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Research Article

Synthesis of Ziegler-Natta Catalyst using Malaysian Ilmenite Derived $TiCl_4$ via Recrystallization Method: A Statistical Approach

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Abstract

In the current study, Ziegler-Natta (Z-N) catalyst was synthesized via recrystallization method using $MgCl_2$ as a support, $AlCl_3$ as an activator and $TiCl_4$ as a transition metal source. The $TiCl_4$ used in the study was derived from Malaysian ilmenite through a sequential pyrometallurgical and hydrometallurgical process of ilmenite concentrate conversion to $TiCl_4$. The recrystallization method of synthesis of the heterogeneous Z-N catalyst was studied by varying the synthesis parameters, such as the combined amount of $MgCl_2$ and $AlCl_3$, temperature, and amount of $TiCl_4$, using statistical design of experiments. The investigation aimed at determining the best conditions for synthesizing the heterogeneous Z-N catalyst. The synthesis conditions posed a significant influence on the Ti content present in the catalyst product. The morphological and elemental analysis of SEM-EDX showed good spherical nature of the prepared catalysts. The XRD phase analysis detected the peaks of $MgCl_2$, $MgCl_2$-Ethanol, $MgCl_2/TiCl_x$, and TiO_2. The IR spectra confirmed the presence of the Mg-Cl bond at 1635 cm^{-1} and Ti-Cl bonds at 602 cm^{-1} and 498 cm^{-1}. The produced catalyst contained a small amount of TiO_2, which could be due to the seepage of moisture during the analysis or storage of the sample. The most favourable combination of the studied parameters was determined based on the Ti content in the catalyst product. Therefore, the best conditions for synthesizing the heterogeneous Z-N catalyst with high Ti content (181.1 mg/L) was at a combined amount of 2 g of $MgCl_2$ for 6 g of $AlCl_3$, crystallization temperature of 80 °C, and 2 mL dosage of $TiCl_4$.

Keywords: Malaysian ilmenite; Ziegler-Natta catalyst; Recrystallization method; $TiCl_4$; statistical design of experiments

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1. Introduction

The Ziegler-Natta (Z-N) catalysts have been widely used in olefin polymerization systems and are responsible for the industrial production of millions of tons of polyolefins annually [1,2]. These heterogeneous catalysts enable the production of polymer materials with specific tacticity and broad molecular weight distribution, demonstrating the presence of multiple active sites in their structure [2]. Polypropylene and polyethylene, the two polymers that have

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widespread applications, are most often produced with Z-N catalysts. These catalysts usually contain a carrier or support, such as: $MgCl_2$, electron donors (Lewis bases), $TiCl_4$ active species, and a co-catalyst (alkyl aluminium) [3-7]. One of the important criteria for a good catalyst is the surface structure of the support component. Heterogeneous Z–N catalysts with $MgCl_2$ support have greatly improved the activity and stereospecificity of catalysts, leading to substantial simplifications in polyolefin production processes [8,9]. Several methods using activated $MgCl_2$ as the support or carrier in the synthesis of Z-N catalyst have been proposed [4,8,10,11].

Generally, $MgCl_2$ is mechanically or chemically treated to become structurally disordered with more active centers on the surface, or may remain in its crystalline state as well [3,8,11-13]. $MgCl_2$-ethanol adducts have also been gaining the privilege as effective Z-N supports, since these adducts tend to lose the alcohol group on interacting with $TiCl_4$, thereby resulting in a high surface area [14-16]. Other supports have also been used in the synthesis of Z-N catalysts, such as: $MgCl_2$/tetrahydrofuran (THF) complexes that are reported with good catalytic activity [17]. The recrystallization method of Z-N catalyst synthesis using $TiCl_4/TiCl_3$ has also been an industrially recognized process for the catalysis of the commercial polymerization process [5, 18]. This method involves the solubilization of $MgCl_2$ in organic media (R-OH) and the recrystallization of $MgCl_2$ from the solution, and the newly generated porous $MgCl_2$ belongs to a γ-type $MgCl_2$ crystal structure, which is much better in supporting $TiCl_4$ [11,19]. Different conditions of the recrystallization process, such as recrystallization temperature, amount of co-catalyst, amount of $MgCl_2$, and the ratio of Mg/Ti have been investigated so far [5,6,11,18-21].

The preparation of Z-N catalyst involves the reaction between compounds of transition elements of groups IV to VIII (titanium, vanadium or zirconium halides) and compounds, such as the hydrides or alkyls of groups I-III, for instance, $LiEt_3$, $BeEt_3$, $AlEt_3$ or $AlEt_2Cl$ [1,22,23]. $TiCl_4$-based Z-N catalysts have been the commercially preferred catalysts owing to their good catalytic performance [23-25]. The significant cost portion for producing the Ti-based Z-N catalyst is the production of $TiCl_4$ itself. One way to tackle this problem is to synthesize titanium oxycarbonitride ($TiO_xC_yN_z$), produced by the carbothermal reduction-nitridation of ilmenite as the raw material, then chlorinating the $TiO_xC_yN_z$ at lower temperatures less than 500 °C [26]. Preliminary studies on the reduction and nitridation of Malaysian ilmenite in H_2-N_2 and N_2 have been carried out [27-28]. Pure $TiCl_4$ liquid was produced by chlorinating the $TiO_xC_yN_z$ after the removal of Fe in the reduced ilmenite by aeration leaching (Becher's process) [29,30]. Synthesizing $TiCl_4$ or $TiCl_3$ by this new method at low temperatures not only prevents impurities from being chlorinated, but also saves on energy consumption [27,31,32].

The study explores the possibility of synthesizing the Z-N catalyst by utilizing the $TiCl_4$ produced from ilmenite. Conventionally, $TiCl_4$, the precursor for producing the catalyst, is required to be obtained of high purity after a series of intensive pyrometallurgical and separation processes. There is much difficulty in controlling the impurities, as the metallic impurities might get chlorinated due to the high temperature of the chlorination process. However, in this study, $TiCl_4$ derived from Malaysian ilmenite through a low-temperature cost-effective method is used for the synthesis. Since the Ti compound is originated from nitrided ilmenite, it will have traces of impurities, such as $FeCl_3$, $AlCl_3$, VCl_4, and $NbCl_5$ after the chlorination process, while most of the impurities might not have chlorinated at low temperatures. By examining the effect of impurities on the production of the Z-N catalyst, directly from the chlorinated product, the elimination of an intensive purification process can be achieved. The low-cost low-temperature method facilitates the production of $TiCl_4$ from local Malaysian ilmenite, which is then treated with $MgCl_2$-ethanol adduct to form $TiCl_4/MgCl_2/Al\text{-}Et_3$ Z-N catalyst. This will subsequently make the production of the Z-N catalyst more economical and energy-efficient than the current industrial practices, thereby adding more value to Malaysian ilmenite. Moreover, the synthesized $TiCl_4$ based Z-N catalyst has potential applications in the production of high-density polyethylene (HDPE) through the Zieglar Natta process and polymerization of ethylene gas into polypropylene plastics. In the study, the heterogeneous Z-N catalysts were synthesized using the locally-made $TiCl_4$ and $MgCl_2$ support by recrystallization process, wherein the effects of the total amount of $MgCl_2$ and $AlCl_3$, recrystallization temperature and amount of $TiCl_4$ were investigated. According to the amount of Ti in the catalyst synthesized for different experiments considered based on the factorial design, the most favourable conditions for the synthesis of the ZN catalyst were established. The effects of the different studied parameters on the synthesis outcome were evaluated. The resulting catalyst was also characterized to study the surface morphology, bonding nature, and phases of the active catalytic components and the effect of impurities on the synthesis of the catalyst.

2. Materials and Methods

2.1 Chemicals

The main highlight of the study is the use of $TiCl_4$ produced from Malaysian ilmenite for the preparation of the catalyst. Malaysian ilmenite is converted to titanium oxycarbonitride ($Fe\text{-}TiO_xC_yN_z$) in the first phase by carbothermal reduction and nitridation process in the H_2-N_2 atmosphere, followed by the removal of iron impurities through Becher's process and the chlorination of $TiO_xC_yN_z$ to form titanium tetrachloride ($TiCl_4$). All other chemical reagents were of analytical grade. The chemicals used in the research with information on their sources, specifications, and purposes are tabulated in Table 1.

2.2 Preparation of Catalyst

The heterogeneous Ziegler-Natta (Z-N) catalyst was prepared by the recrystallization method [6,10,11], i.e. reacting $TiCl_4$ with $MgCl_2$-ethanol adduct and $AlCl_3$. The 2 g of anhydrous $MgCl_2$ was added to 100 mL of n-heptane, and 3 mL of ethanol (95%) was added to the mixture dropwise. This mixture was stirred at 400 rpm at room temperature until $MgCl_2$ was completely dissolved in 2 hours. Then, 6 g of anhydrous $AlCl_3$ was added to the prepared homogeneous solution and agitated for 2 hours at 80 °C. The hot mixture was allowed to naturally cool down to room temperature. Thereafter, the 2 mL of Malaysian ilmenite derived $TiCl_4$ was added to the mixture and was stirred for 2 hours at room temperature. $TiCl_4$ was added to the mixture after passing through a bottle of phosphorous pentoxide (P_2O_5) in order to absorb the moisture present. The entire sequence of processes was carried out in inert conditions. The sample was washed several times with n-heptane and filtered to obtain the recrystallized sample. The wet recrystallized sample was subsequently dried in Ar atmosphere at 70 °C.

2.3 Factorial Design of Experiments - Recrystallization Method

A fully randomized factorial 2^3 design was applied for the statistical evaluation of different factors influencing the recrystallization process of Z-N catalyst synthesis. The chosen factors and their levels for the study are given in Table 2. The effect of the three factors on the response variable for the process, i.e. the amount of Ti in the catalyst was studied. Local optimization was carried out for the parameters within the studied range of levels.

2.4 Characterization of Synthesized Catalyst

The elemental analysis of $TiCl_4$ derived from Malaysian ilmenite was conducted using

Table 2. Z-N catalyst synthesis: factors and their levels.

Factors	Unit	High	Low
Total amount of $MgCl_2$ and $AlCl_3$ (Ratio 1:3)	g	8	1
Recrystallization temperature	°C	80	100
Amount of $TiCl_4$	mL	2	5

Table 1. Raw materials and chemicals: specifications and purpose

Materials	Specifications	Purpose
Titanium tetrachloride ($TiCl_4$) from Malaysian ilmenite	97.24% purity	Source of Ti compound
Anhydrous magnesium chloride ($MgCl_2$)	Solid	Catalyst support
Anhydrous aluminium chloride ($AlCl_3$)	Powder	Co-catalyst feed
Ethanol	95%	Organic solvent/ washing agent
n-Heptane (dry)	Liquid	Solvent
Phosphorous pentoxide (P_2O_5)	Powder	Moisture absorbent
Argon gas	Gas	Inert atmosphere

Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES, Perkin Elmer). The synthesized catalyst particles were characterized using X-ray diffraction (XRD, Bruker D8 Advance) instrument equipped with a Cu-anode and K_α radiation (λ = 154 Å) to determine the crystalline phases of samples. The x-ray scan was run for a 2θ range of 10-80° operated at 40 mA and 40 kV. ICP-OES was also used to determine the amount of Ti present in the catalyst precursors. The morphology and elemental analysis of the solid catalyst particles were examined using Scanning Electron Microscopy equipped with Energy-dispersive X-ray spectroscopy (SEM-EDS, Quanta FEG 450 Oxford Instruments). Fourier Transform Infrared (FTIR, Perkin Elmer) analysis was also conducted with a resolution of 2 cm^{-1} for eight scans over a wave-number range of 4000–400 cm^{-1} to investigate the bonding nature of the different catalyst components.

3. Results and Discussions

3.1 Characterization of Malaysian Ilmenite Derived $TiCl_4$

In this research, $TiCl_4$ was prepared from nitrided local Malaysian ilmenite. Chlorination of titanium oxycarbonitride samples obtained from carbothermal reduction and nitridation was performed at a temperature of about 400-500 °C for 1-3 hours. The final product of this process was a combination of $TiCl_4$ and $TiCl_3$. The produced $TiCl_4$ was 97.24% pure. The elemental analysis results from ICP-OES for the solution derived from Malaysian ilmenite are presented in Table 3.

Table 3. Comparison of the elemental distribution of synthesized $TiCl_4$ product with commercial $TiCl_4$

Element	Concentration, ppm	
	Laboratory grade $TiCl_4$	Synthesized $TiCl_4$
Ti	414,000	388,060
Fe	16.1	7.2
Mn	0.3	0.14
Al	5.3	9.6
Cr	1.5	2.1
Mo	0.7	1.9
Nb	3700	3003
Ta	1.9	2.6
V	-	-
W	-	6.5
Zr	-	0.15
Ce	0.3	0.14
Dy	-	-
Gd	5.4	4.6
La	-	1.2
Lu	-	0.81
Ge	2.5	3.4
Purity (%)	99.10	97.24

From Table 3, the purity of the author's synthesized $TiCl_4$ was lower than that of the laboratory grade $TiCl_4$ because the synthesized sample has not been run through an extensive distillation process, unlike the laboratory-grade $TiCl_4$, which follows a sequential distillation process of purification. The dominant impurities that may involve in the Z-N catalyst synthesis process are Fe, Va, Al, Cr, W, and some REEs. The study will help to understand the efficiency of using the $TiCl_4$ derived from Malaysian ilmenite and promote the use of cost-effective $TiCl_4$ produced from the low-temperature chlorination method for the heterogeneous Z-N catalyst synthesis. Additional qualitative characterization of the $TiCl_4$ solution has been published elsewhere [33].

3.2 Design of Experiment (DOE) Analysis

The results of the factorial design for the recrystallization method of ZN catalyst synthesis are shown in Table 4. Based on the results, the highest content of Ti was obtained for Run 8 (2 g of $MgCl_2$, 6 g of $AlCl_3$, -crystallization temperature of 80 °C, and 2 mL dosage of $TiCl_4$) whereas the lowest amount of Ti was obtained for Run 7 (4 g of $MgCl_2$, 12 g of $AlCl_3$, -crystallization temperature of 100 °C, and 5 mL dosage of $TiCl_4$). The amount of Ti obtained for different samples directly corresponds to the Ti present in the synthesized catalysts. There is a considerable difference in the amount of Ti between the conditions of the highest and lowest runs. Moreover, the analysis indicated a degree of favorability of the studied recrystallization conditions towards the maximum yield of the catalyst.

The main effects plot helps in identifying the levels for the recrystallization process for which there is the most desired outcome, i.e. Ti content in the catalyst. Figure 1 shows the differences in the Ti content for different conditions of process parameters evaluated in the study. While the factors such as the total amount of $MgCl_2$ and $AlCl_3$, and the amount of $TiCl_4$ had significant effects as denoted by the steeper lines of the effects plot, recrystallization temperature had a relatively lesser contribution to the amount of Ti in the synthesized catalyst. From the main effects plot, it is evident that lower crystallization temperature and higher amounts of $MgCl_2$-$AlCl_3$ and $TiCl_4$ feed solution favoured the increase in the amount of Ti in the catalyst. Therefore, it can be claimed that in the studied range of the process parameters of recrystallization method, a combined amount of 2 g of $MgCl_2$ for 6 g of $AlCl_3$, crystallization temperature of 80 °C, and 2 mL dosage of $TiCl_4$ is the optimal combination to synthesize a larger amount of catalyst.

The contour plots are one way of representing the effects of the interaction of the factors on the studied response. Figures 2a-c show the colour gradient of the variation of response, i.e. within the range of process parameters studied. The darkest zone of the contour indicates the effects of the interacting parameters resulting in the most desirable level of response. From the contour plots for interaction in Figures 2 (a) and 2 (c), a non-linear gradient of contour indicates an intricate relationship of the interacting factors. It can be noted that an increase in the amount of Ti is more favourable with a lower temperature, lower amount of $TiCl_4$, and

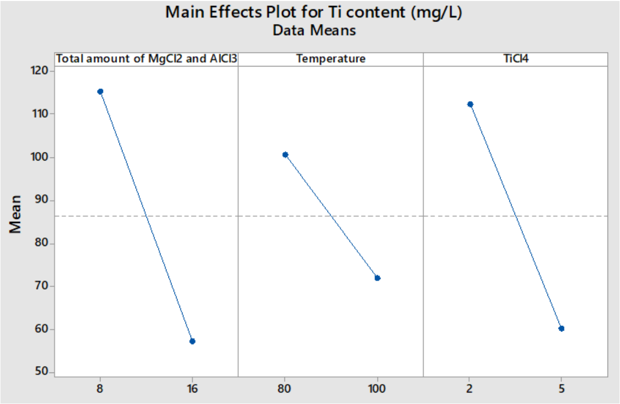


Figure 1. Main effects plot for Ti content in the synthesized catalyst

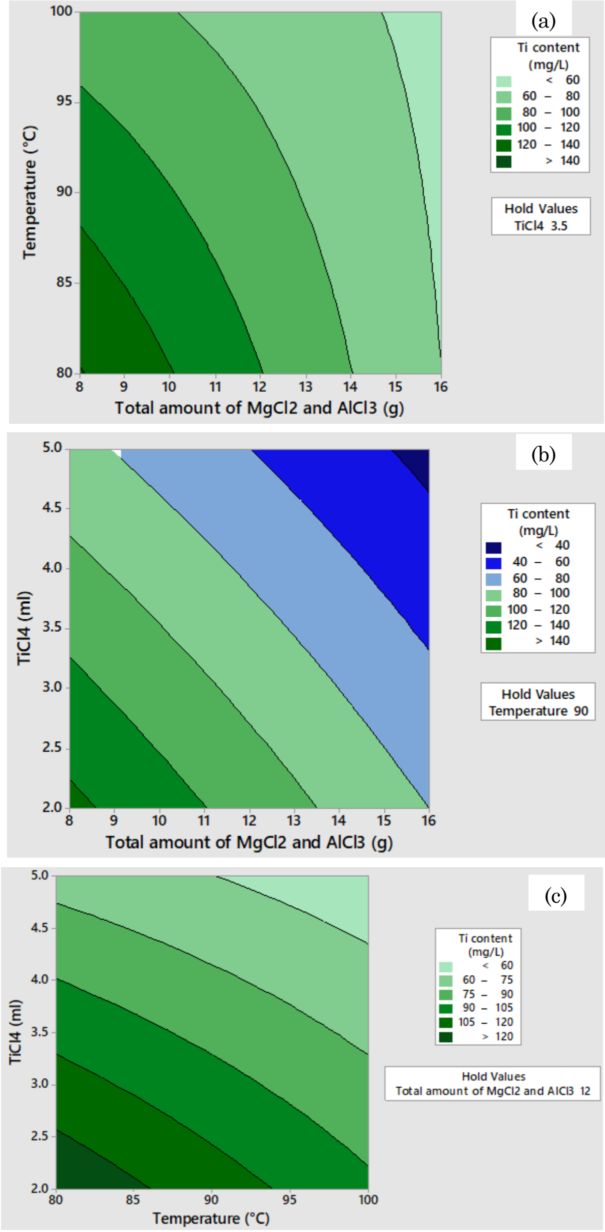


Figure 2. Contour plots of Ti content for 2-way interaction of three factors. (a) Ti content vs Temperature, Total amount of $MgCl_2$ and $AlCl_3$, (b) $TiCl_4$, Total amount of $MgCl_2$ and $AlCl_3$, (c) Ti content (mg/L) vs $TiCl_4$, Temperature.

Table 4. DOE table and responses: recrystallization method of Z-N synthesis

Run order	$MgCl_2$ (g)	$AlCl_3$ (g)	Factor A: Total amount of $MgCl_2$ and $AlCl_3$ (g)	Factor B: Temperature (°C)	Factor C: Amount of $TiCl_4$ (mL)	Response: Ti content (mg/L)
1	4	12	16	80	2	81.81
2	4	12	16	80	5	38.79
3	2	6	8	100	2	108
4	2	6	8	80	5	100.5
5	2	6	8	100	5	71.13
6	4	12	16	100	2	78.04
7	4	12	16	100	5	30.36
8	2	6	8	80	2	181.8

lower total amount of $MgCl_2$ and $AlCl_3$. In Figure 2 (b), the contour exhibits a relatively linear-gradient trend, also suggesting that the lower levels of the factors contributed towards higher Ti amounts in the catalyst. Moreover, additional experiments could help the study to reveal the basis and significance behind the nature of the indicated interactions.

3.3 XRD Studies

The different phases of the synthesized compounds were characterized using XRD analysis, as shown in Figure 3. Since the catalyst synthesis comprised several components, it was not possible to detect and identify the phases accurately. The XRD spectra were characterized by several reflections, which are due to the formation of several complexes between the main catalyst element Ti, co-catalyst Al, and $MgCl_2$ support with organic groups. Based on previous diffraction studies of Z-N, the notable peaks in the synthesized catalyst compounds are $MgCl_2$, $MgCl_2/TiCl_x$, MgEtOH, and unidentified complexes of Ti. The diffractogram of the catalyst with the highest amount of Ti is shown in Figure 3 (Run 8). The diffractogram has characteristic peaks of $MgCl_2$ at $2\theta = 15°$, 30°, 35°, 50°, and 55° [6,14,34]. The additional reflections between 11° to 30° might probably be due to the formation of the Ti complexes during the synthesis of the catalyst [17]. $MgCl_2$ is easily dissolved in alcohols, and during quick precipitation, many defects are produced in $MgCl_2$ and lead to a porous structure [11,14]. $TiCl_3$ peaks were observed as minor phases with some peaks also corresponding to TiO_2, which could be due to the oxidation of $TiCl_4$ as a result of moisture seepage during the synthesis or storage of samples. For a Z-N catalyst to have a good performance, the Ti must form a complex with the $MgCl_2$-ethanol adduct. The formation of complex favours the unstable nature of the catalysts during the polymerization reaction. In addition, the formed complex is not easily washed away during washing and, as a result, leads to higher Ti content in the synthesized catalysts. For Run 8 sample, crystalline peaks were prominent, which could be due to the α- and/or β-$MgCl_2$ dominating the composition of the catalyst. Nevertheless, the broad peaks indicate the structurally disordered $MgCl_2$ undergoing titanation [35]. On the contrary, the diffraction pattern of Run 7 was dominated by phases of $MgCl_2$, which means that the adduct formation is incomplete as a result of which the titanation might not occur [14,21]. Also, there were no amorphous characteristics or broad peaks in the spectrum. i.e. the amount of disordered γ-$MgCl_2$ is low. In that case, the $TiCl_4$ remains unreacted might get oxidized due to the exposure to the OH^- group of the residual alcohol, forming TiO_2. Apart from the above observations, no other impurity phases, like $FeCl_3$, $AlCl_3$, VCl_4, and $NbCl_5$, were noticed in the diffraction studies.

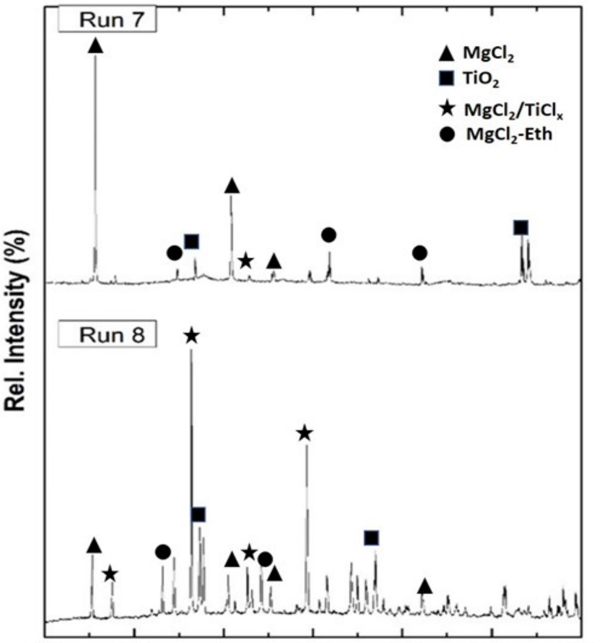


Figure 3. XRD patterns of synthesized Z-N catalysts (Run 8 and Run 7).

3.4 FTIR Analysis

The synthesized Z-N catalyst using Malaysian ilmenite derived $TiCl_4$ was further characterized using the FTIR analysis. The FTIR spectra obtained from two different samples, namely Run 8 and Run 7, corresponding to the highest and lowest amounts of Ti have been compared in Figure 4. From Figure 4, it can be noted that both the spectra are quite identical except for a few positional differences in the absorption peaks. The progress of the reaction is possible to be tracked by observing the band between 3000-3500 cm^{-1}, as the band primarily appears as a result of the -OH bond due to the addition of ethanol for the preparation of the $MgCl_2$-ethanol adduct. This absorption band arises from adsorbed H_2O on the active $MgCl_2$ carrier; therefore, the adsorbed moisture may not favour the oxidation of the $TiCl_4$ to form Ti-O or Ti-O-H groups. However, the final reaction product after the time of a complete reaction may also exhibit this broad band due to the presence of moisture or unreacted alcohol in the reaction mixture. Generally, the nature of $TiCl_4$ is relatively less reactive with alcohol compared to the Al-Et compound in the mixture. Mild inflections were noticed in the spectra between 2000-2500 cm^{-1}, usually ascribed to the absorbed CO_2 and C-H bond of the n-heptane, used to dissolve the $MgCl_2$ to form the adduct. Additionally, two hydrocarbon absorptions were observed at 1384 cm^{-1} and 1326 cm^{-1}, which may also correspond to the n-heptane. A strong peak at 1634 cm^{-1} is evident, which is due to the moisture-present $MgCl_2$. Another peak at 602 cm^{-1}, which can be corresponded to the $MgCl_2$-$TiCl_3$ or the $MgCl_2$-$EtAl(OR)_2$ group, was also observed. The Al-alkyl group showed weak absorption at 1173 cm^{-1}, and a mild inflection at 910 cm^{-1}. The main absorption peaks of Ti-Cl were identified at 602 cm^{-1} and 498 cm^{-1}, which were weaker, but were the only possible indicators of Ti presence in the catalyst. While the spectra of Run 8 exhibited the presence of Ti, Run 7 was not observed of any notable Ti peaks, which could be due to the lower content of Ti in the catalyst. Since the catalyst was prepared using the $TiCl_4$ derived from Malaysian ilmenite, the role of impurities is expected to be influential in affecting the synthesis process; however, the FTIR analysis did not reveal any information on the impurities which is due to their low concentrations (Fe, Al, Nb, Va).

3.5 Morphological Analysis

The morphology of the synthesized catalysts based on conditions of Run 8 and Run 7 are presented in Figures 5 and 6, respectively. The SEM images characterize the physical nature and appearance of the catalysts, as the changes in the synthesis conditions of the catalyst tends to cause changes in their morphology. Agglomerated spherical structures (highlighted in the white box) were observed in the SEM micrographs of the catalyst obtained in Run 8 (Figure 5). On physical observation, the size of the spherical structures was in between the range of 1-1.5 μm. Figures 5 (a) and (b) display masses of spherical particles, which is corresponded to the $MgCl_2$-ethanol adducts. Generally, the removal of alcohol from the $MgCl_2$ adducts makes the surface of the catalyst porous [36]. The surface heterogeneity and porosity of the catalyst structures were not precisely observable, but on comparing the micrographs of the synthesized catalysts in Run 8 and Run 7, the morphological differences were evident. For Run 7 (Figures 6 (a) and (b)), the surface was fragmented and composed of cracks. The distribution of the spherical catalyst structures in the image was very sparse.

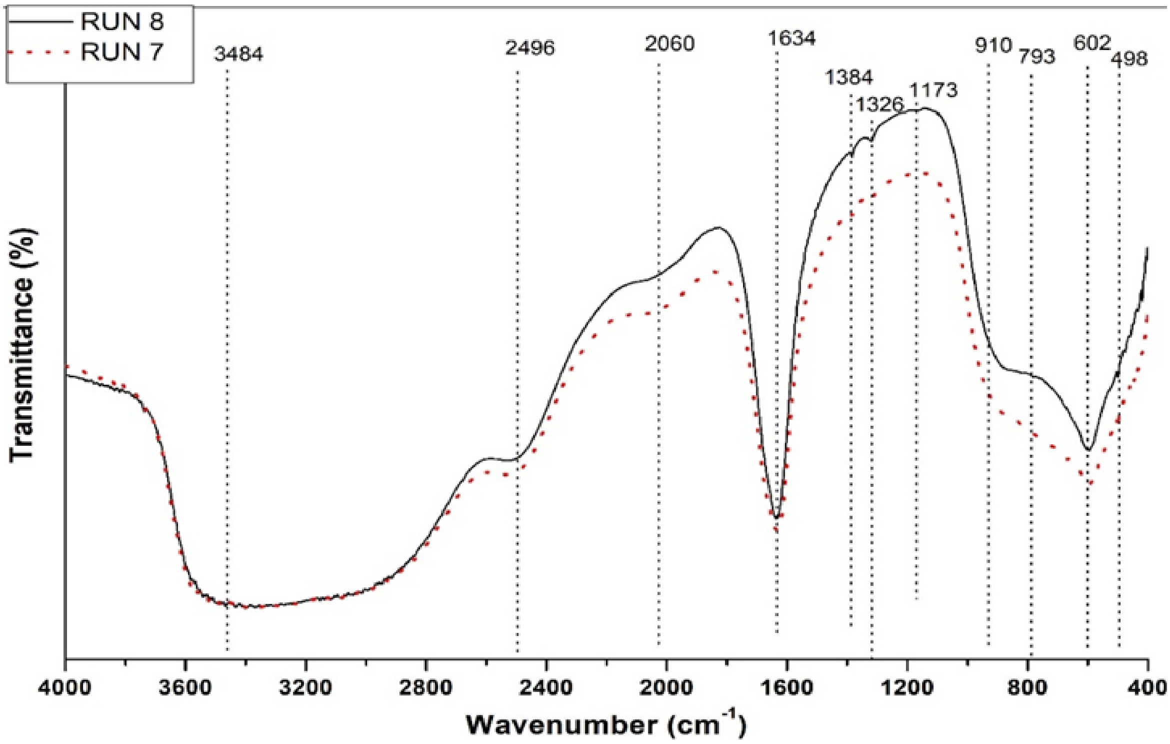


Figure 4. FTIR spectra of the synthesized catalysts: Run 8 (highest amount of Ti content) and Run 7 (lowest amount of Ti content)

A good catalyst comprises a porous and smaller sphere of the catalyst particles, such that the polymers produced during the catalytic activity tend to replicate the shape of the catalyst particles [6,10]. In order to synthesize a catalyst with high catalytic efficiency, it is essential to understand the conditions underlying the formation of $MgCl_2$ support. Usually, when a solvate of $MgCl_2$ in ethanol is dispersed in the inert medium under vigorous stirring, spherical droplets will be formed because of surface tension. However, the absorption of humidity or poor purity of the reagents may affect the morphology of the final adduct obtained [8,36]. The amount of ethanol added during the formation of $MgCl_2$ adducts is crucial in determining the stability and reactive nature of the catalysts as well as the polymer. Besides, the triethyl aluminium (C_2H_5Al), which is the co-catalyst, is influential in regulating the surface area of the catalyst particles.

Elemental analysis of the solid catalyst particles complemented the morphological findings, wherein the spherical particles showed the presence of Ti, Cl, Mg, and Al. The composition of the identified elements differed between the catalyst samples; however, no foreign elements were observed. Figure 7 shows the EDS spectra and composition at two points of the catalyst sample Run 8 from Figure 5 (c). Thus, no impurities or impurity

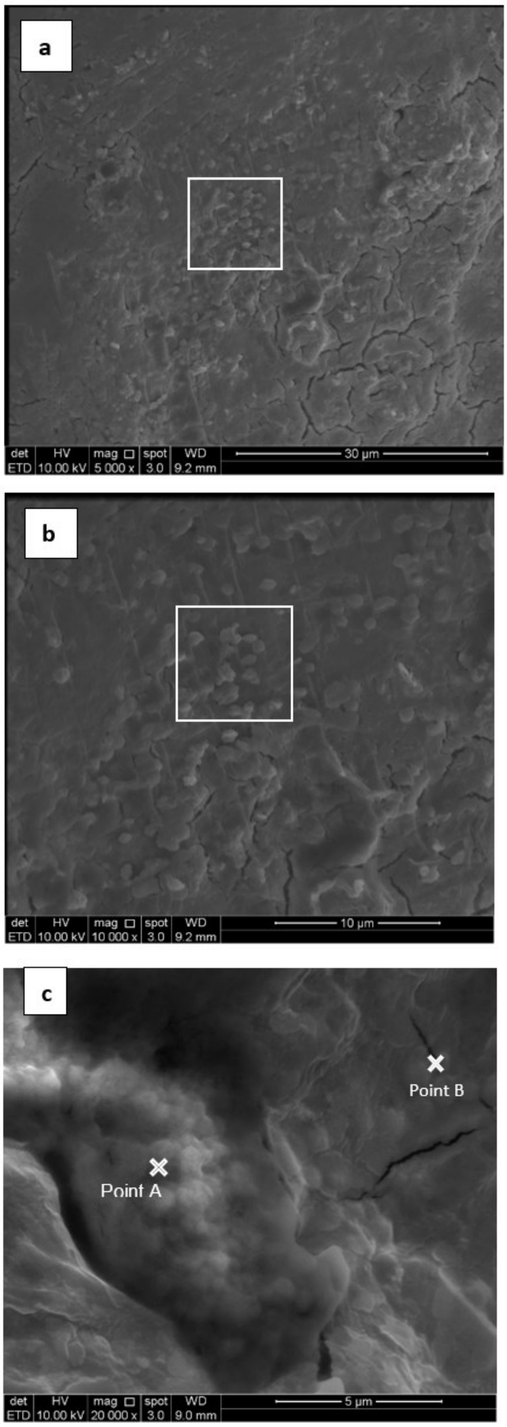


Figure 5. SEM micrographs of catalyst for Run 8 (highest Ti content) at different magnifications

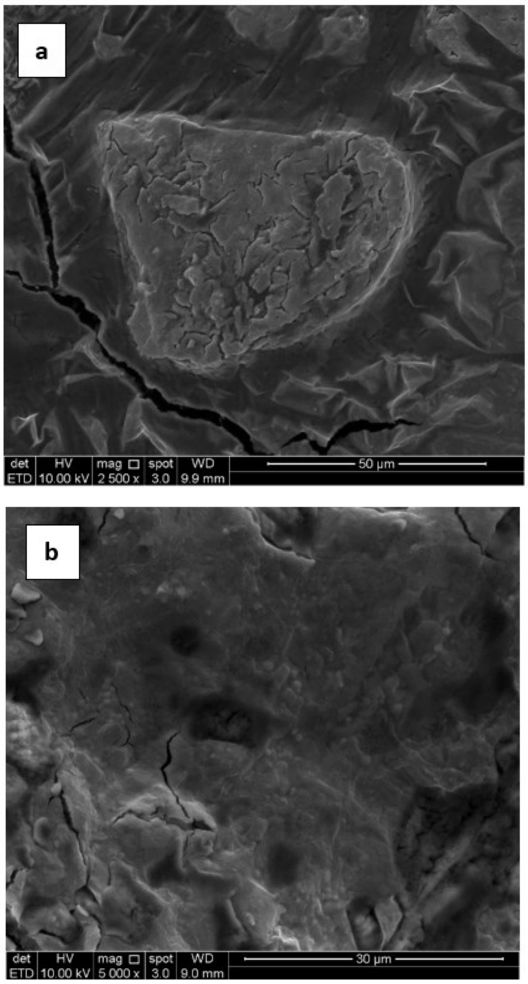
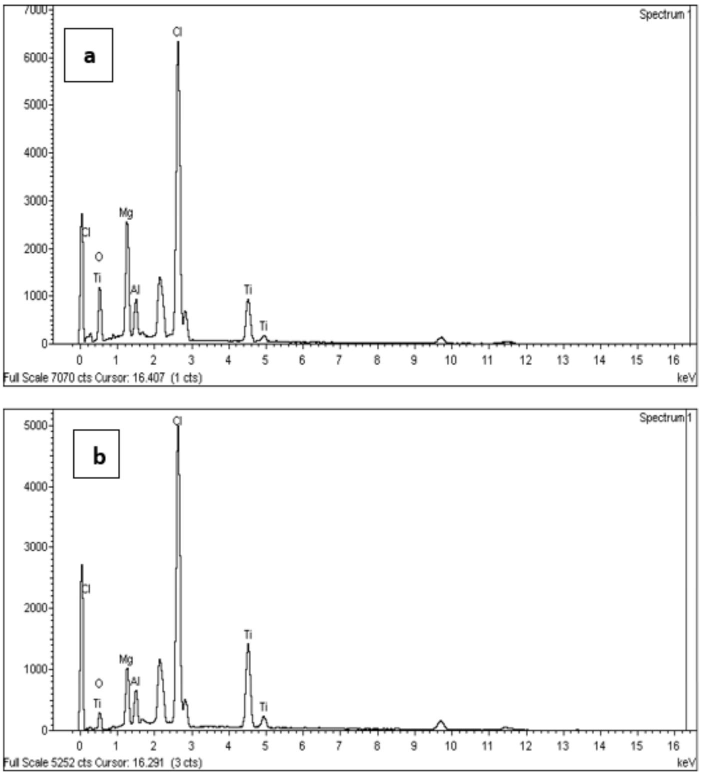


Figure 6. SEM micrographs of catalyst for Run 7 (lowest Ti content)



Element	Wt. %
O	54.69
Mg	11.94
Al	3.40
Cl	24.78
Ti	5.20
Total	100

Element	Wt. %
O	37.80
Mg	8.81
Al	4.48
Cl	34.61
Ti	14.30
Total	100

Figure 7. EDS analysis of the synthesized catalyst (Run 8) at (a) point A and (b) point B marked in Figure 5 (c).

effects were observed during the morphological analysis of the catalyst, thereby approving the successful use of $TiCl_4$ derived from Malaysian ilmenite as a promising source of Ti for the synthesis of Z-N catalysts.

4. Conclusions

Heterogeneous Ziegler-Natta catalyst was successfully synthesized via the recrystallization method using $TiCl_4$ derived from Malaysian ilmenite. The $TiCl_4$ produced from the chlorination of carbothermally reduced ilmenite was found to be 97.24% pure. Using this $TiCl_4$ as the source of Ti compound, the synthesis of the Z-N catalyst was studied using a factorial design of experiments by varying the combined amount of $MgCl_2$ and $AlCl_3$, the recrystallization temperature, and amount of $TiCl_4$. The highest amount of Ti (181.1 mg/L in the synthesized catalyst was obtained for a combined amount of 2 g of $MgCl_2$ for 6 g of $AlCl_3$, crystallization temperature of 80 °C, and 2 mL dosage of $TiCl_4$. The XRD results revealed major phases like $MgCl_2$, $MgCl_2/TiCl_x$ compounds and Ti based complexes. A broad peak was present in the spectrum of the sample with high Ti content, which denotes the presence of structurally distorted $MgCl_2$ in the process of titanation. The spherical morphology of the catalyst particles was observed from the SEM analysis. The concentrations of impurities like Fe, Va, Al, and W were undetected by EDS analysis or were very low to affect the synthesis process and the output. Thus, the findings of the research will open gateways for using Malaysian ilmenite derived $TiCl_4$ as a potential replacement to the currently imported $TiCl_4$ for polymer-based industries.

Conflict of Interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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