



Nicotine/mesoporous solids interactions at increasing temperatures under inert and air environments



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ARTICLE INFO

Article history:

Received 14 October 2015

Accepted 24 February 2016

Available online 15 March 2016

Keywords:

Nicotine
Thermal degradation
Mesoporous catalysts
TGA/FTIR

ABSTRACT

In this work, the pyrolysis of nicotine under N_2 and air atmospheres and in the presence of three mesoporous materials (SBA-15 and two different forms of MCM-41) has been studied by TGA-FTIR. The results obtained show that, in the absence of a catalyst, the thermal evolution of nicotine mainly results in the volatilization of the compound. In an air atmosphere, nicotine evolves at a slightly lower temperature than in N_2 and the oxidation of the small solid residue at around 475 °C is observed. The results obtained suggest that the main interaction of SBA-15 with nicotine is related to adsorption processes, with slight modifications of the reaction pathways in an N_2 atmosphere and enhanced oxidation in the presence of air. The thermal decomposition of nicotine in an inert atmosphere and in the presence of MCM-41 indicates that, besides the desorption processes, an early decomposition step takes place, yielding several derivatives of nicotine. This phenomenon seems to be enhanced in an air atmosphere, where the presence of MCM-41 appears to markedly modify the evaporation and desorption of nicotine processes.

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1. Introduction

Nicotine, (S)-3-(1-methyl-2-pyrrolidinyl) pyridine, is an alkaloid found in plants from the Solanaceae family. The usual content in *Nicotiana tabacum* (tobacco) ranges from 0.6 to 4% or even higher [1]. Tobacco contains more than 20 alkaloids, which significantly affect the taste of tobacco, and nicotine, which is generally synthesized in roots, represents approximately 95% of total tobacco alkaloids [2]. There is general agreement that the addictive agent of cigaret smoking and the reason for smoking is (s)-(-)-nicotine [3]. It is, apart from water, carbon dioxide and carbon monoxide, the major constituent of tobacco smoke [4]. Consequently, the study of its evolution during smoking is of great interest.

Several studies have been performed for years focused on the study of the pyrolysis of nicotine as well as on the fate of nicotine when cigarets are smoked [1,5,6]. In 1944, Woodward et al. [5] studied the pyrolytic reaction of nicotine to β -alkyl and β -alkenyl pyridines and found that in general, the pyrolytic fission of nicotine results in the formation of a variety of products rather than a yield of any one material. The *N*-methylpyrrolidine nucleus of the nicotine molecule showed to be more susceptible to react, yielding ammonia, methylamine, hydrogen cyanide, pyridine, β -picoline, β -ethylpyridine, β -vinylpyridine, 3,2'-nicotyrine, myosmine and a

high boiling non-identified fraction. The volatile products evolved from the pyrolysis of nicotine were also studied in 1961 by Jarboe and Rosene [6]; they discussed their results and those of other authors and describe the influence of the pyrolytic atmosphere in determining the composition of the products. They found that, in an inert atmosphere and in the range of 600–900 °C, a variety of heterocyclic nitrogen compounds and aromatic hydrocarbons were evolved, thus allowing a mechanism for the primary reactions to be established. In addition, a number of secondary products were ascribed to free-radical reactions involving cleavage and recombination. Moldoveanu [1] reports data of the products obtained from the flash pyrolysis of nicotine at 900 °C, reflecting that nicotine represents more than 92% of the pyrolysate. Moreover, a few oxygenated compounds (including cotinine) appeared as a consequence of the presence of traces of oxygen in the pyrolysis atmosphere, and several reactions with methane elimination also occurred. Besides the formation of different nicotine pyrolysis products, racemization was also reported.

The fate of nicotine during pyrolysis and in burning cigarets has been the subject of many studies [7–11]. The conclusions obtained highly depend on the techniques used to study the process, since different products and yields may be obtained accordingly. It has been demonstrated that a substantial portion of the endogenous and exogenous nicotine in cigarets transfers intact into the smoke stream [7], whereas the remaining portion undergoes thermal degradation. According to studies with cigarets containing ^{14}C -labeled nicotine, performed by Schmeltz et al. [7], about 41% of

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the nicotine transfers intact into smoke, about 3–11% is converted to other volatile bases, which are found in the particulate phase (smoke), 12.5% is converted to CO₂, and the remainder likely consists of highly volatile organic compounds. Nevertheless, certain differences were observed when nicotine was thermally degraded in an experimental flash pyrolysis system, mainly due to extensive degradation of nicotine in the pyrolysis tube as opposed to substantial distillation in the burning cigaret. More than 38 compounds were identified in the pyrolysates, and at 600 °C some nicotine still survived pyrolysis. These authors [7] concluded that despite the complex degradative high temperature pyrolysis, pathways do not occur to a great extent in a burning cigaret but may take place to a lesser extent. On the other hand, the products of the pyrolysis of nicotine are also partially a function of the form of nicotine (i.e., salt vs. free form). Stevens and Borgeding [8] established three groups of compounds found in the smoke of nicotine-containing ciga- rets, according to the mechanism produced then:

- Nicotine resulted from distillation-direct transfer of the unchanged compound from cigaret to the smoke.
- Pyridine, 3-methylpyridine, 3-ethylpyridine, 3-ethenylpyridine, 3-allylpyridine, 3-pyridine carbonitrile, produced by pyrolysis from nicotine by simple cleavage reactions without rearrangement of the pyridine ring substituents.
- Myosmine, β-nicotyrine, cotinine formed through oxidation of the nicotine pyrrolidine ring

Baker [9] stated that the majority of the so-called semi-volatile components of cigaret smoke are formed from tobacco at temperatures below 600 °C. A few of these components (e.g., nicotine and other alkaloids) are transferred directly from the tobacco, whereas most are formed principally as a result of pyrolytic decomposition of many tobacco components in parallel. Fournier et al. [10] reported that nicotine volatilizes below 250 °C. Therefore, in online pyrolysis, nicotine is not expected to be exposed to high temperature in the pyrolyzer unit for any significant time. Nevertheless, in another study, Baker and Bishop [11] stated that pyrolysis experiments should be performed under dynamic conditions at 30 °C s⁻¹ from 300 to 900 °C and a flow of 9% of oxygen in nitrogen in order to be relevant to what occurs during cigaret smoking. Under these conditions, 97.7% of nicotine was transferred intact to the smoke as compared to 76.4–100% (from smoking experiments).

The stereochemical configuration of nicotine has an important effect on the actions and potency of nicotine in biological systems [12]. (–)-(*S*)-nicotine, is the dominant alkaloid in tobacco and some studies of nicotine pyrolysis are focused on the investigation of its racemization processes. These studies showed the great influence of the experimental conditions used to carry out the pyrolysis experiments [12,13]. In this way, Liu et al. [13] reported a mechanism for the racemization of *S*-(–)-nicotine to *R*-(+) nicotine in cigaret smoke and found that temperature is a decisive factor for racemization. Nevertheless, the results shown by Clayton et al. [12] indicate that the pyrolytic auto-racemization of nicotine does not occur. This difference is attributed to the different pyrolytic behavior when pyrolysis was conducted in online dynamic conditions or at static offline pyrolysis. The transference of nicotine to the aerosol also depends on the nicotine form. According to Dixon et al. [14], non-protonated nicotine is a high boiling liquid (247 °C) that evaporates with heating, whereas protonated forms must first dissociate, decompose or disproportionate to nicotine free before nicotine can be transferred to the gas phase. Seeman and Carchman [3] reported that when nicotine and protonated nicotine are heated in a flow of gases, nicotine is transferred to the aerosol in near quantitative yield without racemization. These authors [3] proposed three different types of chemical reactions to explain the relative ease in which nicotine carboxylic acid salts found in tobacco are con-

verted to non-protonated nicotine: acid-base dissociation, thermal decomposition of the carboxylic acid anion and disproportion.

Recently, some papers have appeared describing the use of different adsorbents and catalysts in tobacco for different purposes. As an example, Seeofer and Kausch [15] and Li and Hajaligol [16,17] discussed the use of nanoparticles of different oxides to decrease the yield of CO. Chen et al. [18] studied the effect of oxidized carbon nanotubes on the adsorption of nicotine and the composition of the mainstream smoke, and Zhou et al. [19] demonstrated that the presence of carbon nanotubes in cigaret filters absorbs nicotine, among other compounds, more efficiently than commercial activated carbons. On the other hand, Feng et al. [20] showed that mesoporous alumina had no obvious influence on the content of nicotine in smoke. The desorption of nicotine from several materials, focused on the development of articles used as smoking substitutes has been also studied [21,22] as well as the sorption phenomena of nicotine from indoor air [23,24] or aqueous solutions [25–29].

The use of zeolites and other aluminosilicates in the filter or directly mixed with tobacco to reduce nitrosamines and polycyclic aromatics in the tobacco mainstream smoke main has been described by several authors [30–34], who employed NaA, NaY, KA and NaZSM-5, Cu-ZSM-5, SBA-15, MCM-48, Cerium-containing MCM-48 and other calco-silicates. Our research group has studied the use of MCM-41, SBA-15 and other zeolitic catalysts (HUSY, HZSM-5 and Hβ) to reduce the yields of toxicants in tobacco smoke [35,36]. Nevertheless, the mechanisms of action of these types of materials is very complex due to the many possible pathways involved in a non-stationary system with thousands of products being formed and remains as a controversial matter. Adsorption-desorption is always a process present in these types of systems clearly affecting the results, but they may also act modifying the product distribution, even increasing the yields of certain compounds, such as coke or solid residue [37]. In this context, we have found no papers studying the effect of these types of materials on the pyrolysis and oxidation reactions of nicotine. Since nicotine is the more important individual compound in tobacco smoke, the objective of the present paper is to study the pyrolysis of nicotine under different atmospheres and the presence of three mesoporous materials in different concentrations. Thermogravimetric analysis coupled to Fourier-transform infrared spectrometry (TGA-FTIR) is a widely used technique for studying pyrolysis and oxidation reactions and has been widely applied for studying tobacco, tobacco additives and catalysts [38–46]. Thus, in this work, TGA-FTIR equipment has been used in order to obtain some insight into the possible processes involved and to contribute to clarify the mechanisms of action of mesoporous catalyst on the thermal behavior of nicotine. The results obtained provide basic information and a deeper insight in the knowledge of the thermal behavior of nicotine in the presence of the considered catalysts, especially if these materials are intended to be used as adsorbents for the elimination of nicotine from different environments or as ciga- rets additives in order to reduce tobacco smoke toxicity.

2. Experimental

Liquid nicotine for synthesis ((–)-Nicotine reagent grade, Merck ref. 8.20877.0100), with a purity of ≥ 99% according to the provider, has been used as supplied, without further purification. More information about this material can be found in the Merck Chemicals portal (www.merck-chemicals.com).

Three mesoporous materials synthesized in our lab have been used. The catalysts were mesoporous aluminosilicates and have been prepared according to the standard procedures described in the bibliography: a SBA-15 (S sample, according to the nomen-

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