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Thermal release of nicotine and its salts adsorbed on silica gel

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ABSTRACT

Nicotine and its salts adsorbed on silica gel are employed to simulate the nicotine release behaviors of reconstituted tobacco particles (RTPs). Thermogravimetric analysis (TGA) was applied to provide an overview of the thermal behaviors of the nicotine, its salts and the RTPs. Diffuse reflectance infrared spectroscopy (DRIFTS) measurements of pyrolysis processes were performed on a FTIR spectrometer equipped with an in-situ DRIFTS reaction cell and a MCT/A detector. Firstly, the amine groups of nicotine and its salts are mainly adsorbed on the isolated hydroxyl groups of silica gel. Secondly, three adsorption modes of nicotine have been established. Finally, smoking machine was applied to study the release behavior of nicotine from the reconstituted tobacco particles (RTPs). The interaction between nicotine and the adsorbent is identified. Our results show interesting observations on thermal release of nicotine from the different substrates, proving the adsorption and thermal release of nicotine and it salts from RTPs, which have a guiding significance for the development of heat-not-burn cigarettes.

1. Introduction

Nicotine, an addictive component of tobacco smoke, is of interest in its evolution during the smoking process [1–4]. In tobacco leaves, nicotine is mainly in the form of nicotine salts [5,6], most of which are nicotine malate and nicotine citrate. As we all known, cigarette smoke of conventional cigarettes is a highly complex aerosol system, involving over 6000 identified chemicals in a dynamic and reactive mixture [6,7]. These chemicals are generated by incomplete combustion of tobacco [8]. Tar generated in the burning process contains most toxicants from the tobacco smoke. Nowadays, an effective method to reduce the generation of toxicants from tobacco is to develop heat-not-burn cigarettes [9–11], which generates less tar than conventional cigarettes in the smoking process. There are two forms of heat-not-burn cigarettes. One form of heat-not-burn cigarettes looks like a cigarette. It involves a lit carbon tip that heats incoming air, which in turn heats tobacco-based substrates, forming an aerosol containing mainly water, glycerol, nicotine and volatile tobacco components [12–14]. Another type of heat-not-burn cigarettes has a heating device that is powered by a battery, which works with a specially designed tobacco rod [15]. The heating of the tobacco includes heating from the inside of the tobacco rod, or from the external surface of the tobacco rod, or a combination of both. In both of these two forms of heat-not-burn cigarettes, the tobacco heating temperatures are typically below 300 °C [15]. The temperature is high enough for tobacco to release nicotine, but tar generates still much less than conventional cigarettes. The related studies have indicated that the aerosol composition in heat-not-burn cigarette smoke contains less toxicant than that in conventional cigarette smoke [9–11].

The mechanism of nicotine release during smoking of conventional cigarettes is still not fully elucidated. Although the aerosol composition in heat-not-burn cigarette smoke is simpler than that in conventional cigarette smoke, it is difficult to study nicotine release behavior of heat-not-burn cigarettes directly. In order to simplify the experimental sample, silica gel is selected as the adsorbent in our research for the following reasons. Firstly, silica gel has great adsorption capability due to its big Brunner – Emmet – Teller (BET) area, which can adsorb enough nicotine/nicotine salts to show clear pictures of TGA and DRIFTS spectra [16]. Another reason for silica gel selected as the adsorbent in our research is that there are numerous hydroxyl groups present on the surface of silica gel. And the surface of tobacco substrate is polyhydroxy [17–21]. Therefore, silica gel with nicotine adsorbed on and its salts may truly reflect the release behaviors of nicotine from the tobacco substrate.

In this work, thermogravimetric analyses (TGA) was used to provide the thermal behaviors of nicotine and its salts. And diffuse reflectance infrared spectroscopy (DRIFTS) is applied to study the interaction between probes and adsorbent [22–24]. We employed TGA and DRIFTS to study the release behaviors of nicotine and its salts adsorbed on silica gel at selected temperature. TGA draws a continuous mass loss process, and first derivative of the averaged weight loss (DTG) indicates different pyrolysis stages. DRIFTS spectroscopy is capable of carrying out *in situ* characterization of the interaction between nicotine (its salts)

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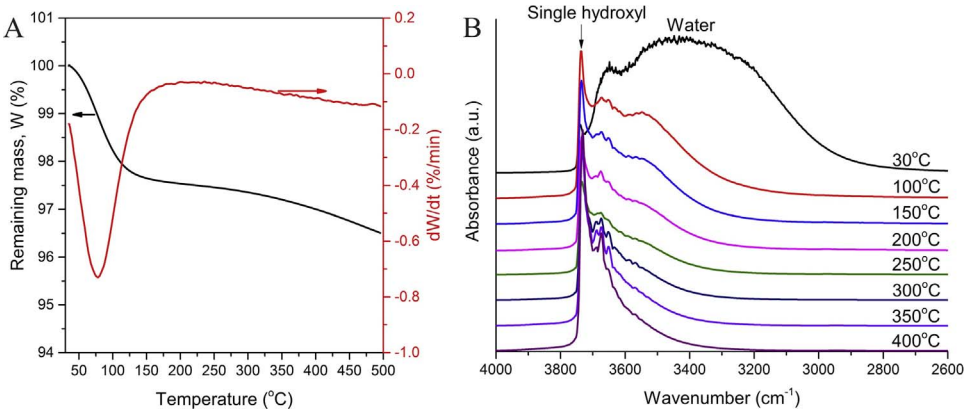

Fig. 1. A: TG (weight loss) and DTG (derivative of weight loss) curves corresponding to the thermal stability of silica gel in N_2. B: DRIFTS spectra at selected temperature for the thermal stability of silica gel in He.

and adsorbent. Combining the TGA and DRIFTS results, desorption/pyrolysis mechanisms of nicotine/nicotine salts can be investigated. Finally, the nicotine release behavior of reconstituted tobacco particles (RTPs) is examined, which completely fulfills our TGA and DRIFTS results. In a word, our results show interesting observations on thermal release of nicotine from the different substrates, proving the adsorption and thermal release of nicotine and it salts from RTPs, which have a guiding significance for the development of heat-not-burn cigarettes.

2. Material and methods

2.1. Material

The nicotine salts were purchased from Huabao International Holdings Limited. The nicotine salts were dissolved in water and the details were in the Table S1 (Supplementary data). The silica gel was purchased from Chemical Division of Silicycle. The reconstituted tobacco particles (noted as RTPs) was purchased from Shanghai Tobacco Group Co., LTD. The RTPs were prepared by 100% reconstituted tobacco sheet by a grinder, and the size of those was between 1 and 2 mm. The total content of nicotine in RTPs was 0.91%, and the moisture content was 16%. The RTPs and all chemicals were used as received.

Nicotine/silica gel samples were denoted followed the typical procedures: 40 μL nicotine, 100 μL anhydrous ethanol and 200 mg silica gel were co-added into a gray GC bottle and adequately mixed by stirring. Finally, the samples were dried in vacuum at room temperature (RT) for 2 h.

Nicotine salts/silica gel samples were denoted followed the typical procedures: 80 μL nicotine salts aqueous solution, 100 μL anhydrous ethanol and 200 mg silica gel were co-added into a gray GC bottle and adequately mixed by stirring. Finally, the samples were dried in vacuum at RT for 2 h.

2.2. Thermogravimetric analyses (TGA)

TGA (PerkinElmer, STA 8000) was performed on the nicotine, its salts and the reconstituted tobacco particles to provide an overview of their thermal behavior. For this experiment, 20–25 mg sample was loaded into a Pt crucible. For each TGA experiment, the temperature ranged from 35 °C to 500 °C in N_2 (sample purge: 20 mL/min; balance purge: 40 mL/min) under 20 °C/min heating rate, and held for 5 min at 500 °C. First derivative of the averaged weight loss (DTG) was also obtained.

2.3. Diffuse reflectance infrared spectroscopy (DRIFTS)

DRIFTS measurements of pyrolysis processes were performed on a Nicolet 5700 FTIR spectrometer equipped with an *in situ* DRIFTS reaction cell (Harrick Scientific Products, INC) and a MCT/A detector. He (flow rate: 20 mL/min) was employed as the carrying gas for the pyrolysis. Silica gel was purged in the He stream (flow rate: 20 mL/min) at 30 °C for 1 h until there were no changes of the DRIFTS spectrum. And the corresponding DRIFTS spectrum was taken as the background spectrum. Nicotine salts adsorbed on silica were pretreated in the He stream (flow rate: 20 mL/min) for 0.5 h to remove the adsorbed water on the surface of silica gel. The pyrolysis process was *in situ* studied by the DRIFTS measurements performed with 64 scans and a resolution of 4 cm^{-1}. The corresponding DRIFTS spectrum was taken when the sample was heated in the He stream (flow rate: 20 mL/min) to desirable temperatures under 10 °C/min heating rate and held at the desirable temperature for 3 min.

2.4. Nicotine release study of reconstituted tobacco particles (RTPs)

The reconstituted tobacco particles (RTPs) and Cambridge filter pads (CFPs, Borgwaldt, Germany) used for our study were conditioned at 22 ± 1 °C and a humidity of 60 ± 2% for at least 48 h. 65 mg RTPs were filled into a U-sharp quartz tube. The heating equipment was a GC oven (Agilent 6890). The RTPs were puffed in a puff volume of 35 mL with 2 s/puff duration in every 15 s by using a 20-port Borgwaldt RM200 smoking machine (Borgwaldt, Germany) according to ISO 4387 at selected temperatures. The smoke particulate matter of the RTPs in one tube was collected in one CFP with a diameter of 44 mm in totally 20 puffs. The schematic diagram was shown in Fig. S1 (Supplementary data).

3. Results and discussion

In this work, silica gel was employed as the adsorbent to adsorb nicotine and its salts to study their pyrolysis behaviors. Silica gel is a common adsorbent, which can adsorb enough nicotine/nicotine salts to show clear TGA and DRIFTS spectra [16].

Firstly, we studied the thermal stability of silica gel (as shown in Fig. 1A). The TG curve of silica gel indicates that the weight loss of silica gel is about 2.5% when the temperature is raised up to 150 °C. When the temperature is raised up to 500 °C, the weight loss of silica gel is about 3.5%. In order to further study the mechanism of the weight loss of silica gel, a series of DRIFTS spectra *in situ* for the thermal stability of silica gel in He acquired at selected temperatures are shown in Fig. 1B. Compared with the DTG curve (Fig. 1A), it is clearly shown that the water adsorbed on the surface of silica gel firstly desorbed before 150 °C. The IR band of silica gel at 3740 cm^{-1} is slowly enhanced, proving the increase in the number of isolated surface hydroxyl groups on the surface of silica gel [21,25].

Silica gel has a considerable adsorption capacity due to its large surface area (~ 500 m^2/g) [16]. Therefore, silica gel is selected as an excellent adsorbent to study the pyrolysis of nicotine and its salts.