



- (51) **International Patent Classification:**  
**C08F 4/52** (2006.01) **C08F 10/00** (2006.01)  
**C08F 4/76** (2006.01)
- (21) **International Application Number:** PCT/IB2015/055276
- (22) **International Filing Date:** 13 July 2015 (13.07.2015)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:** 2267/MUM/2014 11 July 2014 (11.07.2014) IN
- (71) **Applicant:** **RELIANCE INDUSTRIES LIMITED** [IN/IN]; 3rd Floor, Maker Chamber-IV, 222, Nariman Point, Mumbai, Maharashtra 400021 (IN).
- (72) **Inventors:** **PATIL, Yogesh Popatrao**; Elegenta -C, Room No.603, Casabella, Lodha, Builder, near Khidaleshwar Temple, Kalyan-Shil Road, Dombivli (E), Thane, Maharashtra 421204 (IN). **BAGUI, Mahuya**; B-707, Sector-I, Petrochemicals Township, Vadodara, Gujarat 391345 (IN). **PATEL, Viralkumar**; Mota Pore, Near Madhi, Nadiad, Kheda District, Gujarat 387001 (IN). **SARMA, Krishna Renganath**; DF-43, Sector-I, Petrochemicals Township, Vadodara, Gujarat 391345 (IN). **JASRA, Raksh Vir**; B-245, Sundervan Housing Society, New Sama Road, Vadodara, Gujarat 390024 (IN). **MATHUR, Ajit Behari**; D-38, Sector-I, Petrochemicals Township Vadodara, Gujarat 391345 (IN). **VAKIL, Suketu**; A-903/904, Chaitanya Towers, Appa Saheb Marathe Marg, Prabhadevi, Dadar, Mumbai, Maharashtra 400025 (IN).
- (74) **Agent:** **DEWAN, Mohan**; R. K. Dewan & Co., Podar Chambers, S.A. Brelvi Road, Fort, Mumbai, Maharashtra 400001 (IN).
- (81) **Designated States** (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) **Designated States** (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

**Declarations under Rule 4.17:**

- *as to the identity of the inventor (Rule 4.17(i))*
- *of inventorship (Rule 4.17(iv))*

**Published:**

- *with international search report (Art. 21(3))*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

(54) **Title:** SINGLE SITE CATALYST IMMOBILIZED ON INORGANIC OXIDE SUPPORT AND ITS PREPARATION METHOD

(57) **Abstract:** The present disclosure provides a heterogeneous single site catalyst immobilized on an inorganic oxide support and a method for the synthesis of the same using a step of generating a Schiff base imine ligand on the inorganic oxide support followed by lithiation and titanation. The use of the single site catalyst of the present disclosure is for polymerizing ethylene to obtain disentangled ultra-high molecular weight polyethylene.



## **SINGLE SITE CATALYST IMMOBILIZED ON INORGANIC OXIDE SUPPORT AND ITS PREPARATION METHOD**

### **FIELD**

The present disclosure relates to catalysts and methods for preparing the same. Particularly, the present disclosure relates to supported polymerization catalysts.

### **DEFINITION**

As used in the present disclosure, the following term is generally intended to have the meaning as set forth below, except to the extent that the context in which it is used indicates otherwise.

Disentangled polyethylene: The term 'disentangled' is used to describe ultrahigh molecular weight polyethylene - homo-polymer (s) or copolymer(s) of ethylene having molar mass in the range of 0.3 million to 20 million; crystallinity greater than 75%; heat of fusion greater than 200 J/g and bulk density ranging from 0.01 to 0.3 g/cc, wherein the polyethylene chains have low entanglement or are completely disentangled.

Mobil composition of matter No.41 (MCM-41) and Mobil composition of matter No.48 (MCM-48) are the types of mesoporous silica.

### **BACKGROUND**

Conventionally, ultra-high molecular weight polyethylene is prepared by ethylene polymerization catalyzed by metallocene or non-metallocene type homogeneous catalyst compositions. The homogenous catalyst compositions mainly contain transition metal complexes such as complexes of metals including Titanium (Ti), Zirconium (Zr), Hafnium (Hf) and the like. For the activation of these homogenous single site catalyst compositions, relatively larger quantities of costly co-catalyst components such as methylaluminoxane are required. The use of relatively large quantities of the co-catalyst

components results in less kinetic control and consequently reactor fouling by the generation and deposition of polymer lumps on the reactor unit walls and stirrer shaft/paddle assembly. The use of a homogeneous catalyst composition, therefore, leads to increased polymerization cost. Hence, inorganic oxide supported/immobilized single site catalysts is thought to overcome the above mentioned drawbacks and are also preferred for the commercialization. Homogeneous catalysts are known for the production of disentangled ultra-high molecular weight polyethylene. However, for commercial production and overcoming the above mentioned drawbacks, a heterogeneous catalyst system is required for the production of disentangled UHMWPE.

There are immobilized polymerization catalysts in use today. However, they are physically bonded to the support. They have a low resistance to poisoning, which reduces their service life.

Hence, there is a felt need for a heterogeneous catalyst system which is chemically bonded to a support for the production of disentangled UHMWPE which has a long service life.

## **OBJECTS**

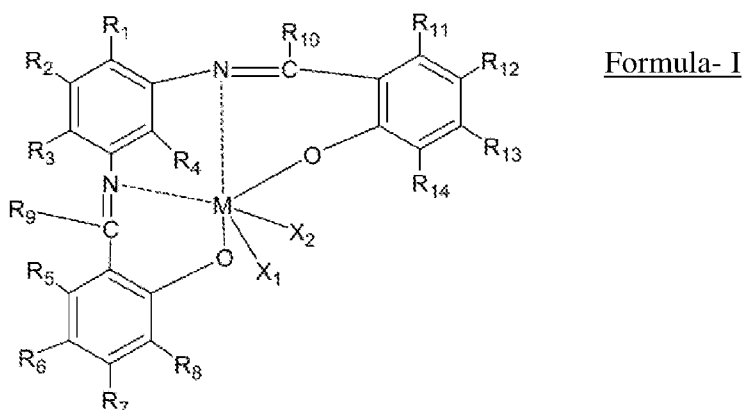
Some of the objects of the present disclosure which at least one embodiment is adapted to provide, are described herein below.

It is an object of the present disclosure to provide a catalyst for the manufacture of ultra-high molecular weight polyethylene, particularly disentangled ultra-high molecular weight polyethylene.

Other objects and advantages of the present disclosure will be more apparent from the following description which is not intended to limit the scope of the present disclosure.

## SUMMARY

In accordance with the present disclosure a heterogeneous single site catalyst immobilized on an inorganic oxide support represented by Formula I is disclosed:

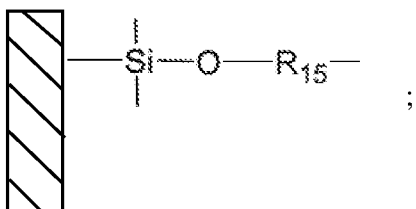


wherein,

M is a Group IV transition metal;

R<sub>1</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub>, R<sub>9</sub>, R<sub>10</sub>, R<sub>11</sub>, R<sub>12</sub>, R<sub>13</sub> are independently a -H or an alkyl group;

R<sub>2</sub> is a functionalized inorganic oxide support selected as



R<sub>8</sub> and R<sub>14</sub> are t-butyl;

R<sub>15</sub> is a -CO- or a -SO<sub>3</sub>H- group; and

X<sub>1</sub> and X<sub>2</sub> are independently one of F, Cl, Br and I.

According to another aspect of the present disclosure, there is provided a method for immobilizing a single site catalyst on an inorganic oxide support. The inorganic oxide support is functionalized by treating with a reagent to obtain a functionalized inorganic oxide support. The functionalized inorganic oxide support is treated with a hydroxyl group containing aldehyde to obtain an inorganic oxide support with Schiff base imine ligand. The inorganic oxide support with the Schiff base imine ligand is lithiated with a

lithiating agent to obtain an inorganic oxide support with a lithiated Schiff base imine ligand; and the inorganic oxide support with the lithiated Schiff base imine ligand is treated with a titanium halide to obtain the immobilized single site catalyst.

In accordance with the present disclosure, a method for synthesis of dis-entangled ultra-high molecular weight polyethylene (UHMWPE) by employing the immobilized single site heterogeneous catalyst of the present disclosure along with a co-catalyst.

### **BRIEF DESCRIPTION OF THE ACCOMPANYING DRAWINGS**

**Figure 1** illustrates an IR spectrum of 3, 5-diamino benzoic acid;

**Figure 2** illustrates an IR spectrum of the immobilized 3, 5-diamino benzoic acid on silica;

**Figure 3** illustrates an IR spectrum of the immobilized Schiff base imine ligand (3-tert-butyl salicylaldehyde based) on silica;

**Figure 4** illustrates a thermo gravimetric analysis of the immobilized catalyst prepared in accordance with the present disclosure;

**Figure 5** illustrates the XRD pattern of the polymer obtained using the immobilized catalyst prepared in accordance with the present disclosure; and

**Figure 6** illustrates the DSC of the polymer obtained using the immobilized catalyst prepared in accordance with the present disclosure.

### **DETAILED DESCRIPTION**

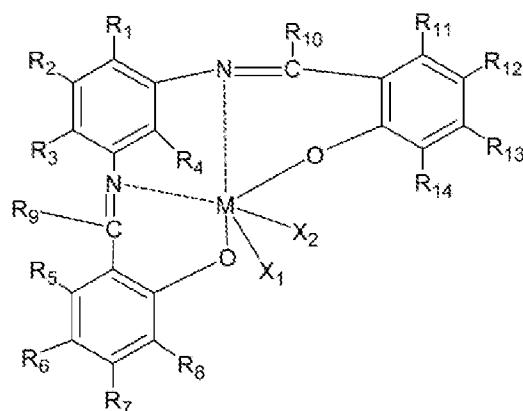
The disclosure will now be described with reference to the accompanying embodiments which do not limit the scope and ambit of the disclosure. The description provided is purely by way of example and illustration.

The embodiments herein and the various features and advantageous details thereof are explained with reference to the non-limiting embodiments in the following description. Descriptions of well-known components and processing techniques are omitted so as to not unnecessarily obscure the embodiments herein. The examples used herein are

intended merely to facilitate an understanding of ways in which the embodiments herein may be practiced and to further enable those of skill in the art to practice the embodiments herein. Accordingly, the examples should not be construed as limiting the scope of the embodiments herein.

Conventionally, direct immobilization of a single site catalyst on an inorganic oxide support is difficult and not easily feasible, especially in the absence of suitable functional groups. The present disclosure provides a novel immobilized heterogeneous single site catalyst, immobilized on an inorganic support, by way of functionalizing the support.

In accordance with the present disclosure, a heterogeneous single site catalyst immobilized on an inorganic oxide support represented by Formula I is herein disclosed:



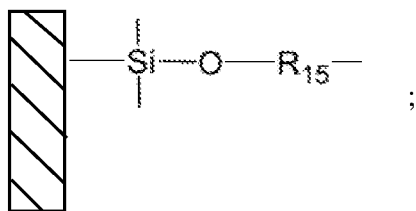
Formula- I

wherein,

M is a Group IV transition metal;

R<sub>1</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub>, R<sub>9</sub>, R<sub>10</sub>, R<sub>11</sub>, R<sub>12</sub>, R<sub>13</sub> are independently a -H or an alkyl group;

R<sub>2</sub> is a functionalized inorganic oxide support selected as



R<sub>8</sub> and R<sub>14</sub> are t-butyl;

R<sub>15</sub> is a -CO- or a -SO<sub>3</sub>H- group; and

X<sub>1</sub> and X<sub>2</sub> are independently F, Cl, Br or I.

A non-limiting example of the inorganic oxide support is at least one of silica, typically mesoporous silica MCM-41 and MCM-48.

Direct immobilization of single site catalysts on inorganic oxide supports is not feasible because of the absence of suitable functional groups (1) on the surface of the inorganic oxide support as well as (2) the catalyst to make a chemical reaction feasible. Further, direct attempts to immobilize single site catalysts on inorganic oxide support results in deactivation of such catalysts due to the reaction of the halide groups with the -OH groups in the support, since it is well known that -OH groups coordinate more strongly. This results in complete catalytic poisoning rendering the catalyst inactive for olefin polymerization. This problem is overcome by the inventors of the present disclosure by devising a synthetic method wherein the -OH groups present in the inorganic oxide support are first suitably functionalized so as to enable reaction with suitable Schiff base chelating ligands thereby immobilizing them.

Accordingly, in another aspect of the present disclosure there is provided a synthetic method for immobilizing a single site catalyst on an inorganic oxide support surface that comprises the following steps:

- a. functionalizing the support by treating with a reagent to obtain a functionalized inorganic oxide support;
- b. treating the functionalized inorganic oxide support with a hydroxy group containing aldehyde to obtain an inorganic oxide support with a Schiff base imine ligand;
- c. lithiating the inorganic oxide support with the Schiff base imine ligand with a lithiating agent to obtain an inorganic oxide support with a lithiated Schiff base imine ligand; and
- d. treating the inorganic oxide support with the lithiated Schiff base imine ligand with a titanium halide to obtain the immobilized single site catalyst.

The reagents used for functionalizing the inorganic oxide support are at least one selected from the group consisting of a diamino carboxylic acid and a diamino sulphonic acid, the non-limiting examples of which include amino substituted carboxylic acids like 3,5-

dianino benzoic acid, amino substituted sulphonic acids of benzene, naphthalene like 3,5-dianino benzene-1- sulphonic acid. According to one exemplary embodiment of the present disclosure, the functionalizing agent used is 3, 5-diamino benzoic acid.

Functionalizing the inorganic oxide support is a critical method step. The idea is to enable reaction between the free -OH groups in the inorganic oxide supports with suitable groups like carboxylic acid or sulphonic acid as in anthranilic acid, benzene/naphthalene sulphonic acids etc. in the amino containing reagents so as to generate an “amino functionalized inorganic oxide support”.

The amino group containing the functionalized silica is then subsequently reacted with a substituted salicylaldehyde, the non-limiting examples of which include 3-tert-butyl salicylaldehyde, 3,5-ditertiary butyl salicylaldehyde, 5-fluoro-3-methyl salicylaldehyde, un-substituted salicylaldehyde and 2-hydroxy-1 naphthaldehyde to generate the Schiff base imine ligand on the functionalized inorganic oxide support.

These immobilized Schiff base imine ligands are subsequently lithiated using a lithiating agent, the non-limiting examples of which include alkyl lithiums, aryl lithiums and lithium hydride.

In one embodiment, n-butyl lithium is used as the lithiating agent. It converts the -OH group in the substituted salicylaldehyde to  $O^- Li^+$ . The immobilized heterogeneous single site titanium catalyst is then prepared by treating the immobilized lithiated Schiff base imine ligand with a titanium halide compound, a non-limiting example of which is titanium tetrachloride.

One of the most advantageous aspects of the immobilized single site heterogeneous catalysts of the present disclosure is that unlike the prior art catalysts they are not physically anchored over inorganic oxide supports. Therefore, these catalysts do not get deactivated quickly.

Furthermore, the polymerization catalyst of the present disclosure also enhances the bulk density of the resultant UHMWPE by capitalizing on the diverse physico-chemical properties like surface area, porosity, average particle size, and particle size distribution,

etc., of the support. Apart from facilitating the increase in the bulk density of the resultant polymer, the selection of a suitable support along with process conditions can produce a diverse range of polymers with varied characteristics by controlling the polymerization activity in a much better way.

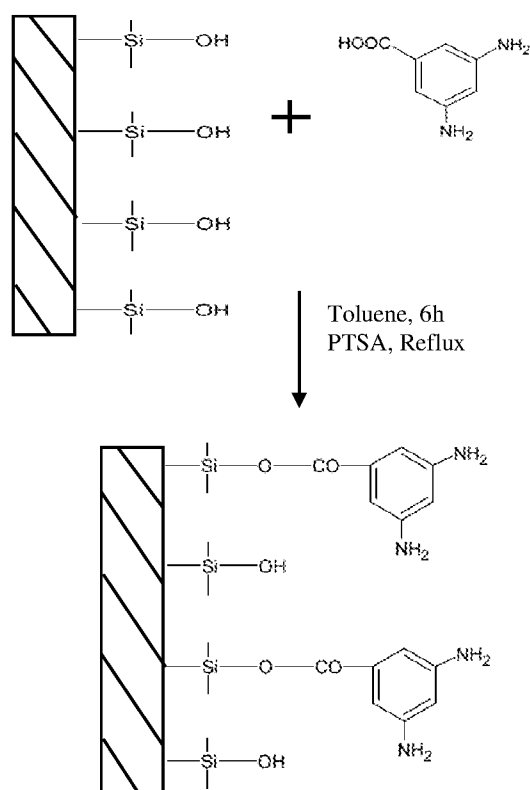
In a still another aspect of the present disclosure, there is provided, a method for synthesis of dis-entangled ultra-high molecular weight polyethylene (UHMWPE) by employing the immobilized single site heterogeneous catalyst of the present disclosure along with a co-catalyst. The method for synthesis of dis-entangled UHMWPE using the immobilized catalyst of the present disclosure is as described below.

To the dry and de-oxygenated polymerization medium, the non-limiting examples of which are hexane, varsol (a mixture of hydrocarbons having boiling point in the range of 140-170 °C.) and toluene, is added a specific amount of a co-catalyst, the non-limiting examples of which are P-MAO (poly methylaluminoxane) and an alkyl aluminium, followed by the immobilized Ti containing catalyst of the present disclosure in such quantity so that the Al/Ti molar ratio as derived from the co-catalyst and catalyst is in the range of 15 to 300. This mixture is charged into a reactor, a non-limiting example of which is a Buchi polyclave reactor, under an inert atmosphere such as nitrogen or argon, and subsequently agitated for different optimized time intervals under different optimized ethylene pressures ranging from atmospheric to 8 bar, preferably higher pressures. The polymerization temperature is also optimized and ranged between 30 to 75 °C. The polymer obtained during the run is filtered, washed with hexane and dried under vacuum for further characterization.

The single site catalyst prepared in accordance with the present disclosure is used for ethylene polymerization using an alkyl aluminium as a co-catalyst under different conditions. Poly methylaluminoxane (P-MAO) as a co-catalyst is found to be very effective for synthesizing disentangled polyethylene with ultra-high molecular weight (3 - 7 million g/mole) as assessed by polymer characteristics including low bulk density, physical appearance (morphology), crystallinity and the like. Also, the catalyst prepared in accordance with the present disclosure is required in comparatively smaller quantity

and hence, prevents fouling of the reactor by not generating and depositing polymer lumps on the reactor walls and the stirrer shaft/paddle assembly.

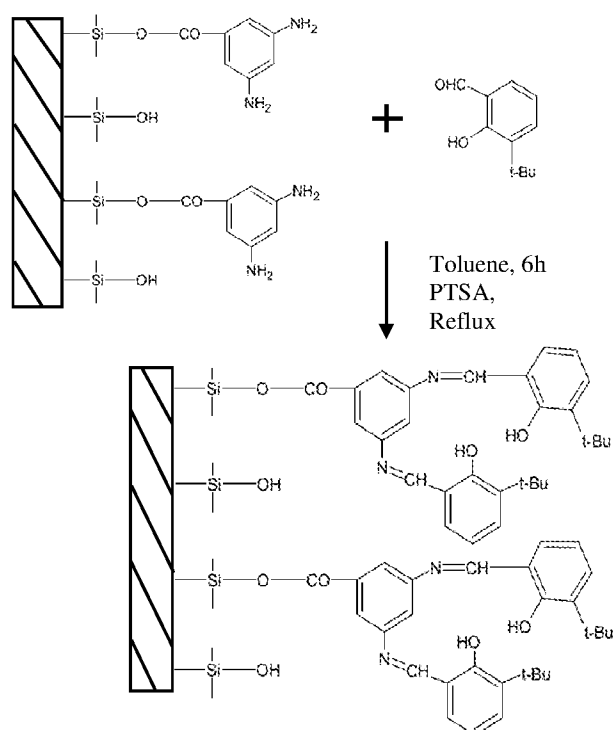
In an embodiment of the present disclosure, 3, 5-diamino benzoic acid is reacted with dry silica to form a mixture. The mixture is then refluxed in dry toluene to a temperature in the range of 115 to 120°C for a time period in the range of 6 to 12 hours to form ester linkage between the hydroxyl group in the silica and the carboxylic acid group in 3, 5-diamino benzoic acid, resulting in synthesis of an esterified and immobilized metaphenylene diamino benzene containing moiety as depicted in **reaction-I**.



**Reaction-I**

The esterified and immobilized metaphenylene diamino benzene containing support is then washed with dry hexane and dried under nitrogen. The dried, esterified and immobilized metaphenylene diamino benzene containing moiety is then reacted with an

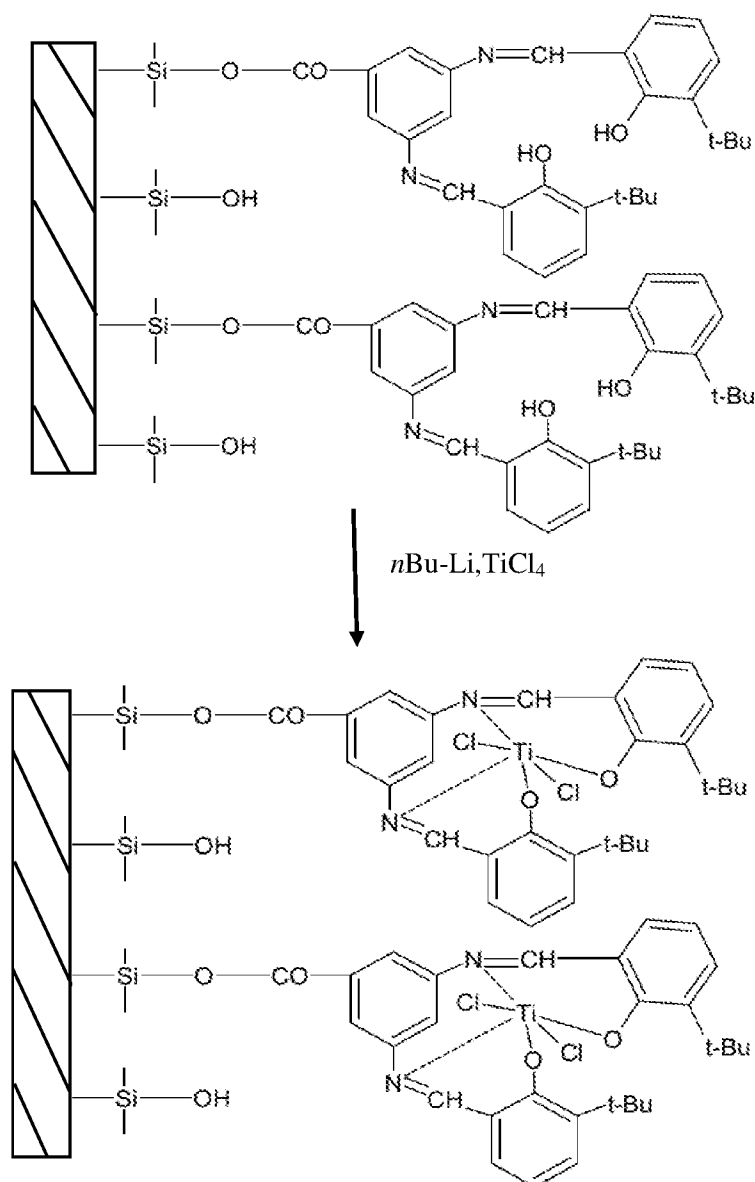
either 3-tert-butyl salicylaldehyde, or 3,5-ditert-butyl salicylaldehyde or any other substituted salicylaldehydes by refluxing in dry toluene to a temperature in the range of 115 to 120°C for a time period in the range of 6 to 12 hours in the presence of catalytic quantity of paratoluene sulphonic acid to obtain the corresponding immobilized Schiff base imine ligands as depicted in **reaction-II**.



## Reaction-II

The immobilized Schiff base imine ligands are then lithiated using *n*-butyl lithium in dry ether to a temperature in the range of -70°C to -75°C for a time period in the range of 1 hour to 4 hours to form a reaction mixture and convert the hydroxyl group to O<sup>-</sup>Li<sup>+</sup> using dry ice and acetone. Temperature of lithiation is further increased to a temperature in the range of 25 to 30°C for a time period in the range of 2 hours to 6 hours. After lithiation, temperature of the reaction mixture is cooled to a temperature in the range of -78°C to -85°C to obtain a cooled reaction mixture. The cooled reaction mixture is reacted with TiCl<sub>4</sub> at a room temperature for a time period in the range of 6 hours to 8 hours followed

by stirring to generate an immobilized transition metal single site catalyst as depicted below in **reaction-III**.



The titanium content of the so-prepared immobilized [bis-(N-3-tert-butylsalicylidene)-3,5-diamino benzoyl]-titanium (IV) dichloride is determined by UV-Vis spectroscopy and the titanium present in the single site catalyst prepared in accordance with the present disclosure is 6.22%.

The single site catalyst prepared in accordance with the present disclosure is used for ethylene polymerization using different co-catalysts. The polymerization is studied under different conditions and the polymer obtained is characterized for its viscosity, molecular weight and bulk density.

The present disclosure is further described in light of the following experiment which are set forth for illustration purpose only and not to be construed for limiting the scope of the disclosure. The following laboratory scale experiment can be scaled up to industrial/commercial scale:

**Experiment:****Preparation of catalyst:**

3, 5-diamino benzoic acid was reacted with dry silica at 25°C to form a mixture. The mixture was then refluxed in dry toluene at 115°C for 6 hours to form ester linkage between the hydroxyl group in the silica and the carboxylic acid group in 3, 5-diamino benzoic acid, resulting in synthesis of an esterified and immobilized metaphenylene diamino benzene.

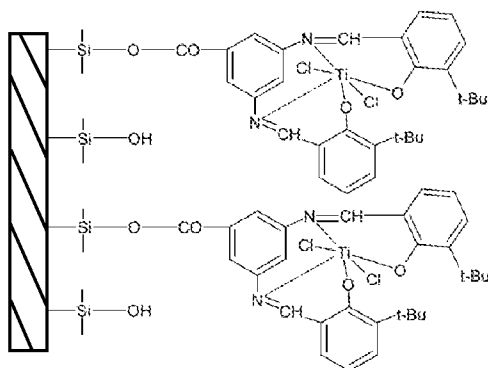
The esterified and immobilized metaphenylene diamino benzene containing support was washed with dry hexane for 30 minutes and dried under nitrogen for 1 hour. The dried, esterified and immobilized metaphenylene diamino benzene containing moiety was then reacted with 3,5-ditert-butyl salicylaldehyde by refluxing in dry toluene at 115°C in the presence of catalytic quantity of paratoluene sulphonic acid for 6 hours to obtain the corresponding immobilized Schiff base imine ligands.

The immobilized Schiff base imine ligands was lithiated using 1.6 moles of *n*-butyl lithium in dry ether at -78°C for 1 hour using dry ice and acetone to form a reaction mixture and convert the hydroxyl group to O<sup>-</sup>Li<sup>+</sup>. Temperature of lithiation was further raised to 25°C for 2 hours. After lithiation, temperature of the reaction mixture was cooled to -78°C to form a cooled reaction mixture. The cooled reaction mixture was then

reacted with 2 mmol of  $\text{TiCl}_4$  at a room temperature for 5 hours followed by stirring to generate an immobilized transition metal single site catalyst.

The catalyst of the present disclosure was used in the polymerization of ethylene. The product of reaction III, as represented by Formula – II below was used as the catalyst for the polymerization.

Formula - II



**Table 1** below summarizes the ethylene polymerization carried out under different conditions.

**Table 1: Polymerization of ethylene with immobilized single site catalyst**

| Run | Solvent<br>(500 mL)        | Catalyst<br>(mg) | Cocatalyst<br>(mL), 15%<br>PMAO | Al/Ti | RSV<br>(dl/g) | MW<br>(M)<br>ASTM | Yield<br>(g) |
|-----|----------------------------|------------------|---------------------------------|-------|---------------|-------------------|--------------|
| 1   | Toluene                    | 30               | 4.5                             | 291   | --            | ---               | 0            |
| 2   | Toluene                    | 200              | 7                               | 68    | ---           | --                | 0            |
| 3   | Mixture of<br>hydrocarbons | 200              | 3                               | 30    | 26            | 4.66              | 10           |
| 4   | Mixture of<br>hydrocarbons | 500              | 4.5                             | 17    | 26            | 4.66              | 10           |

Polymerization conditions:- 1 L Buchi-glasuster polylcave reactor; ~15% PMAO;  
Ti =0.026 mmole to 0.6 mmole of Ti; Al/Ti ~17-291; room temperature to 75 °C;  
2 hr; 500 rpm; Pressure = 2 bar.

From the above result, it is confirmed that the immobilized catalyst:

- is inactive when ethylene polymerization is carried out in toluene; and
- shows good activity towards ethylene polymerization when it is carried out in the mixture of hydrocarbons.

IR spectral study of the single site catalyst prepared shows the carboxylic acid C=O group to be present in 3, 5 diamino benzoic acid at  $1571 - 1633\text{ cm}^{-1}$  as an intense peak as depicted in figure 1, which diminishes significantly in immobilized 3, 5-diamino benzoic acid on silica spectrum as depicted in figure 2, indicating that acid functional group reacted with SiOH group of silica forming an ester linkage. The IR spectra of immobilized Schiff base imine ligand shows a band for C=N in the region of  $1623\text{ cm}^{-1}$  as depicted in figure 3, which confirms the formation of immobilized Schiff base imine ligand.

Thermo gravimetric analysis of the prepared single site catalyst shows that the catalyst contains around 49.39% volatile content or organic content (from the organic Schiff base imine ligand) and 50.61% residue or inorganic content (from the silica and titanium) as depicted in figure 4. The catalyst contains one titanium and 2 chlorine moieties immobilized on the silica support.

The polymer obtained during polymerization using the single site catalyst of the present disclosure is further characterized using X-Ray Diffraction (XRD). It is seen that the crystallinity of the resulting polymer is in the range of 95-99% which is higher than normal UHMWPE (60-65% crystallinity) as depicted in figure 5. The increase in crystallinity compared to normal UHMWPE can be attributed to highly disentangled state of polymer chain obtained using the single site catalyst of the present disclosure.

Differential scanning calorimetry (DSC) of the synthesized polymer is carried out to ascertain the melting and crystallization temperature of the polymer. The melting temperature of polymers synthesized are observed to be around  $138 - 139\text{ }^{\circ}\text{C}$  on first heating and on second heating it got reduced to  $134 - 137\text{ }^{\circ}\text{C}$  as depicted in figure 6. The

crystallization temperature was also observed to be around 118-120 °C. The obtained polymers also exhibited high enthalpy of melting, ranging from 189-190 J/g, compared to normal UHMWPE (enthalpy of melting ~ 140 J/g) indicating a high degree of chain disentanglement in the polymer obtained using the single site catalyst of the present disclosure.

### **Technical advances**

- The present disclosure provides an immobilized single site catalyst on an inorganic oxide support.
- The present disclosure also provides a method for preparation of single site catalyst on an inorganic oxide support.
- The use of single site catalyst of the present disclosure along with poly methylaluminoxane (P-MAO) as a co-catalyst results in polymer chains which are largely disentangled.
- The polyethylene obtained using the single site catalyst of the present disclosure has a high molecular weight and thus can be classified as UHMWPE.
- The catalyst of the present disclosure prevents fouling of the reactor as it is used in a comparatively smaller quantity.

The exemplary embodiments herein quantify the benefits arising out of this disclosure and the various features and advantageous details thereof are explained with reference to the non-limiting embodiments in the description. Descriptions of well-known components and processing techniques are omitted so as to not unnecessarily obscure the embodiments herein. The examples used herein are intended merely to facilitate an understanding of ways in which the embodiments herein may be practiced and to further enable those of skill in the art to practice the embodiments herein. Accordingly, the examples should not be construed as limiting the scope of the embodiments herein.

The foregoing description of the specific embodiments will so fully reveal the general nature of the embodiments herein that others can, by applying current knowledge, readily modify and/or adapt for various applications such specific embodiments without

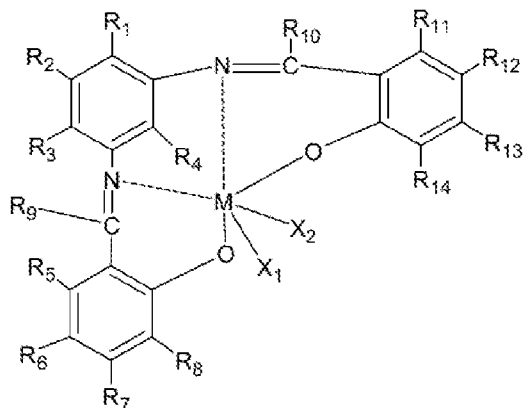
departing from the generic concept, and, therefore, such adaptations and modifications should and are intended to be comprehended within the meaning and range of equivalents of the disclosed embodiments. It is to be understood that the phraseology or terminology employed herein is for the purpose of description and not of limitation. Therefore, while the embodiments herein have been described in terms of preferred embodiments, those skilled in the art will recognize that the embodiments herein can be practiced with modification within the spirit and scope of the embodiments as described herein.

Any discussion of documents, acts, materials, devices, articles and the like that has been included in this specification is solely for the purpose of providing a context for the disclosure. It is not to be taken as an admission that any or all of these matters form a part of the prior art base or were common general knowledge in the field relevant to the disclosure as it existed anywhere before the priority date of this application.

While considerable emphasis has been placed herein on the particular features of this disclosure, it will be appreciated that various modifications can be made, and that many changes can be made in the preferred embodiments without departing from the principles of the disclosure. These and other modifications in the nature of the disclosure or the preferred embodiments will be apparent to those skilled in the art from the disclosure herein, whereby it is to be distinctly understood that the foregoing descriptive matter is to be interpreted merely as illustrative of the disclosure and not as a limitation.

## CLAIMS

1. An immobilized heterogeneous single site catalyst represented by Formula I:



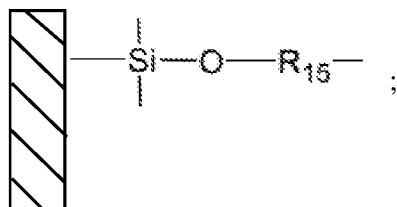
Formula- I

wherein,

M is a Group IV transition metal;

$R_1, R_3, R_4, R_5, R_6, R_7, R_9, R_{10}, R_{11}, R_{12}, R_{13}$  are independently a -H or an alkyl group;

$R_2$  is a functionalized inorganic oxide support selected as



$R_8$  and  $R_{14}$  are t-butyl;

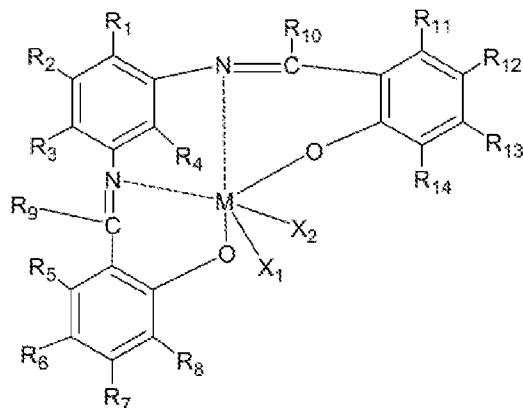
$R_{15}$  is a -CO- or a -SO<sub>3</sub>H- group; and

$X_1$  and  $X_2$  are independently one of F, Cl, Br and I.

2. The catalyst as claimed in claim 1, wherein the Group IV transition metal is titanium.
3. A method for immobilizing a single site catalyst on an inorganic oxide support, said method comprising the following steps:
- functionalizing said support by treating with a reagent to obtain a functionalized inorganic oxide support;

- b. treating said functionalized inorganic oxide support with a hydroxyl group containing aldehyde to obtain an inorganic oxide support with a Schiff base imine ligand;
  - c. lithiating said inorganic oxide support with the Schiff base imine ligand with a lithiating agent to obtain an inorganic oxide support with a lithiated Schiff base imine ligand; and
  - d. treating said inorganic oxide support with the lithiated Schiff base imine ligand with a titanium halide to obtain said immobilized single site catalyst.
4. The method as claimed in claim 3, wherein said inorganic oxide support is at least one of silica, MCM-41 and MCM-48.
5. The method as claimed in claim 3, wherein said reagent is at least one of an amino substituted carboxylic and an amino substituted sulphonic acids.
6. The method as claimed in claim 3, wherein said aldehyde is a substituted hydroxyl group containing aldehyde.
7. The method as claimed in claim 6, wherein said substituted hydroxyl group containing aldehyde is 3-tert-butylsalicylaldehyde.
8. The method as claimed in claim 3, wherein said lithiating agent is n-butyl lithium.
9. The method as claimed in claim 3, wherein said titanium halide is titanium tetrachloride.

10. A method for synthesis of disentangled UHMWPE by employing an immobilized heterogeneous single site catalyst represented by Formula I:



Formula- I

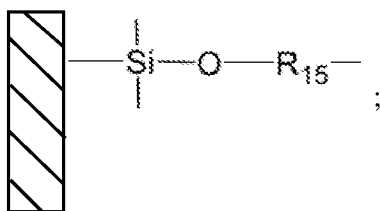
along with a co-catalyst,

wherein,

M is a Group IV transition metal;

R<sub>1</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub>, R<sub>9</sub>, R<sub>10</sub>, R<sub>11</sub>, R<sub>12</sub>, R<sub>13</sub> are independently a -H or an alkyl group;

R<sub>2</sub> is a functionalized inorganic oxide support selected as



R<sub>8</sub> and R<sub>14</sub> are t-butyl;

R<sub>15</sub> is a -CO- or a -SO<sub>3</sub>H- group; and

X<sub>1</sub> and X<sub>2</sub> are independently one of F, Cl, Br and I, said method comprising the following steps:

- mixing said co-catalyst and said immobilized heterogeneous single site catalyst under an inert atmosphere in an inert, dry and oxygen-free hydrocarbon solvent to obtain a mixture; and
- polymerizing ethylene in the presence of the mixture in a reactor to obtain said disentangled UHMWPE.

11. The method as claimed in claim 10, wherein said co-catalyst is at least one selected from the group consisting of poly methylaluminoxane (P-MAO) and an alkyl aluminium.
12. The method as claimed in claim 12, wherein said alkyl aluminium is at least one selected from the group consisting of triethyl aluminium, triisobutyl aluminium and isoprenyl aluminium.
13. The method as claimed in claim 10, wherein said inert atmosphere is an atmosphere of nitrogen or argon.

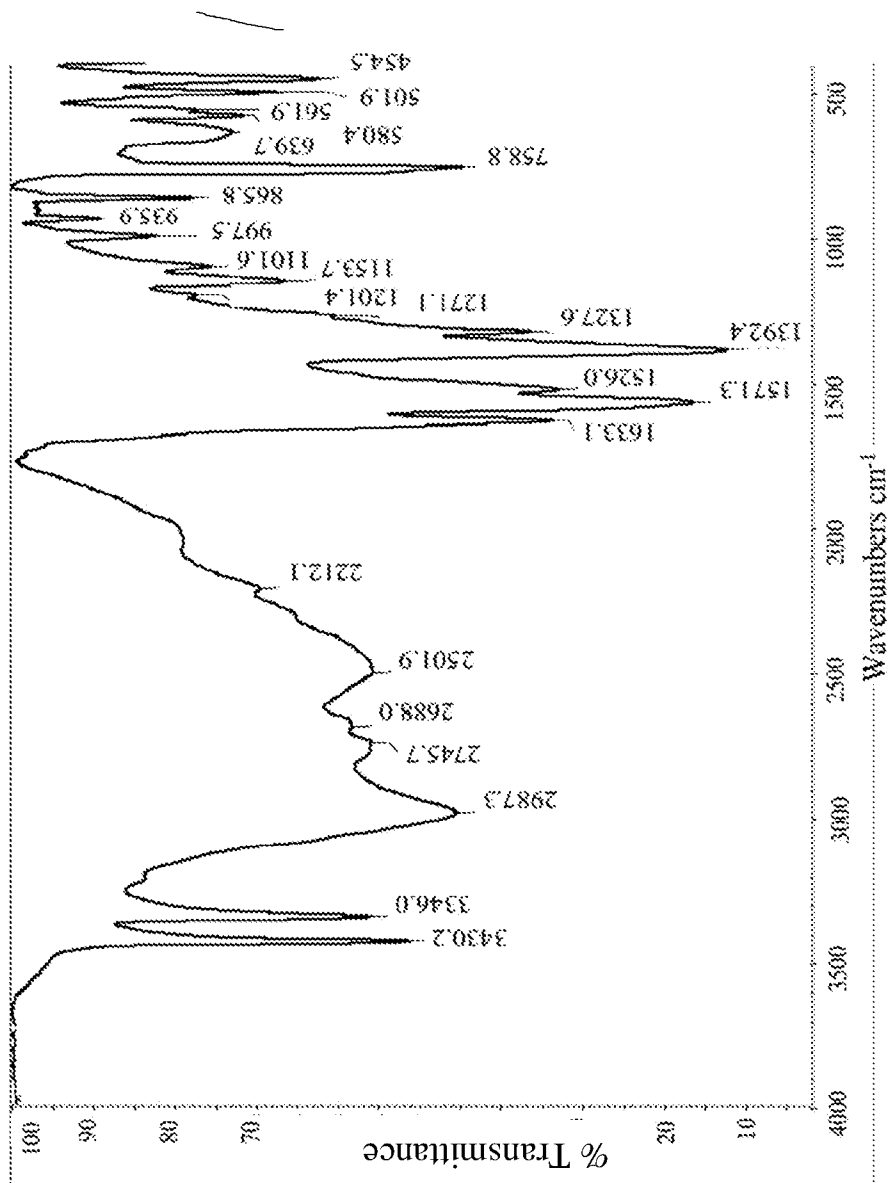
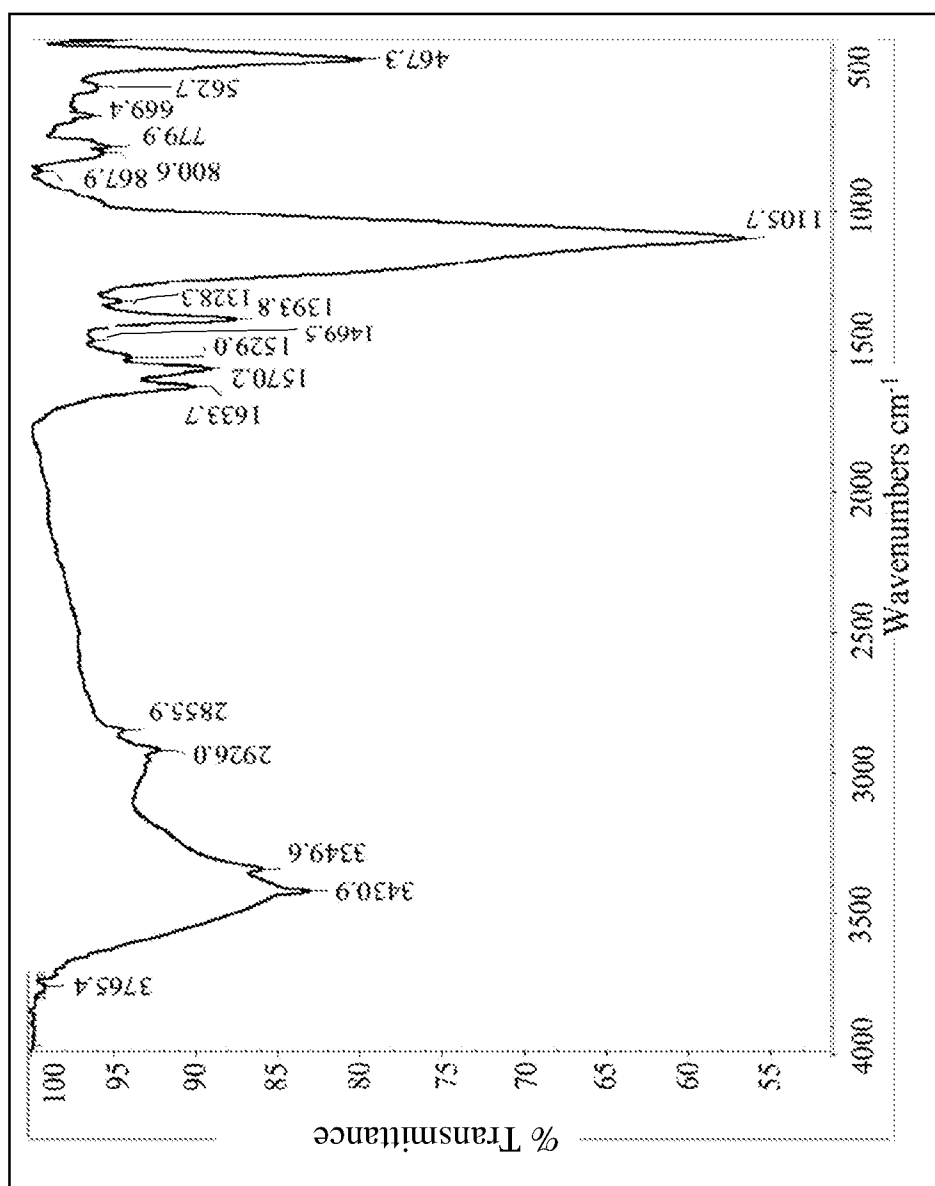


FIGURE 1

**FIGURE 2**

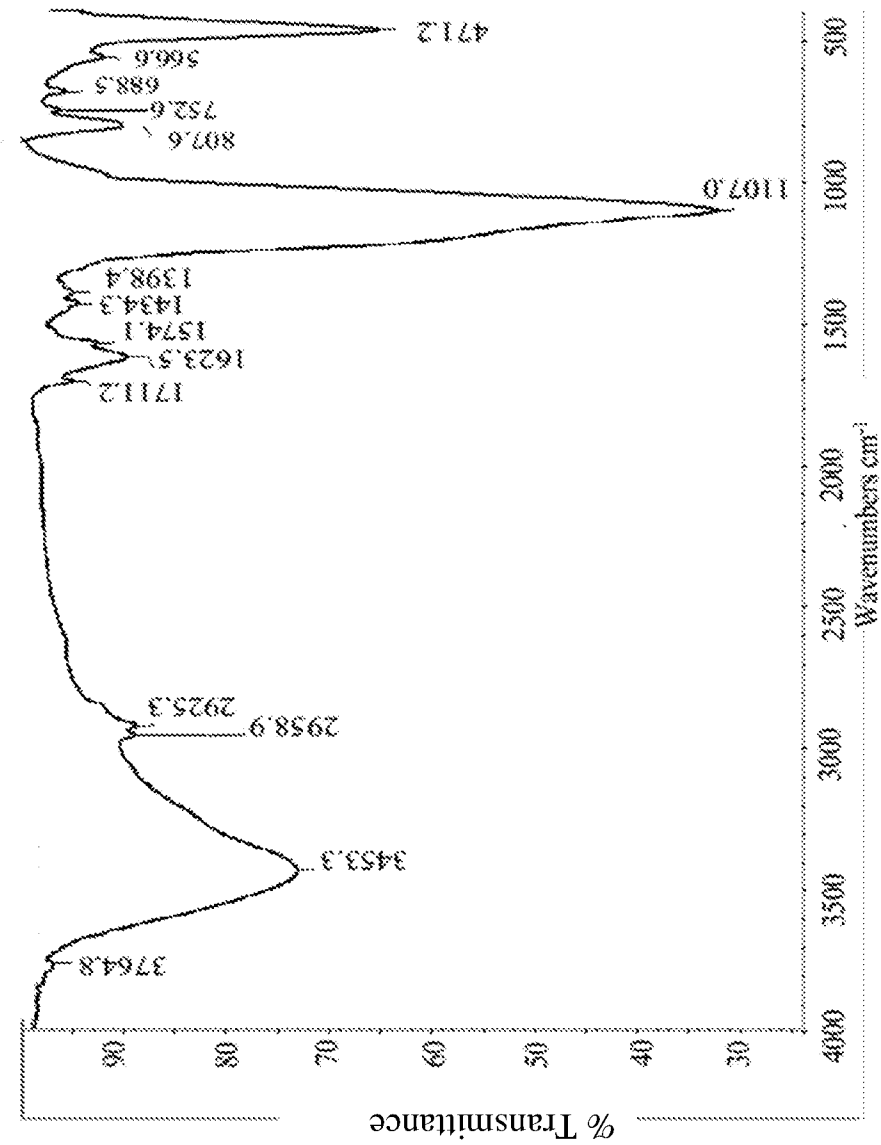


FIGURE 3

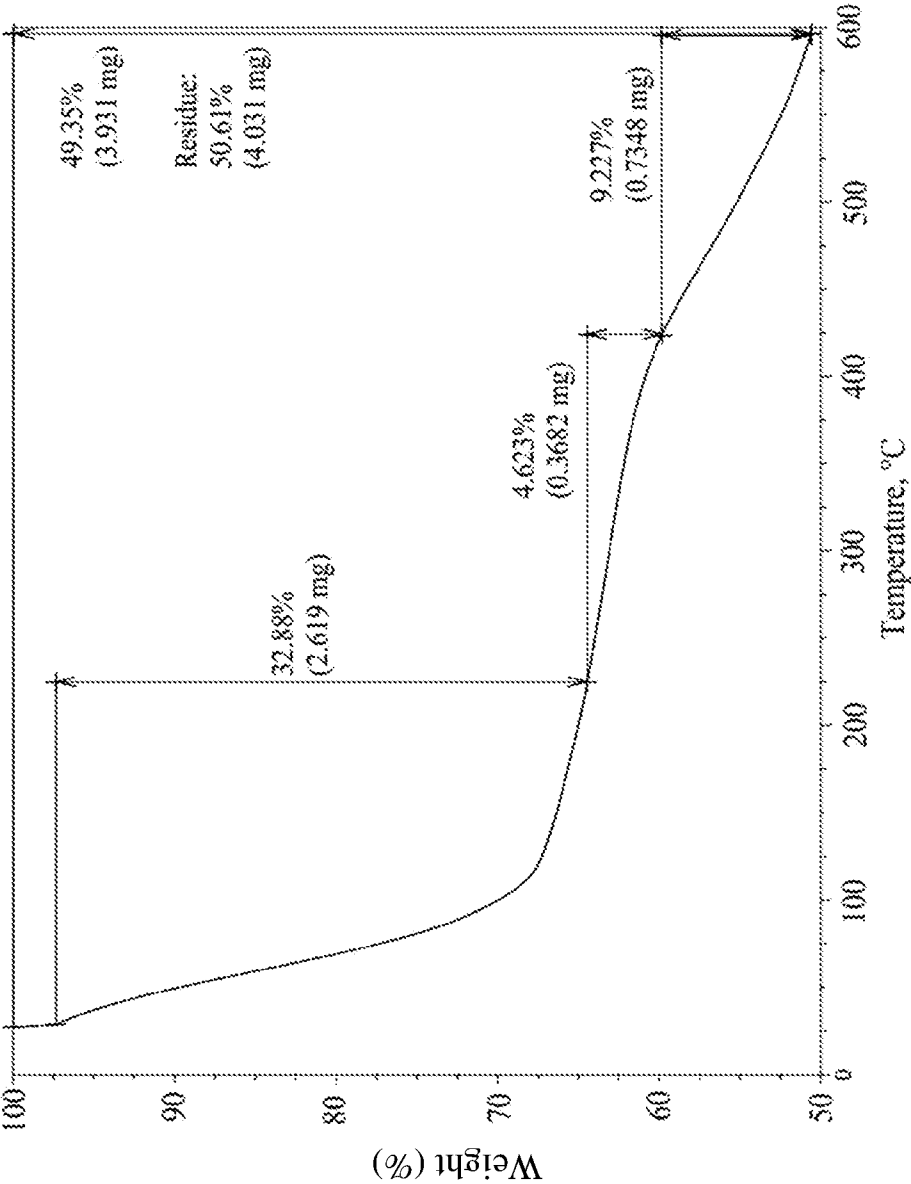


FIGURE 4

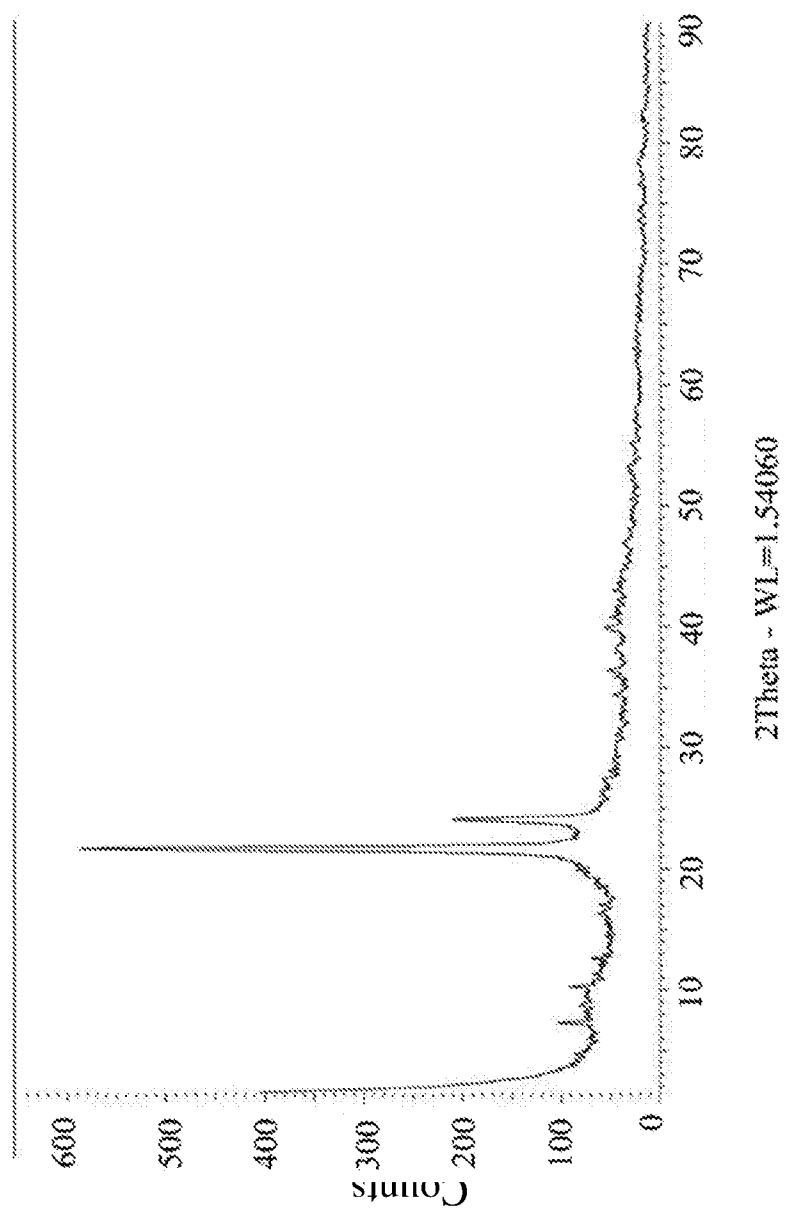


FIGURE 5

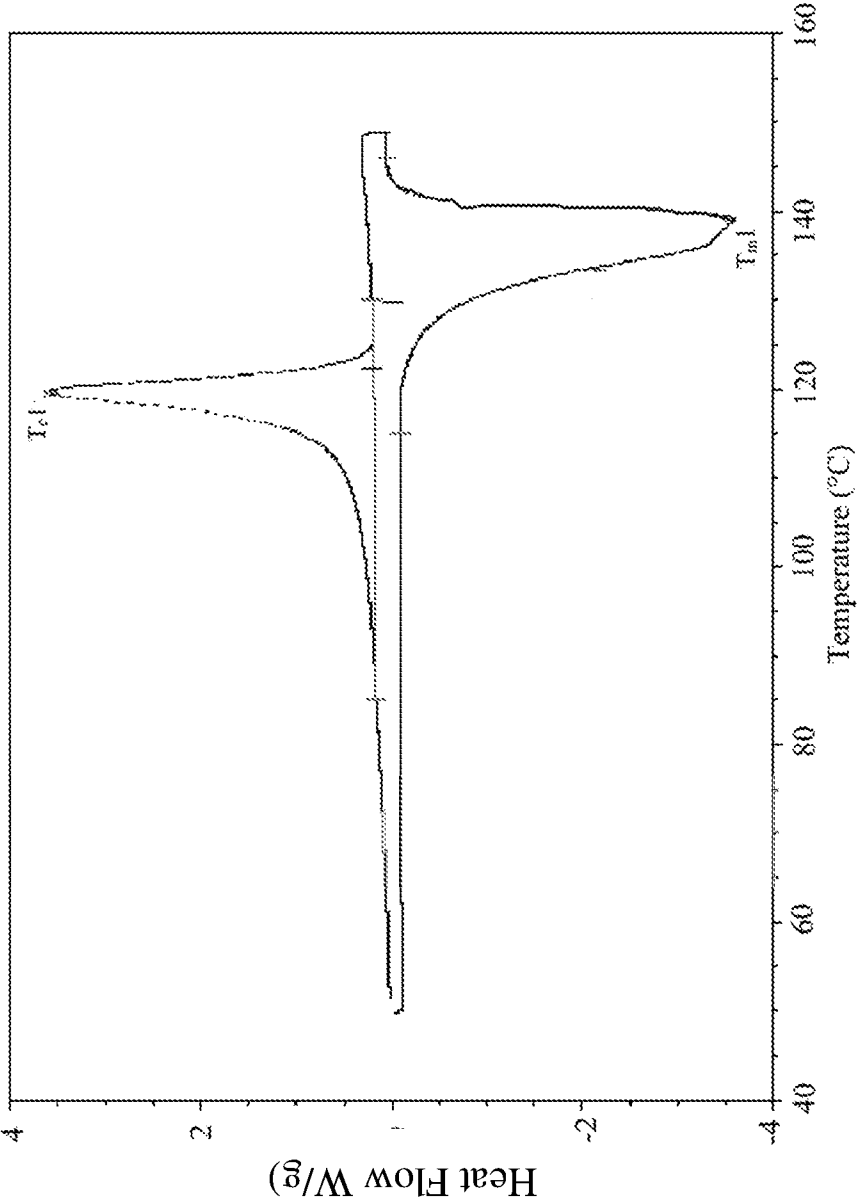


FIGURE 6

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/IB2015/055276

A. CLASSIFICATION OF SUBJECT MATTER  
C08F4/52, C08F4/76, C08F10/00 Version=2015.01

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Patseer, STN, IPO Internal Database.

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                   | Relevant to claim No. |
|-----------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| Y         | US 6875718 B2 (Fujita et al.) Published on, 05 April, 2005. (abstract, page 6, line 3-67; page 7, line 1-67; examples 1-3 & 66; figures 1 & 2(A); claim 1)                                                                                                                           | 1-13                  |
| Y         | WO 2013118140 A2 (Sarma et al.) Published on, 15 August, 2013. (abstract, example 1.1, claim 1-15)                                                                                                                                                                                   | 1-13                  |
| Y         | Design and Use of Nanostructured Single-Site Heterogeneous Catalysts for the Selective Transformation of Fine Chemicals (Dal Santo et al.) Molecules 2010, 15, 3829-3856; DOI:10.3390, ISSN 1420-3049, Published on 26 May 2010. (abstract, pages 3832, 3841 & 3842; figures 1 & 9,) | 1-9                   |

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

|                                                                                                                                                                         |                                                                                                                                                                                                                                                  |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| * Special categories of cited documents:                                                                                                                                | "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention                                              |
| "A" document defining the general state of the art which is not considered to be of particular relevance                                                                |                                                                                                                                                                                                                                                  |
| "E" earlier application or patent but published on or after the international filing date                                                                               | "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone                                                                     |
| "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) | "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art |
| "O" document referring to an oral disclosure, use, exhibition or other means                                                                                            |                                                                                                                                                                                                                                                  |
| "P" document published prior to the international filing date but later than the priority date claimed                                                                  | "&" document member of the same patent family                                                                                                                                                                                                    |

Date of the actual completion of the international search

03-12-2015

Date of mailing of the international search report

03-12-2015

Name and mailing address of the ISA/

Indian Patent Office  
Plot No.32, Sector 14, Dwarka, New Delhi-110075  
Facsimile No.

Authorized officer

Sathish Moorthy

Telephone No. +91-1125300200

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.  
PCT/IB2015/055276

| Citation         | Pub.Date   | Family            | Pub.Date   |
|------------------|------------|-------------------|------------|
| US 6875718 B2    | 05-04-2005 | CN 1199052 A      | 18-11-1998 |
|                  |            | EP 0874005 A1     | 28-10-1998 |
| WO 2013118140 A2 | 15-08-2013 | CN CN104334590 A  | 04-02-2015 |
|                  |            | EP 2812362 A2     | 17-12-2014 |
|                  |            | US 20150005461 A1 | 01-01-2015 |