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Effect of hydrogen accumulation on the surface of Ni-containing nanodiamond catalysts

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The effect of active hydrogen accumulation on the surface of the Ni-nanodiamond catalysts has been demonstrated. Lower bound estimation of the hydrogen capacity is 1.3 wt%. Oxygen-containing functional groups on the nanodiamond surface are presumably responsible for the hydrogen accumulation.

Carbon materials are of interest for hydrogen storage. Activated carbon can physisorb a large amount of hydrogen because of its high specific surface area but only at low temperatures (< 100 K).[1,2] At higher temperatures, hydrogen rapidly desorbs even despite of a large amount of micropores.[3,4] However, many applications require materials operating at room or higher temperatures (*e.g.*, catalysis). This possibility has got unleashed with the introduction of synthetic carbon nanomaterials such as fullerenes, graphens, carbon nanotubes and nanofibers.[1,5,6] It is likely that hydrogen storage is facilitated by H_2 dissociation on transition metals (Fe, Co, Ni, *etc.*), which are used as catalysts for carbon materials synthesis and are usually present in nanomaterials. The presence of a metal allows one to explain contradicting data on the hydrogen storage capacity of various carbon materials.[1] The hydrogen is proposed to 'spill over' from the metal onto the carbon support; that is, H_2 is dissociatively adsorbed on the metal particles and the resulting hydrogen atoms diffuse to the carbon support.[7]

Note that oxidation also significantly affects the hydrogen storage capacity of a material. Oxidizing treatment of activated coals increases the amount of oxygen-containing functional groups on the carbon surface, which raises hydrogen storage capacity.[8,9] Similar research has been performed for Ni-containing carbon materials.[10–14] Zubizarreta *et al.*[10,11] demonstrated that the oxidation of carbon xerogel and carbon nanospheres makes the distribution of Ni particles more homogenous and enhances interactions between Ni nanoparticles and the carbon support. Landau *et al.*[12] reported the effect of surface oxygen-containing groups over multiwall carbon nanotubes on the stabilization of Ni particles. Zielinski *et al.*[14] studied the effect of Ni precipitation method on Ni-activated carbon catalysts. These catalysts easily desorbed hydrogen at room temperature, whereas the hydrogen treatment at 350 °C led to the reversible hydrogen chemisorption on the activated carbon surface. Meanwhile, it was assumed that the formation of C–H bonds at 500 °C is responsible for hydrogen storage, *e.g.*, in the case of Ni- and Co-graphite composites containing up to 20–80% metal.[15]

Therefore, the interaction of active hydrogen formed by the dissociative adsorption on Ni-containing carbon catalysts has not been fully understood yet.

The goal of this work was to investigate the hydrogen storage potential of Ni-containing carbon catalysts with various structures and surface chemical compositions[†] at elevated temperatures. The reaction of acetylene hydrogenation was used because a catalytic method allows one to determine directly the amount of active (*i.e.*, readily available for chemical reactions) hydrogen.[‡]

The specimens obtained differ significantly in the specific surface areas: 284 $m^2\ g^{-1}$ for nanodiamond (ND), 196 $m^2\ g^{-1}$ for sugar carbon (C_{sug}) and 22 $m^2\ g^{-1}$ for synthetic diamond (D_{syn}). The elemental analysis of the carbon supports by X-ray fluorescence showed that the amount of metal impurities was negligible (the iron content was ~0.1%, meanwhile the amount of Ti, Cr and Cu was smaller than 0.02%).

According to SEM and TEM data, the ND consists of aggregates made of nanometer-sized diamond particles; their size is about 5–6 nm. Nickel particles are 10–20 nm in diameter, which is in agreement with the average diameter derived from X-ray powder diffraction data. Synthetic diamond and sugar carbon consist of agglomerates 0.1–1 μm in diameter.

Acetylene hydrogenation in the flow of hydrogen demonstrates that all of the test catalysts are active. They generate a sufficient amount of active hydrogen species for full acetylene conversion at temperatures higher than 250 °C (Figure 1, curves *1*–*3*). The activity of the Ni/ND catalyst is the highest; that is, full acetylene conversion is achieved at the lowest temperature in comparison to the catalysts based on carbon and synthetic diamond.

However, among these catalysts, only Ni/ND was active in the hydrogenation of acetylene by preadsorbed hydrogen (Figure 1, curve *4*). This fact indicates that carbon properties are essential for hydrogen accumulation because, in the opposite case, all of the

† The following catalyst supports were used: UDA-SF detonation nanodiamond (ND) from the Almaznyi Tsentr Ltd, Russia; carbon obtained by sugar carbonization at 400 °C in air (C_{sug}); polydispersed synthetic diamond ('Dalan') obtained from a mixture of explosives and graphite from Chernogolovka, Moscow region, Russia (D_{syn}).

The catalysts containing 2.5 wt% Ni were obtained by the wet impregnation of supports with an aqueous solution of nickel(II) formate using a procedure described elsewhere.[16] Catalytic properties were studied by an impulse microcatalytic method.[17]

‡ The catalyst (0.06 g) was placed in a reactor (a quartz tube 15 cm long and 0.5 cm in diameter). The reactor was positioned in a sealed stainless steel outer tube, which was placed in a resistive heater. A hydrogen flow of 30 ml min^{-1} went through the reactor. Acetylene probes (impulses) of 1 ml (0.04 mmol) were introduced every 20–30 min. Reaction products were analyzed on a Chrom-5 chromatograph equipped with a flame-ionization detector and a column packed with Porapak N (1.3 m long and 5 mm in diameter; temperature, 70 °C). Hydrogen preadsorption was performed using the same apparatus. Catalyst specimens were held in the hydrogen flow at 300 °C for 4 h. Then, hydrogen as a carrier gas was changed to nitrogen with a flow rate of 30 ml min^{-1}, and impulses of acetylene were introduced. The hydrogenation reaction occurred only by the preadsorbed hydrogen.

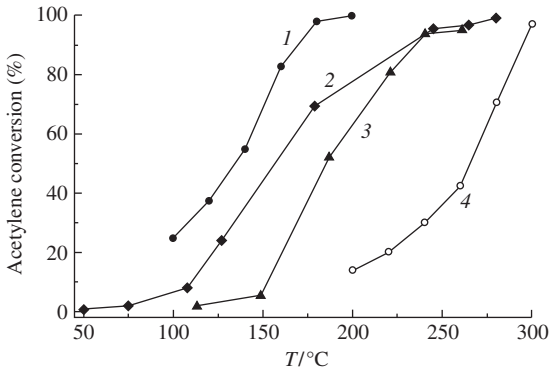

Figure 1 Temperature dependence of acetylene conversion in the flow of hydrogen on (*1*) Ni/ND, (*2*) Ni/D_{syn}, (*3*) and Ni/C_{sug} catalysts; (*4*) acetylene hydrogenation by preadsorbed hydrogen on the Ni/ND catalyst in a nitrogen flow.

catalysts are expected to be of similar activity. Using this catalyst, full conversion was achieved at 300 °C. At this temperature, the hydrogen adsorbed was completely consumed after 20 impulses of acetylene, which allowed us to make a lower boundary estimation of the hydrogen storage capacity as 1.3 wt%. Note that the duration of the reaction was ~6 h, *i.e.*, hydrogen desorption was not accounted. The catalytic measurements vividly reveal the capacity of the material to store active (*i.e.*, one available for chemical reactions) hydrogen.

The catalyst surface was investigated using diffusion reflectance IR spectroscopy (Figure 2). There are bands of carboxyl, carbonyl, ether and anhydride oxygen-containing groups in the regions of 1700–1780 and 3700 cm^{-1}. On the surface of both ND and synthetic diamond, there are oxygen-containing groups, but overall absorbance for ND is significantly higher, which is likely to be caused by larger surface oxygen content. The spectra of the diamond materials have an absorption band at ~1087 cm^{-1}, which is attributed to C_{sp^3}–O stretchning vibrations. It is likely that these oxygen groups on the Ni/ND surface act as active hydrogen acceptors.

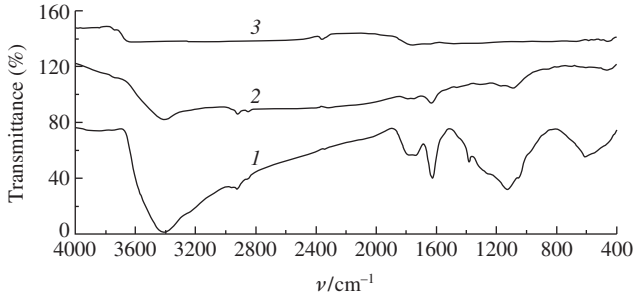

Figure 2 Diffuse reflection IR spectra of (*1*) ND, (*2*) D_{syn} and (*3*) C_{sug}. Spectra *2* and *3* are doubled.

Thus, the effect of active hydrogen accumulation on the Ni/ND surface has been found. A comparative study of the diffuse reflection spectra allowed us to assume that the adsorption of hydrogen likely depends on the presence of oxygen-containing functional groups on the ND surface.

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