

Comparative Investigation of the Hydrogen Production of Zinc/carbons Prepared from Non-activated Carbon and Surface-modified Activated Carbon by Treatment with Zinc Salts

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ABSTRACT

Zn-AC and Zn-H-AC series prepared from non- and surface-modified activated carbon were investigated in terms of their hydrogen production capacity. An increase in the concentration of the zinc salts used with these series was shown to lead to a decrease in the values of the surface textural properties. The existence of zinc complexes on the surface was confirmed from an analysis of XRD data. The SEM micrographs of the two different sample types showed that the transformation of the carbon surface with an acid pre-treatment significantly change the metal contents on the surfaces of the carbon matrix. The EDX spectra indicated that all of the samples were richer in the amount of oxygen and zinc compared to any other elements. The results obtained using the Boehm's titration method showed that the positive introduction of the acidic groups on the carbon surfaces with the acid treatment is correlated with an increase in the amounts of zinc complexes with variation of the acidic groups. In terms of the hydrogen production performance, the volume fractions of the Zn-H-AC series were found to produce higher amounts than the Zn-AC series as a function of the metal contents considering the effects of the acid treatment.

Key words : Carbon, Hydrogen, Zinc, Adsorption/Adsorbents

1. Introduction

Carbon materials are of very high technological importance due to their mechanical and electronic characteristics and their molecular sorption and sieving properties. A large variety of carbon materials determines a wide range of practical applications in heterogeneous catalysis as a catalyst support material in hydrogenation processes. An important step in the design of a material for a particular application is the control of the surface modifications, including the transformation of functional groups and the amount of the free surface^{1,2)} and the formation of micro and mesoporosity via treatment using special metals.^{3,4)} With respect to its potential use as an energy carrier, hydrogen is currently becoming a key and very fashionable element in nowadays scientific, as well as industrial and political life. With environmentally friendly regenerative cycle, hydrogen is likely an ideal energy carrier and is believed to be able to replace petroleum when it becomes an extinct. The high efficiency of hydrogen as a fuel results from the fact that it is very light which however presents a major obstacle in terms of its efficient storage. For the mobile storage applications, the major target has not yet been met by any of the current storage

technologies, such as the use of compressed gas, liquid hydrogen or metal hydrides. An alternative lies in the storage of hydrogen in a porous solid via a physical adsorption process. Activated carbon and their fibers of various morphologies have also been in the focus of the scientific research. However, it has been demonstrated that H₂ adsorption in carbons at high pressures is not efficient because of the large portion of excluded volume.⁵⁾ The surface chemical heterogeneity is due to the presence of heteroatoms such as oxygen, nitrogen, hydrogen, phosphorus and sulfur. The most common functional groups are carboxylic, carbonyls, phenols and lactones. Functional groups on the surface of microporous carbons are most likely subjected to a wide variety of inter- and intra-molecular interactions including inductive, mesomeric, tautomeric, steric and hydrogen bonding. These interactions may severely alter their Brønsted-acid-base characteristics in such a way that in most cases they may not resemble the properties of the parent chemical compounds. These functional groups may play a role in the sorption and deposition of nonpolar molecules and metallic ions for the physical adsorption and halting of molecules from occupying the most energetically-favorable position on the carbon surface.⁶⁻⁹⁾ Generally, metals and their alloys are capable of favorably generating large amounts of hydrogen that react with alkali hydroxides such as NaOH and KOH. Studies of the properties of modified porous carbon for hydrogen generation are very important for the acid treatments that increase the metal ions with an increase in the number of functional groups. The major

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objective of this study is to seek a new storage concept that mitigates severe disadvantages related to compression, liquefaction and the low-temperature operation.

In this work, non- and surface-modified activated carbons treated with Zn ions from an aqueous solution are characterized and investigated in terms of their hydrogen production capacity at room temperature. It is shown that the hydrogen production capacity is correlated with the function of the amount of metallic zinc with the degree of acid treatment on the activated carbon. For the characterization, we attempted that results of analysis for the activated carbon treated with zinc are presented by investigation for the surface properties, XRD, SEM-EDX and production efficiencies of hydrogen.

2. Experimental Procedure

2.1. Preparation procedures

Activated carbon used as a starting material was prepared from coconut shell-based granular typematerial. The carbonized coconut shell was initially heated first at 773 K for burn off, and was then physically activated with water vapor in a the temperature range of 1023~7053 K. $ZnCl_2$ as a metal sources was obtained from Aldrich (99+%, ACS reagent) and used as received. For pretreatment with acid, 5 g of activated carbons was dipped into 100 ml of a 0.1 M hydrochloric acid solution and stirred for 24 h at room temperature. The air and bubbles in the solutions were removed under a pressure of approximately 1.33 Pa for 20 min and the solution was discarded. The prepared samples were dried at 388 K for 48 h in air atmosphere. For the metal treatment, 5 g of pristine activated carbons and activated carbons modified by HCl were dipped into a dissolved aqueous solution of 100 ml of 0.05~0.1 M zinc chloride. This was stirred for 12 h at room temperature.

N_2 adsorption parameters were measured using an ASAP 2010 instrument (Micromeritics, USA) at 77 K. Scanning electron microscopy (SEM, JSM-5200 JOEL, Japan) was used to observe the surface state and pore structure of the metal-activated carbon samples and the state of the transformed zinc salts on the carbon surface. For an elemental analysis of the metal-activated carbon samples, energy dispersive X-ray analysis (EDX) was also used. X-ray diffraction patterns were taken using an X-ray generator (Shimatz XD-D1, Japan) with Cu K α radiation.

2.2. Boehm's titration

Acidic and basic surface functional groups were determined using Boehm's titration.^{7,10} Erlenmeyer flasks containing 1 g of the metal-activated carbon sample had 50 mL of the following 0.05 M solutions added to them: sodium hydroxide, sodium carbonate, sodium bicarbonate for the acidic groups, and hydrochloric acid for the base groups. These additions took place at room temperature and the

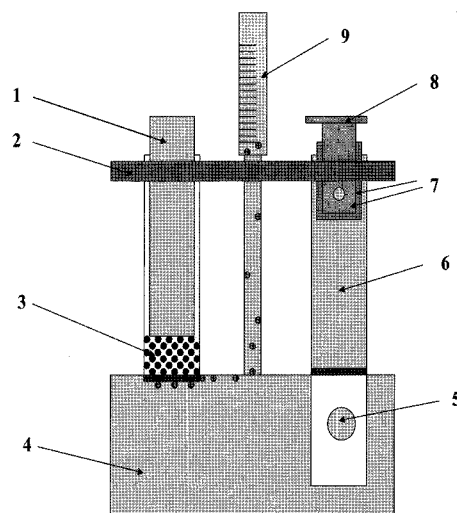


Fig. 1. Schematic apparatus for H_2 gas collection; 1. Syringe, 2. Supporter, 3. Sample, 4. KOH reservoir, 5. Hall, 6. KOH supply tube, 7. Double cock, 8. Rotational valve, 9. Volumetric gauge for H_2 gas collection.

solutions remained for more than 24 h. The Erlenmeyer flasks were sealed and shaken for 24 h and 5 mL of each filtrate was then pipetted. The excess base and acid liquids were titrated with HCl and NaOH, respectively. The numbers of acidic sites of various types were calculated under the assumptions that NaOH neutralizes carboxylic, phenolic, and lactonic groups, Na_2CO_3 neutralizes carboxylic and lactonic groups, and $NaHCO_3$ neutralizes only carboxylic groups. The phenolic groups were determined by the difference between the groups neutralized by Na_2CO_3 and NaOH. The number of surface basic sites was calculated from the amount of hydrochloric acid that reacted with the carbon. Neutralization points were known using pH indicators of a phenolphthalein solution of a titration base with strong acid together with methyl red solution for weak bases with strong acid and a pH meter.

2.3. H_2 gas collection

The schematic apparatus for the collection of H_2 gas is shown in Fig. 1. Column (6) (the KOH supply tube) remained filled with the KOH solution. After a sample reservoirs were completely emptied of the KOH solution, they were filled with Al-ACs. In this state, if a double cock (7) opened, samples were submerged with the KOH solution. Hydrogen gases generated in the sample reservoir were collected using a volumetric gauge (9).

3. Results and discussion

Table 2 shows a comparison of the surface textural properties of the non-activated carbon and surface-modified activated carbon prepared with zinc salts. As shown in the table, S_{BET} was observed at 1645 m^2/g for the pristine acti-

Table 1. Nomenclatures of Non-activated Carbon and Surface-modified Activated Carbon Prepared with Zinc Salts

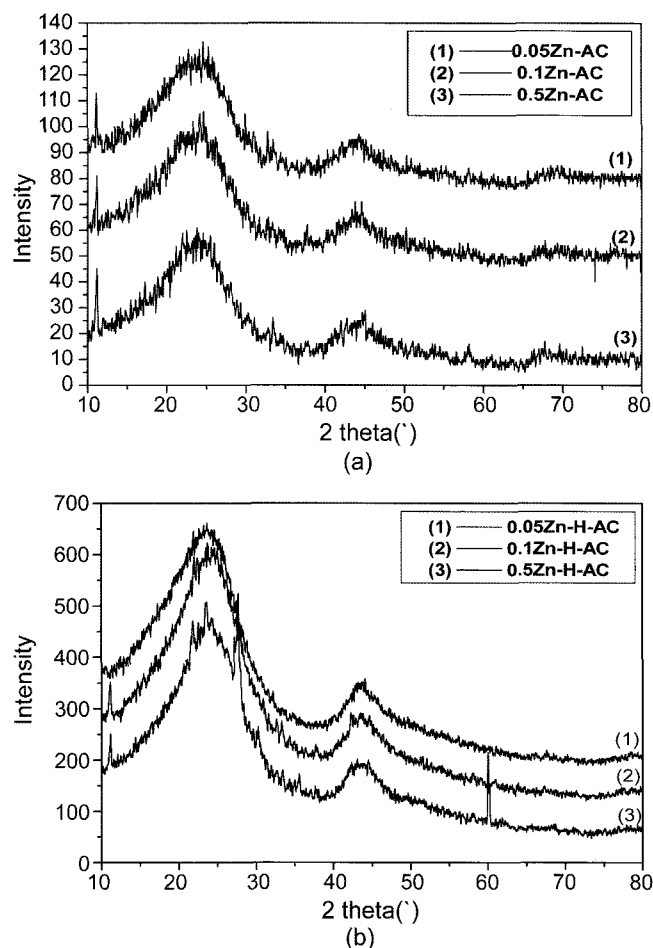
Preparation method	Nomenclatures
Activated Carbon+0.05 M Zinc chloride	0.05Zn-AC
Activated Carbon+0.10 M Zinc chloride	0.10Zn-AC
Activated Carbon+0.50 M Zinc chloride	0.50Zn-AC
0.1 M HCl pre-treated Activated Carbon +0.05 M Zinc chloride	0.05Zn-H-AC
0.1 M HCl pre-treated Activated Carbon +0.10 M Zinc chloride	0.10Zn-H-AC
0.1 M HCl pre-treated Activated Carbon +0.50 M Zinc chloride	0.50Zn-H-AC

Table 2. Comparison of the Physical Parameters of Non-activated Carbon and Surface-modified Activated Carbon Treated with Zinc Salts

Sample	Parameter			
	S_{BET} (m^2/g)	Micropore Volume (cm^3/g)	Internal Surface Area (m^2/g)	Average Pore Diameter (\AA)
As received AC	1645	0.499	1496	18.03
0.05Zn-AC	1301	0.355	967.2	16.63
0.10Zn-AC	1242	0.338	950.2	16.54
0.50Zn-AC	1033	0.323	935.7	16.42
0.05Zn-H-AC	1231	0.344	952.8	16.62
0.10Zn-H-AC	1130	0.337	943.2	16.51
0.50Zn-H-AC	1051	0.331	927.9	16.40

activated carbon, but the surface areas were distributed between 1033 and 1301 m^2/g for the Zn-AC samples and between 1051 and 1231 m^2/g for the Zn-H-AC samples. According to an earlier study,¹¹⁾ it was shown that S_{BET} s for Ag-ACs clearly decrease as the phosphoric acid concentration increases. It is important that the high surface area of dried ACs treated with zinc salts contributes to the temporary storage space of H_2 gas produced from wet Zn-ACs or from Zn-H-ACs reacted with potassium hydroxide. An increase of the concentration of zinc salts led to a decrease in the values of the surface textural properties, including the pore volume, surface area and pore diameter. In particular, post-treatment acid on the carbon surface resulted in considerable transformation to the outer surface states of the activated carbon. It is believed that the post-treatment of acid should increase the amount of functional groups on the carbon surface. It should be noted that the average pore diameter for the samples treated with zinc are distributed in a pore range of 16.42~16.63 \AA for Zn-ACs and 16.40~16.61 \AA for Zn-H-ACs as the micropore volume decreases. From the results, the number of micropores on the Zn-ACs and Zn-H-ACs surface decreases as the concentration of the zinc salts increases. According to these results, a number of pores on the zinc-treated carbon surfaces were blocked with the formation of bulky zinc salts after the acid treatment.

Fig. 2 shows XRD patterns of Zn-AC and Zn-H-AC series

**Fig. 2.** XRD patterns for activated carbon treated with zinc: (a) Zn-AC and (b) Zn-H-AC series.

synthesized under the control (no treatment) as well as various acid treatment conditions. It can be observed that sample Zn-ACs prepared in Fig. 2 (a) exhibit broad amorphous carbon peaks and a number of metallic peaks with weak intensity around 11.5, 22~25, 33.5 and 40~45°. However, sample Zn-H-ACs in Fig. 2 (b) display peaks at approximately 11.5, 22~25, 33.5, 40~45 and 60.5°. The intensity of these peaks increases as the intensity of the acid treatment increases. Therefore, it can be concluded that an acid treatment of activated carbon surfaces can improve the structural state while increasing of the formation of new functional groups on the carbon surface, which may improve the degree of hydrogen production.

The Zn-AC series prepared for hydrogen production was examined by SEM to determine the surface structural conditions and the formation of the metallic state on the surface after the acid treatment. The results for the Zn-H-AC series prepared with surface-modified activated carbon after an acid treatment show a slight change compared to that of the Zn-AC series prepared with non-modified activated carbon. The two sample types had so heavily eroded that the pristine activated carbon appearance of the material had been lost. Particularly, the Zn-AC series formed

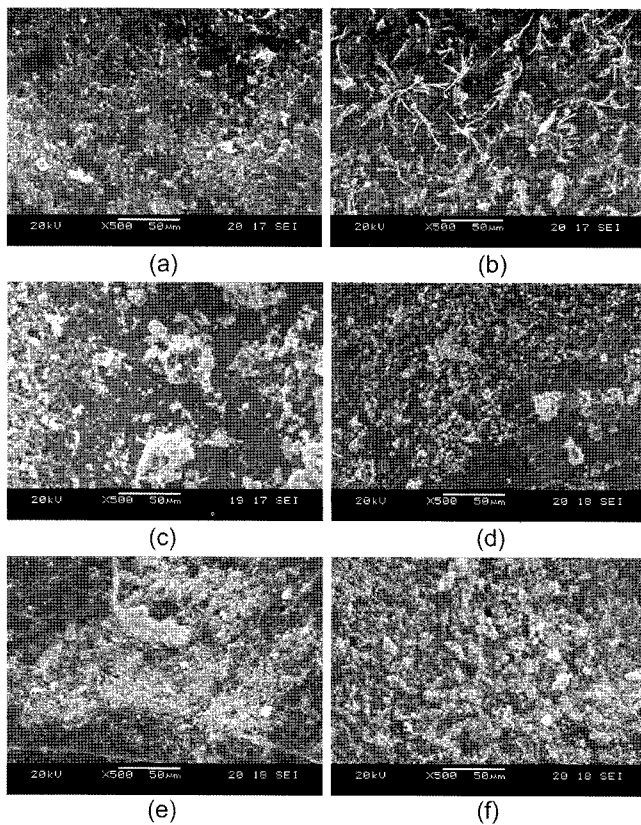


Fig. 3. SEM images obtained from activated carbon treated with zinc: (a) 0.05Zn-AC, (b) 0.1Zn-AC, (c) 0.5Zn-AC, (d) 0.05Zn-H-AC, (e) 0.1Zn-H-AC, and (f) 0.5Zn-H-AC.

frost-like aggregates with the metallic complexes and the surfaces became heavily etched. However, the Zn-H-AC series showed numerous parts of aggregates that resulted in pore blocking with a white metallic complex. This is consistent with the increased surface functional groups after the acid treatment. In another study,²⁾ SEM observation of numerous surfaces and a cross-section of metal complexes containing activated carbon showed that the agglomerates were evenly distributed and irregular in shape and size after an acid treatment. A comparison of these micrographs shows that the transformation of the carbon surface with a pre-treatment of acid significantly changes the amount of metal on the surfaces of the carbon matrix.

Fig. 4 shows the EDX spectra of the Zn-AC and Zn-H-AC series. It is clearly observable that the spectra difference between of Zn-ACs and Zn-H-ACs indicates the treatment effect on the metallic zinc. The spectra show the presence of Zn peaks for samples measured at around 1, 8.6 and 9.6 keV. The tendency of the variation of the EDX spectra is one mechanism that can lead to an increase in the degree of zinc ion adsorption as well as the increased formation of zinc salts on the surfaces after the acid treatment. The EDX observation showed that most of these samples had higher peaks associated with the treated C, Cl and Zn compared to any other element. Quantitative results of the EDX micro-analysis of the Zn-AC and Zn-H-AC series are listed in

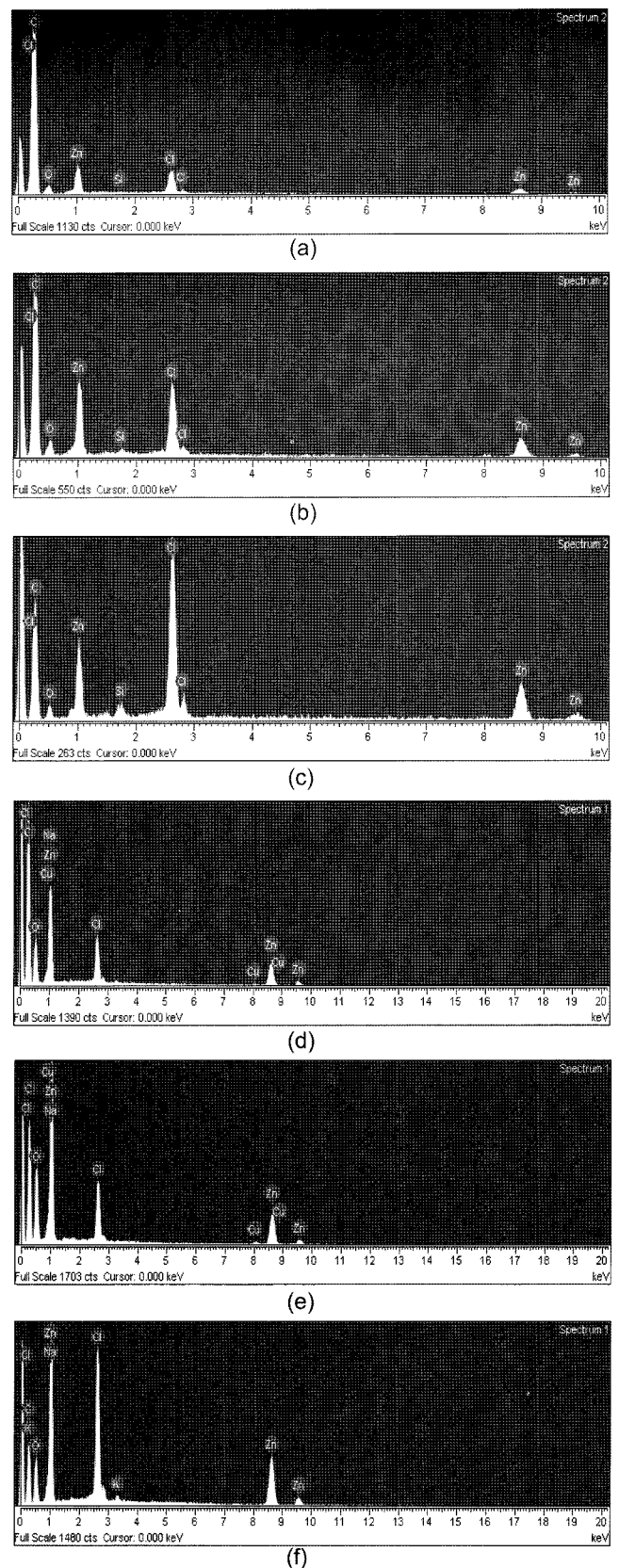


Fig. 4. EDX elemental micro-analysis spectra obtained from activated carbon treated with zinc for the H_2 gas production: (a) 0.05Zn-AC, (b) 0.1Zn-AC, (c) 0.5Zn-AC, (d) 0.05Zn-H-AC, (e) 0.1Zn-H-AC, and (f) 0.5Zn-H-AC.

Table 3. EDX Elemental Microanalysis of Non-activated Carbon and Surface-modified Activated Carbon Treated with Zinc Salts

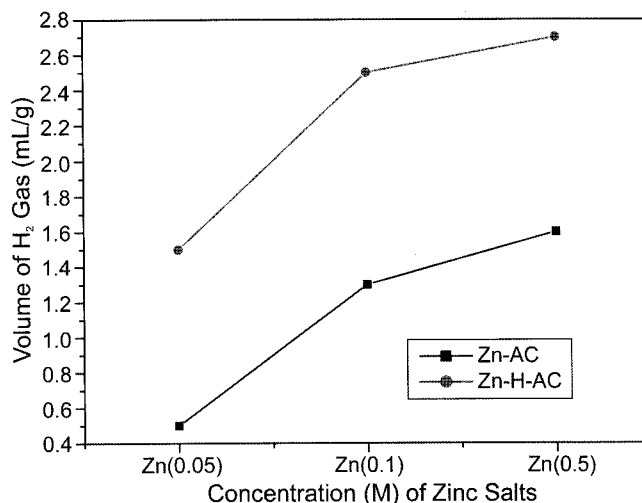
Sample	Elements (%)				
	C	O	Zn	Cl	Si
0.05Zn-AC	81.4	8.24	4.97	2.69	-
0.1Zn-AC	75.4	8.77	10.6	4.97	0.23
0.5Zn-AC	65.8	5.90	17.4	10.44	0.43
0.05Zn-H-AC	51.6	15.7	29.3	6.32	0.15
0.1Zn-H-AC	45.9	14.8	32.9	6.05	0.28
0.5Zn-H-AC	43.7	11.6	36.6	8.54	0.17

Table 4. Number of Surface Species (meq/g) Obtained from Boehm Titration

Sample	Functional Group (meq/g)				
	Carboxylic	Lactonic	Phenolic	Acidic	Basic
0.05Zn-AC	0.009	0.021	0.0001	0.030	0.004
0.10Zn-AC	0.012	0.064	0.004	0.080	0.008
0.50Zn-AC	0.016	0.093	0.007	0.116	0.012
0.05Zn-H-AC	0.008	0.041	0.006	0.055	0.014
0.10Zn-H-AC	0.012	0.072	0.006	0.090	0.020
0.50Zn-H-AC	0.022	0.120	0.008	0.143	0.034

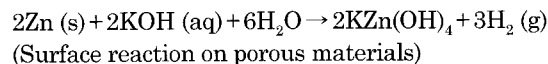
Table 3. From the results for the samples, carbon, oxygen and zinc are presented as the major elements in the Zn-AC and Zn-H-AC series. It was observed that all of the samples were richer in oxygen and zinc than they were in any of the other elements. One possible explanation for this is the formation of surface complexes through the acid treatment including oxygen ions that exhibit zinc oxide complexes for the carbon active sites. It is believed that the increase of the amount of Zn from the aforementioned EDX spectra is due to a modification of the oxygen groups from the carbon matrix by the acid treatment.

The types and quantitative of oxygen groups were traditionally determined using the titration method proposed by Boehm.¹²⁾ The results obtained from the titration method are listed in Table 4. It lists the total acidity and base nature, showing that the distributions of the functional groups have different values. It is believed that complexes treated with acid on carbon surfaces formed due to the capturing of oxygen functional groups as well as via adsorption caused by physico-chemical attraction forces. The effects of the surface acidity and base nature of the solutions were also evaluated from correlations as a function of the NaOH, NaHCO₃ and Na₂CO₃ uptake. It should be noted that 0.50Zn-H-AC has the highest number of oxygen functional groups, including carboxylic, lactonic and phenolic groups. It was considered that the highest values of acidity can be attributed to the lowest local pH of the carbon surfaces due to the hydrochloric acid. It is believed that the affinity of AC for zinc ion depends on the number of surface functional groups. A positive introduction of the acidic groups on the carbon surfaces by the acid treatment was also demonstrated by the increase in the amounts of zinc complexes with variations of the acidic groups. As the distribution of

**Fig. 5.** Hydrogen production capacities of different types of activated carbon treated with zinc.

the acidic groups was properly introduced, metallic sites on the carbon surfaces most likely play an important role in the production of hydrogen.

Zinc and their alloys are capable of favorably generating large amounts of hydrogen that react with alkali hydroxides such as NaOH and KOH. The following reaction describes the production of hydrogen.



Most papers involving theoretical studies of hydrogen absorption in carbon nanostructures focus on the physisorption of H₂ on carbon in conditions of low temperatures and high pressures.¹³⁻¹⁵⁾ Experiments involving hydrogen production in carbon were carried out using different methods under various conditions with numerous small and often samples that were not very well characterized. The hydrogen production results of the Zn-AC and Zn-H-AC series were investigated after treatments with various KOH concentrations and the results are shown in Fig. 5. From the results, it is believed that the metal contents of the Zn-AC and Zn-H-AC series are useful factor in the production of hydrogen. A satisfactory level of hydrogen production with 0.1 M KOH with a zinc source concentration ranging from 0.05-0.5 M was achieved. The amount of hydrogen produced was proportional to the contents of treated metal with the BET surface area of the carbon sample. Their hydrogen volume fraction was high with respect to the entire volume of samples (0.5~1.6 ml/g for Zn-ACs, and 1.5~2.7 mL/g for Zn-H-ACs); this might be associated with the amount of zinc salts in the acid treatment. From a comparison of the two types of samples, the volume fractions of the Zn-H-AC series showed higher amounts compared to that of the Zn-AC series. Upon treatment of a large amount of metal with carbon, a large amount of hydrogen gas will be obtained from the metallic AC series. As shown in the EDX results, the effects of the acid treatment can increase the amount of

metal as the functional groups on the carbon surface increase. The production capacity is correlated to the physical parameters of the carbon samples; however, production stability and safety have to be considered as key factors in relevant applications.

4. Conclusion

In this study, two types of samples for Zn-AC and Zn-H-AC prepared from non- and surface-modified activated carbon using an aqueous solution were characterized and investigated in terms of their hydrogen production capacity at room temperature. An increase of the concentration of zinc salts used in a treatment process leads to a decrease in the values of surface textural properties such as the pore volume, surface area and pore diameter. In particular, post-treatment acid on a carbon surface resulted in considerable transformation of the outer surface states of activated carbon. The existence of metallic zinc and zinc complexes on the surface was confirmed through an analysis of XRD data. From SEM observations, a comparison of micrographs of the two types of samples showed that the transformation of the carbon surface via pre-treatment with acid significantly changes the amount of the metal on the surfaces of the carbon matrix. From the results of the EDX microanalysis, it was shown in these spectra that all of the samples were richer in oxygen and zinc than they were in any other element. The results obtained using the Boehm's titration method showed that the positive introduction of the acidic groups on the carbon surfaces via the acid treatment is also associated with an increase in the amounts of zinc complexes with variations of the acidic groups. From a comparison of the hydrogen production performance, the volume fractions of the Zn-H-AC series showed higher amounts compared to the production amount of the Zn-AC series as a function of metal content with the acid treatment.

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