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Functionalized Mesoporous Silica Utilization for VOCs Adsorption

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Functionalized FDU-12 has been studied in the application for hydrocarbon vapor adsorption. In here, the moieties were phenyl and vinyl which being introduced into FDU-12 synthesis using co-condensation methods with the presence of tri block co-polymer P123 as the template. The adsorption used two different vapors, benzene and n-hexane, at 20^0C. The result suggested that the groups increased the affinity of adsorbing the vapors compared with pure FDU-12.

Keywords: Mesoporous silica, sol-gel, adsorption, VOCs, co-condensation, co-polymer.

INTRODUCTION

Mesoporous silicas, since their invention, has attracted a huge attention due to their ordered structure and with controllable pore size as the most interesting characteristic. Based on these features, the utilizations of the materials for catalyst support, adsorbent, and enzyme immobilization are indispensable.

The recent invention of a unique mesoporous silica called SBA-15 show more promise as to benefits from previous materials by being able to provide bigger pores and a higher thermal stability (Zhao et al. 1998). Furthermore, a recent modification in synthesizing SBA-15 by lowering the temperature and using a swelling agent has been reported and called *FDU-12* (Fan et al. 2005). FDU-12 has several major advantages including low temperature synthesis, broad ranged and controllable pore width, and thermal stable.

Most of the adsorption studies of functionalized mesoporous silica were under environmental concerns, such as adsorbing heavy metal ions in the aqueous solutions. For example, the thiol functional group incorporated in mesoporous silica has been reported to increase the adsorption capacity of Hg(II) (Quintanilla et al. 2006, Liu et al. 2000). While the amino group could enhance the adsorption of Cu(II), Zn(II), Cr(III), and Ni(II) (Liu et al. 2000).

In terms of gas and vapor adsorptions, fewer reports have been documented. For CO_2 adsorption, the effects of aminopropyl group addition have been studied (Hiyoshi, Yogo, and Yashima 2005, Knowles et al. 2005). This group contribution in the adsorption of acetaldehyde on MCM-48 has also been reported (Matsumoto et al. 2002). Then, a recent important hydrocarbon adsorption study has proved that ethylene fragments in PMO increased the capacity and affinity in adsorbing n-hexane compared with pure MCM-48 (Matsumoto, Misran, and Tsutsumi 2004). On the other hand, some enzyme immobilization studies have revealed that by modification of mesoporous silica using phenyl and vinyl the enzyme adsorption affinity can be increased (Chong and Zhao 2004).

The aforementioned results suggest that long alkyl groups incorporated in the mesoporous silica framework exhibit high adsorptivity towards nonpolar hydrocarbon substances. Thus, application of this method for adsorbing harmful gases, such as VOC vapors, deserves further exploration.

In this paper, functionalized FDU-12 by phenyl and vinyl groups have been studied to adsorp benzene and n-hexane vapors. Based on the author's best knowledge this application has not been explored yet. Thus the results will be compared with pure FDU-12 as to adsorption ability and capacity. Phenyltrimethoxysilane (PTMS) and vinyltrietoxysilane (VTES) were the organosilanes being used to bring the functional groups.

EXPERIMENT

PREPARATION OF THE MATERIALS

The preparation of pure FDU-12 followed the method of Fan et al. (2003). The chosen temperature for material synthesis was 15^0C.

Whilst, the functionalized FDU-12 materials were synthesized via co-condensation method. The molar ratio of organosilanes/TEOS has been varied. Then, the sample will be named as *1:n:Z:T;* where, *n* is the proportion of TEOS in the ratio, *Z* is the organosilanes used (PTMS or VTES), and T (^{0}C) is the hydrothermal treatment temperature. Temperatures of 100 and 140 ^{0}C were used in the treatment.

Adsorption of the Vapors

Adsorptions were carried out by a self-assembly gravimetric adsorption apparatus as shown in figure 1.

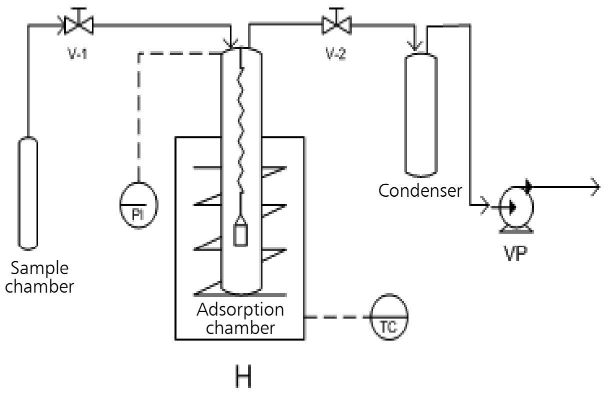


Figure 1. Gravimetric Adsorption Rig Diagram

RESULTS AND DISCUSSION

Material Characteristics

The synthesized materials have been characterized by nitrogen adsorption, small angle X-ray scattering (SAXS), and TEM for investigating the solid structure.

Table 1 shows the summary of the physical adsorption analysis. Several SAXS characterization results will be shown in Figure 2. From the SAXS pattern, it can be seen that the addition of functional groups does not alter much the structure of materials. The higher temperature of hydrothermal treatment caused some peaks to diminish; this result indicates that less ordered materials have been produced.

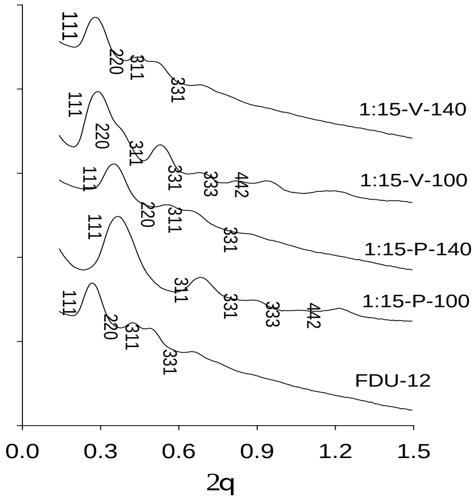


Figure 2. SAXS Patterns for Several Samples.

The peaks emerged at the range of $0.2<2\theta < 1.3$, which can be indexed on planes 111, 220, 311, 331, 333, and 442. This represents a cubic crystal structure similar to that reported Fan et al. (2003).

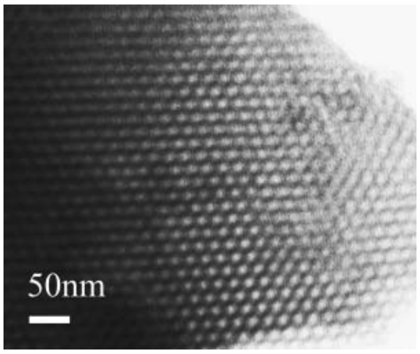
The TEM images in Figure 3 confirmed that ordered materials have been successfully synthesized. The structure of larger pores due to the effect of higher hydrothermal treatment temperature is also obviously presented.

Table 1. Physicochemical Properties of Synthesized Materials.

Sample	S_{BET} *m²/g*	d pore (A)		Vpore *cm³/g*
		Ads	Des.	
1:15:PTMS:100	279.1	62.54	18.67	0.3363
1:15:VTES:100	353.5	96.68	18.72	0.4147
1:5:VTES:100	363.9	62.48	18.68	0.3778
1:15:PTMS:140	279.3	82.39	30.14	0.7772
1:15:VTES:140	231.9	115.60	45.87	0.7813
1:5:VTES:140	338.9	75.64	18.72	0.7262
Pure FDU	239.3	182.7	45.25	0.7662

ADSORPTION

N-Hexane. Adsorption and desorption measurements of n-hexane were conducted at room temperature. The isotherms are depicted in Figure 4. Generally, all the isotherms fall into type IV with hysteresis loops type of H1 and H2. The higher hydrothermal temperature produced larger pores; thus, the materials are able to adsorb more vapor this as shown by the taller isotherms. However, the hysteresis loops became smaller when the temperature increased. This could be a sign of diminishing cage-shape pores by adding a high temperature treatment.



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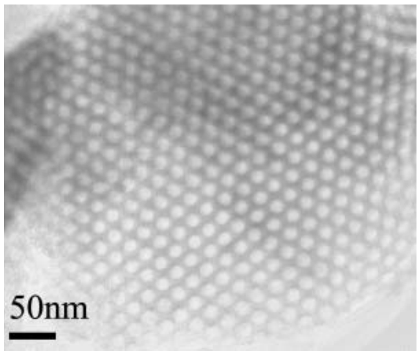

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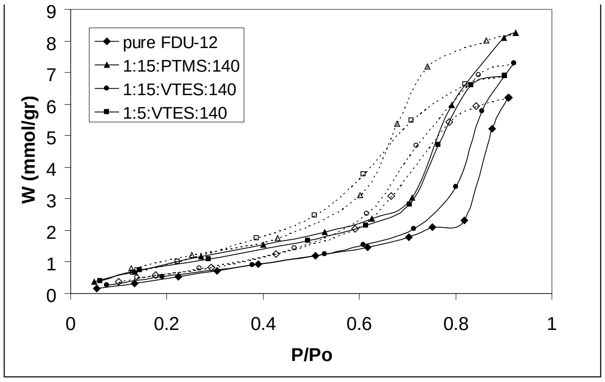
Figure 3. TEM Images of Several Synthesized Materials: (a) 1:15-V-100, and (b) 1:15-V-140

The functional groups are obviously increasing the adsorption capacity. This may be caused by the interaction of moieties with n-hexane molecules. It is noteworthy that the phenyl group showed better performance compared with vinyl, especially at higher hydrothermal temperatures.

Benzene. Benzene vapor adsorption exhibited quite similar results with n-hexane. At the average, benzene isotherms are higher than hexane's. The materials gained better affinity in adsorbing benzene. Thus, the application of the solid for benzene adsorption should be considered.



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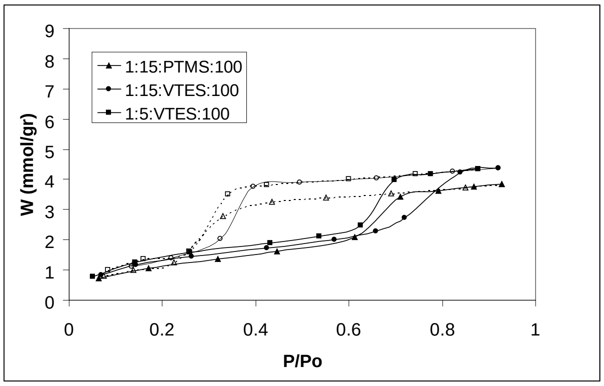

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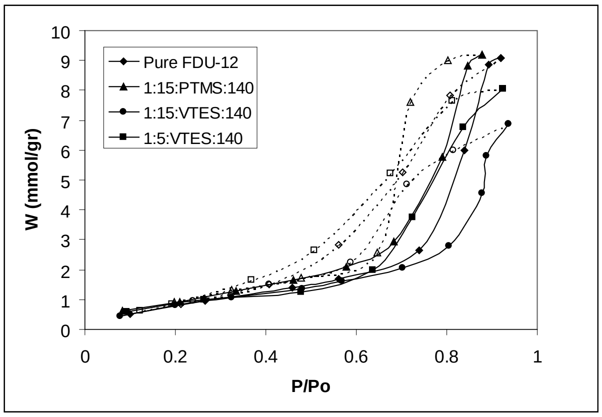
Figure 4. Adsorption Isotherms of n-hexane at Hydrothermal Temperatures (a) 140^{0}C and (b) 100^{0}C (•adsorption and o desorption)

The entire isotherm has a hysteresis loop. This indicates that the pores inside the material is cage-shaped. Hydrothermal treatment alters the entrance pore as the high temperature treatment reduces the cage shape into ordinary cylindrical pores.



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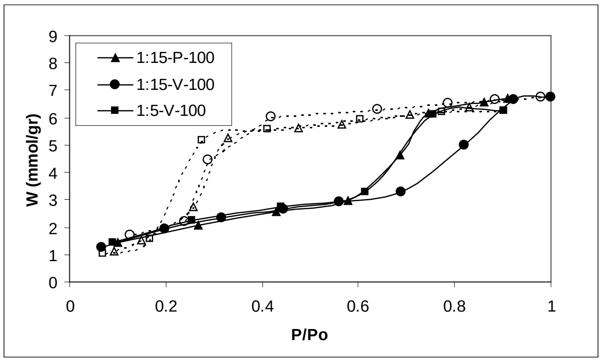

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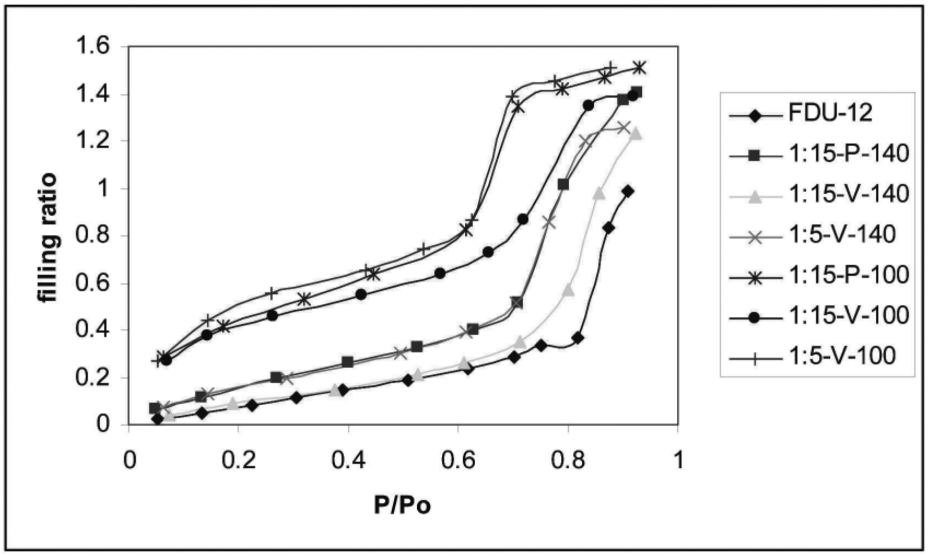
Figure 5. Adsorption Isotherms of Benzene at Hydrothermal Temperatures (a) 140^{0}C and (b) 100^{0}C (•adsorption and o desorption)

Pore filling ratio. In pore filling ratio calculation, the vapor is assumed to fill the pore as liquid. Thus, by knowing the liquid density of all the vapors, the weight-based data of isotherms can be altered into a volumetric adsorption data then being normalized by the available volume of the adsorbent's pores.



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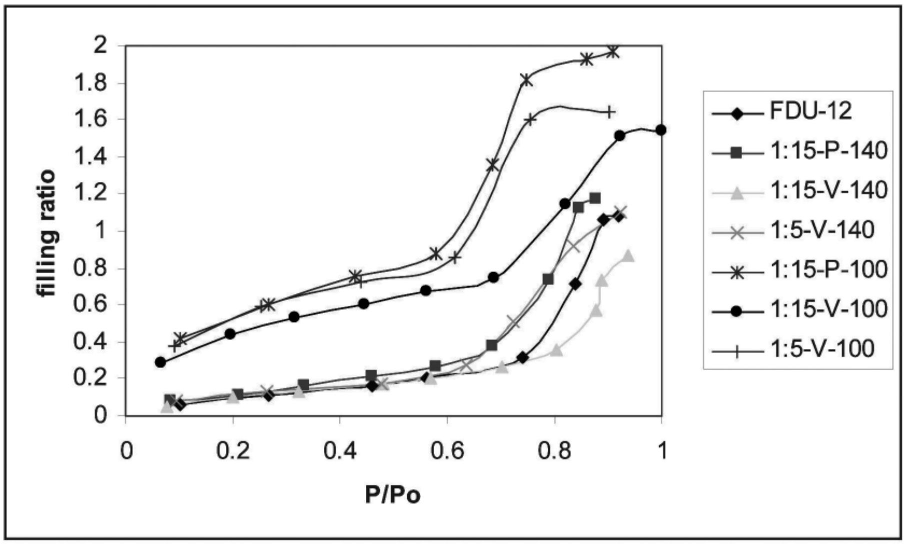

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Figure 6. Adsorption Isotherms Using Filling Ratio Calculation for (a) n-hexane Adsorption and (b) Benzene Adsorption

Thus, this method gives a reliable comparison among the materials in adsorbing the vapor regardless of the shape and capacity of the pores. The bulk liquid density of n-hexane is 0.654 g.cm^{-3} and of benzene is 0.871 g.cm^{-3} (Carrot et al. 2001).

Figure 6 shows that lower temperature hydrothermal materials have better affinity for adsorbing benzene than the higher temperature group. Overall, the phenyl group modified materials delivered the highest adsorptivity. Increasing ratio of vinyl concentration helped to better the performance of the materials as has been shown that materials with 1:5 ratio of VTMS in their synthesis had better affinity than the phenyl functionalized materials.

For n-hexane adsorption, a similar result as that from benzene adsorption of filling ratio calculation has been obtained. The lower temperature of hydrothermal treated materials exhibited better performances. Thus, the overall isotherms give a picture of superiority for phenyl functionalized materials compared to the others.

CONCLUSION

Functional groups can increase the adsorption performance of mesoporous silica. This effect has been due to two reasons. First, the groups increase the affinity of the solids towards vapor molecules. Second, the groups modify the solid pore and the surface area becomes more vapor adsorbent. Phenyl functionalized FDU-12 apparently showed a good affinity and capacity in adsorbing n-hexane and benzene vapors.

Higher hydrothermal treatment temperatures will enhance the pore volume and adsorption capacity, but decrease the adsorption affinity.

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