

Production of 1-Butene via Selective Ethylene Dimerization by Addition of Bromoethane as a New Promoter to Titanium-Based Catalyst in the Presence of Tetrahydropyran Modifier and Triethylaluminum Co-Catalyst

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Abstract

The quantity of by-products and polymeric compounds produced in the ethylene dimerization reaction is a critical factor from the industrial viewpoint. It may lead to the shutting down of 1-butene reactors. It is, therefore, highly desirable to identify the factors that are responsible for the formation of polymeric materials and how the formation of these heavy compounds can be minimized or prevented. A significant way to overcome this drawback is by judicious choice of the catalyst and reaction conditions. In this regard, a systematic study has been carried out on a titanium-based catalyst using tetrahydropyran (THP) and tetrahydrofuran (THF) as modifiers, and bromoethane as a new efficient accelerator in combination with triethylaluminum (Et_3Al) activator. The addition of bromoethane led to dramatic increases in the rate of reaction and yield, and remarkable decreases in the amounts of heavy and polymeric compounds. It is proposed that specific weak coordination of the halide to the dimeric Et_3Al may result in breakage of the Et_3Al dimer and the release of monomeric Et_3Al . The latter is more reactive than Et_3Al dimer and leads to the facile generation of an increased number of the active metal sites that are responsible for the dimerization reaction. Finally, the catalytic performance of the novel homogeneous system [titanium tetrabutoxide $\text{Ti}(\text{OC}_4\text{H}_9)_4/\text{THP}/\text{Et}_3\text{Al}/\text{bromoethane}$] has been examined under various operating conditions.

Keywords: Ethylene dimerization, Heavy Compounds, THP, Promoter, Bromoethane

1. Introduction

One of the strategic trends in petrochemistry is the development of processes for the production of Linear Alpha Olefins (LAOs) through the oligomerization of ethylene. LAOs are of very versatile intermediates for

the production of co-polymers (1-C₄ to C₈), plasticizer alcohols (1-C₆ to 1-C₁₀) detergents and synthetic lubricants (C₁₂ to C₁₄) [1, 2]. 1-Butene is the first member of LAOs, and can be converted into products such as poly(1-butene), butylene oxide, and

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valeraldehyde. The main application of 1-butene is as a co-monomer with ethylene for the production of linear low-density polyethylene (LLDPE) and high-density polyethylene (HDPE). Selective dimerization or oligomerization of ethylene have been considered as economic routes for 1-butene production. However, due to the wide range of products associated with ethylene oligomerization and the limited market for some of these products, ethylene dimerization to 1-butene appears to be a more attractive option for 1-butene production [3, 4].

The selective ethylene dimerization reaction uses a homogeneous catalytic system based on titanium tetrabutoxide ($\text{Ti}(\text{OC}_4\text{H}_9)_4$)/triethylaluminum (Et_3Al)/modifier (electron donor compound) [1, 5]. $\text{Ti}(\text{OC}_4\text{H}_9)_4$ is the main catalyst [6]. Et_3Al is an activator or co-catalyst and plays the following multiple roles [6]:

- 1) The release of free coordination sites in the titanate complex.
- 2) The withdrawal of electron density from around the titanium metal center.
- 3) The generation of one or more Ti-C bonds by exchange.

On the basis of previously reported studies, ethylene dimerization in the presence of a titanium-based catalyst appears to proceed by a mechanism involving the complexation of two molecules of ethylene on a titanium atom to afford a $\text{Ti}(\text{IV})$ cyclopentane intermediate species. This is subsequently converted to a π -bonded 1-butene complex by an intramolecular β -H transfer, and finally Ti species are regenerated [6]. This mechanism has been shown in Fig. 1.

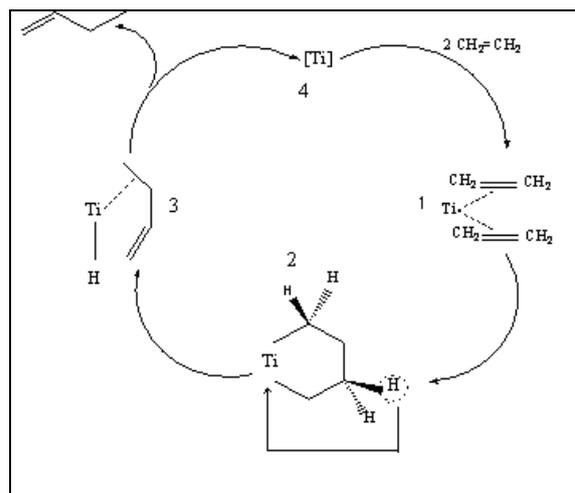


Figure 1. Schematic representation of the cyclic intermediate mechanism

Ziegler-type catalysts based on titanium are primarily known for their ability to polymerize ethylene to high molecular weight materials. This reaction is almost inhibited by adding a modifying agent to the catalytic formula to stabilize the $\text{Ti}(\text{IV})$ complex that is responsible for the production of 1-butene [6, 7]. Indeed, the catalyst modifiers (electron donor ligands) are Lewis bases or polar organic compounds (such as tert-phosphine, phosphite, amine, and cyclic ether), which, when added to the catalyst system, provide better selectivity for the desired reaction. The modifiers influence the mode of linkage of ethylene molecules and inhibit the formation of high molecular weight polymers. Several studies were conducted to elucidate the necessary characteristics of these ligands to catalyze the selective dimerization [4, 6, 7].

Promoters, which are almost always halide compounds, have been widely studied in the tri- and tetramerization of ethylene for the production of 1-hexene and 1-octene, respectively [8–11]. These promoters play an important role in assisting the central metal

of the relevant catalyst system to achieve high selectivity in favor of formation of the desired product and high catalytic activity [11]. However, to the best of our knowledge, there has been no report on their use in the homogeneous ethylene dimerization reaction. In our previous paper, 1,2-dichloroethane (EDC) was introduced as a suitable vicinal dichloro compound to promote the ethylene dimerization reaction for the production of 1-butene [12].

In the present research, we first comprised the effect of two modifiers i.e. tetrahydropyran (THP) and tetrahydrofuran (THF) on the catalyst performance. The experimental results showed that ethylene conversion, selectivity in favor of 1-butene formation, and yield of reaction were all higher for the catalyst system containing THP compared to that containing THF. We then found that the addition of bromoethane boosted the activity of the modified catalyst and increased the rate and the yield of the reaction. Finally, performance of the novel homogeneous $[\text{Ti}(\text{OC}_4\text{H}_9)_4/\text{THP}/\text{Et}_3\text{Al}/\text{bromoethane}]$ catalytic system was investigated under various operating conditions and the optimum values of the relevant parameters were determined.

2. Experimental

2-1. Materials and instruments

THF, THP, and bromoethane were purchased from Merck. Et_3Al was obtained from Crompton Chemicals and was diluted with heptane to obtain a 1 M solution before use. *n*-Heptane was dried over pre-activated molecular sieves (4 Å). Polymerization grade ethylene was supplied by Arak Petrochemical Company (ARPC) and was checked for purity by gas chromatography (GC).

Other chemicals were obtained commercially and were used as received.

Reactions were performed in a 1 L stainless steel Büchi pressure reactor, equipped with a jacket of circulating cooling fluid, a speed-controlled mechanical stirrer, a thermocoupler, gas inlet and outlet ports, and a liquid sampling port. The reactor was set up with a Büchi multi-channel data system (BDS MC) to display and record the temperature, pressure, and stirrer speed with reaction time.

GC/FID analyses were carried out on a Varian 3800 chromatograph using a CP Sil 8 capillary column (25 m × 0.53 mm). The column oven temperature of the GC was programmed to increase from 40 to 280 °C at a rate of 10°C/min.

Differential scanning calorimeter (DSC) analysis was performed on a METTLER TC11 for exact identification and characterization of the polymers formed in certain runs based on the thermal properties (i.e. melting point and degree of crystallinity). The DSC measurements were recorded during the second heating/cooling cycle with the heating rate of 10 °C/min under nitrogen atmosphere. The crystallinity (X_C) is defined as: $X_C = \Delta H_f / \Delta H_f^\circ$

where ΔH_f and ΔH_f° are the melting enthalpy of the polymer and the melting enthalpy of a polyethylene reference with 100% crystallinity. ΔH_f is acquired by integration of the area under the DSC heating curve and $\Delta H_f^\circ = 273 \text{ J/g}$.

2-2. Reaction procedure and product analysis

Before conducting a catalytic batch experiment, the reactor was heated to 100°C for an hour to eliminate traces of water, air,

and impurities. It was then cooled to ambient temperature and flushed with dry nitrogen for 30 minutes. Thereafter, the reactor was charged with 400 mL of *n*-heptane as solvent and was heated to the desired temperature. Ethylene was introduced into the reactor to the desired pressure. The temperature inside of the reactor was controlled using cooling fluid, if required. The calculated quantities of $Ti(OC_4H_9)_4$, THF or THP, bromoethane, and Et_3Al were immediately injected into the reactor. At this stage, agitation was started. The speed of the stirrer was initially set to 900 rpm. As the reaction progressed, a drop in ethylene pressure was observed. The speed of the stirrer was also reduced with increasing reaction time. It is noteworthy that due to the exothermic reaction the reaction temperature first increased slightly and was then reduced to the set level for the reaction. The volume of ethylene introduced through the inlet was measured using a Brooks mass-flow controller (MFC). The total volume of gaseous components was measured by means of a gas flowmeter. After 45 minutes, the reaction was terminated by stopping the stirrer and the mixture was quenched by adding methanol/HCl.

A gas sample was collected in a 150 mL stainless steel bomb and was analyzed by GC. A liquid sample was washed and purified with deionized water in order to remove catalyst, Et_3Al , alcohol, and HCl. Finally, a sample was analyzed by GC/FID. The polymers formed in certain runs were removed, washed with hexane, dried in a vacuum oven at 100 C, weighed, and ultimately characterized by DSC. The melting and degradation points were measured as 129 and 221°C, respectively,

and the degree of crystallinity was 57%. It was found that the polymers formed were linear low-density polyethylene (LLDPE).

The conversions and product selectivities were determined from the mass balance for ethylene consumption based on measured values from the MFC and GC analyses of the gaseous and liquid products, the liquid product weight, and the gas volume. The yield of the reaction was calculated as:

$$Yield(\%) = \frac{(ethylene\ conversion(\%)) \times (overall\ selectivity\ to\ 1-butene(\%))}{100}$$

3. Results and discussion

3-1. Comparison of two cyclic ethers as modifiers

The results showed that ethylene conversion, selectivity in favor of 1-butene formation, and yield of the reaction were all higher for the catalyst system containing THP compared to that containing THF (see Table 1). This can probably be attributed to the larger size of the THP ring compared with the THF ring (see Fig. 2), which leads to increased catalyst solubility and homogeneity [13, 14].

Also, as another proposal, the larger size of THP can inhibit trimerization and oligomerization of ethylene on the active center of the catalyst due to its spatial encumbrance around the central titanium.

3-2. The effect of bromoethane as promoter

In this research it was found that bromoethane, as a new promoter of the ethylene dimerization reaction, increased ethylene conversion and yield of the reaction, and improved overall selectivity in favour of 1-butene. Also, the addition of this promoter to $[Ti(OC_4H_9)_4/THP/Et_3Al]$ led to a decrease in the amount of by-products (see Fig. 3).

Table 1. Effects of two modifiers on the catalyst properties

Entry	Modifier	Modifier/Ti (mol/mol)	Conversion (%)	Overall selectivity to products (% wt)				PE (mg)	Yield (%)
				1-C ₄	C ₆₊	C ₈₊	≥C ₁₀₊		
1		1	68.88	70.22	27.16	1.82	0.80	60	48.37
2		2	70.31	71.74	26.10	1.45	0.71	50	50.44
3	THF	3	71.24	73.00	25.17	1.24	0.59	45	52.00
4		4	72.15	74.28	24.58	0.90	0.24	45	53.59
5		5	70.00	70.75	26.82	1.50	0.93	55	49.52
6		1	78.93	75.12	23.08	1.10	0.70	40	59.29
7		2	80.10	75.90	22.43	1.03	0.64	35	60.79
8	THP	3	81.22	77.18	21.38	0.86	0.58	30	62.68
9		4	80.14	76.26	22.24	0.90	0.60	30	61.11
10		5	79.33	73.45	25.00	0.95	0.60	40	58.27

Reaction conditions: reaction temperature: 50°C, ethylene pressure: 25 bar, Al/Ti=2.5, reaction time: 45 min, stirrer speed: 900 rpm, solvent: n-heptane.

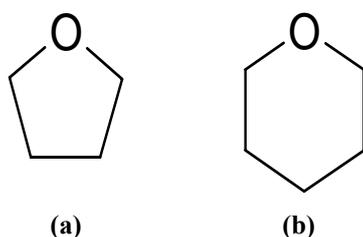


Figure 2. Schematic chemical structure of modifiers: (a) THF, (b) THP

As indicated in Fig. 3, an increase in the bromoethane/Ti molar ratio to 7 resulted in corresponding increases in the ethylene conversion and the overall selectivity in favor of 1-butene, and the yield. When the bromoethane/Ti molar ratio was 7, the conversions, the selectivities to 1-butene, and the yields of reaction were maximum values. However, when the bromoethane/Ti molar ratio was increased further, the values fell. The most probable explanation for this is that

any excess bromoethane may interfere with the formation of the active Ti species due to a coordinative loading of the active sites by more than one halide per metal atom, thus leading to the prevention of ethylene coordination [15].

Reaction conditions: Reaction temperature: 50°C, ethylene pressure: 25 bar, reaction time: 45 min, stirrer speed: 900 rpm, solvent: n-heptane, Ti/THP/Al molar ratio=1:3:2.5.

The mechanism by which promoters exert an effect on homogeneous titanium-based catalysts in the ethylene dimerization is still unclear. In our previous paper [12], we postulated several modes of action for EDC as a new promoter in the ethylene dimerization reaction. With reference to those proposals, the following rationale for the promoting effect of bromoethane is suggested.

Production of 1-Butene via Selective Ethylene Dimerization by Addition of Bromoethane as a New Promoter to Titanium-Based Catalyst in the Presence of Tetrahydropyran Modifier and Triethylaluminum Co-Catalyst

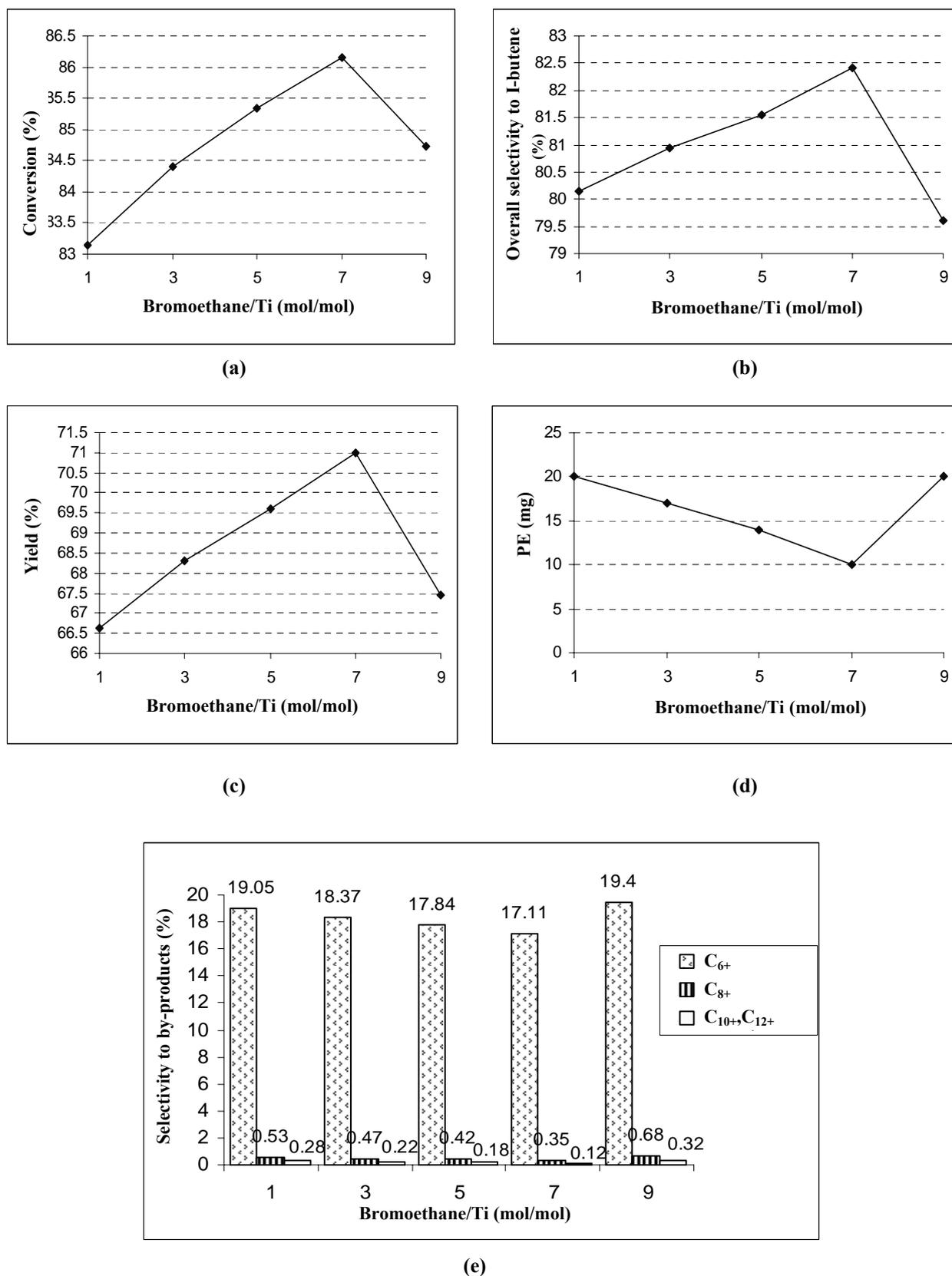


Figure 3. The effect of bromoethane on catalyst performance: (a) conversion, (b) overall selectivity to 1-butene, (c) yield, (d) weight of polyethylene and (e) selectivity to by-products

There is an effective interaction mode between bromoethane and the $[\text{Ti}(\text{OC}_4\text{H}_9)_4/\text{THP}/\text{Et}_3\text{Al}]$ catalyst system. In other words, the suitable coordination ability of bromoethane towards the central titanium of the five-membered Ti metallacyclic transition state may generate a specific structural arrangement of the catalyst system in the reaction medium. Therefore, the chemical micro-environment of the titanium center in the catalyst system is changed. This rearrangement results in the dimeric form of Et_3Al with two ethyl bridging bonds being transformed to monomeric Et_3Al in situ [8, 11]. This transformation is also redolent of the proposal of Christenson and co-workers [16], who suggested that the formation of monomeric Et_3Al by the decomposition of dimeric Et_3Al would be advantageous for the formation of pre-active sites, which are then converted to active species by further reaction with an excess of monomeric Et_3Al due to its better Lewis acid properties which ultimately leads to stabilization of titanium cationic complexes in a higher oxidation state. Since the catalyst system for ethylene dimerization is a dual-functional catalyst, monomeric Et_3Al can modify the spatial and electronic properties

of Ti active sites. Thereby, the dimerization component of the dual-functional catalyst is enhanced and the amounts of heavy and polymeric compounds are concomitantly decreased.

3-3. The effects of temperature, pressure, and Al/Ti ratio on catalyst performance

The conditions of the dimerization reaction influence performance of the catalyst employed and value of the polymer produced. The pendant conditions selected in our previous experiments did not seem to be fully appropriate for the selective ethylene dimerization with relevant catalyst system. Hence, a series of the systematic experiments was performed to investigate the effects of reaction temperature ($^{\circ}\text{C}$), ethylene pressure (bar), and Al/Ti (mol/mol) on the properties of the relevant catalyst system in detail in the Büchi reactor of our laboratory.

3-3-1. The effect of reaction temperature on catalyst performance

The effects of reaction temperature on ethylene conversions, overall selectivities in favor of the products, yields and weights of polymer have been investigated. The results are shown in Table 2.

Table 2. Effect of reaction temperature on catalytic properties

Entry	T ($^{\circ}\text{C}$)	Conversion (%)	Overall selectivity to products (%)				PE (mg)	Yield (%)
			1-C ₄	C ₆₊	C ₈₊	$\geq\text{C}_{10+}$		
1	50	86.00	82.10	17.37	0.38	0.15	15	70.60
2	55	87.82	82.77	16.79	0.32	0.12	12	72.69
3	60	86.14	81.63	17.78	0.41	0.18	20	70.31
4	65	85.27	79.34	19.76	0.65	0.25	40	67.65

Reaction conditions: ethylene pressure: 24 bar, reaction time: 45 min, stirrer speed: 900 rpm, solvent: n-heptane, Ti (IV)/THP/TEA/bromoethane molar ratios: 1:3:4:7.

It was observed that ethylene conversion and overall selectivity for 1-butene initially increased with temperature and reached a maximum at around 55 °C. When the reaction temperature was increased from 55 to 65 °C, ethylene conversion and overall selectivity in favor of 1-butene decreased and the weight of the polymer increased. The decline in ethylene conversion may be attributed to a decrease in monomer solubility at higher reaction temperature [6]. The poor selectivity for 1-butene at higher temperatures may also be ascribed to a higher deactivation rate of active dimerization species, which in turn leads to the generation of oligomeric and heavy compounds [15, 17].

3-3-2. The effect of ethylene pressure on catalyst performance

The effects of reaction pressure on ethylene conversions, overall selectivities in favor of the products, yields, and weights of polymer are reported in Table 3.

Since the relevant reaction is conducted as a bubbling-type process, conversion is directly related to the pressure [3, 5]. As indicated in Table 3, an increase in the ethylene pressure led to an increase in ethylene conversion. Also, both the overall selectivity for 1-butene

and the yield of the reaction were slightly increased. This observation could be interpreted as an indication that higher pressure ensures higher activity of the catalyst due to improved diffusion of the monomer through the reaction mixture to the active dimerization sites [6]. Indeed, due to the fast phase change of ethylene to solvent in the beginning of individual experiments, gas-to-liquid mass transfer rate is greater than the intrinsic reaction rate which means reaction rate is the limiting step. Therefore, it can be inferred that in the higher pressures, ethylene solubility (as molar concentration) in n-heptane and consequently ethylene conversion are increased [17, 18]. The formation of heavy compounds was slightly decreased with increasing pressure in the pressures investigated in this study.

3-3-3. The effect of Al/Ti molar ratio on catalyst performance

The effects of the Al/Ti molar ratio on ethylene conversions, overall selectivities in favor of the products, weights of polymer, and yield of the reaction have also been investigated. The results are shown in Table 4.

Table 3. Effect of reaction pressure on catalytic properties

Entry	P (bar)	Conversion (%)	Overall selectivity to products (%)				PE (mg)	Yield (%)
			1-C ₄	C ₆₊	C ₈₊	≥C ₁₀₊		
1	12	84.52	80.33	18.97	0.46	0.24	25	67.89
2	16	85.83	80.88	18.46	0.44	0.22	22	69.42
3	20	86.95	81.22	18.18	0.39	0.21	20	70.62
4	24	87.78	82.69	16.72	0.41	0.18	15	72.58
5	28	88.00	82.35	16.95	0.52	0.18	18	72.47

Reaction conditions: reaction temperature: 55 °C, reaction time: 45 min, stirrer speed: 900 rpm, solvent: n-heptane, Ti (IV)/THP/TEA/bromoethane molar ratios: 1:3:4:7.

Table 4. Effect of Al/Ti molar ratios on catalytic peroperties

Entry	Al/Ti (mol/mol)	Conversion (%)	Overall selectivity to products (%)				PE (mg)	Yield (%)
			1-C ₄	C ₆₊	C ₈₊	≥C ₁₀₊		
1	3	86.38	82.63	16.82	0.34	0.21	15	71.37
2	4	87.80	82.77	16.74	0.30	0.19	20	72.67
3	5	88.73	81.44	17.60	0.62	0.34	25	72.26
4	6	89.12	77.52	20.62	1.18	0.68	50	69.10

Reaction conditions: reaction temperature: 55 °C, initial ethylene pressure: 24 bar, reaction time: 45 min, stirrer speed: 900 rpm, solvent: n-heptane, Ti (IV)/THP/bromoethane molar ratios: 1:3:7.

The Al/Ti molar ratio is recognized as an important parameter in the dimerization of ethylene to 1-butene [6]. As can be seen in Table 4, with increasing Al/Ti molar ratio, ethylene conversion was increased. When the Al/Ti ratio was increased to 4, the overall selectivity for 1-butene was increased, but when the Al/Ti molar ratio was further increased, the overall selectivity for 1-butene and the yield of the reaction were decreased and the weight of the polymer was remarkably increased. This may be attributed to a rapid deactivation process of the catalyst due to the presence of free Et₃Al at high Al/Ti molar ratios. On the other hand, at high Al/Ti molar ratios, Ti(III) complexes are stabilized by reduction of Ti(IV) species [19, 20]. This causes further formation of polymer and heavy compounds.

As mentioned in the previous paragraph, an excess of Et₃Al co-catalyst participates in the deactivation of the active sites and influences the lifetime of the catalyst [21]. However, the metal center of the catalyst in every run can evidently be stabilized and promoted by the introduction of THP and bromoethane which form complexes with Et₃Al. Therefore, depending on the Et₃Al concentration, it is necessary to maintain a balance between the amount of Et₃Al and titanium precursor/additive.

4. Conclusions

In this research, the effect of two modifiers on the behavior of the catalytic system of the ethylene dimerization reaction was investigated. The experimental results showed the performance of THP was better than THF. The addition of bromoethane, a new promoter for the dimerization reaction, significantly enhanced the reaction rate, ethylene conversion, and yield. Concomitantly, the amounts of oligomeric compounds and polymer were decreased. Therefore, a novel four-component homogeneous [Ti(OC₄H₉)₄/THP/Et₃Al/ bromoethane] catalyst system was introduced. This catalytic system displayed high activity in ethylene dimerization with good selectivity in favor of 1-butene. Finally, the effects of reaction temperature, ethylene pressure, and Al/Ti molar ratio were scrutinized on the aforesaid catalyst system.

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