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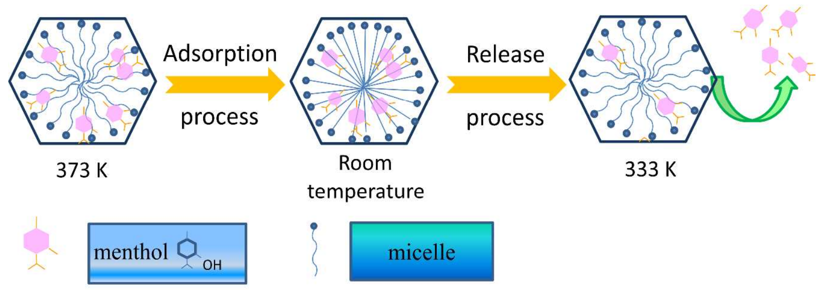

Menthol could be adsorbed in as-synthesized MCM-41 at 373 K, open stored in ambient for 30 days and released at 333 K.

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ARTICLE TYPE

Novel Menthol Releaser Derived from As-synthesized Mesoporous Silica

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Novel menthol releaser is reported for the first time by utilizing the as-synthesized mesoporous silica MCM-41, MCM-48, and SBA-15, which not only saves the energy and time for removal of template, but also opens new application of the micelles. The micelles of CTAB (cetyltrimethylammonium bromide) in the as-synthesized MCM-41 had a flexibility depend on temperature, that is, they were flexible at around 373 K so that menthol could enter the channel, but rigid at ambient temperature so the adsorbed menthol was sealed through physical interception, and they would release the spice at 333 K. The influence of temperature, nature and distribution of micelles on the adsorption and release of menthol was carefully assessed, and among three as-synthesized mesoporous vessels, the as-synthesized MCM-41 exhibited the highest capability in thermal release of menthol at 333 K after open stored in ambient for 30 days or longer. Furthermore, this new menthol releaser was preliminarily used in the filter of cigarette.

1 Introduction

Mesoporous silica has been widely used in many fields such as adsorption, separation and catalysis [1-3] due to its high specific surface area, large pore volume and tunable pore size, along with the advantage of easy modification in chemical composition and geometric structure. Essentially all of these achievements profit from the assembling and condensation of inorganic materials around the surfactant template micelles that are crucial for the fabrication of mesoporous materials. In fact the micelles occluded in the as-synthesized mesoporous silica such as MCM-41 are the unique resource, since they are distributed in the spoke-like configuration to form numerous sub-nanometer gaps between them and the silica walls. This peculiar distribution enables the cation head of CTAB to have the optimal accessibility [4], and the inner structure of the micelles consisted of various extra-fine pores with the sizes smaller than 0.4 nm [5]. However, how to utilize the micelles inside the as-synthesized mesoporous silica is ignored in comparison with the extensive study on these molecular sieves. In general, these templates are removed by calcination or extraction, which not only consumes energy or solvents, but also increases pollution therefore it is necessary to utilize these template micelles orientated inside the channel. At first, these micelles were utilized as sorbent [6, 7] or promoter for high dispersion of metal salts during solid grinding procedure [8]. And then they were used as the special support to coat amine, like weaved web inside tube, enabling the amine to efficiently capture the CO_2 or phenol in gas flow [4, 9, 10]. Recently, the alterable flexibility of the micelles in as-synthesized MCM-41 or MCM-48 (abbreviated as as-M41 or as-M48) at different temperatures was reported, which enabled the micelles to be new releaser: NO could be adsorbed inside the as-synthesized mesoporous silica at 353 K, stored at ambient environment and finally the NO would be released in acidic solution, forming the new acid-trigged NO releaser [4]. However, the adsorbed NO interacted with the CTAB micelles in as-M48 or as-M41 to form surface N_xO_y species hence the NO could be open stored even for several weeks. Can these micelles-occluded vessels work as the releaser without assistance of chemical interaction? Can they hold or seal the volatile guests only through physical interception? This is important for the new application of these template micelles in mesoporous silica as the releaser but unknown to date, which spurs us to explore the thermally releasing of menthol with these template micelles occluded mesoporous silica.

Menthol (5-methyl-2-isopropyl-cyclohexanol) is a natural compound that can provide the typical minty smell and flavour [11]. Apart from pharmaceutical applications like anti-inflammatory, analgesic and anti-fungal, it is often used as the flavoring agent such as tobacco flavor, toothpaste, perfume, beverage and sweets. For instance, addition of menthol into cigarettes can produce the cool and refreshing taste, stimulating the central nervous system and making the respiration unobstructed [12]. Practically, the addition of menthol in cigarette is often performed by spraying the menthol solution or putting the menthol-containing additive in tobacco, filters and packaging materials. However, menthol volatilizes easily so that its function is significantly reduced [13, 14]. To conquer this problem, the as-synthesized mesoporous silica is selected to adsorb and store as well as release menthol based on the variable flexibility of the micelles inside the channel. The gas chromatography-mass spectrometry (GC-MS) combined with headspace technique are employed to explore the influence of channel structure of mesoporous silica and the nature of micelles, temperature of menthol adsorption and storage conditions on the release of menthol. Besides, the vessels pre-adsorbed menthol will be used in the filter of cigarette to assess their actual function in storage and release menthol. It is expected to expand the value of template micelles in mesoporous silica through endowing them the new function of menthol-releaser.

2 Experiment Section

The purity of N_2 and H_2 carrier gases was 99.99%; Menthol (5-methyl-2-isopropyl-cyclohexanol, M = 156.27) and all other agents used here were of AR grade. A Chinese blended type cigarette was purchased from market.

2.1 Synthesis of Mesoporous silica

Mesoporous silica MCM-41, MCM-48 and SBA-15 were synthesized according to the procedures of literature [15-17]. These as-synthesized samples were air-dried and named as as-M41, as-M48 and as-S15, and they contained the template micelles of 49.3%, 57.1% and 40.2%, respectively, as reported previously [8-10]. Part of the as-M48 composite was calcined at 823 K to get the common template-free sample of MCM-48.

2.2 Adsorption and release of menthol

To assess the adsorption of menthol by mesoporous vessels, 0.4 g powder-like as-synthesized mesoporous silica was put on the position above 0.2 g menthol, and then both of them were put into the autoclave in the temperature range of 353 K- 413 K for 12 h. The increased weight of the composite was roughly used to represent the amount of menthol adsorbed. Afterward, the menthol loaded vessel was open stored at ambient temperature for 30 days or longer.

To evaluate the release of menthol from these vessels, a given weight of the menthol-loaded vessel was put into an Agilent 5182-0837 Headspace vial (flat bottom, 20 mL), firstly balanced at a given temperature for a period of time, and then packed in the Agilent G1888 Network Headspace Sampler connected with gas-chromatograph for the second balance prior to sampling. The released menthol was forced into the sample loop and detected with the GC-MS equipped with a 60 m VOCOL capillary column and PerkinElmer Clarus 600T Mass Spectrometer. The detection conditions and parameters were listed in Supporting Information. In the experiment of cycled detection the vessel was taken out and put into another Headspace vial keeping at the temperature for balancing again once the first GC-MS analysis was finished, and the released menthol in the 2^{nd} cycle was then sampled and detected again in the same procedures.

To assess the temperature controllable release of menthol, a give amount of as-M41 vessel pre-adsorbed at 373 K was put into the filter of cigarette and stored for a period prior to smoking. For these sample cigarettes, part of them was sucked for dozens of times without igniting, and then the vessel was taken out to test the release of residual menthol with the GC-MS method aforementioned. Part of them was smoked by the technicians to evaluate the taste of menthol released in smoke.

X-ray diffraction (XRD) patterns of samples were recorded on a D8 ADVANCE diffractometer (40 kV, 40 mA) using Cu-Kα radiation in the 2-theta range from 0.5° to 10°. Fourier Translation - Infrared Spectroscopy (FT-IR) spectra were recorded on a spectrophotometer of NICOLET iS10 with a resolution of 2 cm^{-1} using compressed KBr pellets containing 5 wt% of sample.

3 Results and Discussion

3.1 Characterization of the as-synthesized mesoporous silica

The XRD patterns of as-M41 and as-M48 samples are shown

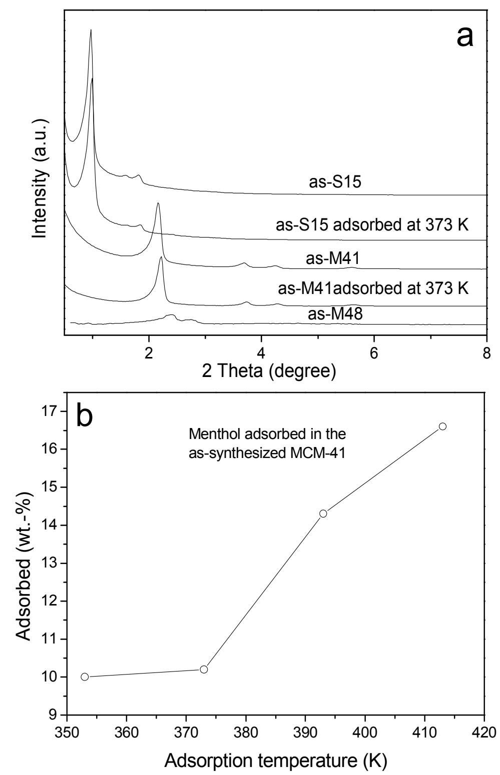

Figure 1. (a) Low-angle XRD patterns of as-synthesized mesoporous silica and (b) menthol adsorbed on as-M41 sample.

in Figure 1a. Three peeks of (100), (110) and (200) appearing on the patterns of as-M41composite can be indexed to a hexagonal phase, but their scattering contrast seems to be lowered in comparison with that of MCM-41 because surfactant molecules occluded inside the mesopore decrease the scattering contrasts between pore spaces and pore walls [10]. After calcination, the MCM-41 sample would preserve the *p6mm* symmetry structure as expected. Similarly, the as-M48 composite possessed cubic *Ia3d* mesostructure, indicating the successful synthesis. Although its channels were occluded by CTAB micelles, the as-M41 composite still adsorbed the menthol of 10~16 wt.-% in 353 K – 413 K (Fig. 1b), due to the flexibility of the micelles at the higher temperature [4]. Adsorption of menthol has a minor influence on the XRD patterns of as-M41 where only the intensity of peaks declined slightly. Similar phenomena were found on the XRD patterns of as-S-15 composite before and after adsorbed menthol (Fig. 1a). They all shown the well-resolved peaks that were indexable as (100), (110), (200), but the intensity of these peaks on the menthol adsorbed samples was slightly weaker. On the FT-IR spectra of as-M41 and as-S15 samples shown in Fig. S1, the bands at 2924 and 2853 cm^{-1} denoted the stretching vibration of C-H bond in CH_2 and CH_3, 1488 cm^{-1} was assigned to bending vibration of C–H bond while 804 cm^{-1} was ascribed to C–C vibration of the surfactants [18, 19]. Due to the doublication of menthol bands with that of vessel, however, no new peak was found on the sample of as-M41 or as-S15 adsorbed menthol no matter they were open stored or purged with nitrogen, even on the mixture of as-M41 ground with 30% menthol (Fig. S2). As a consequence, no evidence was found for the possible chemical interaction between the spice and the micelles of the as-synthesized mesoporous silica.

3.2 Temperature controlled release of menthol

Figure 2 presents the GC-MS analysis of the menthol released from the as-M41 vessel pre-adsorbed at 373 K. As is evident in Fig. 2a, there was only one sharp peak with the retention time of 37 min on the GC spectrum, which mirrors the exclusive release and excludes the possibility of releasing or decomposing micelles. This inference is believable since the template micelles are stable bellow 373 K [8-10], especially, P123 decomposed around 457 K [6] while the Hofmann elimination of trimethylamine in the CTAB template occurred in the range of 423 – 523 K [10]. Figure 2b shows the MS analysis of the component, in which the signals appeared with the m/z ratio of 41, 56, 67, 81, 96, 109, 123, 138 and 154. These signals were recognized to be the characteristics of menthol (Fig. 3), and which confirmed the thermal release of menthol from as-M41 vessel at 333 K. Similar GC-MS spectrum was recorded on the as-M48 pre-adsorbed menthol at 373 K (Fig. S3), in which only one strong GC peak was also recorded at 37th min (Fig. S3a), and whose fragment signals accorded well with the MS spectrum of menthol (Fig. S3b and S3c). Nonetheless, the strength of these signals on the as-M48 was weaker than that on as-M41, meaning the relatively smaller amount of menthol released from the as-M48 than that from the as-M41 under the same conditions. On the basis of GC-MS analysis, it is distinct that the adsorbed menthol does not react with the template micelles inside the channels and not decompose during the thermal release, either. That is, menthol is perfectly loaded inside the channel occluded with micelles and then thermally released in its entirety.

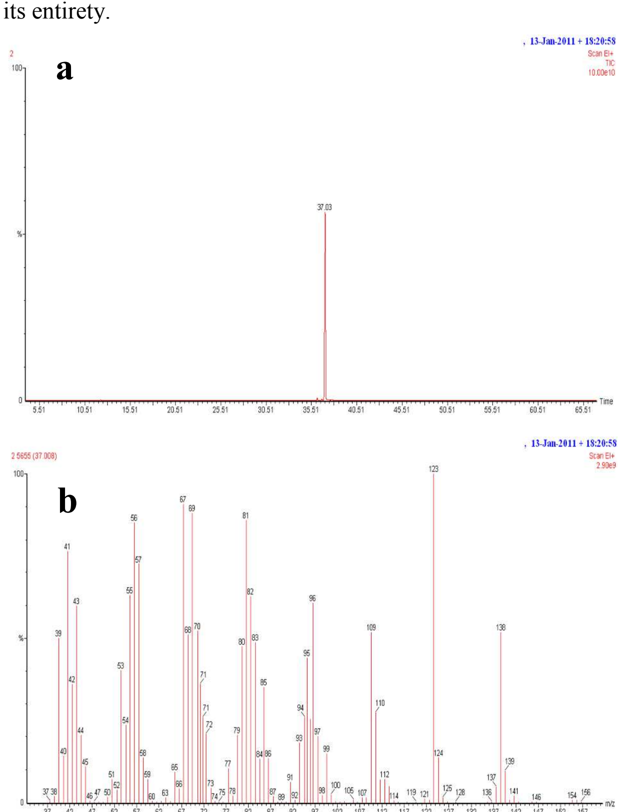

Figure 2. a) GC spectrum and b) MS spectrum of the menthol released from as-M41 vessel adsorbed at 373 K.

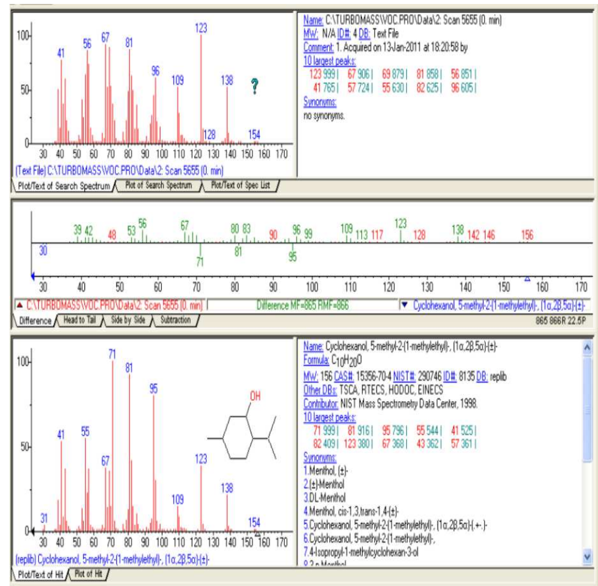

Figure 3. The MS spectrum of the menthol released from as-M41 vessel adsorbed at 373 K was fitting with the standard spectrum of the menthol.

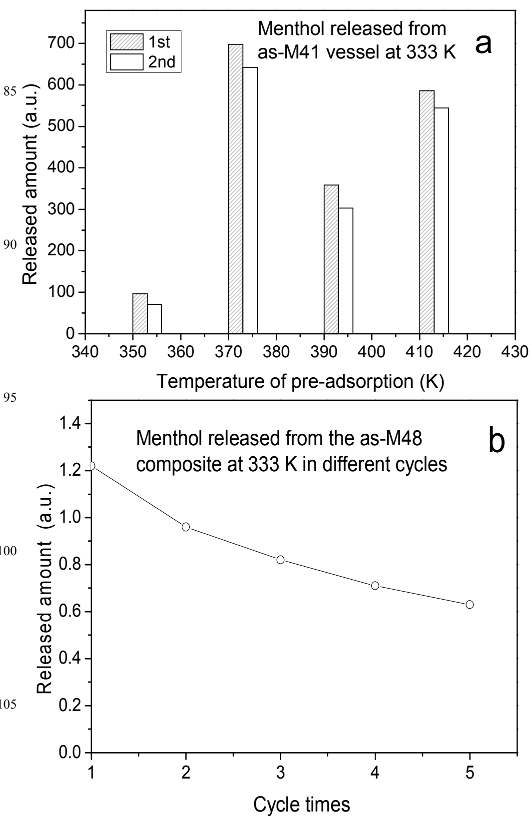

Figure 4. The release of menthol at 333 K from (a) the as-M41 composites adsorbed menthol at different temperatures and (b) the as-M48 vessel adsorbed at 413 K in different cycles.

Figure 4a illustrates the influence of adsorption temperature on the release of menthol from 40 mg as-M41 vessel, in which all of the vessels pre-adsorbed menthol in the range of 353 K - 413 K

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Table 1. The menthol released from the as-M41 vessel adsorbed at 373 K and stored at ambient for 30 days

1st balanced temperature (K)	1st -balanced time (min)	2nd balanced temperature (K)	2nd balanced time (min)	Released amount (a. u.)
278	60	313	1	53.4
293	60	333	1	204.8
313	1	313	60	298.5
333	1	333	60	677.2

Table 2. Release of menthol on the samples adsorbed at different temperatures and stored at ambient for 45 days

Sample	Adsorbed at (K)	1st balanced at (K)	1st balanced time (min)	2nd balanced at (K)	2nd balanced time (min)	Released amount (a. u.)
as-M48	353	293	60	333	60	0.21
		333	60	333	60	0.15
	373	293	60	333	60	0.02
		333	60	333	60	0.10
	393	293	60	333	60	0.01
		333	60	333	60	0.13
	413	293	60	333	60	0.09
		333	60	333	60	1.18
MCM-48	373	293	60	333	60	0
		333	60	333	60	0
as-S15	373	333	60	333	60	0.50
Teflon	373	293	60	333	60	0
		333	60	333	60	0

and then were stored at ambient temperature for 30 days prior to the release at 333 K. According to the results shown in Fig. 4a, all vessels released the menthol indeed even after the long time open storage of 30 days. Among these composites the one adsorbed menthol at 373 K released the largest amount of the spice; rather, it was still the champion among these four composites in the 2nd cycle test (Fig. 4a). The temperature lower than 373 K seems not beneficial for the as-M41 to adsorb menthol since the vessel adsorbed at 353 K only released the spice equalling to 14% of that from the 373 K adsorbed vessel. Nonetheless, the elevated temperature was also unprofitable for the release of menthol on as-M41 because both the vessels adsorbed at 393 K and 413 K released less menthol than that at 373 K, although they could adsorb more the spice (about 16.6% and 20%, respectively) than that at 373 K (11%). Same trend was also observed on the 2nd cycle release at 333 K (Fig. 4a), verifying the effect of adsorption temperature on the menthol release from as-M41 vessel.

Table 1 demonstrates the effect of 1st and 2nd balances temperatures on the release of menthol from as-M41 vessel. For these double balanced vessels, the higher the temperatures of balance, the more menthol to be released, and the sample to be 1st balanced at 293 K released about three times more menthol at 333 K than that from the sample to be 1st balanced at 278 K but released at 313 K. However, it was unclear which temperature of balance, 1st or 2nd, played the major role hence the vessel was tested without 1st balance (Table 1). As a consequence, the vessel released 100% more menthol at 333 K than that at 313 K. It is distinct that the high temperature impels the menthol stored to be released from the vessel more quickly.

With the same CTAB template micelles occluded in channel, the composite as-M48 could also efficiently adsorb and temperature-controllable release menthol, even though they were open stored for 45 days. Table 2 displays the release of menthol from the as-M48 adsorbed at different temperatures, and it is clear that the 1st balance at 333 K is more beneficial than at 293 K for menthol release excepted the vessels adsorbed at 353 K (Table 2) on which reverse situation was observed. Also, the higher adsorption temperature in the range of 353 K - 413 K was also beneficial for the menthol release in as-M48 composite. The vessel adsorbed menthol at 413 K could release 8 times more the spice than that adsorbed at 393 K when they were 1st balanced and released at 333 K. There are two differences between as-M41 and as-M48 vessels. The first, 373 K was the best temperature for as-M41 to release menthol while 413 K was the best one for as-M48. The second, as-M41 seemed to adsorb and release more menthol than as-M48 did. It is known that the micelle in the channel of these vessels will be little bit softer at relatively higher temperature hence the guest molecules can thus enter [4], however

MCM-48 has the double helix *Ia3d* structure so that its surfactant micelles were arranged closer [20]. As a consequence, it is not easy for menthol molecule to enter the occluded channel and diffuses inside due to its relatively large molecular size, resulting in an inferior menthol adsorption performance of as-M48. Nonetheless, without the template micelles inside channels to seal menthol, the common MCM-48 sample failed to hold the volatile spice during the open storage and thus no menthol was detected in the release at 333 K (Table 2). Similar situation was observed on the sample of polytetrafluoroethylene (PTFE) tube without pore structure, which excludes the suspicions whether the mesoporous skeleton structure or the surface adhesion cause the storage of menthol. In contrast, a considerably amount of menthol was released from the as-M48 adsorbed at 413 K, even though in the 5th cycle (Fig. 4b). Of course, the amount of detectable menthol declined as the cycle time increased, say, about half in the 5th cycle, which was comprehensible. To explore the stability of menthol sealed inside the channel of as-synthesized mesoporous silica, the as-M48 vessel that adsorbed menthol at 373 K was divided to two parts. One part was open stored at ambient temperature for 45 days, and another was open stored for 30 day similarly but followed by the purge of nitrogen flow with 30 mL min^{-1} for 15 days. However, two vessels released the similar amount of menthol (0.10 and 0.12 a. u., respectively) at 333 K, which indicates the high stability of menthol sealed in as-M48 vessel during the storage at ambient temperature.

With different template in synthesis, as-S15 contained its micelles of P123 inside channels. However, these non-ionic surfactant micelles could still seal the adsorbed volatile spice and there was a considerably amount of menthol released from the as-S15 vessel that adsorbed menthol at 373 K and open stored for 45 days. Judged from these results, it is clear that the inherent temperature-controllable rigidity of template micelles, rather than their chemical composition, enables them to be novel releaser of menthol within the mesoporous channels.

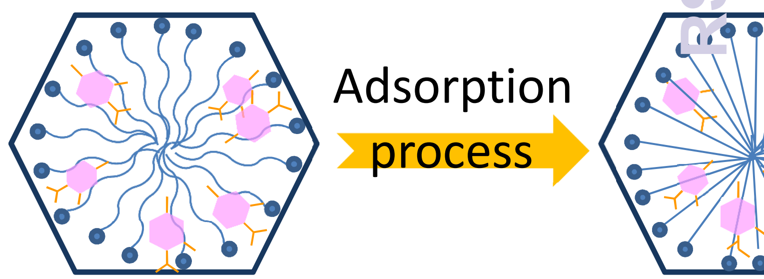
3.3 Preliminary study on the menthol release in cigarette filter

Considering the large amount of menthol released from as-M41 (Table 1, Fig. 4) than that from as-M48 and as-S15 (Table 2), as-M41 composite was selected as the candidate for the thermal release of menthol in cigarette filter. Menthol is well known to be the volatile compound so that its open storage is very difficult [19, 20], even pre-adsorbed inside the as-M41 vessels. For the vessel adsorbed menthol at 353 K, 373 K, 393 K and 413 K, about 0.4%, 2.8%, 7.2% and 2.2% of the spice remained after the open storage of 90 days. However, these values were 1.3, 190.3, 15.2 and 9.2 times higher than the corresponding as-M48 vessels open stored for 45 days. With the same mesoporous channel *p6mm* structures, the menthol released from the 90 days-stored as-M41 (19.8 a. u.) was 38 times more than that form the 45-days stored as-S15 vessel (0.5 a. u.). These results enable the as-M41 vessel, especially the composite adsorbed menthol at 373 K, to be a valuable releaser of menthol in the filter trip. After put into the triacetate filter trip alone for open storage of 90 days followed by 100 suctions at ambient temperature, the as-M41 vessel still released a considerable amount of menthol (3.3 a. u.). However, once 10 mg the as-M41 vessel, which adsorbed menthol at 373 K and open stored for 30 days, was put into the cigarette filter [21] and smoked by technician, it was reported to feel the cool and refreshing of menthol till the 5th puff but absent in 6th-8th puff (usually the puff number of a cigarette is 8). Prolonging the open storage time of as-M41 vessel to 60 days but increasing its amount in filter to 30 mg, the technician still clearly felt the characteristic cool and refreshing of menthol when the cigarette was lighted, which means a potential application of the menthol thermal release controlled by the as-synthesized mesoporous silica.

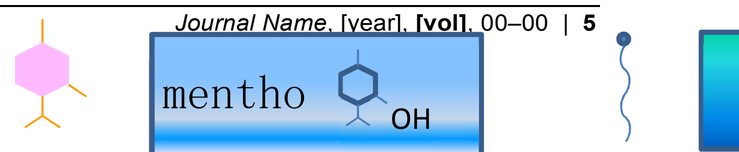
4 Discussion

The tunable flexibility of template micelles in as-synthesized mesoporous silica is crucial for the thermal release of menthol. With the spoke-like configuration, these template micelles tidily occluded the channel of the mesoporous vessel and formed innumerable sub-nanometer gaps between them and silica wall [5, 10]. These micelles play the role of fence to lock-in the channel. They presented flexibility at the high temperature like 373 K, allowing menthol molecule to burst through them and enter into the channel (Scheme 1). Consequently, menthol was adsorbed in the vessel of as-M41 or as-M48, similar to the adsorption of NO [4]. Once the temperature was lowered to ambient, the micelles exhibited inflexibility and became tetanic to block the channel (Scheme 1) so that the adsorbed menthol was sealed even the vessel was open stored. When the temperature was increased to 353 K, the micelle became soft again hence the menthol could escape from the channel to achieve thermal release (Scheme 1). According to GC-MS analysis, these volatile spices could keep their original composition (Fig. 2), implying the success of sealing menthol by as-synthesized mesoporous silica through physical interception.

The nature of micelles affects their function of storing menthol, since as-S15 vessel released much less menthol than as-M41 did (Table 1 and 2) due to the nonionic template Pluronic P123 micelles. Such difference was reported in NO release [4] in which as-S15 failed to store NO even at room temperature. Also, the channel structure of mesoporous silica impacts the storage of menthol, for instance the as-M41 composite could release hundred times more menthol than as-M48 did, although they contained the same CTAB micelles. The former had the one-dimensional channels in the hexagonal *P6mm* structures while the latter was the cubic *Ia3d* mesoporous material with three-dimensional pore systems. Although the structure of common MCM-48 has much more advantages in diffusion and mass transport in comparison with that of MCM-41 [22], it is difficult for



Scheme 1. Temperature-controlled adsorption and storage as well as release of menthol in the as-synthesized mesoporous silica vessels.



menthol to diffuse inside the sinuate channel occluded with micelles because of the micelles oriented with ever-changing directions in the helix structure. As a consequence, as-M48 vessel adsorbed and thus released less menthol. Nonetheless, the adsorbed menthol was tightly held to resist the purge of nitrogen flow. In contrast, the funnel-like channels of MCM-41 enabled the occluded CTAB micelles to be arranged orderly so that the menthol entered and diffused into the channel of as-M41 relatively easier. As the result, relatively large amount of menthol could be adsorbed and stored in the vessel of as-M41, ensuring this composite to thermal release menthol in cigarette smoke.

Apart from the potential economic benefit in application, the success of new menthol releaser derived from the micelles occluded mesoporous silica provides a new concept on the as-synthesized mesoporous composites. Strictly speaking, these composites are the core-shell composite where the micelles core supports the silica shell. Usually the attention is paid on the silica shell on which a lot of study is focused on introducing other metal species or converting the amorphous silica to zeolite [23], meanwhile the micelles core is removed or simply used as the tentatively supports. However, if we change our thinking, this composite is actually a special one where the inorganic shell forms the ordered and limited space and more importantly, the organic core also forms a magical delicate configuration, dividing further the limited space to numerous sub-nanometer gaps such as the superfine pores with the size less than 0.4 nm [5]. That is, the common surfactant micelles actually form an unusual precise sub-nanometer structure within the special chemical environment and the limited space isolated by the silica shell. Such elaborate structure is expected to provide a perfect configuration for efficiently containing guest species to fabricate various novel hybrid functional materials, and menthol releaser is only one among them. This new menthol releaser may afford a candidate for tobacco industry to conquer the problem caused by the volatile of the spice. Furthermore, it gives a clue to elevate the value of template micelles oriented in mesoporous silica.

5 Conclusion

Some conclusive remarks can be tentatively derived from the aforementioned results.

(1) The micelles in as-synthesized mesoporous materials such as MCM-41 exhibited a temperature on-off effect, namely, they showed an adjustable flexibility at different temperature and then switched the sub-nanometer space in the mesoporous channel, allowing and prohibiting guest molecules in and out to realize the temperature controllable storage and release.

(2) Menthol could be adsorbed in the vessel at 373 K and open stored in ambient for 30 days or longer, and finally released at 333 K.

(3) Among the sample of as-synthesized mesoporous silica, as-M41 exhibited a higher capability than as-M48 or as-S15 did in thermal release of menthol at 333 K.

(4) 373 K was the optimal temperature for the adsorption of menthol in the as-synthesized MCM-41, while 413 K was the best one for as-synthesized MCM-48.

(5) The as-M-41 vessel adsorbed menthol at 373 K and open stored for 30 days could release the spice in filter when the cigarette was smoked.

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Notes and references

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†Electronic Supplementary Information (ESI) available: The instrument and condition used for the detection of menthol released from mesoporous silica vessels, FT-IR spectra of menthol-mesoporous silica composites and GC-MS spectrum of the released menthol from as-M48. See DOI: 10.1039/b000000x/

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