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Dimerization of 1-butene via zirconium-based Ziegler–Natta catalyst

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A zirconium-based Ziegler–Natta catalytic system has been tested in the dimerization of 1-butene. It was found that the concentration of Et_2AlCl, Ph_3P and PhONa as well as the reaction temperature had great influences on the activity and selectivity of the catalyst. Under the optimum reaction conditions, the conversion of 1-butene is 91.9%, and the selectivity of dimers is 76.7%. Basic ligands such as Ph_3P and PhONa can inhibit isomerization of 1-butene to 2-butene effectively. In addition, the metal hydride mechanism was also suggested and some indirect evidence was obtained in favor of this mechanism.

Keywords: 1-butene, dimerization, homogeneous catalysis, Ziegler–Natta catalyst, reaction mechanism

1. Introduction

C_8 olefins dimerized from 1-butene are used widely in industry, such as in the manufacture of linear low-density polyethylene (LLDPE) comonomers, special detergents, synthetic lubricating oils, etc. The dimerization of 1-butene in the presence of homogeneous Group 8 transition metal catalysts has been extensively studied [1–3]. However, the practical application has been hindered by the fact that the activity of this kind of catalyst is relatively low, for example, the conversion of 1-butene was not more than 60% based on a substituted fluoroacetylacetonate nickel complex [1,3]. On the other hand, the complicated ligands in this catalytic system are difficult to prepare. Group 4 transition metal zirconium-based Ziegler–Natta catalysts have been used primarily for olefin polymerization [4], especially in recent years. The zirconium-based metallocene catalysts have become the hot spot in this field [5,6]. Our previous studies showed that zirconium-based Ziegler–Natta catalysts can also be employed for ethylene oligomerization to linear lower α-olefins like 1-$C_6^=$, 1-$C_8^=$, 1-$C_{10}^=$, etc. after careful modification [7–10]. There are few reports in literature concerning the dimerization of 1-butene via zirconium-based Ziegler–Natta catalysts. Thus, this research is of considerable industrial interest as well as academic value. In this paper, we report a study of 1-butene dimerization by zirconium-based Ziegler–Natta catalysts, and the reaction mechanism is also discussed.

2. Experimental

2.1. Materials

All reactions were performed under a purified nitrogen atmosphere using standard glove box and Schlenk techniques. Oxygen and moisture levels were maintained at less than 10 ppm. All solvents were purified by distillation from appropriate drying agents under inert atmosphere. Polymerization grade of 1-butene (Panjin Ethylene Co., China) was further purified by activated γ-Al_2O_3. Zirconium tetrachloride ($ZrCl_4$) was obtained from Merck-chuchardt (Germany). Et_2AlCl (from Shanghai Institute of Chemical Engineering, China) was used as a 6% solution in cyclohexane. n-Bu_2Mg without ether was prepared by literature procedures [11]. Ph_3P and PhONa were purified in an ethanol solvent under nitrogen protection [7,8].

2.2. Dimerization experiment and product analysis

Dimerization of 1-butene was performed in a 75 ml stainless-steel autoclave equipped with a magnetic stirrer. The autoclave was carefully flushed with dry, oxygen-free nitrogen before each experiment by successive evacuation, nitrogen back-fill cycles. A typical experiment was carried out by charging 0.05 mmol $ZrCl_4$ and the desired amount of Et_2AlCl, Ph_3P or PhONa in 30 ml benzene chloride to the autoclave via a syringe. The reactor was immersed in a 373 K oil bath for aging 0.5 h. The bath temperature was then set to a desired temperature. The dimerization reaction was started by injecting 0.05 mol 1-butene. The reaction was stopped by introducing 25 ml ethanol-containing NaOH (5 wt%) into the reactor.

The reaction products were analyzed by a gas chromatograph (Varian 3700) equipped with a flame ionization detector and a 30 m long capillary column (SE 54). The column oven temperature was programmed from 313 to 553 K at 5 K min^{-1}. The compositions on the liquid products were identified by GC-MS (Finnigan MAT 312/SS200).

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3. Results and discussion

3.1. Effect of the Al/Zr ratio

The catalytic activity of the zirconium catalytic system is strongly dependent on the amount of Et_2AlCl used for activation. Table 1 gives the results of 1-butene dimerization via the $ZrCl_4/Et_2AlCl/Ph_3P$ catalytic system with various Al/Zr ratios. It can be seen that the conversion of 1-butene increases significantly with Al/Zr ratio, then decreases when the Al/Zr ratio reaches 60. The selectivity of dimers ($C_8^=$) varies the same as the conversion of 1-butene. The optimum Al/Zr ratio is found to be around 60. Under such conditions, the conversion of 1-butene is 91.9%, and the selectivity of dimers is 76.7%. It is also found from table 1 that this catalytic system can isomerize 1-butene to 2-butene, whose space bulk is so large as to result in the deactivation of the catalyst. GC-MS spectra show that the main product in the dimers is 2-ethyl-1-hexene ($m/e = 55, 70, 83, 112$). In addition, there are $C_6^=$ in the products, which can be explained in the following reaction mechanism discussion, i.e., after coordination 1-butene inserts into the $Zr–C_2H_5$ bond and then β-H is eliminated to produce $C_6^=$.

Table 1
Effect of Al/Zr ratio on the dimerization of 1-butene.[a]

	Al/Zr ratio				
	40	50	60	70	80
Conversion of 1-butene (%)	29.2	57.8	91.9	59.0	42.0
Selectivity					
$C_8^=$ (%)	21.7	55.9	76.7	40.4	50.4
$C_6^=$ (%)	41.2	27.1	13.5	27.4	40.5
2-butene (%)	0	0	4.2	14.5	0

[a] Reaction at 353 K for 2 h, P/Zr = 1.0, solvent: C_6H_5Cl.

3.2. Effect of the reaction temperature

Dimerization initiated by $ZrCl_4/Et_2AlCl/Ph_3P$ was performed between 343 and 383 K at Al/Zr = 60 and P/Zr = 1.0. As shown in figure 1, when the reaction temperature increases, the conversion of 1-butene and selectivity of dimers all increase, but for reaction temperatures above 353 K, they all decrease. This demonstrates that higher reaction temperature may kill the active species and lead to the catalyst deactivation.

3.3. Effect of the reaction time

Figure 2 indicates that the profiles of the 1-butene dimerization depend on the reaction time. When the reaction time is over 2 h, the activity decreases slightly, but with prolonged reaction time, the conversion of 1-butene almost

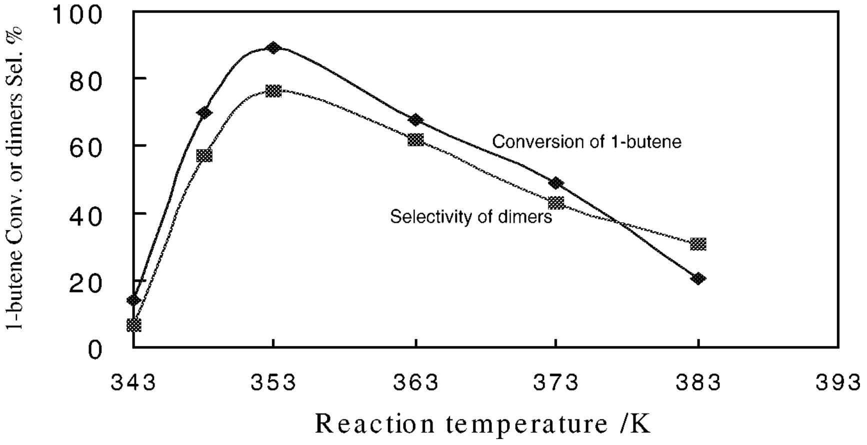


Figure 1. Dependence of 1-butene conversion and dimers selectivity on the reaction temperature.

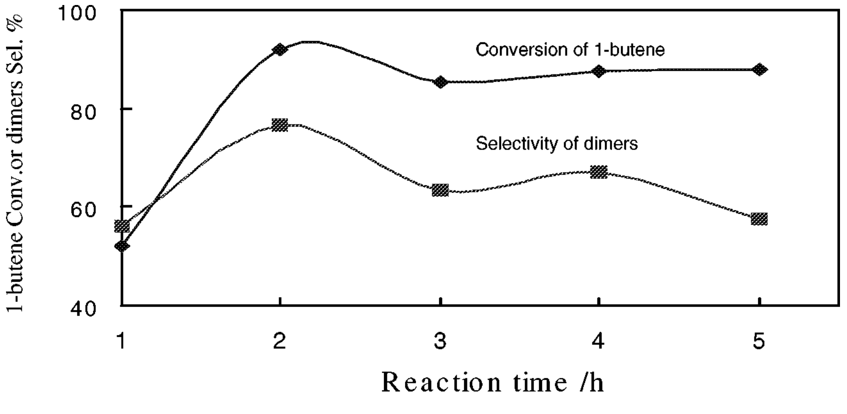


Figure 2. Dependence of 1-butene conversion and dimers selectivity on the reaction time.

Table 2
Effect of P/Zr ratio on the dimerization of 1-butene.[a]

	P/Zr ratio				
	0	0.5	1.0	2.0	3.0
Conversion of 1-butene (%)	98.1	92.8	91.9	59.2	42.1
Selectivity					
$C_8^=$ (%)	52.9	60.1	76.7	45.2	14.4
$C_6^=$ (%)	34.4	26.1	13.5	30.5	47.1
2-butene (%)	11.2	9.6	4.2	2.8	0

[a] Reaction at 353 K for 2 h, Al/Zr = 60, solvent: C_6H_5Cl.

Table 3
Effect of addition of PhONa on the dimerization of 1-butene.[a]

	Na/Zr ratio				
	0	0.5	1.0	1.5	2.0
Conversion of 1-butene (%)	98.1	71.8	73.8	63.6	13.3
Selectivity					
$C_8^=$ (%)	52.9	50.8	71.8	72.6	92.0
$C_6^=$ (%)	34.4	29.0	15.4	17.6	2.5
2-butene (%)	11.2	0	0	0	0

[a] Reaction at 353 K for 2 h, Al/Zr = 60, solvent: C_6H_5Cl.

keeps constant. Thus the optimum reaction time for this catalytic system is ca. 2 h.

3.4. Effect of the P/Zr ratio

Table 2 lists the effect of addition of Ph_3P on the 1-butene dimerization. With increased amount of Ph_3P, the conversion of 1-butene decreases, while the selectivity of dimers increases. But excessive addition of Ph_3P (such as P/Zr ratio >1.0) will lead to decrease of both the conversion of 1-butene and selectivity of dimers. Moreover, the addition of basic phosphine ligand will prevent isomerization of 1-butene to 2-butene. When the P/Zr ratio is over 3.0, 1-butene isomerization reaction will not take place. These are due to the phosphine ligand weakening the Lewis acidic centers in the system which results in the reduction of catalyst activity.

3.5. Effect of the addition of PhONa

Table 3 gives the results of the 1-butene dimerization catalyzed by the $ZrCl_4/Et_2AlCl/PhONa$ system. It can be seen that the addition of PhONa reduces the catalyst activity strongly and increases the selectivity of dimers. Compared with Ph_3P (see table 2), a small quantity of PhONa will inhibit 1-butene isomerization completely. Our previous IR studies showed that a Zr–O bond and not a Zr–P bond was formed in this catalytic system during the catalyst aging period [8]. This demonstrates that PhONa is a more basic ligand which can occupy the empty coordination edge in the active species. Therefore, the coordination of 1-butene is rather difficult while the β-H elimination of the dimers is relatively easy. This gives an explanation for the above results.

Table 4
Dimerization of 1-butene via $ZrCl_4/n\text{-}Bu_2Mg/Ph_3P$ catalytic system.[a]

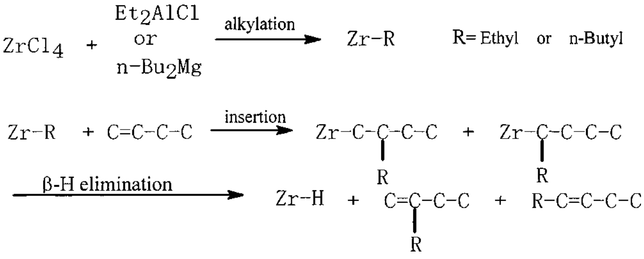
Mg/Zr ratio	2-butene (%)	$C_6^=$ (%)	$C_8^=$ (%)	$C_{12,16}^=$, etc. (%)
10	0	0	0	100
20	0	0	0	100
30	0	0	little	over 99

[a] Reaction at 353 K for 2 h, P/Zr = 1.0, solvent: C_6H_5Cl.

3.6. Mechanism of the 1-butene dimerization

The metal hydride mechanism for 1-butene dimerization was suggested by Keim et al. [1] and Jones et al. [12] in their study using a nickel complex as the catalyst. In this study, we found some $C_6^=$ in the 1-butene dimerization products catalyzed by the zirconium-based Ziegler–Natta system (see tables 1–3). Since $C_6^=$ impurities were not introduced in the reaction, we presume that $C_6^=$ originate from the process of forming the Zr–H active species. In order to test this idea, we used ether-free n-Bu_2Mg as the promoter and employed the $ZrCl_4/n\text{-}Bu_2Mg/Ph_3P$ system to catalyze dimerization of 1-butene. The results are listed in table 4. It can be seen that the main products are $C_{12}^=$, $C_{16}^=$, while no $C_8^=$ was found. This may be due to the stronger alkylation ability of n-Bu_2Mg. However, the most important point is that there are no $C_6^=$ in the products. This further suggests that $C_6^=$ are formed by 1-butene inserting into the Zr–C_2H_5 bond and then β-H elimination.

In summary, we suggest the process of forming the Zr–H active species is as follows:

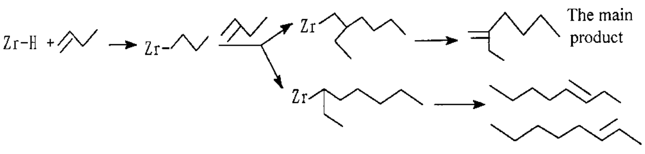


$$ZrCl_4 + \begin{matrix}Et_2AlCl\\ \text{or}\\ n\text{-}Bu_2Mg\end{matrix} \xrightarrow{\text{alkylation}} Zr\text{-}R \qquad R = \text{Ethyl or n-Butyl}$$

$$Zr\text{-}R + C{=}C\text{-}C\text{-}C \xrightarrow{\text{insertion}} Zr\text{-}C\text{-}\underset{R}{C}\text{-}C\text{-}C + Zr\text{-}\underset{R}{C}\text{-}C\text{-}C\text{-}C$$

$$\xrightarrow{\beta\text{-H elimination}} Zr\text{-}H + C{=}\underset{R}{C}\text{-}C\text{-}C + R\text{-}C{=}C\text{-}C\text{-}C$$

If R is ethyl, $C_6^=$ can be detected in the products, while if R is n-butyl, there are $C_8^=$, not $C_6^=$ in the products. The Zr–H active species react with 1-butene to produce dimers as follows:



Our results support the metal hydride mechanism for olefin oligomerization via homogeneous catalysis.

4. Conclusions

(1) After careful modifications, a zirconium-based Ziegler–Natta catalyst can be employed successfully to catalyze

the dimerization of 1-butene. Under the optimum conditions, the conversion of 1-butene is 91.9%, the selectivity of dimers is 76.7%. In addition, basic ligands can prevent isomerization of 1-butene to 2-butene effectively.

(2) Based on the facts that there are C_6 olefins in the products using Et_2AlCl as a promoter while using n-Bu_2Mg as a promoter there are not at all, a metal hydride mechanism for the dimerization of 1-butene is suggested.

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