Effective nitrosamines trap derived from the in situ carbonized mesoporous silica MCM-41

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ABSTRACT

A new route to modify the mesoporous silica MCM-41 with carbon, using the inherent surfactant template in the as-synthesized sample as the carbon precursor, is reported in this article. Apart from the advantage of omitting energy and time required for removal of template, the resulting silica–carbon composites exhibit a high efficiency in adsorption and catalytic decomposition of *N*-nitrosopyrrolidine (NPYR), the typical carcinogenic pollutant in environment. The influence of carbonization temperature on the structure and performance of the resulting carbon–silica composite was investigated by use of XRD, N_2 adsorption–desorption, FTIR and TG-DSC techniques, and the instantaneous adsorption and the temperature-programmed surface reaction (TPSR) of NPYR as well as the reduction of nitrosamines level of cigarette smoke were also utilized to assess the actual function of these composites. The carbonization performed in the range of 773–973 K enabled the resulting composites to possess a higher activity than parent MCM-41 in eliminating volatile nitrosamines, which is beneficial for controlling carcinogenic pollutants in environment.

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1. Introduction

Mesoporous silica is the valuable candidate for controlling the carcinogenic pollutants in environment because its specific channel structure enables the large amount of fluid to pass through within a short time while the target carcinogens can be selectively captured. As the important member of the family of ordered mesoporous silicates [1], MCM-41 with the relatively small pore diameters and high surface area has been tried in various adsorptions [2]. However, these siliceous mesoporous materials lack metal ions to be adsorptive and catalytic active sites due to their inherent chemical composition hence their modification is crucial [3–5]. Among the various modifiers such as metal oxides and organic species, carbon is often to be loaded on the mesoporous silica because of the excellent properties of carbon in hydrogen storage, adsorption, catalyst supports and electrode materials [6–9]. Mesoporous carbon–silica composites can possess the improved physical and chemical properties, and the confined-space effects would certainly modify the unique chemical behaviors of carbon particles inside the nanospace of mesostructures [10]. There are many methods to prepare the carbon–silica porous composite, such as surfactant intercalation [11], combination of triblock copolymer Pluronic P123 and phenol as structure-directing agent [12], and the evaporation-induced

triconstituent co-assembly method [13]. Nonetheless, all of them need the added carbon precursor accompanied with extra operative procedure, enhancing inevitably the cost of the resulting composite. Thus, new economical and time-saving route is sought to prepare the carbon-modified mesoporous silica. Herein, we report the new attempt of using the surfactant template micelles in the as-synthesized MCM-41 sample as the carbon precursor for three advantages. Firstly, it can farthest utilize the template micelles in the synthesis of mesoporous silica, since these hydrocarbons can be further employed as a kind of carbon source. Otherwise, they will be removed through calcination or extraction, consuming a lot of energy and time. Secondly, these template micelles inherently locate inside the channel of the mesoporous silica, which is beneficial to realize the aim of modifying the inner surface of the porous host with carbon. Thirdly, the carbon derived from the in situ carbonization of the template micelles cannot fill the whole channel but distribute inside the channel to change the surface curve of the pore wall, and the existence of carbonous particles in the channel will enlarge the adsorbate–adsorbent collision probability, which is profitable for the resulting composite to adsorb tiny molecules. We have tried this new preparative route in SBA-15, and the carbonized sample really exhibited a better performance than the parent SBA-15 in the adsorption and catalytic decomposition of volatile nitrosamines [14]. Here we try to extend this attempt to MCM-41 because the as-synthesized MCM-41, prepared with the direction of CTAB (cetyltrimethylammonium bromide, ionic surfactant), has two differences in comparison with the as-

synthesized SBA-15: the first, the ionic surfactants CTAB have a stronger interaction with silica wall than the amphiphilic block copolymers in SBA-15. The second, CTAB disperses in the channel of as-synthesized MCM-41 like the spoke in wheel with cation head rooted on the silica wall [15], which will affect the carbonization of micelles and the distribution of newly formed carbon. Besides, MCM-41 can provide the stronger geometric confinement than SBA-15 toward the tiny adsorbates such as volatile nitrosamines due to its smaller pore size [15,16], which is useful for the efforts of eliminating the carcinogenic pollutant in environment.

Another aim of this research is to assess the actual ability of these carbon–silica composites in trapping volatile nitrosamines in the complex environment. For this purpose the carbon–silica composite will be applied to eliminate the nitrosamines in the main smoke of cigarette, because tobacco smoke contains 5200 compounds and in which it is very difficult to selectively remove nitrosamines [17]. On the other hand, N-nitrosopyrrolidine (NPYR) is chosen as the probe for laboratory experiments since it is a common volatile nitrosamine in smoke with a structure of five-member ring [16,18], and its adsorption and catalytic degradation have been investigated on many porous samples [19].

2. Experimental

2.1. Materials and reagents

N-Nitrosopyrrolidine (NPYR) was provided by Sigma and dissolved in dichloromethane (A.R.) at the ratio of 1:19 (v/v). Cetyltrimethylammonium bromide (CTAB) and silica aerosol were produced by Nanjing Chemical Reagents and Qingdao Haiyang (China), respectively. The Chinese Virginia type cigarettes with the tar of 13 mg cig^{-1} and nicotine value of 1.2 mg cig^{-1} were purchased from the market.

Fabrication of MCM-41 was performed according to literatures [20]. Silica aerosol (3 g) was added to NaOH solution (0.5 M, 45 mL) under stirring and heated at 333 K to dissolve the additive, and then a solution (25 mL) containing CTAB (4.5 g) was added dropwise with stirring at room temperature. The pH value of the solution was adjusted to 11.5 using HCl solution (2 M). After being stirred for 6 h, the gel mixture was heated statically at 403 K for 72 h. The solid was recovered by filtration, washed with distilled water, and air-dried to give the as-MCM-41 sample. To in situ carbonize the as-MCM-41, 1 g sample was mixed with 5 g water and 0.2 g concentrated sulfuric acid (98%) by ultrasonic wave, and the mixture was heated at 373 K for 6 h and then to 433 K for another 6 h. Subsequently, the resulting dark brown material was heated at different temperatures in nitrogen atmosphere for 5 h to get the samples of AM-n (n = 773, 873, 973, 1073, indicating the carbonization temperature). For comparison part of the as-MCM-41 sample was calcined in air at 823 K or 773 K for 5 h to obtain MCM-41 or MCM-41(773).

2.2. Methods

The X-ray diffraction (XRD) patterns were recorded on an ARL XTRA diffractometer with Cu Kα radiation in the 2θ range from 0.5 to 8 [15]. Nitrogen adsorption and desorption isotherms were measured at 77 K by using a Micromeritics ASAP 2000 volumetric adsorption analyzer [15]. To get the FTIR spectrum of sample, compressed KBr flakes containing 2 wt% of sample were used, and the spectrum was recorded on a Bruker 22 infrared spectrophotometer in 4000–400 cm^{-1} with a resolution of 4 cm^{-1}. The carbon content of composite was determined by use of a varioEL CHNS analyzer. Thermo-gravimetric and differential scanning calorimetric (TG-DSC) analysis was performed on a NETZSCH STA449C apparatus in oxygen from 293 K to 1073 K with a heating rate of 10 K min^{-1}.
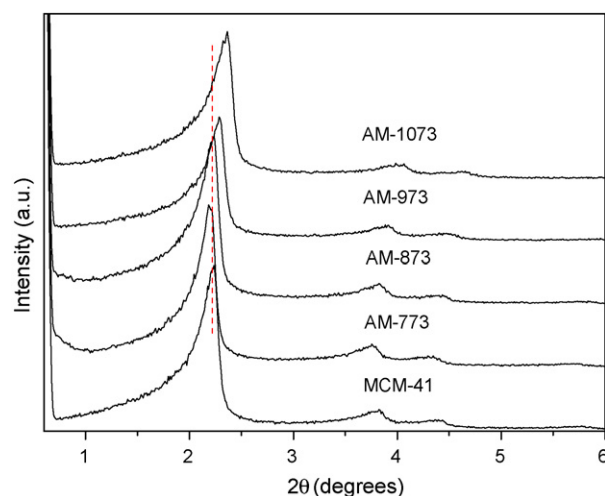

Fig. 1. Low-angle XRD patterns of carbonized MCM-41 samples.

Instantaneous adsorption of nitrosamines was carried out by gas chromatography (GC) method [18]. 5-mg samples (20–40 meshes) were filled in a stainless steel microreactor; it has a 1.4 mm diameter (i.d.) and 150 mm length, with one end inserted deeply into the injector port and the other end connected with the separation column of a Varian 3380 gas chromatograph. The sample was directly heated to 453 K in the flow of carrier gas with a rate of 30 mL min^{-1}, and the solution of nitrosamine was pulse injected with the amount of 2 μL each time. The flame ionization detector (FID) of the GC was used to analyze the gaseous effluent, and the decrement in the ratio of solute to solvent was utilized to calculate the adsorbed amount [18].

TPSR (temperature-programmed surface reaction) test was employed to assess the ability of composite in the catalytic degradation of nitrosamines. A certain mass of sample (20–40 meshes) was first activated at 773 K for 2 h, and then cooled to 313 K to contact 100 μL dichloromethane solution of NPYR. After the sample was purged by N$_2$ for 0.5 h, the temperature was raised to 773 K at a heating rate of 10 K min^{-1} while the nitrogen oxide products formed in the decomposition of nitrosamines were detected by use of an advanced photometric method [17]. And the amount of NO$_x$ determined in the TPSR procedure represented the amount of nitrosamines decomposed in the heating process [19].

To evaluate the efficiency of carbon-containing MCM-41 samples for eliminating nitrosamines in cigarette smoke, 40 mg samples, in 20–40 meshes, were carefully added into the filter to replace part of cellulose matrix with a same volume [21]. 20 cigarettes were smoked in the glass-made chamber designed by Miyake and Shibamoto [22], and mainstream was pulled through 100 mL citrate-phosphate buffer containing 0.02 mole of ascorbic acid with a pH value of 4.5 to absorb nitrosamines. Then the solution was extracted with dichloromethane and the residual nitrosamines content was determined by use of spectrophotometric technique [19], and the decrease in the nitrosamines content represented the amount trapped by the adsorbent.

3. Results and discussion

3.1. Textural properties

Fig. 1 shows the low-angle XRD patterns of MCM-41 and its carbonized analogues AM-773, AM-873, AM-973 and AM-1073, in which three peaks of (1 0 0), (1 1 0) and (2 0 0) can be indexed to a well ordered hexagonal phase. However, the unit cell parameter of the mesoporous materials, a_0, gradually decreased once the

Table 1
The texture properties and catalytic performance of MCM-41 and carbon-containing samples.

Sample	MCM-41(773)	MCM-41[a]	AM-773	AM-873	AM-973	AM-1073
S_{BET} (m^2 g^{-1})	1057	1052	999	973	949	880
S_{mic} (m^2 g^{-1})	57.0	32.6	35.4	4.0	0	0
V_p (cm^3 g^{-1})	0.93	0.92	0.87	0.81	0.79	0.69
V_{mic} (cm^3 g^{-1})	0.0133	0.0012	0.0032	0	0	0
D_p[a] (nm)	2.9	2.9	2.8	2.8	2.5	2.5
a_0 (nm)	–	4.6	4.6	4.6	4.4	4.3
Carbon content (%)	–	–	5.7	6.3	5.4	6.4
Released NO$_x$ (μmol g^{-1})	–	18.1	25.4	23.9	22.8	14.4
(nmol m^{-2})	–	17.2	25.4	24.6	24.1	16.4
T_{max} (K)	–	493	493	493	493	493
Residual nitrosamines in the mainstream smoke[b] (nmol cig^{-1})	–	1.88	1.46	1.46	1.67	1.88

[a] The carbon content of the as-synthesized of MCM-41 is 37.2 wt%.

[b] The original amount of nitrosamines in mainstream smoke is 2.29 nmol cig^{-1}.

carbonization temperature exceeded 873 K (Table 1), and the intensity of diffraction peaks also declined (Fig. 1), resulting from the lattice contraction occurred at high temperature [23]. Since the reflection intensities are related to the extent of pore filling and the scattering contrast between the pore walls and the inside of the pores [24], the loss of scattering intensity in these composites implies the lowered scattering contrast owing to the existence of the carbon particles inside the channel.

Fig. 2A illustrates the N$_2$ adsorption–desorption isotherms of these mesoporous samples, in which a sharp inflection emerges around $p/p_0 = 0.30$. This inflection is well known to be a typical capillary condensation process and the p/p_0 value corresponds to a pore size of about 2.9 nm [20]. However, the onset of inflections slightly shifted toward lower value of p/p_0 while the amount of adsorbed N$_2$ decreased as the sample had been carbonized at higher temperature. Since the capillary condensation pressure rose as the pore diameter of the sample increased, these phenomena indicated the smaller pore size of the composite carbonized at high temperature (Fig. 2B and Table 1). Two factors could be responsible for this variation. One is the framework shrinkage of the mesoporous sample at the high temperature [23], as demonstrated by the smaller microporous area and volume of MCM-41 than that of MCM-41(773) sample (Table 1), and the other is the special state of the carbon formed in the composite, as AM-773 has smaller microporous area and volume than MCM-41(773) sample (Table 1), which is determined by many factors including the temperature of carbonization. As demonstrated in Table 1, the as-synthesized MCM-41 owned the carbon content of 37 wt%, but all of the four carbon–silica composites only had the carbon of less than 7 wt%, probably due to the decomposition of the micelles in the procedure of in situ carbonization. Again, the different temperature should affect the state of new-formed carbon in the composite, because hydrogen may remain in the sample carbonized at below 873 K, but seldom in the sample prepared at 1073 K while a graphite-like structure formed at the higher temperature [25]. Apart from the varied composition of the carbon formed at different temperatures, the distribution of carbon is also changed. Theoretically, the amount of carbon to form a monolayer in MCM-41 is about 18 wt%, but the actual carbon content of these composites is only 5–6 wt% therefore the majority of the newly engendered carbon only form the nanoparticles by twos and threes on the pore walls of MCM-41 (Scheme 1). Furthermore, about 1.3 wt% of carbon is enough to block the micropores of MCM-41 according to the calculation; As the result, the major of carbon will distribute in the channel once the micropores are filled hence the morphology of pore wall is changed. On the basis of the data shown in Table 1, it is clear that only the sample of AM-773 kept the microporous feature similar to MCM-41, while other three composites not only lost their micropores, but also possessed a declined mesoporous volume.
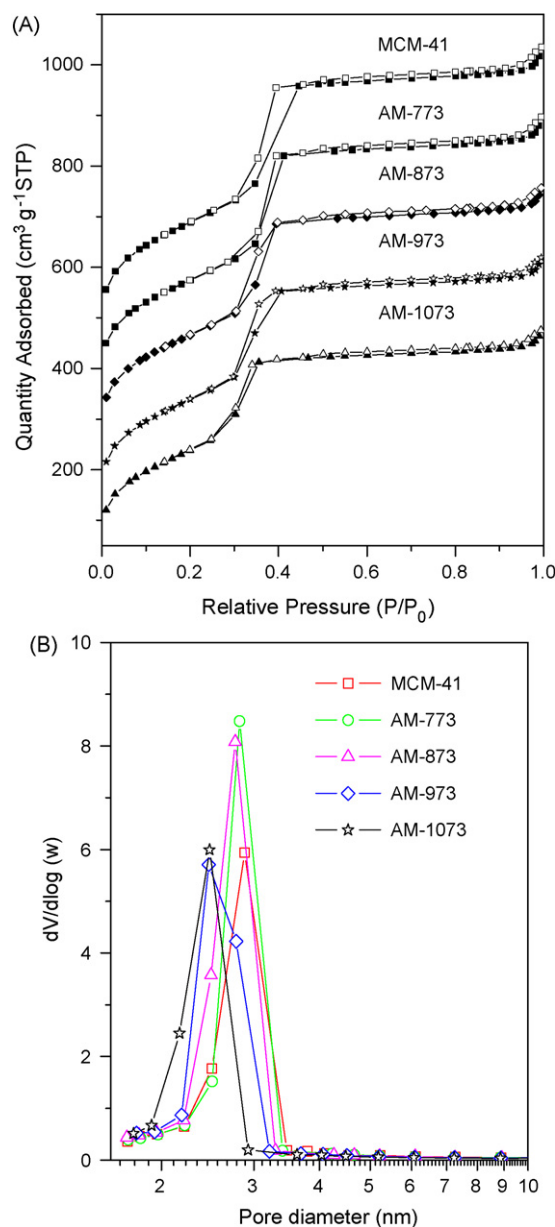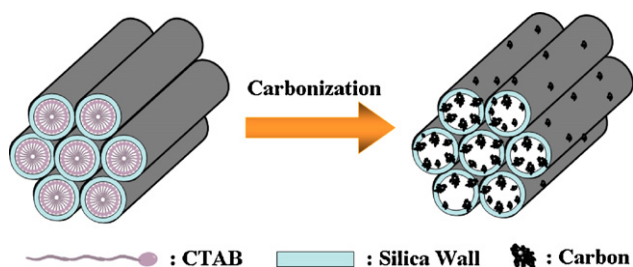

Fig. 2. (A) Nitrogen adsorption–desorption isotherm (filled points—adsorption and opened points—desorption) and (B) pore size distribution of carbonized series samples and MCM-41. The isotherms were offset vertically by AM-973, 70 cm^3 g^{-1}; AM-873, 200 cm^3 g^{-1}; AM-773, 300 cm^3 g^{-1}; MCM-41, 400 cm^3 g^{-1} respectively.

Scheme 1. Formation of mesophase carbon/MCM-41 in situ.

Fig. 3. The FTIR spectra of KBr flakes containing the MCM-41 and its analogues that had been carbonized at different temperatures.

Fig. 3 displays the FTIR spectra of as-synthesized MCM-41 and the carbonized samples. A broad band on the spectrum around $3400\,cm^{-1}$ was attributed to the O–H stretching vibration of the adsorbed water molecules, together with their bending vibration mode responsible for the band recorded at $1630\,cm^{-1}$ [26]. Three peaks at 1483, 2853 and $2925\,cm^{-1}$, assigned to C–H stretching and bending vibrations of the template [26] were observed on the spectrum of as-synthesized MCM-41 but absent on MCM-41 and carbonized samples, confirming the decomposition of template micelles in either calcination or carbonization. In general, the stretching modes of surface silanol groups ($\equiv$Si–OH) give rise to the bands in $960–990\,cm^{-1}$ on the IR spectra of both amorphous and crystalline silicates [27], and the $960\,cm^{-1}$ band in most ordered mesoporous materials indicates the presence of perturbing or defect groups, originating from the asymmetric stretching of Si–O bond neighboring surface silanol groups [28]. There was only a tiny $960\,cm^{-1}$ band on the spectrum of as-MCM-41 due to the existence of surfactant micelles that connected with the silanol group. Likewise, the intensity of $960\,cm^{-1}$ band was weakened on
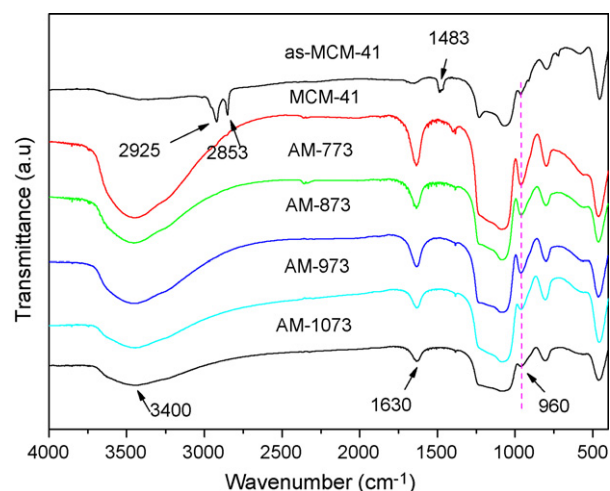
the spectra of AM-n sample as the temperature of carbonization increased, probably due to the condensation of Si–OH groups on the pore surfaces at high temperature [23]. One may argue whether the carbon covered the silanol group to weaken the $960\,cm^{-1}$ band, however, this argument was not justified by the experiment. The $960\,cm^{-1}$ band of both AM-773 and AM-873 was much weaker than that of MCM-41 but this band still existed, which excludes the possibility that the Si–OH was covered by the carbon modifier but confirms the co-existence of both carbon nanoparticles and the silanol group on the composite.
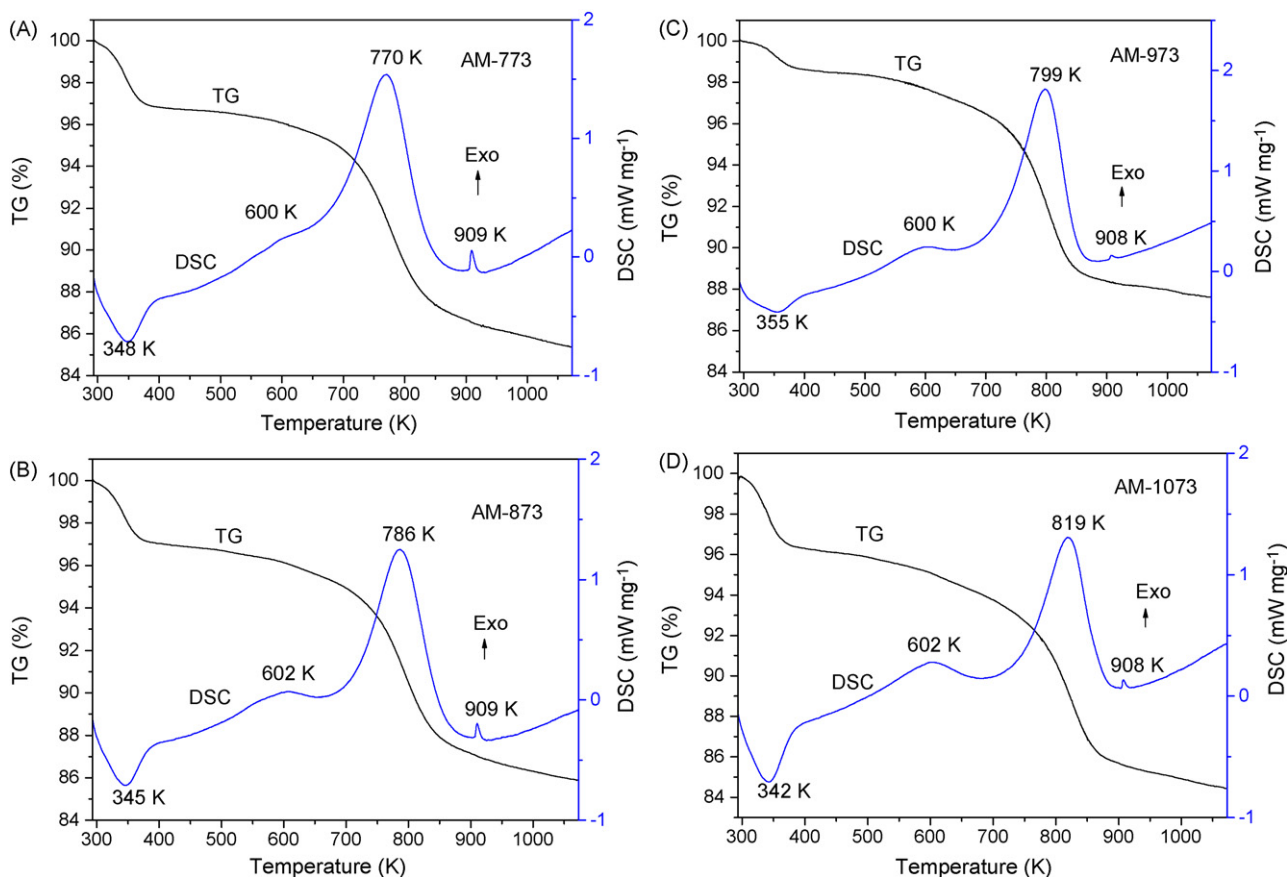

Fig. 4. The TG-DSC measurements of the samples carbonized at different temperatures: (A) AM-773, (B) AM-873, (C) AM-973 and (D) AM-1073 composites.
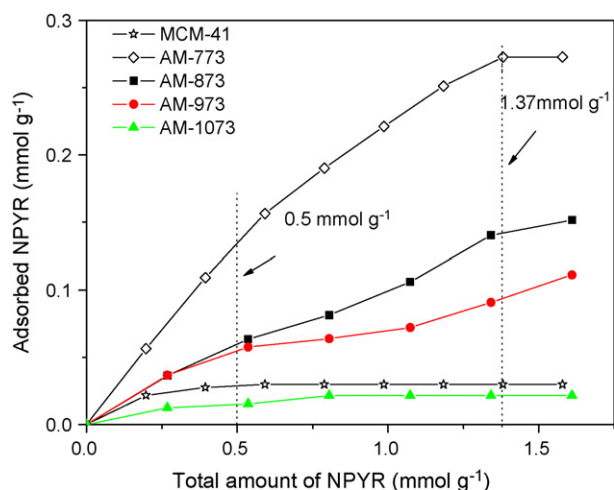
Fig. 5. Instantaneous adsorption of NPYR at 453 K on MCM-41 and the carbonized analogues.

Table 2
Freundlich constants of the adsorption isotherms of NPYR in porous materials at 453 K.

Adsorbent	K_F	n	R^2
MCM-41	0.031	5.76	0.810
AM-773	0.216	1.20	0.983
AM-873	0.103	1.24	0.993
AM-973	0.077	1.75	0.961
AM-1073	0.020	2.94	0.873

Conditions: 1 atm.; the rate of carrier gas was 30 mL min^{-1}.

As the TG-DSC results in Fig. 4 showed, two main processes took place on the carbon-containing composite when the sample was heated; physically adsorbed water was removed below 423 K at first [29], followed by the combustion of carbon engendered from the carbonization accompanied with an obvious weight loss from 550 K to 950 K, including dehydroxylation of silanol group and residual coke combustion [29]. In general the combustion of amorphous carbon occurs between 573 K and 673 K whereas oxidation of graphite takes place at around 973 K [30,31]. Accordingly the carbon combusted in the TG-DSC test can be tentatively divided to amorphous carbon (573–673 K), a kind of graphite (908 K) and the intermediate between amorphous and graphite (673–900 K). The combustion climax of the intermediate carbon shifted to higher value, from 770 K to 819 K as the sample had been carbonized from 773 K to 1073 K, implying the higher thermal stability of the carbon formed on mesoporous silica at higher temperatures though the total carbon content was almost the same. Likewise, other properties of the carbon formed at different temperatures were different, for instance the carbon formed at lower temperature was relatively pliable/viscous more or less, which should be beneficial for trapping the molecules collided on the surface of carbon. When the target molecule collides to the surface of the carbon inside the channel of the composite, it is much easier to be trapped by the viscous and/or pliable species. Otherwise, it will rebound on the hard surface of the carbon.

3.2. Adsorption and catalytic characteristics

Fig. 5 demonstrates the instantaneous adsorption of NPYR by various mesoporous samples at 453 K, in which the contact time between the adsorbent and the adsorbate is less than 0.1 s [18]. Most of the carbonized samples except AM-1073 exhibited the capability higher than parent MCM-41 in the adsorption. When 0.5 mmol g^{-1} of NPYR passed through the mesoporous materials, AM-773 adsorbed 27%, AM-873 trapped 12%, AM-973 captured 11% while MCM-41 and AM-1083 only removed 6% and 3%, respectively. As the accumulated amount of NPYR reached 1.37 mmol g^{-1}, the difference among these carbonized materials was more obvious and the sample of AM-773 still possessed the highest capability. This result is not unexpected because AM-773 possessed the microporous feature of MCM-41 as aforementioned along with the specific performance of carbon modifier, and these features are known to be profitable for capturing volatile nitrosamines [14,18]. For an overall analysis of these adsorption isotherms, they were

fitted with Freundlich equation [18], in which the exponent of $1 < n < 10$ indicates the favorable nature of adsorbent-NPYR system (Table 2). The smallest value of n, that meant a strong affinity between the composite and NPYR, was observed on AM-773 sample as expected. K_F is known as the Freundlich constant related to the adsorption capacity of the sample [18], and the varied values of K_F in Table 2 mirrors that the adsorptive ability of the composite changed inverse proportional with the temperature of carbonization. For instance the K_F value of AM-773 is ninefold larger than that of AM-1073, coincided with the adsorption at the accumulated amount of NPYR reaching 1.37 mmol g^{-1} (Fig. 5). Judged from the variation of n and K_F values, it is clear that relatively low temperature of carbonization is beneficial for the resulting composite to adsorb NPYR in gas flow.

Fig. 6 and Table 1 exhibit the catalytic performance of MCM-41 and its carbon-containing analogues. All of the carbonized samples except AM-1073 showed the higher ability than MCM-41 in the TPSR process of NPYR. AM-773 also degraded the most volatile nitrosamines in the test, 40% more than that by MCM-41, and AM-1073 was the lowest, consistent with the results of the adsorption. To have a deep inspection on the TPSR data, we calculated the catalytic performance of composite in unit area instead of unit weight, that is, to calculate the concentration of nitrogen oxides to μmol m^{-2}. Accordingly, there was NO$_x$ of 17.2 nmol m^{-2} formed on MCM-41 and 25.4 nmol m^{-2} on AM-773. For AM-873, AM-973 and AM-1073 sample, this value changed to 24.6, 24.1 and 16.4 nmol m^{-2}. This varying sequence is also consistent with the adsorption results. On the other hand, the value of temperature T_{max}, at which the maximum value of nitrogen oxide products emerged, is the same (493 K) on all of the porous samples (Table 1). This phenomenon indicates the helpless of carbon modification on MCM-41 toward the degradation of volatile nitrosamines, because NPYR will be decomposed at the lower temperature if the modifier improves the catalytic function of the composite [14,17].
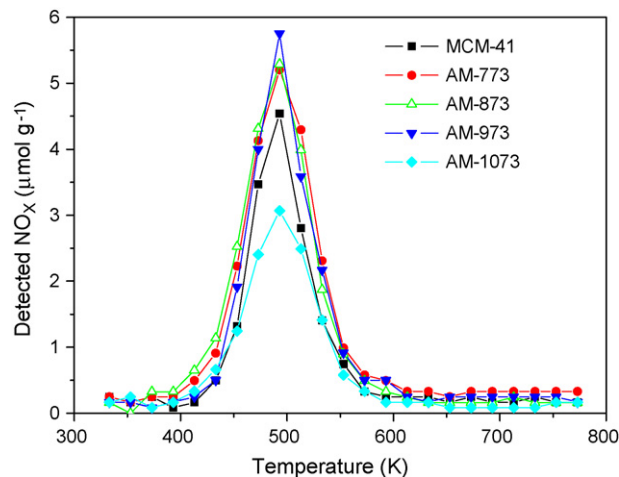

Fig. 6. Profiles of nitrogen oxide detected in the TPSR of NPYR on MCM-41, AM-773, AM-873, AM-973 and AM-1073 samples.
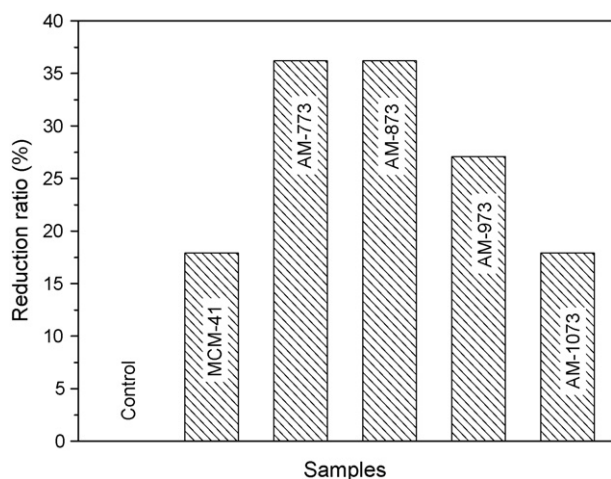
Fig. 7. Removal of nitrosamines in the mainstream smoke of cigarette by MCM-41 series samples.

In order to evaluate the selective adsorption of carbonized MCM-41 samples in complex system, these composites were added into cigarette filter as a triple segment model to trap the nitrosamines in the mainstream smoke and Fig. 7 displays their actual efficiency in reducing the nitrosamines content of smoke. There were 2.29 nmol cig^{-1} of nitrosamine in the main smoke, and MCM-41 adsorbed about 18% of them, similar to that reported previously [16]. Most of the carbonized samples had the higher efficiency than parent MCM-41 in eliminating nitrosamines in tobacco smoke, with the exception of AM-1073 whose performance (18%) was the same as that of MCM-41. AM-773 and AM-873 eliminated about 36% of the carcinogens, twice of that by MCM-41, lowering the nitrosamines content of smoke to 1.46 nmol cig^{-1} (Table 1). This value (36%) is higher than that of activated carbon (18%) and copper-modified MCM-41 (15–33%) [16,32]. It should be pointed out that both AM-773 and AM-873 composites contain the carbon of about 6 wt% that derived from the inherent template micelles, so the proportion of expensive mesoporous silica in the adsorbent is lowered. Together with the economization of energy and time for removal of template, these composites are considerable cheaper than common MCM-41 materials, which is beneficial for controlling the carcinogenic pollutants in environment.

4. Conclusion

Some conclusive remarks can be tentatively made on the basis of the results mentioned above:

(1) It is feasible to modify the mesoporous silica with carbon through the in situ carbonization of the inherent template micelles of the as-synthesized MCM-41, and the amount of carbon remained in the composite was 5–6 wt% no matter how the carbonization temperature varied from 773 K to 1073 K.
(2) The carbonization temperature strongly affects the adsorptive and catalytic performances of resulting composites toward NPYR, the typical volatile nitrosamines, among the samples AM-773 owned the highest activity probably due to the proper surface area of the composite and the appropriate state of the carbon engendered at the low temperature. As the carbonization temperature rose, the carbon filled the micropores of the host at first, and then distributed in the channel of MCM-41.

This investigation is our preliminary studies to farthest utilize the inherent template micelles in the channel of mesoporous silica in order to modify the surface state of the channel wall. Further comprehensive investigations are required to clearly identify the state and distribution of carbon in situ formed in the mesoporous composite.

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