Low-cost metal oxide activated carbon prepared and modified by microwave heating method for hydrogen storage

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Abstract−Novel microporous activated carbon (MAC) with high surface area and pore volume has been synthesized by microwave heating. Iron oxide nanoparticles were loaded into MAC by using $Fe(NO_3)_3 \cdot 9H_2O$ followed by microwave irradiation for up to five minutes. The surface modified microporous activated carbon was characterized by BET, XRD, SEM and thermogravimetric examinations. Adsorption data of H_2 on the unmodified and modified MACs were collected with PCT method for a pressure range up to 120 bar at 303 K. Greater hydrogen adsorption was observed on the carbon adsorbents doped with 1.45 wt% of iron oxide nanoparticle loaded due to the joint properties of hydrogen adsorption on the carbon surface and the spill-over of hydrogen molecules into carbon structures.

Keywords: Microporous Activated Carbon, Iron Oxide Nanoparticles, Microwave Synthesis, Surface Modification, Hydrogen Storage

INTRODUCTION

Hydrogen is a model fuel because of its zero or little contaminant production during burning. In the 21st century, it is estimated to increasingly replace the current fossil fuels that are rapidly depleted and cause heavy environmental problems. However, one of the most important problems of hydrogen use as a fuel is storage. There are different procedures to store hydrogen. All those systems have to meet the provisional Department of Energy of the United States (DOE) standard. The DOE has established goals for onboard hydrogen storage schemes, with the minimum "gravimetric" and "volumetric" capacity and the reversibility of the charging/discharging procedures. For the 2015 year, the storing method should have a gravimetric capacity of 1.8 kWh/kg (5.5 wt% of H_2) and a volumetric capacity of 1.3 kWh/L (0.040 kg H_2/l) [1,2].

There are numerous physico-chemical approaches for separation and storage of hydrogen for its effectual usage in some later times [3-5]. Among all known hydrogen storage methods, physisorption on solid substrates seems to be very adaptive because of clear explanations, for instance, the adsorbed gas can be released reversibly [6]. In recent years, novel carbon materials, such as carbon nanotubes (CNTs), mesoporous carbons, and novel activated carbons, have generated considerable interest [7-11]. However, the standards for their hydrogen storage capacity scatter over several orders of magnitude [12]. These carbon materials usually have large specific surface areas and high pore volumes, which are useful for effective physisorption of H_2. Also, the ordered networks may provide fast transportation in the materials, a noticeable volume of micropores can efficiently adsorb hydrogen, and the micro- and the mesoporosity can be adjusted by changing the synthetic method [13]. In fact, hydrogen adsorption on carbon nanomaterials is closely attrib-

uted to surface heterogeneity, depending in its turn on their preparation and formulation. Surface heterogeneity can increase not only as of surface irregularities, including bound impurities and functional groups, but also from nanoporous structural heterogeneity.

In this work, we prepared novel microporous activated carbon with high surface area by grapevine rhytidome as a plentiful and low-cost precursor via H_3PO_4 chemical activation under microwave; after that, additional microwave modification was done using $Fe(NO_3)_3 \cdot 9H_2O$. Additionally, we examined the effects of specific surface area and surface functional group on hydrogen uptake, which may aid to comprehend the H_2 adsorption mechanism and direct the design of carbon-based hydrogen adsorbents. We measured H_2 sorption densities of the materials at 303 K over the hydrogen pressure variety to 120 bar.

EXPERIMENTAL

1. Materials

The reactant used in this work was the grapevine rhytidome which was collected from Sari city's agricultural province and washed numerous times with distilled water and derived in an oven at 70 ℃ overnight. The dried materials were crushed to small pieces. Phosphoric acid (85 wt%, Merck Co.) as an activating agent and $Fe(NO_3)_3 \cdot 9H_2O$ (99 wt%, Merck Co.) as functionalization agent were used.

2. Adsorbent Preparation

2-1. Microporous Activated Carbon Samples

The novel activated carbon was prepared according to the procedure reported by Hejazifar et al. [14]. In optimum condition; the grapevine rhytidome was added to phosphoric acid with 85 wt% concentration and acid/precursor weight ratio (5 : 1) for 24 at room temperature. The impregnated samples were heated in a microwave oven (LG, WD700, 2450 MHZ) with microwave power 400 W, microwave radiation time 2 min. Then, the samples were placed in an oven at 110 ℃ for 24 hr. The obtained samples were washed several times with hot and then cold distilled water to the pH of 7, and

dried in an oven at 50 °C overnight. Lastly, activated carbons were crushed and sieved to particle mesh size of 20 and stored in a desiccator.

2-2. Iron Oxide Doped Samples

The experimental process was carried out using $Fe(NO_3)_3 \cdot 9H_2O$ with prepared activated carbon, and the composition ratio 5.4 gr activated carbon, 2.5 gr of $Fe(NO_3)_3 \cdot 9H_2O$ and 5 gr water was used. The combinations were then heated under microwave irradiation (LG, WD700, 2450 MHZ) by microwave power 400 W for 1 to 5 minutes (1-Fe-MAC to 5-Fe-MAC). Nanostructured carbon impregnated with the acetone solution was then filtered and dried at 60 °C for 4 hr. The activation temperature was 1,033 K and optimal N_2 gas flow rates (250 cc/min) for 2 hours were used [15].

3. Textural and Structural Studies

The structure of the surface improved materials was determined by powder XRD (Philips 1830 diffractometer) by graphite monochromated CuKa radiation. Adsorption isotherms of the samples were gained by an N_2 gas microporosimeter (Micromeritics model ASAP 2010 sorptometer) at 77 K. Pore size distribution and specific surface area were calculated by Dollimore-Heal [16] and BET [17] methods. Pore volume was estimated from the amount of adsorbed N_2 gas at 0.963 in relative pressure, which derives from 25 nm radii pores. Micropore volume was calculated by t-plot. SEM images were obtained with a JEOL 6300F SEM. Thermal analysis was by means of NETZSCH STA449C analyzer. The tool settings were as follows: heating rate 10 °C/min and an air atmosphere with 100 mL/min flow rate. For each measurement about 25 mg of a ground adsorbent sample was used. From the weight loss curve the differential weight loss was calculated where peaks represent the weight loss.

4. Hydrogen Adsorption

Hydrogen adsorption capacities at 303 K over the hydrogen pressure variety up to 120 bar were measured by the PCT technique (AnySorb 7) with a mechanically controlled device for high-pressure adsorption. The hydrogen adsorption capacities were measured after all samples were pretreated at 423 K for 90 min in helium flow and sequentially reduced in situ in a hydrogen/nitrogen mixture flow.

The dead volume was calibrated with Helium gas at room temperature. High-purity hydrogen (99.999%) was used in this study. The quantities of hydrogen adsorbed were calculated using the Redlich/Kwong equation. Steps were taken to ensure the precision of the experimental results. The major portion of the device was detained in an air thermostat to keep its temperature at 303 K. The device was formerly verified for leakage and calibrated with the empty sample cell and well-known standard samples. The time adopted for equilibration was 30 min at each step. About 300 mg of the nanostructured carbon samples was used for hydrogen adsorption.

RESULTS AND DISCUSSION

1. Textural Characterization

Nitrogen physisorption is the technique of choice to gain information about nanoporous materials. This technique gives information on the specific surface area and the pore diameter. Calculating pore diameters of nanoporous materials by the BJH theory is com-
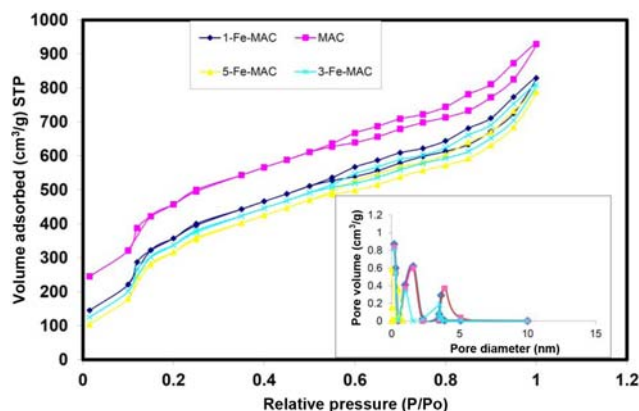

Fig. 1. Adsorption-desorption isotherms of nitrogen at 77 K on MAC, 1-Fe-MAC, 3-Fe-MAC and 5-Fe-MAC. The insert shows the BJH pore size distribution calculated from the desorption branch of the isotherm.

Table 1. Textural parameters of the MAC, 1-Fe-MAC, 3-Fe-MAC and 5-Fe-MAC employed in this study

Adsorbent	Average pore diameter (nm)	A_{BET} ($m^2\,g^{-1}$)	Total pore volume ($cm^3\,g^{-1}$)	Micropore volume ($cm^3\,g^{-1}$)
MAC	2.3	1640	0.93	0.73
1-Fe-MAC	2.2	1547	0.88	0.72
3-Fe-MAC	2.22	1531	0.86	0.69
5-Fe-MAC	2.21	1511	0.81	0.64

Table 2. Hydrogen adsorption in nanomaterials

Material	Specific surface area [$m^2\,g^{-1}$]	Pore volume [$cm^3\,g^{-1}$]	H_2 uptake [wt%]	Conditions	Reference
Iron oxide modified activated carbon	1531	0.86	1.45 wt%	120 bar, 303 K	This work
Nickel doped mesoporous carbon	1434	3.62	0.8 wt%	300 bar, 297 K	[23]
MOF-5	3840	--	0.9	60 bar, 200 K	[24]
Carbon nanotube	--	1.0	0.7	110 bar, 300 K	[25]
ZBDh	1674	0.59	0.51	17.4 bar, 77 K	[26]
CND	1375	0.47	0.33	17.4 bar, 77 K	[26]

munal. Previous studies demonstrate that the application of the BJH theory gives suitable qualitative consequences which permit a straight comparison of relative changes between different nanoporous materials.

Nitrogen adsorption isotherms of the MAC and Fe-MACs are shown in Fig. 1. A high adsorption at a low relative pressure reveals that MACs is mainly microporous. The rise in the adsorption by a high relative pressure is because of multilayer adsorption on the mesoporous, macroporous and on the external surface [16,17]. The existence of hysteresis loop possibly will be due to the existence of mesoporous. Table 1 shows the textural properties of the nanostructured samples as showed by the N_2 adsorption isotherms. The iron oxide doped MAC samples manifested a decreasing specific surface area in addition to decreasing total and microporous volumes with increasing electroplating time. The pore size distributions (see the insets of Figs. 1) are somewhat moved to smaller values in contradiction of the host materials. This effect is attributable to the mesoporous filling with the iron oxide. Alongside the reduction of the pore sizes, a small expansion of the distributions is detected for the host-guest compounds.

The XRD data of carbonaceous adsorbents were gotten on Philips 1830 diffractometer using Cu Kα radiation of wavelength 0.154 nm. In Fig. 2 the XRD patterns of MAC and 3-Fe-MAC are shown. Well-defined peaks at 30.1°, 35.4°, 57°, and 62.5° 2θ, distinctive of Fe_3O_4, appear after iron oxide modification. The strong and sharp peaks (in the case of 3-Fe-MAC) show that large iron crystals formed outside of the carbon surface. The same result has been mentioned by Prakash group [18].

To comprehend the surface morphology, shape and size of iron oxide microporous activated carbon, SEM analysis was performed on 3-Fe-MAC sample (Fig. 3). SEM image displays a rough surface. This result is in accompaniment with the research which has done by Khiew et al. [19]. Moreover, the micrograph also exposed obviously that the subsequent particles were almost flawlessly loaded on carbon surface.

Fig. 4 shows thermogravimetric analysis (TGA/DTA) curve of the 3-Fe-MAC using a heating rate of 5 °C min⁻¹. The 3-Fe-MAC

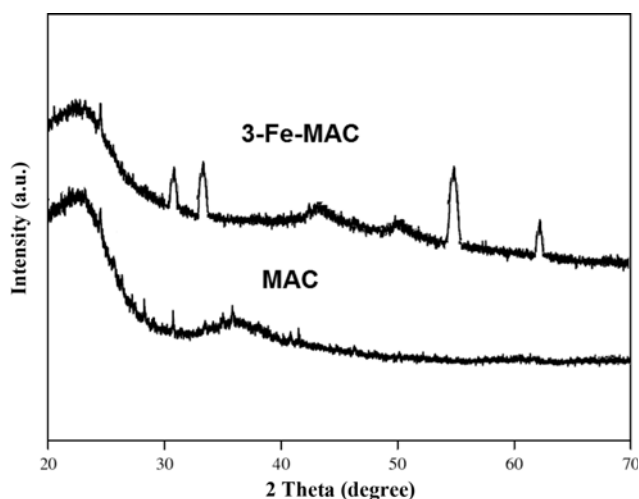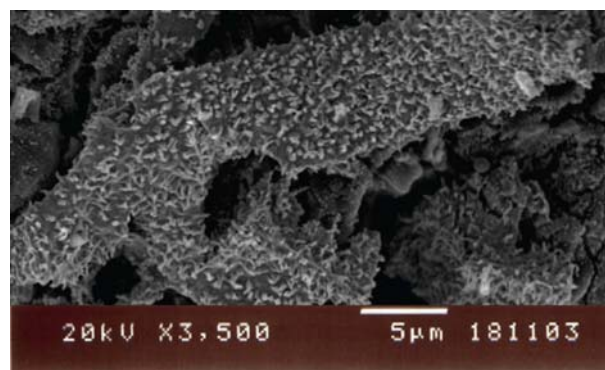Fig. 3. SEM images of the 3-Fe-MAC.

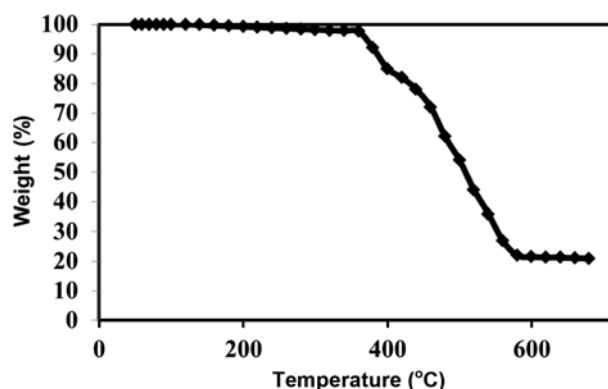Fig. 4. The thermogravimetric analysis (TGA) plots of the 3-Fe-MAC.

presented a 78% endothermic weight loss from 360 to 520 °C linked to the oxidation of the carbon. A weight of 22% is found after oxidation of the activated carbon, which is related to the Fe oxide in the prepared nanocomposite.

2. Hydrogen Adsorption

The hydrogen storage capacity of MAC and Fe-MACs was valued with the PCT technique. Fig. 5 displays hydrogen adsorption isotherms of unmodified and iron oxide modified microporous activated carbons (MAC and 3-Fe-MAC) calculated over hydrogen pressure up to 120 bar at 303 K. We found similar shapes of hydro-
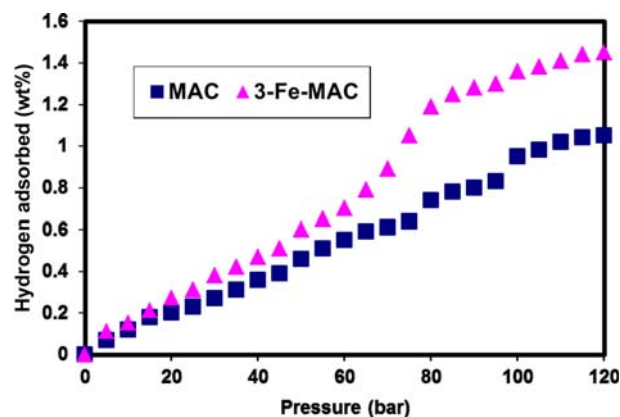

Fig. 2. Wide angle XRD patterns of the microporous activated carbon adsorbents (MAC and 3-Fe-MAC).

Fig. 5. Hydrogen adsorption isotherm of the MAC and iron oxide activated carbon (3-Fe-MAC) at 303 K.
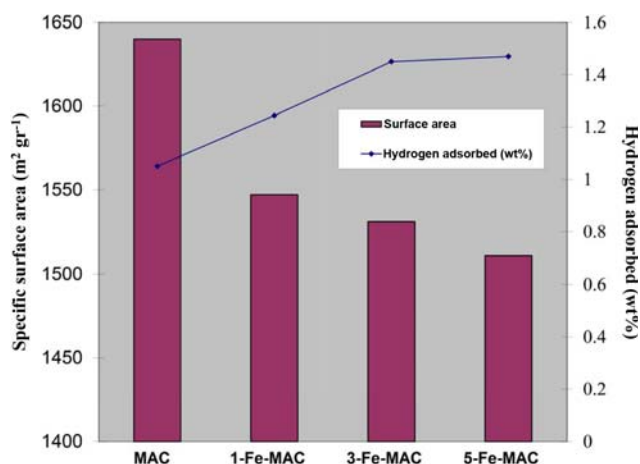
Fig. 6. The effect of specific surface area and modification time on the hydrogen adsorption capacity of unmodified and modified carbonaceous adsorbents at 120 bar, 303 K.

gen adsorption isotherms despite surface modification for MAC adsorbent calculated. Hydrogen adsorption capacity is a linear function of pressure, which can be clarified by Henry's law. These results designated that iron oxide was well dispersed on the surface of novel carbonaceous adsorbent.

By microwave modification, the hydrogen storage capacity was enlarged by refining the pore structure and inducing functional groups in the 3-Fe-MAC sample. The quantity of hydrogen adsorbed amplified with increasing pressure. The quantities of hydrogen adsorbed on iron oxide loaded microporous activated carbon adsorbent (3-Fe-MAC) were much larger than pristine microporous activated carbon adsorbent (MAC). In the records showing in Fig. 6, the effect of activation of iron oxide is more prominent, and therefore led to more hydrogen adsorption. It could be confirmed that loading of iron oxide nanoparticles on carbon surface plays an important role in determining the porous structure and amounts of hydrogen adsorbed.

Fig. 6 also shows the hydrogen adsorption capacity as a function of the iron oxide loading time. The hydrogen adsorption capacity of the 1-Fe-MAC, 3-Fe-MAC samples was found to be greatly better than that of the unmodified sample. But in the case of 5-Fe-MAC it can see that hydrogen adsorption capacity hasn't changed properly. Yang et al. [18] reported that hydrogen-uptake capacity can be remarkably enhanced in the presence of transition metals, as a result of the spill over of hydrogen molecules into carbon structures. The existence of iron oxide nanoparticles can also encourage the hydrogen adsorption of Fe-MACs through hydrogen molecule spill over and much better transition interaction between metal oxide and adsorbed hydrogen molecule [20-22]. In Table 2 the hydrogen adsorption capacity of different nanostructured carbon has been given. From the table it can be seen that the iron oxide modified activated carbon adsorbent has good hydrogen adsorption capacity [23-26].

CONCLUSIONS

Carbonaceous sorbents have been synthesized from grapevine rhytidome and modified by iron oxide nanoparticles by microwave heating. The textural properties of the modified and unmodified

microporous activated carbon adsorbents were studied by XRD and nitrogen adsorption analyses. The effect of iron oxide loading on the hydrogen adsorption abilities of MACs was investigated. Microwave modification, as a function of treatment time, led to an increase of Fe_3O_4 content and a reduction of specific surface area and micropore volume. The hydrogen storage ability was enhanced in the presence of iron oxide nanoparticles. Enhanced hydrogen adsorption was observed on the carbon adsorbents doped with 1.45 wt% of iron oxide modified microporous activated carbon at hydrogen pressures about 120 bar, 303 K.

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