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THERMOANALYTICAL AND MÖSSBAUER SPECTROSCOPIC STUDIES OF PHASE TRANSFORMATIONS OF AMORPHOUS CHROMIUM HYDROXIDE

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To establish the structures of the phase transformation products of amorphous chromium hydroxide and the region of their stability, the thermally initiated transformations were studied at normal and reduced pressure (0.133 Pa) by differential thermal analysis, Mössbauer spectroscopy (on admixed ^{57}Fe atoms) and X-ray diffraction phase analysis.

At reduced pressure the region of stability of amorphous chromium oxide formed during hydroxide dehydration is wider.

The Mössbauer shift of admixed ^{57}Fe atoms in amorphous chromium hydroxide is characteristic of Fe^{3+}, but the magnitude of the quadrupole splitting considerably exceeds those for simple and compound iron oxides and oxide-hydroxides. From this, it can be concluded that the symmetry of the local environment of the chromium atoms in amorphous chromium hydroxide is anomalously low.

The practical application of chromium hydroxide in the production of catalysts, sorbents, pigments, etc. leads to the necessity of further investigation of the phase transformations of the initial amorphous chromium hydroxide [1, 2]. However, the X-ray amorphous state of the majority of the products of the solid-phase transformations of chromium hydroxide challenges the application of modern structure-sensitive methods for this purpose.

To establish the structures of the products of the phase transformations and the regions of their stability, the thermally initiated transformations were studied in a wide range of low pressure (down to 0.133 Pa) by means of differential thermal analysis, nuclear gamma resonance (Mössbauer) spectroscopy and X-ray diffraction phase analysis.

Experimental

Thermal analysis at low pressures was performed with a photorecording pyrometer, according to the technique described in [3, 4].

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TG–DTG–DTA diagrams were obtained with a derivatograph. X-ray diffraction phase analysis was performed in a DROV diffractometer and also in the installation of URS–60 type in the RKD chamber, with the use of cobalt and iron radiation. Samples were identified by comparison with published data [5]. Mössbauer spectra of ^{57}Fe were recorded at 80 and 295 K with a YGRS–4m spectrometer with a ^{57}Co source in palladium at 295 K. The surface density was 0.1 mg cm^{-2} for ^{57}Fe [6, 7]. The measured shifts are presented with respect to α-Fe. The method of Mössbauer spectroscopy on impurity atoms of ^{57}Fe was used to study the structure of the nearest order of amorphous chromium hydroxide. For this purpose, in the process of chromium hydroxide synthesis, a preparation enriched up to 92% of iron isotope ^{57}Fe was introduced into its composition. It was assumed that iron atoms substitute chromium atoms in the amorphous hydroxide and that the parameters of the ^{57}Fe Mössbauer spectra provide information on the chemical nature and symmetry of the local surroundings of the chromium atoms. For comparison, the synthesis of iron hydroxide was carried out simultaneously under similar conditions. The difference in the parameters of the Mössbauer spectra of ^{57}Fe for iron and chromium hydroxides was an additional indication that admixed iron atoms penetrate into the chromium hydroxide (and do not generate a phase of their own).

Samples of chromium and iron hydroxides were obtained by rapid pouring of 1 N ammonium hydroxide into 1 N solutions of nitrate salts, under intensive stirring. The final pH value was equal to 10 at temperatures close to 273 K.

For the doping of chromium hydroxide with iron(III), the preliminary mixtures of the initial chromium and iron salts in the necessary concentrations were prepared with an iron concentration of 0.3 M. The sediments obtained were then purified by washing with water, decantation and centrifugation. The purified hydroxide sediment was dried over P_2O_5 in a desiccator at low pressures. The water content of the chromium hydroxide was about 45%.

Results and discussion

The DTA curve of the initially X-ray amorphous chromium hydroxide at atmospheric pressure shows superimposed endothermic effects of dehydration in the temperature range 378–573 K (Fig. 1, curve 1). Removal of the last mole of water occurs prior to the exothermic effect. Up to the onset temperature of the exothermic effect, the decomposition product is amorphous to X-rays. The exothermic effect at 753–793 K corresponds to the crystallization of chromium oxide. The present investigation of the solid-phase transformations of amorphous chromium hydroxide in a wide range of low pressures showed that, with decreasing external pressure, the region of existence of amorphous chromium oxide is

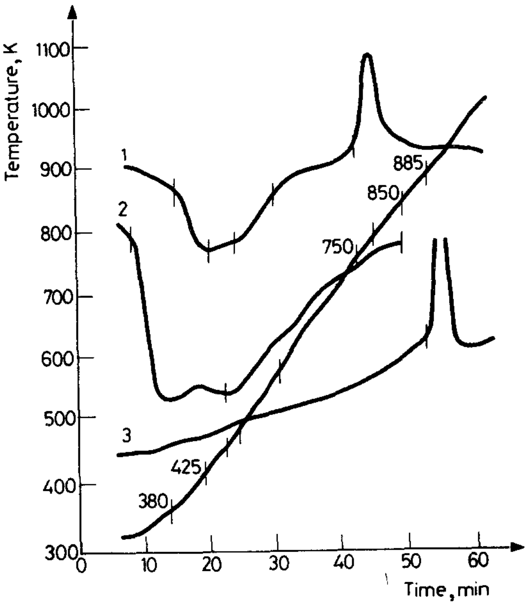

Fig. 1 DTA curves of chromium hydroxide heating, at: 1 – atmospheric pressure, 2 – 266.6 Pa up to 843 K, 3 – reheating of sample 2 above the exoeffect, 4 – temperature curve

increased by two factor. Firstly, both the temperature of the crystallization exoeffect and its peak height in the DTA curve are increased at reduced pressure. Thus, at 266.6 Pa the temperature of the exothermic effect of crystallization is increased by more than 100 deg. Secondly, the temperature of the dehydration decreases with decreasing pressure. The wider region of existence of amorphous chromium oxide is due to the fact that at reduced pressure the water contained in the amorphous hydroxide is removed at lower temperatures. Thus, its catalytic effect on the crystallization processes is excluded. Consequently, the DTA curve of the sample heated up to 843 K at 266.6 Pa (Fig. 1, curve 2) does not show the exothermic effect of crystallization. This temperature is approximately 80 deg higher than that of the crystallization at atmospheric pressure. The X-ray diffractogram of the given sample does not reveal any peaks; the product is in an amorphous state (Fig. 2, curve 1). The DTA curve obtained upon reheating of this sample under the same conditions shows only one exothermic effect of crystallization, beginning at 833 K (Fig. 1, curve 3). The X-ray diffractogram (Fig. 2, curve 2) indicates that, during the exothermic effect, crystalline α-Cr_2O_3 is formed. The temperature range of the stability region of X-ray amorphous chromium oxide, as determined from the data of thermal analysis, is > 350 deg at 266.6 Pa < 150 deg at

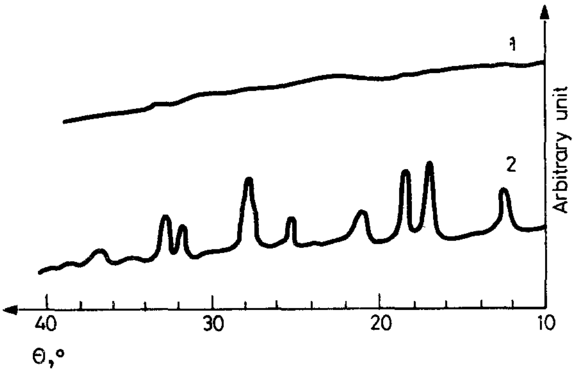

Fig. 2 X-ray diffractograms of thermal treatment products of amorphous chromium hydroxide: 1 – heated to the outset temperature of the exoeffect, 2 – heated to the final temperature of the exoeffect

atmospheric pressure. Thus, by decreasing the pressure, it is possible to extend the region of X-ray amorphous chromium oxide 2–3 fold.

Amorphous oxide samples were obtained in a dynamic mode, i.e. under conditions of simultaneous recording of thermal curves at low pressures at heating rates of 5–10 deg min^{-1}. The samples were abruptly cooled down until the attainment of the stability regions of the amorphous oxides (this was usually 50–30 deg below the onset temperature of crystallization under dynamic conditions). The oxide samples obtained in this way X-ray amorphous. Crystalline

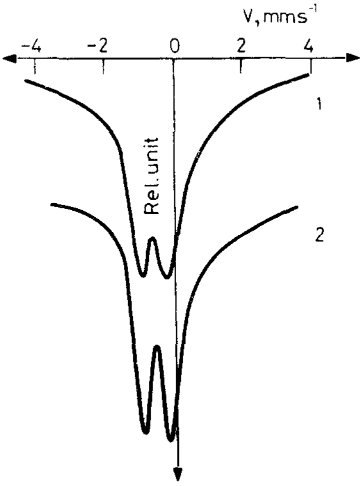

Fig. 3 Mössbauer spectra of amorphous iron hydroxide: 1 – at 80 K, 2 – at 295 K

Table 1 Mössbauer spectral parameters for ^{57}Fe in amorphous chromium(III) and iron(III) hydroxides

Composition	T,	δ, mm/s	Δ, mm/s	H. K.
Chromium hydroxide	295	0.35	1.40	—
	80	0.38	1.40	—
Iron hydroxide	295	0.45	0.74	—
	80	0.50	0.73	—
α-Cr_2O_3	295	0.35	0.3	—
	80	0.35	—	410
Errors		±2	±0.03	±5

Note: δ, Δ, and H are the isomeric shift, the quadrupole splitting and the effective magnetic field acting on the ^{57}Fe nuclei, respectively.

products of dehydration, i.e. oxides, were obtained on abrupt cooling of the samples after the attainment of the final temperature of the crystallization exoeffect.

The Mössbauer spectra of amorphous iron hydroxide at 80 and 295 K exhibit a quadrupole doublet (Fig. 3), corresponding to trivalent iron in an environment with less than cubic symmetry. Amorphous iron hydroxide was subjected to Mössbauer studies, and our Mössbauer spectral parameters (see the Table 1) are in good agreement with available data [7]. The Mössbauer spectra of impurity atoms of ^{57}Fe in amorphous chromium hydroxide at 80 and 295 K also display a quadrupole doublet (Fig. 4), corresponding to trivalent iron, but the value of the quadrupole

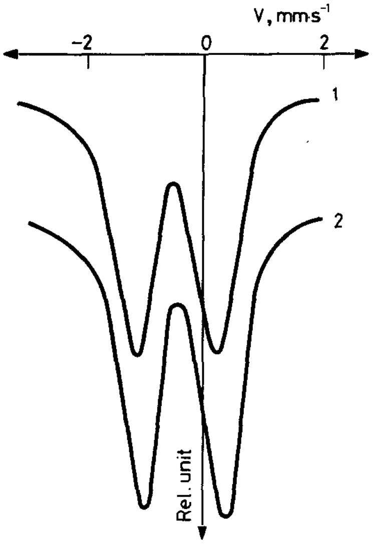

Fig. 4 Mössbauer spectra of ^{57}Fe in amorphous chromium hydroxide at: 1 – 80 K, 2 – 295 K

splitting is much higher than for the spectrum of amorphous iron hydroxide (see the Table). This result confirms that, during the precipitation of chromium hydroxide, the impurity ions of Fe^{+3} do not form a separate phase of iron hydroxide, but are included in the structure of the amorphous chromium hydroxide as a substitution impurity (instead of Cr^{+3} ions). The isomeric shift in the spectra of the ^{57}Fe impurity atoms in the amorphous hydroxide is typical of trivalent iron having oxygen atoms in the first coordination sphere, but those known for simple and mixed oxides and hydroxides of trivalent iron [1]. On the basis of these results, it should be concluded that the local surroundings of the chromium atoms in amorphous chromium hydroxide have abnormally low symmetry. The Mössbauer spectra of crystalline α-Fe_2O_3 obtained during the dehydration of amorphous iron hydroxide reveal typical magnetic sextuplets, and the values obtained for the effective magnetic fields on the ^{57}Fe nuclei (see the Table) are in agreement with the available data [7]. The fine structure of the Mössbauer spectra of the ^{57}Fe impurity atoms in crystalline α-Cr_2O_3 depends on the measurement temperature (Fig. 5). At 295 K, there is a single broad line (G = 0.96 mm/s) (curve 2), corresponding to trivalent iron, while at 80 K, there is a magnetic sextuplet (Fig. 5, curve 1). Such spectra behaviour agrees with the fact that at low temperature α-Cr_2O_3 is an antiferromagnet in a superparamagnetic state according to [7]. the Néel temperature of α-Cr_2O_3 is not constant, depending on the dispersion degree, and in any case is below 320 K. According to the Mössbauer spectra, it is possible to conclude that the dispersity of the crystalline particles does not exceed 100–200 Å.

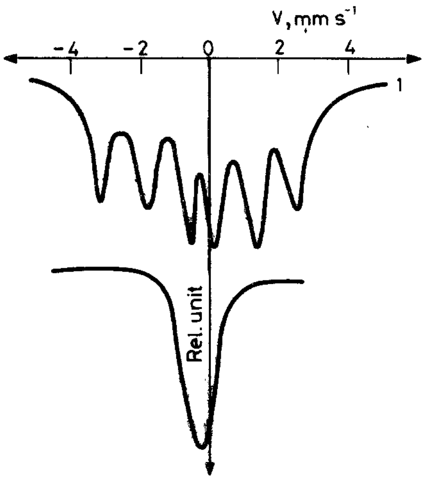

Fig. 5 Mössbauer spectra of ^{57}Fe in crystalline Cr_2O_3: 1 – at 80 K, 2 – 295 K

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Zusammenfassung — Um die Struktur der Umwandlungsprodukte des amorphen Chrom(III)-oxids und seinen Existenzbereich zu ermitteln, wurden die thermischen Umwandlungen bei normalem und vermindertem Druck (0,133 Pa) durch DTA, Mössbauer-Spektroskopie (an zugesetzten ^{57}Fe-Atomen) und Röntgenbeugungs-Phasenanalyse untersucht. Unter vermindertem Druck wird der Stabilitätsbereich des bei der Entwässerung des Hydroxids gebildeten amorphen Chrom(III)-oxids erweitert. Die Mössbauer-Verschiebung von zugesetzten ^{57}Fe-Atomen in amorphem Chrom(III)-oxid ist charakteristisch für Fe^{3+}, die Quadrupol-Aufspaltung übertrifft die für einfache und komplexe Eisenoxide und -oxid-hydroxide beträchtlich. Daraus wird geschlossen, dass die Symmetrie der Umgebung der Chromatome im amorphen Chrom(III)-oxid ungewöhnlich niedrig ist.

Резюме — С целью определения строения продуктов фазового перехода гидроокиси хрома и областей их устойчивости, термически наведенные превращения его были изучены при нормальном и пониженном давлении (0.133 Па) с помощью ДТА, мёззбауэровской спектроскопии на примесных ^{57}Fe атомах и рентгенофазового анализа. Установлен более широкий интервал устойчивости аморфной окиси хрома, образующейся при дегидратации гидроокиси при пониженном давлении. Мёссбауэровский сдвиг примесных ^{57}Fe атомов в аморфной гидроокиси хрома является характеристичным для Fe^{3+}, но величина квадрупольного расщепления значительно превышает таковое для простых и сложных окислов железа и смесей окись–гидроокись железа. Сделано заключение об аномально низкой симметрии локального окружения атомов хрома в аморфной гидроокиси хрома.