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ORIGINAL PAPER

Preparing a modified and promoted homogeneous titanium catalyst for ethylene dimerization to butene-1

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ABSTRACT

Ethylene dimerization is a significant process among the other petrochemical processes due to the production of alpha olefins as the most widely used industrial intermediate. Titanium tetra butoxide/tetrahydrofuran/triethyl aluminum is the main homogeneous catalyst complex that has been used in this process. On the other hand, the formation of polymer or oligomerization side reactions are the salient obstacles in the ethylene dimerization process. The effect of various promoters from the group of halo hydrocarbons, along with different modifiers from the group of esters and silane compounds has been investigated to conquer the barriers mentioned above. The reaction conversion, selectivity, and polymer production are the remarkable parameters that have been evaluated to study the components' impacts. The results indicated that the addition of promoters through reaction with triethyl aluminum (TEA) (co-catalyst) increased the reaction rate and thus augmented the conversion of the reaction to 88.26% and reduced the reaction time to 60 min. Among the promoters, the reaction conversion and selectivity of dichloromethane were, respectively, 88.26% and 78.45%, higher than that of dibromopropane (48.52% and 39.52%), but a higher amount of polymer was produced by dichloromethane. Moreover, esters strongly decreased the catalyst activity, resulting in a decrease in the conversion to under 25%. On the other hand, silanes showed a significant effect on the control of the polymer chains in Ziegler-Natta homogeneous catalysts. Dicyclopentyldimethoxysilane (DCPDS) modifier caused an increase of 1.5% in ethylene conversion and a 6% increase in the 1-butene selectivity. At the same time, the polymer formation also prevented a significant amount, so the amount of polymer decreased to about 2.1 mg. DCPDS modifier performed better than the cyclohexylmethyldimethoxysilane (CHMDS) donor.
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Keywords: Butene-1; homogeneous catalyst; dimerization; ethylene conversion; modifier; promotor.

INTRODUCTION

Oligomerization or dimerization of alkenes is an important method for the production of alpha-olefins, which have been widely used as industrial intermediates [1,2]. One of the most important alpha-olefin compounds is butene-1, which is used as a comonomer in ethylene polymerization reactions. About 40% of all linear polyethylene products are produced via butene-1 comonomer in the world [3-5]. The catalysts used in these systems are from the family of Ziegler-Natta catalysts, and the most important of them is the homogeneous TTBO/THF catalyst with a TEA promotor. The homogeneous catalytic systems used in the ethylene dimerization contain active metal (TTBO), Lewis acid or modifier (triethyl aluminum), modifier, and solvent. TEA is a Lewis acid that increases the rate of dimerization [6,7].

Aluminum trialkyl (AlR_3) is widely used in different processes containing olefins. The kinetics of homogeneous dimerization of ethylene to butene-1 with TEA catalyst ($AlEt_3$) was studied in the gas phase

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and temperature range of 160-230°C. The rate of the ethylene conversion was low, but the selectivity and yield of butene-1 were high. The most important side product of this system was high polymer content. Also, at higher conversions of ethylene (>20%), significant amounts of C8 alkenes were produced along with butene-1 [8, 9]. The study of the reaction between TEA and ethylene in the temperature range of 80-220°C and 1-9 atm pressure showed that the reaction rate was the first-order according to the concentration of ethylene dissolved in the liquid phase and the composition of TEA. The reaction rate increased with increasing temperature, although it was slow below 120°C. Butene-1 was the main gaseous product [10-12].

Modifiers such as ethers or silanes are usually added to the catalyst system to provide better selectivity for the reaction. Modifiers affect the bonding mode of ethylene molecules and prevent the formation of high molecular-weight polymers. Solvents usually play an important role in increasing dimerization speed and improving catalytic activity due to their appropriate reducing power. Paraffinic hydrocarbons, including hexane and heptane, are the most important solvents in titanium homogeneous catalytic systems [13, 14].

The versatility of Ziegler-Natta catalysts shows that ethylene dimerization or oligomerization can be considered as the alignment of the polymerization reaction. It can also be interpreted as an indication of the coexistence of a competitive process between dimerization, oligomerization, and polymerization [15-17]. The dimerization reaction is considered the polymerization reaction of aligned ethylene, and as a result, the formation of oligomeric compounds with six carbon atoms and more is expected. However, the predominance of each of these three reactions depends on the metal catalyst, oxidation state, and reaction conditions. The most important factors affecting the reaction activity and selectivity of the homogeneous titanium catalytic systems for the production of butene-1 include Al/Ti molar ratio, titanate complex concentration, modifier nature, promotor effect, ethylene content, reaction temperature, and reaction time [12,18].

The use of synthetic homogeneous catalytic compounds, despite the results being very close to the industrial catalyst, has an inappropriate amount of produced polymer, which is the most important problem of this type of catalyst. To reduce this amount of polymer or to improve the catalytic complex, it is necessary to use suitable modifiers or promotors [19]. Henrici-Olivé and Olivé [20] studied Cp_2TiCl_2 and $Cp_2TiEtCl$ (Cp= cyclopentadienyl, Et= ethyl) in combination with aluminum alkyls as catalyst systems for the polymerization of ethylene in toluene. They proposed that the growth phase starts from a configuration in which the monomer is coordinated with the metal in the six-membered (I) or four-membered (II) transition state. The formation of each of these intermediates and subsequently the product distribution (dimer vs. oligomer) is thought to be influenced by the nature of the coordinated ligands [21,22].

Increasing the concentration of titanate has the opposite effect on the selectivity of the catalyst towards butene-1. The reason is that higher concentrations of titanium metal lead to the formation of clusters around the active centers and as a result prevent the access of monomers to them [23]. Pillai *et al.,* [23] investigated the dimerization of ethylene to 1-butene by $Ti(OC_4H_9\text{-}n)_4\text{-}A1R_3$ (R = CH_3, C_2H_6, i-C_4H_9) at 1-12.5 kg/cm^2 of ethylene pressure and 25-45°C in a hydrocarbon solvent. They showed that the efficiency of the catalyst and the intensity of the dimerization reaction depends on the molar ratio of Al/Ti, and different ratios of Al/Ti are related to different ratios of catalyst deactivation. That is, at lower Al/Ti molar ratios, the intensity of the dimerization reaction increases, although this value increases up to a ratio of about 11, above that, the intensity of the dimerization reaction decreases and instead, the intensity of the polymerization reaction increases [24]. The research of Mahdaviani *et al.,* [19] also showed that among various modifiers, THF has the best selectivity to butene-1 with a good degree of ethylene conversion. Cyclic ethers, especially THF, have the best properties to fulfill these prerequisites. It is thought that THF molecules stabilize the titanate complex through the formation of six-coordinated species that are not formed otherwise [19,25].

Mahdaviani *et al.,* [18] showed that increasing the Al/Ti molar ratio up to 4 increases ethylene conversion. If it is higher than 4, it reduces the selectivity of butene-1 and increases the amount of polymer compounds. Comparing the effect of THF and THP modifiers on the catalyst properties, ethylene conversion rate, butene-1 selectivity, and the catalyst efficiency are higher when THP is used [19]. Recently, the use of alkoxysilanes (tetramethoxysilane and tetraethoxysilane) as the new modifiers has been investigated, and the results indicate a 50% increase in the yield and a 60% decrease in the amount of polymer produced [26].

On the other hand, the most important modifiers identified in the homogeneous dimerization catalysts are halo hydrocarbon compounds, including dibromoethane and chloroethane [27].

In this work, DCM and DBP are used to improve the performance of Ti-base homogeneous catalyst in ethylene conversion, selectivity in 1-butene formation and reaction efficiency. Also, the family of esters, compounds of DEHP, DIBP and TREA and the family of silanes, compounds of CHMDS and DCPDS were used as catalyst structure modifiers. Finally, after comparing these catalysts with experimental catalysts, the optimal values of relevant parameters were determined under different operating conditions and the optimal combination was introduced for these catalytic systems.

EXPERIMENTAL

Materials

In this study, TTBO, THF, DBP, DCM, TREA, DEHP, DIBP, CHMDS, and DCPDS were purchased as the catalyst, modifiers, and promotor components from Merck. TEA was obtained from Crompton Chemicals and was diluted in n-hexane. n-Heptane (as solvent) was obtained from Merck and polymerization grade ethylene gas (purity of 99.95 wt.%) was supplied from Jam Petrochemical Company and was checked for its purity by gas chromatography (GC).

Equipment

A 1000 mL Buchi reactor of stainless steel was used to perform the dimerization reaction of ethylene to butene-1 by a titanium catalyst in the homogeneous phase. The reaction vessel was an SS316 tank with a design pressure of 60 bar and a design temperature of 250°C, which was equipped with temperature and pressure sensors and gas inlet and outlet paths. Also, the second wall of the reactor (thermal jacket) was made of SS304, which heats/cools the tank with the help of a fluid heat exchanger (usually an oil circulator). The reactor system was equipped with the catalyst and chemical injection system, gas flow measurement system (mass flow controller, MFC), and pressure safety valves for emergency pressure relief (set pressure 60 bar). The flow diagram of the reactor system is shown in Figure 1.

Experimental methods

All stages of preparation of the catalyst, modifier, and promotor samples were done under a nitrogen gas atmosphere or in a Glove Box. For this purpose, the reactor was heated to 70°C for 30 min to remove water, air, and impurities. It was then cooled to ambient temperature and dried by nitrogen and then ethylene was poured into the system for 10 min. Then, the following steps were performed: injecting 400 mL of the solvent into the reactor and then adjusting the circulator temperature (between 55°C). The reactor pressure was set to 17 bar by ethylene feed. The main compounds of the catalyst including TTBO, THF, TEA (TEA 25 wt.% in hexane), modifier, and promotors were injected respectively and according to certain ratios.

The reaction was started by stirring the mixture, and at the end, the gas sample from the reactor was analyzed by a GC device. The output liquid sample (including solvent and 1-butene, ethylene and other compounds) was first washed with distilled water, alcohol, and

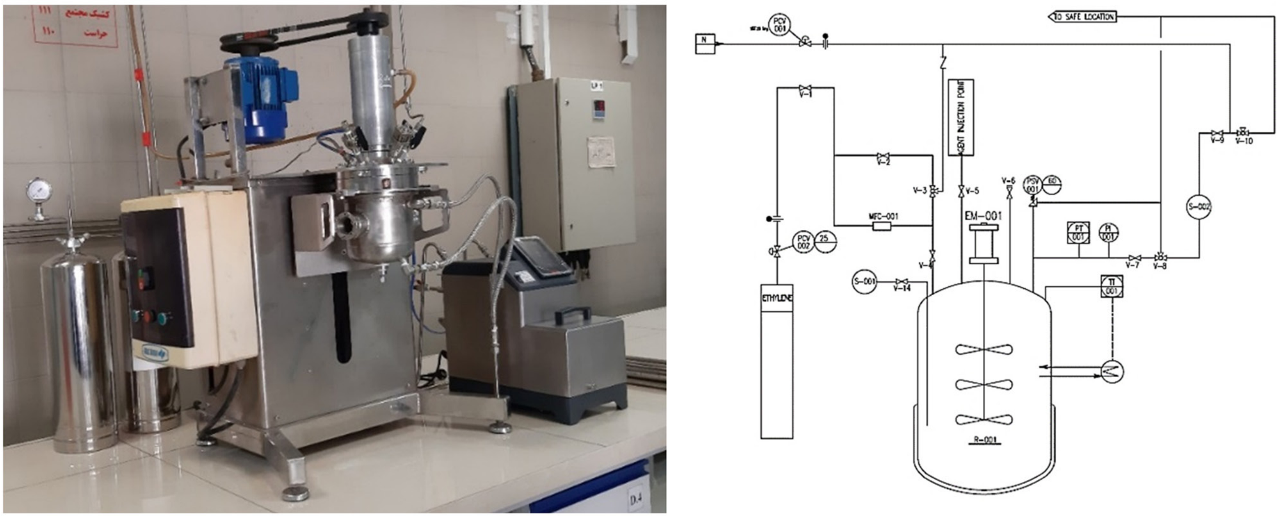

Figure 1. Photo and schematic diagram of the laboratory set-up of the reactor system.

hydrochloric acid (to remove titanium particles and also the remaining triethyl aluminum) and then distilled. To measure the hydrocarbon compounds of the liquid part, the DHA method was used by removing the average metal components of relatively concentrated hydrochloric acid in several steps.

All tests of gas exiting from the reactor have been done with a GC-450 Varian (the method for hydrocarbons and impurities was ASTM D6159 and ASTM D4429, respectively). Because C4 cleavage isomers may change to other isomers due to the passage of time, the gas sample from the reactor was injected into the GC device immediately. The output liquid sample was first washed with distilled water, alcohol, and hydrochloric acid (to remove titanium particles and the remaining triethyl aluminum) and then was distilled. To measure the hydrocarbon compounds of the liquid part, the DHA method was used by removing the average metal components of relatively concentrated hydrochloric acid in several steps.

In each batch, the polymers formed on the reactor wall and around the stirring blade were collected and after washing with hexane or heptane, dried in a vacuum oven at a temperature of 100°C and then weighed. In addition, to ensure the accuracy of the results, each test was repeated at least three times.

Briefly, the reaction conditions were as follows: temperature 55°C, pressure 17 bar, reaction time 60 min, stirring speed 900 rpm, amount of solvent used 400 mL (heptane), amount of catalyst used 1 mL, ratio Al/Ti, Modifier/Ti, Promotor/Ti adjusted according to certain ratios and amount of ethylene consumption 150 ml.

Experiments were carried out in 3 steps:

Step 1: Investigation of the performance of several available commercial catalysts and synthesized catalyst.

After determining the main components of typical homogeneous catalysts for ethylene dimerization and incorporating the modifier, the synthesis of the catalyst was investigated. The co-catalyst for this type of catalyst was triethyl aluminum (TEA). To synthesize the catalyst complex, first, 1 mL of the catalytic compound (including THF and TTBO) was added to 8 mL of TEA dissolved in hexane (15% TEA +75% hexane). This solution was added to 50 mL of hexane. The resulting solution was used as a catalyst complex in the dimerization experiment. To achieve the optimal ratio of modifier THF to TTBO (THF/Ti), their different volume ratios (30:70 to 70:30) were tested. The optimal ratio was obtained based on the ethylene conversion, butene-1 product selectivity, and catalyst efficiency.

Step 2: Evaluation of the effect of DCM and DBP modifiers on the performance of the catalyst in the dimerization reaction and determination of the optimal molar ratio of DCM to TTBO (DCM/Ti) in the range of 1 to 9.

Step 3: Investigation of the effect of different modifiers from the two groups of esters and silanes to improve the catalyst performance. Ethylene conversion percentage was calculated from the mass balance of ethylene consumption using MFC and the selectivity of butene-1 product by GC analysis of gaseous and liquid products, liquid product weight, and gas volume. Equations 1, 2, and 3 were used to calculate the conversion rate of the reaction, selectivity of butene-1, and yield, respectively:

$$\text{Conversion (\%)} = \left(\frac{(\text{mole of Ethylene input}) - (\text{mole of residual Ethylene})}{(\text{mole of Ethylene input})}\right) \times 100 \qquad (1)$$

The selectivity of butene-1 output from the reaction is the total mass percentage of butene-1 in the liquid and gas phases, calculated from the following equation:

$$\begin{aligned}&\text{Selectivity(\%) to 1 - Butene} = (\text{1 - Butene mass fraction in gas phase}) + \\ &(\text{1 - Butene mass fraction in liquid phase})\end{aligned} \qquad (2)$$

Yield calculation:

$$\text{Yield (\%)} = \left(\frac{(\text{Ethylene conversion (\%)}) \times (\text{Selectivity to 1 - Butene (\%)})}{100}\right) \qquad (3)$$

RESULTS AND DISCUSSION

Effect of co-catalyst

In this work, two commercial catalyst samples (named C.Cat-1 and C.Cat-2) have been used. C.Cat-1 and 2 are commercial catalyst produced by Jam Petrochemical Co. for synthesizing ethylene to butene-1. The main components of these common commercial catalysts in industrial units are presented in Table 1. The results show that typical industrial catalysts contain on average 43-47 wt.% of THF and on average 53-57 wt.% of TTBO. Free butanol is also around 500-1500 ppm and chlorides are around 30-50 ppm in the composition of these catalysts. It is necessary to explain that the composition of TTBO is obtained from the reaction of butanol with titanium

Table 1. Main components of commercial homogeneous catalysts for ethylene dimerization.

Main components	Min	Max
Free Butanol, ppm	500	1500
THF, wt.%	43	47
TTBO, wt.%	53	57
Chlorides, ppm	30	50

dioxide. The presence of two butanol compounds and TiO_2 can be a sign of the presence of TTBO compound in the structure of commercial catalysts.

Figure 2 shows the FTIR spectra of commercial catalyst samples as well as pure THF. In both catalysts, the peak of 600-750 cm^{-1} is related to the C-Cl bond, which is not seen in pure THF. The peak area of 1070 cm^{-1} related to the C-O bond or the C-O group in commercial catalysts is also present in THF [28]. There is also a peak of 1040 cm^{-1} in commercial catalysts, which is due to the presence of a butoxide agent in them. The peak at 1375 cm^{-1} corresponds to the Ti-O group with symmetric stretching vibration. The peak of 1440 cm^{-1}, which is common to all of them, is related to the C-H group [29-31]. From the FTIR analysis, it can be concluded that in industrial catalysts, there is the butoxide and titanium Ti-O group as the base and main component of the catalyst, as well as THF as a modifier.

FTIR analysis on several commercial catalyst samples showed that TTBO and THF are the two main components of homogeneous ethylene dimerization catalysts. To achieve the optimal ratio of THF to TTBO (THF/Ti) modifier, different volume ratios of TEA as co-catalyst were investigated. The results of conversion rate, selectivity and yield of butene-1 product are shown in Table 2 and Figure 3. Increasing the amount of THF to THF/Ti=45/55, the conversion rate reaches its maximum value of 81.6%. But at higher ratios of THF, the activity of the catalyst and thus the conversion rate decreases. On the other hand, with the use of industrial catalysts, the conversion amount is about 70.3%. To be sure, the experiment was repeated three times.

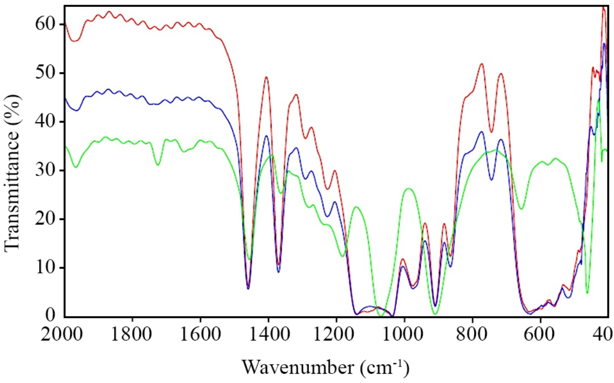

Figure 2. FTIR analysis of two commercial catalysts and THF, C.Cat-1=Red, C.Cat-2=Blue, and THF = Green.

It has been shown that in THF/Ti=45/55, the highest selectivity value of 82.3% was obtained. This value was slightly higher than the selectivity of the butene-1 value caused by the industrial catalyst. The comparison of the yield (Figure 3) showed that the trend of changes in yield (which is the product of the percentage of conversion and selectivity) is similar to the trend of changes in the graphs of conversion rate and selectivity. That is, in the ratio of THF/Ti = 45/55, the maximum efficiency is observed at the rate of 66.4%.

In theory, modifiers such as THF are Lewis base or polar organic compounds of sufficiently soft (nonionic) nature that control the acidity of the Lewis acid co-catalyst or TEA. THF, which has strong Lewis base properties, can break the dimeric state of TEA in the solution and transform it into its monomeric state, as a result of which the ethyl group in TEA is released more easily and causes the formation of species that are active Ti [9, 12, 18]. It is thought that the molecules of this type of cyclic ethers, as well as combined ligands, stabilize the titanate complex through the formation of a hexa core species. It is also expected that any additional enhancers could interfere with the formation of the active Ti species or may prevent ethylene coordination at the active dimerization sites [18, 19]. This is the reason that by increasing the amount of THF or the ratio of THF/Ti above 50/50, the activity of the catalyst gradually decreases.

The amount of polymer produced due to the dimerization reaction in different ratios of THF/Ti is shown in Figure 4. The amount of the polymer is significant. In this way, without a new modifier and only with the existing promotor or modifier (THF), a large amount of polymer is formed (around 130-140

Table 2. The performance results of THF as co-catalyst in the conversion of butene-1 (T=55°C، P=17 bar، Reaction Time= 60 min، Stirrer Speed= 900 rpm، Al/Ti= 6، Ethylene Consumption= 150 mL).

	Conversion, %	Selectivity, %	Yield, %
Com. Catalyst	70.3	81.3	57.2
THF/Ti= 30/70	45.2	69.2	31.1
THF/Ti= 40/60	65.6	78.5	51.5
THF/Ti= 45/55	71.4	82.3	66.4
THF/Ti= 50/50	72.8	80.7	58.7
THF/Ti= 60/40	57.5	70.3	40.3
THF/Ti= 70/30	23.3	34.1	8.2

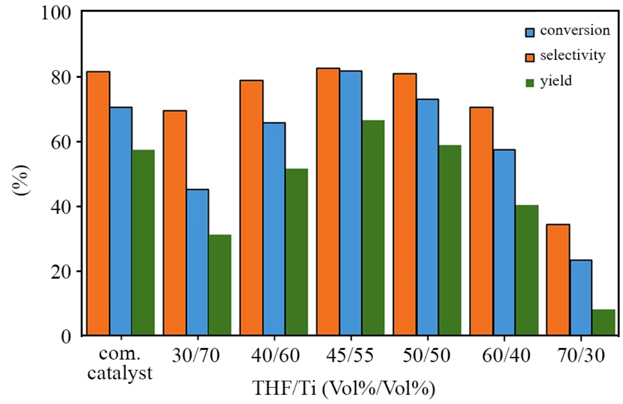

Figure 3. Reaction conversion, reaction efficiency, and selectivity of butene-1 at different volume ratios of THF/Ti. T=55°C, P=17 bar, Reaction Time= 60 min, Stirrer Speed= 900 rpm, Al/Ti= 6, Ethylene Consumption= 150 mL.

mg). This is while commercial catalysts produce up to 180 mg of polymer in the reaction. The presence of THF causes the formation of monomeric species of TEA, and these monomeric species increase the activity of the catalyst, as a result, the formation of polymer reactions can be predicted.

The formation of monomeric TEA through the decomposition of the TEA dimer is useful for the formation of proactive sites. With the excess reaction of TEA monomer, they become active species due to the better properties of Lewis acid. Therefore, it leads to the stabilization of titanium cationic complexes in a higher oxidation state. Since the catalytic system for ethylene dimerization is a bifunctional catalyst, the TEA monomer can change the physical and electronic properties of Ti active sites. As a result, the dimerization component of the bifunctional catalyst increases, and the amounts of heavy and polymeric compounds decrease simultaneously [18, 19].

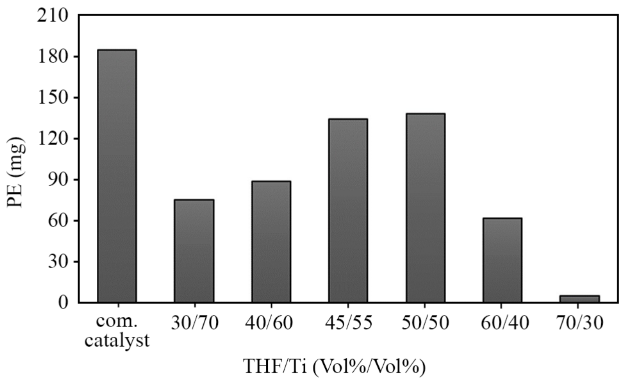

Figure 4. The amount of polymer formed in the different ratios of THF/Ti in catalyst synthesis. T=55oC, P=17 bar, Reaction Time= 60 min, Stirrer Speed= 900 rpm, Al/Ti= 6, Ethylene Consumption= 150 mL.

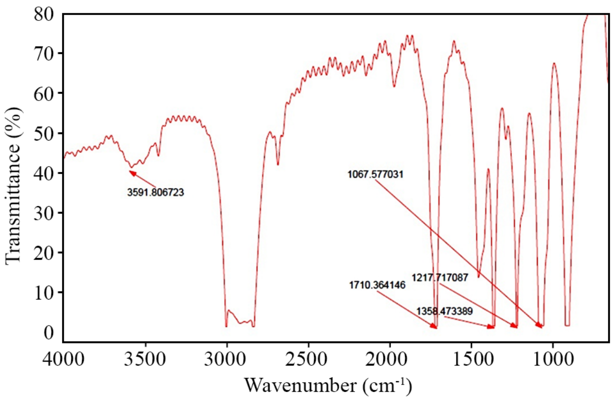

Figure 5. FTIR pattern of the synthesized TTBO/THF catalyst complex.

Figure 5 shows the FTIR spectrum of the TTBO/THF complex. The peak area of 1067 cm^{-1} is related to the C-O bond or the C-O alcohol group, which is also present in THF. The peak at 1217 cm^{-1} corresponds to C-O ether. The peak of 1359 cm^{-1} corresponds to the Ti-O group with symmetric stretching vibration. The peak in the region of 1710 cm^{-1} is also observed due to the butoxide agent in the catalyst complex. In 2800-3000 cm^{-1}, C-H alkane or alkane agents can be identified in the catalyst composition. The peak of 3591 cm^{-1} also corresponds to the O-H alcohol group [32,33]. Therefore, it can be concluded that in the synthesized catalyst, there are butoxide agents, titanium or Ti-O group as the base and main component of the catalyst, C-O groups, and also C-H groups of alkane as the constituent groups of the catalyst complex [31].

According to the percentage of the conversion and butene-1 selectivity, the volume ratio of THF/Ti=45/55 – 50/50 (equivalent to the mass ratio around THF/Ti=42/58 – 47/53) showed reasonable results and it can be considered an optimal ratio. Of course, the amount of polymer in this compound is considered the most important problem of this type of catalyst, and to reduce it, the use of modifiers or new promotors is essential.

Investigating the effect of promoters

Figure 6 shows the promoting effect of dichloromethane (DCM) on the dimerization reaction. As it can be seen, despite the increase in conversion percentage, the decrease in selectivity compared to the unpromoted catalyst is quite evident. Increasing the ratio of DCM/Ti has increased the selectivity, which in the molar ratio of 5, the selectivity has increased to about 78%, but with the increase of the ratio of DCM/Ti above 5, the selectivity of butene-1 has decreased.

The reason for the decrease of the selectivity, in general, can be due to the increase in the activity of the catalyst, which caused side reactions subsequently.

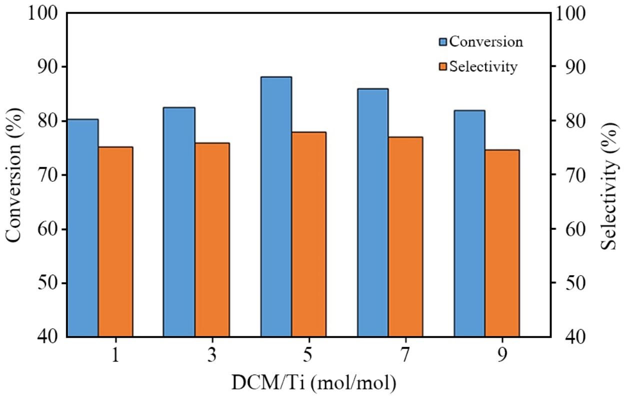

Figure 6. Degree of selectivity and conversion percentage of butene-1 at different ratios of DCM/Ti. T=55°C, P=17 bar, Reaction Time= 60 min, Stirrer Speed= 900 rpm, Al/Ti= 6, Ethylene Consumption= 150 mL.

For this purpose, the amount of polymer formed in these ratios was also measured and shown in Figure 7. The amount of polymer formed has increased to 180 mg, which indicates that the addition of DCM under the same conditions has increased the activity of the catalyst and increased the conversion percentage subsequently. However, increasing the activity has caused a decrease in the selectivity of butene-1 and an increase in the amount of polymer formed in the reaction. Therefore, the catalyst synthesized with ratio of DCM/T=5 has an average amount of polymer produced around that of the commercial catalyst.

In this work, a 1,2-dibromo propane (DBP) promotor was also used. Figure 8 shows the ethylene conversion percentage after adding DBP as a promotor. By increasing the ratio of 1.2DBP/Ti, the ethylene conversion percentage decreased significantly until 1.2DBP/Ti=9, and the ethylene conversion rate decreased to 10%. Achieving this amount of conversion is after a long time of reaction; so that after about 120 minutes of the reaction, practically no change in ethylene pressure was observed and the reaction was stopped at a pressure of about 14 bar, and sampling was done. Table 3 shows the comparison between different promoters.

The reason for this is that any additional DBP species may interfere with the formation of active Ti species due to the coordinated loading of the active sites by more than one halide per metal atom, thus preventing ethylene coordination [19, 34].

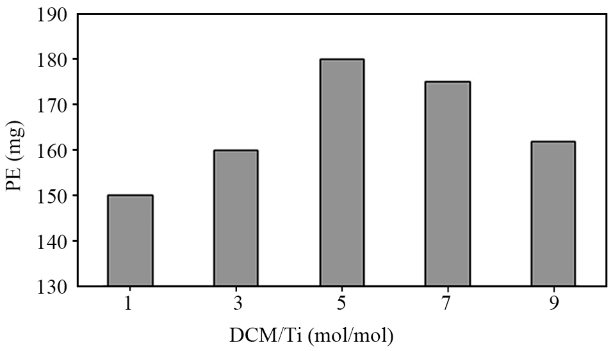

Figure 7. The amount of polymer formed in the reaction at different ratios of DCM/Ti. T=55°C, P=17 bar, Reaction Time= 60 min, Stirrer Speed= 900 rpm, Al/Ti= 6, Ethylene Consumption= 150 mL.

Due to the proper coordination ability of DBP to the central titanium of the five-membered metallacyclic transition state of Ti, a special structural arrangement of the catalyst system may be created in the reaction environment. Therefore, the chemical environment of the titanium center in the catalyst system changes. This rearrangement leads to the formation of a TEA dimer with two ethyl bridging bonds, which is converted into a TEA monomer [35].

Regarding the selectivity, it was also observed that by changing the ratio of 1,2DBP/Ti, the selectivity reached a maximum of 40% at a molar ratio of 1,2DBP/Ti=3, and after that, with increasing of the promotor the 1-butene selectivity decreased, until 1,2DBP/Ti=9, the 1-butene selectivity reached below 5%. The amount of polymer formed due to the reaction can be seen in Figure 9.

The addition of promoter through reaction with TEA (co-catalyst) increased the reaction speed and thus increased the conversion of the reaction and reduced the reaction time significantly. By comparing two types of DCM and DBP promoters, it can be concluded that DCM increased the activity of the catalyst and the conversion percentage, and reduced the reaction time to some extent. On the other hand, DBP increased the

Table 3. A comparison between the results of the findings of different promoters.

Promotor	Promotor/Ti	Conversion (%)	Product selectivity (wt.%)	PE (mg)	Yield (%)	Ref.
1, 2-Dichloroethane	5	97.78	1-C4: 82.86	15	81.02	[18]
Bromoethane	7	86.15	1-C4: 82.42	10	70.98	[19]
Chloroethane	6	86.10	1-C4: 83.12	10	71.56	[27]
1,2-Dibromopropane	3	46.52	1-C4: 39.67	95	18.45	This work
Dichloromethane	5	88.26	1-C4: 78.24	180	69.06	

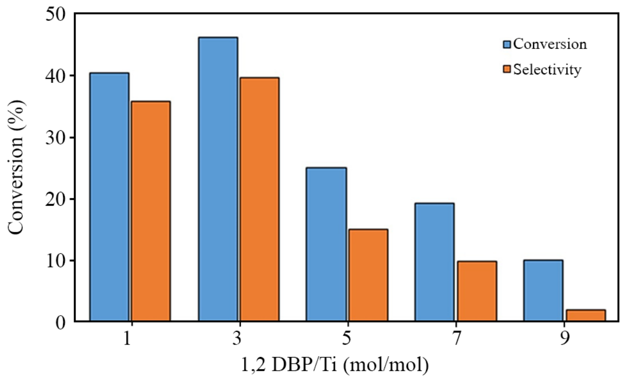

Figure 8. Conversion percentage and selectivity rate in 1.2DBP/Ti molar ratios. T=55°C, P=17 bar, Reaction Time= 60 min, Stirrer Speed= 900 rpm, Al/Ti= 6, Ethylene Consumption= 150 mL.

activity and conversion of the reaction to some extent, but from the molar ratio 1,2DBP/Ti=3 onwards, it decreased the activity of the catalyst and, as a result, the butene-1 selectivity decreased. The excess amount of TEA catalyst caused deactivation of active sites and affected the lifetime of the catalyst. However, the metal center of the catalyst could be stabilized and promoted using THP and bromoethane, which form complexes with TEA. Therefore, depending on the concentration of TEA, it is necessary to balance the amount of TEA and titanium precursor/additive [35].

As a result, by using the DBP promotor, the maximum ethylene conversion rate was about 46% and the maximum butene-1 selectivity was about 40%, which practically cannot be considered as a suitable promotor. An important point common to both promoter compounds was the increase in side reactions, especially polymer production. As a general result, it can be said that the DCM promoter was more effective in improving ethylene conversion and buten-1 selectivity than DBP. However, its weakness compared to the catalyst without a promoter is the high amount of polymer produced by it.

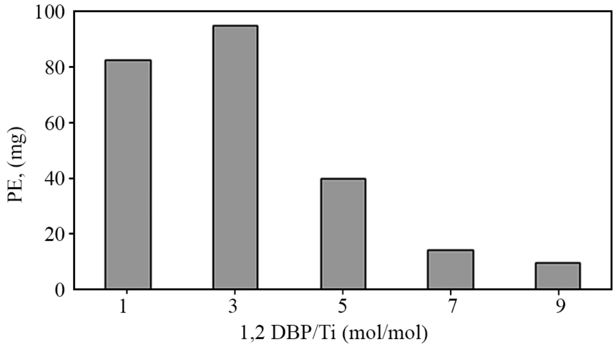

Figure 9. Changes in the amount of polymer formed in molar ratios of 1,2DBP/Ti. T=55°C, P=17 bar, Reaction Time= 60 min, Stirrer Speed= 900 rpm, Al/Ti= 6, Ethylene Consumption= 150 mL.

Modifier effect

In this article, three compounds from the ester group, including 2-ethylehexyl phthalate (DEHP), diisobutyl phthalate (DIBP), and triethylamine (TREA), were added as modifiers to the catalyst composition, and the obtained complex was used in the dimerization reaction. In Table 4, a summary of the results obtained from the types of modifiers added to the catalyst is presented. As can be seen from the results, the addition of esters in dimerization reactions reduced the activity of the catalyst and as a result decreased the ethylene conversion, so that even by increasing the reaction time to several hours, no noticeable change in the reaction is observed.

The use of donors or modifiers from the silane group has a significant effect on the control of polymer chains in Ziegler-Natta catalysts. As an example of two types of this modifier, we can mention CHMDS and DCPDS, which are widely used in polypropylene and polyethylene polymerization reactions and reactors. The use of these donors in the polymerization reactions is to control the polymer chains to control the properties of the polymer. In this article, two modifiers (CHMDS and DCPDS) are used in the catalyst complex and dimerization reaction. Table 5 shows the ethylene conversion, 1-butene selectivity, and also the amount of polymer.

The results in Table 5 show that DCPDS modifier performed better than CHMDS. There is still no clear reason for the different performance between DCPDS and CHMDS. But probably, the number, size, and composition of alkoxy or alkyl groups on siloxanes play an important role in controlling the simultaneous production of insoluble polymers during ethylene. When siloxanes are introduced into

Table 4. The results of adding different modifiers from the group of esters in the catalyst composition TTBO/THF/TEA (T=55oC، P=17 bar، Reaction Time= 60 min، Stirrer Speed= 900 rpm، Al/Ti= 6، Ethylene Consumption= 150 mL).

Modifier	Conversion (%)	Selectivity (%)	PE (mg)
Commercial catalysts	78.3	80.0	185 (Ave.)
Synthesized catalyst	81.2	82.3	136
2-Ethylehexyl phthalate (DEHP)	4.0	2.0	--
Diisobutyl phthalate (DIBP)	2.5	--	--
Triethylamine (TREA)	24.2	12.0	2

Table 5. The results of adding different modifiers from the group of silanes in the catalyst composition TTBO/THF/TEA. (T=55°C، P=17 bar، Reaction Time= 60 min، Stirrer (Speed= 900 rpm، Al/Ti= 6، Ethylene Consumption= 150 mL

Modifier	Conversion (%)	Selectivity (%)	PE (mg)
Commercial catalysts	78.3	80.0	185 (Ave.)
Synthesized catalyst	81.2	82.3	136.0
CHMDS	11.0	6.2	8.0
DCPDS	82.7	88	2.1

ion pairs, oligomerization creates an additional steric barrier around the iron centers. Meanwhile, the trend of relative changes when increasing the concentration of siloxanes in these systems strongly indicates the existence of some limitations in further reducing polymer formation. Such limitations may be due to the distance between the cationic iron centers and the anionic cages of TTB/THF or the coordination number of siloxane molecules on the TTB/THF surface [36]. The results showed that DCPDS caused a 1.5% increase in ethylene conversion and a 6% increase in 1-butene selectivity. On the other hand, polymer formation was significantly reduced, about 2.1 mg (i.e., 64% less than the unmodified catalyst).

CONCLUSIONS

One of the most important catalytic complexes used in ethylene dimerization to produce butene-1 is the titanium tetra butoxide/tetrahydrofuran/triethyl aluminum homogeneous catalyst complex. The main problem of this catalyst is the formation of polymer or oligomerization side reactions. To reduce the formation of polymer in these reactions, from the group of halo hydrocarbons, 1, 2-dibromo propane, and chloromethane as promoters, as well as from the group of esters compounds of ethyl hexyl phthalate, diisobutyl phthalate, and tetra ethylamine and the group of silanes compounds of cyclohexylmethyl dimethoxysilane and dicyclopentyldimethoxysilane were used as modifiers in the catalyst complex. In the end, a suitable combination for improving this type of catalyst was identified. Among the modifiers, the reaction conversion and selectivity of dichloromethane were higher than that of dibromopropane, but a higher amount of polymer was produced by dichloromethane. Esters strongly decreased the catalyst activity, resulting in a decrease in the conversion percentage. On the other hand, silanes showed a significant effect on the control of the polymer chains in Ziegler-Natta homogeneous catalysts. The DCPDS modifier performed better than the CHMDS donor did.

Terminology and abbreviations

Term	Chemical formula	Abb.
Titanium tetrabutoxide	$Ti(C_4H_9O)_4$	TTBO
Tetrahydrofuran	C_4H_8O	THF
Tetrahydropyran	$C_5H_{10}O$	THP
Triethyl aluminum	$C_6H_{15}Al$	TEA
Triethylamine	$N(CH_2CH_3)_3$	TREA
2-Ethylhexyl phthalate	$C_6H_4(CO_2C_8H_{17})_2$	DEHP
Diisobutyl phthalate	$C_{16}H_{22}O_4$	DIBP
Cyclohexylmethyldimethoxysilane	$C_9H_{20}O_2Si$	CHMDS
Dicyclopentyldimethoxysilane	$C_{12}H_{24}O_2Si$	DCPDS
1,2-Dibromopropane	$C_3H_6Br_2$	DBP
Dichloromethane	CH_2Cl_2	DCM

CONFLICTS OF INTEREST

The authors declare that they have no conflicts of interest.

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