



Adsorption of formaldehyde vapor by amine-functionalized mesoporous silica materials

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Abstract

The amine-functionalized mesoporous silica materials were prepared via the co-condensation reaction of tetraethoxysilane and three types of organoalkoxysilanes: 3-aminopropyl-trimethoxysilane, *n*-(2-aminoethyl)-3-aminopropyltrimethoxysilane, and 3-(2-(2-aminoethylamino)ethylamino) propyl-trimethoxysilane. Cetyltrimethylammonium bromide was used as a template for forming pores. Specific surface area and pore volume of the amine-functionalized mesoporous silica materials were determined using surface area and pore size analyzer. Fourier transform infrared (FTIR) spectroscopy was employed for identifying the functional groups on pore surface. In addition, the amine-functionalized mesoporous silica materials were applied as adsorbents for adsorbing formaldehyde vapor. FTIR spectra showed the evidence of the reaction between formaldehyde molecules and amine groups on pore surface of adsorbents. The equilibrium data of formaldehyde adsorbed on the adsorbents were analyzed using the Langmuir, Freundlich and Temkin isotherm. The sample functionalized from *n*-(2-aminoethyl)-3-aminopropyltrimethoxysilane showed the highest adsorption capacity owing to its amine groups and the large pore diameter.

Key words: adsorption; characterization; amine; formaldehyde

Introduction

Formaldehyde emitted from the building materials and household products industry is a colorless and pungent-smelling gas. It can cause a serious air pollution problem. Sources of formaldehyde in the home include some decorated materials, paint and binder of some combination furniture and chemical fiber carpet. Thus, it may be present in high concentration both indoors and outdoors. Formaldehyde can cause watery eyes burning sensations in the eyes and throat, nausea and difficulty in breathing in some humans exposed at elevated levels (above 0.1 ppmv). Environment Protection Agency (USEPA) reported that exposed to formaldehyde can cause cancer in animals and may cause cancer in human beings.

The carbonaceous adsorbents were most widely used for removing formaldehyde from atmosphere (Haiqin *et al.*, 2003; Krisztina, 2005). Nevertheless, the formaldehyde is not efficiently removed by the activated carbon. Prior to this work, our group reported the adsorption of formaldehyde by the adsorbents derived from coffee activated carbons (Virote *et al.*, 2005) and mesoporous silica materials. The experimental results indicated that the adsorption capacity of mesoporous silica material is more

than 1 g/g-adsorbent which is around three times higher than that of activated carbon.

The ordered mesoporous materials synthesized via sol-gel route were firstly discovered by mobil company researchers (Beck *et al.*, 1992; Kresge *et al.*, 1992). The ordered mesoporous materials were known for using in many applications such as catalysts (Wang *et al.*, 1999; Isa and Brent, 2005), adsorbents (Zhao *et al.*, 2000; Ghiaci *et al.*, 2004; Lu and Yan, 2004) and sensor (Kumaran *et al.*, 2001; Baohong *et al.*, 2003; Xu *et al.*, 2005), and so on. In particular, the functionalized mesoporous materials has been paid more attention for the application in removal and recovery of metal ions (Liu *et al.*, 2000; Nooney *et al.*, 2001; Hee-Jung *et al.*, 2004), in adsorption of organic dyes (Wu *et al.*, 2004), and in immobilization of enzymes or protein (Han *et al.*, 1999; Lei *et al.*, 2004; Yurii *et al.*, 2004; Maria and Zhao, 2004), that all relate to the surface functional groups which can be appropriately modified. However, the application of the hybrid mesoporous materials in formaldehyde adsorption has not been explored yet. Therefore, here we reported the synthesis, characterization and efficiency of formaldehyde adsorbents. The co-condensation method is used to introduce the organic groups into the silica network.

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1 Experimental

1.1 Materials

Tetraethoxysilane ($\text{Si}-(\text{OC}_2\text{H}_5)_4$, TEOS) was used as the silica precursor. The functional groups on pore surface of adsorbent were generated from non-hydrolysed ligand of trifunctional organoalkoxysilanes ($\text{R}'-\text{Si}-(\text{OR})_3$): 3-aminopropyltrimethoxysilane or APTMS), *n*-(2-aminoethyl)-3-amino-propyltrimethoxysilane or AEAP) and 3-(2-(2-aminoethylamino)ethylamino) propyltrimethoxysilane or AEEA). The cationic surfactant, cetyltrimethyl ammonium bromide ($\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{NBr}$, CTAB) was used as template or pore-forming agent. Formaldehyde vapor generated by formaldehyde solution (37%, W/W) was used as adsorbate in adsorption experiments.

1.2 Synthesis of amine-functionalized mesoporous silica materials

The synthesis process involved mixing of known amounts of CTAB, ethanol and deionized water by stirring for 30 min. Then TEOS and $\text{R}'-\text{Si}-(\text{OR})_3$ were simultaneously added to the vigorously stirred mixture. The molar ratio of TEOS: $\text{R}'-\text{Si}-(\text{OR})_3$:CTAB:EtOH is 0.85:0.15:0.22:5. The molar ratio of H_2O /precursors ($\text{TEOS} + \text{R}'-\text{Si}-(\text{OR})_3$) was varied for three values of 160, 80 and 16. The mixture was stirred at 60°C for 24 h. The resulting precipitate was filtered and air dried for 24 h. The product was then washed by 1.0 mol/L HCl/EtOH (50 ml of HCl/EtOH per gram of sample) at 70°C for 24 h to remove surfactant template from silica network and form pore without destroying the functional ligands on pore surface. After that the sample was filtered and washed with ethanol until pH > 6. Then, the sample was dried in hot air oven at 90°C for 24 h. Names of the derived samples are in form of $x\text{NS}_y\text{W}$, where, x is 1, 2 or 3 and y is 160, 80 or 16. “ x ” stands for the number of amine group from organoalkoxysilane precursor and “ y ” stands for the molar ratio of H_2O /precursors.

1.3 Characterization

Surface area and pore size analyzer (AUTOSORB-1, Quantachrome Corp., USA) is the equipment for measuring the nitrogen adsorption-desorption isotherms of the samples. These isotherms were used to determine the specific surface area and pore volume of the adsorbents. Prior to each measurement, the hybrid mesoporous materials were outgassed at 110°C under nitrogen flow for 3 h. The nitrogen adsorption-desorption data were recorded at liquid nitrogen temperature (77 K). The specific surface areas were calculated using Brunauer-Emmett-Teller (BET) equation (Brunauer *et al.*, 1938). Micropore volume and mesopore surface area were evaluated using t-plot method. This is the plot of the volume of N_2 adsorbed versus the statistical adsorbed film thickness, t ($\times 10^{-10}$ m) calculated from Halsey equation (Halsey, 1948). In addition, pore diameter and pore size distribution were investigated by using Barrett-Joyner-Halenda (BJH) method (Barrett *et al.*, 1951).

Fourier transform infrared (FT-IR) spectroscopy was used to qualitatively identify the chemical functionality of the synthesized adsorbents before and after adsorption process. To obtain the observable adsorption spectra, the samples were ground to the average diameter of 0.5 μm . The transmission spectra of the samples were recorded using the KBr pellet containing 0.1% of sample. The pellets of 12.7 mm in diameter and 1 mm thick were prepared in a manual hydraulic press at 10 t and dried overnight at 100°C before the spectra were recorded. The spectra were measured from 4000 to 400 cm^{-1} and recorded on a 1760X spectrometer, Perkin-Elmer, German.

1.4 Adsorption experiment

The adsorption capacity of adsorbents was determined using desiccator method. Firstly, water was pre-adsorbed on the adsorbents in the first desiccator in which the relative humidity was controlled near to the level of relative humidity in formaldehyde vapor by salt solution. Then, the samples were moved to the second desiccator containing a beaker of formaldehyde solution to adsorb the vapor from formaldehyde solution. The formaldehyde concentration was varied for five values of 5 wt.%, 10 wt.%, 20 wt.%, 30 wt.%, 37 wt.%. The adsorption data were fitted by Langmuir, Freundlich and Temkin isotherms.

2 Results and discussion

2.1 N_2 isotherms and pore size distributions

Most solids are inherently porous and many techniques have been developed to characterize the porous structure of solids. Among them the nitrogen adsorption technique is the most popular one that can obtain the data on the BET surface area, total pore volume and pore size distribution. The adsorption-desorption isotherms are grouped into six types followed the International Union of Pure and Applied Chemistry (IUPAC). The N_2 adsorption-desorption isotherms for extracted amine-functionalized silica materials synthesized using H_2O /precursors ratio of 160, 80 and 16 are shown in Fig.1. The isotherms are similar to type IV isotherms with a hysteresis loop for samples 1NS160W, 2NS160W, 1NS80W, 2NS80W, 3NS80W and 1NS16W. The hysteresis loops are associated with capillary condensation taking place in mesopores (Sing *et al.*, 1985). For samples 3NS160W and 3NS16W, the isotherms cannot be specified to any type but they are similar to type II of nonporous solid with the small loops that look like those of type IV isotherms. These samples contain small specific surface area and their pores are in the range of mesopore.

Table 1 summarizes the results of specific surface area, pore volume and average pore diameter of the derived hybrid materials. It is observed that specific surface areas (S_{BET}) are relatively high for samples containing short amino chain. The sample of 1NS demonstrates the highest S_{BET} where as the sample of 3NS shows the lowest S_{BET} for every molar ratios of water to precursors. The results of total pore volume (V_{T}) show somewhat similar trend as of S_{BET} . The decrease of specific surface with increasing the

length of amino chain was also observed by Macquarrie *et al.* (1999). They reported that changing amino ligand from aminopropyl- to aminoethyl- aminopropylled to a decline of specific surface area from 750 to 650 m²/g.

The results of pore size in Table 1 and Fig.2 indicate that pore size increases with the increase of amino chain length from one amine group to two amine groups (samples 1NS and 2NS). However, it decreases when using the precursor with three amine groups to synthesize sample 3NS. The decrease of pore size in the sample of 3NS may be ascribed to the inhibition of the co-condensation between TEOS and AEEA by the long ligands of precursor resulting in the homo-condensation of TEOS. Thus, there are both mesopore and micropore in structure of sample 3NS and the average pore diameter is rather small.

In addition, the amount of water used during synthesis also influences the specific surface area of the derived materials. The samples prepared using the H₂O/precursors ratio of 80 yield the highest S_{BET} for all precursors. This ratio is the most appropriate condition among the others for synthesizing the amine-functionalized hybrid materials in this study. The H₂O/precursors ratio of 16 is insufficient

to complete the hydrolysis and condensation whereas the excess water at H₂O/precursors ratio of 160 may cause the incomplete reaction and the intermediate species are generated instead (Brinker and Scherer, 1990).

2.2 Fourier transform infrared spectroscopy

The functional groups contained in the samples were identified using FTIR technique. The IR patterns of the hybrid materials before and after adsorbing formaldehyde vapor are shown in Fig.3 for APTMS, AEAP and AEEA precursors, respectively. The large broad band between 3700 and 3200 cm⁻¹ is referred to O–H bond stretching of the surface silanol groups which is one of the main features of the spectrum. A strong peak between 1090 and 1010 cm⁻¹ is the band of siloxane, –Si–O–Si–. Another position for siloxane band is between 625 and 480 cm⁻¹. Si–O bond stretching of silanol group was observed as a small band at 990–945 cm⁻¹. A peak between 810 and 790 cm⁻¹ is the band of Si–OR, the remained alkoxide groups because of the incomplete hydrolysis reaction. A small peak at band number 1650–1600 cm⁻¹ is caused by deformational vibrations of adsorbed water molecules (Socrates, 2001).

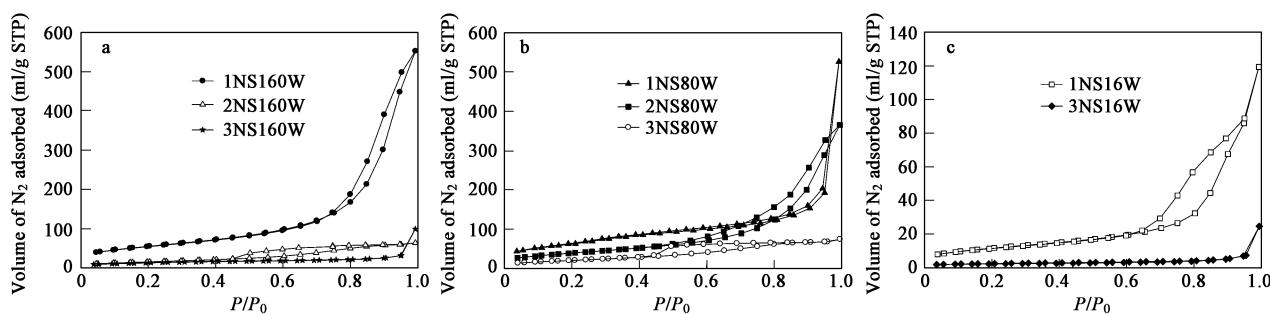


Fig. 1 N₂ adsorption-desorption isotherms for amine-functionalized silica materials synthesized using H₂O/precursors of 160 (a), 80 (b), and 16 (c).

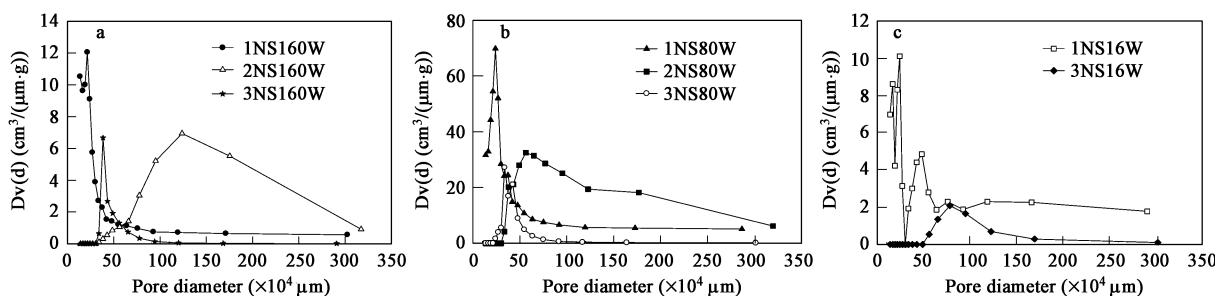


Fig. 2 Pore size distribution of amine-functionalized hybrid materials synthesized using H₂O/precursors of 160 (a), 80 (b), and 60 (c).

Table 1 Texture characteristics and percent yields of amine-functionalized hybrid materials

Sample	Pore volume (cm ³ /g)			Surface area (m ² /g)			D ($\times 10^{-10}$ m)
	V_T	V_{me}	V_{mi}	S_{BET}	S_{me}	S_{mi}	
1NS160W	0.859	0.859	0.000	198.00	198.00	0.00	127.9
2NS160W	0.153	0.152	0.001	57.68	55.42	2.26	172.4
3NS160W	0.099	0.086	0.013	47.88	44.22	3.66	68.4
1NS80W	0.814	0.755	0.059	237.30	128.20	109.10	137.2
2NS80W	0.565	0.565	0.000	141.40	141.10	0.00	159.8
3NS80W	0.114	0.025	0.089	75.67	9.47	66.20	60.4
1NS16W	0.185	0.184	0.001	41.54	39.50	2.04	186.5
2NS16W	N/A	N/A	N/A	N/A	N/A	N/A	N/A
3NS16W	0.038	0.038	0.001	8.14	6.58	1.56	177.7

V_T : Total pore volume; V_{me} : mesopore volume; V_{mi} : micropore volume; S_{BET} : BET surface area; S_{me} : mesopore surface area; S_{mi} : micropore surface area; D : average pore diameter.

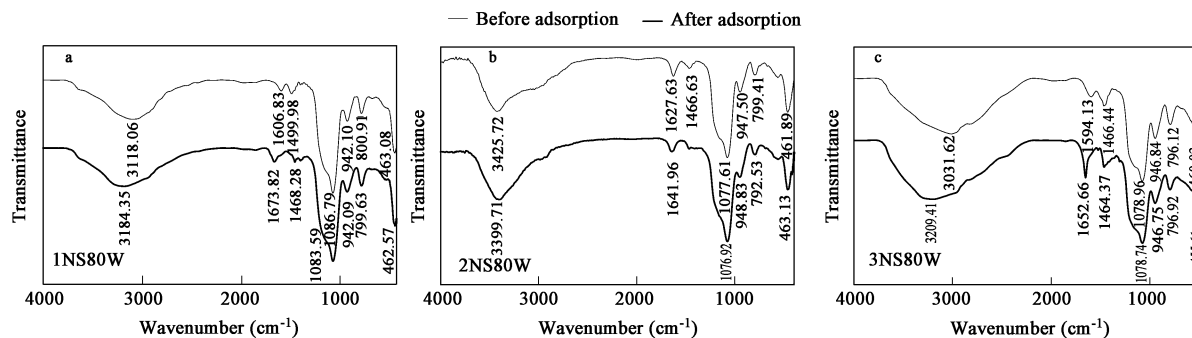


Fig. 3 FTIR spectra of sample 1NS80W (a), 2NS80W (b), 3NS80W (c) before and after formaldehyde adsorption.

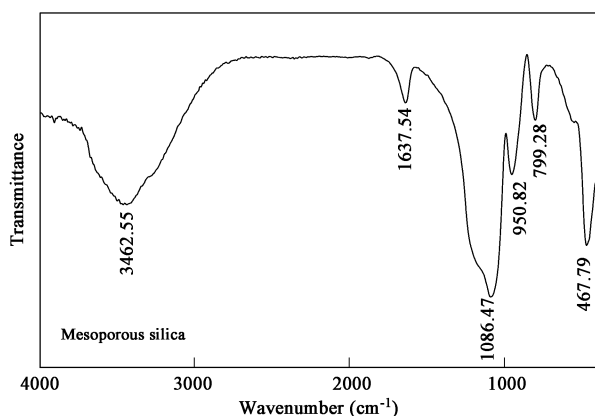
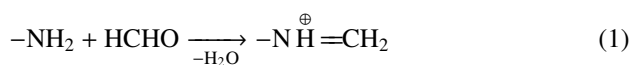


Fig. 4 FTIR spectra of mesoporous silica synthesized from TEOS.

These groups (Si–OH and –Si–O–Si–) are typical groups found on the surface of silica materials (Asomoza *et al.*, 1998; Park *et al.*, 2003; Liu *et al.*, 2005). The band of aliphatic C–H stretching vibration for alkyl chain in ligands of AEAP and AEEA precursors is presented around 3000–2800 cm^{-1} . The band around 1470–1430 cm^{-1} illustrates the NH_2 stretching and N–H deformation peak is displayed around 1145–1130 cm^{-1} (Socrates, 2001). The peaks of amine groups are obviously observed when comparing to FTIR spectrum of mesoporous silica synthesized from pure TEOS (Fig.4). The band of alkyl groups in ligands of precursors was not changed after adsorbing formaldehyde vapor because the formaldehyde molecules were not trapped by the alkyl groups. Nevertheless, NH_2 and N–H bands which illustrate the existence of amine ligands on pore surface of adsorbents are clearly changed after formaldehyde adsorption and a peak of imine appears subsequently. The imine ($-\text{N}=\text{C}=\text{}$) is the product of the reaction between amine and formaldehyde as shown in Reaction (1) (Suzuki, 2001). The imine band displays around 1690–1640 cm^{-1} (Socrates, 2001).



2.3 Adsorption experiment

The adsorption capacity for formaldehyde vapor on the derived adsorbents were tested. The data were recorded at equilibrium condition for five concentrations of formaldehyde vapor. Three isotherm models including Langmuir,

Freundlich, and Temkin were used to elucidate the equilibrium characteristics of adsorption.

The linear form of Langmuir isotherm (Irving, 1918) is expressed as:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{1}{q_{\max}} C_e \quad (2)$$

where, q_e is the equilibrium amount of gas adsorbed on adsorbent (mg/g), C_e is the concentration of adsorbate under equilibrium condition (ppmv), q_{\max} is the maximum amount of gas adsorbed on adsorbent (mg/g) and K_L is the adsorption equilibrium constant (l/mg). By plotting C_e/q_e versus C_e , a straight line with slope $1/q_{\max}$ and intercept $1/K_L q_{\max}$ could be achieved.

The Freundlich isotherm (Freundlich, 1906) is an empirical equation based on a heterogeneous surface. The isotherm is expressed by the following equation:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (3)$$

where, K_F ($\text{mg}^{(1-1/n)}\text{l}/\text{g}$) and n are the Freundlich constants, indicating the adsorption capacity and the adsorption intensity, respectively. The magnitude of n is an indication of system suitability, with values of $n > 1$ representing favorable adsorption conditions. To simplify the derivation of K_F and $\frac{1}{n}$, Eq.(2) can be linearized in logarithmic form:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

The Temkin isotherm (Temkin and Pyzhev, 1940) considered the effects of indirect adsorbate/adsorbate interactions on adsorption isotherms. The heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbate/adsorbate interaction. The Temkin isotherm is given as:

$$q_e = B_T \ln(K_T C_e) \quad (5)$$

which can be linearized as:

$$q_e = B_T \ln K_T + B_T \ln C_e \quad (6)$$

where, K_T is the constant of Temkin isotherm (l/g) and B_T is the Temkin isotherm constant related to the heat of adsorption (kJ/mol).

Table 2 Isotherm parameters for formaldehyde adsorption

Sample	Langmuir parameters			Freundlich parameters			Temkin parameters		
	q_{\max} (mg/g)	K_L (l/mg)	r^2	K_F (mg ^(1-1/n) l ^{1/n} /g)	n	r^2	K_T (l/g)	B_T (kJ/mol)	r^2
1NS160W	817.66	2.03E-04	0.9809	147.77	6.91	0.9190	0.12	81.41	0.8596
2NS160W	957.13	3.22E-04	0.9951	175.59	6.64	0.9858	0.14	99.89	0.9851
3NS160W	590.99	2.32E-04	0.9930	47.77	4.48	0.996	0.02	79.04	0.9751
1NS80W	629.17	2.53E-04	0.9898	87.24	5.78	0.9937	0.05	71.72	0.9660
2NS80W	1,208.09	1.10E-04	0.9603	65.09	4.01	0.9465	0.01	160.90	0.8596
3NS80W	670.78	1.98E-04	0.9881	92.36	5.89	0.9296	0.05	74.84	0.8834
1NS16W	488.26	7.58E-04	0.9994	176.73	11.00	0.9920	9.79	36.02	0.9871
2NS16W	1,140.97	2.13E-04	0.9811	252.81	7.93	0.8827	0.31	103.03	0.8257
3NS16W	613.88	3.45E-04	0.9935	173.30	9.17	0.9758	1.34	50.76	0.9468

The adsorption data were fitted to the above equations. The parameters of the three isotherms are shown in Table 2. Langmuir isotherm was applied for the evaluation of maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbents. The highest value of q_{\max} was obtained from sample 2NS80W. On the contrary, K_F parameter of Freundlich isotherm which indicates the adsorption capacity is not in good agreement with the result of q_{\max} . However, the adsorption intensity (n) of formaldehyde on the adsorbents showed values more than unity representing favorable adsorption conditions. This implies that the adsorption can take place even at high formaldehyde concentration. Temkin adsorption isotherm was used to estimate the adsorption potentials of the adsorbents for formaldehyde vapor. The high value of B_T that related to the heat of formaldehyde adsorption onto the adsorbent indicates a strong interaction between formaldehyde molecules and the surface sites on pores of adsorbent.

The experimental data are found to fit well to Langmuir isotherm in term of R^2 value. The q_{\max} parameter of this model could be the representative adsorption capacity of the adsorbents. As mentioned in FTIR result, formaldehyde can be adsorbed on surface sites of adsorbent by interacting with amine groups on adsorbent. Thus, q_{\max} of sample depended on the number of amine groups or the length of amino chain. Sample 2NS can adsorb formaldehyde vapor more than that of sample 1NS because of the more amine groups and the longer amino chain on the pore surface. Another reason is that sample 2NS yielded the larger pore diameter than sample 1NS. However, q_{\max} of sample 3NS was not the highest although they possess the maximum amine groups and the longest amino chain on pore surface. This can be attributed by the lowest specific surface area and the smallest pore diameter.

3 Conclusions

The organic-inorganic hybrid mesoporous materials were successfully synthesized by co-condensation of tetraethoxysilane (TEOS) and organoalkoxysilanes with amine groups. Specific surface area of the derived materials depends on the length of amino ligand and molar ratio of water to precursors. The hybrid materials synthesized from TEOS and APTMS which contains the shortest amino ligand yielded the highest specific surface

area of 237.30 m²/g and the longest ligand containing sample yielded only 8.14 m²/g of the specific surface area. These hybrid materials were used as adsorbents for formaldehyde vapor. During adsorption, formaldehyde reacted with amine groups on pore surface of the hybrid materials. However, the alkyl groups did not play the role in the formaldehyde adsorption. These were confirmed by FTIR spectra. The bands of amine groups are clearly changed after adsorption and consequently the imine bands appear whereas the alkyl bands remained intact. Langmuir isotherm could be used to fit the data well in term of R^2 (0.98–0.99). One gram of the sample synthesized from TEOS and AEAP can adsorb 1208 mg of formaldehyde vapor which was the highest amount among all samples because of its two amine groups and large pore diameter. On the contrary, the sample prepared from TEOS and AEEA with the maximum number of amine groups did not yield the highest formaldehyde adsorption capacity (590–670 mg/g-adsorbent) because of the low amount of specific surface area and small pore size. Thus, the factors which influenced the formaldehyde adsorption capacity of the hybrid materials synthesized under this study were both of the number of amine groups and the average diameter of pore.

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