Cl/SiO_2$.

*Recyclable of **C** catalytic system.

An IL membrane forms on the surface of SiO_2 after IL treatment. A possible reaction between this membrane and the central metal Rh could weaken the complexing ability of other ligands such as chloride, which would help to activate the alkene, and the electriferous IL membrane could stabilize the intermediate states. It can also be speculated that steric hindrance of the substituents attached to the cation membrane has some effect on the reaction pathway, and the selectivity of the formation of the β-adduct is increased. At the same time, some ethylbenzene was produced. The experimental details will be described and discussed in a subsequent article. The hydrosilylation reactions were examined in the presence of different amounts of rhodium loading (entries 3–6, Table II). It was found that the conversion of styrene increases with increasing amounts of rhodium loading, while the selectivity is almost constant.

Table III Effect of modified silica on the hydrosilylation reaction of alkenes with triethoxysilane catalyzed with $Rh(PPh_3)_3Cl$

Entry	Amount of catalyst (g)	Alkene	Conv. (%)	Selectivity (%) β	α	Alkane
1	$Rh(PPh_3)_3Cl$/B, 0.01	Hexene	100	93.6	—	6.4
2	$Rh(PPh_3)_3Cl$/B, 0.01	Heptene	100	93.3	—	6.7
3	$Rh(PPh_3)_3Cl$/B, 0.01	Octene	100	93.3	—	6.7
4	$Rh(PPh_3)_3Cl$/B, 0.01	Undecene	100	93.0	—	7.0

Reaction conditions: alkene, 2.5 mmol; triethoxysilane, 3.0 mmol; 90°C, 2 h; Catalyst: 0.24% $Rh(PPh_3)_3Cl/SiO_2$.

When aliphatic alkenes such as 1-hexene, 1-heptene, 1-octene, or 1-undecene instead of styrene are use as substrates, excellent conversions and selectivities are obtained with different $Rh(PPh_3)_3Cl/B$ also (Table III).

The use of $Rh(PPh_3)_3Cl$/modified-SiO_2 as a catalyst is advantageous for the product separation at the end of the reaction. In general, $Rh(PPh_3)_3Cl$/modified SiO_2 showed excellent stability for the hydrosilylation of styrene and triethoxysilane. For example, the $Rh(PPh_3)_3Cl/SiO_2{-}(CH_2CH_2CH_2)MimPF_6$ catalyst system could be recovered easily and reused more than 10 times without any notable loss of catalytic activity or selectivity (Table II).

CONCLUSION

The catalytic activity and the β-adduct selectivity of supported catalysts $Rh(PPh_3)_3Cl$/ionic-liquid–modified-SiO_2 for the hydrosilylation reaction of alkenes with triethoxysilane is significantly improved. The $Rh(PPh_3)_3Cl$/modified-SiO_2 catalyst system can be recovered easily and reused more than 10 times without any notable loss of catalytic activity or selectivity.

EXPERIMENTAL

Pretreatment of Silica

SiO_2 (200–300 mesh) was dried at 150°C in a vacuum to constant weight.

Preparation of IL-Functionalized Silica According to Scheme 3

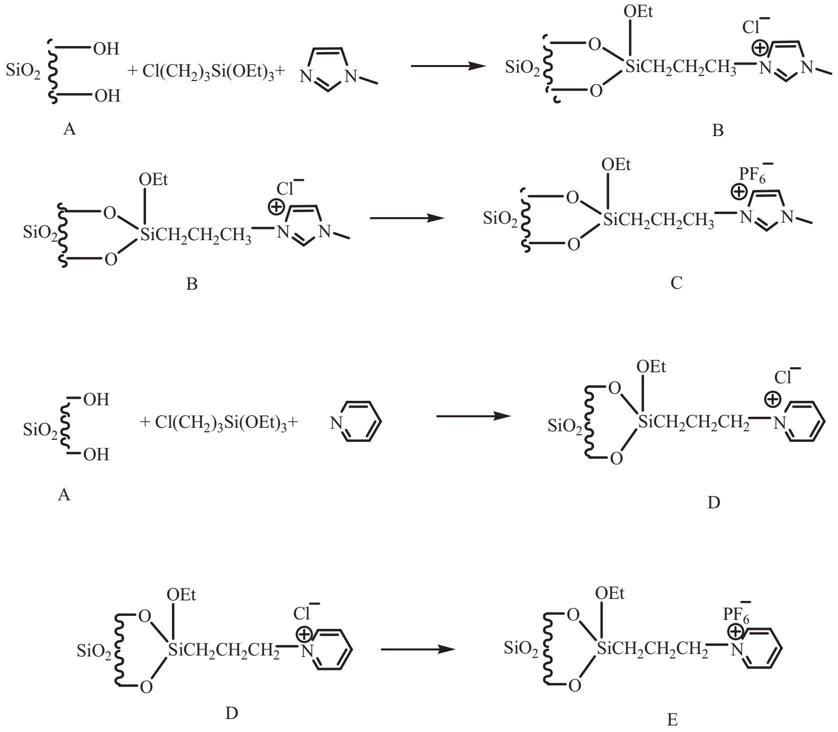
SiO_2 (5 g, 200–300 mesh), 3-chloropropyltriethoxysilane (0.95 g), and *N*-methylimidazole (0.31 g) or pyridine (0.32 g) were dissolved in acetone, then stirred for 2 h and evaporated under reduced pressure. The sample was placed in a 10-mL stainless steel autoclave, which was evacuated, sealed, and then heated to 110°C for 24 h. The residue was washed with ethyl acetate/diethyl ether and dried at 80°C in a vacuum for 24 h to afford **B** or **D**. **B** or **D** and NH_4PF_6 in H_2O were stirred overnight at room temperature. The residue was washed with H_2O and dried at 90°C in a vacuum for 24 h to afford **C** or **E**.

Preparation of the $Rh(PPh_3)_3Cl$-Modified-SiO_2 Catalyst

IL-functionalized silica (2 g) was mixed with $Rh(PPh_3)_3Cl$ (0.0048 g) in 10 mL of $CHCl_3$. The mixture was stirred overnight under nitrogen. The solvent was evaporated under reduced pressure and the residue dried at 90°C in a vacuum to afford the $Rh(PPh_3)_3Cl$/modified-SiO_2 catalyst.

Hydrosilylation of Alkenes with Triethoxysilane

A given amount of catalyst was charged into a 10-mL round-bottomed flask equipped with a magnetic stirrer, and the alkene and silane were added under ambient conditions. This mixture was heated to the desired temperature, and the hydrosilylation reaction proceeded with constant stirring for 2 h. At the end of the reaction, the product phase was separated



Scheme 3 Preparation of IL-functionalized silica.

from the catalyst by decantation, and the alkene conversion and selectivity were determined by GC-MS [Trace DSQ GC-MS system using a DB-5 column (30 m × 2.5 mm, 0.25 μm)]. The catalyst was recharged with fresh alkene and silane for the next catalytic run.

Characterization of IL-Functionalized Silica

Elemental analyses were performed on a VARIO EL-3 elemental analyzer and IR spectra were recorded on a Nicolet 5700 instrument.

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