

Adsorption of Acetone Vapors by SBA-16 and MCM-48 Synthesized from Rice Husk Ash

Wanting Zeng, Hsunling Bai

Abstract—Silica was extracted from agriculture waste rice husk ash (RHA) and was used as the silica source for synthesis of RMCM-48 and RSBA-16. An alkali fusion process was utilized to separate silicate supernatant and the sediment effectively. The CTAB/Si and F127/Si molar ratio was employed to control the structure properties of the obtained RMCM-48 and RSBA-16 materials. The N₂ adsorption-desorption results showed the micro-mesoporous RSBA-16 possessed high specific surface areas (662-1001 m²/g). All the obtained RSBA-16 materials were applied as the adsorbents for acetone adsorption. And the breakthrough tests clearly revealed that the RSBA-16(0.004) materials could achieve the highest acetone adsorption capacity of 181 mg/g under 1000 ppmv acetone vapor concentration at 25°C, which was also superior to ZSM-5 (71mg/g) and MCM-41 (157mg/g) under same test conditions. This can help to reduce the solid waste and the high adsorption performance of the obtained materials could consider as potential adsorbents for acetone adsorption.

Keywords—Acetone, adsorption, micro-mesoporous material, rice husk ash (RHA), RSBA-16.

I. INTRODUCTION

VOLATILE Organic Compounds (VOCs) are major air pollutants in industrial processes, which would affect human health and cause serious environmental problems such as destruction of ozone layer and photochemical smog. Therefore they need to be controlled using modern technologies. There are a number of commercialized VOCs control technologies such as combustion, adsorption, absorption, biofiltration, and catalytic oxidation. And adsorption is one of the most commercialized methods for industrial VOCs pollution control because of the easy operation and low cost [1].

Porous adsorbents such as activated carbon (AC) and zeolite are commercially available for VOCs treatment. Recently the highly ordered mesoporous silica molecular sieves have received much attention because of their potential applications in the fields of adsorption, separation, catalysis, and environmental pollution control [2]-[4]. Mobil researchers [5] reported the first family of highly ordered mesoporous molecular sieves (M41S) by using long-chain cationic surfactant as the template or pore forming agent during the hydrothermal sol-gel synthesis. Since then, numerous mesoporous silica and other metal oxides with narrowly

distributed meso-pore diameters of 2-50 nm have been synthesized through various synthetic routes for obtaining materials in different chemical compositions and pore structures. And their potential applications as adsorbents have been extensively studied [6]-[14]. However, both the economic and environmental costs for the manufacture of mesoporous silica are high due to the high costs of silica precursors and surfactants.

Recently, the uses of waste products such as rice husks have been utilized as the silica source for the synthesis of mesoporous silica such as MCM-41 and SBA-15 [15], [16]. This would be economically beneficial in industrial manufacture of the adsorbents. An ideal mesoporous silica support for a variety of applications is MCM-48 and SBA-16 due to its hydrothermally stable cubic cage structure and large multidirectional pore system [17], [18]. However, to the best of authors' knowledge, there is no report yet on MCM-48 and SBA-16 as adsorbent materials for the removal of VOCs.

In this study, rice husk ash (RHA) was used as the silica source for the synthesis of RSBA-16. Different CTAB/Si and F127/Si ratios were employed to control the textural properties of the obtained RSBA-16 materials, and their performance on acetone adsorption were investigated.

II. EXPERIMENTAL

A. Extraction of Silica from Rice Husk

The rice husk ash was obtained by pre-heating the rice husk at the temperature of 400°C. The alkali extraction method was used to concentrate the silica. In this process, the RHA was mixed with aqueous NaOH solution at 70°C for 12 h and the resulting mixture was then centrifuged to separate supernatant and sediment. The silicate supernatant was utilized as the silica precursor for the synthesis of RMCM-48 and RSBA-16.

B. Synthesis of RMCM-48 and RSBA-16

Mesoporous RMCM-48 was synthesized by the hydrothermal treatment method using the silicate supernatant extracted from RHA as the silica precursor and cetyltrimethylammonium bromide (CTAB) was employed as the structure-directing template in the synthesis. The molar composition of the gel mixture was 1 SiO₂: X CTAB: 0.89 H₂SO₄: 120 H₂O. In a typical procedure, 63 ml of waste silicate solution was acidified by adding approximately 40 ml of 4N H₂SO₄ to bring down the pH to 10.5 with constant stirring to form a gel. After stirring, calculated amount of CTAB (dissolved in 25 ml of DI water) was added drop by drop into the above mixture and the combined mixture was stirred for three additional hours. The resulting gel mixture was

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transferred into a Teflon coated autoclave and kept in an oven at 145°C for 36 h. After cooling to room temperature, the resultant solid was recovered by filtration, washed with DI water and dried in an oven at 110°C for 8 h. Finally, the organic template was removed by using a muffle furnace in air at 550°C for 6 h. The synthesized mesoporous silica was denoted as RMCM-48(X), where X corresponds to the molar ratio of CTAB/Si.

RSBA-16 was synthesized using a tri-block copolymer, EO₂₀-PO₇₀-EO₂₀ (Pluronic F127, BASF) as the template and rice husk derived silicate solution as the silica source. 1 SiO₂: 0.002~0.010 F127: 4.2 HCl: 286 H₂O. For a typical synthesis, given amount of F127 was dissolved in 20 g of DI water; meanwhile, 82 ml of silicate solution was added to 70 ml of 1 M H₂SO₄ to achieve the pH value of 2. Subsequently, calculated amounts of 6 M NaOH were added to the above silicate mixture to bring up the pH to 5 to accelerate the hydrolytic condensation reaction. After stirring, the surfactant solution was added slowly into the above mixture and the combined mixture was stirred for 15 min. The resulting gel mixture was transferred into a Teflon coated autoclave and kept in an oven at 100 °C for 24 h. After cooling to room temperature, the resultant solid was recovered by filtration, washed with DI water and dried in an oven at 60°C for 24 h. Finally, the organic template was removed by using a muffle furnace in air at 500°C for 6 h. The RSBA-16 adsorbents synthesized from RHA with different F127/Si molar ratios were named as RSBA-16(0.002), RSBA-16(0.004), RSBA-16(0.006), RSBA-16(0.008), and RSBA-16 (0.010).

C. Acetone Adsorption Test

The dynamic adsorption experiment was carried out on the experimental set-up, as shown in Fig. 1. Acetone vapor adsorption experiments over RMCM-48 and RSBA-16 were performed by a packed column test. The RMCM-48 and RSBA-16 materials were crushed and sieved between 16-30 mesh. A total of 500mg adsorbent in pelletized form was packed inside an adsorption column with internal diameter of 0.7cm. Before adsorption process, sorbents were pretreated under N₂ flow of 0.1L/min at 200°C for 1h, and it was then cooled to 25°C. Under a typical adsorption test, the acetone vapor concentration was controlled at 1000ppmv.

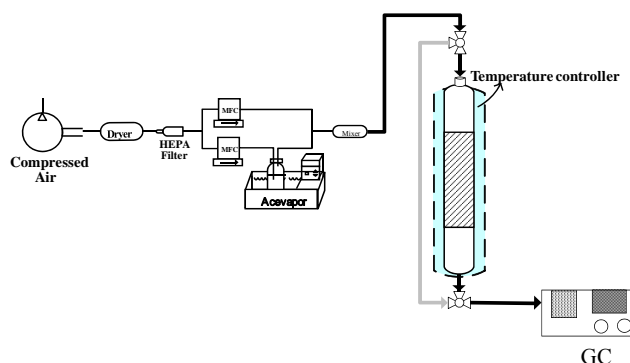


Fig. 1 Experimental setup for acetone adsorption experiments

III. RESULTS AND DISCUSSIONS

The results of the N₂ adsorption-desorption analysis for the RMCM-48 and RSBA-16 material with various CTAB/Si and F127/Si molar ratios are listed in Table I. The specific surface area for RSBA-16 samples ranges from 577 to 1001 m²/g, and it increases with increasing the F127/Si ratio up to RSBA-16(0.004). However, the specific surface area was decreased with further increasing the F127/Si ratio up to RSBA-16(0.010). On the other hand, the specific surface area for RMCM-48 is also strongly influenced by the CTAB/Si molar ratio, and it increases with increasing the CTAB/Si ratio up to RMCM-48(0.04). And the specific surface area was decreased with further increasing the CTAB/Si ratio up to RMCM-48(0.08). Therefore, the textural porosity of the RSBA-16 silica material can be adjusted by the CTAB/Si and F127/Si molar ratios.

In order to figure out the acetone adsorption performance on meso/micro-porous RSBA-16 and mesoporous RMCM-48 material, acetone adsorption removals by RSBA-16 and RMCM-48 with different F127/Si and CTAB/Si ratios were investigated. Fig. 2 displays the breakthrough curves of the RSBA-16 materials with various F127/Si ratios, and the acetone saturated capacities (Sat. q_e) were summarized in Table 1. It can be seen that the acetone capacities of RSBA-16(0.002), RSBA-16(0.003), RSBA-16(0.004), RSBA-16(0.006), RSBA-16(0.008) and RSBA-16(0.010) was 118, 147, 181, 178, 157,98 mg-acetone/g-adsorbents, respectively, and RSBA-16(0.004) exhibited the highest adsorption capacity of 186 mg/g among all tested adsorbents. This is probably due to its higher specific surface area which can provide more adsorption sites.

Fig. 3 depicts the breakthrough curves of the RMCM-48 materials with various CTAB/Si ratios, and the acetone saturated capacities (Sat. q_e) were summarized in Table I. The acetone capacities of RMCM-48(0.02), RMCM-48(0.03), RMCM-48(0.04), RMCM-48(0.06), and RMCM-48(0.08) was 166, 174, 187, 181, and 179 mg-acetone/g-adsorbents, respectively, and RMCM-48(0.04) exhibited the highest adsorption capacity of 187 mg/g among all tested adsorbents.

It is noteworthy in Table I that both RSBA-16(0.004) and RMCM-48(0.03) exhibited similar acetone adsorption capacities, even though RSBA-16(0.004) showed lower specific surface area (1001 m²/g) than that of RMCM-48(0.03) (1341 m²/g). In addition, the acetone capacity of RSBA-16(0.004) was superior to the commercial ZSM-5 zeolite material (71 mg/g) and mesoporous MCM-41 material (115 mg/g) made from pure silica source under the same conditions tested on the freshly made adsorbents. It is interesting to note that RSBA-16(0.004) showed much higher acetone adsorption capacity than that of MCM-41, even though they had similar specific surface area. It has been reported that the presence of micropores in the micro/mesoporous materials is beneficial for the VOCs adsorption [19]–[21]. Therefore, taking into account the adsorption performance and textural properties of MCM-41, RMCM-48(0.03) and RSBA-16(0.004), it is reasonable to deduce that the existence of micropores in

RSBA-16 might play a role in enhancing the acetone adsorption.

TABLE I
BET ANALYSIS OF RSBA-16 ADSORBENTS

| | S_{BET} (m^2/g) | V_p (cm^3/g) | D_p (nm) | V_{micro} (cm^3/g) | Sat. q_e |
|----------------|--------------------------|-----------------------|---------------|-----------------------------|------------|
| RSBA-16(0.002) | 662 | 0.60 | 3.6 | 0.11 | 118 |
| RSBA-16(0.003) | 785 | 0.60 | 3.6 | 0.10 | 147 |
| RSBA-16(0.004) | 1001 | 0.72 | 3.5 | 0.18 | 181 |
| RSBA-16(0.006) | 901 | 0.60 | 3.4 | 0.16 | 178 |
| RSBA-16(0.008) | 808 | 0.54 | 3.2 | 0.10 | 157 |
| RSBA-16(0.010) | 577 | 0.38 | 3.1 | 0.07 | 98 |
| MCM-41 | 1064 | 1.00 | 3.0 | - | 157 |
| ZSM-5 | 395 | 0.24 | 2.4 | 0.24 | 98 |

TABLE II
BET ANALYSIS OF RMCM-48 ADSORBENTS

| | S_{BET} (m^2/g) | V_p (cm^3/g) | D_p (nm) | V_{micro} (cm^3/g) | Sat. q_e |
|---------------|--------------------------|-----------------------|---------------|-----------------------------|------------|
| RMCM-48(0.02) | 1295 | 0.73 | 2.60 | - | 166 |
| RMCM-48(0.03) | 1341 | 0.75 | 2.59 | - | 174 |
| RMCM-48(0.04) | 1576 | 0.87 | 2.62 | - | 187 |
| RMCM-48(0.06) | 1430 | 0.83 | 2.62 | - | 181 |
| RMCM-48(0.08) | 1382 | 0.77 | 2.60 | - | 179 |

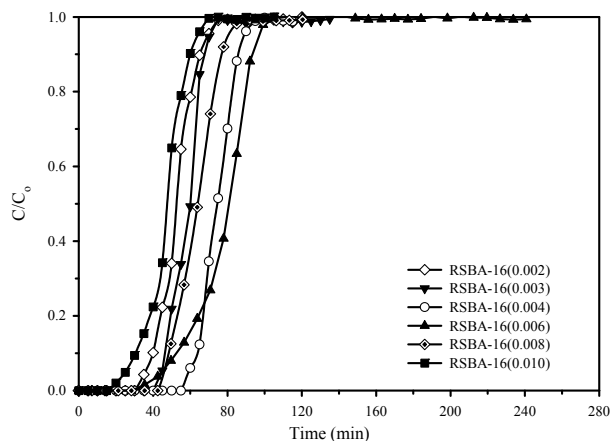


Fig. 2 The breakthrough curves of acetone on RSBA-16 materials

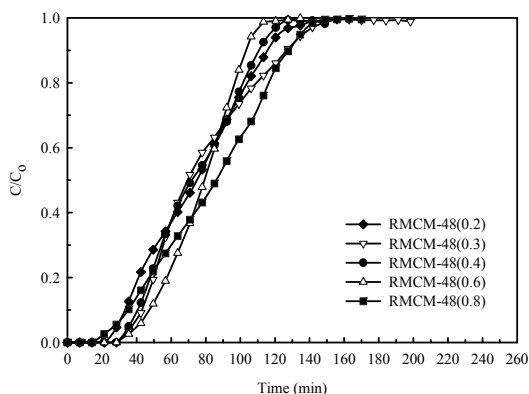


Fig. 3 The breakthrough curves of acetone on RMCM-48 materials

IV. CONCLUSIONS

The RMCM-48 and RSBA-16 materials can be prepared using the silicate supernatant extracted from rice husk ash as the silica source with CTAB and copolymer F127 as the structuring agent. Among all tested samples, RSBA-16(0.004) and RMCM-48(0.04) showed superior performance as the adsorbent for acetone vapor removal. This could be ascribed to their higher specific surface area which provides more adsorption sites for acetone removal. Furthermore, RSBA-16 exhibits higher capacity than those of zeolite ZSM-5 and MCM-41 which could be attributed to the presence of micropores in the micro/mesoporous materials. In conclusion, the RSBA-16 and RMCM-48 materials synthesized from agricultural waste with high adsorption performance could be considered as cost-effective adsorbents for the acetone vapor adsorption.

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