STRUCTURE AND FERROMAGNETIC RESONANCE OF NICKEL-FORMATE CATALYSTS FOR FAT HYDROGENATION

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STRUCTURE AND FERROMAGNETIC RESONANCE OF NICKEL-FORMATE CATALYSTS FOR FAT HYDROGENATION

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To obtain highly active nickel-formate catalysts for the hydrogenation of fats, it is essential to clarify the relationship between the activity of the catalyst, the presence of hydrogen in it, its structure, and its magnetic properties.

The catalysts were prepared by thermal decomposition of nickel formate in sunflower oil with simultaneous purging by H_2; it was shown ([2]) that H_2 promotes the decomposition of nickel formate and the formation of a highly active catalyst.

The following catalysts were investigated, obtained by degreasing active nickel powder with dioxane and drying in vacuum:

No. 1. An ordinary nickel catalyst obtained by decomposition of nickel formate in sunflower oil while purging with H_2.

No. 1a. Catalyst No. 1, sintered in vacuum at 300°.

No. 1b. Catalyst No. 1, sintered in air at 340°.

No. 2. A nickel catalyst obtained by decomposition of nickel formate in sunflower oil while purging with N_2.

No. 3. Catalyst No. 1, dehydrogenated by heating with nitrobenzene.

No. 3a. Catalyst No. 3, sintered in vacuum at $t = 300°$.

No. 4. Catalyst No. 3, treated with quinone for complete removal of hydrogen.

No. 5. Catalyst No. 4, sintered in air at $t = 300°$.

X-ray structural studies were carried out on a URS-55a-type apparatus with K_αCu radiation and a Ni filter, in RKD cameras, by the asymmetric method. The size of the coherent-scattering blocks was determined from the width of the nickel (200) line.

The magnetic susceptibility of the catalysts was studied by the Faraday method in the range $H = 1700$–4500 oersteds. For all catalysts, saturation was observed at 2500 oersteds. The ferromagnetic resonance (f.r.) spectra were recorded

Fig. 1

Figure 1: Fig. 1

on an RE13-01 spectrometer at a frequency of 9326 MHz. The line width was determined between the points of maximum slope, and the g factor was calculated using DPPH. A parallel investigation of the magnetic properties of samples in vacuum and in air showed that exposing degreased nickel powder to air does not lead to any changes in the intensity or shape of the ferromagnetic-resonance signal or in the magnetic susceptibility.

The main results of the X-ray structural and magnetic study of the catalysts are given in Table 1. Of greatest interest is the small width of the f.r. lines of the catalysts studied, especially 2 and 3. In work ([3]), in a study of colloidal Ni particles, it was shown that the line ΔH, depending on the method of preparation of the colloidal system, was 450–500 oersteds, and $g = 2.22$. This g factor was obtained when the resonance condition was calculated in the form $h\nu = g\beta Hz$, i.e., without taking account of the demagnetizing factor, which indicates the spherical shape of the colloidal particles. The closeness of the values of ΔH and g in the case of powdered nickel catalysts to these values for colloidal nickel particles allows one to assume that we are dealing with a "solid colloidal" system of spherical nickel particles of high dispersity. The high dispersity of the Ni particles in these catalysts is indicated both by the data

of X-ray analysis, as well as the extremely low values of σ for a number of nickel catalysts (Table 1). It may be thought that resonance in individual particles, which apparently are close to single-domain ones, takes place under conditions of uniform magnetization of the substance (the influence of the skin effect is small), i.e., the line width is not due to magnetization inhomogeneity. The small line width of catalysts 2 and 3 is also not related to the spin-lattice relaxation time (ΔH does not change at $-195°$) and is probably caused by processes of spin-electron relaxation (interaction of the ferromagnetic system with conduction electrons) and by dipole-dipole interaction between Ni crystallites, leading to line narrowing [4].

Fig. 1. Ferromagnetic resonance spectra of nickel-formate catalysts: a – catalyst No. 1; b –catalyst No. 2; v –catalyst No. 3.

Considering the data obtained, it may be noted that the changes in ΔH and σ do not correlate in any regular way with the presence or absence of H_2 in the catalysts. In contrast to the work [5], where it was shown that removal of H_2 from Raney Ni led to an increase in σ, in some of the catalysts studied the removal of hydrogen leads to a sharp decrease in σ (compare catalysts 1, 3, and 4), while at the same time, in catalyst 2, which contains hydrogen, σ has the same value as in the dehydrogenated catalysts 3 and 4.

Calculation of the lattice parameter shows that hydrogen forms with Ni neither the hexagonal form NiH_2 nor the cubic modification β-NiH_2 [6]; however, it is

Fig. 3

Figure 2: Fig. 3

not excluded that it partially enters the lattice in the form of a solid solution*. At the same time, hydrogen has a decisive influence on catalytic activity, and its removal from Ni leads to irreversible changes in the activity and structure of the catalyst (X-ray diffraction patterns 2 and 3 in Fig. 2, see inset on p. 1338). This is the fundamental difference between catalysts of this type and Raney Ni, removal of hydrogen from which does not cause significant structural changes, while the activity is restored upon repeated treatment of the catalyst with H_2 at 300° [7].

Fig. 3. Ferromagnetic resonance spectra of thermally treated nickel-formate catalyst No. 3: *a* —initial catalyst; *b* —catalyst sintered in air at 300° for 2 h (at the same amplification); *v* —catalyst sintered in vacuum at 300° for 4 h; *g* — catalyst sintered in vacuum at 300° for 4 h.

The reason for this difference is that nickel-formate catalysts, unlike Raney Ni, have a much "looser" and therefore very labile structure. This is especially evident from experiments on sintering in vacuum and in air of dehydrogenated catalyst 3 (Fig. 3). Heating highly dispersed Ni in air at 300° for 2 h leads to a sharp increase in the intensity of the ferromagnetic-resonance signal and in the value of σ (Fig. 3a, b). An analogous picture is also observed for catalyst 4. This is due to the fact that, for the very labile structure of catalyst 3, sintering that occurs upon heating in air and leads to an increase in the size of Ni particles and, correspondingly, to an increase in σ and in the intensity of the ferromagnetic-resonance signal, proceeds at a much higher rate than the process of oxidation of Ni to NiO. Such a process of intense sintering does not occur in cataly-

* The catalyst contains 110 ml H_2 per 1 g.

catalyst 1, in which there is H_2, i.e., in this case the presence of hydrogen prevents sintering, as was also observed for Raney Ni ([7]). It should be noted that sintering in air and in vacuum leads to a substantially different form of the f.r. signal (Figs. 3 and). The strong asymmetry of the f.r. signal for the sample sintered in air is apparently due to the larger size of the Ni particles in this case (Table 1, catalysts 1, 1a, and 1b), as well as to chemical inhomogeneity (the appearance of NiO), and therefore is associated with an increase in the inhomogeneity of magnetization, which usually leads to asymmetry of the line shape.

We have already said above that the presence of hydrogen in the catalyst structure ensures high activity, whereas the removal of hydrogen leads to irreversible deactivation of the catalyst. How, then, is the hydrogen distributed in the catalyst? Apparently, the distribution of hydrogen in nickel-formate catalysts is analogous to its distribution in Raney Ni ([7]), i.e., part of the hydrogen is located between the primary Ni crystallites, and part between secondary particles built

up from the primary crystallites. These forms of hydrogen are not equivalent in their influence on the activity of the catalyst. Thus, considering the data of Table 1 and Fig. 1, one can see that catalysts 2 and 3 are completely identical in physical properties and sharply different in activity. Apparently, treatment of the catalyst with nitrobenzene leads to removal of the most active hydrogen, and the resulting catalyst 3 is inactive, although it still contains hydrogen. Catalyst 2 also contains hydrogen, which is obtained upon decomposition of Ni formate, but this hydrogen is in an active form and the catalyst is active. It is still unclear which of the two forms of hydrogen is the more active and how the hydrogen is bound to Ni (ionic or radical form).

Table 1

Catalyst No.	111	200	220	311	222	400	331	420	Block size, Å	Lattice parameter a^*, Å	Saturation magnetization b, CGS	Line width $\Delta H'$, Oe	g	Activity, l/g·h
1	s.	med.	med.	med.	weak	v. weak	weak	weak	80 – 120	3.52	7.2	540	2.22	96.5
1a	s.	med.	med.	med.	weak	v. weak	weak	weak	130 – 150	3.51	20.0	1400	–	5–10
1b	s.	med.	med.	med.	weak	v. weak	weak	weak	200 – 250	3.53	–	600	–	inactive
2	med.	weak	v. weak	–	–	–	–	–	50 – 60	3.58	0.38	300 **	2.22	90.0
3	med.	weak	v. weak	–	–	–	–	–	40 – 60	3.58	0.30	300	2.22	inactive
3a	s.	weak	med.	weak	v. weak	v. weak	v. weak	v. weak	170 – 200	–	14.0	900	–	inactive
4	–	–	–	–	–	–	–	–	–	–	0.50	720	–	inactive
5	s.	med.	med.	med.	weak	v. weak	weak	weak	170 – 200	3.53	1.5	840	–	inactive

* From the 200 or 220 line.

** The line width at −195° did not change.

Consideration of the data presented, and especially of the characteristics of the f.r. spectra, shows that the high dispersity and activity of the nickel powder obtained are due first of all to carrying out the process of nickel formate decomposition in a viscous, high-boiling medium ([2]), which prevents aggregation of the particles and leads to the creation of a "solid" colloidal system of Ni particles.

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CITED LITERATURE

[1] *Technological instruction for fat processing*, 1955. [2] B. N. Tyutyunnikov, I. I. Novitskaya, *Oil-and-Fat Industry*, No. 12 (1961); I. I. Novitskaya, Dissertation, Kharkov, 1963. [3] D. M. S. Bagguley, *Proc. Roy. Soc.*, A228, 549 (1955). [4] E. A. Turov, in the collection *Ferromagnetic Resonance*, ed. by S. V. Vonsovskii, M., 1961, p. 252. [5] R. J. Kokes, P. H. Emmett, *J. Am. Chem. Soc.*, 81, 5032 (1959). [6] B. Baranowski, Z. Szklarska-Smialowska, M. Smialowski, *Bull. Acad. Pol. Sci. (Ser. Sci. Chim.)*, 6, 179 (1958); T. Boniszewski, G. C. Smith, *J. Phys. Chem. Solids*, 21, 115 (1961). [7] V. D. Krylov, L. Kh. Freidlin, K. G. Rudneva, *Izv. AN SSSR, OKhN*, 1957, 546.

Note: Figure translations are in progress. See original paper for figures.