

SO₂ adsorption on active carbons: the effect of certain metal compounds

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Specific preparations are needed to obtain active carbons with optimal behaviour; oxidating thermal treatments favour the formation, on the carbon surface, of certain oxygenated compounds with acidic and basic nature, often enhancing the adsorption properties of polar substances. Other parameters (surface heterogeneity, specific area, type of pores and their size distribution, etc.) can influence the carbon reactivity. In particular, the process of SO₂ adsorption on active carbon can also be greatly influenced by the presence of metallic derivatives [1]. Moreover, a linear correlation is reported [2] between the molar heat of SO₂ adsorption on carbon (ΔH_{ads}) and the amount of SO₂ adsorbed per unit of BET surface area of the carbon itself. Based on this, the aim of this investigation is the study of the variation of the molar heat of SO₂ adsorption on oxidated active carbons, related to the presence of derivatives of certain metals (such as: V, Fe, Cr, Ni), correlating the results obtained with the SO₂ sorbent characteristics of the carbons.

For this investigation, a commercial vegetal active carbon is treated with boiling acidic aqueous solutions (in order to minimise its ash content). The sample obtained is suitably washed and then treated at 1200°C in H₂ flow and quickly cooled in N₂ flow (obtaining a so called "deoxygenated carbon"). By heating part of this sample at 350°C in air or in N₂ containing 2% of O₂ at 800°C, two new samples of carbon are obtained (called carbons A° and B°) that are used as supports for the metallic derivatives. To carry out this step, parts of the samples A° and B° are immersed in aqueous solutions with a suitable concentration of each of the metallic derivatives (VOSO₄, FeSO₄, Cr₂(SO₄)₃ and TiSO₄) and filtered and dried. The amount of metal present on each sample is detected by elementary analysis. Two series of carbons are obtained, called A and B samples, deriving, by supportation, from the samples A° and B°. The measurement of the molar heat of SO₂ adsorption on the various carbons is carried out with the gas chromatographic method [3]. Some cycles of SO₂ adsorption and desorption are carried out adsorbing SO₂ at 25°C (from N₂ containing 2000 ppm of SO₂) followed by room temperature settlement (24h) and by the desorption step (with N₂ flow at 360°C).

The results obtained show that the treatment with boiling acidic solutions markedly decreases the ash

content of the raw commercial carbon. The A° sample (obtained by air oxidation at 350°C) shows an oxygen percentage that is higher than that of the B° sample (obtained by oxidation with 2% of O₂ in N₂ at 850°C). In more detail, we observe that surface oxygenated compounds on A° sample have predominantly acidic characteristics while those on B° sample are predominantly basic. The BET area values of the A° and B° samples are, however, very close to each other and also close to that of deoxygenated carbon (obtained by H₂ treatment at 1200°C) and so not dependent on the thermal treatment undergone. The ΔH_{ads} of SO₂ value are, closely correlated with the respective surface oxygenated characteristics, according to those described in the literature [2]: 7.2 and 6.1 Kcal/mole for the sample A° and B°, respectively. The ΔH_{ads} of the deoxygenated sample shows results rather lower (5.4 Kcal/mole) and demonstrate that the presence of oxygen chemically bonded to the carbonaceous surface can have a marked importance in the adsorption process of SO₂ on these matrices. The ΔH_{ads} of SO₂ for the samples A and B (containing metallic derivatives of certain metals: V, Fe, Cr, Ni) appears to increase, in a practically linear manner, versus the amount of the supported metal. Also if ΔH_{ads} of the sample A° is lower than the corresponding value of ΔH_{ads} of the sample B°, we observe that supported samples A show more marked increases of ΔH_{ads} values than supported samples B. Figure 1 reports, as an example, the behaviour of the A sample.

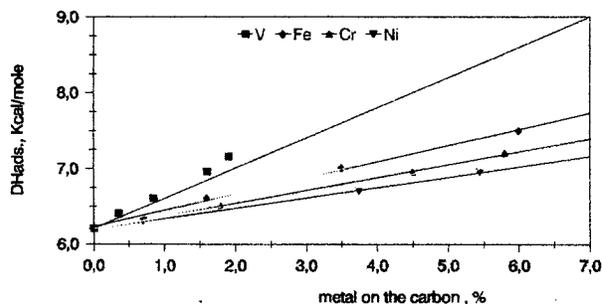
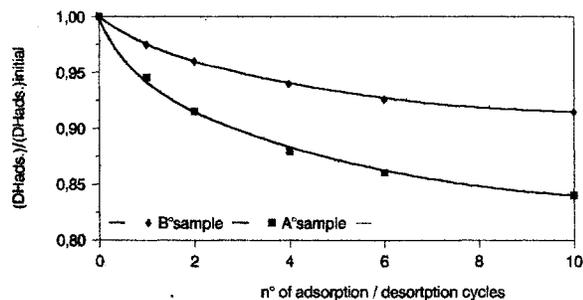


Fig. 1 ΔH_{ads} of A samples vs. the percentage of metal

Otherwise, we observe that the vanadium presence is always related, "ceteribus paribus", with higher ΔH_{ads} of SO₂ values while the effect related to the presence of Fe, Cr and Ni however appears quite different, according to the type of metal and to the nature of the

supporting carbonaceous matrix. In particular, the Fe presence appears related to higher values of ΔH_{ads} . when it is supported by carbon A (with surface characteristics predominantly acidic) while ΔH_{ads} is lower when Fe is supported by carbon B (with surface characteristics predominantly basic). Also Cr and Ni show rather similar behaviour, even if their effect is inverted in two types of carbons. The high values related to the presence of the vanadium can be connected to the properties of this metal that, as a well recognised strong oxidation catalyst, can favour the formation of larger amounts of SO_3 (or SO_2 -surface oxygen complexes with similar nature). This particular behaviour favours the formation of stronger bonds between SO_2 and the carbon and in this way influences the value of the SO_2 molar heat on carbon. The behaviour of the carbon containing Fe appears, instead, to be markedly influenced by the amount and by the nature of the surface oxygenated groups present on the carbon itself. This particular behaviour could be related to the existence of real interactions between Fe and the oxygenated groups with acidic characteristics, with the consequent larger participation of the Fe itself in the reaction between SO_2 and surface oxygenated groups. Also for Cr and Ni a mechanism quite similar to that described for Fe can be hypothesised, even if the overall results related to their presence appear somewhat different, probably closely related to the dimensions and the activity of these elements.

By submitting the carbons A° and B° to cycles of adsorption and desorption of SO_2 we can observe that ΔH_{ads} values decrease with the increase in the number of cycles themselves. In particular, carbon A° shows a more marked decrease of ΔH_{ads} values (see Figure 2).



The general decrease of the ΔH_{ads} values (shown by both the carbons) in the adsorption/desorption cycles could be related to the overall process of thermal destruction of part of the surface oxygenated groups in the desorption step (carried out at 360°C in N_2 flow). Naturally, this thermal destruction is more marked for the surface oxygenated groups with acidic nature. From these results it can be understood that ΔH_{ads} value can vary in a different way for the two carbon samples A°

and B°; in particular, A° carbon shows a more marked decrease of ΔH_{ads} with the increase in the number of cycles. Carbons A and B (supporting the metals) show a different variation of ΔH_{ads} in relation to the type of carbon, to the type of metal (and its percentage) and to the number of the adsorption/desorption cycles. Figure 3 shows, for example, the behaviour of A sample supporting Fe.

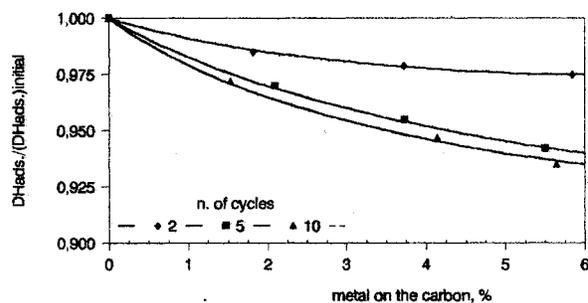


Fig. 3 - SO_2 ads./des. cycles on A sample supporting Fe

From all the obtained data (not reported as detailed plots in this short text) it is possible to note that supported samples A and B show, during the said cycles, a variation of ΔH_{ads} value rather less pronounced than that previously observed for the A° and B° samples. The percentage of oxygen remaining on the carbons supported by the metals, after the tenth cycle of adsorption/desorption, is in general higher than the correspondent amount remaining in the same conditions on the non supported carbons (A° and B°). This behaviour seems due to a partial process of stabilisation of the surface oxygenated derivatives by interaction with the metallic derivatives present on the carbons with the consequent decrease and/or inhibition of their thermal destruction process. Furthermore, the B supported carbons themselves show a variation of ΔH_{ads} that is globally less marked than that of the A supported carbons.

In conclusion, it is shown that, in the cyclic process of adsorption and desorption of SO_2 (mixed with N_2) on surface oxidated carbons, the type and the respective percentage of supported metals play a very important role. They can limit and reduce the effects connected with the degradation of the carbonaceous matrix due to the high temperature of the desorption step. The phenomenon described appears to be relevant for carbons with surface oxygenated acidic characteristics (at least in the experimental conditions used in this investigation).

References

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