



Zinc ferrites hosted in activated carbon from waste precursors as catalysts in methanol decomposition



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ABSTRACT

Activated carbons from peach stones and waste polyolefin wax were prepared and tested as a host matrix of nanodispersed zinc ferrite. Nitrogen physisorption, Boehm method, XRD, TPR with hydrogen, FTIR, UV–Vis and Moessbauer spectroscopy were applied to investigate the activated carbon characteristics and the state of loaded on it metal oxide particles. The higher microporosity and lower surface functionality, typical of activated carbon from waste biomass, facilitated the formation of more finely dispersed, located into the micropores iron and zinc oxide nanoparticles. This promoted formation of Zn rich ferrite phase which ensures high catalytic activity in methanol decomposition.

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1. Introduction

The tuneable and attractive electronic, optical and magnetic properties of nanosized individual and dual metal oxides provoke their wide application [1]. The controlled growth of metal oxide nanoparticles is of primary importance for the preparation of high quality materials and among variety of techniques, their deposition on porous supports have been considered as a promising approach. Activated carbon has been reported as perspective host matrix due to its high surface area and pore volume, tunable texture and surface characteristics, chemical inertness and temperature stability in inert atmosphere [2]. Nowadays many efforts have been done to decrease the price of the activated carbons by elaboration of the preparation techniques and utilization of waste materials as carbon precursor [3–6]. In our previous study we demonstrated that the phase composition of the loaded on the activated carbon metal oxides could be tuned by variation of texture parameters, surface functionality and reduction ability of carbon support [7–10]. This makes difficult to predict the

oxidative state, dispersion and location of metal oxide species into the carbon matrix, especially in case of binary systems, where the intimate contact between various individual oxide particles becomes a decisive factor. Nano ferrites gain a considerable interest due to their low cost, high density memory capacity, high resistivity, and promising catalytic activity [11]. The substitution of Fe cation sites by other metal (M) atom in ferrites generally promotes formation of normal ($\delta = 0$), mixed ($0 < \delta < 1$) or inverse ($\delta = 1$) $A_{(1-\delta)}B_{\delta}[A_{\delta}B_{(2-\delta)}]O_4$ spinel [12]. The physicochemical properties of ferrites strongly depend on the site, nature, and amount of metal substituted at the A and B sites in the structure. Zinc ferrites are known as materials with normal spinel structure and paramagnetic features down to very low temperature [13], which provides their wide application in gas sensor, magnetic and electrical devices and catalysis [14–18]. The current study is aimed at the investigation of the effect of activated carbon support, obtained from various waste precursors (biomass and polyolefin wax) on the formation of binary iron and zinc oxide materials. The catalytic behaviour of thus obtained composites as catalysts in methanol decomposition with a potential application as clean and efficient alternative fuel [19] was also in the focus of investigation.

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2. Experimental

2.1. Materials

The activated carbon, denoted as ACP, was obtained from peach stones by two-step technology: (i) carbonization of peach stones in nitrogen atmosphere (99.996%) at 873 K with heating rate 10 K min^{-1} and treatment at the final temperature for 30 min and (ii) activation of the obtained product in flow of water vapour (1.2 L h^{-1}) up to 1123 K with heating rate 15 K min^{-1} and treatment at 1123 K for 1 h. The activated carbon, denoted as ACO, was synthesized by treatment of polyolefin wax with concentrated solution of sulphur acid at 393 K until solidification of the precursor followed by carbonization of the solid product at 823 K for 30 min and water steam activation at 1073 K for 1 h, as described above. The carbons were modified by three-fold incipient wetness impregnation with 4% solutions of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and/or $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (for the bi-component materials the mol ratio Fe/Zn was 2) in methanol. After each impregnation step the samples were dried at room temperature for 2 h and then, in vacuum at 323 K also for 2 h. The precursor decomposition was carried out in nitrogen flow (99.996%) with heating rate of 3 K min^{-1} up to 773 K, followed by 2 h treatment at 773 K. The total metal amount in all samples was 8 wt%. The modifications were denoted as Fe/AC; Zn/AC and FeZn/AC, where AC was the corresponding activated carbon.

2.2. Methods of characterization

The texture characteristics were determined by low-temperature 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 (SBET) 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 micropores volume (V_{mic}) and their specific surface area (S_{mic}) were evaluated according to V-t-method. The micropore size distribution was calculated by the Dubinin-Astakhov (DA) method. The amount of various acidic oxygen-containing functional groups was determined by Boehm method according to procedure described in Ref. [20]. Powder X-ray diffraction patterns were collected within the range from 5.3 to $80^\circ 2\theta$ with a constant step $0.02^\circ 2\theta$ on 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 software package using the fundamental parameters peak shape description including appropriate corrections for the instrumental broadening and diffractometer geometry [21]. 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 TPR/TG (temperature-programmed reduction/thermo-gravimetric) analyses were performed on 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} . The TEM investigation was performed on a JEOL JEM-2100 instrument at an accelerating voltage of 200 kV. The specimens were prepared by grinding and dispersing them in ethanol by ultrasonic treatment. The suspensions were dripped on standard holey carbon/copper

grids. SEM analyses were performed on a JSM 6390 electron microscope (Japan) in conjunction with energy disperse X-ray spectroscopy (EDS, Oxford INCA Energy 350) equipped with ultrahigh resolution scanning system (ASID-3D) in regimes of secondary electron image (SEI) and back scattered electrons (BEC) image. The sample is mounted on a double coated conjunctive carbon tape that holds the sample firmly to the stage surface and can be used as a ground strap from the samples surface to sample holder. The accelerating voltage was 20 kV, $I \approx 65 \text{ mA}$. The pressure was of the order of 10^{-4} Pa .

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 thermo-conductivity detectors, on a PLOT Q column, using an absolute calibration method and a carbon based material balance.

3. Results and discussion

3.1. Physicochemical characterization

3.1.1. Carbon supports

In Fig. 1 are presented nitrogen physisorption isotherms and pore size distribution for parent activated carbons and the corresponding texture parameters are listed in Table 1. The isotherms exhibit a steep slope at low relative pressure and well defined hysteresis loop in the range of $P/P_0 = 0.4\text{--}1.0$. According to IUPAC classification the isotherms are of mixed I/IV type which is typical of porous materials with micro-mesoporous structure. The shape of hysteresis loop reveals that the mesopores are predominantly of ink-bottle type with average pore diameter 2–3 nm. The ACP possesses higher BET surface area, but lower total pore volume, determined by the presence of larger portion of micropores as compared to ACO. In Fig. 2 are presented XRD patterns of activated carbon supports. The broad diffraction reflections centred at about 24° and $43^\circ 2\theta$ are due to (002) and (100) planes of crystalline carbonaceous structures [22,23]. The additional narrow reflections in the pattern of ACO are due to the presence of well crystallized graphite phase (JCPDS 25-0284). FTIR spectroscopy was applied to characterize the surface properties of activated carbons (Fig. 3a, inset). The broad band at c. a. 1690 cm^{-1} could be due to C=O stretching vibrations in ketones, aldehydes, lactones and carboxyl groups [24,25 and refs therein]. The bands at c.a. $1400\text{--}1370 \text{ cm}^{-1}$ are ascribed to highly conjugated C=O and C–O stretching in carboxylic, carboxylate moieties or basic groups. The band at c.a. 1530 cm^{-1} corresponds to C=C vibrations in the aromatic ring. The broad band at c.a. 1145 cm^{-1} could be assigned to C–C and C–O vibrations in ethers, phenols, esters, alcohols and carboxylic groups. The broad absorption band located at around 3400 cm^{-1} is typically attributed to O–H stretching vibrations in carboxyl and phenol groups or water adsorbed. The presence of methylene and methyl groups in the said chains is confirmed with the broad absorption band in $3000\text{--}2400 \text{ cm}^{-1}$ range. The strong absorption peak at ca. 670 cm^{-1} belongs to $\gamma(\text{OH})$ vibrations. The amount of various accessible oxygen containing surface functional groups was measured by Boehm method (Table 2). The overall amount of carboxyl, lactone and hydroxyl groups is higher for ACO, while carbonyl groups are mainly detected for ACP.

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