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Dimerization of Propylene by Nickel (II) and Cobalt (II) Catalysts Based on Bidentate Nitrogen-phosphino Chelating Ligands

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Abstracts: The catalytic property of propylene dimerization by several nickel (II), cobalt (II) complexes containing N-P bidentate ligands was studied in combination with organoaluminum co-catalysts. The effects of the type of aluminum co-catalysts and its relative amount, the nature of precursors in terms of ligand backbone and metal center were investigated. The results indicated that precursor **I** (N,N-dimethyl-2-(diphenylphosphino)aniline nickel (II) dichloride) exhibited high activity in propylene dimerization in the presence of the strong Lewis acid $Et_3Al_2Cl_3$, whereas low productivity by its cobalt analogues was observed under identical reaction conditions.

Keywords: Bidentate nitrogen-phosphino ligands, nickel (II) and cobalt (II) complexes, propylene dimerization, Al co-catalyst.

It is well known that the SHOP (Shell Higher Olefin Process) makes use of neutral nickel catalysts $[Ni(PO)(PR_3)(R)]$ to manufacture highly linear α-olefin[1-3]. Subsequently great interests in bidentate P-X (X=N, O) ligands in the activation of alkene were encouraged[4-9]. Recently, W. Keim published the application of either cationic or neutral 2-(diphenylphosphino)nicotinate nickel (II) complexes in ethylene oligomerization[10]. Then ethylene oligomerization by neutral imine-phosphino palladium (II) complex was also reported[11]. The reactivity in the propylene oligomerization by cationic P-N nickel (II) complexes has been examined too[12]. Notwithstanding it is generally considered that direct use of the neutral or cationic catalysts makes easy formation of coordination site for alkene molecule in the alkene activation process, the nickel (II), iron (II) and cobalt (II) halide complexes based on either bidentate or polydentate imine chelating ligands in combination with proper activator displayed extremely high productivity in olefin polymerization[13, 14]. More recently, R. He reported that the iron (II) and cobalt (II) halide complexes bound to potentially tridentate $RN(CH_2CH_2PPh_2)_2$ chelating ligand combined with EAO (ethylaluminoxane) exhibited appreciable activity in the oligomerization of ethylene[15].

It is interesting to further explore the potential catalytic behavior of hemilabile N-P

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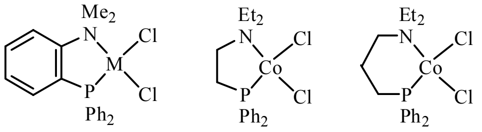
ligands incorporated complexes in the activation of alkene. Here the catalytic performance of several nickel (II) and cobalt (II) complexes based on bidentate nitrogen-phosphino ligands in the presence of Al co-catalyst was examined in the dimerization of propylene. Particular attention was devoted to the influence of the nature of precursor, in terms of the ligand backbone and metal center. Furthermore, the type of Al activators and Al/Ni ratio would be discussed here in order to improve the catalytic performance.

Experimental

Figure 1



M=Ni **I**
M=Co **II**

III

IV

Various N-P bidentate ligands and their nickel (Ⅱ), cobalt (Ⅱ) complexes (**Figure 1**, **I**, **II**, **III** and **IV**) were prepared with known methods[15-17]. EAO was prepared by partial hydrolysis of Et_3Al in toluene at -15~-10 ℃ with ground $CuSO_4 \cdot 5H_2O$ as water source ($Al/H_2O=1$, molar ratio).

Catalytic batch experiments were carried out in a 100 mL stainless steel autoclave according to reported procedures[18], and the products were analyzed by GC.

Results and Discussion

Influence of the Al/Ni ratio and the type of Al co-catalysts on the catalytic performance

Primarily, the dimerization reaction was carried out by nickel precursor **I** in combination with organoaluminum co-catalyst. The effects of Al/Ni ratio and the type of Al co-catalysts on catalytic behavior were checked. The results were described in **Table 1**.

The nickel precursor **I** exhibited no activity at all in propylene dimerization in the absence of aluminum activator, as shown in entry 1. When $Et_3Al_2Cl_3$ was used as a co-catalyst (Al/Ni=50, entry 2), a rather high productivity was observed. As increasing the Al/Ni molar ratio from 50 to 100 and 200 (entries 2-4), a continuous improvement of productivity was observed. No further enhancement of catalytic activity in the system was ascertained as further increasing the Al/Ni molar ratio higher than 200 (entries 5-7). It clearly indicated that the proper value of Al/Ni molar ratio was at about 200.

When Et_2AlCl was employed as a co-catalyst instead of $Et_3Al_2Cl_3$, a marked drop of catalytic activity was observed (entry 8). It led to further reduction of catalytic productivity when treated with $AlEt_3$ as evidenced in entry 9. Poor activity was achieved as well in the case of $Al(i\text{-Bu})_3$, and as EAO was adopted no activity at all was confirmed (entries 10 and 11). All the data allowed us to conclude that, in addition to its properly alkylating ability, strong Lewis acidity of organoaluminum was also required for the activation of nickel precursors incorporated N-P ligands in the propylene dimerization.

Table 1 Effects of the Al/Ni ratio and type of Al co-catalysts on the catalytic performance

Entry	Al co-catalyst		TOF	$C_6^=$	Distribution of dimer (wt %)			
	Type	Al/Ni	(h^{-1})	(wt %)	4MP	2MP	Hex	2,3DMB
1	$Et_3Al_2Cl_3$	0	0	0	-	-	-	-
2	$Et_3Al_2Cl_3$	50	98600	78.0	52.9	27.3	16.0	3.8
3	$Et_3Al_2Cl_3$	100	99107	80.2	42.0	38.0	15.9	4.1
4	$Et_3Al_2Cl_3$	200	149000	82.5	44.2	34.0	16.2	5.6
5	$Et_3Al_2Cl_3$	300	116000	82.1	50.2	30.1	16.7	3.0
6	$Et_3Al_2Cl_3$	400	89300	81.3	43.1	36.8	15.9	4.2
7	$Et_3Al_2Cl_3$	600	90800	78.9	52.1	27.8	18.4	1.7
8	Et_2AlCl	200	42300	87.3	51.9	28.4	16.0	3.7
9	$AlEt_3$	200	18000	85.2	55.2	26.3	14.9	3.6
10	$Al(i\text{-}Bu)_3$	200	5400	83.0	57.6	25.2	14.7	2.5
11	EAO	200	0	0	-	-	-	-

Reaction conditions: 8 μ mol precursor **I**, 18 mL PhCl, 0.4 MPa $C_3^=$, 25 ℃, 60 min.
[*]TOF: Turnover Frequency expressed as moles of propylene converted/(moles of Ni × h)
[**]MP=methylpentenes, HEX=hexenes and DMB=dimethylbutenes.

The results in **Table 1** also showed that, selectivity of the catalytic process, in terms of selectivity to dimers and regioselectivity in dimers, was relatively unaffected with varying the concentration and the type of organoaluminum co-catalysts, at least under the adopted reaction conditions.

Influence of the nature of precursors on the catalytic performance

Taking account into that the structural characteristics and stability of nickel (II), cobalt (II) complexes are closely dependent on the nature of N-P ligands, thus it is possible to modify the catalytic behavior by carefully tuning the ligands as well as the metal centers in the system. Therefore the catalytic performance of several nickel (II) and cobalt (II) catalysts based on different nitrogen-phosphino chelating ligands under propylene atmosphere was checked in combination with aluminum promoters.

As shown in **Table 2**, when cobalt complex **II** was adopted as a precursor (entries 12 and 13), a drastic reduction of activity was observed compared to the analogous nickel one despite of the type of co-catalysts used (entries 4 and 8). No activity at all was given by precursor **II** and $AlEt_3$ co-catalyst (entry 14). When cobalt species **III** and **IV** characterized by alkyl chain backbones were employed as precursors (entries 15 and 16), lower productivity was detected as well compared with **II** system. This behavior may be attributed to the presence of conjugated system in complex **II**.

Notwithstanding certain modification concerning the catalytic activity occurred with adjusting the nature of precursors, no variation of the catalytic selectivity was observed whenever any kind of precursors were used. It may be concluded that the insertion fashion of either the first or the second propylene molecule into the nickel (or cobalt) species was essentially unchanged with adjusting the structural character in the range of similar coordination mode, at least under the adopted reaction parameters.

Table 2 Effect of the type of precursors on the catalytic performance

Entry	Precursor	Al co-catalyst	TOF (h^{-1})	$C_6^=$ (wt %)	Distribution of dimers (wt %)			
					4MP	2MP	Hex	2,3DMB
12	**II**	$Et_3Al_2Cl_3$	39000	80.7	49.8	30.7	17.2	2.3
13	**II**	Et_2AlCl	11600	83.2	52.6	26.9	17.8	2.7
14	**II**	Et_3Al	0	-	-	-	-	-
15	**III**	$Et_3Al_2Cl_3$	12200	78.6	50.1	27.6	17.4	4.9
16	**IV**	$Et_3Al_2Cl_3$	11500	80.1	49.8	28.5	17.3	4.4

Reaction conditions: Al/Ni =200 (molar ratio), the other conditions are the same as shown in **Table 1**.

Further investigation on other multidentate N-P chelating ligands coordinated nickel catalysts in the propylene dimerization is in progress.

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