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Figure 1

Figure 1: Figure 1

Abstract

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Work Function and Catalytic Activity of Iron Contacts for Ammonia Synthesis

Industrial production of ammonia is based on the use of iron catalysts, into which potassium oxide and aluminum oxide are introduced in order to increase activity and stability. Despite numerous studies, the chemical state and mechanism of action of additives in the working contact have still not been definitively clarified. This applies to an even greater extent to other additives (CaO, SiO_2), by means of which it has recently been possible to improve ammonia catalysts considerably (^1). In a number of theoretical studies that have appeared in the literature (^2), the catalytic activity and adsorption capacity of semiconductors and metals are associated with the electron work function. For NiO and ZnO, E. Kh. Enikeev, L. Ya. Margolis, and S. Z. Roginskii (^3) established a direct relation between the change in the work function and the change in the activation energy of catalysis and chemisorption caused by the introduction of various modifying additives. For metallic catalysts there are almost no similar experimental studies. It was therefore of interest to compare the change in work function with the catalytic activity of modified iron catalysts for ammonia synthesis.

Fig. 1. Dependence of the specific catalytic activities K (I) and K' (II) on the change in the initial work function

The electron work function φ was determined from the contact potential difference, measured by the vibrating-condenser method (^3) with an accuracy of 0.01 eV. The reproducibility of measurements in different experiments was $±$0.05 eV. To establish a direct relation between $\Delta\varphi$ and catalytic activity, it would be desirable to carry out measurements under catalytic conditions; however, the very severe conditions of the ammonia synthesis process (high temperature, pressure) do not yet make this possible. For determining the work function,

passivated samples were taken after their activity had been determined in a column. The catalysts were ground into a fine powder in a nitrogen atmosphere. Activation was carried out by heating in vacuum or in a hydrogen atmosphere at a temperature of 320–340° in the special cell described previously (^3). The design of the apparatus ensured identical activation conditions and minimized the influence of fluctuations of the reference electrode on the measured quantity. The work function of all passivated catalysts in air was the same, and differences between samples appeared only after activation; this gives grounds to believe that oxygen had been removed from the main part of the surface. Table 1 gives the values of the con-

contact potential difference V_k, i.e., the difference between the work functions of the given sample and the standard gold electrode, and the quantity $\Delta\varphi$, which represents the change in the work function of various promoted catalysts relative to the work function of the unpromoted catalyst.

The catalyst samples were prepared under industrial conditions by the method of oxidative melting of iron with the introduction of various additives. The chemical

Table 1

Catalytic activity and electron work function of promoted iron catalysts*

Sample No.	FeO	Fe_2O_3	Al_2O_3	K_2O	CaO	SiO_2	Volumetric rate, h^{-1}	NH_3, %***	Total surface, S, m^2/g	Condition surface free of iron, S_{Fe}, m^2/g	Specific rate constants, $K_{ud} = K/S$	Specific rate constants, $K'_{ud} = K/S_{Fe}$	Contact potential difference, V_k, V	Change in the work function upon introduction of additives, $-\Delta\varphi$, eV
1	25.2	74.1	0.2 (impurity)	—	—	—	14500	0.25	0.5	0.325	2.8 · 10^{-1}	4.3 · 10^{-1}	−0.5	0
2	37.2	52.1	10.2	—	—	—	14800	3.6	17	3.9	1.8	7.95	−0.3	0.2

Sample No.	FeO	Fe_2O_3	Al_2O_3	K_2O	CaO	SiO_2	Volumetric rate, h^{-1}**	NH_3, %***	Total surface, S, m^2/g	Conditional surface free of iron, S_{Fe}, m^2/g	Specific rate constants, $K_{ud} = K/S$	Specific rate constants, $K'_{ud} = K/S_{Fe}$	Contact potential difference V_k, V	Change in the work function upon introduction of additives, $-\Delta\varphi$, eV
3	22.1	75.1	0.3 (impurity)	2.0	—	—	15000	3.5	0.7	0.35	$4.3 \cdot 10$ $h^{-1} \cdot atm^{-0.5} \cdot m^{-2}$	$8.6 \cdot 10$ $h^{-1} \cdot atm^{-0.5} \cdot m^{-2}$	+0.6	1.1
4	25.0	66.95	4.8	2.3	0.3 (impurity)	0.15 (impurity)	30000	11.0	11.0	2.2	$5.5 \cdot 10$	$2.7 \cdot 10^2$	+0.8	1.3
5	30.8	59.7	3.2	0.9	4.0	0.9	29600	16.4	13.0	1.04	$1.1 \cdot 10^2$	$1.3 \cdot 10^3$	+1.0	1.5
6	39.3	54.4	3.1	0.7	2.0	—	30000	17.8	12.0	1.44	$1.3 \cdot 10^2$	$1.1 \cdot 10^3$	+1.5	2.0

* We also investigated the catalytic activity and work function of Armco iron. Armco filings with a total surface area of 1 m^2 at 550°, 300 atm, and a volumetric rate of 15000 h^{-1} practically had no catalytic activity; the sample had the greatest value of the work function.

** About 0.5% in each sample consisted of other impurities: MgO, MnO, P_2O_5, SO_3, Cr_2O_3, NiO, etc.

*** Test conditions: $p = 300$ atm, $T = 400°$.

**** The value of S_{Fe} for this sample was not determined. The table gives the value of S_{Fe} from literature data (7) for a catalyst of similar chemical composition.

composition of the catalysts studied before reduction is presented in the left-hand part of Table 1. The activity of the samples was determined by a flow method in a five-channel high-pressure column (4), into which 1-2 ml of each catalyst sample with a grain size of 2-3 mm was loaded. Before activity testing,

the catalysts were reduced at a pressure of 100 atm with a nitrogen–hydrogen mixture of stoichiometric composition (volumetric rate 30000 h^{-1}) by a stepwise temperature increase method. Reduction was completed by holding the catalyst for 2 h at a temperature of 550°. The total duration of reduction was 32 h. The percentage of ammonia in the gas mixture was determined at a pressure of 300 atm, a temperature of 350–550°, and volumetric rates of 15000–30000 h^{-1}. After activity testing, the catalyst samples were passivated in a stream of nitrogen containing 0.1% oxygen at room temperature. The total surface of the passivated samples (S) was determined by the BET method from low-temperature adsorption of nitrogen. From the chemisorption of carbon monoxide at −78° (5), a conditional value was determined for the part of the surface free of promoters (S_{Fe}, see Table 1).*

The catalytic activity of the samples is presented in Table 1 in the form of a reaction rate constant calculated from the percentage of ammonia at the outlet of the column according to Temkin' s equation (6) and referred to a unit of total surface

* This interpretation of S_{Fe}, calculated from the saturation limit of CO_{chem}, is conditional, but it gives an idea of the surface capacity for chemisorption of N_2. The surface measurements were performed by V. N. Shishkova, to whom the authors express their gratitude.

activity: $K_{sp} = K/S_{tot}$ and per unit conventional surface of iron free of promoters: $K'_{sp} = K/S_{Fe}$. It is seen from the table that upon introduction of 10% aluminum oxide, which was previously considered only a stabilizing additive (sample 2), the specific catalytic activity K_{sp} increases somewhat in comparison with the unpromoted catalyst (sample 1). This change in activity corresponds to a slight decrease in the work function (0.2 eV). The addition of 2% potassium oxide (sample 3) increases the catalytic activity 150-fold. The work function is thereby decreased by 1.1 eV. The activity of the doubly promoted catalyst (sample 4), containing 2.3% K_2O and 4.8% Al_2O_3, increased 200-fold, while the work function decreased by 1.3 eV. Addition of CaO (sample 6) and CaO + SiO_2 (sample 5) increases the catalytic activity still more and decreases the work function.

Figure 1 shows a strong, smooth increase of $\lg K_{sp}$ with decreasing electron work function (I). The extreme samples differ by 2 eV in work function and by 450-fold in specific catalytic activity. In view of the fact that the chemisorption capacity of N_2 per 1 cm^2 of catalyst surface decreases upon promotion, it was of interest to compare the work function with the specific catalytic activity referred to a conventional unit of iron surface. In the same figure, II shows the change in the quantity $\lg K'_{sp}$ with change in $\Delta\varphi$. The range of variation of K'_{sp} approaches 4 orders of magnitude, and the obtained dependence can be represented by a straight line.*

At constant temperature and K_0 in the Arrhenius equation, the change in catalytic activity for different samples is related to the change in activation energy

by the equation

$$j\Delta \lg K'_{\text{sp}} = \Delta E. \tag{1}$$

According to the experimental data obtained,

$$j\Delta \lg K'_{\text{sp}} = \alpha\Delta\varphi, \tag{2}$$

therefore, one may expect that

$$\Delta E = \alpha\Delta\varphi. \tag{3}$$

The most reliable values of the activation energy are available for catalysts 1 and 4 in Table 1. E changes from 65 ± 4 kcal/mole (sample 1) to 40 ± 2 kcal/mole (sample 4), i.e., $\Delta E_{\text{kin}\,1,4} \sim 25$ kcal/mole. The change in work function $\Delta\varphi_{1,4} = \varphi_4 - \varphi_1 = 1.3$ eV. Converting electron-volts into kilocalories per mole, we obtain ΔE_{el} of about 30 kcal/mole, which is close to $\Delta E_{\text{kin}\,1,4}$, i.e., in equation (3) $\alpha \sim 1$. Thus, the change in activation energy with change in work function is larger than the effects expected according to Boudart' s theory for metals, and corresponds to the effects theoretically obtained for semiconductors ([8]).

The value of the coefficient α, determined from the slope of straight line II in Fig. 1, is considerably less than 1 ($\alpha' = 0.26$), which may be explained by the presence of a compensation effect or by insufficient accuracy of the values used for $E_{\text{kin}\,1}$ and $E_{\text{kin}\,4}$. For a deeper understanding of the relationship between catalytic activity and work function, it is necessary to study a larger number of catalysts and to carry out measurements of φ under conditions of catalysis. A quantitative comparison of ΔE_{kin} and ΔE_{el} and an estimate of the magnitude of the compensation effect require more careful measurement of activation energies.

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* For final establishment of the character of the dependence $\lg K' - (-\Delta\varphi)$, it is necessary to study a larger number of catalysts, which is presently being carried out by us.

Despite the noted gaps, the data of the present work show an approximately exponential increase in the rate constant of ammonia synthesis, referred to a conventional unit of free iron surface, with decreasing work function on iron promoted catalysts:

$$K'_{\text{unit, promoted}} = K'_{\text{unit, unpromoted}} \exp(-\alpha\Delta\varphi).$$

Apparently, the decrease in φ primarily affects the E of the reaction, lowering the latter. This argues in favor of an electronic mechanism of the action of

the additives and explains the reason for the superiority of three- and four-component catalysts.

A more detailed analysis of the mechanism of action of the additives lies beyond the scope of the present communication.

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