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SHORT COMMUNICATIONS

Interaction of Metallic Iron Particles with Molecular Hydrogen

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In the context of the problem of hydrogen-based energetics, which is currently gaining in importance, metal-hydrogen systems, specifically Fe-H₂ systems, came to the attention of researchers. It is known [1] that bulk metallic iron absorbs molecular H₂ to yield interstitial solid solutions with a hydrogen content no higher than 0.1 wt %. On the other hand, bulk hydrides FeH_x $(x \le 1)$ arise in iron-hydrogen systems only at sufficiently high pressures [2–4], at which they are thermodynamically instable. Meanwhile, using the molecular beam technique [5, 6], it was shown that, at 110 K in a deep vacuum, small clusters of metallic iron (to several tens of Fe atoms) retain ~2 H atoms per Fe atom in the cluster. We have found an analogous effect in the reduction of iron oxide nanostructures: the absorption of hydrogen in excess of the stoichiometric amount.

Iron oxide nanostructures were obtained by the method of isolation in a matrix: in-situ thermal oxidative decomposition of a Fe-containing precursor adsorbed in a porous inorganic matrix. For the precursor, trinuclear iron dodecacarbonyl $Fe_3(CO)_{12}$ was used. Porous crystalline materials (molecular sieves with spatially ordered systems of channels and cavities)—microporous NaY zeolite (pore size 0.8 nm) and mesoporous MCM-41 silicate (3.0 nm)—and amorphous Silochrom S-120 silica gel (30 nm) were used as matrices.

Iron carbonyl Fe₃(CO)₁₂ used as the precursor was dissolved in toluene and introduced into the matrices so that the total Fe content of samples was no higher than 1 wt %. After the removal of the solvent, the samples were oxidized at 550°C in a flow of air for 6 h. Iron oxide formed in pores of the support was reduced in a flow of Ar containing 3.5 vol % H₂. A bulk Fe₂O₃ sample was investigated for reference. The reduction was carried out in the regime of linear rise of temperature (8 K/min) to 1000°C with the measurement of the rate of absorption of hydrogen. The total absorbed amount of hydrogen was determined by the area under the obtained temperature-programmed reduction (TPR) curve.

TPR curves of the investigated samples have two temperature regions of reduction of iron oxide with maximums at 480 and 800°C. In the bulk sample, Fe_2O_3 is reduced to Fe_3O_4 at 380–397°C, and Fe_3O_4 , to

metallic Fe at 465–597°C [7]. According to the data [8–10], such a significant temperature shift in the reduction of iron oxides points to the formation of oxide nano-structures, which are located in pores of the matrix and not on its outer surface.

Total absorbed amounts of H_2 for the reduction of iron oxide in the investigated samples and bulk Fe_2O_3 are listed below:

Matrix		NaY		MCM-41		SiO ₂ Fe ₂ O ₃ *	
Fe, wt %	0.12	0.41	0.69	0.15	0.13	0.31	70
H ₂ /Fe	3.5	2.5	1.7	4.3	3.6	2.8	1.5
H/Fe**	4	2	0.5	5	4	2	-

*Bulk oxide.

**Less the amount consumed for the reduction.

From the data obtained, it follows that the total absorbed amount of H_2 in the TPR of bulk Fe_2O_3 corresponds to the stoichiometric ratio (1.50) for the complete reduction of the sample to metallic iron. In check experiments on TPR with initial matrices, H_2 was not absorbed over the entire investigated temperature range (20–1000°C); therefore, the difference between the total absorbed amount of H_2 measured for an Fe-containing sample and the amount required for its complete reduction corresponds to the amount of hydrogen held in metallic iron nanoclusters. Quantitative estimates of this amount are listed above as H/Fe atomic ratios.

For Fe₁₀ metallic iron clusters in conditions of high vacuum, H/Fe = 1.8 [6], which is in sufficiently close agreement with our data obtained in the regime of temperature-programmed reduction of iron oxide at a partial H₂ pressure of ~3.5 kPa. From the obtained data, it follows that, at the lowest metallic iron concentration in the zeolite matrix, the nanophase holds to 6–8 wt % of hydrogen.

Thus, metallic iron nanoclusters absorb molecular hydrogen not only in a vacuum but also in ordinary conditions; in this case, hydride-like compounds formed are significantly enriched in hydrogen as compared to the bulk phase. This work was supported by the Russian Foundation for Basic Research (project no. 05-03-32045-a) and the "Program for Support of Leading Scientific Schools of the Russian Federation" (project nos. NSh-1275.2003.3 and RI-112/001/056).

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