



Activated carbons from waste biomass and low rank coals as catalyst supports for hydrogen production by methanol decomposition



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ABSTRACT

Activated carbons with different textural and chemical surface characteristics were synthesized from waste biomass and low rank coals, and furthermore used as a host matrix for cobalt species, varying the preparation and modification methods. The obtained activated carbons and modified samples were characterized by complex of various physicochemical methods, such as: low temperature physisorption of nitrogen, XRD, EPR, XPS, UV–Vis and TPR with hydrogen. Boehm method was applied for qualitative and quantitative determination of oxygen-containing groups on the carbon surface before and after cobalt deposition. The catalytic properties of cobalt modifications were tested in methanol decomposition. The dominant effect of activated carbon texture over the surface chemistry on the state and catalytic behavior of cobalt species was discussed.

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1. Introduction

As a catalyst support, activated carbon has many advantages, such as high surface area, tunable pore structure and surface chemistry, resistance to acidic or basic media, stability at high temperatures in inert or reduction atmosphere, as well as ability to recover the supported active metals [1,2]. Activated carbon structure is developed by imperfect aromatic sheets of carbon atoms, as well as incompletely saturated valences and unpaired electrons on the surface. This determines high adsorption capacity of carbon materials, especially towards polar or polarizable molecules [3].

The surface functional groups, formed as a result of thermal or chemical treatments, influence the acid–base properties of carbon surface and could be considered as potential active sites for adsorption and catalysis [4,5].

Carbon precursor selection and treatment conditions are feasible way for tuning the surface chemistry of carbon materials. On the other hand, porous structure of activated carbon is an important factor for preparation of efficient carbon-supported catalysts and it could be successfully regulated by the method of carbon synthesis and subsequent activation. It is well known, that the synthesis of porous carbon materials from lignocellulose precursors using conventional physical

and chemical activation is the most economical and easy approach for large-scale production [5]. Thus synthesized activated carbons exhibit well-developed, however predominantly microporous structure [6,7]. Previous studies report the benefits of addition of metal species (such as calcium) which increases the amount of volatile products during the pyrolysis process, and thus provides formation of carbon products with much broader pore size distribution (development of meso- and macroporosity) [8].

Supported cobalt materials have been investigated in a range of catalytic reactions including Fischer–Tropsch synthesis (FTS) [9,10], methane [11,12] and propane combustion [13], cyclohexane [14], ethyl acetate [15], cyclohexanol [16] and CO oxidation [17]. It was demonstrated that the chemical nature of the support [18,20], the texture and surface acidity [15,19,20], the composition of the metal precursor, the modification method and the intended metal loading influence the dispersion, reduction and catalytic properties, and the extent of metal–support interactions [15]. Various supports have been used for preparation of cobalt based catalysts, such as SiO₂, Al₂O₃, MgO, TiO₂, Nb₂O₅, CeO₂, and ZrO₂, but in some cases, formation of solid solutions between cobalt phase and support significantly changed the coordination and catalytic properties of cobalt [21–23]. The effect of carbon support on the formation of complex mixture of cobalt species in different oxidative state was discussed [24].

There are a lot of reports for the application of activated carbon supported cobalt catalysts for NO_x reduction [22,23,25–31], oxidation

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of phenol with peroxymonosulphate [32], CO-PROX reaction [33], etc.

The aims of this paper are:

- 1) To obtain activated carbons with different surface and texture features from different precursors—waste agricultural products (peach stones, olive stones) and low rank coal treatment products, using various preparation technologies;
- 2) The synthesized activated carbons to be modified with cobalt and tested as catalysts in methanol decomposition. Recently methanol has been considered as a promising carrier of hydrogen due to methanol production by well developed technologies from waste biomass, and possibility for easy release of hydrogen if needed [34–37].
- 3) Finally, this investigation is focused on the possibility for fine tuning and improving catalyst behavior by tailoring the properties of carbon support, by varying the nature of the precursor and the preparation procedures. In this way, the scope of this study is related to the problem of hydrogen production and storage by utilization of waste biomass and coal treatment products.

2. Materials and methods

2.1. Synthesis of activated carbons

Olive stone based activated carbon, denoted as OSAC, was produced by one-step hydro-pyrolysis process, which is well studied and used for a long time in our laboratory [38–42]. Crushed olive stones are used as a precursor. Carbonization and subsequent activation procedures were performed in the presence of water vapor at 1023 K for 1 h. The flow of water vapor was started at 573 K.

Peach stone based activated carbon, denoted as PSAC, was produced by two-step process, including carbonization of crushed peach stones at 823 K for 1 h and subsequent activation of the carbonizate with water vapor at 1023 K for 1 h.

The synthetic activated carbon, denoted as SACS, was prepared by method, developed in our institute [42], using the following procedure: treatment of a mixture from coal tar pitch and furfural (1:1 by weight) with H_2SO_4 at 393 K until solidification. The solid product was subjected to further carbonization up to 873 K; the activation of the obtained carbonizate was performed at 1073 K in the presence of water vapor, followed by thermal treatment in Ar (99.996% purity, SIAD) atmosphere at 1473 K for 1 h.

The synthetic activated carbon, denoted SACN, was prepared from mixture from coal tar pitch and furfural (1:1 by weight) with HNO_3 at 393 K until solidification. The obtained solid product was subjected to further carbonization up to 873 K; the activation of the obtained carbonizate was performed at 1073 K in the presence of water vapor.

Ordered mesoporous silica of SBA-15 type (used as a reference support) was prepared according to the special synthesis procedure [43], using Pluronic 123 as a structure directing agent and decomposition of the template after heating at 823 K for 6 h in air.

2.2. Modification of activated carbons

The activated carbons and mesoporous silica were modified with Co by incipient wetness impregnation with aqueous solution of cobalt nitrate precursor. The nitrate decomposition was carried out by heating at 773 K for 6 h in a flow of nitrogen (99.96% purity, SIAD). The metal content in all samples is about 8 wt.%, determined by atomic absorption spectroscopy. The cobalt modifications samples are denoted as Co/OSAC, Co/PSAC, Co/SACS and Co/SACN, respectively. The reference silica supported sample was denoted as Co/SBA-15.

2.3. Methods of characterization

The porous structure of all investigated activated carbons was studied by nitrogen adsorption at 77 K, carried out in an automatic Micromeritics ASAP 2010 volumetric 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 by using the method of density functional theory (DFT) [44].

The amount of various acidic oxygen-containing functional groups was determined by Boehm method using aqueous solutions of NaHCO_3 , Na_2CO_3 , NaOH , and $\text{C}_2\text{H}_5\text{ONa}$, according to the procedure described by Boehm [45]. The amount of basic sites was determined with 0.05 N HCl, according to the procedure described by Papirer et al. [46]. The pH of activated carbons was determined after boiling for 5 min in 100 cm^3 distilled water, followed by decantation and cooling down the solution to ambient temperature.

The electron paramagnetic resonance (EPR) measurements were performed by an X-band spectrometer Radiopan, working at 9.3 GHz and modulation of 100 kHz. The measurements were taken with attenuation of 20 dB (about 0.7 mW) to avoid microwave saturation. The spectral data were processed by an on-line computer. In the EPR investigations ultramarine was used as a reference for the determination of concentration of paramagnetic centers, and a ruby crystal, permanently placed in the spectrometer cavity, was the secondary reference.

Powder X-ray diffraction patterns were collected by a Bruker D8 Advance diffractometer with CuK_α radiation and LynxEye detector; the average crystallite size was evaluated according to Scherrer equation. The ultraviolet–visible light (UV–Vis) spectra were recorded using a Jasco V-650 UV–Vis spectrophotometer equipped with a diffuse reflectance unit. X-ray photoelectron spectra (XPS) measurements have been carried out on ESCALAB MkII (VG Scientific) electron spectrometer with pressure of 5×10^{-10} mbar in the analysis chamber, using twin anode $\text{MgK}_\alpha/\text{AlK}_\alpha$ X-ray source with excitation energies of 1253.6 and 1486.6 eV, respectively. The spectra are recorded at total instrumental resolution (as it was measured with the FWHM of $\text{Ag3d}_{5/2}$ photoelectron line) of 1.06 eV and 1.18 eV, for MgK_α and AlK_α , respectively. Temperature-programmed reduction and thermo-gravimetric (TPR–TG) analysis was performed in a Setaram TG92 instrument in a flow of 50 vol.% H_2 in Ar (100 $\text{cm}^3 \text{min}^{-1}$) and heating rate of 5 K min^{-1} .

2.4. Catalytic tests

Methanol decomposition was carried out in a fixed-bed reactor at atmospheric pressure. The catalyst (0.055 mg) with a particle size of 0.2–0.8 mm was diluted with three-fold higher amount (by volume) of glass spheres. The catalysts were tested under conditions of a temperature-programmed regime within the range of 350–770 K with a heating rate of 1 K min^{-1} .

Typically, the catalytic experiments include: (i) catalyst pretreatment at 373 K in Ar for 1 h; (ii) GC analysis of the non-converted reaction mixture of methanol (1.57 kPa) in argon (50 ml/min); and (iii) inserting the reaction mixture into the reactor at 350 K. After GC analysis of the output composition, the temperature in the reactor was increased with 20 K (1 K/min). The last procedure was repeated every 20 K in the whole investigated temperature interval (350–770 K).

The changes in the catalysts during catalytic test were elucidated by in-situ measurements of the catalytic activity of the used catalysts at selected temperatures. During the experiments the reactant (methanol) as well as all carbon-containing products (CO , CO_2 , methane, methyl formate and dimethyl ether) was in a gas phase and their amounts were determined by on-line GC analyses, using HP apparatus equipped with flame ionization and thermo-conductivity detectors, and a 30 m PLOT Q column. The methanol conversion $X(T)$ at specific temperature T was calculated by the equation $X(T) = 100\% (C_{\text{input}} - C_{\text{output}}) / C_{\text{output}}$.

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