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Surface Physico-Chemical State of CO-Prereduced Phillips CrO_x/SiO_2 Catalyst and Unique Polymerization Behavior in the Presence of Al-Alkyl Cocatalyst

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Summary: In this work, a CO-prereduced Phillips CrO_x/SiO_2 catalyst (PC600/CO) was characterized by X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption with mass spectrometer (TPD-MS) in comparison with a calcined catalyst (PC600). It was found that surface chromate Cr(VI) species had not been completely reduced into Cr(II) species, meanwhile, CO and CO_2 still strongly adsorbed on the PC600/CO catalyst. Subsequently, the unique real-time profiles of ethylene polymerization rate using PC600/CO in the presence of TEA indicated the existence of two types of active sites: the first type derived from the desorption of CO or CO_2 from Cr(II) species by alkyl-Al and featured with fast activation, higher activity and fast decay; the second type generated from the further reduction of residual chromate Cr(VI) species by alkyl-Al and featured with slow activation, lower activity and slow decay.

Keywords: ethylene polymerization; Phillips CrO_x/SiO_2 catalyst; polyethylene; temperature programmed desorption (TPD); X-ray photoelectron spectroscopy (XPS)

Introduction

As one of the most important industrial catalysts for olefin polymerization, Phillips CrO_x/SiO_2 catalyst is still producing several million tons of high density polyethylene (HDPE) per year in the world. This catalyst system can be very easily prepared through a simple calcination process but shows quite unique polymerization behavior compared with Ziegler-Natta and metallocene catalysts. For example, it can be activated for ethylene polymerization solely by ethylene monomer or CO, as well as alkyl-Al cocatalyst, furthermore, its HDPE products usually featured with ultra-broad molecular weight distribution, unsaturated chain end and

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long chain branching.[1] All these above-mentioned properties have been proven to be very difficult to realize utilizing either Ziegler-Natta or metallocene catalyst within the past 50 years. In spite of its spectacular success in the industrial field and great research effort since early 1950s, its main mechanistic aspects concerning active sites and polymerization still remain mysterious.[1, 2]

Our recent studies on the induction period of ethylene polymerization using Phillips catalyst activated by ethylene monomer have elucidated some important mechanistic points concerning the induction period and subsequent typical accelerating-type polymerization behavior.[3, 4] The induction period is corresponding to the reduction of surface chromate Cr(VI) species into Cr(II) species. Whereas, the Cr(II) species during induction period can only act as ethylene metathesis active precursor due to the adsorption of formaldehyde, a byproduct of the redox reaction between chromate species and ethylene. The subsequent accelerating-type polymerization period is considered to be resulted from a gradual transformation of metathesis active sites into polymerization active sites due to the desorption of formaldehyde molecules.[4] It has also been shown that desorption of formaldehyde from the Cr(II) species became very difficult at even high temperature (e.g. up to 500°C) when ethylene monomer is absent.[3, 4] Therefore, for the CO-prereduced Phillips catalyst, it can be expected that CO, which present similar electron property with formaldehyde molecule, could strongly adsorbed to the surface Cr(II) species and can not be easily desorbed at even high temperature (typically 350°C) in N_2 atmosphere. This may explain why only the induction period can be eliminated, while similar accelerating-type polymerization kinetic can still be observed for the CO-prereduced Phillips catalyst,[1] which can be most probably interpreted in terms of similar active sites transformation due to the gradual desorption of CO from the Cr(II) species in the presence of ethylene monomer. To confirm these speculations, a CO-prereduced Phillips catalyst was prepared and characterized by XPS and TPD-MS in this study. It was found that the surface chromate Cr(VI) species on the calcined Phillips catalyst cannot be completely reduced to Cr(II) species even after 1.5h`s calcination in CO flow under 350°C, which are typical conditions for preparing CO-prereduced Phillips catalyst in the literature. Moreover, the existence of residual CO and $CO_2$ adsorbed on the CO-prereduced Phillips catalyst was confirmed by the TPD-MS method even after 1.5h`s further calcination in N_2 flow under the same temperature (350°C). Based on these preliminary evidences, ethylene polymerization tests using the CO-prereduced Phillips catalyst were designated to combine with the use of alkyl-Al cocatalyst, which has never been studied before. The alkyl-Al cocatalyst was expected to facilitate the formation of active sites for the CO-prereduced Phillips catalyst through both instant removing the CO or CO_2 from the Cr(II) species and further reduction of the residual chromate Cr(VI) species. Subsequently, a unique polymerization behavior was demonstrated in these ethylene polymerization tests using the CO-prereduced Phillips catalyst in the presence of alkyl-Al cocatalyst indicating the existence of two types of active sites: the first type featured with instant site formation, higher activity and fast decay, which was considered to be derived from the desorption of CO or CO_2 from Cr(II) species by alkyl-Al; the second type featured with slow site formation, lower activity and very slow decay, which was postulated to be generated from the further reduction of residual chromate Cr(VI) species by alkyl-Al.

Experimental

Raw Materials

Nitrogen of G2-grade (total impurity < 2ppm, in which O_2 < 0.3ppm, CO < 0.3ppm, CO_2 < 0.3ppm, CH_4 < 0.1ppm, NO_x < 0.1ppm, SO_2 < 0.1ppm, dew point of H_2O < −80°C), high purity helium gas (total impurity < 1ppm, in which O_2 < 0.05ppm, N_2 < 0.1ppm, CO < 0.02ppm, CO_2 < 0.02ppm, CH_4 < 0.01ppm, dew point of H_2O < −80°C), pure air of G1-grade (total impurity < 1ppm, CO < 0.1ppm, CO_2 < 0.1ppm, THC < 0.1ppm, NO_X < 0.01ppm, SO_2 < 0.01ppm, dew point of H_2O < −80°C) and high purity CO gas (CO > 99.95%, O_2 < 75ppm, N_2 < 175ppm, CO_2 < 30ppm, H_2 < 15ppm, THC < 0.5ppm, dew point of H_2O < −70°C) were purchased from Uno Sanso Co. Ethylene of research grade (C_2H_4 > 99.9%, air < 0.03%, methane < 0.01%, ethane < 0.05%, propane < 0.01%, analyzed by Gas Chromatography method) was donated by Mitsubishi Chemical Co. Molecular sieves 4A and molecular sieves 13X, which were purchased from Wako Pure Chemical Industries, Ltd., were used as moisture scavenger for gas purification. Q-5 reactant catalyst (13 wt.% of copper (II) oxide on alumina), which was purchased from Aldrich, was used as oxygen scavenger for gas purification. A catalyst precursor of Crosfield ES370X with 1.0wt% of Cr loading and surface area of 280~350 m^2/g, which was donated from Asahi Kasei Co., was used for preparation of Phillips CrO_x/SiO_2 catalysts.

Figure 1. Schematic diagram of the calcination device of Phillips catalyst, a: spouted fluidized-bed quartz reactor; b: electronic heater with temperature-program-controller; c: catalyst powder.

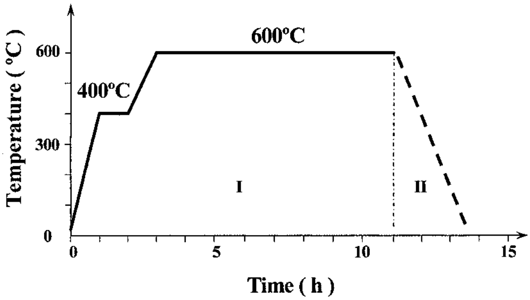


Figure 2. Temperature program for the preparation of the calcined Phillips catalyst, gas flow rate: 200ml/min, stage I: in dry air; stage II: in N_2.

Catalyst Preparation

About 15g of catalyst precursor was added into a spouted fluidized-bed quartz reactor (see Figure 1). Thereafter, a calcination process was performed to obtain a 600°C-calcined Phillips catalyst (named as PC600) according to a temperature program as shown in Figure 2. During the first stage (I) of this calcination process, pure air with a flow rate of 200ml/min was used as gas media. It was switched to nitrogen (200ml/min) during the second stage (II) of cooling. Another CO-prereduced PC600 catalyst (named as PC600/CO) was prepared following a typical temperature-controlling program as shown in Figure 3. Up to the second stage (I to II), the calcination process is almost the same as the PC600 catalyst.

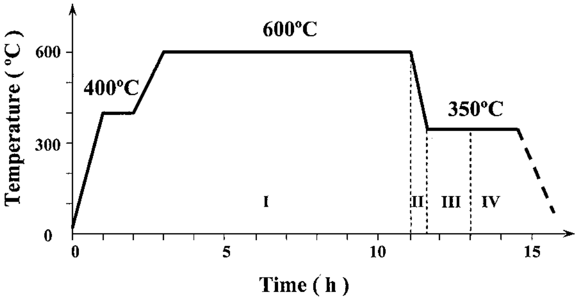


Figure 3. Temperature program for the preparation of the CO-prereduced Phillips catalyst, gas flow rate: 200ml/min, stage I: in dry air; stage II: in N_2; stage III: in CO; stage IV: in N_2.

After being cooled down to 350°C, the gas media was switched to CO (200ml/min) and kept at the same temperature for 1.5 h followed by the final stage (IV) at 350°C in N_2 for 1.5 h before cooling down to room temperature. After preparation, both catalyst samples were distributed and sealed into several large glass tubes within N_2 for storage. Finally, each catalyst sample was distributed and sealed in small glass ampoule bottles under nitrogen atmosphere. The amount of catalyst in each small glass ampoule bottle could be controlled at ca. 100mg and precisely weighed.

XPS and TPD-MS Measurements

The specific procedures and instrumental conditions of XPS and TPD-MS measurements for Phillips catalyst have been described in detail in our previous report.[3~5] Hereafter only a simplified introduction was given. XPS data were obtained on a Physical Electronics Perkin-Elmer Model Phi-5600 ESCA spectrometer with monochromated Al Kα radiation (1486.6eV) operated at 300W. A vacuum transfer vessel (Phi Model 04-110, Perkin-Elmer Co., Ltd.) was used for sample transformation from catalyst storage vessel into the XPS instrument in N_2 atmosphere. XPS high resolution scan measurements for Si 2p, Cr 2p regions of each sample was performed within 10min in order to minimize the X-ray induced reduction to the surface Chromate species during XPS measurement. All spectra were internally referenced to the Si 2p peak from silica gel at 103.3eV to correct for the charging effect during acquisition. The objective of the TPD-MS measurements of the PC600/CO catalyst is to check if there still exist residual CO and CO_2, which were considered to be very difficultly desorbed from the highly-coordinative-unsaturated Cr(II) species even at 350°C under N_2 atmosphere for 1.5 h. Firstly the PC600/CO catalyst sample (ca.100mg) was set into a quartz micro-reactor for the TPD measurement in a glove box. Then TPD-MS spectra were obtained from a Multi-task TPD instrument produced by Bel Japan, Inc. equipped with a quadrupole mass spectrometer (MS). The typical TPD-MS conditions are shown as follows: helium gas flow rate 50ml/min, mass spectrometer sampling time interval 15s, bridge current 2mA, vacuum for MS at ca. 2.5×10^{-8} Torr, etc. The temperature was elevated at a linear rate of 2 °C/min from room temperature (RT) to 600°C. The gaseous components of CO (m/e=28) and CO_2 (m/e=44) were continuously monitored.

Ethylene Polymerization

Schematic diagram of the experimental system for semi-batch slurry ethylene polymerization using the PC600/CO catalyst was shown in Figure 4. N_2 was further purified by passing through a Q-5 catalyst column and a 13X molecular sieve column before entering the polymerization system. Heptane was passed through a column of 13X molecular sieve followed by 24h`s bubbling by high purity N_2 before use. One ampoule bottle with ca. 100mg of PC600/CO was set in the top part of the glass polymerization reactor (volume ca.100ml). Then, the reactor system was vacuumed for 2 h before introduction of heptane solvent, TEA cocatalyst and ethylene. The polymerization was initiated after breaking of the catalyst ampoule bottle by a steel bar. Ethylene monomer was further purified by passing through a 4A molecular sieve column, a Q-5 catalyst column and a 13X molecular sieve column before entering the polymerization reactor. The polymerization conditions are shown as follows: ethylene pressure 0.13MPa, polymerization temperature: 60°C, 20 ml purified heptane, Al/Cr molar ratio at 7.5~22.5 using 1M TEA heptane solution. The real-time ethylene consumption was continuously monitored by a on-line mass flowmeter. The polymerization was stopped by adding 20ml ethanol/HCl after 1.5 h. The polymer was washed and dried in vacuum at 60°C for 6 h.

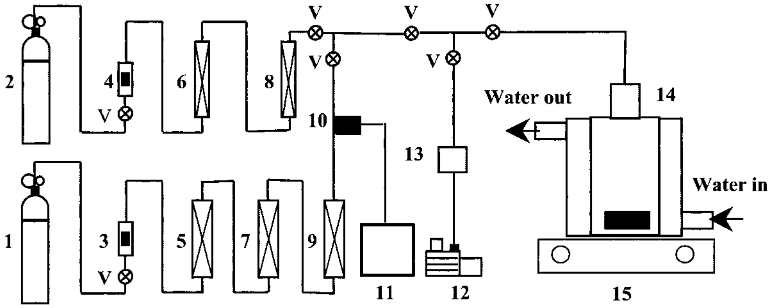


Figure 4. Schematic diagram of the experimental system for ethylene homopolymerization using the CO-prereduced Phillips CrO_x/SiO_2 catalyst, 1: ethylene gas cylinder; 2: N_2 gas cylinder; 3, 4: gas flow meter; 5: 4A molecular sieve column, 6, 7: Q-5 catalyst column; 8, 9: 13X molecular sieve column; 10: mass flow meter; 11: monitor and recorder of mass flow meter; 12: vacuum pump; 13: liquid N_2 trap; 14: polymerization reactor with water-jacket and magnetic stirrer; 15: controller of magnetic stirrer; V: valve.

Table 1. Oxidation states of surface Cr species on the calcined and CO-prereduced Phillips catalyst measured by XPS method.

Sample	BE a) (eV)	Percentage (%)	Assignment	BE a) (eV)	Percentage (%)	Assignment
PC600	581.0	96.9	Cr^{6+}	577.6	3.1	Cr^{3+}
PC600/CO	581.0	36.7	Cr^{6+}	576.7	63.3	Cr^{2+}

a) BE: binding energy of Cr2p (3/2)

Results and Discussions

The oxidation states of surface Cr species on PC600 (calcined) and PC600/CO (CO-prereduced) catalysts measured by XPS method are shown in Table 1.

As it can be seen, about 97% (atomic percentage) surface Cr species is chromate species (monochromate, dichromate or polychromate species) with a binding energy (BE) of 581eV (Cr2p(3/2)) in PC600 catalyst. Only ca. 3% surface Cr species was thermally reduced into surface stabilized Cr(III) species with a BE of 577.6eV.[5] For PC600/CO catalyst, about 63% of surface Cr species was reduced into surface stabilized Cr(II) species with a BE of 576.6eV by CO.[6] It was interesting to find that there still exists ca.37% of residual chromate species, which has not been reduced by CO in PC600/CO catalyst. The TPD-MS evolution curves of CO (m/e=28) and CO_2 (m/e=44) from the PC600/CO catalyst were shown in Figure 5 and Figure 6, respectively. It was clearly confirmed that CO and CO_2 were still strongly adsorbed on the surface Cr(II) species and cannot be desorbed at even high temperature (up to 600°C)

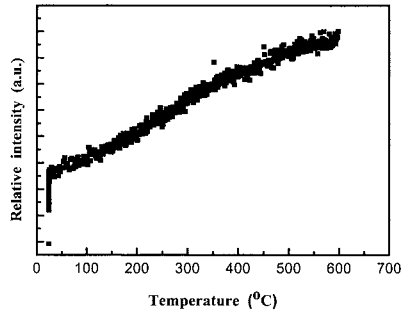


Figure 5. TPD-MS evolution curve of CO (m/e=28) from the CO-prereduced Phillips catalyst, TPD conditions: temperature elevation rate 2°C/min, RT ~ 600 °C, helium gas flow rate 50ml/min.

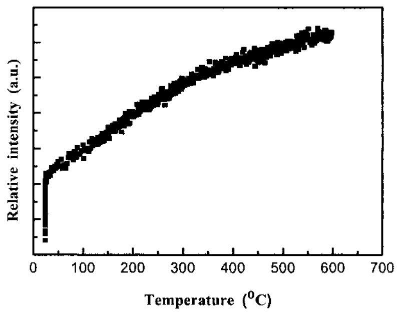


Figure 6. TPD-MS evolution curve of CO_2 (m/e=44) from the CO-prereduced Phillips catalyst, TPD conditions: temperature elevation rate 2°C/min, RT ~ 600 °C, helium gas flow rate 50ml/min.

in the absence of ethylene monomer. The style of the evolution curves of CO and CO_2 was similar with that of formaldehyde as reported in our previous work.[3, 4] The evolution of N_2 (also with m/e=28) from the PC600/CO was considered to be negligible due to its much weaker electron donating power and thus much weaker adsorption to Cr(II) species compared with CO.

So far, two experimental facts have been demonstrated as follows: firstly, considerable amount of surface chromate Cr(VI) species still remained on the PC600/CO catalyst. Secondly, CO and CO_2 still strongly adsorbed on the PC600/CO catalyst and can not be completely removed at even 600°C without ethylene. Based on these experimental evidences, ethylene polymerization tests using the PC600/CO catalyst in the presence of alkyl-Al cocatalyst were carried out. The alkyl-Al cocatalyst was expected to enhance the formation of active sites through fast removing CO or CO_2 from Cr(II) species and further reduction of residual chromate Cr(VI) species on the PC600/CO catalyst. Three semi-batch slurry ethylene homopolymerization experiments were performed in heptane at 60°C for 1.5 h with Al/Cr molar ratio at 7.5, 15.0 and 22.5 (using TEA as cocatalyst), respectively. The average activity of PC600/CO catalyst was found to decrease from 44.0 to 37.5 and 16.4 kg-PE/mol-Cr·h when Al/Cr molar ratio was increased from 7.5 to 15.0 and 22.5, respectively. The most interesting and important point disclosed in this study is the quite unique polymerization kinetics which has never been reported for the Phillips Cr-based catalysts up to now. As shown in Figure 7, the real-time polymerization kinetic curves seem to be a hybrid type comprised of two basic types of polymerization kinetics: one is a fast formation and fast decay type and the other is a slow formation and slow decay type. According to the surface physico-chemical state of the PC600/CO catalyst clarified by XPS and TPD-MS, it is reasonable to ascribe the origins of the two basic types of polymerization kinetics to two different types of active sites produced on PC600/CO by TEA namely Cr(II) species after desorption of CO or CO_2 by TEA (Site-A in Scheme 1) and Cr(II) species from reduction of residual chromate Cr(VI) species by TEA (Site-B in Scheme 1). Site-A is very exposed and can be easily deactivated due to over-reduction from further contact with TEA cocatalyt, while, Site-B might be protected and/or stabilized by the coordination with Al-alkoxyl groups. This is also consistent with previous polymerization kinetics reports relating to organometal-modified Phillips CrO_x/SiO_2 catalysts by McDaniel et al.[7] The Al-alkoxyl ligands coordinated on Site-B

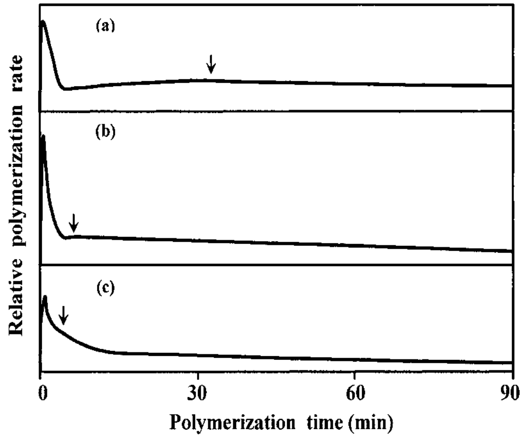
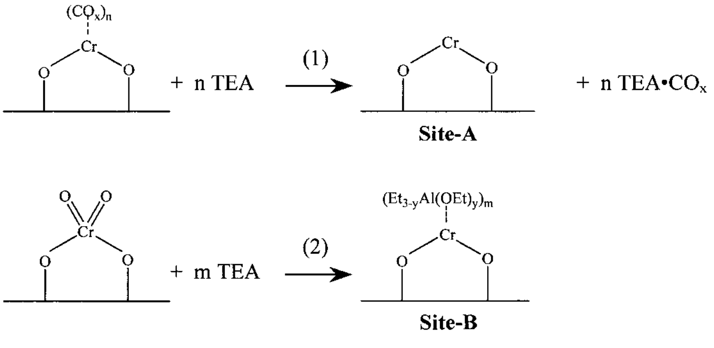


Figure 7. Polymerization kinetics profiles of ethylene homopolymerization using the CO-prereduced Phillips catalyst in the presence of TEA cocatalyst, polymerization conditions: catalyst amount 100mg, polymerization temperature 60°C, polymerization time 1.5 h, ethylene pressure 0.13 MPa, solvent heptane (20ml), cocatalyst TEA in heptane (1M), Al/Cr molar ratio (a) 7.5; (b) 15.0; (c) 22.5.

were not poisonous by-product for polymerization as indicated by McDaniel et al..[7] Figure 7 also showed that the time to reach the maximum activity for Site-B was shortened from ca. 30min to ca 5min (as shown by arrows in Figure 7) accompanied with faster decay of Site-B when Al/Cr molar ratio was increased from 7.5 to 22.5. The decrease of average activity with



Scheme 1. Plausible mechanism of the formation of two kinds of active sites on the CO-prereduced Phillips catalyst in the presence of TEA cocatalyst for ethylene polymerization, x=1 or 2; n=1 or 2; y=1 or 2, m=1 or 2.

increasing Al/Cr molar ratio could be ascribed to enhancement of active site deactivation of both Site-A and Site-B (especially the latter).

Conclusion

It has been shown that surface chromate Cr(VI) species has not been completely reduced into Cr(II) species, meanwhile, CO and CO_2 still strongly adsorbed on the PC600/CO catalyst. Subsequent unique ethylene polymerization behavior using PC600/CO in the presence of TEA demonstrated the existence of two types of active sites: the first type derived from the desorption of CO or CO_2 from Cr(II) species by alkyl-Al and featured with fast activation, higher activity and fast decay; the second type generated from the further reduction of residual chromate Cr(VI) species by alkyl-Al and featured with slow activation, lower activity and slow decay.

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