

# Optimization of a new catalyst composition for trimerization of ethylene

Mohammad Javad Sharifi<sup>1</sup>, Alireza Fazlali<sup>1,\*</sup>, Seyed Hamed Mahdaviani<sup>2</sup>, Davood Soudbar<sup>2</sup>

<sup>1</sup>Department of Chemical Engineering, Faculty of Engineering, Arak University, Arak 38156-8-8349, Iran

<sup>2</sup>R&D Center, Shazand Petrochemical Company (ARPC), Arak 575, Iran

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## ABSTRACT

The performance of the catalyst system [chromium(III)/pyrrole/co-catalyst/halide] on the trimerization of ethylene has been studied using the combined experimental and response surface method (RSM). The chromium(III) tris(2-ethylhexanoate) was synthesized and characterized by FTIR, <sup>1</sup>HNMR and <sup>13</sup>CNMR, to study chemical properties and identify molecular structures. The effect of four variables Al/Cr molar ratio, halide/Cr molar ratio, reaction temperature and catalyst dosage have been considered on catalyst activity, 1-hexene selectivity and polymer content. The central composite design (CCD) model with three main parameters in three response levels for each factor was applied to analyze the effects of the parameters. The comparative studies showed that carbon-tetra-chloride (CCl<sub>4</sub>) and tri-n-octyl-aluminum (TNOA) were the best candidates for this catalyst system, demonstrating high selectivity of 1-hexene formation, higher catalytic activity and lower polymer content. Based on the RSM results, the best trimerization condition for ethylene at 25 bar and 91.2°C was obtained at the catalytic system [Cr(2-EH)<sub>3</sub>/2,5-DMP/CCl<sub>4</sub>/TNOA] molar ratio of 1:6:10.8:201.5, which showed the activity of 105328 (g 1-C<sub>6</sub>/(g Cr.h)), 99.21% selectivity for 1-hexene and no polymer was formed. The predicted process parameters were also verified by actual experiments at the optimized conditions. **Polyolefins J (2024) 11: 219-233**

**Keywords:** Ethylene trimerization; 1-hexene; co-catalyst; halide; response surface methodology.

## INTRODUCTION

Olefins, particularly  $\alpha$ -olefins, are compounds of great significance in industries due to their versatility in synthesis and their utility in materials production [1]. Linear  $\alpha$ -olefins (LAOs) are highly versatile chemical building blocks, commonly used as precursors for detergents, synthetic lubricants, plasticizers alcohols [2] and as co-monomers in the manufacture of linear low-density polyethylene (LLDPE) [3-5]. Additionally,  $\alpha$ -olefins such as 1-butene, 1-hexene, 1-octene, and 1-decene are widely employed as co-monomers in

polymerization reactions [6, 7]. The growing demand for LLDPE has sparked renewed interest in selective ethylene oligomerizations, as 1-butene, 1-hexene, and 1-octene enhance polymer properties, including melt index, density, and molecular weight distribution [8]. The mechanical properties of LLDPE produced with 1-hexene and 1-octene comonomers are much better than the polymer obtained with 1-butene comonomer [9]. Also, due to the high price of 1-octene, it is rarely used in the production of this type of polymer. Conventional

\*Corresponding Author - E-mail: a-fazlali@araku.ac.ir

approaches to produce 1-hexene involved non-selective oligomerization of ethylene using methods such as thermal cracking of paraffinic wax and steam cracking of lighter alkanes. These methods required complex separation processes due to the production of  $\alpha$ -olefins with Schulz-Flory or Poisson distributions [10]. However, in recent years, selective ethylene trimerization has emerged as a successful commercial method to meet the growing demand for 1-hexene [11]. Selective ethylene trimerization offers significant advantages over traditional techniques, including high atomic efficiency and a simplified reaction procedure [12]. The first instance of ethylene trimerization was reported in 1967, and subsequent research efforts led to the development of a selective catalyst system for producing 1-hexene. Chevron-Phillips Company successfully commercialized this catalyst system in 1990 [13]. In 1989, Briggs discovered that the selectivity of 1-hexene could be enhanced by incorporating 1,2-dimethoxyethane (DME) into the same Cr-based catalyst system [14]. Building upon this finding, numerous studies focused on improving product selectivity and catalytic activity of ethylene trimerization. These investigations resulted in the development of new homogeneous Cr-based catalysts with various ligands [15-17].

The combined catalytic system of Cr(III) compound/pyrrole/alkylaluminum has garnered significant attention as a noteworthy homogeneous catalyst for ethylene trimerization among reported selective ethylene trimerization catalytic systems [12]. To enhance the performance of this system, various Lewis bases such as amines, phosphides, ethers, and halides have been incorporated, aiming to improve their catalytic capabilities [18]. Particularly, compounds containing chlorides as Lewis base additives have shown promising results in effectively modifying the catalytic activity and selectivity of this homogeneous catalyst system for ethylene trimerization [19].

This study investigates the ethylene trimerization catalyst system [chromium(III) tris(2-ethylhexanoate)/2,5-dimethyl-pyrrole/co-catalyst/halide]. Effects of compositions of the catalytic components (co-catalyst, halide), catalyst dosage and temperature as crucial operating parameters on catalyst activity, 1-hexene selectivity and polymer formation as a by-product were evaluated using combined response surface methodology (RSM) and central composite design (CCD) techniques.

## EXPERIMENTAL

### Raw materials and instruments

The raw materials used in the experiments included chromium nitrate nonahydrate, 2-ethylhexanoic acid, sodium hydroxide, 2,5-dimethyl-pyrrole(2,5-DMP), hexa-chloro-ethane ( $C_2Cl_6$ ), carbon-tetra-chloride ( $CCl_4$ ), chloroform ( $CHCl_3$ ), tri-ethyl-aluminum (TEA), tri-methyl-aluminum (TMA), tri-n-octyl-aluminum (TNOA), di-ethyl-aluminum chloride (DEAC), and ethyl-aluminum-sesqui-chloride (EASC). These materials were obtained from Merck and Aldrich and were used as received. Additionally, n-heptane and n-hexane were purchased from Merck and refluxed with Na slices and freshly distilled before usage. Nitrogen for purging (99.99%) was purchased from Roham Gas Co., and ethylene (99.99%, polymer grade) was supplied from Shazand Petrochemical Co. The experimental setup for the catalytic batch experiments involved a 1000 mL double-walled stainless steel Buchi pressure reactor equipped with a speed-controlled mechanical stirrer, thermocouple, gas inlet and outlet port, and external circulation bath. Gas chromatography analyses, with flame ionization detection (GC/FID), were conducted using a Varian 3800 chromatograph with a CP Sil 8 capillary column (50 m in length  $\times$  0.32 mm internal diameter, 1.2mm film thickness). The synthesized Cr(III) catalyst was subjected to analytical techniques to gain insights into its properties. The Fourier transform-infrared (FTIR) spectrum was obtained using a Nicolet 550 spectrometer, which provided information about the functional groups present and their chemical bonding. To further investigate the structure of the catalyst, nuclear magnetic resonance (NMR) spectroscopy was employed using a Bruker 250 MHz instrument. By analyzing the NMR spectrum, valuable information about the catalyst's structural features could be obtained.

### Synthesis of chromium(III) tris(2-ethylhexanoate)

The synthesis of chromium(III) tris(2-ethylhexanoate) ( $Cr(2-EH)_3$ ) was carried out by the method outlined in Steele's patent [20]. First, a solution was prepared by dissolving 120g (3.0 moles) of sodium hydroxide in 500 ml of distilled water. Next, with continuous stirring, 491g (3.3 moles) of 2-ethylhexanoic acid was added to the sodium hydroxide solution. The reaction between these components yielded sodium 2-ethylhexanoate. Simultaneously, in a separate container, 200g (0.5 mole) of chromium nitrate

nonahydrate was dissolved in 500 ml of distilled water, forming a chromium nitrate solution. The chromium nitrate solution was then slowly added to the sodium 2-ethylhexanoate solution while stirring thoroughly. When the addition was complete, 500 ml of hexane was added and stirring was continued for 10 minutes. After separating the layers, the hexane layer containing the aquated  $\text{Cr}(2\text{-EH})_3$  was washed with dilute NaOH solution, water, dilute  $\text{Na}_2\text{CO}_3$  solution, and distilled water sequentially to remove impurities. The hexane solution was then dried over anhydrous  $\text{MgSO}_4$ . Following this, the majority of the hexane was removed under vacuum to yield  $\text{Cr}(2\text{-EH})_3$ . The resulting chromium salt was found to be inactive due to the occupation of its six coordination sites by water and carboxylate anions. To activate the catalyst, it was placed in 140-200°C for 6 hours under acidic condition so that the coordination sites were free of water.

### Ethylene trimerization and product analysis

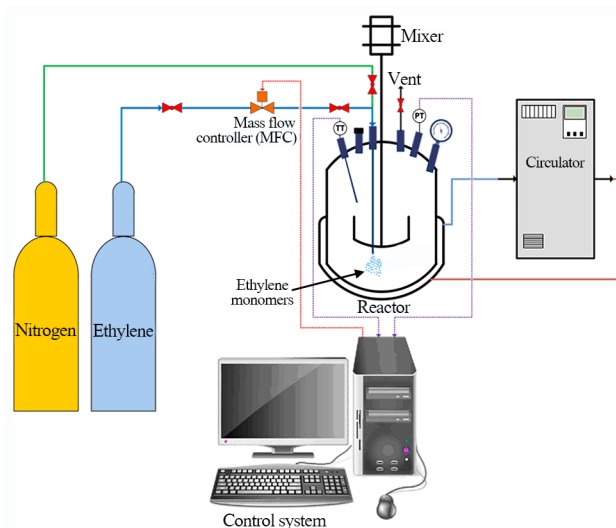
As illustrated in Figure 1, the experiments were carried out in a 1000 mL pressure reactor equipped with a stirrer, thermocouple, gas inlet (fitted with a regulator and Brooks SLA5860S ethylene MFC (mass flow controller)), gas outlet, and a circulator for providing cooling and heating. To eliminate any residual water and oxygen, the autoclave was heated to 90°C and purged several times with high-purity  $\text{N}_2$  prior to the experiments.

The experiments were conducted based on the methods reported by Mr. Araki and his colleagues, who examined similar reaction conditions in their study [21]. The reactor was then allowed to cool down to the lower temperatures,  $5.19 \times 10^{-5}$  mol of  $\text{Cr}(2\text{-EH})_3$  and 2,5-DMP (DMP/Cr 6 (mol/mol)) added to 50 mL of n-heptane. The sample was stirred for 30 minutes under a nitrogen atmosphere. The n-heptane (350 mL) together with the calculated quantities of co-catalyst (Al/Cr 200(mol/mol)) and promoter (promoter/Cr 10(mol/mol)) were immediately transferred to the evacuated reactor under ethylene atmosphere. Then the reactor was heated to the desired temperature (90°C) and the stirring speed was initially set at 900 rpm. In the next step, the  $\text{Cr}(2\text{-EH})_3$  and 2,5-DMP mixture were transferred to the reactor and finally, the reactor was pressurized with ethylene to start the reaction. The volume of ethylene added to the reactor was measured using a Brooks mass-flow controller (MFC). All reactions were performed at a constant reaction temperature. As the reaction progressed, a drop in the ethylene pressure was observed. After 30

min, the reaction was terminated by switching off the stirrer, allowing the reactor to cool down to 10°C and slowly vented and opened. The reaction solution was discharged through the bottom valve and a sample of the liquid reaction mixture was quenched by adding methanol/HCl (10 wt.%) to remove the catalyst and co-catalyst, and finally filtered. The organic layer was taken for GC/FID analysis. A solid by-product was collected by filtration, washed with hexane and dried in an oven at 60 °C and ultimately weighted. The activity and product selectivity were determined from the mass balance for the ethylene-uptake data and GC analyses.

### Design of Experiments (DOE) establishment

The study investigated the influence of various components of a chromium catalyst system on the efficiency of ethylene trimerization using a response surface methodology (RSM) approach. A central composite design (CCD) was established using Design Expert software (v.13, Stat-Ease) to examine the impact of mole ratios of Al/Cr,  $\text{CCl}_4/\text{Cr}$ , catalyst dosage, and reaction temperature as the input parameters. Each variable was assigned three levels, and 27 randomized experiments were suggested, including 3 replicates for mid-points. The performance of the catalyst in the ethylene trimerization process was assessed in terms of catalyst activity, 1-Hexene selectivity, and polymer content in each experiment. A quadratic response-surface model was employed to characterize the relationship between the target factors and the ratios of catalyst components [21].



**Figure 1.** Schematic of the experimental apparatus with a 1000 mL semi-batch-type autoclave.

$$R = \beta_0 + \sum_{i=1}^n \beta_i x_i + \sum_{i=1}^n \beta_{ii} x_i^2 + \sum_{i=1}^n \sum_{j=i+1}^n \beta_{ij} x_i x_j + \varepsilon \quad (1)$$

The model included response factors (catalyst activity, 1-hexene selectivity, and polymer content) represented by  $R$ , independent variables  $x_i$  and  $x_j$ , regression coefficients  $\beta_0$ ,  $\beta_i$ ,  $\beta_{ii}$ , and  $\beta_{ij}$ , and estimation error  $\varepsilon$ . The proposed models' predictive capability for the experimental data was assessed by considering several criteria, including p-values, lack-of-fit significance, normal distribution of residuals, and regression coefficients such as  $R^2$ , adjusted- $R^2$ , and predicted- $R^2$ . These indicators were used to evaluate the adequacy of the models and their ability to accurately represent the experimental data.

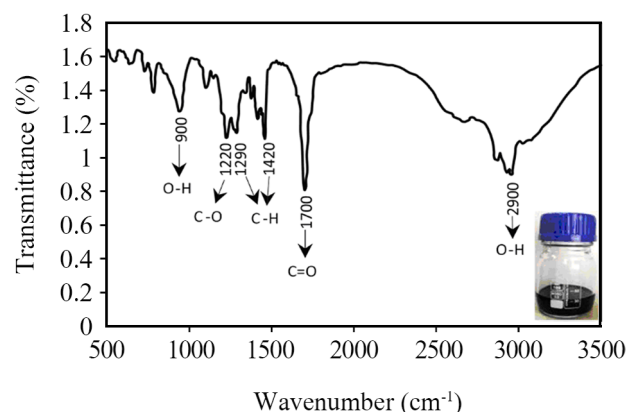
## RESULTS AND DISCUSSION

### FT-IR spectrum of the synthesized $\text{Cr}(\text{2-EH})_3$ catalyst

The FT-IR spectrum of synthesized  $\text{Cr}(\text{2-EH})_3$  is given in Figure 2, the wide band in the  $1290 \text{ cm}^{-1}$  region is related to aliphatic C-H stretching. The broad absorption peak at  $1700 \text{ cm}^{-1}$  indicates the presence of carbonyl group C=O. The absorption peak in the region of  $1420 \text{ cm}^{-1}$  is related to the bending C-H bond. The broad band in the region of  $2900 \text{ cm}^{-1}$  corresponds to the OH stretching. The average absorption peak in the  $1220 \text{ cm}^{-1}$  region is related to the simple carbon-oxygen C-O bond. The absorption opeak at  $900 \text{ cm}^{-1}$  is related to the out-of-plane bending vibration of OH.

### $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectroscopy

The synthesized  $\text{Cr}(\text{2-EH})_3$  analyzed by  $^1\text{H}$ NMR and  $^{13}\text{C}$ NMR spectroscopy is shown in Figure 3. Chemical shifts were acquired in ppm, referenced to the peaks



**Figure 2.** FTIR spectrum of synthesized  $\text{Cr}(\text{2-EH})_3$ .

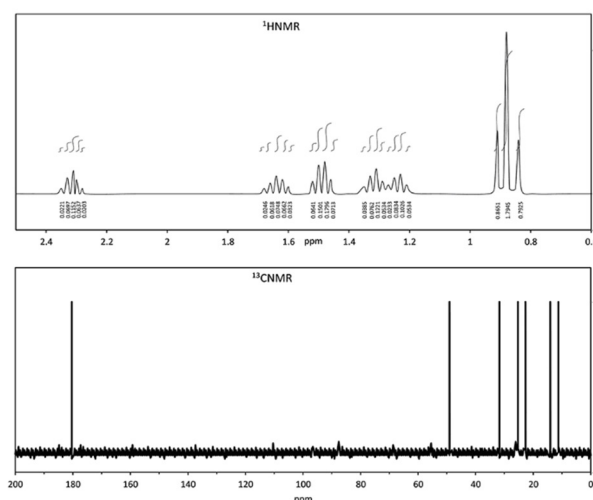
of:  $^1\text{H}$ -NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  0.91(3H, t,  $\text{CH}_3$ ), 1.25-1.67(2H, m,  $\text{CH}_2$ ), 2.28(H, m, CH).  $^{13}\text{C}$ -NMR (250MHz,  $\text{CDCl}_3$ ):  $\delta$  11.787( $\text{C}_6$ ), 13.93( $\text{C}_5$ ), 15.909( $\text{C}_4$ ), 22.643 ( $\text{C}_3$ ), 25.19 ( $\text{C}_2$ ), 29.52( $\text{CH}_3$ ), 31.48( $\text{CH}_2$ ), 183( $\text{C}=\text{O}$ ).

### Investigating the effect of the molar ratio of catalyst components on ethylene trimerization

The study conducted on the ethylene trimerization catalytic system has shown that the ratio of compounds including co-catalysts and halides in the four-component chromium catalyst system is effective on the production efficiency of 1-hexene. Therefore, in the trimerization of ethylene based on the catalytic system [ $\text{Cr}(\text{2-EH})_3/2,5\text{-DMP}/\text{C}_2\text{Cl}_6/\text{TEA}$ ], the molar ratio of the co-catalyst to the catalyst and the promoter to the catalyst on the activity and selectivity of 1-hexene and the amount of polymer was investigated.

The trimerization reaction was carried out at  $90^\circ\text{C}$  and 25 bar ethylene pressure for 30 minutes, using TEA,  $\text{C}_2\text{Cl}_6$  promoter and 400 ml normal heptane as solvent. Figures 4 (a), (b) and (c) show the effects of the molar ratio of TEA to the catalyst ( $\text{Al}/\text{Cr}$ ) and Figures 4 (d), (e) and (f) show the effect of the molar ratio of  $\text{C}_2\text{Cl}_6$  to the catalyst on the activity, selectivity, and amount of polymer, respectively.

Figures 4(a) and (b) show that by increasing the amount of co-catalyst, the activity and selectivity of 1-hexene increase first and then decrease after  $\text{Al}/\text{Cr}$  becomes 200. The highest values of activity and selectivity are related to the  $\text{Al}/\text{Cr}=200$  ratio, which are 43373.82 (g 1- $\text{C}_6/\text{g Cr}\cdot\text{h}$ ) and 92.69%, respectively. As it is clear in Figure 4(c), with the increase of  $\text{Al}/\text{Cr}$



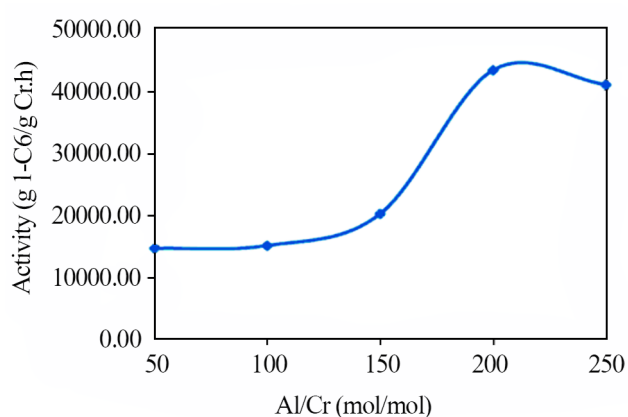
**Figure 3.**  $^1\text{H}$ NMR and  $^{13}\text{C}$ NMR spectroscopies of synthesized  $\text{Cr}(\text{2-EH})_3$ .

ratio, the system faces a decrease in polymer, but after the Al/Cr=150 ratio, the amount of polymer increases.

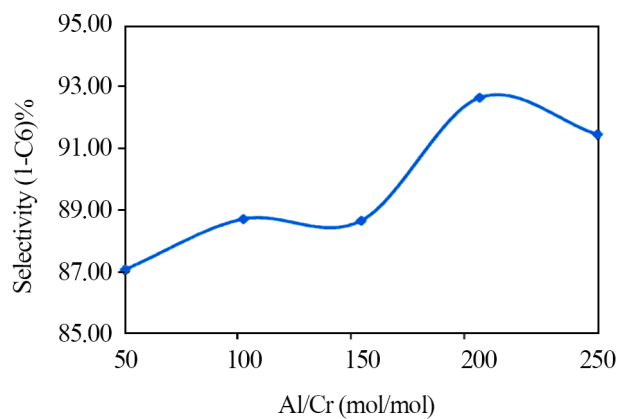
According to the trend shown in Figure 4, the activity and selectivity of 1-hexene production increase up to the range of Al/Cr equal to 200 with the increase in the concentration of the co-catalyst. As a result, increasing Al/Cr ratio by more than 200 decreases the activity and selectivity of 1-hexene production. The decrease in efficiency in higher ratios is related to the

absorption of catalyst aid on the catalytic center in competition with ethylene monomer [22].

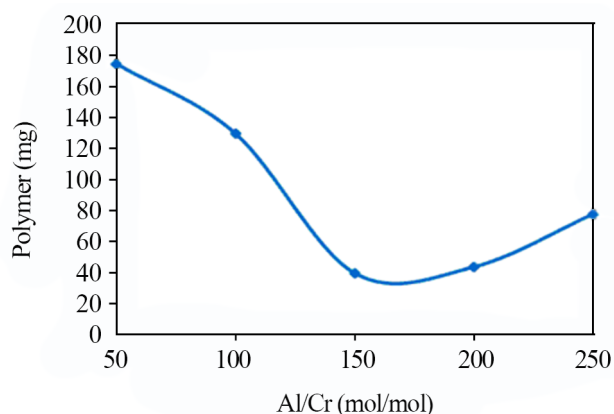
According to Figures 4(d), (e) and (f), catalyst activity and 1-C<sub>6</sub> selectivity increase and polymer content decreases with the increase of the ratio of C<sub>2</sub>Cl<sub>6</sub> to the catalyst, respectively, until the molar ratio of C<sub>2</sub>Cl<sub>6</sub>/Cr is about 10, which decreases with the further increase of the ratio of C<sub>2</sub>Cl<sub>6</sub> to the Cr, and the activity and selectivity both decrease and together



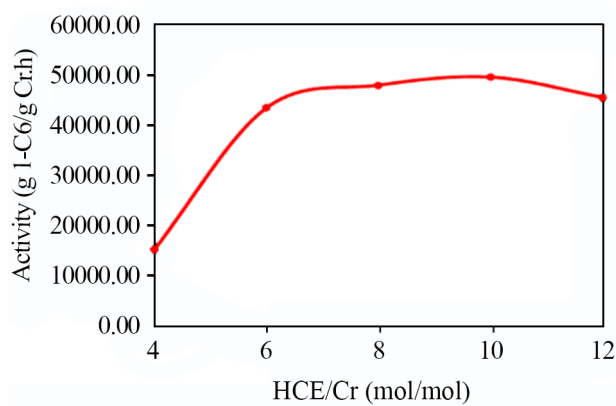
(a)



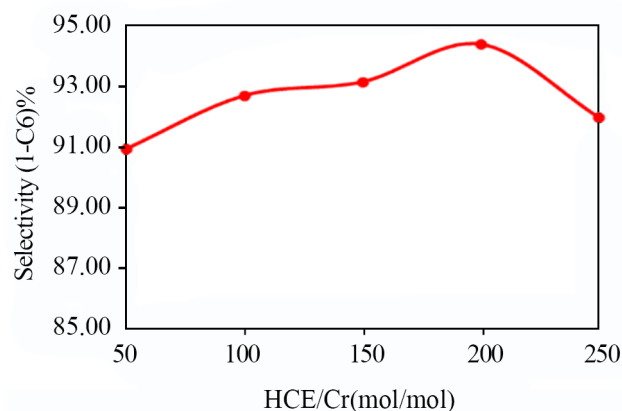
(b)



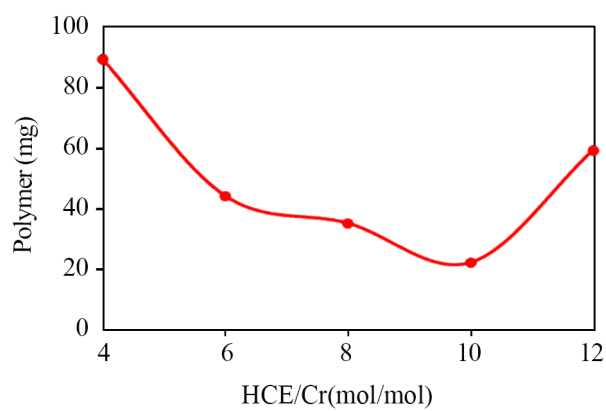
(c)



(d)

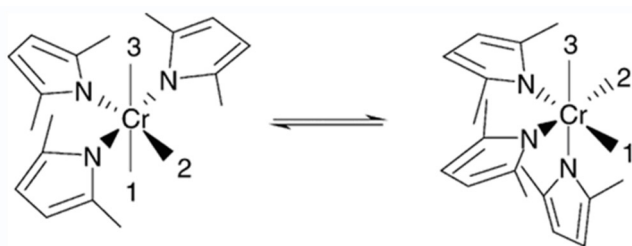


(e)



(f)

**Figure 4.** Effects of the molar ratio of TEA to the catalyst (Al/Cr) (a, b and c) and the effect of the molar ratio of C<sub>2</sub>Cl<sub>6</sub> to the catalyst (d, e and f) on the activity, selectivity, and amount of polymer, respectively.



**Figure 5.** Structures in balance: (A) Meridional and (B) Facial [23]

with 1-hexene of the compounds more polymer is also obtained.

Luo and colleagues [23] proposed a chromium catalytic system model, suggesting an eight-site or six-coordination configuration. In this configuration, the ligand takes up three sites, while the other three are designated for ethylene trimerization. The catalyst system can exist in two spatial modes as depicted in Figure 5: Meridional(A) and Facial(B), with both modes being in equilibrium. Luo suggests that the Facial structure (B) is more spatially conducive for ethylene trimerization, while the Meridional state (A) leads to polymerization and formation of heavy compounds.

In terms of thermodynamics, structure (A) has a lower energy level, the reason being the less spatial hindrance of 2,5-dimethyl pyrrole ligands in this spatial state, therefore, in a normal state and without using chlorine compounds, structure (A) had a higher concentration, leading to the creation of heavy and polymeric compounds. However, by using chlorinated compounds, the stability of the structure (B) increases due to the coordination of the chlorine atom with the chromium atom [24]. By increasing the molar ratio of  $C_2Cl_6/Cr$ , the selectivity of the catalyst increases from 90.93% to 94.39%, as well as the activity of

the catalyst increases from 15159.96 to 49515.57 ( $g\ 1-C_6/(g\ Cr.h)$ ). The amount of  $C_2Cl_6$  is sufficient for the stability of the facial form, but the further increase of  $C_2Cl_6$  prevents the coordination of ethylene to the chromium atom and causes a decrease in activity. When the molar ratio of  $C_2Cl_6/Cr$  is equal to 12, the activity of the catalyst decreases to 45464.99 ( $g\ 1-C_6/(g\ Cr.h)$ ).

### Effects of different halides and co-catalysts

#### *Effects of different halide compounds on the ethylene trimerization*

The effect of halides type on the catalytic system of  $Cr(2-EH)_3/2,5-DMP/co-catalyst/halide$ , for three types of halide including  $C_2Cl_6$ ,  $CCl_4$  and  $CHCl_3$ , were considered in the selectivity of 1-hexene, catalyst activity and polymer amount. The reaction conditions included trimerization at 90 °C under ethylene pressure of 25 bar for 30 minutes using 400 ml of normal heptane as solvent. Catalyst preparation was done under a nitrogen atmosphere ( $Cr(2EH)_3/2,5-DMP/TEA=1:6:200$ ).

According to the results presented in Table 1, it can be concluded that all three halides can form 1-hexene, although the promoter capacity of different halides is different. According to the investigation of the ratio of halide to catalyst in the range of 8 to 12 (mol/mol) for all three promoters, 1-hexene selectivity, catalyst activity and polymer content for  $CCl_4$  in  $CCl_4/Cr=10$  due to the ability of the proper coordination with the chromium center is better than those for  $C_2Cl_6$  and  $CHCl_3$ .

#### *Effects of different co-catalyst compounds on the ethylene trimerization*

The co-catalysts play a crucial role in activating

**Table 1.** Effects of different halide compounds on the ethylene trimerization.

Halide		Composition					Activity ( $g\ 1-C_6/g\ Cr.h$ )	Selectivity( $1-C_6$ ) %	Polymer (mg)
		$C_4$	$C_6$	$C_8$	$C_{10}$	$C_{10+}$			
$C_2Cl_6$	$C_2Cl_6/Cr=8$	3.356	90.442	3.748	0.864	1.590	47900.05	93.14	35
	$C_2Cl_6/Cr=10$	3.255	91.928	3.270	0.918	0.628	49515.57	94.39	22
	$C_2Cl_6/Cr=12$	3.7425	93.016	2.767	0.001	0.472	45464.99	91.97	75
$CCl_4$	$CCl_4/Cr=8$	3.657	94.472	1.066	0.002	0.803	45465.12	94.17	16
	$CCl_4/Cr=10$	1.741	94.981	1.586	0.872	0.818	57494.88	96.52	10
	$CCl_4/Cr=12$	3.064	94.503	0.701	0.002	1.728	53718.17	95.74	18
$CHCl_3$	$CHCl_3/Cr=8$	3.98	94.917	0.886	0.003	0.213	48635.91	91.90	50
	$CHCl_3/Cr=10$	2.581	95.386	1.005	0.901	0.126	43876.89	90.33	64
	$CHCl_3/Cr=12$	2.104	95.953	0.825	0.675	0.442	46278.27	92.73	58

The reaction was carried out at 90°C under 25 bar ethylene pressure for 30 minutes, RPM900 stirrer, molar ratio DMP/CAT=6, TEA/CAT=200 and catalyst dosage= $5.19 \times 10^{-5}$ .

the reaction and significantly impact the catalytic performance of ethylene selective oligomerization catalyst systems. In this study, five different organometallic co-catalysts (TEA, TMA, TNOA, DEAC, and EASC) were evaluated in accordance with Table 2 to identify the most suitable co-catalyst with optimal performance. The catalytic systems employing DEAC and EASC as co-catalysts exhibited no activity for ethylene trimerization. When TEA and TMA were used as cocatalysts, the production of 1-butene and polymer increased. This may be due to a wider range of unsaturated Cr(II) species, where not all Cr centers are accessible to the ligand, preventing the formation of a pure trimerization catalyst. The remaining uncoordinated sites likely function either as spectator species or polymerization-active sites.

Based on the experimental results, TNOA was identified as the ideal co-catalyst for this catalyst system due to its strong reducibility and favorable steric effects. Additionally, the optimal halide compound for this catalytic system was determined to be  $\text{CCl}_4$ . Subsequent investigations were conducted using the catalytic system composed of TNOA,  $\text{CCl}_4$ , 2,5-DMP, and a chromium source.

$\text{CCl}_4$  leads to the production of the TNOA monomer. Monomeric TNOA is thought to be beneficial for the formation of active chromium species due to its enhanced Lewis acid properties. This results in a tendency toward forming a dimer with two ethylene bridge bonds and two specifically arranged aluminum Lewis acid sites. TNOA's role in ethylene trimerization is primarily associated with its Lewis acidity, which facilitates the removal of carboxylate ligands from Cr(III), creating vacant coordination sites for reactants. Furthermore, TNOA extracts a proton ( $\text{H}^+$ ) from the N-H group of the pyrrole compound, leading to the

formation of a pyrrolide ligand.

Table 2 demonstrates that the activity of the catalytic system increased with an increasing TNOA/Cr molar ratio. The highest 1-hexene selectivity was observed at a TNOA/Cr molar ratio of 200. When TNOA/Cr=250 was used instead of 200, the activity increased and 1-hexene selectivity decreased from 68717.71 (g  $1\text{-C}_6/\text{g Cr.h}$ ) to 72073.53 (g  $1\text{-C}_6/\text{g Cr.h}$ ) and 97.81% to 96.85%, respectively.

The role of the cocatalyst in a catalytic system is closely tied to the catalytic activity and product selectivity. The optimal molar ratio of cocatalyst to Cr(III) is required due to its role in generating the pyrrolide anion from pyrrole and activating the stable 6-coordinated Cr(III) complex. Additionally, the cocatalyst, acting as a Lewis acid, aids in removing 2-ethylhexanoate ligands from the Cr(III) complex, further enhancing its activation.

### RSM analysis

In this study, the desired test conditions for RSM were obtained based on the four main variables of Al/Cr molar ratio,  $\text{CCl}_4/\text{Cr}$  molar ratio, catalyst concentration and reaction temperature using the CCD method at their lower and upper levels, the details of which are shown in Table 3.

Using these values and performing three stages of reproducibility of experimental tests, the activity of the catalyst, 1-hexene selectivity and polymer content were calculated, and the results are shown in Table 4.

To develop the best-fitting model, the resulting data are adjusted by selecting the general equation. Then, the probability value of P is calculated and parameters with a value of P greater than 0.05 are removed. According to Table 2 and the values of P in Table 5, all four variables are effective on the reactivity of the

**Table 2.** Effects of different co-catalyst compounds on the ethylene trimerization.

Co-Catalyst		Composition					Activity (g $1\text{-C}_6/\text{g Cr.h}$ )	Selectivity( $1\text{-C}_6$ )%	Polymer(mg)
		$\text{C}_4$	$\text{C}_6$	$\text{C}_8$	$\text{C}_{10}$	$\text{C}_{10+}$			
TEA	Al/Cr=150	3.657	94.472	1.066	0.002	0.804	45465.00	94.17	16
	Al/Cr=200	1.742	94.981	1.587	0.872	0.819	57494.88	96.53	10
	Al/Cr=250	3.065	94.504	0.701	0.002	1.728	53718.17	95.75	18
TMA	Al/Cr=150	5.475	92.168	2.283	0.070	0.004	19068.05	87.52	105
	Al/Cr=200	4.216	93.727	2.007	0.044	0.006	26455.83	89.12	60
	Al/Cr=250	3.752	94.549	1.630	0.062	0.007	31692.42	90.43	86
TNOA	Al/Cr=150	2.201	95.324	2.039	0.093	0.343	47224.75	96.78	21
	Al/Cr=200	2.018	96.055	1.723	0.071	0.133	68717.71	97.81	5
	Al/Cr=250	1.720	96.161	1.819	0.089	0.211	72073.53	96.85	34

The reaction was carried out at 90°C under 25 bar ethylene pressure for 30 minutes, RPM900 stirrer, molar ratio DMP/CAT=6,  $\text{CCl}_4/\text{CAT}=10$  and catalyst dosage= $5.19 \times 10^{-5}$ .

**Table 3.** Coded and experimental values of independent variables.

Factors	level		
	+1	0	-1
Al/Cr (mol/mol)	150	200	250
CCl <sub>4</sub> /Cr (mol/mol)	8	10	12
Catalyst dosage (mmol)	2.59×10 <sup>-5</sup>	5.19×10 <sup>-5</sup>	7.78×10 <sup>-5</sup>
T(°C)	80	90	100

catalyst. The prediction results of the model and the real data are presented in Table 5.

Table 5 displays the ANOVA (Analysis of Variance) table for the response surface quadratic model used to analyze catalyst activity. The P-value listed in Table 5 for the model is less than 0.05, indicating that the model is statistically significant. This is desirable as it suggests that the terms included in the model have a significant impact on the response variable.

The main effects of Al/Cr (A), halide/Cr (B), catalyst dosage (C) and temperature (D) are significant model terms. The two-level interaction terms can be said to be not significant. However, the main effect of all variables and their second-order effect are the significant model terms.

The predicted R<sup>2</sup> of 0.9230 is in reasonable

agreement with the adjusted R<sup>2</sup> of 0.9645; i.e. the difference is less than 0.2. The adjusted R<sup>2</sup> value is instrumental when comparing models with different numbers of terms. The Adeq Precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. Your ratio of 29.365 indicates an adequate signal. This model can be used to navigate the design space. The catalyst activity was related to the coded values via the following equation:

$$\begin{aligned} \text{Activity} = & 78645.70 + (3359.33 \times A) + (3859 \times B) - (6175.67 \times C) + \\ & (2182.33 \times D) + (328.87 \times AB) + (64.87 \times AC) + (182.62 \times AD) - \\ & (154.88 \times BC) + (177.37 \times BD) - (833.63 \times CD) - (13283.56 \times A^2) - \\ & (5168.56 \times B^2) + (16131.44 \times C^2) - (21968.56 \times D^2) \end{aligned} \quad (2)$$

The same procedure is applied to response selectivity and the resulting ANOVA table for the quadratic model is shown in Table 6. For selectivity, the main effects of Al/Cr (A), halide/Cr (B), catalyst dosage (C), temperature (D) and second-order effect there are the significant model terms.

The reasonably close agreement between the predicted R<sup>2</sup> value of 0.8609 and the adjusted R<sup>2</sup> value of 0.9418, with a difference of less than 0.2,

**Table 4.** 1-Hexene production from the experimental design for the Response Surface Quadratic Model (RSM).

Run	A-Al/Cr (mol/mol)	B-CCl <sub>4</sub> /Cr (mol/mol)	C-Catalyst dosage(mol)×10 <sup>-5</sup>	D-T(°C)	Activity (g 1-C <sub>6</sub> / g Cr.h)	Selectivity(%)	Polymer(mg)
1	200	8	5.185	90	65700	92.01	24
2	250	8	7.78	100	50700	92.92	54
3	150	12	2.59	100	64290	89.54	42
4	150	8	2.59	80	52500	83.57	60
5	200	10	5.185	80	53400	91.03	40
6	250	12	2.59	80	63000	88.51	64
7	200	10	5.185	90	80700	96.38	15
8	200	12	5.185	90	79500	96.21	14
9	250	12	2.59	100	71700	92.72	56
10	200	10	2.59	90	103500	99.34	0
11	200	10	5.185	90	78000	95.31	16
12	150	12	2.59	80	56400	86.22	50
13	250	8	7.78	80	46038	91.04	58
14	150	10	5.185	90	60900	91.64	30
15	200	10	5.185	100	58200	93.33	34
16	150	8	7.78	100	44340	88.21	44
17	250	8	2.59	100	62220	90.52	74
18	150	12	7.78	80	47250	88.11	50
19	250	12	7.78	100	55920	93.91	46
20	200	10	5.185	90	82500	95.76	19
21	200	10	7.78	90	84300	99.24	3
22	150	8	7.78	80	40500	87.21	46
23	150	12	7.78	100	49200	91.23	36
24	250	10	5.185	90	68070	93.18	36
25	150	8	2.59	100	54600	86.31	52
26	250	12	7.78	80	55800	93.02	60
27	250	8	2.59	80	57000	86.16	86



**Table 5.** The resulting ANOVA table (partial sum of squares) for the quadratic model for activity.

Source	Sum of Square	df	Mean Square	F-value	P-value	
<b>Model</b>	5.510E+09	14	3.935E+08	51.41	< 0.0001	significant
<b>A-Al/Cr</b>	2.031E+08	1	2.031E+08	26.53	0.0002	-
<b>B-CCl<sub>4</sub>/Cr</b>	2.681E+08	1	2.681E+08	35.01	< 0.0001	-
<b>C-Catalyst dosage</b>	6.865E+08	1	6.865E+08	89.67	< 0.0001	-
<b>D-T</b>	8.573E+07	1	8.573E+07	11.20	0.0058	-
<b>AB</b>	1.731E+06	1	1.731E+06	0.2260	0.6430	-
<b>AC</b>	6.734 E+04	1	67340.25	0.0088	0.9268	-
<b>AD</b>	5.336E+05	1	5.336E+05	0.0697	0.7962	-
<b>BC</b>	3.838E+05	1	3.838E+05	0.0501	0.8266	-
<b>BD</b>	5.034E+05	1	5.034E+05	0.0658	0.8020	-
<b>CD</b>	1.112E+07	1	1.112E+07	1.45	0.2514	-
<b>A<sup>2</sup></b>	4.537E+08	1	4.537E+08	59.27	< 0.0001	-
<b>B<sup>2</sup></b>	6.869E+07	1	6.869E+07	8.97	0.0112	-
<b>C<sup>2</sup></b>	6.691E+08	1	6.691E+08	87.40	< 0.0001	-
<b>D<sup>2</sup></b>	1.241E+09	1	1.241E+09	162.10	< 0.0001	-
<b>Residual</b>	9.187E+07	12	7.656E+06	-	-	-
<b>Lack of Fit</b>	8.161E+07	10	8.161E+06	1.59	0.4468	not significant
<b>Pure Error</b>	1.026E+07	2	5.130E+06	-	-	-
<b>Cor Total</b>	5.601E+09	26	-	-	-	-

suggests that the model provides a reliable prediction of the response variable. The Adeq Precision, which measures the signal-to-noise ratio, is also important in evaluating the model's quality. A ratio greater than 4 is considered desirable. In this case, the calculated ratio of 23.479 indicates a strong signal relative to the noise, further supporting the model's usefulness. Overall, these findings indicate that the developed model can effectively navigate the design space and be utilized for predicting and optimizing the response variable. The following equations are the final empirical models in terms of coded factors:

$$\begin{aligned} \text{Selectivity} = & 95.92 + (1.69 \times A) + (1.21 \times B) + (1.24 \times C) + (1.33 \times D) - \\ & (0.1438 \times AB) + (0.2312 \times AC) + (0.0687 \times AD) - \\ & (0.2313 \times BC) + (0.1062 \times BD) - (0.4688 \times CD) - (3.75 \times A^2) - \\ & (2.05 \times B^2) + (3.20 \times C^2) - (4.05 \times D^2) \end{aligned} \quad (3)$$

Table 7 presents the ANOVA results for the polymer content models, which employ a statistical technique to assess the significance of the proposed models and their associated parameters, as indicated by their respective p-values. A p-value of less than 0.05 is typically considered the criterion for determining the significance of a model or its individual terms. In this case, it is observed that the A, B, C, D, and second-

**Table 6.** The resulting ANOVA table (partial sum of squares) for the quadratic model for selectivity.

Source	Sum of Square	df	Mean Square	F-value	P-value	
<b>Model</b>	410.86	14	29.35	31.04	< 0.0001	significant
<b>A-Al/Cr</b>	51.68	1	51.68	54.67	< 0.0001	-
<b>B-CCl<sub>4</sub>/Cr</b>	26.16	1	26.16	27.67	0.0002	-
<b>C-Catalyst dosage</b>	27.88	1	27.88	29.49	0.0002	-
<b>D-T</b>	31.73	1	31.73	33.57	< 0.0001	-
<b>AB</b>	0.3306	1	0.3306	0.3498	0.5652	-
<b>AC</b>	0.8556	1	0.8556	0.9051	0.3602	-
<b>AD</b>	0.0756	1	0.0756	0.0800	0.7821	-
<b>BC</b>	0.8556	1	0.8556	0.9051	0.3602	-
<b>BD</b>	0.1806	1	0.1806	0.1911	0.6698	-
<b>CD</b>	3.52	1	3.52	3.72	0.0778	-
<b>A<sup>2</sup></b>	36.23	1	36.23	38.33	< 0.0001	-
<b>B<sup>2</sup></b>	10.85	1	10.85	11.47	0.0054	-
<b>C<sup>2</sup></b>	26.27	1	26.27	27.79	0.0002	-
<b>D<sup>2</sup></b>	42.26	1	42.26	44.70	< 0.0001	-
<b>Residual</b>	11.34	12	0.9453	-	-	-
<b>Lack of Fit</b>	10.50	10	1.05	2.48	0.3215	not significant
<b>Pure Error</b>	0.8467	2	0.4233	-	-	-
<b>Cor Total</b>	422.20	26	-	-	-	-

**Table 7.** The resulting ANOVA table (partial sum of squares) for the quadratic model for polymer content.

Source	Sum of Square	df	Mean Square	F-value	P-value	
<b>Model</b>	11275.00	14	805.36	39.07	< 0.0001	significant
<b>A-Al/Cr</b>	854.22	1	854.22	41.44	< 0.0001	-
<b>B-CCl<sub>4</sub>/Cr</b>	355.56	1	355.56	17.25	0.0013	-
<b>C-Catalyst dosage</b>	420.50	1	420.50	20.40	0.0007	-
<b>D-T</b>	320.89	1	320.89	15.57	0.0019	-
<b>AB</b>	30.25	1	30.25	1.47	0.2490	-
<b>AC</b>	72.25	1	72.25	3.51	0.0857	-
<b>AD</b>	2.25	1	2.25	0.1092	0.7468	-
<b>BC</b>	156.25	1	156.25	7.58	0.0175	-
<b>BD</b>	20.25	1	20.25	0.9824	0.3412	-
<b>CD</b>	0.2500	1	0.2500	0.0121	0.9141	-
<b>A<sup>2</sup></b>	1088.86	1	1088.86	52.83	< 0.0001	-
<b>B<sup>2</sup></b>	111.26	1	111.26	5.40	0.0385	-
<b>C<sup>2</sup></b>	306.76	1	306.76	14.88	0.0023	-
<b>D<sup>2</sup></b>	1553.32	1	1553.32	75.36	< 0.0001	-
<b>Residual</b>	247.34	12	20.61	-	-	-
<b>Lack of Fit</b>	236.70	10	23.67	4.45	0.1974	not significant
<b>Pure Error</b>	10.64	2	5.32	-	-	-
<b>Cor Total</b>	11522.35	26	-	-	-	-

order effects are deemed significant model terms, as their p-values are below 0.05. This suggests that the suggested models are capable of accurately estimating the experimental data for polymer content.

The predicted R<sup>2</sup> of 0.8894 is in reasonable agreement with the adjusted R<sup>2</sup> of 0.9535; i.e. the difference is less than 0.2. The Adeq Precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. Your ratio of 24.514 indicates an adequate signal. This model can be used to navigate the design space.

The polymer content coded values via the following equation:

$$\text{Polymer content} = 13.88 + (6.89 \times A) - (4.44 \times B) - (4.83 \times C) - (4.22 \times D) - (1.38 \times AB) - (2.13 \times AC) + (0.3750 \times AD) + (3.13 \times BC) - (1.12 \times BD) + (0.1250 \times CD) + (20.58 \times A^2) + (6.58 \times B^2) - (10.92 \times C^2) + (24.58 \times D^2) \quad (4)$$

Figures 6(a–c) display the normal probability plots of residuals for the regression models described by Equations 2–4, respectively. The residuals for all models exhibit a linear form, indicating a normal distribution. The regression coefficients for R<sup>2</sup>, adjusted-R<sup>2</sup>, and predicted-R<sup>2</sup> for activity, selectivity, and polymer were found to be close to 1, suggesting a strong agreement between the predicted values from the models presented by Equations 2–4 and the experimental data. Additionally, the proximity of the actual data to the predicted values from the empirical models is demonstrated in Figures 6(d–f).

Normal possibility residual plots of catalyst activity, 1-hexene selectivity and polymer content are shown in

Figure 6. Almost > 85% of points exist on the standard line (Figure 6) confirming the fitness of the model.

Figure 7 shows the interactive effect of the Al/Cr, CCl<sub>4</sub>/Cr, catalyst dosage and temperature on the catalyst activity during the trimerization of the ethylene process in 3D plots.

The interactive impact of Al/Cr and CCl<sub>4</sub>/Cr is shown in Figure 7(a). It can be seen that a rise in Al/Cr and CCl<sub>4</sub>/Cr leads to an increase in catalyst activity, but only up to a certain limit. This is because if the Al/Cr is above 200, the active centers of Cr undergo an over-reduction which is not active for the trimerization of ethylene [25].

This highlights that the most possible number of Cr active centers is in Al/Cr=200 mole ratio.

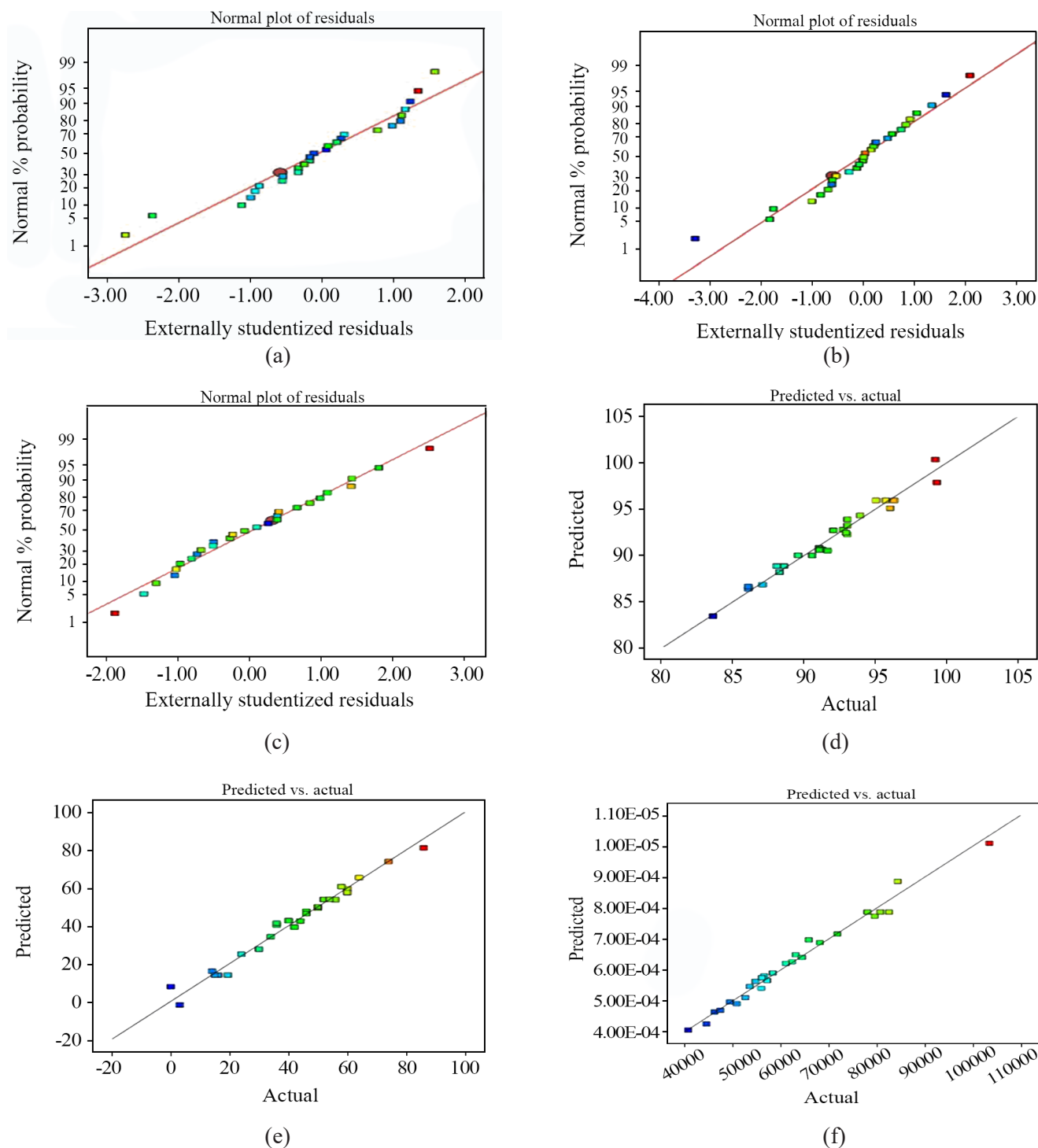
According to Figure 7(a), when CCl<sub>4</sub>/Cr molar ratio was increased from 8 to 10, the catalytic activity was increased from 65700 to 82500 (g 1-C<sub>6</sub>/g Cr.h). Because too much CCl<sub>4</sub> could prevent the coordination of ethylene with the chromium center [26], a further increase in CCl<sub>4</sub>/Cr molar ratio from 10 to 12 causes a decrease of catalytic activity, which is decreased from 82500 to 79500 (g 1-C<sub>6</sub>/g Cr.h). So the effect of CCl<sub>4</sub>/Cr molar ratio in ethylene trimerization is interpreted well.

The mutual effect of temperature and Al/Cr for the activity of the catalyst is shown in Figure 7(b). The activity of the catalyst enhanced with temperature, but only a certain limit. Investigation showed that 90°C is the optimum temperature. The catalyst dosage and Al/Cr impact on the activity are shown in Figure 7(c). The

catalyst dosage also affected the activity of the catalyst. It has been shown that as catalyst dosage has been decreased, the activity of the catalyst also increased. Conclusively,  $2.59 \times 10^{-5}$  mol is the optimum catalyst dosage for the production of 103500 (g 1-C<sub>6</sub>/g Cr.h).

Figures 7 (d, e and f) illustrate the 3D surface plots of the 1-C<sub>6</sub> selectivity against the interaction of Al/Cr, CCl<sub>4</sub>/Cr, catalyst dosage and temperature variables. In

each graph, the two residual variables are kept fixed at their center points. The Al/Cr molar ratio is one of the initial parameters that affect the 1-C<sub>6</sub> selectivity. Figure 7(d, e, and f) depicts the increment of 1-C<sub>6</sub> selectivity by increasing the Al/Cr molar ratio. The maximum 1-C<sub>6</sub> selectivity was 96% at the Al/Cr molar ratio of 200. Also, an increase in the TNOA amounts would move the reaction toward the establishment of



**Figure 6.** Normal probability plot of residuals for activity (a), selectivity (b) and polymer (c). Predicted vs actual plots for activity (d), selectivity (e) and polymer (f).

oligomers and polymers.

The quantity of the  $\text{CCl}_4/\text{Cr}$  was varied from 8 to 12 as can be seen in Figure 7(d). By increasing the molar ratio of  $\text{CCl}_4/\text{Cr}$ , the selectivity of the catalyst for the production of  $1\text{-C}_6$  also increases. However, more increments than 10 could prevent the coordination of ethylene with the chromium center, and consequently, the  $1\text{-C}_6$  selectivity decreases.

Figure 7(e) illustrates that the selectivity initially increases gradually with the rise in reaction temperature but then experiences a significant decline at higher temperatures. The relationship between selectivity and temperature can be categorized into two groups: temperatures below  $90^\circ\text{C}$  and temperatures above  $90^\circ\text{C}$ .

At lower temperatures, the selectivity demonstrates an upward trend as the reaction temperature increases. However, at temperatures exceeding  $90^\circ\text{C}$ , the activity noticeably decreases with higher temperatures. This decline in activity could be attributed to either the deactivation of active sites or the transformation of active sites into less active forms. Although the specific mechanism behind the temperature-dependent behavior in the chromium-containing catalyst system has not been confirmed, a study by Overett on the influence of elevated temperatures on catalyst systems suggests that a ligand rearrangement occurs in the presence of  $\text{AlEt}_3$  [27]. While this mechanism has not been verified for the chromium-containing catalyst system, a similar process may provide a plausible explanation for the observed catalyst deactivation.

The 3D surface graphs for polymer content are shown in Figures 7(g, h and i). Polymer formation in the ethylene trimerization reaction is undesirable and causes fouling in the reactor. The effect of reaction variables such as  $\text{Al}/\text{Cr}$ ,  $\text{CCl}_4/\text{Cr}$ , temperature and catalyst dosage for the polymer content are shown in Figures 7(g, h and i). It is clear from Figure 7(g), the minimum polymer formation is obtainable when the  $\text{Al}/\text{Cr}$  molar ratio is 200. Also at the lower and higher molar ratio, more polymer is produced. The alkyl groups in the above ratio of the catalyst structure can selectively activate the active centers of Cr responsible for producing  $1\text{-C}_6$ . Hence, the selectivity of the final product will be considerably enhanced.

In Figure 7 (g), when  $\text{CCl}_4/\text{Cr}$  molar ratio was increased from 9 to 10, polymer formation was decreased from 24 mg to 16 mg. When  $\text{CCl}_4/\text{Cr}$  molar ratio was at 10, the amount of  $\text{CCl}_4$  was enough to stabilize facial coordination (B) to assist the chromium center in achieving high 1-hexene formation

selectivity. Further increase of  $\text{CCl}_4/\text{Cr}$  molar ratio from 10 to 11, increases polymer production.

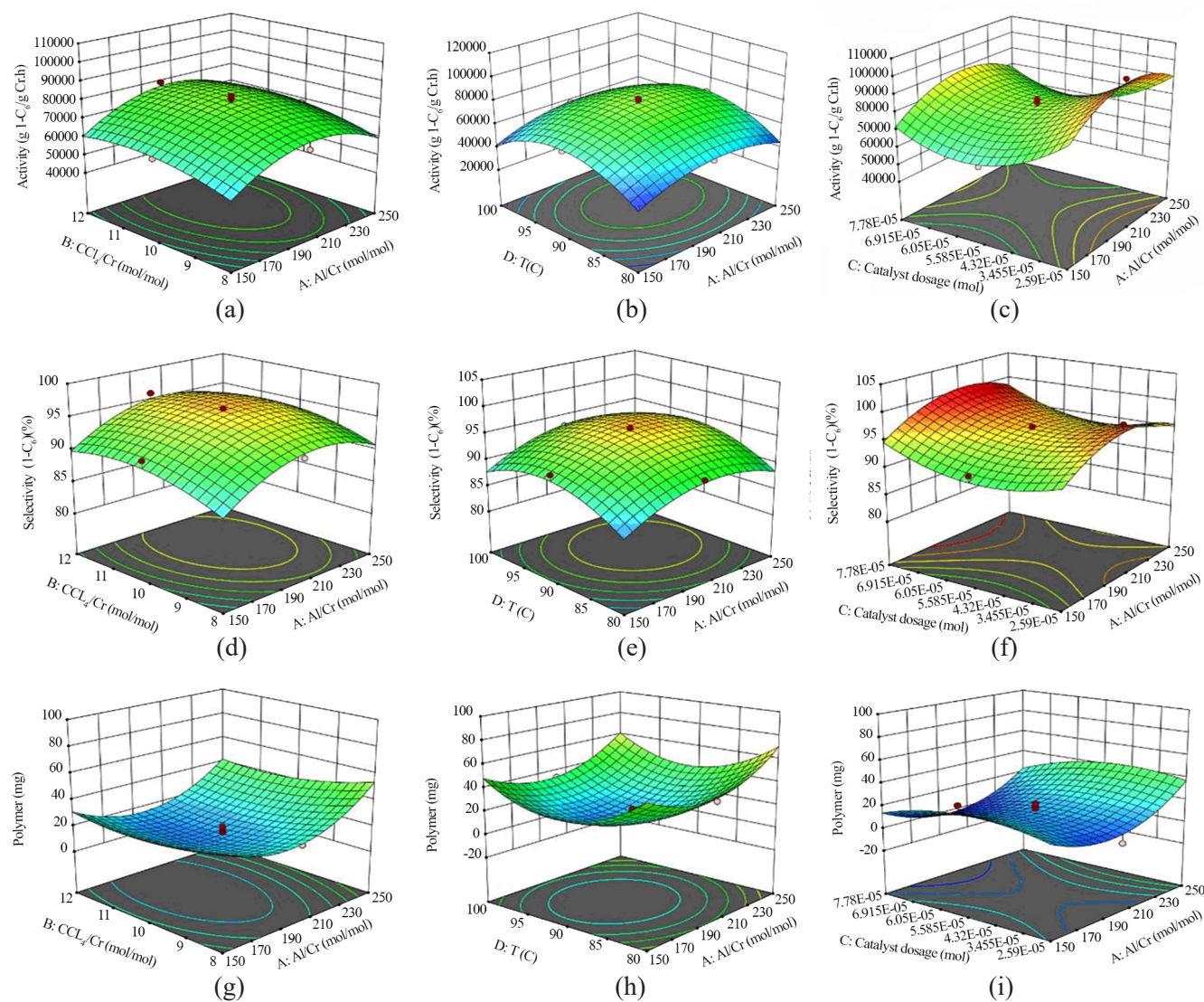
Among the two variables, temperature and catalyst dosage, the influence of temperature is found to be more significant than catalyst dosage (Figure 7 (h)), While the changes in the catalyst dosage did not have a significant effect on polymer formation, due to the decrease in catalyst consumption,  $2.59 \times 10^{-5}$  was chosen as the optimal dosage (Figure 7(i)). According to the experimental results, the temperature of  $90^\circ\text{C}$  was chosen as the ethylene trimerization temperature.

#### Parameter optimization

The process of ethylene trimerization was optimized using the Response Surface Methodology (RSM) numerical approach to optimize the parameters within the studied range by considering the standard error that happened in the model. The quadratic polynomial model was used for maximum activity and selectivity and minimum polymer formation. According to the experimental data provided, the design-expert parameter optimization module is utilized to optimize the  $\text{Al}/\text{Cr}$  molar ratio,  $\text{CCl}_4/\text{Cr}$  molar ratio, reaction temperature, and catalyst dosage. The outcomes of this optimization process are presented in Table 5. To confirm the effectiveness of the optimized process conditions, the experiments were replicated as closely as possible to the optimum conditions. The results closely aligned with the optimized values, thus affirming the validity of the optimization process. Table 8 presents a comparison of the optimal operating parameters and the highest achievable yield as determined by both experimental and predicted data. In a molar ratio of the catalytic system  $[\text{Cr}(2\text{-EH})_3/2,5\text{-DMP}/\text{CCl}_4/\text{TNOA}]$  equal to 1:6:10.8:201.5, ethylene pressure of 25 bar and temperature of  $91.2^\circ\text{C}$ , the highest catalyst activity and  $1\text{-C}_6$  selectivity and minimum polymer content were obtained 105328 (g  $1\text{-C}_6/\text{g Cr.h}$ ), 99.21% and 0 mg under optimum experimental conditions, while it was predicted 103500 (g  $1\text{-C}_6/\text{g Cr.h}$ ), 99.34% and 2 mg by the model, respectively. A good agreement between the experimental and predicted data is observed with an acceptable relative error.

**Table 8.** Optimized ethylene trimerization conditions.

	Experimental	Predicted
Activity(g $1\text{-C}_6/\text{g Cr.h}$ )	105328	103500
Selectivity( $1\text{-C}_6$ )%	99.21	99.34
Polymer(mg)	0	2



**Figure 7.** 3-D response surface plots displaying the effects of Al/Cr,  $\text{CCl}_4/\text{Cr}$ , catalyst dosage and temperature on catalyst activity (a, b and c), 1- $\text{C}_6$  selectivity (d, e and f), and polymer content (g, h and i).

## CONCLUSION

In the present research,  $\text{Cr}(2\text{-EH})_3$  catalyst was synthesized and characterized by FTIR,  $^1\text{H}$ NMR and  $^{13}\text{C}$ NMR to study chemical properties and identify molecular structures. A four-component homogeneous catalyst system [ $\text{Cr}(2\text{-EH})_3$  /2,5-dimethyl pyrrole/ co-catalyst/halide] was investigated for trimerization of ethylene in terms of catalyst activity, 1-hexene selectivity and polymer formation. The effects of three kinds of organic halides and five types of organometallic co-catalysts were tested. The influences of compositions of the catalytic components (co-catalyst, halide, catalyst dosage) and temperature were evaluated using combined response surface methodology (RSM) and central composite design (CCD) techniques.

The results showed that carbon tetrachloride ( $\text{CCl}_4$ ) and tri-n-octylaluminum (TNOA) were the best candidates for this catalyst system, demonstrating high 1-hexene formation selectivity, highly catalytic activity and lower polymer content. In the catalytic system [ $\text{Cr}(2\text{-EH})_3$ /2,5-DMP/ $\text{CCl}_4$ /TNOA] with the molar ratio of 1:6:10.8:201.5, ethylene pressure of 25 bar and temperature of 91.2°C, under optimum experimental conditions, the activity of 105328 (g 1- $\text{C}_6$ /(g Cr.h)), 99.21% selectivity to 1-hexene and no polymer formation were obtained.

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## CONFLICTS OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## REFERENCES

1. Kwon M-H, Chae H-J, Park MB (2018) Oligomerization of 1-hexene over designed SBA-15 acid catalysts. *J Ind Eng Chem* 65: 397-405
2. Alzamly A, Bakiro M, Hussein Ahmed S, Siddig LA, Nguyen HL (2022) Linear  $\alpha$ -olefin oligomerization and polymerization catalyzed by metal-organic frameworks. *Coord Chem Rev* 462: 214522
3. Gharajedaghi S, Mohamadnia Z, Ahmadi E, Marefat M, Pareras G, Simon S, Poater A, Bahri-Laleh N (2021) Experimental and DFT study on titanium-based half-sandwich metallocene catalysts and their application for production of 1-hexene from ethylene. *Mol Catal* 509: 111636
4. Kong W, Ma X, Zuo J, Zhao X, Zhang J (2023) Ethylene tri-/tetramerization catalysts supported by phenylene-bridged mixed alkyl/aryl diphosphine ligands. *Organometallics* 42: 651-659
5. Ma J, Fan H, Hao B, Jiang T (2022) Highly efficient asymmetric (diphenylphosphino) benzene-based chromium catalysts for selective ethylene trimerization. *Appl Organomet Chem* 36: 6907
6. Kitphaitun S, Takeshita H, Nomura K (2022) Analysis of ethylene copolymers with long-chain  $\alpha$ -olefins (1-dodecene, 1-tetradecene, 1-hexadecene): A transition between main chain crystallization and side chain crystallization. *ACS Omega* 7: 6900-6910
7. Shao H, Wang R, Li H, Guo X, Jiang T (2020) Synthesis of low-molecular-weight poly- $\alpha$ -olefins using silicon-bridged zirconocene catalyst for lubricant basestock. *Arab J Chem* 13: 2715-2721
8. Salian SM, Bagui M, Jasra RV (2021) Industrially relevant ethylene trimerization catalysts and processes. *Appl Petrochem Res* 11: 267-279
9. Meng W, Li H, Li J, Chen B (2011) The effect of comonomer type and content on the properties of Ziegler-Natta bimodal high-density polyethylene. *J Korean Chem Soc* 55: 673-679
10. Almuqati NS, Aldawsari AM, Alharbi KN, González-Cortés S, Alotibi MF, Alzaidi F, Dilworth JR, Edwards PP (2024) Catalytic production of light olefins: Perspective and prospective. *Fuel* 366: 131270
11. Ishii S, Nakano T, Kawamura K, Kinoshita S, Ichikawa S, Fujita T (2018) Development of new selective ethylene trimerization catalysts based on highly active ethylene polymerization catalysts. *Catal Today* 303: 263-270
12. Dixon JT, Green MJ, Hess FM, Morgan DH (2004) Advances in selective ethylene trimerization – a critical overview. *J Organomet Chem* 689: 3641-3668
13. Hao B, Alam F, Jiang Y, Wang L, Fan H, Ma J, Chen Y, Wang Y, Jiang T (2023) Selective ethylene tetramerization: An overview. *Inorg Chem Front* 10: 2860-2902
14. Briggs JR (1989) The selective trimerization of ethylene to 1-hexene. *J Chem Soc Chem Commun* 11: 674-675
15. Drzeżdżon J, Sikorski A, Chmurzyński L, Jacewicz D (2018) New type of highly active chromium(III) catalysts containing both organic cations and anions designed for polymerization of beta-olefin derivatives. *Sci Rep* 8: 2315
16. McGuinness DS, Wasserscheid P, Keim W, Morgan D, Dixon JT, Bollmann A, Maumela H, Hess F, Englert U (2003) First Cr(III)-SNS complexes and their use as highly efficient catalysts for the trimerization of ethylene to 1-hexene. *J Am Chem Soc* 125: 5272-5273
17. Overett MJ, Blann K, Bollmann A, Dixon JT, Hess F, Killian E, Maumela H, Morgan DH, Neveling A, Otto S (2005) Ethylene trimerisation and tetramerisation catalysts with polar-substituted diphosphinoamine ligands. *Chem Commun*: 622-624
18. Agapie T (2011) Selective ethylene oligomerization: Recent advances in chromium catalysis and mechanistic investigations. *Coord Chem Rev* 255: 861-880
19. Salakhov II, Mikenas TB, Zakharov VA, Kozlov VG, Matsko MA, Suslova TN (2022) Effect of mono- and multichlorinated organic compounds-

- chlorocyclohexane and hexachloro-p-xylene-on the catalytic properties of titanium–magnesium catalysts in the homo- and copolymerization of ethylene with 1-hexene. *Int J Mol Sci* 23: 10335
20. Steele RB, Katzakian AJ, Scigliano JJ, Hamel EE (1976) Imide oxirane reactions, US Pat: US 3962182
  21. Araki H N, Nanba Y, Okano T (1997) Process for producing  $\alpha$ -olefin oligomer, US Pat: US5856612
  22. Farzami F, Askari M, Eraghi MA (2022) Sensitivity analysis and multi-objective optimization of gas-phase polymerization of propylene using Ziegler-Natta catalysts. *Chem Eng Res Des* 184: 457-472
  23. Carter A, Cohen SA, Cooley NA, Murphy A, Scutt J, Wass DF (2002) High activity ethylene trimerisation catalysts based on diphosphine ligands. *Chem Commun*: 858-859
  24. Luo H-K, Li D-G, Li S (2004) The effect of halide and the coordination geometry of chromium center in homogeneous catalyst system for ethylene trimerization. *J Mol Catal A Chem* 221: 9-17
  25. Köhn RD, Haufe M, Kociok-Köhn G, Grimm S, Wasserscheid P, Keim W (2000) Selective trimerization of  $\alpha$ -olefins with triazacyclohexane complexes of chromium as catalysts. *Angew Chem Int Ed* 39: 4337-4339
  26. Jiang T, Ji R, Chen H, Cao C, Mao G, Ning Y (2011) Effect of alkylaluminum activators on ethylene trimerization based on 2,5-DMP/Cr(III)/TCE catalyst system. *Chin J Chem* 29: 1149-1153
  27. Yang Y, Kim H, Lee J, Paik H, Jang HG (2000) Roles of chloro compound in homogeneous [Cr(2-ethylhexanoate)<sub>3</sub>/2,5-dimethylpyrrole/triethylaluminum/chloro compound] catalyst system for ethylene trimerization. *Appl Catal A Gen* 193: 29-38
  28. Overett MJ, Blann K, Bollmann A, Dixon JT, Haasbroek D, Killian E, Maumela H, McGuinness DS, Morgan DH (2005) Mechanistic investigations of the ethylene tetramerisation reaction. *J Am Chem Soc* 127: 10723-10730