Impregnation of Nickel on Mesoporous ZSM-5 Templated Carbons as Candidate Material for Hydrogen Storage

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ABSTRACT

A series of carbon with the ZSM-5 mesoporous template (ZMC) and nickel impregnated ZMC (Ni/ZMC) were synthesized and gravimetrically determined its adsorption capacity for H_2 gas. ZMC carbon was synthesized using a hard template method at a carbonation temperature of 900 °C with sucrose as a source of carbon. A mesoporous ZSM-5 template was synthesized using a hydrothermal method at aging and crystallization temperatures of respectively 60 and 150 °C for as long as 24 h. The isothermal results of adsorption-desorption of N_2 showed that the larger the Ni loading on the supporting ZMC carbon, the smaller the surface area of the ZMC specific carbon. The distribution of the pore size that was counted by using the BJH method, which was applied to all the samples, was as big as 3.8 nm. The adsorption capacity of H_2 was measured using the gravimetry method at ambient temperature for Ni/ZMC-5, Ni/ZMC-15, and Ni/ZMC-25, which each gave a weight percentage of 0.33, 0.66 and 0.65% respectively, whilst the ZMC carbon has a weight percentage of 2.18%.

Keywords: *mesoporous ZSM-5; mesoporous carbon; Ni/ZMC; hydrogen storage*

ABSTRAK

Karbon bertemplat ZSM-5 mesopori (ZMC) dan Ni/ZMC telah berhasil disintesis dan diketahui kapasitas adsorpsinya terhadap gas H_2 secara gravimetri. Karbon ZMC disintesis melalui metode templat keras pada suhu karbonasi 900 °C dengan sukrosa sebagai sumber karbon. Templat ZSM-5 mesopori disintesis dengan metode hidrotermal pada suhu aging dan kristalisasi masing-masing 60 dan 150 °C selama 24 jam. Hasil isotermal adsorpsi-desorpsi N_2 menunjukkan bahwa semakin besar loading Ni pada pendukung karbon ZMC, maka luas permukaan spesifik karbon ZMC semakin menurun. Distribusi ukuran pori dihitung dengan metode BJH untuk seluruh sampel adalah sebesar 3,8 nm. Kapasitas adsorpsi H_2 diukur dengan metode gravimetri pada suhu ambien untuk Ni/ZMC-5, Ni/ZMC-15, dan Ni/ZMC-25 memberikan nilai masing-masing sebesar 0,33; 0,63; dan 0,65% berat, sedangkan untuk karbon ZMC adalah 2,18% berat.

Kata Kunci: *ZSM-5 mesopori; karbon mesopori; Ni/ZSM-5; penyimpan hydrogen*

INTRODUCTION

Being one of the renewable sources of energy, the hydrogen has attracted attention and studied in depth because it has a couple of advantages which has been seen as very profitable when compared with other chemical energy sources. Using hydrogen as an alternative fuel on motorized vehicles is limited on its storage techniques. Hydrogen has to able to be kept in high density and at the same time not giving an additional weight on the vehicle itself. One of the storage methods which has been thought to be the most appropriate and applicable on motorized vehicles is the physical adsorption method [1].

A couple of carbon based hydrogen storing materials prepared by using porous materials template like zeolite Y, β, L, 13X as well as SBA-15, SBA-16 and KIT-6 mesoporous silica have been widely reported [2-3]. But taking advantage of a mesoporous ZSM-5 zeolite as a carbon template has not been much reported, therefore it is very interesting to study the material characteristics and its H_2 uptake capabilities from mesoporous carbon with ZSM-5 mesoporous template.

As it has been known, the ZSM-5 is one of the synthesized zeolite materials which have been used a lot in catalysis reaction. ZSM-5 is a porous material with a large surface area and pore volume, have a micro-meso pore size that is structured and it is affected by its synthesized condition [4-7]. With the characteristics of mesoporous ZSM-5, it is expected

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that it can be used as the right template in forming mesoporous carbon material.

Besides from structuring porous materials, adding certain metals can increase the effects of storing hydrogen by means of spillover mechanism, one of which is by impregnating transition metals such as Ni [8-10]. Doping Ni on the mesoporous carbon with zeolite material template has not been done much and can be studied further, especially when using mesoporous carbon with mesoporous ZSM-5 zeolite as a template as a material to store hydrogen.

In this research, a mesoporous ZSM-5 was synthesized in which then used as a mesoporous carbon template (ZMC). Next, as a part of synthesized mesoporous carbon, it was impregnated with Ni at a different level of concentration of weight, which was 5, 15 and 25%. The mesoporous carbon that was created, was respectively noted as Ni/ZMC-5, Ni/ZMC-15, and Ni/ZMC-25, in which then its characteristics were studied based on their analysis results by using XRD, SEM-EDX and N_2 isothermal adsorption.

EXPERIMENTAL SECTION

Materials

The chemicals used in this research were: tetra propylammonium hydroxide (TPAOH, 40% mixed with water), sodium aluminate ($NaAlO_2$), tetraethyl orthosilicate (TEOS, 99%), sucrose (99%), hydrofluoric acid (99%), sulphuric acid (98%), sodium hydroxide (98%) and nickel sulphate hexahydrate (99%) from Merck, while cetyltrimethylammonium bromide (CTABr, 99%) from Applichem and demineralized water. All the chemicals were used as received. The ultra-high purity of nitrogen gas was purchased from Samator Gas.

Instrumentation

The diffraction patterns of the samples were measured by X-ray diffraction (XRD) technique using Philip X'Pert PN-1830 X-ray diffractometer with a graphite monochromator and Cu Kα radiaton (λ = 1.5405 Å) at 40 kV and 30 mA. The diffraction patterns were recorded in 2θ range of 0-90° with a step of 0.02°. The scanning electron microscopy (SEM) observations were performed on a AMETEK microscope. The BET surface areas and pore size distributions of samples were determined from N_2 adsorption desorption isotherms at liquid nitrogen temperature (-196 °C) using a Quantachrome NovaWin2 Instrument. The samples were degassed at a temperature of 300 °C prior to analysis.

Procedure

Synthesis of mesoporous ZSM-5

Mesoporous ZSM-5 materials were synthesized by using the hydrothermal method as reported by Gonçalves [11]. $NaAlO_2$ was used as an alumina source which was added to the TPAOH solution and stirred until perfectly mixed together. Next, TEOS, which was a source of silicon, was added and the whole solution was stirred for 15 min, in order to obtain a molecular ratio of materials in the amount of $1SiO_2$: $20Al_2O_3$: 0,2TPAOH : $38H_2O$. The solution was then put in an oven at a temperature of 60 °C for 24 h as a part of the aging process. The process was continued by adding CTABr to the solution until a molar ratio of SiO_2/CTABr = 3.85 was obtained and stirred until the solution was perfectly mixed together. The crystallization process was done at a temperature of 150 °C for 48 h. The obtained solids were then filtered, washed with demineralized water until the filtrate reached a neutral pH level, followed by a drying process, which was done at temperatures of 60 and 110 °C, each for as long as 24 h. Surfactant (CTA^+) and organic template (TPA^+) were removed via a calcination process at a temperature of 550 °C for 10 h [11]. The obtained mesoporous ZSM-5 solids were then used as a hard template in the synthesis of nanoporous carbon.

Synthesis of ZMC carbon began with mixing 1 g of ZSM-5 into a solution which composed from 1.1 g of sucrose and 0.14 g of sulphuric acid in a 5 mL of deionized water. The mixture was then heated in an oven gradually at the temperatures of 100 and 160 °C, each for 6 h. Furthermore, 0.65 g of sucrose and 90 mg H_2SO_4 were added into a 5 mL of deionized water and put into an oven gradually at temperatures of 100 and 160 °C, each for 6 h. The composites of sucrose and ZSM-5 were then carbonized at a temperature of 900 °C for 5 h (the average heating speed was 2 °C per min) underneath the flow of N_2. The black solids with the ZSM-5 mesoporous template (ZMC) were dissolved in fluoride acid (HF) 48% at a room temperature in order to take out the anorganic/inorganic ZSM-5 template frames. The obtained ZMC carbon solids were filtered, washed with deionized water until the filtrate reached a neutral pH level and dried at a temperature of 90 °C for 12 h [8,12].

The method used for Ni impregnation on the surface of the mesoporous carbon was the Incipient Wetness Impregnation (IWI) method, in which the $NiSO_4.6H_2O$ was used as the Ni source. The synthesized carbon material was vacuumed for 12 h followed by addition of Ni solution with a variation of concentration each as much as 5, 15 and 25%, whilst being stirred for 6 h. The mixture was then dried at a temperature of 80 °C for 24 h in order to separate the solid of the Ni impregnated carbon from water. The solid was then calcined at a temperature of 450 °C for 5 h in a stream of N_2 gas in order to get rid of the traces water as well as separating it from salt sulphate (SO_3^{2-}), so that an Ni/ZMC mesoporous carbon was obtained.

The hydrogen storage capacity test for ZMC carbon and ZMC carbon which had been impregnated with Ni, i.e. Ni/ZMC-5, Ni/ZMC-15 and Ni/ZMC-25, was done by using the gravimetry method at a room temperature of 30 °C and at atmospheric pressure. Prior to measurement, all the samples were cleaned from pollutants such as water and gases, and this process was done in two stages. The first stage was to heat the sample at 105 °C for 2 h in order to get rid of the water contents. Then the second stage, the sample was degassed at 260 °C for 2 h in order to remove the crystal water and other pollutants that still remained on the surface and on the inside of the carbon pores, both of which could slow the adsorption process of H_2 gas. After the degassing process, adsorption of the H_2 began by flowing the gas at a flow rate of 20 mL/min. Mass changes were observed on an analytical balance and was recorded every 1 minute to 50 minutes. The mass difference of the sample before and after the H_2 gas flowing was recorded and calculated as a weight percent of the H_2 adsorbed on the sample.

RESULT AND DISCUSSION

X-Ray Diffraction, XRD

Synthesis of mesoporous ZSM-5 was done by using hydrothermal method with cetyltrimethyl ammonium bromide cationic surfactants (CTABr) as a mesostructure steering substance [9], with a ratio of Si/AL = 20. TPAOH was used as an MFI structure directing organic template as well as an alkaline agent. The success in synthesizing is shown in Fig. 1, which is a diffractogram pattern of the obtained solids. As is shown in Fig. 1, The characteristic diffraction peaks of ZSM-5 with high intensity appeared at 2θ of 7.9 and 8.8°, respectively, followed by diffraction peaks at 2θ of 23.1, 23.9 and 24.4° [10].

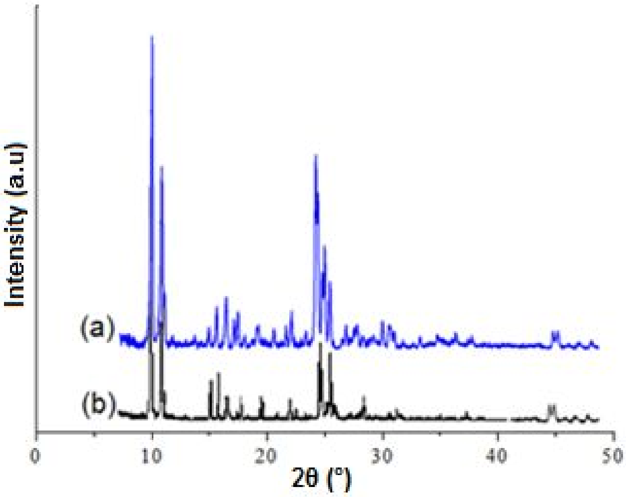

Fig 1. (a) XRD patterns of mesoporous ZSM-5; (b) mesoporous ZSM-5 reference [10]

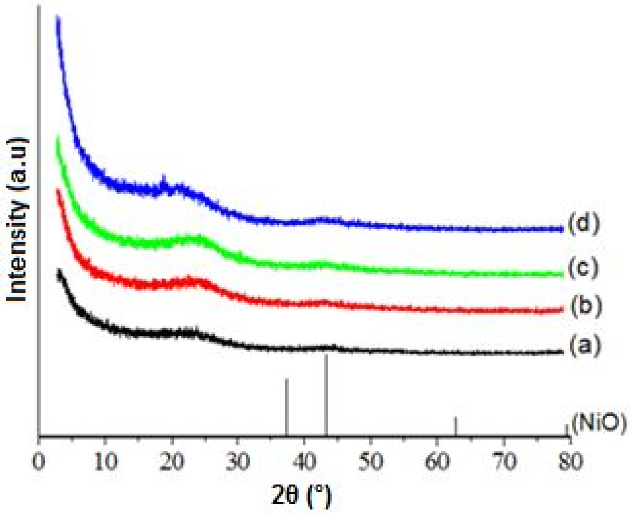

Fig 2. XRD patterns of sample (a) ZMC, (b) Ni/ZMC-5, (c) Ni/ZMC-15 and (d) Ni/ZMC-25

Fig. 2 shows the diffractograms of the synthesized (ZMC) amorphous carbon and the Ni-ZMC carbons after the ZMC was impregnated with Ni. The diffractogram of the ZMC carbon shows that there is a heap centered at a local angle of 2θ, each between the angles of approximately 25° and 43°. This heap marks the diffracted region [002] with the widen peak, or hump, at 2θ of approximately 25° and diffracted region [001] at approximately 43°. The concentration of the widen peak (hump) at region [002] is a typical graphitic carbon with interlayer distance values of 0.342 nm, which is bigger when compared to the interlayer distance value of a graphite when being cut, which is 0.335 nm [11].

A graphitic carbon was formed due to a number of sucrose derivatives that underwent self-condensation was located on the outer side of the ZSM-5 template micelles, which were then deposited on the external layer template throughout the whole process of carbonization. This condition caused the formation of carbon structure that was unable to replicate the ZSM-5 template and had a random shape [13].

There was a little heap that widens and centered at an angle of around 43° at diffraction region of [001], with the interlayer distance of 0.210 nm, which is a typical turbostratic carbon that took shape in the form of a small amount of parallel graphite sheets. The replication of synthesized carbon against the ZSM-5

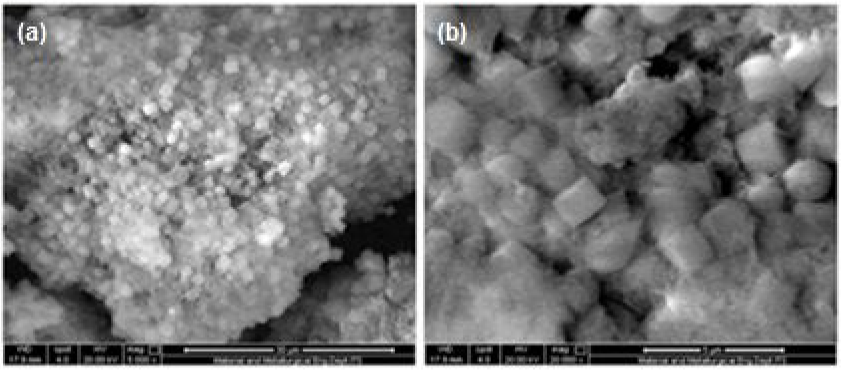

Fig 3. SEM micrograph of mesoporous ZSM-5: (a) 5,000x and (b) 20,000x

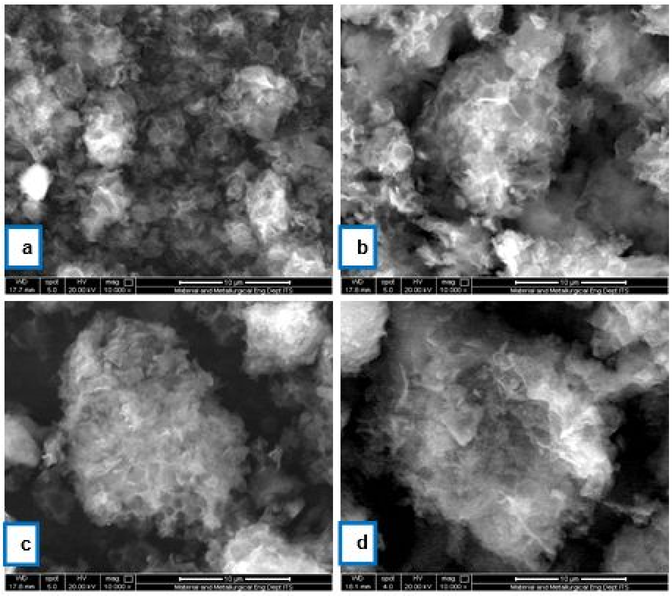

Fig 4. SEM micrographs at 10,000x of (a) ZMC carbon, (b) Ni/ZMC-5, (c) Ni/ZMC-15 and (d) Ni/ZMC-25

Table 1. Estimated Percentage of Elements

Samples	Percentage of Elements (% Weight)			
	C	O	Al	Ni
ZMC	82.96	16.21	0.83	-
Ni/ZMC-5	83.69	13.68	0.35	1.43
Ni/ZMC-15	76.17	19.47	0.11	3.34
Ni/ZMC-25	75.57	18.26	0.4	5.76

mesoporous template can be seen on the characterized diffracted area of the ZSM-5 mesoporous solids, which is located at an angle of 2θ between 7 to 8°, which had high intensities.

The hard template method used in the process of synthesizing a mesoporous carbon by using a ZSM-5 template involved migrating glucose and fructose molecules as derivatives of the sucrose precursors. The migration force of each of the molecules surfaced as an effect of capillarity which happened when there is an interaction in the bonds between the hydroxyl clusters inside the surface of the pore template with the glucose and fructose molecules [11]. The process of heating the composites between ZSM-5 and the sucrose derivative in stages and then followed by the carbonization process at a temperature of 900 °C have the possibilities of polymerization to occur and replicate a huge amount of sucrose derivatives inside the pore template.

Impregnating Ni to the ZMC carbon with the concentration of each 5, 15 and 25% in overall do not show the peaks which can be clearly identified as characterized peaks of NiO. As it is known, typical diffraction peaks of NiO can be identified at an angle of 2θ = 37.4°, 43.3° and 62.8° (JCPDS, No.44-1159). These characterized peaks which could not be seen are possible because they were covered by the noise coming from the amorphous carbon which acted as a support.

Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX) Scanning

The micrograph of the synthesized mesoporous ZSM-5 is shown in Fig. 3, whilst for the ZMC carbon can be seen in Fig. 4. The ratio of the synthesized ZSM-5 solids morphology compared with the molar ratio is CTABr/Si = 0.385, which took form in the shape of stacked piles (agglomerated) cubical particles.

The SEM results of the ZMC carbon in Fig. 4 show the morphology in the shape of amorphous carbon clusters which could not perfectly replicate the shape of the ZMS-5 mesoporous template. SEM micrograph showed that the porous carbon material could be prepared by using a ZSM-5 mesoporous template. The EDX spectrum data in Table 1 showed the elements that were found in Ni/ZMC-5, Ni/ZMC-15, and Ni/ZMC-25 carbons. All three of the carbon samples with the different mass ratio of Ni/ZMC all contained the main elements which were C, O, Al, and Ni.

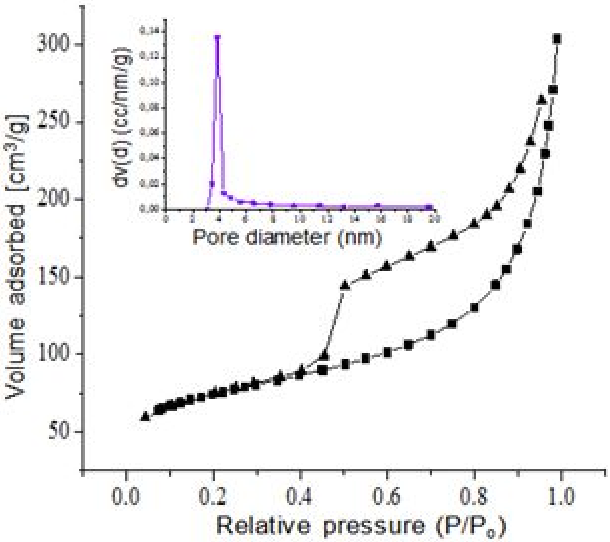

Fig 5. N_2 adsorption-desorption isotherms for mesoporous ZSM-5 (adsorption ■, desorption ▲) and BJH pore size distribution (inset)

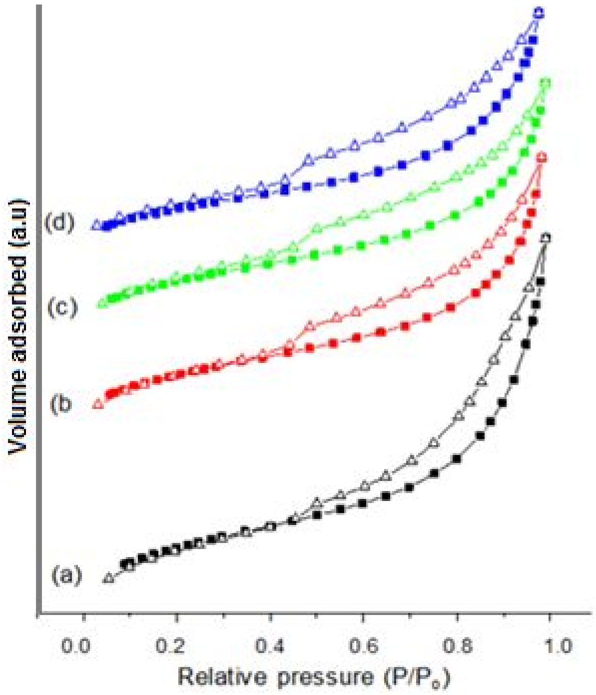

Fig 6. N_2 adsorption-desorption isotherms of (a) ZMC carbon, (b) Ni/ZMC-5, (c) Ni/ZMC-15 and (d) Ni/ZMC-25. (adsorption ■, desorption Δ)

Isothermal Adsorption–Desorption of Nitrogen

The N_2 isothermal adsorption-desorption patterns of ZSM-5 samples are shown in Fig. 5. According to Fig. 5, there was a high level of nitrogen being retrieved during the low partial pressure and there was an existence of a loop hysteresis above P/P_0 of around 0.45 [14-15]. According to IUPAC, the presence of a loop hysteresis at a pressure of $P/P_0 < 1$ is a classification of type IV isothermal adsorption-desorption of nitrogen and a characteristic of a type of a mesoporous material. The specific surface area measurement of a synthesized ZSM-5 resulted in a value of 246.23 m^2/g and a pore volume of 0.39 cc/g. On the other hand, the measurement of the pore diameter by using the BJH method resulted in a pore diameter of 3.85 nm.

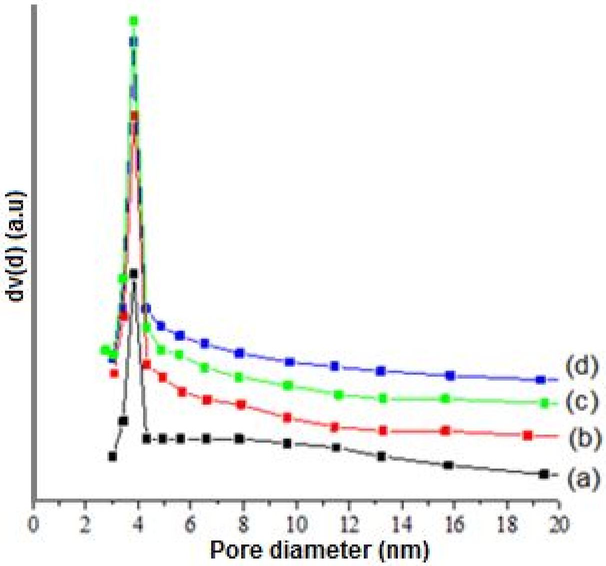

Fig 7. BJH pore size distribution of (a) ZMC carbon, (b) Ni/ZMC-5, (c) Ni/ZMC-15 and (d) Ni/ZMC-25

The N_2 adsorption-desorption isothermal graph of the ZMC carbon samples before and after they were impregnated with Ni is shown in Fig. 6. On the whole, the solids showed the same isothermal pattern, which was type IV with a loop hysteresis at $P/P_0 > 0.45$, which is a typical loop hysteresis for mesoporous solids. The measured value of the surface area (S_{BET}) for ZMC carbon is 910,46 m^2/g, whilst for Ni/ZMC-5, Ni/ZMC-15 and Ni/ZMV-25 respectively are 833.85, 737.08 and 563.97 m^2/g. Overall the samples have a uniform distribution of pore sizes which were measured by using the BJH method with the average pore diameter of 3.8 nm (Fig. 7). The ZMC carbon before it was impregnated with Ni had larger N_2 gas adsorption capacity and loop hysteresis shape compared to when the ZMC carbon was already impregnated with Ni on its supporting surface. The width of the loop hysteresis on the ZMC carbon before it was being impregnated indicated that there was an increase in the proportion or the amount of mesopores. The larger the Ni loading on the ZMC carbon, the specific surface area of the ZMC carbon material decreases.

Table 2. Specific surface area, pore volume and H_2 uptake on all the carbon samples

Materials	S_{BET} (m^2/g)	Pore Volume (cm^3/g)	H_2 Uptake (% weight)
ZMC	910.458	0.713	2.124
Ni/ZMC-5	833.853	0.602	0.331
Ni/ZMC-15	737.075	0.544	0.633
Ni/ZMC-25	563.973	0.497	0.649

The Hydrogen Uptake Test

Table 2 shows the H_2 gas adsorption capacity data at ambient condition for all the carbon samples. The ability of ZMC carbon to uptake H_2 experimentally gave a value of 2.18% of mass, whilst according to the calculations, the value that was found was 2.07% of mass at a low temperature condition (22 Kelvin or 1 bar). According to Ströbel [16], determining the adsorption capacity (m_{ads}) of H_2 gas at low temperature can be calculated based on the value of the specific surface area (S*spe*) of the carbon with the following equation:

$$m_{ads} \approx \text{Sspe} \times 2.27 \times 10.3\% \text{ weight}$$

The uptake test for H_2 gas for Ni/ZMC-5, Ni/ZMC-15 and Ni/ZMC-25 each respectively gave a result of 0.36, 0.63 and 0.65% of the mass. The more Ni being loaded on ZMC carbon, the more effect it will have towards the adsorption capacity of the H_2 gas. These results matched with the previous research being done about the effects of loading Ni towards the H_2 gas adsorption capacity of a mesoporous carbon material (Ni/OMC), in which each used an SBA-15 template and a Phloroglucinol/F127 template [2,7-8].

Besides from affecting its adsorption ability of H_2 gas, the effects of loading Ni yielded in longer time rate in order to be able to undergo the process of adsorption when compared to a pure ZMC carbon. During the first minute of the H_2 gas adsorption process, by observing the adsorption speed pattern of a pure ZMC carbon without Ni, it was able to adsorb hydrogen gas faster as compared to when carbon was already being impregnated with Ni. This condition aroused because the adsorption process of a H_2 gas of a pure ZMC carbon happened without passing through the stage of breaking down H_2 molecules first, thus the spillover effect of Ni on the Ni/ZMC-5, Ni/ZMC-15 and Ni/ZMC-25 carbon caused parts of the H_2 molecules to be broken down first by the Ni metal, turning it into an H atom before it was being diffused or spread out on the support [17-18]. The spillover effect caused the bonds between the hydrogen atoms (H-H) to be unstable, thus the H-H bonds were easily broken down and resulted in H atom alone. The H atoms fused together with the carbon by entering the carbon via its pores in larger quantities than the H_2 molecule, hence this resulted in a larger hydrogen storing capacity on the carbon.

CONCLUSION

Carbon with a mesoporous ZSM-5 template (ZMC carbon) and impregnated with Ni at a different level of concentrations (5, 15 and 25% of weight) was successfully synthesized. The characterization of ZMC carbon by using the XRD powder showed the diffraction pattern of amorphous carbon which had the type of graphite carbon with random morphology. The isothermal results of N_2 adsorption showed that the larger the Ni loading on the ZMC carbon support, the smaller the specific surface area of a ZMC carbon material. The pore size distribution that was calculated by using the BJH method for all the samples, was found as large as around 3.8 nm.

The more Ni loading given on the carbon with mesoporous ZSM-5 template caused the surface area and the pore volume to decrease significantly, while the adsorption capacity of H_2 gas increased due to the spillover effect of Ni transition metal.

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