SYNTHESIS AND STRUCTURAL/ADSORPTION CHARACTERISTICS OF UNMODIFIED AND MODIFIED HYBRID CARBON/MINERAL ADSORBENTS

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Abstract. Several series of pyrocarbon/silica adsorbents were prepared using fumed oxides of different specific surface areas, and mesoporous silica gel Si-100, as inorganic matrices. Different synthetic and natural polymers as well as glucose were used as carbon precursors. Solutions of phosphoric acid at various concentrations were utilized to prepare functionalized hybrid carbon-silica adsorbents. Nitrogen, p-nitrophenol and Cd(II) adsorption isotherms as well as AFM, XRD and XRF methods were used to estimate the structural and adsorption characteristics of the adsorbents.

Keywords: carbon-silica adsorbents, fumed silica, pyrolysis, glucose, starch, cellulose, phosphoric acid, polyvinylpyrrolidone, polystyrene, structural characteristics.

1. Introduction

Carbon/silica adsorbents with pure or functionalized carbon deposits, or functionalized silica surfaces, are of interest for many purposes. An improvement of the structural and adsorption characteristics of carbon deposits is desirable.¹ Pyrocarbon deposits formed by carbonization of low-molecular organic precursors (dichloromethane, cyclohexene, alcohols, acetylacetone, acenaphthene, etc.) at oxide surfaces typically possess a low inner specific

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surface area. The outer surface of these deposits is the main contributor to the specific surface area of the pyrocarbon.\textsuperscript{1,3} For many applications of carbon or carbon-mineral adsorbents, appropriate contributions of both nano- and mesopores are necessary.\textsuperscript{1,4} This problem is difficult to solve in the case of hybrid carbon-mineral adsorbents, because the pyrocarbon synthesis results in deposition of practically nonporous carbon particles (similar to carbon black) onto the support. Additionally, grafted carbon particles can block a significant portion of the pores on the substrate, particularly nanopores. Porous matrices with silica or other oxides, and grafted porous carbon particles, can provide a very wide spectrum of adsorption properties for polar and nonpolar adsorbates.\textsuperscript{5-7} The aim of this paper is to prepare hybrid adsorbents with functionalized carbon deposits possessing inner porosity, and to investigate the properties of these complex materials in gaseous (nitrogen adsorption) and liquid (p-nitrophenol and metal ion adsorption) media.

2. Experimental

2.1. PREPARATION OF ADSORBENTS

A series of fumed silicas A-150, A-200, A-300, and A-380 (Institute of Surface Chemistry, Kalush, Ukraine), OX-50 (Degussa), and silica gel Si-100 (Merck) were used as the initial oxide matrices. Starch (St), methylcellulose (MC), polyvinylpyrrolidone (PVP), polystyrene (PS), and cellulose (C), were deposited onto fumed silicas matrices and carbonised under dynamic conditions to prepare carbosil samples (Tables 1 and 2). Before carbonization polymers were deposited from aqueous solution with subsequent drying of the residue at 320-335 K (Table 1). Sample C/A\textsuperscript{A380-PVP20-1} was prepared using a mixture of silica and PVP/ethanol stirred and heated at 313 K for 5 h in a reactor, and sample C/A\textsuperscript{A380-PVP20-2} was prepared using silica and 25 wt.% solution of PVP in water/ethanol (1:1) treated in a ball mill for 5 h. Precursors of samples shown in Table 2 were prepared by deposition of starch (St) and cellulose (C) by mechanical mixing of weighted portions of A-200 and polymer, and saturated with water vapour in a dessicator for 48 h. Glucose was deposited onto porous silica Si-100 and carbonized under dynamic (rotary reactor, R) or static (autoclave, A) conditions to obtain carbosil samples (Table 3). Selected samples from the carbosil series were modified by phosphorus compounds using phosphoric acid solution before carbonization (Table 4).

Carbonization of grafted polymers and glucose (Tables 1-4) was performed under dynamic conditions in a flow rotary quartz reactor (with a nitrogen stream of 100 cm\textsuperscript{3}/min). The sample was heated from 293 K to 773 K for 2 h, then kept at 773 K for 5 h, and finally cooled to 293 K for 1 h. A series of carbosil samples (Table 3, labelled A) was carbonized in a steel autoclave.