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Effects of Various Mixed Metal Chlorides-$AlCl_3$ in $TiCl_4/MgCl_2$/THF Catalytic System on Ethylene Polymerization

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In this research, the modification of $TiCl_4/MgCl_2$/THF catalyst system with various metal chlorides was investigated on ethylene polymerization. Experimentally, metal chlorides ($CaCl_2$, $FeCl_2$ and $ZnCl_2$) were simultaneously introduced different with $TiCl_4/MgCl_2$/THF catalyst. ICP analysis was used to determine the total amount of each metal in the catalyst. For polymerization reaction, TEA was used as cocatalyst and hexane was used as a medium solvent. The Al/Ti molar ratio was 140. The activity result of Ca-Al, Zn-Al and Fe-Al was 979, 1009 and 1476 kgPE/molTi.h, respectively. The coaddition of $AlCl_3$ and $FeCl_2$ in $TiCl_4/MgCl_2$/THF catalyst system exhibited the highest activity. It suggested that the co-addition of $AlCl_3$ and $FeCl_2$ has higher electronegativity (EN) and the radius of Fe^{2+} is closer to Mg^{2+} resulting in an increased efficiency of the THF removal. This result led to improve the catalyst performance.

Keywords : Ziegler-Natta catalyst; ethylene polymerization; Lewis acids; $TiCl_4/MgCl_2$/THF catalyst

INTRODUCTION

The Ziegler-Natta (ZN) catalyst system for polymerization of ethylene by combinations of transition metal and organometallic compound has been discovered since 1950s (Eisch 2012). In general, heterogeneous ZN catalyst is based on titanium chloride supported on magnesium dichloride ($TiCl_4/MgCl_2$). $MgCl_2$ is suitable support for $TiCl_4$ due to its crystal and electronic structure, high activity, low cost and good control of polymer particle morphology (Jiang *et al.* 2011, Wilke 2003). The tetrahydrofuran (THF) and alcohol as Lewis base are commonly used to improve the surface of $MgCl_2$ support before treatment with an excess of $TiCl_4$ in order to obtain highly active catalysts (Grau *et al.* 2013).

Although today, alcohol is used as Lewis base greater, there are many researches that use THF because the process of catalyst preparation is easy leading to low cost, controlling of polymer morphology and good hydrogen response ability (Luo 2002, Pirinen *et al*. 2013). Sobota (2004) also reported that the most commonly used selectivity control agent for ethylene polymerization is THF. Moreover, there are many researches that study to improve the $TiCl_4/MgCl_2$/THF catalytic system (Grau *et al*. 2013, Bialek *et al*. 2014). So, the $TiCl_4/MgCl_2$/THF catalytic system is one of the most important ZN catalysts for the production of polyethylene. However, the remaining THF in the final catalyst leads to decrease in catalytic activity due to the excess THF may have poisoned the catalyst sites (Marin 1995). So, the removal of THF is very crucial for preparation of the catalyst.

In our previous research, the addition of mixed metal chlorides such as $ZnCl_2/SiCl_4$ could remove the THF in catalyst better than the single metal chloride leading to remarkably enhance the catalytic activity both in homo- and co-polymerization (Phiwkliang *et al*. 2013, Phiwkliang *et al*. 2014). Therefore, in this present work, we focused on the modification of $TiCl_4/MgCl_2$/THF catalyst system with various metal chlorides ($CaCl_2$, $FeCl_2$ and $ZnCl_2$) used in combination with $AlCl_3$. Since the presence of $AlCl_3$ in the $TiCl_4/MgCl_2$ could change the active center distribution resulting in the formation of more active center leading to influence on performance of the catalyst and polymer properties (Chen *et al*. 2006, Chen and Fan 2006).

EXPERIMENTAL

Materials

Because of the sensitivity of the ZN catalyst system to air and moisture, all the operations were carried out under an inert atmosphere of nitrogen (standard Schlenk techniques) and argon (glove box). Hexane was purified before use by distillation and refluxing over sodium metal and benzophenone as an indicator. Polymerization grade ethylene and TEA were donated by Thai Polyethylene Co., Ltd. Ultra-high purity nitrogen and argon (99.999%) were purchased from Thai Industrial Gas Co., Ltd. $TiCl_4$ was purchased from Merck Ltd., anhydrous $MgCl_2$, $AlCl_3$, $CaCl_2$, $FeCl_2$, $ZnCl_2$ and THF were purchased from Sigma-Aldrich Inc.

Catalysts Preparation

The catalyst of type $TiCl_4/MgCl_2/THF/AlCl_3 + MxCl_2$ (Mx is Ca, Fe and Zn) was prepared via a chemical route using $MgCl_2$ as a support precursor according to a procedure that was previously published (Phiwkliang *et al*. 2013). 2 g of anhydrous $MgCl_2$ was added in a four-necked 500 mL round bottom flask equipped with a magnetic stirrer. Then, 150 mL of THF was added into the flask. Later, $AlCl_3$ and $MxCl_2$ (molar ratio of $AlCl_3/MgCl_2$ and $MxCl_2/MgCl_2$ is equal to 0.063) were added. After that, 2 mL of $TiCl_4$ was injected dropwise into the flask under continuous stirring. The temperature was gradually increased to 68 °C and held at this temperature for 3 h. After the reaction mixture was cooled to 40 °C, the solid part was filtered and washed with 100 mL of n-hexane for several times. Finally, the catalyst obtained was dried under a vacuum at room temperature and catalyst powder was stored under argon atmosphere in a glove box. The abbreviations of obtained catalysts are listed in Table 1.

Table 1. The abbreviation of catalyst

Catalysts	Abbreviation
$TiCl_4/MgCl_2$/THF/$AlCl_3$+$CaCl_2$	Ca-Al
$TiCl_4/MgCl_2$/THF/$AlCl_3$+$FeCl_2$	Fe-Al
$TiCl_4/MgCl_2$/THF/$AlCl_3$+$ZnCl_2$	Zn-Al

Ethylene Polymerization

The polymerization of ethylene was carried out in a slurry 100 mL semi-batch autoclave reactor equipped with magnetic stirrer. Haxane as medium agent for reaction (total volume of 30 mL), TEA solution as cocatalyst were injected into the reactor (Al/Ti molar ratio of 140). Then, 10 mg of catalyst powder was added into the autoclave reactor. The feeding of ethylene with the pressure of 50 psi was performed to start polymerization reaction and the amount of ethylene was fixed at 0.018 mmol. Finally, the reaction was terminated by adding acidic methanol. The product was washed with methanol and dried under vacuum.

RESULTS AND DISCUSSION

The total element content in catalysts such as Ti, Mg, Ca, Fe, Zn and Al upon various mixed metal chlorides is listed in Table 2. The external surface compositions of all catalyst also were approximated by EDX technique, as shown in Table 2. The results showed that Fe-Al catalyst exhibited the highest of Ti content among other catalysts. Comparison with ICP technique, it was observed that the Ti content in the bulk observed by ICP for Fe-Al is the lowest suggesting that Fe-Al catalyst is mostly contained Ti atoms located on the catalyst surface. Conversely, in the Zn-Al catalyst, most Ti atoms were located in the catalyst pores.

From our previous research (Phiwkliang *et al.* 2013), the XRD patterns of the $TiCl_4/MgCl_2$/THF system shows peak of the $MgCl_2$/THF complex at 2θ = 10.4°, 20.2° and 32.3°, the $TiCl_4$/THF complex at 2θ = 11.1° and 13.2°, and $TiCl_3$/THF complexes at 2θ = 12.2°, 16.7° and 16.9°. Moreover, $TiCl_4/MgCl_2$/THF complex shows peaks around 2θ = 11.5° and 18.3°. Figure 1 shows the XRD patterns of catalysts with

Table 2. The element content and catalytic activity of catalysts

Catalysts	Element content in bulk[a] (wt %)				Ti on surface[c] (wt %)
	Ti	Mg	Mx[b]	Al	
Ca-Al	3.70	6.09	0.92	0.55	10.26
Fe-Al	3.44	3.26	3.74	0.58	11.17
Zn-Al	4.28	6.12	1.43	0.59	9.51

[a] Results from ICP, [b] Mx refer to Ca, Fe and Zn and [c] Results from EDX

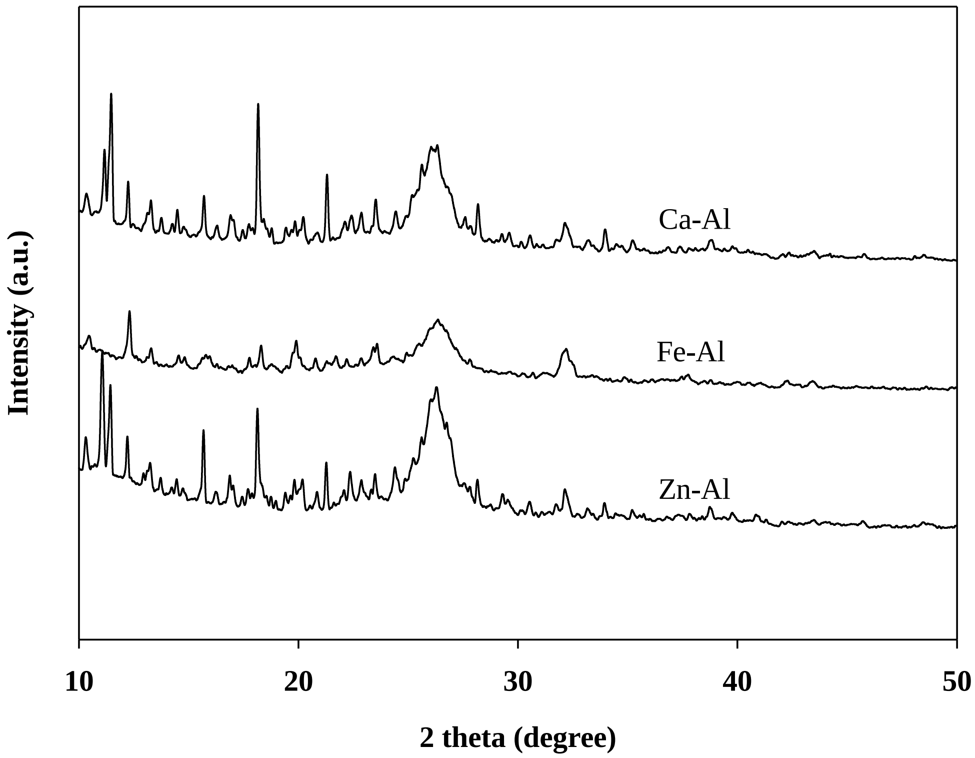

Fig. 1: The XRD patterns of Ca-Al, Fe-Al and Zn-Al catalysts.

different addition of mixed metal chlorides. It was found that for the Fe-Al catalyst, the intensity of XRD patterns involving with structure of THF complex apparently decreased indicating that the THF in the structure of $TiCl_4/MgCl_2/THF$ complex could be better removed by adding the Fe-Al. However, the XRD cannot detect the metal in catalyst due to its crystallite sizes are smaller than 3 nm.

Figure 2 shows the absorption bands of THF examined by FT-IR technique. In general, a symmetrical and an asymmetrical C-O-C stretching band of THF is around 913 cm^{-1} and 1071 cm^{-1}, respectively (Kim 1995, Chu *et al.* 1994). However, after mixed metal chloride was introduced into the catalyst, the IR peaks of the C-O-C stretching bands of THF were slightly shifted from 913 cm^{-1} to 872 cm^{-1} and from 1071 cm^{-1} to 1020 cm^{-1} as a result of the strong Lewis acidity of Ti and Mg (Kim 1995). These results are also similar with those reported by Chu *et al.* 1994, Kim 1995, Pirinen *et al.* 2013 and Phiwkliang *et al.* 2014. The FT-IR results were corresponding to the XRD results indicating that THF was partially removed from the structure of $MgCl_2/THF$ complex by the modification of mixed metal chlorides. It is clear that the Fe-Al catalyst displays the most efficiency in removal of THF, while in the Ca-Al catalyst, the removal of THF is the lowest.

The catalytic activity for ethylene polymerization with various mixed metal chlorides in $TiCl_4/MgCl_2/THF$ catalysts is shown in Table 3. The results show that the catalytic activity increases in order of Fe-Al > Zn-Al > Ca-Al. All catalysts provide the higher activity than the unmodified one from our previous research

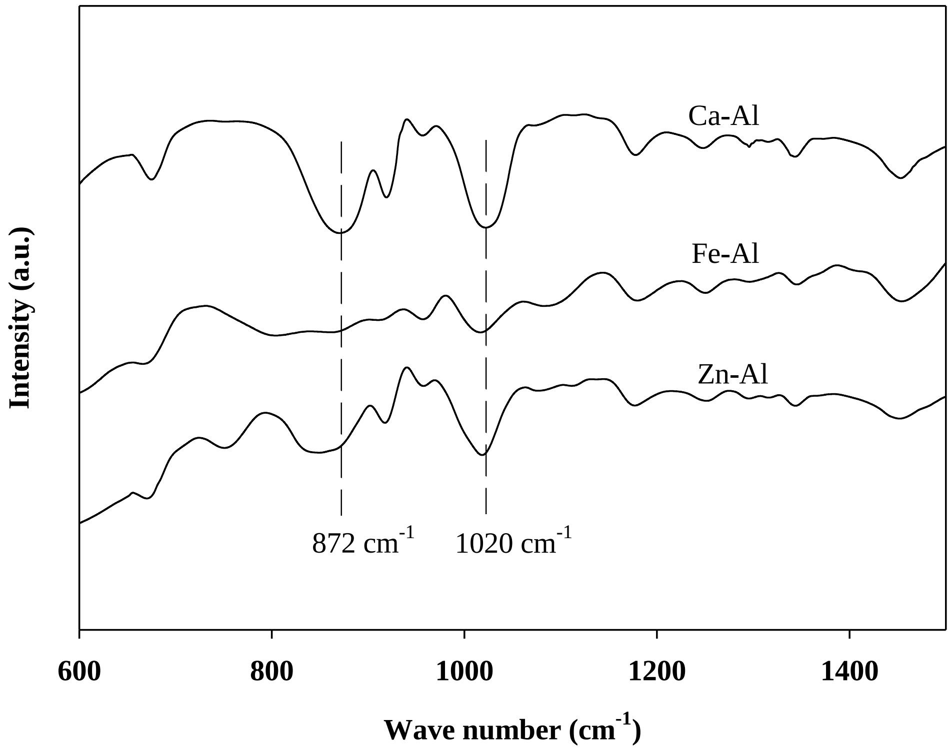

Fig. 2: The FT-IR patterns of Ca-Al, Fe-Al and Zn-Al catalyst

Table 3. The effect of mixed metal chlorides on catalytic activity for ethylene polymerization and polymer properties

Catalysts	Activity	Polymer properties		
	(kgPE/molTi h)	T_m (°C)	$\%\chi_c$[b]	Density (g/cm^3)[b]
unmodified[a]	406	134	53	-
Ca-Al	979	131	54	0.941
Fe-Al	1476	132	54	0.941
Zn-Al	1009	130	52	0.939

[a] Phiwkliang *et al*. 2013

[b] $\chi_c = [\Delta H/(\Delta H°)] \times 100$, density = $(2195+\Delta H)/2500$ (Phiwkliang *et al*. 2014)

(Phiwkliang *et al*. 2013). The modification of $AlCl_3$ and $FeCl_2$ in $TiCl_4/MgCl_2$/THF catalyst provides the highest activity due to Fe-Al had an efficiency to remove higher amount of THF, which can be confirmed by XRD and FT-IR. Comparison for electronegativity (EN) values of Ca, Fe and Zn, they are 1.04, 1.64 and 1.66, respectively. Although EN values of Fe is as high as Zn, the radius of Fe^{2+} (0.61 Å) is closer to Mg^{2+} (0.65 Å) than Zn^{2+} (0.74 Å) and Ca^{2+} (0.99 Å). Therefore, the compatibility efficiency of $FeCl_2$ with $MgCl_2$ could be better than of $ZnCl_2$ or $CaCl_2$ with $MgCl_2$. This reason suggested that the coaddition of $AlCl_3$ and $FeCl_2$ resulting in higher THF removal. However, the Ca-Al catalyst provides the lowest activity due to the remaining THF may have poisoned the catalyst sites leading to the catalyst deactivation (Maria 1995).

The melting point (T_m), percentage of crystallinity ($\%\chi_c$) and density of polyethylene obtained were analyzed by DSC techniques as shown in Table 3. It shows that these properties are similar. Therefore, the modification of $TiCl_4/MgCl_2$/THF catalyst system with various metal chlorides did not significantly affect the thermal behavior of polyethylene.

CONCLUSION

The modification of $TiCl_4/MgCl_2$/THF catalyst system with various metal chlorides ($CaCl_2$, $FeCl_2$ and $ZnCl_2$) combination with $AlCl_3$ was investigated on ethylene polymerization. The catalytic activity shows an increase in order of Fe-Al > Zn-Al > Ca-Al. In case of the Fe-Al catalyst, it provides the highest activity due to it has an efficiency to remove more THF, which can be confirmed by XRD and FT-IR. Moreover, this modification did not affect the thermal behavior of polyethylene.

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