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Research Article

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Studies on NaY zeolites used to remove benzo[a]pyrene and phenol in cigarette mainstream smoke

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ABSTRACT

NaY zeolites were added into cut tobacco and filter tip of a commercial brand of cigarettes substitute for activated carbon. Cigarettes with NaY zeolite were prepared and smoked in a smoking machine and the mainstream smoke was collected. The effect of NaY zeolite was investigated on the release of benzo[a]pyrene(B[a]P) and phenol in flue-cured cigarette mainstream smoke. The results showed that the removal efficiency of NaY zeolite added into cut tobacco was clearly higher than that added into filter tip for reducing B[a]P and phenol in cigarette mainstream smoke.

Key words: NaY zeolites, cut tobacco , filter tip, cigarette mainstream smoke, B[a]P, phenol

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INTRODUCTION

Zeolites are the inorganic porous aluminosilicate materials with unique and regular crystal structure. Each category of zeolites have nano channels with specific shape, size and large specific surface area[1].For most types of zeolites, there are strong acid sites on their surface and large Coulomb field and polarity inside the crystal lattices. Therefore, they show unique shape-selective catalytic functions and strong adsorption-separation performance. Substances can be separated according to the difference in molecular shape, diameter, polarity level, boiling point and saturation extent et al. Furthermore, Being cheap, noncombustible and harmless to human body, zeolites have been used as tobacco additives in harm reduction of smoking. Meier[2,3] described the treatment of tobacco with zeolitic materials as additives for reducing toxic components in tobacco smoke. Cvetkovic et al.[4] used a catalyst based on Cu-ZSM-5 zeolite in order to reduce the amount of NO and NOx in mainstream cigarette smoke. Xu et al.[5] reported that zeolites were added into filter tip or directly into tobacco in order to catalytically degrade tobacco specific nitrosamines (TSNAs) in mainstream smoke. They considered that zeolites were activated in cigarette burning zone and catalytic activity was generated, while the taste of cigarettes was hardly changed.

Moreover, it was reported in some articles that zeolites which were added into tobacco or filter tip could selectively eliminate other harmful components such as B[a]P and TSNAs in mainstream or side stream smoke[6-9]. However, most of these studies devoted to removing only one harmful ingredient, few studies focused on the effect of zeolite on removing B[a]P and phenol in mainstream smoke simultaneously. To our knowledge, there are no reports on the influence of different adding mode of zeolites and other factors except zeolite aperture for removing harmful components. Therefore, the typical NaY zeolites were selected in this paper and added into cut tobacco or filter tip. The removal efficiency on B[a]P and phenol in mainstream cigarette smoke was investigated and the elimination mechanism of zeolites was analyzed as well.

EXPERIMENTAL SECTION

2.1Apparatus

Electronic balance (Mettler Toledo, Switzerland); Milli-Q ultrapure water meter (Millipore, France); miniature cigarette maker(Gizeh, Germany); cambridge filter(Φ44mm, Whatmann, England); KQ3200E ultrasonic cleaner (Kunshan Ultrasonic Instrument Co., China); Sep-Pak Silica (50mg) solid phase extraction column (Sep-Pak Si, Waters, U.S.);automated solid-phase extraction device (GX-274,Gilson, France);gas chromatography-mass spectrometer instrument(6890N-5973, Agilent, U.S.); high performance liquid chromatography instrument (HP1100, Agilent, U.S.).

2.2 Reagents and chemicals

Methanol(HPLC, Merck), hexamethylene(HPLC, Tedia), acetonitrile(HPLC, Tedia), phenol(Tianjin Hengxing Chemical Reagent Co., Ltd., China), B[a]P(purity≥98.5%, Ehrenstorfer), B[a]P-D_{12}(purity 99%, Ehrenstorfer), Glacial acetic acid(AR, Sinopharm Chemical Reagent Co., Ltd, China), NaY zeolite(Nankai catalyst Factory, China), Flue-cured cut tobacco, finished cigarette of certain domestic brand (commercially available).

2.3 Cigarette Sample Preparation

Sample 1:The manufactured cigarettes were Selected according to the standard GB/T5606.1- 2004, the filter tips were drawn out and cut off from the middle; then different mass (10, 20, 30, 40mg) of NaY zeolite particles(20 to 40 mesh) were added into filter tip respectively and cigarettes without adding zeolite were as control samples.

Sample 2: Several copies of cut tobacco with the same weight (0.75 ± 0.01) g were weighed accurately, then NaY zeolite was added into cut tobacco according to its weight (1%, 2%, 3%, 4%, 5%) respectively. They were stirred evenly. Both the cut tobacco with zeolite and without zeolite was rolled into finished cigarette by means of a miniature cigarette maker.

The above finished sample 1 and sample 2 were put into a constant temperature and constant humidity box for 48 h, with temperature of 22 ± 1℃ and relative humidity of 60 ± 2%.Select the samples according to each group of cigarette with the average weight (± 0.02 g) and the average draw resistance(± 50 mm H_2O).

2.4 Sample treatment and analysis

Cigarette samples after equilibrium were aspirated according to the standard GB/T 16450-2004, after that, the cambridge filter on the smoking machine was taken down and the contents of B[a]P and phenol from total particulate matter of mainstream smoke were detected. The detection conditions of B[a]P and phenol was on the basis of GB/T21130-2007 and industry standards respectively.

RESULTS AND DISCUSSION

3.1The effects of NaY zeolite added into filter tip on removing B[a]P and phenol

Physical parameters and conventional parameters of test cigarettes with NaY zeolite added into filter tip was shown in Table 1.It was observed that the average weight of the test cigarettes increases with the increase of adding amount of NaY zeolite and the average weight of the cigarettes was with the increase of adding amount of NaY zeolite and the average weight of the cigarettes was gaining about 0.03 g when the weight of NaY zeolite was 40 mg. Compared with the blank sample(without adding NaY zeolite),there were little change for average draw resistance among each sample when different amount of NaY zeolite was added. It indicated that the addition of NaY zeolite particles in cigarette had almost no effect on the average adsorption resistance. The total particulate matter (TPM) decreased first and then increased with the increasing amount of NaY zeolite. TPM decreased by 1.38 mg/cig at most in contrast with control samples.

Table 1.Physical and conventional gas parameters of test cigarettes with NaY zeolite added in filter tip

Mass of NaY zeolite / (mg)	Average weight (g/cig.)	Average draw resistance (mmH_2O/cig.)	TPM (mg/cig)
0	0.894	114.2	14.48
10	0.912	114.9	14.18
20	0.914	114.2	13.13
30	0.919	114.0	13.10
40	0.923	114.2	13.26

Fig.1 indicated the removal efficiencies of different amount of NaY zeolite in filter tip for B[a]P and phenol. From the figure we can see that the release of B[a]P and phenol in mainstream smoke was decreasing with the increase of the amount of NaY zeolite added into filter tip. The release of phenol was reduced about 2% by every 10 mg of NaY zeolite added and 4% for B[a]P. Nevertheless, for the reduction of B[a]P emissions, NaY zeolite did not produce superposition effect, that is, the release of B[a]P decreased by 6.8% when the amount of NaY zeolite in filter tip was 10 mg and 10.9% for 20 mg which was equal to 5.5% or so for 10 mg. As the same rule, 19.4% for 40 mg was equal to about 4.8% for 10 mg. It may be related to the contact area of NaY zeolite when the smoke flew through the filter tip.

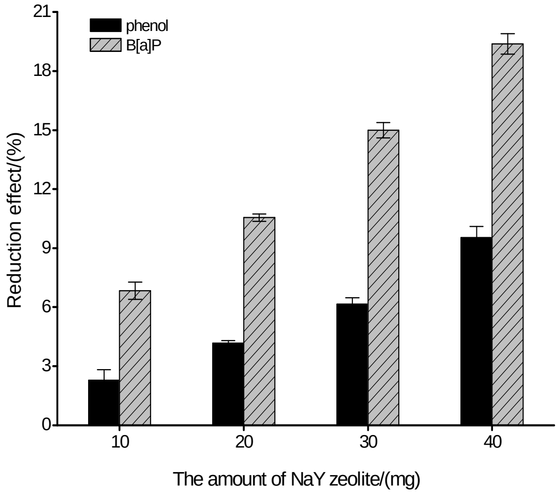

Fig.1 Removal efficiencies of NaY zeolite in filter tip for B[a]P and phenol in cigarette mainstream smoke

3.2 The effects of NaY zeolite added into cut tobacco on removing B[a]P and phenol

Average weight, average draw resistance and TPM parameters of test cigarette with NaY zeolite added in cut tobacco was shown in Table 2.

Table 2. Physical and conventional gas parameters of test cigarette with NaY zeolite added in cut tobacco

Proportion of added NaY zeolite（%）	Average weight (g/cig.)	Average draw resistance (mmH_2O/cig.）	TPM (mg/cig.)
0	0.947	96.2	18.10
1	0.954	96.8	17.25
2	0.963	103.2	16.99
3	0.971	105.4	15.74
4	0.977	111.3	15.84
5	0.984	113.2	17.58

As can be seen from table 2, the average weight and average adsorption resistance of cigarettes increased with the incremental amount of NaY zeolite. When the amount of NaY zeolite reached to 5% of the weight of cut tobacco, the average weight of cigarettes increased by 0.04g/cig. Compared with the blank sample, the average draw resistance increased with the increasing amount of NaY zeolite and increased by 17mmH_2O when the amount of NaY zeolite reached to 5% of the weight of cut tobacco. It may be due to the increase of the filling ability of cigarette because of adding NaY zeolite. TPM decreased first and then increased along with the increase of the amount of NaY zeolite added. When the weight of NaY zeolite reached to 3% of cut tobacco, TPM decreased by 2.36mg/cig. compared with the control sample. This phenomenon that TPM first decreased and then increased is probably related with burning rate of the cigarettes. NaY zeolite can't burn but can absorb and consume heat produced by burning cigarettes, which results in the increase of puff number. The above speculation needs more experiments to prove it such as increasing the adding amount of NaY zeolite from 6% to 10%.

As is shown in figure 2, with the increase of the amount of NaY zeolite in cut tobacco, the release of B[a]P and phenol in mainstream smoke is decreasing. But when the weight of NaY zeolite added was increased from 4% of the weight of cut tobacco to 5%, the release of B[a]P and phenol in mainstream smoke increased instead. This phenomenon may be correlated with the excessive of NaY zeolite which can alter the burning rate of cigarettes.

As can be seen from Fig.1 and Fig.2, when 30mg NaY zeolite(4% of the weight of cut tobacco) was added into filter tip, the release of B[a]P and phenol in mainstream smoke decreased by 15% and 6.2% respectively compared with the blank sample. When 30mg NaY zeolite was added into cut tobacco, the release of B[a]P and phenol in mainstream smoke decreased by 27.6% and 16.3%.When 7.5mg NaY zeolite(1% of the weight of cut tobacco) was added into cut tobacco, the release of B[a]P and phenol in mainstream smoke decreased by 8% and 3% respectively.

However, when 10mg NaY zeolite was added into filter tip, the release of B[a]P and phenol in mainstream smoke decreased by 6.8% and 2.3% respectively. When 22.5mg NaY zeolite(3% of the weight of cut tobacco) was added into cut tobacco, the release of B[a]P and phenol in mainstream smoke decreased by 26.3% and 10.8% respectively, nevertheless, when 20mg NaY zeolite was added into filter tip, the release of B[a]P and phenol in mainstream smoke decreased 10.6% and 4.2% respectively.

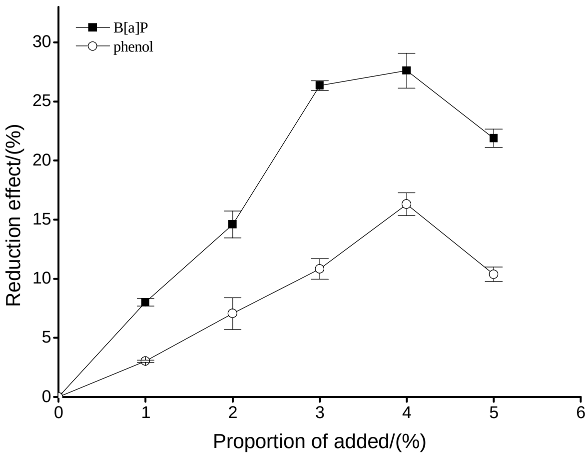

Fig.2 Removal efficiencies of NaY zeolite for B[a]P and phenol in cigarette mainstream smoke

All of the above data showed that for B[a]P and phenol, the removal efficiency of NaY zeolite added into cut tobacco was clearly higher than that added into filter tip when the amount of NaY zeolite was almost equal. There are mainly two reasons as follows：

Firstly,B[a]P in cigarette mainstream smoke is a compound which is formed through the pyrolysis, high-temperature synthesis and a variety of primary hydro- carbon radical reaction of terpene wax, sugar, cellulose, amino acids and so on, while phenol is produced by thermal pyrolysis and high-temperature synthesis of tobacco sugars and polyphenols (rutin, chlorogenic acid, etc) during smoking[10]. Therefore, the intermediates for forming B[a]P and phenol in cigarette smoke may be adsorbed by NaY zeolite added in cut tobacco[11],which leads to reducing the amount of intermediates to form B[a]P and phenol.So it results in reducing the release of B[a]P and phenol.

Secondly, NaY zeolite has excellent adsorption because of its particular spatial structure. It also has shape-selective catalysis according to the molecular size, shape, saturation etc. The reason why NaY zeolite in cut tobacco can remove B[a]P and phenol in mainstream smoke is not just due to its adsorption. Zeolite inside the burning cigarette is activated (activation temperature of NaY zeolite is 700℃,while the internal temperature of cigarette in the combustion process is up to 900℃.As a result, burning cigarette can make zeolite activated.),thus possesses high catalytic activity and it can involve in the formation of harmful substances and catalytically decompose the adsorbed molecules and the intermediates inside the NaY zeolite into other substances, thus the contents of B[a]P and phenol in cigarette mainstream smoke are reduced. However, NaY zeolite added into filter tip can not be activated because the temperature of filter tip is lower than 100℃during smoking, so NaY zeolite can not involve in the formation of harmful substances, but mainly depends on its adsorption to remove them.

CONCLUSION

NaY zeolites added into either filter tip or cut tobacco can both effectively remove B[a]P and phenol in cigarette mainstream smoke. Since NaY zeolite added into cut tobacco is activated inside the burning cigarette, it possesses catalytic activity and can involve in the formation of harmful substances. Consequently, for B[a]P and phenol, the removal efficiency of NaY zeolite added into cut tobacco is superior to that added into filter tip.

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