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Review

Non-carcinogenic carbon sorbents for respiratory protection

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ABSTRACT

Activated carbons impregnated with compounds of chromium, copper and silver (Cr-Cu-Ag) are widely used for removing toxic substances from air, mainly in respiratory protection for industrial and military applications. Toxicological and epidemiological studies have shown chromium (especially hexavalent Cr) to have carcinogenic properties. Hence, research has been launched to develop a new adsorption-catalytic complex without chromium, which is intended to replace the activated carbon-catalyst (Cr-Cu-Ag) system. In this work activated carbon obtained from plum stones as carrier and molybdenum, copper and silver salts as impregnates were studied. The porous structure of the carbon carrier was investigated using low temperature nitrogen adsorption. Cyanogen chloride breakthrough dynamics was analyzed in order to characterize the protection properties. Studies on the substitution of chromium by non-carcinogenic metals will be continued.

Contents

1. Introduction

Many catalysts consist of metals or metal compounds supported on an appropriate carrier, the basic role of which is to maintain the catalytically active phase in a highly dispersed state [1,2]. It is well documented that the role of the support is not merely that of a carrier; it may actually contribute to the overall catalytic activity during the manufacturing process. Interaction between the active and support phases can also affect the catalytic activity. Selection of the support is based on a series of desirable characteristics: inertness; stability under reaction and regeneration conditions; suitable mechanical properties; appropriate physical form for the given reactor; high surface area (not always desirable); porosity; chemical nature. Of a wide range of possible supports, in practice only three combines these characteristics optimally – alumina, silica and carbon – and they are indeed the most commonly used catalyst supports. Although many types of carbon materials have been used to prepare carbon-supported catalysts (graphite, carbon black, activated carbon, activated carbon fibers, carbon-covered alumina, graphite intercalation compounds, glassy carbon, pyrolytic carbon, polymer-derived carbon, fullerenes, nanotubes, etc.), high-surface-area activated carbons are the carbon materials of choice for most carbon-supported catalysts. They are common in industrial, environmental and some other, special applications. One example of this last type is Cu-Cr-Ag/activated carbon (Whetlerite), used in respiratory protection devices for military purposes [3,4]. It is known that adsorption takes place mainly in the micropores of activated carbon. Meso- and macropores play very important roles in any adsorption process, because they serve as a passage for the adsorbate to the micropores, since only a few of these are situated on the outer surface of a carbon particle [5,6].

This work had two objectives: (1) to obtain a carbon sorbent without hexavalent chromium that provides a level of protection no less than that obtainable with chromium-containing sorbents, and

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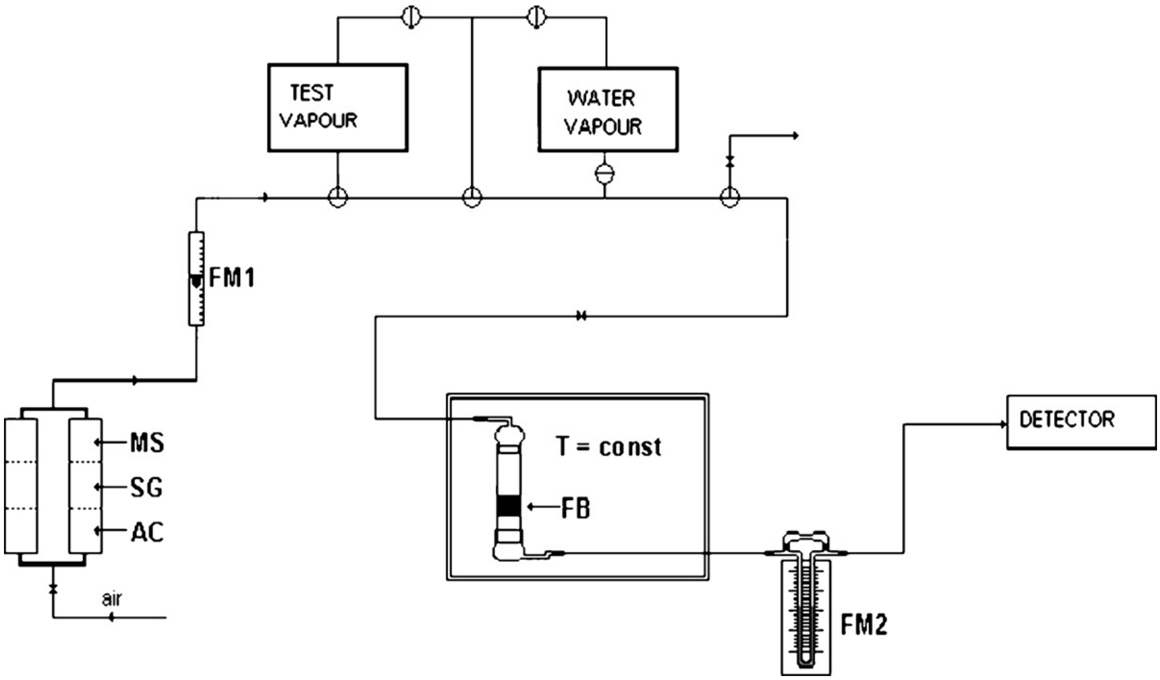

Fig. 1. Testing setup used for breakthrough measurements. AC – activated carbon for purification; SG – silica gel; MS – molecular sieve; flow meters: FM1 (for dry air), FM2 (for air saturated with water vapor and containing vapor of the test substance; it is placed after the carbon bed); FB – activated carbon fixed bed.

(2) to investigate and compare the dynamic sorption capacities and protection times against cyanogen chloride of both sorbent types.

2. Materials and methods

Activated carbon AC, produced from plum stones (steam activation at 1193 K for 1.5 h), was used as a support for incipient-wetness impregnation with MoCuZnAg (AC-Mo) and CuCrAg (AC-Cr) salts. Active components percentage: AC-Cr: Cr-3, Cu-7, Ag-0.1, TEDA-3; AC-Mo: Mo-5, Zn-3, Cu-5, Ag-0.1, TEDA-3. Their structural and adsorptive characteristics were studied by means of nitrogen adsorption and desorption isotherms determined at 77.4 K using a Micromeritics ASAP 2020 analyzer. Cyanogen chloride breakthrough times were measured using the set-up shown in Fig. 1. Compressed air was purified on columns with activated carbon, molecular sieves and silica gel. Dry air, charged with the required amount of cyanogen chloride vapor, was supplied through a glass tube (internal section 5.187 cm^2) filled with the tested carbon. The initial concentration of cyanogen chloride was $c_0 = 3\,\text{mg}\,\text{dm}^{-3}$; the carbon bed depth was constant $L = 2.5\,\text{cm}$; the carbon bed was temperature-controlled at 293 K. The volumetric flow rate was $0.35\,\text{dm}^3\,\text{min}^{-1}\,\text{cm}^{-2}$ and the linear air velocity $5.8\,\text{cm}\,\text{s}^{-1}$.

An accelerated artificial aging procedure was implemented. The carbon was first equilibrated in a stream of moist air (relative humidity 80% at 293 K) to constant weight, then hermetically sealed in a glass tube and maintained at 383 K for 25 h. The glass tube was then broken and the sample moved to the breakthrough setup for further analysis.

3. Results and discussion

The nitrogen adsorption isotherms for the activated carbon samples at 77.4 K are presented in Fig. 2. The adsorption abilities are highest in non-impregnated activated carbon (AC). The lowering of the AC-Mo isotherm with respect to the AC isotherm is greater than that of the AC-Cr isotherm.

Pore size distribution (PSD) was determined on the basis of the isotherms using the DFT method (from ASAP 2020 software – with

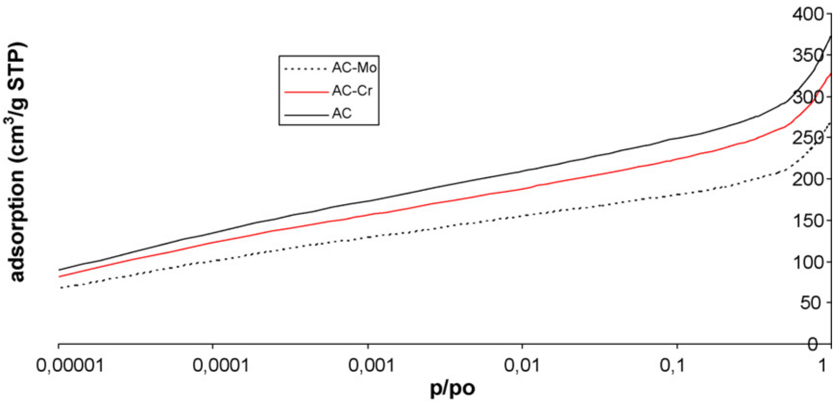

Fig. 2. Nitrogen adsorption isotherms measured at 77.4 K in the following samples: activated carbon, impregnated activated carbon with MoCuZnAg, impregnated activated carbon with CuCrAg.

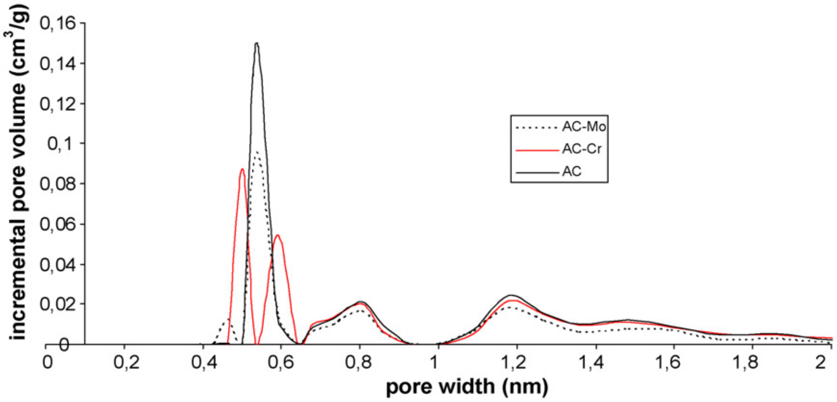

Fig. 3. Incremental micropore size distributions with respect to pore volume in the following samples: activated carbon, impregnated activated carbon with MoCuZnAg, impregnated activated carbon with CuCrAg.

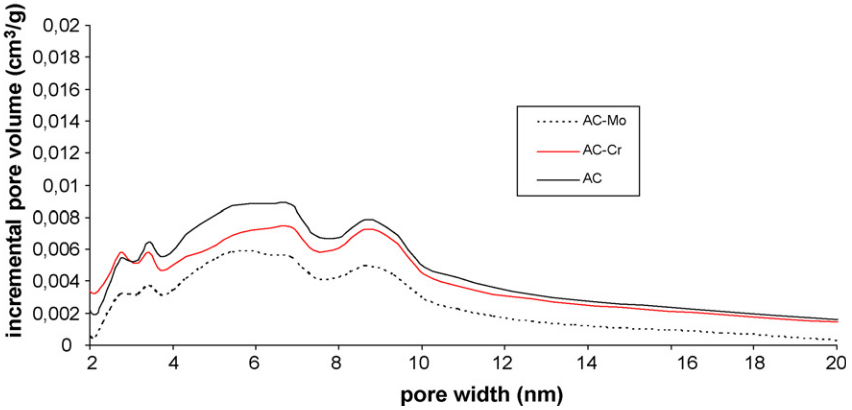

Fig. 4. Incremental mesopore size distributions with respect to pore volume in the following samples: activated carbon 1251, impregnated activated carbon with MoCuZnAg, impregnated activated carbon with CuCrAg.

Table 1
Structural characteristics of the adsorbents

Adsorbent	V_p (cm^3/g)	V_{mic} (cm^3/g)	S_{BET} (m^2/g)
AC	0.57	0.31	978
AC-Cr	0.51	0.28	887
AC-Mo	0.41	0.22	713

V_p – total pore volume calculated from the nitrogen adsorption-desorption isotherm; V_{mic} – micropore volume calculated from the DFT model, S_{BET} – BET surface area.

Table 3
Cyanogen chloride breakthrough times

Adsorbent	$t_b^{(1)}$ (min)	$t_b^{(2)}$ (min)
AC-Cr	47; 45	32; 26
AC-Mo	56; 49	48; 42

$t_b^{(1)}$ – breakthrough time for humidified bed (RH = 80%, t = 20 °C).
$t_b^{(2)}$ – breakthrough time for pre-humidified bed (RH = 80%, t = 20 °C) after accelerated artificial ageing.

“none” regularization level). Microspore distributions are shown in Fig. 3 and the mesopore distribution in Fig. 4. PSDs are very similar; there are small differences in the pore volume for a particular pore size but not in the shape of the whole PSD curve.

The porous structure characteristics and the surface micro- and mesopore volumes determined by the BET model are presented in Table 1. The comparison of these values in Table 2 shows that the decreases are comparable with the total amount of impregnate on AC. There is also good correlation between the results obtained by different methods and models.

Table 2
Relative parameters of the structural characteristics of the adsorbents

Adsorbent	V_p	V_{mic}	S_{BET}
AC	100	100	100
AC-Cr	89	90	90
AC-Mo	80	79	80

The values of AC parameters were set at 100.

Breakthrough measurement was the final test the samples were subjected to. Cyanogen chloride was the test substance. Other authors [7] commonly use this adsorbate because of its ability to test the chemical activity of deposited catalysts, that is, its ability to decompose an air pollutant in a chemical reaction. Moreover, ClCN is representative of other weakly physically adsorbing substances such as HCN, $COCl_2$, AsH_3 and PH_3. The results of the breakthrough experiment are shown in Table 3.

Breakthrough times for AC–Cr are slightly shorter than for AC–Mo with unaged samples. Following the ageing procedure, the differences are more significant.

4. Conclusion

The aims of the work were achieved: impregnated activated carbon without chromium salts was obtained; the characteristics of its pore structure and its adsorptive properties vis-à-vis ClCN were determined and compared with typical chromium-containing sorbents. Further studies are planned in order to elucidate fully such problems as the part played by the porous structure of the carbon carrier and the chemical properties of its surface.

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