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Experimental and theoretical studies on ethylene polymerization using SiO_2-supported silyl chromate type catalysts prepared by a green method

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ABSTRACT

SiO_2-supported silyl chromate catalyst (UCC S-2 catalyst) is an important catalyst for the commercial production of polyethylene. Cann first reported a possible green synthesis route for the preparation of S-2 catalyst through transformation from Phillips catalyst by addition of triphenylsilanol (TPS) to avoid the use of toxic bis(triphenylsilyl) chromate (BC). In this work, this green synthesis route was further investigated by the combination of experimental and theoretical methods. The obtained catalyst was named as PS catalyst based on the incomplete conversion of Phillips catalyst to S-2 catalyst. Polymerization activity of PS1.5 catalyst was higher than that of S-2 catalyst with either TEA or MAO as cocatalyst. The existence of the simultaneously formed hydroxyl group and its coordination to the reduced Cr site was favorable to the PS catalyst, and this might attribute to the higher polymerization activity of PS catalyst than that of S-2 catalyst. A further modification of PS catalyst by a series of alkyl chlorosilane compounds showed that the role of the electron-withdrawing group only limited at a certain distance away from Cr active site. This preliminary study provided a solid basis for a further innovation of PS catalysts and final substitution of S-2 catalyst in commercial processes.

1. Introduction

Polyethylene (PE) is a most commonly used plastic with the largest market. Chromium based catalyst systems, including Phillips (chromium oxide) and silyl chromate supported on silica, have long been among the most important catalysts for the production of PE [1–5]. The silyl chromate catalyst, namely S-2 catalyst, was commercialized by Union Carbide Corporation (UCC) with a gas phase UNIPOL process for HDPE production. Until now, S-2 catalyst still produces several millions tons of HDPE, which have desirable molecular weight characteristics meeting different market demanding [6].

However, compared with Phillips catalyst, S-2 catalyst has not been fully investigated during the past several decades. Traditionally, S-2 catalyst is directly prepared from bis(triphenylsilyl) chromate (BC) using thermal treated silica gel as support by wet impregnation method as shown in Scheme 1(A) [3]. It is well known that the catalytic activity is markedly increased when BC is supported on silica gel and then treated with aluminum alkyl [3]. And the unsupported BC is also an active catalyst for ethylene polymerization under relatively high temperature and pressure [7]. Gaspar et al. found that S-2 catalyst showed lower polymerization activity than Phillips catalyst due to S-2 catalyst with less Cr^{6+} and Cr^{2+} active species in their calcined and reduced states, respectively [8,9]. However, S-2 catalyst using aluminum alkyl cocatalyst could produce polyethylene with broader molecular weight distribution (MWD) on both ends of high and low molecular weight than that of Phillips catalyst without using cocatalyst [5].

Generally, BC is prepared from triphenylsilanol (TPS) and chromium trioxide, and a higher BC product yield has been developed by Li et al. using triphenyl chlorosilane, potassium dichromate [10]. Nevertheless, the highly toxic BC does not meet the trend of the modern world with increasing concerns about environment and human health. In 2004, a pioneering work of a possible transformation from Phillips catalyst to silyl chromate catalyst through introduction of a silyl ligand from reaction with TPS was reported by Cann and co-workers [5,11]. It was found that the polymerization performance between the obtained catalyst and the silyl chromate catalyst tended to be similar in the case of two equivalents TPS to Cr on Phillips catalyst. The reaction was illustrated in Scheme 1(B). Furthermore, Liu et al. used different organo-silanol compound to modify Phillips catalyst and successfully developed a new SiO_2-supported Cr-based catalysts for olefin polymerization [6]. In our opinion, the reports mentioned above indicated a possible green synthesis route for the preparation of silyl chromate type

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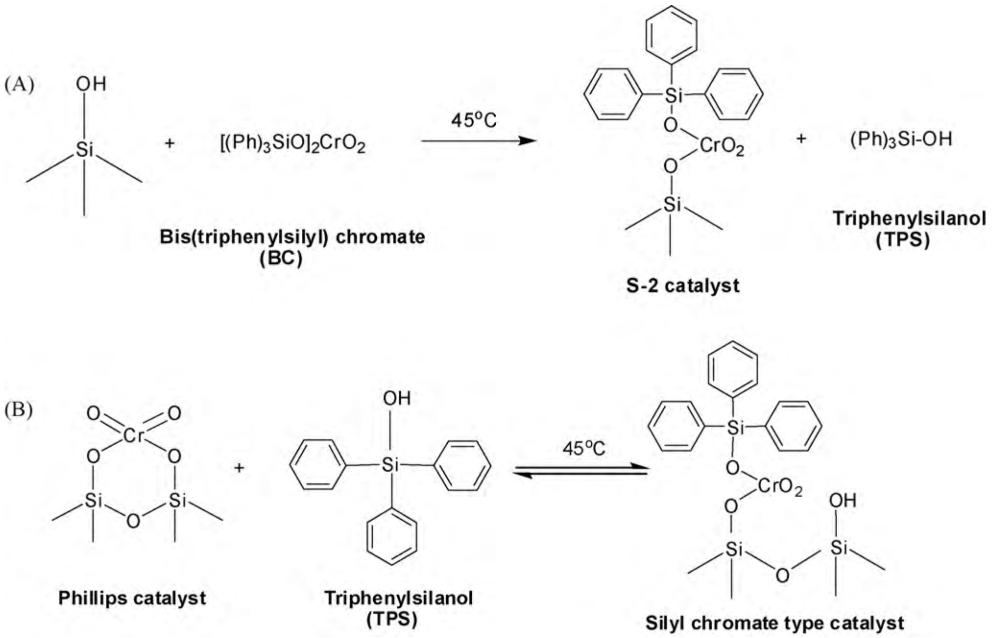

Scheme 1. Two methods for preparation of silyl chromate type catalyst: (A) S-2 catalyst prepared from bis(triphenylsilyl) chromate (BC); (B) Conversion of Phillips catalyst to silyl chromate type catalyst by the addition of triphenylsilanol (TPS).

polyethylene catalyst. However, it was noticeable that a hydroxyl group appeared next to the Cr active site accompanied by the addition of TPS, while this kind of neighboring hydroxyl did not exist in the S-2 catalyst obtained through traditional preparation process. And also, this point was not considered within the previous work by Cann [5]. Considering the strong reverse correlation between the hydroxyl population on the silica surface and polymerization activity in Phillips catalyst [4], effect of the introduced hydroxyl group next to the Cr active site on the polymerization behavior of PS catalyst should be seriously considered.

In recent years, molecular modeling based on density functional theory (DFT) method was increasingly used for the study of the Phillips catalyst [12–19]. Most work was focused on achieving a deeper understanding of the polymerization mechanisms on Phillips-type catalyst. Espelid and Borve [19] compared different routes of initiation and chain propagation with respect to structural, thermodynamic and kinetic properties, and concluded that only a three-coordinate mono-alkylchromium species was found to support chain propagation with the reaction barrier compatible with catalytic activity based on the model of disiloxanochromium site. Liu et al. [15] used a novel silsesquioxane-supported Phillips Cr catalyst as realistic model to elucidate the effects of surface chemistry of silica gel in terms of ligand variation on the catalytic properties of Phillips catalyst. And also, possible reaction mechanisms of olefin polymerization catalyzed by surface supported Cr(IV) species have been investigated using DFT method by Ziegler [13]. However, up to now, there has no theoretical study using DFT method on the silyl chromate type catalyst.

In order to achieve the green synthesis of S-2 catalyst, the preparation of Phillips catalyst in a green method is principal. As a matter of fact, from about 1978, trivalent Cr compound, mostly basic chromium(III) acetate with much weaker toxicity, has been developed as raw material instead of chromium(VI) trioxide for the preparation of Phillips catalyst owing to the environmental and health considerations [9,10,20–25]. Ruddick et al. [22] studied the calcination process of Phillips catalysts using basic chromium(III) acetate and chromium(III) acetylacetonate, and concluded that chromium(III) acetate supported on silica decomposed in a way similar to that observed for bulk chromium acetate. A mechanism for the activation of silica-supported basic chromium acetate in oxidizing, inert, and reducing environments was proposed by Augustine and Blitz [25]. Liu et al. [24] utilized XPS to elucidate the specific transformation process of chromium(III) acetate into bulky CrO_3 and subsequently into $Cr(VI)O_{x,surf}$ as a function of calcination temperatures between 120 and 800 °C.

Thus, in this work, the silica supported Phillips catalyst was first prepared from basic chromium(III) acetate with much lower toxicity compared with the commonly used chromium(VI) trioxide according to our previous report [26]. Subsequently, TPS was added to react with oxo chromate species in Phillips CrO_x/SiO_2 catalyst to form the silyl chromate type catalyst system, which was denoted as PS catalyst. Therefore, in this green synthesis route, highly toxic bis(triphenylsilyl) chromate(VI) (BC) was replaced by chromium (III) compound and TPS. Series PS catalysts and the obtained PE products were characterized. The ethylene polymerization kinetics of the PS1.5 catalysts was compared with those of Phillips catalyst and traditional S-2 catalyst. Specially, the simultaneously formed hydroxyl group next to the Cr active site during the preparation of PS catalyst was investigated by the theoretical method. This was the first theoretical investigation using DFT method for the silyl chromate type catalyst. Additionally, a further modification of the PS catalyst by alkyl chlorosilane compound to remove the nearby surface hydroxyl group was carried out by the combination of theoretical and experimental methods. Much deeper understanding on the SiO_2-supported silyl chromate type catalyst for ethylene polymerization has been demonstrated.

2. Experimental

2.1. Raw materials

Chromium(III) acetate hydroxide (with 24 wt% Cr) was purchased from Johnson Matthey Company. Bis(triphenylsilyl) chromate (>96%) was obtained from Aldrich. Silica gel (Davison 955, surface area 270.4 m^2/g, pore volume 1.65 cm^3/g and average pore size 24.5 nm) was donated by Qilu Branch Co., SINOPEC. Triphenylsilanol (TPS, >98%) and triethylaluminum (TEA, 25%, w/w, in hexane, >95%) were purchased from Alfa Aesar. Methylalumox-