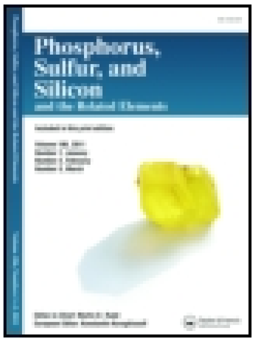

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The catalytic activity of alkali metal alkoxides and titanium alkoxides in the hydrosilylation of unfunctionalized olefins

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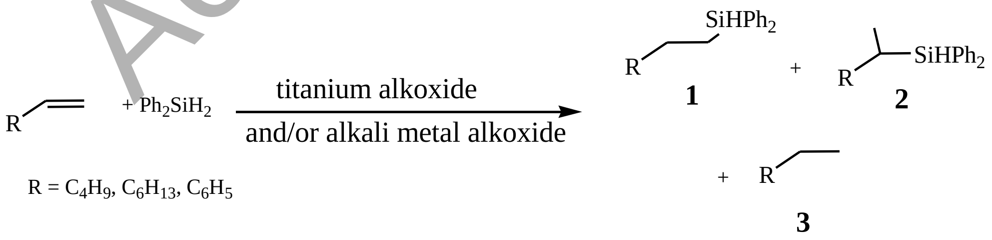
Abstract The catalytic activities of titanium alkoxides and alkali metal alkoxides for hydrosilylation of unfunctionalized olefins have been studied. Titanium(IV) alkoxides showed excellent catalytic activity, while alkali metal alkoxides have low catalytic activity for the hydrosilylation of olefins. However, by using titanocene dichloride as an additive, alkali metal alkoxides showed also excellent catalytic property for hydrosilylation. In comparison with titanium alkoxides, no α-adduct was obtained by using alkali metal alkoxides/Cp_2TiCl_2 as catalysts.



Keywords Hydrosilylation; Titanium alkoxide; Alkali metal alkoxide; Olefin

1. Introduction

Silicon-containing organic compounds and organosilicon polymers are of significant interest for their chemical, electronic, optical as well as physical properties [1]. The hydrosilylation of unsaturated bond, e.g. C=C, C=O, C≡C is an efficient method for preparing organosilicon compounds and polymers. The catalytic hydrosilylation of the carbon-carbon double bond has been widely studied and applied, and the hydrosilylation of the carbon carbon double bond was effectively promoted by transition metals including platinum and rhodium complexes [2,3]. However, the high cost of these noble metal complexes was the main drawback for their application in industrial processes [4,5]. Hence, an ongoing challenge is the development of low-cost metal catalyst system. Recently, the hydrosilylation of alkenes catalyzed with iron[6-8], cobalt[9-12] and nickel complexes [13] have been reported. Harder *et al* reported the first hydrosilylation catalysts based on alkaline-earth metals (Ca, Sr and Ba) [14]. The group Ⅳ transition metal complexes used as hydrosilylation catalysts had also been reported. Both dehydrogenative coupling of hydrosilanes and hydrosilylation reaction could be conducted in the presence of $Cp_2Ti(OPh)_2$ [15]. 1,4-Hydrosilylation of dienes can be carried out in the presence of Cp_2TiF_2 [16]. Silyltitanocene complexes [17] and metallocene-type Ti(Ⅲ) complexes [18] were reported to catalyze the hydrosilylation reaction under mild conditions and the results of $Cp_2MCl_2/n\text{BuLi}$ as a catalyst, have also been reported [19]. Considerable efforts are being made to develop the application group Ⅳ metal complexes as catalysts, and titanium alkoxides have been considered as Lewis acids for catalytic reactions and polymerizations [20-23]. Buchwald *et al* [24] reported that $Ti(O^iPr)_4$ could efficiently catalyze the hydrosilylation of carboxylic esters. Tertiary phosphine oxides could be reduced using hydrosiloxanes in the presence of a catalytic amount of titanium alkoxides [25-28].

In comparison to titanium alkoxides as a Lewis acid, alkali metal alkoxides are always used as organic bases as well as catalysts for catalytic reactions, e.g. transfer hydrogenation of ketones [29], hydrosilylation of ketones [30] and tertiary amides [31], Claisen-Tishchenko reaction [32] and hetero-Aldol-Tishchenko reaction [33]. Herein, we describe our investigation into the use of titanium alkoxides and/or alkali metal alkoxides as catalysts for the hydrosilylation of olefins (Scheme 1).

[Insert Scheme 1]

2. Results and discussion

Initially, the hydrosilylation of olefins in the presence of different titanium alkoxides was investigated (Table 1). The results indicated that $Ti(OEt)_4$ exhibits the highest catalytic activity among $Ti(OEt)_4$, $Ti(O^nBu)_4$ and $Ti(O^iPr)_4$, and α-adduct, β-adduct and hydrogenation product were detected, while no dehydrosilylation product **4** was detected (Entries 1-4, Table 1). Other hydrosilanes such as $(EtO)_3SiH$ and alkenes such as 1-octene and 1-dodecene were also examined under the same conditions (Entries 5-7, Table 1). While the polymerization of styrene was detected (Entry 8, Table 1), no reaction could be conducted by using cyclohexene nor Et_3SiH as one of the substrates.

[Insert Table 1]

Secondly, we examined the hydrosilylation of olefins catalyzed with alkali metal alkoxides and/or additives (Table 2). Lower conversion of 1-octene with high selectivity of β-adduct was obtained by using LiO^tBu or KO^tBu as catalyst (Entries 1-2, Table 2). Slightly enhanced catalytic activity of KO^tBu was observed in the presence of 1 mol% benzo-18-crown-6 (Entry 3, Table 2). Titanocene dichloride exhibits no catalytic activity for the hydrosilylation under the same conditions (Entry 4, Table 2). Titanocene dichloride can effectively improve the catalytic activity of alkali metal alkoxides (Entries 5-11, Table 2). When the amount of titanocene dichloride was increased from 1% to 3%, the conversion of 1-octene increased from 96.3% to 98.3% (Entries 5-7, Table 2). The catalytic activity of titanium alkoxides for hydrosilylation of 1-octene was determined in the initially experiments (Table 1) and furthermore, we examined the catalytic activity of alkali metal alkoxide combined with titanium alkoxide. However, depress of activity was observed when the mixture of two kinds of metal alkoxides was used as catalyst (Entries 12-14, Table 2). The formation of MTi(OR)$_5$ (M=Li, Na, K) or their dimeric complexes by reaction of alkali metal alkoxides with titanium alkoxides had been reported [34], which resulted in a reduced activity. Additionally, in comparison with titanium alkoxides, no α-adduct was obtained by using alkali metal alkoxides alone and alkali metal alkoxides/Cp_2TiCl_2 as catalysts.

[Insert Table 2]

Using LiO^{t}Bu/Cp_2TiCl_2 as catalyst, the influence of reaction temperature on the catalytic hydrosilylation of 1-octene with diphenylsilane was investigated (Table 3). The results indicated that activity increased along with the temperature raising from room temperature to 100 ℃.

[Insert Table 3]

To speculate the mechanism of catalytic reaction, Shimada *et al* [18] demonstrated that silyltitanium (Ⅲ) complex was the intermediate, therefore, the possible reaction path for hydrosilylation of olefin catalyzed with titanium alkoxides was proposed in Scheme 2. On the other hand, Okuda [35] reported that the alkali-metal silyl catalyzed the hydrosilylation of activated carbon carbon double bond and a silyl migration mechanism is operative. Thus, the mechanism of alkali metal alkoxides catalyzed hydrosilylation is proposed in Scheme 3.

[Insert Scheme 2]

[Insert Scheme 3]

To investigate the reaction mechanism, the ^{29}Si NMR of the reaction mixture (Cp_2TiCl_2+LiO^{t}Bu+Ph_2SiH_2 at 90℃ for 2h) were measured. Ph_3SiH (δ-18.85 ppm),

Ph_2SiH_2(δ-33.03 ppm), $(Ph_2SiH)_2$ (δ-34.73 ppm) and $Cp_2Ti(III)SiHPh$ (δ-23.42 ppm)[36] were determined. Thus the silyltitanium (III) complex as the intermediate was demonstrated. The ^{29}Si NMR of the reaction mixture [$Ti(OEt)_4$+ Ph_2SiH_2 at 90℃ for 2h] was also measured; the peak of δ-45.98～-45.83ppm should be attributed to $Ti(III)(OEt)_2SiHPh_2$, thus the low value titanium species should the intermediate. (Figures S 1 and S 2, Supplemental Materials).

3. Conclusion

In summary, the catalytic activities of titanium alkoxides for hydrosilylation of olefins has been studied. Titanium(IV) ethoxide showed the highest catalytic activity among the titanium alkoxides tested. The hydrosilylation of olefins catalyzed with alkali metal alkoxides and/or additives had also been investigated. By using titanocene dichloride as additive, alkali metal alkoxides showed excellent catalytic properties for hydrosilylation.

Experimental section

4.1 General information

Cp_2TiCl_2, LiO^tBu, NaO^tBu, KO^tBu, $Ti(OEt)_4$, $Ti(O^iPr)_4$, $Ti(O^nBu)_4$, cyclohexene, styrene, 1-octene, 1-hexene, 1-dodecene, diphenylsilane, $(EtO)_3SiH$ and other reagents were commercially available and were used without further purification.

^1H, ^{13}C and ^{29}Si spectra were measured using a Bruker AV400 MHz spectrometer operating at 400.1, 100.6 and 79.5MHz, respectively. GC-MS analysis on an Agilent 7890B-5977B apparatus equipped with a HP-5MS column (30 m × 0.25 mm × 0.25μm). Gas Chromatography: Trace DSQ GC Column = DB-5 30 m×2.5 mm×0.25 μm, split = 50:1, flow = 1 mL min^{-1} constant flow, inlet temperature = 260 ºC, column temperature = 50 ºC (hold 1 min) then 15 ºC min^{-1} up to 260 ºC (hold 10 min).

4.2 General procedure for the catalytic hydrosilylation of olefins

The calculated amount of catalyst was charged into a 10 mL round-bottomed flask equipped with magnetic stirring under nitrogen, and then olefin (4.0 mmol) and hydrosilane (4.4 mmol) were added into the flask. The resulting mixture was stirred at the desired reaction temperature for the desired time. At the end of the reaction, the reaction mixture was analyzed by GC/MS, and the conversion of alkene as well as the selectivity of products were determined by GC.

Acknowledgments

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Table 1 Hydrosilylation of olefins catalyzed with titanium alkoxides

Entry	$Ti(OR)_4$/mol%	Olefin	Silane	Conv (%)	Select.(%)		
					1	**2**	**3**
1	$Ti(OEt)_4$/3	1-octene	Ph_2SiH_2	85.7	86.0	10.7	3.3
2	$Ti(OEt)_4$/5	1-octene	Ph_2SiH_2	98.7	85.4(78.8)[b]	13.2	1.4
3	$Ti(O^{n}Bu)_4$/5	1-octene	Ph_2SiH_2	93.3	68.6	29.2	2.2
4	$Ti(O^{i}Pr)_4$/5	1-octene	Ph_2SiH_2	97.3	53.2	43.9	2.9
5	$Ti(OEt)_4$/5	1-octene	$(EtO)_3SiH$	58.1	81.4	/	18.6
6	$Ti(OEt)_4$/5	1-hexene	Ph_2SiH_2	99.5	75.6	22.9	1.5
7	$Ti(OEt)_4$/5	1-dodecene	Ph_2SiH_2	96.1	67.6	28.3	4.1
8[a]	$Ti(OEt)_4$/5	styrene	Ph_2SiH_2	/	/	/	/
9	$Ti(OEt)_4$/5	cyclohexene	Ph_2SiH_2	/	/	/	/
10	$Ti(OEt)_4$/5	1-octene	Et_3SiH	/	/	/	/

[a] Polymerization of styrene was determined

[b] isolated yield in bracket

Reaction conditions: olefin 4.0 mmol，hydrosilane 4.4 mmol，90°C, 12h

Table 2 Alkali metal alkoxides and/or additive catalyzed hydrosilylation of 1-octene

Entry	Alkali metal alkoxide/ mol%	Additive/mol%	Conv. (%)	Select.(%)		
				1	**2**	**3**
1	LiO^{t}Bu/5	/	17.0	100	/	/
2	KO^{t}Bu/5	/	15.2	100	/	/
3	KO^{t}Bu/5	Benzo-18-crown-6/1	28.6	100	/	/
4	/	Cp_2TiCl_2/3	/	/	/	/
5	LiO^{t}Bu/5	Cp_2TiCl_2/1	96.3	84.4	/	15.6
6	LiO^{t}Bu/5	Cp_2TiCl_2/2	96.8	84.9	/	15.1
7	LiO^{t}Bu/5	Cp_2TiCl_2/3	98.3	87.3	/	12.7
8	LiO^{t}Bu/4	Cp_2TiCl_2/3	80.6	86.5	/	13.5
9	LiO^{t}Bu/3	Cp_2TiCl_2/3	67.5	87.1	/	12.9
10	NaO^{t}Bu/5	Cp_2TiCl_2/3	99.3	85.4	/	14.6
11	KO^{t}Bu/5	Cp_2TiCl_2/3	97.4	86.3	/	13.7
12	LiO^{t}Bu/5	$Ti(OEt)_4$/0.5	30.4	100	/	/
13	LiO^{t}Bu/5	$Ti(OEt)_4$/1	/	/	/	/
14	LiO^{t}Bu/1	$Ti(OEt)_4$/5	71.9	86.4	7.5	6.1

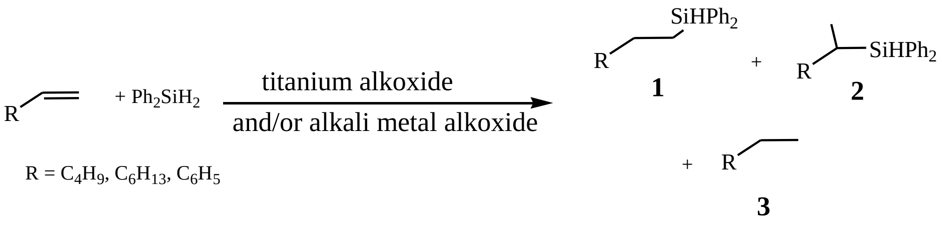
Reaction conditions: 1-octene 4.0 mmol，Ph_2SiH_2 4.4 mmol，90℃，6h.

Table 3 Influence of reaction temperature on LiO^{t}Bu/Cp_2TiCl_2 catalyzed hydrosilylation

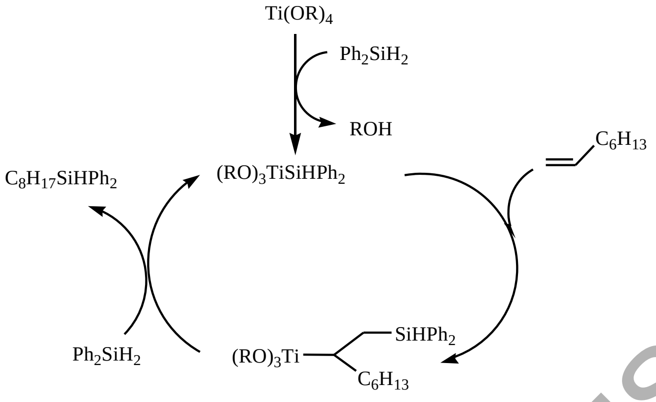
Entry	Temp.（℃）	Conv. (%)	Select.(%)		
			1	**2**	**3**
1	r.t.	/	/	/	/
2	50	73.7	84.5	/	15.5
3	70	93.9	86.4	/	13.6
4	80	94.0	84.8	/	15.2
5	90	98.2	87.4 (79.6)[a]	/	12.6
6	100	98.3	87.7	/	12.3

[a] isolated yield in bracket

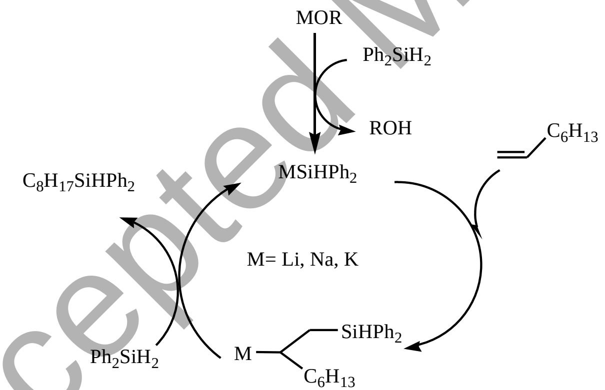
Reaction conditions: 1-octene 4.0 mmol，Ph_2SiH_2 4.4 mmol，Cp_2TiCl_2 3 mol %，LiO^{t}Bu 5 mol %, 6h.



Scheme 1 Hydrosilylation of olefins catalyzed with titanium alkoxides and /or alkali metal alkoxides



Scheme 2 Titanium alkoxide catalyzed hydrosilylation



Scheme 3 Alkali metal alkoxide catalyzed hydrosilylation