Study of the coordinative nature of alkylaluminum modified Phillips $\text{CrO}_x/\text{SiO}_2$ catalyst by multinuclear solid-state NMR

Zhang Qin-Hui, Yan Fang, Xia Wei* and Liu Chenguang

State Key Laboratory of Heavy Oil Processing, College of Chemical Engineering, China University of Petroleum, Qingdao, Shandong 266580, China

© China University of Petroleum (Beijing) and Springer-Verlag Berlin Heidelberg 2013

Abstract: Solid-state nuclear magnetic resonance spectroscopy was used to investigate the coordinative states of surface Al species on various alkylaluminum-modified Phillips $\text{CrO}_x/\text{SiO}_2$ catalysts. The alkylaluminum-modified Phillips $\text{CrO}_x/\text{SiO}_2$ catalysts were examined via ethylene homopolymerization. ^1H and ^{27}Al magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra clearly demonstrated that the existing states of surface Al species in alkylaluminum-modified catalysts strongly depended on the type of alkylaluminum cocatalyst, concentration of alkylaluminum and the calcination temperature. ^1H MAS NMR spectra of alkylaluminum-modified Phillips $\text{CrO}_x/\text{SiO}_2$ catalysts, calcined at two different temperatures, exhibited similar trends in peak shift. ^1H spectra showed that with an increase of Al/Cr ratio and calcination temperature, the main peak shifted to high field, indicating that the dominant surface proton species changed from hydroxyl to ethoxyl and ethyl groups. ^{27}Al MAS NMR spectra showed the presence of three different coordination states (6-, 5-, and 4-coordinated Al species) in the alkylaluminum-modified Phillips catalysts. In comparison of different alkylaluminum cocatalysts, it was found that the reactivity of alkylaluminum modified Phillips catalyst decreased in the order of TEA>DEAH>DEAE. The amount of 4-coordinated Al species of Phillips catalysts modified by TEA, DEAE and DEAH also decreased in the order of TEA>DEAH>DEAE, indicating that the presence of 4-coordinated Al species is related to the polymerization activity.

Key words: Phillips catalyst, alkylaluminum, ethylene polymerization, solid-state NMR

1 Introduction

Among all the olefin polymerization catalysts, including Ziegler–Natta catalysts, Phillips catalysts, and metallocene catalysts, Phillips $\text{CrO}_x/\text{SiO}_2$ catalyst is well known as one of the most important industrial ethylene polymerization catalysts. About one-third of the world high-density polyethylene (HDPE) is currently produced using this catalyst. Compared with Ziegler–Natta and metallocene catalysts, Phillips catalyst exhibits unique polymerization behavior, and the products (polyethylene) have many unique chain microstructures such as long chain branching, unsaturated chain ends and ultra-broad molecular weight distribution, which contribute to excellent properties for both processing and final applications (Pullukat and Hoff, 1999). Unfortunately, notwithstanding remarkable success in the industrial field and almost 50 years research work, there still exist many problems need to be resolved (Bade, 1998; Clark, 1970; Yermakov and Zakhrov, 1975; McDaniel,

1985; Weckhuysen and Schoonheydt, 1999; Thune et al, 2001; Gaspar and Dieguez, 2004; Liu and Terano, 2001; Liu et al, 2002; 2003; 2004a; 2004b; 2004c; 2005; Xia et al, 2006a; 2006b; 2009). In general, the states of active sites and polymerization mechanisms still remain unclear and controversial.

Phillips $\text{Cr(VI)O}_x/\text{SiO}_2$ catalyst can be prepared by impregnating an aqueous solution of Cr compounds (mostly chromium(III) acetate or chromium(VI) trioxide) onto amorphous silica gel support, followed by calcination in dry air at a temperature around 600–800 °C for several hours. The obtained Phillips $\text{CrO}_x/\text{SiO}_2$ catalyst can be used directly to catalyze the polymerization of ethylene at 100–150 °C without a preliminary activation step using organometallic cocatalysts or other reducing agents. With the development of olefin polymerization technology, nowadays, new Phillips catalyst systems using metal-alkyl cocatalyst have attracted much interest in the industrial field. However, activation of Phillips catalysts by using metal-alkyl cocatalysts has not been fully investigated up to now. To our knowledge, typically there are three stages for the introduction of metal-alkyl cocatalyst: 1) the catalyst preparation stage, 2) the catalyst aging or

*Corresponding author. email: xiawei@upc.edu.cn
Received June 22, 2013

pretreatment stage in the polymerization reactor just before the introduction of the monomer and 3) the polymerization stage with simultaneous interaction of catalyst with metal-alkyl cocatalyst and monomer. Spitz and coworkers (Spitz et al, 1979) introduced small amounts of triethylaluminum (TEA), during the Phillips catalyst aging or pretreatment stage in a polymerization reactor just before the introduction of the monomer, to study the effect of small amounts of TEA on the activity, kinetics, and 1-hexene incorporation in ethylene and 1-hexene copolymerization. McDaniel and Johnson (1986; 1987) introduced triethylborane (TEB), during the Phillips catalyst aging or pretreatment stage in a polymerization reactor just before introduction of the monomer, to investigate the effect of TEB on the polymerization kinetics and chain transfer of Phillips catalyst with different supports (AlPO_4 , SiO_2 , Al_2O_3). Wang et al (1991) introduced tri-isobutylaluminum (TIBA), during the catalyst (Phillips $\text{CrO}_x/\text{SiO}_2$ catalyst) aging or pretreatment stage in polymerization reactor just before introduction of the monomer, to study the effect of TIBA on the polymerization kinetics and polymer morphology. Woo and Woo (1990) also investigated the effect of TIBA on the polymerization kinetics and active sites of a Phillips $\text{CrO}_x/\text{SiO}_2$ catalyst. Instead of introducing TIBA during the catalyst aging or pretreatment stages, they introduced TIBA during the polymerization stage, with simultaneous interaction of the catalyst with the metal-alkyl cocatalyst and the monomer. Polymerization reaction was started by breaking a glass ampoule containing the Phillips catalyst within the polymerization reactor (Woo and Woo, 1990). Our group has systematically investigated the effect of the introduction of metal-alkyl cocatalyst in different stages from catalyst preparation to polymerization using Phillips catalyst (Liu et al, 2005; Xia et al, 2006; 2010). From the above investigations and the work of our research group, it is found that organometallic compounds not only can assist active site formation through reduction or alkylation, but also can substantially affect the catalytic properties of Phillips type catalysts, as well as the structures and properties of the produced polymers, through ligand modification of active sites or even creation of completely new active sites. Furthermore, the knowledge on the state and structure of alkylaluminum adsorbed on Phillips catalyst can help to understand the composition of the active component of the catalyst as well as the polymerization mechanism. Therefore, precise and systematic characterization of the state and structure of alkylaluminum-modified Phillips catalysts is very important.

Recently, high-resolution solid-state nuclear magnetic resonance (NMR) spectroscopy has been widely used to study the coordinative states of surface Al species on solid catalysts. Coordination states of four, five, or six on the catalyst surface can be revealed by high-resolution ^{27}Al magic angle spinning (MAS) NMR, which has been used in the study of heterogeneous industrial Ziegler-Natta catalysts (Mori et al, 2000). In our recent studies on triethylaluminum (TEA)-modified Phillips catalysts (Liu et al, 2005; Xia et al, 2010), Phillips $\text{CrO}_x/\text{SiO}_2$ catalysts calcined at different temperatures (400, 600, and 800 °C) were modified by TEA at different Al/Cr molar ratios during the catalyst preparation

stage. High-resolution solid-state nuclear magnetic resonance (NMR) spectroscopy has been utilized for investigation of coordinative states of surface Al species on TEA pre-modified Phillips catalysts. In order to investigate the effect of different alkylaluminum cocatalysts on the Phillips catalyst, in this work, solid-state NMR was used to investigate the coordinative states of surface Al species on Phillips $\text{CrO}_x/\text{SiO}_2$ catalysts modified by various alkylaluminum cocatalysts (triethyl aluminum (TEA), diethyl aluminum hydride (DEAH) and diethyl aluminum ethoxide (DEAE)). Solid-state ^1H and ^{27}Al MAS NMR spectra demonstrated that existing states of surface Al species in the alkylaluminum-modified catalysts strongly depended on the type of alkylaluminum cocatalyst, concentration of alkylaluminum and on the calcination temperature during the catalyst preparation process.

2 Experimental

2.1 Raw materials

In this work, all the gas medium used in the preparation procedure including nitrogen (grade G-2), and pure air (grade G-1) were purchased from Uno Sanso Co. (Japan). Ethylene monomer was donated by Mitsubishi Chemical Co. (Japan). Molecular sieves (13X and 4A) as moisture scavengers used for further purification of gas medium were purchased from Wako Pure Chemical Industries, Ltd. (Japan). Q-5 catalyst (13 wt% copper (II) oxide supported on alumina), which was purchased from Aldrich, was used as an oxygen scavenger for gas purification.

The catalyst precursor used for catalyst preparation was Crosfield ES370X with 1.0 wt% Cr loading and a surface area of 280-350 m^2/g , donated by Asahi Kasei Co. (Japan). DEAH and DEAE, donated by Tosoh Fine Chem. Co. (Japan), were used without further purification. Heptane, purchased from Wako Pure Chemical Industries, Ltd. (Japan), was purified by passing through a column of 13X molecular sieves and subsequently purged by bubbling pure nitrogen for more than 2 hours prior to preparation of the DEAH and DEAE solutions.

2.2 Preparation of catalyst

Details about catalyst preparation of the Phillips catalyst can be found in our previous work (Liu et al, 2004a; 2005; Xia et al, 2006; 2010). About 15 g of catalyst precursor was calcined at a temperature of 600 or 800 °C for 6 hours under 200 mL/min flow of dry air in a spouted fluidized-bed reactor using a temperature-programmed heating controller. The dry air was purified by passing through a 13X molecular sieve column before entering the catalyst preparation system. The calcined catalyst was cooled to room temperature under nitrogen (200 mL/min), which had been purified by passing it through a Q-5 catalyst column and a 13X molecular sieve column before entering the catalyst preparation system. The two calcined Phillips catalysts (at 600 and 800 °C, respectively) were denoted as PC600 and PC800, and used for further modification by alkylaluminum cocatalysts. The alkylaluminum modification was carried out under nitrogen in a glass reactor connected to a high-vacuum line. Heptane (30 mL) and about 1 g of calcined catalyst were introduced to the

reactor; thereafter a controlled amount of alkylaluminum was added to achieve prescribed Al/Cr molar ratios. The mixture was allowed to react for 30 minutes at room temperature. The solution was decanted before drying the modified catalyst under vacuum. The alkylaluminum-modified catalysts were divided into two categories according to the unmodified catalysts' calcination temperatures (600 and 800 °C) and were denoted as PC600/alkylaluminum and PC800/alkylaluminum, respectively. Finally, the alkylaluminum-modified catalyst was distributed and sealed into several glass tubes for storage under nitrogen. Before polymerization, the alkylaluminum-modified catalysts were further distributed and sealed in many smaller glass ampoule bottles and the amount of catalyst in each ampoule bottle was regulated at about 100 mg, which was weighed precisely before polymerization.

2.3 Catalyst characterization by ^1H MAS and ^{27}Al MAS solid state NMR

All the catalyst samples were characterized by solid-state ^1H and ^{27}Al MAS NMR to elucidate the existing states of Al species on the modified catalysts. A Varian UNITY-400 NMR spectrometer was operated at room temperature with a Varian Room Temperature/Cross Polarization Magic Angle Spin (RT/CP MAS) probe. Each sample (ca. 80 mg) was packed into an Φ -7-mm zirconia rotor under nitrogen before measurement. The ^1H and ^{27}Al MAS NMR spectra were obtained at 400.47 and 104.35 MHz, respectively, and were recorded for samples rotating at ca. 3 kHz. The ^1H MAS NMR spectra were obtained with a 30° pulse of 3 μs and a relaxation delay of 1 s. The ^1H MAS NMR spectra of the samples were referenced relative to external tetramethylsilane (TMS). The ^{27}Al MAS NMR spectra were obtained with a 12° pulse of 1.75 μs and a relaxation delay of 0.2 s. $\text{Al}(\text{NO}_3)_3$ was used as an external reference.

2.4 Ethylene polymerization

The same semi-batch slurry polymerization system was utilized as in our previous work (Xia et al, 2006; Mori et al, 2000). One ampoule bottle including ca. 100 mg of alkylaluminum-modified catalyst was set in the top part of a glass polymerization reactor (volume ca. 100 mL) with water-jacket and a magnetic stirrer inside. The reactor system was heated and evacuated for 2 h before introduction of heptane. Heptane solvent was purified with 13X molecular sieve and 24-hours bubbling under high purity nitrogen. The solution was then saturated with 0.15 MPa of ethylene, which was purified by passing through a 4A molecular sieve column, a Q-5 catalyst column and a 13X molecular sieve column. The polymerization was initiated by breaking the catalyst ampoule bottle with a steel bar. Polymerization was carried out at 60 °C for 90 minutes. An on-line mass flowmeter was used to record the real-time ethylene consumption profile. The polymerization was terminated by the addition of 20 mL Ethanol/HCl solution. The polymer was washed with ethanol and dried under vacuum at 60 °C for 6 hours.

3 Results and discussion

The DEAH-modified Phillips catalysts were divided into

two categories according to the calcination temperatures (600 and 800 °C) of the unmodified catalysts. These were named PC600/DEAH and PC800/DEAH and were characterized by solid-state ^1H and ^{27}Al MAS NMR. The chemical shifts of the ^1H MAS NMR peaks of all samples are listed in Table 1. The ^1H MAS NMR spectra of PC600/DEAH catalysts with various Al/Cr molar ratios (3.1 and 4.2) are shown in Fig. 1 (spectra *a* and *b*). For PC600/DEAH with an Al/Cr molar ratio of 3.1 (Fig. 1, spectrum *a*), there were two peaks found at 1.77 and 0.79 ppm, which are usually assigned to the protons in isolated hydroxyl groups (Potapov et al, 1997) on the silica support and ethyl groups in Al-alkyl, respectively. For PC600/DEAH with Al/Cr a molar ratio of 4.2 (Fig. 1, spectrum *b*), similar two peaks were found at 1.77 and 0.77 ppm. However for the PC800/DEAH with an Al/Cr molar ratio of 3.1 (Fig. 1, spectrum *c*), only one peak assigned to an ethyl group in Al-alkyl was found at 0.77 ppm (here, the proton in methene and methyl could not be distinguished because of the heterogeneity of the support surface).

Table 1 Precise chemical shift of alkylaluminum-modified catalysts in ^1H MAS NMR spectra

Samples	Al/Cr molar ratio	Chemical shift of main peaks in ^1H MAS NMR spectra, ppm
PC600/DEAH	3.1	1.77 0.79
PC600/DEAH	4.2	1.77 0.77
PC800/DEAH	3.1	0.77
PC600/DEAE	3.1	1.0
PC800/DEAE	3.1	0.74
PC600/TEA	3.1	1.77
PC800/TEA	3.1	0.75

Fig. 1 ^1H MAS NMR spectra of PC600 and PC800 catalyst modified by DEAH at various Al/Cr molar ratios (a) PC600/DEAH, Al/Cr molar ratio of 3.1; (b) PC600/DEAH, Al/Cr molar ratio of 4.2; (c) PC800/DEAH, Al/Cr molar ratio of 3.1

The DEAE-modified Phillips catalysts were also divided into two categories according to the calcination temperatures (600 and 800 °C) of the unmodified catalysts.

These were named PC600/DEAE and PC800/DEAE and were characterized by solid-state ^1H and ^{27}Al MAS NMR. The chemical shifts of the ^1H MAS NMR peaks of the two catalyst samples are listed in Table 1. The ^1H MAS NMR spectra of PC600/DEAE and PC800/DEAE catalysts with an Al/Cr molar ratio of 3.1 are shown in Fig. 2. In the ^1H MAS NMR spectra of PC600/DEAE catalyst, there was only one broad peak found at 1.0 ppm, which was the ethoxyl group and the ethyl group. For the ^1H MAS NMR spectra of PC800/DEAE catalyst, there was also only one narrow peak found at 0.74 ppm, which was assigned to the ethyl group in Al-alkyl. The amount of hydroxyl on PC600 is more than that on PC800 Phillips catalyst, furthermore, the heterogeneity of the silica support used here resulted in a broadened ^1H MAS NMR peak for PC600/DEAE compared with PC800/DEAE.

Fig. 2 ^1H MAS NMR spectra of PC600 and PC800 catalyst modified by DEAE (a) PC600/DEAE, Al/Cr molar ratio of 3.1; (b) PC800/DEAE, Al/Cr molar ratio of 3.1

The ^{27}Al MAS NMR spectra of PC600/DEAH are shown in Fig. 3 (spectra *a* and *b*). We observed three peaks at 0, 26, and 58 ppm, which were assigned to 6-, 5-, and 4-coordinated Al species on the DEAH-modified catalyst surface, respectively (Liu et al, 2004c; Hussin et al, 2002; Temuujin et al, 2002; Deng et al, 2002). For PC600/DEAH with an Al/Cr molar ratio of 3.1 (Fig. 3, spectrum *a*), the intensity of the ^{27}Al MAS NMR peak at 58 ppm and at 0 ppm is similar. It seems that the 6-coordinated Al species was the dominant Al species in the PC600/DEAH catalyst at the relatively low Al/Cr molar ratio of 3.1. With increasing Al/Cr molar ratio from 3.1 to 4.2 (Fig. 3, spectra *b*), the peak intensity of the 4-coordinated Al species increased, and that of the 6-coordinated Al species decreased. The 4-coordinated Al species became the dominant Al species in the PC600/DEAH catalyst at an Al/Cr molar ratio of 4.2. The DEAH reacted with the hydroxyl group on the silica support or reduced the surface chromate or on the chromium site. These formed Al species simultaneously coordinated with neighboring oxygen atoms of siloxane bridges or surface chromium species.

At low DEAH concentration, the large number of oxygen atoms surrounding each Al species would have resulted in the dominance of the 6-coordination state of Al. An increase in DEAH concentration then could decrease the number of oxygen atoms surrounding each Al species, and consequently the amount of 4-coordinated Al species would have increased with increasing Al/Cr molar ratio. For PC800/DEAH catalysts (Fig. 3, spectrum *c*), three kinds of Al species with 6-, 5-, and 4-coordination states were distinguished as mentioned for the PC600/DEAH. The peak intensity of the 4-coordinated Al species was significantly higher in PC800/DEAH than in the PC600/DEAH catalyst (Fig. 3, spectrum *a*). When the calcination temperature increased from 600 to 800 °C, the hydroxyl groups on the Phillips catalyst decreased, which decreased the number of oxygen atoms surrounding each Al species, and consequently the amount of 4-coordinated Al species increased with increasing calcination temperature.

Fig. 3 ^{27}Al MAS NMR spectra of PC600 and PC800 catalyst modified by DEAH at various Al/Cr molar ratios (a) PC600/DEAH, Al/Cr molar ratio of 3.1; (b) PC600/DEAH, Al/Cr molar ratio of 4.2; (c) PC800/DEAH, Al/Cr molar ratio of 3.1 (I: 4-coordinated Al; II: 5-coordinated Al; III: 6-coordinated Al)

The ^{27}Al MAS NMR spectra of PC600/DEAE and PC800/DEAE catalysts with an Al/Cr molar ratio of 3.1 are shown in Fig. 4. From the ^{27}Al MAS NMR spectra of PC600/DEAE catalyst we observed that 6-coordinated Al species was the dominant at an Al/Cr molar ratio of 3.1 (Fig. 4, spectrum *a*). However for PC800/DEAE with an Al/Cr molar ratio of 3.1 (Fig. 4, spectrum *b*), the 4-coordinated Al species increased sharply, and the 4-coordinated Al species became the dominant Al species on the catalyst. The trend was similar to the ^{27}Al MAS NMR spectra of PC600/DEAH and PC800/DEAH. At low DEAE concentration (Al/Cr ratio is 3.1), the large number of oxygen atoms surrounding each Al species would have resulted in the dominance of the 6-coordination state of Al. When the calcination temperature increased

from 600 to 800 °C, the hydroxyl groups on the Phillips catalyst decreased, which decreased the number of oxygen atoms surrounding each Al species, increasing the amount of 4-coordinated Al species.

Fig. 4 ^{27}Al MAS NMR spectra of PC600 and PC800 catalyst modified by DEAE (a) PC600/DEAE, Al/Cr molar ratio of 3.1; (b) PC800/DEAE, Al/Cr molar ratio of 3.1 (I: 4-coordinated Al; II: 5-coordinated Al; III: 6-coordinated Al)

For comparison, the ^1H MAS NMR spectra of PC600/TEA (Xia et al, 2010) PC600/DEAE and PC600/DEAH catalysts with an Al/Cr molar ratio of 3.1 are shown in Fig. 5. In the ^1H MAS NMR spectra of PC600/TEA catalyst, there was only one peak at 1.77 ppm which was assigned to hydroxyl on the silica surface. The ^1H MAS NMR spectra of PC600/DEAH catalyst shows two peaks, at 1.77 and 0.79 ppm, which were assigned to hydroxyl and ethyl groups. In the ^1H MAS NMR spectra of PC600/DEAE catalyst, there was only one peak found at 1.0 ppm, which was assigned to ethoxyl and ethyl groups.

Fig. 5 ^1H MAS NMR spectra of PC600 catalyst modified by various alkylaluminum cocatalysts at an Al/Cr molar ratio of 3.1 (a) PC600/TEA; (b) PC600/DEAH; (c) PC600/DEAE

Fig. 6 shows the ^{27}Al MAS NMR spectra of PC600/alkylaluminum catalyst with an Al/Cr molar ratio of 3.1. In the ^{27}Al MAS NMR spectra of PC600/DEAE catalysts we

observed that 6-coordinated Al species was dominant at an Al/Cr molar ratio of 3.1. For the PC600/DEAH catalysts, the 6-coordinated Al species decreased and the 4-coordinated Al species increased sharply compared with the ^{27}Al MAS NMR spectra of PC600/DEAE, the 4-coordinated Al species became the dominant Al species on the catalyst. For the PC600/TEA catalysts, the 4-coordinated Al species appeared to increase compared the 4-coordinated Al species on the PC600/DEAH catalysts. At the same Al/Cr ratio, the amount of 4-coordinated Al species decreased in the order as TEA>DEAH>DEAE. Ethylene homopolymerization results are shown in Table 2. The polymerization activity for the three catalysts also decreased in the order TEA>DEAH>DEAE. Our previously reported results for ethylene polymerization activity and solid-state MAS NMR results using TEA modified-Phillips catalyst demonstrate the variation in coordinated states on the Al/Cr molar ratio was similar to the variation in polymerization activity on the Al/Cr molar ratio for PC400/TEA, PC600/TEA, and PC800/TEA catalysts. The trend of the polymerization activity on the Al/Cr molar ratio is similar to the amount of 4-coordinated Al species. Our previous results and the present solid-state MAS NMR results thus suggest that the presence of 4-coordinated Al seems related to the polymerization activity.

Fig. 6 ^{27}Al MAS NMR spectra of PC600 catalyst modified by various alkylaluminum cocatalysts at an Al/Cr molar ratio of 3.1 (a) PC600/TEA (b) PC600/DEAH (c) PC600/DEAE (I: 4-coordinated Al; II: 5-coordinated Al; III: 6-coordinated Al)

Table 2 Activity of ethylene homopolymerization using various alkylaluminum-modified Phillips catalysts

Catalyst	Cocatalyst	Activity (gPE/geat·M[C ₂ H ₄]-h)
PC600	TEA	878
	DEAE	325
	DEAH	673
PC800	TEA	1203
	DEAE	460
	DEAH	800

Fig. 7 shows the ^1H MAS NMR spectra of PC800/TEA, PC800/DEAH and PC800/DEAE catalysts with an Al/Cr molar ratio 3.1. The spectra of PC800/TEA exhibited one main peak at 0.75 ppm. PC800/DEAE catalysts exhibited similar one main peak at about 0.74 ppm. The spectrum of PC800/DEAH showed a main peak at about 0.77 ppm. Owing to the heterogeneity of the silica support used here, the electron environment of each ethyl or ethoxide was slightly different, resulting in a broadened ^1H MAS NMR peak.

Fig. 7 ^1H MAS NMR spectra of PC800 catalyst modified by various alkylaluminum cocatalysts at an Al/Cr molar ratio of 3.1 (a) PC800/TEA, (b) PC800/DEAH, (c) PC800/DEAE

Fig. 8 shows the ^{27}Al MAS NMR spectra of PC800/TEA, PC800/DEAH and PC800/DEAE catalysts with an Al/Cr molar ratio 3.1. In the ^{27}Al MAS NMR spectra of PC800/DEAE catalysts we observed that 4-coordinated Al species was dominant at an Al/Cr molar ratio of 3.1. For the PC800/DEAH catalysts, the 6-coordinated Al species decreased and the 4-coordinated Al species increased sharply. For the PC800/TEA catalyst, the 4-coordinated Al species decreased and the 6-coordinated Al species became the dominant Al species. At the same Al/Cr ratio, the relative content of 4-coordinated Al decreases in the order DEAH>DEAE>TEA. The polymerization reaction results are shown in Table 2. It was shown the reactivity with Phillips catalyst in decreasing order as follows: TEA>DEAH>DEAE. This difference in relative amounts of coordinated Al species could be also contributed to two factors affecting the nature of catalysts calcined at different temperatures. The first factor was the different amount of residual hydroxyl groups present on the calcined PC600 and PC800 catalysts. The second factor was related to the intrinsic electronic state in terms of higher electron deficiency for chromate species (Cr(VI)O_x on the surface) of the original Phillips catalysts calcined at higher temperatures as confirmed in our previous work

(Liu et al, 2004b). This Cr(VI)O_x electron deficiency in turn might have affected the electron deficiency of the Cr(II)O_x species reduced from Cr(VI)O_x species on the correlative alkylaluminum-modified Phillips catalysts.

Fig. 8 ^{27}Al MAS NMR spectra of PC800 catalyst modified by various alkylaluminum cocatalysts at an Al/Cr molar ratio of 3.1 (a) PC800/TEA; (b) PC800/DEAH; (c) PC800/DEAE (I: 4-coordinated Al; II: 5-coordinated Al; III: 6-coordinated Al)

4 Conclusions

Surface Al species on various alkylaluminum-modified Phillips $\text{CrO}_x/\text{SiO}_2$ catalysts with different Al/Cr molar ratios were studied by solid-state NMR. Ethylene homopolymerization was carried out using these alkylaluminum-modified Phillips $\text{CrO}_x/\text{SiO}_2$ catalysts. ^1H and ^{27}Al MAS NMR spectra clearly demonstrated that the existing states of surface Al species in alkylaluminum-modified catalysts strongly depended on the type of alkylaluminum cocatalyst, the concentration of alkylaluminum and on the calcination temperature used during the catalyst preparation process. ^1H MAS NMR spectra of alkylaluminum-modified Phillips $\text{CrO}_x/\text{SiO}_2$ catalysts calcined at two different temperatures (600 and 800 $^\circ\text{C}$) exhibited similar trends in peak shifts. With an increase in the Al/Cr ratio and calcination temperature, ^1H spectra show a main peak shift to high field, this indicates the dominant surface proton species change from hydroxyl to ethoxyl and ethyl groups. ^{27}Al MAS NMR spectra showed the presence of three different coordination states (6-, 5-, and 4-coordinated Al species) in the alkylaluminum-modified Phillips catalysts. With an increase in the Al/Cr ratio and calcination temperature, ^{27}Al spectra of catalysts modified by DEAH and DEAE show similar change that 6-coordinated Al decreases and 4-coordinated Al increases. In the comparison of different alkylaluminum cocatalysts, it was shown the reactivity with Phillips catalyst in decreasing order is TEA>DEAH>DEAE. The amount of 4-coordinated Al on Phillips catalysts modified by TEA,

DEAE and DEAH decrease in the order of TEA>DEAH>DEAE. The presence of 4-coordinated Al species seems related to the polymerization activity. The results of the past and present study thus suggest that the multinuclear solid state NMR has a great potential as an effective tool for understanding Phillips catalyzed polymerization.

Acknowledgements

This work is a project sponsored by the Fundamental Research Funds for the Central Universities (No. 13CX05011A and R1304013A).

References

- Bade O, Blom R and Ystenes M. A study of the catalyst formed when reacting lithium-alkyls with Cr(II)/SiO₂: ethylene polymerization, diffuse reflectance infrared Fourier transform spectroscopy and gas chromatography results. *Journal of Molecular Catalysis A: Chemical*. 1998. 135: 163-179
- Clark A. Olefin polymerization on supported chromium oxide catalysts. *Catalysis Review*. 1970. 3: 145-173
- Deng W, Bodart P, Pruski et al. Characterization of mesoporous alumina molecular sieves synthesized by nonionic templating. *Microporous and Mesoporous Materials*. 2002. 52: 169-177
- Gaspar A B and Dieguez, L C. Characterization of Cr²⁺ and ethylene polymerization on Cr/SiO₂ catalysts. *Journal of Molecular Catalysis A: Chemical*. 2004. 219: 357-362
- Hussin R, Holland D and Dupree R. A MAS NMR structural study of cadmium phosphate glasses. *Journal of Non-Crystalline Solids*. 2002. 298: 32-42
- Liu B and Terano M. Investigation of the physico-chemical state and aggregation mechanism of surface Cr species on a Phillips CrO_x/SiO₂ catalyst by XPS and EPMA. *Journal of Molecular Catalysis A: Chemical*. 2001. 172: 227-240
- Liu B, Nakatani H and Terano M. New aspects of the introduction period of ethene polymerization using Phillips CrO_x/SiO₂ catalyst probed by XPS, TPD and EPMA. *Journal of Molecular Catalysis A: Chemical*. 2002. 184: 387-398
- Liu B, Nakatani H and Terano M. Mechanistic implications of the unprecedented transformations of ethene into propene and butene over Phillips CrO_x/SiO₂ catalyst during introduction period. *Journal of Molecular Catalysis A: Chemical*. 2003. 201: 189-197
- Liu B, Fang Y, Nakatani H, et al. Surface physico-chemical state of CO-prereduced Phillips CrO_x/SiO₂ catalyst and unique polymerization behavior in the presence of Al-alkyl cocatalyst. *Macromolecular Symposia*. 2004a. 213: 37-46
- Liu B, Fang Y and Terano M. High resolution X-ray photoelectron spectroscopic analysis of transformation of surface chromium species on Phillips CrO_x/SiO₂ catalyst isothermally calcined at various temperatures. *Journal of Molecular Catalysis A: Chemical*. 2004b. 219: 165-173
- Liu B, Sinderlar P, Fang Y, et al. Correlation of oxidation states of surface chromium species with ethylene polymerization activity for Phillips CrO_x/SiO₂ catalysts modified Al-alkyl cocatalyst. *Journal of Molecular Catalysis A: Chemical*. 2005. 238: 142-150
- Liu B, Fukuda K, Nakatani H, et al. ²⁷Al MAS solid state NMR study on coordinative nature of alkyl-Al cocatalysts on a novel SiO₂-supported Ziegler–Natta catalyst for controlled multiplicity of molecular weight distribution. *Journal of Molecular Catalysis A: Chemical*. 2004c. 219: 363-370
- McDaniel M. Supported chromium catalysts for ethylene polymerization. *Advances in Catalysis*. 1985. 33: 47-98
- McDaniel M and Johnson M. A comparison of Cr/SiO₂ and Cr/AlPO₄ polymerization catalysts 1: Kinetics. *Journal of Catalysis*. 1986. 101: 446-457
- McDaniel M and Johnson M. Comparison of Cr/SiO₂ and Cr/AlPO₄ polymerization catalysts 2: Chain transfer. *Macromolecules*. 1987. 20: 773-778
- Mori H, Kono H, Terano M, et al. In-situ multinuclear solid-state NMR spectroscopy under continuous-flow conditions for investigations of Ziegler–Natta catalyzed propene polymerization. *Journal of Molecular Catalysis A: Chemical*. 2000. 164: 235-243
- Potapov A G, Terskikh V V, Bukatov G D, et al. ²⁷Al NMR MAS study of AlEt₃/MgCl₂ systems. *Journal of Molecular Catalysis A: Chemical*. 1997. 122: 61-65
- Pullukat T J and Hoff R E. Silica-based Ziegler–Natta catalysts: a patent review. *Catalysis Reviews—Science and Engineering*. 1999. 41: 389-428
- Spitz R, Florin B and Guyot A. Ethylene-hexene-1 copolymers through modified Phillips catalysts. *European Polymer Journal*. 1979. 15: 441-444
- Temuujin J, Okada K and Mackenzie K J D. Preparation and properties of potassium aluminosilicate prepared from the waste solution of selectively leached calcined kaolinite. *Applied Clay Science*. 2002. 21: 125-131
- Thune P C, Linke R, van Gennip W J H, et al. Bonding of supported chromium during thermal activation of the CrO_x/SiO₂ (Phillips) ethylene polymerization catalyst. *The Journal of Physical Chemistry B*. 2001. 105: 3073-3078
- Weckhuysen B M and Schoonheydt R A. Olefin polymerization over supported chromium oxide catalysts. *Catalysis Today*. 1999. 51: 215-221
- Wang S, Tait P and Marsden C. Phillips-type polymerization catalysts: kinetic behavior and active center determination. *Journal of Molecular Catalysis*. 1991. 65: 237-252
- Woo T and Woo S. Ethylene polymerization with Phillips catalyst Co-catalyzed with Al(*i*-Bu)₃. *Journal of Catalysis*. 1990. 123: 215-227
- Xia W, Liu B, Fang Y, et al. Unique polymerization kinetics obtained from simultaneous interaction of Phillips Cr(VI)O₃/SiO₂ catalyst with Al-alkyl cocatalyst and ethylene monomer. *Journal of Molecular Catalysis A: Chemical*. 2006a. 256: 301-308
- Xia W, Tonosaki K, Taniike T, et al. Copolymerization of ethylene and cyclopentene with Phillips CrO_x/SiO₂ catalyst in the presence of Al-alkyl cocatalyst. *Journal of Applied Polymer Science*. 2009. 111: 1869-1877
- Xia W, Liu B, Fang Y, et al. Plausible mechanism for the formation and transformation of active sites on novel Phillips type catalyst with new organo-siloxane ligand. *Studies in Surface Science and Catalysis*. 2006b. 161: 225-228
- Xia W, Liu B, Fang Y, et al. Multinuclear solid-state NMR study of coordinative nature of Alkylaluminum cocatalyst on Phillips CrO_x/SiO₂ catalyst. *Applied Catalysis A: General*. 2010. 389: 186-194
- Yermakov Y and Zakhrov V. One-component Catalysts for Polymerization of Olefins. *Advances in Catalysis*. 1975. 24: 173-219

(Edited by Zhu Xiuqin)