



Mesoporous alumina infiltrated with a very thin and complete carbon layer



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ABSTRACT

The mesoporous composite material “carbon-infiltrated alumina” was synthesized via chemical vapor infiltration of pyrocarbon in a porous alumina (γ -Al₂O₃) matrix. The process was carried out under continuous flow conditions at 650–800 °C and 1 bar of the reaction gas mixture containing ethylene (5 or 15 vol. %) and Ar (balance). A number of the synthesis parameters were examined to determine the conditions that are necessary for the formation of a thin but complete carbon layer over the alumina surface. A special acquisition mode of X-ray photoelectron spectroscopy was suggested and validated for the fast and reliable testing of completeness and uniformity of the carbon deposits on the outer alumina surface. Low-temperature N₂ adsorption and electron microscopy were used to study the porous structure of γ -Al₂O₃ after high-temperature pretreatments and the carbon-infiltrated materials as well as the same samples after treatment with an aqueous hydrochloric acid solution. As a result of these studies, the mesoporous carbon-infiltrated aluminas with an extremely thin (1–1.5 carbon layers) and complete carbon coating, high electrical conductivity and excellent endurance in acidic medium have been prepared.

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1. Introduction

Various porous carbon materials have attracted a growing attention as the promising supports for commercial metal catalysts. Among evidently useful properties of such materials are, in particular, the chemically inert nature of their surface, which can be easily functionalized, the weak metal-support interaction as well as good electrical and thermal conductivity. However, most of the commercially available carbon materials are microporous, which prevents their application in catalytic transformations of large molecules. Mesoporous structure significantly facilitates the diffusion transfer, but most of the known mesoporous carbons have poor mechanical strength and wear resistance or low surface area. To combine the useful properties of mesoporous carbon-based supports with the enhanced mechanical strength, an obvious yet challenging approach to the synthesis of such materials was suggested. The idea was to synthesize a composite material via coating both the inner and outer walls of the chosen mesoporous matrix

with a continuous pyrolytic carbon layer [1–17]. Among the suitable matrices, alumina is the most widely used support for commercial catalysts [18–20]. It was supposed that the novel material, carbon-coated alumina (C/Al₂O₃, CCA), would inherit the advantages of both the alumina (its perfect mechanical strength and mesoporous texture) and carbon. According to the literature, there is a synergistic effect between the alumina and carbon phases in CCA materials [6–8]. This effect becomes more pronounced when carbon completely covers the alumina matrix to form a thin and uniformly dispersed surface layer. Vissers et al. [4] used CCA as a support for cobalt sulfide hydrodesulphurization catalysts and achieved a threefold increase in the catalytic activity as compared to Co/Al₂O₃. According to the authors, this fact indicated that the intermediate carbon layer reduces or eliminates the strong Co–alumina interaction. The work [7] highlights a high antibacterial efficiency of silver nanoparticles deposited over carbon-coated alumina in drinking water purification. The significantly higher catalytic activities were obtained in hydrazine decomposition when CCA materials were used as the supports for molybdenum carbide, nitride and phosphide catalysts instead of conventional alumina [8]. With a monolayer coating of carbon on alumina, the CCA supported catalysts showed the best hydrazine decomposition

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performance. When the carbon deposit was in either sub-monolayer or multilayer form, the catalysts demonstrated relatively low activities due to strong metal-support interaction or low dispersion of metal on the support.

Two main approaches to the synthesis of carbon-coated materials were reported. Alumina materials completely and uniformly coated with carbon were obtained by a two-step procedure [8–13] that included the impregnation of the alumina matrix with a strongly diluted solution of a suitable organic moiety (sucrose [11], grafted 4,4-methylenebis-(phenylisocyanate) [12], polyurethane [13], etc.) with subsequent pyrolysis of the carbon precursor at 600–1250 °C. To obtain a desired amount of pyrocarbon on the matrix surface, the impregnation and carbonization steps were repeated. An alternative approach to CCA synthesis is based on pyrolysis of light hydrocarbons on the alumina surface at temperatures above 400 °C [4–8,14,15]. According to the current terminology, the coating process that includes the decomposition of gas phase precursor on hot bulk surfaces is called the chemical vapor deposition (CVD), while in the case of decomposition on porous substrates (fibrous carbon felts and bundles, carbon nanotubes, *e.g.*) this is the chemical vapor infiltration (CVI) [21–24]. The benefits of pyrocarbon infiltration in mesoporous alumina for the synthesis of CCA composites are obvious: the process is technologically simple (a single-step procedure), the necessary reagents are available in abundance and at affordable prices. However, the CVI process has some drawbacks: (1) it is a long-term process, (2) as the mechanism of CVI/CVD reactions on the surface of porous substrates is very complex, it is a challenge to reveal conditions ensuring the complete and continuous coating of alumina surface with a thin layer of pyrolytic carbon [22,23,25]. Herein we report that the mesoporous carbon-infiltrated alumina composite with a very thin (1–1.5 carbon layers) and uniformly dispersed carbon coating was obtained by CVI of pyrocarbon in the γ -Al₂O₃ matrix at 750–800 °C using the C₂H₄/Ar gas feedstock (1 bar). To the best of our knowledge, a very thin and perfect carbon layer has never been achieved so far via light hydrocarbons CVI in porous alumina.

2. Experimental

2.1. Materials

The low-surface γ -Al₂O₃ (AOC 63-14, Russia) with the specific surface area, S_{BET} , of 140 m² g⁻¹, total pore volume, V_{S} , of 0.305 cm³ g⁻¹ and true density, ρ_{Al} , of 3.52 g cm⁻³, which was calcined at 700 °C (4 h), was used as a matrix to prepare CCA composites. The total content of transition metal impurities in the material did not exceed 0.01 wt.%. TEM images show that mesoporous γ -Al₂O₃ clearly revealed a disordered mixture of lamellar nanocrystallites and long fibrous nanoparticles (Fig. 1) agglomerated into aggregates with the size up to 1 μm . The mesoporous space of parent alumina is the inter-particle space with the average pore diameter of 8.7 nm, which is typical of the “lamellar” or “prismatic” low-surface γ -Al₂O₃ [26]. Other characteristics of parent γ -Al₂O₃ are given in Section 3.

Granular γ -Al₂O₃ with the grain size of 100–200 μm was used in all the experiments. The commercial gases C₂H₄ and Ar were of >99.99% purity. Air was purified from traces of H₂O, CO₂ and organic contaminations by passing through a BIGAS cleaner system before introduction into the reactor.

2.2. Estimation of the required amount of carbon to be deposited on the γ -Al₂O₃ surface

On the basis of the area of single graphene ring in the perfect graphene, 0.052 nm², the amount of elementary carbon sufficient to form a monolayer coverage was estimated as 0.07 g per 1 g of γ -Al₂O₃ with $S_{\text{BET}} = 140 \text{ m}^2 \text{ g}^{-1}$ (or ~7 wt.% C in CCA). However, taking into account the curvature of the pore surface and a very complicated mechanism of hydrocarbons CVI in porous solids, it is unlikely that the carbon deposition in alumina granules would form the perfect graphene. Thus, a more realistic estimation should employ the density of pyrolytic (turbostratic) carbon, $\rho \sim 2 \text{ g cm}^{-3}$. In this case, the adequate amount of carbon for a complete carbon

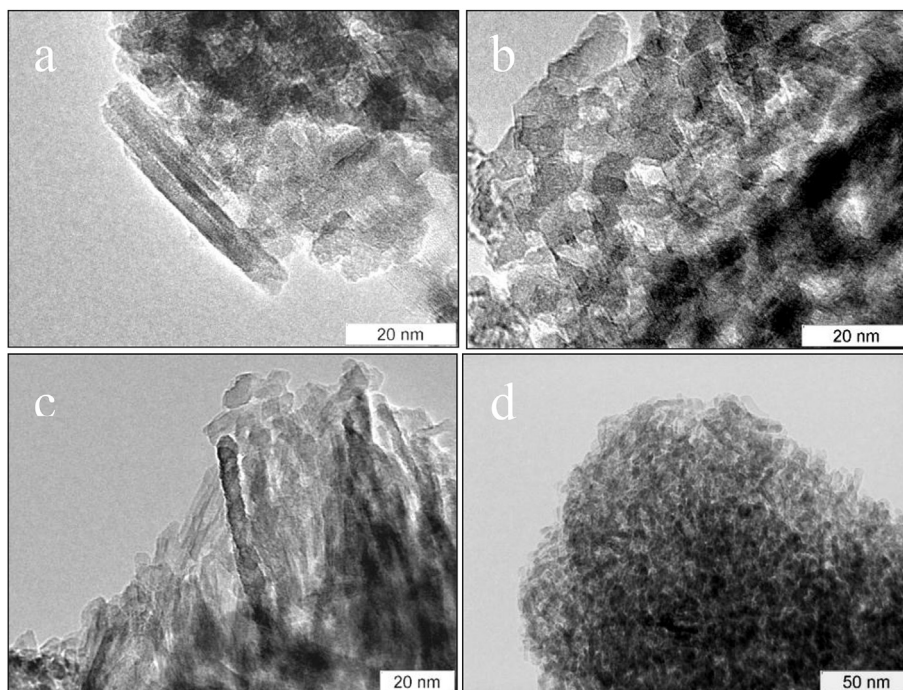


Fig. 1. TEM images of γ -Al₂O₃: faceted nanocrystallites (a, b) and long fibrous nanoparticles (c); the aggregate of primary particles (d).

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