Alkylalumination of arylacetylene catalyzed by zirconocene catalysts supported on solid materials

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ABSTRACT

Zirconocene dichloride (Cp$_2$ZrCl$_2$) supported on montmorillonite K-10, which has previously been shown to be an efficient catalytic system for olefin polymerization, was found to be comparable to the highly activated homogeneous combination of Cp$_2$ZrCl$_2$ and methylaluminoxane (MAO), and more reactive than the originally reported homogeneous catalytic system of Cp$_2$ZrCl$_2$/Me$_3$Al in the methylalumination reaction of an aryl substituted terminal alkyne. Examination of solvent effects in the ethylalumination reaction using Cp$_2$ZrCl$_2$ supported on montmorillonite K-10, SiO$_2$/LiOH, and SiO$_2$/MgO, indicated that the anionic counterpart of the actual catalytically active zirconocenium cation is highly delocalized, thus suggesting that the actual active zirconocenium cation is only very weakly coordinating with the anionic moiety. This accounts for the high activity of systems using solids such as co-catalysts and as supporting materials in olefin polymerization in general.

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1. Introduction

Zirconocene catalysts have been attracting much attention due to their applications in olefin polymerization [1] and organic synthesis [2,3]. In these reactions, the zirconocene catalysts are generally used in a combination with trialkylaluminium. Disproportionation between the zirconocene catalysts and trialkylaluminiums afford monoalkyl zirconocenium cation intermediates (Cp$_2$ZrR$^+$) as the actual catalytic species [4]. In the olefin polymerization reaction, these monoalkyl zirconocenium cations have also been generated by the addition of co-catalysts such as borates, boranes, and methylaluminoxane (MAO), which also serve to "stabilize" the cations by forming weakly coordinating Lewis bases (Fig. 1) [5]. The necessity of heterogeneous systems for industrial gas phase and slurry processes in olefin polymerization has stimulated studies on supported zirconocene catalysts [6] and acidic catalysts such as clay have been found to be highly effective [7].

The Negishi carboalumination reaction (Scheme 1) has been widely used as a versatile method for introducing alkyl groups on to alkynes using zirconocene dichloride (Cp$_2$ZrCl$_2$) with alkylaluminiums [3,8,9]. Notable improvements to this reaction have been reported by Wipf and Lim who have disclosed that reactivity is significantly increased by using MAO in the place of Me$_3$Al [10], and by Lipshutz et al. who have found that the use of Cp modified catalysts improves the regioselectivity [9]. Otherwise there have been relatively few studies on modifications. In this study, we have examined how the reactivity would change upon using various supported zirconocene catalysts, which are useful for olefin polymerization.

2. Experimental

2.1. General

All reactions involving air- and moisture-sensitive reagents were carried out under N$_2$. Tetrahydrofuran (THF) was distilled after refluxing over Na-benzophenone prior to use. CH$_2$Cl$_2$ and benzene were distilled over CaH$_2$ prior to use.

^{1}H and ^{13}C NMR spectra were recorded at 500 and 125 MHz, respectively. The internal reference for ^{1}H NMR spectra was 0.0 ppm (Me$_4$Si) for CDCl$_3$. Chemical shifts for ^{13}C NMR spectra were referenced to CDCl$_3$ (77.0 ppm). MS were recorded under electron ionization (EI; 70 eV) conditions. SiO$_2$ (P-10) [11] was purchased from Fuji Silysia Chemicals Co. Montmorillonite K-10 [12] was purchased from Aldrich and dried at 220 °C for 2 h under reduced pressure.

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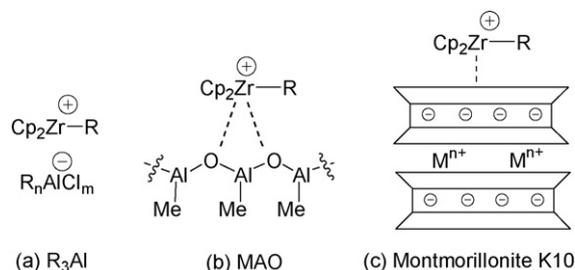**Fig. 1.** Examples of ion pairs between zirconium monoalkyl cation (Cp$_2$ZrR$^+$) and co-catalysts.

2.2. Preparation of modified solid materials

2.2.1. SiO$_2$ modification with MAO (SiO$_2$/MAO)

5.8 g of SiO$_2$ (P-10) and 9.0 mL of MAO (19.5 wt% MAO in toluene) were mixed at 40 °C to give a slurry. The slurry was then dried at 40 °C in vacuo. The resulting solid, SiO$_2$/MAO, was stored under nitrogen.

2.2.2. SiO$_2$ modification with LiOH (SiO$_2$/LiOH) [11]

1 g of SiO$_2$ (P-10) and 71.4 mg of LiOH were mixed in 20 mL of H$_2$O and the mixture was refluxed for 4 h. Then the mixture was heated to 150 °C with an oil bath to remove H$_2$O, to furnish a white solid. The solid was dried for an additional 2 h at 200 °C in vacuo and the resulting solid was stored under nitrogen.

2.2.3. SiO$_2$ modification with MgO (SiO$_2$/MgO) [11]

1 g of SiO$_2$ (P-10) and 0.12 g of MgO were mixed in 20 mL of H$_2$O and the mixture was refluxed for 1 hour. Then the mixture was heated to 150 °C with an oil bath to remove H$_2$O, to furnish a white solid. The solid was dried for an additional 2 h at 200 °C in vacuo and the resulting solid was stored under nitrogen.

2.3. General procedure for the alkylalumination of acetylene 1

2.3.1. Homogeneous alkylalumination

To a solution of Cp$_2$ZrCl$_2$ (0.1 equiv.) was added trialkylaluminium (2.0 equiv., Me$_3$Al: 2.0 M in hexane, Et$_3$Al: 1.0 M in hexane, MAO: 6.5 wt% in toluene) at room temperature. After stirring the

mixture for 1 h, a solution of acetylene 1 was added at room temperature. The reaction mixture was stirred at room temperature and quenched with 1N HCl at 0 °C. The resulting mixture was extracted with Et$_2$O. The combined organic layer was washed with H$_2$O and brine, dried over MgSO$_4$, and evaporated. The resulting residue was purified by silica gel column chromatography.

2.3.2. Heterogeneous alkylalumination

Trialkylaluminium (2.0 equiv.) was added to a solid material (100.0 mg) in a solvent at room temperature. After stirring the mixture for 1 h, Cp$_2$ZrCl$_2$ (0.1 equiv., 25.0 mg, 85 μmol) was added. To the mixture was added acetylene 1 (135.0 mg, 0.85 mmol). The reaction mixture was stirred at room temperature and quenched with 1N HCl at 0 °C. The resulting mixture was filtered through Celite and the filtrate was extracted with Et$_2$O. The combined organic layer was washed with H$_2$O and brine, dried over MgSO$_4$, and evaporated. The resulting residue was purified by silica gel column chromatography.

2.3.3. 2-(4-tert-Butylphenyl)-1-propene (2a) [13]

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.44–7.33 (m, 4 H), 5.35 (s, 1 H), 5.04 (dq, J = 3.0, 1.5 Hz, 1 H), 2.14 (s, 3 H), 1.32 (s, 9 H).

2.3.4. 2-(4-tert-Butylphenyl)-1-butene (2b) [14]

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.38–7.33 (m, 4 H), 5.27 (s, 1 H), 5.02 (q, J = 1.5 Hz, 1 H), 2.51 (q, J = 7.4 Hz, 2 H), 1.32 (s, 9 H), 1.11 (t, J = 7.4 Hz, 3 H).

2.4. (1E)-1-(4-tert-Butylphenyl)-1-butene (2c) [15]

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.33–7.26 (m, 4 H), 6.35 (d, J = 16.0 Hz, 1 H), 6.22 (dt, J = 16.0, 6.5 Hz, 1 H), 2.25–2.18 (m, 2 H), 1.31 (s, 9 H), 1.08 (t, J = 7.5 Hz, 3 H).

2.5. (1Z)-1-(4-tert-Butylphenyl)-1-butene (2d) [15]

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.33–7.26 (m, 4 H), 6.34 (d, J = 11.4 Hz, 1 H), 5.61 (dt, J = 11.4, 7.3 Hz, 1 H), 2.39–2.32 (m, 2 H), 1.31 (s, 9 H), 0.88 (t, J = 7.5 Hz, 3 H).

2.6. 1-tert-Butyl-4-vinylbenzene (2e) [16]

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.35 (s, 4 H), 6.70 (dd, J = 17.7, 11.0 Hz, 1 H), 5.70 (dd, J = 17.7, 1.0 Hz, 1 H), 5.19 (dd, J = 11.0, 1.1 Hz, 1.0 H), 1.32 (s, 9 H).

2.7. 2,4-Bis-(4-tert-butylphenyl)-1,3-hexadiene (2f)

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.44–7.28 (m, 8 H), 6.40 (s, 1 H), 5.61 (s, 1 H), 5.19 (s, 1 H), 2.66 (q, J = 7.5 Hz, 2 H), 1.34 (s, 9 H), 1.32 (s, 9 H), 0.97 (t, J = 7.5 Hz, 3 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 150.7, 150.1, 145.0, 144.9, 139.1, 137.9, 126.9, 126.2 (×2), 126.1 (×2), 125.2 (×2), 125.1 (×2), 113.1, 34.5, 34.5, 31.4 (×3), 31.3 (×3), 23.2, 13.9; HR-EIMS m/z: calcd. for C$_{26}$H$_{34}$ [M$^+$] 346.2661. Found 346.2657.
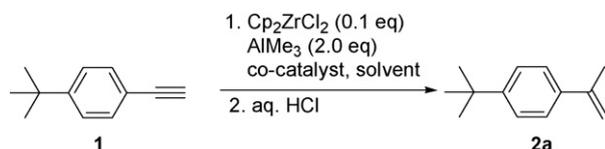
2.8. 1-(4-tert-Butylphenyl)-1-butanone (3) [17]

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.92–7.89 (m, 2 H), 7.49–7.45 (m, 2 H), 2.93 (t, J = 7.2 Hz, 2 H), 1.81–1.83 (m, 2 H), 1.34 (s, 9 H), 1.00 (t, J = 7.4 Hz, 3 H).

2.9. 3-(4-tert-Butylphenyl)-3-buten-1-ol (4) [18]

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.36 (s, 4 H), 5.41 (d, J = 1.3 Hz, 1 H), 5.12 (q, J = 1.3 Hz, 1 H), 3.74 (t, J = 6.4 Hz, 2 H), 2.79 (td, J = 6.4, 1.3 Hz,
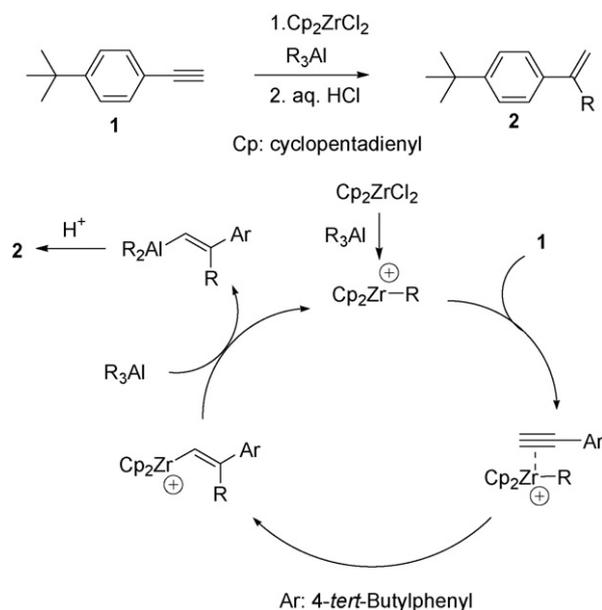
Scheme 1. Alkylalumination of acetylene 1.

Scheme 2. Methylalumination of 1.

2 H), 1.32 (s, 9 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 150.7, 144.4, 137.3, 125.7 ($\times$2), 125.3 ($\times$2), 113.8, 61.0, 38.5, 34.5, 31.3.

2.10. (3E)-(4-tert-Butylphenyl)-3-buten-1ol (5) [19]

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.35–7.28 (m, 4 H), 6.48 (d, J = 15.5 Hz, 1 H), 6.16 (dt, J = 15.5, 7.2 Hz, 1 H), 3.74 (t, J = 6.2 Hz, 2 H), 2.52–2.45 (m, 2 H), 1.31 (s, 9 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 150.4, 134.4, 132.6, 125.7 ($\times$2), 125.5 ($\times$2), 125.4, 62.1, 36.4, 34.7, 34.5, 31.3.

3. Results and discussion

The alkylalumination reaction of *tert*-butylphenylacetylene **1** was chosen as the type reaction [20] to evaluate zirconocene catalysts supported on solid materials (SiO$_2$/MAO, montmorillonite K-10) (Scheme 2). In order to choose an appropriate solvent for the reaction, several solvents were examined under the conventional homogeneous reaction conditions using only Cp$_2$ZrCl$_2$ and Me$_3$Al as the catalyst and methylating reagent (Fig. 2). The time-course of the methylalumination was monitored by the measuring the ^{1}H NMR of the crude product. When CH$_2$Cl$_2$ was used as the solvent, most of acetylene **1** was converted to styrene **2** after 24 h. THF, benzene, and hexane were also examined. The reaction rates increased in the order of CH$_2$Cl$_2$ > hexane > benzene > THF. These results suggest that moderate polarity and low nucleophilicity are favorable for high reactivity. This is the same tendency observed for zirconocene catalyzed olefin polymerization and is in accord with cationic nature of the actual active catalytic species [4a,21].

On the basis of the examination of solvents, the time-courses of the methylalumination catalyzed by zirconocene supported on solid material were measured in CH$_2$Cl$_2$ and compared with reactions carried out under conventional homogeneous conditions (Fig. 3). Negishi carboalumination of alkynes [10] and alkenes [22], and zirconocene catalyzed olefin polymerization [4a,23] are considerably accelerated when MAO or Me$_3$Al treated with a small amount of water are used in the place of Me$_3$Al. The accelerating ability of MAO and water treated Me$_3$Al was also confirmed
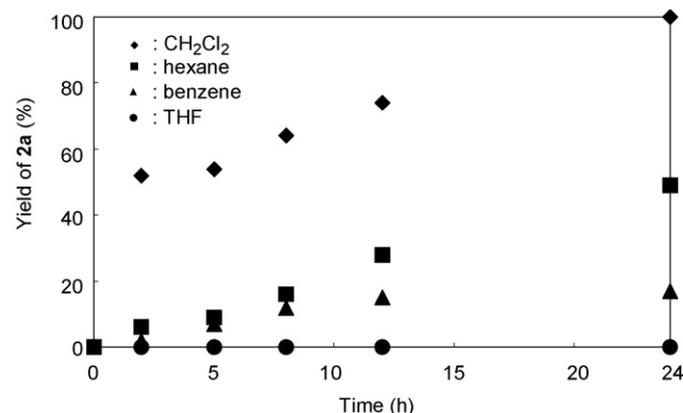

Fig. 2. Screening of solvents in homogeneous methylalumination using Cp$_2$ZrCl$_2$ and Me$_3$Al (0.53 M solution of **1**).
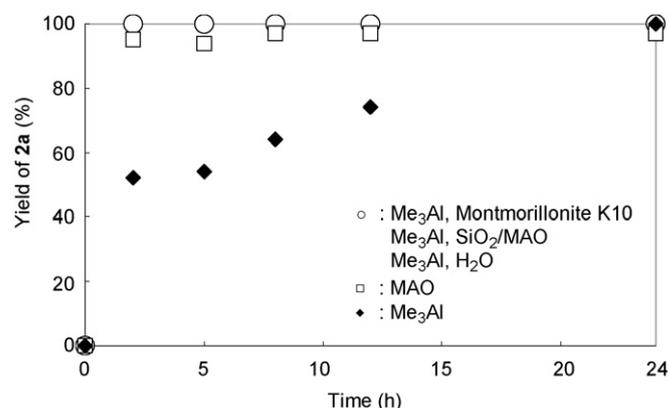

Fig. 3. Time-course of the methylalumination in CH$_2$Cl$_2$. Me$_3$Al, MAO, Me$_3$Al–H$_2$O: 0.53 M solution of **1**. Me$_3$Al–montmorillonite K-10, Me$_3$Al–SiO$_2$/MAO: 0.32 M solution of **1**.

in our studies and most of acetylene **1** was consumed after 2 h. Heterogeneous systems using solid materials (SiO$_2$/MAO and montmorillonite K-10), previously reported to be highly effective in olefin polymerization [6,24], were found to be equally effective as the homogeneous reaction using MAO. Especially noteworthy is the reaction of montmorillonite K-10 which clearly showed that MAO is not necessarily required for rate accelerating.

The similarity in high reactivity between the homogeneous (MAO; Me$_3$Al-H$_2$O) and heterogeneous MAO (Me$_3$Al, SiO$_2$/MAO) systems indicates the counteranion moiety of the actual catalytically active zirconocenium cation to be similar between the two systems, with coordination between the cation and the counteranion moiety being weak. Because of its similar high reactivity, a similar situation is anticipated for the montmorillonite K-10 supported zirconocene system using Me$_3$Al, although the identity of the added aluminium agent is quite different.

Next, we decided to examine the ethylalumination of acetylene **1** catalyzed by zirconocene supported on solid materials in CH$_2$Cl$_2$ and hexane (Scheme 3). Precedence shows that when Et$_3$Al is used, in addition to products corresponding to those in the carboalumination reaction using Me$_3$Al, which is speculated to involve zirconocenium cation intermediates, products that can be attributed to arise via zirconacycles are produced [20b,25]. An examination of the reaction of 1-decene using (NMI)$_2$ZrCl as catalyst revealed that the products were dependent on the polarity of solvent, with products involving zirconocenium cation intermediates favored in polar solvents such as (CH$_2$Cl)$_2$, whereas products via the zirconacycle intermediate were preferred in nonpolar solvents such as hexane (Scheme 4) [25]. These results indicate that the ion pair of the zirconocenium cation and its counteranion, generated from the disproportionation between Cp$_2$ZrCl$_2$ and triethylaluminium, was destabilized in nonpolar hexane due to the highly polar nature of the ion pair, thereby favoring product formation via the relatively nonpolar zirconacycle intermediate [26–28].

For our supported system, since the cation moiety is common with the homogeneous system (Cp$_2$ZrCl$_2$/R$_3$Al), and the negative charge of the anionic moiety is delocalized on the support surface, the polarity of the active cationic catalyst–counterion ion pair as
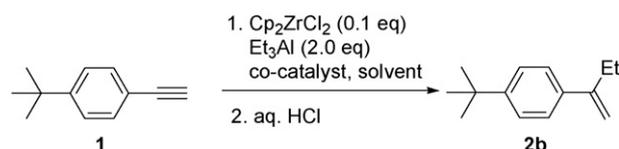
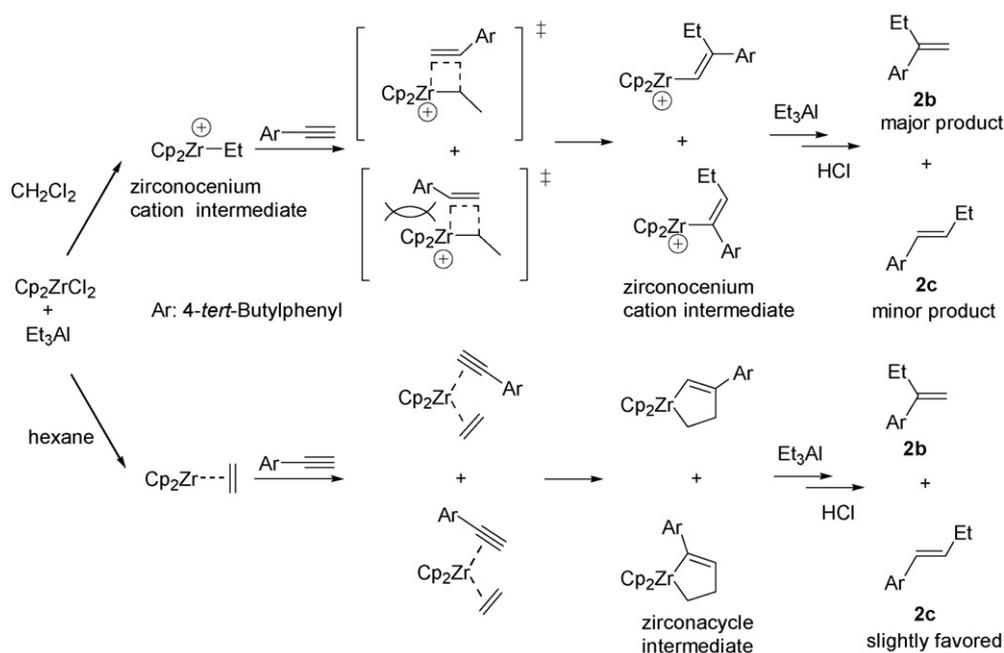
Scheme 3. Ethylalumination of **1**.
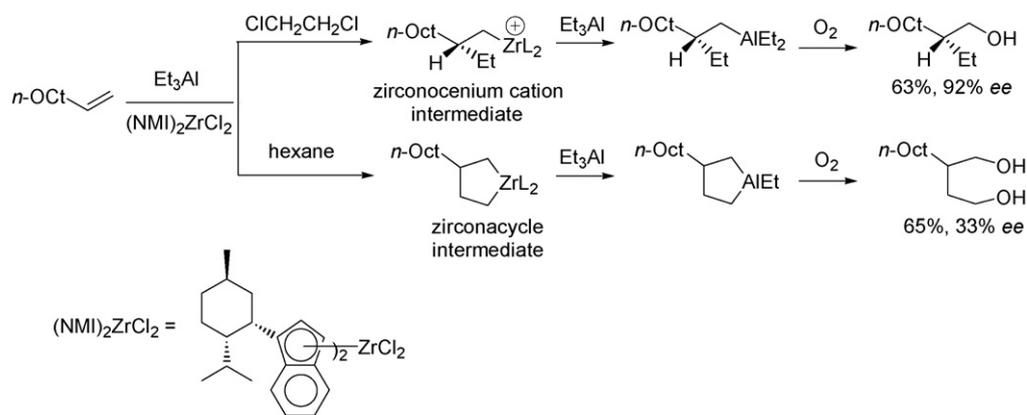
Scheme 4. Solvent effect in the ethylalumination of 1-decene.

a whole is expected to be low compared with that of the homogeneous system. This would mean that the active zirconocenium ion pair from the supported catalyst should be relatively more stable than that from the homogeneous catalyst in nonpolar solvents. Thus, it was anticipated that an increase in the proportion of product **2b** would be observed in reactions using solid supports carried out in nonpolar solvents, in comparison with homogeneous reactions carried out in the absence of solid supports (Scheme 5). To verify this hypothesis, we carried out the ethylalumination reaction in nonpolar hexane.

The ethylalumination of **1** was first examined in CH_2Cl_2 (Table 1). When the ethylalumination reaction was performed for 8 h in the absence of solid materials, styrene **2b** was preferentially obtained as the major product along with a small amount (16%) of recovered acetylene **1** (**2b**:**2c** = ca. 5:1, Table 1, entry 1) and minute amounts of by-products **2d–f**. Extending the reaction time to 24 h did not conduce to improvement of the conversion of **1** [29]. For reactions using solid supports, SiO_2/MAO gave results similar to those of the homogenous reaction (Table 1, entry 2). However, when montmorillonite K-10 was used as the solid support, the proportion of **2c** increased somewhat (**2b**:**2c** = ca. 5:2) (Table 1, entry 5). We had recently disclosed the efficiency of zirconocene

supported on base modified SiO_2 (namely SiO_2/MgO, SiO_2/LiOH, and SiO_2/NaOH) as catalysts for non-MAO ethylene polymerization [11]. It was found that in the ethylene polymerization reaction, the performance of the catalysts were on the same high level with activity being 67 kg PE/g Zr/h for SiO_2/MgO (3.0 mmol base/g SiO_2), 57.5 kg PE/g Zr/h for SiO_2/LiOH (0.8 mmol base/g SiO_2), and 11.5 kg PE/g Zr/h for SiO_2/NaOH (0.5 mmol base/g SiO_2), respectively. On the premise of these results, we examined these solid materials in the ethylalumination reaction. Results using SiO_2/LiOH, and SiO_2/MgO turned out to be practically the same as those of the homogeneous system and the reaction using SiO_2/MAO (Table 1, entries 2–4).

Results of reactions carried out in hexane are summarized in Table 2. When acetylene **1** was treated with Cp_2ZrCl_2 (0.1 equiv.) and Et_3Al (2.0 equiv.) in hexane for 8 h, a mixture of styrene derivatives **2b**, **c** and **2e**, **f** was obtained along with the oxygenated products **3–5**, which probably formed by the adventitious traces of oxygen in the solvents (Table 2, entry 1). In contrast with the reaction in CH_2Cl_2, **2c** was slightly favored over **2b**. The increase of styrene **2c** in this nonpolar solvent implies the preference for the zirconacycle pathway (Scheme 6). The use of SiO_2/MAO resulted in an even distribution of **2b** and **2c** (Table 2, entry 2). On the
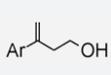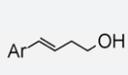

Scheme 5. Proposed mechanism of the ethylalumination of acetylene **1**.

Table 1
Ethylalumination of **1** catalyzed by zirconocene supported on solid materials in CH_2Cl_2.[a]

Entry	Co-catalyst	Product (%)[b]					
		2b	2c	2d	2e	2f	1
1	–	53	11	1	3	0.5	16
2	SiO$_2$/MAO	47	8	0.5	2	1	18
3	SiO$_2$/LiOH	49	9	0.9	2	0.4	7
4	SiO$_2$/MgO	48	10	0.8	2	0.7	6
5	Montmorillonite K-10	44	17	1	2	3	6

[a] Acetylene **1** was treated with Cp$_2$ZrCl$_2$ (0.1 equiv.), Et$_3$Al (2.0 equiv.) and/or co-catalyst in CH$_2$Cl$_2$ (0.17 M solution of **1**) at room temperature for 8 h.
[b] Isolated yield.

Table 2
Ethylalumination of **1** catalyzed by zirconocene supported on solid materials in hexane.[a]

Entry	Co-catalyst	Product (%)[b]							
		2b	2c	2e	2f	3	4	5	1
1	–	19	23	1	–	2	2	2	20
2	SiO$_2$/MAO	26	27	0.6	–	2	3	3	7
3	SiO$_2$/LiOH	31	26	1	1	1	2	3	5
4	SiO$_2$/MgO	29	22	1	1	1	1	2	5
5	Montmorillonite K-10	23	17	1	2	1	2	2	4

[a] Acetylene **1** was treated with Cp$_2$ZrCl$_2$ (0.1 equiv.), Et$_3$Al (2.0 equiv.) and/or co-catalyst in hexane (0.17 M solution of **1**) at room temperature for 8 h.
[b] Isolated yield.
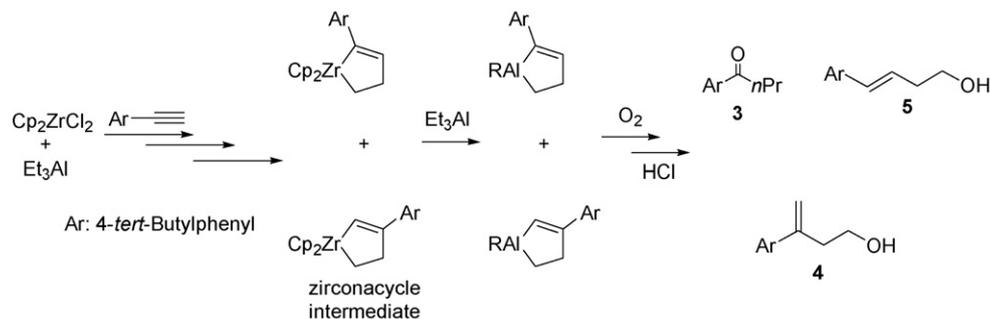
Scheme 6. Plausible reaction mechanism for generation of **3–5**.

other hand, the addition of solid materials, montmorillonite K-10, SiO$_2$/LiOH, and SiO$_2$/MgO, to the zirconocene catalyst system lead to a reversal of selectivity, slightly favoring styrene **2b** (Table 2, entries 3–5). These results suggest that the zirconocenium cation pathway is more favorable with supported systems compared with the conventional homogeneous system (Cp$_2$ZrCl$_2$/R$_3$Al). Thus, the supported systems can be considered to be less polar than the homogeneous system (Cp$_2$ZrCl$_2$/R$_3$Al).

4. Conclusion

Zirconocene catalysts supported on solid materials have been known to be highly efficient catalysts in practical homogenous olefin polymerization. In order to see whether such catalytic systems could be applied to other organic reactions and to obtain insight on the properties of the solid catalysts as feedback for gaining an understanding of polymerization reactions, we have examined the zirconocene catalyzed alkylalumination reaction. In the methylalumination of acetylene **1**, it was found that the use of montmorillonite K-10 in conjunction with Me$_3$Al gives rise to reactivity comparable to that exerted by the homogeneous reaction using MAO. Therefore, negating the use of MAO for activation of this reaction is possible by using montmorillonite K-10 which functions as both solid support and co-catalyst. In the ethylalumination reaction, which is known to give rise to products via uncharged zirconacycle intermediates in addition to zirconocenium cation catalyzed products, examination of solvent effects revealed that in contrast to the homogenous catalyst system (Cp$_2$ZrCl$_2$/R$_3$Al), the heterogeneous systems using montmorillonite K-10, SiO$_2$/LiOH, and SiO$_2$/MgO are affected only slightly. This solvent effect indicated that the coordinating ability of the anionic moiety to the actual active zirconocenium cation is weakened by the delocalization of negative charge and the polar nature of the active catalyst–counterion ion pair is low in polarity. This should account for the high activity observed using montmorillonite K-10, SiO$_2$/LiOH, and SiO$_2$/MgO as supporting materials in the ethylene polymerization reaction.

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