Research on the Ordered Mesoporous Silica for Tobacco Harm Reduction

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Abstract. For reducing tobacco harm, this paper prepared an ordered mesoporous silica by using triblock copolymer Pluronic P123 as template. The property of this material was characterized by the X-ray scattering spectrum (XRD), Transmission electron microscopy (TEM), Scanning electron microscopy (SEM) and Nitrogen adsorption/desorption. Then this ordered mesoporous silica was added into the cigarette filter in order to researching its effect of cigarette harm index. The result shows that the feature of SBA-15 was grain morphology, ordered arrangement, tubular porous 2-D hexagonal structure. The application of SBA-15 in cigarette filter can selectively reduce harmful components in cigarette smoke such as crotonaldehyde, hydrogen cyanide, benzo pyrene and tar. The synthesized SBA-15 could properly reduce cigarette harm index.

1. Introduction
The influencing factors of tobacco harm index (H) is related to seven kinds of harmful ingredients in cigarette smoke. There are mainly HCN, NNK, NH3, B[α]P, phenol and crotonaldehyde of the harmful ingredient. At present, the study on cigarette smoke harm index is publicly reported less, mainly including cigarette auxiliary materials design and cigarette paper, etc. Which has become a research hotspot in recent years is to select reducing one or more among seven kinds of harmful ingredients in cigarette smoke, like crotonaldehyde that has intense stimulation to the person’s eyes, skin and respiratory tract. The method of selective reduction use mainly traditional adsorbent, such as molecular sieves, chitosan, activated carbon and porous resin, etc. Compared with traditional adsorbent, Ordered mesoporous silica (SBA-15) materials have uniform adjustable large aperture, controllable mesoscopic structure, high specific surface area and functional surface. Silica is an
excellent adsorbent and food additives[1]. So far, little researches focus on the effect of SBA-15 on cigarette harm index. Therefore, SBA-15 materials with different aperture are synthesized on a large scale, then detailed characterization of them are performed. And to study the adsorption of harmful ingredients in flue gas and the impact on the H value, they are applied to the cigarette filter as adsorbent.

2. Materials and methods

2.1. Preparing of SBA-15
2kg three block copolymer P123 is added to 15kg deionized water and 60kg 2M hydrochloric acid, then dissolve into solution. By stirring violently, one can get homogeneous solution; By heating, when the temperature reaches 40°C, 4.25g ethyl silicate under the condition of intense stirring is added. After 24h and then transferring into 100°C oven, it occurs to static crystallization; After cooling, by filtering and 100°C drying, and then the sample is placed in muffle furnace, which is heated up to 550°C at a rate of about 1°C /min in air atmosphere. After roasting 6h, one can remove the template agent. After finishing above operations, one can obtain SBA-15.

2.2. Characterization of SBA-15
Small angle X-ray scattering spectrum can be gathered in Nanostar U-type small Angle X-ray scattering (Cu Ka). Then they were observed by SEM and TEM images obtained by SEM. And Nitrogen adsorption/desorption isotherm can be get by using Micromeritics Tristar 3020 adsorption apparatus in 77K [2].

2.3. Preparation of cigarette samples
Weight ratio about 35% SBA-15 is added into a certain weight of starch adhesive, then is mixed evenly. Add the moderate amount of water under stirring. Through granular molding machine, microwave drying and spheroid granulate machine, the particle is divided into 20~60 mesh by screen. According to the production technology of cigarette, one can roll two kinds of rods respectively into control and test tobacco.

2.4. Analysis of physical and chemical cigarette smoke
After balancing contrast cigarette and test cigarette respectively for 48h in (22±1) °C, relative humidity conditions (60±2)%. According to the method of YC/T 28.2-2002, resistance, weight, circumference and rigidity are measured respectively; According to GB/T 19609-2004 and YC/T 156-2001 respectively, smoke tar and release amount of nicotine are measured; According to GB/T 23356-2009, YC/T 254-2008, YC/T 253-2008, YC/T 377-2010, YC/T 255-2008, YQ/T 17-2012 and GB/T 21130-2007 respectively, the release amount of seven kinds of mainstream smoke harmful ingredients including CO, crotonaldehyde, HCN, NH3, phenol, NNK and B[α]P are measured.

3. Results and discussion

3.1. XRD analysis
Characterization of SBA-15 uses the X-ray scattering spectral to investigate mesoscopic order. The result is shown in Figure 1. As can be seen from the Figure 1, SBA-15 within small Angle appear three obvious diffraction peak, whose ratio of interplanar distance (d) is 1:1.73:2, corresponding to typical two-dimensional six-party mesoscopic structure. And space group is p6m.
3.2. SEM and TEM observation
Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are carried out on the Characterization of SBA-15, so as to investigate surface structure characteristics and internal fine structure shown in Figure 2.

As can be seen from Figure 2, SBA-15 which is observed by SEM shows typical wheat-like morphology. Further amplification can be seen that wheat-like morphology SBA-15 is made of about 1 μm particles (Figure 2a, Figure 2b). TEM pictures shows the tubular channel of orderly arrangement, corresponding to two-dimensional six-party mesoscopic structure and consistent with the results of X-ray scattering spectrum (Figure 2c, Figure 2d).

3.3. Characterization of SBA-15
In order to investigate the nature of the hole of SBA-15, ordered mesoporous materials that are synthesized under the condition of different hydrothermal temperature are characterized with Nitrogen adsorption-desorption. Mesoporous pore size distribution can be calculated by BJH. The results are shown in Table 1.
Table 1. The physical and chemical properties of SBA-15

| Samples     | $S_{\text{BET}}$/(m$^2$/g) $^\circledast$ | $S_{\text{micropore}}$/(m$^2$/g) $^\circledast$ | $V$/(cm$^3$/g) $^\circledast$ | bore diameter/nm | $S_{\text{mesopore}}$/(m$^2$/g) $^\circledast$ |
|-------------|------------------------------------------|---------------------------------|-------------------------------|-------------------|------------------------------------------|
| SBA-15-HT80 | 660                                      | 107                             | 0.80                          | 7.4               | 553                                      |
| SBA-15-HT100| 780                                      | 89                              | 1.1                           | 9.3               | 691                                      |
| SBA-15-HT130| 430                                      | 34                              | 1.1                           | 12.4              | 396                                      |

Note: (1) BET specific surface area; (2) micro pore specific surface area; (3) pore volume calculated by BET method; (4) mesoporous aperture calculated by BJH; (5) mesoporous specific surface area

According to the Table 1, all Nitrogen isothermal adsorption-desorption of SBA-15 samples shows typical IV curve. The adsorption section shows an obvious capillary condensation phenomenon belong to a type H1 hysteresis loop. That indicates that it has homogeneous mesoporous and tubular mesoporous channel. The aperture size of SBA-15 increased from 7.4 nm to 9.3 nm and 12.4 nm, as the hot water temperature increasing from 80 °C to 80 °C and 100 °C. The specific surface area of the samples that are measured under different hydrothermal temperature are among 430~780 m$^2$/g. Among of those, BET specific surface area of SBA -15 by 100 °C water heat treatment is the largest and is780 m$^2$/g. Therefore, SBA - 15 under 100 °C water heat treatment is chose as cigarette filter additives.

3.4. Application of SBA-15

Through the laboratory screening of SBA-15, SBA-15 under 100°C water heat treatment is chose as cigarette filter additives. In terms of 1.2.3 the flue gas chemical indicators of cigarette samples were shown in Table 2.

Table 2. Flue gas chemical indicators of cigarette samples (mg/branch)

| Samples | tar   | nicotine | CO    | crotonaldehyde | HCN  | NH3   | phenol | NNK | B[α]P |
|---------|-------|----------|-------|----------------|------|-------|--------|-----|-------|
| Control | 12.5  | 1.36     | 13.3  | 18.4           | 117.9| 8.4   | 16.0   | 4.7 | 10.8  |
| SBA-15  | 11.7  | 1.29     | 13.4  | 12.7           | 114.9| 8.4   | 16.4   | 5.1 | 10.5  |

Table 2 illustrates that compared with the contrast cigarette, H value of test cigarettes adding SBA-15 reduces 0.3/branch, among of which the release quantity of tar reduces 0.8 mg/branch; Nicotine reduces 0.07 mg/branch; HCN reduces 3 µg/branch; B[α]P reduce 0.3 µg/branch; Crotonaldehyde reduces 5.7g/branch, reduced by 30.9%. Experimental results show that adding SBA - 15 can reduce the H value. Meanwhile, the amount of release of tar, nicotine, crotonaldehyde, HCN and B[α]P in cigarette smoke reduce in different degree.

4. Conclusion

Through the synthesis and characterization of SBA-15, the characteristics of the SBA-15 was two-dimensional six-party mesoscopic structure with wheat-like morphology, ordered arrangement, Tubular channel. In the application of SBA-15 in cigarette filter, compared with the contrast cigarette, adding SBA-15 can reduce H value. Meanwhile, the amount of release of tar, nicotine, crotonaldehyde, HCN and B[α]P in cigarette smoke reduce in different degree. Results show that adding SBA-15 can reduce cigarette smoke hazard index and plays an role in reducing tar and decreasing pollution to a certain extent.
References
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