Comparison of Catalytic Behaviors of Various Silica-Supported Metallocene Catalysts in Syndiospecific Polymerization of Styrene

Jin-Heong Yim,[1] Son-Ki Ihm[2]

[1]Division of Advanced Materials Engineering, Kongju National University, 182 Sinkwan-dong, Gongju City, Chungnam, 314-701, Korea
[2]Department of Chemical & Biomolecular Engineering, Korea Advanced Institute of Science and Technology, 373-1, Guseong-dong, Yuseong, Daejeon, 305-701, Korea

ABSTRACT: Homogeneous metallocene catalysts and several kinds of silica-supported metallocene catalysts were employed to investigate their catalytic behavior for styrene polymerization. Half metallocene directly supported on silica catalysts showed better performance than metallocene supported on silica treated with aluminum compounds with regard to syndiospecific styrene polymerization. The silica-supported metallocene catalysts had optimum conditions for Al/Ti mole ratio and polymerization temperature. Among these, the $Cp^*TiCl_3/$ SiO_2 catalyst showed fairly good catalytic activity and yielded enhanced properties of syndiotactic polystyrene, even at a relatively low (< 300) Al/Ti mole ratio in styrene polymerization. Active sites formed on SiO_2 appear to be more thermally stable as compared with their homogeneous counterparts. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 2293–2298, 2006

Key words: syndiotactic polystyrene; metallocene; polymeriztion; catalyst

INTRODUCTION

Ishihara et al.[1] first reported the syndiospecific polymerization of styrene by organotitanium compounds with methylaluminoxane (MAO) as a cocatalyst. The catalytic activity decreased in the order $CpTiCl_3$ (Cp is .5-cyclopentadienyl) $\sim Cp^*TiCl_3$ (Cp* is .5-pentamethyl-cyclopentadienyl) $> CpTiCl_2H \sim Ti(OEt)_4 > Ti(OMe)_4 > TiBr_4$. Ready et al.[2] found that $IndTiCl_3$ (Ind is indenyl)-MAO catalyst displayed fairly good activity and enhanced properties of syndiotactic polystyrene (sPS) as compared with the $CpTiCl_3$-MAO catalyst system. They suggested that the greater activity for $IndTiCl_3$ might be attributable to the higher propagation rate due to the greater electron-donating ability of the indenyl ring relative to the Cp moiety. However, these homogeneous catalysts require a large amount of expensive methylaluminoxane (MAO).

Several attempts have been made to reduce the MAO/Ti mole ratio as well as to exclude the use of MAO as a cocatalyst.[3–11] One approach for the latter is to develop an anionic cocatalyst such as boron compounds instead of MAO. Pellecchia et al.[3,4] found that monocyclopentadienyltitaniumalkyls combined with tris (pentafluorophenyl) boron effectively catalyzed the syndiospecific polymerization of styrene without using MAO. Another approach is immobilization of titanium compounds on a porous solid such as SiO_2, Al_2O_3, $MgCl_2$, polymer, Al_2O_3–SiO_2 gels, and so forth. Soga et al.[5] reported that catalysts prepared by supporting Cp^*TiCl_3 (or $CpTiCl_3$) on Al_2O_3 treated with trialkylaluminium showed activity, although very low, for syndiotactic polymerization of styrene with common trialkylaluminium as a cocatalyst. The $MgCl_2$ supported $Ti(OEt)_4$ catalyst was reported to show still lower activity than their homogeneous counterparts.[6] Soga et al.[7,8] found that a silica-supported $Ti(OBu)_4$ catalyst displayed good performance at a relatively low MAO/Ti mole ratio (< 40) in styrene polymerization. Polymer supported $TiCl_4$ has also been introduced as a catalyst for sPS production.[9] In order to investigate the effect of acid-base properties of support, D. Jamanek et al. have reported that Al_2O_3–SiO_2 gels could be used as a catalyst support for syndiospecific styrene polymerization.[10] In our previous paper, we reported that a silica-supported $CpTiCl_3$ catalyst displayed higher activity than a homogeneous $CpTiCl_3$ catalyst in a low Al/Ti mole ratio.[11]

There are additional advantages to using a heterogeneous catalyst system in syndiotactic polystyrene production. First, the use of supported catalysts allows syndiospecific styrene polymerization to be conducted in a fluidized bed process (i.e., a solventless process). Second, the supports used in these catalyst systems may also serve as fillers, which improve the mechanical properties of sPS.

In this article, various metallocene compounds ($CpTiCl_3$, $Cp*TiCl_3$, and $IndTiCl_3$) were immobilized on several kinds of silica in order to make efficient supported metallocene catalysts for styrene polymerization. Styrene polymerizations were carried out over silica-supported catalysts and homogeneous catalysts. The stability of the catalyst was assessed through comparisons of the catalytic activity and the properties of syndiotactic polystyrene over various metallocene catalysts under various polymerization conditions.

EXPERIMENTAL

Materials

Nitrogen was purified by removing traces of residual oxygen and moisture with columns packed with an oxygen scavenger (Fisher RIDOX, Pittsburgh, PA) and a 5A molecular sieve (Aldrich, Milwaukee, WI), respectively. Styrene (Junsei Chemical) was washed with an aqueous solution of sodium hydroxide, dried over calcium hydride for 12 h, and distilled under reduced pressure. Purified styrene was stored under nitrogen at $-25°C$. Toluene (J.T. Baker, Phillipsburg, NJ) was used as a solvent for the polymerization reaction and the catalyst preparation. The solvent was purified by drying after refluxing through a distillation column over sodium metal under dry nitrogen. $CpTiCl_3$ (Aldrich), $Cp*TiCl_3$ (Strem, Tully Town, PA), $IndTiCl_3$ (Strem), $Al(CH_3)_3$ (Aldrich), and modified methylaluminoxane (Tosoh Akzo, Tokyo, Japan) were used as received without further purification. All operations were carried out under a dry nitrogen atmosphere by using a glove-box and the Schlenk line technique.

Preparation of catalysts

Silica (Davison 952) was dehydrated at $600°C$ for 10 h under a nitrogen atmosphere. The hydroxyl content of dehydrated silica measured by a thermal gravimeter analyzer (Dupont 990) was controlled at 1 mmol/g silica. 5 g of SiO_2 was reacted with 80 mmol of MAO or trimethylaluminium (TMA) at $50°C$ for 1 h (MAO/ SiO_2 and TMA/SiO_2). 5 g of undehydrated SiO_2 was reacted with 80 mmol of TMA at $50°C$ for 1 h (TMA/ undehydrated SiO_2). The solid part was washed with an excess of toluene and dried with nitrogen purging. 3 g of SiO_2 treated with aluminum compound (MAO/ SiO_2, TMA/SiO_2, and TMA/undehydrated SiO_2) was reacted with 1.5 mmol of $CpTiCl_3$ in 100 ml of toluene at $50°C$ for 1 h, washed with an excess of toluene and dried ($CpTiCl_3/MAO/SiO_2$, $CpTiCl_3/TMA/SiO_2$, and $CpTiCl_3/TMA/Undehydrated SiO_2$). 3 g of SiO_2 was reacted with 1.5 mmol of metallocene ($CpTiCl_3$, $Cp*TiCl_3$, and $IndTiCl_3$) in 100 ml of toluene at $110°C$ for 2 h, washed with an excess of toluene, and dried ($CpTiCl_3/SiO_2$, $Cp*TiCl_3/SiO_2$, and $IndTiCl_3/SiO_2$).

Polymerization procedures

Styrene polymerization was carried out in a glass reactor. Styrene monomer and toluene were fed into the reactor together with the catalysts under a nitrogen atmosphere. The polymerization was started with MAO added as a cocatalyst and it was stopped by adding acidic ethanol. The precipitated polymer was washed with an excess of ethanol and dried at $80°C$ for 6 h in vacuum.

Analytical procedures

The contents of metals in the prepared catalysts were measured using an inductively coupled plasma (ARL-3510) spectrophotometer. The surface area of the prepared catalysts was measured by the BET method (Area-meter II, STROHLEIN Instruments, Viersen, Germany). The syndiotacticity of the polymers was measured by ^{13}C NMR (Bruker AMX 500 FT-NMR, Billerica, MA) at $130°C$ with O-dichlorobenzene as a solvent. A differential thermal analysis was carried out with a calorimeter (Thermal Analyst 2000, Dupont Instruments, Raleigh, NC) under a nitrogen atmosphere at a heating rate of $10°C$ /min. The molecular weight and molecular weight distribution were determined by gel permeation chromatography (Waters 150CV) at $145°C$ with 1,3,5-trichlorobenzene as a solvent.

RESULTS AND DISCUSSION

Analysis of supports and catalyst

Table I shows the results of the surface area and elemental analyses of the prepared silica supports and silica-supported metallocene catalysts. The surface area of the MAO/SiO_2 support was lower than that of SiO_2. It is speculated that micropores on the silica were covered with MAO, which has an oligomeric structure $—[—Al(CH_3)—O—]_n—$, with $n = 4$–20). Therefore, the surface area of metallocene directly supported on the silica catalyst ($CpTiCl_3/SiO_2$) was higher than that of metallocene immobilized on silica treated with MAO ($CpTiCl_3/MAO/SiO_2$). Metallocene directly supported on silica catalysts also displayed higher Ti content. The surface areas and Ti content of metallocene directly supported on silica catalysts ($CpTiCl_3/SiO_2$, $Cp*TiCl_3$ $/SiO_2$, and $IndTiCl_3/SiO_2$) showed little variation for different metallocene precursors.

Styrene polymerization over various metallocene catalysts

The results for styrene polymerization over silica-supported $CpTiCl_3$ catalysts and a homogeneous $CpTiCl_3$ catalyst with methylaluminoxane (MAO) or trimethylaluminium (TMA) as a cocatalyst are listed in Table II, in which some data have been quoted from our pre-

TABLE I
Results of Surface Area and Metal Content of Prepared Silica Supports
and Silica Supported Metallocene Catalysts

	Surface area	Metal content	
	(m^2/g)	Al (mmol/g)	Ti (mmol/g)
Supports			
Undehydrated SiO_2	238	n.d.[a]	n.d.[a]
SiO_2	274	n.d.[a]	n.d.[a]
MAO/SiO_2	181	5.16	n.d.[a]
TMA/Undehydrated SiO_2	—	1.97	n.d.[a]
TMA/SiO_2	—	0.90	n.d.[a]
Catalysts			
$CpTiCl_3/SiO_2$	206	n.d.[a]	0.25
Cp^*TiCl_3/SiO_2	229	n.d.[a]	0.20
$IndTiCl_3/SiO_2$	218	n.d.[a]	0.24
$CpTiCl_3/MAO/SiO_2$	161	5.03	0.16
$CpTiCl_3TMA/Undehydrated SiO_2$	—	1.78	0.12
$CpTiCl_3TMA/SiO_2$	—	0.87	0.08

[a] Not detected.

vious work.[11] In styrene polymerization, the activity of the $CpTiCl_3/SiO_2$ catalyst was higher than that of the $CpTiCl_3$ supported on MAO or TMA treated SiO_2 catalyst Based on a study of the active sites of catalyst systems by means of electron spin resonance (ESR) spectroscopy, we suggested that $CpTiCl_3/SiO_2$ catalyst is more easily activated to active sites than its homogeneous counterpart or $CpTiCl_3/MAO/SiO_2$ catalyst in styrene polymerization.[11] It is postulated that the formation of cationic titanium sites via μ-oxo bonding seems to be more favorable for syndiospecific polymerization of styrene when a half-metallocene precursor is used. From the above results, metallocene directly supported on silica catalysts showed better performance than metallocene supported on silica treated with aluminum compounds with regard to syndiospecific styrene polymerization. Therefore, pure silica could be selected as a best support for syndiospecific styrene polymerization.

The results for styrene polymerization over silica-supported various metallocene compounds and the homogeneous metallocene catalyst with MAO as a cocatalyst are compared in Table III. The catalytic activities of silica-supported metallocene catalysts were higher than those of their homogeneous counterparts under our experimental conditions. In addition, the properties of syndiotactic polystyrene (stereoregularity, melting point, and molecular weight) were slightly improved. Moreover, the silica-supported catalysts had fairly good catalytic activity even when a small amount of MAO was used (Al/Ti $\sim$ 100). However, the properties of syndiotactic polystyrene prepared with $CpTiCl_3/SiO_2$ catalyst were not adequate. The properties of syndiotactic polystyrene could be improved by utilizing metallocene precursors having more electron-donating ligands such as pentamethylcyclopentadienyl (Cp*) or indenyl (Ind) ring.

TABLE II
Styrene Polymerization Over Silica-Supported $CpTiCl_3$ Catalysts and Homogeneous
$CpTiCl_3$ Catalyst with MAO or TMA as a Cocatalyst[a]

Catalysts	Cocatalyst	Activity[b]	S.Y.[c] (%)	T_m (°C)	M_w ($\times 10^{-3}$)
$CpTiCl_3/SiO_2$[e]	MAO	237	88	258	44.6
$CpTiCl_3/SiO_2$[e]	TMA	n.g.[d]	—	—	—
$CpTiCl_3/MAO/SiO_2$[e]	MAO	38	80	255	38.6
$CpTiCl_3/MAO/SiO_2$[e]	TMA	n.g.[d]	—	—	—
$CpTiCl_3/TMA/SiO_2$[e]	MAO	24	64	256	29.1
$CpTiCl_3/TMA/undehydrated SiO_2$	MAO	29	49	253	36.3
$CpTiCl_3$ (homo.)[e]	MAO	90	81	255	25.0
$CpTiCl_3$ (homo.)[e]	TMA	n.g.[d]	—	—	—

[a] Polymerization conditions: styrene conc. is 4.36 mol/l; Al/Ti is 300 (the mole ratio Al/Ti is based on the MAO added during polymerization only); polymerization temperature is 50°C; solvent is toluene (100 ml).
[b] Unit is Kg PS · (mol Ti · mol S · hrs)$^{-1}$.
[c] Syndiotacticity measured by ^{13}C NMR.
[d] Negligible.
[e] Data have been quoted.[11]

TABLE III
Results of Styrene Polymerization over Various Silica-Supported Metallocene Catalysts and
Homogeneous Metallocene Catalysts with MAO as a Cocatalyst[a]

Catalysts	Al/Ti[b]	$T_p{}^c$ (°C)	Activity[d]	S.Y. (%)	T_m (°C)	M_w (× 10^{-3})	M_w/M_n
CpTiCl$_3$/SiO$_2$ CpTiCl$_3$/SiO$_2$	100	70	655	81	249	—	—
CpTiCl$_3$/SiO$_2$	600	50	786	90	261	25.9	2.0
CpTiCl$_3$/SiO$_2$	600	110	2998	40	238	—	—
Cp*TiCl$_3$/SiO$_2$	100	70	229	99	274	—	—
Cp*TiCl$_3$/SiO$_2$	600	50	126	99	273	161.3	2.1
Cp*TiCl$_3$/SiO$_2$	600	110	4191	97	270	—	—
IndTiCl$_3$/SiO$_2$	100	70	525	98	271	—	—
IndTiCl$_3$/SiO$_2$	600	50	64	99	271	126.2	1.9
IndTiCl$_3$/SiO$_2$	600	110	1098	81	256	—	—
CpTiCl$_3$ (Homo.)	600	50	245	86	257	24.9	1.9
Cp*TiCl$_3$ (Homo.)	600	50	152	96	273	116.2	1.9
IndTiCl$_3$ (Homo.)	600	50	28	96	270	105.2	1.7

[a] Polymerization conditions: styrene conc. is 0.87 mol/l, [Al] is 1.46×10^{-2} mol, solvent is toluene (100 ml).
[b] The mole ratio Al/Ti is based on the MAO added during polymerization only.
[c] Polymerization temperature.
[d] Unit is Kg PS · (mol Ti · mol S · h)$^{-1}$.

Judging from polydispersities (M_w/M_n), although these catalyst systems are heterogeneous, the active sites are considered to be uniform.

Effect of polymerization temperature

The effect of polymerization temperature on the catalytic activity in terms of styrene polymerization over a silica-supported metallocene catalyst and a homogeneous metallocene catalyst with MAO as a cocatalyst are shown in Figure 1. While the catalytic activities of the heterogeneous catalyst and homogeneous catalyst were relatively similar, the activity of the silica-supported catalyst at a temperature beyond 50°C was much higher than that of the homogeneous metallocene catalyst. It is suggested that the bimolecular deactivation process[12] usually observed in a homogeneous catalyst system is inhibited by the site isolation effect in the heterogeneous catalyst. In other words, the active site of silica-supported metallocene catalyst appears to be thermally stable. The optimum polymerization temperature for the catalytic activity varies according to the nature of the metallocene precursors.

The effects of the polymerization temperature on the melting point of syndiotactic polystyrene over various silica-supported metallocene catalysts with MAO are shown in Figure 2(a). The melting point of syndiotactic polystyrene slightly decreases with increasing polymerization temperature. This might be due to a decrease of the molecular weight and stereoregularity of syndiotactic polystyrene with increasing polymerization temperature, as reported by Chien and Salajka.[13] In the case of CpTiCl$_3$/SiO$_2$ catalyst, this phenomenon was severe as compared with the other catalysts. However, the melting point of syndiotactic
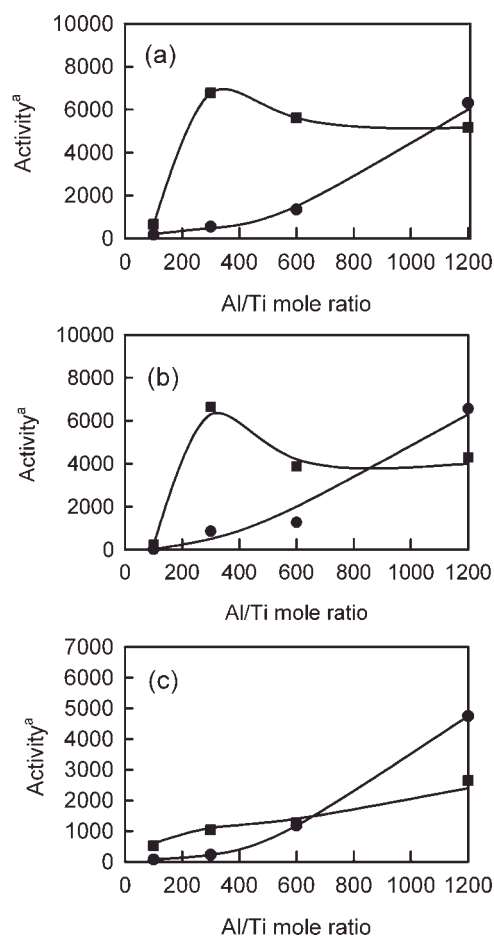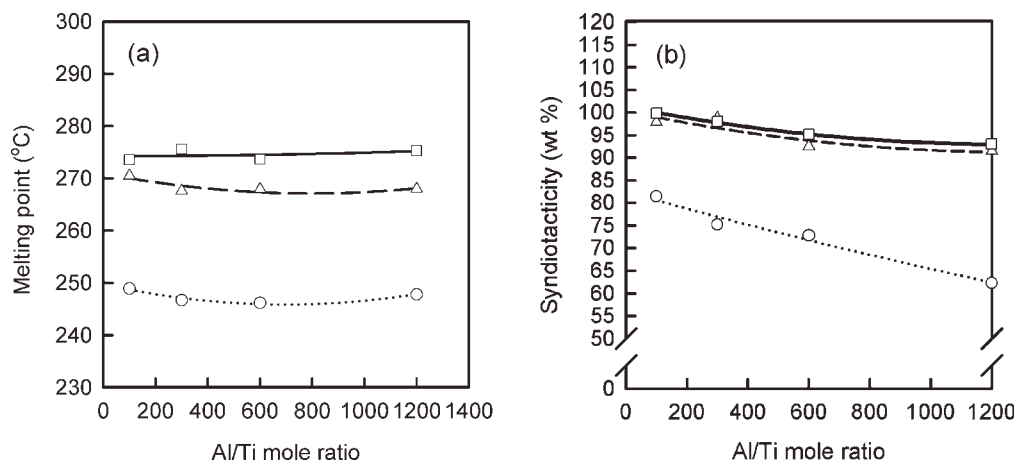

Figure 1 Effect of polymerization temperature on the catalytic activity over various metallocene catalysts with MAO as a cocatalyst with [Ti] = 2.43×10^{-5} mol, [Al] = 1.46×10^{-2} mol, and Al/Ti = 600 for (a) CpTiCl$_3$, (b) Cp*TiCl$_3$, and (c) IndTiCl$_3$ catalyst systems: (■) heterogeneous system; (●) homogeneous system. ^{a}Activity unit is Kg PS · (mol Ti · mol S · h)$^{-1}$.

Figure 2 Effect of polymerization temperature on the (a) melting point and (b) syndiotacticity of sPS over various silica-supported metallocene catalysts with MAO as a cocatalyst, $[Ti] = 2.43 \times 10^{-5}$ mol, $[Al] = 1.46 \times 10^{-2}$ mol, and Al/Ti = 600: (○) CpTiCl$_3$/SiO$_2$; (□) Cp*TiCl$_3$/SiO$_2$; (Δ)IndTiCl$_3$/SiO$_2$.

polystyrene over Cp*TiCl$_3$/SiO$_2$ catalyst was very similar with increasing polymerization temperature.

Figure 2(b) shows the effect of polymerization temperature on the syndiotacticity of syndiotactic polystyrene prepared with various silica-supported metallocene catalysts. Similar to the variation of melting point, the syndiotacticity of syndiotactic polystyrene over Cp*TiCl$_3$/SiO$_2$ catalyst was almost unchanged with increasing polymerization temperature. From the results of variation of melting temperature and syndiotacticity over polymerization temperature, it appears that the active sites of Cp*TiCl$_3$/SiO$_2$ catalyst may be the most thermally stable among the prepared catalysts.
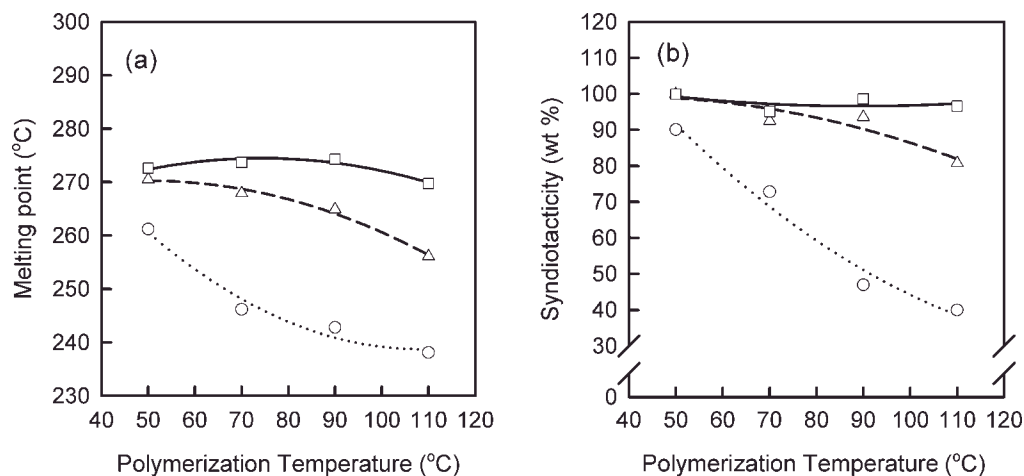
Effect of Al/Ti mole ratio

The effects of the Al/Ti mole ratio on the catalytic activity in styrene polymerization over a silica-supported metallocene catalyst and a homogeneous metallocene catalyst with MAO as a cocatalyst are shown in Figure 3. The catalytic activity drastically increased with increasing Al/Ti mole ratio in the homogeneous metallocene catalyst, as has been reported by several authors.[13–16] On the other hand, the optimum conditions for catalytic activity were found with increasing Al/Ti mole ratio in silica-supported metallocene catalyst. Although only a small amount of MAO was used, the catalytic activity obtained for the homogeneous catalyst under a relatively high Al/Ti mole ratio (∼ 1200) could be achieved by using a silica-supported metallocene catalyst. Considering economic aspects, these catalyst systems appear to be viable, as they require a lesser amount of expensive cocatalyst (MAO).

The effect of the Al/Ti mole ratio on the melting point of syndiotactic polystyrene over various silica-supported metallocene catalysts with MAO is shown
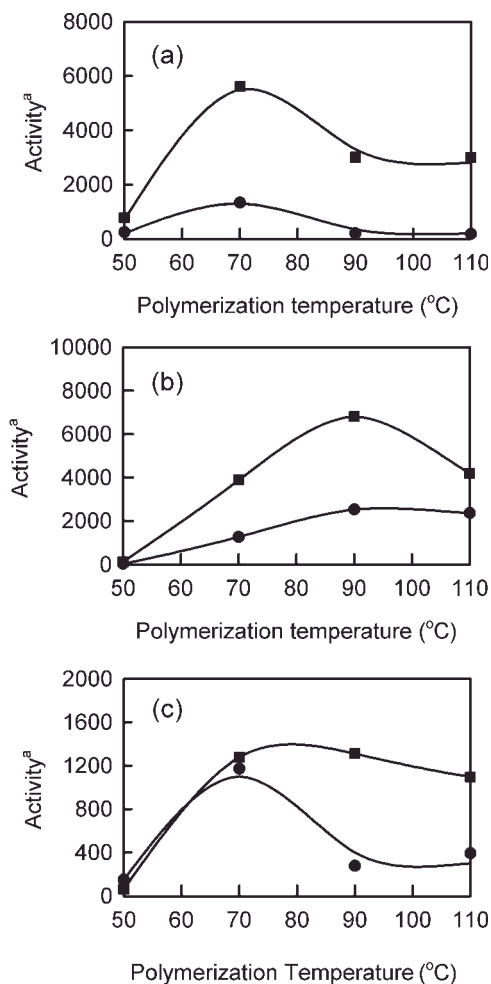
Figure 3 Effect of Al/Ti mole ratio on the catalytic activity over various metallocene catalysts with MAO as a cocatalyst, polymerization temperature of 70°C, and $[Al] = 1.46 \times 10^{-2}$ mol for (a) CpTiCl$_3$, (b) Cp*TiCl$_3$, and (c) IndTiCl$_3$ catalyst systems: (■) heterogeneous system; (●) homogeneous system. [a]Activity unit is Kg PS · (mol Ti · mol S · h)$^{-1}$.

Figure 4 Effect of Al/Ti mole ratio on the (a) melting point and (b) syndiotacticity of sPS over various silica-supported metallocene catalysts with MAO as a cocatalyst, polymerization temperature = 70°C, and [Al] = 1.46 × 10⁻² mol: (○) CpTiCl$_3$/SiO$_2$, (□) Cp*TiCl$_3$/SiO$_2$, (Δ) IndTiCl$_3$/SiO$_2$.

in Figure 4(a). The melting point of syndiotactic polystyrene was almost unchanged in our experimented Al/Ti mole ratio conditions. It is believed that stable active sites were formed even when a small amount of MAO was used (Al/Ti ∼ 100). The melting point of syndiotactic polystyrene, which was produced by various silica-supported catalysts, decreased in the following order: Cp*TiCl$_3$/SiO$_2$ > IndTiCl$_3$/SiO$_2$ > CpTiCl$_3$/SiO$_2$.

Figure 4(b) shows the effect of the Al/Ti mole ratio on the syndiotacticity of syndiotactic polystyrene prepared with various silica-supported metallocene catalysts. The syndiotacticity of syndiotactic polystyrene slightly decreased with increasing Al/Ti mole ratio. This phenomenon cannot be clearly explained at present. In terms of syndiotacticity, however, the use of excess MAO is not favorable for these supported metallocene catalysts. The order of syndiotacticity of syndiotactic polystyrene, which was produced by various silica-supported catalysts, was as follows: Cp*TiCl$_3$/SiO$_2$ ∼ IndTiCl$_3$/SiO$_2$ > CpTiCl$_3$/SiO$_2$.

CONCLUSIONS

Metallocene directly supported on silica catalysts displayed good performance for the synthesis of syndiotactic polystyrene. In particular, Cp*TiCl$_3$/SiO$_2$ catalyst was effective not only in terms of catalytic activity but also with regard to the properties of the produced syndiotactic polystyrene in styrene polymerization. In addition, even with only small amount of MAO, high activity could be achieved by using a silica-supported catalyst. Active sites of silica-supported catalysts are more thermally stable than those of homogeneous catalysts.

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