염처리를 이용한 MCM-48의 수열 안정성 및 휘발성 유기용제 흡착특성

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Hydrothermal and Mechanical Stability of MCM-48 Improved by Post-Synthesis Restructuring in Salt Solution and Adsorption Characteristics of Volatile Organic Compounds

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Introduction

Recently, discovery of a new family of mesoporous molecular sieves named M41S has been receiving a great deal of attention after introducing by Mobil researchers. The M41S family is classified into several members: MCM-41, MCM-48 and other species. MCM-41 has a hexagonal array of unidirectional pores while MCM-48 has a bicontinuous cubic pore system. Their synthesis and utilization have been investigated by many researchers because of their peculiar characteristics such as large internal surface area, uniformity of pore size, and easily controlled size of pore. However, the range of application has been limited by the instability of the structure of the mesoporous molecular sieves.

Mechanical stability is an important characteristic of an adsorbent or catalyst for most practical applications. MCM-41 and MCM-48 exhibit high thermal stability (~1173K) in dry air or in air having a low water vapor pressure. This is a low hydrothermal stability in water and even in air saturated with water vapor. Further, the structure collapses by mechanical compression through the hydrolysis of siloxane bonds in the presence of adsorbed water.

The hydrothermal stability can be improved by increasing the hydrophobicity, i.e., by decreasing the number of silanol groups in the framework structure. Recently, Igarashi et al. reported increased stability of organically modified MCM-41 synthesized by a single-step procedure, in comparison to the unfunctionalized species. On the other hand, Gusev et al. reported that the ordered mesoporous structure of pure silica MCM-41 was mechanically unstable compared to zeolite, silica gels and alumina. The adsorption isotherm of benzene, n-heptane, and cyclohexane on MCM-48 was studied by Hartman et al. to investigate the mechanical stability. Anyway, from an engineering point of view, it is very important to acquire technologies for the modification of surface properties.

Therefore, we synthesized mesoporous MCM-48 by conventional hydrothermal reaction, and modified by post-synthetic treatment in salt solution to increase the hydrothermal and mechanical stabilities. The mesoporous material is characterized by a number of techniques including XRD, IR, SEM and NMR. Further, adsorption equilibrium of VOCs was obtained to examine the influences of mechanical compression on adsorption equilibrium.

Experimental

Synthesis of mesoporous materials

MCM-48 sample was synthesized by conventional hydrothermal method as follows. 12.4 g of cethyltrimethylammonium bromide (CTMABr, $C_{19}H_{42}BrN$, Aldrich), 2.16 g LE-4 (polyoxyethylene lauryl ether, $C_{12}H_{25}(OCH_2CH_2)_4OH$, Aldrich) were dissolved in Teflon bottle containing 130 g of deionized water at 333 K. This aqueous solution was added dropwise to a another aqueous solution in Teflon bottle containing 40 g of Ludox AS-40 (Du Pont, 40 wt% colloidal silica in water), 5 g of NaOH, and 130 g of deionized water under vigorous stirring. The solution mixture was preheated in a water bath kept at 313 K and was stirred at 500 rpm for 20 min. The resultant gel was loaded to autoclaves, and the mixture was hydrothermally treated at 373 K for 78 h. The mixture was then filtered and washed with 500 mL deionized water. The washing procedure was repeated 4-5 times to assure the complete removal of the bromide and other free ions. After drying at 333K for overnight, the dried solid was then calcined in air at 873 K for 10 h at a heating rate of 272 K/min.

Post-synthesis treatments in salt solution

The MCM-48 samples containing the surfactants as synthesized were added to an aqueous solution of $EDTANa_4$ (Acros, 99%) or NaCl, in the ratio of 1 g MCM-48 to 25 g solution. The concentration of the salt solution was varied from 0 to 6 wt.%. The pH of the $EDTANa_4$ solution was approximately 10. The MCM-48 samples in the salt solutions were heated in an oven for the desired periods of time (2-20 d) at 373 K.

Measurement of hydrothermal and mechanical stability

0.1 g of calcined MCM-48 was boiled for 12 h in 100 ml of distilled water, using a Pyrex flask equipped with reflux condenser. XRD pattern was obtained after this boiled sample was subsequently filtered and dried in an oven at 413 K. Mechanical stability was investigated as follows: all the samples were calcined in air at 813 K for 6 h using a muffle furnace immediately before compression. The samples (0.15 g) were pressed in a steel die of 10 mm diameter by a pressing apparatus under ambient air for 10 min. The external pressure applied was 100, 200, and 300 kg/cm^2. The obtained pellet was crushed and sieved to obtain pellets with a diameter of 0.2 to 0.3 mm, that were used for adsorption equilibriumThe structure of pressed samples was examined by XRD and N2 adsorption measurements.

Characterization

Nitrogen adsorption and desorption isotherms, BET surface areas, and BJH (Barrett, Joyner and Halenda) pore size distributions of the synthesized sorbents were measured at 77 K using a Micromeritics ASAP 2000 automatic analyzer. Prior to measurment, the samples were outgassed at 623 K for 10 h. X-ray powder diffraction data of mesoporous sorbents were collected on Phillips PW3123 diffractometer equipped with a graphite monochromater and Cu K_α radiation of wavelength 0.154 nm. XRD patterns were obtained between 2^o and 50^o with a scan speed of 1^o/min.

Adsorption Equilibrium

Adsorption amounts are measured using gravimetric apparatus. The vapor of VOC was generated in a small chamber. The thermostat bath surrounding the chamber was maintained at the required temperature within ± 0.5 ^oC. The adsorption amount was measured by a quartz spring balance, which was placed in a closed glass system. Prior to adsorption, MCM-48 was vacuumed to remove volatile impurities from the sorbents for 15 hours at 523 K. The purity of adsorbate was greater than 99% and they were used without further purification. The adsorption equilibrium was usually attained within 20-30min.

Theoretical Model

Adsorption isotherms play a key role in either the design of the adsorption-based process for the disposal of wastes containing VOCs or modeling the catalytic oxidation process. The equilibrium data for mesoporous sorbents are fitted to combined model of Langmuir and Sips equations. This hybrid isotherm model with four isotherm parameters (q_m, b_1, b_2, n) is as below:

$$q = q_m \left[\frac{b_1 P}{1 + b_1 P} + \frac{b_2 P^n}{1 + b_2 P^n} \right] \tag{1}$$

The number of independent parameters in hybrid temperature-independent isotherm (Eq. 1) is four (q_m, b_1, b_2, n). On the other hand, inhomogeneous D-A equation is used for polar organic compounds on MCM-48.

$$q = q_m \left[\exp\left(\frac{-A}{\beta E_1} \right)^{n_1} + \exp\left(\frac{-A}{\beta E_2} \right)^{n_2} \right] \tag{2}$$

where, $A = RT \ln\left(\frac{P_s}{P} \right)$, $\beta = \frac{V}{V_{ref}}$ is 1 for benzene

The isotherm parameters were determined using Nelder-Mead simplex method by minimizing the sum of residual, namely, the differences between experimental and estimated adsorption amount.

Results and Discussion

Characterization

The XRD pattern of synthesized pure silica MCM-48 materials matched well with the reported one. Figure 1 shows the N_2 adsorption isotherms of pure silica MCM-48 sample. The N_2 adsorption isotherm of MCM-48 before compression was characteristic of mesoporous materials with uniform pore size. The isotherm is reversible and does not exhibit hysterisis between adsorption and desorption. The average pore diameter determined by BJH method was 3.2 nm. By applying pressure under ambient air the steep increase in adsorption at P/P_0 around 0.3 due to the ordered mesoporous structure faced and the amount of adsorbed N_2 was reduced. It should be noted that the sharp distribution of the pore size and the average pore size remained unchanged while the pore volume decreased with increasing applied pressure. These findings suggest that a part of the pores were destroyed by mechanical compression and that the destroyed portion increased with increasing pressure. It is inconceivable that all the pores were simultaneously deformed by degrees. We will be present this in conference.

Adsorption Equilibrium.

The adsorption isotherms of benzene on compressed MCM-48 are shown in Figure 2. All isotherms are type IV according to the IUPAC classification, with a steep increase between P/P_o =0.20 ~ 0.30. The last linear part of the isotherm is suggested to be due to adsorption on the outersurface of particles and interparticle voids.

The hybrid isotherm model for a pure adsorbate was found to fit the individual isotherm data very well. The parameters of the hybrid equations are listed in Table 1.

Table 1 Hybrid Isotherm Parameters

	External Pressure 100 Kg/cm^2	External Pressure 200 Kg/cm^2	External Pressure 300 Kg/cm^2
q_m	4.73E+00	3.81E+00	3.19E+00
b_1	4.08E-01	5.81E-01	5.51E-01
b_2	3.67E-08	3.21E+01	2.72E-06
n	1.46E+01	3.27E+01	1.04E+01
Residual	1.64E-01	1.76E-01	3.36E-01

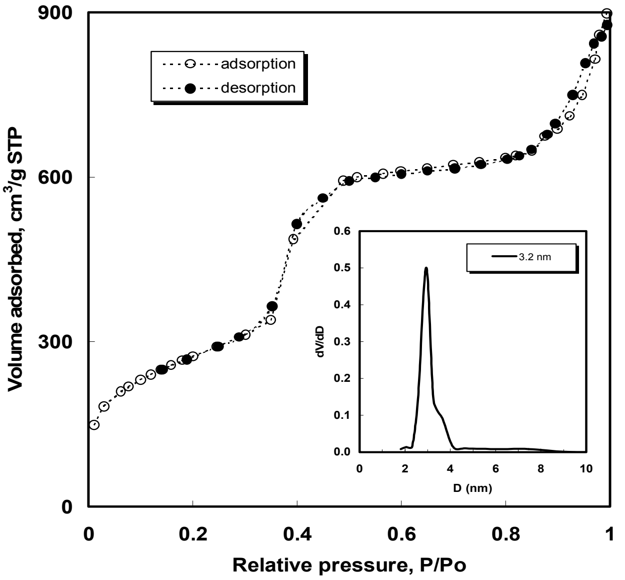

Figure 1. Nitrogen adsorption and desorption isotherm on MCM-48 at 77K.

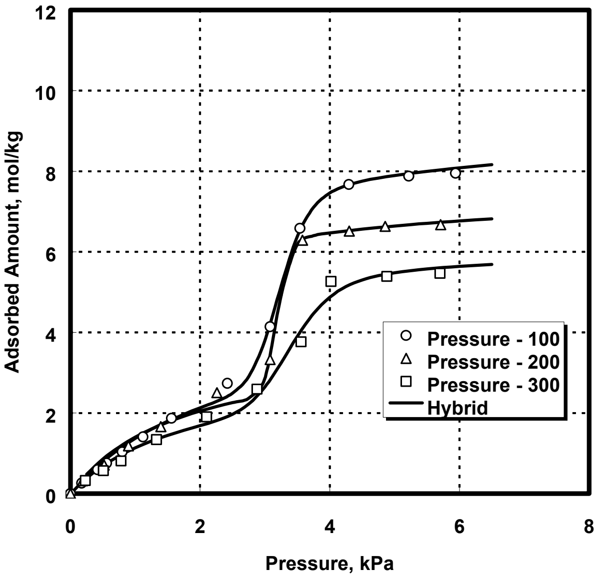

Figure 2. Adsorption isotherms of benzene at 300K on MCM-48.

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