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Formation of Bulk and Two-Dimensional Metal Oxide Nanostructures by Transport Reduction

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Abstract—The use of transport chemical reactions for preparing finely dispersed and two-dimensional structures based on transition metal oxides is considered. A procedure for preparing bulk and film oxide mixtures with a given content of Fe(II) and Fe(III) is described. The samples are characterized by chemical analysis and Mössbauer spectroscopy. A diagram describing the effect of the support on the degree of iron reduction in a film is presented.

INTRODUCTION

Dispersed materials based on transition metal oxides play an important role in modern technologies. The properties of such materials strongly depend on the degree of dispersity and on the macroscopic structure organization, which, in their turn, are determined by the synthesis conditions [1]. Here we discuss preparation of nanostructures by transport reactions. Using this method, it is possible not only to obtain structures of various dispersities, but also to control their phase and chemical composition, as well as to form a composition gradient along a given direction. Transport reactions can be performed in a 10–15 cm^3 glass ampule at 670–870 K. The initial metal oxide (e.g., Fe_2O_3, NiO) and a metal-reductant (Mg, Ca) are placed in the opposite ends of the ampule. Also, 2–3 mg of water in a sealed glass capillary is placed inside the ampule, after which the ampule is evacuated and sealed. On heating, the capillary is broken, and the following reactions occur:

$$Mg + H_2O \rightarrow MgO + H_2, \quad (1)$$

$$3Fe_2O_3 + H_2 \rightarrow 2Fe_3O_4 + H_2O. \quad (2)$$

By adjusting the amount of the transport agent (water), it is possible to perform the process at a required rate and obtain spatially uniform phase mixtures of a given composition. The process is described in detail in [2–4].

PREPARATION AND PROPERTIES OF BULK NANOSTRUCTURES BASED ON IRON OXIDES

Consider the transport process in the system Fe_2O_3–Mg–H_2O. Since reaction (1) is irreversible under the above conditions, the reaction proceeds until magnesium is fully exhausted. By setting the amount of Mg in the system, it is possible to obtain any binary phase complex in the series Fe_2O_3–Fe_3O_4–FeO–Fe [4]. Table 1 represents data on obtaining mixtures of FeO_x phases with a given ratio α = Fe(II)/[Fe(II) + Fe(III)]. The chemical composition of the samples obtained was determined colorimetrically with *o*-phenanthroline [4].

It can be readily seen that, in the range $0 < \alpha < 0.46$, the experimental degree of reduction is larger than the calculated value, whereas in the range $0.46 < \alpha < 1.00$ it is smaller. This is due to the transition from the Fe_2O_3–Fe_3O_4 mixture to the Fe_3O_4–FeO mixture in the range $0.33 < \alpha < 0.4$, so that a part of a reductant (Fe, Na, Mg, Ca) is consumed for creating an atmosphere with a higher H_2 content. Such phenomena can be predicted and taken into account using the corresponding phase diagrams (Fe–O). Mössbauer spectroscopy, combined with ordinary chemical anal-

Table 1. Reactant ratios and calculated (α_t) and experimental (α_{ex}) degrees of Fe(III)→Fe(II) conversion in transport reduction of Fe_2O_3

M_{Mg}	$M_{Fe_2O_3}$	M_{H_2O}	α_t	α_{ex}
mg				
6.8	156.8	0.22	0.289	0.293
8.0	159.6	1.0	0.333	0.351
9.6	160.4	1.1	0.400	0.457
11.9	160.1	1.0	0.464	0.467
15.3	160.3	1.1	0.603	0.560
21.3	160.1	0.9	0.887	0.780

Table 2. Mössbauer parameters and ratio of iron species in transport reduction of Fe_2O_3 (hematite) in the system Fe_2O_3–Mg–H_2O at 653–673 K [5]

Parameter[a]	Fe_2O_3	Fe_3O_4	A[b]	B[b]	FeO_s[c]	$Fe_{1-x}O$	Fe(II)	Fe(0)
				Parameters of Mössbauer spectra				
Δ, mm s^{-1}	0.37	–	0.37	0.64	1.06	0.86	0.44	0.01
ΔE, mm s^{-1}	0.22	–	0.02	0.01	0.29	0.74	1.20	0.02
H, kOe	517.5	–	491.2	460.5	–	–	–	330.1
				Iron speciation in reduction products, %				
1	85.0	11.0	4.2	6.8	–	–	–	–
2	36.0	59.7	24.4	35.3	–	–	–	–
3	–	93.6	35.3	58.3	3.9	–	–	–
4	–	62.2	25.3	36.9	29.1	–	–	–
5	–	19.9	6.8	13.1	47.6	32.5	–	–
6	–	8.8	2.3	6.5	17.7	20.1	4.1	49.3
7	–	–	–	–	–	–	1.4	98.6

[a] (Δ) Isomeric shift, (ΔE) quadrupole splitting, and (H) effective hyperfine magnetic field. [b] (A, B) Structural sublattices of magnetite. [c] (FeO_s) Stoichiometric Fe(II) oxide.

ysis, furnishes the most exhaustive information on the state of iron in the complexes obtained. Table 2 presents data on the iron speciation [5].

It should be noted that two phases of FeO are present (stoichiometric and oxygen-deficient), and also that the sample with 43% metallic iron contains the Fe_3O_4 phase. These specific features are attributable to the stabilizing effect of the substrate (one of the main phases of the complex) on the dispersed impurity phase.

Figure 1 shows experimental data on the dependence of the specific surface area S_{sp} of the phase complex Fe_2O_3–Fe_3O_4 on the Fe_3O_4 content in the mixture (BET method, air adsorption at a temperature of liquid nitrogen). It is seen that the dependence has a clear minimum at the degree of $Fe_2O_3 \rightarrow Fe_3O_4$ conversion in the range 0.3–0.4. A model was proposed for interpreting these results. The specific surface area of the initial Fe_2O_3 is 15.7 $m^2\ g^{-1}$, and that of the final product, Fe_3O_4, is 12 $m^2\ g^{-1}$. Since the sample weight only slightly changes in the course of reduction, the difference in the specific surface areas is due to different sizes of Fe_2O_3 and Fe_3O_4 particles. The sharp minimum in the plot can be rationalized by assuming that a part of the surface of a reduced Fe_2O_3 particle is shielded by magnetite particles. In this case, the sample surface area can be expressed as

$$S_{sp} = S_{sp}^{Fe_3O_4}L + S_{sp}^{Fe_2O_3}(1 - L)(1 - P), \qquad (3)$$

where $S_{sp}^{Fe_3O_4}$ and $S_{sp}^{Fe_2O_3}$ are the specific surface areas of particles of Fe_3O_4 and Fe_2O_3, respectively, L is the degree of conversion of Fe_2O_3 into Fe_3O_4, and P is the shielding coefficient. An empirical expression for P was suggested: $P = kL$ at $L < 1/k$ and $P = 1$ at $L > 1/k$, where k is an empirical coefficient. Then we can distinguish two portions in the curve $S_{sp}(L)$. At $0 < L < 1/k$, the dependence is parabolic:

$$S_{sp}(L) = 12L + 15.7(1 - L)(1 - kL). \qquad (4)$$

At $L > 1/k$, the dependence is linear: $S_{sp}(L) = 12L$. This means that, starting from the degree of conversion equal to $1/k$, Fe_2O_3 ceases to contribute to the overall specific surface area owing to complete shielding by reduction products and acts only as an Fe_3O_4 precursor. The coefficient k was calculated as the average of the results of measuring S_{sp} in the descending curve portion; k amounts to 2.76 from data in Fig. 1.

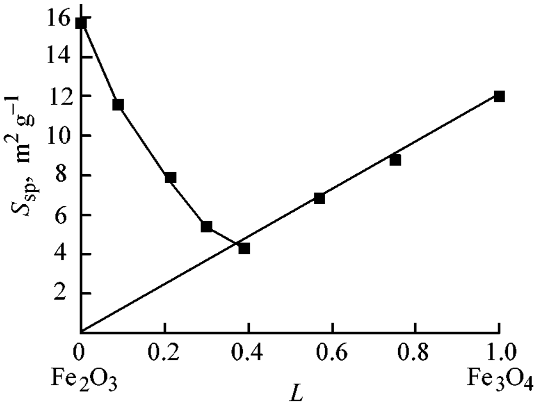

Fig. 1. Specific surface area S_{sp} of the phase complex Fe_2O_3–Fe_3O_4 as a function of the Fe_3O_4 fraction L in the mixture.

DRIVING FORCE OF HOMOGENIZATION OF A MIXTURE OF TWO DISPERSED SOLID PHASES IN THE COURSE OF TRANSPORT REDUCTION

When preparing binary phase complexes of a given composition, we noticed that they are highly homogeneous. A Mössbauer study of products of transport reduction in the systems Fe_3O_4–FeO–H_2O and FeO–Fe–H_2O [5] showed that the spectral characteristics of samples become identical by the end of the experiment, irrespective of their initial composition. These results cannot be explained by local transport processes inside a sample, since the composition of the equilibrium gas phase over a binary phase complex is independent of the phase ratio. The observed effect can be understood by considering the role of surface phenomena in the transport reduction.

Consider a mixture of dispersed phases FeO–Fe_3O_4 at thermodynamic equilibrium with the gas mixture H_2–H_2O. At the constancy of the external conditions and of the gas phase composition, at least two processes can occur in the system: variation of the total surface area of each solid phase and variation of their contact surface area. In the process, the surface free energy of the system should always decrease [6]. Single crystals have the lowest surface free energy. However, their growth requires long time, whereas the equalization of the sample chemical composition in the course of the experiment takes 2–6 h. This is due to the fact that the uniform distribution of particles of the FeO and Fe_3O_4 phases in the sample bulk corresponds to a conditional minimum of the surface free energy of the system. For the system FeO–Fe_3O_4–gas (H_2 + H_2O),

$$E = E_{13}(S_1 - G) + E_{23}(S_2 - G) + E_{12}G, \quad (5)$$

where E is the surface free energy of the system; S_1 and S_2, the surface areas of FeO and Fe_3O_4, respectively; and G, their total contact area. The quantities E_{12}, E_{13}, and E_{23} are the specific surface free energies of the interfaces FeO–Fe_3O_4, FeO–gas, and Fe_3O_4–gas, respectively. $\delta E = 0$ at the point of a conditional minimum. Differentiating function E with respect to the variable G at constant S_1 and S_2, we obtain

$$dE/dG = -(E_{13} + E_{23} - E_{12}). \quad (6)$$

Since the FeO and Fe_3O_4 phases differ in their properties from each other to a much lesser extent than from the gas phase, one can expect that $E_{23} \sim E_{13}$, $E_{12} << E_{13}$, and $E_{12} << E_{23}$. Therefore, $dE/dG < 0$. Thus, the function G should have a conditional minimum, and this is attained by redistribution of phase particles in the sample volume. From this condition and from the analysis of experimental data, it can be concluded that the peculiar mutual mixing of solid phases is characteristic for the macroscopic structural organization of phase complexes obtained by transport reduction. Although the final state of the system is not equilibrium with respect to the whole set of possible surface phenomena, such phase mixing is thermodynamically favorable and can be used in the preparative practice.

PREPARATION AND PROPERTIES OF TWO-DIMENSIONAL NANOSTRUCTURES WITH A GIVEN DEGREE OF REDUCTION OF METAL CATIONS

The chemical transport allows production of a wide spectrum of metal oxide films, but, for this purpose, it requires modification taking into account the chemistry of surface compounds [4, 7]. First of all, the amounts of reactants to be used are extremely small. The typical content of Fe in an ultrathin iron oxide film amounts to 10–100 $\mu g\, m^{-2}$ of substrate surface area [1]. This is smaller than the amount of reactive impurities even on the ampule walls and on the surface of other reactants. Therefore, all the reactants and the reaction ampule itself should be carefully purified. In our experiments, this was attained by prolonged calcination in air at the temperature of the experiment (600–800 K). As the initial nanostructure, we took iron(III) oxide deposited on the surface of Al_2O_3 (37) and MgO (30) by physical adsorption from a solution of $FeCl_3$ in diethyl ether or by deposition from the gas phase of the composition CH_4–O_2–HCl–$FeCl_3$ (the Fe_2O_3 content, μg per 1 m^2 of the support surface area, is indicated in parentheses). The first successful experiments on obtaining two-phase complexes on the support surface were performed with Fe, FeO, and Fe_3O_4 as bulk reductants [4]. The amount of a bulk oxide in experiments (0.2–0.5 g) greatly exceeded the amount of Fe_2O_3 in the film. At a small volume of the gas phase in the ampule (~10 cm^3), this allowed the oxygen pressure in the system to be set as equal to the dissociation pressure of the corresponding oxide. In the process, the bulk oxide played the role of an infinitely large reservoir (chemostat) of oxygen whose chemical potential was determining for the two-dimensional oxide phase. By this procedure, we obtained films of the composition FeO_x with the Fe(II) content gradually changing within the range 0–100%. Table 3 presents the data on the degree of conversion Fe(II)→Fe(III) in relation to the composition of the bulk phase complex.

In some experiments, we used microscopic amounts of organic compounds (CH_3OH, CH_2O, C_2H_5OH) which were also introduced into the ampule in a sealed capillary. The equilibrium oxygen partial pressure was calculated assuming the ideality of the gas mixture of pyrolysis products of an organic compound. This modification of the method allowed finer control of the degree of iron reduction in the films. Using the data of Table 3, we can construct correlations between the degrees of reduction of iron oxide deposited on different supports at equal compositions of the gas phase. Figure 2 represents the diagram for the pair FeO_x/Al_2O_3–FeO_x/MgO. The thermodynamic interpretation of these diagrams remains unclear so far, but they somewhat resemble the classical diagrams of two-component gas–liquid equilibria. Therefore, we can expect a number of model theories to be applicable to this case. For example, considering both the films as solutions of Fe(II) and Fe(III) in the oxygen sublattice, we can write

$$\mu^{Mg}_{Fe(II)} = \mu^{Al}_{Fe(II)}, \quad (7)$$

$$\mu^{Mg}_{Fe(III)} = \mu^{Al}_{Fe(III)} \quad (8)$$

for the state of thermodynamic equilibrium. Here $\mu_{Fe(II)}$ and $\mu_{Fe(III)}$ are the chemical potentials of Fe(II) and Fe(III) in the films, and the support is indicated by superscripts. The activity coefficients of the film components can be estimated from the theory of binary regular solutions as

$$RT \ln \gamma_i = A(1 - x_i)^2, \quad (9)$$

where R = 8.31 J K^{-1} mol^{-1}, γ_i is the activity coefficient of component i with the mole fraction x_i, T is temperature (K), and A is the energetic interaction parameter. Substituting (9) in Eqs. (7) and (8), we obtain after simple transformations

$$RT \ln(x/y) = \Delta\mu^0_{(Mg-Al)} - A(1 - x)^2 + B(1 - y)^2. \quad (10)$$

Table 3. Fe(II) content (%) in equilibrium films of FeO_x/Al_2O_3 and FeO_x/MgO at 870 K and various ratios H_2/H_2O

Reductant	$\log\left(\frac{[H_2]}{[H_2O]}\right)$	FeO_x/Al_2O_3	FeO_x/MgO
FeO/Al_2O_3	–	38	15–20
Fe_2O_3–Fe_3O_4	–5.5	72	30–48
CH_2O (1 mg)	–2	80	55–70
Fe_3O_4–FeO	0	95	82–92
FeO–Fe	1.1	100	92–100

Here y and x are the mole fractions of Fe(II) in the films on MgO and Al_2O_3, $\Delta\mu^0_{(Mg-Al)}$ is the difference of the standard chemical potentials of Fe(II) for the MgO and Al_2O_3 supports, and A and B are the energetic parameters of Eq. (12) for the films on Al_2O_3 and MgO, respectively. The coefficients in (13) can be calculated using the linear regression equation $Z = A_1 + A_2X + A_3Y$, where $X = (1 - x)^2$ and $Y = (1 - y)^2$. From the data of Table 3, we obtained the following film characteristics: $\Delta\mu^0_{(Mg-Al)}$ = 412 J mol^{-1} for Fe(II) and $\Delta\mu^0_{(Mg-Al)}$ = −670 J mol^{-1} for Fe(III). The parameters A and B amount to 9.4 and 8.4 kJ mol^{-1}, respectively. The activity coefficients of film components are 1.33 for the film on magnesium oxide and 1.38 for the film on aluminium oxide at $x_1 = x_2 = 0.5$. Without going into details, we note that the Al_2O_3 support stabilizes Fe(II) (the prototype compound is $FeAl_2O_4$), whereas the MgO support stabilizes Fe(III) (the prototype compound is $MgFe_2O_4$). This is in agreement with the chemical properties of the supports and with the earlier results reporting the stabilization of Fe(II) on TiO_2 and SiO_2 supports [7].

The above two-dimensional nanostructures can be successfully used in studying the catalytic properties of metal oxide compositions. The rates of formation of formaldehyde by photocatalytic oxidation of methane on the surface of the catalyst FeO_x/Al_2O_3 are plotted in Fig. 3. The experiments were performed in a closed quartz reactor at 293 K. The radiation source was a medium-pressure mercury lamp with the radiation intensity (λ = 254 nm) of 400 μE m^{-2} s^{-1}. The amount of CH_2O formed was determined by gas chromatography. The content of Fe(II) in the catalytic

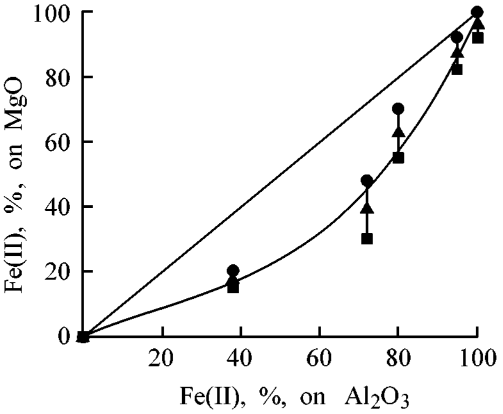

Fig. 2. Equilibrium degrees of reduction of FeO_x films on MgO and Al_2O_3 supports.

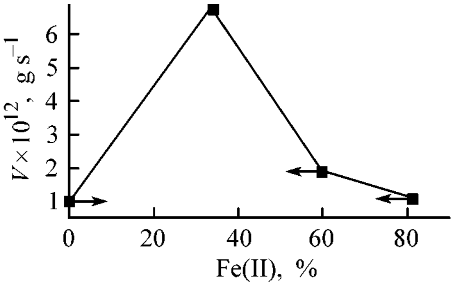

Fig. 3. Rate of formaldehyde formation *V* by photoinduced oxidation of methane on the surface of FeO_x/Al_2O_3 films.

film was determined twice: before and after the experiment. The direction of changes in the catalyst composition is shown with *arrows* in Fig. 3. As seen, the Fe_3O_4 phase appeared to be the most stable and catalytically active under the experimental conditions.

SYNTHESIS OF SPATIALLY ORDERED STRUCTURES ON FLAT SUPPORTS

Whereas the concepts and methods of classical thermodynamics are applicable to obtaining spatially uniform two-dimensional and bulk nanostructures, the preparation of metal oxide films with a composition gradient required such concepts of the thermodynamics of irreversible processes as a steady state and a local equilibrium. It was shown before that the transport reduction can proceed in a steady-state mode for a fairly long time at a proper choice of the reactant amounts, transport agent, temperature, and system volume [3]. In the process, a steady gradient of H_2 and H_2O concentrations arises along the line connecting the metal oxide and metal-reductant. The concentration ratio $[H_2]/[H_2O]$ gradually increases from the near-zero value in the vicinity of Fe_2O_3 to a fairly high value near Mg. If a flat Fe_2O_3 film on some support is arranged along this line, iron oxide should rapidly come to equilibrium with the gas phase at any point of the film. Since the amount of oxide in the whole film is considerably smaller than the amount of reactants in the bulk phases, the film reduction should not disturb the steady-state oxygen transport from Fe_2O_3 to Mg.

Preparation of metal oxide films with a composition gradient was realized with FeO_x/Al_2O_3 as example. The initial Fe_2O_3 films on flat and cylindrical Al_2O_3 supports were prepared by deposition from the methane–oxygen flame with a given content of $FeCl_3$ vapor and HCl. A wash bottle with concentrated HCl was used as a source of HCl, and iron gauze placed at the blue cone edge of the flame was a source of $FeCl_3$. The deposition conditions were chosen empirically to obtain a coating containing 10 μg of Fe_2O_3 per 1 cm^2 of the support surface within a period of 10–15 min. Such surface density corresponded to 10–15 monolayers of iron oxide, which, in its turn, was required by the sensitivity of chemical analysis. The composition gradient was obtained in the steady-state mode of chemical transport of oxygen from the bulk phase of Fe_2O_3 to Fe_3O_4. The substrate with the film was placed along the line connecting the bulk phases. To avoid convection, the empty space in the ampule were filled with coarse crumbs of melted quartz. In such a system, it is possible to obtain films with the variation of the Fe(II) mole fraction from 0.25 to 0.31 per 3 cm of the film length.

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