Nanoparticle supported bis (cyclopentadienyl) zirconium dichloride catalysts for styrene polymerization

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Abstract

Heterogeneous nanoparticle NA-MgO-MAO/NA-TiO$_2$ (anatase)-MAO supported bis (cyclopentadienyl) zirconium dichloride (Cp$_2$ZrCl$_2$) are synthesized and used for the polymerization of styrene monomer. The supporting process is confirmed via X-ray photoelectron spectroscopy (XPS) and FTIR. Characterization of the obtained polymer is done by gel permeation chromatography (GPC), ^{13}C NMR spectroscopy and differential scanning calorimetry (DSC).
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1. Introduction

Metallocenes [1] in combination with suitable activating agents, especially methylaluminoxane (MAO) are extremely active catalysts for olefin polymerization [2–4]. It is extremely important to heterogenise the homogeneous metallocene/activator catalyst systems for large scale industrial processes involving gas phase and slurry polymerization of olefins, since heterogenisation offers many advantages such as ease of separation, possible higher product yields and narrow molecular weight distribution due to pore size distribution control, mild reaction conditions and catalyst reusability. Moreover, heterogenised metallocene catalysts require a smaller amount of MAO than soluble systems to achieve high activity [5]. Silica [6,7], zeolite [8] and alumina [9] supported bis (cyclopentadienyl) zirconium dichloride catalysts have been reported for polymerization reactions, but most of these studies are confined to ethylene polymerization reactions. In principle, polystyrene can occur in isotactic, atactic or syndiotactic configurations, but the latter was unknown until very recently. Atactic polysyrene is non-crystalline (T_g = 100 °C), isotactic polystyrene has slow crystallization rate (T_g = 99 °C, T_m = 240 °C) and syndiotactic polystyrene has fast crystallization rate (T_g = 100 °C, T_m = 270 °C). Furthermore, the low specific gravity, low dielectric constant, high modulus of elasticity and excellent resistance to water and a wide range of solvents, including acids, bases, and most organic solvents except organic solvents with solubility parameters close to styrenic polymer, such as benzene and toluene make syndiotactic polystyrene a promising material for a large number of applications in many market areas. Supported titanocene catalyst shows good catalytic activity for styrene polymerization [10], wherein both syndiotactic and atactic polystyrenes are formed. Polystyrene [11–13] is the most extensively used one in plastics, which has above average growth rate in world market. This increase has been largely prompted by new catalysts, which are able to tailor the stereoselectivity and morphology. Herein we report the design and synthesis of heterogenised bis (cyclopentadienyl) zirconium dichloride (Cp$_2$ZrCl$_2$)-MAO supported on nanomagnesium oxide
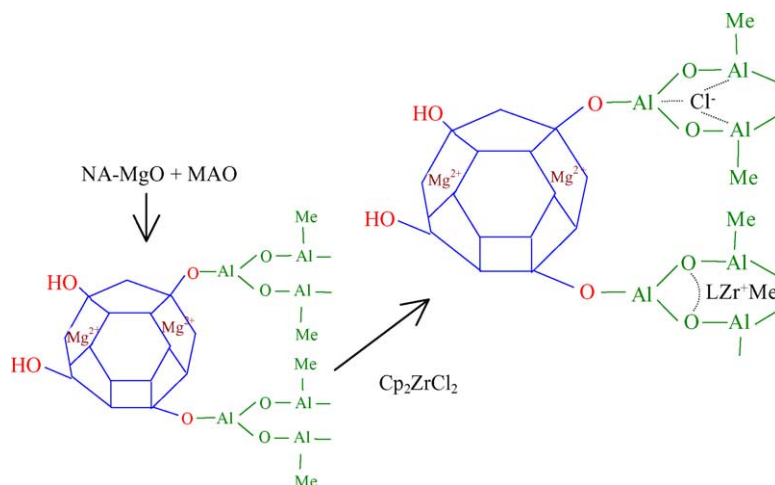
Scheme 1.

(aerogel prepared MgO denoted as NA-MgO), i.e., catalyst 1 (or cat 1) and nanoTiO$_2$ denoted as NA-TiO$_2$ (anatase), i.e., catalyst 2 (cat 2) for the polymerization of styrene to afford syndiotactic polystyrene selectively with high yields having high molecular weight with narrow distribution over the other supported bis (cyclopentadienyl) zirconium dichloride catalysts reported so far (Scheme 1). These heterogenous catalysts are reused for two cycles. Further, heterogeneous commercial MgO (CM-MgO)-MAO/TiO$_2$ (anatase) (commercial)-MAO supported Cp$_2$ZrCl$_2$ are also synthesised and used for styrene polymerzation reactions to understand how the morphology and the particle shape of the support molecules influence the activity of the heterogeneous catalysts.

2. Experimental

2.1. Materials

ZrCl$_4$, dicyclopentadiene and styrene are procured from Aldrich.

MAO prepared from trimethylaluminium (Aldrich). NA-MgO (aerogel prepared) with surface area 590 m^2/g is purchased from Nanotec, USA, and NA-TiO$_2$ (anatase) with surface area 350 m^2/g from Kanto Chemical Co., Inc., Japan. CMMgO with surface area 30 m^2/g and commercial TiO$_2$ (anatase) with surface area 20 m^2/g are procured from Loba Chemie, India.

2.2. Preparation of the catalyst

The catalyst bis (cyclopentadienyl) zirconium dichloride is synthesized following the reported literature procedure [14]. Sodium metal (2.4 g, 0.1 mol) is dispersed in 15 ml toluene at 115 °C to obtain particle size ca. 50 (under a blanket of nitrogen). To this dispersion, the cyclopentadiene monomer (10 ml, 0.12 mol) is added dropwise at 0 °C over a period of 15 min and then allowed to stir at room temperature for 4 h under nitrogen atmosphere to obtain sodium cyclopentadienide. A suspension of zirconium tetrachloride (11.6 g, 0.05 mol) is prepared using dry THF (10 ml) under nitrogen atmosphere and the formed sodium cyclopentadienide is added to it dropwise over a period of 20 min, and then allowed to stir for 4 h. The reaction mixture is concentrated by rotavapor and the solid obtained is subjected to Soxhlet extraction with chloroform saturated with HCl gas for 6 h. The chloroform extract is concentrated to ca. 10 ml and crystallized at −30 °C (dry ice/acetone) to get bis (cyclopentadienyl) zirconium dichloride (9.1 g, 62% yield). m.p. 243–245 °C (lit. m.p. 242–245° C). ^{1}H NMR (200 MHz, CDCl$_3$) (6.45 (s, 10 H)) [15].

Synthesis of MAO [16] is carried out as reported in the literature [13].

2.2.1. Supported catalyst preparation
2.2.1.1. NA-MgO (590) supported bis (cyclopentadienyl) zirconium dichloride catalyst. 0.670 g of NA-MgO (590) is heated for 12 h at 140 °C under vacuum at 0.1 Torr. Then it is suspended in a solution of MAO [0.2331 g MAO in 10 ml toluene] and stirred at 50 °C for 4 h. It is filtered under nitrogen atmosphere, washed five times with toluene until no more aluminium is found in the washing and dried under vacuum. The MAO/NA-MgO contains 8.57% of aluminium. MAO/NA-MgO is added to 100 ml of toluene containing 0.01 g of Cp$_2$ZrCl$_2$, stirred overnight, washed five times with toluene, and dried in vacuo.

2.2.1.2. NA-TiO$_2$ supported bis (cyclopentadienyl) zirconium dichloride catalyst. Same procedure is followed as above (except that in place of NA-MgO as a support, TiO$_2$ is used) and the supported catalyst is denoted as NA-TiO$_2$/MAO/Cp$_2$ZrCl$_2$.

2.2.1.3. Commercial MgO (CM-MgO)/TiO$_2$ supported bis (cyclopentadienyl) zirconium dichloride catalysts. Same

procedure is followed as above. In place of NA-MgO/NA-TiO$_2$, commercial MgO/TiO$_2$ are used as supports.

2.3. Characterization

X-ray photoelectron spectroscopy studies are carried out for cat 1, cat 2, commercial MgO and commercial TiO$_2$ supported catalysts. We have determined the following ratios Zr/Al, Zr/Mg, Mg/Al and Zr/Al, Zr/Ti, Ti/Al for catalysts 1 and 2, respectively, at two different take-off angles (45° and 75°).

X-ray induced photoelectron spectra are taken with a Kratos Axis 165 ESCA system using monochromatic Mg Kα (1253.4 eV) radiation. Acquisition is carried out at room temperature in high-resolution mode [0.1 eV step, 40 eV pass energy] for the Mg 2p, Al 2p and Zr 3d regions. The samples are mounted as thin films on an adhesive copper tape in a glove box, introduced into a transfer chamber, and then evacuated to 10^{-9} Torr in 90 min using a turbo molecular pump. During data collection, an ion-getter pump kept the pressure in the analysis chamber under 10^{-9} Torr. To control the sampling depth in the XPS experiment, the samples were analyzed at take-off angles (angle between the surface plane and the irradiator) 45° and 75°. For each of the reported X-ray photoelectron spectra, an attempt has been made to deconvolute the experimental curve into a series of peaks representing photoelectron emissions from atoms in different chemical environments. These peaks are described as a mixture of Gaussian and Lorentzian contributions to take instrumental error into account together the characteristic shape of photoemission peaks. All binding energy values are charge referenced to C 1s peak at 284.6 eV. XPS experiments are done at two different angles. At 45°, the results obtained correspond to the catalyst surface, while at 75° the information obtained is from a depth near 5 nm.

FTIR analysis is recorded on Biorad 175C spectrometer in the wave number region 400 and 4000 cm^{-1} and number of scans are 64. DSC analysis is carried out on Mettler Toledo 821^e system in the temperature range 25–600 °C at a heating rate of 10 °C/min in nitrogen atmosphere. ^{1}H NMR are recorded on Gemini (200 MHz) spectrometer in CDCl$_3$ and ^{13}C NMR spectra on Bruker Advance 300 MHz spectrometer.

2.4. Polymerization procedure

Polymerization reactions are carried out in a two-necked 250-ml round bottom flask at room temperature. Prior to polymerization, the reactor is heated at 45 °C for 30 min and purged five times with argon gas. The flask is charged successively with the catalyst, dry toluene and the cocatalyst solution. Polymerization started on addition of the styrene monomer. The styrene is outgassed with N$_2$ for 15 min prior to the addition. When the monomer is completely polymerized, the polymer solution is separated from the catalyst by filtration and quenched with acidified methanol. The polymer is isolated by filtration and the residue is washed several times with toluene, methanol and water and dried in vacuum until a constant weight is obtained. The polymerization reactions are repeated three times to ensure reproducibility and reusability of the catalyst.

3. Results and discussion

3.1. XPS of supported metallocene catalysts

The supporting process is confirmed by XPS [17]. The XPS technique is widely used to identify and quantify surface species, as well as to study the chemical environment of metal atoms in catalysts. Survey scan of the supported catalyst clearly indicates all the constituent atoms (Mg, O, Ti, Al, Zr and C) present in the cat 1 and cat 2 are observed within the XPS sampling depth (approximately 3 nm). XPS core level spectra of Mg, Al, Ti, O and Zr are recorded in high resolution mode both at 45° and 75° take-off angles to probe the nature of distribution of these elements (Tables 1–3; Fig. 1). Both Al and Mg are present as respective oxides. In case of Zr, cat

Table 1
XPS Data on NA-MgO/MAO/Cp$_2$ZrCl$_2$

Element	Angle (°)	BE (eV)	FWHM (eV)	%
Mg	45	49.299	1.83	100
	75	49.321	1.77	100
Al	45	74.136	1.923	100
	75	74.179	1.938	100
Zr	45	182.434–184.74	1.63–1.579	61.2–38.8
	75	182.482–184.84	1.566–1.722	60.4–39.6

Table 2
XPS Data on NA-TiO$_2$/MAO/Cp$_2$ZrCl$_2$

Element	Angle (°)	BE (eV)	FWHM (eV)	%
Ti	45	458.5–464.2	1.282–1.986	69.8–30.2
	75	458.5–464.2	1.245–1.885	70.3–29.7
Al	45	74.5	1.97	100
	75	74.52	1.88	100
Zr	45	182.41–184.8	1.4–1.575	58.3–41.7
	75	182.45–184.81	1.42	59.9–40.1

Table 3
XPS ratios of the prepared catalysts

Catalyst	Angle (°)	Zr/Al	Zr/Mg	Mg/Al
NA-MgO/MAO/Cp$_2$ZrCl$_2$	45	0.031	0.103	0.304
	75	0.027	0.093	0.291
Commercial-MgO/MAO/Cp$_2$ZrCl$_2$	45	0.010	0.069	0.150
	75	0.007	0.057	0.123

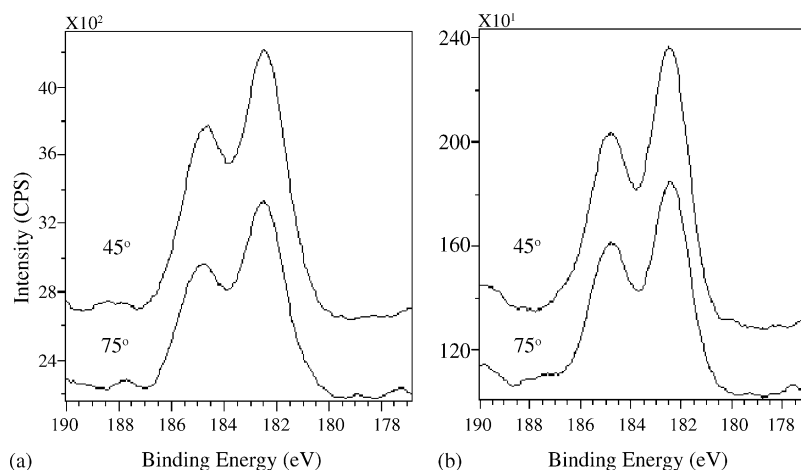| Catalyst	Angle (°)	Zr/Al	Zr/Ti	Ti/Al
NA-TiO$_2$/MAO/Cp$_2$ZrCl$_2$	45	0.096	0.087	1.102
	75	0.091	0.081	1.130
Commercial-TiO$_2$/MAO/Cp$_2$ZrCl$_2$	45	0.041	0.042	0.098
	75	0.045	0.081	0.056

Fig. 1. XPS narrow scans of Zr $3d_{5/2}$ and $3d_{3/2}$ for (a) NA-MgO-MAO-Cp$_2$ZrCl$_2$ and (b) NA-TiO$_2$-MAO-Cp$_2$ZrCl$_2$ at 45° and 75° take-off angles.

1 the $3d_{5/2}$ and $3d_{3/2}$ lines appear at 182.43 eV (61.2%) and 184.74 eV (38.85%) at 45° measuring angle and 182.48 eV (60.4%) and 184.84 eV (39.6%) at 75° angle, respectively. The perceptible shift in binding energy of Zr ($3d_{5/2}$) in the cat 1 is noticed from its pure complex, Cp$_2$ZrCl$_2$, which appears at 181.7 eV and the increase in binding energy, suggests that Zr is electron deficient in the supported metallocene catalyst. Ti 2p core level spectra also shows two signals that are due to spin orbit coupling of 2p electrons of Ti: ca. 458.6 eV ($2p_{3/2}$) and 465.4 eV ($2p_{1/2}$). The similar binding energy values (458.5 and 464.2 eV) both at 45° and 75° suggest that Ti is bonded to oxygen and is in TiO$_2$ form. In both of these supported catalysts Cl is detected at 199.2 eV, which implies that the metallocene catalyst is adsorbed on both the supports. The observed values of Zr/Mg = 0.103, Mg/Al = 0.304 at 45° and Zr/Mg = 0.093, Mg/Al = 0.291 at 75° in cat 1 and Zr/Ti = 0.087, Ti/Al = 1.102 at 45° and Zr/Ti = 0.081, Ti/Al = 1.130 at 75° in cat 2 indicate that both metallocene and MAO have been uniformly distributed in the support. From the Zr/Mg and Zr/Ti ratios both at 45° and 75°, it can be seen that Zr loading is higher in cat 1 than in cat 2.

In case of commercial supports, metallocene and MAO are not distributed uniformly. Here the concentrations of metallocene and MAO on surface are less compared to the nanoparticle supported catalyst.

3.2. FTIR spectra of nanoparticle supported metallocene catalysts

FTIR spectrum shows a decrease in the intensity of O−H peak (at 3500–3600 cm^{-1}) on addition of MAO on the nanoparticles (Fig. 2). This clearly indicates that MAO is forming a complex with the O−H on the support. No significant decrease in the intensity of O−H peak is observed when zirconocene is added which shows that zirconocene is not directly attached to the O−H. On the other hand, the presence of C=C (at 1450 and 810 cm^{-1}) peak in the final catalyst can be attributed due to the insertion of zirconocene, which is not present in the support or in MAO supported nanoparticle metal oxide (Fig. 3).

3.3. Polymerization

Cat 1 and cat 2 are used for stereoselective polymerization of styrene. Higher conversions of monomer to polymer (for cat 1 and cat 2) are obtained with the heterogeneous catalysts compared to the homogeneous system, Cp$_2$ZrCl$_2$-MAO. Moreover, the amount of MAO needed for the polymerization reaction using heterogeneous catalysts is much less when compared to the homogeneous polymerization reactions (to prepare the same amount of
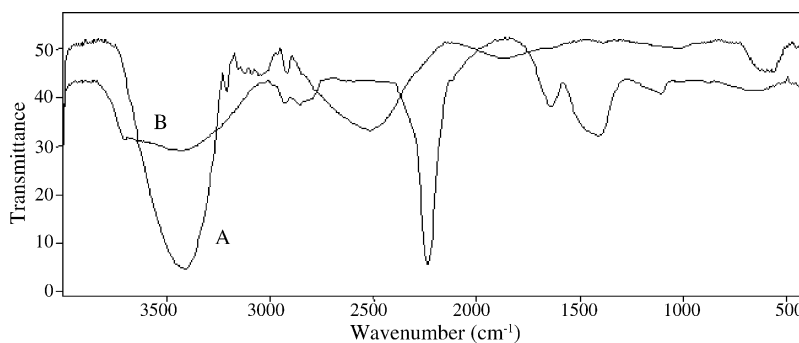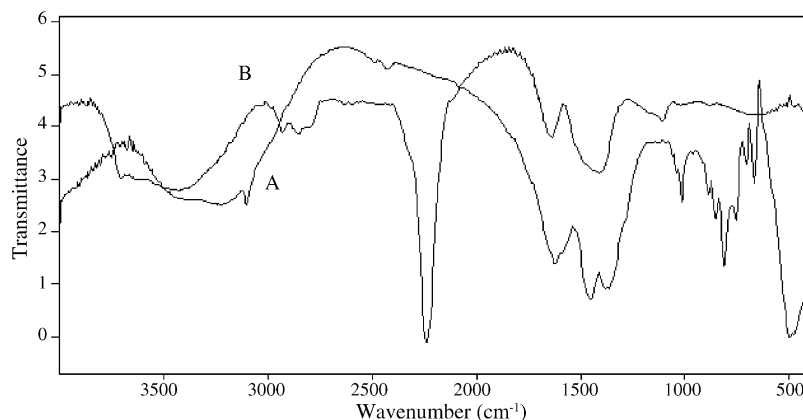

Fig. 2. IR spectra of (A) NA-MgO and (B) NA-MgO-MAO.

Fig. 3. IR spectra of (A) NA-MgO-MAO-Cp$_2$ZrCl$_2$ and (B) NA-MgO-MAO.

Table 4
Results of polymerization reactions

Entry no.	Catalyst	[Al]/[Zr][a]	A	M_n	M_w	T_g/T_m (°C)	S (%)	M_w/M_n
1	Cat 1	52.6	4,540	10,000	20,000	100/266	80	2.0
2		639	5,175	44,000	66,000	100/264	84	1.5
3		1958	10,403	63,636	70,000	100/266	79	1.1
4		4682	9,500	35,000	66,000	100/264	76	1.9
5	Cat 2	52.6	5,100	80,000	126,000	100/266	77	1.6
6		639	6,424	62,000	117,000	100/264	84	1.8
7		1958	11,704	118,081	142,381	100/266	86	1.2
8		4682	11,339	60,000	108,000	100/266	80	1.8
9	Homogeneous	2000	250	1,000	2,500	99/–	–	2.5

S = Triad syndiotacticity using data on C^{13} NMR spectra.
Cat 1: NA-MgO/MAO/Cp$_2$ZrCl$_2$.
Cat 2: NA-TiO$_2$/MAO/Cp$_2$ZrCl$_2$.
A = Activity (gps/mol Zr h).
   [a] [Zr] = 1.602 μmol.

polystyrene). Results of polymerization reactions are given in Table 4.

During the optimization studies of the catalysts, it is observed that the activity of the catalyst critically depends upon [Zr] [17] and [Al] [18].

Fig. 4(i) shows the relationship between the concentration of Al in MAO and yield of polymer produced. The yield of polymer is increased with an increase in MAO. The productivity rises to its maximum value up to 3720 μmol of Al, whereas >3720 μmol shows a slight decrease in the yield of the polymer. Similar trends are observed in earlier reports [10,19]. Fig. 4(ii) shows the relation between the concen-

tration of Zr and the yield of polymer produced. After the optimal concentration [1.602 μmol], the activity is reduced.

Here, in this study, we have found that both nanoparticle supported catalysts viz., cat 1 and cat 2 exhibit very good catalytic activity and produce polystyrene with high molecular weight and narrow polydispersity even with smaller amount of MAO ([Al]/[Zr]) = 52.6 compared to the other supported catalysts reported so far. Cat 2 exhibits better activity, giving high molecular weight and narrow polydispersity compared to cat 1 in all these experiments. Thus, NA-TiO$_2$ is found to be a better (slightly) support than NA-MgO, which may be due to its surface acidity.
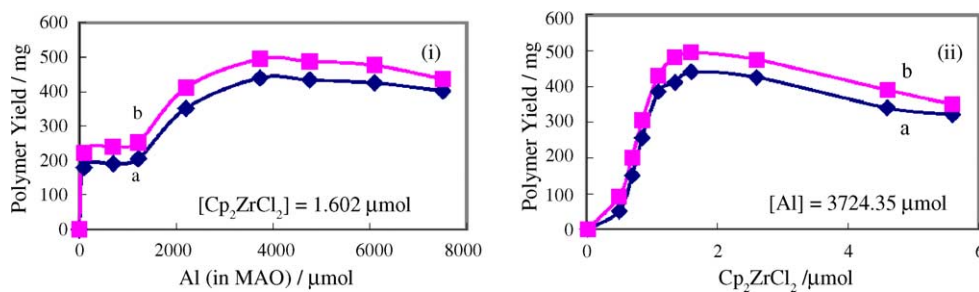
Fig. 4. Effect of (i) cocatalyst and (ii) Cp$_2$ZrCl$_2$ in styrene polymerization (a) cat 1 and (b) cat 2.
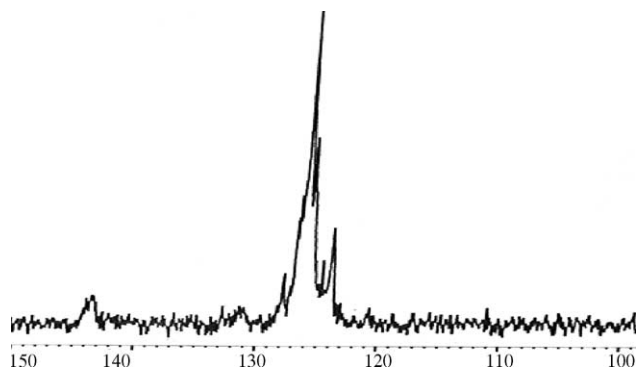
Fig. 5. ^{13}C NMR spectra of polystyrene prepared by cat 1.

Polymerization with CM-MgO-MAO and TiO$_2$-MAO (commercially available) supported Cp$_2$ZrCl$_2$ produces polystyrene in negligible yield. CM-MgO-MAO-Cp$_2$ZrCl$_2$ is found to have A [activity (gps/mol Zr h)] < 50 and commercial TiO$_2$-MAO-Cp$_2$ZrCl$_2$ is found to have A [activity (gps/mol Zr h)] < 50 and they produce low molecular weight polystyrene (<1000) with broader polydispersity (even with 3720 µmol of Al and 1.602 µmol of Zr) compared to nanoparticle supported catalysts. The higher activity of the supported catalysts is attributed to the higher surface area of the nano support because the accumulation of the catalyst and cocatalyst molecules is more on the surface (from XPS result). Moreover, the uniformity of active centers present on the nanoparticle surface during polymerization is much higher than the ordinary support as is observed from XPS studies. Therefore, the polymers obtained are with narrow molecular weight distribution and low polydispersity.

The polystyrenes thus obtained are examined by ^{13}C NMR. Fig. 5 shows that the polymers obtained using these supported catalysts are predominantly syndiotactic in nature [10]. On the other hand, atactic polystyrene is obtained by polymerization with homogeneous bis (cyclopentadienyl) zirconium dichloride catalyst [13].

The glass transition temperature and melting point of the polymers synthesized are determined by using DSC technique. The regular structure of syndiotactic polystyrene is reflected by high melting point and hardness of the polymer. These heterogeneous catalysts are reused for two cycles.

3.4. Recycling studies

After the completion of the first polymerization reaction, the catalyst is separated by filtration and dried. Styrene is added to the used catalyst and it is observed that the polymerization is slow when compared to the first reaction. It infers that some active moieties are still present in the catalyst either as initiating or growing species. The molecular weight is increased in the second polymerization reaction (entry 1, Table 4 for cat 1: $M_{n1} = 10,000$, $M_{n2} = 13,100$, $M_{n3} = 13,950$ and entry 5 for cat 2 $M_{n1} = 80,000$, $M_{n2} = 82,120$, $M_{n3} = 83,520$) whereas

the polydispersity decreased, indicating the growth of the existing polymer chains. Due to a possible blockage of the active sites by the existing chains, few new polymer chains are formed, limiting the diffusion of new monomer molecules to the active moieties [18]. Thermal analysis and IR analysis of the catalyst after use showed the presence of polystyrene. Moreover, the surface area of the catalysts after use is significantly reduced by 50–100 m^2/g for both NA-MgO supported and NA-TiO$_2$ supported catalysts. These results explain the drop in the activity of the reused catalysts, NA-MgO/MAO/Cp$_2$ZrCl$_2$ and NA-TiO$_2$/MAO/Cp$_2$ZrCl$_2$ in the styrene polymerization reaction.

4. Conclusions

Heterogeneous NA-MgO-MAO and NA-TiO$_2$-MAO supported b*is* (cyclopentadienyl) zirconium dichloride (Cp$_2$ZrCl$_2$) catalysts are synthesized and used for stereoselective polymerization of styrene monomer. The supporting process is confirmed by XPS and FTIR. Nanoparticle supported zirconocene catalysts gave higher yield of syndiotactic styrene polymer with high M_n and M_w and narrow molecular weight distribution when compared with the other supported zirconocene catalysts. These heterogeneous catalysts are reused for two cycles. Further experiments are in progress on polymerization of ethylene.

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