

Problems of the creation of nanoreactors for the synthesis of metallic nanoparticles in carbon shells

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Abstract

For the synthesis of metallic nanoparticles and nanowires in carbon shells, it is expedient to use the metal ions that can be reduced in nanoreactors by the interaction with the negatively charged walls of nanoreactors. The synthesis is a reduction-oxidation process, therefore aromatic hydrocarbons or organic polymers together with metal salts are reduction-oxidation pairs. Within the framework of Hartree-Fock theory with the minimal basis 3-21G, the energies of molecules and molecular fragments are calculated. In this energy model, the equilibrium atomic geometry of the fragments and the interaction energy of the reaction centers are determined.

The modeling results are realized in the experiments starting with mixing melts or solutions of the 3d metal chlorides (Cr, Mn, Fe, Co, Ni, Cu) with aromatic hydrocarbons or polyvinyl alcohol solution.

Heating of the reaction masses up to 400°C is carried out in a step-like manner. The control over the processes is performed using spectral, microscopic and chemical methods. Nanoproducts are studied with the use of X-ray photoelectron spectroscopy, transmission electron and scanning electron microscopy, diffractometry and the method of electron microdiffraction. Depending on the conditions of the process, giant fullerenes and tubulenes inclusive of metals and metal-containing compounds are formed.

Introduction

During last years, chemistry in nanoreactors is evolving rapidly. At present, the term "nanoreactor" is regarded in a wider implication as the field with one of the linear parameters less than 1 μm where the synthesis of nanoparticles or their reactions can occur. Under this definition, the term 'nanoreactor' may include the defect regions of metal salt polycrystals; interlayer region in melts and substances with a layer structure; extended cavities formed by macro-molecules in gels or solutions of polymers. The requirement to develop ecologically clean productions will give an opportunity of wide application of nanoreactors in chemistry and metallurgy. However, it is difficult to implement directed syntheses in nanoreactors without preliminary calculation experiment predicting the behavior of chemical particles and their transformations in nanoreactors. For obtaining metallic nanoparticles and nanowires in carbon shells, it is expedient to evaluate the possibilities of reduction-oxidation coupled reactions with participation of the ions of metals and organic compounds; then the results of modeling should be experimentally confirmed. The aromatic such as hydrocarbons naphthalene, anthracene, phenanthrene, and polymeric functional compounds like polyvinyl alcohol are offered for a source of carbon. For the matrices with nanoreactors (with cavities or interlayer regions where the formation of nanoparticles takes place) we have chosen eutectic melts of 3d metal chlorides (Cr, Mn, Fe, Co, Ni, Cu), gels of polyvinyl alcohol and polyva-

nadium acid and its derivatives intercalated with metals.

Mathematical modeling of nanoreactor processes

Mathematical modeling was conducted in several steps. In connection with the task to determine the possibility of the formation of globular or cylinder nanoparticles, at the first step, the fragments of interacting particles and active centers of the nanoreactor walls were singled out. In case of aromatic hydrocarbons, it was suggested that in the metal chloride matrix, the mobility of the metal ions in the cavities of nanoreactors with the walls positively charged is sufficient for the formation of the complexes with aromatic nuclei of compounds, "drawn" into these cavities. In the calculations, the molecules of benzene and naphthalene were used for the molecules imitating the aromatic hydrocarbons used in the experiment. The mechanism of the interaction and the evolution of the dehydropolycondensation are displayed in Fig. 1.

In this model 'erosion' of the nanoreactor walls is suggested accompanied by the liberation of hydrogen chloride and its partial absorption in the matrix.

The modeling of the processes occurring in the gels of polyvanadium acid and its derivatives during the penetration of the polyvinyl alcohol molecules into their interlayer structure was conducted using the fragment of polyvanadium acid and ethanol or hexanetriol 1, 3, 5. As this took place, the processes of dehydration and dehydrogenation were evaluated; it gave the basis for the

formation of polyene chains and carbonized tubulenes that are later condensed.

For the quantum-chemical calculations of the processes in the polyvinyl alcohol gels, the interaction of the metal ions from the related chlorides was suggested; then they penetrated into negatively charged cavities of the nanoreactors formed in the polyvinyl alcohol gels containing alcohol fragments; hexanetriol 1, 3, 5 was selected for the alcohol.

After selection and substantiation of the fragments for the modeling, the semi-empirical quantum-chemical calculations were conducted. At this step, the minimal basis MINI or 3-21G was used, and the search of equilibrium geometrical configuration of the formed complexes was performed for any projection of the energy gradient.

At the next step, the calculations were conducted with the help of the extended basis TZV and also the method ZINDO/1 using the software product Hyperchem and the computer technology of the Bio-Technology Institute, Granada University.

At the fourth step, the first-principles calculations with the use of Hartree-Fock method and the software complex GAMESS were carried out. At the same time, the activation energy and the specific rate of the process were evaluated; they were used for determination of the preferential progress of the reactions. The possibilities of the formation of fullerenes and tubulens were defined in the framework of the molecular dynamics model MM+ [1].

For the first case, the C-H binding energies were calculated as the dif-

ference of the energy of the complex in the equilibrium configuration and its energy in the absence of hydrogen (the energy of H was taken equal to zero):

$$E_{C-H} = E(C_6H_6M)^{n+} - E(C_6H_6M)^{(n-1)+};$$

and for the estimation of the metal cation interaction the following formula was used:

$$E_{M-C_6H_6} = [E(C_6H_6) + E(M^{n+})] - E(C_6H_6M)^{n+}.$$

As it follows from Tables 1 and 2, where the binding energies of C-H and of the metal-aromatic ring are given, the best stimulant for the hydrogen detachment from the ring, causing the disturbance of its coplanarity, is an ion of bivalent nickel. In this case, the ring acquires the form similar to the conformation of the cyclohexane "bath".

Table 1. The binding energy of C-H (Hartree)

The scheme of the hydrogen detachment	Energy
$C_6H_6 \rightarrow C_6H_5^- + H^+$	0,674485
$(C_6H_6Cu)^+ \rightarrow C_6H_5Cu + H^+$	0,501245
$(C_6H_6Co)^+ \rightarrow C_6H_5Co + H^+$	0,498053
$(C_6H_6Mn)^+ \rightarrow C_6H_5Mn + H^+$	0,498126
$(C_6H_6Ni)^+ \rightarrow C_6H_5Ni + H^+$	0,305434

Table 2. The energy of the metal-aromatic ring (Hartree)

The scheme of the interaction	Energy (TZV)
$(C_6H_6M)^{n+} \rightarrow C_6H_6 + M^{n+}$	TZV
$(C_6H_6Cu)^+ \rightarrow C_6H_6 + Cu^+$	-0,05210
$(C_6H_6Co)^+ \rightarrow C_6H_6 + Co^+$	-0,05588
$(C_6H_6Mn)^+ \rightarrow C_6H_6 + Mn^+$	-0,05392
$(C_6H_6Ni)^{2+} \rightarrow C_6H_6 + Ni^{2+}$	-0,22156

The results of the calculations are given in works [2 – 4]. The modeling results allowed to carry out the experiments for obtaining metal nanoparticles and nanowires in the

carbon shells with a comparatively little consumption of energy.

For the modeling of the nanoparticles synthesis from polyvinyl alcohol into polyvanadic acid derivatives as nanoreactors the fragments of polyvanadic acid and ethanol are used. The purpose of this investigation is to determine the alcohol dehydration possibility with the following dehydrogenation and polymerization during their interaction with the layers of vanadium oxide systems, on the example of vanadium oxide and vanadiñ acids and ethanol.

The direct modeling of chemical interaction of ethanol molecule with complexes containing two V_2O_5 pyramids is also carried out. The case when all oxygen atoms are bound with hydrogen atoms in the complex is considered (Fig. 2), as well as the case when each pyramid has one stopped chemical bond on oxygen atom with system charge -2 (Fig. 3).

During the model experiment shown in Fig. 3 two hydrogen atoms from ethyl alcohol molecule transfer to oxygen atom of one of vanadium pyramids and to oxygen bridge atom. This proves the possibility of ethyl alcohol dehydrogenation in the interaction process with flat layer of vanadium oxide.

The formation of metal nanoparticles and nanowires in the carbon shells from the solutions and melts of the mixtures of metal chlorides and organic compounds.

For one of the variants of obtaining nanostructures from aromatic hydrocarbons, the mixture of anthra-

cene was used in the eutectic melt containing aluminum chloride, sodium (better, lithium) chloride and chloride of one of the 3d metals (Cu, Ni, Co or Mn). The temperature of the melt was kept in the range of 300° - 500° C depending on the transition metal used. The time of holding was established based on the change of the optical spectra, the absence of the HCl liberation and the appearance of the practically stable surface geometry. After the end of the process the reaction mass was washed with hydrochloric acid, hot water, acetone and ortho xylene for the separation of the nanoprodut from the matrix. The nanoprodut obtained was dispersed in acetone in the ultrasound field and then was investigated by means of the transmission electron and scanning electron microscopes, the methods of electron microdiffraction and X-ray photoelectron spectroscopy. These investigations revealed nanostructures in the form of tubulenes, fullerenes and nanocrystals. The output of carbon multi-wall nanotubes increases when the process is carried out on the processed metal foils. In Fig. 4, one can see micrographs of nanotubes obtained on the anodized foil.

For the synthesis of nanoparticles and nanowires from the mixture of metal salts and polyvinyl alcohol (PVA), the aqueous solutions of salts were mixed in a certain ratio with the aqueous solution of PVA. The mean molar ratio of PVA in the mixture was 5. The experiments were carried out on the glass substrates; after the obtained mixtures had been dried, they formed colored transparent films. On some samples, the films were broken due to a large surface tension. The

films were heated at $t = 250^{\circ}\text{C}$ until their color, composition and morphology changed. For the control over the process, a complex of methods was used, i.e. photocolourimetry, optical microscopy, X-ray photoelectron spectroscopy and atomic power microscopy.

When PVA was added to the powders of metal chlorides, the color of the mixture changed: the mixture of copper chloride became yellow-green, the cobalt chloride mixture – blue, and nickel chloride – pale-green. Observing the color changes, one can draw a conclusion that when PVA interacts with metal chlorides, the formation of complex compounds takes place (Fig. 5)..

Among the above-discussed metals, iron is most active. Brown-red inclusions on the photograph evidence the formation of the complex iron compounds. In addition, on all the photographs depicting the mixtures containing metal chlorides, one can see a net of weaves, which are most likely the reflections of nanostructures.

In order to compare these structures, the investigations of the morphology of the films changing over a certain range of temperatures were carried out with the help of atomic power microscopy (Fig. 6).

When the nanoproduct pictures obtained by atomic power microscopy and optical microscopy are compared with the TEM micrograph of the nanoproduct treated thermally and with aqueous solution for the matrix removal, one can notice some correspondence between them. The nanoproduct represents interweaving tubulens containing Cu(I), Cu(II). In Fig. 7, there are also optical effects

indicating light polarization at light transmission through the films owing to the defects appearing during the formation of the complex compounds at the initial stage of the process.

Due to the fact, that metal ions are active, in the polymer medium they immediately appear in the environment of the PVA molecules and form bonds with the hydroxyl groups of this polymer. Polyvinyl alcohol replicates the structure of the particle that it surrounds; however, due to the tendency of the molecules of the metal salts or other metal compounds to combine, PVA as if envelops the powder particles, and therefore the forms of the obtained nanostructures can be different. The optical microscopy method allows to determine the structure of the nanostructures at the early stage.

When the samples are heated, dehydration occurs, and as a result, metal-containing nanotubes form. These processes are thoroughly described in works [5-6]. Dehydration leads to the darkening of the film. After the samples have been heated, on the photograph the remaining net of weaves can be seen, i.e. the structure morphology has remained. To some extent, this fact indicates that the initially formed structure of matrices is inherited. The methods of optical spectroscopy and X-ray photoelectron spectroscopy allow to determine the energy of the interaction of the chemical particles in the nanoreactors with the active centers of the nanoreactor walls, which stimulate reduction-oxidation processes.

Depending on the nature of the metal salt and the electrochemical potential of the metal, different metal reduction nanoproducts in the carbon

shells differing in shape are formed. Based on this result we may speak about a new scientific branch – nanometallurgy.

Conclusion

The possible ways for obtaining metallic nanostructures in carbon shells have been determined. The investigation results allow to speak about the possibility of the isolation of metallic and metal-containing nano-particles in the carbon shells differing in shape and structure. However, there are still problems related to the calculation and experiment because using the existing investigation methods it is difficult unambiguously to estimate the geometry and energy parameters of nano-reactors under the condition of ‘erosion’ of their walls during the formation of metallic nanostructures in them.

References

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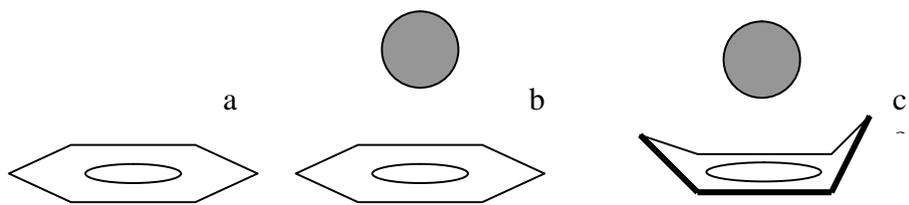


Fig. 1.

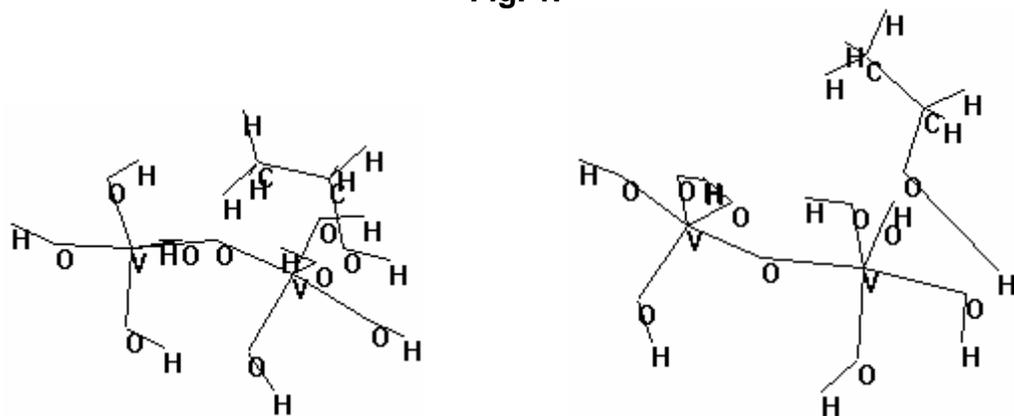


Fig. 2.

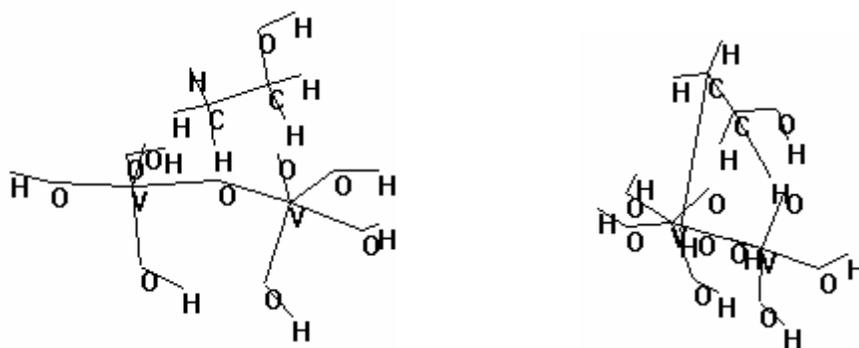


Fig. 3.

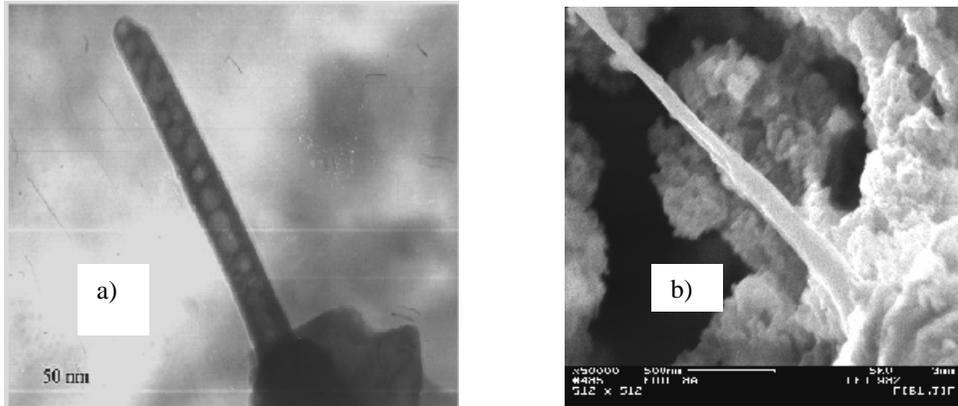


Fig. 4.

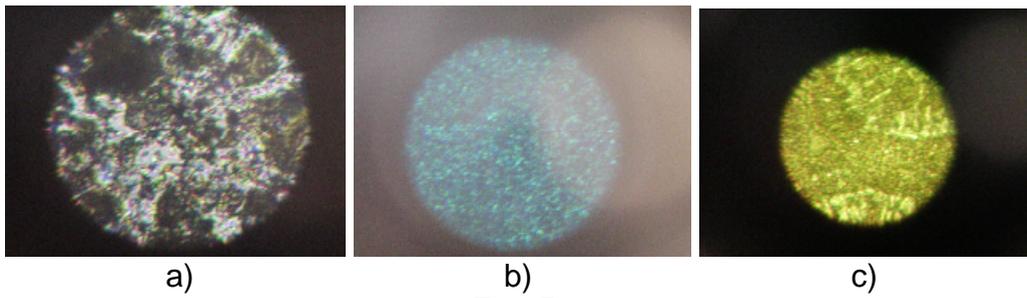


Fig. 5.

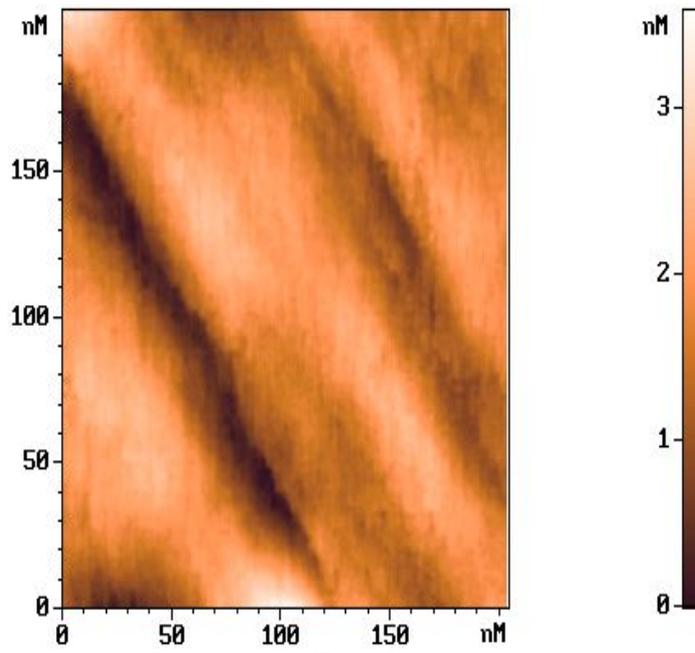


Fig. 6.



Fig. 7.

Captions

Fig. 1. Scheme of interaction of benzene with metals: a) ring structure of benzene, b) complex metal / benzene ring with Cu, c) complex metal / benzene ring with Co and Ni

Fig. 2. Scheme of ethanol interaction with Vanadium Oxide fragment in which Oxygen atoms are connected with Hydrogen

Fig. 3. Scheme of ethanol interaction with Vanadium Oxide fragment having two non compensated Oxygen atoms and the charge -2

Fig. 4. Micrographs of multi-wall nanotubes on the anodized aluminum foil:
a) – the TEM micrograph;
b) – the SEM micrograph.

Fig. 5. The photographs of the samples containing PVA and copper chloride (a), cobalt chloride (b), and nickel chloride (c).

Fig. 6. The Micrographs of the surface geometry of the PVA film with nickel chloride.

Fig. 7. Micrographs of tubulenes.

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