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Storage time effect on dynamic structure of MgCl$_2$.nEtOH adducts in heterogeneous Ziegler-Natta catalysts

Najmeh Hadian, Shokoufeh Hakim, Mehdi Nekoomanesh-Haghighi, Naeimeh Bahri-Laleh*

Department of Polymerization Engineering, Iran Polymer and Petrochemical Institute,

P.O. Box:14965/115, Tehran, Iran.

ABSTRACT

Primary MgCl$_2$.3.3EtOH adduct (PCT1) was prepared by melt quenching method and then submitted into a programmed thermal dealcoholation process using a fluidized bed reactor. During thermal dealcoholation program, different MgCl$_2$.nEtOH support samples with n= 3.0, 2.7, 2.4, and 2.1 were selected and named as PCT2 to PCT5, respectively. Structural analysis of the support samples, by moving from PCT1 to PCT5, showed a significant increase in the surface area from 7.4 m^2/g to 12.8 m^2/g, together with reduced peak heights at $2\theta \approx 8.9$ and 9.7°. After characterization of support samples, the final catalysts were prepared by reaction of the samples with TiCl$_4$ and tested in slurry phase propylene polymerization. The prepared catalysts showed similar stereospecificities but different activities in polymerization tests, so that, with progression of dealcoholation from PCT1 to PCT2 the catalyst activity was reached its maximum value of 2.9 kgPP/g Cat.h, and then by further dealcoholation, from PCT2 to PCT5, the activity decreased gradually. In the last stage of the project, the effect of time interval between thermal dealcoholation and catalyst preparation, termed as "storage time" was studied on crystal and morphological characteristics of the two best adduct samples, namely MgCl$_2$.2.4EtOH and MgCl$_2$.3.0EtOH. The storage time greatly affected the adducts and the resulting catalysts, and in this respect the best catalyst activity was achieved for those prepared immediately after adduct formation. **Polyolefins J (2014) 1:33-41**

Keywords: Ziegler-Natta, adduct, MgCl$_2$, thermal dealcoholation, polyolefin, dynamic structure.

INTRODUCTION

The discovery of Ziegler Natta (ZN) polymerization in 1953 was still probably the most important achievement in the field of synthetic polymer chemistry during the past half-century[1, 2]. Modern ZN catalysts for the industrial production of polyolefins are based on TiCl$_4$ supported on activated MgCl$_2$ because, MgCl$_2$ has layered crystal structure similar to that of "vio-let" TiCl$_3$ (originally with much lower performance) catalyst developed by Natta [3-5], and acts as a template for TiCl$_4$ surface deposition. The relevant crystal structure is α-MgCl$_2$ which has a layered crystal structure that belongs to the R$_{3m}$ space group. Each layer is composed of 6-fold Mg atoms and 3-fold Cl atoms. In this layered structure, the (001) surface is the cleavage surface. However, the (001) surface is chemically inert and needs to be activated. Different methods have

been proposed for the proper activation of primitive α-MgCl$_2$ support [2, 6, 7]. These methods transform α-MgCl$_2$ into the active δ form of MgCl$_2$, in which the stacking sequence no longer corresponds to a cubically close packed structure, but it is disordered due to translation and rotation of the layers [8]. These methods include purely mechanical activation of MgCl$_2$, mechanical plus chemical routes and purely chemical methods [9-12]. It has been found that chemical activation of MgCl$_2$ is more effective than mechanical activation by ball milling [11].

In chemical activation, the treatment of α-MgCl$_2$ with a Lewis base, especially ethanol, produces some well defined adducts, and a successive and suitable elimination of the Lewis base from these adducts gives rise to a solid support whose crystal structure is disordered and which in practice it is very active in polymerization catalysis [13].

So, a widely used approach in ZN catalyst synthesis involves the use of adducts of type MgCl$_2$.nEtOH, in which the value of n may vary from 1 to 6 [14]. Presence of ethanol in these adducts prevents the unsaturated Mg from re-aggregation and the formation of a very perfect crystal structures; therefore, it increases defects in the substrate, which are manifested in the broadening of some peaks and disappearance of others in the XRD spectra [15].

Many reports describe the preparation of MgCl$_2$.nEtOH liquid adducts, followed by a controlled regeneration of the active support through recrystallization by quick cooling [16] or by solvent evaporation [6], with subsequent substratum washing. However, there are a few reports which describe crystal structure change during support preparation [17,18]. Therefore, a deep knowledge about the crystal structure of the support precursor and prepared support has not been achieved yet, and many concepts are still under discussion. Further, to the best of our knowledge there is not a systematic study on the effect of storage time on the crystal structure of prepared support and on the catalytic behavior of the catalysts prepared thereof.

In this contribution we will try to fill this gap. In order to acquire an insight into the effect of dealcoholation level on the crystal structure and morphology of MgCl$_2$, primary MgCl$_2$. 3.3 EtOH powder was synthesized by liquid phase quenching of fused emulsified adducts and then proceeded by successive alcohol extraction using thermal route to prepare MgCl$_2$. n EtOH adducts with n=3.0 to 2.1. Then, all MgCl$_2$. nEtOH adducts were turned into their related catalysts and examined in propylene polymerization to compare catalysts activities and polymer properties. Finally, structural changes of prepared supports besides the activity of resulted catalysts were studied during storage time to make a new suggestion about the best catalyst preparation period.

EXPERIMENTAL

Materials

MgCl$_2$ (98%), absolute ethanol (>99.9%), potassium hydroxide, and titanium tetrachloride (99%) were obtained from Merck (Darmstadt, Germany). Silicon oil (99% with viscosity of 500 cP) was obtained from Dow Corning Chemical (USA). n-Heptane, n-hexane and toluene were supplied by Bandar Imam Petrochemical Co. (Mahshahr, Iran), distilled over calcium hydride, and stored over 13X and 4Å type activated molecular sieves and sodium wire. Diisobutylphthalate and diphenyldimethoxysilane were obtained from Arak Petrochemical Co. (Arak, Iran) and distilled over calcium hydride before use. Triethylaluminium (TEA) was acquired from Schering Co. Ltd (Bergkaman, Germany). Nitrogen gas was supplied from Roham Co (Tehran, Iran), then purified and dried by passage through KOH, activated silica gel and 4Å molecular sieve columns.

Procedures

Liquid-phase quenching of fused emulsified adducts
Spherical MgCl$_2$ adduct was prepared according to a method that was published by our group, previously [11]. A typical procedure was as follows:
A definite weight of dried MgCl$_2$ powder (20 g) was placed in a two-jacketed stainless steel reactor under dry N$_2$ atmosphere. Then, a calculated amount of absolute EtOH ([EtOH]/ [MgCl$_2$] = 3.7) was added into the reactor. The mixture was mixed and the temperature was increased up to 50°C. At this stage, silicon oil (200 mL) was added into the reactor and then the mixture was heated up to 120°C under vigorous stirring. The suspension was kept for 6 h at this temperature, and then transferred to another jacket vessel containing n-hexane (500 mL) at -30°C. The suspension was held at this temperature for 1 h under stirring and after decanting, a solid product was collected in a nitrogen

atmosphere. The solid was repeatedly washed with n-hexane to remove paraffin oil, filtered, and dried at room temperature in vacuum. Molar ratio of EtOH to $MgCl_2$ equal to 3.3 was obtained by NMR analysis [19].

Thermal dealcoholation of the $MgCl_2$ 3.3 EtOH adduct
In thermal dealcoholation, the addition compound of $MgCl_2.3.3EtOH$ was packed into a fluidized bed reactor. Temperature and pressure of the reactor were regulated by passing a nitrogen stream through the packed reactor. Figure 1 shows pressure and temperature programming used in this study. During dealcoholation, five different samples were selected at time 0, 90, 120, 150, and 180 min and designated as PCT1 to PCT5, respectively. Using NMR spectroscopy, EtOH to $MgCl_2$ molar ratio of 3.0, 2.7, 2.4, and 2.1 were obtained for PC2 to PC5 adduct samples, respectively.

Preparation of the catalysts
A volume of 45 mL of $TiCl_4$ was added drop-wise on 2 g of the dealcoholated support at -5°C and kept at this temperature for 30 min with continuous stirring. Then the temperature was gradually raised to 60°C and 0.5 mL of diisobutylphthalate (internal electron donor) was added at this temperature. The system was kept under these conditions for 40 min. After the first impregnation, the supernatant was removed and the catalytic solid was washed three times with 80 mL of dry toluene. Then, another 40 mL $TiCl_4$ (40 mL) was added into the reactor and the temperature was raised to 124°C and kept 1 h at this condition after which the supernatant was removed and the catalytic solid was washed again with dry toluene at 124, 105, and 90°C until no residue of HCl was observed. Finally,

the catalyst was washed three times with dry heptane at 90°C. The obtained catalyst was dried until constant weight under nitrogen flow.

Propylene polymerization
Propylene polymerization was carried out in a 1 L Buchi stainless steel reactor equipped with a mechanical stirrer (Buchi bmd 300, Switzerland). Before each polymerization procedure, the reactor was purged with nitrogen gas at 100°C for about 1.5 h to ensure the absence of moisture and oxygen. After cooling the reactor to 70°C, nitrogen was replaced by propylene and the reagents were added in the following order: 500 mL n-heptane, 5 mL TEA (1 M solution) as co-catalyst, and 5 mL diphenyl-dimethoxysilane (0.1 M) as external donor. The suspension containing 0.05 g supported catalyst was injected into the reactor and propylene pressure was increased up to 5 bar. During polymerization the stirrer and temperature were set at 800 rpm and 75°C, respectively. After 1 h, the reactor was discharged, and the polymer powder was dried at 70°C in vacuum oven, over night.

Characterization
Surface area of the catalyst was determined using BET method by Quantachrome Corp. Nova2200, Version 7.11. For determination of Ti content, after sample digestion in H_2SO_4, Ti was oxidized with H_2O_2 and analyzed by visible spectrophotometer (λ= 410 nm) in a Shimadzu spectrophotometer model 6800. The isotactic index (II, wt% of heptane-insoluble polypropylene) was determined through soxhlet extraction for 8 h.

Solution NMR analysis for the determination of $MgCl_2.nEtOH$ composition was carried out as reported in the literature [19]. The $EtOH/MgCl_2$ molar ratio of the samples was determined by dissolving a weighed amount (ca. 30 mg) of the compounds in 1 mL of D_2O completely and adding a weighed amount of the reference compound THF (ca. 20 mg). The 1H NMR spectra, as recorded at 400 MHz on a Bruker Avance spectrometer, can resolve all the signals of ethanol and THF. The integration of the signals gives the EtOH/THF molar ratio and the absolute amount of ethanol in the given sample. Thus, "n" as $EtOH/MgCl_2$ molar ratios are calculated. Powder X-ray diffraction (XRD) patterns were measured on a Siemens D-5000 X-ray diffractometer operating at 40 kV and
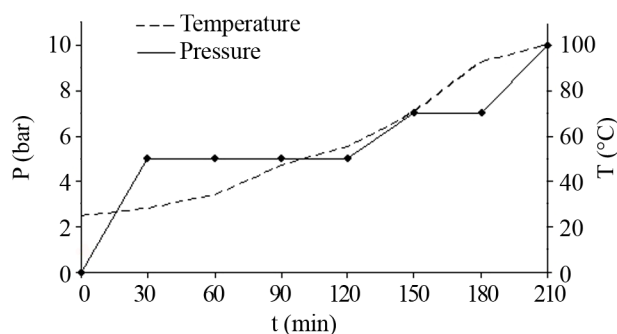

Figure 1. Temperature and pressure programming during thermal dealcoholation

Table 1. Characteristic supports prepared by thermal dealcolation method

| Sample	n (EtOH/MgCl$_2$)	Temp of dealcoholation (°C)	Time of dealcoholation (min)	Surface area (m^2/g)
PCT1	3.3	-	0	7.4
PCT2	3.0	47	90	7.7
PCT3	2.7	55	120	8.7
PCT4	2.4	70	150	12.0
PCT5	2.1	92	180	12.8

25 mA with a copper target ($\lambda = 1.54$ Å) and at a scanning rate of 3 ° min^{-1}.

RESULTS AND DISCUSSION

The crystal structure of MgCl$_2$ is an important critical factor when used as support in Ziegler-Natta type catalyst preparation. Study of thermal dealcoholation of support precursor has the objective of evaluating its influence on the crystal structure, surface area and amount of titanium fixed on the surface of the MgCl$_2$ crystal, and consequently on the polymer properties obtained by the resulted catalysts.

To obtain primary MgCl$_2$.nEtOH sphere, MgCl$_2$ was dissolved in ethanol and then recrystallized by quick cooling to -30°C. The content of ethanol in recrystallized MgCl$_2$.nEtOH compound was 3.3, calculated by NMR analysis (ref. [19]), then the primary adduct was obtained in this work had the composition of MgCl$_2$.3.3EtOH.

EtOH is eliminated slightly through melt quenching. However, the remained EtOH in the support reacts with TiCl$_4$ during impregnation producing titanium alkoxides that are inactive for polymerization [20], so, high amounts of EtOH are undesirable. Then, further elimination of EtOH was carried out thermally.
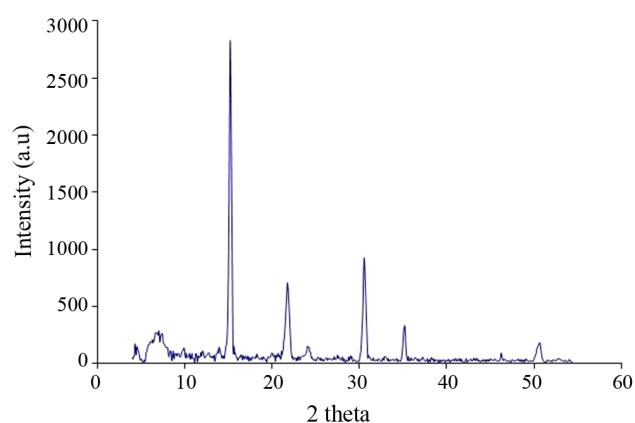
Figure 2. XRD spectrum of primitive MgCl$_2$

It is believed that adducts with n>3 have a low melting temperature (below 20-30°C). To avoid adduct melting; which results in re-aggregation and decreased surface area, dealcoholation should be done at low temperatures and pressures. In these circumstances, only the alcohol molecules from the surface would be eliminated. By the gradual elimination of the EtOH, melting temperature increases which it allows gradual increase in dealcoholation temperature. Therefore, in our study, primary MgCl$_2$.3.3EtOH was subjected into a programmed pressure-temperature project (Figure 1) during which the temperature increased gradually. During dealcoholation, five different samples were selected at times 0, 90, 120, 150, and 180 min and designated as PCT1 to PCT5, respectively.

Ethanol/magnesium chloride molar ratio of the samples was calculated by NMR spectroscopy according to the literature [19] and it is listed in Table 1. In shorter dealcoholation times (or low temperatures of nitrogen) only the ethanol molecules of the surface were evaporated, while, by the proceeding of dealcoholation, ethanol of the interior parts of support was eliminated, as well, and the value of n decreased from 3.3 for PCT1 to 3.0, 2.7, 2.4, 2.1 change PCT2 to PCT5, respectively.

Surface areas of support samples were obtained by BET method and they are listed in Table 1. The results showed a significant increase in the surface area of MgCl$_2$.nEtOH adducts by the progression of the dealcoholation (and/or elimination of more EtOH molecules), in which the surface area was increased from 7.4 m^2/g for PCT1 to 12.8 m^2/g for PCT5 adduct sample.

In order to determine that to what extent a support would be able to activate a particular catalyst depends on its crystal structure, primitive MgCl$_2$ and all MgCl$_2$.nEtOH adduct samples were characterized by XRD analysis. Primitive MgCl$_2$ showed sharp peaks centered at 2θ ≈ 7, 15, 22, 24, 32, 35 and 50° (Figure 2). Peak at 2θ ≈ 15° was associated with the stacking of Cl-Mg-Cl triple layers along the crystallographic

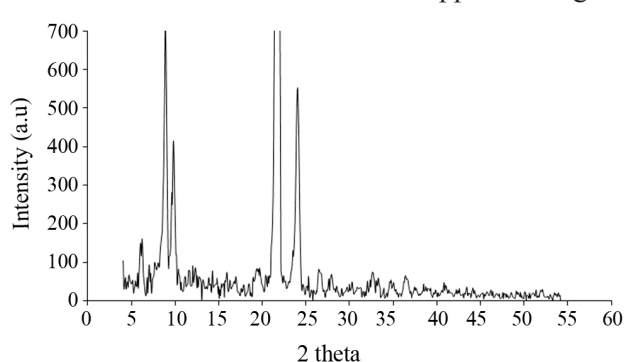**Table 2**. Synthesized catalysts specification and the resulted polymer properties

Catalyst Label	Ti %	Surface area (m²/g)	Activity (kg PP/g Cat. h)	II[a] (wt %)
CT1	0.824	205.4	1.8	99.2
CT2	0.927	236.7	2.9	98.9
CT3	1.096	310.4	2.6	98.1
CT4	1.149	333.8	2.3	98.7
CT5	1.402	360.04	1.5	98.3

(a) Isotacticity Index

direction, and two peaks, at $2\theta \approx 32°$ and $50°$ with stacking faults of the triple layers [21]. The large peaks at $2\theta = 22$ and $24°$ are due to polyethylene film, which is used to protect the catalyst from exposure to the atmosphere.

After activation of $MgCl_2$ with EtOH to prepare primitive $MgCl_2.3.3EtOH$ adduct, EtOH was prevented from $MgCl_2$ segregation and increased the distances between the triple-layers. By increasing layer distances, the peak at $2\theta \approx 15°$, which was assigned to (003) plane, was disappeared and two peaks at $2\theta \approx 8.9°$ and $9.7°$ were emerged (Figure 3). All other samples showed the same XRD spectra however, with different peak heights at $2\theta \approx 8.9°$ and $9.7°$. In the prepared adducts, samples with lower n value would result in lower peak height at $2\theta \approx 8.9°$ and $9.7°$ (Figure 4).

Final catalysts were prepared by reacting support samples with $TiCl_4$ and designated as CT1 to CT5 for PCT1 to PCT5 adducts, respectively. Characterization results of the catalysts were collected in Table 2. The prepared catalysts showed low Ti content, in comparison with similar works which were published before [12, 22, 23]. This can be attributed to several washing times which were applied in catalyst preparation procedure. Moreover, the impregnated content of $TiCl_4$ increased with increasing levels of dealcoholation, and that the surface area of the catalyst drastically increased as well. Increase in Ti content with increasing dealcoholation time (or temperature) was due to an increase in surface area of the support during the

dealcoholation that provided new surfaces for the reaction of $TiCl_4$.

Then, the performance of the catalysts was evaluated in slurry phase polymerization of propylene using triethylaluminum (TEA) as co-catalyst. Activity and stereospecificity results are reported in Table 2. As can be seen, all the catalysts show similar stereospecificity but with different activities, so, here we may discuss over activity results. By moving from CT1 to CT2 the activity was increased by increasing Ti content, however; further increase of Ti content resulted catalysts with lower activity, so that, CT5 had the lowest catalytic activity, although its titanium content was at highest level. This means that titanium species were not all active in the polymerization process [22] and those species, able to generate active Ti, were fractionally lower in CT5 catalyst compared to other samples. According to the literature, titanium content can have a great effect on the polymer molecular weight. In general, catalyst with the less active Ti content (less active catalysts), usually produce polymers with highest molecular weights. The increase of molecular weights can be due to the formation of few active centers, in spite of high concentrations of Ti, since titanium is predominantly found forming titanium chloride alkoxide that is inactive, as it has been previously discussed [12, 23].
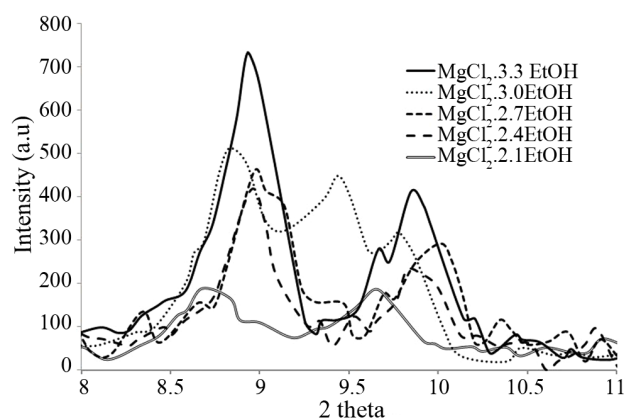

Figure 3. XRD spectrum of $MgCl_2.3.3EtOH$ adduct

Figure 4. XRD spectra of $MgCl_2.nEtOH$ adducts

Table 3. Effect of storage time on the catalytic behavior of $MgCl_2.3.0EtOH$ and $MgCl_2.2.4EtOH$ adducts

Catalyst Label	Time after adduct preparation (day)	Ti (%)	Surface area (m²/g)	Activity (kg PP/g Cat. h)
CT2	0	0.927	236.7	2.9
CT2-1d	1	0.752	227.5	2.7
CT2-9d	9	0.610	218.2	1.8
CT4	0	1.149	333.8	2.3
CT4-1d	1	0.936	307.3	2.0
CT4-9d	9	0.853	295.8	1.7

After exploring the effect of dealcoholation on the structural properties of different adducts and catalytic behavior of the obtained catalysts, in this section structural change of two selected supports, namely $MgCl_2.3.0EtOH$ and $MgCl_2.2.4EtOH$, was studied during storage time. To do this, we left the prepared adducts in a dry box under N_2 blanket. To this end, first, crystal structure of the selected supports was monitored at 0, 2 and 4 h intervals after their preparation. XRD gave spectra with similar patterns but different intensities especially, for the peaks at $2\theta = 8.9$ and 9.9°. As shown in Figures 5a and 5b, intensity of these peaks decreased gradually by passage of time for both supports.

Then, scanning electron microscopy (SEM) was
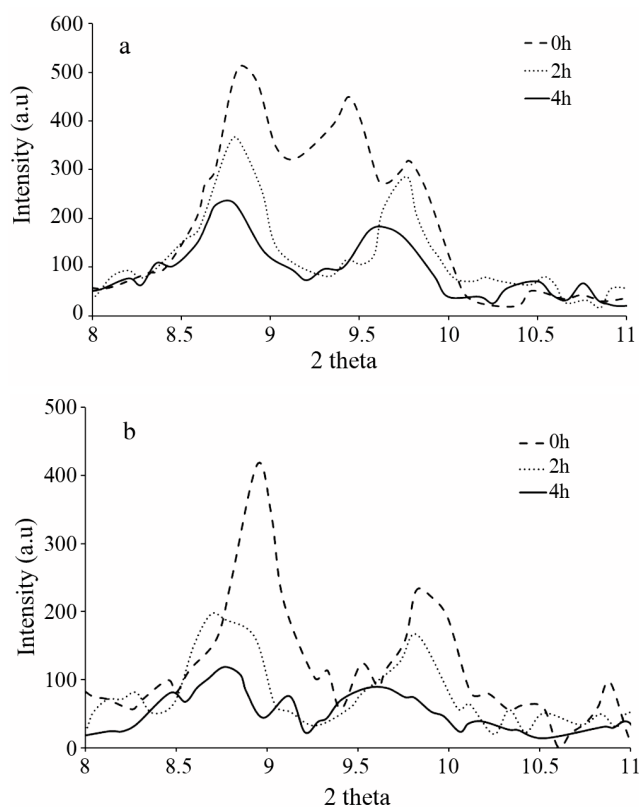
Figure 5. XRD spectra of (a) $MgCl_2.3.0EtOH$ and (b) $MgCl_2.2.4EtOH$ adducts at 0, 2 and 4 h after preparation

employed to monitor storage time effect on the adduct morphology and probably, interpret the findings of XRD spectra. To see the differences clearly, the morphology of as-prepared $MgCl_2.3.0EtOH$ adduct and its storage after 1 and 9 days was scanned by SEM images. As can be seen in Figure 6, a re-arrangement of the particles was happened during time and, by merging support particles together, the morphology receded from highly porous structure to the one with less and small pore sizes.

We can interpret these results by dynamic structure disorder phenomena due to storage time which was published before, by a different route, by Sozzani and coworkers [19] as disordering generated by ethanol dynamics in the crystal. $MgCl_2$ powder was almost in its stable form before treatment. It was kept away from that structure by treatment with EtOH, and resulted in $MgCl_2.nEtOH$ adduct with less stable structure. This low stable form gradually changes by time, as shown by XRD and SEM images. To ensure the absence of water due to absorbance from environment, TGA analysis was performed for both support samples, $MgCl_2.2.4EtOH$ and $MgCl_2.3.0EtOH$, after aging time of 1 day. No extra peak was seen in the TGA curve after 1 day storage, which confirmed the absence of water in the support samples.

To understand storage time effect clearly, two catalysts were prepared immediately after support preparation, and four catalyst samples on the days 2nd (CT2-1d and CT4-1d) and 9th (CT2-9d and CT4-9d) after support preparation. The properties of the catalysts are reported in Table 3. As shown in Table 3, the Ti content incorporated in the final catalyst for all four samples is significantly influenced by the storage time. However, the specific surface areas of the resulting catalysts are slightly different. This means that, suitable $MgCl_2$ surfaces for the $TiCl_4$ coordination are disappeared or replaced during time with the surfaces which are not appropriate for $TiCl_4$ absorption, resulted in the catalysts with less Ti content and activity.
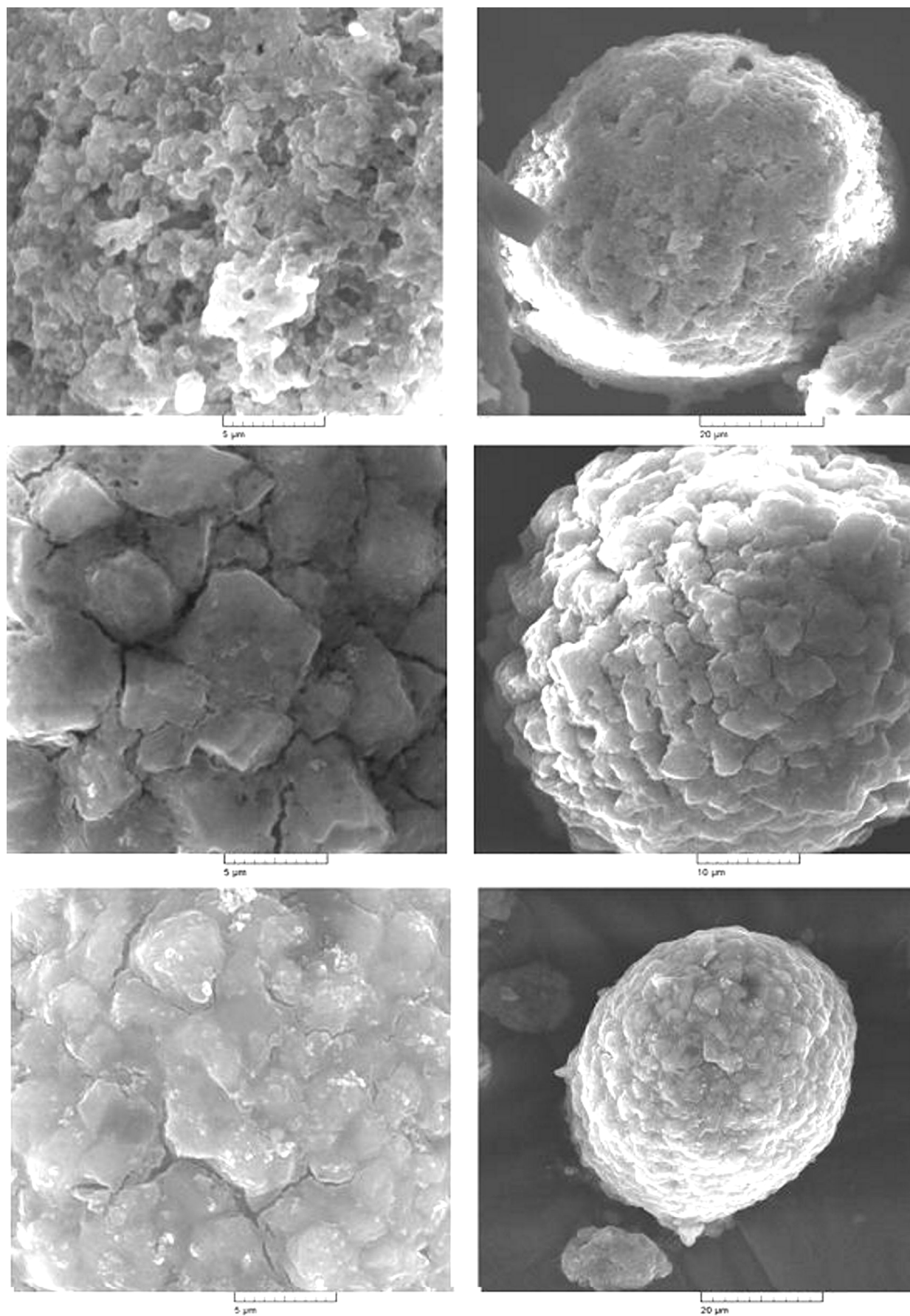
Figure 6. SEM images of MgCl$_2$.3.0EtOH adduct in (a) 0, (b) 1 and (c) 9 days after thermal dealcoholation

In conclusion, our results suggest that catalyst preparation should be done immediately after support dealcoholation, if not; catalyst activity will be decreased drastically. This finding can have great impact on the heterogeneous Z-N catalysts field.

CONCLUSION

Primitive MgCl$_2$.3.3EtOH support precursor was prepared by melt quenching method and subjected into a programmed thermal-pressure dealcoholation treatment. The results showed that:
- In the short dealcoholation time, only the ethanol molecules of the surface were evaporated. By the proceeding of dealcoholation, ethanol in the interior parts of the support was eliminated, and the EtOH content of the samples decreased.
- With decreasing EtOH content, surface area was increased which resulted an increase in TiCl$_4$ uptake.
- Prepared catalysts from dealcoholated supports showed similar stereospecificity but different activities in slurry phase propylene polymerization. At first, by increasing Ti content from CT1 to CT2, the activity was increased. On the other hand; by further increase in Ti content (from CT2 to CT5) catalyst activity was decreased. This means that all the titaniums were not active in the polymerization procedure and the content of titanium species which were able to generate active titanium was lowest in catalyst CT5.
- Finally, crystal structure of MgCl$_2$.2.4EtOH and MgCl$_2$.3.0EtOH adducts was monitored during XRD test and SEM images. The results showed that the structure of the prepared adducts changed gradually by time which significantly affected catalytic behavior. Then, catalyst synthesis was decided to be carried out immediately after support preparation, and if not; the catalyst activity was decreased drastically.

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