Ethylene oligomerization by novel iron (II) diimine complexe

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Abstract: Iron (II) complex ligated by 2-n-propyl–ketimino-1,10-phenanthroline(2,6-diethylanil) has been synthesized and evaluated with different co-catalysts of methylaluminoxane (MAO), modified methylaluminoxane (MMAO) and triethyl aluminum ($AlEt_3$) in ethylene oligomerization. The result shows the catalytic activities activated with MAO or MMAO are much higher than those with $AlEt_3$ under the same conditions, and these investigations provide useful information targeting the potential application in industrial consideration.

Keywords: iron (II) complex, ethylene oligomerization, α-olefin.

1. Introduction

α-Olefins have been extensively used in preparing detergents, lubricants, plasticizers, oil field chemicals, besides the monomers for copolymerization. The full range process of ethylene oligomerization with a range of C_4/C_6 up to C_{20}^+ is currently the major industrial processes for the production of α-olefins, such as Ziegler process, Shell Higher Olefin Process (SHOP).

Since a new class of iron (II) and cobalt (II) complexes bearing bis(imino)pyridyl ligands for the linear polymerization and oligomerization of ethylene was reported independently by Brookhart [1] and Gibson [2] in 1998, many works have been explored through direct modifications of the ligand frame which has led to a range of new tridentate ligand families. However, alternative models for iron (II) complexes with high catalytic activity have been more attractive. The iron (II) complexes ligated by 2-imino-1,10-phenanthrolines were specially interested with high activities for ethylene oligomerization [3,4], and the variation of the substituents of 2-imino-1,10-phenanthroline ligands results in changing their catalytic performances with the active order as aldimine < phenyl-ketimine <methyl-ketimine [3,4]. Subsequently, the iron (II) complex with ethyl-ketimine group exhibited slightly lower activity in ethylene oligmerization [5] than analogs with methyl-ketimino ligands[3], the advantages were but showed better thermal stability (10 ℃ higher in reaction temperature) Therefore, the transition metal complex model with n-propyl-ketimine group is worthy of investigation (Fig. 1) for commercial availability. Herein we report in detail its synthesis, characterization and its catalytic behavior towards ethylene oligomerization.

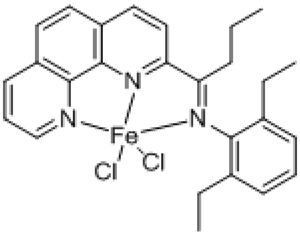

Figure. 1 Structure of iron (II) diimine complexe

2. Experimental

Material and methods. Triethyl aluminum ($AlEt_3$), Methylaluminoxane (MAO) solution (1.4 mol/L) in toluene and modified methylaluminoxane (MMAO) solution (1.8mol/L) in heptane were purchased from Albemarle Corp.

Iron complex Preparation. *N*-(1-(1,10-Phenanthrolin-9-yl)propylidene)-2,6-diethylphenylamine, named as 2-*n*-Propyl ketimino-1,10-phenanthroline, was prepared according to the literature procedure [6].

Ethylene oligomerization. A 300 ml autoclave was used for oligomerization reaction.

3. Results and discussion

Ethylene oligomerization was individually investigated by iron (II) complex (Fig.1) with MMAO, MAO and $AlEt_3$ as co-catalyst and the results are shown in Table 1. According to the data in Table 1, the catalytic activities activated with MAO or MMAO at 1.0 MPa ethylene pressure are higher than those with $AlEt_3$. Elevated temperature (＞20 ℃) and Al/Fe molar ratio (＞600) result in dramatically decreased activity with $AlEt_3$ as co-catalyst.

The amount of co-catalyst MMAO had a significant effect on catalytic activities. At 1.0 MPa of ethylene pressure and Al/Fe molar ratios from 200 to 2000, the best performance was obtained at the ratio of 800 and showed an activity of 3.37×10^7 g mol^{-1} Fe•h^{-1}. The system required an excessive amount of co-catalyst MMAO for scavenging impurities from solvents or gas and producing active species, however, a greater excess of MMAO higher than the Al/Fe ratio 800:1 resulted in a lower activity due to hindering the insertion reaction of ethylene by the isobutyl group [7] and the most active species was formed at the Al/Fe ratio of 800. The amount of MAO had a similar effect on catalytic activities with MMAO, and the highest activity is 3.87×10^7 g mol^{-1} Fe•h^{-1} at the Al/Fe molar ratio of 1000 at 1.0 MPa ethylene pressure.

There is no obvious change of selectivity for α-olefin with the enhancement of co-catalyst MMAO or MAO concentration. However, the product distribution is shifted to higher molecular weight first and then to a little bit lower molecular weight as the molar ratio of Al/Fe increases from 200 to 2000.

Table 1. Effect of different cocatalysts on ethylene oligomerization[a]

Entry	Cat. (μmol)	Cocat.	T (℃)	Al/Fe	Activity[b]	Distribution (wt%)			α-olefin (wt%)	*K*
						C_4-C_{10}	C_{12}-C_{18}	$>C_{20}$		
1	1	MMAO	40	200	14.6	77.8	19.8	2.5	98.4	0.52
2	1	MMAO	40	500	29.1	59.7	26.9	13.5	98.1	0.69
3	1	MMAO	40	800	33.7	61.3	26.5	12.3	97.9	0.68
4	1	MMAO	40	1000	30.2	64.0	26.1	10.0	97.9	0.65
5	1	MMAO	40	1500	25.1	67.7	23.7	8.5	98.1	0.63
6	1	MMAO	40	2000	13.8	62.7	26.0	11.3	98.1	0.67
7	2	MAO	40	200	2.46	80.4	17.3	2.2	98.5	0.51
8	2	MAO	40	500	16.6	77.8	18.8	3.4	97.6	0.53
9	2	MAO	40	1000	38.7	67.5	22.6	9.9	96.1	0.64
10	2	MAO	40	1500	17.7	80.7	15.6	3.7	92.4	0.46
11	2	MAO	40	2000	11.9	78.0	17.7	4.3	97.4	0.51
12	3	$AlEt_3$	4	300	1.96	81.9	17.5	0.6	95.1	0.56
13	3	$AlEt_3$	20	300	4.67	73.6	21.3	5.1	97.6	0.59
14	3	$AlEt_3$	40	300	0.59	88.4	8.6	3.0	71.1	0.5
15	3	$AlEt_3$	20	200	3.75	67.0	24.9	8.1	97.8	0.65
16	3	$AlEt_3$	20	300	4.67	73.6	21.3	5.1	97.6	0.59
17	3	$AlEt_3$	20	400	3.14	68.2	24.8	7.0	95.1	0.63
18	3	$AlEt_3$	20	500	2.59	76.6	20.7	2.7	95.2	0.58
19	2	$AlEt_3$	40	600	0.52	90.5	9.5	0.0	66.9	0.48
20	5	$AlEt_3$	40	1000	0.33	91.4	8.6	0.0	72.9	0.42

a Reaction conditions: 100 ml toluene, 30 min, 1.0 MPa ethylene pressure.

b Catalytic activity: 10^6 g mol^{-1} Fe•h^{-1}

4. Conclusions

Iron (II) complexe ligated by 2-*n*-propyl–ketimino-1,10-phenanthroline(2,6-diethylanil) in the assistance with MMAO as cocatalyst display high activities in ethylene oligomerization with good selectivity to α-olefins. The catalytic activities and distribution of resultant α-olefins closely depend on Al/Fe molar ratio. The iron (II) complex showed comparable catalytic activity by MAO and decreased catalytic activity by $AlEt_3$.

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