



The role of structure and surface chemistry of carbon nanomaterials in catalytic conversion of 1,2-dichloroethane



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ABSTRACT

Catalytic activity of several graphene- and diamond-based carbon nanomaterials was compared in the reaction of the 1,2-dichloroethane (DCE) conversion using the impulse microcatalytic method. Only nanodiamonds and Ni-doped nanodiamonds were active in the reaction. A comparison of XRD, XPS, DRIFTS, and BET studies suggested that nitrogen or oxygen-containing groups could be responsible for the catalytic activity in the DCE reaction. However, nitrogen-doped carbon nanoflakes, which contain much more nitrogen-containing groups, showed no activity in the DCE conversion; hence, it is unlikely that nitrogen-containing groups of nanodiamond surface are active centers in DCE conversion. The role of oxygen-containing groups was studied in a test reaction of 2-propanol dehydrogenation/dehydration – both nanotubes and nanodiamonds were active in the reaction; however, no activity of carbon nanotubes in the DCE conversion suggests that oxygen-containing groups are not active in the DCE conversion. As a result, we suggest that the carbon surface of nanodiamonds might be catalytically active in the DCE reaction.

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1. Introduction

A combination of unique physical and chemical properties attracts a lot of attention to carbon nanomaterials such as carbon nanotubes, graphene, nanodiamond and others [1–5]. In particular, regular structure, electronic properties and easily modifiable surface allows their application in catalysis. Still in the vast majority of cases, carbon materials are used as a catalyst support for metal nanoparticles [6–12]. However, carbon materials can be catalytically active in some reactions without the addition of metal particles, which opens a promising way of decreasing the consumption of expensive and usually toxic metals in catalysis [13–25].

Many authors studied applications of carbon catalysts in the oxidative dehydrogenation of hydrocarbons, where the active sites are functional groups on the sp^2 -hybridized carbon surface [17,19,21–23]. In particular, onion-like carbon structures were active in ethylbenzene oxidative dehydrogenation only after an induction period, which was needed to form catalytically active

oxygen containing groups on the catalyst surface [19]. Bedia et al. [21–23] showed that carbon catalysts containing acidic surface groups are active in 2-propanol dehydration, while basic groups catalyze its dehydrogenation [24,25]. Yang demonstrated that carbon nitride nanosheets can be promising for oxygen reduction reaction, potentially replacing platinum-based metals [20]. There is a vast area of applications of graphene-based materials in photocatalysis [2,26,27].

Much less attention was devoted to the studies of nanodiamond materials [28]. Nanodiamonds look particularly promising because of the sp^3 -hybridized carbon structure, which provides high density of reactive unsaturated atoms, significantly higher than that for sp^2 -hybridised carbon nanomaterials [29,30]. For example, about 15% of the atoms are situated on the surface of 4.2 nm nanodiamond crystals, and hence are potentially catalytically active [31]. Nanodiamond materials were shown to be active in oxidative dehydrogenation of alkanes and dehydrogenation of alcohols on oxygen-containing groups as active centers. Carbonyl groups act as basic Lewis sites and are capable of splitting C–H bonds in alkanes and O–H bonds in alcohols [13,14,16]. Liu et al. [15] proposed that activity of nanodiamond materials in *n*-butane oxidative dehydrogenation is associated with the full restructuring of sp^3 -hybridized carbon structure into a fullerene-like sp^2 -hybridized structure.

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Focusing our attention on the environmental pollution with chlorinated products, we studied the application of carbon catalysts in the dechlorination of 1,2-dichloroethane (DCE) which represents a wide class on industrial chlorinated solvents [32–34]. Chlorinated compounds are not easy to remove safely by incineration as they tend to form highly toxic dioxins; full oxidation takes place only at a combustion temperature of above 800 °C leading to hydrochloric acid [35,36]. Because of very high temperature and resulting high energy consumption, milder alternatives for destruction of chlorinated compounds were studied. Among several alternatives, reductive dechlorination seems to be the most promising as it requires very mild reaction conditions, available and non-toxic chemicals [36,37]. Usually, dechlorination takes place under reducing atmosphere on supported platinum-based bimetallic catalysts [37–47], so the replacement of expensive metals with carbon materials seems promising from both economic and environmental viewpoints. There are a few works where nanodiamond was used as a catalyst support [10,48,49], but the dechlorination activity of nanodiamond materials, to the best of our knowledge, was not investigated before. Hence, in the current work we studied reactions of DCE on nanodiamond materials, comparing their activity with other carbon-based materials such as carbon nanotubes, nanoflakes, and fluorinated graphite.

2. Experimental part

2.1. Materials and catalyst synthesis

Nanodiamond obtained by the detonation synthesis (ND, Almazny Tsentr, St-Petersburg), synthetic diamond “Dalan” (D_{syn} , Institute of Problems of Chemical Physics, Chernogolovka [50]) and fluorinated carbon (FG, HaloPolymer, Kirovochepetsk) were used as purchased.

Carbon nanotubes (CNT) were synthesized in a horizontal quartz reactor by the pyrolysis of hexane vapors. A flow of nitrogen (99.999 vol.%), 100 mL min^{−1} STP, passed through a flask filled with hexane (99.5 wt.%) held at 25 °C and went into a reactor at the temperature of 730 °C filled with the $Co_{0.03}Mo_{0.1}MgO$ catalyst. The catalyst was dissolved washing the materials obtained 3 times with diluted hydrochloric acid and twice with distilled water. Afterwards, non-graphitic carbon forms were removed by oxidation of the materials at 400 °C for 2 h in air. Carbon nanoflakes (CNF) and nitrogen-doped CNF (CNF-N) were obtained by the pyrolysis of benzene (99.5 wt.%) and acetonitrile (99.7 wt.%) vapors, respectively, over MgO catalyst at the reaction temperature of 900 °C in nitrogen flow of 100 mL min^{−1} STP [51].

Synthesis of Ni-containing nanodiamond catalysts was performed by thermal decomposition of nickel (II) formate under dynamic vacuum described in Ref. [52]. Briefly, nanodiamond support material was impregnated with a minimal amount of an aqueous solution of nickel (II) formate, and decomposed by heating up to 280 °C under dynamic vacuum of about 5 Pa. The concentration of the precursor solution was calculated to obtain catalysts containing 2.5 wt.% Ni.

2.2. Material characterization

X-ray diffraction (XRD) studies were performed on a “Dron” diffractometer equipped with a $Co K\alpha$ X-ray tube in the 2θ range of 10–85°, step size 0.05° at the scanning speed of 1° min^{−1}. Infrared (IR) spectra were recorded from powder samples in a diffused reflectance mode using the EQUINOX55/S (Bruker) instrument. BET specific surface areas was measured with a Quantachrome Autosorb-1 analyzer after a thorough sample degassing at 300 °C under the pressure of 0.1 Pa.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Axis Ultra DLD instrument equipped with a monochromatic Al $K\alpha$ source and using pass energies of 160 eV and 40 eV for survey and high-resolution spectra, respectively. Temperature programmed reduction (TPR) studies were conducted placing about 50 mg of the material into a quartz reactor, heating the reactor at 12 °C min^{−1} in the 25 mL min^{−1} STP flow of 5 vol.% H_2 in Ar and studying the response of a thermal conductivity detector calibrated using a series of oxide materials.

2.3. Catalysis

The conversion of DCE (99.5 wt.%) was studied in a microreactor setup described in Refs. [53,54] using an impulse method. About 70 mg of the catalyst was placed between two layers of glass wool into a quartz tubular reactor (4 mm internal diameter and 20 cm long). The reactor was heated using a tubular furnace and connected to the entrance of a Chrom-5 gas chromatograph equipped with a flame ionization detector and a 1.3 m column packed with a Porapak-S adsorbent. A flow of 30 mL min^{−1} (STP) gas (either hydrogen or nitrogen) went through the reactor and impulses of DCE vapors (1 mL at 25 °C) were injected at regular intervals. Regeneration of the catalysts in hydrogen was performed *in situ* for 3.5 h at the reactor temperature of 450 °C. The reduction temperature was selected using TPR data corresponding to the maximum in hydrogen uptake.

Oxygen-containing groups on the catalyst surface were studied in a test reaction of dehydrogenation/dehydration of 2-propanol using the same impulse procedure, but injecting vapors of 2-propanol (99 wt.%) instead of DCE.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 shows electron microscopy characterization of the materials obtained. Diamond-based materials (D_{syn} and ND) contained spheroid agglomerates about 0.5–1 μm in diameter (Fig. 1a). TEM analysis of these agglomerates, however, showed that ND agglomerates were built of crystallites smaller than 10 nm (Fig. 1b), while crystallites of D_{syn} were several orders of magnitude larger, up to 1 μm in diameter. Multiwalled carbon nanotubes were 18–25 nm in diameter and more than 5 μm in length (Fig. 1c). Backscatter electron SEM data showed that metal particles were present at the ends of the nanotubes despite of thorough washing, likely due to encapsulation during the growth. Carbon flakes, both purely carbon CNF and nitrogen-doped CNF-N, had the same morphology and were built of 3–6 layered graphene sheets about 25 by 25 nm (Fig. 1d and e). Fluorinated graphite contained particles 1–10 μm in diameter and a lot of partially exfoliated sheets, which were obtained, likely, due to fluorination treatment (Fig. 1f).

Fig. 2 shows X-ray diffraction patterns of CNT and ND materials. As expected, the structure of ND corresponds to the sp^3 -hybridised diamond structure. Carbon nanotubes are built of sp^2 -hybridised graphene sheets, so the most intensive reflex agrees with that of graphite, while 2 weak reflexes correspond to the molybdenum oxide which is one of the components of the CNT synthesis catalyst and was not fully removed from the CNT material. Average crystallite size of carbon based materials was about 7 nm for ND, while it was about 4 nm for CNT, which agrees with the microscopy data (Fig. 1).

Table 1 shows the surface properties of the studied carbon catalysts. Surface area of the diamond-based materials (ND and D_{syn}) differs by an order of magnitude, likely, because agglomerates of the ND (below 10 nm) are substantially smaller than that

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