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(54) **ALUMINOSILICATE SAB-15 AS AN ADDITIVE FOR REDUCING THE TOXIC AND CARCINOGENIC COMPOUNDS PRESENT IN TOBACCO SMOKE**

(57) The invention relates to the use of the aluminosilicate SAB-15, or the acidic or sodic forms thereof, interchanged with Fe, Na, K, Ca, Ce, Zr, the oxides of Fe, Na, K, Ca, Ce, Zr, and mixtures of same as an additive for reducing the toxic and carcinogenic substances present in tobacco smoke.

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DescriptionField of the Invention

- 5 **[0001]** The present invention relates to the use of aluminosilicates, particularly SAB-15, as an additive for reducing the toxic and carcinogenic compounds present in tobacco smoke.

State of the Art

- 10 **[0002]** The habit of smoking tobacco has been and is a global problem with very negative consequences on human health. Its impact on the departments or ministries of public health is of great importance. More than 4000 different compounds have been identified in tobacco and in the smoke generated when burning same [R.R. Baker, Progress in Energy and Combustion Science, 32 (2006), 373], among which at least 60 are recognized as toxic and carcinogenic. These compounds include tars, carbon monoxide and dioxide, acetaldehyde, phenols, acetone, formaldehyde, benzene, 15 toluene and nicotine. Nicotine is the main addictive component present in tobacco, and in the human body it is converted into a metabolite called cotinine and is used as a reference index for measuring the degree of exposure to tobacco smoke.
- [0003]** The process of smoking a cigarette generates the occurrence of two types of smoke streams, the so-called mainstream and sidestream. The mainstream corresponds to smoke which is generated when burning the tobacco and goes through the cigarette from the lit end to leave through the filter end.
- 20 **[0004]** Patent document EP2092838 describes the use of certain zeolites and other aluminosilicates and mesoporous solids, in different forms and with various compositions, adding them and mixing them directly with tobacco in the form of powder, without having to use any type of special technology or adhesive, as tobacco additives for drastically reducing the amount of toxic and/or carcinogenic compounds that are generated when smoking and are found in the mainstream and sidestream of tobacco smoke.
- 25 **[0005]** Patent application US2005133052 describes the use of mesoporous aluminosilicate molecular sieves modified with aminoalkylsilyl groups in filters for retaining specific compounds.
- [0006]** Patent application US20050133051 proposes the use of filters containing materials formed by a porous alumina or aluminosilicate matrix containing adsorbent activated carbon and zeolite particles for selectively removing specific compounds from tobacco smoke.
- 30 **[0007]** Patent application WO 2004110183 A2 describes filters containing a catalyst dispersed in a porous aluminosilicate matrix, for the purpose of converting the CO in cigarette smoke into CO₂.
- [0008]** Patent application WO 2004086888 describes a filter including at least 2 porous monolithic adsorbent segments that are capable of selectively removing components from the smoke stream, and a mixing segment between both.
- [0009]** Patent application CN 102242527 proposes the use of a cigarette paper containing a microencapsulated adsorbent which allows reducing the content of toxic substances in tobacco smoke. The different adsorbent materials used include, among others, one or more oxides of Cu, Mn, Zn, Fe, Al, Ti, etc., as well as composite materials where the oxides are supported by zeolites, MCM-48, or SBA-15.
- 35 **[0010]** Zhu *et al.* [Zhou, F.N. Gu, L. Gao, J.Y. Yang, W.G. Lin, J., Yang, Y., Wang, J. H. Zhu, Catalysis Today, 166(1), (2011), 39 and Zhou, Gao, Gu, Yang, Yang, Wei, Wang and Zhu, Weinheiman der Bergstrasse, Germany, 15(27), (2009), 6748] have described the use of SBA-15 for selectively reducing the concentration of tobacco-specific nitrosamines (TSNA) in tobacco smoke; however, this article focuses on the synthesis, characterization, adsorption and catalytic activity of SBA-15 and examines a new pathway which allows increasing the efficiency thereof as adsorbents/catalysts with environmental applications through morphology control.
- 40 **[0011]** Patent application WO 2011015861 proposes the use of a filter containing an adsorbent material which is capable of removing phenol from tobacco smoke. The material is formed by a porous solid (with micro- or mesopores) containing an adsorption promoter which is a hydrophilic organic proton donor or acceptor substance.
- [0012]** Patent application CN 101433818 claims the use of a mesoporous material consisting of SBA-15 for adsorbing particulate matter, tar, phenol and nitrosamines in mainstream tobacco smoke.
- [0013]** Patent applications US2006130855-A1 and US2005133047-A1 explicitly mention the possibility of using SBA-15-based substrates.
- 50 **[0014]** The results described in patent document EP0740907 for generating tars or nicotine when using the acidic and sodium forms of zeolite BETA clearly show the minimum differences with respect to the reference cigarette smoked without an additive.
- [0015]** Different types of equipment that facilitate and can even improve incorporating the additive to fine-cut tobacco, such as for example, speed mixers or orbital mixers, fluidized beds and entrained beds, among others, as well as sieves for separating and recirculating the additive that did not attach onto tobacco fibers, can be used for preparing cigarettes.
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Brief Description of the Invention

[0016] Therefore in a first aspect, the present invention relates to aluminosilicate SAB-15 or the acidic or sodium forms thereof, interchanged with Fe, Na, K, Ca, Ce, Zr, the oxides of Fe, Na, K, Ca, Ce, Zr and mixtures thereof as an additive for reducing the toxic and carcinogenic substances present in tobacco smoke, both in mainstream and sidestream tobacco smoke, particularly, toxic substances such as tars, carbon monoxide and nicotine, as well as the components of the liquids and gases generated when burning tobacco in the smoking process.

[0017] In a more particular aspect of the present invention, the aluminosilicate SAB-15 has a spherical morphological shape, tubular morphological shape or rod shape, or any other shape obtained by various synthesis processes and different degrees of acidity obtained by incorporating aluminum in its structure, in a pressurized autoclave that is under stirring or standing still and under reflux at different temperatures, and where it has been interchanged with the cations of metals: Fe, Na, K, Ca, Ce, Zr.

[0018] In a more particular aspect of the present invention, the aluminosilicate SAB-15 has a pore size comprised between 4-10 nm and a mesopore volume preferably greater than 2.2 cm³/g, although the mesopore volume can be less.

[0019] In a second aspect, the present invention relates to a mixture comprising dry tobacco and aluminosilicate SAB-15, or the acidic or sodium forms thereof, interchanged with Fe, Na, K, Ca, Ce, Zr, the oxides of Fe, Na, K, Ca, Ce, Zr and mixtures thereof as an additive and not comprising adhesive agents. Dry tobacco refers to a bright tobacco, dark tobacco, fine-cut tobacco, roll-your-own tobacco, pipe tobacco and any other type of tobacco that can be smoked.

[0020] In the present invention, agent adhesive refers to compounds with the capacity to bind or adhere to tobacco or substances incorporated therein, for example, guar gum, alginates or other compounds having similar characteristics.

[0021] In a more particular aspect of the present invention, the additive is at a concentration comprised between 0.5-10% by weight with respect to the dry tobacco, in another more particular aspect, the additive is at a concentration comprised between 2-7% by weight with respect to the dry tobacco.

Brief Description of the Drawings[0022]

Figure 1 shows the SEM image of a fibrous SBA-15 (A) and a spherical SBA-15 (B).

Figure 2 shows the N₂ adsorption isotherms obtained for SBA-15 materials synthesized in different ways.

Detailed Description of Embodiments and ExampleExample 1: Method for synthesizing the different materials

[0023] The SBA-15 was synthesized according to the following method: a pluronic P 123 solution in acidic medium was first prepared to which an amount of tetraethyl orthosilicate (TEOS) was added. The resulting solution was aged under stirring at 38°C for 20 hours. It was then transferred to an autoclave with a Teflon liner and kept at 100°C for 24 hours. The resulting suspension was washed with water, dried overnight at 100°C and finally burned at 550°C for 5 hours (F. Zhang, Y. Yan, H. Yang, Y. Meng, C. Yu, B. Tu, D. Zhao, Journal of Physical Chemistry B, 109 (18), (2005), 8723).

[0024] The SBA-15_{spherical} was obtained under the following conditions. An amount of pluronic P 123 was dissolved in HCl. A second suspension with CTABr and water was prepared and added to the first suspension. A small amount of ethanol was then added, followed by addition of TEOS. The resulting solution was aged at 35°C for 45 minutes. It was then transferred to an autoclave with a Teflon liner at 75°C for several hours and finally treated at 105°C. The resulting suspension was washed with water, dried overnight at 100°C and finally burned at 550°C, (A. Katiyar, S. Yadav, PG. Smiriotis, NG. Pinto, Journal of Chromatography A, 1122 (1-2), (2006), 13).

[0025] The SBA-15_{reflux} material was obtained under conditions similar to SBA-15, but a flask containing the obtained suspension connected to a reflux condenser at 100°C was used in the final step. The resulting solid was washed with water, dried overnight at 100°C and finally burned at 550°C.

[0026] The SBA-15 material at 125°C was prepared similarly to SBA-15 but modifying the temperature at which it is kept throughout the final temperature of the process, 125°C instead of 100°C.

[0027] The AISBA-15 material was prepared by means of a gel having a molar composition: 1 TEOS: 0.02 Al₂O₃: 0.016 P123: 0.46 HCl: 190 H₂O, according to the method described by Vinu A., Hartmann M., Devassy B.M., Halligudi S.B., Bohlmann W., Applied Catalysis A: General, 281, (2005), 207.

[0028] The Na-AISBA-15 material was prepared by means of ion exchange from the AISBA-15 material, in which 1 gram of material is stirred for 24 hours with a 1 M NaCl solution. The resulting material is filtered, washed with water and dried in an oven at 100°C.

[0029] The FeNa-AISBA-15 material was prepared by means of ion exchange from the Na-AISBA-15 material, in

which in 1 liter of distilled water with 1.26 g of $\text{Fe}(\text{NO}_3)_9\text{H}_2\text{O}$ and 4.5 g of Na-AISBA-15 is added. The resulting solution is stirred for 24 hours and then filtered, washed with water and dried in an oven at 100°C.

[0030] Table 1 shows the chemical and structural characteristics of some of the additives that are studied in this application as representative examples of such materials, corresponding to SBA-15 samples prepared under different synthesis conditions or subjected to post-synthesis modifications. Figure 2 shows the corresponding N_2 adsorption isotherms at 77 K.

Table 1. Textural properties of some of the additives (^aBJH; ^bBET method, N_2 adsorption isotherms; ^ct method, N_2 adsorption isotherms; ^dmeasured at $P/P_0=0.995$, N_2 adsorption isotherms; ^eXRF). The nomenclature refers to SBA-15 materials prepared with different synthesis conditions or subjected to post-synthesis modifications.

PROPERTY	SBA	SBA _{spherical}	SBA _{reflux}	Na-Al-SBA (autoclave)
Pore size (nm) ^a	6.12	6.07	6.39	6.14
BET area (m ² /g) ^b	680.5	847.8	1066	915.9
Outer surface area (m ² /g) ^c	536.3	847.8	668.2	915.9
Pore volume (cm ³ /g) ^d	0.91	1.06	1.24	0.84

[0031] For the purpose of demonstrating the role of the additives proposed in this invention, the following cigarettes were smoked:

- reference commercial cigarettes 3R4F from the University of Kentucky and
- cigarettes to which the additives were incorporated, using a smoking machine that worked according to the following operation variables:

The cigarette smoking conditions and the analysis of the generated products are provided in detail below:

- Fifteen cigarettes were smoked following the specifications of the ISO 3308 standard (2-second drags, 35 mL inhaled volume, 60-second drag frequency and a drag pressure loss of less than 300 Pa).
- The cigarettes were conditioned at room temperature and 60% relative humidity, keeping them in a dryer provided with a saturated sodium nitrite solution at least for 48 hours before being smoked.
- During the smoking process, the smoke, including CO , CO_2 and other non-condensable products went through the cigarette filter as well as a trap (glass fiber filter) located before the gas collection bag. The non-condensable products were collected in a Tedlar gas bag which was kept for subsequent analysis by gas chromatography (GC) and the condensable products were collected in the cigarette filter and in the trap that follows, in which the condensable products directly inhaled by smokers were retained.
- The condensable products retained in the trap located before the filter were extracted with 2-propanol, assuring that all the compounds retained in the trap are recovered. The extract is then dried with sodium sulfate and kept for subsequent analysis by GC.
- The CO and CO_2 content in the non-condensable fraction was determined by GC using a thermal conductivity detector (GC-TCD) and a CTRI concentric column, which was also used for analyzing O_2 , N_2 and CH_4 , in SHIMADZU GC-14A equipment, using calibration by means of external standards. Quantification was performed by calculating the response factor (grams of compound/peak area) of these compounds by means of injecting different volumes (between 0.5 and 2.5 mL) of the corresponding standard (carbon monoxide, carbon dioxide, hydrogen, methane and oxygen).
- The analysis conditions were:

Carrier gas: He
 Injector temperature: 28°C
 Detector temperature: 110°C
 Injected volume: 2.5 mL
 Constant column flow: 40 mL/min
 Oven temperature program: isotherm at 110°C
 Analysis time 20 minutes

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- The rest of the non-condensable components were analyzed by GC with a flame ionization detector (GC-FID), using a GAS-PRO column and the following conditions:

Injector temperature: 150°C
Detector temperature: 210°C
Carrier gas: Helium
Injected sample volume: 150 µL
Constant column flow: 2 mL/min
Oven temperature program:

Initial column temperature 35°C for 10 min
Heating to 100°C with a ramp of 5°C/min
Heating to 200°C with a ramp of 15°C/min
Final time: 10 minutes

- The condensable compounds (extracted with 2-propanol from the cigarette filters and the smoke traps) were analyzed by GC with a detector using mass spectrometry (GC-MS), using an HP-5MS column and the following conditions:

Injector temperature: 250°C
Carrier gas: Helium
Injected sample volume: 1 µL
Constant column flow: 2 mL/min
Oven temperature program:

Initial column temperature 40°C for 5 min
Heating to 320°C with a ramp of 12°C/min
Final Time: 25 minutes

[0032] Nicotine standards of different concentrations (between 5 and 300 ppm) were prepared for quantifying the compounds present in the condensed phase of tobacco smoke. They were injected in the equipment and the value of the corresponding response factor was obtained from the slope of the straight line obtained from the graphs representing the amount of injected compound vs. peak area. The response factor obtained for nicotine was used for the rest of the analyzed compounds since nicotine was the main compound. Quantification was carried out in a similar manner for the gases, in which a mean response factor was used in the cases in which the corresponding response factor was not available.

Cigarette preparation conditions

[0033] To carry out all the tests, cigarettes in which tobacco fibers were mixed by hand with the catalyst were prepared, aided by a few drops of ethanol. This operation was performed on a sieve which allowed separating the catalyst that did not adhere to the tobacco, such that a percentage of catalyst was obtained in the nominal mixtures, corresponding to the amount of initially weighed catalyst, and another real percentage, which was that retained by the sample. Agents other than ethanol which can be used to aid in the process of mixing the tobacco and catalysts are water, glycerin and other similar compounds, commonly present in tobacco preparations and evaporate with relative ease. Nevertheless, mixing can also be satisfactorily performed without having to use any of these substances.

[0034] The characteristics corresponding to some examples which allow illustrating the results that can be achieved with the use of the proposed additives are shown below. The nominal percentage of each type of additive is indicated. The tobacco used, both in the reference cigarettes and in the different mixtures with the additives, was always the reference tobacco 3R4F obtained from the University of Kentucky.

Tobacco-additive mixtures for the conducted tests

[0035] A nominal percentage of 4-6% by weight of additive is used in all the cases. The cigarettes were prepared using the method described in "cigarette preparation conditions" and using the additives indicated below. Table 2 shows the mixtures made in the different tests conducted.

Table 2: tobacco mixtures

Mixtures
3R4F+SBA-15 (4%)
3R4F+SBA-15 (6%)
3R4F+SBA-15 (8%)
3R4F+SBA-15 _{spherical}
3R4F+Na-SBA-15
3R4F+FeNa-SBA
3R4F+AISBA-15 (autoclave)
3R4F+Na-AISBA-15 (autoclave)
3R4F+SBA-15 _{spherical} (125°C)
3R4F+SBA-15 (reflux)

[0036] Tables 3, 4, 5 and 6 show the results obtained when smoking the cigarettes using the cigarette preparation conditions, the smoking conditions and the conditions for analyzing the generated products and the examples corresponding to different tobacco-additive mixtures. The values obtained for the following are shown:

- CO and CO₂, in mg of compound/cigarette
- the amount of some toxic products, in mg of compound/cigarette
- total particulate matter (TPM) in mg/cigarette, calculated as:

$$m_{TPM} = \frac{m_1 - m_0}{q}$$

where m_0 is the mass of the trap located before the filter, in mg, before smoking m_1 is the mass of the trap located before the filter, in mg, after smoking a number q of cigarettes.

Table 3. CO and CO₂ content in tobacco smoke generated under controlled conditions

Sample	CO ₂ (mg/cigarette)	CO (mg/cigarette)
3R4F	40.63	11.22
3R4F+SBA-15	29.85	10.89
3R4F+SBA-15 _{spherical}	31.95	9.02
3R4F+FeNa-SBA-15	37.00	11.45
3R4F+AISBA-15 (autoclave)	39.69	10.11
3R4F+SBA-15 _{spherical} (125°C)	36.97	9.55

Table 4. Number of drags and TPM obtained when smoking tobacco under controlled conditions

Sample	% zeolite	Drags	mg/cigarette	TPM (mg/cigarette)
3R4F	0.0	9	0.76	6.79
3R4F+SBA-15	3.8	9	0.76	2.34
3R4F+SBA-15 _{spherical}	6.3	8.5	0.68	3.07
3R4F+FeNa-SBA-15	3.9	9	0.78	2.91

(continued)

Sample	% zeolite	Drags	mg/cigarette	TPM (mg/cigarette)
3R4F+AISBA-15 (autoclave)	5.9	10	0.80	3.21
3R4F+SBA-15 _{spherical} (125°C)	5.8	8.5	0.77	2.44

Table 5. Generation (mg compound/cigarette) of different toxic compounds present in the gases collected in the Tedlar bag after smoking tobacco under controlled conditions

Sample	Propionaldehyde	Toluene	Benzene	Acetaldehyde
3R4F	0.0208	0.0178	0.0849	0.4214
3R4F+SBA-15	0.0152	0.0135	0.0655	0.2908
3R4F+SBA-15 _{spherical}	0.0118	0.0148	0.1944	1.2061
3R4F+FeNa-SBA-15	0.0203	0.0183	0.0836	0.5511
3R4F+AISBA-15 (autoclave)	0.0135	0.0101	0.0772	0.6541
3R4F+SBA-15 _{spherical} (125°C)	0.0128	0.0099	0.0874	0.4350

Sample	Nicotine	Benzaldehyde	Phenol	p-Cresol
3R4F	5.93E-01	2.93E-04	4.18E-03	5.55E-03
3R4F+SBA-15	3.59E-01	1.10E-04	1.98E-04	9.90E-04
3R4F+SBA-15 _{spherical}	2.33E-01	1.75E-04	3.80E-04	2.91E-04
3R4F+FeNa-SBA-15	1.98E-02	0.00E+00	3.00E-05	1.01E-04
3R4F+AISBA-15 (autoclave)	2.18E-02	0.00E+00	4.13E-05	1.13E-04
3R4F+SBA-15 _{spherical} (125°C)	2.38E-02	0.00E+00	5.40E-05	1.38E-04

Table 6. Generation (mg compound/cigarette) of different toxic compounds present in the condensable products retained in the trap located before the filter when smoking tobacco under controlled conditions

Sample	Hydroquinone	Myosmine	Cotinine
3R4F	1.03E-02	4.01E-03	5.06E-03
3R4F+SBA-15	4.02E-03	8.90E-04	2.82E-03
3R4F+SBA-15 _{spherical}	5.25E-03	1.13E-03	1.56E-03
3R4F+FeNa-SBA-15	1.23E-04	1.16E-04	1.81E-04
3R4F+AISBA-15 (autoclave)	2.84E-04	1.43E-04	1.84E-04
3R4F+SBA-15 _{spherical} (125°C)	3.02E-04	1.43E-04	1.82E-04

Table 6. Continued

[0037] Tables 3 to 6 clearly show that, generally, the proposed additives, mixed with tobacco in the described proportions, provided a significant reduction in the amount of most of the toxic compounds in tobacco smoke. This reduction in turn entailed a decrease of the potential negative effects caused by tobacco smoke in smokers and in passive smokers, without causing significant changes in the organoleptic properties, taste and consistency of the tobacco, and without the apparent generation of other undesired compounds. On the other hand, not only were the toxic compounds reduced, but also the total amount of gases and liquids that are formed when smoking the cigarette (total particulate matter, TPM, plus the liquids retained in the filter) also generally decreased in a significant manner, whereas solid residue together with ash increased. When the process of smoking the cigarette ended, the additives were retained in the ash or in the tobacco that has not been smoked.

[0038] Table 3 shows the yields obtained for CO and CO₂ when smoking cigarettes prepared with the described mixtures. As can be seen, reductions are generally obtained in the amount of CO present in the mainstream tobacco smoke as a result of the presence of almost all the studied materials. As will be seen below, these reductions are particularly interesting for the additive referred to as SBA-15 when it is used in nominal proportions of 6 and 8%. The SBA-15_{spherical}, SBA-15_{spherical} and SBA-15 at 125°C materials also provide significant reductions in CO. That is particularly interesting since CO is one of the substances regulated by laws applicable to commercial cigarettes. The rest of the additives also provide a reduction, although less, in CO, with the only exception of FeNa-SBA-15, which causes a slight increase. It is also seen that reductions in CO₂ are obtained in all the studied cases. It must be pointed out that the results shown in Table 4 depict a significant decrease in the total particulate matter (TPM) as a result of using the proposed additives. These reductions range between a maximum value of 66%, in the case of SBA-15, and a minimum

reduction of 52% in the worst case, which corresponds to AISBA-15 (autoclave). This is also an important feature of these materials since the TPM is closely related to tars that are generated when smoking cigarettes, tars being another regulated substance. In fact, the amount of tars is considered to provide a good measurement of the amount of toxic and harmful substances generated when smoking, all of them considered as a whole. It can therefore be concluded that the capacity of these additives for reducing the formation of said toxic substances is very significant.

[0039] Table 5 shows, by way of example, the results obtained for the production of some toxic and carcinogenic compounds in tobacco smoke. As can be seen, all the additives provided a reduction in the formation of propionaldehyde with respect to the reference cigarette. Interesting reductions were also observed in the case of toluene, with the only exception of the NaFe-SBA-15 material, which caused a slight increase. Similar considerations can be made for benzene and acetaldehyde: reductions are observed for benzene in all cases, except for SBA-15_{spherical} and SBA-15_{spherical} at 125°C, causing a slight increase. In the case of acetaldehyde, the only additive which causes reductions with respect to the reference cigarette is SBA-15. It can therefore be concluded that the sample of the SBA-15 material has an excellent behavior from the viewpoint of applying same as an additive for reducing the toxicity of the mainstream tobacco smoke since, in addition to reducing the generation of CO and TPM, it separately reduces all the analyzed toxic compounds.

[0040] Table 6 shows the results obtained for other compounds present in tobacco smoke in the case of the reference tobacco and with 4 of the studied additives. The excellent behavior shown by the SBA-15 sample can again be confirmed, with reductions ranging between 95% for phenol and 39% for nicotine. The SBA-15_{spherical} material also caused reductions in 7 studied compounds, whereas FeNa-SBA-15 caused an increase in all of said compounds, except benzaldehyde.

[0041] All the described mixtures can also be prepared by means of using speed mixers, fluidized beds or entrained beds and any other type of equipment which favors mixing the tobacco fiber and additive. Sieves can also be used for separating and recirculating the additive that did not attach onto the tobacco fibers. On the other hand, for other different conventional cigarette preparations, in which the tobacco-additive mixtures must be prepared manually by smokers themselves, a dispenser providing the suitable amount of catalyst can be used for preparing bright tobacco, dark tobacco, fine-cut tobacco, roll-your-own tobacco, pipe tobacco and any other product that can be smoked. This dispenser can consist of a blister, in which each cavity contains the selected amount (between 5 and 70 mg, such that between 0.5 and 7% is obtained with respect to the tobacco which will usually be consumed in portions of about 1 g of tobacco), individual capsules containing said amounts, a container including a calibrated or graduated spoon or any another calibrated dispenser. To prepare a ready-to-smoke product (MYO, RYO, pipe or other forms), the content of the calibrated dispenser is poured onto the tobacco fiber and carefully mixed by hand. This method assures excellent results which are as good as those shown in Tables 3 to 6.

Tobacco-additive mixtures with different additive concentration

[0042] The additive used in all the cases was SBA-15. The percentages by weight of catalyst are indicated. The cigarettes were prepared using the method described in "cigarette preparation conditions" and using nominal concentrations (percentage by weight) of 4.6 and 8%.

Results obtained corresponding to tobacco-additive mixtures with different additive concentration

[0043] The influence of additive concentration on additive-tobacco mixtures was also studied. To that end, mixtures were prepared with a nominal percentage of catalyst comprised between 4 and 8% using the method described above. By way of example, Tables 7 and 8 show the results obtained when using SBA-15 as an additive. As can be seen, the best results were achieved when using the maximum additive concentration, although excellent results, which can be adjusted according to the desired reduction in toxic compounds, were also obtained in mixtures with intermediate concentrations.

Sample	% zeolite	Drags	mg/cigarette tobacco	TPM (mg/cigarette)
3R4F	0.0	9	0.76	6.79
3R4F+SBA15 (4%)	3.8	9	0.76	2.34
3R4F+SBA15 (6%)	5.6	9	0.76	1.31
3R4F+SBA15 (8%)	7.3	10	0.76	0.66

Table 7. Number of drags and TPM obtained when smoking tobacco under controlled conditions

Sample	Hydroquinone	Myosmine	Cotinine
3R4F	1.03E-02	4.2E-03	6.5E-03
3R4F+SBA15 (4%)	4.02E-03	8.9E-04	2.8E-03
3R4F+SBA15 (6%)	0.05E+00	9.5E-04	9.7E-04
3R4F+SBA15 (8%)	0.00E+00	0.0E+00	0.0E+00

Table 7. Continued

Sample	CO ₂	CO	Propionaldehyde	Toluene	Benzene	Acetaldehyde
3R4F	40.63	11.220	0.0208	0.0178	0.0849	0.3061
3R4F+SBA15 (4%)	29.85	10.89	0.0152	0.0135	0.0655	0.2908
3R4F+SBA15 (6%)	24.27	7.59	0.0144	0.0088	0.0486	0.2125
3R4F+SBA15 (8%)	22.53	6.50	0.0101	0.0068	0.0356	0.1446

Table 8. Generation (mg compound/cigarette) of different toxic compounds present in the non-condensable products retained in the Tedlar bag when smoking tobacco under controlled conditions

Sample	Nicotine	Benzaldehyde	Phenol	p-Cresol
3R4F	0.593	2.9E-04	4.2E-03	5.6E-03
3R4F+SBA15 (4%)	0.359	1.1 E-04	2.0E-04	9.9E-04
3R4F+SBA15 (6%)	0.233	5.7E-05	0.0E+00	3.8E-04
3R4F+SBA15 (8%)	0.101	9.8E-05	0.0E+00	0.0E+00

Table 8. Continued

[0044] From this point of view, it must be pointed out as being particularly interesting the use of SBA-15 with a nominal concentration of 8% which caused the following reductions: 42% of CO, 90% of TPM, 51% of propionaldehyde, 62% of

toluene, 58% of benzene, 53% of acetaldehyde, 83% of nicotine, 66% of benzaldehyde, and practical disappearance of other compounds.

5 **Claims**

1. Use of aluminosilicate SAB-15, or the acidic or sodium forms thereof, interchanged with Fe, Na, K, Ca, Ce, Zr, the oxides of Fe, Na, K, Ca, Ce, Zr and mixtures thereof as an additive for reducing the toxic and carcinogenic substances present in tobacco smoke.
2. Use according to claim 1, where the aluminosilicate SAB-15 has a spherical morphological shape, tubular morphological shape or rod shape.
3. Use according to any of the preceding claims, where the aluminosilicate SAB-15 has a pore size comprised between 4-10 nm and a mesopore volume preferably greater than 2.2 cm³/g.
4. Mixture comprising dry tobacco and aluminosilicate SAB-15, or the acidic or sodium forms thereof, interchanged with Fe, Na, K, Ca, Ce, Zr, the oxides of Fe, Na, K, Ca, Ce, Zr and mixtures thereof as an additive and not containing adhesive agents.
5. Mixture according to claim 4, **characterized in that** the additive is at a concentration comprised between 0.5-10% by weight with respect to the dry tobacco.
6. Mixture according to claim 5, **characterized in that** the additive is at a concentration comprised between 2-7% by weight with respect to the dry tobacco.

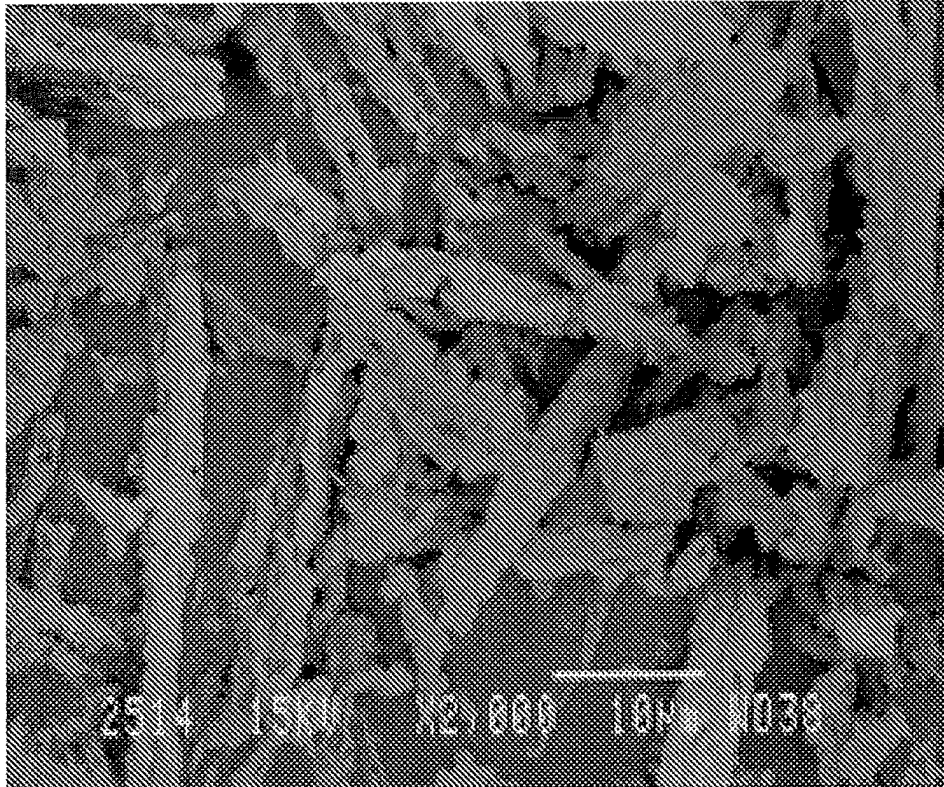


FIG 1-A

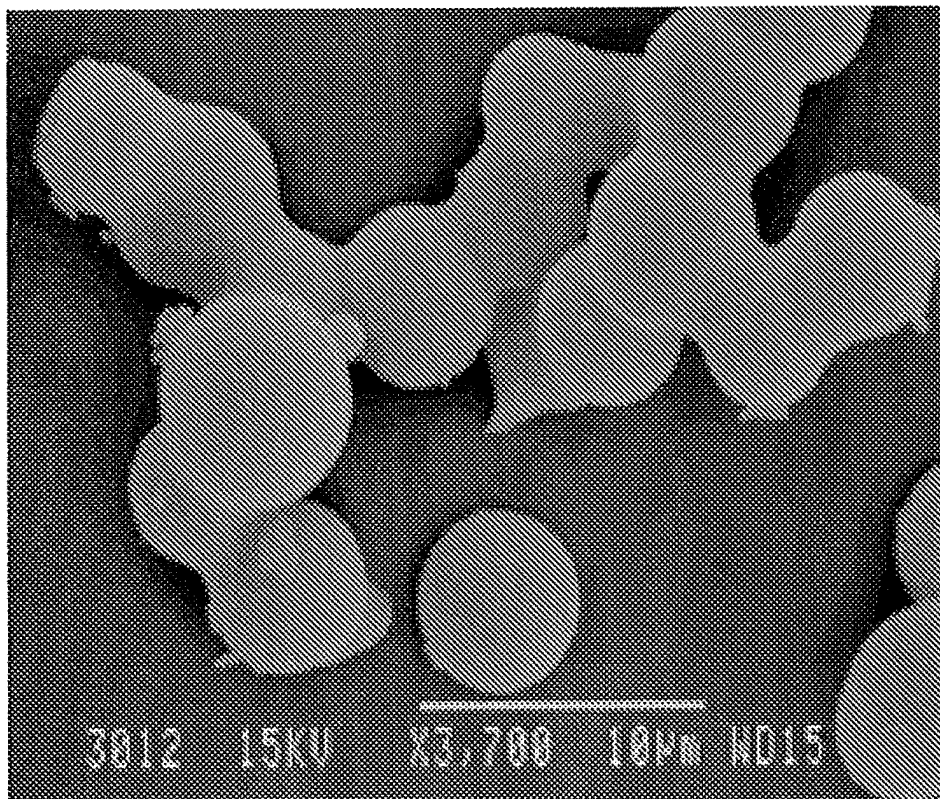


FIG 1-B

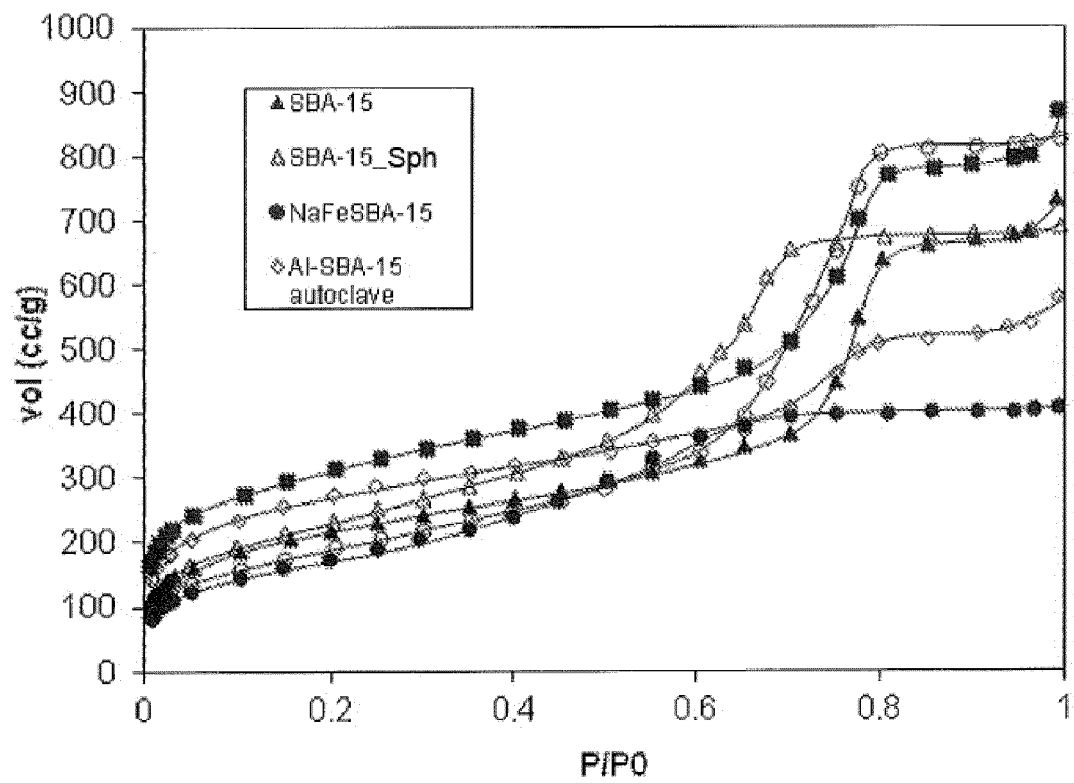


FIG 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/ES2013/070848

A. CLASSIFICATION OF SUBJECT MATTER

A24B15/28 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A24B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC, INVENES, WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2007204807 A1 (RAUSCH ANDY ET AL.) 06/09/2007, abstract; page 2; claims 1,4,5,6,8	1-6
Y	ES 2301392 A1 (UNIV ALICANTE) 16/06/2008, abstract; claims 6 a 13	4-6
A	US 2005133052 A1 (FOURNIER JAY A ET AL.) 23/06/2005, the whole document	1-6

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search
30/12/2013

Date of mailing of the international search report
(08/01/2014)

Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/ES2013/070848

Information on patent family members

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US2005133052 A1	23.06.2005	NONE	

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REFERENCES CITED IN THE DESCRIPTION

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