The preparation and analysis of ceramic fibers with deposited catalytic particles by plasma technology

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Abstract. In this work, the ceramic micro- and nanofibers were formed using atmospheric pressure thermal plasma reactor. The catalytic (copper, titanium) particles and their mixtures were deposited on the surface of zeolite fibers during their formation. The prepared catalytic fibers were analyzed using scanning electron microscopy (SEM), X-ray diffraction analysis (XRD), BET (Brunauer–Emmett–Teller) surface area measurements and Energy-dispersive X-ray spectroscopy (EDS). The SEM analysis showed that the obtained fiber diameters are in the range from 10 µm to few hundred nanometers. Some of the catalytic particles were deposited without changes and some were melted or burst. The XRD analysis showed that the zeolite fiber without the catalytic particles is amorphous as there are no crystal phase peaks. After the deposition of catalytic particles the peaks of the catalytic metals and their oxides appear. The BET method showed that the surface area of the catalytic fiber is 13-18 m²/g. The EDS analysis showed that the quantity of catalytic particles in the catalytic fiber is 7-18 %.

1. Introduction
The Carbon monoxide (CO), nitrogen oxides (NOX) and hydrocarbons (HC) are commonly targeted pollutants worldwide that have caused global warming and environmental pollution [1]. Efficient purification of such exhaust gases is generally carried out using noble metal catalysts such as platinum, rhodium and palladium. However, these noble metals are limited resources and reduction of their usage has become important for wider applications [2].

Zeolite catalysts have been widely used in various industrial field [1]. Usually they are used as supports for platinum as they have a porous structure that can confine molecules in small spaces. The zeolite affords large surface area and large cage with small window structure. This provides the space confinement and strong metal-support interaction for metal nanoparticles with high dispersion, good stability, and adjustable acidic strength when it is used as a catalyst support generally in the form of beads or pellets [3].

Fibrous catalysts made of inexpensive metals, carbons or glasses allow a larger field of applications instead of gauze catalysts woven of wires of fine precious metals (Pt, Ru, Ag). Fibers offer flexibility and endless forms, which do not apply to the usual powdered or granular materials. It is thus possible to adjust the geometric appearance of the fibrous substrates in order to fit it into a flue gas channel of arbitrary shape. Low pressure drop of processed gases, high surface area, safer operation and etc. are identified as other advantages of fiber catalysts [4].
The recently developed ceramic fiber production process using plasma-chemical reactors provides an opportunity to form fine fibers from any kind of ceramic materials by employing the kinetic energy of plasma flow [5]. Such microfiber (in some cases even up to 300 nm in thickness) can be used as catalyst supports for cheaper catalytically active metals like Cu, TiO$_2$ and etc. as its melting temperature is higher than the operating temperatures of the catalysts. Copper is usually used in the catalyst production as additive to Pd for CO oxidation [6], in selective catalytic reduction of NO, and NH$_3$ [7] and etc. The titanium oxide is used in currently commercial catalysts based on V$_2$O$_5$–WO$_3$–TiO$_2$ [8] or in composites with platinum-gold metals for CO oxidation and NO reduction [9]. Chen et al. [10] showed that CuO/TiO$_2$ catalyst had superior catalytic activity with NO conversion and N$_2$ selectivity.

In this work, the ceramic fibers were formed using atmospheric pressure thermal plasma reactor. The catalytic (copper, titanium) particles were deposited on the surface of zeolite fibers during their formation. The

2. Methodology

The zeolite fiber used in this work was prepared using special plasma-chemical reactor, which in detail discussing the thermodynamic processes taking place in the reactor has been described in our other work [11]. The fiber was formed from the zeolite powder (up to 60 μm size).

As the obtained zeolite fiber in the catalyst is used as the support, the catalytically active particles (Cu, TiO$_2$) were deposited on the zeolite fiber during the fiber formation process. The deposition of catalytic particles was designed at the exhaust of the reactor where the formation of the fiber from the melt takes place spraying the catalytic particles on the surface of the formed fiber. Consequently, the catalytically active particles are deposited on the surface of the filaments of formed fiber and can react with the processed gases during catalytic process. The catalytic fiber production process in channel of the plasma chemical reactor is presented in figure 1 (where 1 – the feeder of ceramic particles; 2 – the feeder of catalytic particles; 3 – reactor walls cooled with water; 4 – ceramic melt flow; 5 – produced fibers and granules; G$_1$ – air plasma flow from plasma torch; G$_2$ – air flow for injection of ceramic materials; G$_3$ – air flow for spraying of catalytic particles; G$_c$ – flow of catalytic particles; G$_g$ – propane gas flow; G$_z$ – flow of ceramic (zeolite) particles).

![Figure 1. The schematic view of the catalytic fibre production process.](image)

The channel of plasma-chemical reactor designed for ceramic fiber production was applied for formation of catalytic fiber by, as mentioned above, attaching the feeder of catalytic particles at the outlet nozzle of the reactor, reject the additional air flow rate which is usually used to increase the kinetic energy of plasma flow, decreasing the diameter of outlet nozzle of the reactor from 16mm to 13mm. The parameters of plasma chemical reactor are presented in Table 1.

The copper (Cu), titanium oxide (TiO$_2$) and their mixture were used as catalytically active particles. The mixture was prepared by mixing the equal weights of Cu and TiO$_2$ particles. The size of those particles was between 40-60 μm.

The prepared catalytic fibers were analyzed using scanning electron microscopy (SEM), X-ray diffraction analysis (XRD), surface area measurements and Energy-dispersive spectroscopy (EDS).
Table 1. The plasma-chemical reactor parameters.

| Parameter                                      | Value   |
|------------------------------------------------|---------|
| Plasma torch power, kW                         | 80      |
| Air flow rate (G₁), 10⁻³ kg/s                 | 22      |
| Propane gas flow rate (G₃), 10⁻³ kg/s          | 1.2     |
| Dispersive particle flow rate (G₃), 10⁻³ kg/s  | 1       |
| Plasma flow temperature, leaving the reactor, K| 3100    |
| Plasma flow velocity, leaving the reactor, m/s | ~1200   |
| Plasma torch efficiency, %                     | 80      |

3. Results and discussions

The morphology of formed ceramic fibre with and without catalytic particles is shown in Fig. 2. It can be seen, that the surface of formed fiber is smooth with some small derivatives on surface. The fiber diameters between 10-20 μm dominate. The surface area of such fiber is up to 6 m²/g.

![SEM images of obtained fiber. a) – without, b) – with catalytic particles (Cu).](image)

The sprayed catalytic particles stick to the ceramic fiber at the end of the plasma-chemical reactor where plasma flow temperature is about 3100 K. However, the kinetic energy of plasma flow is very high, so the room temperature catalytic particles are not able to heat up to their melting point and are blown away with the ceramic fiber. In figure 2b it can be seen that the formed catalytic fiber consists of small (up to ~40 μm) size particles and ceramic fiber filaments which are the main component of pure zeolite fiber seen in figure 2a. Some of the catalytic particles were deposited without changes and some were melted or burst. The obtained fiber diameters are in the range from 10 μm to few hundred nanometers. The surface area of ceramic fiber with doped catalytic particles increases from 6 m²/g in case of zeolite up to 18 m²/g after addition of the TiO₂. The addition of Cu increases the surface area up to 13 m²/g.

It was found that zeolite fiber prepared using plasma technology has almost only amorphous phase mullite there are no crystalline phase peaks in the XRD patterns. The XRD patterns of the fiber samples with doped Cu particles (figure 3a) show the crystalline form of Cu, corundum (crystalline form of Al₂O₃), quartz (crystalline form of SiO₂) and synthetic mullite (Al₄.64 Si₁.36 O₉.68). The sample with doped TiO₂ particles (figure 3b) consists of corundum, anatase, and rutile, the crystalline form of quartz and mullite (Al₁₂Si₇O₃₈) and amorphous mullite. The addition of catalytic particles has the influence on the mullite as part of it experiences conversion in phase from amorphous to crystalline. As the crystalline variety shrinks less than the amorphous variety it is an advantage for such catalyst supports [3].
The EDS analysis showed that the quantity of catalytic particles in the catalytic fiber in case of Cu is 6.7 %, while the dominating species are those which compose the zeolite: oxygen – 53.6 %, silicon – 24.1 and aluminum – 12.3 % in normalized atomic concentration. The impurities amount for 3.3 %. In case of TiO$_2$ particle injection, there are 18.1 % of catalytic particles in the fiber. The oxygen amount in the fiber is 51.3 %, silicon – 21.4 %, aluminum – 4.8 % and the impurities – 4.4 % of normalized atomic concentration. The fiber without catalytic particles consist of 55 % of oxygen, 26 % of silicon, 14.6 % of aluminum and 4.4 % of impurities.

Conclusions
The catalytic ceramic fiber can be obtained by spraying the catalytic particles on the fiber during its formation. The addition of catalytic particles has the influence on zeolite fiber as part of it converts from amorphous to crystalline phase. In case of TiO$_2$ and Cu doping, the surface area of the fiber increases up to 3 and 2 times and the catalytically active media amounts for 18.1 % and 6.7 % in the fibrous catalyst, respectively. The further direction of the research – catalytic efficiency of prepared fiber.

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