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On the Mechanism of Promoting Ammonia Synthesis Catalysts by an Alkali

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The mechanism of the promoting effect of an alkali addition in catalytic synthesis of ammonia is described on the basis of a dipole–dipole interaction model. The promoting effect (the increase of the specific rate constant K_{sp}) is considered as a consequence of a decrease in the energy of the dipole $\mu^{\ddagger}$ ($\mu^{\ddagger}$ is the dipole of the activated complex of the reaction limiting step) in the field of promoter dipoles μ. The dependence of the promoting effect magnitude on the concentration of the promoter activating particles N and on $\Delta\varphi$ (the decrease of the iron electron work function resulting from promoting) are calculated. Cases of uniform and maximum nonuniform (two-patch surface) distribution of the promoter activating particles over the catalyst surface are considered. An appraisement of the limiting promoting effect is made.

The possibility of a "chemical" promoting effect, consisting in the decrease of the valency orbital electronegativity of the surface Fe atoms, is considered qualitatively on the basis of the concept of group electronegativity.

1. INTRODUCTION

The introduction of an alkali into a singly promoted iron ammonia synthesis catalyst increases the specific catalytic activity (K_{sp}) and decreases the electron work function (φ). The interrelation between φ and K_{sp} has been studied in a number of works (*1–4*). It served as experimental basis for one of the proposed mechanisms (sometimes called "electronic") of promoting by alkali.

According to this mechanism the limiting step of the process is associated with electron transfer and it is enhanced by a decrease in φ owing to an increase in catalyst donative capability.

Concrete promoting mechanisms based on dipole–dipole interaction and on interaction through the M. I. Temkin surface electron gas have been discussed in Refs. (*5–7*). These promoting mechanisms may be called "physical" in the sense that they consider only the relative change in the energy of the activated complex of the reaction limiting step AC: the AC structure and the mechanism of the chemical process are assumed to remain unchanged.

The present paper contains a more detailed substantiation and further development of the model of dipole–dipole interaction. (This model involves fewer additional assumptions.)

By the electron work function, as used below, we have denoted the work function of an iron surface covered with an alkaline promoter. It differs from the measured value due the presence on the catalyst surface of other phases with different work functions. Calculated values can be compared with experimental data if the differences are small.

2. The Description of the Model of Promotion

Let us denote the AC dipole moment of the limiting step as $\mu^{\ddagger}$. If the limiting step is adsorption of nitrogen, then $\mu^{\ddagger}$ corresponds to the actual AC moment. If hydrogenation of the adsorbed nitrogen is the limiting step, then $\mu^{\ddagger}$ means the difference between the AC dipole moment and the dipole moment of the adsorbed nitrogen.* Since positive charges of dipoles set up during adsorption of alkali metal atoms on the iron surface are directed outwordly, a promoting effect is possible provided that $\mu^{\ddagger}$ corresponds to the dipole moment with the negative charge directed outwardly. It is very difficult to establish an unique relationship between the sign and magnitude of $\mu^{\ddagger}$ and the sign and magnitude of charge transfer from a surface iron atom to a nitrogen molecule or AC: the quantum-mechanical calculations (*8*) of charge distribution in the Fe—N≡N complex show that the effective charges on the nitrogen atoms may differ in sign as well as in magnitude. The contribution of this factor to the $\mu^{\ddagger}$ value can be very significant. (If we had chosen the surface electron gas model for the calculations we would have make the assumption that the charge transfer is from the surface iron atom to the nitrogen molecule and set the value of the transferred charge, but we would not be able to determine the sign and the magnitude of the resulting dipole moment.)

We assumed $\mu^{\ddagger} = 1.55\,\mathrm{D}$ (*5–6*).

Calculation of the promoting effect is possible only if activating promoter particles are taken to mean particles identical with those adsorbed on contact of the catalyst surface with alkali metal vapors.

This assumption has a certain experimental justification:

1. evaporating an alkali metal onto the iron surface *in vacuo* results in a substantial increase of its catalytic activity (*9*);
2. the electron work function of a doubly promoted catalyst (K_2O or Cs_2O plus structure promoter) decreases only after its reduction. Before this it does not differ from the φ of a singly promoted catalyst.

We consider the promoting effect to depend exclusively on the surface concentration of promoter activating particles N and their dipole moment μ.

The maximum possible magnitude of N for a given catalyst can be calculated as the ratio of the number of alkali metal atoms introduced into 1 g of catalyst to its specific surface S (cm^2). The portion of dissociated alkali promoter emerging on the surface—the promoter "utilization factor"—is dependent on the nature of the structure promoter and on the specific surface area. Decreased affinity of the structure promoter for the alkali metal and increased catalyst specific surface area favor an increase in the promoter "utilization factor." Within the framework of the given model the magnitude of the utilization factor is the only characteristic of the structure promoter. With a specific surface of about 10 m^2/g a catalyst with an utilization factor of 0.5 requires the introduction of 0.3–0.5 wt % K_2O to obtain high surface coverages with activating particles but the structure promoter with an "utilization factor" of 0.1 requires 1.5–2.5 wt % K_2O.

Significant differences in the alkali promoter concentration will evidently lead to differences in the pattern of its distribution over the iron surface. This question is discussed below.

Adsorption of Cs or K on the surface of the metal results in the formation of a dipole moment μ. The value of μ decreases considerably with an increase in θ (the fraction of the surface covered by alkali metal particles), since dipole–dipole interaction leads to decreased ionicity (*10, 11*) of the adsorption bond Fe–K (Fe–Cs). The dependence of μ on N is described by the equation

$$\mu = \frac{\mu_0}{1 + 9\alpha N^{3/2}}, \tag{1}$$

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* In this case we assume that the interaction between the dipole moment of the adsorbed nitrogen and the promoter dipoles practically does not affect the concentration of the adsorbed nitrogen.

where μ_0 is the initial dipole moment for $\theta \rightarrow 0$ and α the effective (*10*) polarization coefficient of the alkali metal particle, which depends on the change in the bond ionicity.

N and then μ can be determined from the value of $\Delta\varphi$ ($\Delta\varphi$ is the decrease of φ resulting from the introduction of an alkali):

$$\Delta\varphi = \mu_0 \cdot \frac{4\pi N}{1 + 9\alpha N^{3/2}}. \qquad (2)$$

The constant μ_0 and α must be determined experimentally. No relevant data for Fe are available. We will use the results for plane (111) of W (*11*, *12*), because φ for this plane (4.4 to 4.5 eV) is similar to the work function of α-Fe (4.5 eV). For K on plane (111) of W (*11*) $\mu_0 = 4.8$ D, $\alpha = 28 \times 10^{-24}$ cm^3. For Cs on plane (111) of W (*12*) $\mu_0 = 5.2$ D, $\alpha = 24 \times 10^{-24}$ cm^3.

We also took into account the μ_0-value 3.9 D obtained for the K promoter on doubly promoted ammonia synthesis catalysts by the method of reverse calculation (*6*) (from $\Delta\varphi$ and $\Delta \log K_{\mathrm{sp}}$).

For potassium we assume $\mu_0 = 4.4$ D, $\alpha = 28 \times 10^{-24}$ cm^3 and for cesium $\mu_0 = 4.7$ D, $\alpha = 24 \times 10^{-24}$ cm^3. For K and Cs with monolayer coverage $N_m = 3.9 \times 10^{14}$ cm^{-2} (*11*, *12*).

We further assumed that atoms of the alkali metal form a mobile square lattice on the iron (*6*). This only means that the space between the nearest neighbors is maximal and equal to $N^{-1/2}$. The underlying basis for this assumption is the fact, that the experimental data on the dependence of μ on N for potassium adsorption (*11*) and cesium adsorption [as may be shown on the basis of (*12*)] on plane (111) of W are described by Eq. (1), derived for the mobile dipole lattice (*13*). On the other hand in the case of an immobile dipole lattice (*13*) the dependence of μ on N is described by the following equation: $\mu = \mu_0/(1 + 9\,\alpha N \cdot N_m{}^{1/2})$.

We also assumed that the AC is located in the center of one of the squares.

3. The Calculation of the Promotion Effect

3.1. The Uniform Promoter Distribution

The interaction energy of a dipole $\mu^{\ddagger}$, whose negative end is directed away from the surface, with dipoles of inverse polarity μ is equal (*6*) to the AC enthalpy deviation, $\mu^{\ddagger}$ being situated in the center of one of the squares:

$$\Delta(\Delta \mathrm{H}^{\ddagger}) = -13\mu\mu^{\ddagger}N^{3/2} \qquad (3)^*$$

Polarization of the activated complex was neglected. This may lead to a small error in the case of the limiting stage, nitrogen adsorption, but it is correct if the limiting stage is hydrogenation, since in that case the difference between polarizations of the initial state and the AC is close to zero.

On the other hand, differing in this from (*5–7*), we take into account the polarization of the activating particles of the alkali promoter. $\mu^{\ddagger}$ induces in each particle a dipole moment with the positive charge directed away from the surface. The sum of the induced dipole moments is equal to $(\mu^{\ddagger}/\mu)F\cdot\alpha_2$, where F is the intensity of the electric field at the AC point, and α_2 is the real (not effective) polarization of the alkali promoter (1 to 3×10^{-24} cm^3).

We neglected the energy gain on formation of the induced dipole and took into account solely the increase of energy due to the interaction of the induced dipoles with the electric field of the neighbors. This field is equal to $\frac{9}{13}F$, and the increase of energy is equal to $\frac{9}{13}F^2\,\alpha_2 \times \mu^{\ddagger}/\mu$.

Thus

$$\begin{aligned}\Delta(\Delta H^{\ddagger}) &= -13\mu\mu^{\ddagger}N^{3/2} + \frac{9}{13}\frac{\mu^{\ddagger}}{\mu}\cdot F^2\alpha_2 \\ &= -13\mu\mu^{\ddagger}N^{3/2}(1 - 9\alpha_2 N^{3/2}). \qquad (4)\end{aligned}$$

The polarization effect is very weak in the case of a K promoter $\alpha_2 = (1$ to $0.7)$

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* The numerical factor in Eq. (3) slightly increases with decrease of the space between the dipoles. This effect is insignificant. The limiting value of the factor (for $N \rightarrow 0$) is equal to 16.7 (*6*).

$\times 10^{-24}$ cm³, but it is appreciable in the case of a Cs promoter in the high-coverage range ($\alpha_2 = 2$ to 3×10^{-24} cm³). The increase of the specific catalytic activity $\Delta(\Delta H^{\ddagger})$ was calculated making the assumption that $\Delta \ln K_{sp} = -\Delta(\Delta H^{\ddagger})/RT$, where $\Delta \ln K_{sp} = \ln K_{sp} - \ln K_{sp_0}$ (K_{sp_0} is the specific activity of the catalyst without the alkali promoter). At 400°C

$$\Delta \log K_{sp} = \frac{-\Delta(\Delta H^{\ddagger})}{0.134}. \qquad (5)$$

Thus, all the terms associated with possible variations in the preexponential coefficient (for instance, the formation and disappearance of inactive surface phases) are omitted.

We also assume that the number of active centers does not decrease with increase of θ until very high coverage ($\theta = 1$ or alightly less) is attained, i.e., that the preexponential coefficient is independent of θ.

Let us represent Δ log K_{sp} as a function of N:

$$\Delta \log K_{sp} = \frac{13}{0.134}\mu_0[1/(1 + 9\alpha N^{3/2})] \times \mu^{\ddagger} N^{3/2}(1 - 9\alpha_2 N^{3/2}). \qquad (6)$$

This dependence is given in Fig. 1 by curves 1 and 3 for K and Cs, respectively. For the K promoter the x-axis variable besides N is A/S for two values of the utilization factor of the promoter ($\eta = 0.1$ and $\eta = 0.5$). (A is the weight percentage of K_2O.)

In Fig. 2 Δ log K_{sp} as a function of $\Delta\varphi$ is given by curves 1 and 3 for K and Cs, respectively; Δ log K_{sp} was calculated by Eq. 6.

3.2. The Nonuniform Promoter Distribution

Curves 1 and 3 (Figs. 1 and 2) correspond to a uniform distribution of the activating particles over the surface. It is possible to find the corresponding dependences for the other limiting case, i.e., at maximum nonhomogeneity of the surface. In electronic physics a surface of this type is sometimes called a two-patch surface.

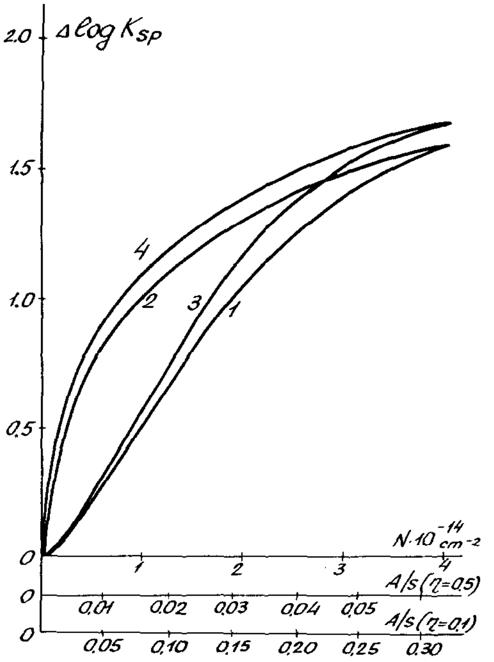

FIG. 1. The dependence of Δ log K_{sp} on the atoms concentration of K (1 and 2) and of Cs (3 and 4) in the case of uniform (1 and 3) and of inhomogeneous (2 and 4) distribution over the surface.

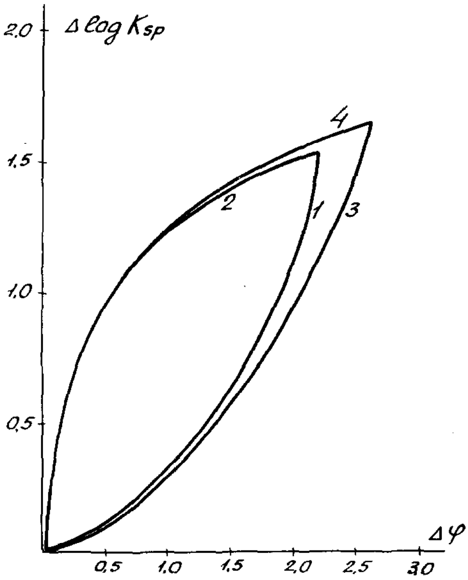

FIG. 2. The dependence of Δ log K_{sp} on $\Delta\varphi$ for the potassium (1 and 2) and for the cesium (3 and 4) promoters in the case of uniform (1 and 3) and of inhomogeneous (2 and 4) distribution over the surface.

This means that a surface with a mean coverage θ consists of places completely covered with promoter ($N = N_m$) and of places entirely free of the promoter ($N = 0$). The fraction of the former places (patch) is θ and the fraction of the latter is $(1 - \theta)$. In this case the dependence of $\Delta \log K_{sp}$ on N (the mean value) is expressed by the equation:

$$\Delta \log K_{sp} = \log[\theta \cdot 10(\Delta \log K_{sp})_{\max} + (1 - \theta)], \quad (7)$$

where $(\Delta \log K_{sp})_{\max}$ is calculated for $N = N_m$ according to Eq. (6). The corresponding curves 2 (for K) and 4 (for Cs) are given in Fig. 1. Compared with the uniform distribution, the uneven one appears to be more profitable from the point of view of specific activity. (This follows from the exponential nature of the dependence of K_{sp} on N*.)

For a given mean N ($N < N_m$) a two-patch surface is the most effective.

In contrast to Eq. (2), the dependence of the work function for this surface on the mean value of θ should be expressed by the equation

$$\Delta\varphi = \theta\Delta\varphi_{\max}. \quad (8)$$

The dependences of $\Delta \log K_{sp}$ on $\Delta\varphi$ corresponding to Eqs. (7) and (8) for nonuniform promoter distribution are given in Fig. 2 (curves 2 and 4).

The dependences of $\Delta \log K_{sp}$ on N or $\Delta\varphi$ for uniform and for maximum nonuniform coverage from a loop, i.e., they coincide for $\theta = 1$ and $\theta = 0$. It is highly probable that the coverage of the Fe surface with activating alkali particles is more uniform for catalysts with a low "utilization factor" (due to a considerable excess of alkali) than for one with a high utilization factor. Experimental data tend toward the lower curves (1, 3) in the first case and in the second, to the upper ones (2, 4) in Figs. 1 and 2.

4. THE LIMITS OF PROMOTING

Thus, for small mean θ-value catalysts with high utilization factors may yield higher activity values. At the same time curves (2 and 4) correspond to the limiting promoting effect of alkali additions to ammonia synthesis Fe catalysts, this effect being independent of the nature of the structural promoter.

Since we have chosen a simplified model, omitting a number of factors and adopting inaccurate constants (μ_0, $\mu^\ddagger$, α and N_m), we can hardly expect to find very precise limits of promotion. Nevertheless the development of iron-based catalysts for which experimental data will considerably exceed the indicated limits (5- to 10-fold for K_{sp} at 400°C) seems highly improbable.

5. CONCLUSIONS. ABOUT POSSIBLE MODEL COMPLICATION

The simple electrostatic model described above corresponds to the classical description of Cs and K adsorption on the surface of the metal (the decrease in the free metal electron work function is equal to the magnitude of the potential jump in the double layer resulting from the adsorption). A complication the model requires the use of new or additional concepts about alkali metals adsorption.

For this purpose we use the concept of the valency orbitals of the surface metal atoms (*14*, *15*). According to it φ (the electron work function of pure metal) may be determined as the neutral orbital electronegativity $x(0)$ of the surface atom of the metal (neutral electronegativity of the surface atom valent state).

According to (*14*, *15*) $\Delta\varphi$ (change in φ resulting from Cs or K adsorption) is equal to the sum of two terms—electrostatic one, corresponding to the potential jump in the double layer and "chemical"

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* For the case of a maximum nonuniform surface with a mean coverage θ, $K_{sp} = K_{sp_0}[(1 - \theta) + \theta \exp(x)]$, where x is the maximum power value (corresponding to $N = N_m$) $\Delta(\Delta H^\ddagger)/RT$. For uniform distribution of promoter particles, $K_{sp} = K_{sp_0} \cdot \exp(x\theta)$. The ratio of the specific activities is equal to

$$\frac{1 + \theta(x + x^2/2! + x^3/3! + \cdots)}{1 + \theta x + \theta^2 x^2/2! + \theta^3 x^3/3! + \cdots}$$

This ratio is evidently always greater than unity for $\theta < 1$.

one ΔX, that correspond to the change in the neutral valency orbital electronegativity of the surface metal atom.

Alkali promoting action corresponding to electrostatic effect has been discussed above. Let us consider the possibility of the "chemical" promoting effect.

As was shown (*16, 17*) electronegativity of valency state is equal to $x = dE/dg$ (E = energy, g = charge).

In first approximation electronegativity of the valency state linearly depends on the excessive charge on the atom δ:

$$x(\delta) = x(0) + b\delta \qquad (9)$$

$$(b = \text{coefficient}).$$

The "equalization of electronegativity with formation of chemical bond" concept (*17, 18*) permits calculating approximately the neutral electronegativity of free valency group $MZ^{\cdot}$ (free radical in valency state) formed atoms Z and M:

$$X_{MZ^{\cdot}}(0) = X_M(\delta_M) = X_M(0) + \delta_M b_M = X_Z(0) + \delta_Z b_Z \qquad (10)$$

$$(\delta_Z = -\delta_M).$$

Apparently the larger the difference $X_M(0) - X_Z(O)$, the larger the magnitude of δ and the larger the difference in the neutral orbital electronegativity of atom $X_M(0)$ and the group $X_{MZ^{\cdot}}(0)$.

The effect of the charge electrostatic interaction is neglected here, which in the case of covalency coupling predominance is justified by the small magnitudes of δ.

However, in the application to Cs or K adsorption on the metal surface the electrostatic effect plays a predominant role in the equalization of electronegativity and in this case Eq. (10) does not apply.

Therefore we approximately define δ_{Fe} (excessive, negative charge on the surface Fe atom) as $(\mu/2l)\cdot(N/N_{Fe})$ where $2l$ is distance between positive charge and its image, and N_{Fe} is the amount of the surface Fe atoms (cm^{-2}). Let us consider the electronegativity of the free valency surface group Fe–$Cs_{(N/N_{Fe})}$ (or Fe–$K_{(N/N_{Fe})}$ group). It is equal to

$$X_{Fc\text{–}Cs(N/N_{Fc})}(O) = X_{Fe}(O) - \frac{\mu}{2l}\frac{N}{N_{Fe}}\,b_{Fe}. \qquad (11)$$

For reactions in solution it was shown (*17*), that the group's electronegativity connected linearly with Taft's σ-values ($\Delta\sigma = \Delta X$)3.

$\Delta\sigma$ is proportional to $\Delta \log K$ (change in reaction rate logarithm) and

$$\Delta \log K = C_1 \Delta X \qquad (12)$$

$$(C_1 = \text{constant}).$$

On the analogy it may be considered that $(\Delta \log K_{sp})_{chem}$ is proportional to $(\mu/21)\ (N/N_{Fe})\ b_{Fe}$.

Giving no quantitative evaluations we note that the concentration dependence of the "chemical" promoting effect differs only insignificantly from that of the electrostatic effect: $(\Delta \log K_{sp})_{electr}$ is proportional to $N^{3/2}/1 + 9\alpha N^{3/2}$ and $(\Delta \log K_{sp})_{chem}$ is proportional to $N/1 + 9\alpha N^{3/2}$.

It follows that the complication of promotion model would have lead to a slight change in the shape of the curves given above.

However, since same time the magnitude μ (in this case $\Delta\varphi > 4\pi\mu N$) and the magnitude $\mu^{\ddagger}$ [obtained on the basis of experimental data (*6*)] would have been reconsidered, the magnitude of the limit promoting effect would not have changed significantly.

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