ON THE QUESTION OF THE SEMICONDUCTOR PROPERTIES OF IRON-COPPER SYNTHESIS CATALYSTS AND THE ACTIVATING ACTION OF AN ALKALINE PROMOTER

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Abstract

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ON THE QUESTION OF THE SEMICONDUCTOR PROPERTIES OF IRON-COPPER SYNTHESIS CATALYSTS AND THE ACTIVATING ACTION OF AN ALKALINE PROMOTER

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One of the factors that most strongly increases the activity of iron-copper catalysts used for the synthesis of oxygen-containing compounds and hydrocarbons from CO and H_2 is their promotion with alkaline additives. The positive influence of alkali on the activity of iron catalysts was noted already in studies ([1]); subsequently this question was studied in greater detail in works ([2]-[4]) and others, as well as by a number of Soviet researchers ([5]). Despite the fact that promotion by alkali is one of the most important stages in the development of iron synthesis catalysts, the mechanism of action of the activator is still insufficiently clear.

With the modern development of ideas about the electronic mechanism of heterogeneous catalytic reactions ([6], [7]) and the theory of semiconductors ([8], [9]), it seems possible to put forward the most probable assumption concerning the action of alkaline promoters on iron-copper synthesis catalysts.

As is known, active Fe—Cu catalysts are prepared by precipitating solutions of nitrates of the corresponding metals with soda. After washing out the precipitant (soda), they are activated (KOH or K_2CO_3), formed, and reduced with hydrogen at low temperatures up to 220-250°. Under these conditions, mainly FeO is formed (not less than 50-60%), as well as compounds of the spinel type: $FeO \cdot Fe_2O_3$ ($Fe \cdot Fe_2O_4$), $CuO \cdot Fe_2O_3$ ($Cu \cdot Fe_2O_4$). If magnesium or manganese is included in the composition of the Fe—Cu catalysts, then the reduced samples also contain $MgO \cdot Fe_2O_3$ or $MnO \cdot Fe_2O_3$. The content of metallic iron usually does not exceed 1.5-2.0%.

It may be assumed that Fe—Cu catalysts should possess semiconductor properties, since after reduction they consist, in the main, as studies have shown, of FeO and spinels, which belong to the class of semiconductors ([10]). In this case the action of the alkaline promoter, by analogy with other semiconductor materials, should consist in the following. The crystal lattice, for example FeO, is characterized by an excess oxygen content and, consequently, has hole conductivity. The excess oxygen atoms (acceptors) pull electrons away from Fe^{2+} to a higher energy level, while the remaining Fe^{3+} (holes) determine the presence of a certain electrical conductivity characteristic of semiconductor materials. The addition of a metal oxide or salts with a metal valence lower than Fe^{2+} (for example K_2CO_3) causes an increase in the number of Fe^{3+}, since the second positive charge missing in the potassium ion is compensated in another place in the lattice. An increase in the number of holes entails an increase in electrical conductivity.

Studies by N. P. Keier, S. Z. Roginskii, and I. S. Sazonova ([11]), and also by Hauffe, Verwey, and Wagner ([6],[7]), have shown that for individual catalysts (for example NiO) there is a direct dependence between their electrical conductivity and activity. We assumed that for Fe—Cu catalysts for the synthesis of oxygen-containing compounds and hydrocarbons from CO and H_2 there should likewise be a direct dependence between the value of the electrical conductivity and the catalytic activity. In this case the activating action of an alkaline promoter should consist in increasing the electrical conductivity of the catalyst. In order to confirm experimentally the assumptions made, studies were carried out, the results of which are presented in the present work.

Experimental part

To measure the electrical conductivity (or its inverse quantity—the electrical resistance), the catalyst was placed in a vessel made of refractory glass. In experiments with reduced catalyst samples, nitrogen free of oxygen was introduced into the vessel. The height of the catalyst bed was 25 mm, and the distance between the electrodes sealed into the vessel was 33 mm. The catalyst was heated by means of an electric furnace equipped with an automatic temperature regulator. The temperature of the catalyst was measured with a thermometer, and the resistance with a universal Wheatstone bridge. The magnitude of the resistance measured was determined by the formula $R = nr$, where $n = r_1/r_2$ is the ratio set on the dial of the ratio arms of the universal Wheatstone bridge; r is the resistance set on the comparison arm. Measurements of the catalyst resistance were made as the temperature was raised, every 10–20° up to 200°, and then every 5° up to 230°.

For the experiments, 6 samples of Fe—Cu catalyst without a carrier were prepared. The first sample contained no alkali. The composition of the other samples included 0.5; 1.0; 2.5; 3.0 and 10% K_2CO_3.

Table 1

Electrical resistance of Fe—Cu catalysts promoted with various amounts of K_2CO_3 (in $\Omega \cdot 10^{-3}$)

T, deg. C	0.0	0.5	1.0	2.5	3.0	10.0
50	41.4	15.8	13.0	15.5	12.5	20.2

Figure 1

Figure 1: Figure 1

T, deg. C	0.0	0.5	1.0	2.5	3.0	10.0
70	20.9	8.7	–	7.6	6.5	17.2
80	16.7	6.9	5.5	5.9	4.5	16.0
100	10.2	4.2	4.0	4.0	2.8	19.1
110	–	4.2	3.4	–	3.1	34.0
120	9.1	4.8	–	3.1	3.9	68.0
140	8.6	6.4	3.4	2.7	4.2	–
150	8.5	5.4	3.9	2.7	4.5	–
170	7.3	4.0	3.2	2.3	4.2	80.0
180	6.2	3.5	2.8	2.2	4.0	59.1
190	5.2	2.8	2.7	–	3.7	44.0
200	4.0	2.4	2.2	1.7	3.2	38.0
205	3.5	2.2	2.1	1.6	3.1	29.0
210	3.1	2.1	2.0	1.5	2.9	24.0
215	2.8	1.9	1.7	–	2.6	–
220	2.2	1.2—1.3	–	1.2	2.5	19.3
225	–	–	–	–	2.4	–
230	–	–	–	0.9	2.3	13.9

Experiments carried out with unreduced catalyst samples showed that these catalysts do not possess any appreciable electrical conductivity even at 230°. Their resistance at all temperatures was above 1,000,000 Ω. The reduced catalyst samples were characterized by entirely different properties. The dependence of their ohmic resistance R on temperature is given in Table 1 and is shown graphically for one of the samples in Fig. 1,a. Considering the data presented, we see that with increasing temperature the ohmic resistance decreases according to an exponential law. This dependence, characteristic of semiconductor materials, shows that the reduced Fe—Cu synthesis catalysts are typical semiconductors. As the resistance decreased and, consequently, as the electrical conductivity of the catalyst increased, its activity increased (Fig. 1,b).

It should be noted that the initial temperature of the synthesis reaction lies at about 160-165° (CO conversion 5%). At this temperature the specific resistance of the catalyst is 1400-1500 Ω ($\lg \rho = 3.145$—3.180). At a temperature of about 205° the specific resistance of the catalyst

Fig. 1. Dependence of the specific resistance and activity of the Fe—Cu catalyst on temperature:
a —logarithm of the specific resistance; b —activity (degree of CO conversion)

was 980 Ω; in this case the normal activity of the catalyst is established, corre-

Figure 2

Figure 2: Figure 2

Fig. 3. Dependence of the specific resistance and activity of the Fe—Cu catalyst on the content of K_2CO_3 in it in the temperature region of synthesis. *a* —logarithm of the specific resistance; *b* —activity (degree of CO conversion). $t = 210°$

Figure 3: Fig. 3. Dependence of the specific resistance and activity of the Fe—Cu catalyst on the content of K_2CO_3 in it in the temperature region of synthesis. *a* —logarithm of the specific resistance; *b* —activity (degree of CO conversion). $t = 210°$

sponding to approximately 80% conversion of carbon monoxide.

Thus, there is a direct dependence between the electrical conductivity of the iron-copper catalyst and its activity in the synthesis reaction.

Fig. 2. Dependence of specific resistance on temperature for samples of the Fe—Cu catalyst containing different amounts of K_2CO_3. 1 —0.0% K_2CO_3; 2 —0.5%; 3—1.0%; 4 —2.5%; 5 —3.0%

The dependence of electrical conductivity on impurity additions, characteristic of semiconductor materials, was also observed for synthesis catalysts. Figure 2 shows the dependence of resistance on temperature for 6 catalyst samples.

The effect of the potash content in the catalyst on its resistance and activity at 210° is shown in Fig. 3. A catalyst sample not containing

containing K_2CO_3 was characterized by a specific resistance of 1880 Ω ($\lg \rho = 3.275$). The introduction of a small addition of potash, 0.5%, increased its electrical conductivity by a factor of 1.5. A further increase in the K_2CO_3 content led to a decrease in resistance and to an increase in the activity of the catalyst.

Consequently, the promoting action of potash, which is an acceptor additive, can be explained by its effect in increasing the electrical conductivity of the catalyst.

Fig. 3. Dependence of the specific resistance and activity of the Fe—Cu catalyst on the content of K_2CO_3 in it in the temperature region of synthesis. *a* —logarithm of the specific resistance; *b* —activity (degree of CO conversion). $t = 210°$

An addition of 2.5% K_2CO_3 imparts to the Fe—Cu catalyst of the given composition the highest electrical conductivity and activity. However, increasing the K_2CO_3 addition to 3.0% caused a decrease in electrical conductivity and activity. In this case the specific resistance was 1750 Ω ($\lg \rho = 3.244$), and the degree of CO conversion was somewhat above 70%. The negative effect of the presence of more than 3% K_2CO_3 is consistent with the effect of impurities on the electrical conductivity of semiconductors. A sharp increase in their conductivity occurs only at a small concentration of impurity, above which the electrical conductivity decreases (10). Measurement of the electrical conductivity of a catalyst sample containing 10% K_2CO_3 showed that even at 210° it was characterized by a very high specific resistance, equal to 14500 Ω ($\lg \rho = 4.161$). The activity of this sample was very low. The degree of CO conversion amounted to only 38%, all other synthesis parameters being equal.

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