

STABILITY AND REACTIVITY OF THE ACTIVE ASSEMBLIES IN MODIFIED GRAPHITES CHARACTERIZED BY TPD AND TPH

L. Chmielarz¹, R. Dziembaj², J. Jamrozik¹, I. Kargulewicz^{1} and W. Makowski¹*

¹Faculty of Chemistry, Jagiellonian University, Cracow

²Regional Laboratory for Physico-Chemical Analyses and Structural Studies, Jagiellonian University, Cracow, Poland

(Received January 22, 1997; in revised form June 9, 1998)

Abstract

Synthetic graphites, as prepared and modified by sulphonation or acetylation, were doped by Fe-, Co-, Ni- and Ca-nitrates. Temperature Programmed Desorption (TPD) and Temperature Programmed Hydrogenation (TPH) were applied to characterize thermal stability and reactivity of the active assemblies formed on the matrix surface. The functional groups lowered the reactivity of the graphites. Thermally less stable carboxylic groups decomposed with formation of secondary groups giving more reactive material. Fe containing as well as sulphonated graphites showed a much lower reactivity than the others. Synergistic effects of Co/Ca and Ni/Ca were confirmed in the graphite materials.

Keywords: active assemblies, carbon materials, hydrogenation, synergistic effects, synthetic graphite, TPD, TPH

Introduction

The 3-D macromolecular structure of condensed aromatic and hydroaromatic layers joined together by aliphatic and etheric bridges has been accepted as the model of natural coals [1]. There are also smaller organic molecules encapsulated inside the empty spaces of the loose macromolecular structure. These molecules can undergo decomposition and/or desorption during thermal treatment and reactions, or they may be extracted during the processes with organic solvents, e.g. liquefaction [2]. In the course of coal pyrolysis or hydrolysis, the remaining organic molecules can react easily, masking the specific reactivity of the 3-D macromolecular structure. Moreover, the reactivity depends strongly

* The present address: Faculty of Foundry, Academy of Mining and Metallurgy, Cracow, Poland

on the kinds and number of functional groups and heterocyclic rings present in the natural coals [3]. For these reasons the studies on defined graphite materials, as model compounds, seems to be of great value to characterize the specific reactivity of 3-D macromolecular structure in abstraction from the properties of smaller molecules.

In our previous paper [4] the synthetic electrode graphite modified by Fe-, Co-, Ni- and Ca-nitrates was used as a model material in studies of the catalytic hydrogenation of carbon. In these studies the synergistic effects of Ca additives as well as of CO₂ and O₂ preadsorption were found.

This was the impulse to implant functional groups into pure and inactive synthetic graphite. The obtained material should allow verifying the introductory hypothesis that metal-functional groups are the active assemblies that catalyze the hydrogenation of graphite matrix more efficiently than metal catalysts alone. The temperature-programmed methods, desorption (TPD) and hydrogenation (TPH), were applied as convenient tools to characterize the thermal stability and reactivity of these assemblies.

Experimental

Samples

All the samples were prepared from pure synthetic graphite powder manufactured by Polgraph SA, Nowy Sącz, Poland. The original graphite contained only very small amounts of metal impurities (Ti:66.0 ppm, Si:37.1 ppm, V:12.6 ppm, Ca:6.0 ppm, other metals:below 2.0 ppm). The total ash content was equal to 375 ppm and the BET surface area was about 100 m² g⁻¹.

The original material was modified in order to introduce the surface functional groups into graphite. One part of the original material was treated with acetyl chloride in CCl₄ solution, in presence of AlCl₃ as the catalyst (like the standard Friedel-Crafts acetylation). Then it was washed thoroughly with distilled water. Another part of graphite was sulphonated in reaction with concentrated H₂SO₄ at temperature 180–190°C for 3 h. Then it was cooled in ice, washed thoroughly with distilled water and dried in vacuum.

Metal catalysts (Ni, Co, Fe, Ca) were introduced by incipient wetness (dry impregnation) technique using methanol solution of nitrates. Then all the samples were dried for 1 h at 120°C. Concentrations of the metal catalysts in the samples were equal to 0.5 wt%. The surface area of the impregnated samples decreased to about 2 m² g⁻¹, probably due to closing of pores by metal nitrates during impregnation.

Experiments

Thermal stability and reactivity of the samples were investigated using the microreactor system presented in Fig. 1. The sample (about 50 mg) was placed in