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Synthesis of Na-A and/or Na-X zeolite/porous carbon composites from carbonized rice husk

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ABSTRACT

Na-A and/or Na-X zeolite/porous carbon composites were prepared under hydrothermal conditions by NaOH dissolution of silica first from carbonized rice husk followed by addition of $NaAlO_2$ and in situ crystallization of zeolites i.e., using a two-step process. When a one-step process was used, both Na-A and Na-X zeolites crystallized on the surface of carbon. Na-A or Na-X zeolite crystals were prepared on the porous carbonized rice husk at 90 °C for 2–6 h by changing the SiO_2/Al_2O_3, H_2O/Na_2O and Na_2O/SiO_2 molar ratios of precursors in the two-step process. The surface area and NH_4^+-cation exchange capacity (CEC) of Na-A zeolite/porous carbon were found to be 171 m^2/g and 506 meq/100 g, respectively, while those of Na-X zeolite/porous carbon composites were 676 m^2/g and 317 meq/100 g, respectively. Na-A and Na-X zeolites are well-known microporous and hydrophilic materials while carbonized rice husk was found to be mesoporous (pores of ~3.9 nm) and hydrophobic. These hybrid microporous–mesoporous and hydrophilic–hydrophobic composites are expected to be useful for decontamination of metal cations as well as organic contaminants simultaneously.

1. Introduction

Rice husk is the milling byproduct of rice and one of the important byproducts of biomass available globally [1,2]. In Japan, around 10% of rice husk is used in the form of porous carbonized rice husk as a soil improvement material, for example, for nursery of rice plants. Carbonized rice husk is commercially produced from rice husk at 500–700 °C in a rotary kiln and it has a porous carbonaceous structure due to the decomposition of cellulose and lignin and evaporation of moisture from raw rice husk during heat treatment. In our previous study [3], we determined the surface area and pore volume of carbonized rice husk treated at 700 °C and they were found to be 121 m^2/g and 0.102 cc/g, respectively, and these values were increased to 224 m^2/g and 0.352 cc/g, respectively, by the dissolution of silica from carbonized rice husk. Furthermore, we prepared ZSM-5/porous carbonized rice husk at 140–160 °C using carbonized rice husk, NaOH, tetrapropylammonium bromide, and deionized water by hydrothermal reaction [3]. The molar ratio of SiO_2:Al_2O_3 of ZSM-5 zeolite prepared at 150 °C was found to be 446 because the content of Al_2O_3 in raw rice husk was only 0.14 wt%. Thus highly siliceous ZSM-5 zeolite/porous carbon composites could be easily prepared from carbonized rice husk by hydrothermal reaction. However, NH_4^+-cation exchange capacity (CEC) of ZSM-5 zeolite was very low and was much lower than that of low silica containing Na-A or Na-Y zeolites. Rice husk ash without carbon was widely used as raw material for the synthesis of some zeolites [4–6] and fabrication of activated carbon and porous SiO_2/C composite from rice husks was previously reported [7,8]. However, only a few studies were conducted with carbonized rice husk, i.e., rice husk transformed to carbon to make composites [3,9]. The objective of the present study was to prepare Na-A and/or Na-X zeolite/porous carbon composites from the carbonized rice husk by in situ crystallization of zeolites using hydrothermal reaction. Activated carbons are commonly used to decontaminate organic pollutants while zeolites are used to decontaminate metal pollutants from solutions. Our objective was to make porous zeolite–carbon composites so that one material could potentially be used for decontamination of both organic and metal ion pollutants. We also investigated some porous properties and CEC of the zeolite/porous carbon composites to determine whether this in situ zeolite crystallization technique is effective for making the above composites from carbonized rice husk.

2. Experimental procedure

2.1. Carbonization of rice husk and dissolution of silica from carbonized rice husk

The chemical composition of starting rice husk was reported previously [3]. Rice husk was carbonized at 600, 800 and 1000 °C for 1 h in N_2 gas flow (100 ml/min). Heating rate was 120 °C/h. The

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content of silica in carbonized rice husk was 49.6–51.8 wt% after carbonization at 600–1000 °C. The dissolution rate of silica from the rice husk (0.5 g) carbonized at 600 and 1000 °C was investigated at 90 °C in 2N-NaOH (50 ml) using hydrothermal treatment. After hydrothermal treatment, the sample was washed with hot water, and then dried at 100 °C for 12 h. The weight loss of silica from carbonized rice husk was calculated.

2.2. Synthesis of zeolite/porous carbon composite

The starting materials used in the synthesis of Na-A and Na-X zeolites were rice husk carbonized at 600 °C, sodium aluminate (Al/NaOH = 0.78, Wako Chemicals Co., Japan), sodium hydroxide (Wako Chemicals Co., Japan) and pure water. Synthesis of Na-A zeolite was done using molar ratios of $SiO_2/Al_2O_3 = 2$, $H_2O/Na_2O = 40$ and $Na_2O/SiO_2 = 2.7$ based on a previous study [10–13], and synthesis of Na-X zeolite was done using molar ratios of $SiO_2/Al_2O_3 = 1.9$, $H_2O/Na_2O = 33$ and $Na_2O/SiO_2 = 3.3$ as reported previously by others [14]. In these experiments, 1.0 g of carbonized rice husk was used along with other chemicals in their appropriate quantities. For example, a mixture of Na-A and Na-X zeolite/porous carbon composite was synthesized from carbonized rice husk (1 g), NaOH (1.37 g), sodium aluminate (0.726 g), and deionized water (15.9 g) in the one-step process as follows: the mixture was mixed thoroughly and treated at 90 °C for 2–6 h in Teflon™-lined stainless steel vessels of 50 ml capacity without agitation. Na-A or Na-X zeolite/porous carbon composites were prepared under hydrothermal conditions by NaOH dissolution of silica first from carbonized rice husk followed by addition of $NaAlO_2$ and in situ crystallization of zeolites, i.e., using the two-step process.

2.3. Characterization of zeolite/porous carbon composites

Carbonized rice husk, zeolites and composites were characterized by powder X-ray diffractometry (XRD; Model X'Pert-MRD, PANalytical Co. Japan) with Cu*K*α radiation and a scanning electron microscope (FE-SEM; Model 6700FS, JEOL, Japan). The BET surface areas were measured using adsorption–desorption isotherms with nitrogen gas as the adsorbent (Model Autosorb 1, Quantachrome Co, Ronkonkoma, NY, USA). Pore-size distributions were calculated using desorption branch by the BJH method. Before the adsorption measurement, the samples were degassed at 200 °C for 2 h under 6.7 Pa. The NH_4^+-CECs of some products were measured by the modified Schöerrenberg method [15]. The charge balancing cations in the samples were replaced by NH_4^+ by equilibrating with 1 M ammonium acetate solution for 1 h. This process was repeated two more times, yielding a total exchanging time of 3 h at 20 °C. The sample was then washed well with 80% ethanol solution to remove excess salts. The NH_4^+ was then replaced by Na^+ using 10% NaCl solution for 1 h. This process was repeated twice. Finally NH_4^+ in the solution was analyzed by the method of Koyama et al. [16] to determine the CEC of the sample.

3. Results and discussion

3.1. The effect of heat treatment on the carbonization of rice husk and the dissolution of silica from carbonized rice husk

To investigate the optimum temperature for carbonization of rice husk, it was treated at 600–1000 °C for 1 h in N_2. Below 600 °C, the carbonization was incomplete and a brown tar substance was partially included in the resultant carbon made from rice husk (referred to hereafter as rice husk carbon or carbonized rice husk). With a heat treatment temperature of 600 °C or more, almost all tar substance was eliminated from the rice husk carbon. Fig. 1 shows XRD patterns of carbonized rice husk at 600, 800, and 1000 °C. The broad reflections in the range of 17–30° 2θ imply amorphous nature of both carbon and silica. With increasing heat treatment, however, the crystallization of silica in rice husk led to a weak α-cristobalite peak (2θ = 21.9°) at 1000 °C.

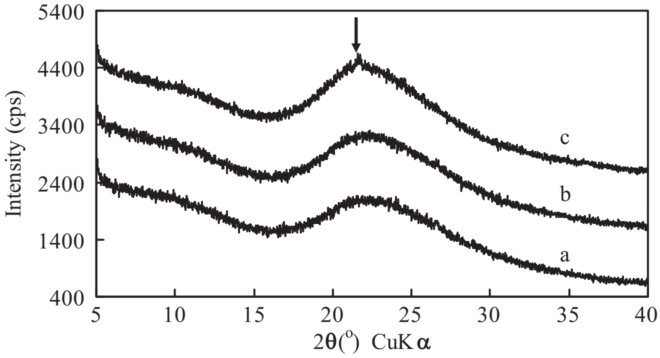

Fig. 1. XRD patterns of the rice husks carbonized at 600 (a), 800 (b), and 1000 °C (c) for 1 h (arrow: 2θ = 21.9°, α-cristobalite).

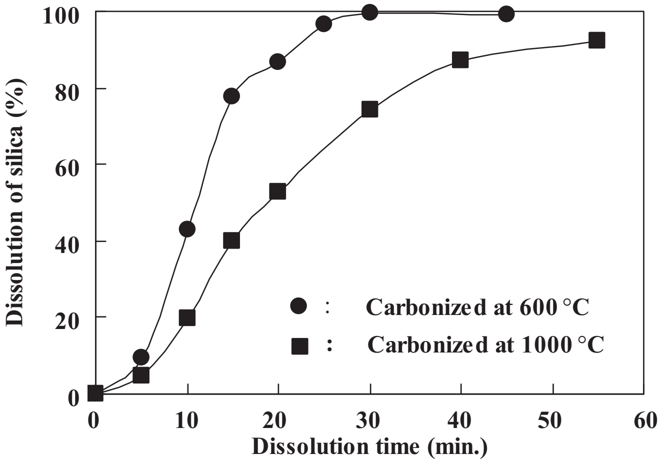

Fig. 2. Dissolution rate of silica from the rice husk carbonized at 600 and 1000 °C for 1 h in N_2.

Fig. 2 shows the effect of heat treatment on the dissolution of silica from the rice husk carbon treated at 600 and 1000 °C. The rice husk carbon samples were treated in 2N-NaOH at 90 °C for 60 min. The dissolved amount was calculated from the weight loss of the rice husk carbon samples. The dissolved amount of silica from the sample treated at 600 °C reached around 100% (Fig. 2) after 30 min. However, the dissolved amount of silica from the sample carbonized at 1000 °C was in the range of 95–96% (Fig. 2) after 55 min. The dissolution of silica from rice husk carbon treated at 1000 °C was suppressed due to the formation of α-cristobalite (Fig. 1). Because the dissolution of silica is faster from rice husk sample carbonized at 600 °C compared to the sample carbonized at 1000 °C (Fig. 1), the 600 °C sample was selected for further studies of zeolite syntheses to make composites (see below).

3.2. The formation of Na-A and/or Na-X zeolite from carbonized rice husk

The rice husk carbon treated at 600 °C was used as the Si precursor for synthesis of zeolites. The chemical composition of

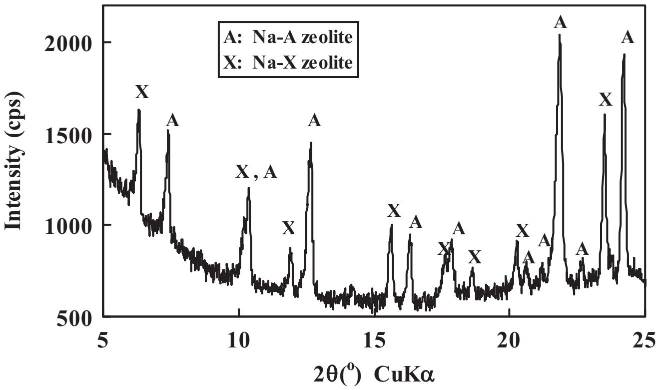

Fig. 3. XRD pattern of zeolite/porous carbon composite showing both Na-A and Na-X type zeolites formed on the carbonized rice husk treated at 90 °C for 8 h using direct (one-step) hydrothermal reaction.

raw materials used was $SiO_2/Al_2O_3 = 2.0$, $H_2O/Na_2O = 40$ and $Na_2O/SiO_2 = 2.7$ based on some previous reports [10–13] for the formation of Na-A zeolite. Fig. 3 shows XRD pattern of the zeolite/porous carbon composite formed at 90 °C for 8 h from the rice husk carbon. By the one-step reaction of rice husk carbon with $NaAlO_2$, the dissolution of silica occurred which led to the crystallization of both zeolite A and X at the same time as the necessary Si was presumed to be available in the liquid during this direct reaction. Therefore, the crystal growth of Na-A and Na-X zeolite simultaneously occurred on the carbonized rice husk. The present results are supported by previous studies which showed that Na-A [LTA: $Na_{96}Al_{96}Si_{96}O_{384}(H_2O)_{216}$] and Na-X [FAU: $Na_{88}Al_{88}Si_{104}O_{384}(H_2O)_{220}$] type zeolites [17] could be prepared by a direct (one-step) hydrothermal reaction, i.e., without prior dissolution of silica in NaOH.

For the selective synthesis of zeolite/carbon composite with either Na-A or Na-X, an aging treatment is found here to be essential, i.e., it is very important to dissolve SiO_2 first from the carbonized rice husk before the reaction with sodium aluminate. For the synthesis of pure Na-A zeolite, the two-step process was used: silica in the carbonized rice husk was dissolved in NaOH solution at 90 °C for 1 h in advance (1st step reaction), and then treated with sodium aluminate at 90 °C for 1–3 h (2nd step reaction). The chemical composition used for Na-A synthesis was $SiO_2/Al_2O_3 = 2.0$, $H_2O/Na_2O = 40$ and $Na_2O/SiO_2 = 2.7$. Fig. 4 shows the XRD pattern of the product formed on the carbon rice husk. By using two-step reaction, only Na-A zeolite was formed after 2 and 3 h treatments (Figs. 4b and c). As for the synthesis of Na-X zeolite, again the two-step reaction was used at 90 °C. The chemical composition used for the Na-X zeolite synthesis, however, was $SiO_2/Al_2O_3 = 1.9$, $H_2O/Na_2O = 33$ and $Na_2O/SiO_2 = 3.3$. Fig. 4 also shows the XRD patterns of the products formed at 90 °C for 3–6 h. In this case, the formation of poorly crystallized Na-X zeolite could be confirmed after 4 h treatment (Fig. 4e) while well crystallized Na-X zeolite was formed after 6 h (Fig. 4f). Compared with the formation of Na-A zeolite, longer reaction time was needed to prepare Na-X zeolite. Fig. 5 shows the morphology of carbonized rice husk (Fig. 5a), carbonized rice husk after silica removal with NaOH (Fig. 5b), Na-X zeolite/porous carbon composite (Fig. 5c) and Na-A zeolite/porous carbon composite (Fig. 5d). Figs. 5c and d clearly show the deposition of zeolites on the surface of carbon after treatment at 90 °C for 3–6 h. Fig. 5 also shows the morphology of Na-X zeolite/porous carbon composite (Fig. 5e) and Na-A zeolite/porous carbon composite (Fig. 5f) at higher magnification. Both types of zeolite crystals showed a chamfered-edge shape and the crystal size was 1–4 μm (Figs. 5e and f).

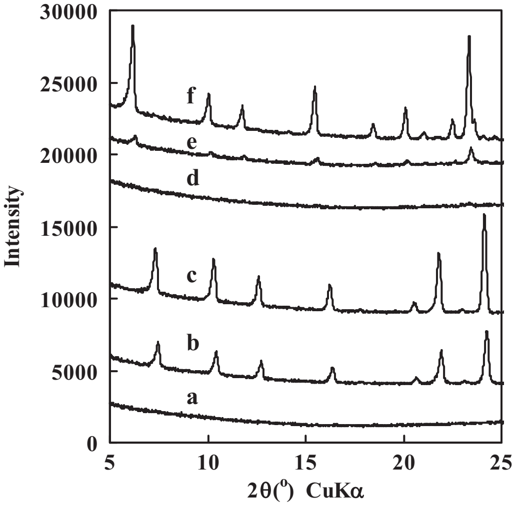

Fig. 4. XRD patterns of Na-A type zeolite/carbonized rice husk composites prepared at 90 °C using a two-step hydrothermal reaction for 1 (a), 2 (b), and 3 h (c) and XRD patterns of Na-X type zeolite/carbonized rice husk composites prepared at 90 °C for 3 (d), 4 (e), and 6 h (f) using a two-step hydrothermal reaction.

3.3. Porous and ion-exchange properties of zeolite/porous carbon composites

Table 1 shows the surface area and NH_4^+-CEC of various synthetic samples. The surface area and NH_4^+-CEC of the carbonized rice husk prepared at 600 °C for 1 h were found to be 159 m^2/g and 27 meq/100 g, respectively. Carbonized rice husk showed a sharp pore-size distribution at ~3.9 nm (Fig. 6). By dissolving all silica from the carbonized rice husk in 2N-NaOH at 90 °C for 1 h, surface area increased to 486 m^2/g due to the formation of more mesopores as can be seen with a strong hump in the 5–20 nm range (Fig. 6b) while NH_4^+-CEC increased to 44 meq/100 g after silica dissolution. From this result it could be seen that porous carbon rice husk with high surface area could be prepared by the dissolution of silica. The increase in NH_4^+-CEC from 27 to 44 meq/100 g can be attributed to increase in carbon content as silica was removed by dissolution.

Surface area and NH_4^+-CEC of Na-X zeolite/carbonized rice husk prepared at 90 °C for 6 h were 676 m^2/g and 317 meq/100 g, respectively (Table 1). Surface area and NH_4^+-CEC of Na-A zeolite/carbonized rice husk prepared at 90 °C for 3 h were 171 m^2/g and 506 meq/100 g, respectively (Table 1). The surface area and CEC results for Na-X and Na-A zeolite powders which were deposited on the bottom of the vessel, i.e., not on rice husk carbon and for a commercial Na-A zeolite (4A, TSC type, Mizusawa Chemical Co., Japan) are shown in Table 1 for comparison. NH_4^+-CEC of the carbonized rice husk was dramatically increased by the hydrothermal deposition of Na-A and Na-X zeolite on the carbon forming zeolite/carbon composites. The Na-A/carbon composite and Na-X zeolite/carbon composite are composed of about 85% and 65% by weight of A and X zeolites, respectively, based on calculation of CEC values of the composites. Surface areas of the synthesized and commercial Na-A zeolite were considerably lower than that of Na-X zeolite, as expected. This is because nitrogen molecule (molecule diameter: 0.375–0.378 nm) cannot enter into Na-A zeolite due to its small pores, while Na-X zeolite has larger pores which let nitrogen molecules go in and that is why the surface area is very high in the Na-X zeolite. The very low surface area of zeolite A deposited on the bottom of the vessel is a result of its large crystal size, which is on the order of about 5 μm

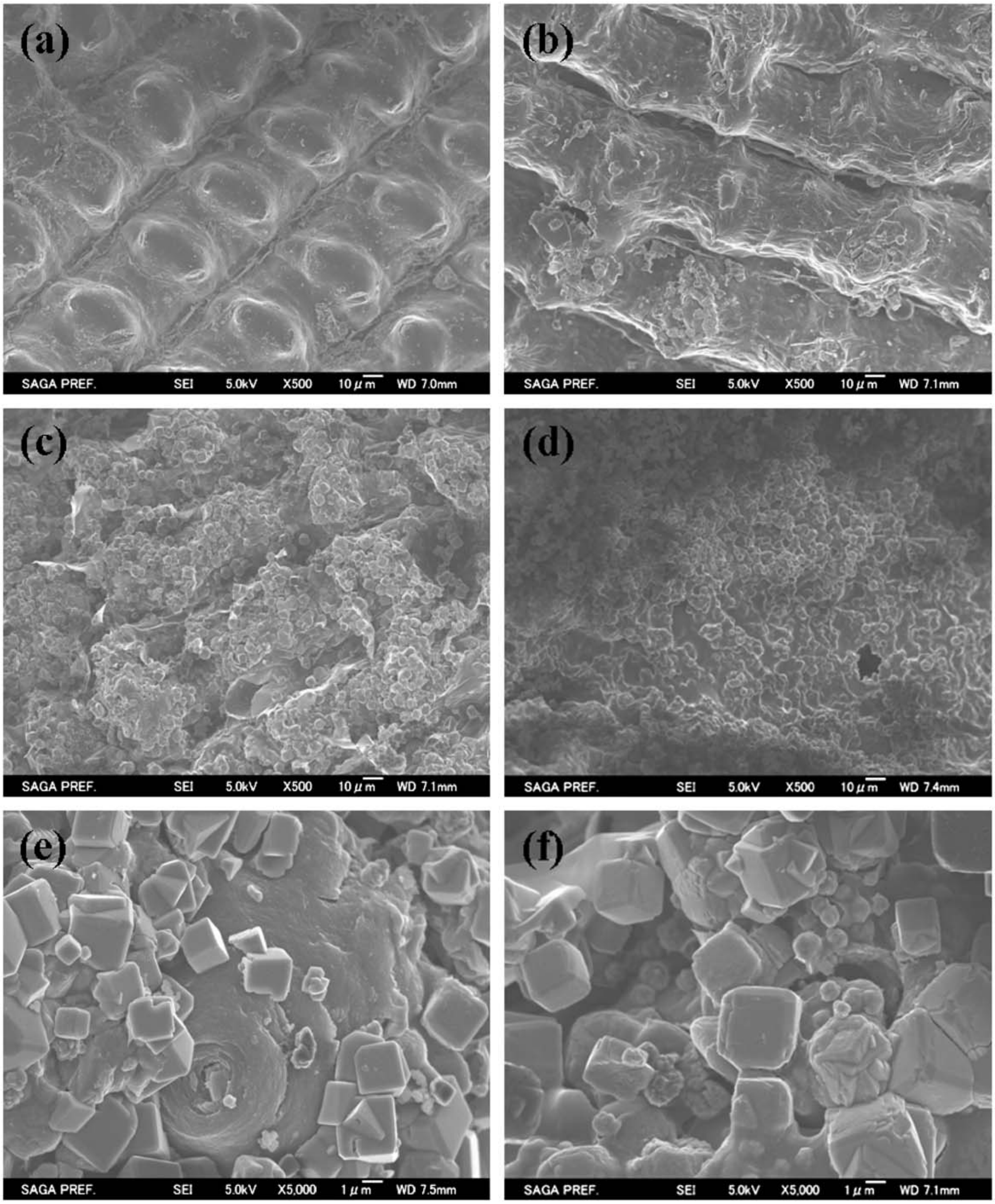

Fig. 5. Morphologies of carbonized rice husk and its composites: (a) carbonized rice husk, (b) carbonized rice husk without silica, i.e., treated with NaOH, (c) Na-X zeolite on carbonized rice husk obtained after treatment at 90 °C for 6 h, (d) Na-A zeolite on carbonized rice husk obtained after treatment at 90 °C for 3 h, (e) Na-X zeolite on carbonized rice husk obtained after treatment at 90 °C for 6 h at higher magnification and (f) Na-A zeolite on carbonized rice husk obtained after treatment at 90 °C for 3 h at higher magnification.

(figure not shown). These results show that Na-X zeolite/carbonized rice husk composite with high surface area and NH_4^+-CEC could be hydrothermally synthesized at 90 °C after treatment for 6 h. Figs. 6c and d show the pore-size distribution of the zeolite/porous rice husk carbon composites and these pore-size distributions do not change significantly after zeolite deposition which suggests that the zeolites are deposited primarily on carbon surface with little or no deposition in the mesopores of carbonized rice husk. Thus, these zeolite/porous rice husk carbon composites were composed of micropores in the zeolites and mesopores in the carbon (Fig. 6).

Nitrogen adsorption–desorption isotherms mainly showed mesoporous nature with large hysteresis for carbonized rice husk before and after silica dissolution and for Na-A zeolite/carbonized rice husk composite. However, when zeolite X was present in the composite, it showed type I adsorption with small hysteresis at high P/P_o, as expected, because of nitrogen accommodating microporosity of zeolite X (figure not shown).

Table 1
Surface area and NH$_4^+$–CEC properties of different materials.

Samples	Reaction	Surface area (m^2/g)	CEC (meq/100 g)
Carbonized rice husk[a]	–	159	27
Carbonized rice husk without silica[b]	90 °C–1 h	486	44
Na-X zeolite/carbonized rice husk	90 °C–6 h	676	317
Na-A zeolite/carbonized rice husk	90 °C–3 h	171	506
Na-X zeolite[c]	90 °C–6 h	553	461
Na-A zeolite[c]	90 °C–3 h	3	585
Commercial Na-A zeolite	–	8	579

[a] Carbonized at 600 °C for 1 h.
[b] Treated with 2N-NaOH.
[c] Zeolite powder deposited in the vessel.

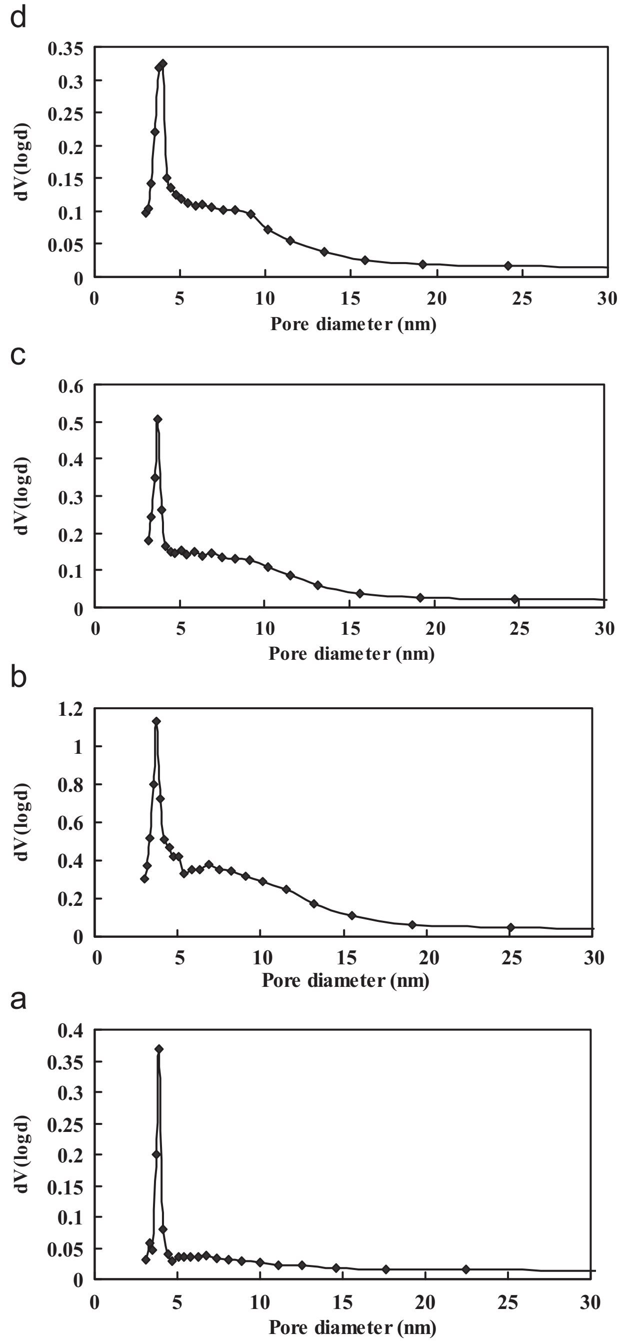

Fig. 6. Pore size distribution of samples calculated by BJH method (desorption): (a) carbonized rice husk, (b) carbonized rice husk after dissolution of silica with NaOH, (c) Na-A/carbonized rice husk composite, and (d) Na-X/carbonized rice husk composite.

4. Conclusions

Synthesis of Na-A and Na-X zeolite/porous carbon composites was achieved using rice husk carbonized at 600 °C, NaOH solution and sodium aluminate by hydrothermal treatment at 90 °C in one-step process. Using two-step process consisting of selective dissolution of silica first from the carbonized rice husk followed by reaction with sodium aluminate, synthesis of Na-A zeolite/porous carbon composite or Na-X zeolite/porous carbon composite could be achieved at 90 °C. Surface area and NH$_4^+$-CEC of the carbonized rice husk/zeolite composites could be optimized by synthesizing Na-A and Na-X zeolite with carbonized rice husk.

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