



Positive studies on the displacement reaction of trialkylaluminum with ethylene catalyzed by cobalt complexes

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Abstract

The catalytic properties of a series of cobalt complexes containing monodentate phosphorus, bidentate phosphorus, bidentate nitrogen ligand for displacement reaction of trialkylaluminum with ethylene is reported. Effect of reaction time, temperature and different ligands on catalyst performance has been investigated. The kinetics of the reaction of tri-isobutylaluminum with ethylene catalyzed by zerovalent cobalt complex has been studied. The displacement reaction rate shows first-order dependence with respect to trialkylaluminum concentration, cobalt complex concentration and ethylene pressure, respectively. The kinetics equation of displacement reaction rate is $r = 1.4 \times 10^6 [R_3Al][Cat][P_{C_2H_4}]$. The activation energy for this reaction is $E_a = 71.9 \text{ kJ/mol}$.

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Keywords: Ethylene; Displacement reaction; Trialkylaluminum; Kinetics; Cobalt complex

1. Introduction

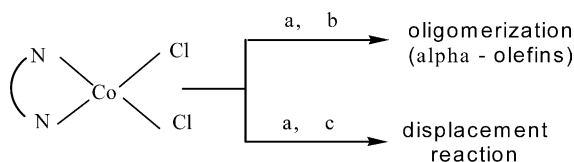
Ethylene oligomerization by late transition metal catalysts have been attracting much attention [1,2]. Oligomerization of ethylene based on phosphorus–oxygen chelates nickel complexes is particularly well-developed, and is employed in industrial process [3–5], it is the first step of the shell higher olefin process (SHOP) [4]. The SHOP process produces linear alpha olefins in the C_4 – C_{20+} range, which are used as comonomers to synthesize LLDPE and in the production of lubricants, plasticizers, surfactants and detergents [6].

We have been interested for some years in studying ethylene oligomerization catalyzed by late transition metal catalysts in combination with ethylaluminumoxane (EAO) [7,8], it was surprising that no oligomerization activity was observed when Et_3Al or $i-Bu_3Al$ was used instead of EAO. Brookhart reported that no active catalyst could be formed when Me_3Al was used as cocatalyst in nickel(II) diimine catalyzed ethylene oligomerization [9]. In fact, trialkylaluminum (R_3Al) reacts with ethylene catalyzed by transition metal (Scheme 1); the reaction of R_3Al with ethylene can also be called the displacement reaction (Scheme 2, path a) [10,11]. The displacement reaction between trialkylaluminum and olefins was first studied by Ziegler in 1954 [12]. Lardica et al. noted that the conversion of $i-Bu_3Al$ was 99.9% in the displacement reaction of $i-Bu_3Al$ with 4-methy-1-hexene catalyzed by bis(*N*-ethylsalicylaidimino) nickel [11].

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Scheme 1. The role of cocatalyst: $a = C_2H_4$; $b = EAO$; $c = R_3Al$.

Although trialkylaluminum deactivated the oligomerization activity of late transition metal catalysts, the research on the catalyzed displacement reaction is still of considerable industrial interest as well as of academic value. Lin et al. have studied the nickel or cobalt-containing displacement catalysts [13]. It has long been known that alpha olefins can be produced through “Alfene” process (Scheme 2, path b) [14]. Such a non-catalytic thermal displacement process, which already have become a commercial production process, suffers from the high energy consumption required by the high displacement reaction temperature (553–573 K), followed by the rapid cooling [13]. On the other hand, the catalyzed displacement reaction can take place at lower temperature, and has industrial application potential. However, very few studies have been devoted to a new type of displacement catalysts. In this paper we report the novel displacement catalysts including a series of cobalt complexes containing monodentate phosphorus, bidentate phosphorus, bidentate nitrogen ligands.

2. Experimental

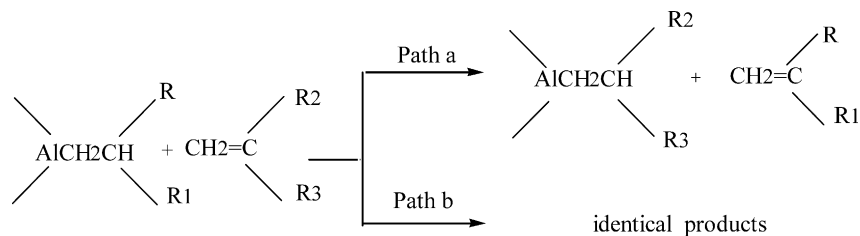
2.1. Materials

All operations were performed with standard Schlenk techniques. Toluene was distilled over

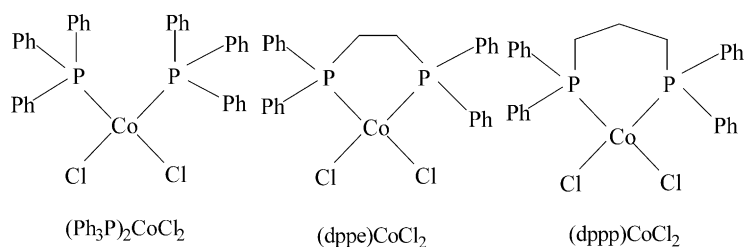
sodium under nitrogen. The complexes were prepared, respectively, according to the literatures: **A**: $CoCl_2(PPh_3)_2$ [15]; **B**: $CoCl_2(dppe)$ ($dppe = Ph_2P(CH_2)_2PPh_2$) [16]; **C**: $CoCl_2(dppp)$ ($dppp = Ph_2P(CH_2)_3PPh_2$) [16]; **D**: $Co(Salen)$ ($Salen = N,N'$ -ethylenebis(salicylideneaminato)) [17]; **E**: $CoCl_2(PhCH=NCH_2CH_2N=CHPh)$ [18]; **F**: $CoN_2(PPh_3)_3$ [19]. The catalyst structures of **A**, **B** and **C** were illustrated in Scheme 3. Trialkylaluminum was an industrial product which contained even number carbon atoms in the range of 4–20 per alkyl group. The gas chromatogram of trialkylaluminum hydrolyzate was illustrated in Fig. 1, and the gas chromatogram of product hydrolyzate was illustrated in Fig. 2. The other materials were commercial products and used without further purification.

2.2. Displacement reaction

The displacement reaction was carried out in a 75 ml stainless autoclave with magnetic stirring. First, the autoclave was kept under vacuum at 100 °C for 1–1.5 h, after cooling was charged by the toluene solution of trialkylaluminum and catalyst with injector under nitrogen. The autoclave was maintained at constant temperature and ethylene pressure. After the reaction, 2 ml reaction products were hydrolyzed and analyzed by a gas chromatograph SRI 8610C, 30 m × 0.32 mm OV-1 column with an FID detector. The column temperature program for liquid sample was from 333 K (hold 8 min, 15 °C/min) to 443 K (hold 5 min, 10 °C/min), up to 523 K (hold 0 min, 15 °C/min), and up to 573 K (hold 30 min). Temperature program for gas sample was from 288 K (hold 6 min, 15 °C/min) up to 313 K (9 °C/min, hold 0 min), then up to 383 K (hold 10 min).



Scheme 2. Displacement reaction: path (a) catalytic displacement, room temperature ~400 K; path (b) non-catalytic thermal displacement, 500–570 K.



Scheme 3. The catalyst structures of A, B and C.

2.3. Kinetics investigation

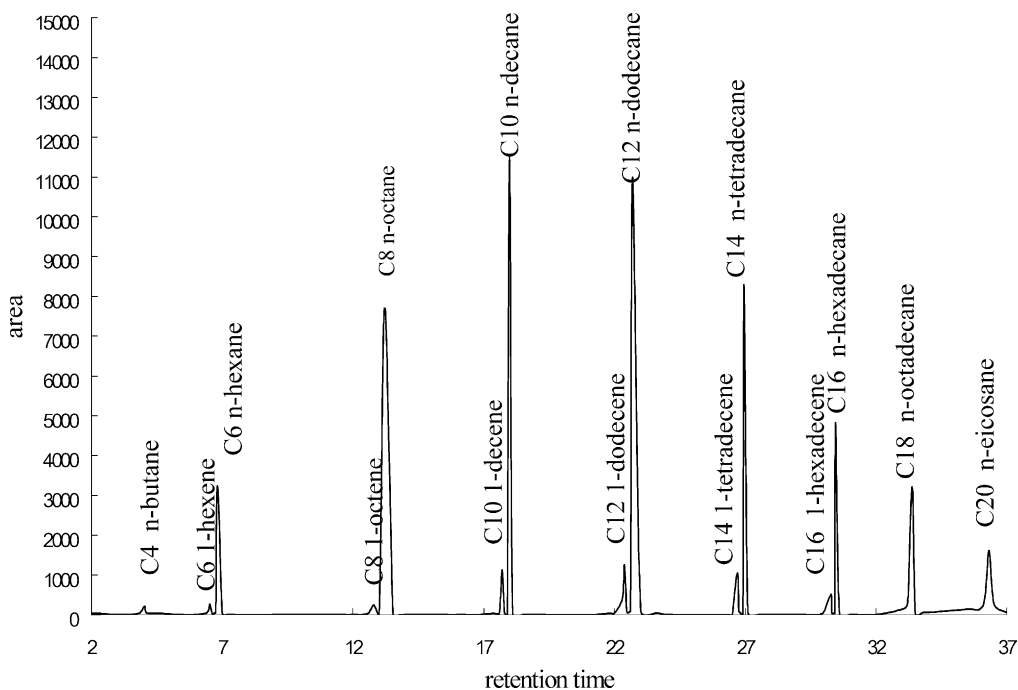
The reaction temperature was controlled with $\pm 0.5^\circ\text{C}$ of the set point, the ethylene was measured with a mass flow sensor TMF-G3, and the catalyst solution was not charged until solvent saturation was reached. This procedure produced the solubility curve of ethylene in solvent for each temperature and pressure conditions used in this work. The kinetic parameters were evaluated in the temperature range from 303 to 318 K, where the diffusion and mass transfer effects can be neglected. Isomerization products were not found at the operating conditions.

3. Results and discussion

3.1. Catalytic behavior of cobalt complexes

3.1.1. Effect of cobalt complexes containing phosphorus ligand

A series of experiments were undertaken in order to determine the effect of different type ligands on catalyst performance. The result are presented in Table 1. When temperature was raised from 343 to 403 K, the conversion of trialkylaluminum went up, high temperature being favorable for the displacement reaction.

Fig. 1. The GC spectrum of R_3Al hydrolyzate.

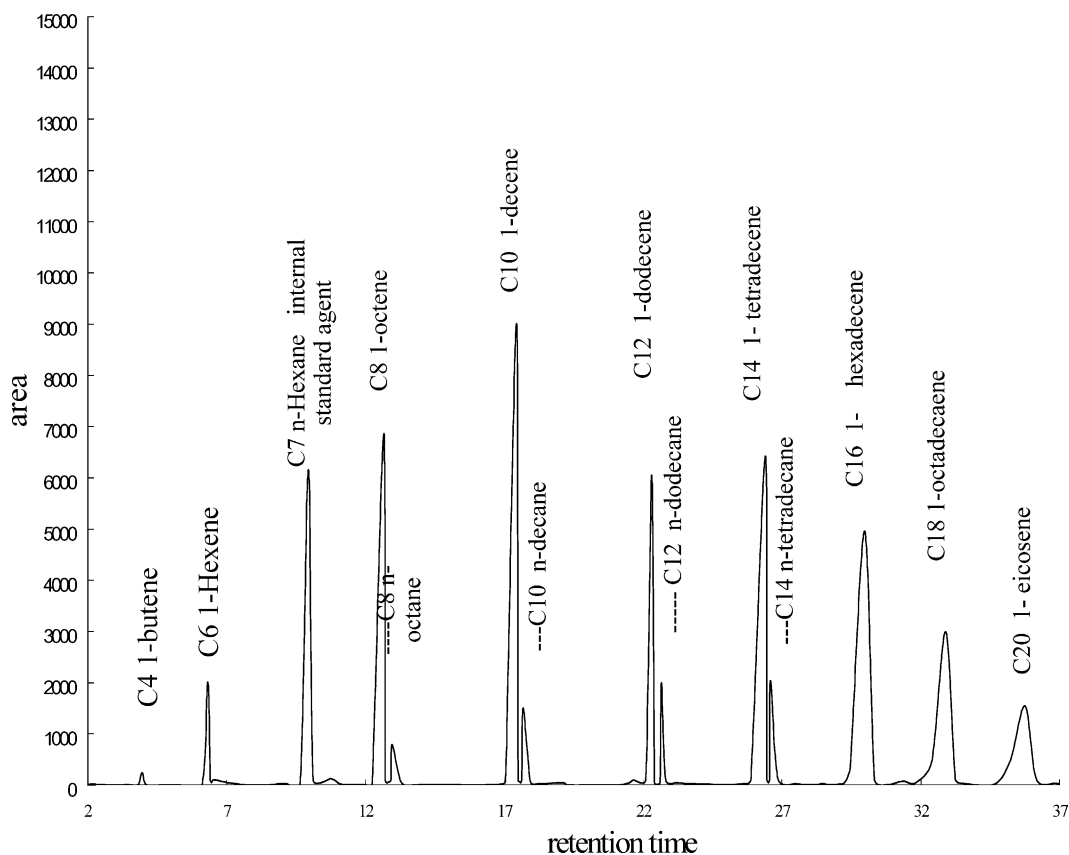


Fig. 2. The GC spectrum of product hydrolyzate.

The cobalt complexes containing monodentate phosphorus ligand (**A**: $\text{CoCl}_2(\text{PPh}_3)_2$; **F**: $\text{CoN}_2(\text{PPh}_3)_3$) performed better than those containing bidentate phosphorus ligand (**B**: $\text{CoCl}_2(\text{dppe})$; **C**: $\text{CoCl}_2(\text{dppp})$).

Table 1
The effect of cobalt complexes containing phosphorus ligand

Catalyst	Conversion (%)	
	343 K	403 K
A	70.4	82.6
B	28.2	53.4
C	15.3	52.2
F	64.0	79.1

Reaction conditions: ethylene pressure: $P_{\text{C}_2\text{H}_4} = 1.4 \text{ MPa}$; reaction time: $t = 0.5 \text{ h}$; trialkylaluminum concentration: $[\text{R}_3\text{Al}] = 1 \text{ mol/l}$; cobalt complex concentration: $[\text{Cat}] = 150 \text{ ppm}$; total liquid volume = 20 ml.

Lardica et al. pointed out a rational mechanism of nickel-catalyzed displacement reaction [11]. Suppose the cobalt-catalyzed displacement reaction also follows the similar path, the first step of displacement reaction will involve the dissociation of ligand (Eq. (1)):



where L represents the ligand, $n \geq 2$.

If the dissociation step is a slow step, and a rate-determining step, the different catalytic behavior between complexes **A** and **B** (or **C**) might in principle be connected with the nature of the ligands bound to the cobalt atom. PPh_3 , which is a monodentate phosphorus ligand, can easily dissociate. In contrast, dppe (or dppp), which is a bidentate phosphorus ligand, associates with cobalt atom and forms a stable complex, so the dissociation rate of dppe (or dppp)

Table 2
The effect of cobalt complexes containing bidentate nitrogen ligand

Catalyst	Conversion (%)	
	343 K	403 K
D	30.1	71.3
E	50.6	60.8

The reaction conditions are the same as those in Table 1.

is slower than PPh_3 . It is adverse for such a stable complex (**B** or **C**) to form active species.

3.1.2. Effect of cobalt complexes containing bidentate nitrogen ligand

For the catalysts **D** and **E**, the result are presented in Table 2. Cobalt complexes containing bidentate nitrogen ligand performed slight better than those containing bidentate phosphorus ligand. It might be caused by the decreased backbonding effect of nitrogen ligand. P atom in dppe (or dppp) has empty d orbit, which interact with filled metal d orbit [20], whereas N atom has no empty d orbit. The backbonding effect strengthens Co–P bond and may cause the slower ligand dissociation rate of P, P complexes than N, N complexes.

3.1.3. Effect of reaction time and temperature

Effect of reaction time, temperature on the conversion of trialkylaluminum catalyzed by cobalt complex $\text{CoCl}_2(\text{PPh}_3)_2$ has been investigated. The result are presented in Table 3. When temperature was raised from 313 to 403 K, the conversion of trialkylaluminum went up smoothly; high temperature was favorable for the displacement reaction. The conversion increased when reaction time was extended from 10 to 30 min. The other catalysts showed similar tendency.

Table 3
Effect of reaction time and temperature on the performance of catalyst

Temperature (K)	Time (min)	Conversion (%)
313	30	40.2
343	30	70.4
373	30	75.8
403	30	82.9
403	10	45.4
403	20	63.2
403	40	83.2

The reaction conditions are the same as those in Table 1.

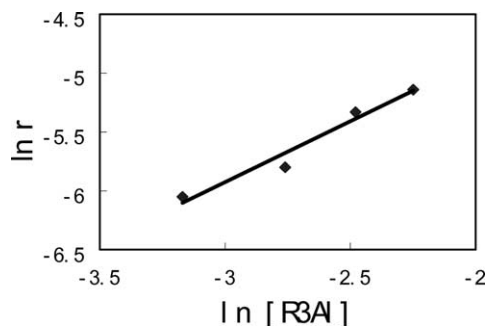


Fig. 3. The effect of tri-isobutylaluminum concentration. Reaction conditions: $P_{\text{C}_2\text{H}_4} = 1.0 \text{ MPa}$; $[\text{Cat}] = 1.11 \times 10^{-4} \text{ mol/l}$; $T = 303 \text{ K}$.

3.2. Kinetic study

The kinetics of the displacement reaction of tri-isobutylaluminum with ethylene catalyzed by zerovalent cobalt complex $\text{CoN}_2(\text{PPh}_3)_3$ (**F**) has been studied.

3.2.1. Effect of tri-isobutylaluminum concentration

It was found that the initial reaction rate rose with increasing concentration of tri-isobutylaluminum. The results are presented in Fig. 3. Since the slope of the line $\ln[\text{Bu}_3\text{Al}]$ versus $\ln r$ is 1, indicating a first-order dependence with respect to trialkylaluminum concentration.

3.2.2. Effect of cobalt(0) complex concentration

Fig. 4 shows the effect of cobalt(0) complex concentration on displacement reaction. As might be anticipated, the reaction rate increased with increasing

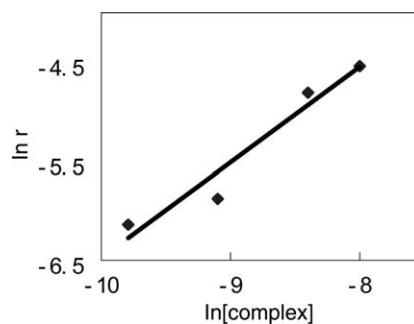


Fig. 4. The effect of catalyst concentration. Reaction conditions: $P_{\text{C}_2\text{H}_4} = 1.0 \text{ MPa}$; $[i\text{-Bu}_3\text{Al}] = 0.063 \text{ mol/l}$; $T = 303 \text{ K}$.

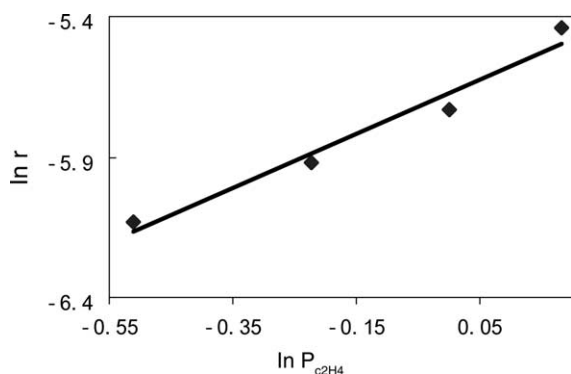


Fig. 5. The effect of ethylene pressure. Reaction conditions: $[i\text{-Bu}_3\text{Al}] = 0.063 \text{ mol/l}$; $[\text{Cat}] = 1.11 \times 10^{-4} \text{ mol/l}$; $T = 303 \text{ K}$.

concentration of cobalt(0) complex, exhibiting first-order dependence on cobalt(0) complex concentration in the range from 5.6×10^{-5} to $3.32 \times 10^{-4} \text{ mol/l}$.

3.2.3. Effect of ethylene pressure

The displacement reaction was carried out in the pressure range from 0.6 to 1.2 MPa. The effect of ethylene pressure on displacement reaction is shown in Fig. 5. It was found that the displacement reaction rate increased significantly with increase in ethylene pressure, exhibiting first-order dependence on ethylene pressure.

3.2.4. Effect of reaction temperature

The effect of reaction temperature on displacement reaction was studied in the temperature range

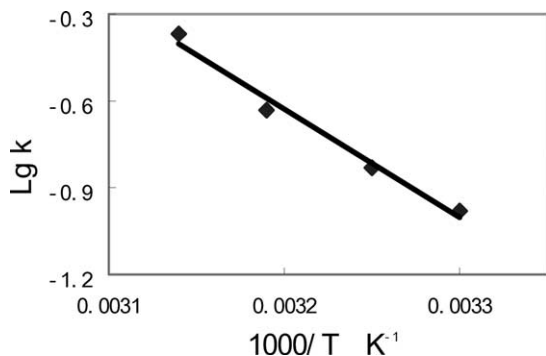


Fig. 6. The effect of reaction temperature. Reaction conditions: $P_{C_2H_4} = 1.0 \text{ MPa}$; $[i\text{-Bu}_3\text{Al}] = 0.063 \text{ mol/l}$; $[\text{Cat}] = 1.11 \times 10^{-4} \text{ mol/l}$.

from 303 to 318 K, and the activation energy of the reaction was determined. The results are illustrated in Fig. 6. Apparent activation energy derived from the plot is 71.9 kJ/mol. The kinetics equation of displacement rate is $r = 1.4 \times 10^6 [\text{R}_3\text{Al}][\text{Cat}][P_{C_2H_4}]$. Further work is in progress, and the mechanism of the cobalt-catalyzed displacement reaction through evaluating the kinetic parameters will be discussed subsequently.

4. Conclusion

No oligomerization activity was observed when trialkylaluminum was used instead of alkylaluminum (MAO or EAO) in ethylene oligomerization catalyzed by late transition metal catalysts. In this case the displacement reaction take place instead of oligomerization. Cobalt complexes containing monodentate phosphorus ligand perform best among the above novel displacement catalysts. The kinetics of the reaction of tri-isobutylaluminum with ethylene catalyzed by zerovalent cobalt complex $\text{CoN}_2(\text{PPh}_3)_3$ shows the first-order dependence with respect to trialkylaluminum concentration, catalyst concentration, and ethylene pressure. The kinetics equation of displacement reaction rate is $r = 1.4 \times 10^6 [\text{R}_3\text{Al}][\text{Cat}][P_{C_2H_4}]$. The activation energy for this reaction is $E_a = 71.9 \text{ kJ/mol}$.

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