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Highly Active Iron/2.6-bis (imino) pyridyl Catalysts for Ethylene Oligomerization

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Abstract: Two novel iron-based catalysts have been synthesized with high catalytic activity (about 10^8g oligomers/molFe·h) for ethylene oligomerization.

Keywords: Iron-based catalyst, ethylene oligomerization, substituent, activity.

Transition-metal-catalyzed oligomerization of ethylene is an important process to convert these basic feedstock into useful value-added products, such as detergents, plasticizers, and many fine chemicals, as well as comonomers for the synthesis of linear low density polyethylene (LLDPE). The pioneering work of Keim in the development of soluble Ni (II)-based catalysts for ethylene oligomerization is the basis for the commercially practiced Shell Higher Olefin Process (SHOP)[1-2]. Brookhart and his coworkers found that by reducing the steric bulk of pyridinebisimine ligands [3-8], the resulting iron-based catalysts could oligomerize ethylene to linear α-olefins with remarkably high activity and selectivity while maintaining desirable oligomer distributions[9].

In order to investigate the steric and electronic effect more closely, we have modified pyridinebisimine ligands by attaching different substituents to the *para* position of aryl group (**Figure 1**). Results of ethylene oligomerization with resultant iron complexes (**1b**, **1c**) are presented in **Table 1**.

Figure 1

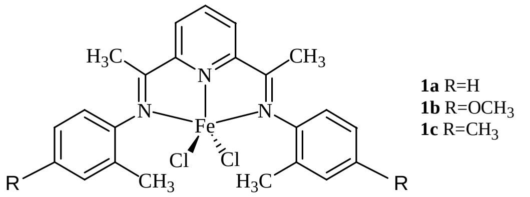

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Table 1 Results of Ethylene Oligomerization with Catalysts[a]

entry	cat.[a]	loading (μmol)	P (MPa)	T (°C)	Activity (10^6g oligomers /molFe·h)	% α-olefin
1	**1a**	1	0.1	30	4.42	95
2	**1a**	1	1	30	15.2	>99
3	**1a**	1	1.5	30	30	>99
4	**1b**	1	0.1	30	12.21	95
5	**1b**	0.4	1	40	288	>99
6	**1b**	0.4	1.5	40	332	>99
7	**1c**	1	0.1	30	15.5	98
8	**1c**	0.5	2	30	340	>99
9	**1c**	0.5	3.2	30	426	>99

[a] All pre-catalysts were activated with MAO(Al/Fe=1500); Time:30min.

Compared with complex **1a**, complexes **1b** and **1c** not only show much higher catalytic activity but also maintain high selectivity of α-olefin (⩾95%).

We suggest that these results can be related to electron-donating substituents on the *para* position of benzene ring. These electron-donating substituents might provide appropriate electron-donating effect on the large conjugated system, which stabilized the active center during oligomerization, and therefore enhanced activity of catalysts.

Similar conclusions have also made by other researchers[10].

From the analytic data of GC-MS and ^{1}HNMR, the resultant oligomers were found to be olefins from C_4 to C_{28} and at least 95% of them were linear α-olefins. Since distribution of oligomers is normally dependent on the size of substituents on *ortho* position of benzene ring, complex **1b** and **1c** still represent high selectivity of α-olefin.

Further investigations of other substituents effects on other position of aryl group are under way.

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