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Studies on the Displacement Reaction of Trialkylaluminum with Ethylene Catalyzed by Nitrogen Chelate Cobalt Complexes

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Abstract: The catalytic properties of a series of cobalt complexes containing bidenated nitrogen ligand for displacement reaction of trialkylaluminum with ethylene is reported. Effect of different reaction time, temperature and cobalt complexes containing different ligand on catalyst performance has been investigated.

Keywords: Ethylene, displacement reaction, trialkylaluminum, cobalt complex.

We have interested for some years in studying ethylene oligomerization catalyzed by late transition metal catalysts in combination with ethylaluminoxane (EAO)[1,2]. It was surprising that no oligomerization activity was observed when Et_3Al or i-Bu_3Al was used instead of EAO. Brookhart reported that it was failure to form an active catalyst when Me_3Al was used as cocatalyst in nickel(II) diimine catalyzed ethylene oligomerization[3]. In fact, the trialkyl aluminum (R_3Al) has reacted with ethylene catalyzed by transition metal (**Scheme 1**), the interaction of the R_3Al with ethylene is also called the displacement reaction[4,5] (**Scheme 2**, path a).

Although the 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 academic value. Lin and Andrew have studied the oxygen-containing nickel or cobalt displacement catalysts[6]. It has long been known that alpha olefins can be produced through "Alfene" process (**Scheme 2**, path b), such a non-catalytic thermal displacement process has already become a production process, but it suffers from the high energy consumption due to the high displacement reaction temperature (553 –573K) and the rapid cooling[6]. So the catalyzed displacement reaction has a potential application in industry due to the lower reaction temperature. However, very few studies describe about such new type of displacement catalyst. In this paper we report the novel displacement catalysts including a series of cobalt complexes containing bidenated nitrogen ligand.

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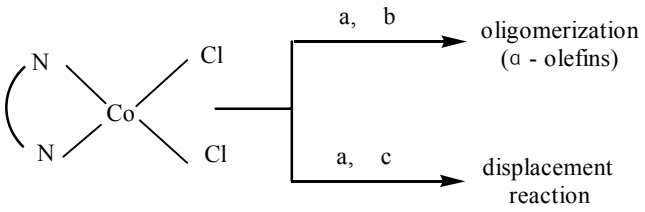
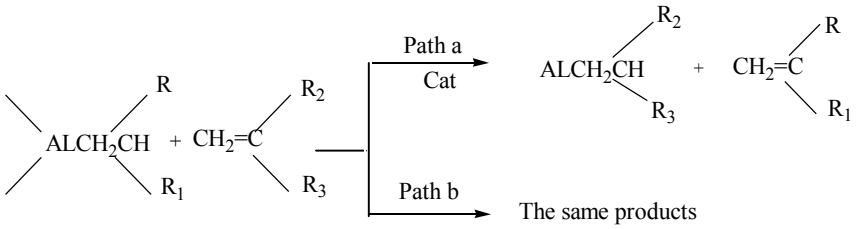
Scheme 1 The role of cocatalyst



a=C_2H_4, b=EAO, c=R_3Al

Scheme 2 Displacement reaction



Path a: catalytic displacement, room temperature ～ 120°C
Path b: non-catalytic themal displacement , 250 ～ 300°C

Experimental

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** : Co(Salen)[7], Salen = N,N′- ethylenebis (salicylideneaminato), **B**: $CoCl_2$ (PhCH=NCH_2CH_2N=CHPh)[8] . The other materials were commercial products and used without further purification.

The displacement reaction was carried out in a 75 mL stainless autoclave with magnetic stirring. Before every experiment, the autoclave was kept under vacuum at 100℃ for 1-1.5 h, after cooling it was charged by the toluene solution of tri-isobutylaluminum and catalyst under nitrogen. The autoclave was maintained at 343K, 403K respectively, and at 1.4MPa ethylene pressure. After the reaction, 2 mL reaction products were hydrolyzed and then analyzed by gas chromatography SRI 8610C with a FID detector, 30m×0.32 mm OV-1 column.

Results and Discussion

A series of experiments were undertaken in order to determine the effect of different bidenated nitrogen ligand on catalyst performance. The results were presented in **Table 1**. The effect of different reaction time, temperature on the conversion of tri-isobutylaluminum with catalyst cobalt complex Co(Salen) has been investigated. The

results were presented in **Table 2**. When temperature was raised from 313 K to 403 K, the conversion of tri-isobutylaluminum went up smoothly, and high temperature was favorable for the displacement reaction. The conversion increased when the reaction time was extended from 10 to 30 minutes. The reaction with other catalysts showed same tendency.

Table 1 The effect of cobalt complexes containing bidenated nitrogen ligand

Catalyst	Conversion (%)	
	343K	403K
A	30.1	71.3
B	50.6	60.8

Reaction conditions: Pressure of ethylene: 1.4Mpa; reaction time: 0.5 h; tri-isobutylaluminum concentration: 1 mol/L; cobalt complex concentration: 150 ppm; Total liquid volume: 20 mL.
A : Co(Salen) ; B : $CoCl_2$ ($PhCH{=}NCH_2CH_2N{=}CHPh$).

Table 2 Effect of reaction time and temperature on the conversion

Tmperature(K)	time (min)	Conversion (%)
313	30	25.8
343	30	30.1
373	30	56.8
403	30	71.3
403	10	27.8
403	20	52.6
403	40	71.6

Reaction conditions: Pressure of ethylene: 1.4Mpa; tri-isobutylaluminum concentration: 1 mol/L; cobalt complex concentration: 150 ppm; Total liquid volume: 20 mL.

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