



Article

Electrochemical Synthesis of Zirconium Pre-Catalysts for Homogeneous Ethylene Oligomerization

Giyjaz E. Bekmukhamedov ^{1,2,*}, Aleksandr V. Sukhov ^{1,2}, Aidar M. Kuchkaev ^{1,2},
Khasan R. Khayarov ¹, Alexander V. Gerasimov ¹, Irina V. Vasilenko ³, Sergei V. Kostjuk ^{3,4,5} 
and Dmitry G. Yakhvarov ^{1,2,*} 

¹ Alexander Butlerov Institute of Chemistry, Kazan Federal University, 18 Kremlevskaya st., Kazan 420008, Russia; alex.suhoff@rambler.ru (A.V.S.); kuchkaev95@mail.ru (A.M.K.); khayarov.kh@mail.ru (K.R.K.); alexander.gerasimov@kpfu.ru (A.V.G.)

² Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center of RAS, 8 Arbuzov st., Kazan 420088, Russia

³ Research Institute for Physical Chemical Problems of the Belarusian State University, 14 Leningradskaya st., Minsk 220006, Belarus; vasilenkoi@bsu.by (I.V.V.); kostjuks@bsu.by (S.V.K.)

⁴ Department of Chemistry, Belarusian State University, 14 Leningradskaya st., Minsk 220006, Belarus

⁵ Institute for Regenerative Medicine, Sechenov University, 8-2 Trubetskaya st., Moscow 119991, Russia

* Correspondence: gbekmouk@kpfu.ru (G.E.B.); yakhvar@iopc.ru (D.G.Y.);
Tel.: +7-843-2337416 (G.E.B.); Fax: +7-843-2732253 (D.G.Y.)

Received: 14 November 2019; Accepted: 9 December 2019; Published: 12 December 2019



Abstract: The catalytic activity of electrochemically synthesized zirconium carboxylates was studied in the process of ethylene oligomerization. Zirconium carboxylates were electrochemically synthesized directly from metallic zirconium and corresponding carboxylic acids (acetic, octanoic and lauric). A comprehensive study (element analysis, nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy, powder X-ray diffraction (PXRD)) of the synthesized zirconium carboxylates showed that these species contain bidentate carboxylate moieties. It was shown that obtained zirconium carboxylates, in combination with $\text{Et}_3\text{Al}_2\text{Cl}_3$ ($\text{Al}/\text{Zr} = 20$), have a moderate activity of $(7.6\text{--}9.9) \times 10^3 \text{ mol}_{\text{C}_2\text{H}_4} \cdot \text{mol}_{\text{Zr}}^{-1} \cdot \text{h}^{-1}$ in terms of ethylene oligomerization (at $T = 80 \text{ }^\circ\text{C}$, $p = 20 \text{ bar}$), leading to even-numbered $\text{C}_4\text{--C}_{10}$ linear alpha-olefins.

Keywords: electrochemical synthesis; zirconium carboxylate; ethylene oligomerization; pre-catalyst; linear alpha-olefins

1. Introduction

The continuous growth of global polymer production leads to the development of new methods and catalysts for the production of olefin monomers; for example, alkane dehydrogenation, methanol-to-olefins, metathesis and olefin oligomerization [1–5]. In its turn, ethylene oligomerization aimed to obtain linear alpha-olefins (LAO), which are used as co-monomers in the production of the demanded types of polyethylene (linear low-density polyethylene, high-density polyethylene), as well as for the production of a wide range of unique chemicals, such as lubricants and additives, plasticizers, surfactants and so forth [6].

From the development of the Ziegler–Natta catalytic system to the present time, zirconium organometallic compounds have been widely investigated in the context of their use as pre-catalysts (substances that acquire catalytic properties after activation) in the reactions of the oligomerization and polymerization of unsaturated hydrocarbons [4,7–12]. For example, zirconium pre-catalysts are used in many industrial processes of homogeneous ethylene oligomerization, such as Alphaselect (IFP Energies Nouvelles, Rueil-Malmaison Cedex, France), Alpha–Sablin (SABIC-Linde, Munich, Germany)