

Co- and Fe-containing Silica-based Catalysts Synthesized in Subcritical Water

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A study of the structure and catalytic properties of the cobalt- and iron-containing catalysts synthesized by the subcritical deposition in the water medium was performed in the current work. The catalyst synthesis was carried out at a temperature of 200 °C and a total pressure of 7.5 MPa using silica as support. The catalytic activity of the synthesized materials was studied in the liquid-phase Fischer-Tropsch synthesis. The study of catalyst structure and composition showed that the use of silica as catalyst support allows the formation of Co- and Fe-containing particles consisted of metal oxides. Testing of the synthesized catalysts in liquid phase Fischer-Tropsch synthesis showed that Co-based catalyst allowed the formation of gasoline-range hydrocarbons. It is noteworthy that Co/SiO₂ showed higher selectivity towards the formation of linear C₅-C₈ hydrocarbons. In the case of Fe-containing catalyst, the formation of a significant amount of oxygenates (C₃-C₄ alcohols) was found.

1. Introduction

The modern tendencies in the industry require the development of highly active and stable catalysts for different processes. Supported metal nanoparticles are one of the most prospective catalysts involved in the majority of the reactions (i.e. hydrogenation, oxidation, hydroformylation, etc.), particularly in the size-sensitive processes (Erkey, 2011). Such nanocatalysts are characterized by unique properties (high surface area, high surface energy) and enhanced reactivity (Zhang and Erkey, 2006). However, the main problem of the metal nanoparticles is fast aggregation. In order to solve this problem, two main directions are used: (i) the search for highly effective stabilizers, and (ii) the development of novel synthesis methods.

The commonly used methods of the catalyst synthesis such as co-precipitation (Ren et al., 2007), incipient wetness impregnation (Antolini et al., 2005), sonochemical synthesis (Angelucci et al., 2007), polyol method (Wang et al., 2006), etc. have numerous disadvantages. The resulted metal nanoparticles are characterized by the broad particle size distribution, in-homogeneity of the catalytically active phase, low dispersity. Moreover, the application of such techniques requires the use of huge volumes of the solvent, high temperatures, toxic compounds or detergents. The solvents typically used in the impregnation have high surface tension and can blockade the pores of the supports. Besides, such techniques as chemical vapor deposition or flame spray pyrolysis are inappropriate for the polymeric and organic supports which are decomposed at the high temperatures.

Last years, the interest in the application of super- and subcritical fluids for the synthesis of the supported nanoparticles is raised. The formation of the metal particles in super- and subcritical fluids is classified as physical and chemical deposition (Türk, 2014). The first one poses as a rapid decompression of anti-solvent transformation. The second type of super/subcritical deposition includes the interaction between the metal precursor and the solvent used through the hydrolysis or reduction (Cansell and Aymonier, 2009). This method is interesting from the point of view of the achievement of high dispersed nanoparticles with unique physical and chemical properties. It can concur with the classical wetness impregnation in terms of efficiency, rapidity, and safety.

The pioneer work on the metal nanoparticle supercritical deposition was performed by Watkins and McCarthy (1995) who synthesized thin Pt film in the alumina. The further investigations were done by Cabanas group (Morere et al., 2011), Türk (2014), Erkey group (Bozbag et al., 2012) and Aymonier group (Pascu et al., 2015). Among the supercritical fluids methanol (Choi et al., 2010), ammonia (Chen et al., 2003), isopropyl alcohol (Lu et al., 2003), cyclohexane (Pestov et al., 2003), carbon dioxide (Morere et al., 2011) and water (Hayashi and Hakuta, 2010) are used for the synthesis of the supported nanoparticles. The last two solvents are the most frequently applied because of ecological compatibility.

The use of water in the sub- or supercritical state in the catalyst synthesis (so-called hydrothermal synthesis) allows obtaining ultrafine metal oxides or metal nanoparticles from inorganic salts (Lester et al., 2006). The metal precursor undergoes hydrolysis resulting in the formation of metal hydroxide, which then is converted into metal oxide or metal particles (Byrappa and Yoshimura, 2001). For example, the structure and catalytic properties of Pd/ZrO₂ and Pd(Rd)/TiO₂ synthesized in supercritical and subcritical water respectively were studied by Galkin et al. (2001). Otsu and Oshima (2005) studied the structure of manganese, lead and silver oxides deposited on γ -Al₂O₃ in supercritical water. Yahya et al. (2001) 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 deposited catalysts shows that in spite of the reaching of the critical region the resulting catalytic systems are characterized by high crystallinity, nanosize and uniform distribution of the active phase. However, since a sharp change in properties (in particular, the dielectric constant, polarity, etc.) is observed for polar liquids in the supercritical state, sub- and near-critical conditions are the most optimal for the synthesis of metal-containing composites (Hayashi and Hakuta, 2010). In this work, we report the study of the structure and catalytic performance of silica-based Co- and Fe-containing catalysts synthesized in subcritical water. Both the porous structure and the composition of the active phase were investigated in order to determine the processes taking place during the hydrothermal synthesis. The catalytic activity of the resulted supported materials was studied in the liquid-phase Fischer-Tropsch synthesis aimed at the production of gasoline-range hydrocarbons.

2. Materials and Methods

2.1 Materials

For the catalysts synthesis the following materials were used: cobalt (II) nitrate (Co(NO₃)₂ · 6H₂O, C.P., Reachim, Russia), iron (III) nitrate (Fe(NO₃)₃ · 6H₂O, C.P., Reachim, Russia), sodium bicarbonate (NaHCO₃, C.P., Reachim, Russia), anhydrous silica (SiO₂, C.P., Reachim, Russia), distilled water.

In the catalyst testing experiments n-dodecane (C₁₀H₂₂, C.P., Reachim, Russia) and a gaseous mixture consisting of 20 vol. % of carbon monoxide (99.9 %, AGA, Russia) and 80 vol. % of hydrogen (99.9 %, AGA, Russia) was used.

2.2 Catalyst synthesis

Synthesis of metal-containing catalysts under subcritical conditions was carried out in a high-pressure reactor PARR-4307 (Parr Instrument, USA). 1 g of silica, metal precursor calculated on 10 wt. % of pure metal and 0.1 g of sodium bicarbonate dissolved in 30 mL of distilled water were inputted into the reactor. The reactor was sealed and purged with nitrogen to remove air oxygen. Then, the operating pressure of nitrogen (6.0 MPa) controlled by the manometer and temperature (T = 200 °C) was set. The total pressure in the reactor after the heating was 7.5 MPa. The process was carried out at continuous stirring at a speed of 750 rpm. The synthesis time was 15 min. After the synthesis, the reaction mixture was cooled to the room temperature, filtered, washed with 15-20 mL of the distilled water until the absence of the reaction to nitrate and carbonate ions, dried in the air, calcinated at 450 °C for 10 h. As the hydrothermal synthesis leads to the oxidation of metals, the resulted catalysts were held in hydrogen flow at 300 °C for 4 h aimed at the partial reduction of metal in order to obtain mixed oxides. The catalyst structure was studied by the low-temperature nitrogen physisorption, X-ray photoelectron spectroscopy, and transmission electron microscopy.

2.3 Catalyst testing

The resulted catalysts were tested in the liquid-phase Fischer-Tropsch synthesis in a steel reactor PARR-4307 (Parr Instrument, USA) using n-dodecane as a solvent. A mixture of CO and H₂ in a volumetric ratio of 1:4 was used as synthesis gas. The high hydrogen content in the gas mixture is due to the need for additional hydrogenation of olefins and oxygen-containing compounds formed in the presence of cobalt- and iron-containing catalyst (Tomasek et al., 2018). The process temperature was 200 °C, the total pressure in the reactor was 2.0 MPa, the catalyst mass was 0.1 g, the solvent volume was 30 mL (Marques and Guirardello, 2018).

The liquid phase was analyzed by GCMS using GC-2010 gas chromatograph and GCMS-QP2010S mass spectrometer (SHIMADZU, Japan). The liquid phase analysis was carried out under the following conditions: the initial temperature of the column 150 °C was maintained for 6 min, then the temperature was raised up to 250 °C at a heating rate of 15 °C/min; injector temperature 280 °C; carrier gas-helium; pressure He 253.5 kPa; total flow He 81.5 mL/min; linear flow rate He 20.8 cm/ s; column HP-1MS: L = 30 m; d = 0.25 mm; film thickness; ion source temperature 260 °C; interface temperature 280 °C; scanning mode from 10 to 800 m/z; scanning speed 625; electron impact ionization.

Analysis of the gas phase was carried out by a chromatographic method using gas chromatograph "Crystallux 4000M", equipped with a flame ionization detector and katharometer. To separate the components of the gas mixture, a 2.5 m long and 3.0 mm diameter Packed column filled with granules of polymer adsorbent MN270 (Purolight Inc., UK) with a fraction of 125-250 μm was used. The gas phase analysis was carried out under the following conditions: initial temperature of the column 40 °C, maintained for 4 min, then, the temperature was raised up to 250 °C at a heating rate of 15 °C/min; temperature of the evaporator and the detector 260 °C; carrier gas-helium; total flow He 30.0 mL/min.

3. Results and Discussion

3.1 Catalyst characterization

The analysis of nitrogen adsorption-desorption isotherms (Figure 1a) showed that the isotherms of the initial silica sample were found to be of type I characterized the microporous substances with a weak adsorbate-adsorbent interaction. The treatment of the SiO_2 in the hydrothermal conditions leads to the changes in the support structure which is specific for hydrothermal treatment of silica, which leads to its recrystallization and the disappearance of micropores (Ioffe and Pismen, 1972). The isotherms for the treated support and the catalysts were found to belong to type IV with the hysteresis loop of H2 form. Such isotherms are typical for micro-mesoporous substances, having a broad size distribution of cylindrical pores, with a strong adsorbate-adsorbent interaction (Donohue and Aranovich, 1998).

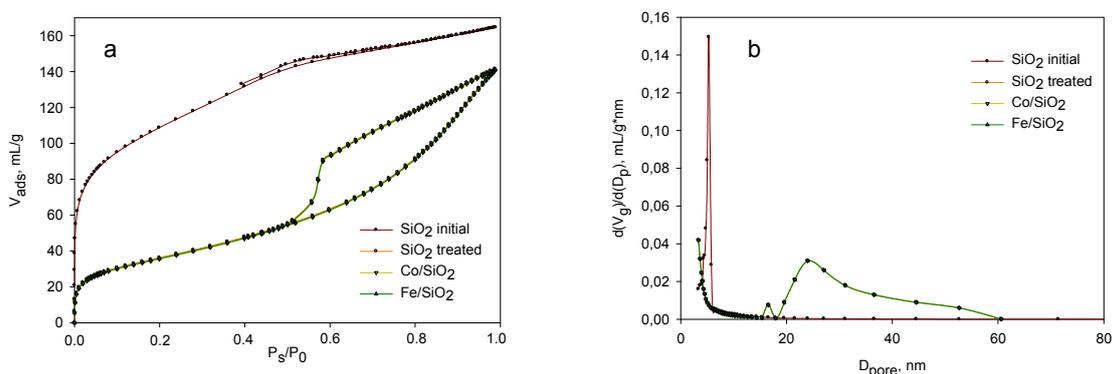


Figure 1: Nitrogen adsorption-desorption isotherms (a) and pore size distribution (b) for the catalyst samples

The appearance of the mesopores with the mean diameter of 20-50 nm for the samples obtained in subcritical water is well seen in Figure 1b. It is interesting to note that during the metal deposition in subcritical water no changes in the silica structure and porosity were observed in comparison with the treated support. The specific surface area and total pore volume for the synthesized catalysts are presented in Table 1. The data presented show that the surface area of the metal-containing catalysts is similar to that for the treated silica. The decrease in the micropore surface area confirms the changes in the support structure.

Table 1: Catalyst characterization results

Sample	Total pore volume, cm^3/g	Surface area, m^2/g	Surface area of micropores, m^2/g	Surface metal concentration, at. %	Metal state
SiO_2	0.25	391.0	121.0	-	-
SiO_2 treated	0.22	128.0	5.5	-	-
Co/ SiO_2	0.22	127.5	5.0	2.8	Co^{2+}
Fe/ SiO_2	0.22	127.0	5.0	2.3	Fe^{2+}

TEM images of the initial (a) and treated (b) support, as well as the resulted catalysts (c and d), are presented in Figure 2. While comparing Figures 2a and 2b, it is well seen that the treatment of silica in the subcritical water leads to the changes in the crystal structure of the support. The analysis of TEM images for the catalyst samples allows concluding the formation of a thin layer of the active phase on the surface of the silica support.

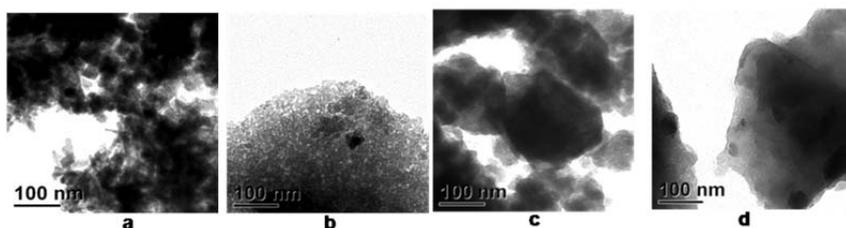


Figure 2: TEM images of the catalyst samples: a) SiO_2 , b) SiO_2 treated, c) Co/SiO_2 , d) Fe/SiO_2

In order to estimate the composition of the catalyst surface and active metal state, XPS analysis was performed. It was found that the surface of the reduced catalysts contains Si, O, C, Co, and Fe atoms. The concentration of the active metal on the catalyst surface was found to be 1.5 and 2.4 at. % for Co/SiO_2 and Fe/SiO_2 , respectively. The surface concentration of the metals in the catalysts indicates the formation of the active phase on the internal surface of the support. Analysis of the high-resolution spectra for Si showed the presence of SiO_2 and hydrated SiO_2 on the catalyst surface. The appearance of the hydrated species of the support is explained by the binding of water $-\text{OH}$ groups with a silica surface. Figure 3 presents the high-resolution XP spectra of Co 2p and Fe 2p sublevels. The analysis of the spectra showed that the active phase of the catalysts is presented by the mixed Co_3O_4 (780.7 eV) and Fe_3O_4 (710.8 eV) oxides. The shift of the high-resolution spectra to the higher binding energies in comparison with a bulk material indicates the formation of a thin layer of the active phase.

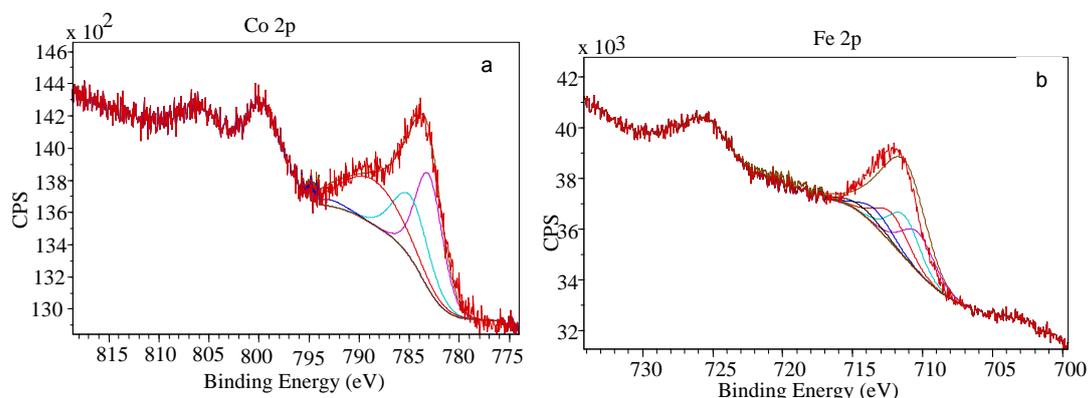


Figure 3: High-resolution XP spectra for: a) Co/SiO_2 , b) Fe/SiO_2

3.2 Catalyst performance in Fischer-Tropsch synthesis

Testing of the obtained silica-based catalysts was carried out in a liquid-phase Fischer-Tropsch synthesis, which allows obtaining a wide range of gaseous, liquid and solid products. Recent years, a great interest of researchers is focused on the liquid-phase process. In the liquid medium of a high-boiling inert solvent, the possibility of the control of the chain growth stage reveals due to the decrease in CO solubility, the formation of oxygen-containing products and preventing the water-gas-shift reaction (Davis, 2002).

Testing of the synthesized catalysts in liquid phase Fischer-Tropsch synthesis showed that Co-based catalyst showed high selectivity (about 45 %) toward the formation of linear $\text{C}_5\text{-C}_8$ gasoline-range hydrocarbons (Figure 4). In the case of Fe-containing catalyst, the formation of a significant amount of oxygenates ($\text{C}_3\text{-C}_4$ alcohols) was found (over 30 %). The formation of the alcohols over Fe/SiO_2 can be explained by the high degree of the hydration of the catalyst surface which was confirmed by XPS study. It is well known, that Fe-based catalysts have high selectivity towards the formation of C_{3+} olefins (up to 50 %) (Khadzhiev and Krylova, 2011). The high surface hydration allows the formation of a high amount of water which reacts with

olefin molecules forming hydroxylic compounds. Moreover, for both catalysts the formation of cyclic and aromatic compounds (mainly cyclohexane and benzene) with total yield ca. 30 wt. % was observed.

The analysis of the catalyst activity has shown that the use of the catalysts synthesized by the hydrothermal deposition provides significantly high reaction rates (0.52 , and $0.57 \text{ mol}_{\text{CO}}\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$ for cobalt and iron-based catalysts respectively) in comparison with the literature data for the liquid-phase process (Davis, 2002).

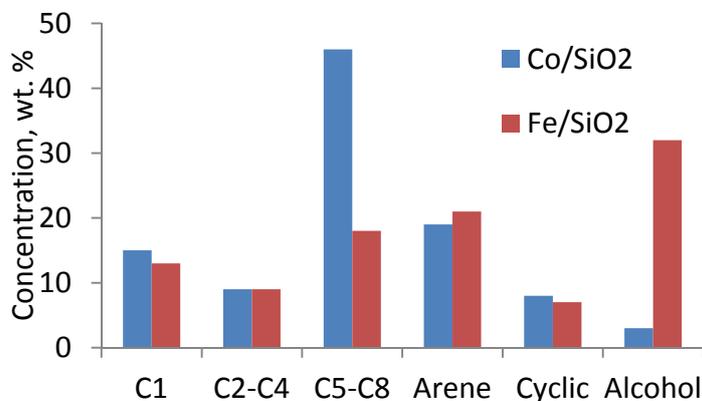


Figure 4: Composition of gaseous and liquid products of the liquid-phase Fischer-Tropsch synthesis over the synthesized catalysts

Analysis of the gas phase composition showed the presence of C₁-C₄ hydrocarbons for all synthesized samples. The formation of a higher amount of C₁-C₂ saturated hydrocarbons was observed while propane and butane presented in the gas phase in trace amounts. It is noteworthy, that the methane selectivity for the synthesized catalysts was found to be lower in comparison with the literature data for Co/SiO₂ (Delgado et al., 2015) and Fe/SiO₂ (Khadzhiev and Krylova, 2011).

The synthesized catalysts showed high long-time performance in the Fischer-Tropsch synthesis. An initial transient period was observed during the first 3 h of the synthesis providing about 25 % of CO conversion. After the achieving of steady-state conditions, the CO conversion degree was found to be over 80 % during at least 50 h. However, Fe-containing catalyst showed slight deactivation (up to 10 %) after 40 h due to the carbonization of the catalyst surface. Co/SiO₂ did not show any decrease in the activity within 50 h in time-on-stream.

4. Conclusions

Hydrothermal method is the permissive way to synthesize the catalysts with the controllable size, structure, and morphology of the metal nanoparticles. The catalysts studied in the current work are characterized by the high specific surface area, a high dispersity of the active phase as well as the stability of the metal nanoparticles towards the aggregation in the high-temperature conditions. The resulted samples showed high catalytic activity in Fischer-Tropsch synthesis allowing the formation of high yield of gasoline-range hydrocarbons.

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References

- Angelucci C.A., D'Villa Silva M., Nart F.C., 2007, Preparation of platinum-ruthenium alloys supported on carbon by a sonochemical method, *Electrochimica Acta*, 52 (25), 7293–7299.
- Antolini E., Salgado J.R.C., Santos L.G.R.A., Garcia G., Ticianelli E.A., Pastor E., Gonzalez E.R., 2005, Carbon-supported Pt–Cr alloys as oxygen-reduction catalysts for direct methanol fuel cells, *Journal of Applied Electrochemistry*, 36, 355-362.

- Bozbag S.E., Sanli D., Erkey C., 2012, Synthesis of nanostructured materials using supercritical CO₂: part II. Chemical transformations, *Journal of Material Science*, 47, 3469–3492.
- Byrappa K., Yoshimura M., 2001, *Handbook of Hydrothermal Technology*, Noyes Publications Park Ridge, New Jersey, 1-39.
- Cansell F., Aymonier C., 2009, Design of functional nanostructured materials using supercritical fluids, *Journal of Supercritical Fluids*, 47, 508–516.
- Chen Q.S., Prasad V., Hu W.R., 2003, Modeling of ammonothermal growth of nitrides, *Journal of Crystal Growth*, 258, 181–187.
- Choi H., Veriansyah B., Kim J., Kim J.-D., Kang J.W., 2010, Continuous synthesis of metal nanoparticles in supercritical methanol, *Journal of Supercritical Fluids*, 52(3), 285–291.
- Davis B.H., 2002, Overview of reactors for liquid phase Fischer–Tropsch synthesis, *Catalysis Today*, 71 (3–4), 249–300.
- Delgado J.A., Claver C., Castillon S., Curulla-Ferre D., Godard C., 2015, Correlation between Hydrocarbon Product Distribution and Solvent Composition in the Fischer–Tropsch Synthesis Catalyzed by Colloidal Cobalt Nanoparticles, *ACS Catalysis*, 5, 4568–4578.
- Donohue M., Aranovich G.L., 1998, Classification of Gibbs adsorption isotherms, *Advances in Colloid and Interface Science*, 76, 137-152.
- Erkey C., 2011, *Supercritical Fluids & Organometallic Compounds*, Elsevier, Amsterdam, Netherlands.
- Galkin A.A., Kostyuk B.G., Kuznetsova N.N., Turakulova A.O., Lunin V.V., Polyakov M., 2001, Unusual Approaches to the Preparation of Heterogeneous Catalysts and Supports Using Water in Subcritical and Supercritical States, *Kinetics and Catalysis*, 42(2), 154-162.
- Hayashi H, Hakuta Y., 2010, Hydrothermal Synthesis of Metal Oxide Nanoparticles in Supercritical Water. *Materials*, 3(7), 3794-3817.
- Ioffe I.I., Pismen L.M. 1972, *Inzhenernaya khimiya geterogennogo kataliza*, Khimiya, Leningrad, Russia.
- Khadzhiev S.N., Krylova A.Yu., 2011, Fischer–Tropsch Synthesis in a ThreePhase System over Nanocatalysts (Review), *Petroleum Chemistry*, 51(2), 74–85.
- Lester E., Blood P., Denyer J., Giddings D., Azzopardi B., Poliakoff M., 2006, Reaction engineering: the supercritical water hydrothermal synthesis of nanoparticles, *Journal of Supercritical Fluids*, 37, 209-214.
- Lu X.M., Hanrath T., Johnston K. P., Korgel B. A., 2003, Growth of single crystal silicon nanowires in supercritical solution from tethered gold particles on a silicon substrate, *Nano Letters*, 3, 93–99.
- Marques F.H., Guirardello R., 2018, Thermodynamic analysis for Fischer-Tropsch synthesis using biomass, *Chemical Engineering Transactions*, 65, 397-402.
- Morère J., Tenorio M.J., Torralvo M.J., Pando C., Renuncio J.A.R., Cabanas A., 2011, Deposition of Pd into mesoporous silica SBA-15 using supercritical carbon dioxide, *Journal of Supercritical Fluids*, 56, 213–222.
- Otsu J., Oshima Y., 2005, New approaches to the preparation of metal or metal oxide particles on the surface of porous materials using supercritical water: Development of supercritical water impregnation method, *Journal of Supercritical Fluids*, 33, 61-67.
- Pascu O., Cacciuttolo B., Marre S., Pucheault M., Aymonier C., 2015, ScCO₂ assisted preparation of supported metal NPs. Application to catalyst design, *Journal of Supercritical Fluids*, 105, 84–91.
- Pestov D., Levit N., Kessick R., Tepper G., 2003, Photosensitive 2,5-distyrylpyrazine particles produced from rapid expansion of supercritical solutions, *Polymer*, 44, 3177-3183.
- Ren G., Shi H., Xing Y. 2007, Synthesis and Composition Evolution of Bimetallic Pd-Pt Alloy Nanoparticles, *Nanotechnology*, 18, 385604-385610.
- Tomasek S., Lonyi F., Valyon J., Wollmann A., Hancsok J., 2018, Fuel production from Fischer-Tropsch paraffin mixtures, *Chemical Engineering Transactions*, 70, 667-672.
- Türk M., 2014, *Particle Formation with Supercritical Fluids*, Elsevier, Amsterdam, Netherlands.
- Wang W.M., Zheng D., Du C., Zou Z.Q., Zhang X.G., Xia B.J., Yang H., Akins D.L., 2007, Carbon-supported Pd–Co bimetallic nanoparticles as electrocatalysts for the oxygen reduction reaction, *Journal of Power Sources*, 167, 243-249.
- Watkins J.J., McCarthy Th. J., 1995, Polymer/Metal nanocomposite synthesis in supercritical CO₂, *Chemistry of Materials*, 7 (11), 1991–1994.
- Yahya R.B., Hayashi H., Nagase T., Ebina T., Onodera Y., Saitoh N., 2001, Hydrothermal synthesis of potassium hexatitanates under subcritical and supercritical water conditions and its application in photocatalysts, *Chemistry of Materials*, 13, 842-847.
- Zhang Y., Erkey C., 2006, Preparation of supported metallic nanoparticles using supercritical fluids: a review, *Journal of Supercritical Fluids*, 38, 252–267.