# Study of the Structure of Cobalt-Containing Catalysts Synthesized under Subcritical Conditions

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Abstract—A physicochemical study of cobalt-containing (10 wt %) silica-supported Fischer—Tropsch catalysts was carried out. The catalysts were obtained under subcritical conditions ( $T = 200^{\circ}$ C, P = 8 MPa) using water ( $T_c = 374.1^{\circ}$ C,  $P_c = 22.1$  MPa) and propanol-2 ( $T_c = 235.6^{\circ}$ C,  $P_c = 5.8$  MPa). The obtained samples were compared with a 10 wt % Co/SiO<sub>2</sub> catalyst prepared by incipient-wetness impregnation. Comparison of the properties of catalysts in the liquid-phase Fischer—Tropsch synthesis showed that the sample prepared in subcritical water was the most active and selective to aliphatic C<sub>6</sub>–C<sub>7</sub> hydrocarbons. This sample is characterized by a high surface area (131.7 m<sup>2</sup>/g), a uniform distribution of particles in the active phase with an average size of 5 nm and higher accessibility of cobalt species for reagents. According to XPS data, the composition of catalyst active phase is mainly represented by two compounds: Co(OH)<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub>.

*Keywords:* cobalt, silica, subcritical conditions, impregnation, Fischer–Tropsch synthesis **DOI:** 10.1134/S0023158419050021

# **INTRODUCTION**

Supported metal catalysts are given considerable attention in various fields of chemical technology. Such heterogeneous systems are characterized by high mechanical strength and surface area and make it possible to decreasing the metal content of a catalyst [1]. Currently, different techniques are used in order to support metal particles on different materials: incipient-wetness impregnation [2], colloidal synthesis [3], microemulsion method [4], sonochemical synthesis [5], precipitation and co-precipitation [6], polyol method [7], etc. Physical and physicochemical properties of the obtained catalysts undergo considerable change depending on the technique used.

Supported metal catalysts are typically prepared by impregnation of supports with a solution of a metal precursor with the subsequent drying, calcination, or reduction of metallic nanoparticles [2]. However, the high viscosity and surface tension of the most liquids used as solvents in the impregnation process lead to a slow diffusion of metal salts in the pores of support, and, as a consequence, to the low dispersion of metal particles and inhomogeneity of the resulting samples [8]. Furthermore, subsequent drying and thermal activation may cause significant changes in the structure of the catalyst leading to a sharp decrease in the surface area and aggregation of the active phase.

Considerable recent attention is given to the synthesis of supported catalysts using sub- and supercritical fluids [9]. Due to the unique properties, the supercritical fluids make it possible to control the size, dispersity, structure, and morphology of the obtained nanoparticles. The low surface tension of supercritical fluids prevents pores of support from clogging during synthesis, while the low viscosity accelerates the diffusion of a metal salt solution. Moreover, the solubility of many compounds increases in supercritical conditions thus expanding the range of metal precursors used [10]. Supercritical metal deposition is carried out in several steps: (1) the dissolution of a precursor in a supercritical fluid; (2) the addition of a porous support to the resulting solution; (3) the adsorption of the solution in the pores and on the surface of the support; (4) the chemical or thermal reduction of the precursor leading to the formation of the active-phase particles [11]. Carbon dioxide [8, 9, 12–15] and water [16–18] are most often used as solvents in the supercritical synthesis of catalysts. In addition, there are data on the use of methanol [19], ammonia [20], isopropyl alcohol [21, 22], cyclohexane [23], and propane [24] as supercritical solvents. Analysis of literature data showed that water can be considered the most promising solvent for sub/supercritical synthesis of catalysts.

For example, the structure and catalytic properties of  $Pd/ZrO_2$  and  $Pd(Rd)/TiO_2$  synthesized in super-

critical and subcritical water, respectively, were studied in [16, 25]. Otsu and Oshima [26] studied the structure of manganese, lead, and silver oxides supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in supercritical water. Sun et al. [27] synthesized nickel-, cobalt-, and iron-containing catalvsts in subcritical ethanol. Yahva et al. [28] studied the structure and photocatalytic properties of potassium hexatitanate synthesized in super- and subcritical water. The use of super- and subcritical conditions for the synthesis of supported catalysts shows that, despite reaching the critical region, the resulting catalytic systems are characterized by high crystallinity, nanoscale size and uniform distribution of the active phase. However, since a sharp change in the properties (dielectric constant, polarity, etc.) is observed for polar liquids in the supercritical state, sub- and nearcritical conditions are optimal for the synthesis of metal-containing composites [17].

In this work, the structure and physicochemical properties of cobalt nanoparticles deposited on silica, synthesized in subcritical conditions using water and propanol-2 as solvents are studied. The obtained nanosystems are compared with the catalyst prepared by impregnation.

# **EXPERIMENTAL**

#### Synthesis of Cobalt-Containing Catalysts

The following materials were used for the synthesis of catalysts: cobalt(II) chloride, sodium bicarbonate, anhydrous silica, propanol-2, ethylene glycol (all reactants were of chemical purity grade purchased from Reakhim, Russia), and distilled water.

# Catalyst Synthesis in Subcritical Conditions

Synthesis of cobalt-containing catalysts under subcritical conditions was carried out in a PARR-4307 high-pressure reactor (Parr Instrument, USA). The reactor was loaded with 1 g of silica, cobalt chloride based on 10 wt % of pure cobalt, and 0.1 g of sodium bicarbonate as a precipitating agent dissolved in  $30 \text{ cm}^3$  of a solvent (distilled water or propanol-2). The reactor was sealed and purged with nitrogen to remove air oxygen. Then the necessary operating pressure of nitrogen (6.0 MPa) controlled by the pressure gauge and temperature ( $T = 200^{\circ}$ C) were set. The total pressure in the reactor after heating was 7.5 and 8 MPa for water and propanol-2, respectively. The process was carried out with continuous stirring at a rate of 750 rpm. The synthesis time was 15 min. After synthesis, the reaction mixture was cooled to room temperature, filtered, washed with  $15-20 \text{ cm}^3$  of the solvent to remove chloride ions and dried in air. The obtained samples were designated as Co/SiO<sub>2</sub>(H<sub>2</sub>O) and  $Co/SiO_2(IPA)$ .

# Catalyst Synthesis by Impregnation

The cobalt-containing catalyst was synthesized by impregnation as follows: 1 g of silica  $(SiO_2)$  dried to a constant weight, was impregnated with a mixture consisting of cobalt chloride based on 10 wt % of pure cobalt, 8 cm<sup>3</sup> of ethylene glycol, and 2 cm<sup>3</sup> of distilled water for 15 min. Then, the sample was filtered and treated with an aqueous solution of sodium bicarbonate with a concentration of 2.76 g/dm<sup>3</sup> for 15 min, washed with distilled water to remove chloride and carbonate ions and dried in air. The resulting sample was denoted as Co/SiO<sub>2</sub>(EG).

The resulting samples were reduced in a hydrogen flow at 300°C for 3 h to convert metal hydroxides into oxides with the subsequent reduction.

#### Physicochemical Study of the Catalysts

**Low-temperature nitrogen adsorption.** The specific surface area and porosity were determined using a Beckman Coulter<sup>TM</sup> SA  $3100^{TM}$  analyzer (Coulter Corporation, USA). The preparation of samples was performed by Beckman Coulter<sup>TM</sup> SA-PREP<sup>TM</sup> device (Coulter Corporation, USA) at a temperature of  $-120^{\circ}$ C for 60 min. In the analysis, Langmuir, Brunauer–Emmett–Teller, and *t*-plot models were used. The Harkins–Jura equation was used to calculate pore distribution.

**Transmission electron microscopy.** Transmission electron microscopy (TEM) of catalyst samples was performed to determine the size and distribution of cobalt-containing particles. The catalyst samples were prepared by the microslice method with a thickness of 50 nm. The analysis was performed at a voltage of 60 kV using JEOLJEM 1010 microscope (JEOL, Japan). Microscopic images were obtained using a Gatan digital camera (Gatan Inc., USA). The analysis of the microscopic images was performed using Adobe Photoshop and Scion Image Processing Toolkit.

X-ray photoelectron spectroscopy. To determine the qualitative composition of the surface and the valence state of the metal, X-ray photoelectron spectroscopy (XPS) of samples was used. The X-ray photoelectron spectra of the samples were obtained on an ES-2403 photoelectron spectrometer equipped with PHOIBOS-100-MCD energy analyzer (Specs GmbH, Germany) and XR-50 X-ray source with a twin-anode Mg/Al. The Al $K_{\alpha 1,2}$  line was used when recording the spectra. The radiation power was 250 W. The survey spectra of the samples were recorded in the range of 0–1200 eV.

The obtained spectra were analyzed using Casa XPS software package. To isolate individual states, model deconvolution of high-resolution spectra was carried out taking into account such characteristics of photoelectron sublevels as the binding energy of components, the ratio of the areas of component peaks, and intra-doublet splitting. Shirley background was chosen as a model background. Minimization was carried out by the Levenberg–Marquardt method.

Diffuse reflectance IR Fourier transform spectroscopy. Diffuse reflectance IR Fourier transform (DRIFT) spectra were measured using the Protege 460 IR spectrometer (Nicolet, USA) equipped with a diffuse-reflectance device. Before the analysis, the samples in the form of 0.25–0.35 mm fraction were treated in vacuum for 2 h at a temperature of 400°C. Carbon monoxide was used as a test molecule. Carbon monoxide was adsorbed at room temperature at an equilibrium pressure of 1599.9 Pa. Carbon monoxide desorption was carried out at room temperature in vacuum. The spectra were measured in the range of  $6000-400 \text{ cm}^{-1}$  with a step of 4 cm<sup>-1</sup>.

# Testing of Synthesized Catalysts in Liquid-Phase Fischer–Tropsch Synthesis

Fischer–Tropsch synthesis in the presence of the obtained catalytic systems was carried out in a PARR-4307 steel reactor (Parr Instrument, USA) using *n*-dodecane as a solvent. A mixture of CO and H<sub>2</sub> in a volumetric ratio of 1 : 6 was used as syngas. The high hydrogen content of the gas mixture is due to the need for additional hydrogenation of olefins and oxygen-containing compounds formed in the presence of a cobalt-containing catalyst [29–32]. The process temperature was 200°C, the total pressure in the reactor was 2.0 MPa, the catalyst weight was 0.1 g, the solvent volume was 30 cm<sup>3</sup>.

The liquid phase was analyzed by GCMS using a GC-2010 gas chromatograph and a GCMS-OP2010S mass spectrometer (SHIMADZU, Japan). Liquid phase samples were taken after 3 h of the reaction after cooling and condensing the liquid products. The analysis of the liquid phase was carried out under the following conditions: the sample volume, 3 mm<sup>3</sup>; the initial temperature of the column 150°C was maintained for 6 min, then the temperature was increased to  $250^{\circ}$ C at a heating rate of  $15^{\circ}$ C/min; injector temperature, 280°C; carrier gas, helium; helium pressure, 253.5 kPa; total flow rate of helium, 81.5 cm<sup>3</sup>/min; linear flow rate of helium, 20.8 cm<sup>3</sup>/s; a HP-1MS column with L = 30 m and a film thickness 0.25 µm and d of 0.25 mm; ion source temperature,  $260^{\circ}$ C; interface temperature, 280°C; scanning mode from 10 to 800 m/z; scanning speed, 625; and electron impact ionization.

The gas phase samples with a volume of 1 cm<sup>3</sup> were taken after 3 h of the reaction after cooling and condensing liquid products. Analysis of the gas phase was carried out by chromatography using a Crystallux 4000M gas chromatograph (MetaKhrom, Russia), equipped with a flame ionization and thermal conductivity detectors. To separate the components of the gas mixture, a Packed column (2.5 m long and 3.0 mm in diameter) filled with granules of a MN270 polymer adsorbent (Purolight Inc., UK) with a fraction of 125–250  $\mu$ m was used. The analysis of gas phase was carried out under the following conditions: the initial temperature of the column (40°C) was maintained for 4 min, then temperature was increased to 250°C at a

heating rate of  $15^{\circ}$ C/min; the temperature of the evaporator and detector was 260°C; the carrier gas was helium; and the total helium flow was 30.0 cm<sup>3</sup>/min.

# **RESULTS AND DISCUSSION**

Table 1 shows the results of analysis of the specific surface area of the synthesized samples. The highest decrease in the specific surface area compared with the initial silicon oxide is observed for the catalyst sample synthesized in the subcritical water medium. In this case, a significant decrease in the surface area of micropores was also noted. Such a change in the porous structure is specific for hydrothermal treatment of silica, which leads to its recrystallization and the disappearance of micropores [33]. A strong decrease in the micropore surface area for the sample synthesized in subcritical water medium can also indicate a complete adsorption of the cobalt chloride precursor in the micropores of the support. For the catalyst synthesized in subcritical propanol-2, a double decrease in the total surface area and a six times decrease in the surface area of micropores was also observed. Due to the polar nature of the solvent used, the treatment of silicon oxide with subcritical propanol-2 is also likely to lead to support recrystallization, which affects its porosity. The minimum decrease in the surface area was observed for the sample synthesized by impregnation. In addition, this cobalt-containing system showed a significant decrease in the total pore volume compared to the support, which may be due to the clogging of pores by the solvent during synthesis.

Analysis of nitrogen adsorption-desorption isotherms (Fig. 1) showed that the isotherms of the initial silica sample (Fig. 1a) and the catalyst synthesized in subcritical propanol-2 (Fig. 1c) were found to be of type I characterized the microporous substances with a weak adsorbate-adsorbent interaction. The isotherms of samples synthesized in subcritical water (Fig. 1b) and by impregnation (Fig. 1d) were found to belong to type IV with the hysteresis loop of H2 form. These isotherms are typical for micro-mesoporous substances, having a wide size distribution of cylindrical pores, with strong adsorbate-adsorbent interaction [34, 35].

The analysis of the pore size distribution for the studied samples (Fig. 2) showed that for the catalysts synthesized in subcritical conditions, the number of pores with a size of less than 6 nm decreased compared with that in the support. This indicates the formation of the particles of active phase in silica micropores, although in the case of the catalyst synthesized by impregnation, the particles of active phase were formed in the mesopores.

Microscopic images of cobalt-containing samples are shown in Fig. 3. For  $Co/SiO_2(H_2O)$  and  $Co/SiO_2(IPA)$  catalysts (Figs. 3a, 3b), the formation of small nanoparticles with average diameters of 5 and 7 nm, respectively, was observed. In this case, a uniform distribution of the particles of active phase

Sample	Specific surface area, m <sup>2</sup> /g			Total pore volume $dm^3/a$
	Langmuir model	BET model	<i>t</i> -plot	Total pole volume, um /g
SiO <sub>2</sub>	391	389	269*	0.25
			121**	0.22
$Co/SiO_2(H_2O)$	128	132	5**	
Co/SiO <sub>2</sub> (IPA)	205	207	179* 25**	0.23
Co/SiO <sub>2</sub> (EG)	315	327	274* 53**	0.21

 Table 1. Specific surface area and total pore volume of cobalt-containing catalysts

\* Surface area of mesopores; \*\* Surface area of micropores.

occurred on the support surface. The highest density of particle distribution was observed for the sample synthesized in subcritical water. It indicates a high content of cobalt on the silica surface. For the catalyst synthesized by impregnation (Fig. 3b), the formation of particles with an average diameter of 20 nm was observed. The lowest density and irregular distribution of the active phase particles on the support surface were detected.

Figure 4 shows the survey XPS spectra of the catalyst samples. The analysis of the elemental composition of the surface showed that cobalt was most fully



Fig. 1. Nitrogen adsorption–desorption isotherms for the samples: (a)  $SiO_2$ , (b)  $Co/SiO_2(H_2O)$ , (c)  $Co/SiO_2$  (IPA), and (d)  $Co/SiO_2(EG)$ .

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Fig. 2. Pore size distribution for samples (a)  $SiO_2$ , (b)  $Co/SiO_2(H_2O)$ , (c)  $Co/SiO_2(IPA)$ , and (d)  $Co/SiO_2(EG)$ .

adsorbed on silica in the subcritical water medium (11.8 at %). In the case of subcritical propanol-2 and ethylene glycol, cobalt was found on the surface in negligible amounts (1.3 and 0.5 at %, respectively), which is confirmed by the results of TEM analysis.

Analysis of high-resolution spectra [36, 37] for cobalt (Fig. 5) showed that the surface composition of Co/SiO<sub>2</sub>(IPA) and Co/SiO<sub>2</sub>(EG) samples (Figs. 5b, 5c) is almost identical and is represented mainly by cobalt(II) hydroxide (binding energies of 781.0 and 785.5 eV). Cobalt(III) and cobalt(II) oxides (797.1 and 802.9 eV, respectively) were also observed on the surface of these samples. For the  $Co/SiO_2(H_2O)$  sample (Fig. 5a), the main surface compounds were found to be cobalt(II) hydroxide (786.2 and 803.5 eV). Also, a mixed cobalt oxide  $(Co_3O_4)$  with 797.7 eV was observed on the surface of the sample synthesized in subcritical water. This compound exhibits catalytic activity in many reactions (hydrogenation of carbon oxides, deoxygenation of organic acids, etc.) [38]. The formation of mixed  $Co^{2+}/Co^{3+}$  oxide can be explained by the oxidative effect of the water molecules in a subcritical state [39].

Figures 6a–6c show the survey CO DRIFT spectra of the catalysts. Comparison of the spectra showed that for the samples synthesized by impregnation and in the subcritical propanol-2 medium, the narrow absorption band at 3740 cm<sup>-1</sup> with a tail extended to the lower frequencies is observed. This band is attributed to the vibrations of the isolated Si-OH groups and OH groups perturbed by the hydrogen bond. In the same spectral region, broad absorption bands of alcohol OH groups were registered. During CO adsorption, especially after prolonged exposure, bands at 3680 cm<sup>-1</sup> appeared in the spectra of the samples, and the intensity of a band at  $3740 \text{ cm}^{-1}$ decreased. The analysis of spectra suggests that the appearance of a new band is associated with the interaction of CO with OH groups on the support surface. In the spectrum of the sample synthesized in the subcritical water medium, a narrow band at 3736 cm<sup>-1</sup> and a broad band at  $\sim$  3669 cm<sup>-1</sup> attributed to the oscillations of the isolated Si-OH and OH groups perturbed by the hydrogen bond are observed. For this sample, no changes in this spectral region were detected during CO adsorption. The analysis of the high-resolution spectra (Fig. 6d) showed that, for all samples after CO adsorption, the absorption bands at  $2160-2180 \text{ cm}^{-1}$  appeared, characterizing the valence vibrations of the C=O bond of carbon monoxide molecule adsorbed in a linear form on  $Co^{2+}$  cations [40]. The positions of these bands almost do not change during long CO adsorption. When CO desorbed into the vacuum at room temperature, these bands disappeared from the spectrum. Comparison of high-resolution spectra for the studied samples showed that the sample synthesized in the medium of subcritical water has the highest accessibility of Co<sup>2+</sup> cations for CO molecules. Thus, the cobalt-containing catalyst synthesized in the medium of subcritical water has better physical and chemical characteristics compared with other studied samples.

The samples were tested in liquid-phase Fischer– Tropsch synthesis, which allows obtaining a wide range of gaseous, liquid and solid products. In the recent years, researchers has focused on the liquidphase process, which makes it possible to control of



Fig. 3. TEM images of cobalt-containing samples: (a) Co/SiO<sub>2</sub>(H<sub>2</sub>O), (b) Co/SiO<sub>2</sub>(IPS), and (c) Co/SiO<sub>2</sub>(EG).



Fig. 4. Survey X-ray photoelectron spectra of cobalt-containing samples: (a) Co/SiO<sub>2</sub>(H<sub>2</sub>O), (b) Co/SiO<sub>2</sub>(IPA), and (c) Co/SiO<sub>2</sub>(EG).



Fig. 5. High-resolution X-ray photoelectron spectra for cobalt-containing samples: (a)  $Co/SiO_2(H_2O)$ , (b)  $Co/SiO_2(IPA)$ , and (c)  $Co/SiO_2(EG)$ .

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Fig. 6. Survey CO DRIFT spectra of the catalysts: (a)  $Co/SiO_2(H_2O)$ , (b)  $Co/SiO_2(IPA)$ , (c)  $Co/SiO_2(EG)$ , and (d) high resolution CO DRIFT spectrum for cobalt-containing samples.

the chain growth stage due to a decrease in CO solubility, the formation of oxygen-containing products and preventing the water-gas shift reaction. Group VIII metals are commonly used as the active sites of the Fischer–Tropsch synthesis catalysts. Ruthenium, cobalt, iron, and nickel are the most active. To increase the surface area, these metals are deposited on the porous supports, such as silica gel. Cobalt and iron catalysts are the most commonly used in industry. Figure 7 shows the results of catalytic tests.

The obtained samples showed high efficiency in the process of the production of liquid  $C_5-C_7$  hydrocarbons (Fig. 7). Analysis of the gas phase showed the presence of methane and ethane for all synthesized samples. However, when using catalysts obtained under subcritical conditions, the formation of a smaller amount of  $C_1-C_2$  alkanes was observed compared with the catalyst obtained by impregnation. Propane and butane in the gas phase were observed in trace amounts. The reuse of the studied catalysts showed that the composition of the gas phase almost did not change for the Co/SiO<sub>2</sub>(H<sub>2</sub>O) and Co/SiO<sub>2</sub>(IPS) samples. For the Co/SiO<sub>2</sub>(H<sub>2</sub>O) catalyst, an increase in the content of methane and ethane in the gas phase was noted, which leads to a decrease in the selectivity to  $C_{5+}$  hydrocarbons.

Analysis of the liquid phase revealed that the synthesized catalysts make it possible to obtain mainly linear and cyclic  $C_5-C_7$  hydrocarbons. When  $Co/SiO_2(H_2O)$  and  $Co/SiO_2(IPA)$  catalysts are used, a shift in the selectivity to  $C_6-C_7$  hydrocarbons was observed. The Co/SiO<sub>2</sub>(EG) catalyst showed a rather high selectivity to the aromatic and cyclic hydrocarbons. When the  $Co/SiO_2(H_2O)$  catalyst is reused, its selectivity to  $C_6-C_7$  hydrocarbons is retained, but there is a slight increase in the heptadecane content and the cyclohexane content due to benzene hydrogenation. This may be due to the transformation of products adsorbed in the pores of the catalyst. In the case of reuse of  $Co/SiO_2(IPA)$ , there is a significant increase in heptadecane content, which indicates a chain growth reaction. For the catalyst synthesized by impregnation, an increase in the content of aromatic and cyclic hydrocarbons was observed, which may be due to hexane cyclization in the pores of support.

The calculation of molecular-weight distribution of the Fischer–Tropsch synthesis products showed

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Fig. 7. Composition of liquid (a) and gas (b) phase of Fischer–Tropsch synthesis.

that in the presence of the catalysts synthesized in the medium of subcritical water and propanol-2 the  $\alpha$ coefficient was found to be 0.77 and 0.68, respectively. These values indicated the maximum yield of C<sub>6</sub> hydrocarbons which correlates well with experimental and literature data [29, 31, 32]. For the catalyst synthesized by incipient-wetness impregnation, the value of  $\alpha$  was found to be 0.61, that indicates a product shift toward low-weight hydrocarbons and high selectivity to methane. Thus, the catalyst synthesized in subcritical water showed the highest efficiency in the liquidphase Fischer-Tropsch synthesis allowing the formation of  $C_5-C_7$  liquid hydrocarbons with the highest yield of C<sub>6</sub> hydrocarbons. The results of catalyst testing correlated well with data on the composition and structure of the catalysts.

# CONCLUSIONS

Comparison of cobalt-containing catalysts synthesized in subcritical conditions and by impregnation

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method showed that subcritical synthesis is a promising alternative to traditional methods, which allows obtaining the samples with the developed internal surface, uniform distribution, smaller size and higher accessibility of active phase particles for reagents. Subcritical water is the optimal medium for the catalyst synthesis. The tests of catalysts in the liquid-phase Fischer–Tropsch synthesis showed that the catalyst synthesized in subcritical water was the most effective.

# ABBREVIATIONS AND NOTATION

$T_{\rm c}$	critical temperature	
P <sub>c</sub>	critical pressure	
TEM	transmission electron microscopy	
BET	Brunauer-Emmet-Teller model	
XPS	X-ray photoelectron spectroscopy	
α	chain growth coefficient	

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## ADDITIONAL INFORMATION

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