



Formation of catalytic active sites in iron modified activated carbons from agriculture residues



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ABSTRACT

Agriculture residues (grape seeds, peach, apricot and olive stones) were used as a precursor of activated carbons with tunable textural characteristics and relatively low surface functionalities (predominantly carbonyl and hydroxyl groups). Thus obtained activated carbons were modified with iron species and tested as catalysts in methanol decomposition. Nitrogen physisorption, XRD, UV–Vis, FTIR, Moessbauer spectroscopy, TPR with hydrogen and Boehm method were applied for complex characterization of the initial activated carbon supports, their iron modifications and the transformations during the catalytic process. The final phase composition and the related with this catalytic activity and selectivity of these materials was considered as a result of complex transformations of active phase by the influence of activated carbon support and reaction medium and this is in close relation with the dispersion and location of iron species into the porous matrix. The decisive role of activated carbon texture characteristics, which is much more significant than the surface functionalities, on the formation of iron catalytic sites is established, and the variation in the nature of the agriculture precursor is assumed as a simple approach for tailoring their properties.

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1. Introduction

Activated carbons (AC) are known as promising materials with wide application as adsorbents, catalysts or catalyst supports due to their tunable surface and textural characteristics, which could be easily controlled by the preparation procedure and the precursor used [1–10]. Particularly, the interest towards their iron modifications is due to wide application of different forms of iron oxides in the environmental engineering for degradation and treatment of toxic pollutants and hazardous chemicals in the soil, air, and water [11–28 and refs. therein]. Magalhães et al. [29] prepared reduced forms of iron by thermal treatment under nitrogen atmosphere of synthetic hematite in tar for degradation of textile dyes. Pereira et al. [22] also used AC as reactive support to produce highly active Fe⁰ and Fe₃O₄ phase for reduction of Cr⁶⁺ and degradation of textile

dye by combined reduction/Fenton process. In our previous study we demonstrated significant activity of iron and binary iron–cobalt modified activated carbons from various waste materials (coal treatment products and biomass) as catalysts in methanol decomposition [30–32]. It was established that the role of activated carbon as catalyst support is difficult to predict since it not only depends on the texture and surface properties of the starting activated carbon, but also it could be affected by the additional surface functionality, which is developed during the modification procedure or by the influence of the reaction medium, as well as by the nature of the reactants and supported active phase. It is assumed that the surface functional groups provide anchoring sites for the catalyst precursor, decrease the carbon hydrophobicity [18,19] or act as active centres in bi-functional reactions due to their redox and acid–base properties [33]. Rodriguez-Reinoso [1] considers that the introduction of surface functional groups affects not only the dispersion of loaded metal but also metal–carbon interaction and the latter could be increased by the development of surface acidic groups [34]. Álvarez-Merino et al. [35] regards AC as

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an organic semiconductor with delocalized π -electrons which provides electron-donor properties. The basic graphitic structure of AC provides hydrophobic sites, which can interact with hydrophobic molecules. Moreover, the phenol groups with unpaired π -electrons in oxygen atom and deprotonated carboxyl groups also could act as electron donors [35]. Muniza et al. [36] describe two mechanisms for iron doping of AC which include non-selective adsorption as well as ion exchange and complexation with surface acidic groups, situated at the edges of the aromatic carbon layers. Zhong et al. [37] established that under low degree of loading, ferric species interacted mainly with surface carboxylic groups, which were responsible for the high catalytic activity in benzene hydroxylation to phenol by hydrogen peroxide. Li et al. [38] found that iron species interact with surface lactonic and carboxyl groups with the formation of surface iron carboxylate species, but do not interact with carbonyl and phenolic groups.

The aim of current investigation is to study the complex effect of surface and textural properties of the activated carbon support on the formation of iron phase and its transformation during the catalytic process. Methanol decomposition was used as a catalytic test, since recently methanol has gained a considerable interest as renewable “reservoir” for safety storage and transport of hydrogen, syngas or methane which could be released in case of need [39–41]. Activated carbons obtained from various agriculture residues (grape seeds or peach, apricot and olive stones) were used as catalysts support due to the world wide tendency to produce cost effective and environmental alternative to coal based carbons [14,21,42 and refs. therein]. Several techniques such as Boehm method, Nitrogen physisorption, XRD, FTIR, UV–Vis, Moessbauer Spectroscopy and TPR with hydrogen were used for catalysts characterization and iron modified mesoporous silica type KIT-6 was also studied as a reference sample.

2. Experimental

2.1. Materials

Activated carbon from peach stones (ACPS) was prepared by two-step procedure of carbonization and activation, using a stainless-steel vertical reactor and a tube furnace. The raw material was subjected to pyrolysis at 823 K (heating rate of 5 K/min) for 30 min. The obtained carbonizate was activated with water vapour at 1123 K for 1 h. The activated carbons from apricot stones (ACAS), grape seed (ACGS) and olive stones (ACOS) were prepared by one-step process, combining carbonization and activation procedure [43–45]. The raw materials were subjected to pyrolysis in the presence of water vapour for 1 h at 1073 K for ACAS, 973 K for ACGS and 1023 K for ACOS.

For comparison, mesoporous silica type KIT-6 was prepared using Pluronic P123 triblock-co-polymer ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) as structure-directing agent according to the procedure described in Ref. [46]. The template was removed by calcination at 823 K for 6 h. Thus prepared carbon and silica materials were modified with iron (6 wt%) by incipient wetness impregnation with methanol solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. The precursor was decomposed in a flow of N_2 at 773 K for 2 h. The obtained samples were denoted as Fe/S, where S was the type of support (ACPS, ACAS, ACGS, ACOS or KIT-6, respectively).

2.2. Methods of investigation

The elemental analysis of the obtained activated carbons was performed on a Carlo Erba 1106-type equipment for C, H and N. Sulfur content was determined by Eshka's method, while the oxygen was determined from the mass balance (Table 1). The texture

Table 1

Data from elemental analyses of various activated carbons.

Sample	W wt.% [*]	A wt.% ^{**}	C wt. %	H wt. %	N wt. %	S wt. %	O wt. %
ACPS	1.7	2.6	88.0	2.5	1.1	0.5	7.9
ACAS	1.6	2.0	89.5	2.4	0.9	0.8	6.4
ACGS	1.8	13.1	84.7	1.3	1.6	0.3	12.1
ACOS	2.7	2.4	90.8	2.0	0.9	0.6	5.7

^{*} W – moisture content (ash free basis).

^{**} A – ash content (dry basis).

characteristics were determined by low-temperature (77.4 K) nitrogen adsorption in a Quantachrome Instruments NOVA 1200e (USA) apparatus. The nitrogen adsorption–desorption isotherms were analyzed to evaluate the following parameters: the specific surface areas (S_{BET}) were determined on the basis of the BET equation, the total pore volume (V_{t}) was estimated in accordance with the Gurvich rule at a relative pressure close to 0.99. The volume of the micropores (V_{mi}) and specific surface area connected to micropores (S_{mi}), as well as the mesoporous specific surface area (S_{mes}) were evaluated according to V-t-method. The volume of the mesopores (V_{mes}) was determined as a difference between V_{t} and V_{mi} . Additionally, the pore size distribution were calculated using nonlocal density functional theory (NLDFT) method using equilibrium models with slit shape pores for carbons and cylindrical pores for KIT-6 silica. The micropore size distribution was made by the Dubinin–Astakhov (DA) method. The amount of various acidic oxygen-containing functional groups was determined by Boehm method according to the procedure described in Ref. [47]. The content of carboxylic groups was determined by neutralization with NaHCO_3 ; both carboxylic and lactonic groups – with Na_2CO_3 ; the sum of carboxylic, lactonic and phenolic groups–with NaOH ; while all carboxylic, lactonic, phenolic and carbonyl groups were determined by neutralization with sodium ethoxide. The amount of basic sites was determined by titration with 0.05 N HCl [48]. Powder X-ray diffraction patterns were collected within the range of 5.3 to 80° 2θ on a Bruker D8 Advance diffractometer with Cu K_α radiation and LynxEye detector. Phase identification was performed with the *DiffraPlus* EVA using ICDD-PDF2 Database. Mean crystallite size were determined with the Topas-4.2 program using the fundamental parameters peak shape description including appropriate corrections for the instrumental broadening and diffractometer geometry. The UV–Vis spectra were recorded on the powder samples using a Jasco V-650 apparatus. The IR spectra (KBr pellets) were recorded on a Bruker Vector 22 FTIR spectrometer at a resolution of 1 cm^{-1} , accumulating 64 scans. The Mossbauer spectra were obtained in air at room temperature (RT) and liquid nitrogen temperature (LNT) with a Wissel (Wissenschaftliche Elektronik GmbH, Germany) electromechanical spectrometer working in a constant acceleration mode. A $^{57}\text{Co}/\text{Rh}$ (activity $\approx 25\text{ mCi}$) source and $\alpha\text{-Fe}$ standard were used. The experimentally obtained spectra were fitted by the least square-method. The TPR/TG (temperature-programmed reduction/thermo-gravimetric) analyses were 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} .

2.3. Catalytic test

Methanol conversion was carried out in a fixed bed flow reactor (0.055 g of catalyst), argon being used as a carrier gas ($50\text{ cm}^3\text{ min}^{-1}$). The methanol partial pressure was 1.57 kPa. The catalysts were tested under conditions of a temperature-programmed regime within the range of 350–770 K with heating rate of 1 K min^{-1} . On-line gas chromatographic analyses were performed on HP apparatus equipped with flame ionization and

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