

# Preparation and Characterization of Silica-Modified Aromatic Polymer-Based Catalysts for Fischer-Tropsch Synthesis

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The polymer can be effectively used as the supports for catalyst preparation. The main disadvantage of the polymer support is the absence of the acid-base sites on its surface. The modification of the polymeric support is one of the ways to solve this problem. In the current work, the modification of the surface of the hypercrosslinked polystyrene was carried out to apply the silicon oxide and provide the acid sites on the polymer. The effect of the silica deposition method and silica precursor was studied by the physics chemical analysis. The precipitation of the silica in subcritical water was found to provide the higher specific surface area of the resulting support (over 700 m<sup>2</sup>/g) in comparison with the wet-impregnation method. The use of ethoxysilanes, particularly 3-aminopropyltriethoxysilane, as a silica precursor was found to lead to the full deposition of Si. The synthesized modified support was used for the preparation of the catalyst for Fischer-Tropsch synthesis. Lewis acid sites on the catalyst support facilitate the CO adsorption and enhance the production of hydrocarbons via Fischer-Tropsch synthesis. The use of the catalysts on the silica-modified support showed a three-fold increase in CO conversion with an increase in the selectivity towards the oxygenates.

## 1. Introduction

Modern industry cannot be imagined without the use of catalysts. In the chemical industry, catalytic processes provide more than 80 % of production and about 10 % of the gross domestic product in developed countries (Makaryan and Sedov, 2020). At least 90-95 % of industrial reactions in chemical and petrochemical industries are catalytic processes. It is well known that the costs of manufacturing of industrial heterogeneous catalysts used in the production cycle account for a small proportion of the overall cost of the target product. However, the parameters of the catalysts used (activity, thermal and chemical stability, resistance to deactivation, mechanical strength, regenerative ability, etc.) determine the effectiveness of the chemical process, its selectivity and economic attractiveness.

In recent years, reactions in the presence of polymer-based catalysts have become increasingly important. Polystyrene, polyacrylamide, poly(alkyl methacrylate) and various resins are widely and successfully used as polymer supports. Polymer compounds are characterized by a high specific surface area, the ability to swell in various solvents, etc. This makes the polymers applicable in catalysis. Hypercrosslinked polymers also attract the attention of scientists, because they have an extremely high surface area and porosity, low density, outstanding adsorption properties, high chemical, and thermal stability (Lyubimov et al., 2019). From this point of view, hypercrosslinked polymers are promising supports for metal catalysts.

Hypercrosslinked polystyrene (HPS) is a three-dimensional polymer obtained by crosslinking polystyrene chains with rigid bridges in solvents. Bis-chloromethyl derivatives of aromatic hydrocarbons, as well as monochlorodimethyl ether, are used as crosslinking agents (Tsyurupa et al., 2020). The polymer matrix is characterized by a high surface area and a high pore volume (Ahn et al., 2006). Depending on the precursor monomers used, as well as the presence of functional groups, HPS can be micro-, meso- and macroporous. At the same time, the surface area can vary from 500 to 2000 m<sup>2</sup>/g (Fontanals et al., 2015).

Despite the enormous advantages of hypercrosslinked polymers as supports for catalysts, their main disadvantages are the hydrophobicity of the surface and the absence of acid-base sites (Vasita et al., 2008).

One of the ways to solve these problems is to modify the surface of polymers in order to give them specific properties. To impart acidic properties to polymer matrices in the work of Guerritore et al. (2020) the introduction of mesoporous silica nanoparticles obtained by the sol-gel method into the polymer during its crosslinking was considered. This method was also used by Castaldo et al. (2019) in the synthesis of catalytic systems PtRu/MoS<sub>2</sub>/HPS.

However, the use of this method can lead to the unavailability of acid sites and negatively affect the degree of crosslinking of the polymer. Thus, the effect of the polymer modification methods on the structure and properties of the resulting materials should be intensively studied. In this paper, for the first time, it is proposed to use the method of precipitation in subcritical water to impart acidic properties to a polymer matrix. This method allows the modifier to be evenly applied to the surface of the hydrophobic support. Since water is considered a green solvent, the proposed method that does not use organic surfactants and precursors can be considered sustainable. The applicability of this method to polymer support was shown earlier by us from the point of view of polymer stability to synthesis conditions (Markova et al., 2023).

To confirm the possibility of the application of the modified polymer composites in the catalysis, the transition metal containing catalysts were synthesized and tested in the Fisher-Tropsch synthesis using n-dodecane as a solvent.

## 2. Methods and techniques

Two methods were used to apply the silicon-containing phase to the HPS polymer matrices: the incipient wetness impregnation and precipitation in subcritical water. Solutions of sodium silicate, tetraethoxysilane (TEOS) and 3-aminopropyltriethoxysilane (APTES) were used as precursors of the silicon-containing phase. HPS MN 100 (Purolight Inc., UK) was washed with acetone to remove impurities, dried at a temperature of  $70 \pm 5$  °C and crushed. A fraction with a particle size of less than 80 µm was used to prepare the catalyst supports.

### 2.1 Modification of hypercrosslinked polystyrene by incipient wetness impregnation

3 g of HPS, 0.5 g of the silicon phase precursor (calculated as 10 wt. % of SiO<sub>2</sub> per mass of HPS) and 3 mL of 0.1 M hydrochloric acid solution were mixed in 5 mL of a solvent consisting of distilled water and ethanol 1:1 at  $25 \pm 3$  °C for 30 min. Then the polymer was filtered, washed with distilled water until the absence of the reaction to chloride ions and dried in air at  $105 \pm 5$  °C for 4 h. The samples were signed as MN-100-Na<sub>2</sub>SiO<sub>3</sub>i, MN-100-TEOSi, and MN-100-APTESI.

### 2.2 Modification of hypercrosslinked polystyrene by precipitation in subcritical water

3 g of HPS, 0.5 g of the silicon phase precursor (calculated as 10 wt. % of SiO<sub>2</sub> per mass of HPS) and 10 mL of distilled water were placed in a high-pressure reactor PARR 4307 (Parr Instrument Ltd., USA). The reactor was sealed and purged with nitrogen three times. The reactor was then heated to  $200 \pm 1$  °C at a nitrogen pressure of 6.0 MPa and maintained for 30 min. The reaction mixture was cooled to room temperature, filtered, washed with distilled water until the absence of the reaction to chloride ions and dried in air at  $105 \pm 5$  °C for 4 h. The samples were signed as MN-100-Na<sub>2</sub>SiO<sub>3</sub>p, MN-100-TEOSp, and MN-100-APTESp.

To remove the water sorbed by the polymer and provide the formation of SiO<sub>2</sub> phase, the samples were dried in a N<sub>2</sub> flow at a temperature of 300 °C for 5 h. The sample was signed as MN-100-Na<sub>2</sub>SiO<sub>3</sub>t, MN-100-TEOS<sub>t</sub>, and MN-100-APTES<sub>t</sub>. The scheme of the catalyst synthesis is shown in Figure 1.

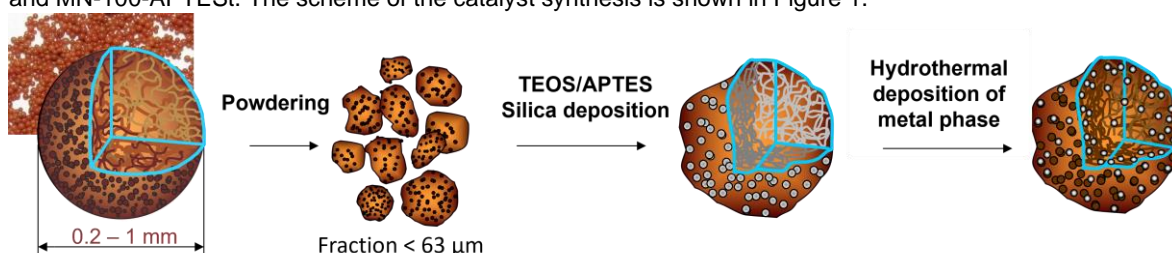


Figure 1: Scheme of the catalysts supported on the silica-modified polymer

### 2.3 Characterization methods

The method of X-ray fluorescence analysis was used to study the quantitative elemental composition of synthesized samples. The method of X-ray photoelectron spectroscopy was used to study the qualitative and quantitative composition of the surface of synthesized samples. The surface area of samples synthesized by

impregnation and precipitation in subcritical water was determined by the low-temperature nitrogen physisorption.

To synthesize the catalytic systems, the deposition of the active phase to the modified HPS was carried out by precipitation in subcritical water according to the procedure described elsewhere (Stepacheva et al., 2019). Catalyst testing was carried out in a liquid-phase Fischer-Tropsch synthesis according to the procedure described by Markova et al. (2019).

### 3. Results and discussions

Table 1 shows the results of a study of the quantitative elemental composition of synthesized samples by X-ray fluorescence analysis. When using sodium silicate as a precursor of the silicon-containing phase, the silicon content in the sample obtained by the incipient wetness impregnation was found to be 3.3 wt. %, which was 3 times less than the calculated (10 wt.%). It can be concluded that the ionic compound (sodium silicate) is not able to be absorbed by weakly polar MN100 in significant quantities. The use of TEOS makes it possible to increase the silicon-containing compound concentration twice, but the Si content remains less than theoretically calculated. The most effective method for the quantitative deposition of silica was found to be the precipitation of APTES into MN100 in subcritical water. Further heating of the obtained sample in a tubular furnace at 300 °C in a nitrogen current did not lead to a significant decrease in Si concentration.

Table 1: Results of the elemental analysis

Sample	Si concentration, wt. % (XFA method)	Surface element concentration, wt. % (XPS method)					
		C	N	O	Na	Cl	Si
MN-100- $\text{Na}_2\text{SiO}_3$ i	3.3	83.2	2.2	8.8	0.3	1.5	4.0
MN-100-TEOSi	7.2	38.0	1.1	26.1	-	0.7	34.1
MN-100-APTESp	9.8	83.2	3.1	6.9	-	1.0	5.8
MN-100-APTES <sub>t</sub>	9.3	86.8	-	8.7	0.6	0.8	3.0

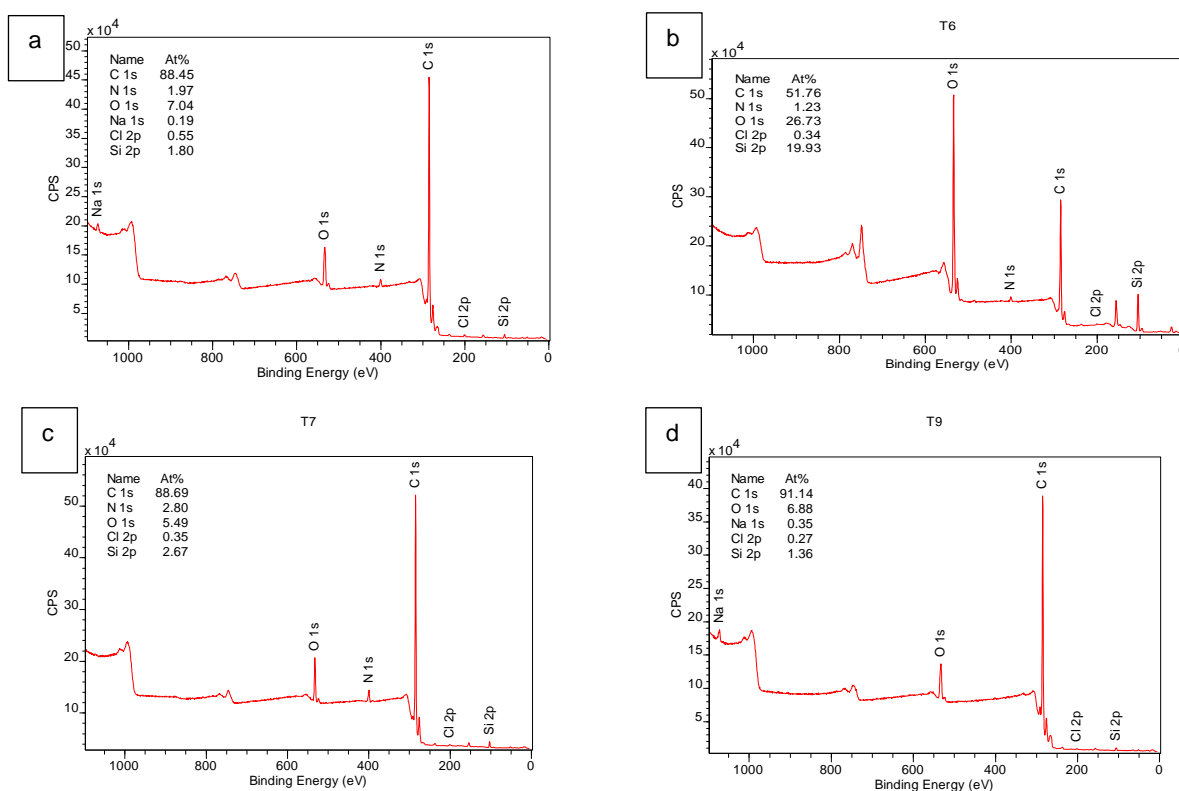


Figure 2: Survey photoelectron spectra and surface composition of samples: a – MN-100- $\text{Na}_2\text{SiO}_3$ i, b – MN-100-TEOSi, c – MN-100-APTESp, d – MN-100-APTES<sub>t</sub>

The results of the study of the qualitative and quantitative composition of the surface of synthesized samples by X-ray photoelectron spectroscopy are shown in Figure 2 a-d. The analysis of the spectra shows that carbon, oxygen, chlorine and silicon in various concentrations were registered on the surface of all samples (Table 1). Samples MN-100- $\text{Na}_2\text{SiO}_3$ , MN-100-TEOSi, MN-100-APTESp also contain nitrogen on their surface. In addition to the indicated elements, Na presents in small amounts on the surface of the MN-100- $\text{Na}_2\text{SiO}_3$  sample. This is explained by the incomplete removal of sodium during treatment of the sample with hydrochloric acid. Chlorine is present in small amounts on the surface of the MN-100-APTES sample. It can be explained by the treatment of the sample with an APTES solution.

A comparison of the methods of the deposition of the silicon-containing phase showed that the highest silicon content on the surface is observed when applying TEOS as a silica precursor by impregnation. However, according to the data of the elemental analysis, the highest silicon content was found in the MN-100-APTESp sample (Table 1). It can be assumed that when using the impregnation method, TEOS is distributed mainly on the surface of the polymer matrix. In the case of precipitation in subcritical water, APTES penetrates into the pores of the polymer due to its weak hydrophilicity, filling it. While sodium silicate, due to its ionic nature, does not penetrate into the polymer structure and is not adsorbed on its surface in significant quantities.

Heat treatment of the MN100-APTSp sample at 300 °C in nitrogen flow to obtain the MN100-APTES sample was shown to decrease in the Si content on the surface of the system by more than ten times, while the volume Si content of silicon has practically not changed. Such a difference in the results of the analysis of volume-sensitive and surface-sensitive methods is explained by the migration of APTES with the front of capillary moisture into the pores of the polymer during drying at high temperatures.

According to the mathematical modeling of Si 2p sublevel in the MN-100- $\text{Na}_2\text{SiO}_3$  sample (Figure 3a), the silicon-containing phase is represented as silicon oxide. It is also possible to note a significant amount of sorbed water on the surface of the sample. In the MN-100-TEOSi sample (Figure 3b), the modifier phase of silicon oxide (103.18 eV) was calculated to be in an amount of 7.3 %. The peak of 104.65 eV in the high-resolution spectrum of the Si 2p sublevel corresponds to silicon hydroxide in amorphous form.

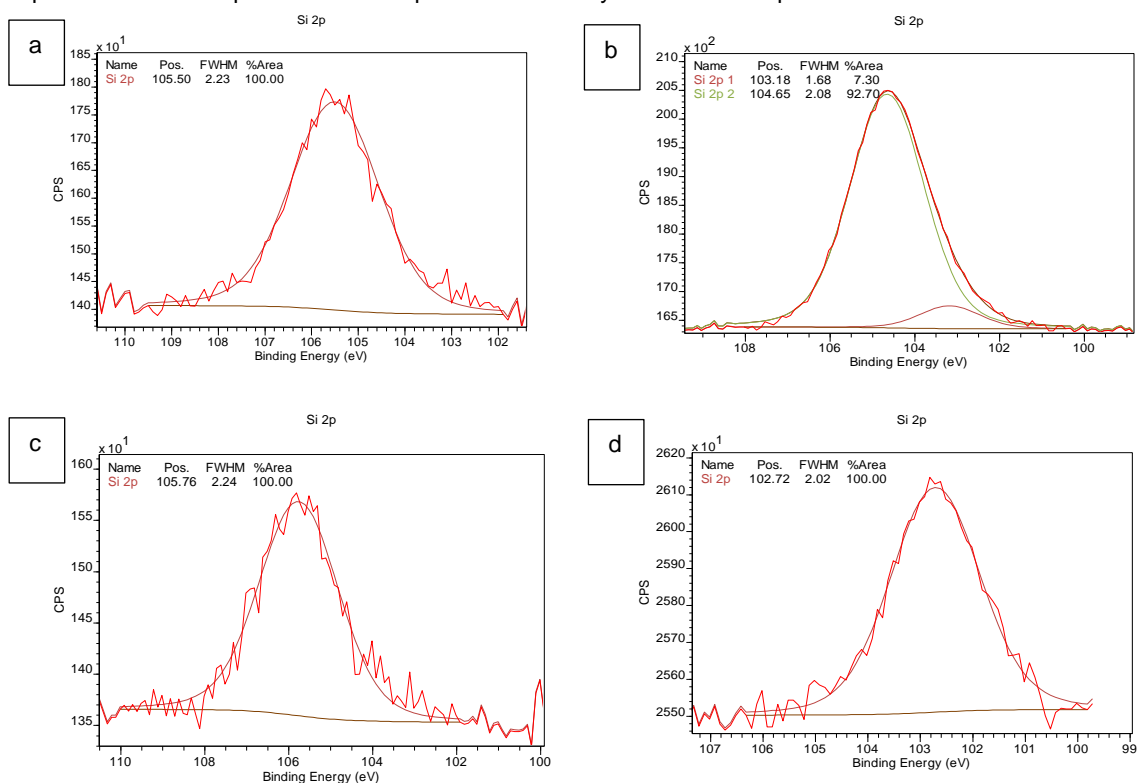


Figure 3: High-resolution photoelectron spectra of the Si 2p sublevels for samples: MN-100- $\text{Na}_2\text{SiO}_3$ i (a), MN-100-TEOSi (b), MN-100-APTESp (c), MN-100-APTES (d)

In the sample obtained by precipitation in subcritical water using APTES as a modifier, the silicon-containing phase is represented by silicon oxide (Figure 3c), surface-adsorbed water also presents. Treatment of the

sample MN-100-APTESp in the flow of N<sub>2</sub> at a temperature of 300 °C for 5 h (abbreviation of the sample MN-100-APTES<sub>t</sub>), leads to the complete removal of adsorbed water (Figure 3d).

According to the results of the studies, it was found that APTES is the most optimal modifier for applying a silicon-containing phase. The surface area of samples synthesized by impregnation and precipitation in subcritical water using this modifier was determined by low-temperature nitrogen adsorption (Table 2).

Table 2: Surface area of synthesized samples

Sample	V <sub>pore</sub> , cm <sup>3</sup> /g	S <sub>BET</sub> , m <sup>2</sup> /g	S <sub>Langmuir</sub> , m <sup>2</sup> /g	S <sub>t-plot</sub> , m <sup>2</sup> /g
MN-100	0.52	814	963	208
MN-100-APTESi	0.34	591	672	696*
MN-100-APTESp	0.40	611	709	198
MN-100-APTES <sub>t</sub>	0.65	951	1072	392*
				197
				435*
				380
				597*

\* surface area of micropores

When compared with the initial polymer MN-100, it can be noted that when deposition of APTES by impregnation, a decrease in the surface area of the polymer sample and the pore volume is observed. At the same time, the surface of the micropores is reduced to a greater extent. This may be due to the fact that APTES, penetrating into the pores of the polymer support, condenses in micropores, which leads to their partial blockage. The application of APTES to the polymer surface in a subcritical water also leads to a decrease in the total surface area and surface area of micropores, but to a lesser extent than using the impregnation method.

To study the effect of surface modification on the composition of products in the Fischer-Tropsch synthesis, monometallic systems deposited on the modified (Me-SiO<sub>2</sub>-HPS) and initial (Me-HPS) polymer were studied. The test results of the samples are presented in Table 3. When silicon oxide is added to catalytic systems, a decrease in the content of low molecular weight C<sub>2</sub>-C<sub>4</sub> products, as well as cyclic and aromatic compounds, is observed. A decrease in the content of C<sub>5</sub>-C<sub>11</sub> hydrocarbons was noted on the iron-containing catalyst. The application of Lewis acid sites rich in oxygen facilitates the adsorption of CO increasing its conversion compared to non-modified catalysts. It also increases the content of oxygen-containing products that react with oligo- and polycondensation. This is most clearly observed when using iron-containing catalysts (Lapidus, 2000).

The long-term stability of the modified support to the leaching of the modifier under conditions of Fischer-Tropsch liquid-phase synthesis was also studied. Stability was determined based on data on the leaching of the silicon-containing phase from the polymer surface. For samples synthesized using sodium silicate as a modifier, a slight decrease in silicon content was observed according to elemental analysis data after 9 hours under reaction conditions. A significant decrease in silicon concentration was noted after 5-fold use of the support. For samples synthesized using TEOS and APTES, there is a high resistance of the silicon-containing phase to leaching. For a sample synthesized using APTES in subcritical water, after heating in a nitrogen current at 300 °C for 5 h, no leaching of the silicon-containing phase was observed for 10 consecutive cycles.

Table 3: CO conversion and selectivity of Fischer-Tropsch synthesis products in the presence of the studied catalysts

Catalyst	Conversion of CO, mol. %	Selectivity, mol. %					
		CH <sub>4</sub>	C <sub>2</sub> -C <sub>4</sub>	C <sub>5</sub> -C <sub>11</sub>	C <sub>13</sub> -C <sub>14</sub>	OxygenatesC <sub>1</sub> -C <sub>5</sub>	Cyclic and aromatic hydrocarbons
Co-SiO <sub>2</sub> -HPS	17.8	8.2	5.9	84.8	0	0.2	0.8
Ni-SiO <sub>2</sub> -HPS	15.8	10.7	9.8	75.9	0	2.5	1.0
Fe-SiO <sub>2</sub> -HPS	24.6	5.9	7.0	68.7	0	17.4	0.9
Co-HPS	13.6	5.2	7.6	84.2	1.2	0.4	1.4
Ni-HPS	27.2	7.5	14.9	75.4	0.0	0.2	1.9
Fe-HPS	8.3	4.6	8.9	78.2	0.0	6.6	1.7

#### 4. Conclusions

The influence of application methods and the precursors of the silicon-containing phase on the composition, structure, and catalytic activity of polymer-based systems were studied in the work. Two methods of the modification of the surface of HPS (wetness impregnation and deposition in subcritical water) were compared in terms of Si concentration and specific surface area. Three silica precursors were investigated. APTES deposited in subcritical water was found to be the most optimal modifier providing full Si deposition with the maintaining the high specific surface area of the resulting support. The use of this technique was noted to lead to a more complete deposition of the modifier without significantly reducing of the surface area.

The Co-, Ni-, and Fe-containing catalysts were synthesized using the modified polymeric support. The catalysts were tested in the liquid-phase Fischer-Tropsch synthesis. The presence of the SiO<sub>2</sub> on the surface of the HPS was found to facilitate Co adsorption with a three-fold increase in its conversion for the Fe-SiO<sub>2</sub>-HPS in comparison with the non-modified catalyst. The resulting catalysts showed a significant increase (up to 3 times) in oxygen-containing products which can undergo into the oligo- and polymerization resulting in the formation of branched liquid hydrocarbons. The future studies will be focused on the analysis of the acidity effect on the conversion and selectivity of the process, as well as the process mechanism in the presence of SiO<sub>2</sub>-HPS supported catalysts.

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