

[Ti(OC₄H₉)₄/2,5-Dimethoxytetrahydrofuran/TEA/Ethylene Chlorobromide] as a Novel Homogeneous Catalyst System Effective for the Ethylene Dimerization Reaction

Seyed Hamed Mahdaviani, Davood Soudbar, Matin Parvari *

Abstract—In the present research, the titanium-catalyzed ethylene dimerization and more specifically, the concomitant by-products and polymer formation have been studied in the presence of 2,5-dimethoxytetrahydrofuran as an electron donor compound in the combination with triethylaluminum (TEA) as activator. Then, we added ethylene chlorobromide as a new efficient promoter to the relevant catalyst system. Finally, the behavior of novel homogeneous [Titanium tetrabutoxide (Ti(OC₄H₉)₄)/2,5-dimethoxytetrahydrofuran/TEA/ethylene chlorobromide] was investigated in the various operating conditions for the optimum production of 1-butene. In the optimum conditions, a very high ethylene conversion (almost 90.77 %), a relative high selectivity to 1-butene (79.00 %), yield of reaction equal to 71.70 % and a significant productivity (turnover frequency equal to 1370 h⁻¹) were achieved.

Keywords—Ethylene dimerization, 2,5-dimethoxytetrahydrofuran, ethylene chlorobromide, polymeric compounds

I. INTRODUCTION

THE dimerization or oligomerization of ethylene has been considered as economic routes for 1-butene production. However, due to the wide range of products associated with ethylene oligomerization and market limitation for some of these products, ethylene dimerization to 1-butene appears to be a more attractive option for the 1-butene production [1]-[3]. The selective ethylene dimerization reaction uses a homogeneous catalytic system based on Titanium tetrabutoxide (Ti(OC₄H₉)₄)/Triethylaluminum (TEA)/modifier [1], [4]. Ti(OC₄H₉)₄ is the main catalyst [2]. TEA is an activator or co-catalyst. The multiple roles plays by the TEA in the dimerization reaction are [2]:

1) The release of free coordination sites in the titanate complex.

2) The withdrawal of the electron density surrounding the titanium metal center.

3) The generation of one or more Ti-C bonds by exchanging its ethyl groups with the butoxide groups of titanate complex.

Ziegler-type catalyst based on titanium is primarily known for their ability to polymerize ethylene to high molecular weight materials. This reaction is inhibited almost by adding a modifying agent to catalyst to stabilize the Ti(IV) complex which is responsible for production of 1-butene [2], [5].

Promoters which almost are halide compounds have been widely studied in tri- and tetramerization of ethylene for production of 1-hexene and 1-octene, respectively [6]-[9], [12]. The promoters play an important role to assist central metal of pertinent catalyst system to achieve high desired product formation selectivity and highly catalytic activity [6]. Previously Y. Yang et al. [8] and H. Chen et al. [9] reported that the addition of geminal chloro compounds and halides to catalyst systems at ethylene trimerization and tetramerization reactions resulted in significant improvement of selectivity to 1-hexene and 1-octene, respectively. However, despite these intense research works, the reports on halides used as the activity promoters for titanium-based catalysts in the dimerization of ethylene are very few.

In the present work, first we used an electron donor compound such as 2,5-dimethoxytetrahydrofuran as modifier and investigated the effect of molar ratios of 2,5-dimethoxytetrahydrofuran/Ti on the total efficiency of reaction. Then, we found that the addition of ethylene chlorobromide could boost the activity of the relevant catalyst and also could increase the overall selectivity to 1-butene and yield of reaction. Therefore, we investigated the influence of molar ratios of ethylene chlorobromide/Ti on the performance of catalyst. Finally, a series of the systematic experiments were undertaken to examine the effect of reaction temperature, ethylene pressure and the molar ratio of TEA/Ti on the catalytic properties of the novel homogeneous [Ti(OC₄H₉)₄/2,5-dimethoxytetrahydrofuran/TEA/ethylene chlorobromide] in detail.

II. EXPERIMENTAL

A. Materials and Instruments

2,5-dimethoxytetrahydrofuran and ethylene chlorobromide

Seyed Hamed Mahdaviani was with the Chemical Engineering Department, Iran University of Science and Technology (IUST), Tehran, Iran. He is now with group of the catalyst and polymer of Research and Development Center (R&D division), Arak Petrochemical Company (ARPC), Arak, Iran (e-mail: hamed_mahdaviani@chemeng.iust.ac.ir).

Davood Soudbar is with group of the catalyst and polymer of Research and Development Center (R&D division), Arak Petrochemical Company (ARPC), Arak, Iran (e-mail: dsoudbar@arpc_ir.net).

Matin Parvari is with the Chemical Engineering Department, Iran University of Science and Technology (IUST), Tehran, Iran. (Phone: +98 (21) 73 91 27 55, Fax: +98 (21) 77 24 04 95, e-mail: parvari@iust.ac.ir).

were purchased from Merck. TEA was obtained from Crompton Chemicals and was diluted to heptane to obtain a 37.5 gr/lit solution before use. n-heptane was dried over preactivated molecular sieve (4 Å). Also, 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 used as received.

A 1-L stainless steel buchhi pressure reactor, equipped with a jacket circulating cooling fluid, a speed-controlled mechanical stirrer, a thermocouple, gas inlet and outlet ports and a liquid sampling port was used. Meanwhile, the reactor was set up with a buchhi 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 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.

B. Ethylene dimerization runs 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. Then, it was cooled to ambient temperature and was swept with dry nitrogen for 30 minutes. Afterwards, the reactor was charged with 400 ml n-heptane as solvent. Subsequently, the reactor was heated to the desired temperature. The ethylene was introduced into the reactor to the desired pressure. The inside temperature of the reactor was controlled using cooling fluid, if required. In A typical run, 1 mL $\text{Ti}(\text{OC}_4\text{H}_9)_4$ (1 mL; content of 2.92 mmol Ti), 2,5-dimethoxytetrahydrofuran (1.14 mL; 2,5-dimethoxytetrahydrofuran/Ti molar ratio of 3), a 37.5 g/lit solution of TEA (44.5 mL; Al/Ti molar ratio of 5), and ethylene chlorobromide (0.73 ml; ethylene chlorobromide/Ti molar ratio of 3) were immediately injected into the reactor. At this moment, 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 reaction time. It is noteworthy that the internal temperature of the reactor was adjusted to that of 4-6 °C lower than the desired value because of the highly exothermic character of ethylene dimerization. The volume of the inlet ethylene was measured using a Brooks Mass-Flow Controller (MFC). Also, the total volume of gaseous components was measured by means of a gas flowmeter. 30 minutes later, the reaction was terminated by stopping the stirrer and was quenched by adding methanol/HCl.

A gas sample was taken into 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, TEA, alcohol and HCl. Finally, a sample was analyzed with 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 differential scanning

calorimetry (DSC). Note that the melting and decomposition points were 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 gas volume. The yield of the reaction was calculated as:

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

Also, TOF was expressed as:

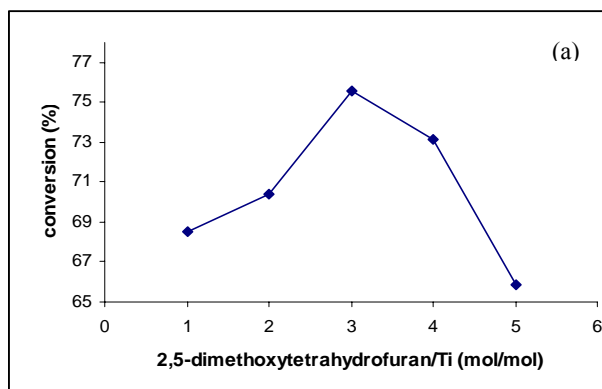
$$\text{TOF (h}^{-1}\text{)} = \frac{\text{moles of converted ethylene}}{(\text{mole of Ti}) \times (\text{reaction time})} \quad (2)$$

III. RESULTS AND DISCUSSION

A. The effect of 2,5-dimethoxytetrahydrofuran on catalytic performance of $\text{Ti}(\text{OC}_4\text{H}_9)_4/\text{TEA}$

Fig. 1 represents the effect of 2,5-dimethoxytetrahydrofuran on the properties of $\text{Ti}(\text{OC}_4\text{H}_9)_4/\text{TEA}$ catalyst system.

The results show that 2,5-dimethoxytetrahydrofuran is a suitable modifier for ethylene dimerization. It is proposed that the high donority of the methoxy fragments in the 2,5-dimethoxytetrahydrofuran leads to the suitable coordination of modifier on the central titanium and generally a well-defined complex with ethylene in a head-on orientation toward the metal center is formed. On the other hands, electronic nature of the methoxy fragments can modify the spatial and electronic properties Ti active sites leading to concomitant generation of of an increased number of these active species [10], [11]. This causes the catalyst performance is improved.



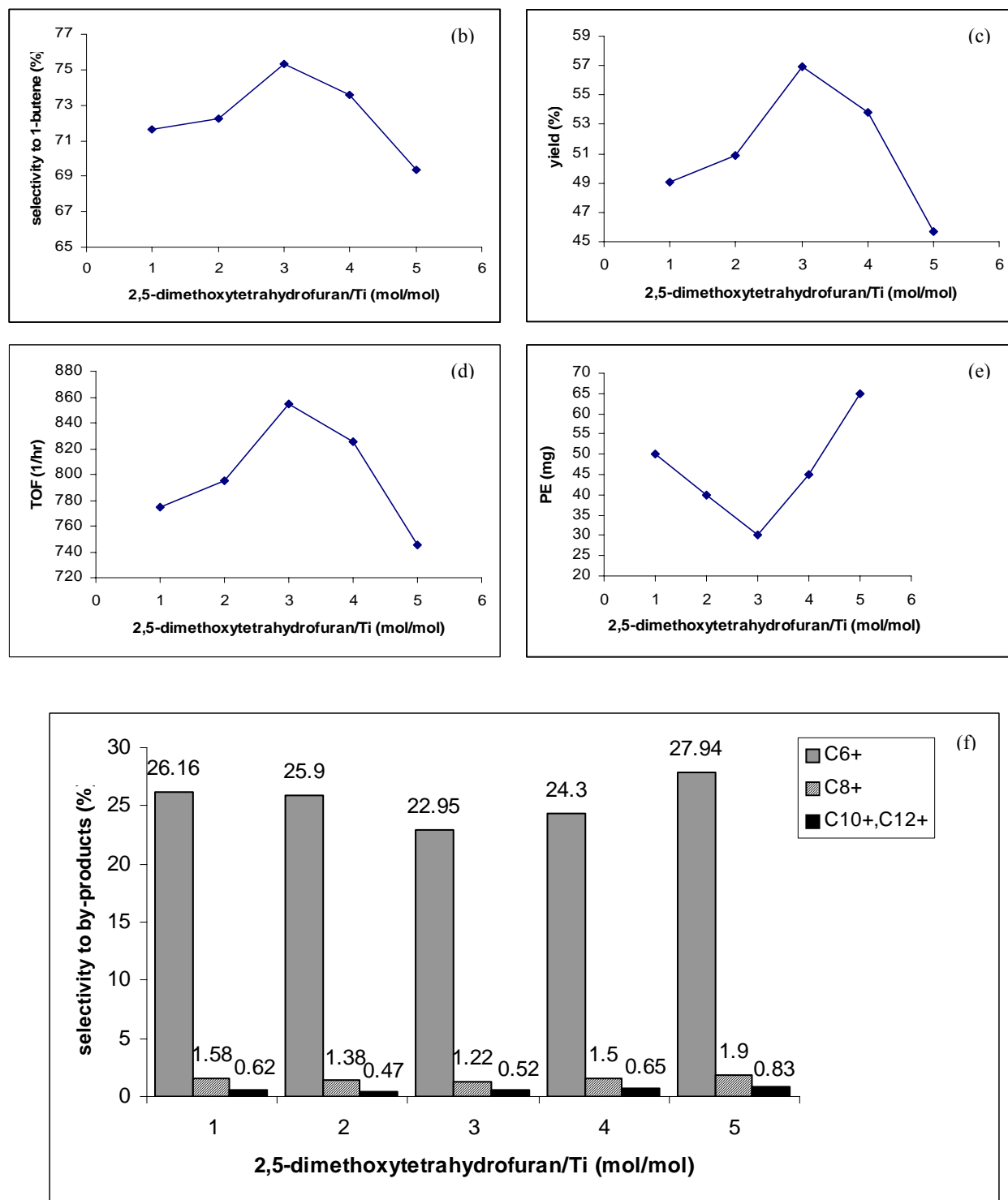


Fig. 1 Effects of molar ratios of 2,5-dimethoxytetrahydrofuran/Ti on catalyst performance: (a) conversion, (b) overall selectivity for 1-butene, (c) yield, (d) TOF, (e) weight of polymer, and (f) selectivity to by-products. Reaction conditions: reaction temperature: 50 °C, initial pressure of ethylene: 15 bar, reaction time: 45 min, solvent: 400 mL n-hexane, Al/Ti=3 (molar ratio)

B. The effect of ethylene chlorobromide as promoter

In this research, we found that ethylene chlorobromide as a new promoter at ethylene dimerization reaction could increase ethylene conversion, yield of reaction, TOF and could improve overall selectivity to 1-butene. Also, the addition of this promoter to $[\text{Ti}(\text{OC}_4\text{H}_9)_4/2,5\text{-dimethoxytetrahydrofuran/TEA}]$ led to the decrease of by-products. The results are listed in Table I.

As reported in Table I, the increase of ethylene chlorobromide/Ti molar ratio to 3 resulted in the relative increase in ethylene conversion, overall selectivity to 1-butene, yield and TOF to a maximum value. However, when the ethylene chlorobromide/Ti molar ratio was further increased, the values fell. This can be probably interpreted that any excess ethylene chlorobromide may poison active titanium centers slightly. Thereupon, Ti(III) species insoluble in solvent are formed and side reactions (ethylene oligomerization reactions) are occurred [12].

The mechanism by which promoters exert an effect on titanium-based catalyst has not been clear up to now. We suggest the following rationale for the promoting effect of ethylene chlorobromide:

Since ethylene chlorobromide (1-bromo-2-chloroethane) is a vicinal halide compound, there is a matching interaction between halogen groups of the promoter with titanocyclopentane intermediate species which leads to the regulation of the coordination fashion of titanium centers in the catalytic cycle and the stabilization of the catalyst's active sites more suitable for the ethylene dimerization [6]. In other words, the suitable coordination ability of ethylene chlorobromide with central titanium of five-membered Ti metallacyclic transition state may generate a specific structural arrangement of the catalyst system in the reactional medium. Therefore, the chemical micro-surroundings of titanium center in catalyst system is changed. This rearrangement causes that the dimeric form of TEA with two ethyl bridge bonds is transformed to monomeric TEA in-situ [6], [8]. The decomposition of TEA dimer to monomeric form is expected to be advantageous for the formation of pre-active sites which finally leads to the stabilization of titanium cationic complex in a higher oxidation state [13]. Monomeric TEA can modify spatial and electronic properties of Ti active sites and finally heavy and polymeric compounds were

The conditions of the dimerization reaction influence the performance of the catalyst employed and the value of the polymer produced. We investigated the effect of addition of a modifier and a promoter and obtained their optimum molar ratios to catalyst in the pendant conditions selected at our previous experiments. In the following steps, optimum operating conditions, devoting particular attention to reaction temperature, ethylene pressure and molar ratio of Al/Ti were determined.

C. The effect of reaction temperature on catalyst performance

The effects of reaction temperature on ethylene conversions, overall selectivities to total products, yields, productivities (TOF) and weight of polymers were investigated. The results are shown in Table II.

It was observed that ethylene conversion and overall selectivity to 1-butene initially increased with temperature and reached a maximum around 55 °C. As reaction temperature increased from 55 to 65 °C, overall selectivity to 1-butene decreased and weight of polymer increased. The decline in ethylene conversion may be attributed to a decrease in monomer solubility at higher reaction temperature. Also, poor selectivity to 1-butene at higher temperature could be ascribed to the higher deactivation rate of active dimerization species which led to generation of oligomer and heavy compounds [2], [12].

D. The effect of reaction pressure on catalyst performance

The effects of reaction pressure on ethylene conversions, overall selectivities to total products, yields, productivities (TOF) and weight of polymers are reported in Table III.

As demonstrated in Table III, the increase of the ethylene pressure led to the increase of ethylene conversion. Also, yield of reaction were slightly increased. This observation could be interpreted as an indication that higher pressure ensures higher activity of catalyst due to improved diffusion of the monomer thought the reaction mixture to the active dimerization sites [2], [12]. The further increase of reaction pressure had a detrimental effect on the overall selectivity to 1-butene (see entry 4 in Table III). The decrease selectivity for 1-butene is probably due to repetitive co-dimerization of ethylene with produced 1-butene, giving rise to the formation of higher oligomers.

TABLE I
EFFECT OF PROMOTER ON CATALYST PROPERTIES

| Entry | Promoter | Promoter/Ti (mol/mol) | Conversion (%) | Overall selectivity to products (% wt) | | | | PE (mg) | Yield (%) | TOF (h ⁻¹) |
|-------|------------------------|--------------------------|-------------------|---|-----------------------------|-----------------------------|-------------------------------|------------|--------------|---------------------------|
| | | | | 1-C ₄ | C ₆ ⁺ | C ₈ ⁺ | ≥C ₁₀ ⁺ | | | |
| 1 | Ethylene chlorobromide | 1 | 79.94 | 77.10 | 21.70 | 0.92 | 0.28 | 40 | 61.63 | 900 |
| 2 | | 3 | 83.82 | 78.16 | 20.87 | 0.77 | 0.20 | 30 | 65.51 | 1300 |
| 3 | | 5 | 81.37 | 77.00 | 21.75 | 0.95 | 0.30 | 35 | 62.65 | 1100 |
| 4 | | 7 | 78.68 | 75.10 | 23.25 | 1.24 | 0.41 | 45 | 59.10 | 890 |

Reaction conditions: reaction temperature: 50 °C, ethylene pressure: 15 bar, reaction time: 45 min, solvent: 400 mL n-heptane, Ti(IV)/2,5-dimethoxytetrahydrofuran/Al molar ratios=1:3:3

TABLE II
EFFECT OF TEMPERATURE ON CATALYST PROPERTIES

| Entry | T (°C) | Conversion (%) | Overall selectivity to products (% wt) | | | | PE (mg) | Yield (%) | TOF (h ⁻¹) |
|-------|-----------|-------------------|---|------------------|------------------|--------------------|------------|--------------|---------------------------|
| | | | 1-C ₄ | C ₆ + | C ₈ + | ≥C ₁₀ + | | | |
| 1 | 50 | 88.68 | 77.56 | 21.32 | 0.87 | 0.25 | 30 | 68.78 | 1335 |
| 2 | 55 | 90.77 | 79.00 | 20.20 | 0.60 | 0.20 | 30 | 71.71 | 1370 |
| 3 | 60 | 89.20 | 77.35 | 21.45 | 0.90 | 0.30 | 35 | 68.99 | 1345 |
| 4 | 65 | 88.00 | 75.84 | 22.51 | 1.24 | 0.41 | 55 | 66.74 | 1325 |

Reaction conditions: ethylene pressure: 22 bar, reaction time: 45 min, solvent: 400 mL n-heptane, Ti(IV)/2, 5-dimethoxytetrahydrofuran/Al /ethylene chlorobromide molar ratios=1:3:4:3.

TABLE III
EFFECT OF PRESSURE ON CATALYST PROPERTIES

| Entry | P (bar) | Conversion (%) | Overall selectivity to products (% wt) | | | | PE (mg) | Yield (%) | TOF (h ⁻¹) |
|-------|------------|-------------------|---|------------------|------------------|--------------------|------------|--------------|---------------------------|
| | | | 1-C ₄ | C ₆ + | C ₈ + | ≥C ₁₀ + | | | |
| 1 | 10 | 86.65 | 77.32 | 21.56 | 0.90 | 0.22 | 20 | 67.00 | 655 |
| 2 | 16 | 88.41 | 78.21 | 20.83 | 0.72 | 0.24 | 25 | 69.14 | 1000 |
| 3 | 22 | 90.22 | 78.85 | 20.25 | 0.66 | 0.24 | 30 | 71.14 | 1360 |
| 4 | 28 | 91.00 | 77.90 | 20.80 | 1.00 | 0.30 | 50 | 70.90 | 1880 |

Reaction conditions: reaction temperature: 55 °C, reaction time: 45 min, solvent: 400 mL n-heptane, Ti(IV)/2, 5-dimethoxytetrahydrofuran/Al/ethylene chlorobromide molar ratios=1:3:4:3.

TABLE IV
EFFECT OF AL/Ti ON CATALYST PROPERTIES

| Entry | Al/Ti (mol/mol) | Conversion (%) | Overall selectivity to products (% wt) | | | | PE (mg) | Yield (%) | TOF (h ⁻¹) |
|-------|--------------------|-------------------|---|------------------|------------------|--------------------|------------|--------------|---------------------------|
| | | | 1-C ₄ | C ₆ + | C ₈ + | ≥C ₁₀ + | | | |
| 1 | 2 | 83.00 | 78.00 | 21.00 | 0.80 | 0.20 | 20 | 64.74 | 1250 |
| 2 | 3 | 85.85 | 78.50 | 20.60 | 0.70 | 0.20 | 25 | 67.39 | 1295 |
| 3 | 4 | 90.90 | 78.90 | 20.30 | 0.60 | 0.20 | 30 | 71.72 | 1370 |
| 4 | 5 | 92.41 | 77.10 | 21.60 | 1.00 | 0.30 | 45 | 71.25 | 1390 |
| 5 | 6 | 92.60 | 74.50 | 23.60 | 1.25 | 0.65 | 65 | 69.00 | 1395 |

Reaction conditions: reaction temperature: 50 °C ethylene pressure: 22 bar, reaction time: 45 min, solvent: 400 mL n-heptane, Ti(IV)/2,5-dimethoxytetrahydrofuran/ethylene chlorobromide molar ratios=1:3:3.

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

The effects of Al/Ti molar ratios on ethylene conversions, overall selectivities to total products, weight of polymers, yield of reaction and productivities (TOF) were investigated. The results are shown in Table IV. The molar ratio of Al/Ti is recognized as an important parameter in the dimerization of ethylene to 1-butene [2], [3]. As seen in Table IV, with increasing Al/Ti molar ratio, ethylene conversion was increased. In addition, with the increase of Al/Ti to 4, overall selectivity to 1-butene was increased but when the molar ratio of Al/Ti was further increased, the overall selectivity to 1-butene and yield of reaction were decreased and the weight of polymer was remarkably increased. This was expected that due to the presence of free AlEt₃ at high Al/Ti molar ratios, a rapid deactivation process of catalyst might be occurred [14].

On the other hand, at high Al/Ti molar ratio Ti(III) complex was stabilized and was formed. This causes which the polymer and heavy compounds are further formed [14].

IV. CONCLUSION

In this research, a novel four-component homogeneous [Ti(OC₄H₉)₄/2,5-dimethoxytetrahydrofuran/TEA/Ethylene chlorobromide] catalyst system was introduced. The aforesaid catalytic system displayed high activities in ethylene dimerization with good selectivities to 1-butene. Ethylene chlorobromide, a new promoter for dimerization of reaction, could significantly enhance ethylene conversion, 1-butene formation selectivity, yield and TOF. Also, oligomeric compounds and polymer were remarkably decreased.

REFERENCES

- [1] G. P. Blov, P. E. Mathkovsky, "Process for the production of higher α -olefins", Petrol. Chem., vol. 50, 2010, pp. 283-289.

- [2] A. W. Al-Sadoun, "Dimerization of ethylene to butene-1 catalyzed by Ti (OR')₄-AlR₃", Appl. Catal. A: General, vol. 105, 1993, pp. 1-40.
- [3] A. M. Al-Jaralleh, J. A. Anabtawi, M. A. B. Siddiqui, A. M. Aitani, "Ethylene dimerization and oligomerization to butene-1 and linear alpha-olefins; A review of catalytic system and processes", Catal. Today, vol. 14, 1992, pp. 1-124.
- [4] V. I. Zhukov, G. V. Val kovich, B. N. Shorik, Yu. M. Petrov., G. P. Blov, "Selective dimerization of ethylene to butene-1 under the conditions of industrial process, I. Influence of temperature and pressure on the rate of the process in a bubbling type reactor", Russ. J. Appl. Chem., vol. 80, 2007, pp. 1195-1200.
- [5] S. M. Pillai, G. L. Tembe, M. Ravindranathan, S. Sivaram, "Dimerization of ethylene to 1-butene catalyzed by titanium alkoxide-trialkylaluminum system", Ind. Eng. Chem. Res., vol. 27, 1988, pp. 1971-1977.
- [6] H. K. Leo, D. G. Li, S. Li, "The effect of halide and the coordination geometry of chromium center in homogeneous catalyst system for ethylene trimerization", Mol. Catal. A: Chemical, vol. 221, 2004, pp. 9-17.
- [7] H. Mahomed, A. Bollmann, J. T. Dixon, V. Gokuln, L. Griesel, C. Grove, F. Hess, H. Maumela, L. Pepler, "Ethylene trimerization catalyst based on substituted cyclopentadienes", Appl. Catal. A: General, vol. 193, 2003, pp. 355-359.
- [8] Y. Yang, H. Kim, J. Lee, H. Paik, H. G. Jang, "Roles of chloro compound in homogeneous [Cr(2-ethylhexanoate)₃/2,5-dimethylpyrrole/triethylaluminum/chloro compound] catalyst system for ethylene trimerization", Appl. Catal. A: General, vol. 193, 2000, pp. 29-38.
- [9] H. Chen, X. Liu, W. Hu, Y. Ning, T. Jian, "Effects of halide in homogeneous Cr(III)/PNP/MAO catalytic systems for ethylene tetramerization toward 1-octene", Mol. Catal. A: Chemical, vol. 270, 2007, pp. 273-277.
- [10] F. A. Carey, R. J. Sunderberg, "Advanced Organic Chemistry", 3rd ed. part A: structure and mechanisms, Plenum Press, New York, 1990, ch. 3, p. 144.
- [11] E. Killian, K. Blann, A. Bollmann, J. T. Dixon, S. Kuhlmann, M. C. Maumela, H. Maumela, D. H. Morgan, P. Nongodlwana, M. J. Overett, M. Pretorius, K. Höfener, P. Wasserscheid, "The use of bis(diphenylphosphino) amines with N-aryl functionalities in selective ethylene tri- and tetramerisation", Mol. Catal. A: Chemical, vol. 270, 2007, pp. 214-218.
- [12] H. T. Jiang, Y. Ning, B. Zhang, J. Li, G. Wang, J. Yi, Q. Huang, "Preparation of 1-octene by the selective tetramerization of ethylene", Mol. Catal. A: Chemical, vol. 259, 2006, pp. 161-165.
- [13] C. P. Christenson, J. A. May, L. E. Freyer in R. P. Quirk (editor), "Transition metal catalyzed polymerization: alkenes and dienes", Harwood Academic, New York, 1983, p. 763.
- [14] T. W. Woo, S. I. Woo, "Kinetics study of ethylene dimerization catalyzed over Ti (O-nC₄H₉)₄/AlEt₃", J. Catal., vol. 132, 1991, pp. 68-78.