



## Preparation of Polyethylene Nano-fibres Using Rod-like MCM-41/TiCl<sub>4</sub>/MgCl<sub>2</sub>/THF Bi-supported Ziegler-Natta Catalytic System

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### ABSTRACT

One of the known groups of mesoporous materials is MCM-41 that has been extensively used as support for different types of catalysts. In the present work, rod-like MCM-41 was synthesized to support TiCl<sub>4</sub>/MgCl<sub>2</sub>/THF catalyst to form the bi-supported rod-like-MCM-41/TiCl<sub>4</sub>/MgCl<sub>2</sub>/THF catalytic system. Then, ethylene polymerization was performed by this synthesized catalytic system under 8 bar ethylene pressure. The formation of rod-like semi-crystalline mesoporous MCM-41 with relatively high surface area (~972 m<sup>2</sup>/g) was confirmed by SEM, XRD, and BET studies. FTIR spectroscopy was used to confirm the omission of the organic template and water from the synthesized MCM-41. Investigating the specific surface area of the prepared catalyst by BET analysis showed that after loading the catalyst on MCM-41 support, the surface area is reduced considerably and it is reached a value of approximately 486 m<sup>2</sup>/g. XRD, SEM, and DSC analyses revealed that the synthesized PE samples contained nano-fibres as their main morphological units. SEM analysis showed the formation of dense polyethylene fibres with nanometer sized diameters and lengths of about 1 to more than 20 micrometers. DSC analysis showed the high melting point of 144°C for the synthesized PE samples and their crystal structure was assigned to be orthorhombic by XRD investigations. Finally a relatively high activity of 11×10<sup>4</sup> g PE/mol Ti.h was obtained for the catalytic system.

### Key Words:

MCM-41/TiCl<sub>4</sub>/MgCl<sub>2</sub>/THF;  
bi-supported;  
ethylene polymerization;  
Ziegler-Natta;  
polyethylene nano-fibres.

### INTRODUCTION

Periodic mesoporous MCM-41 (Mobile Composition of Matter Number 41 [1]) has regular cylindrical/hexagonal mesopores with a simple geometry, tailored pore size, and reproducible surface properties. It is widely used as adsorbent, ion exchanger, and support [2]. Different methods have been used to synthesize these types of materials. In majority of these methods the cationic surfactant cetyltrimethylammonium (CTA) has been used as the

structure-directing agent (template) [3-6] and tetraethylorthosilicate (TEOS) [7-11], fumed silica (FS) [9,12], sodium silicate (Na<sub>2</sub>SiO<sub>3</sub>) [13], or ethyl silicate (ES) [14] have been used as the sources of silica. To remove the organic template, usually the simplest way is the calcination process [12-16]. Furthermore, it is noteworthy that in the industrial scale production of these materials, some foam reducing agents are also used to facilitate autoclaves charging and

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processing enhancement [17].

One of the recent interesting applications of MCM-41 is using as the support for different types of catalysts in ethylene polymerization to produce polyethylene nano-fibres [1,18-22]. For the first time in 1999 Aida et al. showed that crystalline nano-fibres of linear polyethylene with an ultra-high molecular weight (6,200,000 g/mol) and a diameter of 30 to 50 nm can be formed by polymerization of ethylene with titanocene catalyst supported on mesoporous silica fibre (MSF) with methylaluminoxane as cocatalyst. Small angle X-ray scattering showed that the polyethylene fibres consist predominantly of extended chain crystals. This observation indicated a potential utility of the honey-comb-like mesoporous framework as an extruder for nanofabrication of polymeric materials [18]. After this exceptional observation, many scientific groups developed this novel field using rod-like MCM-41 as the support of different catalysts. Ye et al. used metallocene catalyst ( $Cp_2TiCl_2$ ) and studied the morphological and mechanical properties of the produced fibres extensively [1]. In another work, PE nano-fibres were prepared under atmospheric pressure using metallocene catalyst [19]. The effect of polymerization temperature on the formation of nano-fibres was investigated by Dong et al. using  $Cp_2ZrCl_2$  as the catalyst [20]. Also the effect of  $\beta$ -cyclodextrin on the formation of nanofibres was studied using  $TiCl_4$ /MCM-41 catalytic system [21].

Recently, a novel MCM-41/ $MgCl_2$ / $TiCl_4$  catalyst is proposed by Semsarzadeh et al. [22] to produce polyethylene nano-fibres under atmospheric ethylene gas pressure. They optimized the Mg/Ti molar ratio and their findings show that the highest activities can be obtained when this molar ratio is equal to 2.

In another research Jiamwjitkul et al. investigated the effect of boron modification of the MCM-41 support on the results of LLDPE synthesis using dMMAO/zirconocene catalyst. They found that upon modification of MCM-41 by boron the catalyst activity is enhanced, MW increases, and a narrower MWD is obtained [23]. dMMAO stands for the dried and modified methylaluminoxane which is more soluble than MAO in a hydrocarbon such as *n*-heptane.

Wang et al. investigated this field from another

point of view. They considered the synthesized PE as surface modifier of MCM-41 and used this surface modified inorganic filler in melt blending with a commercial PE sample. They observed a significant enhancement in the mechanical properties of the sample in comparison with other simple PE/MCM-41 composites. Therefore, they concluded that the in situ polymerized PE in the pores and on the surface of MCM-41 plays an important role, as an interfacial modifier, in the melt blended samples [24].

As it is mentioned by our other researches [25-27]  $MgCl_2$  is known as a preferred support for highly efficient Z-N catalysts for polymerization of olefins. Since, this support does not result in good polymer morphology it is often used along with other supports especially silica to obtain bi-supported catalysts which results in good morphology together with acceptable efficiencies [26,28].

In another research by Hakim et al., the Mg/Ti molar ratio of 2 was also obtained for  $SiO_2$ / $TiCl_4$ /THF/ $MgCl_2$  catalytic system under high ethylene concentration [26]. In these types of Ziegler-Natta catalytic systems,  $MgCl_2$  helps the catalyst to provide a high polymerization activity while the siliceous support (such as spherical  $SiO_2$  or mesoporous MCM-41) controls the product morphology.

In the present work, the optimized bi-supported MCM-41/ $TiCl_4$ / $MgCl_2$ /THF catalytic system is used to produce in-situ polyethylene nano-fibres under 8 bar ethylene pressure to investigate the effect of the gas pressure (monomer concentration) on the produced fibres properties. The findings show that the high concentration of ethylene monomer used in the polymerization process can be considered as one of the main reasons of producing considerably long fibres with high density. In addition, the polymerization conditions used are very close to industrial conditions. The catalytic system also provided a high degree of conversion in comparison with mono-supported heterogenized Z-N catalysts.

## EXPERIMENTAL

### Materials

The chemicals including TEOS, CTMABr, ammonia

(25 wt%), anhydrous magnesium chloride ( $\text{MgCl}_2$ ), tetrahydrofuran (THF) and titanium tetrachloride ( $\text{TiCl}_4$ ) were purchased from Merck. Triethyl-aluminium (TEA) was supplied by Aldrich and polymerization grade ethylene gas and *n*-hexane were provided from Arak Petrochemical Co., Iran and  $\text{N}_2$  gas (purity: 99.9%) was obtained from Roham Co., Iran. All the solvents (THF, *n*-hexane) were completely dry and all the manipulations involving air and/or water sensitive compounds were performed under  $\text{N}_2$  atmosphere using dry box.

### MCM-41 Synthesis

A sample of CTMABr (1.36 g) was dissolved in 76 g of deionized water under constant stirring speed (magnetic stirrer, 500 rpm) in a 250 mL flask at room temperature. A portion of 10.9 g of aqueous ammonia (25 wt%) was added to this solution and stirred for 10 min. At last 6.67 g of TEOS was added dropwise with vigorous stirring to obtain the final gel of composition of  $\text{SiO}_2$ : 1, CTMABr: 0.12,  $\text{NH}_4\text{OH}$ : 2.5, and  $\text{H}_2\text{O}$ : 150. The stirring was continued for 2 h [5]. The resultant solution was transferred into a 100 mL Teflon-lined bomb and aged for a week at  $105^\circ\text{C}$  in a hot box. The product (white precipitate) was recovered by filtration, washed thoroughly with distilled water and methanol and dried at  $100^\circ\text{C}$  overnight. Removal of the template was accomplished by calcination in air at  $540^\circ\text{C}$  for 6 h followed by cooling to room temperature under  $\text{N}_2$  gas flow [10].

### Synthesis of MCM-41 Supported Catalyst

In a 500-mL flask, 1 g (0.0151 mol) of anhydrous  $\text{MgCl}_2$  was completely dissolved in 50 mL of dry THF under constant stirring speed (500 rpm) at  $60^\circ\text{C}$  under nitrogen atmosphere. After complete dissolution, 0.5 mL (0.0045 mol)  $\text{TiCl}_4$  was injected into the solution to give a yellowish solution. After siphoning of the solvent and drying at  $60^\circ\text{C}$ , a yellowish powder was gained. The detailed procedure is published elsewhere [22,26]. Then, 1 g of the product was mixed with 4 g of MCM-41 in 50 mL of *n*-hexane. This solution was transferred to a special glass reactor for catalyst synthesis. The solution was allowed to be stirred (by glass stirrer). After 1 h, 2 mL TEA (1 molar in *n*-hexane) was added to the solution

which turned its colour from yellow to brown. The stirring was continued over night at  $60^\circ\text{C}$  under nitrogen atmosphere. Then the solvent was siphoned and the brownish product was dried at  $60^\circ\text{C}$  under the flow of nitrogen gas. The product was transferred to a dry box.

### Preparation of Polyethylene Nano-fibres

Polyethylene nano-fibres were prepared using the MCM-41/ $\text{TiCl}_4$ / $\text{MgCl}_2$ /THF catalytic system in a 1 L Buchi reactor. Slurry polymerization of ethylene (in *n*-hexane) was carried out at constant high ethylene pressure (8 bar) and  $70^\circ\text{C}$ . Polymerization was performed for 1 h while the stirrer speed was set at 800 rpm. The detailed procedure can be found elsewhere [26].

### Characterization of MCM-41, Catalyst, and Polyethylene Nano-fibres

X-Ray diffraction data were recorded between  $2\theta = 0^\circ$ - $25^\circ$  for MCM-41 samples on a Philips Analytical (Germany) using  $\text{CuK}\alpha$  radiation of wavelength 0.154056 nm and between  $2\theta = 10^\circ$  -  $30^\circ$  for polyethylene samples on a Siemens D5000 (Germany) using  $\text{CuK}\alpha$  radiation of the same wavelength.

BET analysis was carried out on a CHEMBET 3000 Quantachrome TPRWin v1.0 (USA) to achieve the specific surface areas of the supports and catalysts. The cell of the instrument was filled with adequate amount of sample (7 mg) under nitrogen atmosphere in a dry box.

To investigate the omission of the organic template and the presence of surface hydroxyl groups of MCM-41 samples, IR analysis was carried out by a FTIR Bruker 55- EQUINOX (Germany). The samples were prepared as KBr pellets.

To achieve melting points of the PE samples and also their degree of crystallinity, differential scanning calorimetric analysis was carried out on a DSC-NEUZSCH 200 F3 (Germany). The rate of heating and cooling of the samples were identical and equal to  $10^\circ\text{C}/\text{min}$ .

Finally the morphologies of MCM-41 and polyethylene nano-fibre samples were observed by a scanning electron microscope (VEGA EMITECH K450X, Czech Republic) after sputtering the samples with gold for 2 min.

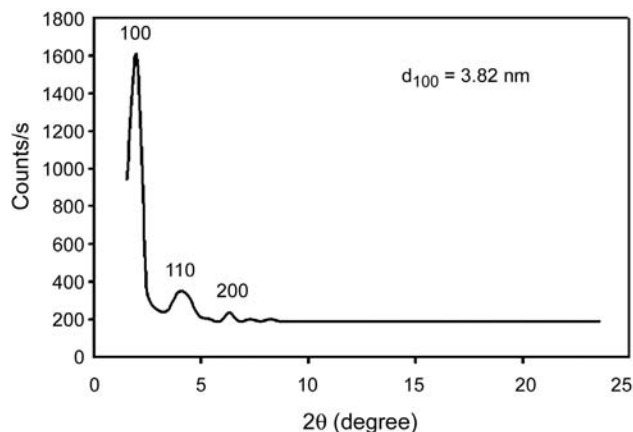


Figure 1. XRD pattern of MCM-41 before calcination.

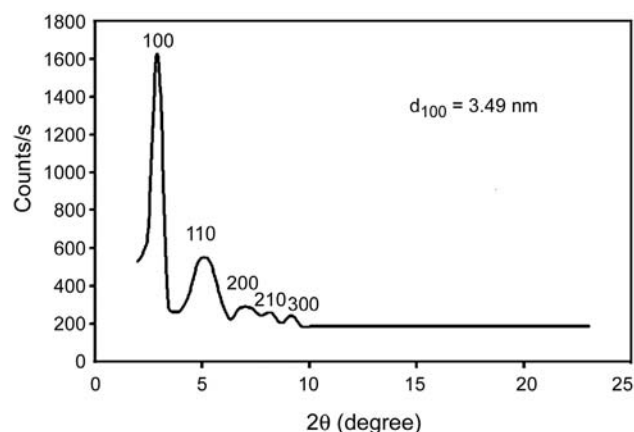


Figure 2. XRD pattern of MCM-41 after calcination [10].

## RESULTS AND DISCUSSION

Typical X-ray diffraction patterns of MCM-41 usually show four Bragg peaks indicating the long range order present in this material [11]. The repeating distance  $a_0$  between two pore centres can be calculated by  $a_0 = (2/\sqrt{3})d_{100}$  [11,17]. Then, the pore diameter can be achieved from this value by subtracting 1.0 nm which is an approximate value for the pore wall thickness [11] (in some reports [19,21] this value is calculated as  $\sim 0.92$  nm).

The XRD patterns of the synthesized samples are shown in Figures 1 and 2. It is clear that when the samples are calcined, the peaks become sharper, and samples' intraplanar distances ( $d_{100}$ ) are reduced. Also, the peaks shift towards higher  $2\theta$  degrees (in accordance with bragg equation  $n\lambda = 2d \sin\theta$ ) shows shrinkage in these porous structures. As it may be observed in Figure 2, even a fifth peak is obtained which is indicative of a very ordered system. The pore diameter of the sample is achieved using  $d_{100}$  value (Table 1).

Table 1. Different parameters of the prepared MCM-41 and catalyst.

Material	$d_{100}$ (nm)	$a_0$ (nm)	Pore diameter XRD $\approx a_0 - 1.0$ (nm)	Specific surface area ( $m^2/g$ )
MCM-41	3.49	4.03	3.03	972.5
Catalyst	-	-	-	486.2

X-ray diffraction analysis of the synthesized polyethylene sample (Figure 3) shows a pattern indicative of extended chain crystals [1]. The amorphous halo around 19.4 is very small, indicative of existence of amorphous regions [20].

BET analysis showed very high surface areas for the synthesized MCM-41. As it is clear from Table 1 after loading the catalyst on MCM-41, its surface area has been considerably reduced. The probable causes of this phenomenon are: first, during the preparation of the catalyst some parts of MCM-41 structure may be destroyed due to applied mechanical force of the stirrer. Second, after loading the catalyst on MCM-41 the radius of its pores becomes smaller leading to the reduction of the specific surface area and third, some of the channels may be filled or blocked by the catalyst.

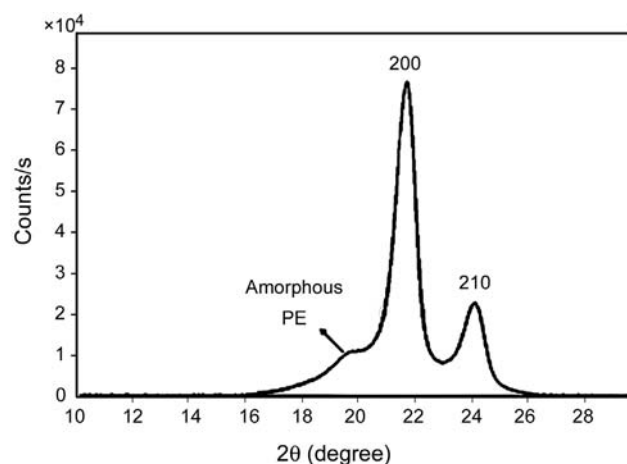


Figure 3. XRD pattern of the synthesized PE sample.

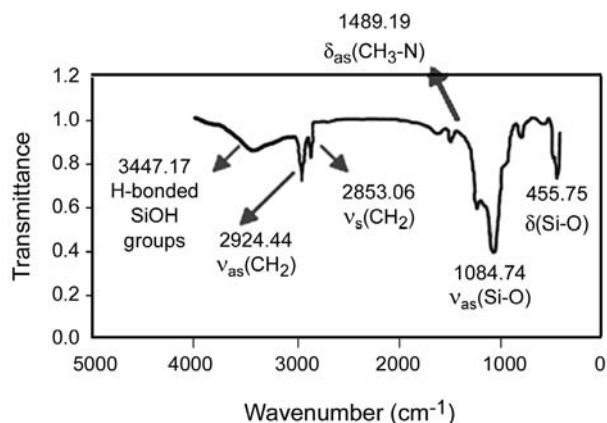


Figure 4. FTIR spectrum of MCM-41 before calcination [10].

FTIR spectra of synthesized MCM-41s before and after calcination are shown in Figures 4 and 5, respectively. As it is indicated in Figure 5, after calcination of the samples, the peaks corresponding to the template structure of 1489  $\text{cm}^{-1}$ , 2853  $\text{cm}^{-1}$ , and 2924  $\text{cm}^{-1}$  [12] have disappeared, which confirm the complete decomposition and removal of the template to verify the calcinations conditions.

Furthermore, a new peak at 3741  $\text{cm}^{-1}$  has appeared which corresponds to free -OH groups on the catalyst surface. This peak is masked and cannot be observed in Figure 4, due to the high intensity of the peak corresponding to H-bonded SiOH, epoxy groups, and also adsorbed water. After calcination, the intensity of this peak is reduced and the peak corresponding to the free OH groups is observed clearly [27]. Therefore, it can be concluded that due to calcination, in addition to disappearance of the template, an agent, such as water that may deactivate the Z-N catalyst is removed. The decomposition of the template occurs through the following Hoffmann elimination reaction [29]:



Table 2. Melting points and degrees of crystallinity based on DSC curves.

$T_m$ (°C)		$\Delta H_m$ (J/g)		Crystallinity <sup>a</sup> (based on first scan) (%)
First scan	Second scan	First scan	Second scan	
144	140	176	154	61

<sup>(a)</sup> crystallinity =  $\Delta H_m / \Delta H_m(100\% \text{ crystalline polyethylene})$  [29].

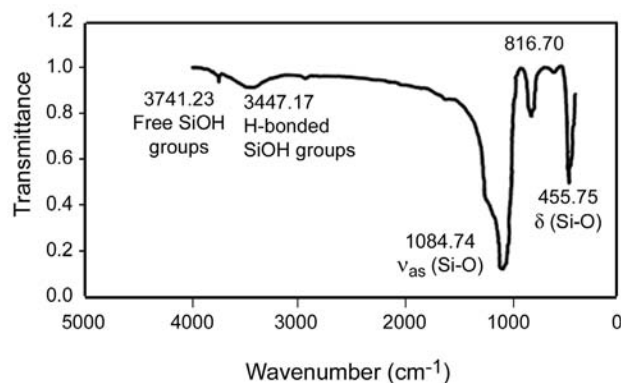
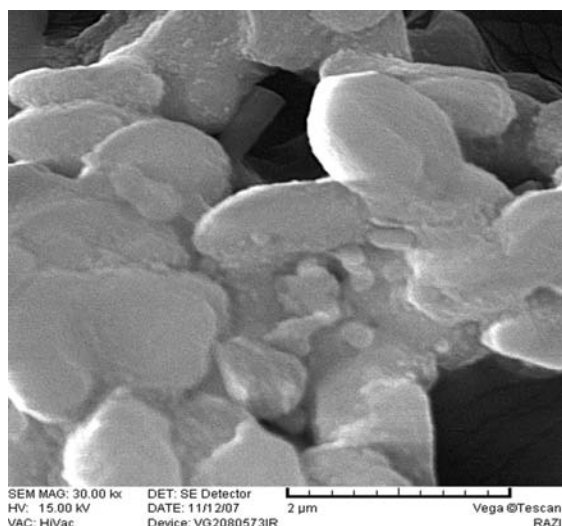


Figure 5. FTIR spectrum of MCM-41 after calcination [10].

DSC analysis of the synthesized polyethylene samples (Table 2) reveals that the melting point of the synthesized sample is relatively higher than the common melting points of polyethylene (120-130°C). This can be attributed to the control of channels by the arrangement of PE chains. The lamellar thickness of the PE folded chain crystals (27.0 nm) [20] is larger than the pore diameter of MCM-41 (3.03 nm in Table 1). Therefore, the chains cannot fold and as a result they form extended chain crystals which are considerably larger than the common PE crystals. Also, the degrees of crystallinity of the samples reported in Table 1 are calculated from DSC data [30].

Figure 6 shows the SEM image of the synthesized MCM-41. This observation confirms the formation of rod-like MCM-41. SEM images of synthesized polyethylene are shown in Figure 7. The formation of considerably long PE fibres along with floccules is obvious in these images and the main morphological units of the samples are nano-fibres rather than floccules. It is also verified that the mesoporous structure of the support has been preserved during the different stages of the work. The catalytic sites, located on the exterior surface of MCM-41 particles



**Figure 6.** SEM micrograph of rod-like MCM-41.

and encountered no restriction in the production of polyethylene are responsible for the formation of the floccules. In contrast, the active sites located in the interior surfaces of nanochannels in MCM-41 particles are responsible for the formation of the nanofibres. The detailed mechanisms for the formation of floccules and nano-fibres are given in literature [31].

As it is indicated in Table 3 using the same catalytic system under atmospheric ethylene pressure, fibres with the length of 1 to 6 micrometers are produced [22], whereas in the present work the lengths of the fibres range from 1 to more than 20 micrometer. Moreover, a close inspection of the images in Figure 7 clarifies that the density of the

produced fibres is higher, as well. It can be said that as higher pressure of ethylene gas (8 bar) is used in this work, the fibres grow longer and more catalytic sites have been activated at the same time. A similar trend may also be observed for the metallocene catalysts (Table 3). A comparison between the metallocene catalysts and Z-N types also show the effect of activity of the catalysts on the length of the fibres. Since the metallocenes are more active than the Z-N types, their produced fibres are much longer and denser. Furthermore, it can be concluded from the Figures 7a and 7b, that the fibres have cross-sections (or thicknesses) in the range of nano-scale. It can be said that the regular nanochannels present in the catalyst support have driven the PE chains to be configured in the form of fibres.

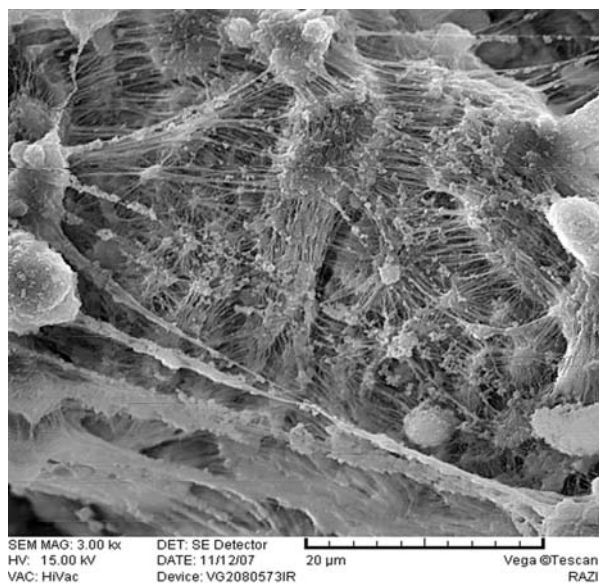
Putting together all the information gathered from XRD, DSC, and SEM investigations of PE samples it may be suggested that the synthesized samples have the same crystal structure as common PE polymers, except that the *c* dimension of these crystals has a very large value. As a result, these considerably larger crystals result at higher temperature as they have higher melting point.

Finally the synthesized catalytic system shows the activity of  $11 \times 10^4$  g PE/mol Ti.h using TEA/Ti = 20 molar ratio, polymerization temperature of 70°C, and ethylene pressure of 8 bar which is an acceptable value in comparison with other activities mentioned by other researchers (Table 3) [1,19-22]. This relatively high activity can be attributed to the presence of MgCl<sub>2</sub> in the structure of the catalyst

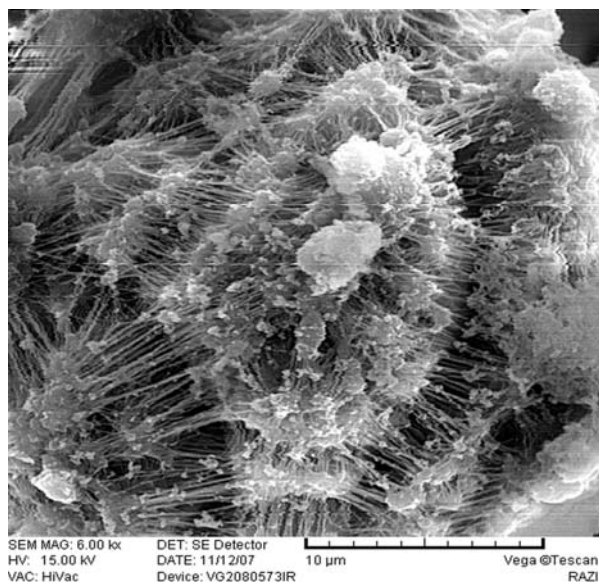
**Table 3.** A comparison of polyethylene polymerization results obtained from different catalytic systems under various pressure conditions.

Catalyst	Cp <sub>2</sub> TiCl <sub>2</sub>	Cp <sub>2</sub> ZrCl <sub>2</sub>	Cp <sub>2</sub> ZrCl <sub>2</sub>	TiCl <sub>4</sub>	TiCl <sub>4</sub> /MgCl <sub>2</sub>	TiCl <sub>4</sub> /MgCl <sub>2</sub>
Cocatalyst	MAO	MAO	MAO	TEA	TEA	TEA
Al/M molar ratio	2000	2000	2000	20	30	20
Pressure (atm)	20	1	1	1	1	7.9
Temperature(°C)	85	50	70	30	50	70
Activity kg PE/mol Ti.h	1262	500	1740	19.3	47.4	111
Length of fibres* (µm)	> 250	> 20	Cannot be estimated	≈ 2	<1 to >6	<1 to >20
T <sub>m</sub> (°C)	140	133	130.4	140.8	142.5	144
ΔH <sub>m</sub> (J/g)	240	Not reported	200.7	176.4	197.3	176
Reference	[1]	[19]	[20]	[21]	[22]	This work

(\*) Obtained from SEM micrographs



(a)



(b)

**Figure 7.** SEM micrographs of PE nano-fibres with magnifications of (a) 3000 $\times$  and (b) 6000 $\times$ .

together with the TEA pretreatment of the catalyst and also the high pressure of ethylene gas feed. As it is mentioned elsewhere [26] the pre-reduction stage results in an enhancement in the catalyst activity through gradual reduction of Ti(IV) into more active Ti(III) species. Furthermore, TEA molecules have replaced some of the coordinated THF molecules in the catalyst structure, thus more active sites have been

available for ethylene polymerization. In contrast, a pressure of 8 bar ethylene gas has provided higher monomer concentration in the polymerization media (*n*-hexane) and it has therefore enhanced their polymerization. In this way, greater productivity of the catalyst has been achieved.

## CONCLUSION

From the results obtained in this research it can be concluded that:

- Calcination causes the MCM-41 structures to shrink and become more ordered. The shrinkage seen in the intraplanar distance (confirmed by XRD analysis) is perhaps due to the disappearance of the template and adsorbed water molecules.

- Upon loading the catalyst on MCM-41 the surface area is being reduced considerably. The reduction in the internal radius of the cylinders due to the loaded catalyst and also the partial destruction of the structures and blocking of some of the channels may be considered as the reasons counted and discussed above.

- Achieving fibrous morphologies using MCM-41/TiCl<sub>4</sub>/MgCl<sub>2</sub>/THF catalytic system under high monomer concentration (8 bar pressure) which is very close to industrial conditions is possible as confirmed by XRD, DSC, and SEM analyses. Perhaps the confining effect of regular cylindrical pores present in the catalyst support guided the PE chains to grow through this morphology.

- Since the PE chains continue their path straight forward over a long micrometer length scale, it can be said that the crystal sizes of the synthesized samples are larger than common PEs and therefore their melting points would be increased considerably.

- Due to the high ethylene concentration (8 bar pressure) used in this work the produced fibres are considerably long and dense.

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