Effect of Halocarbon as Promoter on Activity of Ziegler-Natta Catalyst in 1-Hexene Polymerization

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Abstract
The effect of halocarbon on catalyst activity of 1-hexene polymerization uisng Ziegler-Natta catalyst was investigated. At first, effect of temperature, co-catalyst concentration and monomer concentration was investigated to obtain optimal reaction conditions and maximum catalyst activity. Then, chlorocyclohexane was added in reaction medium and polymerization was carried out using 30ml of 1-hexene and 1.5 ml of Triisobutylaluminum (TIBA) as co-catalyst at Room temperature. It was found that the presence of halocarbon has a crucial role on the catalyst activity when compared to when no promoter was used. In addition, by incresing halocarbon to 2 ml ,the activity incresed and it has a descending trend thereafter.

Keywords: Promotor, Polymerization, 1-Hexene, Ziegler-Natta catalyst

Introduction
Promoters as supplementary modifiers not only enhance the catalyst activity but also affect the end properties of polymers such as number- and weight-average molecular weight, bulk density, particle size, melting point and crystallization temperature [1]. In addition, organohalides are the carbonaceous compositions containing halogens that is utilized within catalyst preparation or introduced during the polymerization reaction. Among them, cyclohexane, chlorobenzene, dichlorobenzene, chloroform and butyl chloride are the widely used organohalides as promoters [2].
Cann et al. made the comparison between vanadium- and titanium-based catalysts and determined the effect of halocarbons. They reported that vanadium-based catalysts showed four to ten times higher activity, this is while the titanium-based catalysts showed solely 50 percent higher activity using the halocarbons [3]. Various type of halides were also investigated on the vanadium-based catalyst. The results showed that most of the times their presence giving rise to enhanced catalyst activity even as much as 8 times higher than the preliminary system [4]. Although organohalides are used to increase vanadium-based Ziegler-Natta catalysts to a large extent [5] and their usage for the titanium-based is limited [6], yet acceptable conclusions were obtained from the experiments. For instance, three type of organohalides including organic halides, organic silicon, aliphatic and aromatic compositions were used for catalysts based on vanadium and it was found that the method of feeding organic halides separately and/or their combination with co-catalyst has got no impact on the

catalyst activity. However they brought about to enhance the catalyst activity [7]. Bahri et al. studies cast light on the effect of the titanium-based catalyst using different sort of organic halides such as chlorocyclohexane, butyl chloride, chloroform and 1 4-dichlorobutane and they concluded that the catalyst activity is dependent to type and amount of organic halides used in the polymerization [8].
In this paper, the effect of chlorocyclohexane on the titanium-based catalyst in 1-hexene polymerization at optimal polymerization conditions at room temprature was investigated.

Experimental

Materials

The TIBA with purity >99% was purchased from Aldrich, 1-hexene as monomer was supplied from Arya Sasol petrochemical company. Also, the Ziegler-Natta catalyst, heptane as solvent and chlorocyclohexane was provided from Bandar Emam petrochemical company.

Faculities

Determination of the titanium amount in catalyst was done through Cecil 1021 UV-Vis Spectrometer apparatus (Cambridge, UK).

Polymerization

The polymerization reaction was achieved in a round-bottom boiling flask as reactor at room temperature and atmospheric pressure in a fixed mixing speed. First, the flask was placed under vacuum system to remove any contamination (if present) and followed by sealing. Then solvent, monomer and catalyst were fed to the reactor, respectively. After 5 min, chlorocyclohexane and then catalyst were introduced to the system and polymerization was done within 140 min. Finally, the end product was dried and prepared for further analysis.

Results and discussion

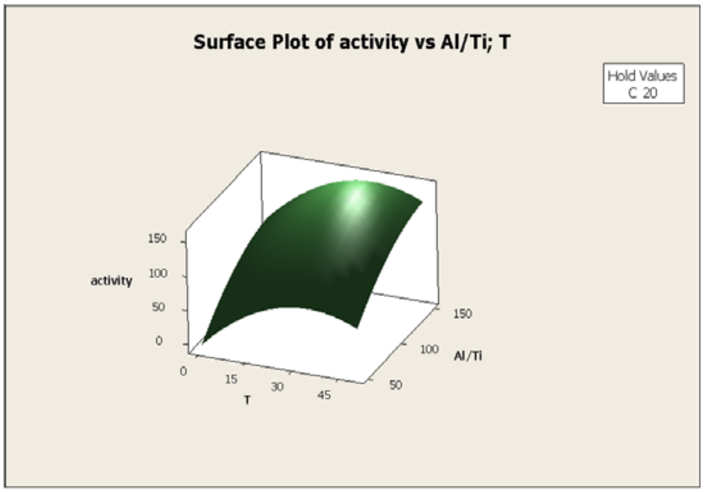
Catalyst activity depends on monomer concentration, catalyst and cocatalyst content, time and temperature of polymerization. 1- Hexene polymerization conditions was presnetd in Table 1.

Table 1. 1-hexene polymerization conditions

Temprature(°C)	1-Hexene(mml)	TIBA(mml)	W(gr)	Activity
25	10	0.5	0.63	33.6
25	30	0.5	2.69	143.46
25	10	1.5	1.41	75.2
25	30	1.5	4.97	265.06
50	20	0.5	0.92	49.06
50	30	1	4.13	220.26
50	10	1	1.16	61.86
50	20	1.5	2.63	140.26

Reaction conditions: Heptane as solvent, catalyst :1.5 ml

As seen in the Table 1, at a constant temperature by increasing the monomer concentration and by increasing the catalyst content in amount of monomer constant, lead to increase activity.



Fiugre 1. Catalyst activity versus temperature and Al/Ti in polymerization of 1-hexene

As seen in the Figure 1,the temperature reached 25 ° C to its maximum value and then decrease during the process. Ziegler-Natta catalyst systems, the catalyst activity in most of Al / Ti, the maximum value is therefore the amount of monomer 30 ml, 1.5 ml catalyst and a temperature of 25 ° C is selected as the optimum conditions.

The results of 1-hexene polymerization using various amounts of chlorocyclohexane halocarbon are listed in Table 2. The catalyst activity enhances as halocarbon concentraion increases up to 2 ml and then it has a descending trend at room temperature.

Table 2. Effect of halocarbon concentraion on 1-hexene polymerization

No.	Chlorocyclohexane(ml)	Activity(gpolymer/g catalyst)	Polymer(g)
1	0	212.27	3.98
2	0.5	242.14	4.54
3	1	282.14	5.29
4	2	385.86	6.86
5	4	275.2	5.16
6	6	177.06	3.32

Polymerization Conditions: 1-hexene (30ml), TIBA (1ml), catalyst (1ml) Heptane (20 CC), polymerization duration (140 min), Temperature (25^0C)

The Ti^{+4} centers show higher activity in comparison to Ti^{+2} centers [6]. Thus, decreasing the catalyst activity may be related to decreasing amount of Ti^{+4}. Halocarbons performance highlighted as promoter of poor Ti^{+2} centers through entering them in the fresh cycle of activating the active centers of catalyst [7-9]. In fact, evolving the Ti^{+2} which resulted from Ti^{+4} reaction with co-catalyst into Ti^{+3} and Ti^{+4} that are capable to become active centers, leads to better catalyst efficiency during polymerization [9].
It is obvious in Table 2 that catalyst activity reached its maximum level at 2 ml of chlorocyclohexane, and then a decreasing trend was observed. Density functional theory

analysis demonstrated, due to higher amount of Ti^{+2} regarding Ti^{+3} active centers in the reaction media [9] and its lower efficiency, the catalyst activity would decrease.

Conclusions

The catalyst activity is dependent to type and amount of organohalides used in the polymerization. The presence of chlorocyclohexane as halocarbon showed great enhancement in the activity of Ziegler-Natta catalyst for 1-hexene polymerization when compared to when no halocarbon was used. Increasing the amount of halocarbon up to 2ml brought about higher catalyst activity in an optimum level and then because of Ti^{+2} active centers it would decrease.

References

[1] Garry L. Fields, Kenneth W. Johnson, Douglas D. Klendworth, Michael W. Lynch,Raghu Menon, Linda N. Winslow L., “Vanadium-containing catalyst system.” EP0862587, 1996.

[2] Bahri-Laleh N., Seifali Abbas-Abadi M., NekoomaneshHaghighi M., Akbari Z., Tavasoli M.R., and Mirjahanmardi S.H., Effect of Halocarbon Promoters on Polyethylene Properties Using $MgCl_2$)ethoxide type)/$TiCl_4$/$AlEt_3$/H_2Catalyst System, J. Appl. Polym. Sci., 117, 1780-1786, 2010.

[3] Cann K.J., Nicoletti J.W., Karol F.J., Marcinkowsky A.E., Spriggs T.E., and Hwu M.C., Ethylene Polymerization Using a Titanium and Vanadium Catalyst System in Staged Reactors, US Pat. 5442018, 1995.

[4] Reinking M.K., Bauer P.D., and Seyler J.W., A Study of Halocarbon Promoter Influence on Catalyst Reactivity and Polymer Mn in Vanadium-based Ethylene Polymerizations, Appl. Catal. A, 189, 23-34, 1999.

[5] Luo H., Tang R., Yang H., Zhao Q., An J., “Studies on highly efficient promoters for titanium-based Ziegler – Natta catalyst for ethylene polymerization,” Appl. Catal. A203, 269-273, (2000).

[6] Naeimeh Bahri-Laleh,Hassan Arabi,Shahram Mehdipor-Ataei,Mehdi Nekoomanesh-Haghighi,Gholamhosein Zohuri,Mehrdad Seifali,Zahra Akbari ., “Activation of Ziegler-Natta Catalysts by Organohalide Promoters: A Combined Experimental and Density Functional Theory Study” J. Appl. Polym. Sci. 2526–2533, (2012).

[7] Bahri-Laleh, N.; Correa, A.; Mehdipour-Ataei, S.; Arabi, H.;Nekoomanesh-Haghighi, M.; Zohuri, G. H.; Cavallo, L. Macromolecules,” Testing DFT ability to predict the stereoselectivity of group 4 metallocenes in propylene polymerization”J. Polyolefins. 44, 4, 778. 2014

[8] Bahri-laleh N., Correa A., Mehdipour-ataei S., Arabi H., Haghighi N., Zohuri G., Cavallo L., “Moving up and down the Titanium Oxidation State in Ziegler - Natta Catalysis,” Macromolecules,44 (4), pp778-783,(2011).

[9] Reza Bazvand, Naeimeh Bahri-Laleh, Mehdi Nekoomanesh-Haghighi, Hossein Abedini,” Effect of Modifiers on the Performance of Ziegler-Natta Catalysts in Olefin Polymerization” IPPI,P.O. 2252-0449,(2014).