

Propylene Dimerization by ($\eta^5\text{-C}_9\text{H}_7$)₂ Nickel(II) Catalytic System

WU, Si-Zhong^{a,b}(吴思忠) LU, Shi-Wei^{*a,b}(陆世维)

^a National Engineering Research Center for Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, Liaoning 116011, China

^b Dalian Chem-Phy Chemical Company Ltd., Dalian, Liaoning 116011, China

The catalytic performance of Ni($\eta^5\text{-Ind}$)₂ complex in the dimerization of propylene was studied in combination with an organoaluminum co-catalyst, eventually in the presence of a phosphine ligand. The effects of the type of aluminum co-catalyst and its relative amount, the nature of phosphine ligand and P/Ni ratio as well as the reaction temperature were examined. The results indicated that the nickel precatalyst exhibited high productivity for the propylene dimerization together with organoaluminum. It was likely to strongly modify the reactivity in the catalytic system when using phosphine ligand as additives, especially at the reaction temperature below 0 °C. The catalytic system based on Ni($\eta^5\text{-Ind}$)₂ complex displayed an extremely high productivity (TOF up to 169000 h⁻¹) and a good regioselectivity to 2,3-dimethylbutenes (2,3-DMB) in dimers (66.4%) under proper reaction parameters.

Keywords Ni($\eta^5\text{-Ind}$)₂ complex, propylene dimerization, Al co-catalyst, phosphine ligand

Introduction

It is well known that olefin polymerization by metallocene catalysts technology has been the center in the area of polyolefin synthesis since the early 1980s.¹⁻⁴ For the last decades, considerable efforts have been devoted to the modification of metallocene catalysts with the aim to either controlling over the properties of resultant polymer or synthesizing new type polyolefin. Currently, an interesting family of group 4 metallocene catalysts based on η^5 -indenyl ligand and its analogues have been one of the most important segment in the field of polyolefin production, particularly some indenyl type metallocene catalysts with specific structure.⁵⁻⁸ Moreover, it was also found that these catalysts exhibited excellent reactivity for the oligomerization of olefin under appropriate reaction parameters.^{9,10} However, the research work was mainly focused on the early transition metal catalytic systems. There appeared few reports regarding the application of η^5 -indenyl late transition metal complexes in the alkene activation.¹¹

Indeed, a large number of transition metal catalysts for the propylene dimerization have been developed since 1960s, especially nickel-based species based on various chelating ligands.^{12,13} However, to the best of our knowledge, there is no report concerning the nickel-based catalysts containing η^5 -in-

denyl and its analogues adopted in the dimerization process of propylene up to now. In this paper, the catalytic behavior of bis(η^5 -indenyl)nickel(II) complex in combination with aluminum co-catalyst was examined under propylene atmosphere. Particular attention would be devoted to the catalytic behavior of the system modified by phosphine ligands, particularly at a controlled temperature.

Experimental

All manipulations were performed under dry argon using standard Schlenk techniques. Anhydrous toluene was obtained by distillation on Na metal and stored on molecular sieves (4A). Chlorobenzene was dried and deoxygenated with P₂O₅ after being treated with anhydrous CaCl₂ for a week. The other chemicals were used as received.

Bis(η^5 -indenyl)nickel(II) complex was prepared by IndLi reacting with anhydrous NiCl₂ according to the reported procedures.¹¹ EAO (ethylaluminumoxane) was obtained by partial hydrolysis of Et₃Al in toluene at -15—-10 °C with finely ground CuSO₄·5H₂O as water source (Al/H₂O = 1, molar ratio).

Catalytic batch experiments were carried out in a 100-mL stainless steel autoclave or a 500-mL rocking stainless steel autoclave. The proper amount of precursor was dissolved in chlorobenzene in a 50-mL Schlenk tube in the presence of desired phosphine ligand. Then the mixture was transferred into the autoclave under propylene atmosphere. The suitable Al co-catalyst was added. Then the temperature was adjusted to the desired value, and the autoclave was finally pressurized with propylene up to 0.4 MPa. The pressure was manually held at that value by repeated propylene feeds. After 60 min, the reaction was stopped by carefully degassing unreacted propylene and the liquid products were collected, weighed and analyzed by gas chromatography (GC).

The oligomeric mixture was analyzed by GC on HP-4890D equipped with FID and a 30 m SE-54 capillary column. *n*-Heptane was used as an internal standard. The distribution of dimers was analyzed by GC-910 equipped with a 4 m × 3 mm stainless steel column, with a stationary phase of

* E-mail: lusw.183@online.ln.cn; Tel.: +86-411-3698749; Fax: +86-411-3698749

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30% DMS. The column temperature was kept at 30 °C.

Results and discussion

Influence of the Al/Ni ratio on the catalytic performance

Preliminarily, the dimerization reaction was run by Ni(η^5 -Ind)₂ complex in the presence of Et₃Al₂Cl₃, and the effect of the relative amount of aluminum co-catalyst with respect to nickel metal was discussed.

As shown in Table 1, when Al/Ni molar ratio was varied in the range of 20 to 400 through 50, 100, 200 and 300 respectively (Entries 1–6), the activity increased with raising the aluminum concentration in the catalytic system. No any more improvement of activity was observed as further increasing the Al/Ni molar ratio higher than 400 (Entry 7). The results also showed that selectivity of the catalytic process, in terms of selectivity to dimers and regioselectivity in C₆ cut, was essentially independent on the aluminum concentration. The results indicated that the appropriate Al/Ni molar ratio in the activation of Ni(η^5 -Ind)₂ precatalyst under propylene atmosphere was around in the range of 200–400.

Table 1 Effect of the Al/Ni ratio on catalytic activity and selectivity^a

Entry	Al/Ni (molar ratio)	TOF ^b (h ⁻¹)	C ₆ ^c (wt%)	Distribution of dimers ^c (wt%)			
				D ₁ ^c	D ₂ ^c	D ₃ ^c	D ₄ ^c
1	20	14000	83.9	60.9	23.1	15.0	1.0
2	50	20300	85.5	58.2	24.5	16.4	0.9
3	100	28600	82.8	60.0	22.9	16.6	0.5
4	200	53000	81.2	63.1	19.4	16.8	0.7
5	300	56400	81.9	55.6	25.4	17.6	1.4
6	400	57000	80.5	57.9	23.4	17.2	1.5
7	600	50000	78.4	60.3	21.8	16.1	1.8

^a Reaction conditions: 0.01 mmol of Ni(η^5 -Ind)₂, Et₃Al₂Cl₃ as co-catalyst, 18 mL of PhCl, pressure of propylene = 0.4 MPa, 25 °C, 60 min. ^b TOF: "turnover frequency" expressed as the moles of propylene converted/(moles of Ni × h). ^c D₁ = 4-methylpentenes, D₂ = 2-methylpentenes, D₃ = hexenes, D₄ = 2,3-dimethylbutenes.

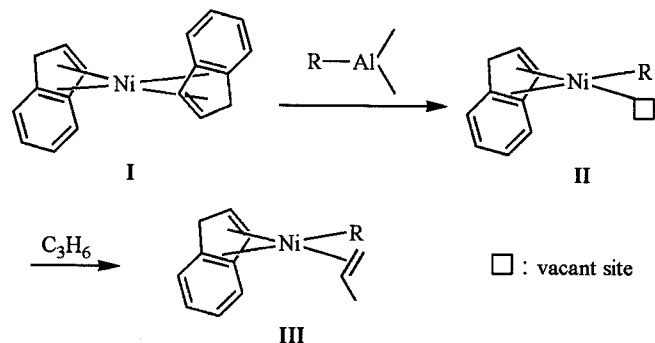
It is well developed that the active nickel species is *in situ* generated from the Ni(acac)₂ complexes when they were treated with alkyl aluminum promoters in the activation of olefin.¹⁴⁻¹⁶ Thus it allowed to assume that, treatment of Ni(η^5 -Ind)₂ complex with organoaluminum co-catalyst would result in releasing an η^5 -indenyl ligand from the nickel precursor (I, Scheme 1) with the formation of the active monoidenyl nickel intermediate (II, Scheme 1), which instantly coordinated with propylene molecule to afford III under propylene atmosphere due to its labile characteristics.

Influence of the type of aluminum co-catalyst on the catalytic performance

It was confirmed that a significant activity for the propy-

lene dimerization was obtained by Ni(η^5 -Ind)₂ species when using Et₃Al₂Cl₃ as alkylating agent at suitable Al/Ni ratio. Herein the effect of different type of aluminum co-catalyst was also tested.

Scheme 1



As demonstrated in Table 2, when Et₃Al₂Cl₃ was replaced by Et₂AlCl as an alkylating agent, a significant reduction of activity was detected (Entry 8). And a lower productivity was observed when AlEt₃ was employed as compared to that of Et₂AlCl (Entry 9). Being treated with EAO co-catalyst, no activity at all was obtained as shown in Entry 11. The results indicated that the catalytic activity was declined with the drop of Lewis acidity of Al co-catalyst. The data seemed to confirm that, in addition to its proper alkylating capability, strong acid strength of aluminum co-catalyst was also required in order to obtain high activity by Ni(η^5 -Ind)₂ catalyst, at least under the adopted reaction conditions. In the case of Al(*i*-Bu)₃ activator (Entry 10), the catalytic system also exhibited a poor productivity. The observation may be due to its scarce alkylating ability as mentioned above.

Table 2 Effect of the type of organoaluminum on catalytic activity and selectivity^a

Entry	Al co-catalyst	TOF (h ⁻¹)	C ₆ ^c (wt%)	Distribution of dimers (wt%)			
				D ₁	D ₂	D ₃	D ₄
5	Et ₃ Al ₂ Cl ₃	56400	81.9	55.6	25.4	17.6	1.4
8	Et ₂ AlCl	37400	89.7	53.3	25.6	15.3	5.8
9	AlEt ₃	17000	86.4	58.0	22.8	14.7	4.5
10	Al(<i>i</i> -Bu) ₃	8900	85.0	54.4	26.7	13.9	5.0
11	EAO	0	—	—	—	—	—

^a Reaction conditions: Al/Ni = 300 (molar ratio), the other conditions are the same as those in Table 1.

It was also found that the products distribution was relatively unchanged by varying the type of aluminum co-catalyst in the Ni(η^5 -Ind)₂ system, at least under the reaction parameters used.

Influence of the P/Ni ratio on the catalytic performance

It is well known that the catalytic behavior for propylene dimerization of various nickel-based catalysts might be

Table 3 Effect of the presence of PCy₃ and P/Ni ratio on catalytic activity and selectivity at ambient temperature^a

Entry	Phosphine		TOF (h ⁻¹)	C ₆ ⁼ (wt%)	Distribution of dimers (wt%)			
	Type	P/Ni			D ₁	D ₂	D ₃	D ₄
5	—	—	56400	81.9	55.6	25.4	17.6	1.4
12	PCy ₃	1	58900	78.8	58.2	14.1	13.8	13.9
13	PCy ₃	2	65500	75.9	53.6	14.3	14.3	17.8
14	PCy ₃	5	61600	74.4	47.0	17.7	11.2	24.1
15	PCy ₃	10	71000	81.7	40.7	14.5	6.3	38.5
16	PCy ₃	20	74000	98.2	27.9	19.8	4.2	48.1
17	PCy ₃	30	84800	87.9	23.6	20.1	3.2	53.1
18	PCy ₃	40	82400	86.6	23.5	20.3	3.2	53.0
19	PCy ₃	60	70200	85.7	23.0	24.3	4.5	48.2

^a Reaction conditions: 0.01 mmol of precursor, Et₃Al₂Cl₃ as co-catalyst, Al/Ni (molar ratio) = 300, 18 mL of PhCl, pressure of propylene = 0.4 MPa, 25 °C, 60 min.

substantially modified by adding phosphine ligands.^{17,18} Taking account into that no marked improvement of selectivity was achieved with adjusting the type of aluminum co-catalyst and its concentration in the Ni(η^5 -Ind)₂ system, hence the effect of phosphine ligand on the dimerization process would be investigated as well at room temperature.

When PCy₃ was added with a P/Ni molar ratio equal to 1 (Table 3, Entry 12), the catalytic activity in system was essentially unchanged as compared with that obtained in the absence of phosphine ligand in Entry 5, whereas a certain enhancement of the content of 2,3-DMB (2,3-dimethylbutenes) in dimers products occurred. The productivity of the catalytic system was gradually improved with increasing the PCy₃/Ni molar ratio in the range of 2 to 30 (Entries 13—17), accompanied with a continuous enhancement of regioselectivity to 2,3-DMB. But as further raising the PCy₃/Ni molar ratio up to 40 and 60 respectively (Entries 18 and 19), the catalytic activity as well as the selectivity of 2,3-DMB within C₆ cut was not up any more. It indicated that the proper value of P/Ni molar ratio in Ni(η^5 -Ind)₂ system was at about 30 at room temperature.

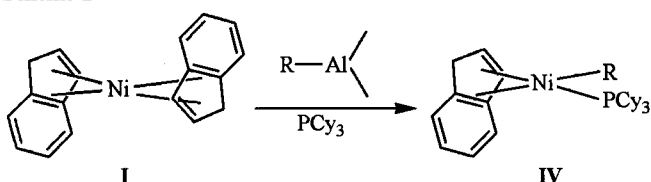
Combining the above observation with what obtained in the absence of phosphine ligand, it allowed to form the active (monoindenyl) (phosphino) nickel species (IV, Scheme 2) when treatment of Ni(η^5 -Ind)₂ complex with alkyl aluminum co-catalyst in the presence of excess phosphine ligands. Indeed, the products distribution was mainly influenced by the insertion mode of active nickel species (nickel hydride or alkyl nickel) into propylene molecule in the catalytic process (Ni → C₁ or Ni → C₂). According to what observed for the

effect of phosphine ligands in other nickel-based catalysts,^{12,13,17,18} it could be concluded that, in the first step, Ni—H inserts into propylene molecule in the Ni → C₂ mode, which is essentially unaffected by the phosphine ligands; however, in the second step, the insertion mode is steadily changed from Ni → C₂ to Ni → C₁ through bulky interference of PCy₃, thus leads to higher regioselectivity to 2,3-DMB in the dimerization process, as shown in Scheme 3.

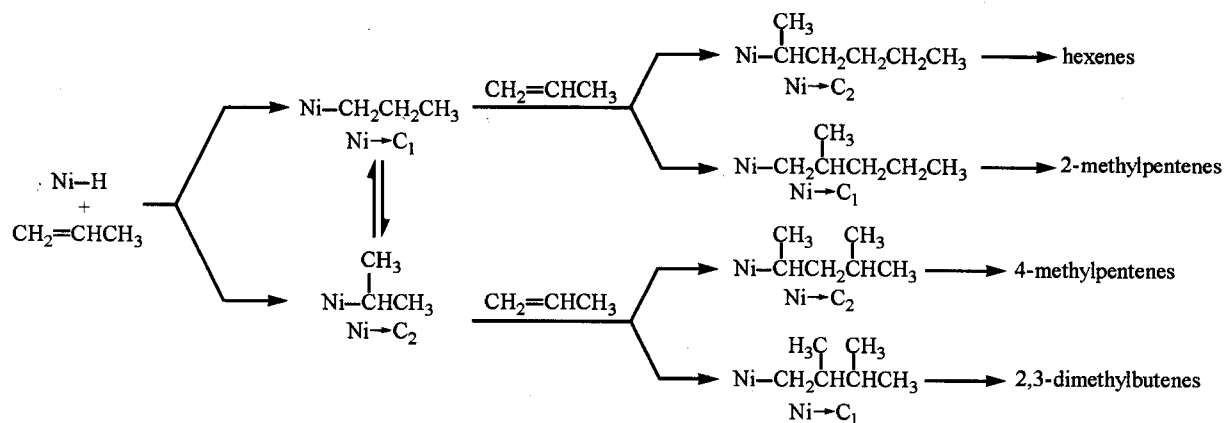
Influence of the type of phosphine ligand and P/Ni ratio on the catalytic performance

It was ascertained that pronounced improvement of regioselectivity to 2,3-DMB followed by a certain enhancement of activity in the dimerization reaction was observed in the presence of large excess of PCy₃ ligand. Herein the effect of different type of phosphine ligands on the Ni(η^5 -Ind)₂ system was studied as well, especially at a given reaction temperature.

Firstly, experiments were performed to test the influence of the reaction temperature on the catalytic behavior using Ni(η^5 -Ind)₂ catalyst in combination with Et₃Al₂Cl₃ and excess amount of PCy₃. When the reaction temperature was changed from 15 °C over 5 °C to -5 °C with the Al/Ni molar ratio equal to 4 (Entries 20, 22 and 29), a sharp enhancement of productivity was achieved, accompanied by a substantial improvement of regioselectivity towards 2,3-DMB in C₆ fraction. As further decreasing the reaction temperature to -15 °C (Entry 30), a certain drop of selectivity occurred whereas the activity essentially remained unchanged. Moreover, it seemed that the effect of the PCy₃/Ni ratio on the catalytic performance at lower temperatures (Entries 21—23 and 27—29), especially in terms of the regioselectivity to 2,3-DMB, became more significant as compared to those previously obtained at room temperature in Table 3. For example, when the dimerization process was carried out at -5 °C, turnover frequency as high as 123000 h⁻¹ in addition to a moderate selectivity of 2,3-DMB in C₆ fraction (48.6%)

Scheme 2

Scheme 3

Table 4 Effect of the type of phosphine ligand on catalytic activity and selectivity at a controlled temperature^a

Entry	Phosphine		T^b (°C)	TOF (h ⁻¹)	C_6^c (wt%)	Distribution of dimers (wt%)			
	Type	P/Ni				D ₁	D ₂	D ₃	D ₄
20	PCy ₃	4	15	86500	73.6	45.9	15.5	10.2	28.4
21	PCy ₃	2	5	95200	76.7	49.8	14.7	10.9	24.6
22	PCy ₃	4	5	135000	77.2	36.1	14.6	7.0	42.3
23	PCy ₃	8	5	101000	82.4	30.5	13.8	6.6	49.1
24	PPh ₃	4	5	68000	69.6	60.2	17.9	15.1	6.8
25	P(<i>n</i> -Bu) ₃	4	5	274000	82.7	36.4	36.0	5.2	22.4
26	PEt ₃	4	5	122000	78.3	59.7	16.8	11.1	12.4
27	PCy ₃	1	-5	123000	87.0	26.4	21.2	3.8	48.6
28	PCy ₃	2	-5	184000	91.6	25.6	9.2	0.8	64.4
29	PCy ₃	4	-5	169000	94.0	18.2	14.1	1.3	66.4
30	PCy ₃	4	-15	167000	72.6	26.1	15.4	2.1	56.4

^a Reaction conditions: 0.02 mmol of precursor, 10% Et₃Al₂Cl₃ in toluene, Al/Ni (molar ratio) = 300, 36 mL of PhCl, pressure of propylene = 0.4 MPa, 60 min. ^b T = reaction temperature.

was obtained even in the presence of equimolar amount of PCy₃ relative to nickel species (Entry 27). A good value of the regioselectivity towards 2,3-DMB within C₆ cut (66.4%) was obtained when PCy₃/Ni molar ratio was 4 at -5 °C (Entry 29).

All the above results concerning the relationship between selectivity and temperature may be interpreted that the difference of the energy barrier between the primary and the secondary insertion of the second propylene molecule into the nickel-carbon bond was increased with lowering the reaction temperature. Thus the modification of bulky and basic PCy₃ orientating the catalytic process toward preferred formation of 2,3-DMB became more efficient. The observation concerning the dependence of activity on reaction temperature in the presence of phosphine ligand could be attributed to the solubility of propylene in the reaction medium which was substantially enhanced at lower temperatures, hence the insertion rate of propylene molecule into active nickel species was improved and led to higher productivity. In the other hand, a drop of temperature might increase stability of the nickel intermediates involved in the catalytic process.

However, when P(*n*-Bu)₃, PPh₃ and PEt₃ were applied respectively (Entries 24–26), no significant modulation of products distribution in the catalytic system was obtained compared to that obtained with PCy₃ ligand (Entry 22). For example in the case of P(*n*-Bu)₃ system (Entry 25), the regioselective towards 2,3-DMB in dimers was rather low in contrast to Entry 22, even an extremely high activity (274000 h⁻¹) was given. The behavior may be due to the lower steric hindrance and higher flexibility of *n*-butyl although P(*n*-Bu)₃ displayed lower basicity as compared with PCy₃.^{19,20} These data allowed to conclude that high bulkiness and strong basicity of phosphine ligand were necessary to direct the dimerization reaction towards predominant formation of 2,3-DMB in C₆ fraction.

Conclusions

On the basis of all the obtained results, the following conclusions can be drawn:

(1) The treatment of Ni(η^5 -Ind)₂ with organoaluminum acti-

vator *in situ* generated active nickel catalyst for the dimerization of propylene.

(2) The presence of phosphine ligand deeply affected the catalytic behavior of the system, and higher regioselectivity to 2,3-DMB in dimers was achieved in the presence of the bulky and basic PCy₃, particularly at lower temperatures.

(3) Propylene turnover frequencies as high as 169000 h⁻¹ by Ni(η^5 -Ind)₂ precursor accompanied by moderate regioselectivity value of 2,3-DMB (66.4%) within C₆ fraction as well as rather high selectivity to dimers was achieved under appropriate reaction conditions.

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