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Gas Phase Polymerization of Ethylene with Supported Titanium-Nickel Catalysts

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Abstract: A new ditransition-metal catalyst system $TiCl_4$-$NiCl_2/MgCl_2$-SiO_2/AlR_3 was prepared. Gas phase polymerization of ethylene with the catalysts has been studied. The kinetic curves of gas phase polymerization showed a decline. The catalystic efficiency and polymerization reaction rates have a optimum value when Ni content of the catalysts was 12.5%(mol).The products obtained are branched polyethylene.

Keywords: Gas phase polymerization, $NiCl_2$, catalysts, branched polyethylene.

Olefins gas phase polymerization uses generally supported titanium catalyst systems in industrial production. The polymerization of olefins with late transition metal catalyst has recently attracted considerable interest[1-2]. The new catalyst family shares many of the advantages of metallocene catalysts in terms of activity and control of polymer properties and, in addition, the new catalysts yield homopolymer of ethylene with very high branching degrees and branching degree can be controlled .

A new ditransition-metal catalyst system **$TiCl_4$-$NiCl_2/MgCl_2$-SiO_2/AlR_3** was prepared by precipitating reaction procedure. The performance of the catalysts was evaluated based on homopolymerization of ethlyene in gas phase process. As shown

Table 1 Effect of $NiCl_2$ content on polymerization of ethylene

Cat.	Ni concn. (mol%)	Cat. Efficiency (gPE/g metal)	Density (g/cm^3)	Branch concn Per 1000c
TN-0	0.0	6000	0.958	1.5
TN-1	6.6	1733	0.948	3.6
TN-2	12.5	3428	0.950	4.3
TN-3	17.5	2243	0.942	6.0
TN-4	22.2	840	0.940	7.2

*Ni concn.=Ni/(Ni+Ti)(mol), metal is transition metal (Ni+Ti).
Polymerization condition: M_{Al}/M_{Ti}=100, T=80℃, t=1.5h, P=106.7Kpa

in **Table 1**, the properties of catalysts are affectd by Ni contents of the catalysts. When Ni content was 12.5% (mol),catalystic effiency and polymerization rates of the Ti-Ni catalysts achieved highest values. As nickel compound supported, the β-hydride elimination was decreased[3], and thus permits formation of high polymers. However

titanium and nickel can form complex active centres for gas phase polymerization of ethylene.

The products obtained from gas phase polymerization of ethylene were characterized by **^{13}C-NMR** and **IR,** the results show the products were branched polyethylene with branching concentration from 3.6 to 7.2/1000c and the density was lower (see **Table 1**). This shows that new catalyst system has characteristics of oligomerization and copolymerization *in-situ*:

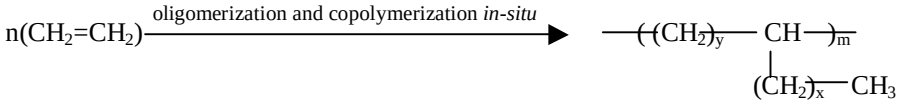
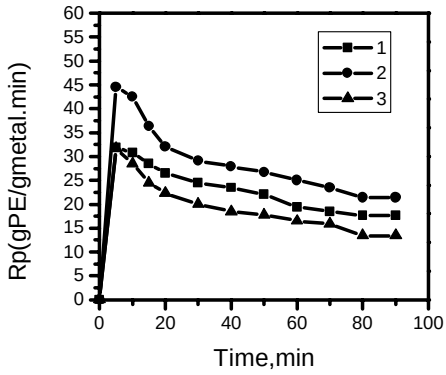


Figure.1. Kinetic curves of ethylene polymerization:
1.TN-1, 2.TN-2, 3.TN-4, Polymerization condition see **Table 1**



The kinetic curves of polymerization exhibited decaying properties (**Figure 1**).

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