Morphological Study of Spherical $MgCl_2$.nEtOH Supported $TiCl_4$ Ziegler-Natta Catalyst for Polymerization of Ethylene

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ABSTRACT: Spherical $MgCl_2$·nEtOH was prepared by adducting ethanol to $MgCl_2$ using melt quenching method. Effect of molar ratio of [EtOH]/[$MgCl_2$] = 2.8–3.05 on the morphology and particle size of the $MgCl_2$·nEtOH were studied. The best adduct of spherical morphology was obtained when 2.9 mol ethanol to 1 mol $MgCl_2$ was used. An emulsion of dissolved $MgCl_2$ in ethanol was prepared in a reactor containing silicon oil. Stirrer speed of the emulsion and its transfer rate to quenching section that work at −10 to −40°C are affected by the particle size of the adduct particle. The adducted ethanol was partially removed with controlled heat primary to catalyst preparation (support). Treatment of the support with excess $TiCl_4$ increased its surface area from 13.1 to 184.4 m^2/g. Heterogeneous Ziegler-Natta catalyst system of $MgCl_2$ (spherical)/$TiCl_4$ was prepared using the spherical support. Scanning electron microscopy studies of adduct, support, and catalyst obtained shown spherical particles, however, the polyethylene particles obtained have no regular morphology. The behavior indicates harsh conditions used for catalyst preparation, prepolymerization, and polymerization method used. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3829–3834, 2006

Key words: Ziegler-Natta catalyst; morphology; spherical support; adducted support; polyethylene

INTRODUCTION

Several factors influencing on polymer morphology were obtained using heterogeneous Ziegler-Natta catalyst. The most important factor is the morphology of the catalyst particles replicated from its support; therefore, morphology and particle size distribution (PSD) of the support could be key factors in the field of heterogeneous Ziegler-Natta catalyst polymerization.[1–5]

In general, reactor fouling could be avoided in the slurry and gas phase process by heterogenizing the catalyst through supporting on suitable carrier.[2,6]

The lower the fine particles in support, the less is the fine polymer particles obtained, and less fouling of polymerization reactor. With regard to the facts, majority of the work on the improvement of the morphology of the polymer has focused on the morphology of the support and catalyst preparation methods. However, polymerization procedure could affect seriously.

So far $MgCl_2$ is known as the best support for Ziegler-Natta catalyst polymerization. The active $MgCl_2$ that is not morphologically controlled may produce polymer powder particles of nonuniform size and shape. To control morphology of the support to uniform particles in general and spherical in particular have many advantage. $MgCl_2$ has some solubility in solvents such as alcohol and ether which could be useful for controlling its morphology.[7] Adduct such as $MgCl_2$·nEtOH, $MgCl_2$.nCH_3OH, and $MgCl_2$.nC_4H_9 are obtained by dissolving the $MgCl_2$ in methanol, ethanol, or tetrahydrofuran.[7] Spherical $MgCl_2$ has been used in the preparation of the spherical catalyst for its controllable morphology. Spherical $MgCl_2$-supported catalyst prepared under control condition produced polymer with high bulk density and desired spherical morphology.[2,6,8–10]

The absence of fine polymer particles prevent reactor fouling, and the absence of coarse particles eliminate undesirable fluidization and agglomeration effect. Therefore, producing an optimal polymer particle morphology is one of the important goals in catalyst development.[2] Control of the particle morphology is based on the fact that the polymer tends to replicate the shape of the catalyst particle on which it is produced and the catalyst get the shape from its support.[2–5]

As $MgCl_2$ is the best support for Ziegler-Natta catalyst, major studies on morphology have been done on $MgCl_2$ compound. The common important methods of morphological improvement of the support are

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(a) melt quenching,[11–13] (b) spray drying,[14] (c) spray cooling,[15] and (d) recrystallization.[16–17]

In addition to the morphology of the catalyst, the polymerization procedure and its conditions also affect the polymer powder morphology. Both physical and chemical phenomena influences the morphology. The phenomena include stirrer type and its speed, mass transfer limitation, rate and temperature of polymerization, and monomer and H_2 concentration. Prepolymerization is also a very important step in the morphological development.[2,18]

EXPERIMENTAL

Chemicals

$MgCl_2$ (98%), ethanol (98%), potassium hydroxide, phosphorous pentoxide (99.5%), 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). Other chemical are used as described by Zohuri et al.[19]

Preparation of spherical adducted $MgCl_2$

Spherical adduct of $MgCl_2$ was prepared using melt quenching method. A series of stainless steel reactor containing stirrer with speed control and heating systems was used. Silicon oil was used as an emulsifying media. Anhydrous $MgCl_2$ (20 g) was added to a reactor containing ethanol (first reactor) [EtOH]/[$MgCl_2$] = 2.5–4. The content of the reactor was heated to 125°C while stirring. Then, the content was added to the second reactor containing the silicon oil (200 mL). The mixture was stirred to a uniform emulsion. The emulsion was transferred to the third reactor containing *n*-hexane (500 mL) at temperature −10 to −40°C. On adding, the solid adducted $MgCl_2$·nEtOH was formed. The white solid precipitated particles were washed using *n*-hexane and dried under vacuum at ambient temperature. Because of the sensitivity of the $MgCl_2$ to air and moisture, all the procedures were carried out under an atmosphere of dried N_2.

Catalyst preparation

$MgCl_2$(spherical)/$TiCl_4$ catalyst was prepared using the adduct $MgCl_2$·nEtOH. To remove some of the alcohol, the support was heated to 120°C. The support (5 g) was added to a catalyst preparation reactor containing *n*-heptane (100 mL). $TiCl_4$ (150 mL) was added at room temperature while stirring the content of the reactor. The temperature of the mixture was increased to 90°C and was maintained for at least 2 h. The obtained product was filtered. *n*-Heptane (100 mL) and $TiCl_4$ (100 mL) were added. The temperature was raised to 120°C and the mixture was stirred for another 2 h. The prepared catalyst was filtered, washed with *n*-heptane, and dried. All the procedures were carried out under an atmosphere of dried N_2.

TABLE I
Effect of [EtOH]/[$MgCl_2$] Molar Ratio on Particle Size of the Adduct

Sample	[EtOH]/[$MgCl_2$] molar ratio	Mean volume	Span[a]	Medium size[b] (μm)
AS1	2.8:1	31	1.47	38
AS2	2.9:1	38	1.37	40
AS3	3.1:1	36	1.67	37
AS4	3.3:1	40	1.53	39
AS5	3.5:1	38	1.79	41

Stirrer speed of different steps of the preparation = 500, 1000, 4000 rpm, respectively.

[a] Volume dispersity index (ratio of volume polydispersity to diameter).

[b] Particle size at the maximum PSD spectrum.

Polymerization of ethylene

Ethylene polymerization was carried out using the catalyst. Triethylaluminium (TEA) was used as cocatalyst. The polymerization procedure is explained elsewhere.[19]

Characterization

Morphological study of the support, catalyst, and polymer particle was carried out using Stero Scan 360 scanning electron microscopy (SEM) model (Cambridge Instrument). The PSD of the support, catalyst, and polymer particles was measured by laser diffraction method using instrument model Master Size X long bed Ver. 2.15 (Malvern). Surface area of the solid particle was determined using BET method by CHEM BET 3000 (Quantachrom).

RESULTS AND DISCUSSION

It is well known that in the case of Ziegler-Natta olefin polymerization at controlled conditions, shape replication of the catalyst to polymer is desired.[1–5,18] In the project, spherical particles of $MgCl_2$·nEtOH was prepared by adducting anhydrous $MgCl_2$ dissolved in ethanol.

Effect of [EtOH]/[$MgCl_2$] molar ratio

Effect of [EtOH]/[$MgCl_2$] molar ratio of 2.8:1 to 3.5:1 on particle size and volume dispersity index was studied (Table I). At molar ratio of [EtOH]/[$MgCl_2$] less than 2, the $MgCl_2$ does not completely dissolve in the ethanol.[11] On other hand, at the molar ratio higher than 4, the $MgCl_2$ does not precipitate well, and con-

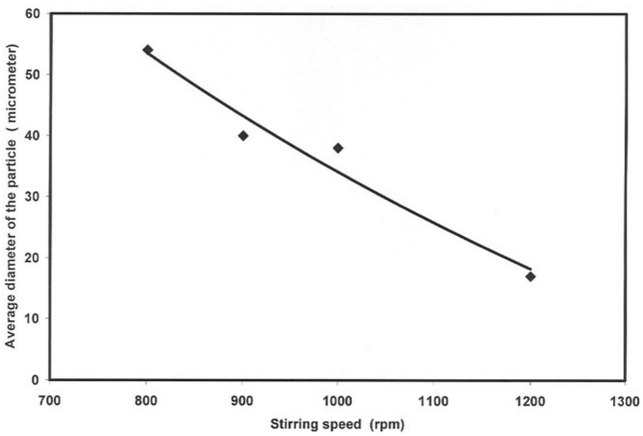

Figure 1 Effect of stirrer speed of the emulsion section on average diameter particles.

trol of morphology is impossible.[12] Table I shows the particle size obtained at $[EtOH]/[MgCl_2] = 2.9:1$, which is a narrow distribution that was chosen for preparing the $MgCl_2 \cdot nEtOH$ adduct.

Effect of stirrer speed

In the melt quenching method used for adducting $MgCl_2$, an emulsion of the adduct in an oil bath is required. The stirrer speed plays a key role to prepare a uniform desirable emulsion. The effect of stirrer speed from 800 rpm to 1200 rpm was studied. Figure 1 shows the stirrer speed effect on average diameter of the particles obtained. The higher the speed of the stirrer the lower is the average diameter of the particles. The behavior could be due to fine droplet of emulsion formed at higher stirrer speed. Therefore, the higher speed prevents coalescence and agglomeration of the particle in emulsion state.

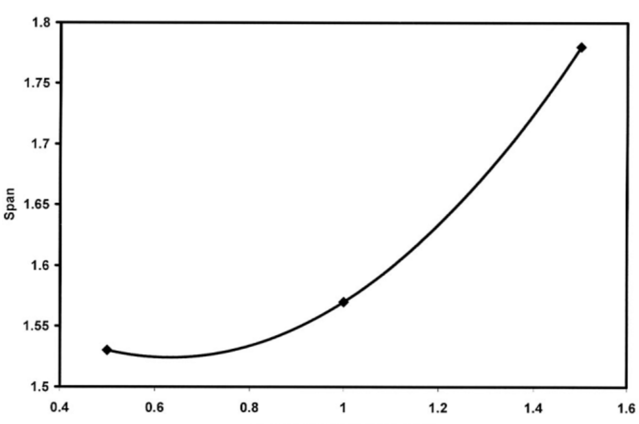

Figure 2 The effect of emulsion transfer rate on particle size.

TABLE II
Prepolymerization Condition

Catalyst (ml)	2
Cocatalyst (ml)	5
Heptane (ml)	50
Temperature (°C)	30
Time (min)	10

Catalyst slurry, 1 g catalyst in 30 ml heptane; [TEA] = 1*M*.

Effect of transfer rate of the adduct

The adducted $MgCl_2$ as emulsion was transferred to quenching section (the third reactor) via a stainless steel tube. The rate of the emulsion is influenced by morphology of the adduct.[7] Figure 2 shows the effect of the emulsion transfer rate on span (volume dispersity index or most probably the broadness of the PSD) obtained. The mean particle size increased slightly to a higher value with increasing transfer rate of the emulsion. When the transition rate is low, the amount of emulsion reaching the quenching section per unit time is low. The low amount of the adduct prevent agglomeration of the particles to bigger size, which may happen at higher value.

Polymerization

Prepolymerization of ethylene was carried out at room temperature in the presence of a low amount of cocatalyst (TEA) and monomer; prepolymerization generates a thin layer of polymer around the catalyst particles and protects the particle from uncontrolled fragmentation and therefore, increases the activity of the catalyst during main polymerization.[20]

Polymerization of ethylene was carried out using the slurry of the prepolymer. Tables II and III show the condition for prepolymerization and polymerization result obtained, respectively.

Surface area and morphological study

Surface area and morphology of the $MgCl_2 \cdot nEtOH$, adduct, support, prepared catalyst, and the polymer was studied. Table IV shows the result of surface area studies obtained. Removing some of the alcohol from

TABLE III
Polymerization of Ethylene

Run No.	Yield (kg PE/mmol Ti h)
1	18.34
2	20.23
3	19.68

Polymerization condition: monomer pressure, 1.5 bar; temperature, 60°C; [TEA], 5 mmol; time, 1 h; [Ti], 0.002 mol/L.

TABLE IV
Surface Area of the Adduct, Support, and Catalysts

Compound	Surface area (m^2/g)
$MgCl_2$.nEtOH	2.7
Support[a]	13.1
$MgCl_2$ (spherical)/$TiCl_4$	184.4

[a] Support is dealcoholated $MgCl_2$.nEtOH using heat.

the $MgCl_2$·nEtOH by heat increases the surface area of the support (Table IV).

SEM study of the $MgCl_2$·nEtOH, support, catalyst, and the main polymerized polyethylene obtained are shown in Figures 3–6, respectively. As can be seen from the SEM micrograph, the $MgCl_2$·nEtOH has large number of spherical particles with smooth surface. The very few pores on the surface indicate very low surface area of the particles. The diameter of the particles is mainly in the range of 20–45 μm with short amount of dusty particles. Removing some amount of the alcohol from adduct makes the surface of the so-called support bit coarse and porous. The surface area was increased from 2.7 to 13.1 m^2/g. Treatment of the support with excess $TiCl_4$ to the catalyst $MgCl_2$(spherical)/$TiCl_4$ increases sharply the surface area to 184.4 m^2/g. Figure 5 shows SEM of the catalyst particles that are mainly still spherical with porous surface compared with the surface of the support and adduct. The sharp increase of the porosity is due to removal of the ethanol from the support during the catalyst preparation procedure via a chemical reaction. The same behavior has been reported earlier.[1,21,22] SEM micrograph of the polyethylene obtained using the catalyst shows particles with no good morphology. The loss of the morphology could be due to uncontrolled fragmentation occuring during the prepolymerization and polymerization. In any case, the amount of dusty polymer particles obtained was very small. In general overview SEM of the $MgCl_2$·nEtOH, the support and the catalyst show morphological replications, which do not take place in polymer particles to such extent.

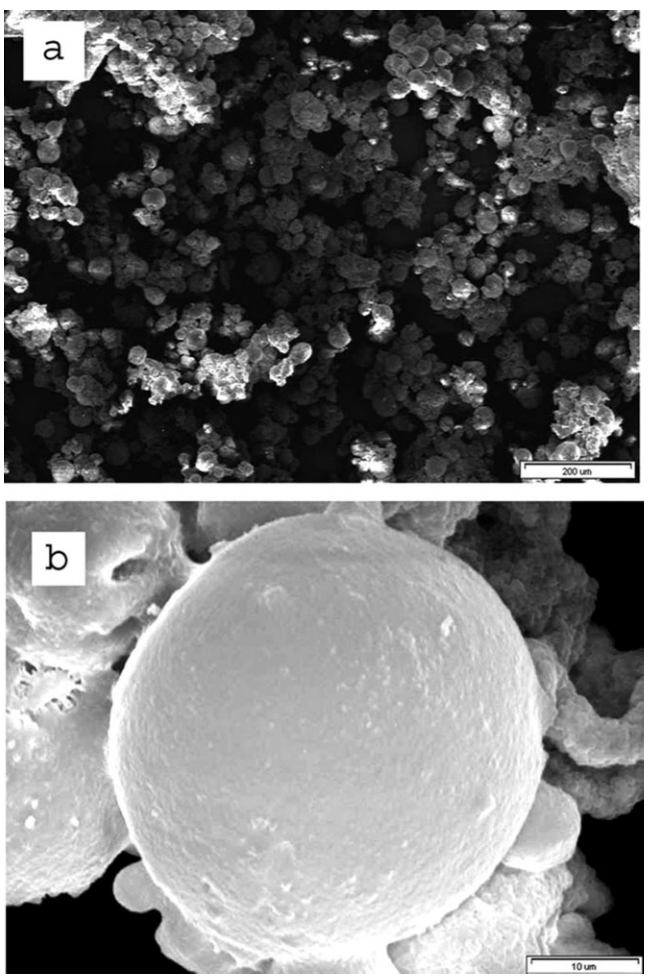

Figure 3 SEM micrograph of $MgCl_2$·nEtOH: (a) magnification 100×; (b) magnification 1500×.

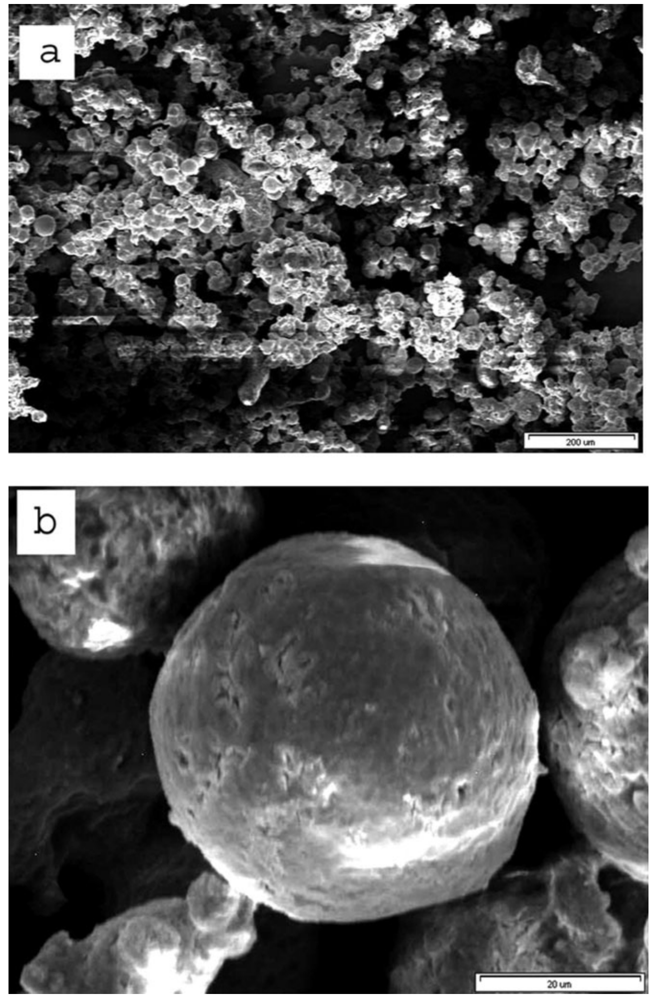

Figure 4. SEM micrograph of the support: (a) magnification 100×; (b) magnification 1500×.

CONCLUSIONS

1. Process conditions for preparation of the support, catalyst, and polymerization have a great effect on morphology of the support, catalyst, and polymer particles.
2. Stirrer speed of emulsion section in the melt quenching method for the preparation of spherical support of $MgCl_2$ is influenced by PSD and the morphology of the particles obtained.
3. Melt quenching method for the preparation of spherical particles of $MgCl_2$·nEtOH gives particles with good spherical morphology.
4. Transfer rate of emulsion is affected by the particle size of the $MgCl_2$·nEtOH adduct.
5. Heat removal of ethanol from the $MgCl_2$·nEtOH increases its surface area. Treatment of the support with $TiCl_4$ also significantly increases its surface area.

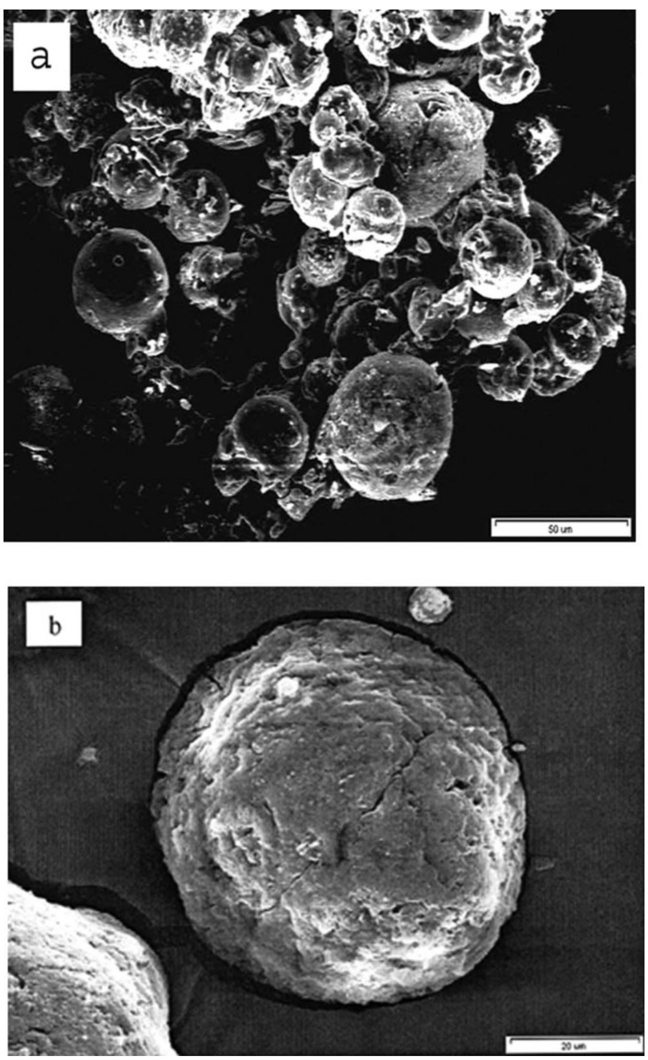

Figure 5 SEM micrograph of MgCl2(spherical)/TiCl4 catalyst: (a) magnification 500×; (b) magnification 1200×.

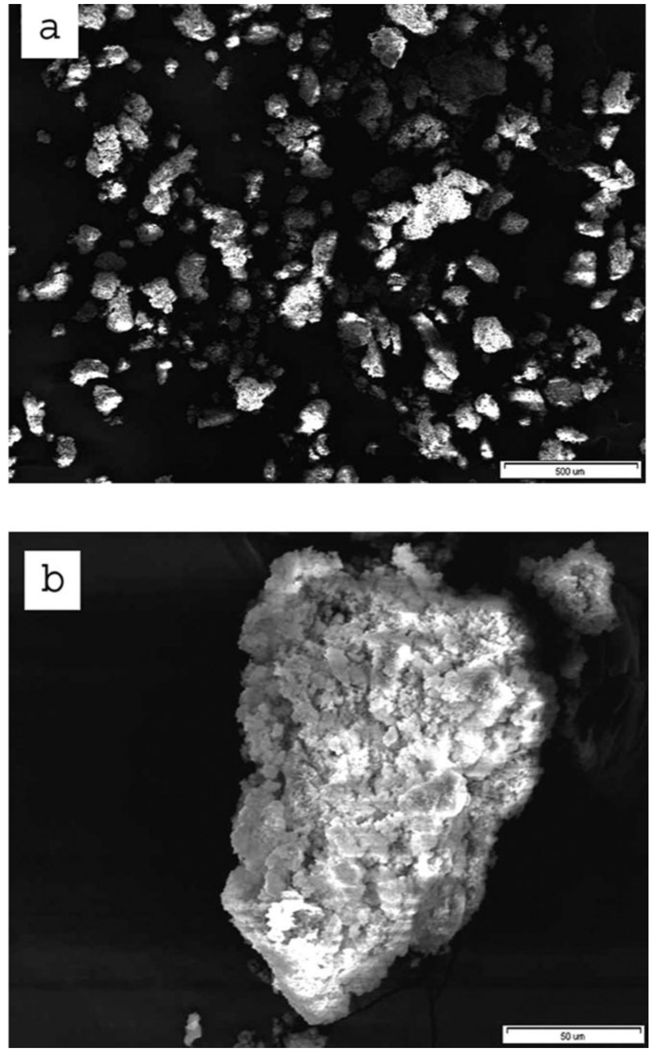

Figure 6 SEM micrograph of main polymerized polyethylene obtained: (a) magnification 500×; (b) magnification.

6. Ziegler-Natta catalyst of $MgCl_2$(spherical)/$TiCl_4$ prepared using $MgCl_2$·nEtOH with $TiCl_4$ gives an active catalyst for ethylene polymerization.
7. SEM study of the polyethylene obtained using the $MgCl_2$(spherical)/$TiCl_4$/TEA catalyst system of spherical morphology obtained from spherical support shows particles with no regular shape.

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