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Catalytic effect of MCM-41 on the pyrolysis and combustion processes of tobacco. Effect of the aluminium content

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ABSTRACT

The hydrothermal stability and the acidity of mesoporous MCM-41 materials are strongly related with their aluminium content. In this work, the influence of the concentration of Al on the textural and acidic properties of MCM-41, as well as on its role as tobacco additive for reducing the toxicity of the smoke generated in the smoking process has been studied. The results obtained show that the material with an intermediate content of aluminium presents acceptable hydrothermal stability, and higher values for the decrease of the yields of CO, CO_2, and the condensed and non-condensed products, thus showing the best results from the point of view of reducing the toxicity associated with the generation of toxic and carcinogenic compounds in tobacco smoke.

1. Introduction

Tobacco smoking is the largest preventable cause of disease and death in the world, causing about five million deaths annually, a toll projected to rise to 10 million by the 2020s, 70% of which will be in developing countries [1].

The health hazard caused by smoking cigarettes has been well established [2]. Besides nicotine, the major inducer of tobacco dependence, cigarette smoke also contains various toxic compounds and noticeably carcinogenic agents such as nitrosamines and polycyclic aromatic hydrocarbons (PAHs). Zeolites and molecular sieves such as MCM-41 have been employed as additives in cigarettes in order to remove such dangerous products [3–9].

Since the disclosure by Mobil [10], in the early 1990s, of the synthesis of mesoporous materials with regular structure, the so-called MCM-41 series has drawn considerable attention. These materials present a long range ordered structure with a regular hexagonal array of one-dimensional mesopores, whose diameters can be adjusted in the range of 2–10 nm, depending on the surfactant agent, on various additives and on the synthesis conditions. This set of characteristics makes them attractive for fundamental studies, as well as for applications in the fields of adsorption and catalysis, especially when bulky molecules, which do not fit into the pores of usual adsorbents and catalysts such as zeolites, are involved. However, this material has as a disadvantage its sensitivity to moisture at ambient temperature, which can limit its use in some applications.

The hydrothermal stability of MCM-41 in boiling water or steam at high temperatures has been studied in several publications [11], and it seems to be dependent on the synthesis conditions [12] and, in particular, on the aluminium content.

It has been reported that structural degradation of pure silica MCM-41 materials can occur even at 298 K if the material is exposed to water vapour for long periods [13]. Improvement of stability can be achieved by modification of the surface with organosilanes [14], by pyrolytic carbon deposition [15] or by post-synthesis treatment such as silanization, using tetraethoxysilane in hexane [16].

Therefore, the low hydrothermal stability of MCM-41 is a factor which must be considered, and if it is possible be improved, in a parallel way to the studies focused on its catalytic role in the tobacco pyrolysis and combustion processes, before trying to exploit its use as a tobacco additive for reducing toxicity at an industrial scale. In this work, the behaviour of several samples of MCM-41with different contents of aluminium, obtained by a post-synthesis Al-ion exchange treatment has been studied. The structure and acidity of these materials, as well as their role as tobacco additives for reducing the toxicity of the smoking process have been studied.

2. Experimental

2.1. Synthesis of materials

MCM-41 not including aluminium (so-called "M" in the nomenclature used in this work) was prepared according to the procedure

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Table 1
Characterization of the different catalysts studied in this work.

Material	BET (m^2/g)	Vol. total pore (cm^3/g, 0.995)	Pore size (Å), BJH	Acidity (mmol/g)	Si/Al
M	964	0.78	29	0.10	157
AM	923	0.74	29	0.26	119
2AM	869	0.69	27	0.28	48
4AM	877	0.74	27	0.35	23

reported in literature [17]: CTMACl (25 wt% aqueous solution, Aldrich) and dissolved in distilled water under constant stirring. An aqueous ammonia solution was added to this solution, which was stirred for 10 min. Finally, the silica source (TEOS, Aldrich, 99 wt%) was added dropwise with vigorous stirring to obtain the final gel. The stirring was continued for a period of 4 h. The product was recovered by filtration, washed thoroughly with distilled water and then dried at 100 °C for 4 h. The removal of the template was accomplished by calcination in air at 550 °C for 6 h.

Additionally, aluminium containing MCM-41 materials (so-called "AM" in the nomenclature used in this work) were prepared by stirring the M sample prepared according to the previous procedure in aqueous solutions of $Al(NO_3)_3{\cdot}9H_2O$ of different concentrations at 60 °C, for 3 h. The exchanged solid product was recovered by filtration, washed with distilled water, and dried at 100 °C. Three concentrations of Aluminium were checked, and materials AM, 2AM and 4AM were prepared, respectively, from 0.25 mol/L, 0.5 mol/L and 2 mol/L aqueous $Al(NO_3)_3{\cdot}9H_2O$ solutions in order to obtain materials with the Si/Al ratios shown in Table 1.

2.2. *Catalyst characterization*

The textural characteristics of the different samples studied were established from the measurement of the N_2 adsorption isotherms at 77 K. The equipment used was an automatic Quantachrome AUTOSORB-6. The surface area measurements were done according to the BET method. The pore size distributions were obtained applying the BJH model with cylindrical geometry of the pores and using the Harkins and Jura equation for determining the adsorbed layer thickness (t) and the external surface area.

The acidity of the materials was measured by temperature-programmed desorption (TPD) of ammonia, performed in a Netzsch TG 209 thermobalance, following the procedure described elsewhere [18].

The Si/Al ratio was measured by X-ray fluorescence (XRF) in a sequential spectrometer of V rays PHILIPS MAGIX PRO, model PW2400.

2.3. *Smoking experiments*

In order to check the influence of the aluminium content on the activity of the aluminium containing MCM41 materials for reducing tobacco toxicity, cigarettes were prepared with mixtures of tobacco and the different samples of catalysts. Such cigarettes have been smoked in a smoking machine described elsewhere [9]. Then, the results obtained for the chemical composition of the gaseous and condensed products were compared with those corresponding to a reference cigarette, where the same tobacco was used, but without the catalyst. The smoking machine permits five cigarettes to be smoked simultaneously under some specifications of the ISO 3308 conditions [19]. During the smoking process, the mainstream smoke crosses the filter of the cigarette as well as a trap placed after the cigarette, for the purpose of retaining the condensable products, and finally, the non-condensable products in these conditions are collected in a Tedlar bag. It is interesting to point out that the trap located after the cigarette captures the condensable products which could condensate in the mouth and the lungs of active smokers.

The cigarettes, with a nominal percentage of catalyst of around 4% (wt), were prepared and then kept at 25 °C and 60% relative humidity for at least 48 h before the smoking process (i.e., in a drier provided with a saturated sodium nitrite solution). The pressure of aspiration of the machine is of the order of 1.5 kPa.

The condensable products retained in the filter of the cigarette and in the trap were extracted with 2-propanol as solvent and analyzed by GC/MS using a HP-5MS column.

The measurement of the content of CO and CO_2 in the gaseous product was carried out by GC-TCD using a CTR I column. Finally, the rest of non-condensable products were analyzed by GC-FID using a GAS-PRO column.

3. Results and discussion

The results of the characterization of the catalysts prepared (M sample) and modified in the post-synthesis ion exchange procedure (AM, 2AM and 4AM) are shown in Table 1. The stabilizing role of aluminium in the structure, and the corresponding improvement of the hydrothermal resistance have been pointed out elsewhere [9,20]. As expected, when the aluminium concentration in the solution used to carry out the ion exchange increases, the aluminium content in the structure also increases, and the Si/Al ratio decreases. However, some kind of saturating effect seems to appear, and the highest incorporation of aluminium in the structure occurs in the presence of low concentrations of aluminium. In fact, above 0.5 mol/L of Al^{3+}, the increase in the aluminium content is relatively low. The acidity of the samples increases as its aluminium content also increases, and a near linear relationship between Si/Al and acidity can be observed. However, the textural properties are hardly modified by the introduction of aluminium in the structure, despite some apparent worsening.

The catalytic role of the samples prepared in this work in the pyrolysis and combustion processes of tobacco has been analyzed through smoking experiments performed following the procedure described in Section 2. Table 2 shows the yields of CO, CO_2 and other

Table 2
Yields (mg comp./g tobacco fumed) of CO, CO_2 and other gases and liquids condensed in filters and traps obtained when smoking the reference tobacco in the absence of (R) and in the presence of catalysts with different Al contents (R + M, R + AM, R + 2AM and R + 4AM).

Compound	R	R + M	R + AM	R + 2AM	R + 4AM
CO	5.47	3.88	4.08	2.27	4.89
CO_2	39.8	31.0	32.5	22.0	37.6
Non-condensed	2.51	2.00	1.82	1.37	2.18
Condensed in traps	959	411	539	327	599
Condensed in filters	962	512	663	475	693

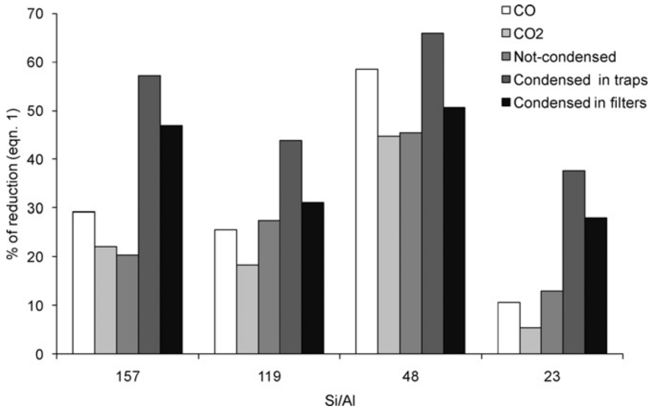

Fig. 1. Percentages of reduction (calculated with Eq. (1)) of the yields of CO, CO_2, liquids and gases achieved with the catalysts studied in this work.

non-condensed compounds as well as of the condensed materials collected in the traps placed after the cigarettes and in the filters of the cigarettes. It is interesting to point out that the amount of CO, nicotine and tar generated when cigarettes are smoked is restricted by law. Nicotine is enclosed in the condensed products, and tar is defined as the condensed products, after the water and nicotine content have been discounted. As can be seen, all the catalysts checked have the ability to reduce the yields of the products evolved from the smoking process. Fig. 1 shows the percentages of reduction achieved with each catalyst, calculated as follows:

$$\%\,\text{reduction} = \frac{\text{yield in the reference tobacco} - \text{yield in the presence of catalyst}}{\text{yield in the reference tobacco}} \times 100 \qquad (1)$$

As can be seen, in all the cases the best results correspond to the sample 2AM, followed by M, AM and 4AM which act in a relatively similar way, with the only exception of M, which is slightly better at reducing the liquids (but worse than 2AM). From the point of view of the reduction of toxic compound generation in a smoking tobacco process, when the MCM-41 catalysts have relatively similar textural properties, these results suggest that the best catalyst is that having a Si/Al ratio of around 50. Thus, the results obtained indicate that the relationship between the percentages of reduction of the yields of different compounds evolved in the smoking process and the acidity of the catalysts shows a maximum corresponding to an intermediate value of acidity. It must be considered that, according to [20] the incorporation of high levels of Al may destroy the porous structure, and consequently a maximum of the activity with the Al content would be expectable.

Fig. 2 presents the yields for the main components of the non-condensed fraction of the mainstream smoke obtained in different smoking experiments. The 10 compounds shown represent 80% of this fraction. As can be seen, in good agreement with the previous statements, 2AM could be considered as the best additive, and is the catalyst which reduces in higher extent the yields of all the compounds, with the only exception of isobutene and acetone. On the other hand, other minor components (around 20 compounds) also appear, and 2M is also the catalyst providing the highest reductions with respect to the reference tobacco.

The analysis of the particulate matter retained (i.e., liquids or condensed fraction) in the filters of cigarettes and in the traps located after the cigarettes in the smoking experiments is a complex task due to the appearance of more than 100 peaks, i.e., more than 100 different compounds, most of them at very low levels. Tables 3 and 4 show the yields obtained for some compounds which have been identified with a matching factor higher than 80% with the aid of the library of the GC/MS equipment, in the traps and in the filters, respectively. As can be expected, there are compounds appearing in the filters which have not been detected in the traps, thus indicating that these materials have been retained almost completely. In good agreement with the results previously presented and commented on, 2AM seems to be the best catalyst from the point of view of the reduction of tobacco toxicity. Similar behaviour can be observed for the rest of compounds (not identified by the library used) of the liquid fraction. At this point, it is worth mentioning that, in accordance with Ref. [21], the complexity of the mainstream smoke suggests that the toxicity of the condensed products evolved from tobacco in the smoking process, and the effect of additives for reducing its toxicity, could be evaluated through the overall yield of particulate matter. In this way, it is interesting to consider the effect of the additives studied in this work on all the compounds appearing in the chromatograms, even those where the identification of peaks is doubtful. Figs. 3 and 4 show the percentages of reduction, calculated with Eq. (1), for all

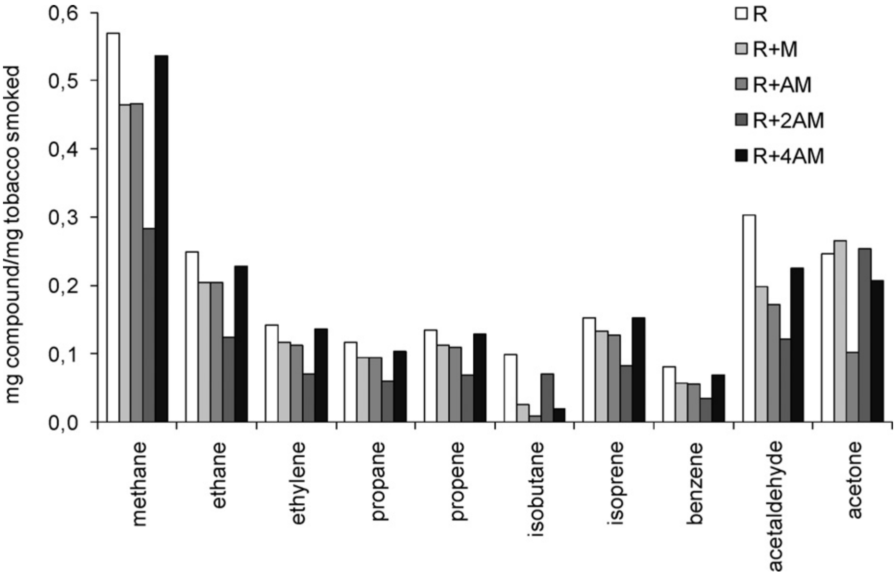

Fig. 2. Yields corresponding to the major compounds of the non-condensed fraction of the mainstream smoke.

Table 3
Yields of the different compounds identified and analyzed in the condensed fraction retained in the traps located after the cigarettes in a smoking experiment in the absence (R) and in the presence of catalysts with different Al contents (R + M, R + AM, R + 2AM and R + 4AM).

Residence time (min)	Compound	mg/g tobacco smoked				
		R	R + M	R + AM	R + 2AM	R + 4AM
8.62	Furfural	3.29	4.95	4.56	4.31	4.19
9.66	2-Furanmethanol	1.01	7.02	3.51	7.77	1.74
10.09	4-Cyclopentene-1,3-dione	2.02	1.17	0.66	1.54	1.11
10.77	2-Methyl-2-cyclopenten-1-one	0.60	0.38	0.01	0.20	0.39
11.00	2(5H)-furanone	1.32	0.55	0.97	0.86	1.04
11.30	2-Hydroxycyclopent-2-en-1-one	1.53	0.32	0.38	0.27	0.43
12.55	5-Methyl-2-furfural	0.82	0.34	0.52	0.37	0.38
13.39	Phenol	8.87	0.37	4.47	2.55	4.91
14.50	2-Hydroxy-3-methyl-2-cyclopenten-1-one	2.27	0.43	0.70	0.33	0.79
14.57	Limonene	2.07	0.86	0.76	0.78	1.15
14.90	2,3-Dimethyl-2-cyclopenten-1-one	1.11	0.38	0.18	0.24	0.72
15.41	o-Cresol	3.79	1.25	2.05	0.24	3.25
15.55	2-Acetylpyrrole	0.75	0.43	0.62	0.27	0.65
16.03	p-Cresol	8.21	2.36	3.79	2.28	5.68
17.96	Benzeneacetonitrile	0.98	0.44	0.54	0.39	0.86
18.11	2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one	2.08	0.52	1.71	0.62	4.85
18.26	3,5-Dimethyl-phenol	3.10	2.05	3.34	1.11	3.61
18.83	4-Ethyl-phenol	4.06	0.30	0.89	0.69	1.24
19.27	Naphthalene	0.86	0.35	0.26	0.28	0.61
22.10	Hydroquinone	10.7	1.41	5.63	1.54	1.21
23.00	4-Vinyl-2-methoxy-phenol	4.10	1.70	2.86	1.42	3.57
23.87	Nicotine	654	256	335	196	370
24.97	3-Methyl-1H-indole	3.91	2.32	2.34	1.48	3.36
32.55	Cotinine	6.14	2.45	3.65	1.94	4.81
34.13	N(b)-formylnornicotine	4.44	2.22	2.96	1.86	2.91
35.29	Neophytadiene	37.0	16.5	22.9	13.2	25.5
55.92	Vitamin E	3.35	3.07	3.17	1.92	3.80

Table 4
Yields of the different compounds identified and analyzed in the condensed fraction retained in the filters of the cigarettes in a smoking experiment.

Residence time (min)	Compound	mg/g tobacco smoked				
		R	R + M	R + AM	R + 2AM	R + 4AM
8.08	3-Furaldehyde	1.70	1.19	1.17	1.26	1.70
8.24	2-Methyl-pyridine	2.80	0.84	1.36	0.95	1.82
8.37	Methyl-pyrazine	3.19	1.34	1.27	1.11	2.55
8.62	Furfural	26.5	10.5	17.3	10.9	20.9
9.66	2-Furanmethanol	3.80	1.04	1.38	0.85	3.18
10.09	4-Cyclopentene-1,3-dione	7.08	3.48	6.23	5.52	8.98
10.25	Styrene	1.00	0.51	0.83	0.91	1.28
10.77	2-Methyl-2-cyclopenten-1-one	9.95	4.63	7.22	4.68	9.42
10.91	2(5H)-furanone	10.77	4.56	6.31	4.74	9.35
11.30	2-Hydroxycyclopent-2-en-1-one	3.07	1.49	2.42	1.89	3.53
11.48	3,5-Dimethyl-pyridine	0.94	0.37	0.65	0.45	0.60
11.61	2,5-Dimethyl-2-cyclopentenone	0.34	0.32	0.32	0.31	0.29
12.55	5-Methyl-2-furfural	15.88	5.38	9.44	6.21	12.39
13.39	Phenol	23.8	10.0	16.7	12.1	19.2
14.50	2-Hydroxy-3-methyl-2-cyclopenten-1-one	7.87	4.03	6.04	3.47	6.67
14.57	Limonene	6.31	4.34	6.15	2.27	5.12
14.83	Benzenemethanol	0.73	0.37	0.58	0.44	0.69
14.90	2,3-Dimethyl-2-cyclopenten-1-one	7.32	3.01	4.45	2.97	5.78
15.42	o-Cresol	8.39	4.27	6.38	4.47	7.09
15.55	2-Acetylpyrrole	2.67	1.31	2.00	1.34	1.74
16.03	p-Cresol	12.7	6.20	11.3	7.87	13.4
17.96	Benzeneacetonitrile	2.69	1.48	2.06	1.56	2.66
18.11	2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one	0.83	0.57	0.61	0.61	0.95
18.26	3,5-dimethyl-Phenol	3.49	2.83	4.74	3.14	4.55
18.83	4-Ethyl-phenol	1.81	1.00	0.73	1.15	1.68
19.27	Naphthalene	1.58	1.34	1.53	0.88	1.52
22.10	Hydroquinone	3.61	2.03	3.41	1.84	2.33
23.00	4-Vinyl-2-methoxy-phenol	3.41	2.22	2.73	2.09	2.01
23.87	Nicotine	537	262	331	244	341
24.97	3-Methyl-1H-indole	4.01	2.42	3.12	2.33	2.59
32.55	Cotinine	2.97	1.40	2.40	2.04	2.88
34.13	N(b)-formylnornicotine	2.42	1.39	1.79	0.90	1.57
35.29	Neophytadiene	27.5	19.5	22.9	18.7	25.6
55.92	Vitamin E	1.66	3.28	1.24	0.68	0.94

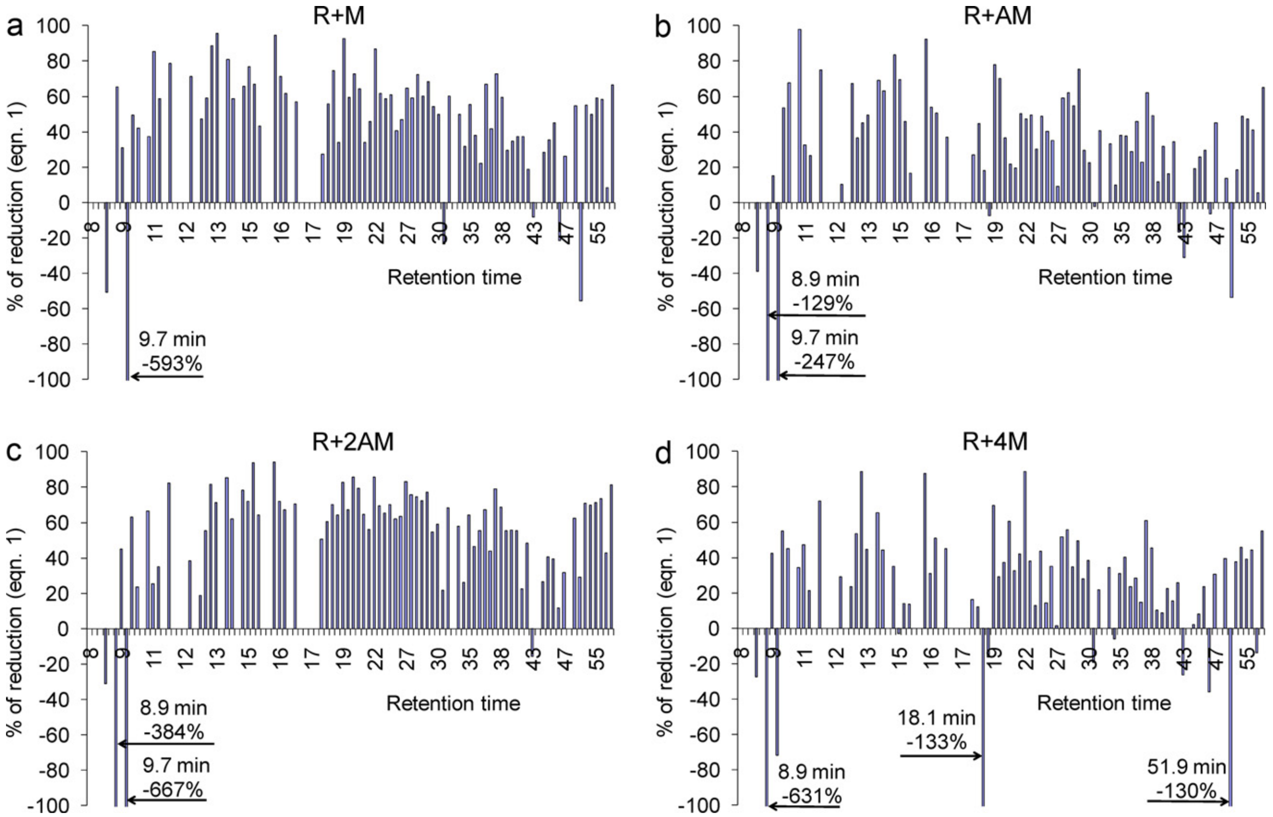

Fig. 3. Percentages of reduction of the yields of the different compounds obtained in the condensed fraction retained in the traps after cigarettes when (a) M, (b) AM, (c) 2AM, and (d) 4AM were used as tobacco additives. Components out of scale are marked, and the corresponding retention times in the chromatograms are shown. The equivalence for the identified compounds can be seen in Table 3.

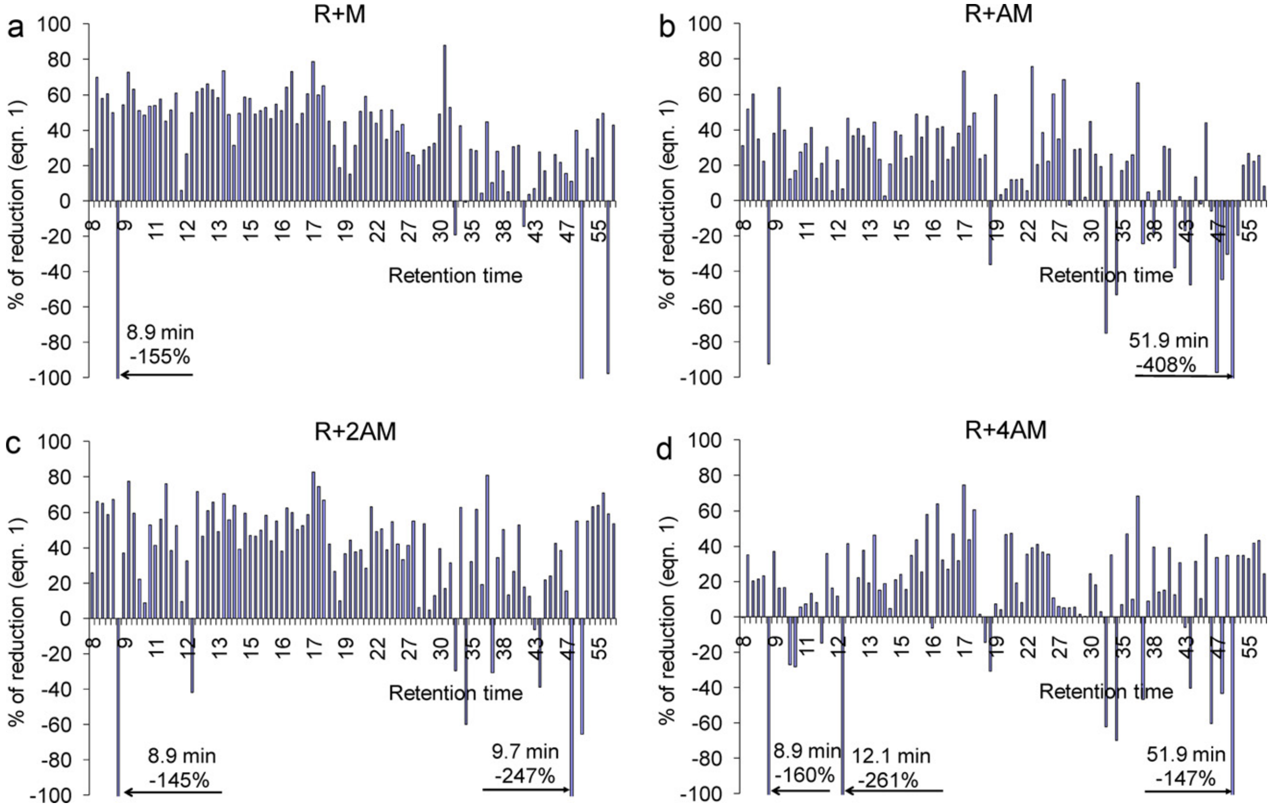

Fig. 4. Percentages of reduction of the yields of the different compounds obtained in the condensed fraction retained in the filters after cigarettes when (a) M, (b) AM, (c) 2AM, and (d) 4AM were used as tobacco additives. Components out of scale are marked, and the corresponding retention times in the chromatograms are shown. The equivalence for the identified compounds can be seen in Table 4.

the compounds appearing in the condensed products retained by the traps and by the filters, respectively. In these figures the *X* axis represents the retention time corresponding to each peak. The negative values in the *Y* axis indicate an increase occurring as a consequence of the presence of the catalyst, whereas the positive values correspond to the percentage of reduction obtained. As can be seen, an overview of Figs. 3 and 4 indicates that, in general, as expected from the previous results, 2AM is the catalyst showing the best properties for reducing tobacco toxicity, followed by M and by AM and 4AM.

4. Conclusions

In this work, the ability of MCM-41 materials with different aluminium contents, prepared by aluminium ion exchange, to act as catalysts in order to reduce tobacco toxicity has been studied. The results obtained indicate that the catalytic activity of such materials in the processes of pyrolysis and combustion of tobacco not only depends on the textural properties of the samples, but also on the acidity, and the material with acceptable catalytic properties should show good textural properties and an intermediate value of acidity (Si/Al ratio around 50 and acidity around 0.28 mmol/g).

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