

AN IMPREGNATED ACTIVATED CARBON FOR THE SEPARATION OF VOC MIXTURES INTO THEIR INDIVIDUAL COMPONENTS

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Deposition of impregnation chemicals on the internal surface of suitable activated carbon optimizes the existing properties of the activated carbon for the chemisorption of certain gas pollutants giving a synergism between the chemicals and the carbon. Various qualities of impregnated activated carbon are available and have been used for many years in the fields of gas purification, civil and military gas protection and catalysis. For the manufacture of impregnated activated carbon, an activated carbon of suitable quality for the particular application is impregnated with solutions of salts or other chemicals which, after drying or other after-treatment steps, remain on the internal surface of the activated carbon. Usually, homogeneous distribution of the impregnating agents on the internal surface without any blocking of the micropores and macropores is considered to be important to keep the impregnation agent accessible for the reactants. However, in this case, the impregnated activated carbon is not selective: the adsorptive removal of further gas impurities can also take place.

In this work, we propose a new impregnated activated carbon for the selective removal and the fractionation of VOC's mixtures in exhaust humid gas. One seeks to separate by adsorption and thermodesorption on activated carbon four organic solvents: chlorinated (dichloromethane : DCM, 1,2-dichloroethane : DCE) and oxygenated (methanol : MET, methylethylketone : MEK) present in low concentration ($< 0.5 \text{ mole/m}^3$) in wet air (c. 70% of relative humidity). While seeking to avoid any degradation, the solvents must be selectively trapped at ambient temperature and selectively thermodesorbed by electric heating under a flow of nitrogen. Thermodesorption must perfectly regenerate the activated carbon in order to make it possible to apply a sequence of cycles of adsorption-desorption modulated in temperature. That implies a high selective adsorption capacity and a fast desorption at low temperature.

A preliminary work undertaken on carbon adsorbents chemically activated with phosphoric acid (SA 1817 from Atochem and Picazine from Pica), or on activated carbon oxidized by a mixture of nitric and sulfuric acid, showed us that, after washing, the residual mineral acid (acid phosphoric or acid sulfuric) gave a beginning of selectivity to the carbonaceous supports: the chlorinated solvents (DCM, DCE) tend to be better retained on the acid loaded support than the oxygenated ones (MET, MEK). We took benefit from this observation by impregnating the carbonaceous support (activated carbons in grains or fiber) with a mineral substance (ZnCl_2) having acid properties by simple cold agitation in aqueous concentrated solutions (c. 1.25 g ml^{-1}). Electron microscopy showed that the grains are coated with the product of impregnation and the adsorptiometry put in evidence that the impregnation plugs the whole porosity of the carbonaceous material. However the effect of the support is very important. Various supports were tested (powdered /granular from coal or coconut, carbon cloth). The best results were obtained with the most mesoporous activated carbons - for instance with a granular activated carbon prepared with the lignite of Lubstov (Poland) at the University of Wrocław (Table 1).

The most remarkable result is that on the ZnCl_2 impregnated CA, the DCM and the DCE are not retained at all, whereas methanol and MEK are trapped and completely desorbed by isothermal heating at 100°C during a few minutes under a flow of nitrogen, while on the non-impregnated support, the peaks of desorption of the oxygenated VOC "strongly tails". The impregnated support remains perfectly stable during more than 15 cycles of adsorption in a flow of air charged with 70% moisture followed by a thermodesorption at 150°C under a nitrogen flow (Figure 1). The disadvantage of the method lies in the fact that the impregnation's product is toxic, corrosive and hygroscopic. That implies constraints of storage, and requires to use reactor protected from corrosion and to work in short cycles of adsorption-desorption. In fact, MEK breakthrough appears before that of methanol and water. The improvement of the process is currently in hand by seeking a better acidic substance of impregnation for the selective removal of ppm concentration of various VOC's and HAP's in humid effluents.

Table 1. Porosity parameters of the activated carbon (AC) before and after impregnation

	Pore volume, $\text{cm}^3 \text{g}^{-1}$			BET m^2
	Micropores	Mesopores	Micro+Meso	
Non-impregnated AC	0.205	0.504	0.709	740
ZnCl_2 impregnated AC	0.028	0.057	0.085	17

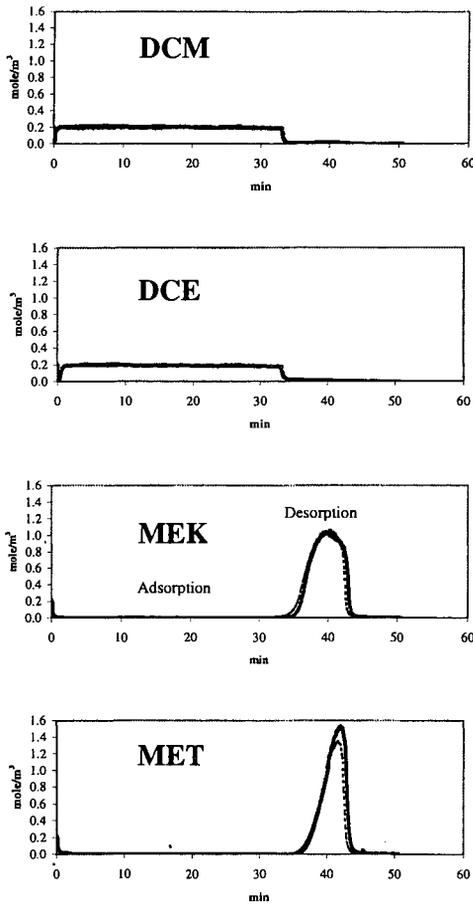


Figure 1. Profile of dynamic adsorption at 25°C and desorption at 150°C of a mixture of dichloromethane (DCM), 1,2-dichloroethane (DCE), methylethylketone (MEK) and methanol (MET) (individual VOC concentration : 0.2 mole /m³, water vapour concentration : 70% of the saturation pressure at 25°C, flow rate : 20 ml/min) on a column filled with 83 mg of ZnCl_2 -impregnated activated carbon (impregnation rate : c. 50 wt %, dashed line : 2nd adsorption-desorption cycle, solid line : 15th adsorption-desorption cycle). The adsorption stage is stopped at the breakthrough point of MEK.