

OXIDIZED GRAPHITES AS CATALYST SUPPORTS

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Introduction

Oxidized graphites, due to their layered structure and high content of oxygen-containing groups embedded in the carbon layers [1] and related to this easy exfoliation in polar solvents, and high adsorptive capacity to metal ions [2], should be considered as potential carbon precursors of carbon-metal catalysts and composites.

In terms of the kind of carbon precursors, preparation methods of such catalysts are divided into four groups:

- 1 - use of the oxidized graphites as host substances for intercalation and surface modification with metal ions;
- 2 - deposition of metal films and clusters on the modified surface of the oxidized graphites;
- 3 - thermal decomposition of graphite oxide-metal derivatives;
- 4 - fabrication of graphite-oxide thin surface films utilized as matrices in which to incorporate a range of metal ions.

This work deals with the preparation and structure of oxidized graphites modified and intercalated with Cu(2+), Ni(2+), Co(3+), Cr(3+), and Ag(+) amino complexes and the catalysts production through their thermal decomposition, and chemical plating with Ni. The preparation of self-assembled films from aqueous colloids of the exfoliated graphite oxide on the mineral oxides surface of the different nature and sorptive properties of the obtained materials toward transition metal ions have also been studied. Oxidized graphites of two different oxidation degrees have been investigated: the graphite oxide (GO), in which every carbon layer has oxygen-containing groups in its structure [1], and the highly dispersed oxidized graphite (HDOG), in which only 2-3 near-surface carbon layers are of the approximate composition of the graphite oxide carbon layers [3].

Experimental

The GO was prepared by oxidation of graphite with KMnO_4 in concentrated H_2SO_4 . The HDOG was prepared by the mechanical dispersing of graphite bisulphate followed by the hydrolysis. The HDOG particle thickness was about 100 nm. The GO and HDOG were used as their aqueous dispersions.

The modification of the oxidized graphites with metal ions was carried out in metal ammoniate solutions. After stirring for 2 h the mixture was filtered off. The residue was washed with water, dried under vacuum and characterized by IR (Perkin-Elmer 325 instrument) and UV-Vis (PU-800 instrument) spectroscopy.

The thermal decomposition of the resultant GO-metal

complexes [GO-M] was performed by heating the samples in air up to 300°C and in Ar flow up to 800°C. The decomposition products, indicated as [C-M-3] and [C-M-8], respectively, were characterized by XRD (DRON-1, $\text{CuK}\alpha$ -radiation) and SEM (SCAN-SEAM instrument) methods.

The HDOG modified with metal ions [HDOG-M] was subjected to chemical plating with Ni by stirring the mixture of the [HDOG-M] and aqueous solution containing 50g/l NiSO_4 , 20g/l NaH_2PO_2 , 50g/l NH_4Cl , 70g/l NaCit, 85 ml/l 25% NH_3 for 15 h at 80°C.

The Al_2O_3 , MgO, ZnO, and fumed silica powders were investigated as substrates on which to deposit GO films from the diluted aqueous GO dispersion. After 1 h stirring, the suspension was decanted and the residue was dried at room temperature. The adsorption of Cu(2+) ions on obtained compounds was investigated in aqueous and aqueous ammonia solutions at room temperature.

Results and Discussion

1. The quantity of Cu(2+), Ni(2+), Co(3+), Cr(3+), and Ag(+) amino complexes adsorbed on the GO and HDOG depends on pH of the medium. The maximum number of bound ions (Table) is observed in pH range of 10-11 for GO and 12-13 for HDOG. The interaction of the metal ions with the GO and HDOG results in a decrease of reaction mixture pH and an increase of GO interlayer spacing by 0.7-0.8Å (Table), which indicates that the metal ions are bound by acidic functional groups situated both on the oxidized graphites surface and in the interlayer space. The comparative study of the IR and electronic spectra of the initial GO and GO containing metal amine ions allow us to suggest that GO forms complexes with metal amino complexes due to the replacement of amine molecules in the coordination sphere of a metal ion by oxygen-containing groups of GO carbon layers.

2. The chemical metallization of the [HDOG-M] results in the precipitation of 1.17g/g and 1.45 g/g metallic Ni on the surface of [HDOG-Cu] and [HDOG-Ag], respectively. No Ni precipitation is observed on the surface of the initial HDOG. So chemisorption of the metal ions can be used for the HDOG surface activation instead of the expensive two-step method of graphite impregnation with solutions of Sn(2+;4+) and Pd(2+) salts, which is commonly used prior to the chemical plating of graphite powders with Ni. Though the quantity of Ag(+) ions fixed on the HDOG surface is 2.24 times less than that of Cu(2+) ions, the quantity of Ni precipitated on the [HDOG-Ag] is 1.24 times more than that precipitated on

Table. Characterization of oxidized graphites-metal catalysts by chemical and BET surface area analysis, UV-Vis spectroscopy XRD, SEM, electrical resistance measurements

| Sample* | Metal compound (UV-Vis, XRD) | Metal content, wt% (chemical) | As BET m^2/g | 2θ $d\alpha$, A (XRD) | Average metal particles size, nm (XRD, SEM) | Electrical resistance, Ohm.m |
|---------------------------------------|------------------------------|-------------------------------|----------------|-------------------------------|---|------------------------------|
| GO | | | 0.7 | 12.8 6.916 | | 6.10^7 |
| GO-Cu | $Cu(NH_3)_2O_4$ | 23.0 | 0.8 | 11.5 7.695 | atomic level | 2.10^8 |
| GO-Ni | $Ni(NH_3)_2O_3$ | 15.3 | 0.8 | 11.7 7.563 | atomic level | |
| C** | | | 2.4 | 3.5 | | 0.03 |
| C-Cu-3 | CuO, Cu(w) | 48.5 | 11.9 | 10.5 8.425 | | 87.5 |
| C-Cu-8 | Cu, $Cu_2O(w)$ | 52.3 | 36.2 | 10.4 8.506 | 15 | 0.03 |
| C-Ni-3 | | 24.5 | 6.0 | 10.6 8.346 | | 2.0 |
| C-Ni-8 | Ni | 38.4 | 23.5 | 10.4 8.506 | 10 | 0.08 |
| HODG-Cu | $Cu(NH_3)_nO_{6-n}$ | 4.9 | 0.7 | | atomic level | |
| HODG-Ag | $AgNH_3O$ | 3.7 | 0.7 | | atomic level | |
| HODG-Cu-Ni | Ni | 117.0 | 0.7 | | 250- 800 | |
| HODG-Ag-Ni | Ni | 145.0 | 0.7 | | 300-1000 | |
| SiO ₂ /GO-Cu(1) | $Cu(NH_3)_2O_4$ | 5.8 | 152.0 | | atomic level | |
| SiO ₂ /GO-Cu(2) | $Cu(NH_3)_2O_4$ | 10.2 | 121.0 | | atomic level | |
| SiO ₂ /GO-Cu(3) | $Cu(NH_3)_2O_4$ | 13.8 | 85.0 | | atomic level | |
| ZnO/GO-Cu | $Cu(NH_3)_2O_4$ | 3.8 | 4.0 | | atomic level | |
| Al ₂ O ₃ /GO-Cu | $Cu(NH_3)_2O_4$ | 1.0 | 38.0 | | atomic level | |

* SiO₂/GO samples with GO content: (1)- 4.1 wt%, (2)- 15.5 wt%, (3)- 58.7 wt%; ZnO/GO sample with GO content 19.3 wt%; Al₂O₃/GO sample with GO content 0.6 wt%. ** GO heat-treated at 600° C

the [HDOG-Cu]. This fact indicates that Ag(+) ions have higher catalytic activity in the Ni(2+) reduction. The SEM photographs of the metallized HDOG show even distribution of the Ni particles over the surface.

3. The heat of GO complexes with Cu(2+) and Ni(2+) ammoniates in air up to 300°C results in the removal of water, ammonia and oxygen-containing groups of the GO carbon layers. XRD patterns of the heat treated samples indicate that Cu species present as crystallized CuO essentially, while Ni species are in amorphous state or dispersed at atomic level. We have shown by XRD and SEM methods that the heat of the GO metal complexes in inert atmosphere up to 800°C leads to the formation of carbon composites containing nanometer-sized metal oxide or metal clusters which are situated both on the surface and inside the carbon matrix particle (Table). The conductivity of the [C-Ni-8] is four times higher than that of the carbon matrix whereas the [C-Cu-8] conductivity does not differ from that of the carbon matrix. The higher Cu content and the formation of the bigger crystals may result in a comparatively larger number of carbon matrix defects due to reduction of the metal ions by carbon. Such defect formation in near-surface carbon layers might create pores and be a possible cause of 10-15-time increase of the [C-M-8] surface area (Table).

4. Maximum quantities of GO deposited on the surface of each metal oxide were determined as 19.3%, 14.6% and 0.56% for ZnO, MgO and Al₂O₃, respectively. The GO quantity precipitated on the SiO₂ surface was negligible. The decrease of the GO + SiO₂ reaction mixture pH to 2-3, the area where the SiO₂ isoelectric

point is observed and the hydrogen bonds formation is the most effective, does not improve the GO deposition. Hence hydrogen and van der Waals bonds do not play a significant role in GO-SiO₂ interaction. To deposit GO film on SiO₂ surface, the preliminary modification by triethoxy(aminopropyl)silane was used. This fact and the comparison of the maximum quantities of GO deposited on the MgO and Al₂O₃ surface indicate that the GO deposition occurs due to electrostatic interaction. The SEM photographs of the metal oxide-GO samples show that GO forms nanostructured film with particle size less than 1 μm, which completely covers the ZnO and MgO surface and forms separate islands on the Al₂O₃ surface.

Investigation of Cu(2+) ions adsorption on the obtained compounds has shown that, depending on the nature of the mineral support, adsorptive capacity of the GO films to Cu(2+) ammoniate increases in the order of Al₂O₃, ZnO, SiO₂ and runs to the value of that of the pure GO (Table). In adsorption of metal aqua complexes, synergism of the sorptive properties of the GO and the support is observed.

Thus the described above methods offer new routes for preparing a variety of composites that possess all the necessary characteristics of effective heterogeneous catalysts: redox activity, acid sites, good metal dispersion, porous matrix, and stability in water and organic solvents.

References

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