2496 Russian Chemical Bulletin, International Edition, Vol. 53, No. 11, pp. 2496—2498, November, 2004

Synthesis of silver nanoparticles in mesoporous high-aluminum aluminosilicate matrices

I. V. Kolesnik, A. A. Eliseev, A. V. Garshev, A. V. Lukashin, and Yu. D. Tret´yakov★

Department of Material Sciences, M. V. Lomonosov Moscow State University,
1 Leninskie Gory, 119992 Moscow, Russian Federation.
Fax: +7 (095) 939 0998. E-mail: eliseev@inorg.chem.msu.ru

A new method for the synthesis of $Ag/Al_xSi_{1-x}O_{2-0.5x}$ nanocomposite materials was proposed. The method is based on the use of charged mesoporous aluminosilicate matrices as nanoreactors. The porous structure of the matrices was characterized by ^{27}Al NMR spectroscopy and nitrogen capillary sorption at 77 K. An increase in the aluminum loading destroys the matrix structure and decreases the specific surface area. The resulting aluminosilicates were used as matrices for the synthesis of silver nanoparticles. The nanocomposites were examined by transmission electron microscopy and chemical analysis to estimate the silver percentage in specimens. Silver nanowires (~20% Ag) are formed in the low-aluminum (<10 mol.%) matrices, whereas an increase in the aluminum percentage affords both nanowires and spherical particles 3—10 nm in size and decreases the total amount of silver in the nanocomposite.

Key words: synthesis, silver, silver nanoparticles, mesoporous aluminosilicate, nanoreactor.

Mesoporous aluminosilicates are promising matrices for preparing nanocomposites with an ordered arrangement of active elements due to well-ordered pore system with uniform size distribution and a high specific surface areas.[1] Mesoporous structures with the hexagonal arrangement of cylindrical pores with the length about 1000 nm (in some cases, it can exceed hundreds micrometers) and the diameter ranging from 2 to 50 nm, are of special interest. These structures possess the highest anisotropy parameters of all known porous materials and can be considered as one-dimensional.

The structure of mesoporous aluminosilicate can be considered as mesoporous silica in which the silicon atoms are partially substituted by aluminum, producing a negative charge on the matrix. The alkaline metal cations and weakly bonded protons, which are located inside pores and compensate the charge of the matrix, can be exchanged in aqueous solutions and easily substituted by transition metal ions, including Ag^+, Cu^{2+}, Pt^{2+}, Pd^{2+}, Fe^{3+}, *etc*. As a result, metal atoms are uniformly distributed in the pores of mesoporous aluminosilicate, and one can expect the formation of uniformyl-sized nanoparticles upon the chemical modification of cation-substituted matrices. In addition, the open pores of aluminosilicates do not prevent gas diffusion in the system, and pore walls restrict the particle growth.[1] These conditions are similar to those in one-dimensional nanoreactors, such as reverse micelles or liquid-crystalline phases. The content of cations in the aluminosilicate is determined by the matrix charge, *i.e.*, the aluminum percentage in the SiO_2 structure, which can widely be varied in the synthesis. Such an approach makes it possible to prepare nanocomposites with a desired metal content.

The successful preparation of one-dimensional metal nanoparticles in mesoporous matrices is described in a number of works.[2—4] However, matrices of mesoporous aluminosilicates with a controlled charge of the structure have not been used so far for preparing nanocomposites.

In this work, we synthesized nanocomposites $Ag/Al_xSi_{1-x}O_{2-0.5x}$ by cation exchange followed by reduction and established a correlation between the composite structure and the matrix charge of mesoporous aluminosilicate. Silver was chosen as a model system due to the low charge and high atomic number of Ag^+ ion, which is an important factor that provides a maximum contrast for studying nanocomposites by transmission electron microscopy.

Results and Discussion

The plot of the silver content *vs*. aluminum content is presented in Fig. 1. It should be noted that the high silver content corresponds to specimens with a high aluminum loading and also to those containing <10 mol.% aluminum. Such a dependence is caused, most likely, by competitive tendencies in the system. First, an increase in the aluminum content increases the matrix charge and, hence, increases the content of silver introduced by the ion exchange procedure. At the same time, an increase in the aluminum content partially destroys the mesoporous

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2391—2393, November, 2004.

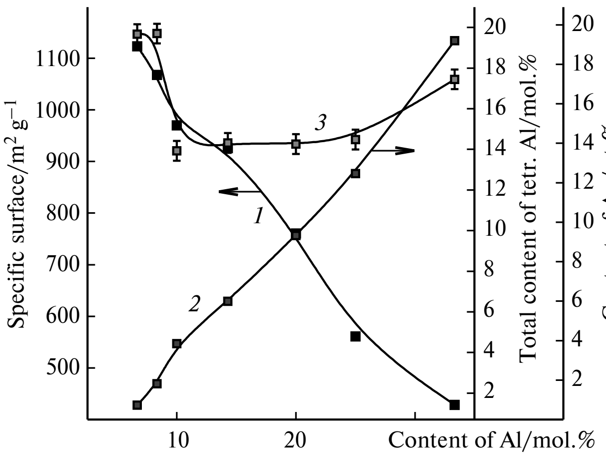

Fig. 1. Specific surface area (*1*) of mesoporous aluminosilicates, the content of aluminum in the tetrahedral coordination (*2*), and the silver content (*3*) in nanocomposites $Ag/Si_{1-x}Al_xO_{2-0.5x}$.

structure and blocks mesopores with aluminum polyhydroxo complexes formed upon joint hydrolysis of $Si(OEt)_4$ and $Al(OPr^i)_3$. Therefore, the silver content decreases proportionally to the ordering of the mesoporous phase. In addition, due to high specific surface area of the mesoporous matrices, intercalation of additional silver ions occurs due to ion exchange and also as a result of ion adsorption on silanol groups Si—OH bearing no negative charge. A rather high silver content (~9 wt.%) in the sample obtained by the impregnation of pure mesoporous silica confirms this assumption.

A difference between efficiencies of these processes has a strong influence on the microstructure of the prepared nanocomposites, whose microphotographs are presented in Fig. 2 (JEM-2000FXII, JEOL, accelerating voltage 200 kV, and JEM-4000EX, JEOL, accelerating voltage 400 kV). For example, silver nanowires 1—3 nm in diameter are formed in pores of the low-aluminum (<10 mol.%) aluminosilicate matrix, whereas in the case of higher-aluminum matrices spherical silver particles 3—10 nm in size are mainly formed on the aluminosilicate particle surface (see Fig. 2). The formation of a metal silver phase is confirmed by the electron diffraction data. The occurrence of spherical particles on the surface can be due to a nonuniform distribution of silver ions in the high-aluminum aluminosilicates, because mesopores are partially blocked and the aluminosilicate particle decreased in size. At the same time, an increase in the aluminum content in the structure is accompanied by an increase in the number of Lewis acid sites Al—O$^-$ on the internal surface of pores, resulting in a considerable increase in the mobility of silver ions and favoring their escape from the structure.[5]

Thus, the approach proposed in this work makes it possible to prepare nanocomposites containing filamentary silver particles in the case of using aluminosilicates with a low matrix charge (below 10 mol.% Al); an increase in the matrix charge is accompanied by its partial destruction and an increase in the mobility of silver ions, resulting in the formation of both nanowires and spherical silver nanoparticles 3—10 nm in size on the surface of the aluminosilicate particles. The total silver content in the prepared nanocomposite is determined by the matrix charge and the specific surface of aluminosilicate. The proposed approach can be used for preparing a wide scope of nanosized materials with a controlled amount of the nanophase. Due to the microstructure of the resulting nanocomposites and a high metal content, they can be considered promising for the use in catalysis.

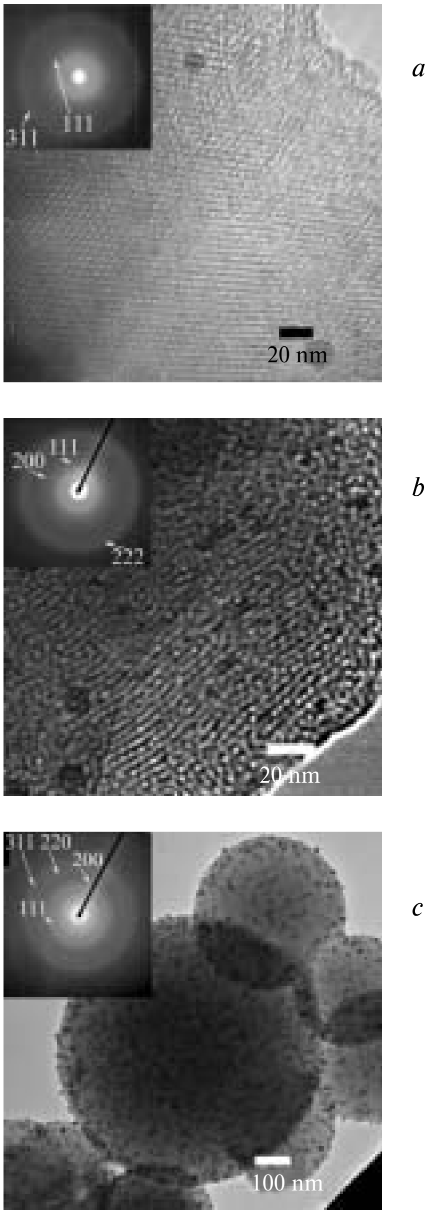

Fig. 2. Electron microphotographs of nanocomposites Ag/SiO_2 (*a*), $Ag/Si_{0.93}Al_{0.07}O_{1.97}$ (*b*), and $Ag/Si_{0.67}Al_{0.33}O_{1.83}$ (*c*).

Experimental

Mesoporous aluminosilicates were prepared by the combined hydrolysis of aluminum isopropoxide and tetraethyl orthosilicate (TEOS) in the presence of a template (cetyltrimethylammonium bromide, CTAB).[6,7] The calculated amount of a solution of aluminum isopropoxide in anhydrous isopropyl alcohol (6.4 wt.%) was mixed with TEOS (5 mL), the mixture was added dropwise to an aqueous solution of CTAB (0.057 mol L^{-1}) and ammonia (1 mol L^{-1}), and the resulting solution was stirred for 1 h. The precipitates were stored for aging, filtered off, washed to pH ~7, and dried in air at 95 °C. The template was removed by annealing the specimens for 10 h in an oxygen flow at 550 °C (heating and cooling rates 1 °C min^{-1}). As a result, white fragile powders were obtained (series Si_nAliP, where n = 2, 3, 4, 6, 9, 11, and 14).

Aluminosilicate matrices were studied by ^{27}Al NMR spectroscopy (Bruker MSL-300, frequency 78.205 MHz with a polarizing field induction of 7.05 T, duration of excitation pulses 1 μs, "dead" time 10 μs, interval between pulses 0.5 s) and nitrogen capillary sorption at 77 K (Sorptomatic 1900, Karlo Erba Instruments).

According to the results of studies of the aluminosilicate matrices,[7] an increase in the aluminum content is accompanied by the partial disordering of the structure and decreases the sizes of crystallites of the mesoporous aluminosilicate. Nevertheless, even at the maximum ratio Al : Si = 1 : 2, the surface area remains rather large (~420 $m^2 g^{-1}$). At the same time, the ^{27}Al NMR spectroscopic data indicate that an increase in the total aluminum content in the samples increases the fraction of tetrahedrally coordinated aluminum and, correspondingly, the negative charge of the matrix increases (see Fig. 1).

The H^+ form of the mesoporous aluminosilicates was transformed into the Ag^+ form using direct ion exchange in a 10% excess of an 0.05 *M* aqueous solution of $AgNO_3$ in the cold in the absence of direct solar light. Silver was reduced in a hydrogen flow at 300 °C.

The silver content in specimens was analyzed by rhodanometric titration[8] of mother solutions of silver nitrate after impregnating aluminosilicates. Aliquots of the mother liquors (10 mL) were titrated with a 0.1 *M* solution of NH_4SCN in the presence of an indicator (1 mL of a saturated solution of $NH_4Fe(SO_4)_3$) in an acidic medium.

This work was financially supported in part by the Russian Foundation for Basic Research (Project No. 03-03-32182), the Foundation of the President of the Russian Federation (Program for Support of Leading Scientific Schools, Grant 00-15-97435), the INTAS (Grants 2001-204; 03-55-1523), the Foundation for Assistance of Domestic Science, and the LG Chemical and Haldor Topsoe Companies.

References

1. J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonovicz, C. T. Kresge, K. D. Shmitt, C. T-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins, and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10834.
2. K. S. Napolsky, A. A. Eliseev, A. V. Knotko, A. V. Lukashin, A. A. Vertegel, Yu. D. Tretyakov, *Materials Science and Engineering C*, 2003, **23**, 151.
3. M. Sasaki, M. Osada, N. Higasimoto, T. Yamaoto, A. Fukuoka, and M. Ichikava, *J. Mol. Catal. A: Chemical*, 1999, **141**, 223.
4. M. H. Huang, A. Choudrey, and P. Yang, *Chem. Commun.*, 2000, 1063.
5. S. Besson, T. Gacoin, C. Ricolleau, and J. P. Boilot, *Chem. Commun.*, 2003, 360.
6. A. Matsumoto, H. Chen, K. Tsutsumi, M. Grun, and K. Unger, *Micropor. Mesopor. Mat.*, 1999, **32**, 55.
7. I. V. Kolesnik, A. A. Eliseev, A. P. Malakho, A. V. Garshev, V. P. Tarasov, A. V. Lukashin, and Yu. D. Tret´yakov, *Dokl. Akad. Nauk*, 2004, **395**, 776 [*Dokl. Chem.*, 2004, **395** (Engl. Transl.)].
8. A. P. Kreshkov, *Osnovy analiticheskoi khimii* [*Foundations of Analytical Chemistry*], Moscow, Khimiya, 1971, Vol. **2**, 455 pp. (in Russian).

Received September 22, 2004