REDUCTION OF HARMFUL COMPONENTS OF CIGARETTE SMOKE USING MCM-48

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Mesoporous MCM-48 molecular sieves were synthesized using cetyltrimethylammonium bromide (CTAB) as template and tetraethylorthosilicate (TEOS) as silica source. This ordered mesoporous silica was added into cigarette filter in order to establish how this influences the harmful toxicity effect of smoke. The presence of the catalyst seems to reduce the yield of polycyclic aromatic hydrocarbons (PAHs) compounds found in the mainstream cigarette smoke. Thus, although the three silica prepared by varying different synthesis parameters, such as stirring time and temperature, are able to reduce smoke toxicity, the best results where obtain for that synthesized at 15 h stirring time.

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1. Introduction

From the first discovery of this new family of mesoporous sieves by Mobil scientists in 1992, a great interest was targeted by their properties. This M41S material including MCM-41, MCM-48 and MCM-50 have attracted attention mostly in separation and catalysis [1]. M41S materials possess especially large and uniform well-defined pores whose diameter can be varied in the range of approximately 15-100Å. Large channels of these materials with very regular pore openings ordered in different arrays hexagonal (MCM-41), cubic (MCM-48) and lamellar (MCM-50) [2]. Elimination of template, after MCM-48 synthesis, it is a necessary step in order to obtain the porous framework and to provide the adequate catalytic properties.

Besides the well-known applications of molecular sieves as catalysts, these species have also been involved in a wide range of process. The mesoporous silica catalyst is well known that shows promising catalytic performance for reactions and could be used for different chemical purposes with different type of suitable metallic phase [3-5].

Air is the most important environmental factor for the diffusion of pollutants, therefore being the most environmentally friendly medium for transport, the surveillance of air quality is the first in monitoring activity of a country. Potentially, air pollution is the most serious problem as it has short, medium and long term effects. In the short and medium term, pollutions are likely to endanger human health, damage ecosystems and cause economic damage. In the long run, pollution causes environmental changes by greenhouse effect, acid rain, ozone depletion.

Tobacco smoking is a controversial issue of great concern for people. During the smoking of a cigarette several mechanisms occur, which cause the generation of tobacco smoke. Reducing the polycyclic aromatic hydrocarbons (HAPs) delivery of cigarettes, is the most important step in decreasing this type of pollution. The addition of catalyst to different part of cigarette has different requirements. The morphology of catalyst particles may also influence.

It should be noted that introduction of catalysts to cigarette paper can reduce harmful substance delivery; its cost effectiveness may still need to be improved, so the commercial application of future technologies in this field can advance.

One the other hand the catalysts can, for example, colors the cigarette paper which may not be promising in term of commercial use respecting the required standards. The concept of

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catalysts impregnation to cigarette paper is rather promising and great development is expected in this area.

Due to the high interest in the subject and to the promising results obtained, in the last year new papers have appeared on this topic of cigarette smoke reducing using different types of catalyst.Young et al. [6] have demonstrated that MCM-48 and Ce-MCM-48 act as a good catalyst for reducing harmful hydrocarbons in mainstream smoke of cigarettes. The authors describe for the first time a method for reducing the amount of undesirable bulky hydrocarbons in the cigarette smoke using mesoporous materials, which are attached to the tobacco or put into the cigarette filter tips.

Shen et al. [7] makes an overall review regarding the reduction of carbon monoxide provided by smoke cigarette. The authors proposed several concepts to decrease CO delivery that includes: (1) increasing the porosity/air permeability of cigarette paper, (2) increasing the dosage of burn additives, (3) decreasing the fiber basis weight of cigarette paper, (4) optimization of the use of catalysts raw materials source, (5) incorporation of catalysts and/or oxidants. The authors finally concluded that fundamental studies related to catalytic oxidation of CO during smoking would be important for the development of more efficient technologies. They also mentioned that reduction of toxic emissions other than carbon monoxide is also of critical importance.

Marcilla et al. [8] studied the ability of MCM-41 as catalyst in order to reduce tobacco toxicity. The authors also concluded that for catalyst steps preparation involving template elimination the treatment with H_2O_2 is better instead of HCl/Ethanol. Moreover the catalysts supported on MCM-41 show good textural properties and hydrothermal stability as tobacco additives. In other publication Marcilla et al. [9] studied the ability of three mesoporous aluminosilicate solids to reduce different compounds from the mainstream smoke of two brands of cigarette. The material with the highest pore size SBA-15 seems to provide a better reduction than MCM-41 samples. The authors have concise that the important mechanism involved in the tobacco compounds reduction by mesoporous silica is the filtration of the particles in smoke caused by the fiber like morphology of the catalyst. The SBA-15 presents larger pore size and pore volume; both properties increase the reduction effect.

In [10] Marcilla et al. analyzed the effect of two zeolites HUSY, NaY and mesoporous Al/MCM-41, on the smoke composition of commercial cigarette. They concluded that NaY zeolite is the material with the poorest behavior and Al/MCM-41 is the most effective in reducing of this harmful cigarette components. Regarding the families of compounds, the highest component reduction was achieved in the case of nitrogenous compounds followed by aromatics.

The objective of the present paper is to study the effect of the preparation condition of MCM-48 samples to be used as catalysts for reducing the toxicity of the tobacco smoke. However, the scope of the present work is not only to present alternative synthesis for MCM-48, but also to study the stability of the catalysts obtained and their effect as additives for reducing smoke toxicity.

2. Materials and methods

2.1. Catalyst synthesis and characterization

Cetyltrimethylammonium bromide CTAB (98%, Aldrich) was used as the structure directing agent and tetraethyl orthosilicate TEOS (98%, Aldrich) as source of silica. Deionized water, ethanol C_2H_5OH (99,2% Chemical) and aqueous ammonia solution NH_4OH (20% Chemical) were used as reagents for the synthesis.

The catalysts is mesoporous silica MCM-48 and has been prepared according to the standard procedure described elsewhere [8]. Briefly in a typical synthesis of mesoporous MCM-48 molecular sieve, few grams of CTAB were added to deionized water and ethanol under stirring. After the solution turned clear, aqueous ammonia solution was added to the system and it was allowed to mix for several minutes. After that, TEOS were poured into the solution immediately under vigorous stirring. Stirring was continued for 15 h at room temperature. The solid product was recovered by filtration and dried at room temperature overnight. The dried materials were calcined at 560^0C for 6 h in order to remove the surfactant molecules.

X-ray powder diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer with CuKα radiation in the 2θ range of 1°-10° at scanning rate of 1°/min. N_2 sorption isotherms at 77 K were recorded with an automatic Quantachrome Autosorb Gas Sorption system. BET surface and pore distribution were determined from the desorption isotherms. The morphology of the sample was examined by scanning electron microscopy (SEM) using a FE-SEM Nova NanoSEM 630.

More details about the synthesis and catalysts characterization can be found in a previous research [11].

Table 1. The catalyst samples synthesized.

Sample	Synthesis time (h)	Calcination temperature (^{0}C)	S_{BET} (m^2/g)
MCM-48	2h	560^{0}C	946.60
MCM-48	9h	560^{0}C	958.71
MCM-48	15h	560^{0}C	1028.95

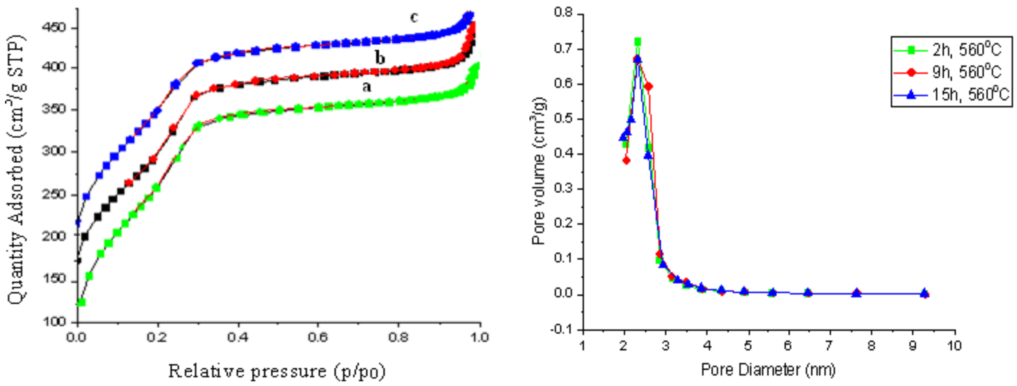

Fig. 1. Nitrogen adsorption-desorption isotherms and pore size distribution for MCM-48 synthesized at different stirring time (a) 2h (b) 9h and (c) 15 h and calcinations temperature 560^{0}C.

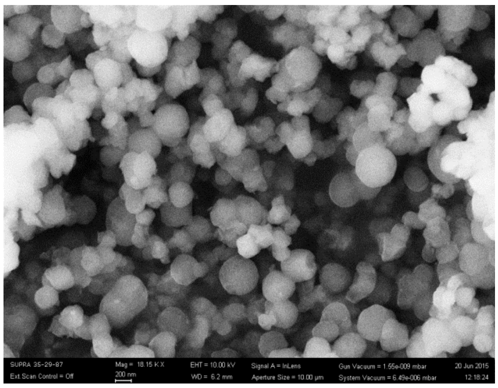

Fig. 2. Scanning electron micrographs of the MCM-48 synthesized at 560^{0}C for synthesized time stirring of 15 h.

2.2. Cigarettes

In this work, three reference cigarettes (A, B and C) have been used in order to check the behavior of the studied catalyst. The main characteristics according to the supplier are shown in Table 2.

Table 2. Design data of the commercial brands cigarette used.

Brand type	**Weight of tobacco** (mg/cigarette)	**Filter length** (mm)	**Filter weight** (mg/cigarette)	**Paper length** (mm)	**Paper weight** (mg/cigarette)
A	550	18.9	110	57,3	41
B	504	25.8	146.7	50,3	35,6
C	506	20.1	106.6	59,7	42,4

Is worth mentioned that the test cigarettes were hand rolled with filter tips. The weight of tobacco was exactly weight for each cigarette. Several milligrams of MCM-48 were added to the layer and the tobacco was mixed with the mesoporous material powder until the mix looked perfectly uniform. The mixture formed by tobacco and catalyst was prepared by manually mixing the catalyst powder with tobacco contained in each cigarette analyzed. A certain quantity (amount) of ethanol was added to wet the tobacco and predefine the mixture of tobacco with the catalyst. The refilled cigarettes were kept at 25^0C for at least 48 h. The ethanol was evaporated prior to the refilling.

2.3. Smoking experiments

In order to check the influence of adding catalyst for reducing tobacco toxicity, cigarettes prepared with mixtures of tobacco and catalyst were smoked, and the results obtained were compared with those corresponding to the standard cigarettes with no catalyst added.

Three cigarettes were consumed simultaneously at each cycle. The working regime was set according to ISO 3308 standard with the difference that 8 puffs were performed here. The condensed products were collected in a 44 mm filter located between the smoke extraction side and the chromatograph. The condensed particles and cigarette filters were separately treated with isopropanol and analyzed. After performing the previous operations, the smoke was collected in a standard bag as a gaseous fraction for analyses. The mixture passes through the chromatographic system, being trained by the mobile phase. The uneven distribution is determined either by the different affinity of the components of the mixture relative to the two phases or by the different capacity to diffuse therein. The apparatus used in gas chromatography is characterized by a variety of different types of complexity. In this paper a GC/MS using a HP-5MS column was used.

3. Results and discussion

In order to investigate the effect of MCM-48 mesoporous material on polycyclic aromatic hydrocarbons (PAHs), the types of PAHs formed were analyzed as mentioned before using GC-MS.

The results obtained in table 3 illustrate that MCM-48 comports as a good selective adsorption catalyst. Smaller PAHs molecules do not appear, whereas the bulky PAHs are selectivity eliminated, using MCM-48 catalyst. The results obtained for MCM-48 (2 h) are not significant for this study and have not been take in account for future explanations.

Table 3. Catalytic reduction of PAHs for C reference brand cigarette.

PAHs	**% Reduction MCM-48 (9 h)**		**% Reduction MCM-48 (15 h)**	
	In filter tip	**In tobacco**	**In filter tip**	**In tobacco**
1. Naphtalene	19.21	7.73	0	19.43
2. Phenanthrene	8.12	1.87	5.82	5.02
3. Anthracene	4.65	3.21	3.42	3.58
4. Pyrene	9.13	4.20	4.11	2.01
5. Benzopyrene	19.31	20.07	59.40	40.22
The total reduction of PAHs (take in account unidentified substance).	**16.41**	**14.13**	**24.00**	**32.18**

It should be noted that by comparison with MCM-48 (9h), MCM-48 (15h) exhibits highly catalytic activity, when added to the tobacco or filter tip as present in Fig. 3.

This fact revealed that longer synthesis time can effectively improve the catalytic activity.

Moreover the mesoporous silica catalysts are more activated when they are near the hot zone in the smoking cigarette while burning, where temperature reaches around 800^0C, as a conclusion, the reduction of PAHs by MCM-48 (15h) in the tobacco is higher than that in filter tips. The brand C of cigarette presents the most important reductions of PAHs, while brands A and B show lower reductions and has not been taken into account for further analyses.

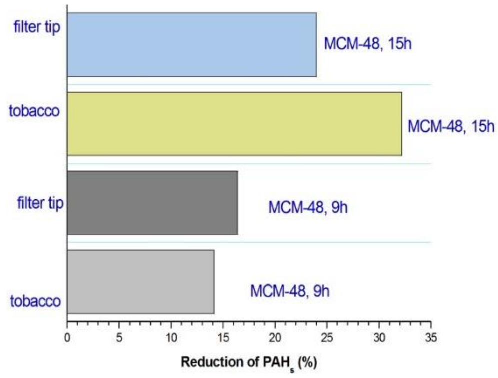

Fig. 3. Reduction of PAHs in mainstream smoke of cigarette brand C by MCM-48 (9h) and MCM-48 (15h)

4. Conclusions

The effect of potential mesoporous additives for reducing the amount of toxic compounds in the tobacco smoke have been investigated on commercial cigarette brands.

In this paper MCM-48 (15h) material acts as selective adsorption catalysts on the tobacco and provides a good means to reduce the PAHs in the smoke of cigarettes.

The results obtained suggest that the three mesoporous catalyst prepared exhibit normal textural properties but the preparation steps seems to conduct to higher catalytic activity for the catalyst synthesized for 15h. In the long run, more research work is needed to explain the negative effect of smoking and to find the most suitable catalyst/additive for reducing the harmful smoke components.

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