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Synthesis and characterization of KOH/boron modified activated carbons from coal and their hydrogen sorption characteristics

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ABSTRACT

Activated carbons from bituminous coal taken from the area of Zonguldak Kilimli region in Turkey were synthesized by chemical activation using a mixed combination of KOH and as a boron source borax decahydrate. The modification process consists of chemical activation of the demineralized coal with KOH (KOH/coal:4/1) and various concentrations of borax decahydrate solutions (0.025–0.1 M). Textural properties such as surface area and pore structure were studied by volumetric methods using N₂ adsorption data at 77.4 K (P/P₀ = 0–1). The samples obtained have high microporosity, in the form of irregular structures. The EDAX spectra indicate that Boron heteroatoms are attached to surface of AC41, and as BDH concentration increases from 0.025 M to 0.1 M, higher atomic percent of boron is accumulated at the surfaces. AC41 exhibits amorphous structures, whereas BDH modified AC41 consists of predominantly amorphous structure and disordered graphitic carbon. Among the synthesized boron modified samples, the highest surface area, total pore volume and average pore diameters were found for the 0.025 M_{BDH}-AC41 sample. As the BDH concentration increases, the volume of N₂ adsorbed decreases. Surface area of CC and AC41 samples were 52.62 and 2228 m²/g, respectively, whereas surface area of the boron modified samples were found in the range of 2190–2704 m²/g. Hydrogen sorption capacities of the KOH/boron modified samples were found in the range between 2.08 and 3.74% wt. Hydrogen sorption capacity of AC41 obtained was 4.11% wt. Increasing boron concentration resulted in the decrease of hydrogen sorption capacities. Boron modified activated carbons were prepared successfully from coal samples by chemical activation using a mixed combination of KOH and BDH.

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Introduction

Hydrogen is regarded as an alternative energy source for the future. Although hydrogen is a green energy source which can be used instead of fossil fuels, it has many problems as energy efficiency, storing, transferring and cost [1–3].

Hydrogen storage techniques can be classified into three main methods: Mechanical storage, the solid form of chemical hydrides and adsorption processes on porous materials. Mechanical storage is still the most commonly used method, which can be carried out with high pressure tanks, cryogenic storage and cryo-compressed storage, even though it has high

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cost. The solid form of chemical hydride based storage is safer than mechanical storage. Desorption of hydrogen from the chemical hydride is provided at high temperatures, because of requiring large endothermic energy for the desorption. Physical adsorption on porous materials presents the advantage over compressed gas system of a lower pressure and over cryogenic liquid system of a faster sorption kinetics at room temperature [4]. The most studied adsorption materials are activated carbons [5–7], modified activated carbons [8,9], metal–organic frameworks [10,11], zeolites [12,13] and carbon nanotubes [14,15]. The investigations have shown that hydrogen adsorption on carbonaceous materials has provided lots of advantages such as low mass density, rapid adsorption kinetics, and high-capacity storage [16–19].

Activated carbon is a unique adsorbent for hydrogen adsorption on account of the surface area, surface functionality, pore size distribution (especially microporosity) and chemical compositions, compared to other adsorbents [20]. Activated carbon can be produced from two main sources: These are coal and agricultural products or lignocellulosic materials [21]. Most of the commercial activated carbons are produced from coal, lignite, peat, wood and coconut shell [22–25]. Coal is the most commonly used raw material for preparation of activated carbon because of its low cost, availability and especially physical and chemical properties. Compared to the other raw materials, coal generally provides more highly developed surface area and chemical resistance [26,27].

Activated carbon can be produced with two different methods: Physical activation and chemical activation. Physical activation is carried out in two steps, carbonization and steam or CO₂ activation. Chemical activation is performed with impregnation process to the raw material and simultaneous carbonization-activation process to the impregnated material under inert atmosphere [28]. Impregnation can be provided with various chemicals such as KOH, NaOH, ZnCl₂ and H₃PO₄ at temperature ranging between 400 and 900 °C. Chemical activation is more advantageous than physical activation because of its low energy cost, high efficiency and better porosity [29–31].

Modification of the activated carbon changes physico-chemical properties of the product. The surface structures of activated carbons significantly affect their properties such as adsorption, electrochemical, catalytic, acid–base, redox, hydrophilous–hydrophobic, etc. Many heteroatoms can be transferred to the structure of activated carbon by using various modification methods. Many heteroatoms such as nitrogen, boron, palladium, platinum, copper can be transferred to the structure of activated carbon by using various modification methods [32]. Preparation of the boron modified activated carbon can be provided by two prominent methods: Impregnation and chemical doping [33–37]. Several investigations have indicated that hydrogen adsorption capacity of boron modified carbon is higher than carbonaceous materials with similar surface area [38–42].

Many investigations have been carried out on material development and characterization for hydrogen adsorption studies. Fierro et al. [43] studied hydrogen storage in activated anthracites. The samples were prepared by chemical activation method using sodium and potassium hydroxide,

according to various impregnation ratios at different activation temperatures (700–800 °C). The maximum hydrogen uptake was measured as 5.3% wt at 77 K and 4 MPa for the sample prepared with KOH. Wróbel-Iwaniec et al. [44] investigated the impact of experimental conditions of potassium hydroxide activation on hydrogen storage capacities of microporous chitosan-based activated carbons. They studied various carbonization/activation temperatures (700–1000 °C) and impregnation ratios (KOH/chitosan char: 1–4). The maximum hydrogen adsorption capacity of 2.95% wt (77 K, 0.1 MPa) was obtained for the sample carbonized at 800 °C and activated at 700 °C (KOH/chitosan char:3). Xu et al. [45] studied the hydrogen storage capacity of various carbon materials which were activated carbons, single-walled carbon nanohorns, single-walled carbon nanotubes and graphitic carbon nanofibers at 77 and 303 K for pressure range of 0.1–10 MPa. The best hydrogen adsorption capacity was 5.7% wt at 77 K and 3 MPa for the sample of Maxsorb activated carbon. Hydrogen adsorption capacity values of 2.85% wt (77 K and 1 bar) and 6 wt% (77 K and 4 MPa) for activated carbons have been reported by Zhang et al. [46] and Zhao et al. [47], respectively.

Marco-Lozar et al. [48] investigated hydrogen storage capacities of Maxsorb3000, MOF-5 and anthracite-based activated carbons. The amount of hydrogen adsorbed reported was in the following order, MOF-5 < Maxsorb300 < AC1, and the highest value was found as 5.1% wt at 77 K and 4 MPa for the AC1 sample. Guo and Gao [49] studied porous carbon materials derived from citric acid and boric acid for determining hydrogen adsorption capacities. After pretreatment procedures with nickel chloride and ammonia, the pyrolysis/carbonization (at 900 °C for 4 h) and the activation processes with potassium hydroxide (at 750 °C for 1 h) were carried out. The maximum surface area, micropore volume and hydrogen uptake reported were 2930 m²/g, 1.00 cm³/g, and 6.24% wt (77 K and 2 MPa), respectively. Ozturk et al. [50] investigated the hydrogen storage ability and surface characteristics of 2D micro porous MOF, and reported a hydrogen storage capacity of 1.382% wt. Yang et al. [51] investigated the impact of surface modifications with various chemicals on the hydrogen adsorption capacity of MOF-5, and reported a maximum hydrogen uptake as 2% wt. Xiang et al. [52] studied the effect of lithium doping on various MOFs for developing hydrogen storage, and reported that lithium doping increased the hydrogen storage capacities, because of the strong affinity of lithium towards hydrogen. The maximum hydrogen storage capacity was observed as 3.50% wt at 77 K and 1 bar. Martyla et al. [53] investigated the effects of the preparing methods and molar ratio of boron oxide/alumina on hydrogen storage properties. Although the preparing methods which are sol–gel and sol–gel template were not observed to have significant effects on adsorption mechanism, the lower molar ratio of boron oxide/alumina was determined to increase the hydrogen adsorption capacities. Jeong and Chung [54] studied the characterization and hydrogen storage properties of super-activated carbons containing substitutional boron obtained by polycondensation reaction of phenyl diacetylene and boron trichloride. The highest hydrogen uptake observed was 3.8% wt at 77 K and 60 bar for the sample of BC₆. It was also reported that, although the boron content reduced the

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