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REFUSE-DERIVED FUEL BASED COBALT CATALYSTS FOR HYDROGEN PRODUCTION

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Abstract

Refuse-derived fuel (RDF) is a mixed industrial waste, which often contains combustible materials (cellulose, polymers, rubber, biomass, etc.). The RDF waste precursor is subjected to thermo-oxidation treatment at 300 °C, followed by carbonizations at 600 °C, and high temperature hydropyrolysis at 800 °C. The obtained nanoporous carbon material was subjected to detailed characterization by low temperature nitrogen sorption, elemental analysis, etc. Carbon derived from RDF is distinguished by micro/mesoporous texture and moderately high surface area (650 m^2 g^{-1}). The catalyst obtained is tested in the process of methanol decomposition, leading to production of hydrogen as a fuel. The influence of the physico-chemical characteristics of the synthesized carbon on the catalytic activity of carbon-based cobalt catalyst is studied.

Key words: RDF fuel, nanoporous carbon, catalyst supports

1. Introduction. Nowadays in Bulgaria big amounts of municipal and industrial wastes are deposited in the landfills. Meanwhile, cities continue to expand and often overload local waste management systems. In some European countries landfilling is reduced to a minimum, whereas the waste is used for alternative

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fuel. RDF (refuse-derived fuel) is a mixture of industrial and municipal wastes, and usually contains highly flammable components (paper, plastic, etc.). The main characteristics of solid fuel derived from waste are the energy value, ash content and moisture content. Solid waste fuel is used dominantly in industrial and thermal power plants. RDF is mainly used within the European Union – in countries with high standard for waste recycling, such as Austria, Germany, and the Netherlands. However, this waste is difficult to be recycled, determined by technology limitations and lack of available installations. This leads to environmental contamination – the air, water, soil and plants are polluted with carbon, sulphur and nitrogen oxides, polycyclic hydrocarbons, heavy metals, as well as fine dust particles formed by the non-combustible materials present in RDF [1,2].

Activated carbons (AC) are widely allied as adsorbents, catalysts or catalyst supports, due to their surface and textural characteristics, which could be easily controlled by the preparation procedure and the precursor used. It is well known that the influence of the physico-chemical characteristics of the synthesized carbon affects the catalytic activity of carbon-based catalysts. The characteristics of the activated carbons produced from various agricultural [3–7] and polymer by-products [8,9] depend on the composition and structure of the raw materials [3–9]. Previous investigations demonstrated that different catalysts are used for methanol decomposition, leading to production of hydrogen as a fuel [10–13], whereas cobalt containing catalysts are distinguished by high catalytic activity and selectivity towards CO and H_2 [14].

The main objective of the present study is utilization of RDF by conversion to liquid and gas for energy, as well as solid product – porous carbon. The raw materials used are waste from roof-covering materials, made of polyvinyl chloride and polyolefins. The investigations will allow us to determine the treatment conditions for obtaining porous carbon with optimal characteristics for application as catalyst support, using suitable active phase on its surface. The catalyst obtained will be tested in the process of methanol decomposition, leading to production of hydrogen as a fuel. The influence of the physico-chemical characteristics of the synthesized carbon on the catalytic activity of carbon-based cobalt catalyst will be studied. Another contribution of this work is the utilization of by-products from industry and construction business.

2. Materials and methods. ***2.1. Adsorbent preparation.*** RDF building waste, which contains polyvinyl chloride (PVC), was provided by the University of Architecture, Civil Engineering and Geodesy, Sofia, Bulgaria. The raw materials used are waste from roof-covering materials, made of PVC resin (55%) as basic material, 28% plasticizers (phthalic anhydride esters), 7% fillers, and 10% pigments, processing oil, biocides and stabilizers.

Concentrated sulphuric acid was used in the thermal oxidation treatment, which continues 60 min. One hundred grams waste product from RDF was heated up to 100 °C and 10 cm^3 98% H_2SO_4 was added by drops with continuous stirring,

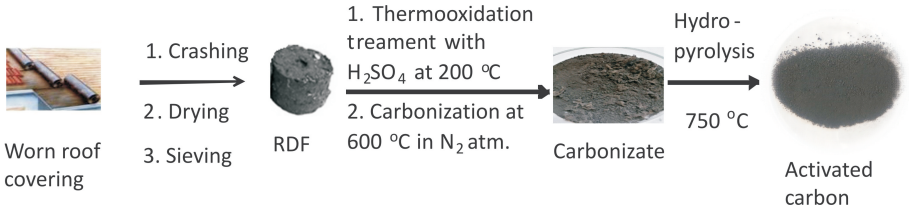


Fig. 1. Scheme of synthesis of activated carbon from RDF

and the mixture was heated up to 200—300 °C. The obtained solid product was washed with water, dried at 150 °C, and carbonized at 600 °C (30 min). Then the carbonizate was subjected to water steam activation at 800 °C for 60 min (Fig. 1). The obtained solid product is denoted as AC-RDF. Mohr's method, using titration with $AgNO_3$ of solution obtained by continuous washing of synthesized carbon, was applied to check the presence of Cl^- anions in obtained carbon – chlorides were below detection limits.

2.2. Deposition of cobalt on activated carbon. Ten grams activated carbon was modified with Co by incipient wetness impregnation with 10 cm^3 saturated (0.84 g cm^3) aqueous solution of cobalt (II) nitrate. The nitrate decomposition was carried out by heating at 500 °C for 6 h in a flow of nitrogen (99.96% purity, SIAD). The metal content in the sample is about 8 mass %, determined by atomic absorption spectroscopy. Cobalt catalyst sample is denoted as Co/AC-RDF.

2.3. Methods of characterization. The textural characteristics were determined by low-temperature (−196 °C) nitrogen adsorption on a Quantachrome Autosorb iQ-C-XR/MP apparatus. Before the experiments, the samples were outgassed under vacuum at 300 °C overnight. The obtained isotherms were used to calculate the specific surface area S_{BET}, pore volumes and pore size distribution.

The elemental analysis was carried out on a Vario Macro Cube apparatus (ELEMENTAR), in order to determine carbon, hydrogen, nitrogen and sulphur content.

The temperature-programmed reduction/thermo-gravimetric (TPR/TG) analysis was performed with Simultaneous Thermal Analyzer – STA 449 F3 (Netzsch) instrument in a flow of 50 vol % H_2 in Ar (100 cm^3 min^{-1}) and heating rate of 5 °C min^{-1}.

2.4. Catalytic tests. Methanol conversion was carried out in a fixed bed flow quartz reactor (0.05 g of catalyst), argon being used as a carrier gas (50 cm^3 min^{-1}). The methanol partial pressure was 1.6 kPa. The catalysts were tested under conditions of a temperature programmed regime within the range of 100–500 °C with heating rate of 1 °C min^{-1}. On-line gas chromatography analysis was performed on HP apparatus equipped with flame ionization and thermo-conductivity detectors, on a PLOT Q column, using an absolute calibration method and a carbon-based material balance.

3. Results and discussion. Table 1 presents the results from the elemental analysis of activated carbon from RDF. Data show that the higher number of condensation reactions, which occur during the carbonization and synthesis of activated carbon, lead to formation of condensed aromatic structures, related with high carbon and low hydrogen content. Ash (39% inorganic impurities; determined by measuring the mass after heating in air at 800 °C for 1 h) contains $CaCO_3$, $CaSO_4$, $Ca(OH)_2$, detected by X-day diffraction.

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Elemental analysis of activated carbon from RDF

Sample	C, mass %	C, atomic %	H, mass %	H, atomic %	N, mass %	N, atomic %	S, mass %	S, atomic %
AC-RDF	47.10	3.93	2.25	2.25	4.20	0.30	2.30	0.07

Results from nitrogen physisorption (−196 °C) of activated carbon from RDF are shown in Fig. 2. The calculated textural parameters are as follows: specific surface area S_{BET}, $m^2/g = 650$ m^2/g, total pore volume micropore volume is 0.22 cm^3/g, mesopore volume – 0.02 cm^3/g and macropore volume – 0.01 cm^3/g.

The isotherm presents a type I–IV hybrid shape, according to the BET classification, with a hysteresis loop (H4 types) in the desorption branch at relative pressures > 0.5, which is associated with capillary condensation in slit-shaped

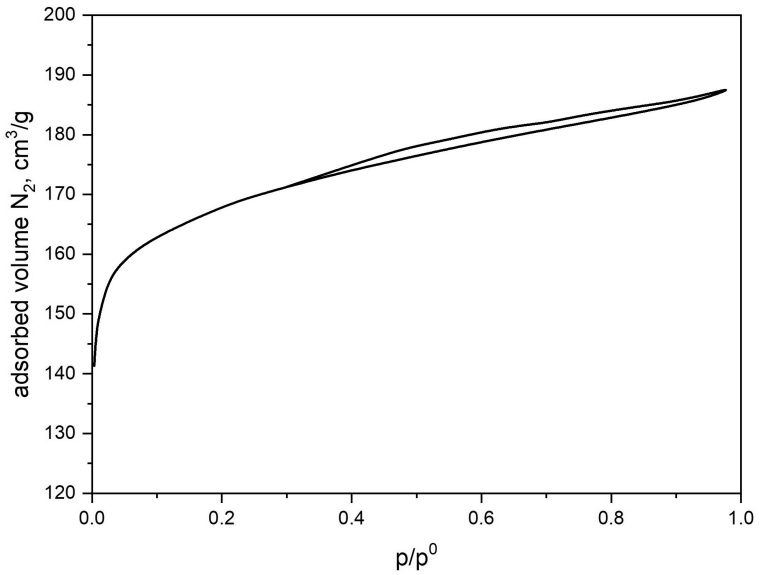


Fig. 2. Nitrogen physisorption (−196 °C) isotherm of activated carbon from RDF

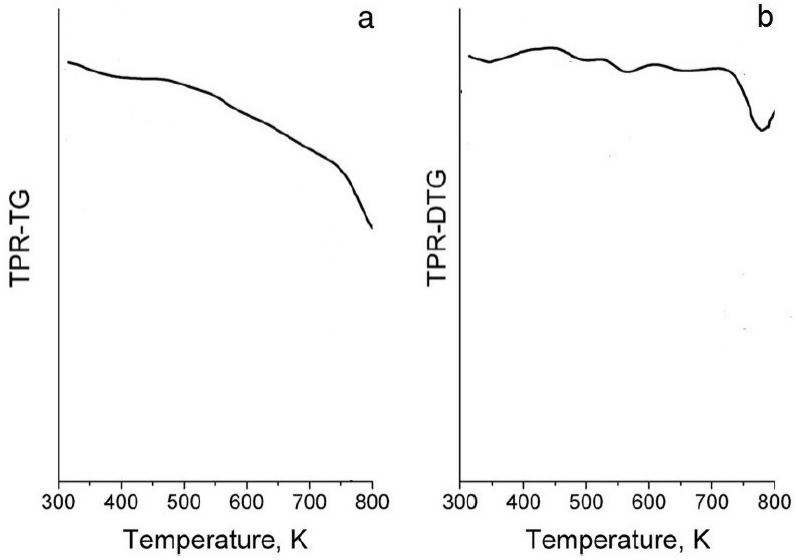


Fig. 3. TPR-TG (a) and TPR-DTG (b) profiles of Co modified activated carbon

mesopores [15]. The obtained carbons present relatively narrow pore size distribution within the micropore range, with a maximum at 1–2 nm. This finding is in good agreement with earlier investigation about the effect of raw material composition on the final porous and chemical properties [16].

Carbon from RDF is distinguished by moderate specific surface area and presence of micro- and mesopores, whereas the micropores prevail. The results suggest that obtained nanoporous carbon is appropriate to be used for adsorbent and catalyst support.

The results from temperature-programmed reduction with thermo-gravimetry and differential thermo-gravimetry (TPR-TG and TPR-DTG) are presented in Fig. 3. The main reduction effects for cobalt catalyst based on AC-RDF occur in the range 475–600 K (200–325 °C) and above 650 K (400 °C), which could be due to stepwise reduction of cobalt oxides to metallic cobalt. The effects below 600 K are related to reduction of Co_2O_3 to CoO, whereas, the effects above 650 K are connected with reduction of CoO to Co [17].

The results about temperature dependence of methanol conversion show that CO, methane and CO_2 are the only registered carbon-containing products. During catalytic tests AC-RDF supported cobalt catalyst demonstrated conversion up to 40% at 450 °C. The selectivity of the reaction to the main product CO, which is directly related to the hydrogen production from methanol, is 45% within the range 400–500 °C. Moderate catalytic activity and selectivity towards CO, both lower than other cobalt catalysts [14], are most probably due to high ash content, whereas inorganic impurities have negative effect on this catalytic reaction.

4. Conclusions. RDF waste was successfully applied as precursor for synthesis of nanoporous carbon. The obtained nanoporous carbon materials were subjected to detailed characterization by low temperature nitrogen sorption, elemental analysis, etc. The obtained nanoporous carbon materials are distinguished by micro/mesoporous texture and moderately high surface area (650 m^2 g^{-1}).

The catalyst obtained is tested in the process of methanol decomposition, leading to production of hydrogen as a fuel. The influence of the physico-chemical characteristics of the synthesized carbon on the catalytic activity of carbon-based cobalt catalyst is studied. After methanol degradation, CO, methane, and CO_2 were detected in the gas products. CO selectivity is directly related to the hydrogen production from methanol ($CO:H_2$ = 1:2). Main factors which determine the catalytic activity and selectivity are the dispersion and location of cobalt species into the porous matrix, as well as the texture and surface chemistry of the nanoporous carbon support used.

Catalytic support strongly affects the formation of active phase in this monocomponent cobalt catalyst. Activated carbon contributes to the formation of partially reduced highly dispersed cobalt species, which possess relatively high catalytic activity and selectivity in methanol decomposition to H_2 and CO. The results suggest that the obtained nanoporous carbon is suitable for application as a catalyst support for the degradation of methanol.

The results suggest that the obtained waste-based nanoporous carbon is appropriate to be used for adsorbent and catalyst support for cobalt catalyst for methanol decomposition, despite its moderate catalytic activity and selectivity towards CO, due to inorganic impurities with negative effect on this catalytic reaction.

The conversion of waste materials to catalysts with moderate activity and selectivity for production of hydrogen is an important contribution. In the future work the catalyst properties could be improved by modifying the precursors and synthesis procedure.

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