ORIGINAL ARTICLE

Analysis of nitrogen and carbon tetrachloride adsorption isotherms and pore size distribution for siliceous MCM-41 synthesized from rice husk silica

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Abstract

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Analysis of nitrogen and carbon tetrachloride adsorption isotherms and pore size distribution for siliceous MCM-41 synthesized from rice husk silica

Songklanakarin J. Sci. Technol., 2004, 26(Suppl. 1) : 37-44

RH-MCM-41 particles were synthesized using sodium silicate prepared from rice husk as a silica source and hexadecyltrimethylammonium bromide (CTAB) as a surfactant. The molar compositions were 1.0SiO_2: 1.1NaOH: 0.13CTAB: 0.12H_2O. This material was used for adsorption isotherm studies of carbon tetrachloride (CT) at 25 °C using a magnetically coupled microbalance, and compared with adsorption isotherms using nitrogen at 77 K. The CT isotherms were classified as reversible Type V isotherms, and the nitrogen adsorption isotherm was Type IVc. Capillary condensation was found in a very narrow pressure range, indicating the presence of nearly uniform pores in the RH-MCM-41 particles, which agrees very well with TEM results. The surface area estimated by using the BET method was (800 ± 8) $m^2 g^{-1}$. Pore size distributions (PSD) of nitrogen and CT adsorption isotherms for a series of MCM-41 were calculated by using method recommended by Naono and Hakuman (1997). The pore size distributions from the nitrogen isotherm using the BJH and Naono methods showed quite narrow pore diameter distributions, centered around 27 and 29 Å, respectively. Similarly, the peak pore diameters calculated from CT isotherms using the BJH and Naono methods were 24 and 28 Å. It was found that the PSDs analyzed by the BJH method were underestimated compared to that from Naono method.

Key words : MCM-41, rice husk silica, microbalance, carbon tetrachloride, pore size distribution

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Received, 8 March 2003 Accepted, 10 May 2004

บทคัดย่อ

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การวิเคราะห์ไอโซเทอมการดูดซับของไนโตรเจนและคาร์บอนเตตระคลอไรด์และการกระจายตัวของรูพรุนด้วยวัสดุซิลิกา เอ็มซีเอ็ม 41 สังเคราะห์จากแกลบข้าว

ว.สงขลานครินทร์ วทท. 2547 26(ฉบับพิเศษ 1) : 37-44

ซิลิกาจากแกลบข้าวสามารถนำมาใช้เป็นแหล่งซิลิกาสำหรับการสังเคราะห์เอ็มซีเอ็ม 41 โดยสังเคราะห์จากสารละลายโซเดียมซิลิเกตที่ได้จากซิลิกาแกลบกับเฮกซะเดคซิลไตรเมธิลแอมโมเนียมโบไมด์ (ซีทีเอบี) ด้วยอัตราส่วนโดยโมลเป็น 1.0 ซิลิกา ต่อ 1.1 โซเดียมไฮดรอกไซด์ ต่อ 0.13 ซีทีเอบี ต่อ 0.12 น้ำวัสดุที่สังเคราะห์ได้สามารถนำมาศึกษาไอโซเทอมของการดูดซับของคาร์บอนเตตระคลอไรด์ที่อุณหภูมิ 25 °C ด้วยตาชั่งระบบแม่เหล็กที่มีความละเอียดระดับไมโครโดยเปรียบเทียบกับไอโซเทอมของการดูดซับของไนโตรเจนที่ 77 เคลวิน จากการทดลองพบว่าไอโซเทอมของคาร์บอนเตตระคลอไรด์เป็นชนิดที่ 5 ขณะที่ไอโซเทอมของไนโตรเจนเป็นชนิดที่ 4 ซี ค่าแคปิราริคอนเดนเซชันอยู่ในช่วงแคบแสดงถึงลักษณะของรูพรุนที่สม่ำเสมอซึ่งสามารถยืนยันได้จากผลของทีอีเอ็ม พื้นที่ผิวคำนวณโดยวิธีของบีอีทีมีค่า 800±8 ตร.เมตร/กรัม ขนาดของรูพรุนและการกระจายตัวของรูพรุนที่ได้จากไอโซเทอมของไนโตรเจนคำนวณด้วยสมการของบีเจเอชและนาโอโนพบว่ารูพรุนมีขนาด 27 และ 29 อังสตรอม ตามลำดับ ขณะที่ขนาดของรูพรุนและการกระจายตัวของรูพรุนที่ได้จากไอโซเทอมของคาร์บอนเตตระคลอไรด์พบว่ารูพรุนมีขนาด 24 และ 28 อังสตรอม ตามลำดับ ซึ่งพบว่าการกระจายตัวของรูพรุนที่วิเคราะห์โดยสมการของบีเจเอชมีค่าต่ำกว่าค่าที่ได้จากสมการของนาโอโน

Carbon tetrachloride (CT) is a hazardous solvent produced for uses in cleaning, degreasing, and paint strippers. By means of poor solvent handling practices and careless disposal of these hazardous materials have greatly contributed to subsurface environmental pollution (Hudson, 2003). The difficulty in cleanup is the lack of knowledge of the controlling processes in contaminant transport and fate. To improve current fate and transport models for subsurface contaminations, it is necessary to understand the individual contributions of each fundamental factor affecting transport phenomena.

Recently, a new procedure for gas phase sorption studies was carried out by using a microbalance. The studies of sorption isotherms and kinetic of CT on mesoporous and microporous silicas were performed on a magnetically coupled microbalance, manufactured by Rubotherm in Bochum, Germany (Hudson, 2003; Miller *et al.*, 2002). With this instrument, both equilibrium and kinetic measurements can be made by direct mass determination with real time and long term stability. It was shown through comparison with nitrogen results, that CT isotherms were well defined in the microbalance and comparable to literature values of both nitrogen adsorption and CT adsorption on these types of porous particles.

The pore size distribution (PSD) is one of the essential factors in characterizing mesoporous materials. The BJH model and nitrogen adsorption isotherms at 77 K have been utilized to calculate the PSD of many porous adsorbents (Gregg and Sing, 1982; Rouqerol *et al.*, 1999; Grisdanurak *et al.*, 2003). By this method, the Kelvin equation and the adsorbed thickness on the flat surface have been used. However, it was found that the difference of the adsorbed thickness between flat sur-

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face and pore surface has significantly affected the PSD of micro and mesoporous materials (Rouqerol *et al.*, 1999; Naono and Hakuman, 1997). Recently, a new method for PSD calculation of nitrogen and CT adsorption on mesoporous silica was suggested to be more accurate compared to the BJH model (Naono and Hakuman, 2001).

In this present work, RH-MCM-41 synthesized from rice husk silica was used as a mesoporous adsorbent (Kumar *et al.*, 2001). The sorption studies of CT measured at 25 °C were determined on a magnetically coupled microbalance. To see whether the PSD calculated from the adsorption isotherm of CT agrees with the distribution curve obtained from the nitrogen isotherm measured at 77 K, the BJH method was utilized and then compared with Naono model (Naono and Hakuman, 1997).

Theoretical background

Studies of CT equilibrium and kinetics on microporous silicas were performed on a magnetically coupled microbalance, manufactured by Rubotherm in Bochum, Germany. The microbalance system allows direct mass measurements of a silica sample, and changes in mass during adsorption and desorption, all within a controlled atmosphere cell.

A schematic of the entire system is shown in Figure 1. The measurement cell and coupling housing above it were surrounded by a thermal jacket with a circulating fluid from a constant temperature circulator (TP-6 Heating Circulator, Julabo® USA, Inc.) with a precision of 0.01 °C and accurate to 0.1 °C. The system was connected to the contaminant source cylinder, which was maintained in a constant temperature bath. The cell also had a vent line to an atmospheric hood, which con-

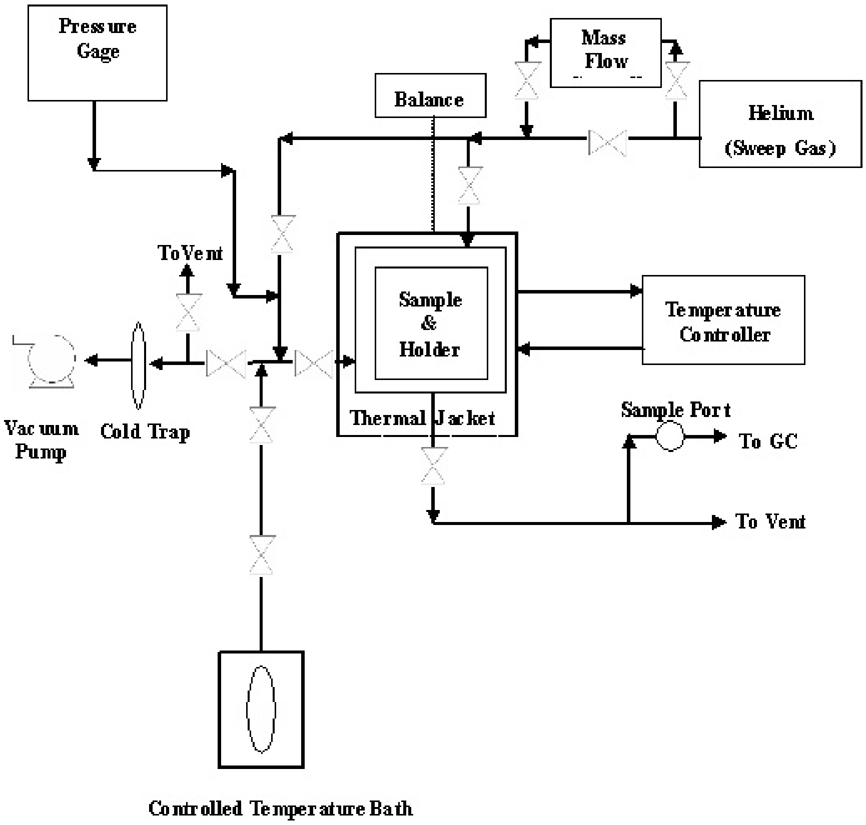

Figure 1. Schematic of sorption system using microbalance.

tained a sample port for syringe sampling of the off-gas. The cell was connected to a vacuum pump, so that it could be evacuated in preparation for a run, and a liquid nitrogen cold trap was located in the vacuum line to prevent any organic contaminant from entering the pump.

Materials and Methods

Preparation of RH-MCM-41

The RH-MCM-41 particles were synthesized using CTAB as template and sodium silicate prepared from sodium hydroxide and rice husk silica as silica source. The molar compositions were $1.0SiO_2$: 1.1NaOH: 0.13CTAB: $0.12H_2O$. The CTAB was dissolved in sodium hydroxide solution and vigorously stirred until the solution was clear. Sodium silicate was prepared and mixed with CTAB solution. Then, the solution was stirred at room temperature for 2 days. The pH was adjusted to 11 by adding 1% HCl. Finally, the suspended solid was filtered, washed and dried before calcined at 550 °C for 5 h under airflow. The XRD, FTIR and TEM characterizations were carried out for the analysis of product properties.

Adsorption isotherms of nitrogen gas on RH-MCM-41

Prior to adsorption measurements, a 0.1 g sample was outgassed under vacuum at 350 °C for 12 h. Nitrogen physisorption was performed on a Micromeritics ASAP 2010 volumetric adsorption analyzer at 77 K, in the range of relative pressure from 0.01 – 0.90.

Adsorption isotherms of carbon tetrachloride vapor on RH-MCM-41

A desorption isotherm was carried out at 25 °C by filling the microbalance cell (Rubotherm®) with CT vapor at 0.13 atm (CT sample temperature of 24 °C) and allowing the mass and pressure to come to equilibrium. Then, the vacuum system was used to remove some CT (deposited in the cold trap) and obtain a new equilibrium condition. The equilibrium points were measured from 0.11 atm to 0.01 atm. Before starting a subsequent adsorption isotherm, the cell was evacuated at 25 °C for 30 minutes, and then CT vapor was added incrementally, by varying the CT sample bath temperature from -30 °C to 15 °C.

Results and Discussion

XRD and FTIR characterizations for the synthesized MCM-41

The well defined XRD pattern of MCM-41 is illustrated in Figure 2. The highly distinct pattern appears at the 2q values equal to 2.6, 4.2, 4.8, and 6.3 degree corresponding to the *hkl* reflection plane 100, 110, 200, and 210, respectively. This result is in good agreement with the pattern from a pure siliceous MCM-41 reported elsewhere (Kumar *et al.*, 2001; Naono and Hakuman, 2001).

The FTIR result is presented in Figure 3. A broad absorption band around 3400 cm^{-1} was assigned to H-bonded silanols. The three characteristic peaks commonly found in the MCM-41 material appeared at 790 cm^{-1} attributed to symmetrical Si-O-Si stretching vibration and at

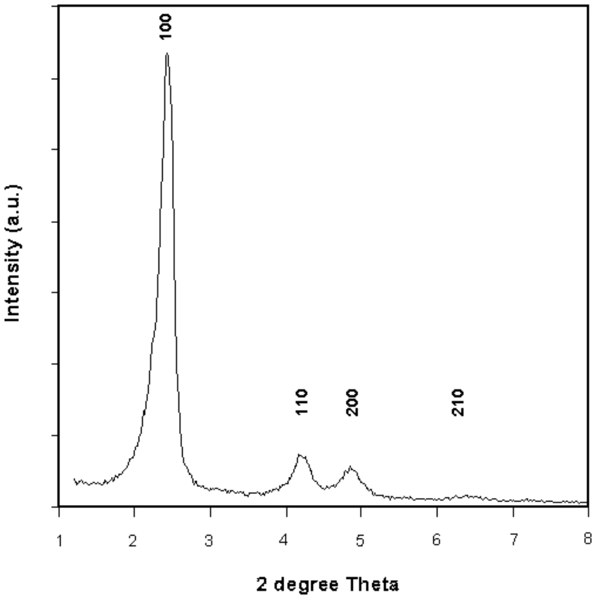

Figure 2. XRD pattern of MCM-41.

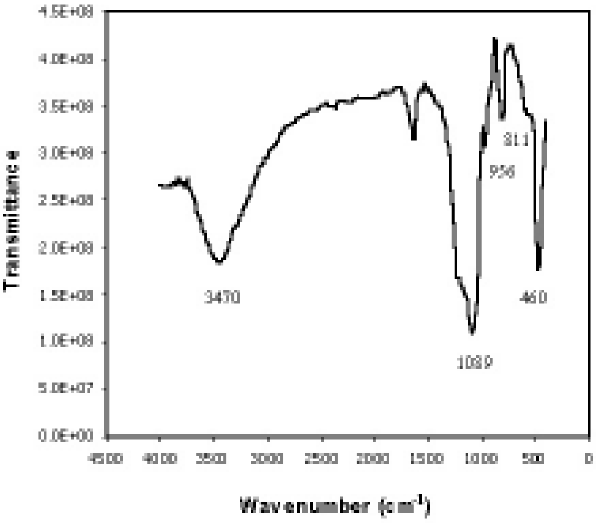

Figure 3. FTIR spectra of MCM-41.

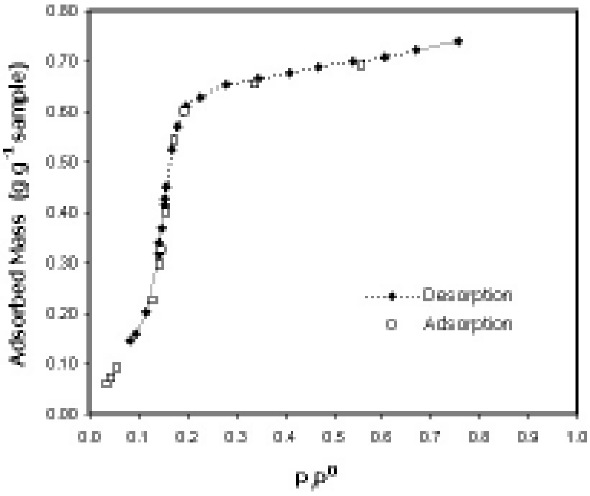

Figure 4. Adsorption and desorption isotherms of MCM-41 with CT at 25 °C.

952 cm^{-1} assigned to symmetric stretching vibration of Si-O-H groups. A strong peak at 1078 cm^{-1} was referred to Si-O-Si anti-symmetric stretching. These results confirm that the surface of MCM-41 possess silanol groups, a required adsorption property.

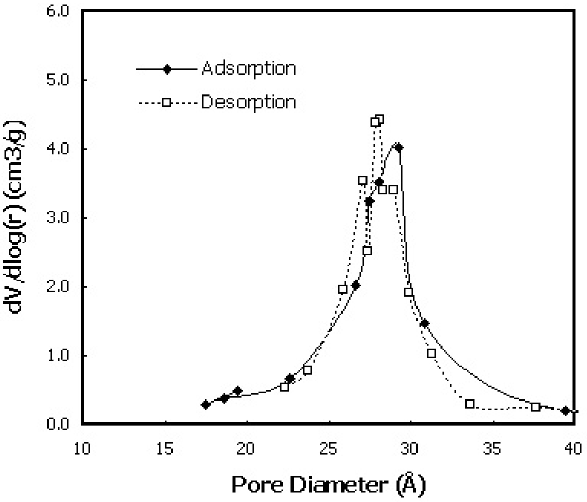

Figure 5. Pore size distribution curve for MCM-41 calculated from the CT isotherms at 25 °C.

Carbon tetrachloride isotherm and pore size distribution

The CT isotherms presented in Figure 4 were classified as reversible Type V isotherms (Brunauer *et al.*, 1942), which agrees very well with those found in the literature (Hudson, 2003; Naono and Hakuman, 2001). No significant hysteresis was found between the adsorption and desorption isotherms. The capillary condensation occurs in a very narrow relative pressure range ($P/P^{o} = 0.16 \pm 0.02$). This steep region in the isotherm indicates the presence of nearly uniform pores in the MCM-41 particles.

The calculations of PSDs for mesoporous materials which have pore diameter in the range of 1-5 nm were derived from Naono's equations (Naono and Hakuman, 2001) as utilized by Hudson (2003). The PSD plot from the adsorption and desorption CT isotherms is shown in Figure 5. Both adsorption and desorption results are in agreement with each other. The pore diameter of the MCM-41 particles was found to be centered at 28 Å, with a narrow distribution (halfwidth of about 2 Å). This was in good agreement with TEM results as presented in Figure 6.

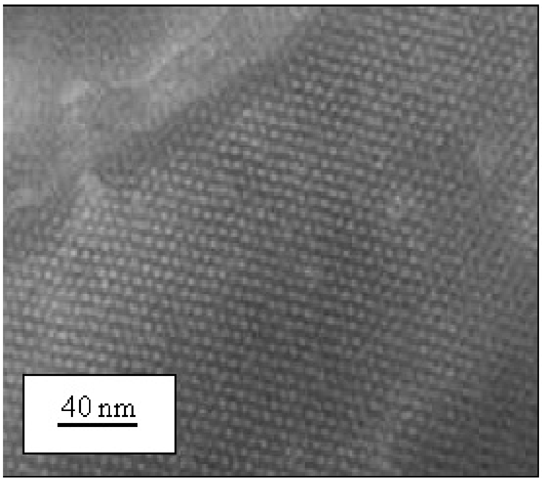

Figure 6. TEM image of MCM-41 synthesized from rice husk silica.

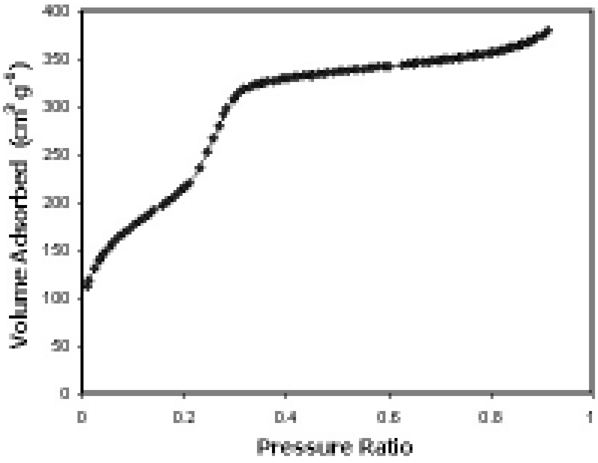

Figure 7. Adsorption isotherm of nitrogen gas at 77 K for MCM-41 particles.

Nitrogen isotherm and pore size distribution

The nitrogen adsorption isotherm for the MCM-41 particles is shown in Figure 7. According to the IUPAC classification (Brunauer *et al.*, 1940), the isotherm was Type IVc, which is the same type of isotherm found by Naono and coworkers [Naono and Hakuman, 1997; 2001]. As the relative pressure increases, the isotherms exhibit sharp inflection, which is the characteristic of capillary condensation within uniform mesopores. The ratio P/P^o at the inflection point is related to the diameter of the mesopores. The capillary condensation in a very narrow range $0.2 < P/P^o < 0.3$ suggests that the MCM-41 particles have nearly uniform pore size.

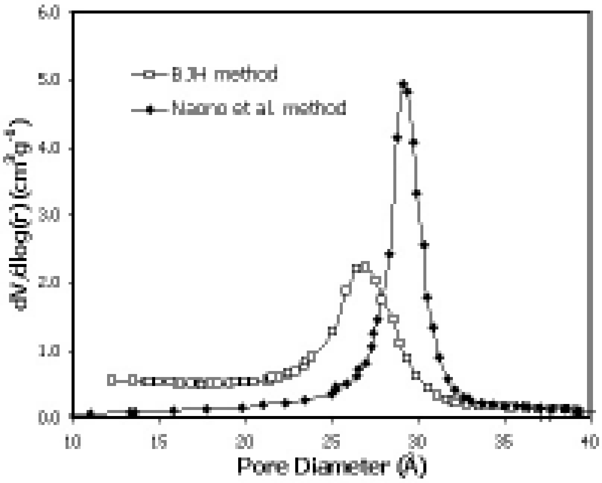

Figure 8. Pore Size Distribution of MCM-41 particles from Nitrogen adsorption isotherms using the BJH method and the method suggested by Naono (Naono and Hakuman, 1997).

The total surface area of the MCM-41 particles evaluated by using the BET theory was (800 ± 8) m^2 g^{-1}. The PSDs from the nitrogen isotherm produced by using the BJH and Naono methods are shown in Figure 8. The BJH and Naono pore size distribution curves show the MCM particles with a quite narrow pore diameter distribution, which are centered around 27 and 29 Å, respectively. The PSD calculated by Naono's method is shifted to the higher position in comparison with of that calculated by the BJH method. This distinguishable difference found is in agreement with Naono *et al.* According to Naono's paper (Naono and Hakuman, 2001), there is an appreciable difference between the adsorbed thickness on the flat surface (t_{pore}) and on the pore wall (t_{flat}). It is the fact that t_{pore} is larger than t_{flat} due to the enhanced adsorption force on the curved surface.

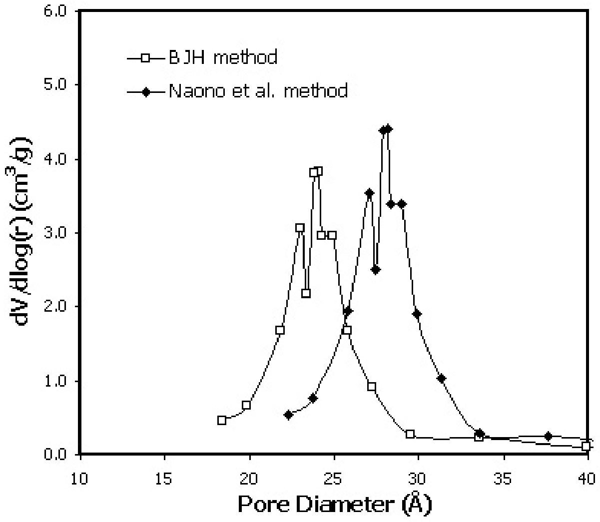

Figure 9. Pore Size Distribution of MCM-41 particles from CT isotherms by using the BJH method and the method suggested by Naono [Naono and Hakuman, 2001].

Similar to the one from the nitrogen isotherm, the PSD from the CT isotherms analyzed by the BJH method (shown in Figure 9) was underestimated compared to that from Naono's method (Naono and Hakuman, 2001). The BJH method predicted the pore diameter from the CT isotherm at a lower value (24 Å) than Naono's method (28 Å).

Conclusion

The MCM-41 particles synthesized from rice husk silica manifest the excellent sorption properties. The sorption studies using the magnetically coupled microbalance provided the well-defined isotherms, which were comparable with reports in the literature. The adsorption isotherm studies of carbon tetrachloride (CT) at 25 °C were classified as reversible Type V isotherms, and the nitrogen adsorption isotherm was Type IVc. Capillary condensation found in a very narrow pressure range indicated the uniformity of pores in the MCM-41 particles, which agrees very well with TEM results. The BET surface area was (800 ± 8) $m^2 g^{-1}$. Comparisons of different methods for evaluating the pore size in MCM-41 from nitrogen and CT isotherms were performed. The pore size distributions of nitrogen adsorption isotherms calculated by using the BJH and Naono methods showed quite narrow pore diameter distributions centered around 27 Å and 29 Å, respectively. Similarly, the peak pore diameters calculated from CT isotherms using the BJH and Naono methods were 24 Å and 28 Å.

Acknowledgements

This research was supported by National Research Center for Environmental and Hazardous Waste Management, Chulalongkorn University. The authors wish to express their sincere thanks to Dr. David Yonge, Center for Multiphase Environmental Research, Washington State University, U.S.A. for instrumental support.

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