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CHEMICAL MODIFICATION OF ACTIVATED CARBONS

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Abstract

Mesoporous activated carbons and silica gel (Kieselgel 100, Merck) were modified as follows: (i) treatment with vinyltrimethoxysilane; or (ii) chlorination with CCl_4 followed by the reaction with a Grignard reagent. Modification of silica gel was proved by methods FTIR, NMR-^{13}C and element analysis on carbon. The chemical modification of coals by alkans and olefins was supported by comparison of results of thermogravimetry for modified coals and modified silica gels. Polymerization of vinyl groups on carbon surface is shown by methods thermogravimetric analysis and differential scanning calorimetry.

Keywords: activated carbons, chemical modification, differential scanning calorimetry, thermogravimetry

Introduction

Activated carbons (AC) as catalyst supports in catalytic organic reactions offer potential advantages over traditional carriers such as SiO_2 and Al_2O_3. AC have unrivaled adsorption capacity towards organic molecules. They can also stabilize transition metals in low valence states. Chemical modification of carbon surface, in particular, hydrophobization by attaching non-polar organic radicals may improve their performance in reactions involving non-polar species and solvents, as well as increase selectivity of catalyst.

Experimental

Made in-house polymer-pyrolyzed mesoporous AC (SCN) and charcoal from fruit stones (CAU) were modified as follows: before chemical modification by organic functional groups all AC were oxidized by hydrogen peroxide (500 ml of 15% hydrogen peroxide was added to 10 g of AC and the mixture was refluxed for 1 h. After that coal was filtered off, thoroughly washed with water and dried on air). The sample of AC, obtained by the

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method described above, was decarboxylated by heating at 450°C in inert atmosphere for 2 h till no more CO_2 evolution was detected in IR spectra. Total CO_2 was equal 0.4–0.7 mmol g^{-1}. For reducing ketonic groups contents on coal surface all AC were reduced by sodium borohydride (0.5 g of sodium borohydride was added to the stirred suspension of 5 g CAU in 100 ml of absolute methanol. The mixture was stirred for 4 h at room temperature. Then 100 ml of water was added and the obtained mixture was boiled for 10 min and cooled. Following filtration and washing with water gave 5 g of coal with hydroxylated surface). The last stage of coals and silica gel (Kieselgel 100, Merck) hydrophobization was carried out by two methods: (i) treatment with vinyltrimethoxysilane (VTMS) in toluene at 125°C; or (ii) chlorination with CCl_4 followed by the reaction with Grignard reagent. The Grignard reagent was prepared by adding 4-bromobutene-1 or *n*-butyl bromide (2 mmol per gram of adsorbent) in Na-dried ether to an excess of Mg turnings (4 mmol per gram of adsorbent). Details of these procedures have been given in [1].

Chlorination was performed by treatment with CCl_4 vapour in Ar at 500°C for 1 h. Kinetics of AC chlorination with CCl_4 was studied using FTIR technique by measuring CO_2 formation according to the reaction:

$$\mathrm{AC{-}OH{+}CCl_4 \rightarrow AC{-}Cl{+}CO_2{+}COCl_2{+}HCl} \tag{1}$$

followed by the reaction with a Grignard reagent:

$$\begin{gathered}\mathrm{AC{-}Cl{+}CH_2{=}CH{-}CH_2{-}CH_2{-}MgBr \rightarrow} \\ \mathrm{AC{-}CH_2{-}CH_2{-}CH{=}CH_2{+}MgBrCl}\end{gathered} \tag{2}$$

Surface area and pore size distribution were determined with SA analyzer from C_6H_6 and N_2 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^{-1}) under a flow of nitrogen from 20 to 1000°C. IR spectra were recorded using. Perkin Elmer 1720 FTIR.

Results and discussion

Hydrophobization of carbon surface has been obtained by elimination of carboxyl, carbonyl and hydroxyl groups. Presence of these groups determined by IR-spectroscopic method [2]. The reduction of carbonyl groups of quinone type after treatment of coal with $NaBH_4$ was proved to vanishing peak of absorption on frequency 1585 cm^{-1} [3, 4]. The element analysis on chlorine has shown that 4 mmol g^{-1} of chlorine is contained on surface of the coal after treatment with CCl_4. Some surface properties of initial and modified AC are given in Table 1.

Both surface area and micropore volume decrease on modified AC. TG and DSC data show that VTMS forms a separate phase inside the pores and it is weakly bound to the carbon surface. A sharp loss of mass in AC samples takes place at 375°C that is 170°C 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. 1).

Table 1 BET specific surface area and micropore volume of initial and modified activated carbons

Sample	Specific surface area, S/m^2 g^{-1}	Micropore volume, V/cm^3 g^{-1}
Activated carbon SCN	820	0.28
SCN, modified by VTMS	740	0.25
SCN with grafted 1-butene	750	0.26
Activated carbon CAU	870	0.36
CAU modified by VTMS	710	0.22

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^{-1}) of the reaction (1) for both AC and silica gel shows that the interaction of CCl_4 with surface OH-groups involves free radicals. TG analysis of silica and AC modified via route (ii) with 4-bromo-

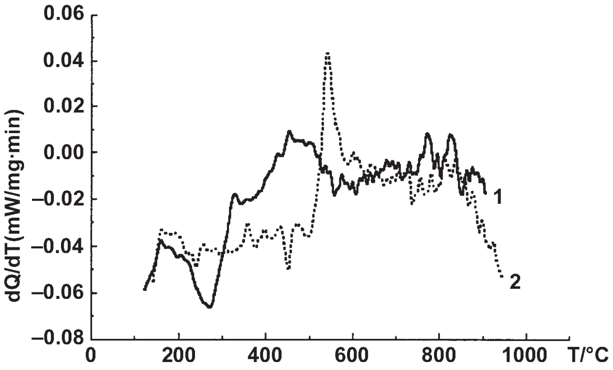

Fig. 1 Differential scanning calorimetry of carbon SCN (1) and silica gel (2) modified by vinyltrimethoxysilane

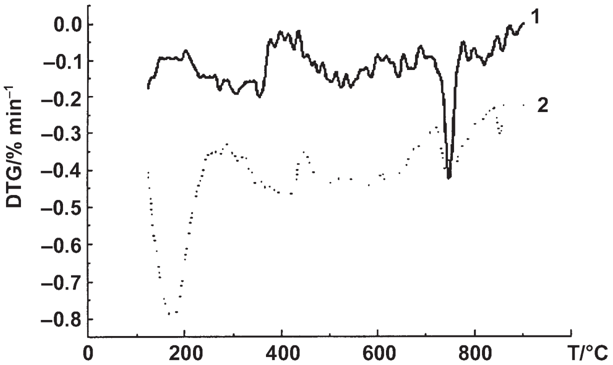

Fig. 2 Thermogravimetric analysis of chlorinated silica gel (1) and chlorinated carbon SCN (2) both treated by Grignard reagent (1-butenemagnesium bromide)

butene-1 allows us to suggest that the mass loss of AC samples occurs due to the desorption of butene (Fig. 2).

The mass loss corresponds to the evolution of 0.8 mmol of butene per g of carbon and SiO_2. It is interesting to note that the dependence of changing of mass with temperature both for silica gel and for coal are very similar. There are three maxima on these curves (near 400, 600 and 750°C).

The decomposition of organic compounds on the surface at high temperatures (600–800°C) indicates on formation of polymeric film. TG analysis of AC modified via route (ii) with *n*-butyl bromide with mass-spectrometric registration shows two peaks at low temperatures for butyl and ethyl radicals (135 and 225°C).

Conclusions

It is shown that hydrophobization of activated carbons can be achieved by treating the surface phenolic groups with vinyltrimethoxysilane or by treating the chlorinated phenolic groups with a Grignard reagent.

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