Chapter 4

Melamine formaldehyde supported titanium based heterogeneous Ziegler-Natta catalyst for ethylene polymerization in slurry process
4.1. Introduction

In this chapter, we have reported melamine-formaldehyde as a polymer support for TiCl$_4$. Since functionalized polymer could provide enough flexibility in designing these catalysts by various physico-chemical ways. Melamine formaldehyde has the potential functional polar site such as -NH group which is expected to hold the catalytic groups. Also melamine formaldehyde ensures good thermal stability to be applied as a support in Ziegler-Natta catalyst systems for ethylene polymerization. Moreover, to the best of our knowledge, there appears no report in the literature for the use of melamine-formaldehyde as a support in Ziegler-Natta catalyst for ethylene polymerization in slurry process.

In this study, we have reported the preparation of novel melamine formaldehyde supported Ziegler-Natta catalyst in hexane medium. The performance and storability of the hybrid catalysts was evaluated with triethyl aluminium as a co-catalyst for polymerization of ethylene in slurry process.

4.2. Experimental

All experiments involving air sensitive compounds were performed inside an inert atmosphere glove box continuously purged with high purity dry nitrogen.

4.2.1. Materials

Titanium tetrachloride and triethylaluminium (TEA) purchased from Aldrich were used without further purification. Ethylene (>99.99 % purity) was taken from Chemtron Science Lab. Pvt Ltd. (Bombay) and used after passing over a BTS copper catalyst, Selexsorb COS, Selexsorb CD, CaCl$_2$ and a molecular sieve (3Å, 4Å, 10Å, 13X) to remove O$_2$, moisture and other impurities. Nitrogen (purity >99.99 %, Rass Cryogenics) was also purified with reduced BASF 3R-11 catalysts and molecular sieves (3Å, 4Å, 13X, Sigma-Aldrich). Melamine, formaldehyde (37%) and NaOH were of analytical reagent grade chemicals (Aldrich) and used as received. Toluene was fresh-distilled before each polymerization from Na/K alloy and stored on molecular sieves and BTS catalysts afterwards. Hexane, ethanol, and methanol were distilled and kept over molecular sieves catalyst before use. For all purposes double distilled water was used.

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4.2.2. Experimental set-up

All ethylene polymerization reactions were conducted in a 150 ml, high pressure autoclave (Amar Equipment, Mumbai). The schematic diagram of the apparatus is already shown in chapter 2. The stainless steel reactor can withstand a pressure up to 100 kg/cm² (advised to perform below 70 kg/cm²). The pressure inside the reactor was measured with a pressure transducer and a digital display. The equipment is attached with the high pressure ethylene cylinder, high pressure metering pump, high efficient cooler and a regulated supply of dry nitrogen and ethylene. The internal temperature of the reactor was measured with thermocouple. The temperature controlling is done via some internal water circulating coil inside the reactor, heating with the help of highly efficient jacket thermocouple.

4.2.3. Procedure

4.2.3.1. Synthesis of melamine formaldehyde (MF)

In a 500 ml round bottom flask equipped with three inlets was used for the polycondensation reaction of melamine and formaldehyde. The unreacted formaldehyde was removed by distillation. For the synthesis of melamine-formaldehyde, calculated amount of melamine (0.2M) and 37% formaldehyde aqueous solution (0.6M) were added into the flask in an inert atmosphere. Before carrying out the reaction the pH of the solution was adjusted to 8.5 ± 0.1 by adding 0.1 N NaOH solution. The polymerization reaction was carried out at 80°C with a mechanical stirrer. When the reaction mixture became white cloud, the temperature was raised to 90°C and the reaction was lasted for 1.5 hr. Finally, the pH of the sample was adjusted to 10 with 0.1 N NaOH solutions and the reaction was quenched with ice. The cross-linked polycondensate was precipitated and washed with distilled water followed by vacuum drying at 40°C.

4.2.3.2. Preparation of MF supported TiCl₄ catalysts (MFT1-3)

MF-supported Ziegler-Natta catalysts were prepared using melamine formaldehyde as a starting material. Three catalysts were prepared by varying the weight ratio of TiCl₄/MF (Table 4.1). In a typical reaction, TiCl₄ was loaded directly onto the polymer support without modifier in dry nitrogen inert atmosphere inside the glove box.
Melamine formaldehyde supported titanium based heterogeneous Ziegler-Natta catalyst for ethylene polymerization in slurry process

MF powders (1.5 g) were suspended in 40 ml hexane in a round bottom flask placed over a magnetic stirrer and the dry nitrogen atmosphere was maintained in the flask. With a gas tight syringe prescribed amount of TiCl$_4$ solution in toluene was added dropwise to the solution of MF with constant stirring at ambient temperature. After the addition was complete, the mixture was kept stirred for further 5 h at room temperature. The resulting solid product was then filtered and rinsed with ample amounts of dry toluene to remove the unreacted TiCl$_4$ and dried under reduced pressure at 55 ºC for 24 h. The dried catalysts were subjected to titanium estimation.

**Table 4.1: Recipe of MF supported titanium-based catalysts**

<table>
<thead>
<tr>
<th>Entry</th>
<th>MFT1</th>
<th>MFT2</th>
<th>MFT3</th>
</tr>
</thead>
<tbody>
<tr>
<td>MF(g)</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>TiCl$_4$(g)</td>
<td>0.964</td>
<td>2.892</td>
<td>4.82</td>
</tr>
<tr>
<td>TiCl$_4$/M-F wt ratio</td>
<td>0.642</td>
<td>1.928</td>
<td>3.21</td>
</tr>
<tr>
<td>Physical nature</td>
<td>Pale yellow powder</td>
<td>Pale yellow powder</td>
<td>Pale yellow powder</td>
</tr>
</tbody>
</table>

**4.2.3.3. Polymerization of ethylene using polymer supported titanium based catalyst**

Polymerization of ethylene with the synthesised three supported titanium based catalysts was performed in the presence of triethylaluminium (TEA) as a co catalyst. After exhaustion of all moisture and oxygen, 80 ml dry hexane was added to the reactor under nitrogen pressure. The solution was then saturated with ethylene followed by addition of TEA (10%, v/v; Al/Ti mole ratio = 250) (Table 4.5). Finally the catalyst (0.04 g) was introduced to the reactor to start the polymerization at 40 ºC and atmospheric pressure. The ethylene flow was maintained during the initial 60 minutes of polymerization to maintain the saturated ethylene concentration at atmospheric pressure. After the polymerization was completed, the reaction was terminated with ethanol containing 20 vol% of conc. HCl and subsequently the untreated gases were slowly released. The precipitated polymer was filtered, washed with methanol and dried in vacuum at 70 ºC.
4.2.4. Characterization

4.2.4.1. X-ray photoelectron Spectroscopy (XPS)

The XP spectra of all the samples were recorded on Shimadzu (ESCA 3400) spectrometer using monochromatic Al Kα (1486.6 eV) X-ray radiation as the excitation source. The binding energy of the samples was corrected by setting the binding energy of the adventitious carbon (C1s) at 284.6 eV. The XPS analysis was performed at ambient temperature and pressure typically in the order of less than $10^{-6}$ Pa.

4.2.4.2. UV-visible spectra

The titanium content of the synthesised catalysts was determined by colorimetric method. UV-visible spectra of the complexes were recorded on a Hitachi U-2001UV–visible spectrophotometer. The peak intensity at 410 nm was used to quantify the titanium content.

4.2.4.3. Determination of the Acidity of the Polymer supported TiCl₄ Complex

The catalyst was hydrolysed in 60% acetone solution in water at room temperature. The pH of the resultant solution was measured by a standard pH (Orion multiparameter kit).

4.2.4.4. Fourier Transform-Infrared (FT-IR) spectra

The infrared (IR) spectra of the catalysts were recorded in Nicolet Impact-410 IR spectrometer in KBr medium at room temperature in the region 4000–450 cm⁻¹.

4.2.4.5. Scanning electron microscopy and energy dispersive X-ray detector (SEM-EDX)

The morphology of the powdered polymer particles and composition were examined by using the JEOL-JSM-6390LV scanning electron microscope attached with energy dispersive X-ray detector. Samples were coated with platinum to a thickness of 200 Å. The voltage and working distance was varied during the measurements. The EDX instrument was operated at 20 kV which was conducted on the same specimen in an effort to obtain semi quantitative compositional information.
4.2.4.6. Thermogravimetric analysis (TGA)

Thermogravimetric analysis of pure polymer and polymer supported-TiCl$_4$ catalysts were studied in a Shimadzu TGA-50 Thermal analyzer over a temperature range of 30 °C to 600 °C with the heating rate 5 °C/min under N$_2$ atmosphere.

4.2.4.7. X-Ray diffraction analysis (XRD)

Powder X-ray diffraction (XRD) data were collected on a Rigaku Miniflex X-ray diffractometer with Cu $K_a$ radiation ($\lambda= 0.15418$ nm) at 30 kV and 15 mA using a scanning rate of 0.05°/s in 2θ ranges from 10° to 70°.

4.2.4.8. Gel permeation chromatography (GPC)

Molecular weight of the polyethylene was determined by gel permeation chromatography (GPC, Waters, USA) using 1, 2, 4-trichlorobenzene as a mobile phase.

4.2.4.9. Differential Scanning Calorimetry (DSC)

The melting point of polymers was measured by Differential Scanning Calorimetry (DSC, Model DSC-60, Shimadzu) at a heating rate of 5 °C/min under the nitrogen flow rate of 30 ml/min from 0 to 400 °C.

4.2.4.10. Computational work

All the density functional calculation are carried out using the DMol$^3$ program with VWN correlation functional and double numeric (DN) basis set. We performed all electron calculations on the neat polymer (MF), TiCl$_4$ and TiCl$_4$ incorporated MF. For the simplicity of our calculation in case of TiCl$_4$ modified polymer we consider only a unit of MF considering of 13 no of carbons.

4.3. Results and discussion

4.3.1. Characterization of MF and MF supported TiCl$_4$ catalysts

4.3.1.1. Synthesis of MF and MF supported TiCl$_4$ catalysts

MF has been synthesized by the reaction of melamine and formaldehyde which is catalysed by NaOH as a base (Scheme 4.1). Two main steps are involved in the reaction of melamine and formaldehyde to synthesised MF precursors. First, nucleophilic addition reactions of -NH$_2$ groups of melamine with formaldehyde under basic condition to give methylol groups (-NH-CH$_2$OH-). Next, these methylol groups condensed with
Melamine formaldehyde supported titanium based heterogeneous Ziegler-Natta catalyst for ethylene polymerization in slurry process

either another methyol group or an amino group of the triazine ring resulting in ethylene ether or methylene bridges.\textsuperscript{13}

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{N} & \quad \text{N} & \quad \text{N} & \quad \text{NH} & \quad \text{H} \\
\text{H} & \quad \text{N} & \quad \text{H} & \quad \text{N} & \quad \text{NH} & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{N} & \quad \text{N} & \quad \text{N} & \quad \text{NH} & \quad \text{H} \\
\text{H} & \quad \text{N} & \quad \text{H} & \quad \text{N} & \quad \text{NH} & \quad \text{H} \\
\end{align*}
\]

Melamine 

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{N} & \quad \text{N} & \quad \text{N} & \quad \text{NH} & \quad \text{H} \\
\text{H} & \quad \text{N} & \quad \text{H} & \quad \text{N} & \quad \text{NH} & \quad \text{H} \\
\end{align*}
\]

Formaldehyde 

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{N} & \quad \text{N} & \quad \text{N} & \quad \text{NH} & \quad \text{H} \\
\text{H} & \quad \text{N} & \quad \text{H} & \quad \text{N} & \quad \text{NH} & \quad \text{H} \\
\end{align*}
\]

Melamine-Formaldehyde pre-polymer

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{N} & \quad \text{N} & \quad \text{N} & \quad \text{NH} & \quad \text{H} \\
\text{H} & \quad \text{N} & \quad \text{H} & \quad \text{N} & \quad \text{NH} & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{N} & \quad \text{N} & \quad \text{N} & \quad \text{NH} & \quad \text{H} \\
\text{H} & \quad \text{N} & \quad \text{H} & \quad \text{N} & \quad \text{NH} & \quad \text{H} \\
\end{align*}
\]

Melamine-Formaldehyde micro-sphere via polycondensation

Scheme 4.1: Reaction mechanism for melamine and formaldehyde

FT-IR spectra of MF and MF supported catalysts are shown in Figure 4.1. The characteristic absorption peak at around 3430.38 cm\textsuperscript{-1} and 1569.66 cm\textsuperscript{-1} are attributed to the stretching and bending vibration of N-H bond of amine group. The methylene C-H stretching vibration peak appears at 2965.89 cm\textsuperscript{-1}, C-N absorption at 1381.24 cm\textsuperscript{-1} and the distinctive absorption peak at 1206 cm\textsuperscript{-1} indicates the stretching vibration of the ether C-O-C bond. These characteristic bands imply the formation of MF.

After incorporation of TiCl\textsubscript{4} into the polymer matrix the FT-IR spectrum of MF also shows noticeable changes in the absorption bands. The peak intensity of N-H bending absorption at 1569.66 cm\textsuperscript{-1} decreases and a new absorption at 1630.25 cm\textsuperscript{-1} is observed in case of MFT1. The shift of the absorption peak at 1569.66 cm\textsuperscript{-1} to higher frequency is the characteristic for complexation of the TiCl\textsubscript{4} to polymer through coordination bond with –NH group. With the increase in the amount of TiCl\textsubscript{4} (MFT2 and
Melamine formaldehyde supported titanium based heterogeneous Ziegler-Natta catalyst for ethylene polymerization in slurry process

MFT3), the typical absorption peak intensity of the 1569.66 cm\(^{-1}\) band almost diminish and is shifted to higher frequency. Also, the absorption peak of N-H bond at 3430.38 cm\(^{-1}\) in the bare polymer shifted to a lower value (3396.67 cm\(^{-1}\)) for all synthesized catalysts. These significant changes revealed that TiCl\(_4\) is coordinated with MF through N-H bond. The white M-F polymer becomes pale yellow after the heterogenation with TiCl\(_4\).

![Infrared spectra of (a) MF, (b) MFT1, (c) MFT2 and (d) MFT3](image)

**Figure 4.1:** Infrared spectra of (a) MF, (b) MFT1, (c) MFT2 and (d) MFT3

An XPS survey scan was performed on the virgin polymer (MF) and polymer supported catalysts for the purpose to assess the state and chemical environment of the titanium species and the functional groups of the MF and MF-TiCl\(_4\) (MFT2) catalyst. The representative survey spectra of the pure polymer and the polymer supported catalyst are shown in **Figure 4.2.** The binding energy of N\(_{1s}\) atom for neat MF polymer is 399.97 eV. In case of polymer supported catalyst the N\(_{1s}\) binding energy is shifted to a higher binding energy region i.e. 402.7 eV. In addition, the O\(_{1s}\) binding energy 533.5 eV attributed to
oxygen singly bound to carbon. No significant difference in O₁s binding energy between MF and MF-TiCl₄ (533.6 eV) is observed. To investigate the states of the titanium species, an XPS scan of the Ti region was also performed for the polymer supported catalyst. The doublet at 458.5 and 464.6 eV is reported to be due to the 2p₃/2 and 2p₁/2 photoelectrons from titanium atoms in TiCl₄ in its molecular solid state. Thus the doublet shown in Figure 4.2 (e) is ascribed to the 2p₃/2 and 2p₁/2 photoelectrons from titanium atoms in the TiCl₄ existing on the M-F supported catalyst. From the comparison between the supported catalyst and TiCl₃ along with TiCl₄, the Ti binding energy of the peak was found to be higher for the supported catalyst (458.1 eV) than that for TiCl₃ (457.8 eV) and lower than TiCl₄ in its molecular states. This lowering in Ti binding energy value of TiCl₄ on adsorption at MF support indicates transfer of electronic charge from support to titanium atom in MF supported catalysts. And the transfer of electron density taking place from the –NH moiety of MF polymer due to which N₁s binding energy shifted to a higher region. Thus it is reasonable that the -NH group of MF co-ordinates with Ti⁴⁺ through nitrogen atom.

Figure 4.2: XPS spectra of N₁s binding energy (a) MF, (b) MFT2; O₁s binding energy in (a) MF, (b) MFT2 and (c) Ti₂p level of MFT2
Melamine formaldehyde supported titanium based heterogeneous Ziegler-Natta catalyst for ethylene polymerization in slurry process

4.3.1.2. UV-visible spectroscopy

Figure 4.3 displays the UV-visible spectra of the solution of the neat MF polymer and its complexes with TiCl₄. It is well known that Ziegler-Natta catalyst does not show any absorption band in the UV-visible region. In order to confirm the existence of titanium in the supported catalysts (MFT1- MFT3), catalysts were digested with 20% of conc. H₂SO₄ at 150 °C followed by filtration. Subsequently on addition of 30% (w/v) H₂O₂ into the filtrate the colour of the solution changes from pale yellow to yellow. This confirmed the formation of a peroxotitanium complex [TiO₂(H₂O₂)].

The yellow peroxocomplex solution shows a broad peak at 350-480 nm [Figure 4.3 (b)], which is attributed to π→d transition of lone pair of electrons on oxygen of H₂O₂ to the vacant d-orbital of Ti⁴⁺ of TiCl₄. The presence of the broad spectrum at 350-480 nm implies the formation of peroxotitanium complex which subsequently confirms the presence of Ti in the polymer matrix. Interestingly, on increasing the amount of TiCl₄, the absorption peak intensity also increases gradually [Figure 4.3 (c), (d)] indicating the successfully incorporation of TiCl₄ into the polymer matrix. The peak intensity at 410 nm is used to quantify the titanium content of the catalysts followed by colorimetric method. It is observed that the wt% of Ti in the catalysts [MFT1- MFT3] is in the range of 1.6-5.3 (Table 4.5). On the other hand, pristine polymer presented absorption at around 280 nm. This absorption may be related to n→π* transition of the triazine ring of the neat MF polymer matrix [Figure 4.3 (a)].

![Figure 4.3: UV-visible spectra of pristine (a) MF, (b) MFT1, (c) MFT2 and (d) MFT3](image-url)
4.3.1.3. Acidity of the solution obtained on hydrolysis of MF supported TiCl₄ catalysts

It is found that the pH of acetone-water solution (60%) containing MFT1, MFT2 and MFT3 gradually increases with time (Figure 4.4). This may be due to the release of HCl on hydrolysis of TiCl₄ with water to the acetone-water solution (Scheme 4.2). This reveals the presence of TiCl₄ into the MF supported TiCl₄ complex.

![Figure 4.4: Change of the pH of 50 ml acetone-water solution (60%) containing 1g M-F supported TiCl₄ catalyst with time; (a) MFT1, (b) MFT2 and (c) MFT3](image)

![Scheme 4.2: Probable way of hydrolysis of MF supported TiCl₄ catalyst](image)

4.3.1.4. SEM and EDX analysis

Scanning electron microscopy is used to study the surface morphological changes occurring of the polymer after loading of TiCl₄ to the polymer chain. It is observed that
Melamine formaldehyde supported titanium based heterogeneous Ziegler-Natta catalyst for ethylene polymerization in slurry process

MF shows rough morphology with randomly aggregated chunky particles [Figure 4.5 (a)]. MFT1 shows agglomerated surface of the polymer [Figure 4.5 (b)]. The particle size of the MFT1 is bigger than that of the pristine MF which is possibly due to the incorporation of TiCl₄ on the surface of MF, thereby combining the polymer particles. Similar noticeable trend is observed for the other two catalysts [Figure 4.5 (c), (d)].

![Figure 4.5: SEM micrographs of the (a) MF, (b) MFT1, (c) MFT2 and (d) MFT3](image)

EDX technique is an effective tool to observe the presence of relative amount of Ti and Cl on the surface of polymeric particles (Figure 4.6). With the increase of TiCl₄ amount into the polymer matrix, incorporation of Ti content in the sample also increases and reaches to maximum of 64.28 wt% (Table 4.2). On the other hand, the amount of chlorine on the polymer matrix gradually decreases with increase in amount of TiCl₄. Generally, EDX quantifies only the presence of titanium and chlorine in the uttermost catalyst surface. The result shows that the titanium is exclusively present in the surface of the catalysts as expected. In addition, the distribution of Ti and Cl on the surface of MF of the hybrid catalyst (MFT2) is shown in Figure 4.7. It is seen that, Ti and Cl are evenly distributed throughout the surface without leaving any void space. Similar fashion is also noted for the other two catalysts (MFT1 and MFT3) suggesting the homogeneous surface composition of the three catalysts following the aforementioned preparation methods.
Table 4.2: Surface composition of the MF supported TiCl₄ catalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ti (wt %)</th>
<th>Cl (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFT1</td>
<td>41.12</td>
<td>58.88</td>
</tr>
<tr>
<td>MFT2</td>
<td>53.28</td>
<td>46.72</td>
</tr>
<tr>
<td>MFT3</td>
<td>64.28</td>
<td>35.72</td>
</tr>
</tbody>
</table>

Figure 4.6: EDX patterns of the (a) MFT1, (b) MFT2 and (c) MFT3

Figure 4.7: Distribution of (a) Ti and (b) Cl on the surface of catalyst (MFT2)

4.3.1.5. XRD analysis

The X-ray diffraction patterns for MF, MFT1, MFT2 and MFT3 are shown in Figure 4.8. A wide reflection peak is observed at 2θ=25-30° diffraction angles for pristine MF polymer due to the crystalline nature of MF. The diffraction peak position is found to be unaltered by the incorporation of TiCl₄ into the polymer matrix (MFT1-MFT3). But interestingly, the diffraction peak intensity (at 2θ = 25.3-25.9) of the catalysts amazingly decrease with the increase in amount of TiCl₄ and become totally amorphous
in nature (Table 4.3). This phenomenon confirms the presence of TiCl$_4$ in to the polymer matrix. To our knowledge, the decrease in peak intensity occurred because of the accommodation of TiCl$_4$ molecules onto the MF polymer matrix which disrupts the packing of polymer chain.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Angle (20)</th>
<th>Peak intensity (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MF</td>
<td>25.9</td>
<td>210</td>
</tr>
<tr>
<td>MFT1</td>
<td>25.55</td>
<td>60</td>
</tr>
<tr>
<td>MFT2</td>
<td>25.5</td>
<td>25</td>
</tr>
<tr>
<td>MFT3</td>
<td>25.3</td>
<td>10</td>
</tr>
</tbody>
</table>

4.3.1.6. Thermal Analysis (TGA)

Thermo gravimetric analysis is of the widely used to evaluate the thermal stability of the polymer matrix and hybrid catalysts. Figure 4.9 illustrates the TGA curves of the MF polymer and MF supported TiCl$_4$ catalysts. The characteristic degradation temperature of the polymer and catalysts are presented in Table 4.4.

The first stage weight loss (7% weight loss) of the pristine MF polymer matrix is occurred at the temperature range 110 °C-170 °C, could be due the evaporation of water. The second stage thermal degradation occurred in the temperature 180-390 °C may be due to the loss of alkyl chain, formaldehyde, methanol and the ether linkage present in the MF polymer matrix. Also at higher temperature it is possible to taking place the
Melamine formaldehyde supported titanium based heterogeneous Ziegler-Natta catalyst for ethylene polymerization in slurry process

oxidation of the activated methylene of the N-CH$_2$-O- linkage. The third weight loss is occurring in the temperature range 400-510 °C due to the degradation of main polymer chain and simultaneously released of CO$_2$ and NH$_3$. Interestingly, TiCl$_4$ incorporated MF catalysts (MFT1- MFT3) shows first weight loss in the range 90-125 °C with a little deviation from that of pristine polymer. This weight loss at lower temperature compared to neat MF polymer due to the loss of HCl and residual solvent. The 2$^{nd}$ and 3$^{rd}$ degradation temperature of catalysts are lower than that of the pristine polymer which is attribute to an outlet of TiCl$_4$ from the polymer matrix.

TG analyse reveals that MF supported TiCl$_4$ hybrid catalysts are thermally stable upto 90-125 °C (depending on % of TiCl$_4$ loading). Since olefin polymerization with conventional Ziegler-Natta catalyst system is carried out at 60-80 °C; so it may be inferred that these newly synthesised catalysts are sufficiently thermal stable to be used as supports for Ziegler- Natta catalyst for olefin polymerization.

Figure 4.9: TGA curves of (a) MF, (b) MFT1, (c) MFT2 and (d) MFT3
Table 4.4: Degradation temperatures of the MF and catalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>1st phase (°C)</th>
<th>2nd phase (°C)</th>
<th>3rd phase (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MF</td>
<td>160</td>
<td>330</td>
<td>590</td>
</tr>
<tr>
<td>MFT1</td>
<td>125</td>
<td>300</td>
<td>470</td>
</tr>
<tr>
<td>MFT2</td>
<td>120</td>
<td>290</td>
<td>465</td>
</tr>
<tr>
<td>MFT3</td>
<td>90</td>
<td>286</td>
<td>460</td>
</tr>
</tbody>
</table>

4.3.1.7. Theoretical calculation

Density functional calculation was carried out to explore the nature of the interaction between TiCl$_4$ and the polymer matrix. A system comprising of a unit of MF polymer and TiCl$_4$ is subjected to geometry optimization using double numerical (DN) basis set in combination with the Vosko-Wilk-Nusair (VWN) co-relation functional as provided in the DMol$^3$ program.$^{11}$ In the optimized geometry, the C=N, C-H, N-H, >C-O and Ti-Cl bond lengths are found to be 1.510, 1.140, 1.110, 1.510 and 2.237 Å respectively and are within considerable range. The distance between Ti and N atom of -NH group of polymer moiety is found to be 2.113 Å which is found to be 11% shorter than the sum of the covalent radii of Ti and N (2.31 Å) [Figure 4.10].$^{16}$ Thus, the incorporation of TiCl$_4$ into the polymer matrix takes place via an interaction between the N atom of the -NH group of the polymer matrix and Ti atom of TiCl$_4$. Further, the hybrid material is found to be stabilized by 427.335 kcal mol$^{-1}$ than the individual moieties.

![Figure 4.10: Probable complex of MF-TiCl$_4$ and selected bond length of the optimized geometry](image)
4.3.1.8. Catalytic activity of MF supported TiCl$_4$ catalysts on ethylene polymerization

Polymerization of ethylene is performed with developed MF-supported Ziegler-Natta catalyst in the presence of TEA in hexane at 40 °C and atmospheric pressure, which is rather mild than the typical industrial condition. TEA has been the most commonly used co-catalyst which has the significant capability of alkylation of the titanium tetrachloride species. The polymerization of ethylene proceeded in a heterogeneous system, where the catalyst is dispersed in hexane medium. It is well known that the co-catalyst TEA reduces Ti$^{4+}$ to Ti$^{3+}$ in TiCl$_4$ by shifting the alkyl group to Ti leading to the formation of active site for ethylene polymerization.

The catalytic activity of these catalysts (MFT1, MFT2 and MFT3) is evaluated for polymerization of ethylene at 40 °C and 1 atmosphere pressure. The activity is determined in terms of weight of polyethylene produced per g of Ti used in one hour polymerization. All the catalyst shows the productivity in the range of 2950.16-4721.09 g of PE/g of Ti/h (Table 4.5). It is observed that the activity of the catalyst MFT2 is higher than that of MFT1 due to the more amount of Ti into polymer matrix which increases the active site for ethylene polymerization after alkylation. But after a certain limit of Ti, the activity gradually decreases (MFT3). More is the amount of TiCl$_4$ anchored into the polymer matrix; more is the probability of formation of TiCl$_4$ clusters which reduces the active site.

Table 4.5: Experimental condition and activity of three catalysts in ethylene polymerization

<table>
<thead>
<tr>
<th>Entry</th>
<th>MFT1</th>
<th>MFT2</th>
<th>MFT3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti wt % (UV-visible)</td>
<td>1.6</td>
<td>3.5</td>
<td>5.3</td>
</tr>
<tr>
<td>Catalyst amount (g)</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Al/Ti mole ratio</td>
<td>250</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>Ethylene pressure (atm.)</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Reaction temperature (°C)</td>
<td>40</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Solvent (ml)</td>
<td>80</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>Polymerization time (h)</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Productivity (g of polyethylene/g of Ti/h)</td>
<td>2950.16</td>
<td>4721.09</td>
<td>3885.34</td>
</tr>
</tbody>
</table>
4.3.1.9. **Stability of the supported catalysts**

We have seen that supported catalysts are effective in ethylene polymerization. In the catalysts TiCl₄ is anchored on the support through co-ordination bond formation between >NH with Ti. There is a chance of leaching of TiCl₄ from the support during polymerization. Therefore, stability of the supported catalysts is an important factor to assess the suitability of the catalysts. UV-visible spectroscopy is a very useful method to evaluate the leaching property of the catalysts. For this purpose the following experiment was conducted. In a 250 ml three necked round bottom flask, 0.05 g MFT2 was dispersed in dry heptane in an inert nitrogen atmosphere. Calculated amount of TEA (Al/Ti = 300) was injected into the solution with a gas tight syringe. After vigorously stirring at 40 °C for about 2 h, the mixture was filtered in dry nitrogen atmosphere. The titanium content of the filtrate was estimated using UV-visible spectroscopy as mentioned above. Furthermore, a same experiment is also carried out without alkylation with the MFT2 catalyst. Interestingly, no absorption peak was found in the 350-410 nm characteristic ranges for both experiments. The absence of trace amount of titanium reveals no leaching of TiCl₄ from the polymer matrix during alkylation and without alkylation. The same experiment was performed for the other two catalysts (MFT1 and MFT3) and no leaching of Ti was found. It is confirmed that Ti complex is anchored firmly on MF matrix.

4.3.1.10. **Catalytic activity of the catalysts with storage time**

In Ziegler-Natta catalyst the major drawback arises in storing and handling of TiCl₄ and Et₃Al since; they are highly moisture sensitive and corrosive in nature. But interestingly synthesised MF supported Ziegler-Natta catalyst can be stored easily in a stopper vessel at nitrogen atmosphere. In order to evaluate the catalytic activity vs. storability of the catalysts, ethylene polymerization is conducted by maintaining the aforementioned specific conditions. It is observed that the synthesised catalysts (MFT1-MFT3) retain their catalytic activity for ethylene polymerization up to 120 days (Figure 4.11). The aptitude of these developed MF supported TiCl₄ catalysts is apparently different from that of the conventional inorganic supported Ziegler-Natta catalyst, which has an initial high productivity followed by a drastic rot.
Melamine formaldehyde supported titanium based heterogeneous Ziegler-Natta catalyst for ethylene polymerization in slurry process

Figure 4.11: Catalytic productivity with storage time (a) MFT1, (b) MFT2 and (c) MFT3

4.3.1.11. Characterization of the obtained PE

The FT-IR spectra of the resulting polymer synthesized with MF supported Ziegler-Natta catalyst (MFT1, MFT2 and MFT3) are shown in Figure 4.12. In comparison with the pure PE, the characteristic absorption band at 2929 and 2856 cm$^{-1}$ corresponding to C-H stretching mode is observed. In addition, two strong band at 1468 and 719 cm$^{-1}$ is also found for the deformations of methylene group. The occurrence of all these significant bands indicates that PE has been formed in the presence of MF support during polymerization. The broad band at about 3460 cm$^{-1}$ is due to O-H of the moisture adsorbed in PE.$^6$

The SEM micrographs of polyethylene at various magnifications are shown in Figure 4.13. At lower magnification of 350x, the polymer seems to be representing a colony of clouds, but at higher magnification, one observes that polymer granules seem to be engulfed with fibre like polymer which is exhibited on further magnification (5500x). It is noticed that the sizes of the PE granules were much larger than that of the polymer supported catalysts. This might be attributed to the fact that during polymerization, the resulting polymer particles pack together to form well-built PE granules where, the catalyst particles act as a template for growth of the polymer particles. The absence of
Melamine formaldehyde supported titanium based heterogeneous Ziegler-Natta catalyst for ethylene polymerization in slurry process

fine particle also eliminated the insurmountable obstacles such as reactor fouling, discharge from the reactor, filtration and drying etc.

Figure 4.12: FT-IR spectra of PE synthesized from (a) MFT1, (b) MFT2 and (c) MFT3

Table 4.6: Characterization of PE synthesized by MF-supported titanium catalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>$M_n$(GPC) g/mol</th>
<th>$M_w$(GPC) g/mol</th>
<th>PDI</th>
<th>$T_m$(°C)</th>
<th>$T_c$(°C)</th>
<th>MFI (g/10 min)</th>
<th>BD (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFT1</td>
<td>29,753</td>
<td>2,46,950</td>
<td>8.3</td>
<td>132.1</td>
<td>116</td>
<td>1.87</td>
<td>0.18</td>
</tr>
<tr>
<td>MFT2</td>
<td>35,397</td>
<td>2,79,640</td>
<td>7.9</td>
<td>135.2</td>
<td>118</td>
<td>1.33</td>
<td>0.28</td>
</tr>
<tr>
<td>MFT3</td>
<td>21,857</td>
<td>2,20,760</td>
<td>10.1</td>
<td>132.9</td>
<td>111</td>
<td>1.90</td>
<td>0.20</td>
</tr>
</tbody>
</table>

MFI (230 °C/2.16 Kg)
Melamine formaldehyde supported titanium based heterogeneous Ziegler-Natta catalyst for ethylene polymerization in slurry process

Figure 4.13: SEM images PE synthesized from MF-TiCl₄ supported titanium catalyst (MFT2) collected at magnification of (a) x350, (b) x1000, (c) x2000 and (d) x5500

The molecular weight of the PE is measured by GPC and the results are present in Table 4.6. The PE exhibited number-average molecular weights ($M_n$) in the range of 21,857-35,397 g/mol with broad molecular weight distribution of 7.9-10.1. It is worth noting that the broadening of the molecular weight in PE, caused primarily by the presence of multiple active centres of Ziegler-Natta catalyst due to which monomer diffusion resistance may be low. Since, the catalysts are heterogeneous in nature so it is very taxing to produce polyethylene with narrow polydispersity ($\text{PDI} = < 2$) PE.

The melt flow index (MFI) of the resulting polyethylene is decrease with increase in molecular weight of the resulting PE. The bulk density (BD) of the ensuing PE increases with increasing the polymerization activity (Table 4.6). However, the bulk density of the PE is relatively low (0.18-0.28 g/cm³, runs MFT1, MFT2 and MFT3) which is due to the lower ethylene pressure.
Figure 4.14: DSC plots of PE synthesized from (a) MFT1, (b) MFT2 and (c) MFT3

Differential scanning calorimetry (DSC) analyses of polyethylene have been carried out under nitrogen atmosphere in the heating rate of 10 °C /min. DSC curves of the polymers are shown in Figure 4.14. The melting point (T<sub>m</sub>) of the PE is found to be in the range of 132.1-135.2 °C (Table 4.6). It is observed that with the increase of molecular weight of the synthesised PE the melting point and crystallization temperature (T<sub>c</sub>) also increases. This indicates the less branch structure of the resulting PE.<sup>3, 6</sup> The thermal stability of the resulting polyethylene is also studied with thermogravimetric analysis. From the TGA curves as shown in Figure 4.15, it is observed that the resulting polyethylene are relatively thermally stable upto 300 °C and after the onset degradation temperature of 340 °C, the degradation rate of polyethylene accelerates. Above 530 °C only 1% char or residue is visible for all the resulting polyethylene.
Figure 4.15: TGA plots of PE synthesized from (a) MFT1, (b) MFT2 and (c) MFT3
4.4. Conclusions

The major findings of the above work are described below:

- MF supported Ti based Ziegler-Natta catalyst (MFT1, MFT2 and MFT3) has been successfully synthesized by varying different weight ratio of TiCl₄.
- XPS analysis provides the evidence for the successful incorporation of TiCl₄ into the polymer matrix through the coordination of -NH group of MF. DFT calculation and FT-IR spectral analysis further significantly reveal the interaction of TiCl₄ with the MF polymer through -NH moiety.
- UV-visible spectroscopy reveals that the Ti content in the polymer matrix gradually increases (1.6-5.3wt %) with the increase in amount of TiCl₄.
- It is found that the pristine MF polymer lost its crystallinity with the incorporation of TiCl₄ and becomes completely amorphous.
- MF-TiCl₄ catalysts are stable up to 90-125 °C (depending on % of TiCl₄ loading).
- After pre-treated with TEA, the hybrid catalysts were found to be active for ethylene polymerization in the slurry process at 40 °C and 1 atm. pressure.
- These catalysts with different composition (1.6-5.3 wt %) of titanium in polymer matrix showed productivity 2950.16-4721.09 g of PE/g of Ti/h.
- Catalyst with 3.5 wt% of titanium showed maximum activity. This gives unambiguous indication that not only quantity of titanium but also the uniform distribution of Ti in the polymer matrix is a foremost factor for catalytic activity.
- The MF supportedTiCl₄ catalysts retained their catalytic activity up to 120 days when stored in an inert atmosphere.
- The resulting PE exhibited number-average molecular weights (\(M_n\)) in the range of 21,857-35,397 g/mol with broad molecular weight distribution of 7.9-10.1 due to the multicenter nature of the catalysts.
Melamine formaldehyde supported titanium based heterogeneous Ziegler-Natta catalyst for ethylene polymerization in slurry process

References