



Decene formation in ethylene trimerization reaction catalyzed by Cr–pyrrole system

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ABSTRACT

Decene formation in the ethylene trimerization reaction was studied using a chromium(III) 2-ethylhexanoate/2,5-dimethylpyrrole/triethylaluminum/diethylaluminum chloride catalyst system. Kinetic investigations revealed that some decene formation reactions did not depend on 1-hexene concentration, because 1-hexene and catalyst may react with ethylene before dissociation of 1-hexene–catalyst complex after 1-hexene formation. The results demonstrated that decene formation is an intrinsic part of the trimerization reaction mechanism. It was also shown that a stepwise elimination mechanism for the decomposition of the chromacycloheptane intermediate cannot explain the observed product distribution. The dependencies found allow selection of appropriate conditions for low or high decene formation in the ethylene trimerization reaction.

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1. Introduction

The ethylene trimerization reaction predominantly produces 1-hexene, which is chiefly used as a comonomer in polyethylene production. The reaction, which has been applied industrially by Chevron Phillips since 2004, is catalyzed by transition metal complexes which are typically chromium-based and activated by organoaluminum compounds. Comprehensive reviews on trimerization catalysts and the mechanism of the reaction have been published [1–3].

It is generally accepted that the reaction mechanism includes the formation of metallacyclic intermediates. The basic mechanism proposed by Briggs [4] (Scheme 1) was later supported by experimental [5,6] and theoretical [7,8] findings. It involves the coordination of two ethylene molecules to the catalyst center, followed by metallacyclopentane formation. A metallacycloheptane is then formed by expansion of the ring with a third ethylene molecule. The metallacycloheptane presumably undergoes β -elimination and reductive elimination, which results in

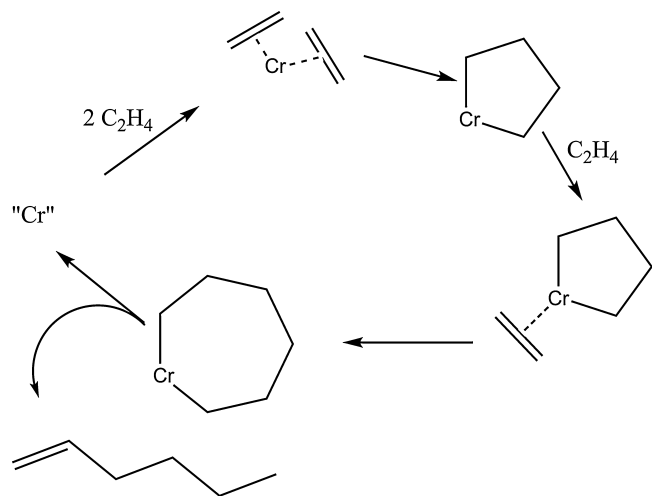
1-hexene formation and regeneration of the catalyst. An alternative explanation suggests a concerted 3,7-hydrogen shift in the metallacycloheptane leading to the same product.

By-products of the reaction, usually about 10% in total, include 1-butene, 1-octene, internal hexenes, decenes, and higher olefins. 1-Butene may be formed due to non-selective oligomerization, or from the metallacyclopentane. 1-Octene is believed to be formed due to further metallacycle expansion to metallacyclononane, which also undergoes reactions analogous to the metallacycloheptane. Decene isomers are formed in a co-trimerization reaction of 1-hexene and two ethylene molecules [9,10]. Decenes are often the most significant by-products in the reaction, regardless of the catalyst used [1,9–11]. Heavier olefins can be formed through other co-trimerization reactions [10].

Most kinetics studies of the ethylene trimerization reaction have considered the formation of the main product, 1-hexene, or studied the total ethylene consumption or the catalyst productivity [11–16]. Details of the decene formation kinetics in the ethylene trimerization reaction remain unknown. We have not found studies devoted to the topic, although there are papers that consider the formation of co-trimerization products using various conditions and catalysts [6,10,17]. This work was intended to investigate the key features of decene formation kinetics in the ethylene trimerization reaction, as it affects the 1-hexene selectivity in the reaction. These data could also help to increase the understanding of the reaction mechanism.

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Scheme 1. Ethylene trimerization mechanism.

2. Experimental

2.1. Materials

Chromium(III) 2-ethylhexanoate ($\text{Cr}(\text{EH})_3$) was prepared by a known method from aqueous chromium(III) chloride and sodium 2-ethylhexanoate [18], but the final drying with ethylhexanoic acid was carried out at 200 °C and 200 Pa, in order to maximize the associated water removal. A 25% solution of triethylaluminum (TEA) in toluene and 2,5-dimethylpyrrole (DMP) were purchased from Aldrich. 1-Hexene, 1-octene and 1-decene for standards and diethylaluminum chloride (DEAC) (1.0 M solution in hexanes) were purchased from Acros Organics. These reagents were used without further purification. Hydrocarbon solvents were refluxed over Na and NaH, and freshly distilled before use. The polymer-grade ethylene was further purified by passing it through a steel bottle filled with activated molecular sieves 5 Å.

2.2. Instruments

A stainless steel jacketed reactor (0.5l) equipped with an overhead stirrer, thermostat, pressure and temperature sensors, nitrogen line, hydrogen line, bottom needle valve, and ethylene dosing line with a flow meter was used for the study. A computer-based control system was used to control the stirrer speed, reactor and jacket temperatures, flow rate of ethylene, and other parameters.

Reaction products were analyzed using gas chromatography (Agilent 7890A with FID-detector, Agilent 7890A with 5975C mass-selective detector) with HP-5 capillary column. NMR spectra were recorded in CDCl_3 using Bruker Avance III 400 (400 MHz) spectrometer.

2.3. Procedures

2.3.1. Catalyst preparation

The catalyst was prepared according to a previously described enhanced method [19] by using $\text{Cr}(\text{EH})_3$ /DMP/TEA/DEAC in the ratio 1:5:36:14. $\text{Cr}(\text{EH})_3$ (29 mg, 60 μmol) and DMP (29 mg, 305 μmol) were placed in a flask. Then 5 ml of ethylbenzene was added. The mixture of 1.15 ml of 1.9 M TEA solution in toluene (2.2 mmol) and 0.84 ml of 1 M heptane solution of DEAC (0.84 mmol) was microwave-irradiated in a polypropylene syringe using CEM MARS 5 microwave oven at rated power 400 W for 6 min (with little heating). Then, within 30 s after the end of the

irradiation, the TEA/DEAC solution was added to the mixture of $\text{Cr}(\text{EH})_3$ and DMP in ethylbenzene. After 15 min since TEA/DEAC addition, solvents were removed in vacuo at 40 °C. The residue in the flask was diluted with 20 ml of cyclohexane to obtain the catalyst solution (0.003 M Cr).

2.3.2. Ethylene trimerization

The reactor was dried at 120 °C under nitrogen flow, and then evacuated and filled with hydrogen. Cyclohexane (200 ml) was added with a dosing pump under a hydrogen atmosphere. The solvent was saturated with hydrogen at atmospheric pressure and the desired reaction temperature. The catalyst solution in cyclohexane (2 ml, 6 μmol Cr) was injected into the reactor via a syringe under hydrogen counter flow. Ethylene was swiftly added to build up the desired pressure, and then ethylene was dosed to maintain the pressure constant. Reactor temperature was maintained at the set value by an automated system. Sampling was performed from the bottom valve during the reaction. The pressure was reduced and the reaction mixture was unloaded after 60 min.

During each run, seven samples were collected for GC analysis at 2, 5, 10, 15, 30, 45 and 60 min after ethylene addition (sample volume 1–1.5 ml).

2.3.3. Distillation of decene fraction

The combined reaction mixtures were exposed to air for 2 h, which resulted in precipitation of small amount of brown solids. These were filtered off, and the filtrate was distilled using a laboratory distillation column to obtain a bottom residue containing about 50% cyclohexane and hexenes, 40% decenes, and 10% heavy products. The residue was additionally distilled using a laboratory column in vacuo, and a fraction with the boiling point 108–112 °C/18 kPa was collected. GC/MS analysis confirmed a content of 94% C_{10} olefins. The sample also contained about 2% of cyclohexane, 1.8% of ethylbenzene and 1.3% of 1-octene.

3. Results and discussion

3.1. The scope of the experiments

We performed a series of trimerization runs, varying the ethylene pressure and reaction temperature. Our measurements allowed us to determine the average reaction rate between sampling points for every product, including the decene isomers. The average reaction rates for 1-hexene and the decenes at 15–30 min intervals were calculated from GC data for all runs. The results are listed in Table 1.

The typical time course of product formation during the ethylene trimerization reaction is shown in Fig. 1.

3.2. Identification of the decenes

Scheme 2 illustrates pathways for decene formation in accordance with the metallacycle mechanism. Seven main decenes were formed, including 1-decene (6), 4-decene (7) and 5-decene (5). GC analysis could not distinguish 5 and 7, so only six major decene peaks were discerned by GC/MS.

The decenes were distilled from the reaction products for identification purposes. The fraction contained about 94% decenes, according to GC/MS analysis. The mixture also contained small amounts of 1-octene (1.3%) and ethylbenzene (1.8%) which had been used in the catalyst preparation. The remainder was mostly cyclohexane solvent. Decenes were identified by ^{13}C NMR analysis of the decenes mixture. The Distortionless Enhancement by Polarization Transfer (DEPT) method was used to establish the signal positions of the vinyl CH_2 and CH carbons, as well as the aliphatic CH (branching points). 5-Methyl-1-nonene (1) and *cis*-4-decene (7)

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