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Preparation of Supported Iron-Containing Catalysts from a $FeSo_4$ Solution: The Effect of the Support

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Abstract—The iron compounds resulting from the impregnation of the most common supports—alumina and silica gel—with an aqueous $FeSO_4 \cdot 7H_2O$ solution and subsequent heat treatment in air are identified by thermal analysis and Mössbauer spectroscopy. The state of the active component of the iron-containing catalysts depends strongly on the nature of the support.

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Iron-containing systems are catalytically active in a variety of chemical reactions. Iron oxide catalysts are active in ethylbenzene dehydrogenation into styrene [1], the water gas shift reaction [2], selective methane oxidation into formaldehyde [3], and selective hydrogen sulfide oxidation into sulfur [4]. Iron sulfide is active in the hydrodechlorination of chlorinated organic compounds [5] and coal liquefaction [6]. Iron metal is used as a catalyst for ethane decomposition to obtain fibrous materials [7].

The synthesis of supported Fe-containing catalysts from iron(III) nitrate was studied in detail [8–12]. These catalysts contain α-Fe_2O_3 particles, whose size depends on the iron concentration in the solution and on the heat treatment temperature. The preparation of catalysts from iron(II) sulfate received little attention, even though this compound is cheap waste from metallurgy.

Here, we report the surface compounds of iron that result from the impregnation of the most common supports—alumina and silica gel—with an aqueous $FeSO_4 \cdot 7H_2O$ solution and the conversions of these compounds upon subsequent heat treatment in air.

EXPERIMENTAL

Catalysts were prepared from alumina with a specific surface area of 224 m^2/g, a mean pore diameter of 122 Å, and a pore volume of 0.73 cm^3/g (ZAO Promyshlennye Katalizatory); silica gel KSKG with a specific surface area of 287 m^2/g, a mean pore diameter of 141 Å, and a pore volume of 0.35 cm^3/g (OOO KhromAnalit); and $FeSO_4 \cdot 7H_2O$ (Iron(II) sulfate heptahydrate, ACS, 99%, CAS 7782-63-0). Alumina and silica gel (0.25–0.50 mm size fraction) were impregnated once with an aqueous solution of iron(II) sulfate at room temperature and were dried at room temperature and then at 110°C for 4 h. $FeSO_4/Al_2O_3$ was calcined at 500°C, and $FeSO_4/SiO_2$ was calcined at 450, 500, or 550°C, both in argon for 4 h. Fe/Al_2O_3 and Fe/SiO_2 samples will be designated FA and FS, respectively, with a number in parentheses indicating the calcination temperature (°C). According to chemical analysis data, the Fe content of the FS(500) sample is 3.47 wt %, and that of the FA(500) sample is 2.92 wt %.

Thermal analyses (TGA and DSC) were carried out on a Netzsch STA 449 C Jupiter thermal analyzer between 25 and 600°C in flowing air at a heating rate of 10 K/min. The sample (20 mg) was placed in a corundum crucible. The reference sample was calcined alumina.

Mössbauer spectra were recorded at 22°C on an NP-610 spectrometer with a $^{57}Co(Ru)$ source. The error in the measurements of the chemical shift δ (relative to α-Fe) and the quadrupole splitting ε was 0.01 and 0.02 mm/s, respectively.

Analyses for Fe and SO_4^{2-} were carried out by inductively coupled plasma atomic emission spectroscopy using an Optima 4300 DV instrument (Perkin Elmer).

RESULTS AND DISCUSSION

The iron compounds that resulted from the impregnation of alumina and silica gel with an iron(II) sulfate solution followed by heat treatment turned out to be X-ray-amorphous. For this reason, we used thermal analysis and Mössbauer spectroscopy in their identification.

Figure 1 shows the Mössbauer spectra of the initial salt $FeSO_4 \cdot 7H_2O$ and alumina pellets impregnated with a solution of this salt and dried at 110°C. The spectrum of the salt is a quadrupole doublet with a

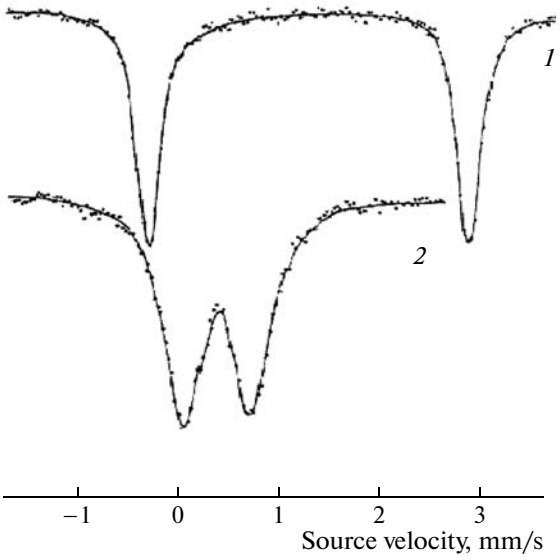

Fig. 1. Mössbauer spectra of (*1*) $FeSO_4 \cdot 7H_2O$ and (*2*) FA(110).

chemical shift of $\delta = 1.26$ mm/s and a quadrupole splitting of $\varepsilon = 3.20$ mm/s. These parameters are typical of the Fe^{2+} ion and are in agreement with the data reported for iron(II) sulfate heptahydrate [13]. The spectrum of the pellets impregnated with the salt solution appears as a quadrupole doublet of broad lines. Its parameters ($\delta = 0.36$ mm/s and $\varepsilon = 0.66$ mm/s) are characteristic of the Fe^{3+} ion in amorphous iron(III) hydroxide [14]. These data suggest that the Fe^{3+} ions on the alumina surface are in hydroxide form.

Figure 2 shows the Mössbauer spectra of the reference sample α-Fe_2O_3 and the FA(500) sample. The spectrum of FA(500) is a superposition of the lines due to magnetically ordered Fe^{3+} ions and the quadrupole doublet. The first group of lines is characteristic of Fe^{3+} in α-Fe_2O_3. This is indicated by the similarity between the observed value of the effective magnetic field on the iron nuclei ($H_{eff} \sim 480$ kOe) and the same parameter for crystalline iron oxide (515 kOe). The decrease in H_{eff} and the marked broadening of spectral lines are typical indications of the small size and poor crystallinity of iron(III) oxide particles on the catalyst surface [15]. We believe that the doublets in the central part of the spectrum are due to the paramagnetic form of Fe_2O_3 with a particle size of ~100 Å.

The Mössbauer spectra of FS(110), FS(450), and FS(550) are presented in Fig. 3. The spectrum of FS(110) is a superposition of two quadrupole doublets of noticeably broadened lines. The first, main doublet is due to Fe^{3+} ($\delta = 0.43$ mm/s, $\varepsilon = 0.78$ mm/s, $\Gamma = 0.62$ mm/s), and the other is due to Fe^{2+} (only the right component is visible, occurring at $\delta = 2.35$ mm/s). The Fe^{3+} chemical shift for FS(110) is higher than the chemical shift for iron(III) hydroxide, indicating a greater Fe–O bond strength in the former,

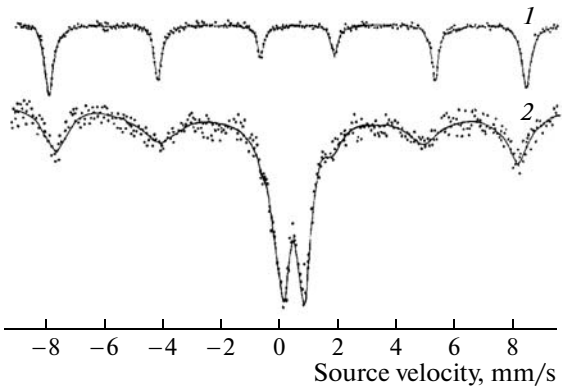

Fig. 2. Mössbauer spectra of (*1*) α-Fe_2O_3 and (*2*) FA(500).

and the large ε value suggests that the Fe^{3+} ions in FS(110) are significantly inequivalent. This inequivalence can result from both hydroxyl and sulfate groups being present in the first coordination sphere of the iron atoms. The spectrum of FS(450) shows only the main doublet, which occurs at the same δ as in the spectrum of FS(110) and is characterized by a still higher quadrupole splitting and line widths. This is evidence of a still greater covalence anisotropy of the Fe–O bonds and a heavier distortion of the coordination sphere around the metal atom. This is likely due to the larger number of sulfate groups and the smaller number of hydroxyl groups in the closest environment of the iron atoms. As the calcination temperature is further raised, the quadrupole splitting vanishes, giving way to a singlet at a rather large δ of 0.55 mm/s.

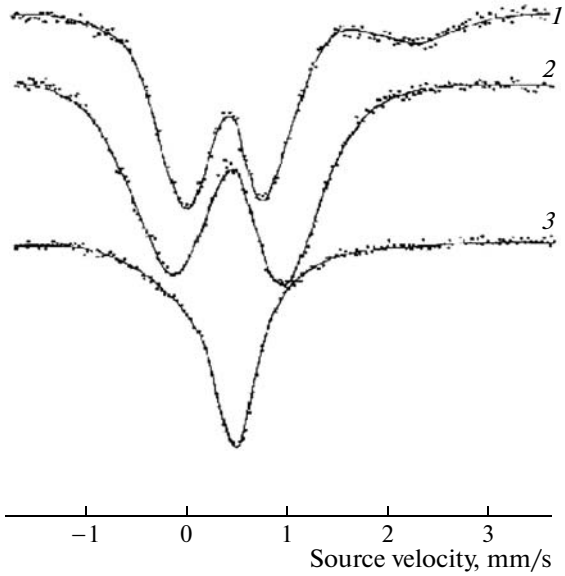

Fig. 3. Mössbauer spectra of (*1*) FS(110), (*2*) FS(450), and (*3*) FS(550).

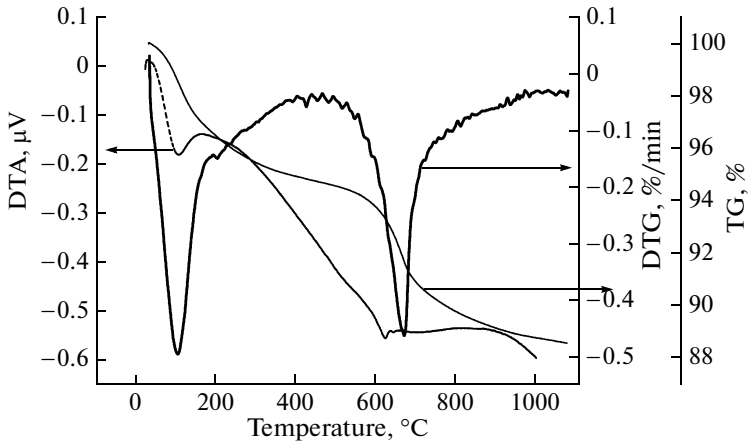

Fig. 4. Thermal analysis of FS(110).

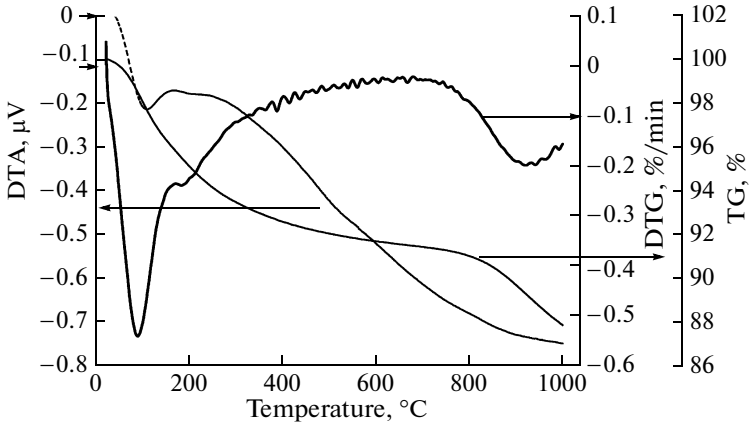

Fig. 5. Thermal analysis of FA(110).

The corresponding iron species in FS(550) was identified as anhydrous iron(III) sulfate.

The TG, DTG, and DSC curves of FS(110) are shown in Fig. 4, and those of FA(110) are presented in Fig. 5. Either DTG curve indicates two weight loss regions. The first region (70–120°C) is associated with the release of adsorbed water, and the second is due to the decomposition of the sulfates that resulted from impregnation. Sulfate decomposition takes place at 580–700°C in FS(110) and above 800°C in FA(110). This difference can be explained by the different chemical natures of the compounds into which the sulfate ion incorporates upon impregnation and subsequent drying: the decomposition temperature of 600°C is characteristic of iron(III) sulfate, while decomposition above 800°C is typical of aluminum sulfate [16]. This inference is confirmed by the dynamics of the SO_4/Fe ratio in the samples as a function of the heat treatment temperature (table). The silica gel–based sample is almost free of sulfate ions at 700°C. The SO_4/Fe ratio in the alumina-based sample is independent of the heat treatment temperature, suggesting that the sulfate ion is involved in the formation of aluminum sulfate, a more stable compound. The deviation of this ratio from the stoichiometry of

Fe and SO_4^{2-} contents as a function of the calcination temperature according to chemical analysis data

Sample	Fe, wt %	SO_4^{2-}, wt %	SO_4/Fe, mol/mol
FS(110)	3.59	6.27	1.01
FS(500)	3.47	3.69	0.61
FS(600)	3.71	0.97	0.15
FS(700)	3.78	0.11	0.014
FA(110)	2.94	4.26	0.85
FA(500)	2.92	3.73	0.75
FA(600)	2.84	3.87	0.78

the starting compound ($FeSO_4$) is attributable to the errors in chemical analysis arising from the poor solubility of aluminum oxide and sulfate.

Thus, our Mössbauer study demonstrated that the impregnation of alumina with an iron(II) sulfate solution followed by drying at 110°C yields iron(III) sulfate in the sample. Upon calcination at 500°C this compound turns into α-Fe_2O_3. The impregnation of SiO_2 with an iron(II) sulfate solution followed by drying at 110°C yields iron(III) hydroxysulfates of variable composition on the sample surface, which turn into iron(III) sulfate upon calcination at 550°C.

The fact that different compounds result from the impregnation of alumina and silica gel with an iron(II) sulfate solution can be explained in terms of the chemistry of this solution and the acid–base properties of the support surfaces. The iron(II) sulfate solution has pH ~ 5, while the isoelectric point is pI ~ 1.8–2.2 for silica gel and pI ~ 7–8 for alumina. The alumina surface has a considerable amount of basic groups [17]. The interaction of the impregnating solution with these groups raises the pH of the solution, and this favors the deprotonation and hydrolysis of the iron aqua complex $[Fe(H_2O)_6]^{2+}$ and the oxidation of Fe^{2+} into Fe^{3+} [18]. As a result, iron(III) hydroxide forms already at the impregnation stage, as is indicated by the brown color of the freshly prepared sample.

The silica gel surface does not affect the chemical nature of the dissolved compounds. In this case, the supported phase results from the precipitation of white $FeSO_4 \cdot 7H_2O$ from the supersaturated iron(II) sulfate solution in the pore space of the support. Upon subsequent drying at 110°C, water molecules in the inner coordination sphere of the iron cation are replaced by sulfate ions and Fe^{2+} is oxidized to Fe^{3+}, yielding iron(III) hydroxysulfates of variable composition. This process is accompanied by the sample changing from white to brown.

Thus the nature of the support is of considerable significance in the formation of the active component of the iron-containing catalysts prepared using an aqueous solution of $FeSO_4 \cdot 7H_2O$ as the precursor. The forthcoming study of the effect of the heat treatment temperature on the reduction and sulfidation resistances of the resulting material will make it possible to optimize the methods of preparation of catalysts containing iron as oxides, sulfates, sulfides, or metal particles.

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