Catalysis Communications 83 (2016) 39–42

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short communication

Electrochemically assisted ethylene (co-)polymerization with a vanadium-based Ziegler-Natta catalyst

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ARTICLE INFO

Article history:
Received 14 March 2016
Received in revised form 27 April 2016
Accepted 29 April 2016
Available online 1 May 2016

Keywords:
Electrochemistry
Polymerization
Polyolefin
Vanadium catalyst

ABSTRACT

A facile and efficient electrochemically assisted ethylene polymerization and ethylene-propylene copolymerization with the widely used $VOCl_3$/ethylaluminum sesquichloride (EASC) catalyst system was demonstrated. The low-activity and/or inactive low-valence-state V species present in the catalyst were oxidized to high-valence-state V through electrochemical methodology. Thus, the catalytic activity of the $VOCl_3$/EASC catalyst system was significantly improved. The effects of electrochemical application on the resultant polymer structure and properties were investigated. This work provides a new strategy to improve the performance of Ziegler-Natta catalysts.

1. Introduction

Electrochemistry is a powerful tool with a wide range of applications in areas such as analysis [1–3], catalysis [4–6], polymerization [7–9], and material sciences [10,11]. It deals with the relationship between electrical energy and chemical change, and offers multiple readily adjustable parameters (e.g., applied current, potential, and total charge passed) to influence the oxidation or reduction of chemicals. Recently, there has been growing interest in the application of electrochemical methodology to radical polymerization. Matyjaszewski et al. [12–14] have reported an electrochemically mediated atom-transfer radical polymerization (eATRP) technique to control the polymerization of methacrylate monomers. By adjusting the electrochemical potential, the higher-oxidation-state Cu(II) salt was reduced to Cu(I) through one-electron reduction. Thus, a new environment-friendly procedure for the control of polymerization processes with predetermined molecular weights and narrow molecular weight distributions of the product was developed. However, compared with electrochemical oxidation polymerization, the application of electrochemical methods to other types of polymerization reactions has been rarely reported.

Coordination polymerization is a form of addition polymerization in which a monomer adds to a growing macromolecule through an active organometallic center. In these processes, the valence state of the transition metal is a very important parameter. Taking advantage of the facile control of the valence state of elements available with this method, it would be highly desirable to apply this technology to coordination polymerization. However, to our knowledge, there are currently no reports concerning electrochemically assisted coordination polymerization.

V-based complexes are one of the most useful Ziegler–Natta catalysts, and are extensively applied in the production of polyethylene (PE) and ethylene/propylene/diene elastomers, as well as ethylene/α-olefin copolymers. However, the easy reduction of high-valence-state V species to low-activity and/or inactive low-valence V species significantly reduces catalytic activity, especially at high reaction temperatures and high cocatalyst (i.e., aluminum compounds) feed rates [15–20]. Therefore, the development of a new strategy that maintains the high valence state of V species during polymerization is of great interest.

Herein, we report an example of electrochemically assisted ethylene polymerization and copolymerization catalyzed by a $VOCl_3$/ethylaluminum sesquichloride (EASC) catalyst system. This method provides a new strategy to improve the performance of Ziegler-Natta catalysts.

Scheme 1 shows the mechanism of electrochemically assisted olefin polymerization. The application of an electrochemical stimulus reversibly activates the V-based catalyst by oxidation of the low-activity and/or inactive low-valence-state V species, thereby enhancing the catalytic activity of the electrochemically assisted system.

The reaction was carried out in an electrochemical cell with a three-electrode system under argon atmosphere. A constant potential was applied to continually oxidize the generated low-activity or inactive low-valence-state V species during the polymerization process. Prior to the polymerization experiments, cyclic voltammograms (CV) of the supporting electrolyte ($Bu_4N^+PF_6^-$ in CH_2Cl_2) over a potential range of 4.0 V (from −2.00 to 2.00 V vs Ag/Ag^+) were acquired in order to ensure that no intrinsic redox processes that might interfere with the intended oxidation procedure were occurring in the electrolyte. As

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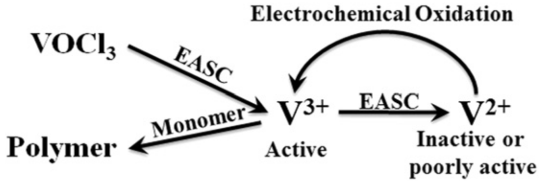
http://dx.doi.org/10.1016/j.catcom.2016.04.024



Scheme 1. Mechanism of electrochemically assisted olefin polymerization.

shown in Fig. 1a, no redox process is observed within the potential window ranging from −2.00 to 2.00 V vs Ag/Ag$^+$. After confirming the stability of the reaction medium, an additional CV measurement in the presence of $VOCl_3$ was taken to investigate the oxidation state of the catalyst under argon atmosphere. $VOCl_3$ displays multi-step reductive chemistry (Fig. 1a), which is only partly reversible. In general, V catalysts exhibit low productivity in olefin polymerization as a result of the reduction of active V^{3+} to low-activity or inactive V^{2+} species after activation with EASC [15–20]. Thus, in the present study, the oxidation-reduction process of the $VOCl_3$/EASC system was further examined. As shown in Fig. 1, the reduction peaks located at −0.86 V, −0.37 V, and 0.85 V shift to lower potential (−1.04 V, −0.34 V, and 0.38 V) with the introduction of the EASC cocatalyst. This may be ascribed to the alkylation of the $VOCl_3$ catalyst and/or coordination of Al compounds to the $VOCl_3$ catalyst. Due to the rapid reaction of $VOCl_3$ with EASC, the intensity of the peaks at 0.85 V and −0.37 V drastically decreases within 10 min. With prolonged reaction time, the intensity of the peak at −1.4 V gradually increases. This result may be attributed to the amount of lower-oxidation-state V (V^{2+}) increasing with prolonged reaction time.

The polymerization of ethylene catalyzed by $VOCl_3$/EASC in the absence and presence of electrochemical potential was examined. It was found that the system is more effective when the polymerization operate at higher [Al]/[V] ratio (Table S1). This could be correspondence to the relatively higher reduction speed of V at higher EASC concentration. Therefore detailed investigations have been carried out employing [Al]/[V] = 4000 through varying the applied potential and polymerization time. As shown in Fig. 2, the catalytic activity increases with increasing applied potential, but levels off at 1.50 V. This result may be due to the rapid oxidation of inactive and low-activity V species at higher applied potential.

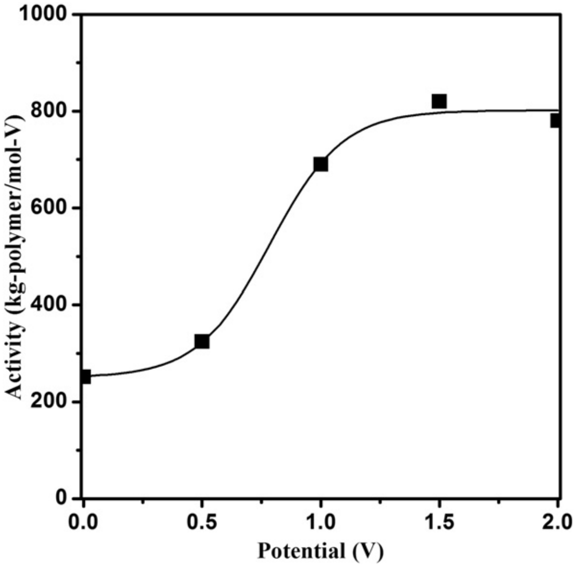


Fig. 2. Effect of potential on catalyst activity.

The melting temperature of the resultant PE was further investigated by differential scanning calorimetry (DSC). As shown in Fig. S3(a) and Table S1, the T_m of the produced PEs are almost same as those of the potential-free PE. This confirms that the application of potential on the polymerization system has no effect on the polymer structure. The PE structure was further confirmed by ^{13}C NMR. As shown in Fig. S3(b), in both cases the polymers have a linear structure, indicating that the polymerization mechanism does not change under the application of potential.

The molecular weight and its distribution were studied by gel permeation chromatography (GPC) analysis and the GPC curves were given in Fig. S4. Regardless of the different potential applied, the GPC curves of the resultant polymers remain unimodal and the molecular weight distribution is relatively narrow (M_w/M_n = 2.0–2.3), demonstrating that no new active species are formed by potential application. In addition, the molecular weight of the polymer increases with an increase in the applied potential. The increased molecular weight maybe ascribed to the increased propagation rate by the potential application.

The dependence of catalyst activity on the polymerization time at different potentials is shown in Fig. 3. The catalyst activity increases with prolonged polymerization time. With regards to shorter polymerization time (15 min), the activities of catalyst prepared with different potential applications are almost equal. The difference in the activities of the catalysts prepared with different potential applications becomes

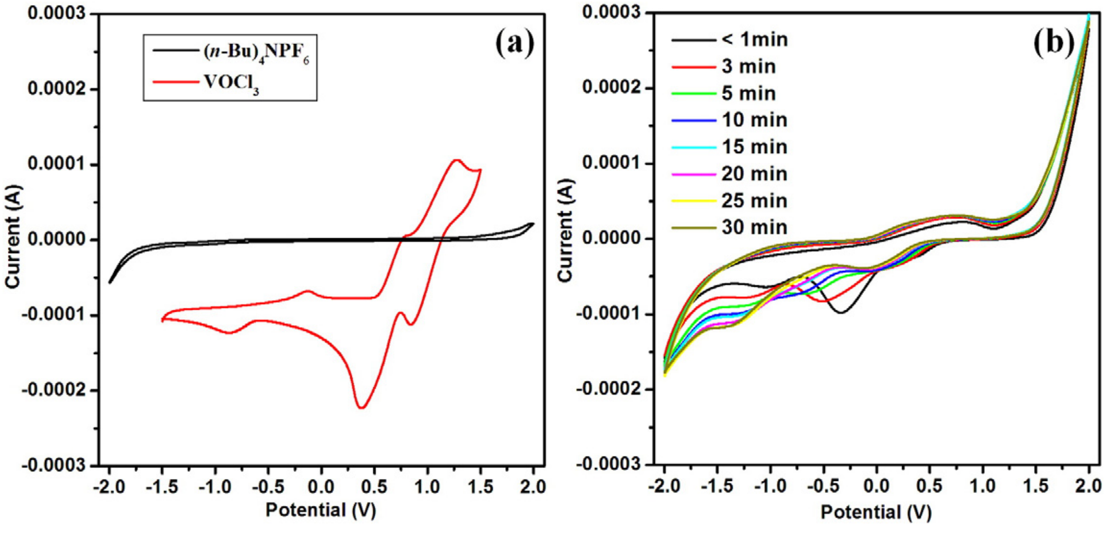


Fig. 1. Cyclic voltammograms of (a) $Bu_4N^+PF_6^-$ (0.1 M), $VOCl_3$ (0.01 M) and (b) $VOCl_3$-EASC ([Al]/[V] = 5) in CH_2Cl_2 at a scan rate of 200 mV s^{-1}.