CHAPTER V

GASEOUS PHASE ISOTHERMS OF CARBON TETRACHLORIDE AND NITROGEN GAS ON RH-MCM-41

The addition experiment mentioned in this chapter was a part of the environmental projects granted by the Pacific North National Laboratory (PNNL), U.S.A. This research was carried out in collaboration with Prof. Reid C. Miller, Dr. Brent Peyton and Oscar M. Flores, Department of Chemical Engineering and Dr. David Yonge, Center for Multiphase Environmental Research (CMER), Washington State University, U.S.A from May – August 2003. The objectives of this work were to exchange knowledge and experiences in the synthesis and characterization of a mesoporous solid, and to study a new technique for the determination of gas phase isotherms by using a gravimetric method. This work was focused on the operation of a magnetically coupled microbalance, the determination of carbon tetrachloride adsorption and desorption isotherms, and the calculation of pore size distribution using a recognized model. The material used for the sorption studies was MCM-41 synthesized from rice husk silica. The experiment results are to be used as a reference for the comparison with other kinds of porous materials in future studies.

5.1 Introduction

Carbon tetrachloride (CT) is a hazardous solvent used in cleaning, degreasing, and paint stripping. Poor solvent handling practices and the careless disposal of these hazardous m aterials h ave greatly contributed t o subsurface e nvironmental p ollution [Hudson, 2003]. Since the 1960s, CT has been found as a subsurface pollutant contaminant at the Hanford site, Washington State, where once the productions of nuclear weapon and hazardous chemicals had been operated. The difficulty in its clean up is a lack of knowledge of the controlling processes in contaminant transport and fate and the sorption behavior. It is necessary to understand the individual contributions of each fundamental factor affecting transport phenomena. The CT gas phase adsorption on porous media with different pore sizes is a current research effort

which has been conducted in the research groups of CMER. The porous adsorbents used as a contaminated media were synthesized from silicate materials in various pore sizes with a narrow pore size distribution. Accordingly, MCM-41, which has a well-defined pore size in the range of 2-50 nm and narrow pore size distribution, was suggested to be one of the media used in the experiment. This led to an interest in the utilization of the synthesized RH-MCM-41 obtained from Chapter IV as the mesoporous media for the study o f adsorption and desorption behavior of CT. The experiment was assumed to be in gas phase and dry condition. The competition of water and other dissolved chemicals has not been included in this experiment.

Recently, new procedures for gas phase sorption studies were carried out [Hudson, 2003 and Miller, 2002]. More reliable sorption techniques and real time measurement have been developed to overcome some of the drawbacks of the batch experiments. Microbalances have been introduced for gravimetric sorption studies. With this instrument, the adsorbed mass can be measured as a function of time with reproducibility and long-term stability. The microbalance system is computer controlled, allowing measurements on samples requiring long equilibration times, as well as long-term release rate studies.

In this present work, MCM-41 synthesized from rice husk silica was used as a mesoporous adsorbent. The synthesis procedure and sample characterizations examined by X-Ray Diffraction, Scanning Electron Microscope, Transmission Electron Microscope and Fourier T ransform I nfrared Spectrometry were previously discussed in Chapter IV. The sorption studies of CT measured at 25 °C were determined on a magnetically coupled microbalance. To determine whether the PSD calculated from the adsorption isotherm of CT agrees with the distribution curve obtained from the standard nitrogen isotherm measured at 77 K, the BJH method was utilized and then compared with corrected Kelvin equations recommended by Naono (2001).

5.2 Experimental

5.2.1 Equipment and Particle Preparation

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 gel sample, and changes in mass during adsorption and desorption, all within a controlled atmosphere cell.
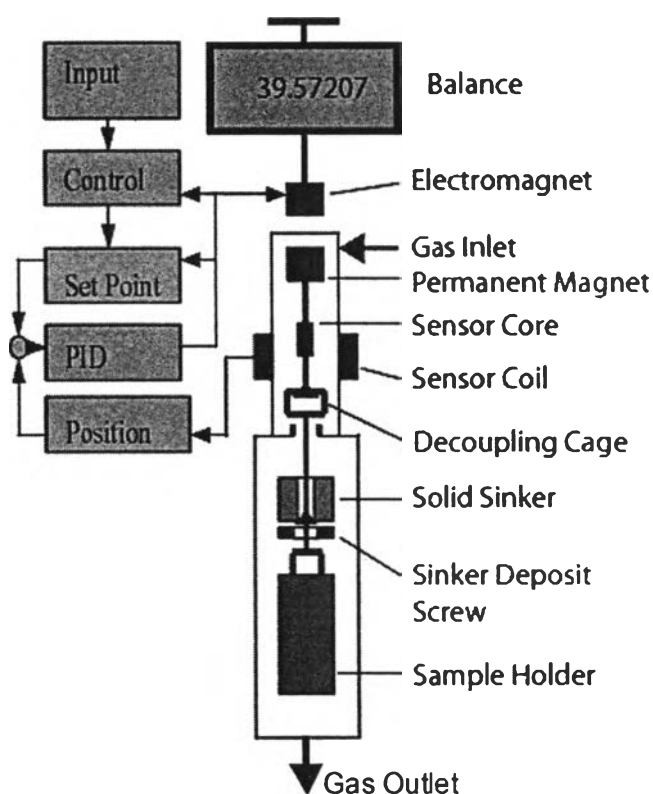

Figure 5-1 Microbalance apparatus [Hudson, 2003].

A schematic of the microbalance is shown in Figure 5-1. A sample holder and solid sinker are suspended in the main cell volume, below a permanent magnet contained within the upper cell coupling housing. The load is transmitted by magnetic force to the electromagnet, which hangs from the bottom hook on the balance pan. The control system allows measurements to be taken in three vertical positions: a tare position, a position with the sample holder (and contents) lifted, and a

position with the sinker lifted as well. The balance can be automatically calibrated against internal standard masses, but corrections have to be made for buoyancy effects of the room air. The precision of the balance is 0.00001 g with a reproducibility and accuracy approaching 0.00002 g.

Due to the fine particle size of the silica samples, a special sample holder (Figure 5-2) was designed to be placed in the microbalance to maximize surface area in contact with CT vapor. The silica sample is contained in four beds with inside diameter of 16 mm, each packed with silica particles 2-3 mm deep, and held in place by stainless steel screens. The sample beds are then stacked on three vertical rods spaced evenly on the perimeter of the holder. There are three spacers on each level of the holder that fit over the rods. The spacers are small (3 mm OD), and do not interfere with gas flow into or out of the sample beds. The sample holder is equipped with a hook to suspend it in the microbalance. The factory mass of the assembled sample holder was initially determined to be 39.57207 g.
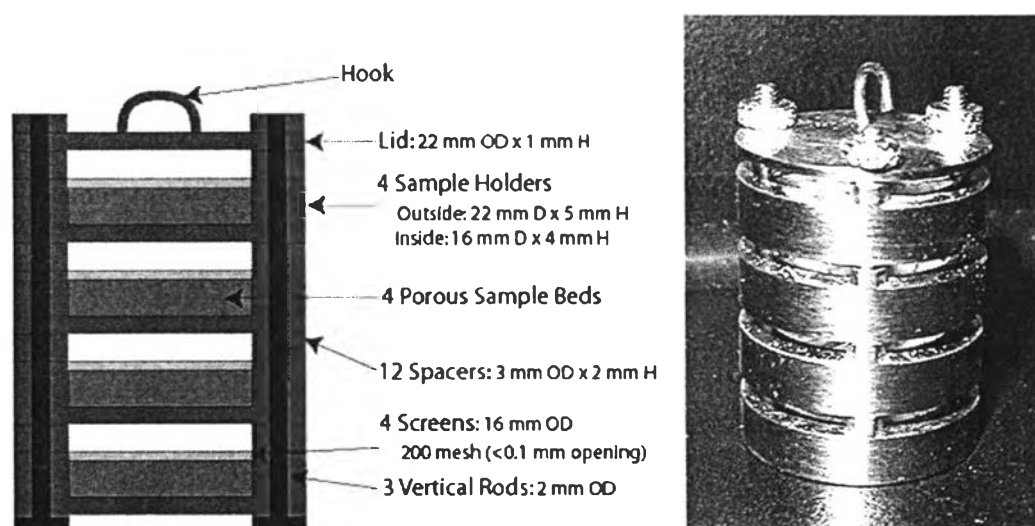
Figure 5-2 Schematic and picture of sample holder [Hudson, 2003].

A schematic of the entire system is shown in Figure 5-3. 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 this circulator, operational temperatures were in the range from 20 °C to 250 °C, and the cell temperature was maintained within ±0.05 °C. Cell

temperatures were measured with a platinum resistance thermometer (supplied by Rubotherm), with a precision of 0.01 °C and accurate to 0.1 °C. Reported temperatures as whole numbers, e.g., 25 °C, should be considered to be representative of (25.0 ± 0.1) °C. Cell pressure was measured by a Ruska quartz spiral gauge, accurate to 0.1 kPa, with a range of (0-1100) kPa. The system was connected to a compressed gas cylinder. It was also connected to the contaminant source cylinder, which was maintained in a constant temperature bath (Julabo® USA, Inc., F83-HP Ultra-Low Refrigerated Circulator, temperature range -80 °C to 50 °C, controllable to ±0.01 °C). The cell also had a vent line to an atmospheric hood located in the lab, which contained 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 [Hudson, 2003].

Mass adsorbed was determined from the microbalance mass readings versus time. The mass adsorbed was calculated by following equation

$$M_{ad} = \frac{M_{app} - M_{true}^{H+S} - \rho V^{H+S}}{1 - \dfrac{\rho}{\rho_{CT(l)}}} \quad \text{................................(5-1)}$$

where $\rho_{CT(l)}$ is the liquid density of CT, M_{true}^{H+S} the true mass of sample plus holder, M_{app} the appearance mass, and V^{H+S} the volume of sample plus holder.
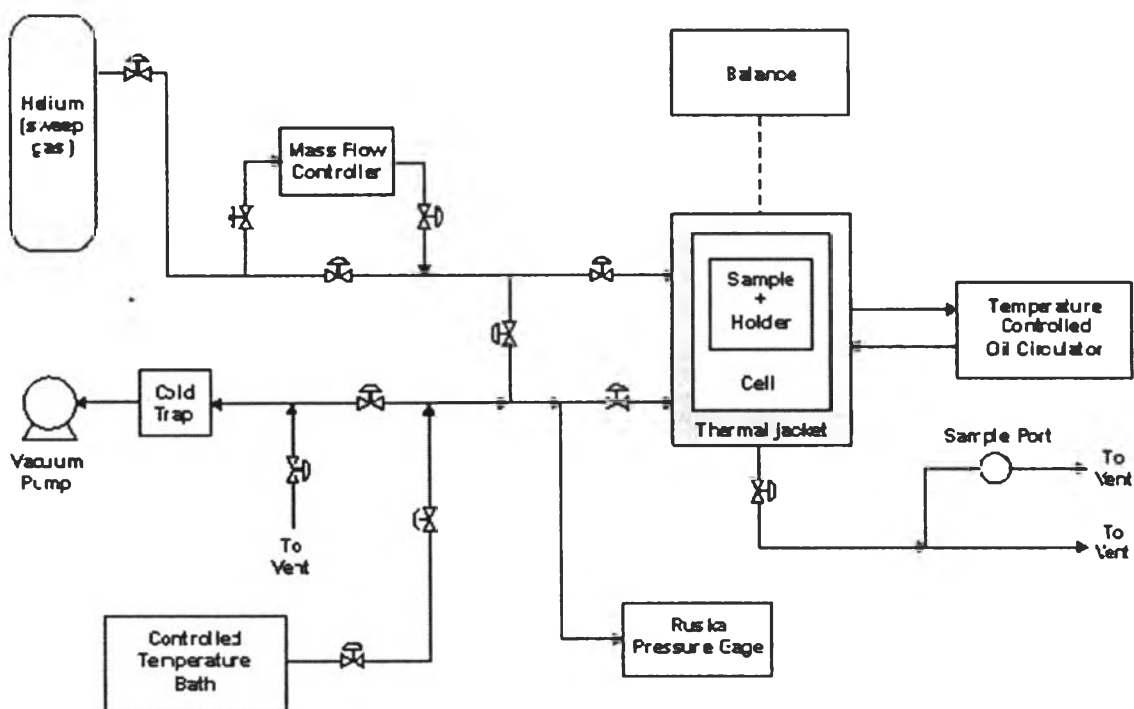
Figure 5-3 Schematic of the sorption system.

The MCM-41 samples used in this experiment were synthesized from rice husk silica. In order to study the desorption of CT from silica particles under dry conditions, sample pretreatment was required. Before running the experiments, samples were ground into fine particles, heated in an oven at 150 °C for 12 h, and then transferred to a dessicator to cool. Then, particles were loaded in the sample holder and dried in the oven again before using. The sample holder was transferred to the hook in the microbalance, and the cell raised quickly, with continuous flushing of helium from the upper part of the cell. Once the cell was assembled, helium flow was terminated, the cell temperature was raised to 70 °C for at least 12 hours, under evacuation, with a liquid nitrogen cold trap in the vacuum line. When the mass reading from the microbalance was steady, the temperature was lowered to 25 °C, and the study of CT isotherms was conducted.

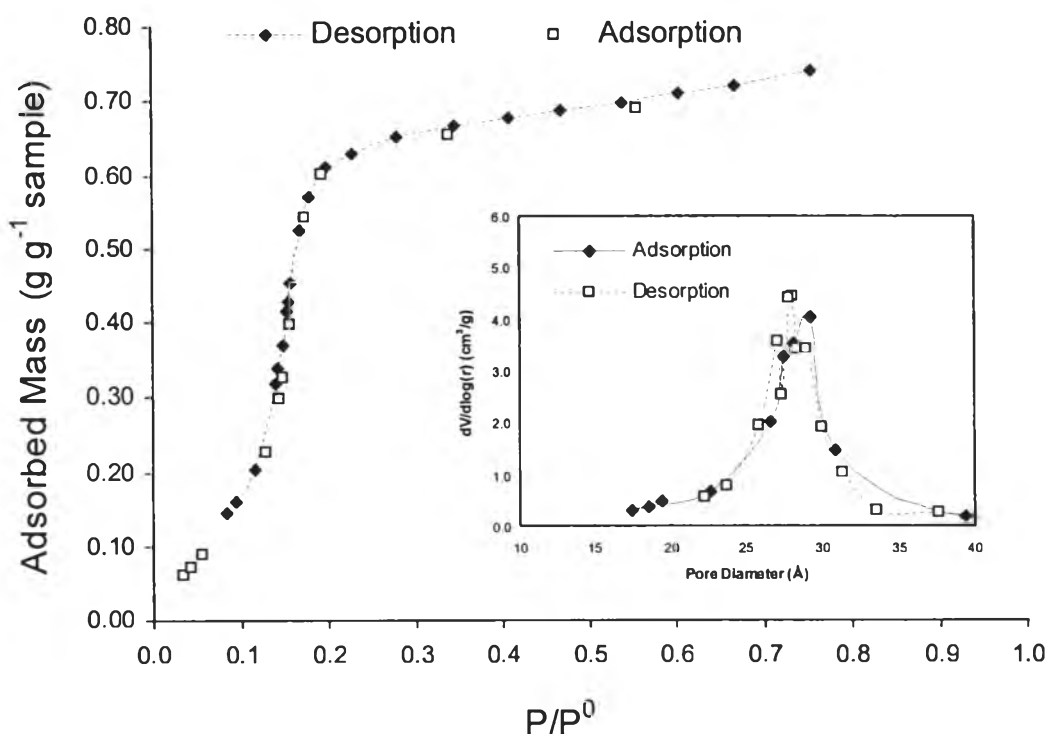### 5.2.2 Carbon Tetrachloride Adsorption and Desorption Isotherms

Experiments to determine CT isotherms were conducted to obtain important information about the pore size distribution, which is one of the essential factors for characterizing mesoporous materials. It was desirable to compare the CT isotherm results with nitrogen adsorption results at 77 K. According to the traditional BJH method, the Kelvin equation is used, in conjunction with information on adsorption onto flat surfaces of the material in question and to calculate the pore size distribution. However, the reliability of this approach has become a concern for mesoporous silicas, because it produces underestimated pore size distributions [Storck, 1998 ; Naono, 2001; Carrott, 2001]. For this reason, a new method to calculate the pore size distributions was utilized to analyze the isotherms. According to Naono and coworkers [Naono, 2001], there are differences of absorbed thickness between curved and flat surfaces, which need to be taken into account. In this experiment, the pore size distributions were calculated by the methods recommended by these investigators.

5.2.2.1 Procedures

A desorption isotherm was carried out at 25 °C by filling the microbalance cell with CT vapor at 0.13 atm (CT sample temperature of 24 °C) and allowing the mass and pressure to come to an equilibrium. The valve between the CT sample and the cell was closed prior to the final approach to an 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. For each point, the cell was opened to the sample cylinder for about 30 min, and then the valve was closed to isolate the cell during the final approach to reaching an equilibrium.

5.2.2.2 Results and Discussion

The CT isotherms and the pore size distribution presented in Figure 5-4 are classified as reversible Type V isotherms [Branton, 1999], which agrees very well with those found in the literature [Pankow, 1996; Naono, 2001]. Type V isotherms indicated the presence of monolayer-multilayer adsorption. The adsorbent-adsorbate interactions are weak when compared to adsorbate-adsorbate interactions. No significant hysteresis was found between the adsorption and desorption isotherms. The capillary condensation occurs in a very narrow relative pressure range ($P/P^0 = 0.16 \pm 0.02$). This steep region in the isotherm indicates the presence of nearly uniform pores in the MCM-41 particles.

Figure 5-4 Adsorption and desorption isotherm of carbon tetrachloride at 25 °C and pore size distribution of MCM-41 particles calculated by the adsorption isotherm using the BJH method and the method suggested by Naono (2001).

The calculations of PSDs were derived from Equations 5-2 and 5-3 following Naono's method (2001), as utilized by Hudson (2003). These two equations provide the fundamental information necessary to calculate the PSD of mesoporous materials

in the range of 1-5 nm. They are used to calculate core radius (r_c), and the thickness of adsorbed CT on the curved surface (t_p). Pore diameter is determined from radius (r_p), which is the sum of r_c and t_p. The volume adsorbed is calculated from the density of liquid CT and the CT mass adsorbed from the microbalance readings. The PSD plot from the adsorption and desorption CT isotherms is inserted in Figure 5-4. 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 formerly in Figure 4-5.

$$\ln\left(\frac{P^0}{P}\right) = 2.17 r_c^{-1}$$

....(5-2)

$$t_p = 0.188 + 0.336\left(\frac{P}{P^0}\right) + 0.382\left(\frac{P}{P^0}\right)^2 \qquad 0.08 < P/P^0 < 0.60$$

...................(5-3)

In these equations, r_c and t_p are in nm, and P^0 is the CT vapor pressure at 25 °C.

5.2.3 Nitrogen Adsorption Isotherm

5.2.3.1 Procedures

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.

5.2.3.2 Results and Discussion

The nitrogen adsorption isotherm for the MCM-41 particles is shown in Figure 5-5. According to the IUPAC classification, the isotherm was Type IVc, which is the

same type of isotherm found by Naono and coworkers (1997, 2003). The isotherm represented a steep vertical section in a range of $0.2 < P/P^0 < 0.3$, which occurs in porous materials with a narrow range of uniform, cylindrical pores [Kumar, 2001].

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 inserted in Figure 5-5. The peak pore diameters calculated from both models are shown in Table 5-1. 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, 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 [Naono, 1997].

The comparisons of the pore diameters calculated from the nitrogen and CT adsorption isotherms using the BJH model and Naono's method are presented in Table 5-1. Similar to the one from the nitrogen isotherm, the PSD from the CT isotherms analyzed by the BJH method (shown in Figure 5-4) was underestimated compared to that from Naono's method. The BJH method predicted the pore diameter from the CT isotherm at a lower value (24 Å) than Naono's method (28 Å).

Table 5-1 Pore diameters for nitrogen and CT adsorption isotherms on MCM-41 particles.

Methods	Pore diameter (Å)
N$_2$ PSD – BJH method	27
N$_2$ PSD – Naono et al. method (1997)	29
CT PSD – BJH method	24
CT PSD – Naono et al. method (2001)	28
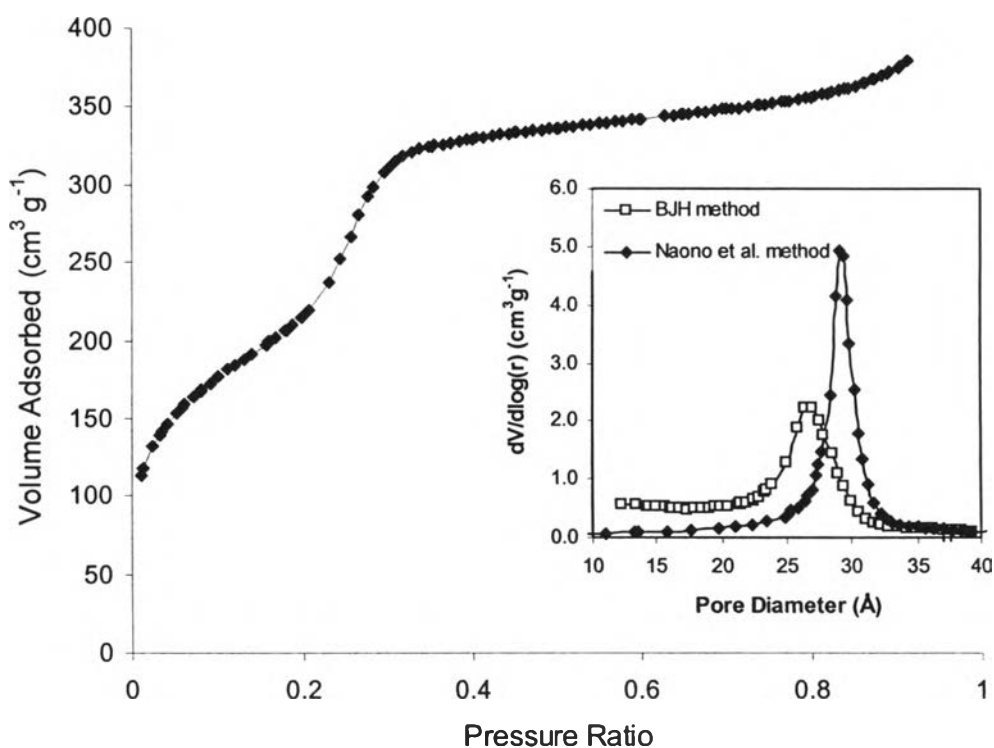
Figure 5-5 Adsorption isotherm of nitrogen gas at 77 K and pore size distribution of MCM-41 particles calculated by using the BJH method and the method suggested by Naono et al. (1997).

5.3 Summary

The s orption s tudies o f C T o n t he M CM-41 p articles sy nthesized f rom rice husk silica using the magnetically coupled microbalance provided the well-defined isotherms, which were comparable with those in the literatures. 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) $m^2 g^{-1}$. The pore size distributions of nitrogen adsorption isotherms calculated by using the BJH and Naono methods [3, 11] 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.