

Roles of chloro compound in homogeneous [Cr(2-ethylhexanoate)₃/2,5-dimethylpyrrole/triethylaluminum/chloro compound] catalyst system for ethylene trimerization

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Abstract

The effects of chloro compounds on the catalytic performance in ethylene trimerization reactions were studied using a homogeneous [Cr(2-ethylhexanoate)₃/2,5-dimethylpyrrole (DMP)/triethylaluminum (TEA)/chloro compound] catalyst system. Chloro compounds of different types showed a broad range of effects on the performance of the catalytic system. The chloro compounds of geminal chloro groups greatly improved the catalytic activity and 1-hexene selectivity of ethylene trimerization reaction.

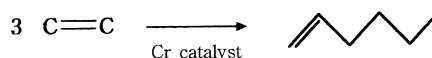
Some specific interaction modes of chloro groups with dimeric TEA and active Cr species in the catalytic cycle were proposed to explain the catalytic activity and 1-hexene selectivity improvement effects of chloro compound in the ethylene trimerization reaction. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Ethylene trimerization; 1-Hexene; Cr catalyst; Chloro group effects

1. Introduction

The linear ethylene trimerization reaction depicted in Scheme 1 has been studied for the future commercial production of 1-hexene, which is one of important co-monomer components for low density polyethylene [1,2].

The first selective formation of 1-hexene from ethylene was reported by Manyik et al. in 1977 [3]. At that time, 1-hexene was detected as an oligomeric by-product in the ethylene polymerization system with Cr-based catalysts.

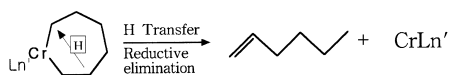


Scheme 1. Selective ethylene trimerization to 1-hexene.

The selective ethylene trimerization, which is different from the usual Ziegler type olefin oligomerization, especially in terms of product distribution, has been studied using Cr-based catalysts by several researchers to figure out the reaction steps and to improve the catalytic activity of the reaction [4,5]. The formation and decomposition of the seven-membered Cr metallacyclic transition state, which may liberate 1-hexene exclusively by reductive elimination in the catalytic cycle as described in Scheme 2, has

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Scheme 2. 1-Hexene formation step by reductive elimination of seven-membered Cr metallacyclic species.

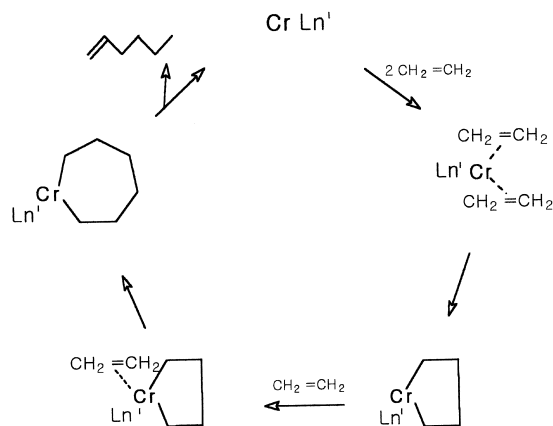
been adopted to explain the unique 1-hexene product selectivity of the ethylene trimerization reaction [4,6].

Recently, a seven-membered Cr metallacyclic compound stabilized by cyclopentadienyl ligand was prepared as a model compound of active catalytic species and was applied to the ethylene trimerization reaction [7]. However, it did not demonstrate the selective ethylene trimerization activity, probably due to the rigidity and stability of the Cr compound with the specific ligand. The Cr metallacyclic compound showed polymerization activity at low ethylene pressure and low reaction temperature.

Other approaches that trace in-situ generated Cr catalytic species during the trimerization reaction and modify catalytic properties of the Cr catalytic species by controlling reaction parameters such as catalyst composition ratio and reaction condition have been used in the improvement of catalytic activity and 1-hexene selectivity [1,2,4]. In these approaches, chemical interactions of each catalytic component with others in the reaction system were more important than the structural identification of active species. The combination of [Cr(III)compound/pyrrole/alkylaluminum] was effective for the homogeneous in-situ generated ethylene trimerization catalyst system. Cr complexes with pyrrole coordinations were also proved to be active for the reaction when alkylaluminum was used as a co-catalyst [8].

Even though the structure of active catalytic species in the homogeneous [Cr(III)compound/pyrrole/alkylaluminum] system has not been defined, it is believed that Cr species with three pyrrolide ligands and three open sites are involved in the catalytic cycle, based on the optimum ratio and chemical functions of each catalytic component [1,2]. As second order for ethylene has been observed in the ethylene trimerization reaction² [3], five-membered Cr

² A preliminary experiment in this study also shows a reaction order of 2 for ethylene over the pressure range of 25–35 atm.



Scheme 3. Proposed ethylene trimerization reaction steps associated with Cr metallacyclic species formation.

metallacyclic species which can be generated by the coordination of two ethylene molecules to the open sites of the Cr species at the same time is being utilized as a key component of the reaction step. Seven-membered Cr metallacyclic species which can possibly be formed from the five-membered Cr species by the ring expansion reaction with one additional ethylene molecule, as shown in Scheme 3, can also be considered as a key part of the catalytic cycle of the reaction to explain the unique 1-hexene product selectivity of the ethylene trimerization reaction [4,7].

The [Cr(III)compound/pyrrole/alkylaluminum] catalytic system has been further modified by Lewis base additives such as amines, phosphines, ethers or halogen compounds to improve the catalytic properties of the system [8]. Especially, chloro compounds have been reported to be effective in modifying catalytic activity and selectivity of the homogeneous catalyst system. However, chemical functions of specific chloro compounds in the catalytic system have not been defined [9].

In this paper, we report chloro compound effects in the homogeneous [Cr(2-ethylhexanoate)₃/2,5-dimethylpyrrole (DMP)/triethylaluminum (TEA)/chloro compound] ethylene trimerization catalyst system. By comparing catalytic activities and selectivities of specific ethylene trimerization catalyst systems, we also propose plausible chemical interaction modes of chloro groups with TEA Cr catalytic species.

2. Experimental

2.1. Materials

Chromium(III)tris-2-ethylhexanoate ($\text{Cr}(\text{2-EH})_3$) was prepared using a patent method [10]. Pyrroles, chloro-containing compounds and other additives purchased from Aldrich were of reagent grade and were purified using CaH_2 under high purity N_2 flowing at room temperature or at boiling points of specific compounds. Alkylaluminum compounds were purchased from Aldrich and were used without purification. Ethylene (lower than 10 ppm moisture and about 0.5 wt.% of saturated lower hydrocarbons; Air Liquid Co.) was of high purity grade, over 99.5%. Heptane as solvent was refluxed with LiAlH_4 and freshly distilled before usage.

2.2. Instruments

A 100 cm^3 stainless steel pressure reactor (Autoclave Engineers) equipped with magnetic drive stirrer, thermocouple, gas inlet, gas outlet port and heating system was used. A separate catalyst injection chamber and a liquid sampling port were attached to the reactor. Mass spectroscopy (HP5971 Mass selective detector) was used for the identification of reaction products. Gas chromatography (HP 5890II) with Supelco SPB-35 capillary column was used for product analysis.

2.3. Catalyst solution preparation

2.3.1. Cr stock solution

To the mixture of 48 mg of solid $\text{Cr}(\text{2-EH})_3$ and 50 mg of LiAlH_4 in 30 cm^3 rubber capped vial was added heptane to make 1.0×10^{-2} M Cr stock solution. The heptane suspension was shaken for 2 h at room temperature to remove possible moisture impurities before use and was then centrifuged to settle down fine solid particles.

2.3.2. DMP stock solution

DMP was dried using CaH_2 under N_2 flowing for 24 h at room temperature. The DMP– CaH_2 suspension was transferred to a glass vial using a syringe tube and was centrifuged to separate DMP from CaH_2 particles.

DMP stock solution 6.0×10^{-2} M was prepared by adding heptane to 6.0×10^{-2} cm^3 of dried DMP.

2.3.3. TEA stock solution

TEA was diluted in a 30 cm^3 vial with purified heptane to prepare 3.0×10^{-1} M TEA stock solution.

2.3.4. Chloro compound stock solutions

Chloro compounds such as, 1,2-dichloroethane, 1-chloroheptane, 2,2-dichloropropane, 1,1,2,2-tetrachloroethane, 1,1,1-trichloroethane (TCE), and chloroform were dried using CaH_2 for 24 h with N_2 flowing. The dried chloro compounds were separated by the same method as in DMP stock solution preparation and diluted to make 6.0×10^{-2} M stock solutions using purified heptane.

2.4. Reaction procedure

Ethylene trimerization was performed in a 100 cm^3 batch-type stirred pressure reactor. A typical reaction procedure is illustrated as follows, using our standard reaction parameters. The reactor and stirrer parts heated in a furnace at 300°C for 2 h and reactor head parts heated with electric heat guns to 150°C were assembled when the parts were hot. After evacuating, the reactor was filled with N_2 and cooled to below 30°C. To remove any impurities on reactor parts, the reactor was washed with 20 cm^3 of 0.5 M tributylaluminum solution. Tributylaluminum solution in the reactor was discharged after 10 min through the needle valve attached to the bottom part of the reactor. 10 cm^3 of [TEA-Chloro]heptane solution containing 1.0 cm^3 of TEA stock solution and 0.5 cm^3 of chloro compound stock solution was introduced to the reactor through the catalyst inlet chamber and an additional 20 cm^3 of heptane was added to the reactor to sweep any TEA and chloro compound remaining in the catalyst inlet chamber. 10 cm^3 of [Cr-DMP]heptane solution containing 1.0 cm^3 of $\text{Cr}(\text{2-EH})_3$ stock solution and 0.5 cm^3 of DMP stock solution was charged to the catalyst inlet chamber. The reactor was heated slowly with stirring. When the reaction temperature of 80°C was reached, [Cr-DMP] solution in the catalyst inlet chamber was added to the [TEA-Chloro] solution in the reactor using pressurized ethylene. Stirrer speed of 750 rpm and ethylene pressure of 35 atm

were maintained at 90°C for 30 min. The total amount of heptane solution in the reactor was 40 cm³ and the amounts of DMP, TCE, TEA and Cr(2-EH)₃ in the reactor were 3.0×10^{-2} , 3.0×10^{-2} , 3.0×10^{-1} and 1.0×10^{-2} mmol, respectively. The trimerization reaction was stopped on closing the ethylene supply valve and by cooling the reactor.

2.5. Analysis

Liquid products were analyzed using gas chromatography. Heptane solutions of authentic compounds with proper mixing ratio were used for the quantitative analysis of products. 1-Decene was used as a standard compound for the analysis of decene isomers in the product. Polymeric material was separated from reaction product and weighted after drying at 100°C for 24 h.

3. Results and discussion

3.1. General scope of ethylene trimerization reaction

Table 1 summarizes the catalytic activities and product selectivities of ethylene trimerization reactions which were carried out using the homogeneous [Cr(2-ethylhexanoate)₃/DMP/TEA/TCE] catalyst system with the variations of catalytic composition.

In general, product compositions of about 90 wt.% of 1-hexene and about 10 wt.% of decenes with small amounts of 1-octene and polymeric material were obtained using the homogeneous [Cr(2-ethylhexanoate)₃/DMP/TEA/TCE] catalyst system. The catalytic activities and selectivities of ethylene trimerization reactions are strongly affected by the variation of molar ratio of each catalytic component. The importance of Cr(2-EH)₃ and TEA components in the catalytic system can be realized by the fact that no ethylene trimerization proceeds without using the components. However, when other components of DMP or TCE are removed from the catalyst system, ethylene trimerization is still observed even though catalytic activity and 1-hexene selectivity decrease to a large extent.

The concentration increase of Cr(2-EH)₃ component in the catalyst system results in gradual decreases in catalytic activity and 1-hexene selectivity. The Cr

concentration dependencies of catalytic activity and 1-hexene selectivity indicate that the formation of active Cr species from Cr(2-EH)₃ is related to the interactions of other catalytic components of proper ratios. The excess amount of Cr(2-EH)₃ component may interfere with the formation of active Cr catalytic species. The importance of proper composition ratio of the catalyst system is also shown in TCE and TEA concentration dependencies of catalytic activity and product selectivity. The optimum molar ratios of TCE/Cr(2-EH)₃ and TEA/Cr(2-EH)₃ for the highest catalytic activity are observed at 3 and 30, respectively. With the addition of excess amounts of TCE or TEA, catalytic activities decrease. The pattern of the activity change with DMP/Cr(2-EH)₃ molar ratio is somewhat different from those of the other three catalytic components. The highest catalytic activity is observed at a DMP/Cr(2-EH)₃ molar ratio of 3 and the catalytic activity is maintained at higher DMP/Cr(2-EH)₃ molar ratio.

To understand the component molar ratio dependency of catalytic activity and the product selectivity of the [Cr(2-ethylhexanoate)₃/DMP/TEA/TCE] catalyst system, the relationship between chemical functions of each catalytic component and the proper composition molar ratio of the catalytic system is to be considered. It is reasonable to propose that the optimum molar ratio values of DMP/Cr(2-EH)₃ and TEA/Cr(2-EH)₃ are related to the formation of the active Cr species of proper number of pyrrolide ligands because these two components have been utilized as ligands and co-catalyst in catalytic reaction systems. The optimum DMP/Cr(2-EH)₃ molar ratio of 3 may stand for the formation of three Cr–pyrrolide bonds in the active catalytic species. The requirement of a relatively large amount of TEA can be justified by the facts that the formation of pyrrolide anion from pyrrole and activation of stable 6-coordinated Cr(2-EH)₃ complex are associated with the chemical actions of TEA. The removal of 2-ethylhexanoate ligands from Cr(2-EH)₃ complex should be facilitated by the Lewis acid property of TEA. It is also expected that any excess amount of TEA may interfere with the formation of active Cr species of proper Cr–pyrrolide ligand ratio by the formation of TEA–pyrrolide acid–base type adduct and/or by the over-reduction of Cr species.

The profound effect of TCE on the activity and product selectivity, however, can not be explained

Table 1
Summary of ethylene trimerization activities using homogeneous $[\text{Cr}(\text{2-ethylhexanoate})_3/\text{DMP}/\text{TEA}/\text{TCE}]$ catalyst systems^a

Catalyst composition [Cr(2-EH) ₃ /DMP/TEA/TCE] (mmol)	Ethylene conversion rate (g/30 min)	Liquid product		Solid product
		1-Hexene selectivity (%)	Decene selectivity (%)	Polymer weight (mg)
–/0.03/0.30/0.03	0.00	–	–	–
0.005/0.03/0.30/0.03	29.93	96.9	2.63	2
0.01/0.03/0.30/0.03	27.10	93.0	6.34	4
0.02/0.03/0.30/0.03	20.98	92.2	6.72	3
0.01/–/0.30/0.03	6.23	87.2	6.80	38
0.01/0.015/0.30/0.03	20.14	89.5	6.47	10
0.01/0.03/0.30/0.03	27.10	93.0	6.34	4
0.01/0.06/0.30/0.03	26.17	92.5	6.65	3
0.01/0.03/–/0.03	0.00	–	–	–
0.01/0.03/0.15/0.03	2.65	93.7	5.10	19
0.01/0.03/0.30/0.03	27.10	93.0	6.34	4
0.01/0.03/0.60/0.03	13.12	89.6	8.91	3
0.01/0.03/0.30/–	4.85	69.6	18.34	5
0.01/0.03/0.30/0.015	15.21	87.9	9.58	3
0.01/0.03/0.30/0.03	27.10	93.0	6.34	4
0.01/0.03/0.30/0.06	23.61	94.9	4.47	4
0.01/0.03/0.30/0.12	6.24	98.0	1.13	103
0.01/0.03/0.30/0.30	2.36	99.2	0.29	228
0.01/–/0.30/–	0.95	93.8	6.12	221

^a Reaction conditions: reaction temperature, 90°C; ethylene pressure, 35 atm; stirrer speed, 750 rpm; catalyst concentration: mmol in 40 cm³ of heptane.

simply because chemical interactions of TCE with catalytic components of ethylene trimerization have not been established even in other catalytic systems. The effects and functions of chloro compounds including TCE in the $[\text{Cr}(\text{2-ethylhexanoate})_3/\text{DMP}/\text{TEA}/\text{chloro compound}]$ ethylene trimerization catalyst system will be discussed in Section 3.3.

3.2. Reaction pathway of decene formation

Regarding the 1-hexene selectivity improvement effect of TCE in the $[\text{Cr}(\text{2-ethylhexanoate})_3/\text{DMP}/\text{TEA}/\text{TCE}]$ catalyst system, the reaction pathway of decene formation should be confirmed because decenes are major by-products in the ethylene trimerization reaction.

An almost linear relationship between decene formation and 1-hexene formation in ethylene trimerization, as shown in Fig. 1, was observed in the $[\text{Cr}(\text{2-ethylhexanoate})_3/\text{DMP}/\text{TEA}/\text{TCE}]$ catalyst sys-

tem. The linear relationship may present two possible pathways for the formation of decenes. One is the reaction pathway in which 1-hexene participates as a reactant with ethylene in the trimerization reaction. The other possible pathway is related to the addition steps of two more ethylene molecules to the Cr metallacycle which renders 1-hexene. In the latter case, the involvement of 1-hexene should be excluded in the catalytic reaction step.

To trace the reaction pathway for the decene formation, a pre-determined amount of 1-hexene or 1-butene was added to the ethylene trimerization system. In Fig. 2, 1-hexene and 1-butene addition effects on the product selectivity are compared at similar 1-hexene formation levels.

In the 1-hexene addition experiment, decene selectivity of 8.7% and octene selectivity of 1.1% were observed. The increase in decene selectivity with the addition of extra 1-hexene implies that 1-hexene is involved in the formation of decenes in the catalytic

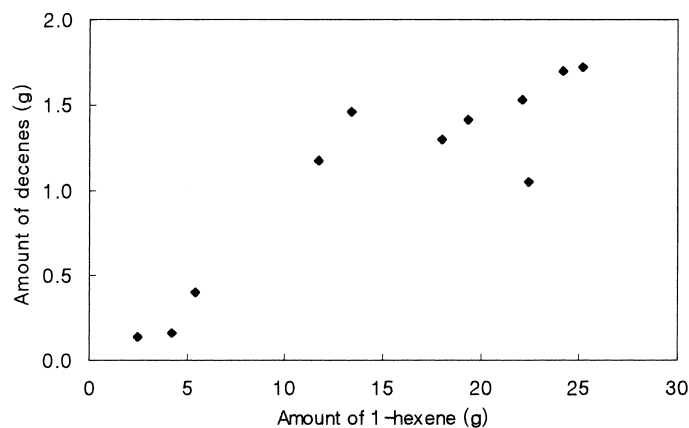


Fig. 1. Correlation of 1-hexene and decene formation in ethylene trimerization reactions.

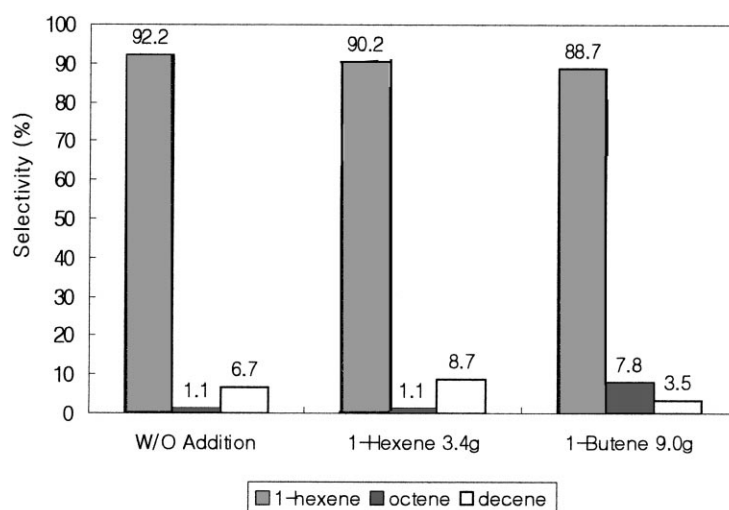


Fig. 2. Effects of 1-hexene and 1-butene addition on product selectivity of the ethylene trimerization reaction at ethylene conversion rates of 21.0, 23.9 and 19.9 g ethylene per 30 min for w/o addition, 1-hexene 3.4 g and 1-butene 9.0 g addition cases, respectively.

cycle. The incorporation of 1-hexene in the trimerization reaction step can also be supported by the product analysis of 1-butene addition experiment. When 1-butene is added to the reactor, octene selectivity increases to a large extent with the decrease in decene selectivity. The changes in octene and decene selectivities in the 1-butene addition experiment can be explained by the preferred coordination of 1-butene in the reaction medium, in which 1-hexene is formed continuously during the ethylene trimerization reaction. The formation of octenes and decenes from 1-butene and 1-hexene, respectively, with the

addition of two molecules of ethylene should be also applied. If 1-hexene or 1-butene is not involved in the catalytic cycle, decene selectivity should be the same. Thus, regarding the formation of decenes, the reaction pathway in which 1-hexene and ethylene react to form five-membered butyl-substituted Cr metallacycle and additional ethylene is inserted to form butyl-substituted seven-membered Cr metallacycle, which decomposes to the mixture of decenes, can be proposed by referring to the previously introduced ethylene trimerization catalytic reaction steps. In the above-proposed decene formation pathway,

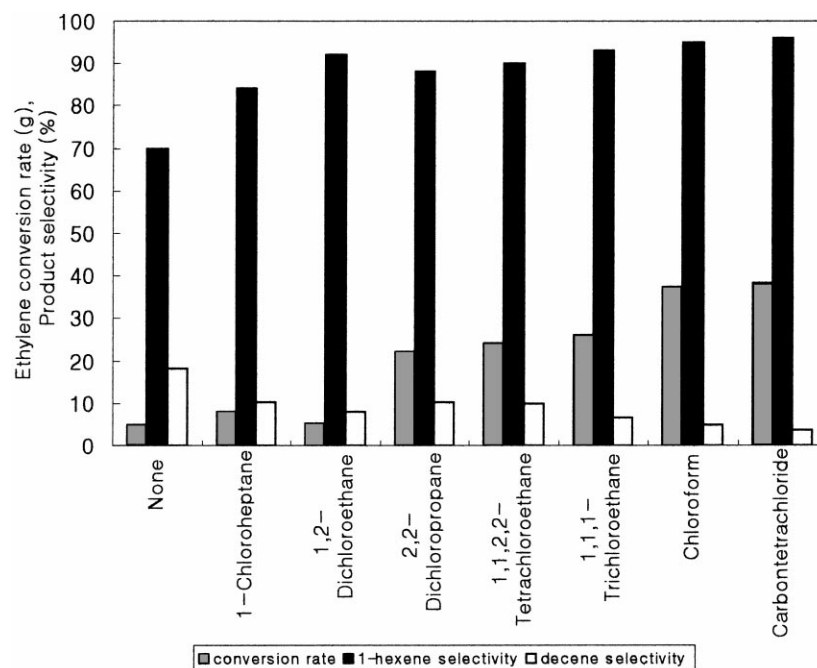


Fig. 3. Effects of various chloro compounds on the activity and selectivity of the ethylene trimerization reaction.

incorporation of 1-hexene in the formation of five-membered Cr metallacycle is preferred rather than the possible incorporation of 1-hexene in the formation of seven-membered Cr metallacycle. Relative exclusion of 1-hexene in the coordination step of seven-membered Cr metallacycle may be suggested based on the relatively crowded environment around the Cr active site.

3.3. Effects and functions of chloro compounds

To elucidate the specific effects of the chloro compound in the $[\text{Cr}(\text{2-ethylhexanoate})_3/\text{DMP}/\text{TEA}/\text{chloro compound}]$ catalyst system, chloro compounds of different types were applied in the homogeneous ethylene trimerization. Effects of various chloro compounds on the activity and product selectivity of ethylene trimerization reaction using the standard reaction conditions are compared in Fig. 3.

As shown in Fig. 3, chloro compounds of different types in the $[\text{Cr}(\text{2-ethylhexanoate})_3/\text{DMP}/\text{TEA}/\text{chloro compound}]$ catalyst system show broad ranges of ethylene conversion rates and product selectivities. In general, with increasing number of chloro substitutions

in chloro compounds, improvements in 1-hexene selectivity and ethylene conversion rate were observed. The variation of 1-hexene selectivity with the number of chloro groups can be emphasized by the comparison of decene selectivity, as shown in Fig. 4. As decene formation in ethylene trimerization reaction is related to the participation of 1-hexene in the catalytic cycle as described in Section 3.2, the decrease in

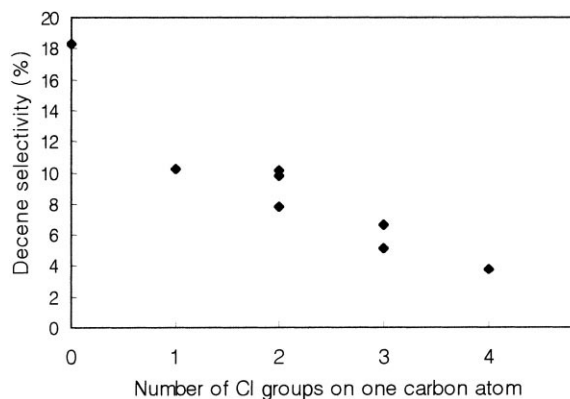


Fig. 4. Correlation of decene selectivity with the number of chloro groups in chloro compounds.

Table 2

Effect of total chloro group concentration on the catalytic performance in the $[\text{Cr}(\text{2-ethylhexanoate})_3/\text{DMP}/\text{TEA}/1,2\text{-dichloroethane}$ or $1\text{-chloroheptane}]$ catalyst system^a

Catalyst composition [Cr(2-EH) ₃ /DMP/TEA/chloro compound] (mmol)	Ethylene conversion rate (g/30 min)	Liquid product		Solid product
		1-Hexene selectivity (%)	Decene selectivity (%)	Polymer weight (mg)
<i>Chloro compound: 1,2-dichloroethane</i>				
0.01/0.03/0.30/0.03	5.29	92.0	7.81	20
0.02/0.03/0.30/0.06	4.14	84.6	15.3	3
<i>Chloro compound: 1-chloroheptane</i>				
0.01/0.03/0.30/0.03	7.77	83.8	10.2	20
0.01/0.06/0.30/0.09	2.99	89.3	10.6	357

^a Reaction conditions: reaction temperature, 90°C; ethylene pressure, 35 atm; stirrer speed, 750 rpm; catalyst concentration, mmol in 40 cm³ of heptane.

decene selectivity with increasing numbers of chloro groups should be attributed to the effective interaction of chloro compound with the active sites of Cr species. Thus, the 1-hexene product selectivity improvement effect of chloro compound can be explained by the spatial effects of weak coordinations of chloro groups on the Cr active species.

When changes in ethylene conversion rates with different types of chloro compounds are compared, it can be shown that the numbers of chloro groups in specific chloro compounds also affect the ethylene conversion rate, as in 1-hexene selectivity variation. However, it should be noted here that the mode of interaction of chloro groups with the active site of Cr species can not be applied for the explanation of the pattern of catalytic activity changes because the effective interaction of chloro groups with the active site of Cr species is also expected to interfere with the coordination of ethylene and to reduce ethylene conversion rate. The pattern of catalytic activity decrease with the increase in TCE concentration at high TCE/Cr molar ratio values, as shown in Table 1, may represent the opposite effects of the interaction between chloro groups and the active Cr species. The activity change patterns with concentration changes of other chloro compounds such as chloroform and carbon tetrachloride were similar to that of TCE. Thus, the device of some other type of interaction of chloro compound by which the activity improvement effect can be illustrated in the $[\text{Cr}(\text{2-ethylhexanoate})_3/\text{DMP}/\text{TEA}/\text{chloro compound}]$ ethylene trimerization catalyst system is required.

One important feature of the chloro compound effect on catalytic activity in the $[\text{Cr}(\text{2-ethylhexanoate})_3/\text{DMP}/\text{TEA}/\text{chloro compound}]$ catalyst system is observed in the cases of 1,2-dichloroethane and 2,2-dichloropropane shown in Fig. 3. 2,2-Dichloropropane shows much higher catalytic activity improvement effect than 1,2-dichloroethane, even though the two compounds have the same number of chloro groups and similar physical properties. The variations in catalytic activity with the chloro group configuration means that cooperative interaction of two geminal chloro groups of 2,2-dichloropropane is involved in the interaction with other catalytic components for the promotion of catalytic activity. The pattern of catalytic activity changes of Fig. 3 is qualitatively more consistent with the numbers of geminal chloro groups of specific chloro compound than with the total numbers of chloro groups. The increase in total chloro group concentration in the reaction system with the addition of three times of 1-chloroheptane or twice of 1,2-dichloroethane more than the standard [chloro compound/Cr] molar ratio of 3 does not improve catalytic activity of the reaction system, as shown in Table 2. The result also shows the importance of geminal chloro group configuration of chloro compound in the ethylene trimerization catalyst system.

In considering possible cooperative interactions of geminal chloro groups in the catalytic system, one should recall that the catalytic component which interacts with geminal chloro groups requires a specific structural arrangement to fit with and a specific

Table 3
Strong Lewis base effects in the $[\text{Cr}(\text{2-ethylhexanoate})_3/\text{DMP}/\text{TEA}/\text{base additive}]$ ethylene trimerization catalyst system^a

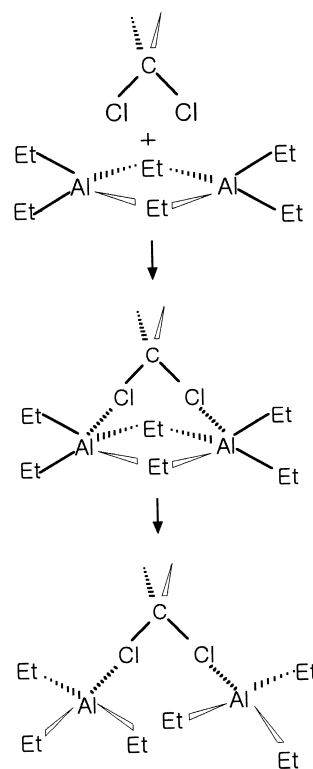
Catalyst composition [Cr(2-EH) ₃ /DMP/TEA/chloro compound] (mmol)	Ethylene conversion rate (g/30 min)	Liquid product		Solid product
		1-Hexene selectivity (%)	Decene selectivity (%)	Polymer weight (mg)
<i>Base compound: sulfur</i> 0.01/0.03/0.30/0.03	4.69	85.8	11.8	10
<i>Base compound: triphenylphosphine</i> 0.01/0.03/0.30/0.03	4.13	70.2	14.6	5
<i>Base compound: ethyleneglycoldimethylether</i> 0.01/0.03/0.30/0.03	4.31	73.7	13.3	100

^a Reaction conditions: reaction temperature, 90°C; ethylene pressure, 35 atm; stirrer speed, 750 rpm; catalyst concentration, mmol in 40 cm³ of heptane.

chemical property to interact with. TEA which prefers dimeric form with two ethyl bridge bonds and two Al Lewis acid sites of specific arrangement may be selected for the verification of the cooperative interaction with geminal chloro groups. The important chemical functions of TEA in catalytic systems can also be counted in the selection. In normal catalytic reactions in which TEA is utilized as a catalytic component, one half order for TEA is observed because the decomposition constant of dimeric TEA into monomeric TEA is too small and dimeric TEA is involved in the catalytic reaction step [11]. However, it can be presented that the catalytic activity improvement is related with the action of in-situ generated monomeric TEA, if the generation of monomeric TEA from dimeric TEA is efficient in catalytic reaction system by kinetic and/or thermodynamic interactions of other catalytic components. As chemical roles of TEA component in the ethylene trimerization reaction are associated with Lewis acid property for the removal of carboxylate ligands from $\text{Cr}(\text{2-EH})_3$ to provide open sites for the reactant coordination and H^+ abstraction from the N–H moiety of pyrrole compound to form pyrrolide ligand, facile formation of monomeric TEA by the decomposition of dimeric TEA is expected to be advantageous for the formation of active Cr species. The decomposition of dimeric TEA to stable monomeric TEA–base type adducts have been well known for the various strong Lewis base compounds of amines, phosphines and ethers [12]. The low ethylene trimerization activities of $[\text{Cr}(\text{2-ethylhexanoate})_3/\text{DMP}/\text{TEA}/\text{Lewis base component}]$ homogeneous catalyst systems, as shown in Table 3, in which monomeric TEA can not act

as a Lewis acid, indirectly support the positive effect of monomeric TEA component on the catalytic activity.

Scheme 4 presents the effective interaction mode between geminal chloro groups and dimeric TEA by



Scheme 4. Possible effective interaction modes between geminal chloro groups and dimeric TEA.

which the contribution of geminal chloro groups to the decomposition of dimeric TEA can be recognized. In the interaction mode, geminal chloro groups act as two-point weak Lewis base sites which fit with two Al Lewis acid sites of dimeric TEA. The specific interaction mode between dimeric TEA and geminal chloro groups is expected to accelerate the decomposition of dimeric TEA into monomeric TEA. In addition, the monomeric TEA may be somewhat stabilized by the formation of weak chloro group mediated bridge bonds.

In discussing the interaction between alkylaluminum compounds and alkylchloro compounds, the radical reaction pathway in which some alkylaluminum compounds and alkylchloro compounds radically decompose into HCl, AlCl₃ and various organic compounds should also be considered [13–16]. TEA and CCl₄ in purified heptane with four times of concentration (TEA/CCl₄ of 0.60 mmol/0.06 mmol in 20 cm³ heptane) of our standard reaction system showed no considerable CCl₄ concentration change even after heat treatment at 80°C for 5 min when CCl₄ concentration was monitored using gas chromatography. The stability of CCl₄ in our catalytic system is consistent with the result of Eden C. et al. who claimed that no radical decomposition of CCl₄ was observed in the dilute mixing solution of CCl₄ and TEA of high purity even though the radical decomposition occurred in the same system when impure TEA which contained chloroalkylaluminum compound was used [15]. As other chloroalkyl compounds have been claimed to be rather more stable than CCl₄ in alkylaluminum solution [16], the radical decomposition of chloro compounds in our chloro compound–TEA combinations may be excluded in discussion of the interaction mode of the two catalytic components.

Thus, it can be presented, based on the reasonably verified reaction schemes and chemical species involved in the catalytic cycle, that the facile decomposition of dimeric TEA into monomeric TEA which is supposed to affect the formation of increased number of active Cr species can be suggested as another important chemical role of chloro compound in the [Cr(2-ethylhexanoate)₃/DMP/TEA/chloro compound] ethylene trimerization catalyst system for the explanation of the activity improvement effect of chloro compound in the ethylene trimerization reaction.

4. Conclusions

In the homogeneous [Cr(2-ethylhexanoate)₃/DMP/TEA/chloro compound] ethylene trimerization catalyst system, chloro compounds of different types showed a broad range of effects on the performance of the catalytic system. The chloro compounds of geminal chloro groups greatly improved the ethylene trimerization catalytic activity. Linear correlation of 1-hexene selectivity with the numbers of chloro group in specific chloro compounds was also observed.

The 1-hexene selectivity and catalytic activity improvement effects of chloro compounds in the homogeneous ethylene trimerization catalyst system could be explained. They are the consequence of specific interactions of chloro groups with active Cr species to modify spatial properties of active sites and those of dimeric TEA to form monomeric TEA for the facile formation of active Cr species in the catalytic system.

References

- [1] R.D. Knudsen, J.W. Freeman, M.E. Lashier, USP 5,563,312 (1996).
- [2] E. Tanaka, H. Urata, USP 5,491,272 (1996).
- [3] R.M. Manyik, W.E. Walker, T.P. Wilson, J. Catal. 47 (1977) 197.
- [4] J.R. Briggs, J. Chem. Soc., Chem. Commun. 11 (1989) 674.
- [5] M.P. McDaniel, Adv. Catal. 33 (1985) 47.
- [6] N. Meijboom, C. Schaveien, A.G. Orpen, Organometallics 9 (1990) 774.
- [7] R. Emrich, O. Heinemann, P.W. Jolly, C. Kruger, G.P.W. Verhovnik, Organometallics 16 (1997) 1511.
- [8] W.K. Reagen, B.K. Conroy, USP 5,470,926 (1995).
- [9] W.K. Reagen, T.M. Pettijohn, J.W. Freeman, USP 5,523,507 (1996).
- [10] R.B. Steele, A. Kazakian, J.J. Scigliano, E.E. Hamel, USP 3,962,182 (1976).
- [11] J.J. Eisch, C.K. Hordis, J. Am. Chem. Soc. 93 (1971) 4496.
- [12] J.J. Eisch, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 3, Pergamon Press, Oxford, 1982, Chapter 6, p. 596.
- [13] J.W. Collette, J. Org. Chem. 28 (1963) 2489.
- [14] A. Priola, S. Cesca, G. Ferraris, Makromolekulare Chemie 160 (1972) 41–57.
- [15] C. Eden, H. Feilchenfeld, J. Phys. Chem. 66 (1962) 1354.
- [16] W.H. Thomas, Ind. Eng. Chem. Prod. Res. Dev. 21 (1982) 120–122.