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Applying Hexagonal Nanostructured Zeolite Particles for Acetone Removal

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ABSTRACT

This study examines the performance of a new adsorbent, hexagonal nanostructured zeolite particles (HNZP) for acetone adsorption and compares the results with that of commercial mobil synthetic zeolite-5 (ZSM-5) type zeolite. The HNZP is a pure siliceous adsorbent with different values of pore diameter and surface area being adjustable by the manufacturing condition. The results indicate that a slight increase in the average pore diameter (d) of HNZP from 2 to 2.5 nm leads to an increase in the acetone adsorption capacity, although its surface area is decreased, in which case (d = 2.5 nm) the adsorption capacity of fresh HNZP is better than that of ZSM-5 zeolite. Even for the fresh HNZP (d = 2 nm) of which the adsorption capacity is less than that of the ZSM-5 zeolite at relative humidity (RH) of 0%, its adsorption capacity is not deteriorated after repeated regeneration, but the adsorption capacity of regenerated ZSM-5 zeolite decays markedly. Thus, after only one regeneration, the adsorption capacity of HNZP (d = 2 nm) becomes better than that of the ZSM-5 zeolite. The decrease in the adsorption capacity of regenerated ZSM-5 zeolite might be because of its aluminum content that catalyzes the acetone into coke and, thus, blocks the adsorption sites. Furthermore, result on the moisture effect shows that because the pure siliceous HNZP was more hydrophobic than the ZSM-5 zeolite, the acetone adsorption efficiency of fresh HNZP (d = 2 nm) is better than that of ZSM-5 zeolite at RH = 50%.

IMPLICATIONS

Nanostructured (also known as mesostructured) materials have advantages of large surface area, controllable pore size, uniform pore distribution, hydrothermal stability, and hydrophobic characteristics. However, the conventional hydrothermal method for manufacturing nanostructured materials is complex and time-consuming, thus limiting its applications. Recently, novel materials of HNZP could be successfully synthesized within several sec using an Association of Academies of Sciences in Asia process. This study synthesized HNZP adsorbents and showed that they have better adsorption/desorption and hydrophobic characteristics as compared with the commercially available ZSM-5 zeolite.

INTRODUCTION

Zeolite concentrator was one of the volatile organic compound (VOC) abatement devices most commonly used by semiconductor manufacturers. The use of hydrophobic zeolite, especially zeolite-5 (ZSM-5) type zeolite, as the solvent adsorbent in a concentrator was efficient for VOC adsorption for a wide range of operation characteristics.[1–4] Additional advantages in using zeolite include the relative lack of requirements regarding the control of relative humidity (RH), fire protection, and the sacrificial adsorbent bed. However, the adsorption capacity of zeolite could be reduced through repeated adsorption/desorption process. This occurs frequently in semiconductor and optoelectronic factories using zeolite concentrators as VOC abatement devices. Besides, the conventional method for manufacturing zeolite is time consuming. It usually requires 3 days to synthesize the zeolite adsorbent by a conventional hydrothermal method. Therefore, additional improvement on zeolite-based adsorbent is necessary.

Recently the novel materials of hexagonal nanostructured zeolite particles (HNZP) could be synthesized within 8 sec using an AASA process.[5] Both synthesizing time and procedure of HNZP were much less than those of traditional hydrothermal method for producing nano-structured material. However, the research on the HNZP made by the Association of Academies of Sciences in Asia process has been focused on the material manufacturing process, such as synthesizing well-structured materials[5,6] or nano-composite mixed with metals.[7,8] Limited information is available in the literature on the applicability of

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HNZP as a VOC adsorbent. This study intends to investigate the adsorption performance of HNZP on the removal of acetone, which is one of the most common VOCs emitted from semiconductor industries. The performance of the HNZP at different values of surface area and pore size was tested, and the results were compared with that of the commercial ZSM-5 zeolite in terms of repeated adsorption/desorption under conditions of with and without moisture.

EXPERIMENTS

The compositions and molar ratio of reagents for synthesizing HNZP were tetraethoxysilane (TEOS):cetyltrimethylammonium bromide (CTAB):ethanol:water:hydrochloric acid = 1:0.1:5:20:0.004. The synthesizing process of HNZP was referred to Lu et al.[5] The commercial ZSM-5 zeolite was obtained from Advchem Laboratories for comparison purpose. The average pore diameter and the average pore size of the adsorbents were determined using the Brunauer-Emmett-Teller (BET) equation with the Micromeritics accelerated surface area and porosimetry (ASAP) analyzer, ASAP 2020. The chemical properties of the adsorbents were analyzed by inductively coupled plasma–atomic emission spectrometer (ICP-atomic emissions spectroscopy, Jarrell-Ash ICAP 9000) and powder X-ray diffraction (XRD, Rigaku D/MAX-B), respectively.

Figure 1 shows a simplified diagram of the acetone adsorption system. The inlet flow was generated from the air cylinder and then passed through a silica gel air dryer and a HEPA filter. The acetone and the moisture in the flow were obtained by passing the air through the midget impingers filled with liquid acetone and di-water, respectively. Mass flow controllers (BROOK 5850E) were used to control the flow rates and concentrations of acetone, moisture, and dilution air.

A total of 0.3 ± 0.001 g of adsorbent was placed into the adsorption column (with i.d. of 2 cm and height of 0.4 cm) under thermostat condition for each experiment. Thus, the vol and the density of adsorption bed were 1.26 cm^3 and 0.24 g/cm^3, respectively. The adsorbate residence time was 0.08 sec as operated at inlet flow rate of 1000 cm^3/min in each adsorption experiment. The adsorption temperature was 45 °C, whereas the desorption temperature was 200 °C, referring to the temperatures in practical adsorption/desorption operation of a zeolite concentrator. The adsorption characteristics of acetone were conducted on the fresh and regenerated materials of both HNZP and ZSM-5 zeolite. Before adsorption experiments, all of the adsorbents were dried at 110 °C for 24 hr to remove humidity interference and then cooled down within a dry cabinet of 45 °C for 5 hr to achieve the temperature condition of adsorption experiments. After adsorption, the regenerated materials were then prepared by desorption of the saturated materials via 200 °C heating in 100 cm^3/min airflow for 24 hr.

The acetone concentrations of process flow before and after the adsorption system were measured using gas chromatography (GC)/flame-ionization detector (FID; China Gas Chromatograph 9800) to obtain the breakthrough curves of the adsorbents. The column used in the GC for analysis was Carbon Wax (2 m), and the temperatures of the injection point, FID, and oven were 100, 150, and 90 °C, respectively. The results shown in all of the figures were the average data of three repeated experiments. The SD of the repeated experiment was ~3% in terms of the acetone removal efficiency.

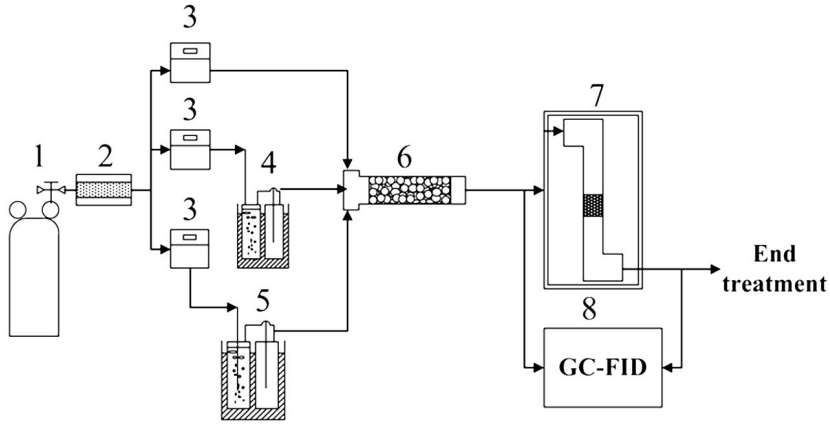

Figure 1. Schematic of the acetone adsorption system.

RESULTS AND DISCUSSION

Table 1 illustrates results on the material analyses of the adsorbents. The surface area of commercial ZSM-5 zeolite was 356 m^2/g, whereas those of HNZP synthesized at 450 and 550 °C were 750 and 872 m^2/g, respectively. The average pore size of commercial ZSM-5 zeolite was 2.7 nm, and those of HNZP synthesized at 450 and 550 °C

Table 1. Material analysis of the adsorbents.

Adsorbents	Surface Area (m^2/g)	Average Pore Size (nm)	Pore Structure	Si:Al Ratio
ZSM-5 zeolite	356	2.7	10-membered rings	48
HNZP synthesized at 450 °C	750	2.5	Two-dimensional hexagonal phase	Pure siliceous material
HNZP synthesized at 550 °C	872	2.0	Two-dimensional hexagonal phase	Pure siliceous material

were 2.5 and 2 nm, respectively. The surface area of the ZSM-5 zeolite was much smaller, but its average pore size was higher than those of the HNZP adsorbents. The pore structure of commercial ZSM-5 zeolite was comprised of 10-membered rings of perpendicular-cross pore channels. The XRD analysis showed that the pore arrangements of HNZP adsorbents synthesized at 550 and 450 °C were comprised of two-dimensional hexagonal phase, similar to the nanostructure of Mobile Crystalline Material (MCM-41).[5,6] Furthermore, the main components of commercial zeolite measured by ICP-atomic emissions spectroscopy were silica (Si) and aluminum (Al) with Si:Al molar ratio of 48, whereas the HNZP was composed of pure siliceous materials.

Figure 2a illustrates the acetone breakthrough curves of fresh HNZP and ZSM-5 zeolite adsorbents. The inlet conditions were flow rate of 1000 cm^3/min, acetone concentration of 1000 ppmv, and RH of 0%. As referred to in Table 1, the BET surface area of HNZP synthesized at 550 °C was 1.5 times of that of ZSM-5 zeolite, but the adsorption efficiency of fresh HNZP synthesized at 550 °C was still less than that of ZSM-5 zeolite as illustrated in Figure 2. This may be because the average pore diameter of HNZP was 0.7 nm less than that of zeolite. The smaller pore could restrain the diffusion of adsorbate in the pore channel because of Knudsen diffusion limitation.

By altering the synthesized temperature from 550 °C to 450 °C, the average pore size of HNZP was increased from 2 to 2.5 nm. But its surface area was slightly decreased from 872 to 750 m^2/g. As observed in Figures 2a and 2b, the HNZP synthesized at 450 °C had better adsorption efficiency and saturated adsorption than those of the commercial ZSM-5 zeolite adsorbent. Thus, the adsorption efficiency of the porous materials was affected by a slight increase in the pore size with a sacrifice in the surface area. Based on the breakthrough curves, the saturated adsorption capacities of fresh ZSM-5 zeolite, HNZP synthesized at 450 °C, and HNZP synthesized at 550 °C, were calculated to be 73.25, 82.53, and 68.91 mg/g sorbent, respectively, at adsorption temperature of 45 °C.

Although the fresh HNZP made at 550 °C had a smaller adsorption capacity than that of the fresh commercial ZSM-5 zeolite at RH of 0%, its performance could be better after repeated regeneration or at a higher RH. The results are demonstrated from Figure 3 to Figure 6.

Figures 3a to 3d compare the adsorption performance of adsorbents after repeated adsorption/regeneration processes. The HNZP synthesized at 550 °C and the commercial ZSM-5 zeolite were both regenerated once and 10 times, respectively, to evaluate their change in the adsorption capacity. Although the adsorption efficiency of fresh

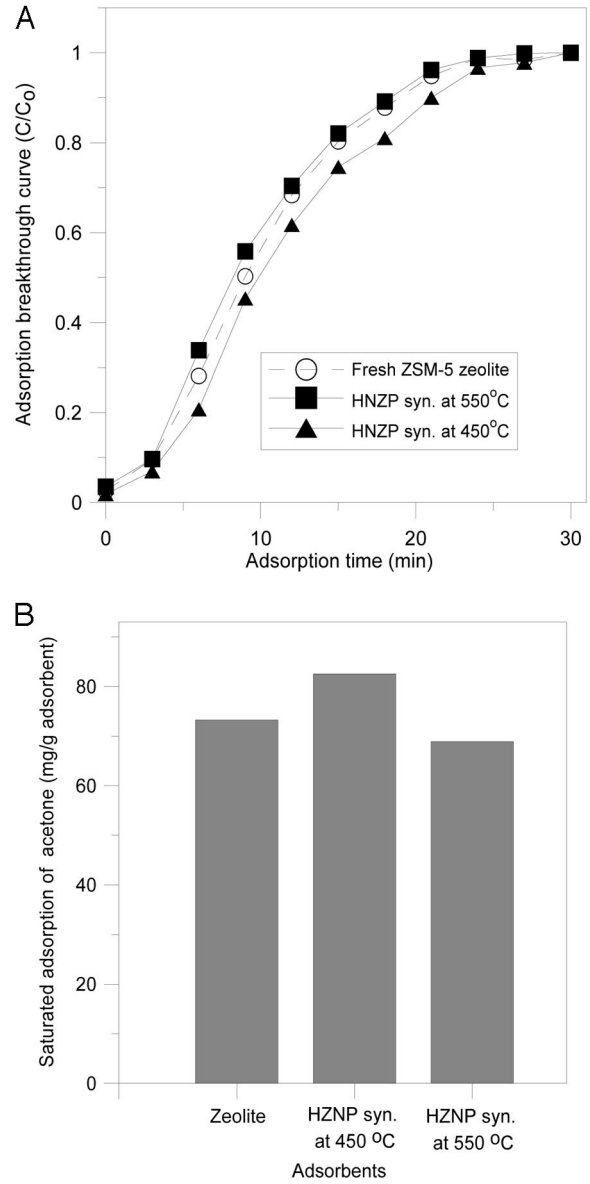

Figure 2. The adsorption performance of the commercial ZSM-5 zeolite adsorbent and the HNZP synthesized at 450 and 550 °C, respectively. (a) Adsorption breakthrough curve and (b) saturated adsorption capacity of acetone vapors.

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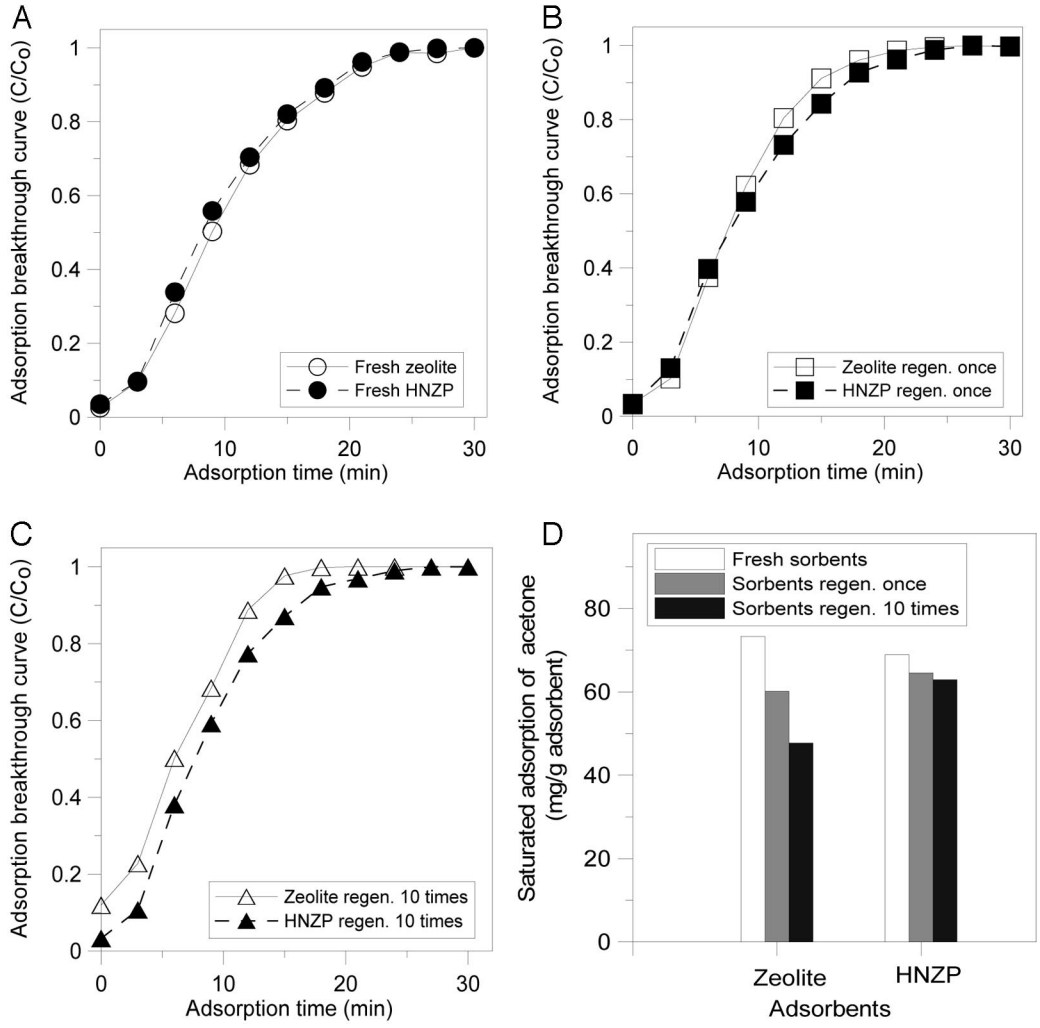

Figure 3. The adsorption performance of HNZP and the commercial ZSM-5 zeolite adsorbents after regeneration. (a), (b), and (c) Adsorption breakthrough curves of fresh zeolite, regenerated 1 and 10 times, respectively; and (d) saturated adsorption capacity of acetone vapors. The HNZP sorbent was synthesized at 550 °C.

HNZP synthesized at 550 °C was inferior to that of ZSM-5 zeolite, its adsorption efficiency after regeneration is comparatively superior. The adsorption efficiency of regenerated ZSM-5 zeolite gradually decreased as the number of regeneration increased. On the other hand, the adsorption efficiency of regenerated HNZP synthesized at 550 °C remained almost unchanged even after 10 regenerations. As illustrated in Figure 3d, the adsorption capacities of regenerated HNZP showed slight differences from the fresh adsorbent. However, the adsorption capacity of regenerated ZSM-5 zeolite after 10 regenerations was reduced to only 65% that of fresh one. Thus, the HNZP adsorbents showed superiority in antidecay for adsorbing acetone and could serve as a good adsorbent for repeated adsorption/desorption process.

The reduction in the adsorption capacity for the regenerated ZSM-5 zeolite could be explained by the analyzed results of the Fourier transform IR spectrometer (FTIR, Bruker Vector 22) and the elemental analyzer (Heraeus Vario EL-III) as illustrated in Figures 4a and 4b, respectively. For FTIR analysis, the samples were pressed into thin tablets of 0.01 g/cm^2, and the IR spectra of the tablets were obtained at 25 °C. It was observed from Figure 4a that the regenerated zeolite displayed coke band peaks at around 1585 cm^{-1}.[9] And the peak intensity increases as the number of regeneration increased from 1 to 10. This indicates the possible presence of coke in the zeolite. The formation of coke may be because of the aluminum content in the ZSM-5 zeolite that catalyzed the adsorbed acetone vapors into coke during the regenerating process. The presence of coke was also observed with the color change from the original adsorbent's white color for fresh ZSM-5 zeolite to the coke's dark brown color for regenerated zeolite. However, no obvious coke band was observed by the FTIR results shown in Figure 4a for the regenerated HNZP materials even after 10 regenerations. Furthermore, no obvious change in color was observed between the fresh and the regenerated HNZP adsorbents.

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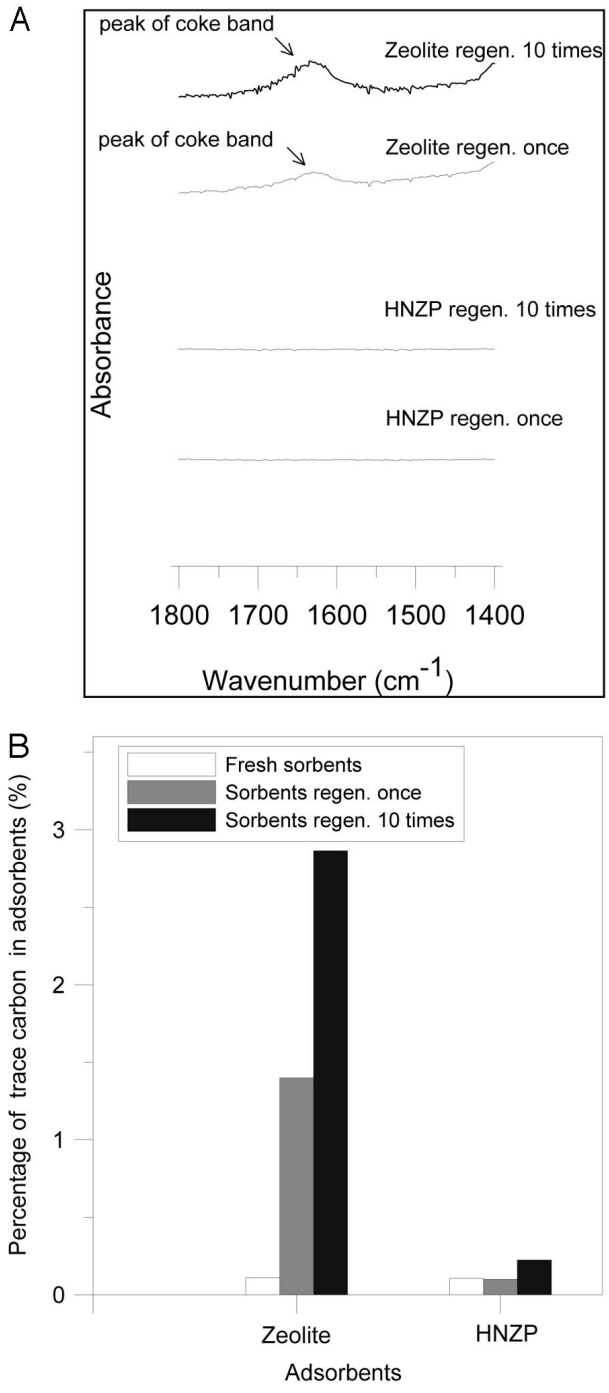

Figure 4. Detection of carbon remained on the adsorbents after repeated regeneration by (a) FTIR analysis and (b) EA analysis.

The percentages of trace carbon in fresh and regenerated adsorbents as analyzed by the elemental analyzer were illustrated in Figure 4b. It shows minimal variation in the percentage of trace carbon between the fresh and regenerated HNZP. On the contrary, the quantity of trace carbon in ZSM-5 zeolite increased conspicuously with the number of regenerations. The amount of trace carbon in zeolite after 10 regenerations was 26 times higher than that in the fresh ZSM-5 zeolite.

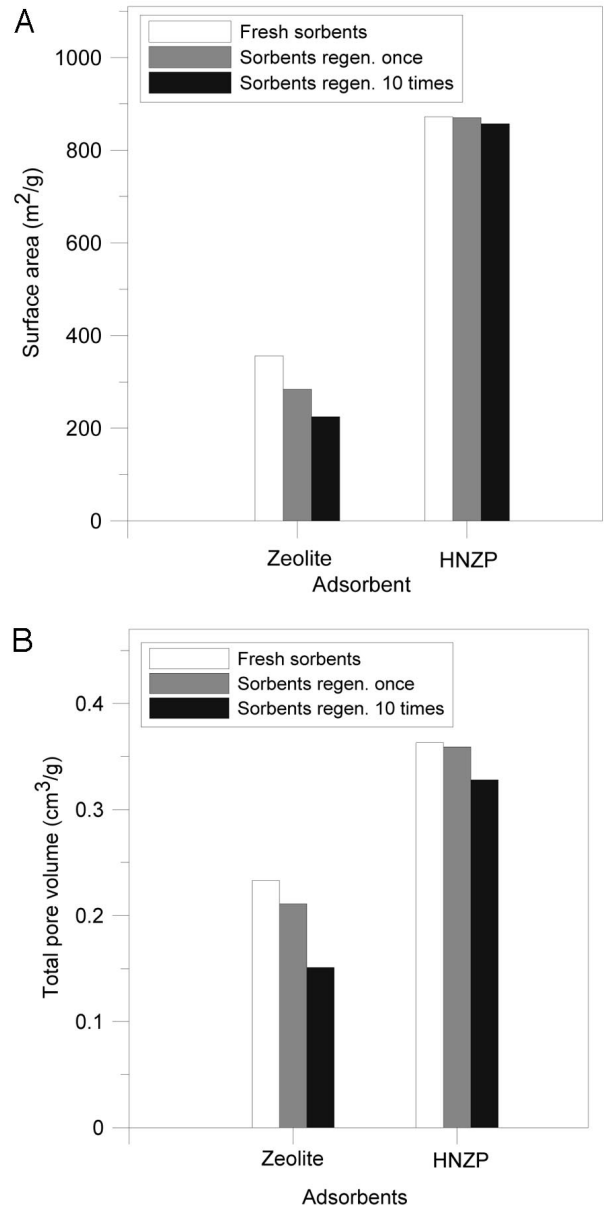

Figure 5. Comparison of (a) the total surface area and (b) the total pore volume between the fresh and regenerated adsorbents. The HNZP was synthesized at 550 °C.

Once coke was formed in the zeolite, the carbonaceous compounds were trapped in the pores of sorbents and gradually blocked the surface of the adsorption sites. Figures 5a and 5b show changes in the surface area and the pore vol of fresh and regenerated sorbents. It was observed that after 1 or 10 times of adsorption/desorption process, the change in the surface area or pore vol of the HNZP adsorbent was not obvious. But the surface area and pore vol of regenerated ZSM-5 zeolite was significantly reduced even after only 1 regeneration. And after 10 regenerations, the surface area and pore vol of regenerated ZSM-5 zeolite were reduced to only 63% and 65%, respectively, of those of the fresh zeolite.

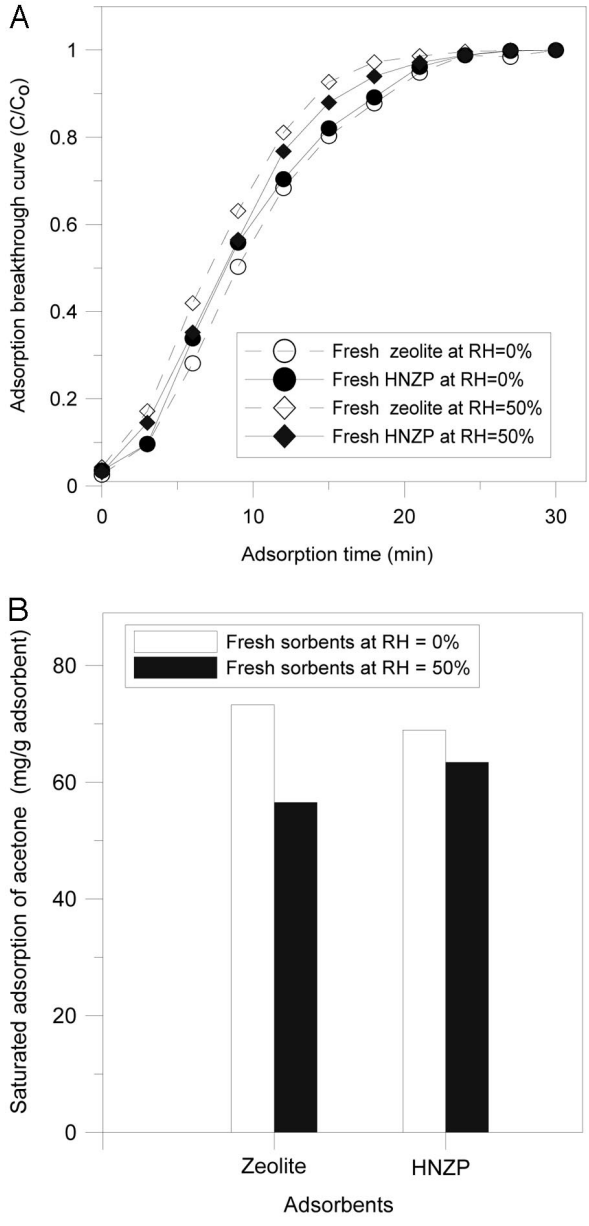

Figure 6. Comparison of (a) the adsorption efficiency and (b) the saturated adsorption capacity of acetone by the fresh adsorbents at RH = 0% and RH = 50%. The HNZP was synthesized at 550 °C.

Because RH can be a very important parameter that affects the adsorption capacity of adsorbent, the performance of the HNZP at a higher value of RH was compared with that of the commercial ZSM-5 zeolite. A RH value of 50% was tested to simulate typical operation of zeolite concentrators at semiconductor factories. Figure 6a shows results on the adsorption efficiency of fresh HNZP and commercial ZSM-5 zeolite adsorbents at RH of 0% and RH of 50%. The difference in the adsorption efficiency was not significant at RH of 50% or at RH of 0% using the HNZP adsorbent. This indicated that HNZP has a hydrophobic characteristic. On the other hand, one can see that at RH of 0% the ZSM-5 zeolite showed a better adsorption efficiency than that of HNZP, but at RH of 50% the adsorption efficiency of zeolite was less than that of HNZP. This is because that the aluminum element in the commercial zeolite resulted in a more hydrophilic characteristic. The hydrophilic characteristic with the presence of Al is in agreement with literature data for the tests on zeolite.[10–12] The adsorbed moisture tends to occupy the adsorption sites, thus reducing the adsorption efficiency.

Figure 6b compares the saturated adsorption capacity of HNZP and ZSM-5 zeolite at RH of 50% and RH of 0%. The saturated adsorption capacity for zeolite tested at RH of 50% was 56.53 mg acetone per gram zeolite, which is 23% less than that at RH of 0%, 73.25 mg/g. But the saturated adsorption capacity of HNZP at RH of 50% was only 8% less than that at RH of 0%. Thus, moisture interference was minimized by the hydrophobic characteristic of the pure siliceous HNZP.

CONCLUSIONS

This study synthesized HNZP adsorbents with different values of surface area and pore size to investigate their adsorption characteristics on acetone and compared their performances with those of commercially available ZSM-5 zeolite. The effects of sorbent regeneration and moisture were also clarified. The results demonstrated that both surface area and pore size were key parameters for the adsorption performance of adsorbents. The adsorption capacity of HNZP could be superior to that of zeolite by a slight increase in the pore size and a small sacrifice in the surface area. The HNZP had a higher antidecay property than the commercial ZSM-5 zeolite after repeated adsorption/desorption process. The significant decrease in the adsorption capacity of ZSM-5 zeolite adsorbents was resulted from blocking of the adsorption sites by the coke formation during regeneration. The high content of coke formation was possibly because of the presence of aluminum in the ZSM-5 zeolite that catalyzed the adsorbed acetone vapors. Additional advantage on the use of HNZP as an adsorbent was its hydrophobic characteristic. The HNZP is a pure siliceous adsorbent that was less affected by moisture than the ZSM-5 zeolite.

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