Effect of Two Halohydrocarbons as New Promoters Suitable for Titanium-catalyzed Ethylene Dimerization Toward 1-butene

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Abstract—**This paper deals with the study related to the suitability of two new promoters for ethylene dimerization to 1-butene which is a potential raw material for polyethylene synthesis and other applications. In this study, the effect of two haloethanes has been carried out on a Ti-based homogeneous catalyst in combination with a cyclic ether as modifier and in the presence of triethylaluminum (TEAl) activator. The experimental results showed that the effect of chloroethane on ethylene conversion, overall selectivity to 1-butene, yield of reaction and productivity (turnover frequency) was better than bromoethane. The specific weak coordination of the halide to TEAl co-catalyst and also, a matching interaction between the halogen group of the promoter and titanocyclopentane intermediate species in the catalytic cycle can be proposed to elucidate the promoting effect of the halides in the ethylene dimerization.**

Index Terms—**Ethylene dimerization, heavy and polymeric compounds, promoter, haloethane**

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 the limited market for some of these products, ethylene dimerization to 1-butene appears to be a more attractive option for 1-butene production [1], [2]. 1-butene, a versatile chemical intermediate to a wide variety of industrial products, is the first member of the even-numbered linear 1-alkenes which have diversified applications. The main application of 1-butene is as a co-monomer for the production of linear low-density polyethylene (LLDPE) and high-density polyethylene (HDPE) [3].

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The dimerization of ethylene is of great interest from both academic and technological viewpoints, since there are a number of different processes that can happen during the reaction, some of which included isomers of 1-butene, linear oligomer formation and polymeric products [2]-[6]. By investigation of previously reported studies, two mechanisms for the ethylene dimerization are more valuable: 1) The bimetallic Titanium-Aluminum complex that was proposed by Angelescu et al. [4]. It was depicted in Fig. 1. 2) Cyclic intermediate mechanism which proceeds by four steps involving the complexation of two molecules of ethylene on a titanium atom affording a Ti(IV) cyclopentane intermediate species. Subsequently, it is converted to the π-bonded 1-butene complex via β-H transfer and finally Ti species are regenerated [3]. This mechanism has been shown in Fig. 2. The ethylene dimerization reaction uses a homogeneous catalytic system based on Titanium tetrabutoxide ($Ti(OC_4H_9)_4$)/ Triethylaluminum (TEAl)/ modifier (an electron donor compound) [1], [5]. $Ti(OC_4H_9)_4$ is the main catalyst [3]. TEAl is an activator which can release free coordination sites in titanate complex and generate one or more Ti-C bonds by exchanging its ethyl groups with the butoxide groups of the titanate complex [3]. It also enhances the dimerization rate and has a profound effect on the course of the reaction. Usually, the catalyst modifiers are polar additives (such as tert-phosphine, phosphate, amine, and cyclic ether) which, when added to the catalyst system, provide better selectivity for the reaction. The modifiers influence the mode of linkage of ethylene molecules and inhibit the formation of heavy compounds [6]. Several studies were conducted to elucidate the necessary characteristics of these ligands to catalyze the selective dimerization [2], [3], [6].

Promoters, which almost always are halide compounds, have been extensively studied in tri- and tetramerization of ethylene [7]-[11]. The 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 [10]. This account is based on the findings of research studies of Y. Yang *et al.* [7] and H. Chen *et al.* [9]. They reported that the addition of geminal chloro compounds and halides to the catalyst systems at ethylene trimerization and tetramerization reactions resulted in significant improvement of selectivity to 1-hexene and 1-octene, respectively.
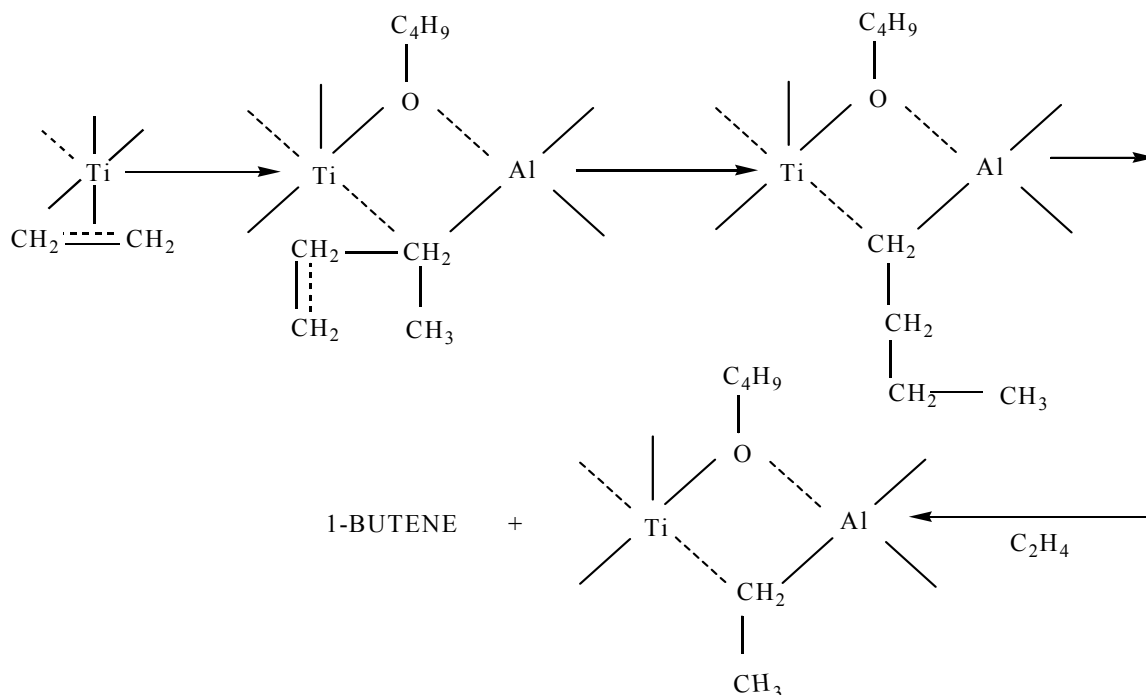
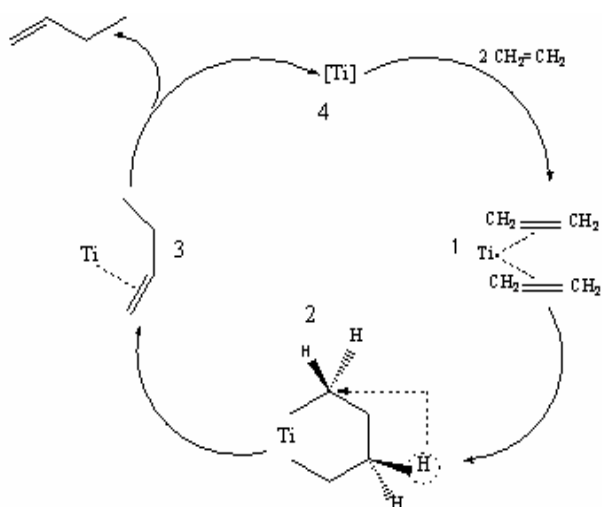Fig. 1. Dimerization of ethylene to bimetallic titanium-aluminium complex.

Fig. 2. Schematic representation of the cyclic intermediate mechanism [3].

However, despite these comprehensive research works, the systematic reports on the use of halides as promotion of activity for the Ti-based catalysts in the homogeneous reaction of the ethylene dimerization are almost unknown.

In the present research, we added chloroethane and bromoethane as new promoters to catalyst system and investigated the catalytic behavior in the various molar ratios of promoter/Ti.

II. EXPERIMENTAL

A. Materials and Instruments

Chloroethane (2 M solution in diethylether) and bromoethane were purchased from Merck. TEA was obtained from Crompton Chemicals and was diluted to a 0.5 M solution in heptane before use. n-heptane was dried over pre-activated molecular sieve (4 $^{\circ}$A). 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.

Reactions were performed in a 1 L stainless steel büchi pressure reactor, equipped with a jacket circulating cooling fluid, a magnetic drive stirrer, a thermocouple, 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. A schematic representation experimental set-up is depicted in Fig. 3.

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 $^{\circ}$C at a rate of 10 $^{\circ}$C/min.
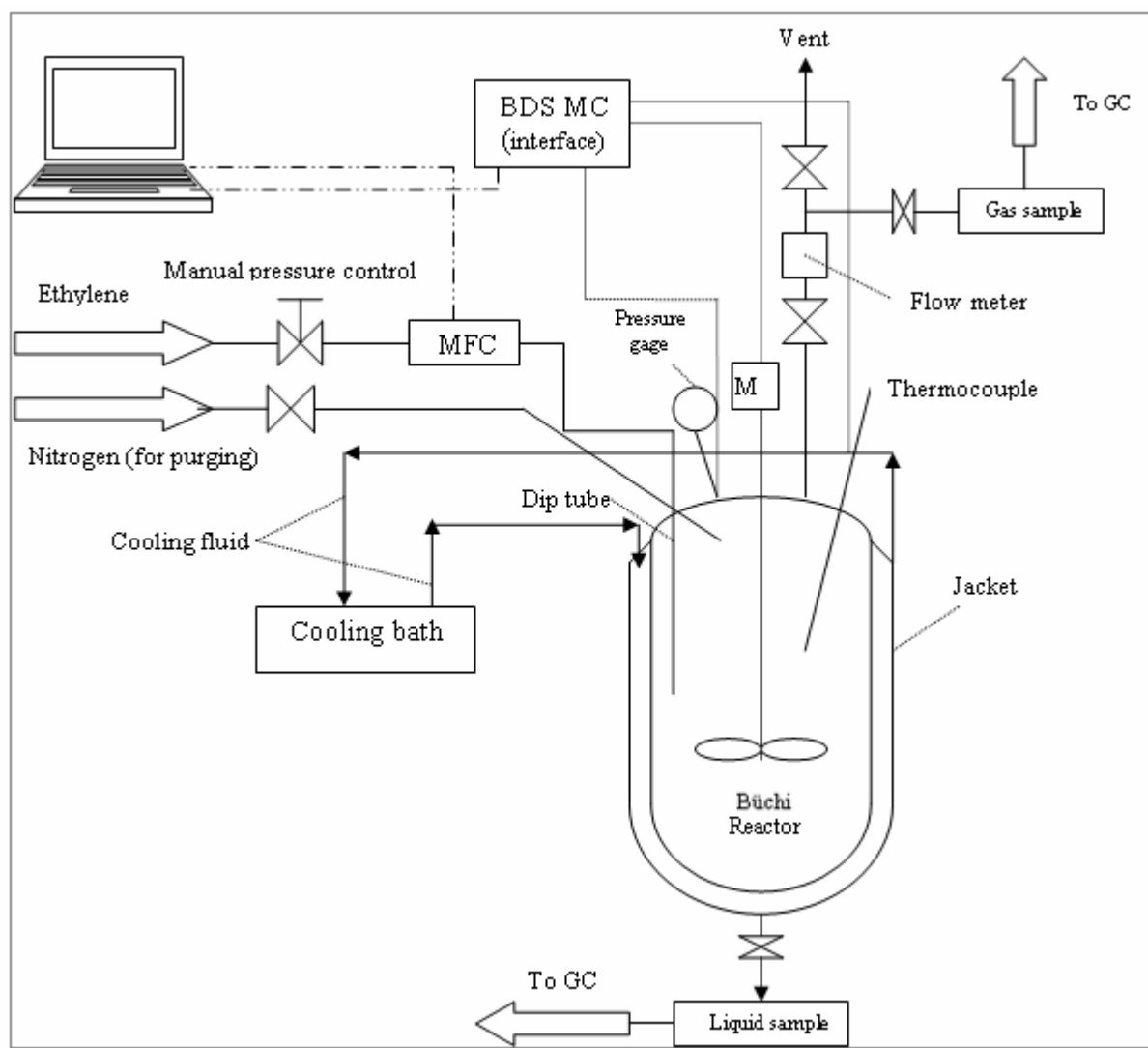
Fig. 3. Schematic set-up of the büchi reactor used in this study.

B. Reaction procedure and product analysis

All manipulations involving air and moisture-sensitive materials have been performed under atmosphere of dry nitrogen using standard Schlenk techniques.

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. Thereafter, the reactor was charged with 400 ml of n-heptane as solvent and was heated to a temperature lower than the desired temperature. It is noteworthy that the internal temperature of the reactor was adjusted to a level 4-6 °C lower than the desired value because of the highly exothermic character of ethylene dimerization. Ethylene was then introduced into the reactor to the desired pressure. The temperature inside of the reactor was controlled using cooling fluid, if required. Then, the calculated quantities of $Ti(OC_4H_9)_4$, TEA, ligand and promoters 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 increasing reaction time.

The volume of ethylene introduced through the inlet was measured using a Brooks mass-flow controller (MFC). Also, the total volume of gaseous components was measured by means of a gas flowmeter. After the dimerization was allowed to proceed for 0.5 h, the reaction was terminated by stopping the stirrer, the mixture was quenched by adding methanol/HCl solution and the products were withdrawn.

A gas sample was collected in a 150 ml stainless steel bomb and then subjected to GC-FID analysis. 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). 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 LLDPE.

The conversions and product selectivities were evaluated from the mass balance for ethylene consumption based on measured values from the MFC, flowmeter 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:

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

Also, turnover frequency (TOF) was expressed as:

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

III. RESULTS AND DISCUSSION

Based on the four-membered homogeneous titanium catalyst system [Ti(OC$_4$H$_9$)$_4$)/cyclic ether/AlEt$_3$/halide compound], effects of chloroethane and bromoethane as halohydrocarbons with various molar ratios of halohydrocarbon/Ti on ethylene conversion, overall selectivity to 1-butene, yield, and productivity (TOF) were investigated. The results are summarized in Table I. A blank reaction in the absence of promoter was carried out. In the relevant experiment, the yield and selectivity for 1-butene were reduced and the proportions of oligomeric compounds and polymer were obtained remarkable values under the given conditions.

According to the Table I, it is apparent that an increase of halide/Ti molar ratio until 6 resulted in a continuous enhancement of ethylene conversion, overall selectivity for 1-butene, yield, and TOF (runs 2-7 and 13-18). Further augmentation of halide/Ti molar ratio has a negative effect on the catalytic performance (runs 8-11 and 19-22). The detrimental effect of halide/Ti at high molar ratios is due to a coordinative loading of the active sites by more than one halide per metal atom was occurred and thus it leads to the preventing ethylene coordination [7], [9]. On the other hands, this trend can be rationalized that any excess promoter may interfere with the formation of the active Ti species or by over-reduction of active Ti species [11]. From Table I, It is seen that conversion, overall selectivity for 1-butene, yield and TOF (respectively 86.10%, 83.12%, 71.56% and 1458 h^{-1} in the optimum molar ratio of halide/Ti equal to 6) of the catalyst system containing chloroethane is better than of a corresponding bromoethane. This result can be likely attributed to the stronger coordination ability of bromo group with titanium center than Cl group. Taking into account that the coordination ability of bromo group with titanium center may be too strong [12], the catalyst system is poisoned slightly comparing with chloride [9], [10]. Thereupon, Ti(III) and Ti(II) species insoluble in solvent are formed and the side reactions- leading to the generation of hexenes, octenes and heavier oligomers- occur.

With more depth investigation on the remarkable effect of chloroethane in the aforementioned catalytic system, the following concluding remarks can be drawn:

Generally, because of compatibility of aluminum alkyls and chlorinated hydrocarbons, an electrophilic process generating what may be looked on as a carbonium counter ion pair, a free carbonium ion, or a well-defined polar complex Et$_3$Al + RX ↔ [R]$^+$ [Et$_3$AlX]$^-$ (1) (at this complex X represents Cl group) which then may react further depending on the reaction conditions and the nature of reactants [13]. Indeed, owning the acidity of TEA and nature of chloroethane and with polarization of the C-Cl bond, the compatible polar complex (1) is generated at reaction media which its chemical property and consecutive specific interaction in a head-on orientation toward metal center of the catalyst system may cause monomeric TEA is released [7]. Considering the fact that the conventional homogeneous catalyst system of ethylene dimerization is a dual functional catalyst system, monomeric TEA can modify spatial and electronic properties of Ti active sites giving concomitant generation of the increased number of these active species whereby the dimerization component of dual functional catalyst is provoked and finally amounts of polymeric compounds are suppressed.

As another proposal, the suitable coordination ability may exist between chloro group of chloroethane and central titanium of five-membered Ti metallacyclic transition state which may generate a specific structural arrangement of catalyst system at reactional mixture [10]. Therefore, the chemical micro-surrondings of titanium center in catalyst system is changed. This geometric regulation stabilizes titanium cationic complex in a higher oxidation state which is responsible for the ethylene dimerization and production of 1-butene.

While the exact geometric structure of possible molecular complexes between halogen group of the used promoters and titanium center of catalyst in the reaction media may be detected by X-ray crystallographic analysis and in-situ ^{13}C-NMR or ^{1}H-NMR and CI- MS (chemical ionization-mass spectroscopy) in order to represent the detailed mechanism in ethylene dimerization, therefore still remain to be elucidated through more extensive studies on quantum chemistry calculations.

IV. CONCLUSION

In this research, the effect of two haloethanes on ethylene dimerization reaction was investigated by comparative study on the ethylene conversion, overall selectivity to 1-butene and oligomers, yield of reaction, TOF, and weight of polymers. The results showed that the chloroethane promoted [Ti(OC$_4$H$_9$)$_4$/TEA/ligand] catalyst system was very active and selective for dimerization of ethylene.

TABLE I
RESULTS OF ETHYLENE DIMERIZATION WITH ADDITION OF TWO HALOHYDROCABONS TO CATALYST SYSTEM

Entry	Promoter	Promoter/Ti (mol/mol)	Conversion (%)	Overall selectivity to products (% wt)				PE (mg)	Yield (%)	TOF (h^{-1})
				1-C$_4$	C$_6$+	C$_8$+	$\geq$C$_{10}$+			
1		0	77.45	75.90	23.25	0.70	0.15	30	58.78	1312
2		1	79.41	77.47	21.77	0.64	0.12	27	61.52	1345
3		2	80.66	78.66	20.63	0.60	0.11	25	63.45	1366
4		3	81.93	79.52	19.84	0.54	0.10	22	65.15	1388
5		4	83.14	80.72	18.69	0.50	0.09	20	67.11	1408
6	chloroethane	5	84.88	81.85	17.65	0.43	0.07	15	69.47	1438
7		6	86.10	83.12	16.55	0.30	0.03	10	71.56	1458
8		7	85.15	82.34	17.26	0.35	0.05	15	70.11	1442
9		8	82.56	80.80	18.70	0.42	0.08	20	66.71	1398
10		9	78.22	77.83	21.47	0.58	0.12	25	60.88	1325
11		10	73.60	74.10	24.98	0.75	0.17	30	54.54	1247
12		0	77.45	75.90	23.25	0.70	0.15	30	58.78	1312
13		1	79.00	76.33	22.86	0.67	0.14	27	60.30	1338
14		2	80.50	77.10	22.15	0.62	0.13	25	62.06	1364
15		3	81.77	78.15	21.16	0.57	0.12	22	63.90	1385
16		4	82.83	79.24	20.12	0.53	0.11	20	65.63	1403
17	bromoethane	5	84.43	80.17	19.25	0.48	0.10	17	67.69	1430
18		6	85.90	81.16	18.37	0.40	0.07	14	69.71	1455
19		7	84.14	80.64	18.82	0.44	0.10	18	67.85	1425
20		8	81.91	78.12	21.24	0.50	0.14	25	63.99	1387
21		9	78.11	75.82	23.34	0.64	0.20	30	59.22	1323
22		10	73.40	72.45	26.52	0.78	0.25	35	53.18	1243

Reaction conditions: reaction temperature: 55°C, ethylene pressure: 25 bar, reaction time: 45 min, stirrer speed: 900 rpm, solvent: n-heptane, Ti(IV)/ligand/TEA molar ratios=1:4:4.

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