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TiCl₄/MgCl₂/MCM-41 Bi-Supported Ziegler–Natta Catalyst: Effects of Catalyst Composition on Ethylene/1-Hexene Copolymerization

Xiaoyu Liu 1,†, Wenqi Guo 1,‡, Xueer Wang 1, Yintian Guo 2,3, Biao Zhang 4, Zhisheng Fu 1, Qi Wang 1 and Zhiqiang Fan 1,*

1. Introduction

Polyethylene (PE) is a general-purpose synthetic resin with the largest production volume (about 100 million tons per annum) among synthetic polymers. Among the three major PE categories (low density polyethylene, high density polyethylene, linear low density polyethylene), high density polyethylene (HDPE) and linear low density polyethylene (LLDPE) are produced by the catalytic copolymerization of ethylene with C₄~C₈ α-olefins. TiCl₄/MgCl₂ (single support) and TiCl₄/MgCl₂/SiO₂ (bi-support) type heterogeneous Ziegler–Natta (Z-N) catalysts play major roles in the production of HDPE and LLDPE [1,2]. Though these Z-N catalysts show excellent performance in large-scale industrial production for their high activity and satisfactory control over the polymer particle morphology, their PE products have rather broad chemical composition distribution (CCD) because of the presence of multiple active sites [3–5]. Because the α-olefin comonomer is highly enriched in fractions of low molecular mass [4–6], HDPE and LLDPE produced with Z-N catalysts show poorer mechanical properties than PE produced with single-site catalysts like metallocenes [7–9]. It is seen that the broad CCD of Z-N based PE resins needs to
be improved. In the past two decades, many efforts have been devoted to improving the ethylene-α-olefin copolymerization performance of Z-N catalysts [10–17]. However, improvements in ethylene copolymer’s CCD were not satisfactory in many of these efforts.

In the last decades, mesoporous inorganic materials (e.g., MCM-41, SBA-15, AAO) with uniform pore size and very large surface area were used as a support of metallocene or other organometallic catalysts and tested for catalytic ethylene polymerization [18–26] and ethylene-α-olefin copolymerization [26–35]. In comparison with homogeneous catalysts, metallocene catalysts immobilized on mesoporous supports show a serious of unique performances, like producing PE with nanofibrous morphology [18,21] and special mechanical properties [20,25]. The space confinement effects of mesoporous support on the active sites were considered as the main reason for the unique performances. Similar concept has been extended to developing MgCl2-supported Z-N catalysts. Semsarzadeh et al. [36] prepared two kinds of bi-supported Z-N catalysts, TiCl4/MgCl2/MCM-41 and TiCl4/MgCl2/SiO2, and found that the catalyst containing MCM-41 showed higher activity than the one with SiO2 in catalyzing ethylene polymerization. Similar ethylene polymerization behaviors of bi-supported catalysts containing a mesoporous support are reported by other researchers [37–40]. To the best of our knowledge, ethylene-α-olefin copolymerization with TiCl4/MgCl2/MCM-41 type bi-supported Z-N catalysts has not been reported in open-published journals.

In the literature on ethylene-α-olefin copolymerization with metallocene immobilized on mesoporous supports, strong effects of support pore size on the copolymerization activity, α-olefin incorporation rate, and copolymer’s CCD were reported [28–34]. Large-pored catalysts were found to exhibit higher 1-hexene incorporation rates [29]. However, the effects of mesoporous support on ethylene-α-olefin copolymerization with TiCl4/MgCl2/MCM-41 type bi-supported Z-N catalysts are still unclear. In this work, MCM-4/MgCl2 bi-supported Z-N catalysts with different MCM-4/MgCl2 mass ratios were prepared by adsorbing TiCl4 onto MgCl2 crystallites that are anchored in nanochannels of MCM-41. These catalysts were used for catalyzing ethylene-1-hexene copolymerization under different ethylene pressure and ethylene/1-hexene feed ratios. Significant effects of the MCM-41 support on the catalytic activities and chain structure of the ethylene-1-hexene copolymers were observed, which are beneficial to the polymer performances.

2. Results and Discussions
2.1. Characterization of Supports and Catalysts

Five supported Ziegler-Natta catalysts were respectively prepared by anchoring TiCl4 on activated MgCl2, MCM-41 and MgCl2/MCM-41 composite supports with different composition. According to literature reports, impregnating MgCl2 in mesoporous silica like MCM-41 lead to anchoring of MgCl2 crystallites in nanopores of the silica, owing to strong interaction of MgCl2 with hydroxyl groups on inner walls of MCM-41 [38,41,42]. The MCM-41 mesoporous silica used to prepare the composite supports was calcinated at 500 °C to remove most of its hydroxyl groups on the outer surface. This can ensure that most MgCl2 in MgCl2/MCM-41 support is anchored in nanopores of MCM-41.

XRD analysis of the activated MgCl2 precipitated from THF solution and the MgCl2/MCM-41 bi-supports were first made and compared with XRD pattern of commercial anhydrous MgCl2 (see Figure 1). The commercial MgCl2 with α-phase and small surface area showed a strong peak at 2θ = 15°, which corresponds to the periodical stacking of Cl-Mg-Cl triple-layers, but this peak was absent in the activated MgCl2 and MgCl2/MCM-41 supports. The appearance of broad asymmetric peaks at 2θ = 35° and 2θ ≈ 50° in XRD of the activated MgCl2 and MgCl2/MCM-41 indicated that both of them contain δ-phase MgCl2 with small crystal size [43]. In the XRD pattern of MgCl2/MCM-41, the peaks appearing at 2θ = 3–6 in the XRD of pure MCM-41 were not observed, possibly attributable to the filling of MgCl2 in the meso-pores of MCM-41 (XRD pattern of calcinated MCM-41 can be seen in Figure S1).
Five supported catalysts were prepared by anchoring TiCl₄ on activated MgCl₂, pure MCM-41, and three MgCl₂/MCM-41 composites, respectively. Ti and Mg contents of these catalysts were determined, and the results are listed in Table 2, which shows that Ti content of the TiCl₄/MCM-41 catalyst (cat-2) was even higher that of the TiCl₄/MgCl₂ catalyst (cat-1), possibly owing to the much larger specific surface area of MCM-41 than the activated MgCl₂. TiCl₄ could react with hydroxyl groups inside the mesopores of MCM-41 to form -SiO-TiCl₃ type anchored Ti species [38]. With the decrease of MgCl₂/MCM-41 mass ratio of the support from 1/1 (cat-3) to 1/2 (cat-4) and 1/3 (cat-5), the Mg/Ti molar ratio of the corresponding catalyst also markedly decreased. It seems that when MgCl₂ occupies the internal surface of the mesopores in MCM-41, less TiCl₄ can be anchored on MCM-41 to form -SiO-TiCl₃ type species. The Mg/Ti molar ratio of cat-3 that has the highest MgCl₂/MCM-41 ratio was close to that of cat-1, which contains no MCM-41, meaning that most of the TiCl₄ in cat-3 is anchored on MgCl₂ crystallites. In cat-4 and cat-5 that have lower MgCl₂ contents, a significant part of TiCl₄ could be directly anchored on the surface of MCM-41.

Table 1. Specific surface area and pore parameters of supports

| Support          | Specific Surface Area (m²/g) | Pore Volume (cm³/g) | Average Pore Radius (nm) |
|------------------|------------------------------|---------------------|--------------------------|
| MgCl₂            | 159.6                        | 0.66                | 3.8                      |
| MCM-41           | 1021.7                       | 1.02                | 2.7                      |
| MM4              | 606.1                        | 0.88                | 2.7                      |
| MM5              | 697.7                        | 0.88                | 3.1                      |

*a Determined by BET method; MM4 and MM5 are MgCl₂/MCM-41 composite with m(MgCl₂)/m(MCM-41) (mass ratio) of 1/2 and 1/3, respectively.*
2.2. Polymerization Activity

The polymerization of ethylene and copolymerization of ethylene/1-hexene with the prepared catalysts were conducted under 1 bar and 4 bar ethylene pressure, respectively. For (co)polymerization under 1 bar, the activity of cat-2 (TiCl₄/MCM-41 mono-supported catalyst) was only 2–10% of that of cat-1 (TiCl₄/MgCl₂ mono-supported catalyst, see Table 3). Similar phenomena have been reported in literatures dealing with similar catalysts [36,37]. It means that MgCl₂ plays an essential role in enhancing polymerization activity of supported Z-N catalyst [44]. The catalysts containing MgCl₂ (cat-1, cat-3, cat-4, and cat-5) showed similar activity at 1 bar ethylene pressure, and the activity evidently increased with increase of 1-hexene concentration. Under 4 bar ethylene pressure, the ethylene/1-hexene copolymerization activity was about 10 times higher than that conducted under 1 bar, while the activity of the MgCl₂/MCM-41 bi-supported catalysts became higher than that of the MgCl₂-supported catalyst (see Figure 2 and Table 3). It is interesting that the activity of the bi-supported catalysts increased with decrease of MgCl₂/MCM-41 ratio (the only exception was the higher activity of cat-4 than cat-5 at [H] = 0.6 mol/L). Explanations on this phenomenon will be given after analyzing chemical structure and particle morphology of the polymerization products.

![Figure 2. Copolymerization activities of cat-1, cat-3, cat-4 and cat-5 under 1 bar and 4 bar ethylene pressure.](image-url)
Table 3. Results of ethylene/1-hexene copolymerization with different Ziegler-Natta catalysts under different ethylene pressure a.

| Entry | Catalyst | Pressure (Bar) | [H] (mol/L) | Activity (kgPE/(gTi·h)) | Mw c (kg/mol) | D c | Tm d (°C) | ∆Hm d (J/g) |
|-------|----------|----------------|-------------|--------------------------|---------------|-----|-----------|-------------|
| 1     | cat-1    | 1              | 0           | 1.47                     | 495           | 8.7 | 133       | 168.4       |
| 2     | cat-1    | 1              | 0.2         | 3.37                     | 255           | 23.8| 124       | 94.5        |
| 3     | cat-1    | 1              | 0.4         | 3.86                     | 208           | 21.0| 123       | 58.4        |
| 4     | cat-1    | 1              | 0.6         | 4.04                     | 156           | 17.7| 123       | 42.5        |
| 5     | cat-2    | 1              | 0           | 0.15                     | –             | –   | 133       | 112.5       |
| 6     | cat-2    | 1              | 0.2         | 0.12                     | –             | –   | 130       | 84.5        |
| 7     | cat-2    | 1              | 0.4         | 0.10                     | –             | –   | 129       | 70.5        |
| 8     | cat-2    | 1              | 0.6         | 0.09                     | –             | –   | 129       | 70.1        |
| 9     | cat-3    | 1              | 0           | 2.39                     | 393           | 9.8 | 134       | 172.7       |
| 10    | cat-3    | 1              | 0.2         | 3.99                     | 167           | 15.2| 125       | 97.1        |
| 11    | cat-3    | 1              | 0.4         | 3.99                     | 166           | 24.1| 124       | 52.1        |
| 12    | cat-3    | 1              | 0.6         | 5.07                     | 138           | 18.7| 123       | 41.4        |
| 13    | cat-4    | 1              | 0           | 1.26                     | 455           | 10.5| 134       | 173.4       |
| 14    | cat-4    | 1              | 0.2         | 2.79                     | 231           | 23.1| 124       | 99.7        |
| 15    | cat-4    | 1              | 0.4         | 3.06                     | 184           | 18.6| 124       | 55.6        |
| 16    | cat-4    | 1              | 0.6         | 3.70                     | 130           | 17.1| 123       | 39.1        |
| 17    | cat-5    | 1              | 0           | 1.17                     | 569           | 9.3 | 133       | 167.5       |
| 18    | cat-5    | 1              | 0.2         | 2.55                     | 291           | 23.5| 124       | 100.5       |
| 19    | cat-5    | 1              | 0.4         | 2.77                     | 173           | 22.5| 123       | 62.8        |
| 20    | cat-5    | 1              | 0.6         | 2.85                     | 195           | 19.9| 123       | 43.0        |
| 21 b  | cat-1    | 4              | 0.2         | 13.58                    | 414           | 5.5 | 127       | 131.4       |
| 22    | cat-1    | 4              | 0.4         | 14.47                    | 287           | 8.9 | 124       | 114.6       |
| 23    | cat-1    | 4              | 0.6         | 14.01                    | 239           | 10.0| 123       | 97.2        |
| 24    | cat-3    | 4              | 0.2         | 21.18                    | 362           | 8.2 | 127       | 132.5       |
| 25    | cat-3    | 4              | 0.4         | 20.33                    | 295           | 10.7| 124       | 117.0       |
| 26    | cat-3    | 4              | 0.6         | 20.07                    | 274           | 9.1 | 123       | 98.0        |
| 27    | cat-4    | 4              | 0.2         | 30.34                    | 405           | 7.4 | 129       | 129.8       |
| 28    | cat-4    | 4              | 0.4         | 32.60                    | 372           | 11.1| 126       | 116.0       |
| 29    | cat-4    | 4              | 0.6         | 48.43                    | 310           | 8.9 | 124       | 113.4       |
| 30    | cat-5    | 4              | 0.2         | 30.27                    | 389           | 6.5 | 128       | 130.8       |
| 31    | cat-5    | 4              | 0.4         | 34.07                    | 417           | 7.9 | 127       | 120.9       |
| 32    | cat-5    | 4              | 0.6         | 34.47                    | 399           | 7.3 | 125       | 111.4       |

a Polymerization conditions: [Ti] = 6 × 10⁻⁴ mol/L; cocatalyst: Al(C₂H₅)₃; n(Al)/n(Ti) = 100; polymerization temperature: 60 °C; time = 30 min; n-heptane as solvent, [H] = initial 1-hexene concentration; b For polymerization runs under 4 bar ethylene pressure, [Ti] was reduced to 2 × 10⁻⁴ mol/L; c Weight-average molecular weight (Mw) and polydispersity index (D) determined by GPC; d Melting temperature (Tm) and melting enthalpy (∆Hm) of polymer determined by DSC.

2.3. Polymer Structure

All copolymer samples produced by cat-1, cat-3, cat-4, and cat-5 were extracted by boiling n-heptane to fractionate each of them into two parts: boiling n-heptane soluble fraction (C7-s) and insoluble fraction (C7-in). Each fraction was analyzed by FT-IR to determine its 1-hexene content, and the results are listed in Tables 4 and S1. As a general trend, the C7-s content of the copolymer increased with increase of 1-hexene concentration ([H]) under both 1 bar and 4 bar ethylene pressure (see Figure 3 and Table S1), similar to the phenomena observed in our previous studies [4,14,17]. C7-s of copolymer produced under 1 bar was higher than that formed under 4 bar at the same [H], since ethylene concentration was higher under higher pressure. For both the copolymerization runs, under 1 bar and 4 bar, C7-s content of copolymer catalyzed by the three bi-supported catalysts was lower than the MgCl₂-supported catalyst (the blank catalyst without MCM-41). The difference became more evident when the copolymers were produced under 4 bar. When cat-5 with the highest MCM-41 load was used as catalyst, the C7-s content of its copolymer formed at
[H] = 0.6 mol/L and 4 bar was only about 30% of the copolymer produced by cat-1 under the same conditions. In contrast, copolymers produced by cat-2 that has a much lower MCM-41 load contained a similar amount of C7-s fraction to those of cat-1.

**Table 4.** Boiling n-heptane extraction results of copolymer catalyzed by cat-1, cat-3, cat-4 and cat-5 under 4 bar.

| Entry | Catalyst | [H] (mol/L) | \(C_6^a\) (mol%) | Conversion (%) | C7-s | C7-in |
|-------|----------|-------------|-----------------|----------------|------|-------|
|       |          |             | Fraction (wt%) | \(C_6^a\) (mol%) | Fraction (wt%) | \(C_6^a\) (mol%) |
| 21    | cat-1    | 0.2         | 2.4             | 27.6           | 1.1  | -     | 98.9 | 2.4  |
| 22    | cat-1    | 0.4         | 2.1             | 13.3           | 10.0 | 6.9  | 90.0 | 1.6  |
| 23    | cat-1    | 0.6         | 3.6             | 14.7           | 27.1 | 8.2  | 72.9 | 2.1  |
| 24    | cat-3    | 0.2         | 0.9             | 16.6           | 3.5  | -     | 96.5 | 0.9  |
| 25    | cat-3    | 0.4         | 2.7             | 23.7           | 13.8 | 8.1  | 86.2 | 1.9  |
| 26    | cat-3    | 0.6         | 3.3             | 19.4           | 26.4 | 7.5  | 73.6 | 1.9  |
| 27    | cat-4    | 0.2         | 1.1             | 28.9           | 3.2  | -     | 96.8 | 1.1  |
| 28    | cat-4    | 0.4         | 2.4             | 34.0           | 10.5 | 10.0 | 89.5 | 1.6  |
| 29    | cat-4    | 0.6         | 3.2             | 45.4           | 14.5 | 9.5  | 85.5 | 2.3  |
| 30    | cat-5    | 0.2         | 1.1             | 28.9           | 2.6  | -     | 97.4 | 1.1  |
| 31    | cat-5    | 0.4         | 2.0             | 29.8           | 7.1  | 8.8  | 92.9 | 1.5  |
| 32    | cat-5    | 0.6         | 2.4             | 24.6           | 8.3  | 9.0  | 91.7 | 1.8  |

\(a\) 1-Hexene content of the whole copolymer determined by FTIR. \(b\) Conversion rate of 1-hexene.

![Figure 3](image1.png)

**Figure 3.** Change C7-s fraction weight of ethylene/1-hexene copolymer with initial 1-hexene concentration.

The 1-Hexene contents of the original copolymer samples and their fractions were determined, and the results are shown in Figures 4 and S2. It can be seen that the hexene content of the copolymer produced under 1 bar was slightly enhanced by introducing MCM-41 in the support, but less 1-hexene was incorporated in the copolymer produced under 4 bar when MCM-41 was introduced. The 1-Hexene contents of the C7-in fraction were hardly changed by MCM-41, but the 1-hexene content of the C7-s fraction slightly increased with increase of MCM-41 in the catalyst.
Figure 4. 1-Hexene content of copolymer fractions produced under 1 bar (a) and 4 bar (b).

Thermal analysis of the copolymer samples and their fractions was performed, which provided information regarding crystalline phases indirectly reflecting the chain structure of the copolymer. As shown in Tables 3, 5 and S2, the melting temperature and melting enthalpy of the copolymer tended to decrease with increase of 1-hexene concentration, since the incorporated 1-hexene units can interrupt the crystallization of polyethylene segments, leading to smaller crystalline phases and thinner crystalline lamellae. Introducing MCM-41 in the catalyst hardly influenced melting temperature, but the melting enthalpy of C7-s part decreased with a decreasing MgCl$_2$/MCM-41 ratio. This can be largely attributed to the higher 1-hexene content of C7-s part formed by the bi-supported catalysts, especially for C7-s formed under 4 bar. For the C7-in fractions, their melting enthalpy was only slightly influenced by the introduction of MCM-41. It seems that the active centers producing this part of the copolymer have the same catalytic features in both TiCl$_4$/MgCl$_2$ and TiCl$_4$/MgCl$_2$/MCM-41 catalysts.

Table 5. Thermal properties of copolymers and their fractions catalyzed by cat-1, cat-3, cat-4 and cat-5 under 4 bar.

| Entry | Catalyst | [H] (mol/L) | C7-s $T_m$ (°C) | \(\Delta H_m\) (J/g) | C7-in $T_m$ (°C) | \(\Delta H_m\) (J/g) |
|-------|----------|-------------|----------------|--------------------|----------------|--------------------|
| 21    | cat-1    | 0.2         | 114            | 104.3             | 127            | 132               |
| 22    | cat-1    | 0.4         | 119            | 60.5              | 124            | 123               |
| 23    | cat-1    | 0.6         | 116            | 53.0              | 123            | 115               |
| 24    | cat-3    | 0.2         | 117            | 73.8              | 127            | 137               |
| 25    | cat-3    | 0.4         | 118            | 59.3              | 124            | 125               |
| 26    | cat-3    | 0.6         | 118            | 50.1              | 123            | 112               |
| 27    | cat-4    | 0.2         | 117            | 54.5              | 129            | 134               |
| 28    | cat-4    | 0.4         | 116            | 41.3              | 125            | 125               |
| 29    | cat-4    | 0.6         | 117            | 41.3              | 124            | 120               |
| 30    | cat-5    | 0.2         | 116            | 41.7              | 128            | 124               |
| 31    | cat-5    | 0.4         | 117            | 42.3              | 124            | 126               |
| 32    | cat-5    | 0.6         | 117            | 46.1              | 125            | 120               |

As shown in Table 3, copolymers produced by bi-supported catalysts under 4 bar had higher $M_w$ than that produced by the blank catalyst when [H] was larger than 0.2 mol/L. This can be explained by the lower C7-s content of the former (see Figure 3). It is well documented that the C7-s fraction of the ethylene-1-hexene copolymer synthesized by Z-N catalysts has a much lower molecular weight than the C7-in fraction [4,14,17]. Therefore,
variation of C7-s content in copolymer will lead to evident changes in its average molecular weight and molecular weight distribution. Because the copolymers produced by different catalysts under 1 bar had similar C7-s contents, their $M_w$ values varied in a narrower range.

Comonomer content and molecular weight of the (co)polymers produced by cat-2 (TiCl$_4$/MCM-41 catalyst) were not determined due to a lack of sufficient samples. DSC analysis on these copolymers showed that they had higher melting temperature and melting enthalpy in comparison with those produced by the catalysts containing MgCl$_2$, meaning that cat-2 had poorer ability of incorporating 1-hexene in the polymer chains.

Summarizing the results of chain structure characterization on the copolymers produced by cat-1, cat-3, cat-4, and cat-5, it is clear that these polymers have similar structural features in terms of 1-hexene content, crystalline structure, and molecular weight. The main differences between the polymers of blank Z-N catalyst and those of the bi-supported Z-N catalysts are evidenced by the lower C7-s content of the latter when ethylene concentration was relatively high. These kinds of change in copolymer structure are beneficial to its application properties. In ethylene-\(\alpha\)-olefin copolymers, the \(\alpha\)-olefin comonomer like 1-hexene is introduced in the polymer chain in order to reduce the crystallinity and lamellae thickness. This kind of polymer shows lower melting temperature, lower stiffness, improved impact strength, and improved optical transparency in comparison with ethylene homopolymer, making the former more suited for applications like polymer films and soft/tough plastics.

In such a polymer, the part of copolymer with high \(\alpha\)-olefin content and low molecular weight hardly contributes to the material’s mechanical properties, but may damage the film performance for its solubility in organic solvents at room temperature. When we compare sample 23 produced by cat-1 and sample 34 produced by cat-5, their melting temperatures are all 10–15 °C lower than that of the ethylene homopolymer ($T_m = 137–140$ °C), meaning that they are all suited for application as plastic film. However, the C7-s content of sample 23 was nearly three times higher than that of sample 34. Such a large amount of soft and weak (for low $M_w$ of the C7-s fraction) components in sample 23 will lead to lower mechanical strength and poorer solvent resistance of its film product as compared with sample 34. Therefore, the bi-supported catalysts, especially those with relatively low MgCl$_2$/MCM-41 ratio, can produce copolymer with better properties than the conventional TiCl$_4$/MgCl$_2$ type Z-N catalyst.

### 2.4. Morphology of Nascent Polymer Particles

The morphology of polyethylene particles produced by the TiCl$_4$/MCM-41 catalyst (cat-2) is shown in Figure 5. The PE particles were loose aggregates of micrometer-sized short rods. Such morphology can be attributed to the replication of the rod-like MCM-41 particles in the polymerization process. A few nano-fibrils can be seen on parts of the short rods, which should be caused by extrusion of PE chains from mesopores of the support [22,23,36,40]. However, the nano-fibrils on PE formed by cat-2 were much shorter, and their space density was much lower than that of MCM-41 supported catalysts reported in the literature, since cat-2 has much lower catalytic activity than those producing high-yield nano-fibrils (the sample of Figure 5 has a polymer/catalyst mass ratio of only 4.5). When most of the active sites are anchored on the internal surface of the nano-pores of MCM-41, a low polymer growth rate over large active surfaces will lead to a slow rate of PE extrusion from the mesopores, and more difficult formation of nano-fibrils. The good replication of support morphology in PE/cat-2 particles implies that most of TiCl$_4$ in cat-2 are anchored inside the meso-pores of MCM-41.
Typical morphologies of PE particles produced by the bi-supported catalysts under 1 bar ethylene pressure are shown in Figure 6. In contrast to the replication phenomenon in PE/cat-2 particles, the morphology of regular short rods of MCM-41 was seriously distorted in these particles. In the PE/cat-3 particles, irregular sub-particles of 0.2~1 μm can be seen, which were tightly connected with each other. In the PE/cat-5 particles, sub-particles were hardly distinguishable, as they were strongly merged in micrometer-sized particles.

Morphologies of nascent copolymer particles produced by the bi-supported catalysts under 4 bar were significantly different from those of PE produced under 1 bar. Unlike the compact particles produced by bi-supported catalysts under 1 bar, the particles formed at 4 bar were very loose aggregates of irregular sub-particles, many of them being covered by randomly distributed thread-like structures (see Figures 7 and S5). This kind of morphology is also present in nascent copolymer particles produced by cat-1 (the mono-supported Z-N catalyst, see Figure S6). It should be noted that the fiber-like and thread-like structures in Figure 7 are clearly different from the long and thin PE nano-fibers reported in the literature, produced with similar MgCl₂/MCM-41 bi-supported catalysts [40]. This means that no PE nano-fibers were formed by the bi-supported catalysts studied in this work. In the literature, the PE nano-fibers formed by MCM-41 supported catalysts are explained as the result of extrusion polymerization, in which the mesopores of MCM-41 confine the movement of
PE chains formed on active centers anchored inside the mesopores [22,23,36,40]. However, the nano-sized channels of MCM-41 could be broken up when the rate of polymer growth inside the channels exceeds a certain threshold level, as the pressure exerted on the walls of channels by the growing polymer will increase with the polymerization rate. This could be the main reason for the absence of nano-fibers in PE produced by bi-supported catalysts under 4 bar. In other words, the mesopores of bi-supported catalysts may be largely broken up during ethylene-1-hexene copolymerization under 4 bar. The space confinement effects on active centers anchored in the mesopores will thus disappear, and the barriers to monomer diffusion from the reaction medium to the active centers will be reduced. As a result, the polymerization rate will be evidently enhanced. This mechanistic model can be used to explain the much larger extent of polymerization rate enhancement of the bi-supported catalysts than the MgCl2-supported catalyst when ethylene pressure was raised from 1 to 4 bar (see Figure 2). The absence of nano-fibers in PE produced with the bi-supported catalysts under 1 bar could be attributed to the low polymerization rate of such catalysts [36,40].

The changes of catalytic activity and copolymer chain structure with decrease of MgCl2/MCM-41 mass ratio can also be explained by the same mechanism. As seen in Figures 2 and 3, the differences between the bi-supported catalyst and the blank Z-N catalyst became more evident when MgCl2/MCM-41 ratio decreased. This means that a larger percentage of MgCl2 is adsorbed on locations outside the mesopores of MCM-41 in bi-supported catalyst with high MgCl2/MCM-41 ratio (cat-3), making cat-3 behave like a mixture of traditional MgCl2-supported catalyst and MgCl2/MCM-41 bi-supported catalyst. The catalyst with the lowest MgCl2/MCM-41 ratio (cat-5) exhibited the largest extent of differences from the blank Z-N catalyst, meaning that most of its MgCl2 and thus TiCl4/MgCl2 species are located inside the mesopores of MCM-41.

The strong differences in catalytic features between the bi-supported catalyst and blank Z-N catalyst could be explained by space confinement effect in MCM-41 mesopores on structure of MgCl2 crystallites. In traditional MgCl2-supported Z-N catalysts, the average size of MgCl2 crystallites varies between 3–13 nm, depending on the method of catalyst preparation [45–49]. In the bi-supported catalysts, the growth of MgCl2 crystallites inside the mesopores with 3.4 nm pore size will be strongly limited, resulting in a relatively small crystallite size and narrower size distribution. It is expectable that a larger fraction of stereochromically open surface sites (e.g., corners) is present on smaller MgCl2 crystallites. TiCl4 adsorbed on such sites will be less congested. As proposed in our previous work, TiCl4 located on open and less congested surface sites could form Ti(II) species that incorporate less α-olefin comonomer [50]. This could be the reason for the lower C7-s content of

Figure 7. Morphology of nascent copolymer particles synthesized under 4 bar ethylene pressure and [H] = 0.2 mol/L with (a) cat-4 and (b) cat-5.
ethylene-1-hexene copolymer produced by the bi-supported catalysts, especially cat-5, which has a higher percentage of active centers inside the mesopores of MCM-41.

3. Materials and Methods

3.1. Chemicals

MCM-41 (3.4 nm pore size, Nanjing Xianfeng Nanomaterials Co. Ltd, Nanjing, China.) was calcinated at 500 °C for 2 h before use. Tetrahydrofuran (THF) and n-heptane (Sinopharm Chemical Reagent Co. Ltd, Shanghai, China.) were purified by refluxing over sodium for 6 h and distilled before use. Triethylaluminum (TEA, Albemarle, NC, USA) was diluted with n-heptane to 2 mol/L before use. Titanium tetrachloride (TiCl₄, Adamas, Shanghai, China) and MgCl₂ (Alfa Aesar Co., Shanghai, China) were used as received. 1-Hexene (98%, J&K Scientific, Shanghai, China) was distilled over metallic sodium before use. Ethylene gas (polymerization grade, SINOPEC, Shanghai, China) used in the polymerizations was purified by passing through columns of 4 Å molecular sieves and PEE deoxygenate catalyst (Dalian Samat Chemicals, Dalian, China).

3.2. Preparation of MgCl₂ and MgCl₂/MCM-41 Support

Anhydrous MgCl₂ (2.5 g) was introduced into a round-bottom flask in a glove box, before 60 mL THF was successively introduced to the flask under nitrogen, and the flask was heated to 95 °C under stirring until MgCl₂ was completely dissolved in THF. Fine MgCl₂/THF adduct particles were precipitated when the solution was cooled to 60 °C, and then THF was removed by evacuating the flask for 2 h, and the solid MgCl₂ support was stored in a glove box. For preparing the MgCl₂/MCM-41 support, a clear MgCl₂/THF solution was first prepared in the same procedures, and the hot solution was transferred to another flask containing designed amount of MCM-41. The suspension was stirred at 95 °C for 2 h, the temperature was reduced to 60 °C under nitrogen atmosphere, then the suspension was kept still for 15 min to settle down the MgCl₂/MCM-41 support. The THF was removed by evacuating the flask for 2 h at 60 °C, and the dried support was stored in a glove box.

3.3. Preparation of Ziegler-Natta Catalysts

Supported Ziegler-Natta catalysts using MgCl₂, MgCl₂/MCM-41, and MCM-41 as the support were respectively prepared by anchoring TiCl₄ on the support in similar procedures adopted in our previous work [51]. The support was first dispersed in 40 mL n-heptane at 40 °C, a calculated amount of TiCl₄ (Ti/Mg = 10 mol/mol) was added into the slurry. It was stirred at 90 °C for 2 h under the protection of nitrogen, then the slurry was cooled to 60 °C, kept still to settle down the solid catalyst, and the solvent was removed using syringe. The catalyst was washed by n-heptane for three times (each time 15 mL) at 60 °C, then dried by vacuum, and stored at −10 °C inside a glove box.

3.4. Ethylene Polymerization and Ethylene/1-Hexene Copolymerization

Ethylene (co)polymerization was carried out in a 100 mL Schlenk flask equipped with a magnetic stirring bar. Firstly, the flask was dried by heating under vacuum and refilling with nitrogen for three times. Then, it was filled with ethylene at 1 bar. Designed amounts of n-heptane, TEA, and 1-hexene (for copolymerization) were successively introduced into the flask. Weighed solid catalyst was then added to start the polymerization at 60 °C. Gaseous ethylene at 1 bar was continuously supplied to the flask during the polymerization. After a designed time, the polymerization was terminated with 95/5 mixture of ethanol and concentrated HCl. The produced polyethylene or ethylene/1-hexene copolymer powder was repeatedly washed with ethanol and filtered, then dried at 60 °C under vacuum for 6 h.

Pressurized ethylene/1-hexene copolymerization was carried out in a 300 mL Büchi autoclave with mechanical stirrer. All procedures were the same as the polymerization runs under atmospheric pressure, while gaseous ethylene at 4 bar was continuously supplied to the autoclave during the copolymerization.
3.5. Polymer Fractionation

Each copolymer was fractionated into two parts by solvent extraction. About 1 g polymer was extracted with boiling \( n \)-heptane in a Soxhlet extractor for 12 h. The boiling \( n \)-heptane soluble fraction (C7-s) was recovered by concentrating the solution and precipitating the polymer with isopropanol. Both the C7-s fraction and the part insoluble in boiling \( n \)-heptane (C7-in) were vacuum dried at 50 °C overnight and weighed.

3.6. Characterization

Powder X-ray diffraction analysis of the support was made using an Ultima IV diffractometer. The scans were performed from diffraction angle \( 2\theta = 5° \) to 60°. The step size was 0.2° and the time per step was 12 s. The sample was placed on a special holder and the holder was sealed with a thin Mylar film to prevent contact of the samples with air and moisture. Nitrogen adsorption measurement was performed on an AUTOSORB-1-C instrument. The surface area and pore-size distribution were calculated by using the Brunauer—Teller (BET) method. The Ti content of the catalyst was determined by the UV-Vis method. A known quantity of catalyst was dissolved in sulfuric acid and treated with hydrogen peroxide to form peroxo-titanium complex, which is a yellow solution. The content of Ti was calculated from the absorbance of the solution at 410 nm recorded by a UV-vis spectrophotometer. The content of Mg was measured by inductively coupled plasma spectrometry (ICP).

The average molecular weight and polydispersity index (\( D \)) of the polymer samples were measured by high temperature gel permeation chromatography (HT-GPC, Agilent PL-220) with three PL mixed B columns (500–107) at 150 °C in 1,2,4-trichlorobenzene. Polystyrene standards were used to make universal calibration of the experimental GPC curves. The content of 1-hexene in the copolymers as well as the copolymer fractions was measured by the FTIR method that was calibrated by \(^{13}\)C NMR analysis [52]. Differential scanning calorimetry (DSC) measurements were carried out on a TA Q200 DSC calorimeter. About 3–5 mg of sample was sealed in an aluminum sample cell. The sample was first melted at 160 °C for 5 min to erase the thermal history, and then cooled to 40 °C at a cooling rate of 10 °C/min, followed by reheating to 160 °C at a scanning rate of 10 °C/min to record the melting behavior. Scanning electron microscope (SEM) analysis of the nascent polymer particles was conducted with a Hitachi S4800 field-emission SEM (Hitachi High-Technologies Corp., Tokyo, Japan). The micrographs were taken at 3-kV acceleration voltage. Before SEM observations, all the sample surfaces were sputtered with a thin layer of gold.

4. Conclusions

\( \text{TiCl}_4/\text{MgCl}_2/\text{MCM-41} \) type bi-supported Z-N catalysts with different \( \text{MgCl}_2/\text{MCM-41} \) ratio were prepared in order to control the active center distribution and tailor the chain structure of the olefin copolymer they produce. The pore volume and specific surface area of MCM-41 were significantly reduced after immobilizing \( \text{MgCl}_2 \) on the mesoporous silica. Ethylene-1-hexene copolymerization activity of the bi-supported catalysts was comparable to that of a \( \text{TiCl}_4/\text{MgCl}_2 \) type Z-N catalyst. Under 4 bar ethylene pressure, the bi-supported catalysts showed a stronger comonomer activation effect than the \( \text{TiCl}_4/\text{MgCl}_2 \) catalyst, rendering higher activity of the former at relatively high 1-hexene concentration. In comparison with the \( \text{TiCl}_4/\text{MgCl}_2 \) catalyst, the bi-supported catalysts produced much less copolymer fraction of low molecular weight and high 1-hexene content, meaning that active center distribution of the catalyst was significantly changed by introducing MCM-41 in the support. The extent of active center distribution variation was enhanced by increasing MCM-41 content in the bi-supported catalyst. Ethylene-1-hexene copolymers produced by the bi-supported catalysts under 4 bar had a narrower composition distribution and molecular weight distribution than that produced by the traditional \( \text{MgCl}_2 \)-supported Z-N catalyst. The copolymer produced by the bi-supported catalysts had a lower content of boiling \( n \)-heptane soluble fraction than that produced by the \( \text{TiCl}_4/\text{MgCl}_2 \) catalyst, but
the former showed greater similarity $T_m$ than the latter. This kind of ethylene copolymer, combining the features of low soluble fraction and low melting temperature, will show better performances for applications such as polymer film. The particle morphology of nascent copolymer produced by the bi-supported catalysts was similar to that produced by the traditional MgCl$_2$-supported Z-N catalyst. Combining low cost and robustness in the industrial process with better copolymer properties, this kind of bi-supported Z-N catalyst could find important applications in the polyolefin industry.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/article/10.3390/catal11121535/s1, Figure S1. XRD curve of MCM-41. Figure S2. Pore size distribution of MgCl$_2$, MCM-41 and two composite supports. Figure S3. 1-Hexene content of ethylene/1-hexene copolymer produced under 1 bar and 4 bar. Figure S4. DSC traces of unfractonated (co)polymers. Figure S5. Morphology of nascent copolymer particles synthesized under 4 bar ethylene pressure and [H] = 0.2 mol/L with cat-4 and cat-5 and Figure S6 Morphology of nascent copolymer particles synthesized under 4 bar ethylene pressure and [H] = 0.2 mol/L with cat-1. Table S1. Boiling point of E-1-hexene copolymer produced under 1 bar and 4 bar. Table S2. Thermal properties of copolymer and C7-s fraction produced by cat-1, cat-3, cat-4 and cat-5 under 1 bar.

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