

Nicotine fast pyrolysis under inert and air environments. Effect of catalysts

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ABSTRACT

Fast pyrolysis of nicotine under He and Air atmospheres and in the presence of three mesoporous materials (two different morphology SBA-15 materials and one MCM-41) has been studied by EGA/Py/GC/MS. Nicotine is more stable under inert atmosphere, still representing around 6.7% of the products at 900 °C, than under oxidizing atmosphere, where it is almost completely decomposed at 700 °C. The products distribution as well as their evolution is also highly affected by the atmosphere, being 3-vinyl pyridine and nornicotyrine the major compounds under inert atmosphere, whereas 3-cyano pyridine and nicotyrine are the major compounds under oxidizing atmosphere, where the significant presence of hydrogen cyanide is also observed at 700 °C. The presence of catalysts modifies and accelerates the degradation of nicotine under both atmospheres studied. MCM-41 and SBA-15p show higher activity than SBA-15 f, probably due to their higher textural properties and accessibility of the nicotine molecule. Under Inert atmosphere, 3-vinyl pyridine is highly reduced by SBA-15p and MCM-41, still being the major compound. Pyridine increases its yield in presence of these two catalysts, as well as quinoline and isoquinoline (products not present when pyrolyzing sole nicotine). Under oxidizing atmosphere, the three catalysts increase the water yield, as well as that of 3-(2,5-dimethyl-1 H-pyrrol-1-yl) pyridine, compound that is almost not obtained in absence of catalyst. HCN as well as the toxicity of the compounds evolved are reduced by the three catalysts.

1. Introduction

Nicotine is the main reason for smoking, since it is the alkaloid responsible of the addictive character of tobacco [1]. Its presence in tobacco leaves and its behavior during tobacco smoking has been studied for many years [2–4]. The pyrolysis of nicotine and the products derived have been the objects of several studies. Woodward et al., [5] as early as in 1944, concluded that the pyrolysis of nicotine resulted in a variety of β -alkyl and β -alkenyl pyridines. The N-methylpyrrolidine group of the nicotine molecule reacted to form ammonia, methylamine, hydrogen cyanide, pyridine, β -picoline, β -ethylpyridine, β -vinylpyridine, 3,2'-nicotyrine (II) and myosmine. Jarboe and Rosene [6] observed the evolution of a range of heterocyclic nitrogen compounds and aromatic hydrocarbons under inert atmosphere at 600–900 °C, as a result of free-radical reactions involving cleavage and recombination. Moldoveanu et al. [2] studied the flash pyrolysis of nicotine at 900 °C, finding that nicotine was the major product, representing more than 92% of the products obtained, as well as the presence of low amounts of different oxygenated compounds (including cotinine), due to the

presence of traces of oxygen in the atmosphere.

Many authors agree in that a substantial portion of the endogenous and exogenous nicotine in cigarettes transfers intact into the smoke stream. According to Schmeltz et al. [7], around 41% of the nicotine passes unaltered to the tobacco smoke, around 12% transforms into carbon dioxide and up to 13% is reacted to other volatile compounds. The results depend on the pyrolysis atmosphere and temperature. At 600 °C around 40 compounds were detected from the nicotine pyrolysis and part of the nicotine was still observed.

Stevens [8] distinguished three groups of compounds found in the smoke of tobacco related to the pyrolysis of nicotine and considering the possible mechanisms of formation:

- Unaltered nicotine resulting from the direct distillation to smoke.
- Pyridine, 3-methylpyridine, 3-ethylpyridine, 3-ethenylpyridine, 3-allylpyridine, 3–3-cyano pyridine, obtained by cleavage reactions without rearrangement of the pyridine ring substituents.
- Myosmine, β -nicotyrine, cotinine resulting from the oxidation of the nicotine pyrrolidine ring

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Fournier et al. [9] concluded that nicotine was unlikely to undergo pyrolysis reactions since it volatilizes below 250 °C. Baker and Bishop [10] in experiments simulating the smoking conditions found that 97.7% of nicotine transferred unaltered to smoke.

Dixon et al. [11] reported that the non-protonated nicotine (boiling at 247 °C) evaporates with heating, whereas the protonated form must first dissociate and decompose to nicotine free before nicotine can be transferred to the gas phase. Seeman and Carchman [1] proposed three possible mechanisms explaining the way nicotine carboxylic acid salts found in tobacco are converted to non-protonated nicotine: i.e.: acid-base dissociation, thermal decomposition of the carboxylic acid anion and disproportion.

Nicotine in tobacco can be found free and in form of different salts (mainly malate and citrate). Nicotine interaction with ammonia has been the object a great controversy regarding the pathway of absorption of nicotine by smokers since it favored the presence of free nicotine [12, 13].

The pyrolysis products form nicotine also depend on the form the nicotine is present [14]. These authors studied the pyrolysis of nicotine adsorbed on silica gel using TG and concluded that the pyrolysis occurred within 200–270 °C. They suggested the possibility of three types of interactions of the nitrogen atoms in nicotine with the hydroxyl groups of the on the surface of silica gel. a) Both two N atoms of nicotine interact with two hydroxyl groups nearby b) The N atom of the pyridine ring interacts with an isolated hydroxyl group and c) The N atom of the 1-methylpyrrolidine ring interacts with an isolated hydroxyl group. Based on the intensity of the interaction $a > c > b$, these authors explained the DTG curve of nicotine obtained.

Borduas et al. [15] reported the first-time evidence of the formation HNCO by nicotine oxidation in the gas phase after the smoking process. Kibet et al. [16] reported a kinetic modelling of nicotine in mainstream smoking indicating that such study was not previously reported. They focused on nicotine pyridine and pyridine radicals.

Several papers have been found describing the use of different adsorbents and catalysts in tobacco with different purposes i.e.: Seeofer and Kausch [17] for reducing CO and nitric oxide; Li and Hajaligol [18], for reducing CO, Pi et al. [19] for the adsorption behavior of nicotine.

The use of zeolites and aluminosilicates in the filter or directly mixed with tobacco has been reported to reduce nitrosamines and polycyclic aromatics in the tobacco mainstream smoke [20–26].

In a previous paper in 2016 [27] we studied by TG-FTIR the pyrolysis and oxidation reactions of nicotine both sole and in the presence of different aluminosilicates (i.e.: SBA-15 and MCM-41). Nevertheless, we have found no papers systematically studying the products evolved in the fast pyrolysis of nicotine at different temperatures, under inert and air atmospheres nor the effect of the presence of aluminosilicate catalysts on these processes. Thus, the objective of this paper is to complete the previous study and to report novel results on the effect of different catalysts, under inert and oxidizing atmospheres, and at different temperatures on the product distribution of the pyrolysis of nicotine.

2. Experimental

(-)-Nicotine reagent grade (Merck ref. 8.20877.0100) has been used as supplied. The catalysts used, three mesoporous aluminosilicates, have been synthesised in our lab. A SBA-15 with a fiber-like morphology, was synthesized according to the procedure described by Zhang et al. (2005) [28] using BASF Pluronic P123 as the surfactant, tetraethyl orthosilicate (Wacker, >99% purity) as the silica source and HCl (Merck 37%). A SBA-15 with platelet morphology, synthesised according to the procedure described by Yeh et al. [29] using cetyl trimethyl ammonium bromide and sodium dodecyl sulphate (both from (Acros Organics, >99% purity) as the surfactants, sulphuric acid (Merck, >99% purity) sodium silicate (Schalau, neutral solution pure) and sodium hydroxide (Sigma Aldrich, >98% purity). The MCM-41 was synthesised as described by Gaydhankar et al. [30], using cetyl trimethyl ammonium

bromide (Acros Organics, >99% purity), ammonia (Merck, 25% solution) and tetraethyl orthosilicate (Wacker, >99% purity). The catalysts obtained have been characterized by 77 K N₂ adsorption isotherms. SBA-15p present the major pore size (7.244 nm) and pore volume (1.281 cm³/g), followed by SBA15f with a pore size of 6.091 nm, and 0.954 cm³/g of pore volume. MCM-41 presents a minor pore size (2.182 nm) and minor pore volume (0.905 cm³/g). With respect to BET area, MCM-41 present the major value (1154 m²/g), followed by SBA-15p (1009 m²/g) and SBA15f (728.1 m²/g).

A Frontier Laboratories EGA/PY-3030D pyrolyzer on line with an Agilent 6890 N GC Gas Chromatographer with an Agilent 5973 Mass spectrometer detector (Py-GC/MS) was used for studying the nicotine pyrolysis under the selected conditions. Typically, around 0.1 mg of nicotine was placed in the sample holder. In the experiments with catalysts to this 0.1 mg of nicotine 0.2 mg of catalysts were added and thoroughly mixed. A 100:1 Split ratio was used and the products generated where introduced into the GC separation column (HP-5MS Ultra Inert, 30 m × 0.25 mm i.d. × 0.25 μm film thickness, Agilent technologies). The pyrolysis temperature was one of the parameters studied, and was accordingly fixed in the corresponding experiment. Pyrolysis time was set to 0.2 min in all experiments. The GC conditions used were as follows: Injection temperature: 300 °C, carrier gas flow (He or air) 2 mL/min, Oven temperature: 45 °C during 5 min, heat at a rate of 12 °C/min up to 285 °C, hold temperature during 5 min. MS conditions: electronic impact ionization energy 70 eV, mass scan 15–300 amu. The ChemStation Data Analysis provided by Agilent Technologies has been used to quantify the area of the peaks and the 2002 NIST MS Search 2.0 and the Wiley 2007 libraries have been used to identify the different products obtained. Several compounds not found in the libraries, with a low match with the libraries or not likely to occur have been identified by analyzing their corresponding mass spectra and comparing them with other literature sources.

3. Results

3.1. EGA fast pyrolysis of sole nicotine

The chromatograms obtained in EGA (all experiments have been run by triplicate and very good reproducibility was observed) in the pyrolysis of pure nicotine in He atmosphere at temperatures within the 650–900 °C shows a range of 178 peaks under inert atmosphere and 172 under air atmosphere. As an example, the chromatograms of Nicotine obtained at different temperatures both atmospheres are shown in the [supplementary material](#), FS1 and FS2. This temperature range is typical in smoking processes and is a range where nicotine significantly decomposes. [Table 1](#) shows the main compounds obtained in the decomposition of nicotine. [Table S1](#) shows the name of up to 56 compounds that present a contribution to the total area greater than 0.5% and have been assigned with a probability greater than 80% ([Tables S2–S4](#)). As can be seen, at lower temperatures nicotine remains practically unaltered, being nicotine the main. At 650 °C is almost the only peak detected and only very small peaks are observed at longer retention times ([Fig. 1](#)). As temperature increases, the intensity of the nicotine peak decreases and the chromatogram presents a large number of peaks ([Tables S2 in supplementary material](#)).

Under air atmosphere, the temperature range selected has been 300–700 °C ([Fig. 1](#)), since under this atmosphere the nicotine is not as stable as in He. In this case intervals of 100 °C have been considered. At temperatures as low as 300 °C the nicotine suffers important reactions and the chromatogram obtained shows a number of peaks of significant relative intensity at retention times longer than that of the nicotine. Again, as the temperature increases the nicotine undergoes increasing reactions, and at 700 °C almost no nicotine is detected. Thermal decomposition occurs at lower temperatures under air atmosphere, nicotine being completely decomposed at temperatures where its decomposition under He atmosphere is hardly starting. Under air,

Table 1
Main compounds of nicotine and nicotine in the presence of the three catalysts used decomposition under inert and oxidative atmosphere at different temperatures (°C).

Inert Atmosphere	Nicotine						N + SBA-15 f						N + SBA-15p						N + MCM-41						
	650	700	750	800	850	900	650	700	750	800	850	900	650	700	750	800	850	900	650	700	750	800	850	900	
Compound	650	700	750	800	850	900	650	700	750	800	850	900	650	700	750	800	850	900	650	700	750	800	850	900	
Ethylene	0.1	-	0.2	1.4	3.6	4.1	-	-	0.2	0.7	2.1	3.9	-	-	0.1	0.8	1.5	2.8	-	-	0.1	0.9	2.0	3.4	
Hydrogen cyanide	-	-	-	-	-	1.4	-	-	-	-	-	2.4	-	-	-	-	-	1.1	-	-	-	-	-	0.7	
Pyridine	-	0.1	0.2	0.7	1.8	3.5	0.1	0.2	0.3	0.9	2.1	4.0	0.3	0.9	1.4	1.9	3.6	6.4	0.8	1.6	1.2	2.0	3.5	5.8	
3-methyl pyridine	-	-	0.1	0.3	1.4	3.0	-	-	0.3	0.6	1.9	3.4	0.6	1.2	1.7	1.3	2.1	5.3	2.3	2.6	2.1	2.2	2.8	3.4	
3-ethyl pyridine	-	-	0.2	0.8	3.0	6.0	-	0.1	0.2	1.2	3.5	6.0	0.1	0.4	0.7	0.9	2.7	5.2	0.8	1.0	0.8	1.0	2.9	5.5	
3-vinyl pyridine	0.2	1.6	3.8	9.0	17.8	23.7	0.8	1.6	4.0	10.6	18.7	23.8	2.7	3.2	4.6	7.8	13.6	17.9	2.7	3.0	3.3	7.4	13.9	17.8	
3-cyano pyridine	-	-	0.1	0.6	2.0	3.9	-	-	0.1	0.7	2.1	3.7	-	-	0.1	0.3	1.2	2.2	-	-	0.1	0.3	1.2	2.2	
Indolizine	-	-	0.6	2.1	4.5	1.2	-	0.2	-	0.4	0.8	1.2	-	-	0.4	0.7	0.3	0.2	0.6	0.5	0.3	-	-	1.5	
Quinolone	-	-	-	-	0.5	1.0	-	-	0.2	0.3	0.8	1.4	0.8	1.7	2.5	3.1	3.5	5.8	2.3	4.3	2.5	3.4	4.3	7.2	
isoquinoline	-	-	-	0.1	0.2	0.4	-	-	0.1	0.2	0.3	0.5	0.1	0.8	1.3	1.6	1.8	3.0	1.9	2.0	1.6	1.8	2.3	3.5	
1 H-pyrrolo[2,3-b]pyridine	-	-	0.5	1.4	3.4	3.5	-	-	-	0.1	1.0	2.4	-	-	-	-	0.6	1.8	-	-	-	0.1	0.6	2.1	
Nicotine	93.4	90.3	82.4	63	28.8	6.7	89.2	87.7	82.6	60.1	26.6	5.1	69.4	66.8	60.5	55.3	28.0	5.0	69.9	62.6	67.6	54.7	29.4	6.0	
Myosmine	2.8	3.8	5.8	10.2	12.4	8.6	2.5	4.0	5.3	11.1	12.8	7.8	4.5	4.9	5.6	7.7	11.5	6.1	1.8	2.9	3.9	7.8	9.8	6.7	
Nicotyrine	0.4	0.7	0.6	0.5	0.4	-	1.7	1.3	0.5	0.4	0.5	0.2	2.2	2.1	1.8	1.0	0.8	0.7	2.3	2.0	1.5	1.0	0.7	0.3	
Nornicotyrine	-	0.1	0.5	1.1	3.7	5.9	-	-	0.2	1.5	4.2	6.0	0.2	0.4	0.8	0.7	2.9	4.6	-	-	0.4	0.6	2.2	3.0	
Cotinine	2.2	1.9	1.8	1.8	1.3	1.0	2.6	2.0	1.8	1.8	1.4	0.8	1.6	1.4	1.1	1.7	1.6	0.7	1.1	1.0	1.2	1.5	1.3	0.7	
Air Atmosphere	Nicotine						N + SBA-15 f						N + SBA-15p						N + MCM-41						
Compound	300	400	500	600	700	300	400	500	600	700	300	400	500	600	700	300	400	500	600	700	300	400	500	600	700
Carbon dioxide	0.3	0.5	1.4	2.8	9.7	0.1	0.4	1.2	4.1	7.8	0.2	0.6	1.4	2.6	5.0	-	0.1	1.9	3.0	6.8	-	-	-	-	
Hydrogen cyanide	-	-	-	0.2	3.8	0.6	-	-	0.2	1.7	-	-	-	0.2	2.0	-	-	-	0.4	0.8	-	-	-	-	
Water	0.3	0.7	1.5	3.6	10.3	0.6	1.7	2.2	8.5	17.1	8	8.7	4.9	10.6	15.1	5.9	10.0	10.0	13.7	21.2	-	-	-	-	
Pyridine	-	-	0.2	0.5	2.4	-	-	0.2	1.4	1.7	-	0.1	0.7	1.7	2.1	-	0.3	0.8	1.4	1.8	-	-	-	-	
3-vinyl pyridine	-	-	1.2	8.6	7.2	-	-	1.1	5.6	10.4	-	-	0.8	5.0	11.3	-	0.3	1.2	5.7	11.8	-	-	-	-	
3-cyano pyridine	-	0.2	1.5	7.0	22.0	0.1	0.1	1.2	4.9	13.9	2.1	0.5	2.1	2.9	14.4	2	1.2	2.0	3.4	7.1	-	-	-	-	
3-hydroxi pyridine	-	-	0.5	1.3	4.0	-	-	0.1	0.6	1.0	-	-	0.1	0.3	1.7	-	-	-	0.3	0.3	-	-	-	-	
Nicotine	89.3	68.5	39.6	8.8	-	81.7	70.6	40.2	7.5	0.8	76.4	59.3	29.8	15.3	0.6	75.1	37.9	29.2	14.0	1.0	-	-	-	-	
N-methylmyosmine	1.2	1.8	0.5	-	-	3.1	2.2	0.8	-	-	2	1.8	0.4	-	-	1	0.8	0.4	-	-	-	-	-	-	
1 H-pyrrolo[2,3-c]pyridine	0.3	3.9	7.2	3.2	-	2.5	2.3	4.6	1.2	-	1.8	1.6	1.2	1.3	-	1.7	2.3	2.1	1.6	-	-	-	-		
Myosmine	3.4	8.1	11.8	12.3	2.3	5	6.5	10.9	11.4	4.7	2.1	5.7	10.3	12.1	5.4	4.2	9.3	8.5	9.2	7.4	-	-	-		
Nicotyrine	1.3	6.3	13.3	16.8	4.2	1.9	5.5	15.2	22.9	8.5	1.8	6.3	14.5	15	7.9	5.2	16.8	16.4	14.5	10.3	-	-	-		
3-(2,5-dimethyl-1 H-pyrrol-1-yl) pyridine	-	0.5	0.5	0.4	-	1.6	2.4	4.5	4.7	0.7	2.1	4.8	8.0	5.5	1.0	3.1	5.8	5.7	4.2	1.2	-	-	-		
Nornicotyrine	-	0.6	3.0	6.9	3.1	-	0.3	2.3	5.8	5.0	-	0.3	2.5	5.4	6.0	-	1.5	2.8	4.8	5.2	-	-	-	-	
Cotinine	3.2	2.8	2.2	1.3	0.1	2	2.1	2.0	1.0	0.4	0.1	1.1	1.3	1.0	0.2	0.1	0.4	0.9	0.6	0.4	-	-	-		

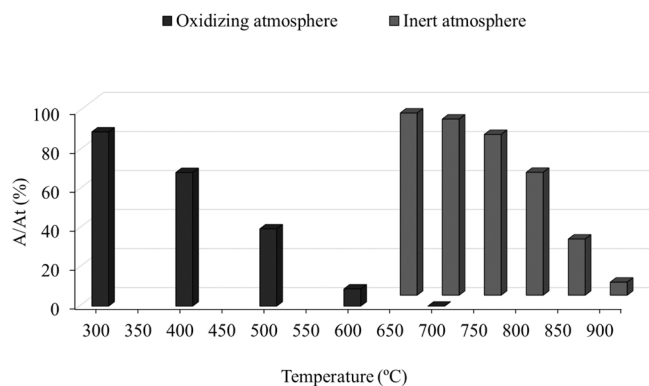


Fig. 1. Evolution of nicotine vs temperature under inert and oxidizing atmosphere.

nicotine represents 89.3% of the chromatogram at 300 °C whereas at 700 °C is almost undetected. Contrarily, under He atmosphere at 700 °C nicotine represents 90.3% of the chromatogram and at 900 °C (the maximum operating temperature of the equipment used), it still represents a 6.7% (Table 1).

Jarobe and Rosene [6] reported eighteen compounds when studying the pyrolysis of nicotine in He atmosphere in a temperature range similar to that in the present study. They used a sample size of 50 g. Eleven of those eighteen compounds have been also detected with in the present work (i.e.: pyridine, 3-methylpyridine, 3-ethyl pyridine, 3-vinyl pyridine, 3-cyano pyridine, 2-cyano pyridine, quinoline, isoquinoline, nornicotirine, myosmine, and 1 H-pyrrolo[2,3-*b*]pyridine). Baker and Bishop [10] reported the presence of nicotyrine, myosmine and cotinine in addition to nicotine in their studies of nicotine pyrolysis under inert atmosphere. These authors published a list of fifteen compounds and functional groups obtained in the slow pyrolysis of nicotine at 600 °C [31]. The list included products as myosmine, quinoline and isoquinoline, in addition to the vinyl pyridines, monomethyl pyridines also detected in the present work, though many of the compounds reported in the paper by Baker and Bishop [10] at 600 °C appear at higher temperatures in the present work, probably as a consequence of the different heating conditions.

Fig. 2 shows the main decomposition products from nicotine and possible routes of formation.

- Medana et al. [32] suggested a mechanism where 3-vinyl pyridine can be formed in nicotine pyrolysis through the initial formation of cotinine and a further loss of the pyrrolidone ring.
- 3-cyano pyridine is mainly obtained under air atmosphere. Kagarlitskii et al. [33] studied the conversion of nicotine to this compound through an oxidative aminolysis at temperatures between 380 y 460 °C, where nicotine transformed into 3-cyano pyridine, pyridine,

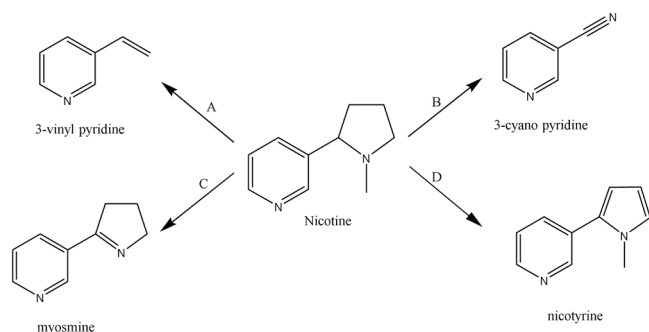


Fig. 2. Main decomposition products from nicotine pyrolysis and possible routes of formation.

ammonium cyanide, CO and CO₂. Lin et al. [24] suggested a mechanism involving myosmine and the loss of ethane.

- Myosmine is the second major compound under inert atmosphere and the third in air. Woodward et al. [5] reported the formation of this compound and nicotyrine, as well as hydrogen cyanide, ammonia and methyl, alkyl and vinyl pyridines when studied the pyrolysis of nicotine at 500 °C. Myosmine can be formed through the nicotine dehydrogenation to N-methyl myosmine, followed by its demethylation.
- Nicotyrine is the second major compound in air and is not very significant under inert atmosphere. Lin et al. [24] propose the conversion of nicotine to nicotirine through the dehydrogenation of the pyrrole ring. Kisaki et al. [34] suggested the formation of nicotirine in air atmosphere by the formation of pseudooxynicotine followed by the loss of water and cyclation to yield N-methylmyosmine that is decomposed to nicotyrine and N-methylnicotinamide.

In this work the major compounds detected in the pyrolysis of nicotine under inert atmosphere were ethylene, pyridine, 3-methyl pyridine, 3-ethyl pyridine, 3-vinyl pyridine, 3-cyano pyridine, indolizine, quinolone, isoquinoline, 1 H-pyrrolo[2,3-*b*]pyridine, myosmine, nicotyrine, nornicotirine and cotinine (Table 1). At 650 °C nicotine represents 93.4% of the total area, myosmine and cotinine (2.8% and 2.2% respectively) are obtained in significant, but much smaller, amounts. When the temperature increases more compounds are generated as a consequence of the nicotine reactions. At 800 °C nicotine decreases to a 63% whereas myosmine is the main degradation product, reaching a 10.2% of the total area. Most compounds increase their contribution as increasing the temperature, except nicotyrine and cotinine that decrease their contribution. At 850 °C, nicotine is only 28.8% and 3-vinyl pyridine is the main decomposition product [6,30]. At 900 °C 3-vinyl pyridine is still markedly growing up to 23.7% of the area (Table 1).

Under air atmosphere the principal compounds detected were carbon dioxide, water, pyridine, 3-vinyl pyridine, 3-cyano pyridine, 3-hydroxy pyridine, 1 H-pyrrolo[2,3-*c*]pyridine, myosmine, nicotyrine, 3-(2,5-dimethyl-1 H-pyrrol-1-yl)pyridine, nornicotirine and cotinine (Table 1). At 500 °C nicotine represents less than 50% of the area (39.6%) and at 600 °C decreases below 10% (8.8%). Myosmine and nicotyrine increase their contribution with the temperature reaching a maximum at 600 °C (12.3% y 16.8% respectively). Contrarily, cotinine reduces its contribution as temperature increases, as observed in inert atmosphere. Finally, at 700 °C, nicotine has been completely degraded and 3-cyano pyridine reaches 22%, water 10.3%, carbon dioxide 9.7% are the major compounds. On another hand, myosmine, nicotyrine and nornicotirine show their maximum contribution at 600 °C, indicating that these compounds are not favored at this high temperature of may undergo secondary reactions.

It can be concluded that the nicotine is more stable under inert than under air atmosphere. Several compounds are common under both atmospheres such as pyridine, 3-vinyl pyridine, 3-cyano pyridine, myosmine, nicotyrine, nornicotirine and cotinine. Pyridine, myosmine, nornicotirine and cotinine show similar contributions and trends in both atmospheres. 3-vinyl pyridine and 3-cyano pyridine show similar trends with temperature in both atmospheres, nevertheless their contributions are opposite, being 3-vinyl pyridine the major compound under inert atmosphere and 3-cyano pyridine the major compound under air atmosphere. Nicotyrine presents very low contributions under inert atmospheres but is the main decomposition product at 500 and 600 °C in air. The case of HCN should be mentioned, which shows a significant presence at high temperatures under oxidizing conditions (Table 1).

3.2. Catalytic pyrolysis of nicotine

In a previous work [27] we studied the effect of three catalysts, two

SBA-15 of different morphology and a MCM-41, in the slow pyrolysis in TG-FTIR of nicotine. We have found almost no references in literature on the effect of temperature on the catalytic fast pyrolysis of nicotine under inert and oxidizing atmosphere as well as on the products obtained. In this part we report and discuss the results obtained when pyrolyzing nicotine mixed with these catalysts.

3.3. Catalytic pyrolysis under inert atmosphere

Fig. 3 shows the nicotine area percentage as a function of temperature for the sole nicotine and the catalytic experiments in He atmosphere.

Similar decreasing trend that nicotine as function of the temperature is observed for all the materials. Moreover, the presence of MCM-41 and SBA-15p between 650 and 750 °C provokes a marked pyrolysis of nicotine, and at high temperatures only little effect on nicotine pyrolysis can be observed for all the catalysts. SBA-15 shows small reductions between 650 and 700 °C, but at high temperatures it shows a similar behavior to the other materials.

Different trends can be observed, though the main trend is an increase of the yields with increasing temperatures (Table 1). Nicotine and nicotyrine show a decreasing trend with temperature, whereas cotinine and myosmine show a maximum with temperature at 800 and 850 °C respectively. SBA-15 f shows little effect when compared with the sole nicotine pyrolysis (Table 1) showing a slight decrease in the yields of indolizine. SBA-15p shows larger differences, 3-vinyl pyridine is highly reduced, mainly at the highest temperatures, though remains as the major product. Similarly, indolizine and ethylene reduce their yields. Pyridine increases as compared with sole nicotine pyrolysis, as well as quinoline and isoquinoline, products almost not present in absence of catalyst at temperatures minor than 800 °C. MCM-41 has a similar effect as SBA-15p, showing better reductions than SBA-15 f.

Ye et al. [35] studied the catalytic flash pyrolysis of nicotine at low temperatures (250–500 °C). They used Pd supported on activated carbon and SBA-15 similar to the SBA-15 f used in the present work. They observed the almost complete conversion of nicotine into nicotyrine. We have observed a slight increase in the nicotyrine formation when using MCM-41 higher than that observed when using SBA-15 f. The presence of Pd must be the responsible of the lower stability of the nicotine that decomposed at much lower temperatures in the work of Ye et al.

3.4. Catalytic pyrolysis under oxidizing atmosphere

The effects of the materials observed are similar to those reported under inert atmosphere. Again SBA-15p and MCM-41 present more marked effects.

Fig. 4 shows the nicotine % area for pure nicotine and for the

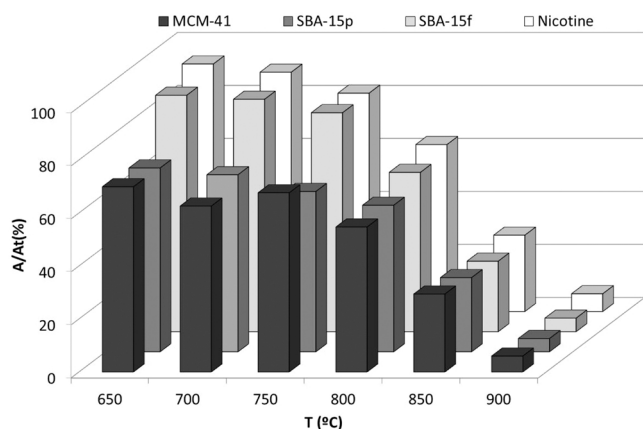


Fig. 3. Evolution of nicotine and nicotine with three catalysts under inert atmosphere.

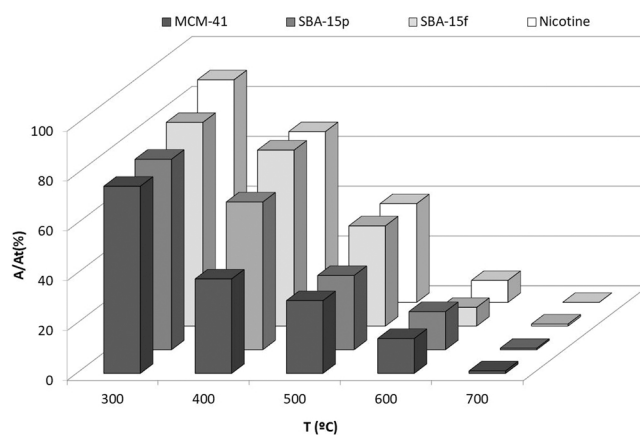


Fig. 4. Evolution of nicotine and nicotine with three catalysts under air atmosphere.

pyrolysis of nicotine with the three catalysts considered as a function of temperature in air atmosphere.

As can be seen, at 300 °C all materials present similar reductions in the Nicotine, moreover at 400 °C an important effect of MCM-41 can be observed. SBA-15 f is the catalyst that produced less modification on the pyrolysis of nicotine. SBA-15p reduces the nicotine % area from 68.5% to 59.3% at 400 °C and from 39.6% to 29.8% at 500 °C, whereas MCM-41 presents a similar effect at 500 °C, reducing the nicotine contribution to 37.9%. At 600 °C both catalysts present higher yields of nicotine, while at 700 °C all materials still show a small amount of nicotine, that Nicotine sample. Similar effects were observed by Marcilla et al. [27] when studied this catalysts in air atmosphere in TG.

The larger surface area of SBA-15p and its morphology, more similar to MCM-41 than to that of SBA-15 f, make the porosity of these two materials more accessible to nicotine than that of the SBA-15 f, and may be responsible of the higher effect observed in both atmospheres.

The three materials provoke an increase in water yield at the four temperatures studied, reaching at 700 °C 17.1% with SBA-15 f, 15.1% with SBA-15p and 21.2% with MCM-41, as compared with 10.3% when pyrolyzing nicotine without catalyst. Water is the major compound at 700 °C. The three catalysts increase the yield of 3-(2,5-dimethyl-1 H-pyrrole-1-yl)pyridine, compound that is almost not obtained in absence of catalyst. At 700 °C, the three catalysts reduce the yield of 3-cyano pyridine that is the major compound in absence of catalyst at 700 °C. Especially remarkable is the decrease in the yield of HCN that passes from a 3.8% in absence of catalyst to 1.8% when using SBA-15 f, 2% with SBA-15p and 0.8% with MCM-41.

SBA-15 f produces a marked increase in nicotyrine a temperatures higher than 500 °C, being the major compound at 600 °C and representing 22.9% of the total area. MCM-41 favors the formation of nicotyrine at low temperatures and decreases when increasing temperature.

Most compounds present an increasing trend with temperature, as water, CO₂ and 3-cyano pyridine. Nicotine and cotinine present a decreasing trend whereas myosmine, nicotyrine, 3-(2,5-dimethyl-1 H-pyrrole-1-yl)pyridine and nornicotyrine present a maximum.

The toxicity of the compounds present in tobacco smoke has been widely studied [36–41]. The effect of the catalysts used has been analysed from this point of view considering the evolution of the compounds generated that appear in the lists of toxic compounds in tobacco smoke. Table 2 shows the effect of the different catalysts on the toxic compounds (i.e.: those appearing in the Hofmann lists of toxic compounds in tobacco smoke [42]) product of the pyrolysis of nicotine. (↑) indicates an increase in the yield as compared to that obtained for sole nicotine and (↓) the contrary case. (–) indicates no change.

HCN, one of the most toxic compounds is reduced by the three

Table 2

Toxic compounds presents in the vapor phase gas generated in the pyrolysis of nicotine under both atmospheres.

Peak	Compound	SBA-15 f		SBA-15p		MCM-41	
		He	air	He	air	He	air
3	HCN	↑	↓	↓	↓	↓	↓
4	Methyl amine	-	-	↑	-	-	-
7	acetaldehyde	-	↑	-	↓	-	↓
8	2-propenal	-	↓	-	↓	-	↓
9	Acetone	-	↑	-	↑	-	↑
10	Acetonitrile	↑	↓	↑	↓	↑	↓
11	2-propennitrile	-	↓	-	↓	-	↓
14	pyridine	↑	↓	↑	↓	↑	↓
16	3-methyl pyridine	↑	↑	↑	↑	↑	↑
19	3-vinyl pyridine	↑	↑	↓	↓	↓	↓
33	quinoline	↑	↑	↑	↑	↑	↑

catalysts, except when using SBA-15 f in He atmosphere. 2-propenal and 2-propen nitrile only was reduced in air atmosphere by the three catalysts, whereas acetone presents the opposite effect. Acetonitrile and pyridine are increased in He atmosphere by all catalysts, whereas are reduced in air atmosphere. SBA-15p and MCM-41 materials reduce the presence of 3-vinyl pyridine in He atmosphere, whereas in air the three materials increase its yield.

The three materials reduce the yield of the toxic compounds in air atmosphere, especially MCM-41 and SBA-15p.

4. Conclusions

Thermal decomposition of nicotine occurs at lower temperatures under oxidizing atmosphere than under inert atmosphere yielding a marked different product distribution highly affected by temperature. The main degradation compounds under inert atmosphere are 3-vinyl pyridine, myosmine and nornicotyrine, while 3-cyano pyridine, myosmine and nicotyrine are the main compounds under oxidizing atmosphere. CO₂ and H₂O are obtained in high yields at high temperatures under oxidizing atmosphere. Compounds such as 3-vinylpyridine, nornicotyrine and 3-cyano pyridine show increasing trends with temperature while myosmine and nicotyrine show a maximum in their evolution.

The presence of catalysts modifies the degradation of nicotine as a function of the catalysis and adsorption processes. All of three catalysts promote the decomposition of nicotine at lower temperatures and generate changes in the degradation product distribution. This effect is more remarkable under inert atmosphere. MCM-41 shows the major modifications and SBA-15 with fiber like morphology the lowest. Also, under oxidizing atmosphere the presence of catalysts favors the formation of CO₂ y H₂O favouring the catalytic decomposition of the starting compound.

A direct relationship can be observed between the textural properties of the mesoporous silicates used and their effect on the catalytic degradation of nicotine. A greater modification of the catalytic degradation of nicotine is observed when using silicates with higher surface area (as is the case of MCM-41 and SBA-15p as compared to the SBA-15 f) and a more accessible porous structure (again, the case of MCM-41, and the laminar morphology of the SBA-15p as compared to the fiber like morphology of the SBA-15 f).

It has been shown that nicotine, in addition to being the main addictive component of tobacco smoke, generates in its thermal degradation, both under inert and oxidizing atmospheres (both conditions present in the smoking process), highly toxic compounds such as HCN, acetaldehyde and others. The catalysts studied are capable of reducing the emission of most toxic compounds. All these aspects are of great interest when considering the use of catalysts in order to reduce the toxicity of tobacco smoke.

CRedit authorship contribution statement

Javier Asensio: Visualization, Methodology, Investigation, Validation, Data curation, Writing – original draft. **Deseada Berenguer:** Data curation, Writing – review & editing. **Antonio Marcilla:** Conceptualization, Methodology, Supervision, Project administration, Writing – review & editing. **Ma Isabel Beltran:** Conceptualization, Methodology, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jaap.2023.105899](https://doi.org/10.1016/j.jaap.2023.105899).

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