

# PHYSICO-CHEMICAL PROPERTIES OF ACTIVATED CARBONS MODIFIED BY ORGANIC FUNCTIONAL GROUPS

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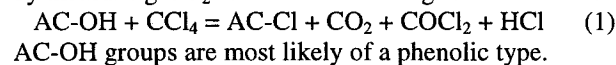
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## Introduction

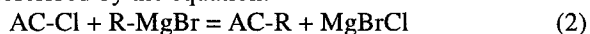
Activated carbons (AC) as catalyst supports in catalytic organic reactions offer potential advantages over traditional carriers such as SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. AC have unrivaled adsorption capacity in organic molecules. They can also stabilise transition metals in low valence states. Chemical modification of carbon surface, in particular, hydrophobisation by attaching nonpolar organic radicals may improve their performance in reactions involving nonpolar species and solvents, as well as increase selectivity of catalysis.

## Experimental

Made in-house polymer-pyrolysed mesoporous AC (SCN), charcoal from fruit stones (KAU), and silica gel (Kieselgel 100, Merck) were modified as follows: (i) treatment with vinyltrimethoxysilane (VTMS) in toluene at 125°C; or (ii) chlorination with CCl<sub>4</sub> followed by the reaction with a Grignard reagent. The Grignard reagent was prepared by adding 4-bromo-butene-1 (2 mmol per gram of adsorbent) in Na-dried ether to an excess of Mg turnings (4 mmol per gram of adsorbent). Chlorination was performed by treatment with CCl<sub>4</sub> vapour in N<sub>2</sub> at 300–400°C for 3 h. Details of these procedures have been given in [1]. Before chemical modification, all AC were heated at 300°C in inert atmosphere for 2 h until no more CO<sub>2</sub> evolution was detected in IR spectra. Kinetics of AC chlorination with CCl<sub>4</sub> was studied using FTIR technique by measuring CO<sub>2</sub> formation according to the reaction:



AC-OH groups are most likely of a phenolic type. Further surface treatment with the Grignard reagent can be described by the equation:



where R: CH<sub>2</sub>=CH-CH<sub>2</sub>-CH<sub>2</sub>-. Surface area and pore size distribution were determined with SA 3100 analyzer from N<sub>2</sub> adsorption – desorption data. Thermogravimetric (TG) analysis and differential scanning calorimetry (DSC) were carried out simultaneously using STA 409C. The sample was heated rapidly (10°C/min) under a flow of nitrogen from 20°C to 1000°C. Infrared spectra were recorded using a Perkin Elmer 1720 FTIR. The results obtained for AC were compared to those for silica gel [1].

## Results and Discussion

Some surface properties of initial and modified AC are given in Table 1. Both surface area and micropore volume decrease on modified AC (Fig. 1 and Table 1). From TG and DSC data it follows that VTMS forms a separate phase inside the pores and it is weakly bound to the carbon surface (Fig. 2 and 3). A sharp loss of mass in AC samples takes place at 375°C that is 170° lower than for silica gel. Unlike silica gel that shows one maximum according to DSC data, there are two maxima dQ/dt for AC (Fig. 3). The first maximum ca. 375°C probably corresponds to the decomposition of VTMS, and the second one at 450°C reflects polymerization of vinyl groups on carbon surface.

Relatively low activation energy (20 kJ/mol) of the rate of reaction (1) for both AC and silica gel shows that interaction of CCl<sub>4</sub> with surface OH-groups involves free radicals. TG analysis of silica and AC modified via route (ii) allows us to suggest that the mass loss of AC samples occurs due to the desorption of butene (Fig. 4). The mass loss corresponds to the evolution of 6.0 · 10<sup>-4</sup> mol of butene per g of carbon. The number of chlorinated surface OH-groups was about 7.0 · 10<sup>-4</sup> mol/g. These calculations suggest that hydrophobisation of AC via reactions (1) and (2) proceeds with a high yield.

## Conclusions

It has been shown that hydrophobisation of AC can be achieved by treatment of the surface phenolic groups with vinyltrimethoxysilane or by treatment of chlorinated phenolic groups with a Grignard reagent.

## References

1. Clark JH, Butterworth AJ, Tavener SJ, Teasdale AJ., Barlow SJ, Bastock TW and Martin K. Environmentally friendly chemistry using supported reagent catalysts: chemically-modified mesoporous solid catalysts. *J.Chem. Tech. Biotechnol.* 1997;68:367-376.

## Acknowledgements

Research sponsored by INTAS-Ukraine Programme, grant 95-141.

**Table 1.** Surface area and micropore volume of activated carbons

Sample	BET Surface Area (m <sup>2</sup> /g)	Micropore Volume (cm <sup>3</sup> /g)
SCN	820	0.28
SCNvtms	740	0.25
SCNbutene	750	0.26
KAU	870	0.36
KAUvtms	710	0.22

