



Novel phenol capturer derived from the as-synthesized MCM-41

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ABSTRACT

Novel phenol-capturer was prepared by modifying the as-synthesized mesoporous silica MCM-41 with tetraethylenepentamine (TEPA), not only saving the energy and time for removal of template, but also opening the way to utilize the micelles for adsorption. Once the organic modifier was distributed in the template micelle of MCM-41 to form a web within the mesoporous channel, the composite could adsorb more phenols in gas stream than activated carbon for the first time. With an unwonted high adsorption capacity, this mesoporous silica-amine composite represented potential application for trapping phenols, especially in tobacco smoke to protect environment.

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1. Introduction

Phenol is the hydroxyl derivate of benzene and is toxic to human through oral exposure; for instance, ingesting one gram of phenol has been reported as lethal with symptoms including muscle weakness and tremors, loss of coordination, paralysis, convulsions and coma [1]. Phenol occurs in domestic and industrial wastewater, natural water, potable water supplies and cigarette smoke [2], and it has a large harmful effect for public health due to its accumulation in environment [3]. Consequently, it is necessary to eliminate the phenol pollutant in environment. Adsorption is efficient to control the phenol pollution, and great interest has been focused on the removal of phenols in aqueous solution in recent years, especially in purifying the phenol-contaminated water [4]. Activated carbon shows an excellent adsorption capability of phenol but it lacks the selectivity toward phenol because of its inherent feature of universal adsorbent [5]. Thus, many researchers studied the adsorption of phenolic compounds by other inorganic materials, e.g., clay materials and natural zeolites [6,7]. Nonetheless, the majority of research has taken place in the area of adsorption of phenols from waste water or other solution [8–10], few are known on the reducing phenol content in gaseous phase such as environmental tobacco smoke (ETS) by zeolite and the relative materials.

In the present investigation, new adsorbent, the as-synthesized MCM-41 material coated with tetraethylenepentamine (TEPA) [11], will be assessed in the gaseous adsorption of phenol. The as-

synthesized MCM-41 with surfactant micelles occluded in the pore can disperse large amount of amine, forming a net-like filter inside the mesoporous channel. In addition, the weak basicity of CTAB template in MCM-41 is in favor of reaction with weak acidic phenol. Accordingly, the TEPA coated as-synthesized MCM-41 is chosen to be the adsorbent of phenol. However, this material easily adsorbed CO₂ [11], so that the inference of CO₂ and moisture on the adsorption of phenol will be examined. Besides, we used the instantaneous adsorption method to investigate the gaseous adsorption of phenol according to the requirement of environment protection. The first, the concentration of phenol in an aeration system of a building is variational so that the phenol should be periodically instead of continuously introduced into the adsorption system. The second, the adsorbents in an aeration system of a building had a very short contact time with the pollutants [12], hence the contact time in this instantaneous adsorption ought to be shorter than 0.1 s. The third, intermittent adsorption instead of continuous adsorption is predominant in the applications of zeolite additives in cigarette filters or the aeration system, thus, an instantaneous rather than static adsorption method should be adopted to critically examine the adsorption of phenol in gas stream. Furthermore, these adsorbents are directly added into the filter of cigarette to reduce the phenol in main stream smoke, in order to check their actual performances of trapping phenol in complex chemical system because tobacco smoke contains more than 4800 compounds.

2. Experimental

Zeolite NaY, mesoporous silica SBA-15, amorphous silica and activated carbon were commercially available in powders [13], and

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Table 1
Structural properties of porous materials and their adsorption capacity.

| Sample | Si/Al | Pore size (nm) | Surface area (m ² g ⁻¹) | Pore volume (cm ³ g ⁻¹) | Adsorbed phenol | |
|-----------------------|-------|-----------------------|--|--|--------------------------------------|-------------------------|
| | | | | | (mmol g ⁻¹) ^b | (μmol m ⁻²) |
| SBA-15 | – | 6.7 | 708 | 1.05 | 0.18 | 0.25 |
| MCM-41 | – | 3.4 | 1331 | 1.01 | 0.14 | 0.11 |
| As-synthesized MCM-41 | – | – | 16 | 0.03 | 3.91 | – |
| NaY | 2.86 | 0.7 | 766 | 0.34 | 1.80 | 2.35 |
| Activated carbon | – | ~1.0 ^a | 1128 | 0.5 | 4.28 | 3.79 |
| SiO ₂ | – | 8.0–10.0 ^a | 350 | 0.91 | 0.09 | 0.25 |
| AS-M-10T | – | – | 3.3 | 0.004 | 4.54 | – |
| M-10T | – | 2.0 | 544 | 0.33 | 2.05 | 3.78 |

^a The average pore size.

^b The total amount of phenol passed through the adsorbent was 5.0 mmol g⁻¹.

the detail synthesis process of SBA-15 could be found in literature [14]; mesoporous silica MCM-41 was synthesized in laboratory [11,15]; and their structural properties are listed in Table 1. Hydrogen (99.999%) and nitrogen (99.99%) were used as the carrier gas of gas chromatograph; phenol was the agent with AR grade. Two brands of Chinese Virginia cigarettes, with 12 mg tar and 1.1 mg nicotine, were purchased from market. These tar and nicotine yields are determined by machine-smoking the cigarettes under a standard (ISO) smoking method [16,17].

TEPA was incorporated in MCM-41 through impregnation process [11], forming the composites denoted as AS-M-*n*T or M-*n*T, where *n* represents the weight percentage of amine in the sample, AS-M meant the as-synthesized MCM-41 while M indicated the calcined MCM-41.

The XRD patterns of samples were recorded on an ARL XTRA diffractometer with Cu K_α radiation in the 2θ range of 0.5–8°. A Netzsch STA449C TG/DSC-MS analyzer was employed to monitor desorption of phenol on AS-M-50T sample. The sample was purged under an Ar flow at 308 K for 1 h, and was then heated to 873 K at the rate of 10 K/min under the protection of Ar flow, meanwhile the released components were sent to the mass spectrometer by the carrier gas. The gas line between TG and MS was heated to 453 K to avoid cold points and thus condensation of some gaseous products.

Instantaneous adsorption of phenol in gas stream was performed in a stainless steel micro-reactor with 3 mm diameter and 150 mm length [18]. To perform the adsorption experiment, 5 mg sample (20–40 meshes) was filled in the reactor and directly heated to 353 K in N₂ flow with a rate of 20 mL min⁻¹, and then the dichloromethane solution of phenol (0.05 M) was pulse injected with amounts of 4 μL each time. The Flame Ionization Detector (FID) of Varian 3380 GC analyzed the gaseous effluent, and the decrement in the ratio of solute to solvent was utilized to calculate the amount of phenol adsorbed by the sample. For some samples with high adsorption capacity, 3 mg sample and the injection of 6 μL were utilized in the experiment, in order to reach the equilibrium of adsorption soon.

To evaluate the effect of porous materials in reducing the phenol level of mainstream smoke, 60 mg of sample, in 20–40 meshes, were carefully added into the filter of cigarette to replace part of cellulose matrix with a same volume. The control sample was the original cigarette whose cellulose filter was cut to be three parts. Four test cigarettes were conditioned at 295 K and 60% relative humidity for 48 h and then smoked using a SM 450 linear Smoking Machine (Cerulean, UK) under the standard ISO machine-smoking regime (35 cm³ puff, 2-s duration every 60 s [16]). Each Cambridge filter pad with trapped smoke particulate was extracted, purified and finally analyzed by HPLC method as described below.

After the last replicate was smoked, the Cambridge pad filter was transferred from the pad holder to a 100-mL centrifuge tube,

which containing 50-mL acetate acid solution (1%, v/v), and then the centrifuge tube was ultrasonic for 20 min. The obtained extractive solution was further cleaned up using filter membrane (0.45 μm). About 1 mL of liquid was transferred to an autosampler vial and analyzed by Agilent 1100 LC system. The system was fitted with a C18 column (4.6 mm × 150 mm i.d. 5 μm) at 313 K and equilibrated with a gradient solvent A (acetate/water solution = 1/99, v/v) and solvent B (acetate/acetonitrile/water = 1/30/69, v/v/v). The flow rate of the mobile solution was 1.0 mL min⁻¹. The initial solution contained 20% solvent B and changed linearly to reach 60% solvent B at 15 min, 100% solvent B at 23 min. Solvent B flowed through the column for another 8 min, and then the composition of the mobile phase changed to be the initial state from 35 min to 40 min, accompanied with a 5 min post run time. Multiple injections with 10 μL of sample or calibration standard were done every 45 min. A fluorescence detector was used to detect the phenol content, and the error was determined to be ±3%. The fluorescence was measured initially at 284 nm λ_{ex} and 332 nm λ_{em}. The conditions were changed to 275 nm λ_{ex} and 315 nm λ_{em} after 5 min, to 277 nm λ_{ex} and 319 nm λ_{em} after 8 min, to 272 nm λ_{ex} and 309 nm λ_{em} after 12 min, then to 273 nm λ_{ex} and 323 nm λ_{em} after 20 min, and finally to 284 nm λ_{ex} and 332 nm λ_{em} after 40 min. Calibration curves with a series of five standards were applied to quantify phenols. The standards were made in a two-step dilution from an initial stock solution, which was obtained by dissolving 199.2 mg hydroquinone, 40 mg resorcinol, 199 mg catechol, 206.4 mg phenol, 102 mg *o*/*m*-cresol, 107 mg *p*-cresol in 1% aqueous acetic acid to a volume of 1000 mL (all chemicals from Aldrich/Sigma). The secondary stock solution was prepared by diluting the initial stock solution ten times with 1% aqueous acetic acid. The calibration standards were obtained by diluting 1, 2, 5, 10, and 50 mL of the secondary stock solution into 100 mL with 1% aqueous acetic acid, respectively. Calibration curves represented linear relation of quantity versus peak areas to the concentration of each phenols (*R*² > 0.999) and were used for the measurement of phenols.

3. Results

3.1. Coating amine in the as-synthesized MCM-41

Fig. 1 illustrates the low-angle XRD patterns of mesoporous silica MCM-41 and their TEPA coated analogues. The as-synthesized MCM-41 sample, AS-M, and the calcined MCM-41 sample, M, had three peaks that could be indexed to (1 0 0), (1 1 0) and (2 0 0) reflections of hexagonal structure. Coating TEPA into the palisade of the micelle only had a minor effect of the scattering contrast, causing only slight variation of the XRD patterns. The only exception was AS-M-50T sample that was loaded equal amount of TEPA on the mesoporous composite, but it still kept the XRD characteristics of MCM-41 (Fig. 1A). Nonetheless, different situations emerged on

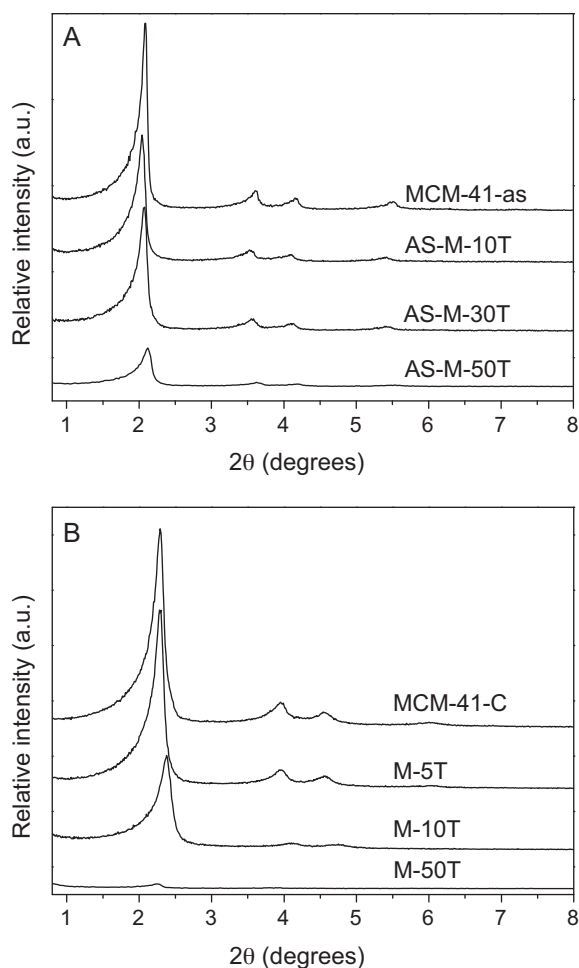


Fig. 1. XRD patterns of mesoporous silica MCM-41 coated with amine.

the sample derived from calcined MCM-41, on which coating TEPA caused a significant change in the scattering contrast. Especially, the reflection intensities of sample M-50T dramatically diminish because TEPA incorporates into the channels of the support, leading to a low scatter contrasts between pore walls and pore space [11].

Fig. 2 shows the nitrogen sorption results of AS-M-10T, the as-synthesized MCM-41 coated with 10% of amine, and M-10T sample, the calcined MCM-41 coated with 10% of amine. The textural properties of these two samples are summarized in Table 1. Calcined MCM-41 had large BET surface area of more than $1000 \text{ m}^2 \text{ g}^{-1}$ and pore volume higher than $1 \text{ cm}^3 \text{ g}^{-1}$, which was different from the as-synthesized MCM-41 that had very small surface area and pore volume (Table 1). Coating 10% TEPA on these two samples caused different textural properties: M-10T also kept high surface area of $544 \text{ m}^2 \text{ g}^{-1}$ and the pore volume of $0.33 \text{ cm}^3 \text{ g}^{-1}$, much larger than AS-M-10T ($3 \text{ m}^2 \text{ g}^{-1}$ and $0.004 \text{ cm}^3 \text{ g}^{-1}$). And the isotherm of M-10T was type IV, similar to calcined MCM-41, with a smaller most probable pore size of 2 nm, because TEPA was coated on the surface of silica wall to decrease pore diameter. Nitrogen failed to enter these extra-fine pores formed by CTAB micelles in the as-synthesized MCM-41 at 77 K so that the inner surface area of this composite could not be detected by the N_2 -adsorption method [10]. This situation is similar to that of zeolite KA. Consequently, it is inferred that these extra-fine pores may have the average size smaller than 0.4 nm therefore nitrogen cannot enter when the micelles became rigid at 77 K [11].

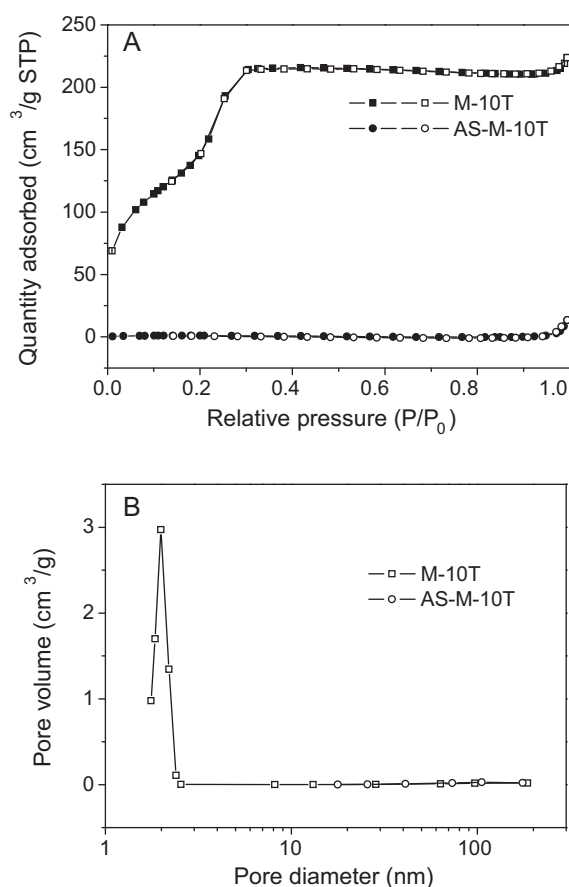


Fig. 2. (A) The nitrogen isotherms and (B) pore size distribution curves of AS-M-10T and M-10T samples.

3.2. Instantaneous adsorption of phenol by molecular sieves

Table 1 describes the instantaneous adsorption of phenol by various porous materials at 353 K. Among these adsorbents the activated carbon exhibited the highest activity in the adsorption, and it could capture 85.7% of the phenol (4.28 mmol g^{-1}) when the phenol of 5 mmol g^{-1} passed through. To assess the repeatability of test, adsorption on activated carbon was repeated and the error was found to be about 1%. Zeolite was the runner-up, and NaY trapped 35.5% of the adsorbate (1.80 mmol g^{-1}) under the same conditions. Among the siliceous adsorbents, amorphous silica owned the large pore volume similar to mesoporous silica like calcined MCM-41 and SBA-15 but had the performance inferior to them in the adsorption of phenol, mirroring the contribution of ordered pore structure. To assess the experimental error in the weak adsorption, the test of SBA-15 was repeated and the error was lower than 1%.

As demonstrated in Fig. 3A, AS-M sample, the as-synthesized MCM-41 whose channels were occluded by the CTAB micelles, exhibited a surprising ability in the instantaneous adsorption of phenol because it could capture 3.91 mmol g^{-1} , close to that of activated carbon (4.28 mmol g^{-1}). Coating TEPA enables the AS-M-*n*T composites to exceed activated carbon in trapping phenol at 353 K, and AS-M-10T adsorbed the phenol of 4.54 mmol g^{-1} under the same conditions. Enhancing the coating amount of amine to 30% (w/w) increased the adsorption ability of composite, and 4.78 mmol g^{-1} of phenol were trapped by the sample of AS-M-30T. The highest activity appeared on the sample of AS-M-50T that adsorbed all of the phenol in the gas stream throughout the whole experimental process, as demonstrated in Fig. 3A. This is the first time to find the powerful mesoporous composites exhibit-

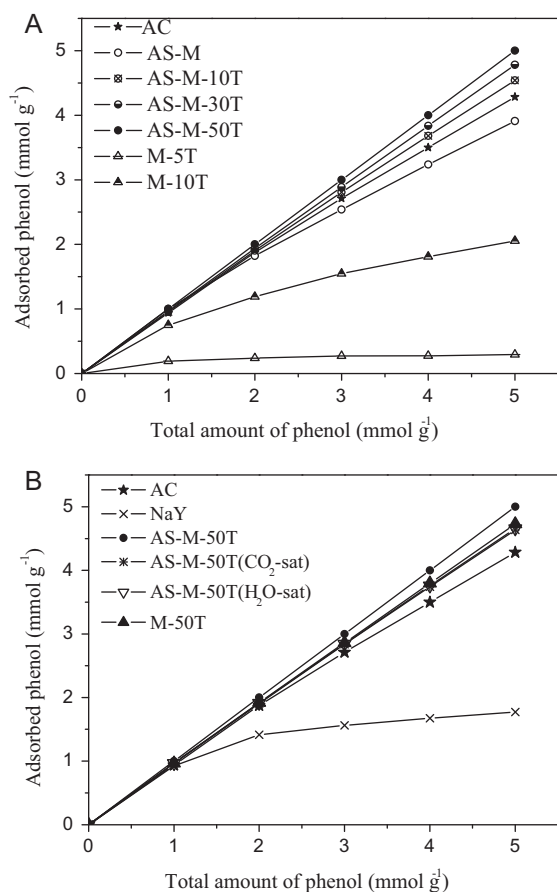


Fig. 3. Adsorption of phenol by (A) as-synthesized or calcined MCM-41 coated with TEPA and (B) other samples.

ing the adsorptive ability higher than the activated carbon derived from coconut, because this microporous activated carbon is a famous excellent adsorbent [5]. Unlike zeolite NaY whose adsorption capacity was soon saturated (Fig. 3B), all AS-M-*n*T samples kept their adsorption ability throughout whole adsorption process. Fig. 4 shows the TG–MS spectrum of AS-M-50T sample adsorbed phenol. The weight loss around 472 K was mainly attributed to desorption of phenol from the composite, since the removal of physically adsorbed water and CO₂ occurred below 413 K, decomposition of the organics via Hoffman degradation happened between 413 K and 473 K, a successive carbon chain (residue of CTAB and TEPA) fragmentation or decomposition with oxidation reactions began around 473 K and reached the maximum near 673 K [11]. Mass signals in Fig. 4B provided the further evidence on the desorption of phenol, in which the signals of phenol with *m/z* ratio of 94 (C₆H₅OH) and 93 (C₆H₅O⁻) emerged near 385 K and vanished at around 600 K. The signal of CO₂ appeared at 550 K and disappeared around 780 K, indicating the thermal decomposition of template micelles and amine in the composite.

To distinguish the role played by the micelles occluded in the channels of MCM-41 on the adsorption of phenol, various amounts of TEPA from 5%, 10% to 50% (w/w), was also coated on the calcined MCM-41, and their adsorption performances are illustrated in Fig. 3. Coating small amount of TEPA on the MCM-41 only had a minor influence in the adsorption of phenol at 353 K, the sample of M-05T was soon saturated in the experiment and it only trapped 0.30 mmol g⁻¹ of phenol (Fig. 3A) when the accumulated amount of phenol reached 5 mmol g⁻¹. M-10T sample was inferior to AS-M-10T in the adsorption, and the difference became larger as more phenol adsorbates past the sample. When accumulated amount

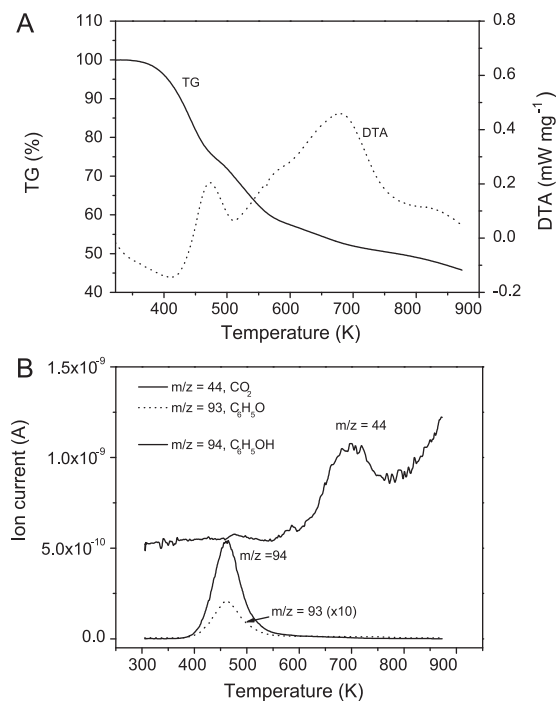


Fig. 4. (A) TG–DTA curves and (B) MS signals of the as-M-50T sample adsorbed phenol.

of phenol achieved 5 mmol g⁻¹, M-10T adsorbed 2.06 mmol g⁻¹, equalling to 45% of that by AS-M-10T (4.54 mmol g⁻¹). Coating more TEPA on the template-free MCM-41 enhanced the adsorption capability of the composite, and the resulting M-50T sample captured the phenol of 4.73 mmol g⁻¹ in gas flow, still inferior to AS-M-50T (5 mmol g⁻¹) but same as that by AS-M-30T (4.78 mmol g⁻¹). Two reasons can be accounted for the phenomenon why AS-M-50T adsorbs more phenol than M-50T. One is the template CTAB that is weak basic hence it can interact with the weak acidic phenol adsorbate. Another is the better distribution of amine guest on the AS-M support, since the micelles inside the channel supply the delicate soft support for coating the amine, dividing the tiny space within the channel into infinitesimal ones [11]. Hence, TEPA can be distributed in the palisade of CTAB micelle, enveloping or interacting with the micelles to acquire a better accessibility to adsorbate.

In order to check the stability of the TEPA coated sample in storage, we saturated the sample of AS-M-50T with moisture or CO₂ prior to adsorption of phenol. AS-M-50T composite lost about 8% of its activity of trapping phenol after the moisture or CO₂ saturation, but the residual adsorption capability was still higher than that of activated carbon and zeolite NaY (Fig. 3B). As is evident from Fig. 3B, the adsorption capability of these two saturated samples was close to that of M-50T throughout the whole experiment procedure. The minor negative influence of moisture and CO₂ saturation on the adsorption of AS-M-50T results from the weak adsorption of water or CO₂ on the amine-coated composites at 353 K [11], which is beneficial for the amine-coated composite to be applied in the environment protection.

3.3. Reducing phenols level of tobacco smoke by porous materials

Table 2 illustrates the performances of AS-M based adsorbents in reducing the phenol contents of tobacco smoke. There were seven phenols in the mainstream smoke, and among them quinol and catechol were the primary ones. However, AS-M only trapped 4% of quinol and 7% of catechol though it captured 15% of resorcinol, so that the phenol contents of smoke were lowered 5%. Coating

Table 2
Reduction of phenols in main stream smoke of cigarette by porous additive in filter.

| Sample | – | AS-M | AS-M-10T | AS-M-30T | AS-M-50T |
|---|-------|-------|----------|----------|----------|
| Quinol ($\mu\text{g cig}^{-1}$) | 95.2 | 91.0 | 78.0 | 84.1 | 99.0 |
| Reduced (%) | – | 4.4 | 18.1 | 11.6 | –4.0 |
| Resorcinol ($\mu\text{g cig}^{-1}$) | 2.0 | 1.7 | 1.7 | 1.6 | 2.2 |
| Reduced (%) | – | 15.0 | 15.0 | 20.0 | –8.0 |
| Catechol ($\mu\text{g cig}^{-1}$) | 72.2 | 67.1 | 58.0 | 60.9 | 75.2 |
| Reduced (%) | – | 7.1 | 19.6 | 15.6 | –4.1 |
| Phenol ($\mu\text{g cig}^{-1}$) | 18.9 | 18.2 | 15.6 | 15.1 | 18.5 |
| Reduced (%) | – | 3.7 | 17.8 | 20.3 | 2.2 |
| <i>m</i> -, <i>p</i> -Cresol ($\mu\text{g cig}^{-1}$) | 17.8 | 17.9 | 15.0 | 14.9 | 18.0 |
| Reduced (%) | – | –0.2 | 15.7 | 16.3 | –1.1 |
| <i>o</i> -Cresol ($\mu\text{g cig}^{-1}$) | 3.9 | 3.9 | 3.1 | 3.2 | 3.9 |
| Reduced (%) | – | 0 | 19.9 | 17.7 | 0 |
| Total amount ($\mu\text{g cig}^{-1}$) | 201.1 | 199.7 | 171.4 | 179.9 | 216.8 |
| Reduced (%) | – | 5.0 | 18.4 | 14.4 | –3.2 |

amine of 10% made the function of AS-M-10T much clear because it reduced 18% of quinol and 15% of catechol in the smoke while other phenol components were decreased about 15% therefore the phenol level of smoke was lowered 18% (Table 2). Nonetheless, modification of AS-M with the amine of 30% slightly declined the activity in adsorbing phenols, though the reduction of quinol became 11% while the elimination of catechol was lowered to 15%. Likewise, loading more amines on AS-M further caused deactivation of AS-M-50T sample, and it hardly reduced the phenol level of smoke (Table 2). Such phenomenon may be attributed to that the micelles become rigid at low temperature during the smoking process (the temperature in the cigarette filter was equal to room temperature at the beginning of the experiment, and increased slightly along with the smoking prolonged, but it was lower than 313 K during the whole smoke process), thus hamper the adsorbate molecules to enter inside the channel deeper. As the TEPA loading amount increases, two contrary factors will influence the actual performance in trapping phenols from smoke gas. One is the increased amount of TEPA that strengthens the adsorbate/adsorbent interaction, and another is more rigid micelles in the channels to disturb the diffusion of adsorbate. In case of loading large amount of TEPA, the influence of former factor cannot remedy the later, thus resulting in the inferior performance of AS-M-50T.

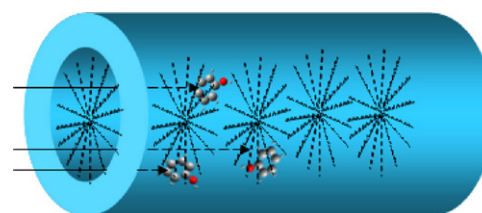
Table 3 reports the reduction of phenol in mainstream smoke of another cigarette by various porous material additives in the filter. M-5T and M-10T prepared by coating amine on calcined MCM-41 are applied to reveal the actual role of CTAB and TEPA in trapping phenols from mainstream smoke gas, while other samples such as activated carbon, NaY, SBA-15 are utilized as controls to illustrate the advantage of the novel phenol capturer in environmental protection. The smoke of this cigarette contained less phenols with total amount reached $117 \mu\text{g cig}^{-1}$, among them quinol and catechol were still the primary components. Activated carbon had a feeble ability to trap quinol and catechol hence the total amount of phenols in the smoke was not reduced. Contrarily, zeolite NaY could trap both quinol (9%) and catechol (13%) as well as cresols (about 10%) in tobacco smoke due to its specific selective adsorption ability, therefore the total amount of phenols in the smoke was thus reduced to 10%. MCM-41 failed to adsorb catechol and resorcinol; hence it exhibited an inconspicuous ability in reducing the phenol level of smoke. SBA-15 adsorbed *o*-cresol among the phenols in tobacco smoke but failed to trap quinol, catechol and phenol. Consequently, SBA-15 could not decrease the total amount of phenols in the smoke. Contrarily, M-5T sample obviously reduced the phenol level of the smoke, similar to that by zeolite NaY, and among the seven phenol components quinol was decreased to 14%, three cresols were reduced around 12% hence the total amount of phenols in the smoke was lowered to 10%. A significant reduction of phenols in smoke was found on the sam-

ple of M-10T. This additive could obviously eliminate the phenol components in the range of 11–26% therefore the phenol level of the mainstream smoke was lowered 16%. As-synthesized MCM-41 could strongly adsorb phenol in instantaneous adsorption process but only exhibited a weak performance in trapping phenols from mainstream smoke gas, while coating TEPA increased the reduction ratio of phenols from mainstream smoke gas. Likewise, M-5T and M-10T also showed similar performance in trapping the phenols from the mainstream smoke, which clearly revealed that it is the TEPA that enhances the trapping efficiency of phenols from mainstream smoke. This achievement implies the possible application of the mesoporous silica coated with liquid film in the protection of environment.

4. Discussion

The contact time between adsorbate and adsorbent in the instantaneous adsorption was very short [19], so that the phenol molecules past through the adsorbent with a high speed. For instance, the volume of adsorbent in our experiments was about 0.016 cm^3 therefore the phenol would quickly past the adsorbent layer with the rate of 21 cm s^{-1} , which certainly affected the adsorption by various porous materials. The as-synthesized MCM-41 sample possessed an optimal hierarchical structure; its mesoporous channel enabled the gas flow to successfully pass through while micelles net efficiently filtered the phenols in the flow. Besides, the micelles provided the soft-collision with the phenols in gas stream, enabling them to be hold instead of rebounding (Scheme 1). Moreover, the weak basicity of CTAB micelles was beneficial for capturing the acidic target. Subsequently, the as-synthesized MCM-41 showed a high capability similar to the coconut-based activated carbon in the instantaneous adsorption, superior to both mesoporous silica and zeolite (Fig. 3).

Apart the special function of fine filter, the template micelle in the as-synthesized MCM-41 sample can be used to distribute TEPA for preparation of the phenol capturers with an elevated efficiency,



As-synthesized MCM-41

Scheme 1. Schematic illustration of the phenol adsorbed on As-synthesized MCM-41.

Table 3
Reduction of phenols in main stream smoke of cigarette by porous additive in filter.

| Sample | – | Activated carbon | NaY zeolite | MCM-41 | SBA-15 | M-5T | M-10T |
|---|--------|------------------|-------------|--------|--------|-------|-------|
| Quinol ($\mu\text{g cig}^{-1}$) | 45.86 | 45.81 | 41.51 | 42.33 | 48.58 | 39.08 | 36.39 |
| Reduced (%) | – | 0.1 | 9.5 | 7.7 | –5.9 | 14.8 | 20.6 |
| Resorcinol ($\mu\text{g cig}^{-1}$) | 0.98 | 0.96 | 0.90 | 0.96 | 0.94 | 0.93 | 0.84 |
| Reduced (%) | – | 2.0 | 8.1 | 2.0 | 4.0 | 5.2 | 14.3 |
| Catechol ($\mu\text{g cig}^{-1}$) | 40.59 | 42.13 | 34.59 | 39.85 | 41.85 | 38.06 | 36.01 |
| Reduced (%) | – | –3.8 | 13.9 | 1.8 | –3.1 | 6.5 | 11.3 |
| Phenol ($\mu\text{g cig}^{-1}$) | 14.41 | 13.97 | 13.88 | 13.88 | 14.36 | 13.19 | 12.31 |
| Reduced (%) | – | 3.0 | 3.7 | 3.6 | 0.3 | 8.5 | 14.6 |
| <i>m</i> -, <i>p</i> -Cresol ($\mu\text{g cig}^{-1}$) | 12.38 | 11.86 | 11.17 | 11.23 | 11.62 | 10.83 | 9.68 |
| Reduced (%) | – | 4.2 | 9.8 | 9.0 | 6.2 | 12.6 | 21.8 |
| <i>o</i> -Cresol ($\mu\text{g cig}^{-1}$) | 3.36 | 2.90 | 2.92 | 2.79 | 2.80 | 2.71 | 2.49 |
| Reduced (%) | – | 13.7 | 13.0 | 16.9 | 16.5 | 19.2 | 26.0 |
| Total amount ($\mu\text{g cig}^{-1}$) | 117.58 | 117.63 | 105.33 | 111.04 | 120.15 | 104.8 | 97.72 |
| Reduced (%) | – | –0.04 | 10.4 | 5.6 | –2.2 | 10.9 | 16.9 |

giving a better accessibility for phenol molecules. As is evident from Fig. 3, AS-M-10T exhibited a higher capacity than M-10T in the instantaneous adsorption of phenol, and AS-M-50T was superior to M-50T. Nonetheless, it should point out that M-50T was more expensive because one gram of M-50T contained 0.5 g MCM-41 while AS-M-50T consisted of about 0.3 g the siliceous matrix plus 0.2 g micelles. Rather, the preparation of AS-M-50T omitted the calcination of templates thereby its cost was no doubt lower than that of M-50T.

The as-synthesized MCM-41 coated with TEPA also had a considerably high capacity in the adsorption of phenol in tobacco smoke (Table 2), and AS-M-10T sample significantly reduced all of the seven phenols in mainstream smoke (Table 2). For the given porous adsorbent, trapping phenol in cigarette filter is much harsher than that in laboratorial test. In our test, for example, as shown in Table S1, 60 mg additives occupied the volume of about 0.12 cm³ in cigarette filter, but the puff volume of machine smoking was 17.5 cm³ s⁻¹ [17], thus the additive only had a very short time, 0.007 s, to contact with the phenols in the smoke, one seventh of that in instantaneous adsorption (about 0.05 s). Probably due to this reason, plus the competitive adsorption of other components in smoke [16], the microporous activated carbon that was very active in laboratorial test was inactive to trap the phenols in mainstream smoke (Table 2), and SBA-15 lost its activity while MCM-41 only showed a weak capability, either. Contrarily, several composites with amine-coated, AS-M-10T and AS-M-30T, along with M-5T and M-10T exhibited a considerable ability to trap the phenols in the mainstream smoke, because the liquid film coated in the channel of MCM-41 could also adhibit the fast-moving targets, preventing these colliding molecules from “bounce off” and finally capturing them.

Utilization of the template in mesoporous materials is economic and environmental benign. After inducing the wall structure of mesoporous material through nanocasting or structure-directing procedure [20,21], these templates must be removed from the synthetic products by calcination or extraction [21–23], which not only costs energy and time, but also releases pollutants in environment sometimes. Here we utilized the template in the as-synthesized MCM-41 to capture the phenol in gas flow for the first time. These micelles form a close congruent net inside the channel of MCM-41 (Scheme 1), enabling the as-synthesized MCM-41 to be the excellent adsorbent forward phenol, which may shed light on the preparation of effective and low-cost functional materials for environment protection.

5. Conclusion

Some conclusive remarks can be tentatively derived from the results mentioned above.

- (1) Instantaneous adsorption of phenol is useful to assess the behavior of porous materials in the gaseous adsorption of phenol.
- (2) The template micelles reserved in the as-synthesized MCM-41 can promote the adsorption of phenol in gaseous phase, especially in the laboratorial instantaneous adsorption at 353 K, and enable TEPA modifier to be well dispersed inside the channel of MCM-41, forming the efficient adsorbent superior to activated carbon.
- (3) Coated with the suitable amount of amines such as TEPA, either as-synthesized or calcined MCM-41 can exert the function of reducing phenol levels of tobacco smoke, offering a new type adsorbent with liquid film for environmental protection.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.02.089.

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