



FORMATION FEATURES OF COMPOSITE MATERIALS CONTAINING COBALT NANOPARTICLES ACTIVE IN FISCHER-TROPSCH SYNTHESIS

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The influence of polymer matrix on the activity of composite material containing cobalt nanoparticles in Fischer-Tropsch synthesis was studied. It was found that the structure of the polymer matrix affects active centers formation. Magnetometry techniques *in situ* and XRD confirmed the presence of the metal cobalt and its oxide phases which are the active centers of different type effect.

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Introduction

Fischer-Tropsch synthesis (hydrocarbon synthesis from carbon monoxide and hydrogen) is a second stage of the most recycling processes of non-oil raw materials (coal, natural or associated gas, peat, etc.) to eco-friendly fuel components.¹

Traditionally, the Fischer-Tropsch synthesis is catalyzed by VIII group metals (iron or cobalt) in bulk state or distributed on the surface of a highly porous support.² Their catalytic activity, selectivity and stability is defined by the shape and size of the applied active component particles.³

In 1925 F. Fischer and H. Tropsch published results for the catalytic hydrogenation of carbon monoxide to hydrocarbons at atmospheric pressure over an iron based catalyst.⁴ Further study of this process has led to the development of cobalt catalysts which have proved to be more active than the iron ones.

In recent years, nanoscale metal-carbon materials as catalysts for the Fischer-Tropsch synthesis have increasingly garnered the interest of the researchers. The introduction of the catalytic active metal particles into carbon matrix is carried out at the stage of carbonization.⁵ IR pyrolyzed polymer materials are used as carbon supports. Under the conditions of IR annealing the carbonization process leading to graphite structure formation occurs. Under the conditions of IR pyrolysis of precursors based on polymers and metal salts the ordered carbon structures are formed and simultaneously the metal reduction occurs with the participation of hydrogen released in the dehydrogenation of the backbone polymer chain.

IR pyrolysis process of the precursor allows to introduce catalytic active metals into the carbon matrix structure directly during its formation providing regular distribution of the active catalytic sites.^{6,7}

Possibility to control nanocomposite structure and properties makes these systems very promising for the using them as catalysts for chemical and petrochemical processes such as Fischer-Tropsch synthesis. In this paper we distinguish the effect of the nature of initial polymer on the catalytic activity and selectivity of Co-containing nanocomposites.

Experimental

For the samples preparation the following polymers were used: polyacrylonitrile ((-CH₂-CH(CN)-)_n) (PAN) polydiphenylamine ((-C₆H₄-NH-C₆H₄-)_n) (PDPhA), polystyrene ((-CH(C₆H₅)-CH₂-)_n) (PS), polyvinyl alcohol ((-CH₂-CH(OH)-)_n) (PVA) and cellulose ((C₆H₁₀O₅)_n) (CE).

For the preparation of common solution of polymer and cobalt salt the following components were used: PAN – DMFA – Co(NO₃)₂·6H₂O, PDPhA – DMFA – Co(CH₃COO)₂, PS – toluene – C₁₀H₁₄CoO₄, PVA – distilled water – Co(NO₃)₂·6H₂O. The cellulose suspension in water was obtained after dissolving Co(NO₃)₂·6H₂O. After common solution or suspension obtained the precursor was dried at 80 °C. IR pyrolysis was performed at temperatures of 250-700 °C in inert atmosphere. The cobalt content in the precursor was 20 wt. %.

Fischer-Tropsch synthesis was conducted in a fix bed reactor at a pressure of 2 MPa and a space velocity of 1000 h⁻¹ (a molar ratio of CO: H₂ = 1: 2) in the temperature range 200-320 °C. The temperature was increased by 20 °C step every 12 h. The gas and liquid samples were taken for analysis at the end of each isothermal mode.

Table 1. The influence of the polymer matrix nature on the basic indicators of the Fischer-Tropsch catalysts based on Co-CMNP (20 atm, 1CO+2H₂, liquid hourly space velocity 1000 h⁻¹)

Sample	Temperature*, °C	Hydrocarbon yield, g m ⁻³		Liquid hydrocarbon productivity, g kg metal ⁻¹ · h ⁻¹	Liquid hydrocarbon selectivity, %
		Gaseous hydrocarbons	Liquid hydrocarbons		
Co-PVA	280	100.4	25.4	2084	20.2
Co-PDPhA	300	46.8	33.3	1744	41.6
Co-CE	300	76.6	38.7	279	33.6
Co-PS	300	36.2	18.9	137	34.3
Co-PAN	300	54.0	72.0	2600	57.0

* The temperature at which the maximum yield of liquid hydrocarbons is shown

The catalytic tests were carried out without pre-reduction stage. The initial synthesis gas and gaseous products of the synthesis were analyzed by a chromatograph "Kristallux-4000M" with two chromatographic columns. Helium was applied as a carrier gas and TCD as a detector. A column packed with CaA molecular sieve (3 mm × 3 m) was applied for CO and N₂ separation. Temperature mode – isothermal, 80 °C. A column packed Haye Sep R (3 m × 3 mm) was applied for CO₂ and C₁-C₄ hydrocarbon separation. Temperature mode - programmed, 80-200 °C, 8 °C min⁻¹.

The catalyst activity review was based on the following parameters: specific activity (CO moles reacted on 1 g of Co per 1 s), CO conversion (percentage ratio of reacted CO weight to the weight of CO logged into the reaction zone), the product yield (number of grams of product obtained by passing of synthesis gas through 1 m³ of catalyst reduced to normal conditions), the selectivity (percentage ratio of carbon, taking participation in the formation of the reaction products, to the total amount of carbon introduced into the reaction zone), productivity (the amount of products produced by 1 kg of catalyst per 1 h).

The magnetic characteristics of the composites were measured with a vibration magnetometer.⁸ Oxidation of the nanocomposites was carried out in an air stream in vibrating magnetometer cell at a programmed temperature rise of 0.42 °C s⁻¹ speed.

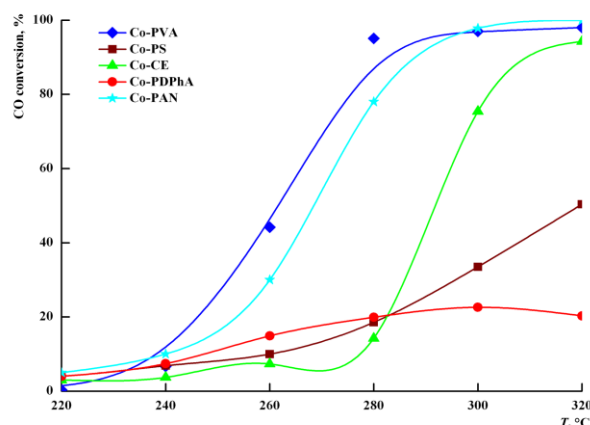
X-ray diffraction analysis was performed at room temperature on a DIFREY-401 diffractometer (Russia) (Cr K α radiation, Bragg-Brentano focusing).

Results and discussion

The most active catalysts for Fischer-Tropsch synthesis are cobalt systems characterized by high selectivity in hydrocarbon formation. In the presence of these systems the synthesis proceeds with a minimum amount of carbonaceous by-products such as CO₂ and monohydric alcohols.⁹ The composite materials containing Co nanoparticles (Co-CMNP) were synthesized via IR pyrolysis of the precursor based on PAN and cobalt salt. The Co-CMNP catalytic activity dependence on the cobalt salt nature, preparation temperature and Fischer-Tropsch synthesis conditions was shown in the previous study.¹⁰

This paper describes the effect of the polymer nature used for Co-CMNP preparation on the catalyst activity in the Fischer-Tropsch process.

Every prepared sample showed activity in the synthesis of hydrocarbons from CO and H₂ (Fig. 1).

**Figure 1.** Temperature dependence of CO conversion of Co-CMNP.

The maximum activity was shown by the samples based on PVA and PAN. These samples CO conversion reached 100% at 300 °C. Also Co-CMNP based on CE showed high catalytic activity. CO conversion tended to 100% at 320 °C. However, this sample CO conversion was started to rise much later than the samples based on PVS or PAN. The drastic increase of the sample was observed only after 280 °C. This indicates that Co-CMNP based on CE has carbon matrix of structure differs from the structure of the carbon matrix formed during the pyrolysis of Co-PAN or Co-PVA. Therefore, adsorption of reagents (first catalytic action) on the surface of the active metal sites may occurs at higher temperatures than in the case of the samples based on Co-PVA or Co-PAN.

The influence of the polymer matrix nature on the basic indicators of the Fischer-Tropsch catalysts based on Co-CMNP is presented in Table 1.

Table 1 show that the synthesized samples with different support have not very high yield of liquid hydrocarbons in comparison with commercial catalysts (~ 100 g m⁻³).

However, the productivity of Co-PAN, CoPDPPhA and Co-PVA is extremely high and is ten times much as industrial catalyst productivity.

The Co-PVA sample showed a low yield (25.4 g m^{-3}) whereas its productivity was very high - $2084 \text{ g kg metal}^{-1}\cdot\text{h}^{-1}$.

The similar indicators were achieved in the presence of Co-PDPPhA. The yield of liquid hydrocarbons was 33.3 g m^{-3} , while the productivity reached $1744 \text{ g kg metal}^{-1}\cdot\text{h}^{-1}$. It should be noted that the yield of gaseous hydrocarbons in the presence of the Co-PDPPhA sample was two times lower than in the presence of the Co-PVA sample (46.8 g m^{-3} and 100.4 g m^{-3} , respectively). The highest yield of liquid hydrocarbons (72 g m^{-3}) and liquid hydrocarbon productivity ($2600 \text{ g kg metal}^{-1}\cdot\text{h}^{-1}$) were reached in the presence of Co-PAN.

The samples of Co-CE and Co-PS showed low yield of liquid hydrocarbons (38.73 g m^{-3} and 18.91 g m^{-3} , respectively) as well as the productivity of the catalysts ($< 279 \text{ g kg metal}^{-1}\cdot\text{h}^{-1}$).

It's important to note that the yield of the main by-product formed in the presence of cobalt catalysts - methane - depends on the nature of the polymer used (Fig. 2).

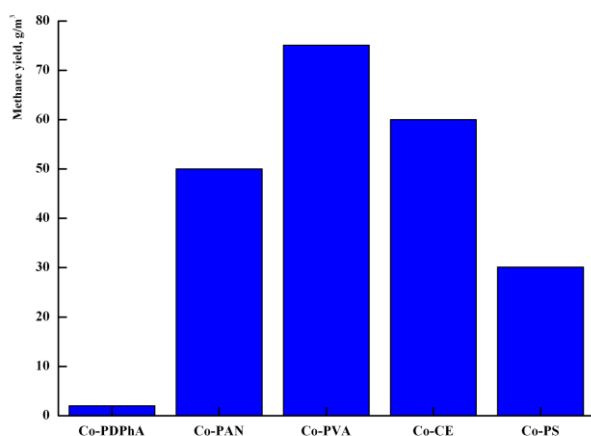


Figure 2. Methane yield in Fischer-Tropsch synthesis in the presence of Co-CMNP.

Co-PVA and Co-CE were characterized by the highest methane yield ($\sim 70 \text{ g m}^{-3}$ and 60 g m^{-3} , respectively). The smallest selectivity of liquid hydrocarbons (Table 1) was observed in the presence of the same samples.

Methane yield was 50 g m^{-3} in the presence of Co-PAN catalyst and in the case of Co-PDPPhA the methanation was almost completely suppressed. The same samples are characterized by the highest liquid hydrocarbon selectivity (57 % and 41.6 %, respectively) (Table 1). It indicates that the use of PDPPhA or PAN as the polymer matrix allows to form different active sites for Co-CMNP.

Thus, in the case of Co-CMNP based on PAN some of the active sites responsible for hydrocarbon formation, are crystallites of metallic Co (so-called type A sites). These sites take part in dissociative adsorption of CO with generation of active surface carbon followed by its

hydrogenation led to the formation of methane.⁹ As concerns Co-CMNP based on PDPPhA bicomponent active sites consisted of metallic and oxide cobalt are mainly formed (so-called type B sites). These sites cause the growth of the hydrocarbon chain in the Fischer-Tropsch synthesis conditions.^{11, 12} Probably, formation of different active sites caused by the formation of polyconjugated systems with different structure due to polymer nature. Thus, in the case of PAN polyconjugated polycyclic system is formed, as opposed to polyconjugated linear cyclic structures in PDPPhA.

Magnetometric technique *in situ* was applied in order to explain the features of the synthesis gas conversion in the presence of Co-PDPPhA, Co-PAN and Co-PVA which showed the highest liquid hydrocarbon productivity.

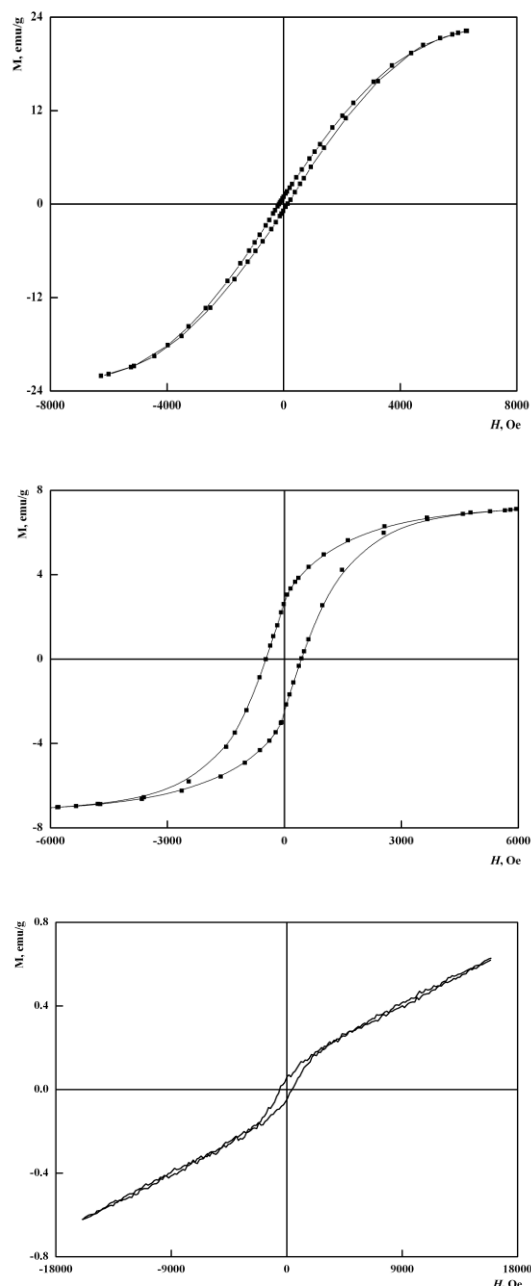


Figure 3. Field dependence of magnetization reversal of Co-PDPPhA (a), Co-PAN (b) and Co-PVA (c) samples.

Field dependence of magnetization reversal of Co-PDPhA and Co-PAN samples showed hysteresis loop (Fig. 3a, b). This shape of the dependence is caused by the presence of ferromagnetic particles in the samples, i.e. cobalt crystallites with an oxidation degree equal to zero. Co-PAN sample hysteresis loop is characterized by a relatively high coercive force (Fig. 3b). This fact can be explained by the presence of particles with size of 15-20 nm in the sample. The hysteresis loop shape of Co-PVA sample (Fig. 3c) differs from the curves of Co-PDPhA and Co-PAN samples (Fig. 3a, b). The distorted hysteresis loop of Co-PVA sample indicates the dominance of the oxide paramagnetic phase of cobalt in the sample.

The synthesized composite samples were studied by the magnetometry method in situ. Fig. 3 shows that Co-PDPhA and Co-PAN samples contain metallic cobalt which forms the active sites of cobalt catalysts of Fischer-Tropsch synthesis. In Co-PVA sample cobalt has the oxide form and metallic cobalt is lack.

The degree of the metal reduction was determined via comparison of the magnetization value of bulk Co (1 mg) and the magnetization value of the studied. The metal reduction degree was approximately 90%, 64% and 1% for systems with Co-PDPhA, Co-PAN and Co-PVA, respectively. However, the fact that all three samples showed activity in the synthesis of hydrocarbons from CO and H₂ (Table 1), indicates that the sample Co-PVA was activated directly in the synthesis.

These conclusions were confirmed by XRD analysis.^{10,13,14} It was shown that metallic cobalt of α - (hexagonal) and β - (face-centered cubic) modifications and amorphous carbon phase were formed in the composite material based on PDPhA.^{13,14} Reflection peaks relating to metallic cobalt of α - (hexagonal) and β - (face-centered cubic) modifications and carbon phase as a PAN pyrolysis product were presented in all diffraction patterns of Co-PAN.¹⁰ Cobalt oxide phase reflection peaks were detected for Co-PAN samples.¹⁰ The XRD pattern of Co-PVA sample is shown in Fig. 4.

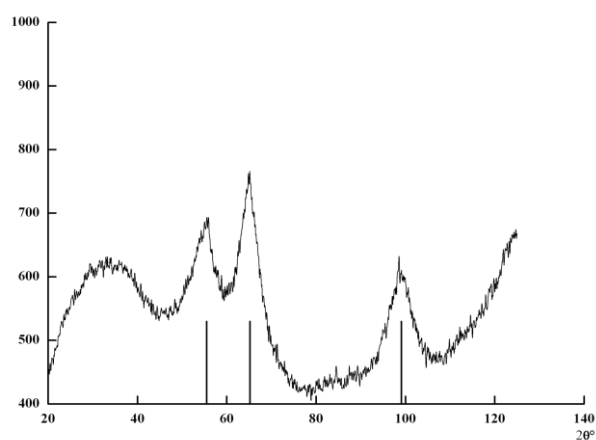


Figure 4. The XRD pattern of Co-PVA sample. The straight lines show CoO phase.

The XRD pattern of Co-PVA sample (Fig. 4) indicates that cobalt oxide phase (where Co²⁺) prevails in the diffractogram. The width of the reflection peaks shows poor crystallinity which can be explained by small size of cobalt oxide particles caused by rapid particle formation under non-equilibrium conditions. Reflection peaks corresponding to metallic cobalt or its other oxides (e.g., Co₃O₄ or Co₂O₃) were not detected. Wide halo around 30° is associated with the amorphous carbon matrix.

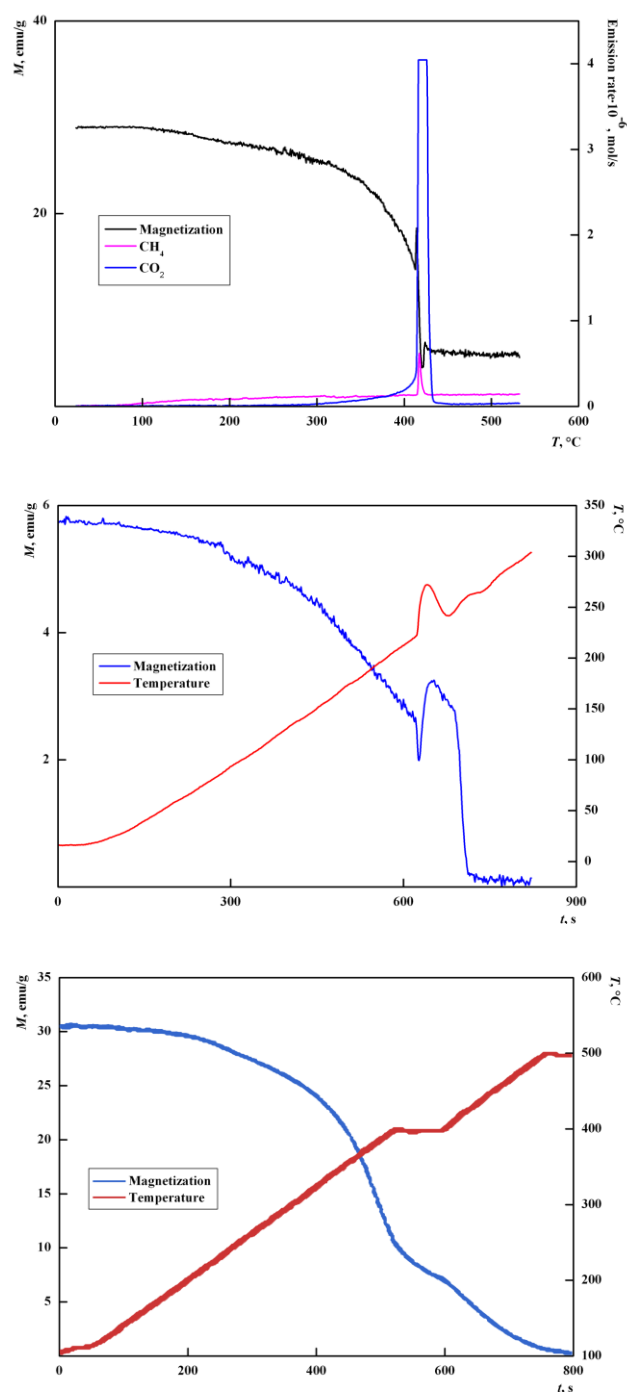


Figure 5. The TPO curves of Co-PDPhA, Co-PAN and Co-PVA samples.

Temperature programmed oxidation (TPO) curves of Co-PDPhA, Co-PAN Co-PVA samples are shown in Fig. 5. The data of Fig. 5a and 5b show that the oxidation of Co-PDPhA and Co-PAN samples occurs via similar scheme - after a "plateau" there is rapid drop of the magnetization indicating burnout of the polymer shell and oxidation of the metal particles. The magnetization rapid drop in Fig. 5 occurs simultaneously with a rapid CO₂ emission that additionally confirms the hypothesis of burnout carbon shell. Also, there is methane emission which may be associated with simultaneous oxidation and pyrolysis processes of the polymer leading to hydrogen and other gaseous products release at the temperature. Methane is formed on the metallic particles due to hydrogenation of oxidation and decomposition products. In Fig. 5a and 5b there is a jump in the magnetization, indicating cobalt reduction partly by oxidation products. At the same time calorification is observed, indicating exothermic process (oxidation of the matrix and cobalt). In the case of Co-PAN the magnetization decrease is observed at 150 °C, and for Co-PDPhA – at 320 °C. Such temperature difference indicates that the applying PDPhA as polymer matrix leads to "covering" active metal particles as described in.¹³ It seems that such a dense shell prevents adsorption of synthesis gas on the active site surface. That is explains the low CO conversion for this catalyst.

There is no rapid drop of the magnetization in the whole investigated temperature range and no rapid calorification in the oxidation curve of Co-PVA sample (Fig. 5c). Burning of the polymer matrix occurs gradually in the case of the PVA.

Conclusions

Thus, the effect of the polymer matrix nature on Co-CMNP activity in the Fischer-Tropsch process was shown. The system based on polyconjugated cyclic structure formed during pyrolysis reaction of polymer exhibited the highest activity. Obviously, different matrix-nanoparticle systems are formed as various types of polymers are applied. In the case of PDPhA the composite formation and cobalt reduction is caused by hydrogen released during the condensation reaction of DPhA oligomer fragments. As a result of thermolysis the system with tightly encapsulated particles is formed. In the case of Co-PAN system the metal reduction occurs with the participation of hydrogen released in the dehydrogenation of the main polymer chain. The system with weakly encapsulated particles is formed. In the Co-PVS the metal reduction does not occur and forming cobalt oxide particles are encapsulated by thermalized polymer matrix.

In the case of PVS conjugation system formation occurs due to the side groups decoupling opposite to PAN where there is formation of conjugated cyclic structures during backbone substituents cyclization followed by carbonization.

Co and CoO phases presence in Co-PDPhA and Co-PAN samples were proved by XRD and *in situ* magnetometry. The phases are responsible for the active sites of different nature activity. In Co-PVA sample metallic cobalt was not found. However, the high catalytic activity of this sample indicates that its activation occurs in synthesis gas medium under reaction condition.

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