Computer Simulation of Nanoparticle Evolution in the Mesoporous Structures

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Abstract. A computer model, describing nanoparticle evolution in the mesoporous structures and enabling to study the influence of the formulation and technological factors on the particle size distribution has been created. The computer model is based on the “method of particles” and is a result of improved computer simulation of the multiphase system.

1. Introduction

Development of nanotechnology brought about an incredible increase in the number and scope of publications related to the subject. The studies of nanoparticle synthesis in mesoporous structures are widespread at present. The most important trend of such studies is application of these materials as catalytic systems. For example, a number of investigations is devoted to the synthesis of copper oxide [1], titanium oxide [2], iron oxide [3] particles in the mesopores of silicon oxide.

Synthesis of nanoparticle materials is extremely laborious, so creation of computer program, enabling to describe a process of nanoparticle evolution and thus to reduce the scope of experimental investigations seems to be very useful. An algorithm and computer model, describing nanoparticle synthesis in the mesoporous structures and enabling to study the influence of the formulation and technological factors on the particle size distribution have been created.

2. Model

Development of computer simulation algorithm is based on the “method of particles” and is a result of improved approach to computer simulation of the multiphase system structure [4-6]. A three-dimensional space with the properties of dispersive medium is described in the model. Evolution of nanoparticles subjected to different formulation and technological factors at the process of their synthesis is investigated. The input data for created computer model are number of particles, nucleation size, degree of mesopore volume filling, temperature, viscosity of the medium, the system shear rate, time step. According to the program algorithm, initial size distribution of the nanoparticle nucleations in three-dimensional space by random-number generator, takes place after source information input. Nanoparticle formation takes place in spherical pore. The pore size is determined as a function of the given degree of volume filling.

\[ R_{pore} = r \cdot \exp\left( \frac{1}{3} \cdot \ln\left( \frac{n}{V} \right) \right) , \]

where \( r \) – particle radius;
\( n \) – number of particles;
\( V \) – volume filling of a mesopore.

The main cyclic algorithm of calculation of resultant forces, acting on every particle, is involved in the work. Velocities and coordinates of the particles are determined in the developed computer model, the following statements being taken into account. The system evolution is considered as a result of the particle interaction not only with each other, but also with a medium. Here Brownian motion of the
particles is taken into account. For Brownian motion to be taken into account, the classical Einstein-Smolukhovsky formula is used in the model.

The next stage is calculation of the current size and number of nanoparticles, nanoparticle motion trajectory, i.e. particle spatial position at every point of time.

Nanoparticle interaction leads to their aggregation into a bigger particle. Here summing of the volumes occurs, and combined particle size is calculated by the formula:

\[
R_{\text{form}} = \exp\left(\frac{1}{3} \cdot \ln\left( r_i^3 + r_j^3 \right)\right),
\]

where \( R_{\text{form}} \) – radius of the nanoparticle formed;
\( r_i, r_j \) - radii of particles, forming a new particle.

Coordinates of the particle formed are calculated by the formulas:

\[
\begin{align*}
x &= (x_i \cdot r_i^3 + x_j \cdot r_j^3) \cdot R_{\text{form}} \\
y &= (y_i \cdot r_i^3 + y_j \cdot r_j^3) \cdot R_{\text{form}} \\
z &= (z_i \cdot r_i^3 + z_j \cdot r_j^3) \cdot R_{\text{form}},
\end{align*}
\]

where \( x, y, z \) – coordinates of the formed nanoparticle;
\( x_i, x_j, y_i, y_j, z_i, z_j \) – coordinates of the particles, forming a new nanoparticles.

The next image of the particle spatial position and coordination numbers distribution are displayed after carrying out of calculation and determination of the new particle coordinates. Interruption of the program, recording of the current data and calculation results, loading and change of the input parameters is possible at every point of time.

A calculation program of nanoparticle evolution in the mesopore is created on the basis of the algorithm developed. Program language is Delphi. An example of initial particle distribution in a pore is presented in figure 1.

The influence of component concentration, synthesis temperature and rate of stirring on nanoparticle size distribution has been studied.
3. Results and discussion

As demonstrated in figure 2, the decrease of the total volume fraction of the initial nanoaggregations in the mesopore leads to the increase of the fraction of synthesized nanoparticles (initial size) in the system, the letter in turn must lead to the higher dispersion of the oxide nanocatalyst.

Relationships, shown in figure 3, confirm the foregoing statement and demonstrate substantial extension of nanoparticle size distribution as a result of the increase of their fraction in the simulated system. However, the dispersity increase at nanoparticle fraction decrease in catalytic system will be followed by decrease of the total fraction of catalytically active component of the material. Thus, determination of specific content and, consequently, dispersity of catalytic system is possible only after additional experiment to be conducted.

![Figure 3](image3.png)

*Figure 3 – size distribution of synthesized nanoparticles (end size) as a function of nucleation concentration in a mesopore.*

![Figure 4](image4.png)

*Figure 4 – The influence of the temperature on kinetics of decrease of the initial size particle fraction*  

Results of the study of the system shear rate (rate of stirring during synthesis) on dispersity of nanooxide part of the system simulated are illustrated in figure 5.

Size distribution of the synthesized nanoparticles is shown in figure 6.

![Figure 5](image5.png)

*Figure 5 – Fraction of initial size nanoparticles as a function of the synthesis duration at different shear rates.*

![Figure 6](image6.png)

*Figure 6 – Shear rate as a function of the end size distribution of the nanoparticles.*

As follows from the results obtained, the flow in the system investigated leads to extension of the particle size distribution. Thus, for the system dispersity to be increased, stirring in the course of the particle synthesis and evolution should be as slow as possible.
The work was carried out at financial support of Russian fund of fundamental research (grant № 05-03-08005-ofi_p and grant № 06-03-32551a).

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