

Chemical modification of silica support to improve the branching ability of Phillips catalyst*

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Abstract: A variety of modified Phillips catalysts were synthesized by employing three kinds of chemical modifiers for silica support: (1) organic modification with silane coupling agents, (2) Lewis acidic modification with typical metal alkyl or alkoxide, and (3) modification with transition-metal alkoxide. The activity and branching ability of these catalysts were investigated for ethylene polymerization. It was revealed that the chemical modification of silica support was a good methodology for controlling the catalyst activity as well as the branching level in resultant polyethylene.

Keywords: catalysts; ethylene; Phillips catalyst; polymerization.

INTRODUCTION

The Phillips catalyst ($\text{CrO}_x/\text{SiO}_2$) is one of the most important industrial ethylene polymerization catalysts due to the ability to produce unique high-density polyethylene (HDPE). Nowadays, Phillips catalyst is responsible for nearly 7 million tons of the annual production of HDPE [1,2]. The distinct properties of HDPE produced by Phillips catalyst are attributed to extremely broad molecular weight distribution (MWD), and short- and long-chain branches (SCBs and LCBs) incorporated into linear main chains, which is suitable for blow molding applications [3–8]. These unique features of Phillips HDPE are attainable through one-step ethylene homo-polymerization, which implies a highly multifunctional nature of the Phillips catalyst [9,10]. Industrial Phillips catalysts are commonly prepared by impregnation of a solution of a Cr salt onto a high-surface-area silica in order to obtain 0.2–1.0 Cr wt %, followed by high-temperature activation under an oxidative condition. Cr species supported on silica are highly heterogeneous in terms of the Cr nuclearity and the environments of bonding and coordination with surface oxygen [11] to realize the catalytic multifunctional nature [12]. Recently, we have reported that mononuclear and binuclear Cr species have a notable difference in short-chain branching [12], and that the heterogeneity of coordination environment around Cr is responsible for broad MWD [13].

The advantages of the Phillips catalyst are not only the ability to produce unique HDPE but also the variability to cover a number of various HDPE grades. In the developmental point of view, there are several factors affecting the catalyst performance and resulting polymer structures, such as activation temperature, Cr loading, and support structure [14,15]. Among these parameters, the activation tem-

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perature is the most powerful variable used in commercial HDPE manufacturing process to control polymer properties [16–19]. The chemical modification of catalyst support has been also an important parameter influencing both the catalyst activity and polymer structure. There has been much research regarding the chemical modification of support for Phillips catalyst [16], but no research has systematically investigated the effects of various modification methods on catalyst performances. Titania-modified silica support is the most popular example, which is known to enhance the activity, MWD, and the uniformity of the branching frequency. In general, the chemical modification brings about the alternations in the support electronic nature and the distribution of surface hydroxyl groups, thus affecting the catalytic performance [16].

The objective of this research is a systematic investigation of the support chemical modification for the Phillips catalyst: (a) organic modification with silane coupling agents, (b) Lewis acidic modification with typical metal alkyl or alkoxide, and (c) modification with transition-metal alkoxide. The obtained catalysts were subjected to ethylene polymerization as well as to various catalyst characterizations.

EXPERIMENTAL

Raw materials

Basic Cr(III) acetate [$\text{Cr}_3(\text{OH})_2(\text{CH}_3\text{COO})_7$] was used as a Cr precursor for all the catalyst preparation. Silica gel (ES70X, 51 μm , 320 m^2/g , donated by PQ Corporation) was used as support. Triethoxyphenyl silane [$\text{PhSi}(\text{OEt})_3$], dimethyldimethoxy silane [$\text{Me}_2\text{Si}(\text{OMe})_2$], boron isopropoxide [$\text{B}(\text{iOPr})_3$], tetraisopropoxide orthotitanate [$\text{Ti}(\text{iOPr})_4$], vanadium tri-*n*-propoxide oxide [$\text{VO}(\text{nOPr})_3$], zirconium tetra-*n*-propoxide [$\text{Zr}(\text{nOPr})_4$], and tungsten tetraisopropoxide [$\text{W}(\text{iOPr})_4$] modifiers were used as purchased. Triisobutyl aluminium (TIBA, $\text{Al}i\text{Bu}_3$) and diethyl zinc (ZnEt_2) modifiers were kindly donated by Tosoh Finechem Corporation. Heptane and toluene were purified using molecular sieves (4A). Modified supports and catalysts as well as solvents were handled and stored under nitrogen atmosphere. Oxygen (purity > 99 %) of research grade was used for calcination. Ethylene (purity > 99.9 %, donated by Asahi Kasei Chemicals Co.) was used for polymerization.

Chemical modification of support

Modification with silane coupling agents

Silica (1.0 g) dehydrated at 200 °C under nitrogen was subjected to dropwise addition of a silane coupling agent diluted in anhydrous alcohol (ethanol or methanol) and stirred for 24 h under nitrogen atmosphere at room temperature, followed by repeated washing with heptane and drying to obtain alkyl silane-modified silica. Assuming that 1.472×10^{21} surface hydroxyl groups are present on the 1.0 g of silica when treated at 200 °C [7] and that the alkoxide groups necessarily react with surface hydroxyl groups, 0.4 mmol of $\text{PhSi}(\text{OEt})_3$ or 0.6 mmol of $\text{Me}_2\text{Si}(\text{OMe})_2$ corresponding to 1/2 molar ratio of alkoxy groups/surface hydroxyl groups was added per 1.0 g of silica.

Modification with typical metal alkyl or metal alkoxide

Typical metal alkyl (0.4 mmol of $\text{Al}i\text{Bu}_3$ or 0.6 mmol of ZnEt_2) or metal alkoxide [0.4 mmol of $\text{B}(\text{iOPr})_3$] dissolved in appropriate anhydrous solvent was dropwise added to pre-dehydrated silica (1.0 g) under nitrogen atmosphere, and stirred over 24 h, followed by washing and drying. The addition of metal alkyl was conducted at –40 °C. Similarly to the modification with silane coupling agents, the added amounts of the modifiers were set to 1/2 molar ratio of alkyl or alkoxy groups/surface hydroxyl groups.

Modification with transition-metal alkoxide

Modified support with various transition-metal alkoxide was prepared by impregnating propanol solution of propoxide [Ti(*i*OPr)₃, VO(*n*OPr)₃, Zr(*n*OPr)₃, or W(*i*OPr)₃] onto 1.0 g of silica for 24 h. The sample was subsequently dried and calcined at 500 °C under oxygen flow for 4 h, followed by cooling under nitrogen. The added amounts were mostly set to 3.0 wt % of metal per silica, and it was varied in the case of Ti[*i*OPr)₃] from 3.0, 5.0 to 7.0 wt %.

Catalyst preparation

Neat or modified silica was impregnated with an aqueous solution of basic Cr(III) acetate, for 1.0 wt % Cr loading and then dried under nitrogen. Thereafter, the solid was calcined in oxygen for 2 h at 250, 350, 400, 450, or 600 °C, followed by cooling under nitrogen to obtain Phillips catalysts.

Polymerization process

Slurry polymerization of ethylene in heptane was carried out using the unmodified and modified Phillips catalysts in a 1 L autoclave for 30 min. The polymerization temperature was kept at 70 °C with continuous supply of ethylene at 0.5 MPa. TIBA (0.2 mmol) as activator and scavenger was added to 200 ml of heptane followed by the injection of 40 mg of catalyst to initiate polymerization. The polymerization was terminated by adding ethanol to polymerization slurry, and the polyethylene obtained was filtered and dried in vacuum at 60 °C for 6 h.

Characterization of polyethylene

The branching frequency in PE was determined by ¹³C NMR operated at 75.43 MHz using Varian Gemini-300 spectrometer. A sample tube was prepared by dissolving ca. 250 mg of PE in 3.1 ml mixture of 1,2,4-trichlorobenzene and 1,1,2,2-tetrachloroethane-*d*₂ (4:1 v/v). The average of peak areas at 14.1, 22.8, and 32.2 for the branches equal to or longer than the *n*-hexyl [20,21] (≥Hex) were normalized by the peak area for the main methylene to give the branching frequency for ≥ Hex.

*M*_n and MWD of the obtained PE were determined by gel permeation chromatography (GPC, Waters Alliance GPCV2000CV) with polystyrene gel columns (Shodex UT-806 M) at 140 °C using 1,2,4-trichlorobenzene as solvent.

Characterization of support and catalysts

The surface analysis of modified supports was performed by X-ray photoelectron spectroscopy (XPS, Kratos Analytical–Shimadzu, AXIS ultra DMD model). Monochromatic Al K α radiation was used as X-ray source. Spectra were acquired for Al 2p B 1s, Zn 2p, Ti 2p, Zr 3d, and W 4f regions of different samples with pass energy 20 and step size 0.01 eV. All binding energy (BE) values were calibrated with Si 2p peak at 103.3 eV [22].

The electronic state of Cr in catalysts was analyzed by using diffuse reflectance UV–vis spectroscopy on a JASCO V670 UV–vis–NIR spectrometer. An active catalyst sample (ca. 1 g) was loaded as powder into a quartz cell kept under N₂. The spectra were recorded at 200–800 nm with 1 nm resolution. The reflectance from neat silica powder was used as background.

The effects of Al*i*Bu₃ modification on the surface acidity of silica were studied with in situ Fourier transform-infrared (FT-IR) spectroscopy (JASCO 6100, Japan) of pyridine adsorption [23]. Sample powder (either Al*i*Bu₃ modified or neat silica) was pressed into a thin transparent disk and was placed in an in situ cell equipped with CaF₂ windows. The disk was dehydrated at 200 °C for 2 h under vacuum prior to the measurements. Subsequently, pyridine vapor pulses were admitted into the cell at room temperature, and a spectrum was acquired at each pulse with resolution of 4 cm⁻¹. The final spec-

trum was obtained at the saturation of pyridine adsorption. Data analysis was performed in terms of a differential spectrum between pyridine-saturated and pre-treated silica.

RESULTS AND DISCUSSION

Characterization of modified supports

Before synthesis of catalysts using the modified supports, their surface chemical compositions as well as the chemical nature of modifier elements were examined with XPS. Only in the case of organically modified silica supports, we evaluated the amounts of grafted organic groups by using thermogravimetric analysis as 41.77 and 13.04 wt % for $\text{PhSi}(\text{OEt})_3$ and $\text{Me}_2\text{Si}(\text{OMe})_2$, respectively. Table 1 summarizes the surface loadings of the modifier elements (M/SiO_2) as well as their BE values, given by XPS analysis. The modifier loadings were found to be in the same order from about 2 to 6 wt % for all the modifier elements except boron and vanadium. In the case of boron and vanadium, because of having very low concentration over the surface of support determined by XPS, it was thought that the precursors might be preferentially incorporated into internal pores, leading to heterogeneous dispersion.

Table 1 XPS results for modified silica support.

Modifier ^a	Binding energy ^b (eV)	%M/SiO ₂ ^c
Al <i>i</i> Bu ₃	73.0 (Al 2p)	3.10
ZnEt ₂	1020.0 (Zn 2p _{3/2})	6.18
B(<i>i</i> OPr) ₃	196.0 (B 1s)	0.21
Ti(<i>i</i> OPr) ₄ (3.0 wt %)	459.5 (Ti 2p _{3/2})	2.44
Ti(<i>i</i> OPr) ₄ (5.0 wt %)	459.4 (Ti 2p _{3/2})	4.40
Ti(<i>i</i> OPr) ₄ (7.0 wt %)	459.1 (Ti 2p _{3/2})	4.85
Zr(<i>n</i> OPr) ₄ (3.0 wt %)	183.0 (Zr 3d _{5/2})	3.25
W(<i>i</i> OPr) ₄ (3.0 wt %)	36.6 (W 4f _{7/2})	2.36

^aVanadium was not detected for VO(*n*OPr)₃-modified support.

^bBinding energy values for Al₂O₃, ZnO, B₂O₃, TiO₂, ZrO₂, and WO₃ are 74.6 (Al 2p), 1021.2 (Zn 2p_{3/2}), 193.6 (B 1s), 458.5 (Ti 2p_{3/2}), 182.6 (Zr 3d_{5/2}), and 36.0 (W 4f_{7/2}), respectively [26].

^cMass concentration in wt % per silica.

The BE values for Lewis acidic elements were found to be lower as compared with those of the corresponding oxides. This suggests that the modification of silica by the Lewis acidic elements makes the support more electron-deficient, which is expected to reduce the electron density of supported Cr [24]. For Ti, the BE values of Ti 2p_{3/2} shifted as a function of the Ti loading. Ti at 3.0 wt % led to the highest BE value, which is 1.0 eV higher than that of pure TiO₂. At higher loadings, the BE values of Ti 2p_{3/2} became closer to that of pure TiO₂. The observed shift in the Ti 2p_{3/2} BE values with respect to the pure TiO₂ value could be associated with the formation of Ti–O–Si bonds, which result in an increase in the effective positive charge on Ti since Si atoms are more electronegative than Ti atoms [25,26]. In turn, the shift of BE value toward the pure TiO₂ value at higher loadings is attributed to the increasing contribution of Ti–O–Ti bonds. Zr and W imparted similar behavior as Ti.

Polymerization results

We have synthesized a variety of modified Phillips catalysts using the modified supports. Tables 2–4 represent the ethylene polymerization results for these modified catalysts.

Table 2 Polymerization results for organically silane modified Phillips catalyst.

Calcination temperature	Modifier	Activity ^a	≥Hex branch ^b /1000C
250 °C	–	0.54	0.14
	PhSi(OEt) ₃	0.40	0.18
	Me ₂ Si(OMe) ₂	0.49	0.23
350 °C	–	1.7	0.31
	PhSi(OEt) ₃	1.1	0.32
	Me ₂ Si(OMe) ₂	1.4	0.46

^aIn ton-PE/mol-Cr h.^bDetermined by ¹³C NMR with the accuracy of ±0.02.**Table 3** Polymerization results for typical metal alkyl- or alkoxide-modified Phillips catalyst.

Calcination temperature	Modifier	Activity ^a	≥Hex branch ^b /1000C
350 °C	–	1.7	0.31
	Al <i>i</i> Bu ₃	1.6	0.50
	ZnEt ₂	0.8	0.46
	B(<i>i</i> OPr) ₃	1.7	0.48
450 °C	–	1.8	0.44
	Al <i>i</i> Bu ₃	1.7	0.61
	ZnEt ₂	1.6	0.48
	B(<i>i</i> OPr) ₃	1.8	0.55
600 °C	–	2.5	0.53
	Al <i>i</i> Bu ₃	2.5	0.71

^aIn ton-PE/mol-Cr h.^bDetermined by ¹³C NMR with the accuracy of ±0.02.**Table 4** Polymerization results for transition metal alkoxide-modified Phillips catalyst^a.

Modifier	Activity ^b	≥Hex branch ^c /1000C
–	2.7	0.41
Ti(<i>i</i> OPr) ₄ (3.0 wt %)	4.4	0.54
Ti(<i>i</i> OPr) ₄ (5.0 wt %)	2.2	0.55
Ti(<i>i</i> OPr) ₄ (7.0 wt %)	2.5	0.52
Zr(<i>n</i> OPr) ₄ (3.0 wt %)	3.2	0.53
VO(<i>n</i> OPr) ₃ (3.0 wt %)	5.2	0.50
W(<i>i</i> OPr) ₄ (3.0 wt %)	3.8	0.61

^aCalcined at 400 °C.^bIn ton-PE/mol-Cr h.^cDetermined by ¹³C NMR with the accuracy of ±0.02.

Table 2 summarizes the data for organically silane-modified Phillips catalysts, where aromatic PhSi(OEt)₃ and aliphatic Me₂Si(OMe)₂ were selected as modifiers. Since the grafted organic groups cannot be retained upon calcination beyond 400 °C, higher calcination temperatures were avoided. For

both of the modifiers, the branching levels increased, while the activities slightly decreased. It is envisaged that organic modification partially cleaves surface hydroxyl concentration to limit the available location for Cr immobilization, leading to poorer Cr dispersion as well as locally higher Cr concentration [27]. Tonosaki et al. reported that a higher activity leads to more in situ formation of α -olefin, resulting in a higher branching level [12]. The slightly lower branching ability for $\text{PhSi}(\text{OEt})_3$ could be explained by its lower activity than for $\text{Me}_2\text{Si}(\text{OMe})_2$.

It is known that the incorporation of Lewis acidic sites tends to enhance the activity and branching of Phillips catalysts [16]. This is because the Lewis acidic centers make Cr more electron-deficient, resulting in stronger π complexation of olefin especially for α -olefin with electron-donating alkyl substituents [24]. The increase of Lewis acidic sites on silica surfaces through the modification with Lewis acidic elements (B, Al, Zn) was confirmed by in situ FT-IR measurements of pyridine adsorption. The spectrum for the $\text{Al}i\text{Bu}_3$ -modified silica is shown in Fig. 1 compared with that for neat silica. The Al-modification brought about ca. 30 % increase in the adsorbed pyridine amount related to Lewis acidic sites. Table 3 lists the polymerization results for catalysts modified with typical metal alkyl and alkoxide with Lewis acidic nature. At 350 °C of calcination temperature, these modifiers gave more or less higher branching abilities as compared with silane coupling agents due to their Lewis acidic natures. Among the three modifiers, $\text{B}(i\text{OPr})_3$ and $\text{Al}i\text{Bu}_3$ led to activities and branching superior to ZnEt_2 . Elevation in calcination temperature enhanced activity and branching irrespectively of modifier type, keeping the superiority of $\text{Al}i\text{Bu}_3$ and $\text{B}(i\text{OPr})_3$. On the contrary, the activities changed in a complicated manner, that is the $\text{B}(i\text{OPr})_3$ and $\text{Al}i\text{Bu}_3$ modifications kept the original activity, but the activity dropped down for ZnEt_2 . This is again plausibly because the $\text{Al}i\text{Bu}_3$ and ZnEt_2 modifications reduce surface hydroxyl concentration at the given modification degrees (Table 1), and limited the place available for the subsequent Cr immobilization (over-modification) [24]. The lowest activity for ZnEt_2 coincided with its highest loading in XPS (Table 1). The opposite is true for $\text{B}(i\text{OPr})_3$ with the lowest loading.

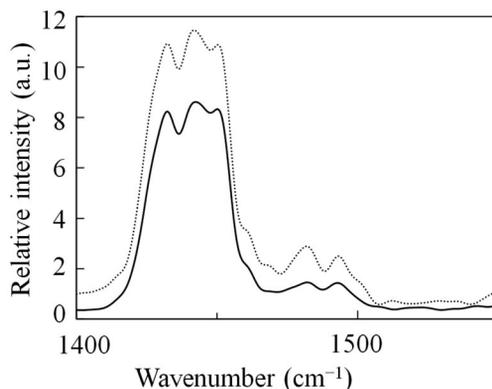


Fig. 1 In situ FT-IR spectra of pyridine adsorption for (—) unmodified and (···) $\text{Al}i\text{Bu}_3$ -modified silica.

Table 4 represents the polymerization results for Phillips catalysts modified with transition-metal alkoxide. In contrast to the prior two kinds of modifiers, the modification with transition-metal alkoxide always increased both activity and branching as compared to the unmodified catalyst. In general, transition-metal oxides dispersed on silica more or less exhibit Lewis acidic nature due to the coordination property [28], which is beneficial to make Cr more electron-deficient for higher activity and branching ability. Moreover, oxidation states of these transition metals equal or higher than that for Si allows the formation of surface M-OH groups and consequently M-O-Cr bonds, thus directly withdrawing electron density from Cr without sacrificing the surface available for the Cr impregnation. It

was postulated by Weckhuysen and Schoonheydt that improved catalytic performance for TiO_2 -modified Phillips catalysts is attributed to the formation of Ti–O–Cr bonds [29]. At 3.0 wt % of the metal loading, the order of the activity became $\text{VO}(n\text{OPr})_3 > \text{Ti}(i\text{OPr})_4 > \text{W}(i\text{OPr})_4 > \text{Zr}(n\text{OPr})_4$, while $\text{W}(i\text{OPr})_4 > \text{Zr}(n\text{OPr})_4 > \text{Ti}(i\text{OPr})_4 > \text{VO}(n\text{OPr})_3$ for the branching. Thus, precise mechanisms for the activity and branching enhancements seem more complicated than explained above. Variation of the distribution of surface hydroxyl groups upon modification must be taken into consideration for further details, which are beyond the scope of the present study. Within $\text{Ti}(i\text{OPr})_4$ -modified catalysts, the modification at 3.0 wt % of Ti exhibited the optimum performance with respect to the activity and branching, plausibly as a result of a balance between the enhanced Lewis acidity and over-modification.

Table 5 summarizes GPC results for the obtained PE and the influences of the support modification on M_n and MWD. In the case of Lewis acidic modification, M_n decreased but MWD got broader. McDaniel et al. stated that electron-deficient Cr active sites induce faster chain-transfer reactions to monomer through stronger β -agostic interaction [30]. It was believed that active sites interacted with Lewis acidic components produce lower MW polymer, which results in the decrease of M_n and the increase of MWD by extending lower MW tail. In the case of transition-metal alkoxide modification, M_n gets decreased with a similar mechanism, while MWD became slightly narrower indicating reduction in the heterogeneity of surface chromate species. This might be attributed to rather uniform modification of the silica surface with transition-metal alkoxide [25]. It is notable that the usage of titania/silica mixed oxide support generally expands MWD [16] plausibly due to co-presence of titania and silica surfaces.

Table 5 GPC results.

Calcination temperature	Modifier	M_n	MWD
600 °C	–	1.4×10^4	32
	$\text{Al}i\text{Bu}_3$	1.0×10^4	44
400 °C	–	1.4×10^4	35
	$\text{Ti}(i\text{OPr})_4$ (3.0 wt %)	9.4×10^3	30

UV–vis DRS analysis of different modified Phillips catalysts

According to Weckhuysen et al., the nature of chromate species can be studied by UV–vis dielectric relaxation spectroscopy (DRS) [31,32]. In general, Phillips catalyst exhibits trimodal UV DRS, comprising three peaks at around 260, 350, and 460 nm for the $\text{O} \rightarrow \text{Cr}^{+6}$ charge transfers [33]. These peaks were always present for the modified and unmodified catalysts (Figs. 2 and 3). The largest change observed was the great intensification of the peak at 460 nm by increasing the calcination temperature from 400 °C (Fig. 3) to 600 °C (Fig. 2). The peak at 460 nm was previously attributed to the dichromate species by Weckhuysen et al. [31]. It is quite reasonable that the ratio of the dichromate species to the monochromate species increases as the concentration of hydroxyl groups decreases. The UV–vis DRS of the catalysts were slightly changed by modifier. In the case of $\text{Al}i\text{Bu}_3$ modification, the three peaks became more isolated from each other. In the case of $\text{Ti}(i\text{OPr})_4$ modification, the center peak was bathochromically shifted. The broad peak for titanosilicate reported to exist at 290 nm and a small amount of Ti^{+4} in silicate network also shows a peak from 222–208 nm [34]. These Ti-related peaks were not obviously seen in the DR spectrum due to their broadness as well as strong absorption of chromate species.

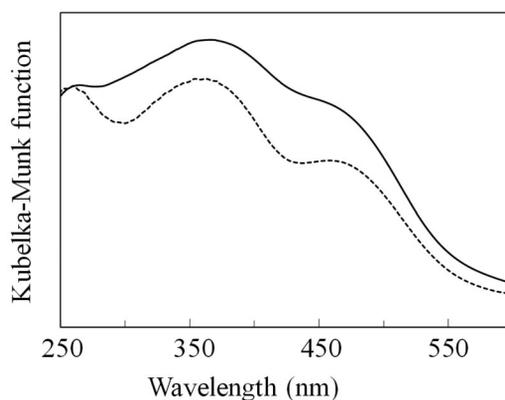


Fig. 2 UV-vis DRS for (—) unmodified and (---) Al*i*Bu₃-modified Phillips catalysts calcined at 600 °C.

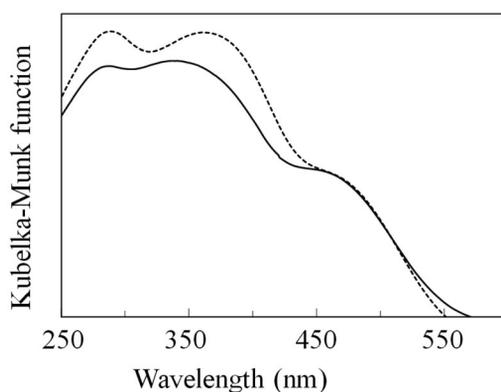


Fig. 3 UV-vis DRS for (—) unmodified and (---) Ti(*i*OPr)₄ (3.0 wt %)-modified Phillips catalysts calcined at 400 °C.

CONCLUSIONS

Ethylene polymerizations were carried out in slurry using a variety of modified Phillips catalysts. The results for the catalyst activity and the branching level suggest that not only the electronic interaction between modifiers and Cr species but also the variation of the surface available for the Cr immobilization play an important role for deciding the catalyst performance. Higher activities were observed in the case of transition-metal alkoxide modifier than that of the unmodified catalyst, which are attributable to the formation of M–O–Cr bonds to directly withdraw electron density from Cr species. On the contrary, the other modifiers lowered the catalyst activity as a result of the cleavage of surface hydroxyl groups to decrease the available surface location for Cr immobilization. However, the branching level increased with all modifiers, which are ascribed to the introduction of Lewis acidic sites to enhance the coordination of α -olefins and/or the local density of active chromate species.

In the conclusion, chemical modification of silica support for Phillips catalysts can be used as an effective strategy to tune the catalyst productivity as well as the branching frequency of PE products. On the contrary, it is an extremely difficult task to precisely identify the origins of variations in the polymerization performance by various modifications. Thus, the mechanistic aspects for polymerization with Phillips catalysts are still a target of research for better understanding and development of more functional olefin polymerization catalysts.

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