



# 1-Hexene polymerization by $\text{Cp}^*\text{TiX}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$ [X: Cl, Me] in the presence of MAO- and MMAO-modified carbonaceous supports

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## ABSTRACT

Various MAO-, MMAO-modified carbonaceous materials with different degrees of coalification, surface areas and amounts of nitrogen in their structures have been prepared, and the nature of Al supported and their compositions of elements close to surface were determined by the XPS method. These materials were effective as supported cocatalysts in 1-hexene polymerization using  $\text{Cp}^*\text{TiX}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$  [X = Cl (1), Me (2)], affording poly(1-hexene)s with unimodal molecular weight distributions; the facts clearly suggest that these polymerizations proceeded with uniform (single-site) catalytically active species. The activities were affected by the nature of the carbonaceous supports employed, whereas the surface area does not strongly affect the activity in this catalysis.

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## 1. Introduction

Design of transition metal complex catalysts for precise olefin polymerization attracts considerable attention in the field of catalysis, organometallic chemistry, and polymer chemistry [1–3]. We have demonstrated that half-titanocenes containing anionic donor ligands exhibit unique characteristics especially for ethylene copolymerizations [3b,4]. Design of supported *single-site* catalysts has also been one of the most attractive subjects especially in the field of catalysis [5,6] in terms of better morphology controls for large-scale production. Approaches using supported catalysts (with homogeneous cocatalysts) or supported cocatalysts (with homogeneous catalysts) have been known [5].

We recently reported that the catalytic activity in styrene polymerization using a catalyst system, composed of  $\text{CpTiCl}_2(\text{O}-4\text{-ClC}_6\text{H}_4)$  loaded on the carbonaceous materials and MAO, was strongly affected by nitrogen heteroatoms in the structure of supported carbonaceous materials [7]. However, the activities significantly decreased compared to the homogeneous system and the resultant polymers possessed several compositions, probably due to partial decomposition of the titanium complex pretreated with carbonaceous materials.

In this article, we thus focused on using MAO-, MMAO-modified carbonaceous materials, instead of using prepared supported Ti complex in the above study [7]. Since physical as well as chemical

properties of the carbonaceous materials with different degrees of coalification and functional groups on the surface can be generally modified by introduction of specific heteroatoms, such as nitrogen, oxygen, sulfur and phosphorus, into their structure [8], we explored the electronic natures and compositions of the surface of the prepared MAO-, MMAO-modified materials with different degrees through measurement by XPS. We then explored possibilities of using these carbonaceous materials as the supported cocatalysts for 1-hexene polymerization using  $\text{Cp}^*\text{TiX}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$  [X = Cl (1), Me (2)] complexes, which exhibit unique characteristics in precise olefin (co)polymerization [3b,4]. Through this study, we wish to develop a possibility of using these materials as the supported cocatalysts for precise olefin (co)polymerization.

## 2. Experimental

### 2.1. General procedure

All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox unless otherwise specified. All chemicals used were of reagent grades and were purified by standard purification procedures. Anhydrous grades of 1-hexene and toluene (Kanto Kagaku Co. Ltd.) were transferred into a bottle containing molecular sieves (mixture of 3A 1/16 and 4A 1/8, and 13X 1/16) in the drybox under a nitrogen stream.  $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$  (1) and  $\text{Cp}^*\text{TiMe}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$  (2) were prepared according to our previous report [9]. Toluene and  $\text{AlMe}_3$  in the commercially available methylaluminoxane [PMAO-S, 9.5 wt.% (Al)] toluene solution, Tosoh Finechem Co.] were removed under

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**Table 1**  
Summary of sample codes of a series of carbonaceous materials, and required amount of MAO and MMAO for their modifications.

Sample code <sup>a</sup>	N <sup>b</sup> [wt.%]	(O+S) <sup>b</sup> [wt.%]	S <sub>BET</sub> <sup>b</sup> [m <sup>2</sup> /g]	MAO <sup>c</sup> [g/g]	MMAO <sup>c</sup> [g/g]
PK	0.4	9.3	313	0.345	0.421
PKA	0.1	11.2	814	0.400	0.487
BDN <sub>2</sub>	23.5	22.6	7	1.74	2.120
BDKN <sub>2</sub>	9.8	17.2	237	0.969	1.179
BDKN <sub>2</sub> A	1.6	11.2	800	0.447	0.544
BDK (NO) <sub>300</sub>	3.9	13.6	13	0.737	0.897
SDK	0.0	7.0	1	0.290	0.353

<sup>a</sup> Sample code: P—plum stones, B—brown coal, S—subbituminous coal, D—demineralization, K—carbonization in 700 °C, A—steam activation in 800 °C, N<sub>2</sub>—amoxidation in 350 °C, (NO)<sub>300</sub>—nitrogenation with NO in 300 °C. More details are described in Section 2 and Ref. [10].

<sup>b</sup> Estimated from Refs. [7] and [10].

<sup>c</sup> Calculated amount of MAO or MMAO (gram) per gram of carbonaceous materials on the basis of molar amount of heteroatoms (oxygen, nitrogen, sulfur).

reduced pressure (at ca. 50 °C for removing toluene, AlMe<sub>3</sub>, and then heated at >100 °C for 1 h for completion) in the drybox to give white solids [9]. A modified methylaluminoxane (MMAO) sample [methyl-isobutylaluminoxane, MMAO 3AT toluene solution, Me<sup>i</sup>Bu = 2.33, Tosoh Finechem Co.] was also used as white solids after removing solvent, AlMe<sub>3</sub>, and Al<sup>i</sup>Bu<sub>3</sub> *in vacuo* according to the analogous procedure as that in PMAO-S except that the resultant solid was re-dissolved in toluene (or in hexane) and then removed *in vacuo* to remove Al<sup>i</sup>Bu<sub>3</sub> completely [4a].

Various carbonaceous materials employed in this study were used as reported previously [7,10], and their physicochemical data (compositions, surface area, etc.) are summarized in Table 1. Raw samples of the carbonaceous materials [i.e. plum stones (P), brown coal (B) and subbituminous coal (S)] were enriched with nitrogen by amoxidation (N) or nitrogenation (NO); the amoxidation (N) was carried out using a mixture of ammonia and air at a volume ratio of 1:3 (250/750 cm<sup>3</sup> min<sup>-1</sup>) in a flow reactor at 350 °C for 5 h [7], whereas samples for the nitrogenation (NO) were exposed to nitrogen(II) oxide (620 mL/min.) in a flow reactor at 300 °C for 2 h [10]. The samples were carbonized (K) accompanied by evolution of gases during the process where the temperature in the vessel was increased at the rate of 5 °C min<sup>-1</sup> to 700 °C and was maintained for 1 h. Activation (A) was then conducted by steam at 800 °C for 1.5 h [7,10]. The sequences of symbols in support's codes are thus corresponded to the sequences of their treatments.

Molecular weights and molecular weight distributions of poly(1-hexene)s were measured by means of gel-permeation chromatography (GPC). HPLC grade THF was used for GPC and were degassed prior to use. GPC were performed at 40 °C on a Shimadzu SCL-10A chromatograph using a RID-10A detector (Shimadzu Co. Ltd.) in THF (containing 0.03 wt.% 2,6-di-*tert*-butyl-*p*-cresol, flow rate 1.0 ml/min). GPC columns (ShimPAC GPC-806, -804 and -802, 30 cm × 8.0 mm Ø) were calibrated versus polystyrene standard samples.

## 2.2. Preparation of carbonaceous materials by modification with MAO, MMAO

Modifications of the carbonaceous materials by MAO and MMAO were typically carried out as follows. These carbonaceous supports were dried under vacuum at 120 °C for 12 h. To a support (1.0 g) containing toluene (20.0 mL) in a Schlenk flask was added a prescribed amount of MAO or MMAO at 25 °C under nitrogen atmosphere (in the drybox), and the mixture was stirred for 16 h [11]. The amounts of MAO and MMAO added were calculated on the basis of total molar amount of heteroatoms (nitrogen, oxygen, and sulfur, according to elemental analysis) estimated by the elemental analysis (Table 1), because Al should strongly bind heteroatoms in these materials. The solvent in the reaction mixture was removed by decantation and the residue was washed twice with toluene (20 mL 2 ×) in order to remove unsupported free MAO or MMAO

completely. The amounts of Al (mmol/g) presented in (loaded on) the supports after modification were estimated according the initial amount of MAO/MMAO employed, not only because the amounts of Al extracted in toluene were small in most cases but also because perfect separation of the supports and the toluene extract by simple decantation seemed somewhat difficult.

Typically in preparation of the PKA/MMAO, PKA (1.0 g) and MMAO (0.487 g) were mixed in toluene at 25 °C for 16 h, the amount of the toluene extract (toluene soluble portion after removing toluene/volatiles *in vacuo*) after decantation was 86 mg, and the amount of the extracts by additional washing with toluene (stirred for >1 h at 25 °C) was negligible. We confirmed that the amount of toluene extracts were negligible especially in the 2nd wash with toluene, suggesting that MAO and MMAO in the resultant supports were strongly absorbed under these conditions.

## 2.3. XPS analysis

Surface compositions of the samples studied were determined by X-ray photoelectron microscopy (XPS) using an AXIS 165 spectrometer (KRATOS) in X-ray radiation Al Kα with the X-ray power of 150 W and the layer depth of ca. 3.5–4 nm.

## 2.4. 1-Hexene polymerization

A prescribed amount of the modified support (calculated amount according to the amount of Al), and 1-hexene (5.0 mL) were added into a Schlenk flask in the drybox. The polymerization was started by the addition of a prescribed amount of catalyst (1 or 2) in toluene. The reaction mixture was stirred at 25 °C for a certain period (60 min). The polymerization was terminated by addition of EtOH (15 mL) containing HCl (5 mL), and the mixture was then extracted with CHCl<sub>3</sub> (50 mL 3 ×). The combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and chloroform and the volatile in the solution were removed *in vacuo* to give poly(1-hexene) as amorphous materials, confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectra and GPC measurements.

## 3. Results and discussion

### 3.1. Preparation of MAO or MMAO-modified carbonaceous materials, and XPS analysis of carbonaceous materials before and after their modification with MAO or MMAO

Various carbonaceous materials, enriched with nitrogen by two different factors [i.e. nitrogenation (NO)<sub>300</sub> and amoxidation (N<sub>2</sub>)] [7,10], were chosen for preparation of MAO- and MMAO-modified supports (cocatalysts). The carbonization (K), steam activation (A) processes were taken for modification of the surface more orderly (K), and for increasing the surface area as well as pores (A). The resultant carbonaceous materials were then pretreated

with a certain amount of MAO or MMAO in toluene and use in preparing high molecular weight polymers with uniform molecular weight distributions in the ethylene copolymerization [4a,9,12] and 1-hexene polymerization using  $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-i-Pr}_2\text{C}_6\text{H}_3)$  (**1**) employed in this study [9,12]. In most preparation runs, certain small amounts of residual MAO/MMAO were collected as the toluene wash, suggesting that all supports were pretreated with MAO or MMAO in a rather excess amount. Moreover, as described in Section 2, we confirmed that the amount of toluene extracts were negligible especially in the 2nd wash with toluene, suggesting that MAO and MMAO in the resultant supports were absorbed under these conditions. Determination of the Al contents by MIP-MS analysis was very difficult due to the fact that most of Al was adsorbed strongly on carbon even after treatment with nitric acid. Therefore, we estimated the Al amount in the support on the basis of the initial ratio.

The electronic nature (binding energy) and composition of elements close to the surface of the MAO- and MMAO-modified materials were explored by XPS analyses, and the results are summarized in Tables 2 and 3. The original supports before impregnation, MAO, and MMAO were also examined for comparison. Fig. 1 shows XPS C 1s spectra of SDK and BDKN<sub>2</sub>A supports before and after their modifications with MAO or MMAO. Fig. 2 also shows the Al 2p spectra of the supports after modification with MAO or MMAO.

As shown in Table 2, the Al contents by XPS in the MAO-modified carbonaceous materials were higher than those calculated based on the amount of MAO loaded into the support, except BDN<sub>2</sub> which possesses the highest heteroatom contents (Table 2). The percentages of the oxygen measured by XPS were also high and the percentages of carbon were low compared to the calculated values in all cases. This is because the XPS analysis measures only few layers on the surface, and the facts clearly suggest that the Al in MAO or MMAO was located on the surface. The Al contents measured by XPS (20.66–27.77 wt.%) were, however, lower than the values of MAO itself [(MeAlO)<sub>n</sub>, Al 46.5 wt.% (calculated), 32.64 wt.% (by XPS)], suggesting that surface of the supported materials was not completely covered by MAO. The latter assumption was confirmed by XPS spectra, because the peaks ascribed to the original supports (SDK, BDKN<sub>2</sub>A) were also seen in the XPS spectra in the prepared supports (Fig. 2a–d, fractional).

According to their elemental analysis results previously reported [7,10], total amount of N, O+S (volatile matter) in the materials derived from brown coal increased in the order: BDN<sub>2</sub> (46.1) > BDKN<sub>2</sub> (27.0) > BDK(NO)<sub>300</sub> (17.5) > BDKN<sub>2</sub>A (12.8). The amount of Al on the surface measured by XPS increased in the order: BDN<sub>2</sub> (27.77) > BDKN<sub>2</sub>A (26.91) > BDKN<sub>2</sub> (25.98) > BDK(NO)<sub>300</sub> (20.66). The observed differences in the order between BDKN<sub>2</sub> and BDKN<sub>2</sub>A can be due to the fact that surface area in BDKN<sub>2</sub>A is much larger than that in BDKN<sub>2</sub>, as a result of increased number of pores after steam activation followed by carbonization. In the supported materials designated as BDK(NO)<sub>300</sub>, the amount of Al supported around the surface was somewhat lower than that supported on BDKN<sub>2</sub>, and this should be due to the different pretreatment procedures (N<sub>2</sub>-ammonoxidation at 350 °C vs. nitrogenation with NO at 300 °C) that introduce nitrogen atoms with different chemical properties. This means that the nitrogen introduced by nitrogenation is present in acidic forms, whereas the nitrogen introduced by ammonoxidation is basic [7,10]; the difference would influence the Al content after MAO modification, although we are not sure why the binding energies were close.

Table 3 summarizes the electronic nature (binding energy) and composition of elements close to the surface of the MMAO-modified materials explored by XPS analyses. The amount of Al on the surface measured by XPS increased in the order: BDKN<sub>2</sub>A (24.92) > BDK(NO)<sub>300</sub> (24.53) > BDKN<sub>2</sub> (20.72) > BDN<sub>2</sub> (20.38). The

**Table 2**  
Summary of XPS data of MAO-modified carbonaceous supports.

Support code <sup>a</sup>	N + (O + S) <sup>b</sup> [wt.%]	S <sub>BET</sub> <sup>b</sup> [m <sup>2</sup> /g]	C 1s			O 1s			Al 2p				
			BE [eV]	Atomic conc. [%]	BE [eV]	Atomic conc. [%]	BE [eV]	Atomic conc. [%]	BE [eV]	Atomic conc. [%]	Al calcd <sup>c</sup> [%] (mmol/g)		
												Before modification	Modified with MAO
PK	9.7	313	285.994	77.22	290.764	12.77	533.035	2.01	532.773	60.38	75.074	26.85	11.9 (4.42)
PKA	11.3	814	285.639	97.03	285.822	19.18	532.891	2.97	531.925	57.56	75.606	23.27	13.3 (4.93)
BDN <sub>2</sub>	46.1	7	286.246	74.55	290.106	13.00	531.270	7.65	532.494	58.60	74.762	27.77	29.6 (10.95)
BDKN <sub>2</sub>	27.0	237	285.512	86.90	288.545	11.56	533.474	7.14	532.619	62.46	74.852	25.98	22.9 (8.48)
BDKN <sub>2</sub> A	12.8	800	289.469	96.62	291.126	11.90	532.289	3.38	533.333	61.19	75.614	26.91	14.4 (5.33)
BDK(NO) <sub>300</sub>	17.5	13	284.710	94.58	290.248	12.87	533.314	5.42	531.183	66.46	74.766	20.66	19.8 (7.32)
SDK	7.0	1	286.169	97.60	290.078	26.27	533.242	2.40	532.675	51.06	74.79	22.67	10.5 (3.88)

<sup>a</sup> Sample code shown in Table 1, and more details are described in Section 2 and Ref. [7].

<sup>b</sup> Contents in the supports before modification cited from Ref. [7].

<sup>c</sup> Calculated on the basis of MAO added (g/g-support). BE (atomic conc.) in MAO: O 1s 531.579 eV (67.36%); Al 2p 75.084 eV (32.64%).

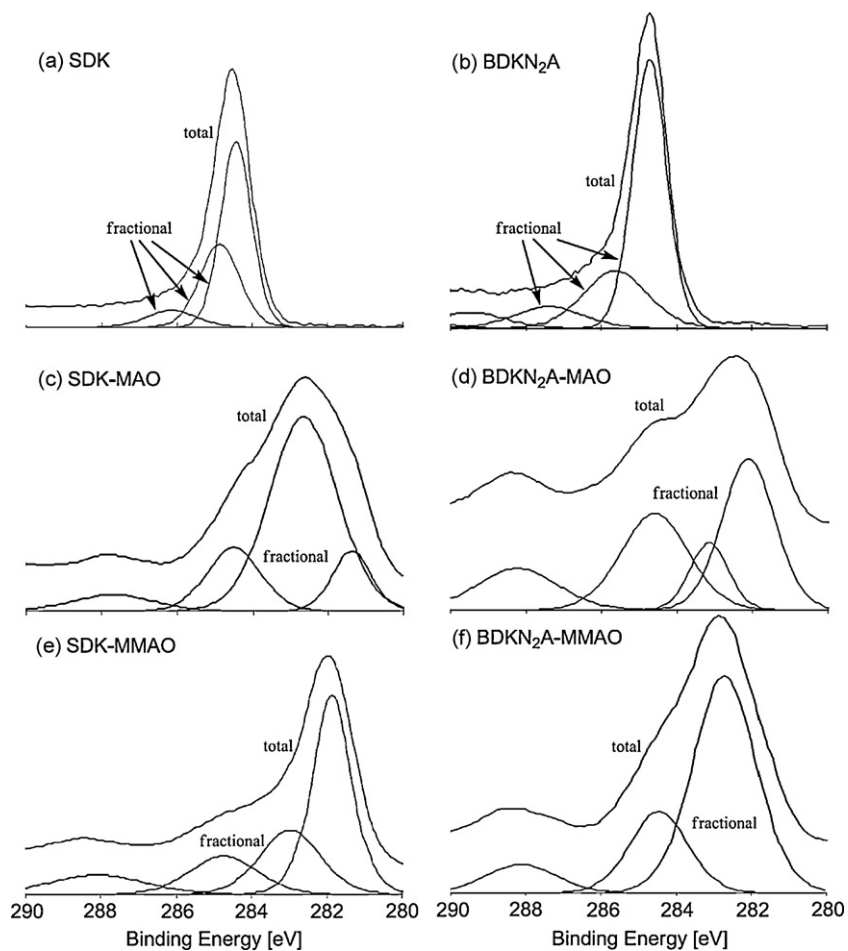


Fig. 1. XPS C 1s spectra of SDK and BDKN<sub>2</sub>A supports before and after their modification with MAO and MMAO (support codes according to Table 1).

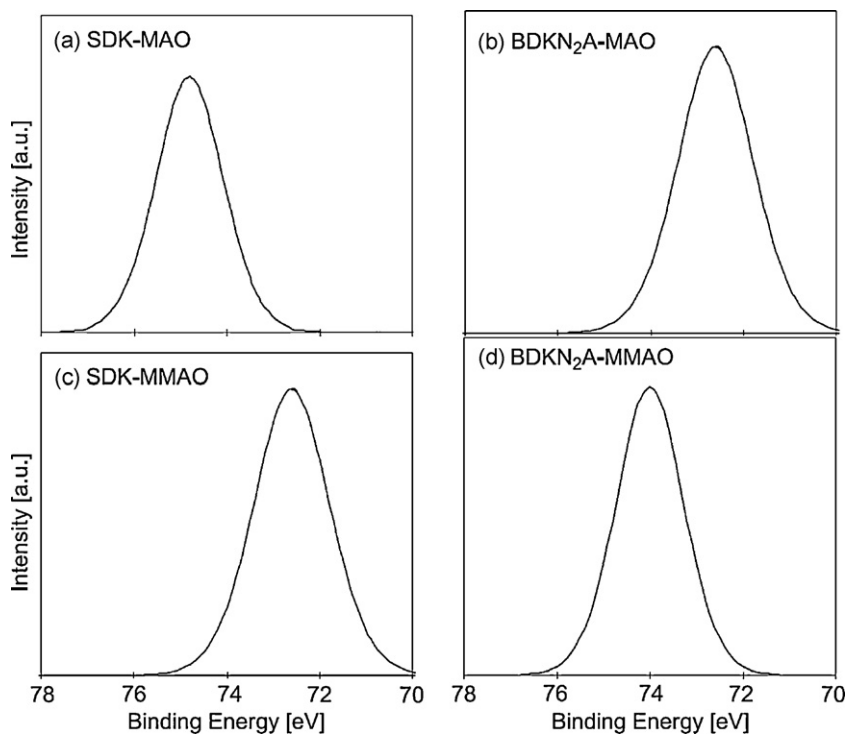


Fig. 2. XPS Al 2p spectra of SDK and BDKN<sub>2</sub>A supports after their modification with MAO and MMAO [support codes according to Table 1, and Binding energy (B.E.) for MAO, MMAO were 75.084, 74.926 eV, respectively].

**Table 3**  
Summary of XPS data of MMAO-modified carbonaceous supports.

Support code <sup>a</sup>	N+(O+S) <sup>b</sup> [wt.%]	S <sub>BET</sub> <sup>b</sup> [m <sup>2</sup> /g]	C 1s		O 1s		Al 2p		Al theoretical [%] (mmol/g) <sup>c</sup>
			BE [eV]	Atomic conc. [%]	BE [eV]	Atomic conc. [%]	BE [eV]	Atomic conc. [%]	
PK	9.7	313	288.147	20.52	530.715	55.94	72.600	21.47	13.8 (5.11)
PKA	11.3	814	291.173	22.68	530.605	54.78	72.619	22.54	15.2 (5.65)
BDN <sub>2</sub>	46.1	7	287.152	25.02	530.542	25.02	72.680	20.38	31.6 (11.72)
BDKN <sub>2</sub>	27.0	237	288.329	27.43	530.740	51.85	72.881	20.72	25.2 (9.33)
BDKN <sub>2</sub> A	12.8	800	288.117	17.83	530.475	57.24	72.699	24.92	16.4 (6.07)
BDK(NO) <sub>300</sub>	17.5	13	287.978	19.18	530.734	56.29	72.694	24.53	22.0 (8.15)
SDK	7.0	1	288.099	28.20	530.845	28.20	72.868	21.43	12.1 (4.50)

<sup>a</sup> Sample code shown in Table 1, and more details are described in Section 2 and Ref. [7].

<sup>b</sup> Contents in the supports before modification cited from Ref. [7].

<sup>c</sup> Calculated on the basis of MAO added (g/g-support). BE (atomic conc.) in MMAO: O 1s 531.448 eV (68.77%); Al 2p 74.926 eV (31.23%).

fact may suggest that the effect of the surface area and the electronic nature of nitrogen seems dominant than the heteroatom content in the MMAO-modified materials (containing isobutyl group on Al).

As exemplified in Fig. 2 (MAO, MMAO-modified SDK, MAO, and MMAO-modified BDKN<sub>2</sub>A), the Al 2p spectra by XPS showed only one relatively sharp peak. The binding energies in the resultant MAO-modified materials increased in the order: BDKN<sub>2</sub>A (75.614 eV) > PKA (75.606) > MAO (75.084) > PK (75.074) > BDKN<sub>2</sub> (74.852) > SDK (74.79) > BDK(NO)<sub>300</sub> (74.766), BDN<sub>2</sub> (74.762). The results clearly suggest that Al in MAO was affected by the carbonaceous supports employed, probably due to certain coordination with the functional groups present on the surface of carbonaceous supports. The values in the MAO-modified materials after steam activation (BDKN<sub>2</sub>A, PKA) were larger than those before the activation (BDKN<sub>2</sub>, PK) and MAO. In contrast, the binding energies in the resultant MMAO-modified materials (72.6–72.881 eV) became lower than MAO (74.916 eV), and no significant differences were seen. The results also suggest that Al in MMAO was affected by the carbonaceous supports employed. The values in the MMAO-modified materials were lower compared to those obtained in the case of MAO-modified materials, probably due to a difference in the alkyl substituents on Al (Me or Me + <sup>i</sup>Bu).

### 3.2. 1-Hexene polymerization by Cp\*TiX<sub>2</sub>(O-2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (X = Cl, Me) in the presence of MAO-, MMAO-modified carbonaceous supports

1-Hexene polymerizations using Cp\*TiCl<sub>2</sub>(O-2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (**1**) were conducted at 25 °C in the presence of MAO- or MMAO-modified SDK with various Al/Ti molar ratios. Complex **1** was chosen because **1** exhibited remarkable catalytic activity in 1-hexene polymerization in the presence of MAO in a homogeneous system, affording high molecular weight polymers with uniform molecular weight distribution [9,12]. SDK was selected to optimize the polymerization conditions, because this support would

be considered as the standard support containing a small amount of nitrogen/oxygen and the most ordered surface. The results are summarized in Table 4.

The catalytic activity estimated on the basis of the polymer yield initially increased upon increasing the Al/Ti molar ratio (Al 1.0–3.0 mmol), but kept constant upon further addition (Al 3.0–5.0 mmol). The activities in the presence of MAO-modified SDK were higher than those in the presence of MMAO-modified SDK, and this implies that the effect of cocatalyst plays a role in the activity. Moreover, the molecular weights of poly(1-hexene) prepared in the presence of MMAO-modified SDK were higher than those prepared in the presence of MAO-modified SDK. These differences would be due to the percentage of the catalytically active species as well as the degree of dominant chain transfer reaction employed in these catalyses. Since the *M<sub>n</sub>* values of the poly(1-hexene) were not strongly affected by the Al/Ti molar ratios under these conditions, we would thus assume that the dominant chain transfer would be β-hydrogen elimination rather than the chain transfer to aluminium, as suggested in the homogeneous system [12]. Molecular weight distributions in the resultant polymers were unimodal in all cases, and the resultant polymers was atactic poly(1-hexene) revealed by <sup>13</sup>C NMR [9,12].

Table 5 summarizes time course in 1-hexene polymerization using **1** in the presence of MAO, MAO-, and MMAO-modified SDK under the optimal conditions (3.0 mmol of Al, Al/Ti molar ratio of 600) at 25 °C. The polymerization using homogeneous **1**-MAO catalyst system proceeded at remarkable rate at the initial stage and decreased gradually, and the observed trend is similar to that in our previous report [12], whereas a first order relationship between the monomer concentration and the reaction rate was seen, suggesting that the apparent decrease in the activity is not due to the deactivation of catalytically active species but the decrease in the 1-hexene concentration [12b]. The activity by **1** in the presence of MAO-modified SDK was initially low, but increased after 1 h probably due to an induction period for generating the catalytically active

**Table 4**  
Selected data on polymerization of 1-hexene by Cp\*TiCl<sub>2</sub>(O-2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (**1**) in the presence of MAO-, MMAO-modified SDK<sup>a</sup>.

Al (mmol)		Yield (g)	Activity <sup>b</sup>	TON <sup>c</sup>	<i>M<sub>n</sub></i> <sup>d</sup> × 10 <sup>-5</sup>	<i>M<sub>w</sub></i> / <i>M<sub>n</sub></i> <sup>d</sup>
1.0	MAO	0.165	33.0	329	6.63	1.53
2.0	MAO	0.238	47.6	567	4.48	1.86
3.0	MAO	0.588	117.6	1400	6.81	1.97
5.0	MAO	0.602	120.4	1433	7.42	1.90
1.0	MMAO	0.067	13.4	160	11.87	1.80
2.0	MMAO	0.086	17.2	204	12.17	1.77
3.0	MMAO	0.196	39.2	467	12.81	1.64
5.0	MMAO	0.201	40.2	478	12.15	1.59

<sup>a</sup> Reaction conditions: (**1**) 5 μmol (10 μmol/mL toluene), 1-hexene 5.0 mL, 25 °C, 60 min.

<sup>b</sup> Activity in kg polymer/mol-Ti h.

<sup>c</sup> TON (turnover number = molar amount of 1-hexene reacted/mol Ti).

<sup>d</sup> GPC data in THF vs. polystyrene standards.

**Table 5**  
Time course for 1-hexene polymerization using Cp\*TiCl<sub>2</sub>(O-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (**1**)—cocatalyst systems<sup>a</sup>.

Cocatalyst (Ti/ $\mu$ mol)	Time (min)	Activity <sup>b</sup>	TON <sup>c</sup>	$M_n^d \times 10^{-5}$	$M_w/M_n^d$
Homogeneous (5.0)	20	344	1350	8.84	2.03
	40	186	1480	8.41	2.04
	60	140	1660	9.06	2.21
	80	107	1690	9.60	2.12
	100	86.1	1710	11.69	2.13
SDK/MAO (5.0)	20	75.2	295	7.52	1.79
	40	66.3	528	4.94	2.02
	60	118	1400	6.81	1.97
	80	92.0	1460	7.53	1.87
	100	74.1	1470	7.31	1.92
SDK/MMAO (5.0)	20	43.6	171	6.01	1.53
	40	32.8	262	11.82	1.83
	60	39.2	467	12.81	1.64
	80	30.2	478	12.96	1.83
	100	24.4	486	13.07	1.87

<sup>a</sup> Reaction conditions: (**1**) 5.0  $\mu$ mol (10  $\mu$ mol/mL toluene), 1-hexene 5.0 mL, 25 °C.

<sup>b</sup> Activity in kg polymer/mol-Ti h.

<sup>c</sup> TON (turnover number = molar amount of 1-hexene reacted/mol-Ti).

<sup>d</sup> GPC data in THF vs. polystyrene standards.

species (proposed cationic alkyl species [13]). In contrast, such an induction period was not seen in the polymerization by **1** in the presence of MMAO-modified SDK. The  $M_n$  values of poly(1-hexene) were not affected by the reaction time and the  $M_w/M_n$  values were constant ( $M_w/M_n = 1.79$ – $2.02$ ), clearly suggesting that the polymerization proceeded with a certain degree of chain transfer reactions.

Table 6 summarizes results for 1-hexene polymerization using Cp\*TiX<sub>2</sub>(O-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) [X = Cl (**1**), Me (**2**)] in the presence of a series of MAO-, and MMAO-modified carbonaceous supports, and the results using **1,2**-MAO, and MMAO catalysts (homogeneous conditions) are shown for comparison. The dimethyl analogue (**2**) showed higher catalytic activities than the dichloro analogue (**1**) irrespective of the kind of MAO-modified carbonaceous supports, whereas no significant differences in the  $M_n$  values in the resultant poly(1-hexene)s were observed in these catalyses; these would be due to the incomplete alkylation of Ti–Cl bonds **1**. As seen in Table 5, the catalytic activities in the presence of MMAO-supported cocatalysts were lower than that in the presence of MAO-supported catalysts. The activity of **2** in the presence of a series of MAO-modified supports

increased in the order: SDK > homogeneous > BDK(NO)<sub>300</sub> > BDN<sub>2</sub>, BDKN<sub>2</sub>A > PKA. The order in the activity of **2** in the presence of a series of MMAO-supported catalyst systems was somewhat similar to that of **2**-MAO-supported catalyst, except that the homogeneous catalyst system showed much higher catalytic activity. We thus assume that this would be due to an influence of (probably) electronic nature of the Al species, although we could not see the distinct trend from the XPS analysis results. One exception it might be interesting to note is that the activity of **2** in the presence of MAO-SDK cocatalyst was higher than that of **2** in the presence of MAO cocatalyst (homogeneous system). In contrast, the order for the dichloro analogue (**1**) was somewhat different from that for the dimethyl analogue (**2**), probably due to the percentage of generated catalytically active species. It also seems likely that the activity was not strongly influenced by the surface area of the supports employed, as reported for the gas phase ethylene polymerization [14].

We have shown that 1-hexene polymerizations using Cp\*TiX<sub>2</sub>(O-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) [X = Cl (**1**), Me (**2**)] in the presence of MAO-, MMAO-modified carbonaceous materials proceed from

**Table 6**  
Polymerization of 1-hexene using Cp\*TiX<sub>2</sub>(O-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) [X = Cl (**1**), Me (**2**)] in the presence of different supports<sup>a</sup>.

Support	N <sup>b</sup> [wt.]	S <sub>BET</sub> <sup>b</sup> [m <sup>2</sup> /g]	Al 2p <sup>c</sup> [eV]	Ti [wt.%]	Activity <sup>d</sup>	TON <sup>e</sup>	$M_n^f$	$M_w/M_n^f$ ( $\times 10^{-5}$ )	
MAO-PKA	0.1	814	75.606	23.27	<b>2</b>	105	1130	6.44	2.08
MAO-BDN <sub>2</sub>	23.5	7	74.762	27.77	<b>2</b>	94.6	1260	5.81	1.91
MAO-BDKN <sub>2</sub> A	1.6	800	75.614	26.91	<b>2</b>	106	1250	7.64	1.99
MAO-BDK(NO) <sub>300</sub>	3.9	13	74.766	20.66	<b>2</b>	130	1550	6.45	2.31
MAO-SDK	0	1	74.790	22.67	<b>2</b>	154	1840	10.23	2.20
MAO-Homogenous			75.084	–	<b>2</b>	144	1720	8.74	2.12
MAO-BDN <sub>2</sub>	23.5	7	74.762	27.77	<b>1</b>	61.4	731	8.5	2.05
MAO-BDKN <sub>2</sub> A	1.6	800	75.614	26.91	<b>1</b>	80.4	957	7.84	2.26
MAO-SDK	0	1	74.790	22.67	<b>1</b>	118	1400	6.81	1.97
MAO-Homogenous			75.084	–	<b>1</b>	140	1660	9.06	2.21
MMAO-PKA	0.1	814	72.619	22.54	<b>2</b>	36.4	433	9.66	1.94
MMAO-BDN <sub>2</sub>	23.5	7	72.680	20.38	<b>2</b>	22.6	269	7.78	1.86
MMAO-BDKN <sub>2</sub> A	1.6	800	72.699	24.92	<b>2</b>	37.8	450	10.18	1.96
MMAO-BDK(NO) <sub>300</sub>	3.9	13	72.694	24.53	<b>2</b>	42.4	505	9.50	1.92
MMAO-SDK	0	1	72.868	21.43	<b>2</b>	54.4	648	10.37	1.57
MMAO-Homogenous			74.926	–	<b>2</b>	137	1630	10.46	2.13

<sup>a</sup> Sample code shown in Table 1, and more details are described in Section 2 and Ref. [7]. Reaction conditions: 1-hexene 5 mL, Cp\*TiX<sub>2</sub>(O-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) [X = Cl (**1**), Me (**2**)] 5.0  $\mu$ mol (10  $\mu$ mol/mL toluene), 25 °C, 60 min.

<sup>b</sup> Values before modification cited from Ref. [7] and [10].

<sup>c</sup> By XPS analysis.

<sup>d</sup> Activity in kg polymer/mol-Ti h.

<sup>e</sup> TON (turnover number = molar amount of 1-hexene reacted/mol-Ti).

<sup>f</sup> GPC data in THF vs. polystyrene standards.

moderate to remarkable catalytic activities affording high molecular weight polymers with unimodal molecular weight distribution. The production of the polymer with uniform molecular weight distribution clearly indicates that these polymerizations took place with uniform catalytically active species. The catalytic activity was influenced by the nature of the carbonaceous support employed, whereas the activity was not strongly influenced by the surface area. Although the details concerning the origin affecting the activity is still not clear, we believe that these are promising and important information for designing supported catalyst for precise olefin polymerization.

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### References

- [1] For example (recent reviews), see:  
 (a) V.C. Gibson, S.K. Spitzmesser, *Chem. Rev.* 103 (2003) 283;  
 (b) P.D. Bolton, P. Mountford, *Adv. Synth. Catal.* 347 (2005) 355;  
 (c) Special issue, Metallocene complexes as catalysts for olefin polymerization, H.G. Alt (Ed.), *Coord. Chem. Rev.* 250 (2006) 1;;  
 (d) J. Cano, K. Kunz, *J. Organomet. Chem.* 692 (2007) 4411.
- [2] (a) G.W. Coates, P.D. Hustad, S. Reinartz, *Angew. Chem. Int. Ed.* 41 (2002) 2236;  
 (b) G.J. Domski, J.M. Rose, G.W. Coates, A.D. Bolig, M. Brookhart, *Prog. Polym. Sci.* 32 (2007) 30.
- [3] (a) D.W. Stephan, *Organometallics* 24 (2005) 2548;  
 (b) K. Nomura, J. Liu, S. Padmanabhan, B. Kitiyanan, *J. Mol. Catal. A* 267 (2007) 1.
- [4] For recent examples;  
 (a) K. Itagaki, M. Fujiki, K. Nomura, *Macromolecules* 40 (2007) 6489;  
 (b) K. Nomura, K. Chin, *J. Polym. Sci.* 26 (2008) 513, Feature article for synthesis of cyclic olefin copolymers;  
 (c) J. Liu, K. Nomura, *Macromolecules* 41 (2008) 1070;  
 (d) K. Nomura, K. Kakinuki, M. Fujiki, K. Itagaki, *Macromolecules* 41 (2008) 8974;  
 (e) K. Kakinuki, M. Fujiki, K. Nomura, *Macromolecules* 42 (2009), ASAP.
- [5] (a) G.G. Hlatky, *Chem. Rev.* 100 (2000) 1347;  
 (b) J.R. Severn, J.C. Chadwick, R. Duchateau, N. Friederichs, *Chem. Rev.* 105 (2005) 4073;  
 (c) J.M. Thomas, R. Raja, D.W. Lewis, *Angew. Chem. Int. Ed.* 44 (2005) 6456.
- [6] J.R. Severn, J.C. Chadwick (Eds.), *Tailor-Made Polymers via Immobilization of Alpha-olefin Polymerization Catalysts*, Wiley-VCH, Weinheim, 2008.
- [7] (a) L. Wachowski, W. Skupinski, M. Hofman, *Appl. Catal. A: Gen.* 303 (2006) 230;  
 (b) L. Wachowski, J.W. Sobczak, M. Hofman, *Appl. Surf. Sci.* 253 (2007) 4456.
- [8] For example;  
 (a) J.R. Pels, F. Kapteijn, J.A. Moulin, Q. Zhu, K.M. Thomas, *Carbon* 33 (1995) 1641;  
 (b) M. Hofman, S. Pasieczna, L. Wachowski, J. Ryzkowski, *J. Phys. IV France* 137 (2006) 287.
- [9] K. Nomura, N. Naga, M. Miki, K. Yanagi, *Macromolecules* 31 (1998) 7588.
- [10] M. Hofman, S. Pasieczna-Patorska, J. Ryzkowski, L. Wachowski, *Eur. Phys. J. Special Top.* 154 (2008) 325.
- [11] H.C. Welborn, US Patent 4,808,561 (1989).
- [12] (a) K. Nomura, T. Komatsu, Y. Imanishi, *J. Mol. Catal. A* 159 (2000) 127;  
 (b) K. Nomura, A. Tanaka, S. Katao, *J. Mol. Catal. A* 254 (2006) 197.
- [13] (a) K. Nomura, A. Fudo, *Inorg. Chim. Acta* 345 (2003) 37;  
 (b) H. Zhang, K. Nomura, *Macromolecules* 39 (2006) 5266.
- [14] (a) P. Kumkaew, S.E. Wanke, P. Preserthdam, D. Danumah, S. Kaliaguine, *J. Appl. Polym. Sci.* 87 (2003) 1161;  
 (b) P. Kumkaew, P. Wu, P. Preserthdam, S.E. Wanke, *Polymer* 44 (2003) 4791.