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Abstract

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STUDY OF THE PHASE COMPOSITION AND ADSORPTION PROPERTIES OF AN IRON-CARBON CATALYST

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An iron–carbon catalyst consisting of activated carbon or generator dust impregnated successively with solutions of FeS_4 and NaOH* is used for the destructive hydrohydrogenation of aromatic hydrocarbons, tar, and petroleum residues ([1]–[10]). Until now the phase composition and adsorption properties of this catalyst have not been studied. In the present work, data were obtained that characterize two unused samples of iron–carbon catalyst prepared as in ([5]): sample 1—with 5.6% Fe on activated carbon; sample 2—with 10.5% Fe on generator dust**. Their activity was evaluated by the reaction of autoclave hydrogenation of 20 g of phenol in the presence of 2.5 g of catalyst for 3 hr at 480° and an initial H_2 pressure of 114 atm, as described in ([12]). In addition, sample 1 after adsorption of H_2 on it was also studied by X-ray diffraction and magnetic methods. The results of the experiments are given in Figs. 1-3 and in Table 1.

Table 1

Specific surface area S, pore volume U, activity in the reaction of phenol hydrogenation under pressure, and magnetic susceptibility χ at 20° of iron–carbon catalysts

Catalyst	S, m^2/g by nitrogen adsorption	S, m^2/g by N_2 adsorption	U, cm^3/g by N_2 adsorption	Degree of phenol conversion, %	H_2 consumption, mol/mol	$\chi \cdot 10^6$	$\chi \cdot 10^6$ per 1 g Fe
Sample No. 1	440	622	0.334	85	2.7	330	5900
Sample No. 2	185			75	2.7	57	540

Figure 1 and Figure 2

Figure 1: Figure 1 and Figure 2

Catalyst	S, m^2/g by nitrogen adsorption	S, m^2/g by N_2 adsorption	U, cm^3/g by N_2 adsorption	Degree of phenol conversion, %	H_2 consumption, mol/mol	$\chi \cdot 10^6$	$\chi \cdot 10^6$ per 1 g Fe
Reduced sample No. 1						1600	29000

Phase X-ray diffraction analysis was carried out in standard powder cameras with Cu K radiation (Ni filter) and Co Kα radiation (Fe filter). From the diffraction pattern, the investigated samples differed only slightly from one another. The interplanar spacings found were close to the interplanar spacings in the following individual compounds: Na_2SO_4, α-Fe_2O_3, γ-Fe_2O_3, Fe_3O_4, β-$Fe_2O_3 \cdot H_2O$ ([13],[14]).

Establishing which of the Fe oxides were actually present in the samples studied proved impossible, since, owing to their high dispersion, the diffraction patterns were incomplete and did not contain a sufficient number of lines for exact identification; moreover, each of the oxide and iron hydroxide lines present on the radiographs could, with equal justification, be assigned to two or several of the above-mentioned Fe compounds. Along with Fe oxides (and possibly β-$Fe_2O_3 \cdot H_2O$), the presence of crystalline Na_2SO_4 was established by the X-ray structural method.

This conclusion is in good agreement with the results of measurements of magnetic susceptibility χ (Table 1), which were carried out as described in [15].

The data of Table 1 should be compared with tabulated data on the magnetic susceptibility χ of those Fe compounds whose presence as a separate phase was possible according to X-ray structural analysis, namely: (a) ferromagnetic γ-Fe_2O_3 and Fe_3O_4, for which, at a field strength $H = 2000$ Oe, $\chi \cdot 10^6 = 47\,500$, and, when recalculated per 1 g Fe, respectively, 68,000 and 67,500; and (b) paramagnetic α-Fe_2O_3 with $\chi \cdot 10^6 = 20$,

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* In the literature this catalyst is often designated No. 10927.
** The Fe content was determined by the Hillebrand method ([11]).

Fig. 1. Thermomagnetic curves of the iron-carbon catalyst: *a* —sample 1; *b* —reduced sample 1. 1 —heating, 2 —cooling, 3 —second heating, 4 —second cooling

Fig. 2. Adsorption isotherms of toluene from its solution in isooctane on iron-carbon catalysts at room temperature. 1 —on sample 1, 2 —on sample 2

as well as FeO and β-$Fe_2O_3 \cdot H_2O$ (for which exact values of χ are not given in the literature). The measurements showed that the values of χ for samples 1 and 2, calculated per 1 g Fe, lie between the corresponding values for γ-Fe_2O_3 and Fe_3O_4 and for α-Fe_2O_3, FeO, β-$Fe_2O_3 \cdot H_2O$. From the fact that the thermomagnetic curve of sample 1 was completely reversible, it follows that metallic iron was absent from it, since on heating in air it would have had to oxidize and, as a result, the χ of the sample would have changed.

This is confirmed by the 1.5-fold decrease in χ of reduced sample 1 upon its oxidation in air (see Fig. 1).

Thus, the results of our determinations of phase composition and magnetic properties refute the statements made in [1,5] ...

that iron enters into the composition of the unused iron-carbon catalyst in the form of only one compound: $Fe(OH)_3$ or $Fe(OH)_2$. The unused catalyst contains a mixture of para- and ferromagnetic iron oxides and, possibly, β-$Fe_2O_3 \cdot H_2O$. Naturally, under hydrogenation conditions (480°, 300-700 atm H_2), in the absence of sulfur compounds, Fe oxides should be reduced to the metal; in the presence of sulfur compounds in the feedstock, sulfurization of Fe should occur.

The adsorption isotherms of toluene from its solution in isooctane (X) and the toluene content in the adsorption volume of the catalysts (A) (Fig. 2) were measured at room temperature, as described in work (16). The specific surface area S was calculated (Table 1) from the molecular area ω_0 of toluene, 50 $Å^2$. The adsorption isotherm of N_2 vapor at the temperature of liquid N_2 was measured on sample 1, as described in work (17), and is shown in Fig. 3 together with the distribution of the pore volume of this sample by effective radii. Comparison of the adsorption properties of the catalysts with the results of phenol hydrogenation shows that, in terms of degree of conversion, sample 1 was more active; its S, determined from toluene adsorption (the size of whose molecule is close to that of the phenol molecule), is 2.4 times larger than the S of sample 2. Since in work (2) it was shown that the activity of the iron-carbon catalyst increases with increasing Fe content only up to 4-5%, after which a further increase in Fe content does not affect the activity, the differences in activity of samples 1 and 2 did not depend on the different Fe content in them.

The selectivity of action of samples 1 and 2 was the same, as can be seen from the consumption of H_2. It should be noted that it considerably (by a factor of 2.7) exceeded the consumption of H_2 required for the reduction of phenol to benzene, which indicates formation, in the presence of the iron-carbon catalyst, not only of aromatic hydrocarbons but also of hydrocarbons richer in hydrogen.

Fig. 3

Figure 2: Fig. 3

These results are of interest in connection with the contradictory literature data (7, 10) on the selectivity of action of the iron-carbon catalyst in the phenol hydrogenation reaction; the results obtained in the present work confirm and supplement the results of work (2) (in which the S of the catalysts was not determined) concerning the influence of the magnitude of the specific surface area of the support on the activity of the catalyst under discussion. The S of sample 1, determined from toluene adsorption, is smaller than that from N_2 adsorption, since in this catalyst a large volume is occupied by ultrafine pores (see Fig. 3).

Fig. 3. Adsorption isotherm (a) of N_2 vapor at −196° on an iron-carbon catalyst (sample 1) (1 −adsorption, 2 −desorption) and distribution of pore volume (b) of sample 1 by effective radii

Adsorption of H_2 was carried out as a series of successive experiments on the same charge of sample 1 at 400° and a constant H_2 pressure of 740 mm Hg, up to complete saturation, in an apparatus analogous to that described in work (18). Before each experiment the catalyst was evacuated at 400° under high vacuum. In the first experiment the catalyst absorbed 15.9 cm^3/g (NTP) of H_2; in subsequent experiments, which were well reproduced, 4.8 cm^3/g (NTP).

Taking ω_0 of the H atom at 400° to be 6.1 Å^2 (19), we find that the surface area of catalyst 1, active in reversible chemisorption of H_2 at 400°, is 16 m^2/g, which amounts to about 3% of the S of this sample, determined from the low-temperature adsorption of N_2 vapor.

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