

Short Communication

Cobalt ferrite nanoparticles hosted in activated carbon from renewable sources as catalyst for methanol decomposition



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ABSTRACT

High quality micro-mesoporous activated carbon was prepared from waste bio-mass (peach shells) and used as a host matrix of cobalt ferrite nanoparticles. The obtained materials were characterized by N₂ physisorption, XRD, FTIR and Moessbauer spectroscopy and tested as catalysts for hydrogen production from methanol. Depending on the Co/Fe ratio formation of pure CoFe₂O₄ or a mixture of CoO and ferrite phases were observed for carbon supported bi-component materials, while under the same condition the silica support provides the formation of non-stoichiometric ferrite phase. The catalytic active phase which is formed by the influence of the reaction medium represents a complex mixture of non-changed ferrite, magnetite, Co-Fe alloy and/or Fe₃C in different proportions.

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1. Introduction

Nowadays, methanol is considered as a promising carrier of hydrogen because it could be produced by well developed technologies, including from bio-mass, and could easily release hydrogen whenever needed by different procedures (e.g. steam reforming, partial oxidation and decomposition). It was demonstrated that spinel ferrites represent a good photocatalytic activity under visible light [1] and they are effective catalysts in photocatalytic splitting of H₂O/methanol [2], reforming of methane [3], steam reforming of methanol [4] and ethanol [5], hydrogen production from dimethyl ether [6] and methanol decomposition [7–12]. Binary oxide spinels are described by the general formulae (Me²⁺)_A[Me₂³⁺]_BO₄. In the case of ferrites, Fe³⁺ ions could be shifted either to octahedral (B) or to tetrahedral (A) position by variation in stoichiometric ratio with other cations. It was established that the distribution of ions in the spinel structure strongly influences their physical and catalytic properties [13,14]. In our previous study we observed that the increase of cobalt content in bulk ferrite materials improved the catalytic activity in methanol decomposition, but this effect was influenced by ferrite deposition on activated carbon (AC) [7]. Besides, we demonstrated high catalytic activity in methanol decomposition for Fe or Co modified AC, obtained from waste agricultures or coal tar pitch [15]. In this paper we focused our attention to the preparation of cobalt

ferrites, supported on AC, which was obtained from bio-mass, and to their potential use as catalysts in methanol decomposition. In order to highlight the effect of carbon support, similar modifications of mesoporous SBA-15 silica were studied.

2. Experimental

2.1. Materials

The activated carbon was produced from peach stones by a one-step carbonization–activation procedure in the presence of water vapor at 1023 K for 1 h. The reference mesoporous SBA-15 silica was prepared according to the procedure described in [16]. The obtained AC and SBA-15 were modified by incipient wetness impregnation with cobalt or/and iron nitrate precursors, followed by treatment in N₂ at 773 K. Metal loading for all materials was 8 wt.%. The samples were denoted as xFeyCo/S, where S was AC or SBA-15 support and the mol x/y ratio was 1:1 or 1:2.

2.2. Methods of characterization

The porous structure of selected samples was studied by nitrogen physisorption at 77 K on a Quantachrome NovaWin2 porosimeter. The FTIR spectra (KBr pellets) were recorded on a Bruker Vector 22 FTIR spectrometer at a resolution of 1–2 cm⁻¹, accumulating 64–128 scans. The amount of acidic oxygen-containing groups was determined by titration with an aqueous solution of NaHCO₃, Na₂CO₃, NaOH, C₂H₅ONa

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Table 1
Nitrogen physisorption data for the parent activated carbon and silica supports.

Sample	S_{BET} , m ² /g	V_{tot} , cm ³ /g	V_{micro} , cm ³ /g	V_{meso} , cm ³ /g	$V_{\text{micro}}/V_{\text{meso}}$
AC	820	0.41	0.27	0.08	3.37
SBA-15	807	0.99	0.12	0.86	0.14

and 0.05 N HCl for basic groups according to the procedures described in [17]. The powder XRD patterns were recorded on a TUR M62 diffractometer with Co K α radiation. The Moessbauer spectra were obtained in air at room temperature and temperature of liquid nitrogen with a Wissel (Wissenschaftliche Elektronik GmbH, Germany) electromechanical spectrometer working in a constant acceleration mode. A ⁵⁷Co/Rh (activity \approx 50 mCi) source and an α -Fe standard were used. The experimentally obtained spectra were fitted by least square-method.

2.3. Catalytic investigation

The conversion of methanol (3.5 mol% methanol in argon) was carried out in a flow-type reactor. The catalysts (0.055 g) were tested under conditions of a temperature-programmed regime (2 K/min) within the range of 403–773 K. Additional experiments under isothermal conditions at selected temperatures were also done. On-line GC analyses were performed on an HP apparatus equipped with flame ionization and thermo-conductivity detectors, on a PLOT Q column (30 m), using an absolute calibration method and a carbon based material balance.

3. Results and discussion

3.1. Physicochemical characterization of AC and SBA-15 supports

The data from nitrogen physisorption analyses (Table 1) reveal that AC obtained from peach shells using the one-step carbonization–activation procedure possesses high specific surface area and well developed micro-mesoporous structure. The observed broad reflections in the XRD pattern of AC around 23° 2 θ (002 plane) and 43° 2 θ (100 plane) are typical of crystalline carbonaceous structures (Fig. 1a). In the FTIR spectrum (Fig. 2) the vibration modes of the aromatic structure of carbon can be clearly seen, the most prominent being the band related to $\nu_{\text{as}}(\text{C}=\text{C})$ situated between 1600 and 1500 cm⁻¹ [18,19]. The weak absorption band at about 800 cm⁻¹ is due to $\gamma(\text{C}-\text{H})$ vibrations of substituted in aromatic structure groups. The band at around 1700 cm⁻¹ is due to C=O stretching vibrations in carboxylic, ester, lactonic or anhydride groups [18]. The band at 1040–1070 cm⁻¹ is due to $\nu_{\text{as}}(\text{C}-\text{O}-\text{C})$ bonds. The band in the 900–950 cm⁻¹ region could be assigned to lactonic O=C–O groups. The strong absorption peak at 665 cm⁻¹

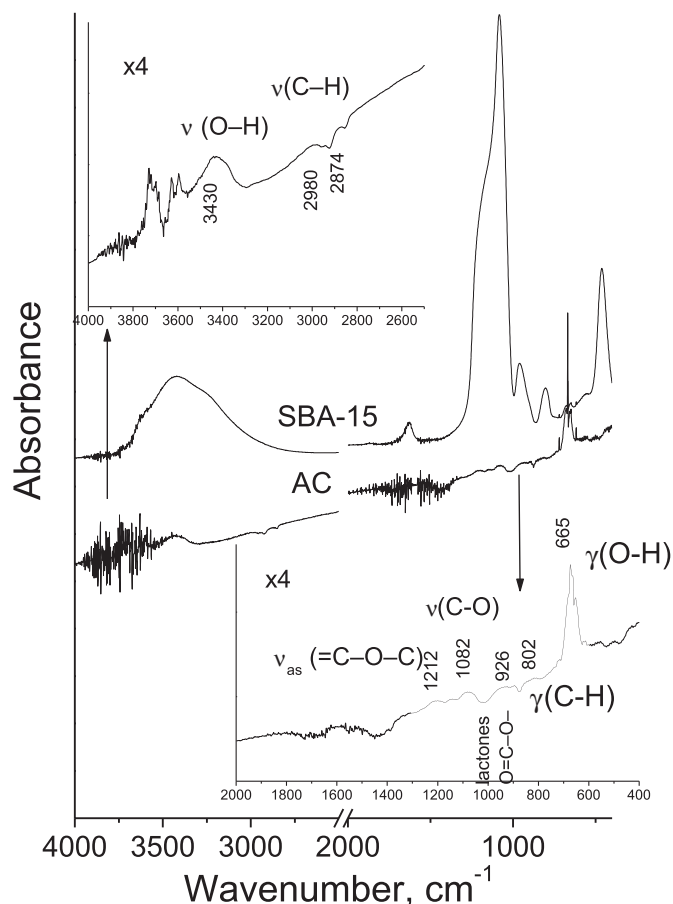


Fig. 2. FTIR spectra of activated carbon and SBA-15 silica supports.

belongs to $\gamma(\text{O}-\text{H})$ stretching vibrations [18]. The absorption band at 3470–3300 cm⁻¹ in the FTIR spectra of AC indicates the presence of surface hydroxyl groups $\nu_{\text{as}}(\text{OH})$. The quantitative chemical analyses of AC confirm the presence of surface acidic functional groups, mainly carboxyl (1.07 meq/g) and hydroxyl (0.29 meq/g) and a significant amount of different basic groups (1.04 meq/g). The reference SBA-15 support is characterized with an almost similar specific surface area, mainly mesoporous structure and about 2 times larger pore volume as compared to AC (Table 1). The XRD pattern of SBA-15 represents all reflections typical of a well ordered hexagonal type mesoporous structure (Fig. 1a). The

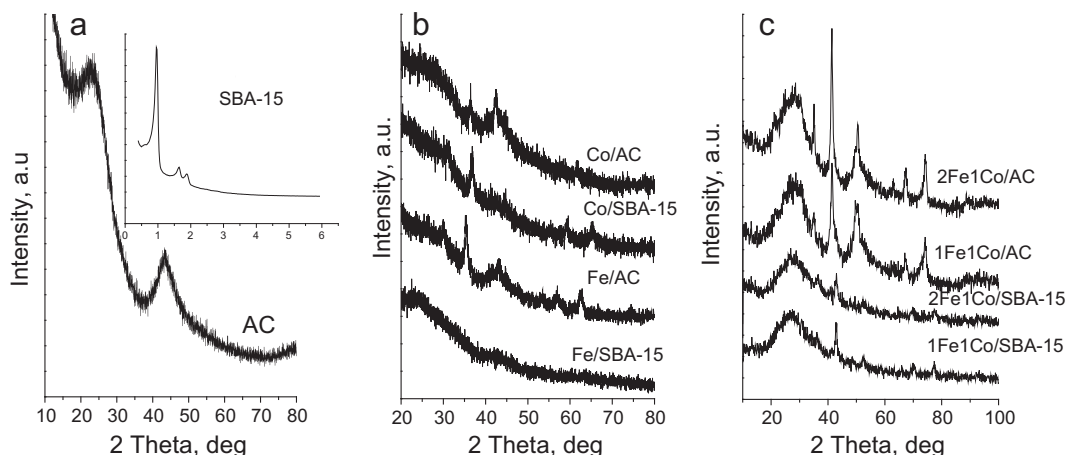


Fig. 1. XRD patterns of parent AC and SBA-15 supports (a) and mono- (b) and bi-component (c) Fe and Co modifications of AC and SBA-15.

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