

Preparation of Shish-Kebab and Nanofiber Polyethylene with Chromium/Santa Barbara Amorphous Silica-15 Catalysts

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ABSTRACT: Cr/SBA-15 catalysts were prepared by the grafting of chromium nitrate nonahydrate [$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] complexes onto SBA-15 mesoporous materials. Shish-kebab and nanofiber polyethylenes (PEs) were prepared under different temperatures via ethylene extrusion polymerization with the $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ catalytic system. The diameter of a single nanofiber was 100–250 nm. Scanning electron microscopy images showed that the polymer obtained from the SBA-15-supported catalyst under different polymerization temperatures produced nanofiber and/or shish-kebab mor-

phologies. X-ray diffraction and differential scanning calorimetry were used to characterize microstructures of the materials. Polymers obtained with all of the catalysts showed a melting temperature, bulk density, and high load melt index; this indicated the formation of linear high-density PE. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 3658–3665, 2010

Key words: catalysts; fibers; polyethylene (PE); supports; templates

INTRODUCTION

The Phillips Cr/silica polymerization catalyst, responsible for perhaps 40% of the world's high-density polyethylene (PE) production, is usually made by the impregnation of a chromium compound, such as CrO_3 onto silica followed by calcination in dry air at a high temperature.^{1,2} The activity of these polymerization catalysts is very sensitive toward the support of textural properties and, particularly, its porosity.³ The recently discovered M41S families of mesoporous solids are amorphous materials with a uniform pore size distribution.⁴

Mesoporous zeolites possess uniform hexagonal channels with diameters of 15–100 Å.⁵ These channels not only control the polymerization locus but also affect the pattern of monomer insertion and chain propagation to obtain fibrous polymers.⁶ Kageyama et al.⁷ first prepared crystalline PE fibers via *in situ* ethylene extrusion polymerization with mesoporous silica film (MSF)-supported titanocene at a pressure of 10 atm. Subsequently, Ye et al.⁸ also prepared PE nanofibers with titanocene dichloride (Cp_2TiCl_2) supported on mobile crystalline material (MCM)-41, under a higher ethylene pressure (20 atm).

SBA-15, was synthesized using amphiphilic tri-block copolymers to direct the organization of silica species under strong acidic conditions. SBA-15 has regular, cylindrical, ordered hexagonal pores, with narrow pore size distribution and large surface area. SBA-15 is another kind of mesoporous silicate zeolite with a diameter of 6–12 nm; it has a larger pore, thicker wall, and higher mechanical intensity than MCM-41.⁹ So, it is a better support for the preparation of fibrous polymers. Recently, Calleja et al.^{10,11} prepared PE with a Cr/Aluminium metal-SBA-15 (AISBA-15) catalyst.

In this study, both nanofiber and shish-kebab PEs were prepared via *in situ* ethylene extrusion polymerization with SBA-15-supported chromium nitrate nonahydrate [$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] as a catalyst under different polymerization temperatures. The effects of the polymerization temperature and silica structure on the catalytic activities and morphologies of the produced nanofibers and shish-kebab PEs have not yet been reported. These Cr/SBA-15 catalysts were compared to a chromium-containing catalyst prepared through grafting of chromium nonahydrate onto Aldrich (Germany) commercial silica.

EXPERIMENTAL

Materials

All manipulations involving air and/or water sensitive compounds were performed under nitrogen atmosphere using standard Schlenk technology.

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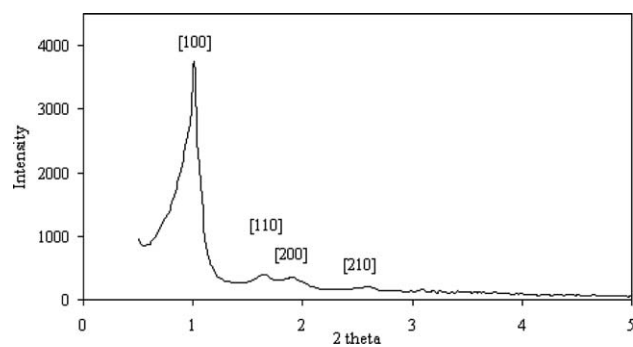


Figure 1 XRD pattern of the Soxhleted SBA-15 support.

TEAL (triethylaluminium) and Pluronic 123 triblock copolymer (EO₂₀-PO₇₀-EO₂₀, poly(ethylene oxide)-block-poly(propyleneoxide)-block-poly(ethylene oxide)) were purchased from Aldrich (Germany). Tetraethylorthosilicate (TEOS) and ethanol were obtained from Merck (Germany). Polymerization-grade ethylene and n-hexane were purchased from Arak Petrochemical Company, Iran and purified using three columns of KOH, CuO, and 5-Å molecular sieves. Hexane was refluxed over sodium with benzophenone as an indicator and distilled under nitrogen atmosphere before use.

Preparation of the support

SBA-15 material was synthesized according to the procedure described by Zhao et al.¹² with Pluronic 123 as a template. In a typical preparation, 4.0 g of Pluronic was dissolved in 30 g of water and 120 g of a 2M HCl solution with stirring at 35°C. Then, 8.50 g of tetraethylorthosilicate was added to the solution with stirring at 35°C for 20 h. The mixture was aged at 80°C overnight under static conditions. The solid product was recovered, washed, and air-dried at room temperature. The template was removed from the as-made mesoporous material by Soxhlet extraction with ethanol for 96 h.

Preparation of the silica-supported catalysts

The chromium grafting procedure was started with the support materials, which were previously out-gassed *in vacuo* overnight. Then, 2 g of the silica was

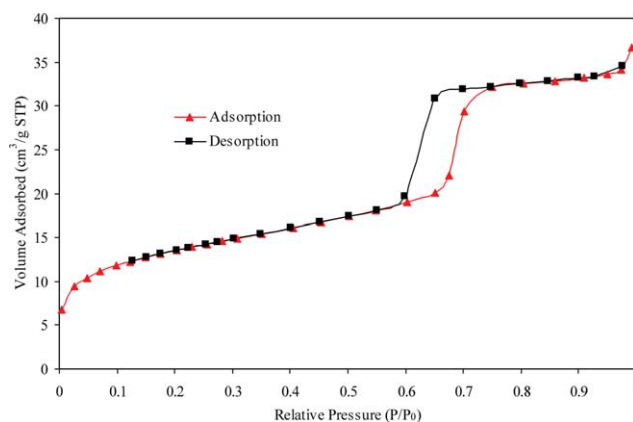


Figure 2 Nitrogen adsorption-desorption isotherm plot of Soxhleted SBA-15. P/P_0 = relative pressure (surface pressure/preliminary pressure). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

stirred with 30 mL of Cr(NO₃)₃·9H₂O solution in dried methanol for 3 h under reflux. Next, the solid product was recovered and washed extensively with methanol. Finally, the grafted materials were calcined in air on a fluidized bed reactor up to 550°C for 3 h at a heating rate of 2.0°C/min. Inductively coupled plasma spectrometry analysis gave us the supported chromium content (0.19 wt %).

Preparation of PE in the slurry phase

Ethylene polymerization reactions were carried out in a 2-L stainless steel stirred Autoclave Engineers apparatus (Buchiglauster bmd300, Switzerland). The reaction conditions were 800 rpm, 90°C, 31.5 bar of ethylene pressure, 0.5 mol of TEAL, and hexane as the solvent. After 1 h of reaction, the resulting PE was recovered, filtered, washed with acetone, and dried for 6 h at 70°C. The polymerization activities [kg of PE (g of Cr)⁻¹ h⁻¹] were calculated for each run.

Physicochemical characterization

Powder X-ray diffraction (XRD) patterns were collected on a Siemens D5000 diffractometer (Siemens, Berlin, Germany) instrument using Cu K α radiation of wavelength 0.154 nm. Nitrogen adsorption-desorption isotherms were obtained at 77 K with an

TABLE I
Structural Parameters of the SBA-15 and SiO₂ Samples

b_p (Å)	d_{100} (Å)	V_p (mL/g)	d_p (Å)	S_{BET} (m ² /g)	Support
34.3	87	0.56	46.8	479	SBA-15(Hex)
12.7	74	0.75	60	500	SiO ₂

S_{BET} = BET specific surface area; V_p = specific pore volume; d_p = average pore diameter, obtained from BJH adsorption data ($d_p = 4V_p/S_{BET}$); d_{100} = XRD interplanar spacing; b_p = pore wall thickness [$b_p = (a_0 - d_p)/2$, $a_0 = (2/\sqrt{3})d_{100}$].

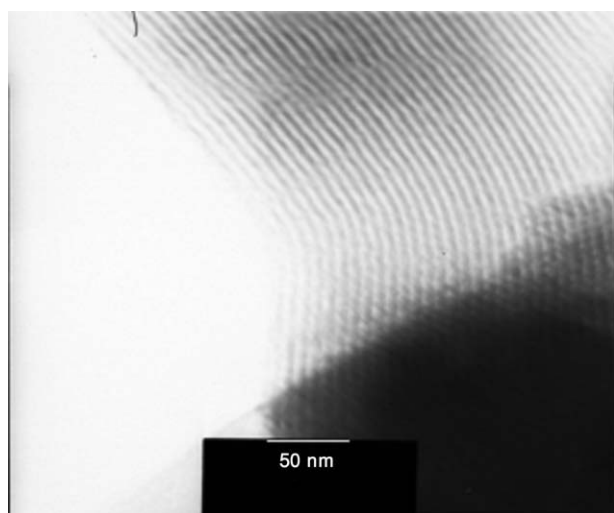


Figure 3 TEM micrograph of the Soxhleted SBA-15.

OMNISORP 100CX VER 1G adsorption apparatus. Samples were outgassed at 473 K for at least 8 h *in vacuo* before the measurements. The SBA-15 and polymer samples were deposited on a sample holder and sputtered with gold. The morphologies were observed on a scanning electron microscopy (SIRION, FEI). Transmission electron micrographs (TEM) were taken on a 2000 JEOL electron micro-

scope (Akishima, Japan) operating at 200 kV. The samples for TEM were prepared by dispersing a large number of particles of the products through a slurry in acetone onto a holey carbon film on a Ni grid. Differential scanning calorimetry (DSC) analysis was carried out on a PerkinElmer DSC 7 instrument (Boston, MA). Ultra-high-purified nitrogen was purged through the calorimeter. The PE samples (≈ 4 mg) were heated to 170°C at a rate of 10°C/min; they were then cooled to 40°C at 10°C/min. Subsequently, a second heating cycle was conducted at a heating rate of 10°C/min. Thermogravimetric analysis (TGA) was performed under nitrogen flow on a thermogravimetric analyzer from PerkinElmer (Pyris1 model) with scanning from 50 to 800°C at a rate of 5°C/min. Fourier transform infrared (FT-IR) spectroscopy (Bruker IFS 48 spectrophotometer, Ettlingen, Germany) was taken in KBr pellets to confirm the structure of the catalyst and polymer.

RESULTS AND DISCUSSION

Characterization of SBA-15

The X-ray pattern of the as-synthesized SBA-15 prepared with poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) (EO₂₀-PO₇₀-EO₂₀)

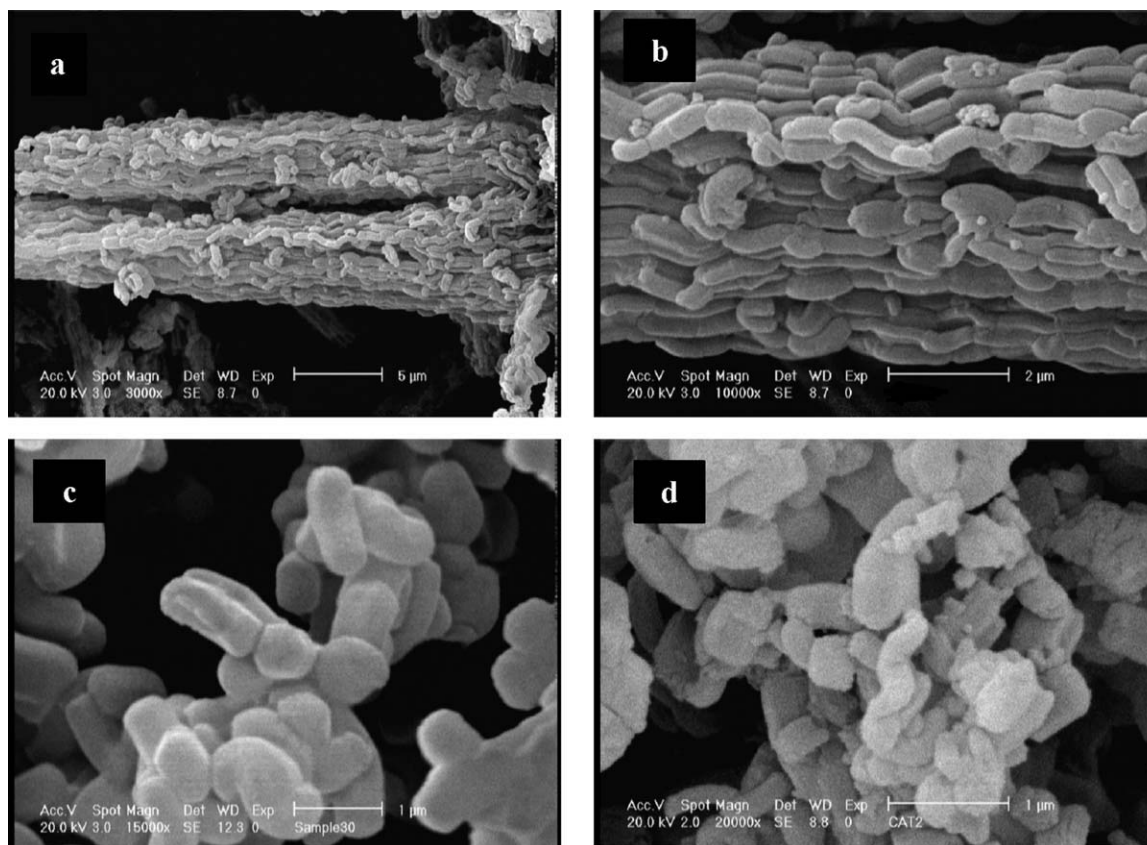


Figure 4 SEM micrographs of SBA-15: (a,b) tubular structure of Soxhleted SBA-15, (c) calcined SBA-15, and (d) Cr/SBA-15 catalyst.

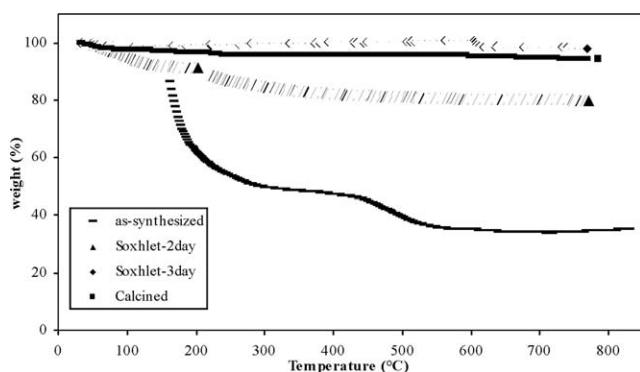


Figure 5 TGA thermograms of (–) uncalcined SBA-15(Hex), (▲) Soxhleted SBA-15 after 2 days, (◆) Soxhleted SBA-15 after 3 days, and (■) calcined SBA-15 (heating rate = 5°C/min under pure N₂).

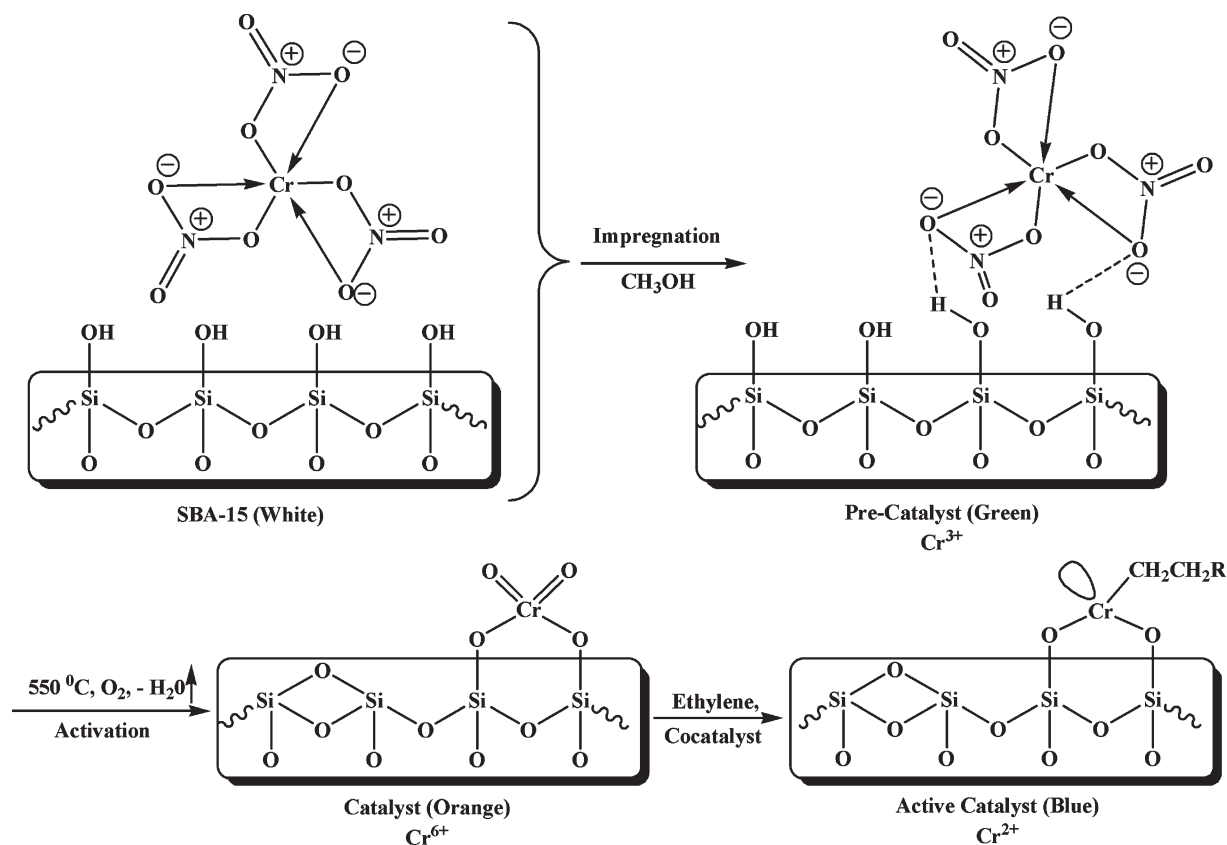
(Pluronic P123) in Figure 1 shows four well-resolved peaks that could be indexed as the (100), (110), (200), and (210) diffraction peaks associated with space group (*p6mm*) hexagonal symmetry. Three additional peaks appeared in the 2θ range 2.5–3.5° that could be indexed as the (300), (220), and (310) scattering reflections, respectively. The intense (100) peak reflected a *d*-spacing of 87 Å, which corresponded to a large unit cell parameter ($a = 90 \text{ \AA}$).^{12,13}

Figure 2 shows the nitrogen adsorption–desorption isotherm plot from the adsorption branch of the Soxhleted hexagonal mesoporous silica SBA-15.^{12,13}

Table I summarizes the textural properties of the SBA-15 supports derived from the nitrogen adsorption–desorption isotherm plot and pore size distribution curve. Table I also displays the textural properties of the commercial silica used as a reference support to prepare the Cr/SiO₂ catalysts for comparison purposes.

As shown in Figure 3, the TEM image of the Soxhleted SBA-15 confirmed that SBA-15 had a two-dimensional *p6mm* hexagonal structure with a well-ordered hexagonal array and a one-dimensional channel structure. The average distance between mesopores was estimated to be about 100 Å; this was consistent with that determined from X-ray diffraction (XRD) data.¹²

SEM was used to determine the size and morphology of the SBA-15. In Figure 4, SBA-15 images reveal that it consisted of many ropelike domains with relatively uniform sizes with lengths of 0.9–1.5 μm and diameters of 0.2–0.3 μm; these were aggregated into wheatlike macrostructures (rodlike primary particles aggregated to form micrometer-sized fibers).



Scheme 1 Cr/SBA-15 catalyst synthesis and activation steps.

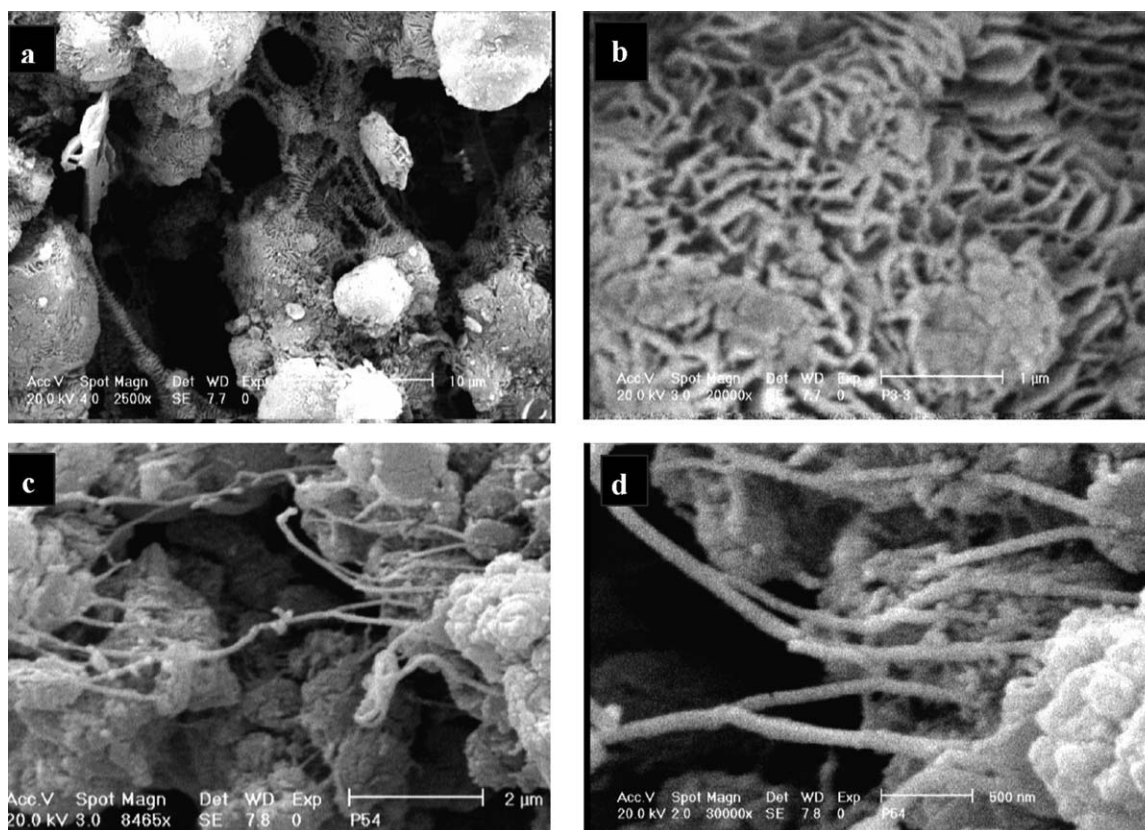


Figure 7 SEM micrographs of the PE produced from the chromium-supported catalysts at a polymerization temperature of 90°C: (a) Cr/SiO₂ (Aldrich), (b) magnified view of part a, (c) Cr/SBA-15, and (d) magnified view of part c.

We calculated the polymerization activities [$\text{kg of PE (g of Cr)}^{-1} \text{h}^{-1}$] by dividing the weight of dry PE produced by the weight of chromium in the catalyst. As shown by the results of activity in Table II, the activity of Cr/SBA-15 was higher than that of Cr/SiO₂. The polymerization temperature increase from 90 to 112°C led to a decrease in the polymerization activity, which could have been due to a decrease in the ethylene solubility in hexane and an increase in the chain transfer.

According to Figure 7(a,b), the SEM micrographs of the PE sample produced in Table II run 1 mainly took on porous morphologies. Figure 7(c,d) shows the SEM micrographs of the samples produced in Table II run 2 mainly took on smooth nanofiber morphologies. The ethylene could disperse into the channels easily and polymerize in the channels, and the channels could control the direction of the chain propagation to form fibers.

As shown by the results of enthalpy change (ΔH) in Table II, the PE prepared by the Cr/SBA-15 catalyst had a higher crystallinity compared to the PE prepared by the Cr/SiO₂ catalyst. The Cr/SBA-15 catalyst prepared by impregnation gave a PE with a slightly higher melting temperature than the PE obtained from the Cr/SiO₂ catalyst. This indicated

that the channels of SBA-15 could control the direction of the chain propagation to increase the crystallinity of the PE.

The DSC curves in Figure 8 show the melting points of the PEs prepared at different polymerization temperatures. The polymerization temperature had a significant effect on the morphology of the resulting PE samples. In this study, three samples prepared at different polymerization temperatures were investigated. Figure 9(a,b) shows the SEM

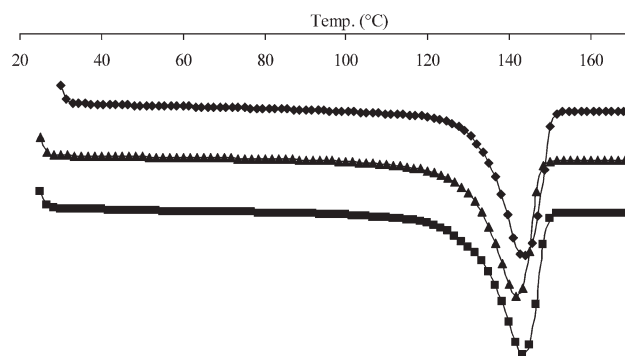


Figure 8 DSC traces for the PE prepared by the Cr/SBA-15 catalysts at different polymerization temperatures: (◆) 90, (▲) 104, and (■) 112°C (heating rate = 5°C/min under pure N₂).

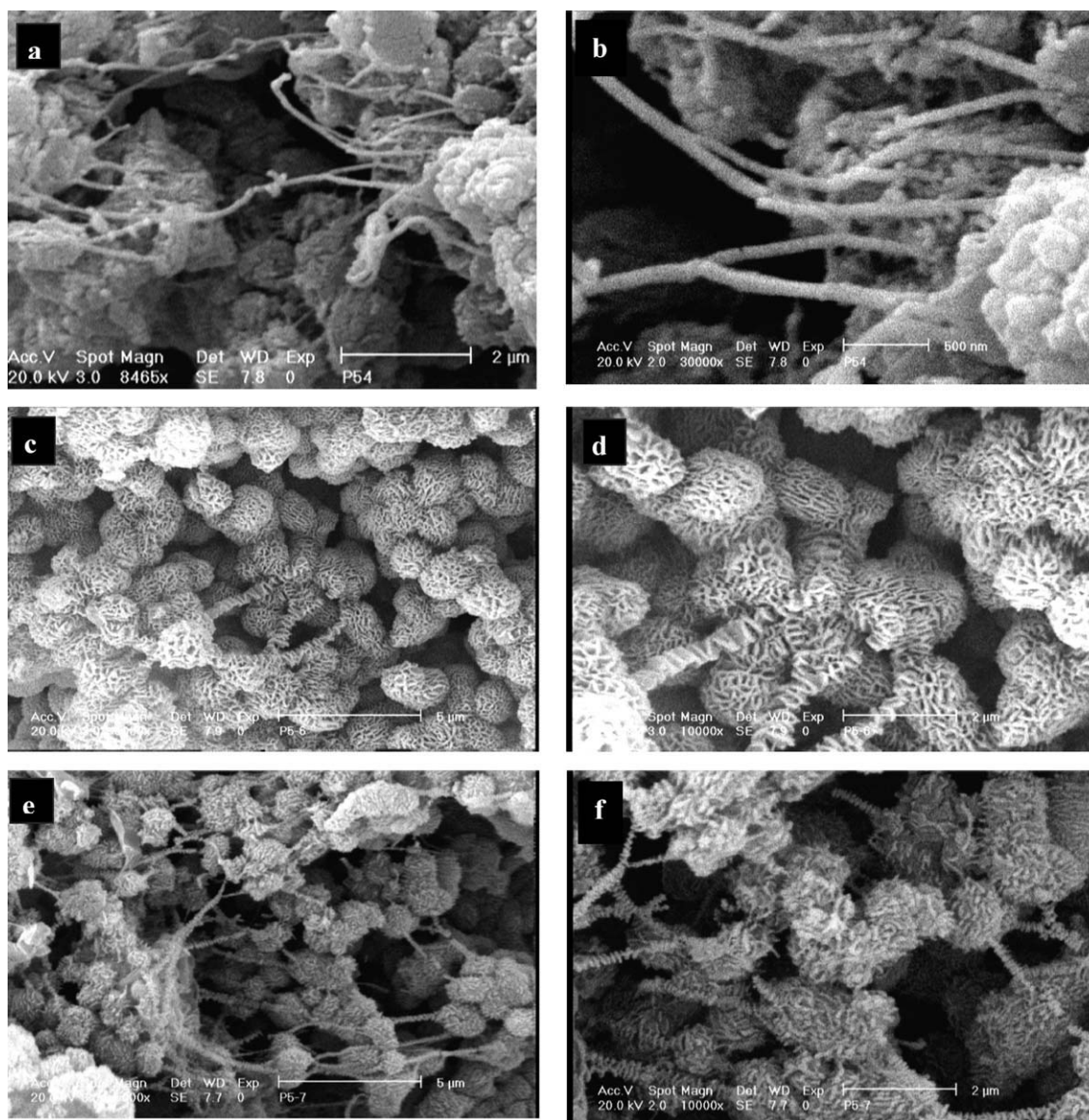
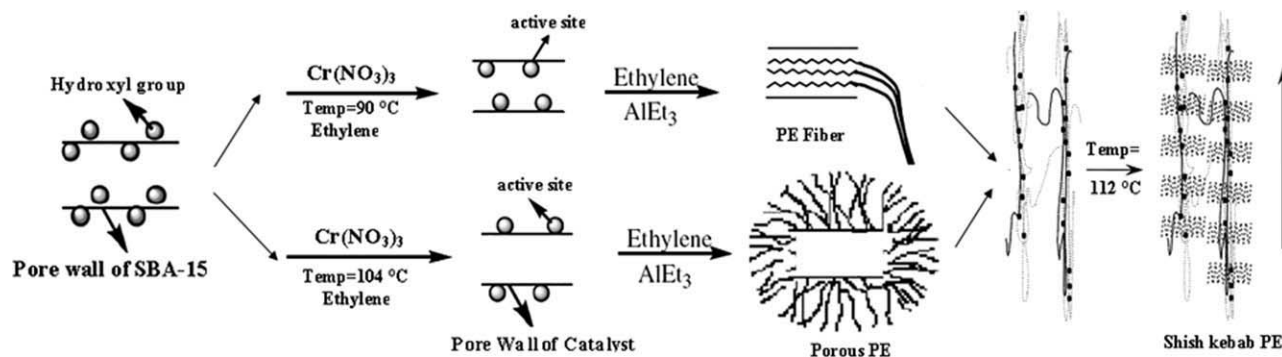


Figure 9 SEM micrographs of the PE produced from the SBA-15 chromium-supported catalysts at different polymerization temperatures: (a) the fibers and floccule morphologies of the sample produced at a 90°C polymerization temperature, (b) magnified view of part a, (c) the porous morphology of the sample produced at a 104°C polymerization temperature, (d) magnified view of part c, (e) the shish-kebab and porous morphologies of the sample produced at 112°C polymerization temperature, and (f) magnified view of part e.



Scheme 2 Possible formation process of the shish-kebab PE.

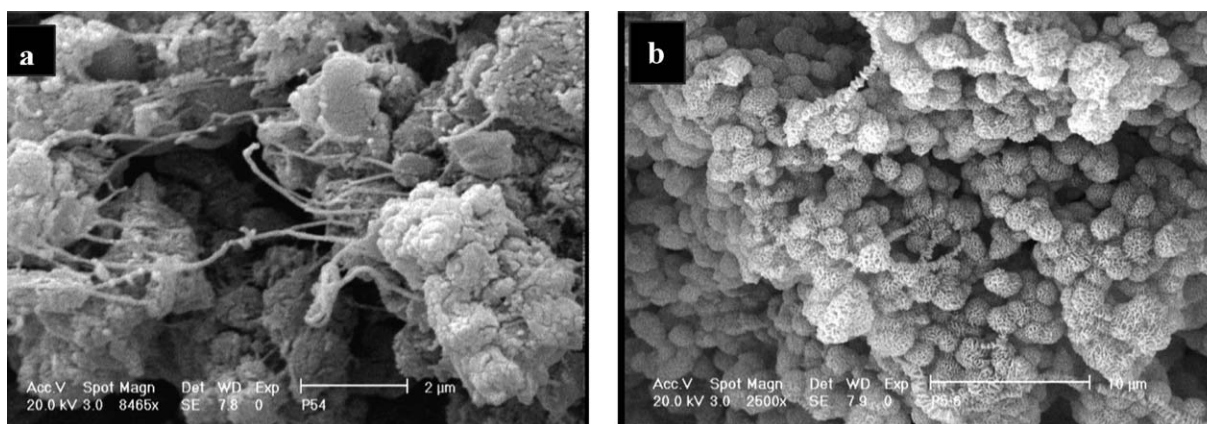


Figure 10 SEM micrographs of the PE produced from the SBA-15(Hex) chromium-supported catalyst at a 90°C polymerization temperature: (a) calcined SBA-15(Hex) and (b) uncalcined SBA-15(Hex).

micrographs of the sample produced in Table II run 2; it indicates that the PE samples mainly took on fiber and floccular morphologies. The SEM micrographs show that fibers were the major morphologies in the PE samples. The diameter of a single nanofiber was 100–250 nm. As the polymerization temperature increased to 104°C, the number of nanofibers decreased, and a porous morphology was observed [Fig. 9(c,d)]. According to Figure 9(e,f), the increase in the polymerization temperature to 112°C led to a shish-kebab morphology.

At 90°C, the internal and external chromium sites of the catalyst had high activities. The channels could control the direction of the chain propagation to form nanofibers with shear-induced cylindrical crystallization.

At 104°C, active internal Cr sites were blocked with the polymer, the activity of polymer was decreased, and a porous morphology was produced by active external Cr sites. As shown in Scheme 2, at 112°C, nanofibers acted as shish nuclei, and porous PE, acting as a kebab, was aligned around the shish.

According to these results, the nanofiber-to-folded-chain ratio in produced PE was controlled by the change in the polymerization temperature. Nanofibers increased the strength, but folded chains increased the elasticity.

There were internal and external hydroxyl groups in Cr/hexagonal SBA-15 (SBA-15(Hex)) nanochannels that covalently bonded with chromium. Nanofibers were attributed to internal Cr sites, and porous PE was due to external chromium sites. To confirm this, the as-synthesized SBA-15 without surfactant extraction from the nanochannel was tested, and Cr was loaded onto the uncalcined support.

As shown in Table II run 5, the activity of this catalyst was lower than that of run 2. SEM micrographs of the samples merely showed porous PE. A comparison between Figures 10(a) and 10(b) confirmed that a long nanofiber was produced in the hexagonal nanochannel of the calcined Cr/SBA-15(Hex).

CONCLUSIONS

Under overpressure, PE nanofibers were prepared via *in situ* ethylene extrusion polymerization with SBA-15-supported $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as a catalytic system. Fibers and floccules were the major morphological units in the samples prepared at low temperature. The diameter of a single nanofiber was 100–250 nm. The single nanofibers aggregated to form fiber aggregates and bundles. With the extension of the polymerization temperature, the number of PE nanofibers decreased, and a porous morphology appeared. At high temperature, a shish-kebab morphology was observed. The melting point of the nanofiber and shish-kebab PE was a little higher than that of common PE.

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