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> LABORATORY TECHNIQUES

Experimental Setup for Investigating Topochemical Transformations of Ferromagnetic Nanoparticles

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Abstract—An experimental setup controlling the topochemical transformations in synthesis of ferromagnetic metal nanoparticles is described. The setup is based on a vibrating magnetometer. The range of operating temperatures in the reaction zone is 300-870 K. The required sensitivity is maintained by a magnetic field of up to 0.6 T. Gases (or gas mixtures) may be blown through the reactor at a flow rate as high as $150 \text{ cm}^3/\text{min}$. The experimental results illustrating the capabilities of the setup are presented.

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INTRODUCTION

The methods for in situ control of the synthesis process have found wide physical application in thin film deposition and in nanocomposite and nanostructure formation. Optical and induction control methods are most frequently used for this purpose. In this case, it is possible to monitor the film thickness, morphology, and, more seldom, anisotropy. At the same time, similar methods for monitoring the film properties when using chemical synthesis techniques are practically absent.

The impossibility of monitoring in situ the properties is particularly pronounced when investigating the physical and chemical properties of nanoparticles, when experimental difficulties caused by the high reaction ability of analyzed samples occur. In particular, nanoparticles of iron-subgroup metals oxidize extremely fast even at small oxygen concentrations in the gas phase [1].

The risk of oxidation complicates transfer of samples from the reaction zone to the measuring facility, thus making it difficult to study the magnetic properties of particles with superparamagnetic sizes in particular. In addition, problems are often encountered in investigations of the kinetics of interaction between metal nanoparticles and the gas phase. These problems have both applied and basic characters.

For the above problems of physical chemistry to be solved, we have developed a setup based on a vibrating magnetometer [2, 3]. This setup is intended for in situ studying transformations of nanoparticles of ferromagnetic metals and their compounds followed by a change in their magnetization.

DESCRIPTION OF THE EXPERIMENTAL SETUP

The structural diagram of the setup for studying the topochemical processes is shown in Fig. 1. The central part of the setup is reactor 4 made of fused silica tubes in which an analyzed sample is located. The diagram of the reactor is shown in the inset in Fig. 1.

The sample mass is selected from the range of 1-50 mg. Gas-permeable heat-resistant spacers-locks made of T3MK fibrous material are used to fix the sample in place inside the reactor. The T3MK material is composed of hyperpure quartz fibers with operating temperatures ranging from 123 to 1500 K.

During investigations, the sample temperature may be set in the limits of 293–873 K for which the reactor core is placed in small-sized high-temperature furnace 11 (a heater), which is controlled by temperature controller 12. The temperature in the reactor center is measured by calibrated platinum–platinum-rhodium thermocouple 13. To protect the sensors and the electromagnet from the heat flow, cylindrical water-cooling jacket 20 is mounted outside furnace 11.

The reactor vibrates with a constant amplitude of 0.5 mm in the vertical plane with a frequency of 73 Hz. The system controlling the magnetic properties embodies the vibrating magnetometer principle. The reactor core is disposed in the gap of magnet I, which creates a magnetic field with a strength as high as 0.63 T and is powered by operator-controlled GPR-30H10D



Fig. 1. Structural diagram of the vibrating magnetometer for studying topochemical processes: (1) electromagnet, (2) power supply of the magnet, (3) magnetic field strength meter, (4) reactor, (5) vibrator, (6) power amplifier, (7) generator, (8) millivoltmeter, (9) gas system, (10) gas analyzer, (11) furnace, (12) thermocontroller, (13) Pt–PtRh thermocouple, (14) cooling system, (15) analog-to-digital converter, and (16) lock-in amplifier. Inset: the general view of the reactor core: (17) sample under investigation, (18) membrane made of T3MK fused silica fibers, (19) quartz tube, (20) cylindrical jacket of the running-water cooling, (21) measuring coils, and (22) glue.

dc source 2. The magnetic field strength is monitored by PIII1-10 meter 3.

Electromagnetic vibrator 5 with a power supply circuit and a stabilizer of the amplitude of oscillations is attached to the tube with the reactor to create mechanical oscillations. The sinusoidal oscillations are formed by Γ 3-123 low-frequency generator 7, amplified by LV103 power amplifier 6, and fed to the power supply circuit of the vibrator. The amplitude of its vibrations is measured by an induction sensor and monitored by a GVT-417B millivoltmeter 8. The signal from this induction sensor is also used in the feedback loop to stabilize the vibrational amplitude of vibrator 5.

Gas or gas mixture with a prescribed composition is blown through the reactor with a preset rate (in the range of $1-150 \text{ cm}^3/\text{min}$) by means of gas system 9, which is connected to the reactor via flexible lines. The gas flow rate is set by the "flow rate–pressure" regulating system. Depending on the goal of the study, the gases used in it are preliminarily cleaned of oxygen and water traces. Cleaning is performed using a system of serially connected columns with the following adsorbers: aluminum oxide, zeolite, and manganese dioxide deposited on silica gel. The gas cleaning system allows regular recovery of the adsorbers. The gases at the exit from the opposite reactor side are fed into the gas analyzer via flexible polymer hoses.

A system of selective photoacoustic detectors 10 developed by the Prokhorov General Physics Institute was used to analyze the composition of the gas released from the microreactor. This system incorporates CO, CO₂, and CH₄ detectors. Its operating principle is based on selective absorption of intensity-modulated

IR radiation by the gas component. Upon absorption of the modulated light beam, the gas generates an acoustic pulse emerging from the region that absorbed the optical energy.

Information on the temperature and composition of the supplied and released gases is digitized by analog-to-digital converter 15 and fed to the computer.

The system measuring the magnetic moment is traditional for vibrational magnetometry and includes two pairs of oppositely connected coils, which are glued to the end faces of the magnetic core of electromagnet *1*. The magnetic moment of the sample is determined from the emf induced in these coils by vibrations of the sample enclosed in the reactor.

The electrical signal produced in the coils is applied to the SR830 DSP dual-phase lock-in amplifier 16, which extracts, by means of synchronous detection, its in-phase U_s and quadrature U_Q components. Its peak-to-peak amplitude

$$U = \sqrt{U_S^2 + U_Q^2} \tag{1}$$

is determined after digitization.

This demodulation method allows us to avoid errors due to possible phase shifts of the input signal relative to the vibrator phase.

EXAMPLES OF SETUP APPLICATIONS

As noted above, the advantage of the setup, primarily, consists in the possibility of exploring a sample in a controlled gas medium and at elevated temperatures. This approach opens special prospects for studying metal-deposited heterogeneous catalysts containing iron-subgroup metals in a superfine state. Such metals



Fig. 2. Time dependences of the magnetization and rate of CH_4 and CO_2 production for the Fe/SiO₂ catalyst.

oxidize at room temperature even in the presence of only traces of oxygen. Recovery of a catalyst in a hydrogen flow directly in the measuring cell of the magnetometer solves this problem and, in addition, helps determine the fraction of the reduced metal and investigate the magnetic characteristics of obtained nanoparticles. In some cases, it is possible to use the magnetic granulometry method to obtain distributions of metal nanoparticles in their size. The last aspect opens up wide prospects for investigating the magnetic properties of various nanocomposites containing ferromagnetic metals.

Studying the Dynamics of CO Hydrogenation on Fe-Supported Catalysts

Apart from synthesis of hydrocarbons on the catalyst surface, topochemical processes take place in the course of CO hydrogenation on Fe-supported catalysts. As a result of the topochemical processes, iron carbides are produced, changing thereby the chemical composition of the catalyst. The used method of continuous magnetization measurements, together with the detection of changes in the compositions of the reacting gases, provides useful information in the dynamics of processes proceeding both on the catalyst surface and in the solid phase.

The time dependences of the magnetization and the rate of CH_4 and CO_2 production for the Fe/SiO₂ catalyst are presented in Fig. 2. In this case, the use of the setup allows us to observe both the change in the magnetization caused by the iron carbide production and the generation rate of methane and carbon dioxide. The magnetization curve makes it possible to determine the time when the maximum carbide generation rate is attained and, thereby, to obtain unique information on the sequence of processes that take place both on the catalyst surface and inside the solid phase [4].

Kinetics of the Metal Oxide Reduction Reaction

The existing methods for studying the kinetics of gas-solid body reactions are not always capable of providing the required accuracy of measurements, which may result in arbitrariness in interpretation of kinetic data. The method of continuous magnetization measurements in the course of the reaction solves this problem, at least, in the case of ferromagnetic samples [4, 5].

Figure 3 presents the temperature dependences of the hydrogen adsorption rate and the magnetization during temperature-programmed Fe_2O_3/SiO_2 reduction. The detector placed immediately behind the microreactor measured the hydrogen adsorption rate by the heat conductivity.

In this case, variations in the magnetization reflect the process of sequential reduction $Fe_2O_3-Fe_3O_4-Fe_3O_4-Fe_3O_4-Fe_3O_4$. FeO-Fe. Besides, the initial increase in the magnetization corresponds to production of magnetite Fe_3O_4 , and its subsequent decline is associated with the formation of antiferromagnetic wustite FeO. A low sluggishness of the microfurnace makes it possible to rapidly change from programmable heating to the isothermal mode, which in turn provides a means for



Fig. 3. Temperature dependences of (1) the hydrogen adsorption rate and (2) the change in the magnetization during temperature-programmed Fe_2O_3/SiO_2 reduction.

"freezing" the state of the analyzed sample and investigating its magnetic properties in this state.

Investigating the Kinetics of Adsorption on Ferromagnetic Metal Nanoparticles

The influence of adsorption on magnetization should undoubtedly be taken into account in investigation of the magnetic properties of ferromagnetic nanoparticles, in particular, topochemical transformations of ferromagnetic particles with nanosizes. This effect is most vivid in the case of adsorption on nickel.

For the deposited nickel catalysts, a linear and reversible dependence of the magnetization on the degree of the surface coverage with hydrogen is observed (i.e., the magnetic isotherm). The isotherm slope expressed in terms of Bohr's magnetons per adsorbed molecule is approximately $1.4\mu_B$. The atomic magnetic moment of nickel μ_{Ni} is $0.6\mu_B$ and, therefore, $\alpha_{H_2} \approx 2\mu_{Ni}$. This means that approximately two nickel atoms are excluded from magnetic interaction during dissociative hydrogen adsorption on nickel.

Figure 4 presents the time dependence of the relative magnetization for the Ni/Cr₂O₃ catalyst upon replacing the hydrogen flow with the argon flow and vice versa at T = 400 K. According to the figure, replacement of hydrogen with argon is followed by an increase in the magnetization, which essentially reflects the hydrogen desorption process. Replacement of argon with hydrogen results in a fast decrease in the magnetization down to the initial level. Varia-



Fig. 4. Time dependence of the relative magnetization for the Ni/Cr₂O₃ catalyst when the hydrogen flow is replaced with argon flow and vice versa at a temperature of 400 K.

tions in the magnetization upon hydrogen adsorption and desorption are essentially the adsorption and desorption isotherms. Therefore, the method is applicable to studying the kinetics of adsorption and desorption on nanoparticles of some metals.

CONCLUSIONS

The presented applications of the developed setup demonstrate the wide potential of the method for studying various materials containing ferromagnetics in a controlled gas medium at temperatures ranging from room temperature to 873 K.

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