Chapter 4

Bulky MgCl$_2$.xROH Molecular Adducts and Its Influence in Polyethylene Production


*Dalton Trans., 2011, 40, 10936-10944.*
Part A: MgCl$_2$.6C$_6$H$_{11}$OH

4.1 Introduction

Though several decades passed after the discovery of Z-N catalyst [1], heterogeneous MgCl$_2$ supported TiCl$_4$/alkylaluminium system still remains the irreplaceable catalyst for many industrial productions of polymers in spite of its multisite in nature [2]. These supported catalysts not only simplify the industrial process of polyolefin production but also can tune the property of polymers by simply controlling the morphology of the active catalysts [3]. Lewis bases such as alcohol, esters, ethers, etc., are important and indispensable components to activate MgCl$_2$ and to act as electron donor (ED) to increase the stereo specificity of propylene polymerization [4−6]. It is also to be underscored that the role of alcohol molecules present in the adduct is to make high surface area and porous support. Further, alcohol molecules do not have the role of an internal donor since all the alcohol molecules will be eventually removed at the final stages of Z−N catalyst preparation. However, very few crystal structures of intermediate and final compounds are available [4]. To date, many generations of heterogeneous Z−N catalytic systems have been reported based on the Lewis bases used [2, 7, 8]. For the design of new Z−N catalytic systems, development of new Lewis bases will be an important criterion. Most importantly, activation of TiCl$_4$/AlR$_3$ (R = Me, Et, etc.) by MgCl$_2$ support depends on the crystallographic structure of the support, which is similar to the role of ligands in the homogeneous catalyst [9].

Though technologically Z−N catalyst has matured to a sophisticated level, the molecular science behind the role of support and various key interactions of the active components in the heterogeneous Z−N catalyst is still unclear [10−16]. Partly it is due to the complex nature of active sites of TiCl$_x$ on MgCl$_2$ under polymerization conditions and the high sensitivity of catalyst components present in Z−N systems toward the atmosphere. Now it is a big challenge to techniques such as surface science, structural, spectroscopy, and
theoretical methods to determine the role of support for surface activation in supported MgCl$_2$ in Z–N catalyst [17–21]. Experimental and theoretical efforts have been taken to identify the key structural aspects of support and its influence in catalytic activity. Indeed, MgCl$_2$ surface exposing certain crystallographic planes, especially (110) lateral cuts of MgCl$_2$, are more active for polymerization [6, 11].

MgCl$_2$·6EtOH is shown as an active support, and it has been reported that the ratio between EtOH/MgCl$_2$ deeply affects the performance of Z–N catalytic system. Among many possible MgCl$_2$·xROH supports, single crystal structure is reported only for two adducts, namely, MgCl$_2$·6EtOH (MgEtOH) and MgCl$_2$·6BzOH [22, 23]. Solid state NMR and crystal structure studies on MgEtOH support clearly indicate the presence of mixed phases of precursor MgCl$_2$·xEtOH ($1 \leq x \leq 3$) present in the synthesized supports [24, 25]. Recently many alcohols having different alkyl chains have been used to prepare the well-defined molecular adduct and its polymerization activity for ethylene was studied [26, 27]. It is clear that the nature of alcohol present in the adduct changes many properties, like electronic, textural, and structural, and hence the final Z–N catalysts also show different activity. With different alcohol, it is possible to tune the polymerization activity, and our ultimate aim is to find a suitable molecular adduct for oligomerization of olefins to value-added petrochemicals. We believe it is possible, and systematic efforts are definitely required to achieve this.

In order to understand the complex system consisting of multicomponent, which are interacting with one another, it is essential to understand the physicochemical properties of each component and then allow them to interact together with increasing complexity [16]. The present chapter describes a synthesis procedure to make well-defined MgCl$_2$ based molecular adducts prepared using cyclohexyl, benzyl alcohol and 9-fluorenemethanol (9-FM). The above molecular adducts were named as MgCyOH, MgBzOH and Mg-9FM-EtOH and used as a support material to synthesize active Z–N catalyst after titanation. Structural
insights of molecular adducts and titanated catalysts have been examined through structural, spectroscopic and textural studies toward a better understanding of Z–N catalysis in polymerization reaction at molecular level. This report is a part of on-going efforts in our laboratory to synthesize new molecular adducts with different Lewis bases, exploiting them for polyolefin synthesis with an emphasis on understanding molecular level properties [26, 27].

4.2. RESULTS AND DISCUSSION

4.2.1. Characterization of Adduct

4.2.1.1. Powder X-ray Diffraction.

![Powder XRD pattern](image)

**Figure 4.1:** Powder XRD pattern of (a) anhydrous MgCl$_2$, (b) MgEtOH adduct, and (c) MgCyOH adduct.

Powder X-ray diffraction pattern (PXRD) of catalyst precursors MgCyOH and MgEtOH are shown and compared with that of anhydrous MgCl$_2$ in Figure 4.1. Anhydrous MgCl$_2$ exhibiting rhombohedral cubic close packing with strong diffraction patterns for (003), (004), and (110) planes at $2\theta = 15.1^\circ$, 35$^\circ$, and 50.4$^\circ$, respectively. First eight intense
features were used for indexing of MgCyOH adduct (see crystallographic data in Table 4.1).

Indexing of MgCyOH

Table 4.1. Crystallographic data

Crystal system: Monoclinic

\[
\begin{align*}
\text{a} &= 17.53157 \, \text{Å} \\
\text{b} &= 10.30281 \, \text{Å} \\
\text{c} &= 14.47035 \, \text{Å}
\end{align*}
\]

\[
\begin{align*}
\alpha &= 90.00000^\circ \\
\beta &= 99.32681^\circ \\
\gamma &= 90.00000^\circ
\end{align*}
\]

Unit cell volume = 2579.15 Å\(^3\)

\[M(20) = 38; \quad M'(20) = 114\]

Total number of observed lines = 9

Number of calculated lines (up to the 20th observed d) = 105

Number of unindexed lines = 0

Number of single indexed lines = 7

Total number of lines = 8

\[
\begin{align*}
\text{a} &= 17.531054 \pm 0.009951 \, \text{Å} \\
\alpha &= 90.000000 \pm 0.000000 \, \text{deg} \\
\text{b} &= 10.301604 \pm 0.009267 \, \text{Å} \\
\beta &= 99.327675 \pm 0.020346 \, \text{deg} \\
\text{c} &= 14.471068 \pm 0.009573 \, \text{Å} \\
\gamma &= 90.000000 \pm 0.000000 \, \text{deg}
\end{align*}
\]

Unit cell volume = 2578.89 Å\(^3\)

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<th>(\text{SST}_{\text{cal}})</th>
<th>(\delta)</th>
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<th>(2\theta_{\text{cal}})</th>
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<td>12.660</td>
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</tbody>
</table>

Number of observed lines = 8

Number of calculated lines = 9
the diffraction patterns clearly indicates that the sample possesses monoclinic symmetry. A strong (002) diffraction peak appeared at $2\theta = 7.2^\circ$ ($d = 12.135 \text{ Å}$), which is higher than the $d$ value of MgEtOH precursor ($d = 9.838 \text{ Å}$). Higher value of $d$ in MgCyOH is attributed to the bulkiness of cyclohexanol moiety in the adduct. Above high intense peak (002) for MgCyOH adduct clearly shows that the crystal growth occurs along the (00l) plane and similar to that of MgEtOH [26,28]. The unit cell parameters calculated are listed in the crystallographic data. A strong (002) diffraction feature observed below $2\theta = 10^\circ$ and with $d = 12.135 \text{ Å}$ clearly demonstrates that the MgCyOH adduct exhibits a layered structure because of interaction of cyclohexanol along z-axis around MgCl$_2$.

4.2.1.2. Thermal Analysis

Thermal analysis of MgCyOH adduct has been carried out in N$_2$ atmosphere at a heating rate of 10 deg/minute, and the results are shown in Figure 4.2. On the basis of the molecular formula MgCl$_2$·6CyOH, expected weight loss (86.1%) matches well with that of the experimental weight loss (85.5%) within ±1% error. From the experimental weight loss, the ratio of cyclohexanol/MgCl$_2$ has been derived and confirmed to be six. The weight loss pattern obtained was not similar to MgEtOH adduct, i.e., stepwise weight loss [26] was not observed in MgCyOH. In TGA analysis, there is only one well defined transition that could be observed at 155 °C corresponding to a weight loss of three cyclohexanol. Further, DTA analysis also shows three peaks ≤154 °C, supporting the successive dealcoholation of cyclohexanol molecules. However, above 155 °C, systematic decomposition of CyOH molecules are not observed, rather a continuous weight loss was observed. This observation could be due to the different kind of dynamics of cyclohexanol around Mg$^{2+}$. Although the boiling point of cyclohexanol is 161 °C, weight loss that occurs below 161 °C indicates a possible weak interaction. Indeed, weight loss that occurs >161 °C hints toward a relatively stronger interaction. The above observations indicate that the nature of interaction of
cyclohexanol with MgCl\textsubscript{2} varies with composition and that all cyclohexanol molecules may not have the same interaction with MgCl\textsubscript{2}. Absence of any weight loss >250 °C clearly indicates that only MgCl\textsubscript{2} remains present without any CyOH.

![Figure 4.2: TG-DTA analysis of MgCyOH adduct.](image)

4.2.1.3. Raman Analysis

Figure 4.3 shows the Raman spectra of MgCyOH, liquid cyclohexanol, and anhydrous MgCl\textsubscript{2}. MgCl\textsubscript{2} belongs to the rhombohedral crystal system with layered structure having D\textsubscript{3d} space group. The A\textsubscript{1g} breathing mode of MgCl\textsubscript{6} octahedra appears as a high intense peak at 243 cm\textsuperscript{-1}. This is attributed to a distorted octahedron environment with Mg\textsuperscript{2+} coordinated to six chloride ions [26,27,29]. Raman spectrum of pure cyclohexanol shows a peak at 966 cm\textsuperscript{-1} for axial C–OH stretching vibration, and a peak at 1024 cm\textsuperscript{-1} is assigned for the equatorial C–OH stretching vibration [30]. Other than these peaks, pure cyclohexanol exhibits a broad and weak –OH phonon observed between 2850 and 3300 cm\textsuperscript{-1} due to strong intermolecular hydrogen bonding. In MgCyOH, some of the Raman features of neat cyclohexanol disappear,
and new features emerge due to the adduct formation between MgCl$_2$ and cyclohexanol. Particularly, a new peak at 712 cm$^{-1}$ in MgCyOH Raman spectrum emerges out. This peak in MgCyOH adduct is attributed to Mg$^{2+}$ ion surrounded by six molecules of cyclohexanol in an octahedral (Mg−O$_6$) arrangement. However, the above feature appears at 685–690, 700, and 703 cm$^{-1}$ for MgEtOH adduct, MgCl$_2$·5EtOH·EtOOCPH, and MgCl$_2$·6PhCH$_2$OH, respectively [29,26,27a]. These observations underscore the sensitive nature of this peak for electronic and structural changes around Mg$^{2+}$ ion in these adducts. A shift in the Mg−O$_6$ Raman active feature in MgCyOH could be due to the bulkiness of cyclohexanol moiety, which could distort the octahedral environment. Further, the above shift (to 712 cm$^{-1}$) suggests an overall stronger interaction between Mg$^{2+}$ and cyclohexanol.

Figure 4.3: Raman spectra of (a) anhydrous MgCl$_2$, (b) CyOH, and (c) MgCyOH.
4.2.1.4. Solid State NMR

Figure 4.4: (a) $^{13}$C CPMAS 75.5 MHz and HPDEC NMR spectra recorded at D1 as 3 s. (b) $^{13}$C CP-MAS NMR spectra of MgCyOH at different relaxation time.

Figure 4.5: $^{13}$C HPDEC NMR 75.5 MHz spectrum of MgCyOH adduct recorded at different D1 relaxation times.
Figure 4.4a shows the $^{13}$C CPMAS and HPDEC spectra of MgCyOH adduct recorded at 3 s of relaxation time (D1). $^{13}$C CPMAS as well as HPDEC spectrum shows eight peaks with chemical shift values of 72.5, 71.9, 36.9, 36.4, 34.8, 33.9, 26.5, and 25.7 ppm. However, only four types of carbon signals are expected for cyclohexanol in the most favored chair configuration with –OH in equatorial position. Therefore, the observation of eight NMR peaks in MgCyOH adduct dictates the presence of two different types of cyclohexanol molecules. These peaks could be assigned as follows: C1 peaks at 72.5 and 71.9 ppm, C2 peaks at 36.9 and 36.4 ppm, C3 peaks at 34.8 and 33.9 ppm, and finally C4 peaks at 26.5 and 25.7 ppm. Absence of any extra peak in $^{13}$C HPDEC clearly signifies that all the cyclohexanol molecules are strongly interacting with MgCl$_2$, in other words, there is no free cyclohexanol molecules in the adduct. However, intensity of the peaks in $^{13}$C CPMAS and $^{13}$C-HPDEC spectra were found to vary significantly. The intensities of one set of signals that are shielded were found to be weaker in the HPDEC spectrum. Because of the contact time dependency of intensities, the CPMAS spectrum shown in Figure 4.4b need not provide quantitative information. In order to quantify the sets of chemically different cyclohexanol (i.e., 3 + 3 or 2 + 4) among six cyclohexanol molecules around MgCl$_2$, $^{13}$C-HPDEC spectra have been recorded at different relaxation delays (D1 at 3, 20, and 120 s), and the results are shown in Figure 4.5. The carbon resonances of one set of cyclohexanol was found to relax very slowly, especially C1, the carbon atom directly attached to –OH, which is coordinated to MgCl$_2$. Spectrum recorded at 120 s (fully relaxed) shows equal intensity for C–OH peaks. Hence, in MgCyOH adduct, cyclohexanol is most likely present in a 3 + 3 chemical environment, and one set of three cyclohexanol molecules experiences very restricted molecular motions, as qualitatively suggested by the longer spin–lattice relaxation time.
4.2.1.5. Surface Morphology

Scanning electron microscope images of MgCyOH adduct is shown in Figure 4.6. MgCyOH adduct has been taken with triblock copolymer to avoid (a) degradation due to the interaction with residual moisture and (b) to minimize agglomeration of particles. Particles are of spherical in shape in a size range of 10−20 µm in diameter. Closer view of the particles clearly shows that each particle consists of many smaller particles. Indeed, this type of inter-particle voids might contribute to the porosity of MgCyOH. This is further supported by surface area measurement, which will be discussed later. The surface of MgCyOH particles is not smoother in nature like MgEtOH particles [27].

![Figure 4.6: SEM image of MgCyOH adduct at different magnification. Scale bar is 50 µm (left) and 20 µm (right).](image)

4.2.2. Characterization of Active Catalyst (Ti-MgCyOH)

4.2.2.1. Powder X-ray Diffraction

PXRD of Ti-MgCyOH catalyst is shown in Figure 4.7. Significantly broad and low intensity diffraction features are observed for titanated MgCyOH catalyst. This is in contrast to narrow and intense features observed for MgCyOH. This indicates that the active catalyst is less crystalline in nature. It is to be noted that, during the addition of TiCl₄ and subsequent washing, cyclohexanol molecules are removed and that TiCl₃/TiCl₄ is incorporated into the
lattice of MgCl₂. This severely decreases the crystallinity of MgCl₂. Removal of organic moiety during the incorporation of TiCl₄ could be the reason for less crystalline nature. Titanated MgCl₂ exhibits peaks at $\sim 2\theta = 17°$ for (003) and broad peaks around 26°, 32°, and 51°. Stacking of Cl–Mg–Cl triple layer is evidenced by the presence of a 17° peak [31,32].

![Figure 4.7: Powder X-ray diffraction pattern of (a) anhydrous MgCl₂ (b) MgCyOH, and (c) Ti-MgCyOH catalyst.](image)

4.2.2.2 Solid State NMR

Figure 4.8a shows a solid state $^1$H MAS NMR spectrum of Ti-MgCyOH catalyst. The peak at 7.5 ppm is attributed to the presence of residual chlorobenzene present inside the pores. Sharp peaks at 1.4 and 1.1 ppm (inset of Figure 4.8a) could be due to the trace amount of hexane, which was used for washing, present inside the pores. Figure 4.8b shows the comparison of the $^{13}$C CPMAS spectrum of Ti- MgCyOH catalyst and MgCyOH adduct. A peak at 127.3 ppm in Ti-MgCyOH catalyst spectrum demonstrates the presence of chlorobenzene in the active catalyst. The presence of signals in the aliphatic region 20–25
ppm is likely to be associated with availability of physisorbed n-hexane on the pores of active catalyst. The absence of all cyclohexanol features in the active catalyst (Figure 4.8b) confirms that the cyclohexanol molecules are washed away during the active catalyst preparation.

![Figure 4.8](image)

Figure 4.8. (a) Solid state $^1$H MAS NMR spectrum of Ti-MgCyOH and (b) $^{13}$C CPMAS spectrum of the Ti-CyOH compared with MgCyOH.

4.2.2.3 Thermal Analysis

Thermal analysis of Ti-MgCyOH has been carried out in N$_2$ atmosphere at a heating rate of 10°deg/minute, and the results are shown in Figure 4.9. Compared to MgCyOH adduct, an entirely different TG-DTA pattern was observed for Ti-MgCyOH. About 35% weight loss has been observed in Ti-MgCyOH. This weight loss could be due to the presence of chlorobenzene residue deposited during the synthesis of active catalyst. Further, some amount of n-hexane that remains even after thorough washing of active titanated catalyst adds to the weight loss. In fact, the presence of the above two organic moieties were very clear from the solid state NMR spectrum (Figure 4.8).
Figure 4.9: TG-DTA analysis of Ti-MgCyOH.

4.2.2.4. Scanning Electron Microscopy

Figure 4.10: SEM image of Ti-MgCyOH catalyst at different magnification. Scale bar is (a) 5 \( \mu m \) and (b) 10 \( \mu m \). A single spherical particle is shown in the SEM image panel b.

Scanning electron microscope images of Ti-MgCyOH are shown at different magnification in Figure 4.10. The porous nature of the active catalyst is clearly evident from
SEM images. A closer view (Figure 10a) shows that the active catalyst contains many sub-micrometres size particles composed together and that each particle exhibits a smooth surface. In addition, there are spherical particles present, which also lead to spherical-shaped polyethylene.

4.2.2.5. Textural Properties.

![Image of Adsorption Isotherm and Pore Size Distribution](image)

**Figure 4.11:** (a) Adsorption isotherm and (b) pore size distribution of Ti-MgCyOH active catalyst.

**Table 4.2:** Textural Characteristics of Molecular Adducts and Titanated Catalyst.

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<th>S.No</th>
<th>Material</th>
<th>Particle Morphology</th>
<th>Pore Volume cc/g</th>
<th>Pore Diameter nm</th>
<th>Surface area m²/g</th>
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*NM, not measurable

N₂ adsorption isotherm and pore size distribution of active catalyst is shown in Figure 4.11 and given in Table 4.2. BET surface area analysis active catalyst Ti- MgCyOH shows a surface area of 236 m²/g, which is extremely high compared with earlier reported and
commercial (MgEtOH, 32 m²/g) Z−N active catalysts [26,27]. High surface area could be due to the removal of bulky cyclohexanol during the active catalyst preparation. Ti-CyOH exhibits an average pore diameter of 12 nm and average pore volume of 0.84 cc/g. The adsorption isotherm of Ti-MgCyOH catalyst shows no adsorption saturation even at high relative pressure (P/P₀ = 1) indicating a Type-IV isotherm with H3 hysteresis loop [33,34]. It clearly indicates the contribution of macropores in the active catalyst. Pore size distribution analysis of active catalyst indicates that a major contribution from mesopores in a close pore diameter range of 8–20 nm occurs, and the rest arise from macro- and micropores together. It is very likely the above meso- and macropores allow easy diffusion of reactants as well as chain growth of polymer. Significantly high polymerization activity is related to high molecular weight; however, low molecular weight distribution is attributed to the above textural characteristics (entry 6 in Table 4.3).

4.2.3. Ethylene Polymerization.

Ti-MgCyOH catalyst has been screened for ethylene polymerization using three different co-catalysts without maximizing polymerization activity. Results presented in Table 4.3 are the average values taken after carrying out three sets of experiments. When pressure was increased from 1 to 5atm, the polymerization activity of all the active catalyst increased as expected. Analysis of activity data given in Table 4.3 leads to the following points: (a) Reasonable high activity was observed with any cocatalyst, even at atmospheric pressure of ethylene. However, the activity increases linearly with increasing size of alkyl group in cocatalyst from Me, Et, to isobutyl group. Molecular weight of polyethylene (PE) also increases with the above activity; however, MWD did not change significantly. (b) A very similar trend to that of point (a) is observed at 5atm pressure of ethylene, however, with much higher PE yield. MWD of PE produced at 5atm pressure is significantly narrow,
Table 4.3: Activity results of catalysts for polymerization reactions

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<th>Condition</th>
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<th>Productivity of PE (gmmol⁻¹ of Ti)</th>
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<td>183</td>
<td>26111 (188000)</td>
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</table>

Catalyst quantity = 0.1g; Al/Ti = 300 for MgCyOH support, Al/Ti = 50 for MgEtOH and Al/Ti = 10. Dry hexane has been used as solvent.
compared to that prepared at atmospheric pressure. (c) Compared to standard MgEtOH, entry 3 exhibits higher activity and PE yield with i-Bu$_3$Al cocatalyst at atmospheric pressure. (d) Among the activity measurements, entry 6 gives the best polymerization activity and comparatively narrow MWD without any external donor. (e) Compared to the activity of titanated catalyst prepared from MgBzOH (MgCl$_2$·6PhCH$_2$OH) [27a], the present set of catalysts exhibits much higher activity even at atmospheric pressure. It is to be noted that high surface area was observed for present Ti-MgCyOH as well as Ti-MgBzOH; nonetheless, a large amount of high boiling PhCH$_2$Cl trapped in the pores of Ti-MgBzOH was attributed to lower polymerization activity [27a]. (f) High porosity and textural properties observed with Ti-MgCyOH and without any impurities, apart from solvents, is likely to be responsible for higher activity.

The difference in polymerization activity with different co-catalysts could be due to different active site formation [35]. Overall performance of Ti-MgCyOH was much better than the commercial Ti-MgEtOH catalyst in terms of activity and MWD. The possible reason could be due to the very high surface area (236 m$^2$/g) of Ti-MgCyOH and lesser content of active TiCl$_x$ species over the catalyst. We believe that, i-Bu$_3$Al cocatalyst integrates well with the Ti-MgCyOH catalyst structurally, due to the bigger size of the iso-butyl group, and leads to higher activity. However, more experiments are necessary to confirm the above aspects.

4.2.4. CONCLUSIONS

A novel adduct of MgCl$_2$ with bulky cyclohexanol (MgCyOH) has been synthesized. Structural insights of adduct have been revealed by various spectroscopic and morphological characterization methods. NMR and Raman data show the presence of six cyclohexanol molecules in an octahedral environment with magnetically non-equivalent CyOH molecules in a 1:1 ratio. Using this novel support, active Ziegler–Natta catalysts with very high surface area and evenly distributed titanium active species have been prepared. This final active
catalyst Ti-CyOH exhibits much better performance in terms of activity and polymer property compared to commercial Z–N catalyst. Multimodal porous nature of catalyst is apparently responsible for high activity. High activity observed with iso-butyl aluminium cocatalyst on Ti-MgCyOH suggests a possible structural integration, which would also make it electronically integrated. If this is true, higher and selective activity could be achieved with other polymerization reactions. Detailed structural and spectral studies are essential to understand the present catalyst system for better activity.
Part A: MgCl$_2$.6C$_6$H$_{11}$OH

4.3. Results and Discussion

4.3.1. Characterization of MgBzOH adduct

4.3.1.1. Powder X-ray Diffraction

Figure 4.12 shows a comparison of the powder XRD patterns of the MgBzOH and MgEtOH adducts and anhydrous MgCl$_2$. Assignment of various features are possible due to the Rietveld refinement analysis, which will be discussed below. A rhombohedral cubic close packing structure is exhibited by anhydrous MgCl$_2$. It gives strong diffraction peaks for the

![Figure 4.12: Comparison of powder XRD pattern of (a) anhydrous MgCl$_2$ adduct (b) MgEtOH adduct (c) MgBzOH adduct. (d) Rietveld plot for MgBzOH adduct observed (crosses), calculated (dark grey line) and difference (grey) powder XRD patterns.](image)
(003), (004) and (110) planes at $2\theta = 15.1^\circ$, $35^\circ$, and $50.4^\circ$, respectively [36]. The XRD pattern of the MgBzOH adduct shows a highly intense peak at $8.2^\circ$ for the (002) plane with other reflections at $16.2^\circ$ and $27.1^\circ$ for the (004) and (106) reflections, respectively. The highly intense reflection for the (002) plane clearly shows the growth of the crystal in this preparation method occurs along (00l) planes. The XRD pattern of the MgBzOH adduct fits with the crystal structure belongs to monoclinic symmetry with the space group $P2_1/c$. Nonetheless, in comparison to the MgBzOH adduct, the XRD pattern of the MgEtOH adduct remains in a rhombohedral structure with a highly intense reflection at $9^\circ$ (001) and other selected reflections at $2\theta \sim 18^\circ$ (002) and $2\theta \sim 36^\circ$ (004). A strong diffraction feature at $2\theta < 10^\circ$ for the MgBzOH adduct highlights the fact that the adduct exhibits a layered structure due to relatively weak interaction of the alcohol along the z-axis. Although the benzyl alcohol moiety is bulkier than ethanol, the MgBzOH adduct exhibits a d value of 10.705 Å for the (002) plane due to compact packing.

Figure 4.13: Ball and stick model representation of crystal structure of MgBzOH adduct, viewed along the b-axis. Small dark grey, blue, red and green spheres represent C, Mg, O and Cl atoms, respectively
Rietveld refinement of the MgBzOH structure with its powder XRD data, based on the atomic positions reported in the literature [22], gave high agreement factors and this may be due to the good quality of the X-ray diffraction data and a possible preferred orientation in the sample along the 00l direction. All of the diffraction features match well with the calculated XRD pattern. The final Rietveld plot is displayed in Figure 4.12d, providing a significant difference in the intensities of the 00l reflections. Figure 4.13 displays a schematic representation of a ball and stick model of the structure of the MgBzOH adduct generated from single crystal data reported in the literature (viewed along the y-axis) [22]. The above structure demonstrates the octahedral coordination of six –OH groups to Mg$^{2+}$.

4.3.1.2. Thermal Analysis

Figure 4.14 shows TG and DTA results for the MgBzOH adduct. However, TG analysis did not show any well-defined weight loss features, though a large weight loss was observed in the temperature range between 75 and 210 °C. The absence of a well-defined weight loss, unlike for MgEtOH and MgCl$_2$.4(CH$_3$)$_2$CHOH adducts [14, 26] shows the absence of successive dissociation of benzyl alcohol from the MgBzOH adduct. The single broad weight loss feature observed for the MgBzOH adduct is likely to be due to the steric bulkiness of the benzyl alcohol molecule in adduct. Nevertheless, DTA shows some sharp features, mainly due to the endothermic desorption of the benzyl alcohol molecule from the MgBzOH adduct. The weight loss feature associated with desorption of the first benzyl alcohol molecule is broad between 75 and 130 °C and the DTA minimum was observed at 80 °C. The second weight loss is narrow between 130–150 °C and the DTA minimum observed at 140 °C. Dissociation of third molecule shows no distinct DTA feature. The fourth weight loss is sharp between 165–180 °C and the DTA minimum is observed at 175 °C. The fifth and final weight losses occurs with exothermic desorption at >180 °C and 210 °C, respectively. The expected total weight loss of the MgBzOH adducts matches well with the
experimental weight loss within ±1% error. The absence of any weight loss above 250 °C indicates the presence of only MgCl$_2$, after dissociation of all benzyl alcohol molecules. The benzyl alcohol/MgCl$_2$ ratio was found to be six, from the experimental weight loss corresponding to 87.2%.

![Graph](image.png)

**Figure 4.14**: TG-DTA analysis of MgBzOH adduct.

### 4.3.1.3. Surface Morphology

![Images](image2.png)

**Figure 4.15**: (a and b) Optimal microscopy, and (c) SEM images of MgBzOH adduct.  
The optical microscopy images of the MgBzOH adduct are presented in Figure 4.15. Figure 4.15a shows the adduct in a thin liquid layer of triblock copolymer solution and Figure 4.15b is in anhydrous hexane solution. In triblock copolymer solution the adducts were
homogeneously dispersed. All particles are spherical in shape and homogeneously distributed without agglomeration. However, in the case of anhydrous hexane solution the particles are agglomerated and a large distribution of particle size is evident (Figure 4.15b). Due to this, the particles are larger in size, and predominantly spherical in shape. Figure 4.15c shows an SEM image of the MgBzOH adduct. The SEM image reveals the particles are spherical in shape; however, the particle size is not uniform. The size of the particles (0.5 µm) is much smaller than in MgEtOH adducts [26] (20 µm, results not shown). The images show the surface of the adduct is smooth in nature.

4.3.1.4. Raman Analysis

Figure 4.16 shows the Raman spectra of the MgBzOH adduct, with (liquid) benzyl alcohol and anhydrous MgCl₂. Crystalline MgCl₂ belongs to a layered rhombohedral Structure with D₃d space group. The Raman spectrum of anhydrous MgCl₂ shows a highly intense peak at 243 cm⁻¹ due to the A₁g breathing mode of the MgCl₆ octahedra in the lattice [29]. This indicates Mg²⁺ is in a distorted octahedral configuration coordinated to six chlorine anions. The Raman spectrum of neat benzyl alcohol shows a very strong Raman band at 1002 cm⁻¹ from the phenyl ring breathing mode and a peak at 1027 cm⁻¹ from the in-plane C–H bending mode [37]. However, the above features of MgCl₂ and neat benzyl alcohol disappear in the Raman spectrum of the adduct and a new peak appears at 703 cm⁻¹ for the MgBzOH adduct. This peak is attributed to the symmetric breathing mode of the Mg–O bond formed due to the interaction of Mg²⁺ with alcoholic oxygen atoms. This peak underscores the fact that Mg²⁺ is in an octahedral environment, and surrounded by six benzyl alcohol moieties forming a MgO₆ octahedron. It is to be noted that the above symmetric breathing mode of Mg–O appears at 690 cm⁻¹ for the MgEtOH adduct [29]. The shift observed to higher frequency for MgBzOH indicates a significant change in the electronic environment around
Mg$^{2+}$ ion in the case of the MgBzOH adduct, and stronger binding between Mg and O especially is reflected in the Raman spectrum.

![Raman spectrum](image)

**Figure 4.16:** Raman spectrum of (a) benzyl alcohol, (b) MgBzOH adduct, and (c) anhydrous MgCl$_2$.

### 4.3.1.5. Solid State NMR

The MgBzOH adduct prepared has been characterized by solid state $^{13}$C CP-MAS NMR. The $^{13}$C CP-MAS spectrum of the MgBzOH adduct is given in Figure 4.17 and shows peaks in the region 63 to 67 ppm for –CH$_2$OH and aromatic peaks between 125 and 140 ppm. Three equally intense peaks were observed for –CH$_2$OH. It clearly indicates that there are three magnetically non-equivalent methylene (–CH$_2$OH) carbons present around the Mg$^{2+}$ ion. The structure of the MgBzOH adduct is similar to that of the MgEtOH adduct where six coordination sites are occupied by benzyl alcohol molecules around an octahedral Mg$^{2+}$ ion [23,24]. Three different –CH$_2$OH signals can be attributed to the fact that each pair of alcohols on the x, y and z-axis are likely to have a slightly different arrangement in the crystal
structure. Indeed three different Mg–O bond lengths (2.094, 2.071, 2.078 Å) with O–Mg–O angles of 90.8 to 92.2° are reported in ref. 22. Two chloride ions are present out of the octahedral coordination sphere in this ionic structure attached through H-bonding with the oxygen of the alcohol. Some of the aromatic carbons that experience the effect of Mg coordination, i.e. the one closer to Mg, also show multiplicities in the MgBzOH adduct. This is clearly visible for the C1 carbon (140 to 134 ppm) and probably also for the C2 (ortho) carbons (127–121 ppm). The other carbons are expected to be less affected by the coordination.

Figure 4.17: 75.5 MHz $^{13}$C CP-MAS NMR spectrum of MgBzOH adduct.

4.3.2. Characterization of Titanated Adduct

4.3.2.1. Powder X-ray Diffraction

Figure. 4.18 shows the powder XRD pattern of the Ti-MgBzOH catalyst and it is compared with that of the pure MgBzOH adduct. A broad peak between 14–21° (003), broad asymmetric halo peaks at 26 and 32° and another peak around 50° were found. This type of XRD pattern has been reported earlier for a titanated catalyst and it corresponds to the
structurally disordered δ-MgCl$_2$ crystal structure [31]. A relatively intense and broad peak at ~18° is related to the stacking of Cl–Mg–Cl triple layers along the crystallographic direction. Two other peaks are related to stacking faults in the Mg–Cl–Mg triple layers [32]. The highly crystalline natures of the virgin MgBzOH adduct changes into a poorly crystalline Ti-MgBzOH material. This is due to the removal of most of the benzyl alcohol organic moieties during the titanated catalyst preparation and the growth of MgCl$_2$ crystallites is restricted by the active TiCl$_4$ incorporation into the lattice.

![XRD pattern of Ti-MgBzOH catalyst compared with MgBzOH adduct.](image)

**Figure 4.18:** XRD pattern of Ti-MgBzOH catalyst compared with MgBzOH adduct.

### 4.3.2.2 Thermal Analysis

Figure 4.19 shows thermal analysis of Ti-MgBzOH catalyst. There is a significant difference in the TG-DTA results of Ti-MgBzOH catalyst compared to MgBzOH adduct. There is no significant weight loss below 100°C indicating no loss of any species from Ti-MgBzOH catalyst. The weight loss associated with Ti-MgBzOH catalyst > 100 °C might be
due to desorption of chlorobenzene (boiling point 131°C) and benzyl chloride (boiling point 179°C). Chlorobenzene is used as the solvent in the titanation step and small amounts of benzyl chloride is a side product in the reaction between TiCl$_4$ and benzyl alcohol. Small amounts of these relatively higher boiling solvents probably remain trapped in the pores. This result is supported further by NMR of Ti-MgBzOH catalyst.

![Thermal analysis of Ti-MgBzOH catalyst.](image)

**Figure 4.19:** Thermal analysis of Ti-MgBzOH catalyst.

### 4.3.2.3. Scanning Electron Microscopy

Figure 4.20 shows SEM images of Ti-MgBzOH catalyst. Highly porous nature of titanated adduct is clearly visible in these pictures. SEM pictures clearly shows that all the particles are of spherical in shape with a narrow particle size distribution. Higher magnification of the particles shows the surface of the particles is smoother in nature.
4.3.2.4. Textural Properties

BET method was used to determine the surface area of the Ti-MgBzOH catalysts from nitrogen adsorption–desorption isotherms (Figure 4.21). The Ti-MgBzOH catalyst surface area was found to be 123 m² g⁻¹ and it is higher than that of the Ti-MgEtOH catalyst (32 m² g⁻¹). This is due to the removal of most of the bulky benzyl molecules from the MgBzOH adduct that leads to bigger pores. It is noteworthy that the average pore diameter of Ti-MgBzOH catalyst is found to be 12.3 nm (Figure 4.21b) with a pore volume of 0.381 cm³.

Figure 4.20: SEM images of Ti-MgBzOH catalyst

Figure 4.21: (a) Adsorption isotherm, and (b) pore size distribution curve of Ti-MgBzOH adduct.
These values are significantly higher than the values reported for commercial polyolefin catalysts [14, 24, 26, 38].

### 4.3.2.5 Solid State NMR

**Figure 4.22:** $^{13}$C CP-MAS spectra of Ti-MgBzOH.

![Figure 4.22](image)

Figure 4.22 shows the solid state $^{13}$C CP-MAS spectrum of the Ti-MgBzOH catalyst. The $^{13}$C CP-MAS spectrum shows the presence of aromatic peaks around 120 to 150 ppm and a peak around 40 ppm. The absence of peaks around 60 to 65 ppm clearly indicates the absence of benzyl alcohol on the MgCl$_2$ surface. Peaks at ~40 ppm in the $^{13}$C CPMAS are probably due to the CH$_2$–Cl carbon of benzyl chloride, a side product expected from the reaction between benzyl alcohol and TiCl$_4$. This benzyl chloride formed seemed to be strongly associated with the Ti-MgBzOH catalyst.

### 4.3.3. Ethylene polymerization

The activity of the Ti-MgBzOH catalyst has been tested for ethylene polymerization activity without any effort to maximize the productivity of polyethylene by optimizing the
reaction conditions. In a typical polymerization, 0.5 L of dry hexane was added to the reactor at 75 °C, followed by alkyl aluminium (methyl, ethyl, isobutyl alkyl aluminium) and the catalyst was introduced into the reactor under a stream of dry N₂ and then evacuated. Ethylene (5 bar) was then fed at a constant pressure. Polymerization was carried out for 1 h at 75 °C. For the polymerization reaction alkyl aluminium has been added as a co-catalyst. The activity of the Ti-MgBzOH catalyst under identical conditions is compared with that of the MgEtOH-Ti catalyst in Table 4.4. Activity data reported in Table 4.3 is the average of data collected from three different batches of catalysts. Among three different co-catalyst used, Et₃Al combination gave best activity for Ti-MgBzOH catalyst. The polyethylene yield from the Ti-MgBzOH catalyst is marginally lower than that of the Ti-MgEtOH catalyst. Though the surface area of the Ti-MgBzOH catalyst was much higher than that of the Ti-MgEtOH catalyst, the activity was lower implying that factors other than surface area influence the activity of the catalyst. The large surface area of the Ti-MgBzOH catalyst leads to a very high impregnation of Ti on the MgCl₂ surface, however, the polymerization results indicate that the number of active sites on the surface with relatively long life time is slightly less in Ti MgBzOH than in Ti-MgEtOH A plausible explanation for this is discussed later on (Section 4.3.5). The activity results suggest a very large amount of Ti species also leads to a decrease in the activity. The optimum surface area with a lower amount of Ti fixation leads to higher polyolefin activity. The molecular weight (Mw) and molecular weight distribution (MWD) are critical for polymer processing as they are important factors in determining the mechanical and rheological properties of polymers. GPC profile results obtained from polyethylene produced by the Ti-BzOH and Ti-MgEtOH catalysts are shown in Table 1. Polyethylene from Ti-MgBzOH shows a MWD of 7.2. However, polyethylene from Ti-MgEtOH shows a MWD of 11.5. It is likely that the different Ti-content, as well as the origin of the MgCl₂ support from different molecular adducts leads to significantly different results.
Table 4.4: Activity results of the Ti-MgBzOH catalysts for polyethylene production.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Support</th>
<th>Ti wt% (mmol)</th>
<th>Co-catalyst</th>
<th>Condition</th>
<th>PE Yield (g/g of catalyst)</th>
<th>PE Yield (g/mmol of Ti)</th>
<th>Mn (Mw) gmol(^{-1})</th>
<th>MWD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MgBzOH</td>
<td>17 (0.51)</td>
<td>Me(_3)Al</td>
<td>75°C, 5atm</td>
<td>378</td>
<td>74.1</td>
<td>18689 (147650)</td>
<td>7.9</td>
</tr>
<tr>
<td>2</td>
<td>MgBzOH</td>
<td>17 (0.51)</td>
<td>Et(_3)Al</td>
<td>75°C, 5atm</td>
<td>960</td>
<td>189</td>
<td>26111 (188000)</td>
<td>7.2</td>
</tr>
<tr>
<td>3</td>
<td>MgBzOH</td>
<td>17 (0.51)</td>
<td>iBu(_3)Al</td>
<td>75°C, 5atm</td>
<td>689</td>
<td>135.1</td>
<td>21955 (210769)</td>
<td>9.6</td>
</tr>
<tr>
<td>7</td>
<td>MgEtOH(^{[14]})</td>
<td>11 (0.23)</td>
<td>Et(_3)Al</td>
<td>75°C, 5atm</td>
<td>1300</td>
<td>572</td>
<td>22173 (255010)</td>
<td>11.5</td>
</tr>
</tbody>
</table>

Catalyst quantity = 0.1g; Al/Ti = 10 and 50 for MgBzOH and MgEtOH respectively; Dry hexane has been used as a solvent.
4.3.4. Polymer morphology

Figure 4.23: SEM image of polyethylene synthesized using the Ti-MgBzOH catalyst.

Figure 4.23 shows an SEM image of polyethylene synthesized using the Ti-BzOH catalyst. The surface morphology of the polymer exhibits a spherical shape and replicates the catalyst particle morphology [39–41]. A few particles are agglomerated and not spherical in shape. This is due to the conditions that have been applied for the polymerization reaction which leads to cracks on the catalyst surface. However, a careful analysis of many images of the polymer suggests a relatively low polydispersity of polyethylene. Indeed this is in agreement with the low MWD values obtained for the polyethylene produced using the Ti-MgBzOH catalyst (Table 4.3).

4.3.5 Origin of activity

The detailed preparation, characterization by structural, spectroscopic and microscopic analytical methods and the evaluation of the titanated adducts for ethylene polymerization presented here provide some new information, especially on the molecular level properties and electronic structure of the molecular adducts and corresponding Ziegler catalysts. Although there is already some similar information available in the literature [42,43], it is derived from the analysis of polymer products and hence in an indirect manner.

A few points are worth highlighting regarding the influence on catalytic activity. (a) The structure and spectral properties of the MgBzOH adduct and Ti-BzOH catalyst have been sufficiently demonstrated by XRD, NMR, and Raman spectroscopy. (b) Significant changes
in the Raman spectra of MgBzOH and MgEtOH have been observed, indicating a stronger interaction between Mg and O in MgBzOH than MgEtOH. (c) A marginally lower polymerization activity is observed with Ti-MgBzOH compared to Ti-MgEtOH in spite of a higher surface area. Ti-MgBzOH in spite of its high titanium content shows a lower specific activity towards polymerization. In Ziegler catalysts, partial reduction of the catalytically active Ti\(^{4+/3+}\) to Ti\(^{2+}\) in a side reaction with TEAL is known to be one of the main catalyst deactivation pathways. In our earlier publication we presented evidence indicating that PhCO\(_2\)Et, a so called internal electron donor, makes the catalyst more resistant towards quick deactivation by co-ordination to the Ti\(^{4+}\) center. In the present case the larger pores probably make the catalytically active Ti\(^{4+/3+}\) sites more accessible to TEAL resulting in over-reduction and deactivation. Further benzyl chloride trapped in the pores might also be blocking some of the active sites. It is known that a higher surface area generally increases the activity of catalysts. However, low polymerization activity observed with Ti-BzOH, in spite of better textural properties, underscoring the origin of decreased activity is not due to textural properties. Hence from the above discussion and our earlier work on different catalytic systems [44], it is clear that the origin of lower catalytic activity in the present Ti-MgBzOH case, compared to the Ti-MgEtOH catalyst, could be attributed to the lower specific activity of Ti which is probably due to the result of relatively rapid deactivation of the active sites due to over reduction by TEAL.

4.3.6. Conclusion

A new single phase supporting material for Z–N catalysts with an aromatic alcohol (benzyl alcohol) adduct of MgCl\(_2\) has been successfully synthesized and characterized by variety of analytical and spectroscopic characterization methods. Notably a stronger interaction between the Mg and O atoms of the OH groups of PhCH\(_2\)OH is observed in structural studies and Raman spectra. The titanated MgBzOH catalyst has been characterized
by variety of techniques. Polymerization activity results suggest the surface area of the catalyst is not an important criterion governing the polymerization activity. A significantly high Ti content on the final catalyst surface indicates a strong interaction between the support and Ti, which reduces the specific activity of Ti towards polymerization
Part C: MgCl$_2$-9FM-EtOH

4.4 Results and Discussion

4.4.1 Characterization of MgCl$_2$-9FM-EtOH Adduct

4.4.1.1. Powder X-ray Diffraction

Figure 4.24: Comparison of powder XRD pattern of (a) anhydrous MgCl$_2$ (b) MgEtOH adduct (c) 9FM and (d) Mg-9FM-EtOH.

Figure 4.24 shows the comparison of powder XRD of pure MgCl$_2$, MgEtOH, 9FM and Mg-9FM-EtOH. Rhombohedral cubic close packing structure exhibited by anhydrous MgCl$_2$ and it gives a strong diffraction peaks for (003), (004) and (110) planes at 2$\theta$ 15.1°, 35°, and 50.4°, respectively. XRD pattern of MgEtOH shows a high intensity and characteristic (001) reflection at 2$\theta$ = 9°; rather, Mg-9FM-EtOH shows high intensity peak reflection at 2$\theta$ = 5.7°. High intense reflection for (001) plane clearly shows the growth of crystal, in azeotropic distillation preparation method, occurs along (00z) planes [26, 28]. Among all XRD patterns, Mg-9FM-EtOH shows significantly different pattern having high intensity peak around 2$\theta$ of 5.7° with d value of 15.49 Å. However, MgEtOH molecular adduct and anhydrous MgCl$_2$ exhibits d value of 9.838 Å and 5.741, respectively, for high intense (00l) peak. Higher d
value for Mg-9FM-EtOH compared with MgEtOH and MgCl₂ could be due to bulkiness of 9-FM as Lewis base. Since 9FM is relatively bulkier than ethanol molecule, the distance between Cl-Mg-Cl triple layer increases when Lewis base interacts with Mg²⁺. Hence, Mg-9FM-EtOH exhibits higher d-value among other adducts. Indeed the 9FM molecule size is 8.76 Å x 7.3 Å, which is much bigger than EtOH molecules.

### 4.4.1.2 Thermal Analysis

![Figure 4.25: TG-DTA analysis of Mg-9FM-EtOH adduct.](image)

Figure 4.25 shows the thermogravimetry and differential thermal analysis of Mg-9FM-EtOH adduct. Temperature of the sample was ramped from ambient to 350 °C at 5 °C/min under flow of dry nitrogen (99.999%) at 40 mL/min. Well defined weight loss features were observed in thermal analysis is attributed to successive loss of ethanol as well as 9FM molecules from the molecular adduct. Similarly well defined DTA curve also confirms the successive dealcoholation process is occurs with Mg-9FM-EtOH adduct. Because of the complex nature of the molecular adduct i.e., two different Lewis bases (EtOH and 9FM) have been used, it is difficult to find the dealcoholation temperature of each entities present in the molecular adduct. From the TG-DTA analysis of MgEtOH adduct, it is
expected that EtOH molecule might dissociate from the adduct first due to its lower boiling point compared to 9FM. It is also expected that from the smaller weight loss between RT and \(\sim 170 \, ^\circ\text{C}\) is attributed to loss of EtOH and 9FM dissociation might occur between 150 \(\, ^\circ\text{C}\) and 250 \(\, ^\circ\text{C}\). Stoichiometry of the molecular adduct containing 9FM and EtOH was also determined separately by liquid state NMR [24] using a known quantity of the adduct in 1 mL of deuterated acetonitrile containing known amount of a reference compound, methanol. The mole fraction of 9FM and EtOH is estimated from the \(^1\text{H}\) integrals and used for the calculation of absolute amount of 9FM and EtOH in the adduct, \textit{vide infra} and found the stoichiometry of \(\text{MgCl}_2\cdot(\text{9FM})_{1.1}\cdot(\text{EtOH})_{1.23}\). The expected total weight loss of the above stoichiometry found by NMR for \(\text{MgCl}_2\cdot\text{9FM-EtOH}\) adduct matches well with the experimental weight loss within \(\pm 1\%\) error. Absence of any weight loss above 250 \(\, ^\circ\text{C}\) indicates the presence of only \(\text{MgCl}_2\), after dissociation of all the alcohol molecules.

4.4.1.3 Solid state NMR

![Figure 4.26: 75.5 MHz \(^{13}\text{C}\) CP-MAS NMR spectrum of (a) 9-FM and (b) Mg-9FM-EtOH.](image)

Figure 4.26 shows \(^{13}\text{C}\) CPMAS solid state NMR spectrum of pure 9-FM and Mg-9FM-EtOH. Pure 9-FM gives
\(-\text{CH}_2\cdot\text{OH}\) peak at 62.3 ppm, \(=\text{CH}\) (five membered) peak at
46.9 ppm and aromatic peaks between 118 to 144 ppm. Ethanol moieties present in Mg-9FM-EtOH gives the peak at 16.3 and 58.5 for $\text{CH}_3$- and –$\text{CH}_2$-OH, respectively. 9FM moieties present in Mg-9FM-EtOH gives the peaks at 46.8, 64.5 and between 117 to 145 for –$\text{CH}$-(five membered), –$\text{CH}_2$-OH and aromatic peaks, respectively. A closer look at the –$\text{CH}_2$-OH peak of 9-FM present in Mg-9FM-EtOH adduct, it is clear that the peak has been shifted to down field compared with pure 9-FM i.e, 64.5 ppm in Mg-9FM-EtOH compared with 62.3 ppm in pure 9-FM. This downfield shift of 2.2 ppm clearly demonstrates the coordination of –$\text{CH}_2$-OH of 9-FM with MgCl$_2$. In other way, it confirms the formation of molecular adduct of 9-FM with MgCl$_2$.

4.4.1.4 Scanning Electron Microscope

![SEM images of Mg-9FM-EtOH.](image)

Figure 4.27: *SEM images of Mg-9FM-EtOH.*

SEM images of Mg-9FM-EtOH molecular adduct is shown in Figure 4.27. Needle like morphology was observed in this present case unlike spherical and rod shape morphologies in MgEtOH, MgMeOH and MgBOH [26, 27]. The length of needle is approximately about 100 µm. Needle shape morphology indicates the growth of particle is unidirectional in nature. However, most of the needles were agglomerated. An increase in the
molecular size from EtOH to 9-FM alters the interaction differently with MgCl$_2$ and leads to a different morphology of adduct and catalyst.

**4.4.2 Characterization of active catalyst**

**4.4.2.1 Synthesis of active catalyst**

2.8 g of Mg-9FM-EtOH adduct was taken with 22 mL of chlorobenzene and stirred for 1 h at 110 °C. Subsequently, 22 mL of TiCl$_4$ has been added over a period of 10 min and stirred further for 1 h. Resulting solid product was washed with two 100 ml portions of TiCl$_4$. Finally, the solid catalyst was filtered and washed several times with dry hexane at 60 °C until all the physisorbed Ti-species was removed. Then, Ti-9FM-EtOH-1 catalyst obtained has been dried under vacuum and stored in dry N$_2$ atmosphere. Amount of titanium content in the active catalyst was found to be 12.5 wt % (0.264 mmol).

In order to see the influence of 9FM on the polymerization activity, we have synthesized the active catalyst without washing step i.e., by simply having 9FM as internal donor on active catalyst. For comparison we have taken same amount of titanium (as found in Ti-9FM-EtOH-1) in this present active catalyst. Required quantity of Mg-9FM-EtOH has been taken in dry hydrocarbon solution then 12.5 % of titanium precursor (TiCl$_4$) has been added and stirred for 48 hours. Finally Ti-9FM-EtOH-2 catalyst has been dried under vacuum and stored in dry N$_2$ atmosphere. Although we presume that TiCl$_4$ is incorporated in a similar way in the above catalysts, we cannot rule out the difference in the nature of TiCl$_x$ species on both the above catalysts.

**4.4.2.2 Solid state NMR of active catalyst**

Figure 4.28 shows the $^{13}$C CPMAS NMR of active catalyst derived from Mg-9FM-EtOH. Ti-9FM-EtOH-1 catalyst shows peak at 25.1, 44.7, 77.5 ppm and broad peak around 129 ppm. Aromatic peak around 129 ppm could be due to the presence of chlorobenzene.
which has been used as a solvent for the synthesis of active catalyst as well as could be due to the contribution from 9FM moieties present in the active catalyst. Peak around 25.8 ppm confirms the presence of aliphatic hydrocarbon i.e., hexane used during the washing step in the synthesis of active catalyst. Peaks at 77.5 ppm and small broad peak around 44.7 could be due to ether or other organic moieties formed during the titanated and others harsh condition involved in the synthesis of active catalyst. In Ti-9FM-EtOH-2 catalyst, peak at 49.5 and 68.1 ppm confirms the presence of 9-FM moieties in active catalyst. –CH$_2$OH feature at 68.1 ppm is shifted down field compared to 9FM and Mg-9FM-EtOH, possibly indicating a stronger interaction. Peak at 25 ppm confirms the presence of hexane used in the synthesis. Peaks between 120 to 144 ppm also evidenced the presence of 9-FM moieties in the active catalyst. Overall solid state NMR characterization confirms Ti-9FM-EtOH-2 catalyst having 9-FM moieties as such as a integral part of active catalyst.

Figure 4.28: $^{13}$C CPMAS NMR spectra of the titanated active catalyst.
4.4.2.3 Thermal analysis

**Figure 4.29: TG-DTA analysis of active catalyst.**

TG and DTA analysis of the titanated active catalysts are shown in Figure 4.29. Among two active catalysts synthesized, significant difference in the weight loss has been observed. Catalyst prepared by conventional synthesis (Ti-9FM-EtOH-1) shows the weight loss of 48% compared to the weight loss of 74% for catalyst prepared by simple stirring (Ti-9FM-EtOH-2). Lower weight loss associated with Ti-9FM-EtOH-1 could be due the presence of lesser organic residues. During the synthesis of active catalyst in conventional synthesis, most of the organic residues will be removed in the hexane washing step. However, in the case of Ti-9FM-EtOH-2, 74% weight loss indicates the presence of more organic residues in the active catalyst. Infact presence of 9-FM moieties in Ti-9FM-EtOH-2 was evidenced by $^{13}$C solid state NMR in figure 4.28. However, in the case of Ti-9FM-EtOH-1, catalyst contains other hydrocarbon, such as chlorobenzene and other organic residues and 9-FM moieties is unlikely to be present.
Figure 4.30: SEM images active catalysts. (a) and (b) for Ti-9FM-EtOH-1 and (c) and (d) for Ti-9FM-EtOH-2.

Figure 4.30 shows the SEM images of the active catalyst. The images were recorded after the sonication of dispersed active catalyst in triblock copolymer and toluene solution to avoid any agglomeration and to resist the atmospheric degradation due to the air-sensitive nature of the catalyst. SEM images clearly show high porous nature of Ti-9FM-EtOH-1. Particle size of the active catalyst was observed below ~1 µm. Ti-9FM-EtOH-2 catalyst exhibits spherical morphology with smooth surface. Size of the particles was measured to be between 2-5 µm. Harsh condition employed in the synthesis of Ti-9FM-EtOH-1 could be the reason for the smaller particle size compared with Ti-9FM-EtOH-2.
4.4.2.5 Textural Properties

$N_2$ adsorption isotherm and pore size distribution of active catalyst is shown in Figure 4.31. Figure I and Figure II represent the isotherm and pore size distributions obtained from Ti-9FM-EtOH-1 and Ti-9FM-EtOH-2 catalyst, respectively. BET method was employed to calculate the surface area of active catalysts. Ti-9FM-EtOH-1 catalyst shows a surface area of 410 $m^2/g$ which is far higher than many commercial and other reported catalysts.

(I) Ti-9FM-EtOH-1  
(II) Ti-9FM-EtOH-2

![Figure 4.31: (I) Ti-9FM-EtOH-1 catalyst (a) Adsorption isotherm and (b) pore size distribution and (II) Ti-9FM-EtOH-2 catalyst (a) adsorption isotherm and (b) pore size distribution](image)

The average pore diameter was calculated and found to be 69.2 nm with the pore volume of 0.711 cc/g. However, Ti-9FM-EtOH-2 exhibits a surface area of 75.1 $m^2/g$ and pore size distribution of 50.3 nm with the pore volume of 0.0946 cc/g. High surface area of Ti-9FM-EtOH-1 compared with Ti-9FM-EtOH-2 could be due to the removal of bulkier organic residue during the washing step in the synthesis of active catalyst. Former active catalyst shows type-IV with H3 isotherm and latter active catalyst shows type-II isotherm. Ti-9FM-EtOH-2 catalyst having less contribution from type-III and more contribution from type-II. Macropore contribution in the active catalysts is evidenced by type-II isotherm. Infact pore
size distribution curve also shows the contribution of macropores in both active catalysts. Macropore contribution could be associated with the removal of bulky 9-FM that was present in the molecular adducts.

4.4.3. Ethylene Polymerization

Ethylene polymerization reactions have been carried out for the two active catalysts derived from Mg-9FM-EtOH. Co-catalysts with three different alkyl chains; namely, methyl, ethyl, and isobutyl (R₃Al; R = CH₃, −CH₂CH₃, and −CH₂CH(CH₃)₂) have been used to activate the catalytic active sites present in the catalysts. For each cocatalyst, reactions were carried out at 5 atm pressure and 75 °C. Average results were taken after carrying out three sets of polymerizations for each condition. Activity results are shown in Table 4.5. (1) Overall polymerization activity of Ti-9FM-EtOH-1 catalyst is higher than Ti-9FM-EtOH-2. (2) Among the ethylene polymerization reactions, entry 3 shows best activity of Ti-9FM-EtOH-1 when iBu₃Al was used as co-catalyst. This activity is ~4.5 times higher than the commercial Z-N catalyst (entry 7). (3) Overall MWD of polymer obtained by using Ti-9FM-EtOH-1 was better than Ti-9FM-EtOH-2 and entry 6 shows the lowest MWD of polyethylene among all the polymers obtained. Overall higher activity of Ti-9FM-EtOH-1 catalyst could be due to the higher surface area (410 m²/g) compared with Ti-9FM-EtOH-2 (surface area of 75 m²/g). The highest polymerization activity for the combination of Ti-9FM-EtOH-1 with iBu₃Al could be due the porous nature associated with active catalyst and macropores (69.2 nm) found in it is likely to contribute to the activity. This bigger pore and comparatively lower lability of iBu₃Al (compared with other alkyl aluminium used) might have influenced the reduction of TiClₓ species in the pores of the active catalyst to Ti³⁺ and thereby lead to the highest activity. Overall lower MWD of PE for Ti-9FM-EtOH-2 catalyst
Table 4.5: *Activity results of catalysts for polymerization reactions.*

<table>
<thead>
<tr>
<th>No</th>
<th>Catalyst</th>
<th>Ti wt% (mmol)</th>
<th>Cocatalyst</th>
<th>Condition</th>
<th>Productivity of PE (g g⁻¹ of catalyst)</th>
<th>Productivity of PE (g mmol⁻¹ of Ti)</th>
<th>Mn (Mw) gmol⁻¹</th>
<th>MWD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ti-9FM-EtOH-1</td>
<td>12.5 (0.264)</td>
<td>Me₃Al</td>
<td>75°C, 5atm</td>
<td>2685</td>
<td>1017.0</td>
<td>17196 (166809)</td>
<td>9.7</td>
</tr>
<tr>
<td>2</td>
<td>Ti-9FM-EtOH-1</td>
<td>12.5 (0.264)</td>
<td>Et₃Al</td>
<td>75°C, 5atm</td>
<td>4841</td>
<td>1833.7</td>
<td>14451 (154631)</td>
<td>10.7</td>
</tr>
<tr>
<td>3</td>
<td>Ti-9FM-EtOH-1</td>
<td>12.5 (0.264)</td>
<td>iBu₃Al</td>
<td>75°C, 5atm</td>
<td>5813</td>
<td>2201</td>
<td>237681 (237681)</td>
<td>12.3</td>
</tr>
<tr>
<td>4</td>
<td>Ti-9FM-EtOH-2</td>
<td>12.5 (0.264)</td>
<td>Me₃Al</td>
<td>75°C, 5atm</td>
<td>1870</td>
<td>26051</td>
<td>26723 (187570)</td>
<td>7.2</td>
</tr>
<tr>
<td>5</td>
<td>Ti-9FM-EtOH-2</td>
<td>12.5 (0.264)</td>
<td>Et₃Al</td>
<td>75°C, 5atm</td>
<td>3303</td>
<td>1251.5</td>
<td>20057 (150430)</td>
<td>7.5</td>
</tr>
<tr>
<td>6</td>
<td>Ti-9FM-EtOH-2</td>
<td>12.5 (0.264)</td>
<td>iBu₃Al</td>
<td>75°C, 5atm</td>
<td>2356</td>
<td>892.4</td>
<td>33696 (215660)</td>
<td>6.4</td>
</tr>
<tr>
<td>7</td>
<td>Ti-MgEtOH[26]</td>
<td>11 (0.23)</td>
<td>Et₃Al</td>
<td>75°C, 5atm</td>
<td>1300</td>
<td>572</td>
<td>22173 (255010)</td>
<td>11.5</td>
</tr>
</tbody>
</table>
derived could be due the influence of 9-FM as internal donor present in the active catalyst.
Presence of higher amount of 9-FM in Ti-9FM-EtOH-2 is evident from NMR and TGA.
Lowest MWD of Ti-9FM-EtOH-2 with iBu₃Al could be again due lower lability as well as the presence of 9-FM internal donor in the surface of catalyst

4.4.4. Conclusion

Mg-9FM-EtOH molecular adduct has been synthesized and subjected to detailed spectroscopic and structural investigations. In order to see the effect of 9-FM molecule as an internal donor, active catalyst have been synthesized by conventional and merely fixing TiCl₄ over the support; both the above catalysts were subjected to detailed investigations. The textural properties of the active catalysts shows higher surface area for conventional synthesized catalyst than the other one. Ethylene polymerization reactions were carried with different co-catalyst and shows iBu₃Al as best cocatalyst for the above supported Z-N catalytic system. Polymerization activity results suggests conventionally synthesized catalyst exhibit ~4.5 times better activity than commercial Z-N catalyst, and still better than merely TiCl₄ fixed over the Mg-9FM-EtOH support. However, the latter catalytic system shows lowest MWD of PE obtained confirms the role of 9-FM as internal donor in the catalytic system. Detailed studies confirm the less lability of iBu₃Al and contribution of macropores are the reason for the conventionally synthesized catalyst to give higher polymerization activity.

4.5 Reference:


34. Sobota, P.; Szafert, S. *Dalton Trans.* **2001**, 1379