Hydrogen sorption characteristics of Zonguldak region coal activated by physical and chemical methods

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Abstract−Hydrogen sorption characteristics of activated carbons (ACs) produced by physical and chemical activations from two coal mines (Kilimli and Armutcuk) in the Zonguldak region, Turkey were investigated by a volumetric technique at 77 K. H_2 adsorption isotherms were obtained on the samples exposed to pyrolytic thermal treatments in a temperature range of 600-900 °C under N_2 flow and chemical activation using different chemical agents such as KOH, NH_4Cl, $ZnCl_2$ from the two mines. Experimental hydrogen adsorption isotherm data at 77 K were used for the evaluation of the adsorption isotherm constants of the Brunauer-Emmett-Teller (BET) and the Langmuir models, and also the amount of hydrogen adsorbed on the various samples was evaluated by using the adsorption isotherm data. Higher hydrogen adsorption capacity values were obtained for all the heat and the chemically treated activated carbon samples from the Kilimli coal samples than Armutcuk. The amount of H_2 adsorbed on the original Kilimli coal samples was 0.020 wt%, and it was increased to 0.89 wt% on the samples pyrolyzed at 800 °C. The highest value of hydrogen adsorption obtained was 1.2 wt% for the samples treated with KOH+NH_4Cl mixture at 750 °C followed by oxidation with $ZnCl_2$. It was shown that chemical activations were much more effective than physical activations in increasing the surface area, pore volume and the hydrogen sorption capacities of the samples.

Key words: Coal, Activated Carbon, Adsorption Isotherms, Chemical Activation, Hydrogen Sorption

INTRODUCTION

Hydrogen is now considered as the potential energy carrier of the future because of having many advantages, and an effective, cheap storage system is necessary for the future utilization of hydrogen as a pollution-free energy carrier [1,2]. Adsorption of hydrogen molecules on porous materials is one possible mechanism for hydrogen storage in different porous materials [3-7]. The most often investigated materials in many hydrogen storage systems are activated carbons (ACs), synthetic carbons, single and multi-wall carbon nanotubes (SWCNTs, MWCNTs), and metal organic framework (MOF) materials [3-8]. Although many investigations are being carried out to improve the methods and to develop the most appropriate adsorbent in hydrogen storage applications, further studies are still needed in this field.

Hydrogen storage capacities in porous materials such as carbon nanomaterial, zeolites and crystalline coordination polymers at room and liquid nitrogen temperatures have been studied extensively [1-18]. Carbon materials are largely investigated in this field. ACs obtained from coals are attractive due to the low cost of production and abundant resources. Also, they posses some specific beneficial properties, such as very well developed surface area, high mechanical and chemical resistance, ease of degradation of the used material and good ion-exchange properties [19].

In the study of Jeong et al. [1], the adsorption isotherms of pure hydrogen, methane and ethylene, and their binary and ternary mixtures were measured on AC at 293.15, 303.15, and 313.15 K and

pressures up to 2 MPa by using a volumetric method. Zielinski et al. [2] studied hydrogen storage in a commercial AC impregnated with nickel using a high-pressure volumetric adsorption-desorption system at high-pressure (20-30 bars). It was reported that nickel catalysts supported on AC could store significant amounts of hydrogen at room temperature and high pressure (up to 0.53% at 30 bars against 0.1% for the AC); and the hydrogen storage depended on the hydrogen pressure, the metal content, the metal precursor nature and the catalyst preparation method. The best performance at 20 bar was obtained with the 1 wt% Ni non-classical hydrazine catalyst which exhibited the largest specific surface area ($1,694 \text{ m}^2 \text{ g}_{cat}^{-1}$) and micropore proportions (80.8%). Jagiello et al. [3] used H_2 and N_2 adsorption isotherms at cryogenic temperatures to characterize the microporosity of a series of ACs. Panella et al. [4] investigated hydrogen adsorption on SWCNTs and AC using thermal-desorption spectroscopy at temperatures down to 20 K, to identify the adsorption sites of hydrogen and to determine quantitatively the amount of hydrogen stored.

Jorda-Beneyto et al. [7] prepared a series of chemically ACs with a wide range of properties (specific surface area and micropore size distribution) for the study of hydrogen adsorption at different temperatures (298 K and 77 K) and high pressures. Other types of carbon materials, such as AC fibers, CNTs and carbon nanofibers were also used to analyze the effect of structure in hydrogen adsorption capacity. It was reported that the hydrogen adsorption capacity depended on both the micropore volume and the micropore size distribution at 298 K. Values of hydrogen adsorption capacities at 298 K of 1.2 wt% and 2.7 wt% were reported for 20 MPa and 50 MPa, respectively, for a chemically AC. Hydrogen adsorption depended on the surface area and the total micropore volume of the AC at

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77 K. Hydrogen adsorption capacities of 5.6 wt% at 4 MPa and 77 K were recorded by a chemically AC. The total hydrogen storage on the best AC at 298 K was reported as 3.2 and 6.8 wt% at 20 MPa and 50 MPa, respectively and 8 wt% at 77 K and 4 MPa.

Hwang et al. [8] determined experimentally the equilibrium data for the adsorption of hydrogen on activated carbon at pressures up to 30 atm at 301 K, 323 K and 348 K. Konstantakou et al. [11] obtained adsorption isotherms of H_2 at 77 K on the AX-21 AC. Kopac and Erdogan [12] studied sorption characteristic of H_2 and N_2 in ACs with different particle sizes in a temperature range of 303-473 K using a dynamic technique and evaluated the adsorption equilibrium constant and heat of adsorption values of H_2 and N_2 on the carbon samples. Shindo et al. [13] investigated the hydrogen physisorption characteristics of mechanically milled AC powders using thermal desorption spectroscopy and the pressure-composition-temperature method. It was observed that hydrogen molecules were easily desorbed in hydrogenated milled AC and the hydrogen physisorption capacity of hydrogenated milled AC was smaller than that of the host AC, as the specific surface area of the host AC was reduced by milling. Concequently, the hydrogen physisorption characteristic of AC with a higher specific surface area was superior to that of milled AC. Kopac and Karaaslan [15] studied sorption of H_2 and N_2 in MWCNT-graphite mixture and determined the adsorption equilibrium parameters using a dynamic technique. Kocabas et al. [16] studied hydrogen sorption on SWCNT modified by thermal treatments and palladium loading, and reported 1.04 and 1.66 wt% hydrogen sorption capacities at 77 K for the heat-treated samples at 400 °C and the palladium loaded samples, respectively. The graphitized MWCNT was modified by KOH impregnation to improve hydrogen storage property by Chen and Huang [10] and the hydrogen uptake of 4.47 wt% was recorded. It was reported that potassium metal could be used to promote hydrogen storage capacity of the CNTs. The defect structure of CNTs was formed via KOH activation in enhancing hydrogen spilling into the inner layers of CNTs. Kang et al. [20] studied the effects of activation temperature, time and impregnation ratio of potassium hydroxide-to-char on the quality of activated carbons and reported that the temperature and impregnation ratio of activating agents have the greatest influence on the quality of activated carbon during the activation step. The influence of pretreatment and activation conditions in the preparation of activated carbons were investigated by Lee and Lee [21].

In our previous study we have reported the preparation of AC samples by physical and chemical activations from coal samples from two mines (Kilimli and Armutcuk) in the Zonguldak region, Turkey [5]. In this study, hydrogen sorption characteristics of these samples were investigated and the effects of heat and chemical activations (KOH, NH_4Cl, $ZnCl_2$) on hydrogen sorption characteristics were compared.

EXPERIMENTAL

Coal samples from the Kilimli and Armutcuk coal mines from Zonguldak, Turkey were used in this research. The preparation of ACs through physical and chemical activations have been extensively explained in our previous work [5]. The experimental adsorption isotherms of hydrogen were measured at 77 K, and pressures up to 1 atm on the raw coal samples and a series of ACs prepared.

The ash-reduced coal samples were activated by pyrolytic thermal treatments under N_2 flow at different temperatures in a temperature range of 600-900 °C. The AC samples from the Kilimli and Armutcuk coal mines obtained in a temperature range of 600-900 °C were named as K600-K900 (Kilimli mine) and A600-A900 (Armutcuk mine), respectively. On the other hand, the ash-reduced coal samples were treated by chemical agents such as KOH, $ZnCl_2$, NH_4Cl at 650 and 750 °C. The AC samples obtained by chemical activations at 650 and 750 °C were named as K650, K750, A650, A750. The samples treated at 650 °C with KOH+$ZnCl_2$ were named as K650(1), A650(1), and samples treated at 650 °C with KOH+NH_4Cl+$ZnCl_2$ were named as K650(2), K650(2) for the samples from the Kilimli and Armutcuk coal mines, respectively. K750(1), A750(1) and K750(2), A750(2) codes correspond to the activated samples at 750 °C with KOH+$ZnCl_2$ and KOH+NH_4Cl+$ZnCl_2$, respectively, for the samples from Kilimli and Armutcuk coal mines. In our previous study, it was shown that the BET surface area of the Kilimli coal samples, which initially had a value of 1.20 m^2/g, were increased to 52.62 m^2/g after pyrolytic heat treatments at 800 °C and increased to 830.5 m^2/g by treating the coals with KOH+NH_4Cl mixture at 750 °C followed by oxidation of the samples mixed with $ZnCl_2$ [5]. Hydrogen sorption experiments on all these samples were carried out at 77 K by using a Quantachrome NOVA 2000 Gas Sorption Analyzer.

RESULTS AND DISCUSSION

1. Hydrogen Sorption Results on Activated Carbons Produced by Pyrolytic Thermal Treatments under N_2 Flow

Activated carbon samples from Kilimli (K) and Armutcuk (A) mines were obtained by heating the samples at 30 °C min⁻¹ from ambient temperature to pyrolysis temperature in the range of 600-900 °C under N_2 flow [5]. Figs. 1 and 2 show the H_2 adsorption isotherms on the A600-A900 and K600-K900 samples, respectively, at 77 K. From Fig. 1, it can be seen that the A800 sample shows a higher H_2 adsorption capacity than the A600, A700 and A900 samples. Likewise, H_2 capacity of K800 is better than the K600, K700
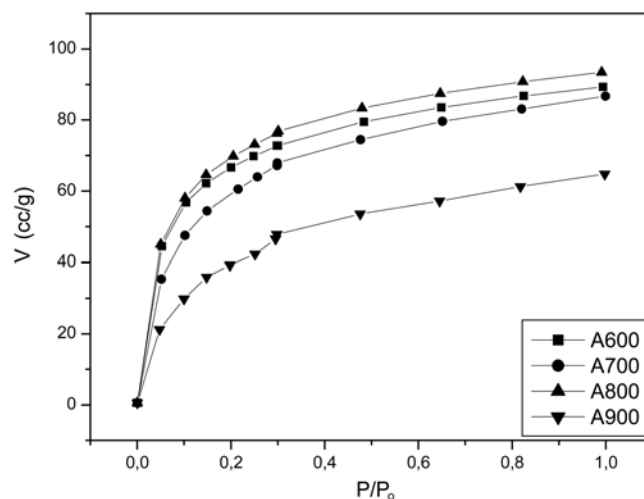

Fig. 1. H_2 adsorption isotherms on Armutcuk coal samples at 77 K ($T_{pyrolysis}$=600-900 °C).
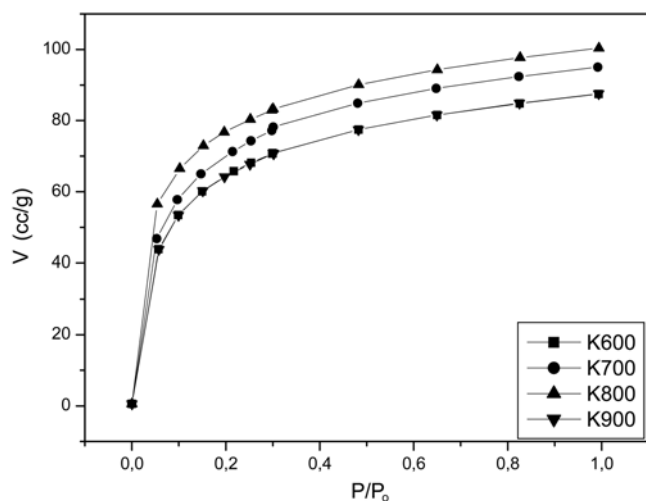
Fig. 2. H₂ adsorption isotherms on Kilimli coal samples at 77 K ($T_{pyrolysis}$=600-900 °C).

and K900 samples, as shown in Fig. 2. Two well known adsorption isotherm models, Brunauer-Emmett-Teller (BET, multilayer) and the Langmuir (monolayer) adsorption isotherm models (Table 1) were applied to analyze the experimental adsorption data of hydro-

Table 1. Adsorption isotherm models [22]

Adsorption isotherms
BET
$$\frac{1}{W\left(\left(\frac{P}{P_o}\right)-1\right)}=\frac{1}{W_mC}+\frac{C-1}{W_mC}\left(\frac{P}{P_o}\right)$$
LANGMUIR
$$\frac{P/P_o}{W_m}=\frac{1}{CW_m}+\frac{P/P_o}{W_m}$$

gen on activated carbons. The comparison of the experimental adsorption isotherm data with the BET and the Langmuir adsorption isotherm models [22] is given in Figs. 1 and 2 and the constants appearing in these models were evaluated. Tables 2 and 3 show the evaluated constants of C, W_m and R^2 for hydrogen adsorption on the A600-A900 and K600-K900 samples. The experimental adsorption isotherm data were in good agreement with the BET and the Langmuir adsorption isotherms models with R^2 values of 0.99 for the pyrolyzed samples. On the other hand, for the raw and the ash-reduced samples no appreciable hydrogen adsorption was observed as seen in Tables 2 and 3, due to the nonporous structure and very low surface area of these untreated samples [5]. For both K800 and A800 samples, highest H_2 adsorption capacity was found at 800 °C. At 800 °C, the adsorption capacities were 0.89 and 0.81 wt%, for K800 and A800 samples, respectively. The BET surface areas of these samples were given in our previous paper [5]. The samples obtained at 800 °C have the highest surface areas among the 600-900 °C range with values of 52.62 and 41.55 m²/g for the K800 and A800 samples, respectively. There was an increase in surface area until 800 °C. H_2 adsorption capacity of the K900 and A900 samples at 900 °C was decreased to 0.78 and 0.56 wt%, respectively, with decrease of surface areas due to the destruction of pores at temperatures higher than 800 °C [5]. The largest increase in the amount of hydrogen adsorbed on the K600-K900 and A600-A900 samples was obtained over the hydrogen relative pressure range 0-0.3. All of the K samples adsorbed more hydrogen than the A samples. According to the results, pyrolysis process applied to the raw and the ash-reduced coal samples in a temperature range of 600-900 °C under N_2 flow affected the H_2 adsorption parameters at 77 K. At 600 °C, the differences in the adsorption isotherms were very little, whereas at 900 °C the differences in the isotherms were considerable for the K900 and A900 samples. The destruction of pores for the A900 samples was significant than the K900 samples. An increase of hydrogen adsorption capacity with an increase in temperature was observed due to the surface area and pore volume increases; however, this increase in hydrogen adsorption capacity with tem-

Table 2. BET isotherm constants for H₂ adsorption on the heat treated samples

Samples	BET constants	Raw	Ash reduced	600 °C	700 °C	800 °C	900 °C
A	C	1.728	1.214	130.8	51.57	103.65	42.22
	W_m (g/g)	0.00009	0.00012	0.0048	0.0045	0.005	0.003
	R^2	0.58	0.03	0.99	0.99	0.99	0.99
K	C	2.342	1.204	88.69	81.73	300.4	73.56
	W_m (g/g)	0	0.0001	0.005	0.005	0.005	0.005
	R^2	0.78	0.20	0.99	0.99	0.99	0.99

Table 3. Langmuir isotherm constants for H₂ adsorption on the heat treated samples

Samples	Langmuir constants	Raw	Ash reduced	600 °C	700 °C	800 °C	900 °C
A	C	0.52	0.11	33.77	73.37	31.10	19.04
	W_m (g/g)	0.0003	0.0001	0.007	0.007	0.007	0.004
	R^2	0.42	0.38	0.99	0.99	0.99	0.97
K	C	-	-	27.77	26.88	41.71	24.37
	W_m (g/g)	-	-	0.007	0.007	0.008	0.007
	R^2	0.52	0.62	0.99	0.99	0.99	0.99

perature was limited.

For all the investigated carbon structures, the shapes of the adsorption isotherms were similar. The amount of H_2 that can be stored in an adsorption system can be determined by the nature of the adsorption material and the temperature of the adsorption system. The increase in H_2 adsorption capacities with an increase in temperature up to 800 °C can be attributed to the release of volatiles to leave the space that was previously occupied by the decomposed samples, and therefore causes an increase in the specific surface area of the samples enhancing the hydrogen adsorption capacities. At temperatures higher than 800 °C, a decrease in the amount of H_2 sorption was observed. This reduction can be due to the breakdown of crosslinks in the carbon matrix with a consequent rearrangement of carbonaceous aggregates and demolishing of pores as pointed out in our previous study [5]. Also the extensive gasification at high temperatures results in destruction of pore structures.

2. Hydrogen Sorption Results on Activated Carbons Produced by Chemical Activation

In chemical activation, the procedure for preparation of activated carbon samples includes the impregnation of the samples with chemical reagents followed by carbonization [5]. It has been known that the chemical activation with KOH is an effective method to prepare AC materials. Treating the coal samples with KOH, activation of the samples takes place as a result of chemical reaction between carbon and potassium hydroxide. The main reactions consist of hydroxides reduction and carbon oxidation; thus porosity is formed by the release of CO, CO_2 and H_2 and the removal of metallic carbonates or metallic potassium during washing, after the activation process. Then the activation of the impregnated coal samples with $ZnCl_2$ was carried out under N_2 environment. Coal samples were also impregnated with KOH and NH_4Cl, then mixed with $ZnCl_2$ (with $ZnCl_2$/coal ratio of 3 : 1), respectively, and then activated at 650 and 750 °C [5]. Figs. 3 and 4 show the H_2 adsorption isotherms of the A and K samples at 77 K. In these figures, hydrogen adsorption isotherms are clearly of Type I. From Fig. 3, the highest adsorption capacity was obtained for the A650(2) samples which were treated with $KOH+NH_4Cl+ZnCl_2$ at 650 °C. On the other hand, for the K750(2) samples which were treated with $KOH+NH_4Cl+ZnCl_2$ at 750 °C, highest adsorption was observed (Fig. 4). The hydrogen sorption capacity increases (decreases) with increasing (decreasing) relative H_2 pressure. The calculation of the experimental data as BET and Langmuir isotherm results is also shown in Tables. 4 and 5. The experimental adsorption isotherm data were also in good agreement for these samples with the BET and the Langmuir
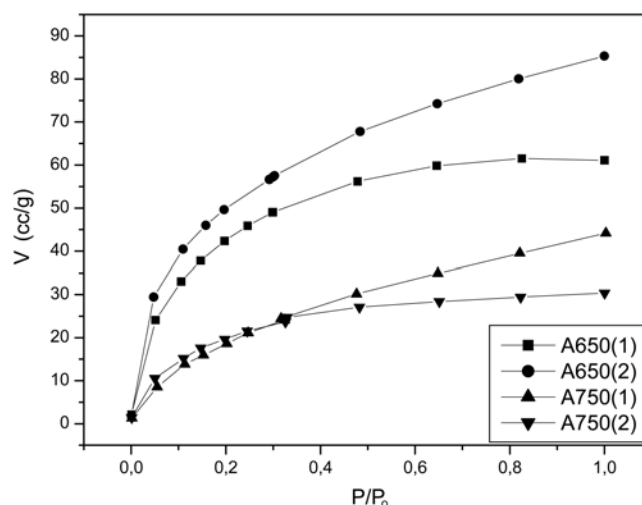

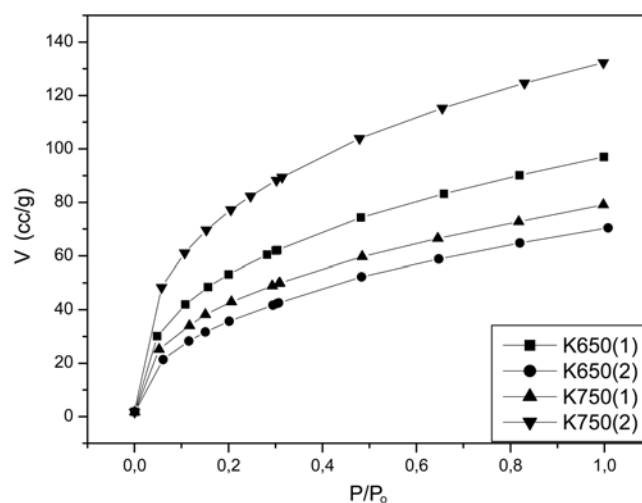**Fig. 3. H_2 adsorption isotherms on Armutcuk coal samples at 77 K (Chemical treatments at 650, 750 °C).**

Fig. 4. H_2 adsorption isotherms on Kilimli coal samples at 77 K (Chemical treatments at 650, 750 °C).

adsorption isotherm models with R^2 values of 0.99. Table 6 shows H_2 sorption % of all the samples. According to the results, higher values of hydrogen sorption were found for the samples from the Kilimli mines (K650(1)) than the Armutcuk samples obtained with chemical activation at 650 °C. In the same way, at 750 °C, hydrogen

Table 4. BET isotherm constants for H_2 adsorption on the chemically treated samples

Samples	BET constants	650 °C		750 °C	
		$KOH+ZnCl_2$ treated (1)	$KOH+NH_4Cl+ZnCl_2$ treated (2)	$KOH+ZnCl_2$ treated (1)	$KOH+NH_4Cl+ZnCl_2$ treated (2)
A	C	44.87	65.18	20.70	50.99
	W_m (g/g)	0.003	0.004	0.002	0.002
	R^2	0.99	0.99	0.98	0.99
K	C	60.90	39.53	51.11	66.54
	W_m (g/g)	0.004	0.003	0.003	0.006
	R^2	0.99	0.99	0.99	0.99

Table 5. Langmuir isotherm constants for H$_2$ adsorption on the chemically treated samples

Samples	Langmuir constants	650 °C		750 °C	
		KOH+ZnCl$_2$ treated (1)	KOH+NH$_4$Cl+ZnCl$_2$ treated (2)	KOH+ZnCl$_2$ treated (1)	KOH+NH$_4$Cl+ZnCl$_2$ treated (2)
A	C	20.25	23.07	10.85	17.72
	W$_m$ (g/g)	0.005	0.005	0.002	0.002
	R^2	0.97	0.98	0.91	0.96
K	C	19.15	15.35	13.44	21.49
	W$_m$ (g/g)	0.006	0.005	0.005	0.009
	R^2	0.98	0.96	0.97	0.97

Table 6. H$_2$ sorption % on various samples at 77 K and atmospheric pressure

Sample	K		A	
	W (g/g)	%W	W (g/g)	%W
Raw	0.00023	0.020	0.00026	0.026
Ash reduced	0.00025	0.025	0.00025	0.025
600	0.0079	0.78	0.008	0.79
700	0.0086	0.85	0.0078	0.77
800	0.0090	0.89	0.008	0.81
900	0.0079	0.78	0.005	0.56
650(1)	0.0087	0.87	0.0055	0.55
650(2)	0.0063	0.63	0.0077	0.76
750(1)	0.0071	0.71	0.004	0.4
750(2)	0.012	1.20	0.0027	0.27

sorption of Kilimli (K750(2)) was higher than Armutcuk coal samples with chemical activation. The maximal hydrogen amount was obtained at 750 °C for samples impregnated with KOH+NH$_4$Cl by chemical agent (ZnCl$_2$) with thermal treatment. According to the results, changing the preparation variables, it was possible to increase the H$_2$ sorption capacity of samples from around 0.020 wt% to 1.2 wt% by applying chemical activations. High extents of microporosity occurring during the chemical activations cannot be obtained by physical activation, because the increase in surface areas occurs together with pore widening. The hydrogen sorption results obtained with the chemically activated carbons compared with the samples exposed to just thermal pyrolysis under N$_2$ flow in a temperature range of 600-900 °C have shown that applying thermal treatments only was not sufficient and that hydrogen sorption capacities could be improved by chemical activations.

CONCLUSIONS

The hydrogen adsorption isotherms of activated carbons obtained by thermal and chemical activations from the Kilimli and Armutcuk coal mines were measured by a volumetric technique at 77 K over the hydrogen relative pressure (P/P$_o$) range 0-1.0. H$_2$ sorption capacities of the Armutcuk and Kilimli samples were increased to a limited extent by pyrolysis in the temperature range of 600-900 °C under N$_2$ flow. The highest amount of H$_2$ adsorbed was obtained for the samples exposed to thermal treatments at 800 °C. The H$_2$ uptake of the Kilimli and Armutcuk coal samples was increased

from 0.020 wt% and 0.026 wt% to 0.89 wt% and 0.81 wt%, respectively, at 800 °C. Chemically activated carbons present higher H$_2$ adsorption capacities due to the increase of surface areas and pore volumes. The highest value of the hydrogen uptake was found as 1.2 wt% for the K750(2) samples, which was obtained by treating the coals with KOH+NH$_4$Cl mixture at 750 °C followed by oxidation of the samples mixed with ZnCl$_2$.

ACKNOWLEDGMENTS

NOMENCLATURE

C　　　: adsorption isotherm constant
P/P$_0$　: relative pressure
T　　　: temperature [°C]
V　　　: volume of gas [cc/g]
W　　　: amount of gas adsorbed per gram of adsorbent [g/g]
W$_m$　: maximum amount of gas adsorbed per gram of adsorbent [g/g]
R^2　　: square of the correlation coefficient

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