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Abstract

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KINETICS OF AMMONIA SYNTHESIS DURING POISONING OF THE CATALYST BY WATER VAPOR

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The influence of oxygen-containing poisons on the activity of an iron catalyst for ammonia synthesis has been investigated in a number of works ($^{1-5}$). Almkvist and Black (^{2}) established that O_2 and H_2O, in equivalent amounts, produce the same poisoning effect, because under synthesis conditions O_2 is converted into H_2O. They found that, in a flow system at constant space velocity, the partial pressure of ammonia at the outlet, $P_{\mathrm{NH_3}}$, is related to the partial pressure of water vapor $P_{\mathrm{H_2O}}$ by the equation

$$P_{\mathrm{NH_3}}\sqrt{P_{\mathrm{H_2O}}} = \text{const.} \tag{1}$$

Emmett and Brunauer (^{3}) indicated that equation (1) can be obtained by integrating an equation of the form

$$\omega = \frac{f(P_{\mathrm{N_2}}, P_{\mathrm{H_2}})}{P_{\mathrm{NH_3}} \cdot P_{\mathrm{H_2O}}}, \tag{2}$$

where ω is the reaction rate, if the partial pressures of nitrogen and hydrogen $P_{\mathrm{N_2}}$ and $P_{\mathrm{H_2}}$ are regarded as constant. S. L. Kiperman (^{6,7}) proposed the equation

$$\omega = \left[k_1 P_{\mathrm{N_2}} \left(\frac{P^3_{\mathrm{H_2}}}{P^2_{\mathrm{NH_3}}}\right)^{\alpha} - k_2 \left(\frac{P^2_{\mathrm{NH_3}}}{P^3_{\mathrm{H_2}}}\right)^{1-\alpha}\right] \frac{P_{\mathrm{H_2}}}{P_{\mathrm{H_2O}}}, \tag{3}$$

which, at $\alpha = 0.5$, gives equation (2), if the term containing k_2, i.e., the rate of the reverse reaction, is neglected.

Equation (3), at $P_{\mathrm{H_2O}} = 0$, does not pass into the kinetic equation for synthesis

$$\omega = k_+ P_{N_2} \left(\frac{P_{H_2}^3}{P_{NH_3}^2} \right)^{\alpha} - k_- \left(\frac{P_{NH_3}^2}{P_{H_2}^3} \right)^{1-\alpha}, \tag{4}$$

which is valid in the absence of catalytic poisons, but gives $\omega = \infty$. Equations (1) and (2) have the same shortcoming.

The derivation of equation (4) assumes (^{8,9}) that, in the course of synthesis, equilibrium is established between adsorbed nitrogen $N_{2\,\mathrm{ads}}$ and the gas phase

$$N_{2\,\mathrm{ads}} + 3H_2 = 2NH_3. \tag{5}$$

The rate of synthesis is determined by the rate of adsorption of nitrogen on the free surface. In addition, we shall assume that, in the presence of water vapor in the gas mixture, the equilibrium

$$O_{\mathrm{ads}} + H_2 = H_2O \tag{6}$$

is established.

The adsorption of two substances on a heterogeneous surface can be considered similarly to the way in which the adsorption of one substance was considered earlier (^{10}). Let a and a' denote the adsorption coefficients of the two gases, and let s denote the ratio of the number of a site on the surface to the total number of sites (the sites may be numbered, for example, in the order of decreasing values of a). Assuming that the surface is uniformly heterogeneous with respect to the standard free energies of adsorption of both gases, we obtain

$$a = a_0 e^{-fs}; \tag{7}$$

$$a' = a'_0 e^{-f's}, \tag{8}$$

where a_0 and a'_0 are the values of a and a' at $s = 0$. For simplicity, let us assume that $f = f'$, i.e., that the change in the standard free energy of adsorption in passing from one surface site to another is the same for both gases.

We shall assume that, during the adsorption process, an equilibrium distribution of particles over the surface sites is established. This could be the result of surface migration; in the case of interest to us, the equilibrium distribution is ensured by the mobile equilibria (5) and (6). The existence of an equilibrium distribution permits the introduction of quantities common to all

instead of the quantities p and p'—the fugacities of the substances in the surface layer, i.e., those partial pressures of these substances in the ideal gas phase that would correspond to equilibrium with the surface layer. The probability that a given site is free is equal to $\frac{1}{1+ap+a'p'}$. Let P denote the partial pressure of the first gas, and let $\varkappa$ denote its adsorption rate constant (which is a function of s); then the rate of adsorption of this substance is

$$v = \int_0^1 \frac{\varkappa P}{1+ap+a'p'}\, ds. \tag{9}$$

Let us assume that

$$\varkappa = Ga^{\alpha}, \tag{10}$$

where α and G are constants ($0 < \alpha < 1$); then $\varkappa = \varkappa_0 e^{-\alpha f s}$, where $\varkappa_0$ is the value of $\varkappa$ at $s = 0$. Substitution of (7) and (8) into (9), after introducing the variable $y = (a_0 p + a_0' p')e^{-fs}$ and transformation, gives

$$v = \frac{\varkappa_0 P}{f(a_0 p + a_0' p')^{\alpha}} \int_{a_1 p + a_1' p'}^{a_0 p + a_0' p'} \frac{y^{\alpha-1}\, dy}{1+y}. \tag{11}$$

Here a_1 and a_1' are the values of a and a' at $s = 1$. In the region of intermediate coverages $a_0 p + a_0' p' \gg 1$ and $a_1 p + a_1' p' \ll 1$. Therefore, for the region of intermediate coverages, the limits of the integral may be replaced by 0 and ∞. This gives

$$v = \frac{\pi}{\sin \alpha\pi} \frac{\varkappa_0 P}{f(a_0 p + a_0' p')^{\alpha}}. \tag{12}$$

For the case of NH_3 synthesis, p is the fugacity of adsorbed N_2, and p' is the fugacity of adsorbed O. These quantities are determined by equilibria (5) and (6); therefore

$$p = K^{-1} \frac{P_{\mathrm{NH3}}^2}{P_{\mathrm{H2}}^3}, \tag{13}$$

where K is the equilibrium constant of ammonia synthesis, and

$$p' = K' \frac{P_{\mathrm{H2O}}}{P_{\mathrm{H2}}}. \tag{14}$$

According to equation (12), the rate of the forward reaction is

$$\omega_+ = k_+ \frac{P_{\mathrm{N2}}}{\left(P_{\mathrm{NH3}}^2 / P_{\mathrm{H2}}^3 + R P_{\mathrm{H2O}} / P_{\mathrm{H2}}\right)^{\alpha}}, \tag{15}$$

where

$$k_{+} = \frac{\pi}{\sin \alpha\pi} \frac{\varkappa_0}{f} \left(\frac{K}{a_0}\right)^{\alpha}$$

and

$$R = \frac{a_0'}{a_0} K K'.$$

It is easy to verify that R is the constant of the following equilibrium:

$$\mathrm{N}_{2\,\mathrm{ads}} + \mathrm{H_2O} + 2\mathrm{H_2} = \mathrm{O_{ads}} + 2\mathrm{NH_3}; \tag{16}$$

reaction (16) has been observed directly ([11]).

A consideration of the reverse reaction analogous to that given above, or application of Horiuti’ s theorem ([12]), gives for the rate of the reverse reaction

$$\omega_{-} = k_{-} \frac{P_{\mathrm{NH3}}^2}{P_{\mathrm{H2}}^3 \left(P_{\mathrm{NH3}}^2 / P_{\mathrm{H2}}^3 + R P_{\mathrm{H2O}} / P_{\mathrm{H2}}\right)^{\alpha}}. \tag{17}$$

The observed reaction rate $\omega = \omega_{+} - \omega_{-}$ is determined by the equation

$$\omega = \frac{k_{+} P_{\mathrm{N2}} - k_{-} \dfrac{P_{\mathrm{NH3}}^2}{P_{\mathrm{H2}}^3}}{\left(P_{\mathrm{NH3}}^2 / P_{\mathrm{H2}}^3 + R P_{\mathrm{H2O}} / P_{\mathrm{H2}}\right)^{\alpha}}. \tag{18}$$

At $P_{\mathrm{H_2O}} = 0$, equation (18) becomes equation (4). When the poisoning is large, i.e. $RP_{\mathrm{H_2O}}/P_{\mathrm{H_2}} \gg P_{\mathrm{NH_3}}^2/P_{\mathrm{H_2}}^3$, and, in addition, the reverse reaction as well as changes in $P_{\mathrm{N_2}}$ and $P_{\mathrm{H_2}}$ can be neglected, equation (18) leads to equation (1) (with $\alpha = 0.5$).

Table 1

Temp., °C	Volumetric velocity $\left(\frac{V}{\mathrm{h}^{-1}}\right) \cdot 10^{-3}$	$\mathrm{NH_3}$, % (100 g)	$\left(\frac{P_{\mathrm{H_2O}}}{\mathrm{atm}}\right) \cdot 10^{4}$	$\frac{k}{\mathrm{h}^{-1}\,\mathrm{atm}^{0.5}} \cdot 10^{-3}$
425	37,0	0,0266	2,2	8,46
425	61,0	0,0201	1,38	8,30
425	61,0	0,104	0	8,50
425	110,0	0,0149	0,763	8,27
425	74,5	0,0177	1,22	8,37

Temp., °C	Volumetric velocity $\left(\frac{V}{\mathrm{h}^{-1}}\right)\cdot 10^{-3}$	NH_3, % (100 g)	$\left(\frac{P_{\mathrm{H_2O}}}{\mathrm{atm}}\right)\cdot 10^4$	$\frac{k}{\mathrm{h}^{-1}\,\mathrm{atm}^{0.5}}\cdot 10^{-3}$
425	74,5	0,0955	0	8,49
425	37,0	0,0161	6,2	8,45
425	61,0	0,0138	2,99	8,35
425	37,0	0,0140	8,37	8,55
425	61,0	0,0101	5,6	8,35
425	61,0	0,1035	0	8,38
450	112,0	0,0895	0	22,7
450	112,0	0,0150	3,0	24,3
450	53,3	0,120	0	23,2
450	53,3	0,0215	6,2	24,1
450	110,0	0,0915	0	22,5
450	110,0	0,0272	0,873	23,8
450	53,3	0,1180	0	22,0
450	53,3	0,0290	2,99	22,8
450	123,0	0,0866	0	23,0
450	123,0	0,0277	0,62	22,9
450	36,0	0,0220	10,15	21,2
475	59,5	0,0283	6,23	54,5
475	37,0	0,0337	10,15	52,4
475	108,0	0,0490	0,553	55,7
475	108,0	0,0955	0	57,0
475	108,0	0,0289	1,97	56,7
475	69,3	0,0272	5,56	57,4
475	109,5	0,0244	2,70	56,5
475	76,5	0,0233	5,60	54,2
475	111,0	0,0212	3,64	57,5
475	76,5	0,0485	1,0	52,0
475	111,0	0,0450	0,52	54,6
475	60,5	0,1120	0	54,7
475	76,5	0,1065	0	56,3
475	111,0	0,0931	0	54,5
500	96,0	0,0580	0,870	125
500	110,0	0,0587	0,618	124
500	59,0	0,0406	6,85	128
500	79,0	0,096	0	120
500	109,0	0,0404	1,97	126
500	126,0	0,0504	0,555	107
500	75,5	0,0320	5,60	112
500	109,0	0,0318	3,60	128
500	110,0	0,0581	0,62	122
500	110,0	0,0891	0	119

Temp., °C	Volumetric velocity $\left(\frac{V}{h^{-1}}\right) \cdot 10^{-3}$	NH_3, % (100 g)	$\left(\frac{P_{H_2O}}{atm}\right) \cdot 10^4$	$\frac{k}{h^{-1}\,atm^{0.5}} \cdot 10^{-3}$
500	159,0	0,0826	0	127
500	62,8	0,1015	0	129
500	157,5	0,0198	4,68	126
500	156,0	0,0338	1,22	115
500	223,0	0,0356	0,765	132,5
500	223,0	0,0736	0	123
525	186,0	0,0734	0	247
525	122,0	0,0796	0	254
525	186,0	0,0450	0,975	250
525	253,0	0,0455	0,552	254
525	186,0	0,0262	4,54	259
525	236,0	0,0284	2,43	264
525	120,0	0,0350	5,80	268
525	121,0	0,0288	8,40	256
525	186,0	0,0231	6,20	261
525	120,0	0,0760	0,105	258
525	120,0	0,0453	2,20	242

To check equation (18), measurements were carried out of the rate of NH_3 synthesis from a stoichiometric nitrogen-hydrogen mixture at atmospheric pressure by a flow-circulation method (13). The apparatus was analogous to the previously described system with double circulation (14), but was supplemented with a device for dosing water vapor and determining its concentration. A small part (on the order

Table 2

Temp., °C	Volumetric velocity $\left(\frac{V}{h^{-1}}\right) \cdot 10^{-3}$	NH_3, % (100 g)	$\left(\frac{P_{H_2O}}{atm}\right) \cdot 10^4$	$\frac{k}{h^{-1}\,atm^{0.5}} \cdot 10^{-3}$
400	25,0	0,147	0	3,62
400	25,0	0,020	0,62	3,60
400	25,0	0,0138	1,40	3,70
400	14,2	0,0185	2,44	3,74
425	36,7	0,0189	1,0	9,70
425	25,0	0,0224	1,39	9,25
425	36,7	0,138	0	10,0
425	14,2	0,0316	2,44	9,90
425	25,0	0,0372	0,485	9,20

Temp., °C	Volumetric velocity $\left(\frac{V}{h^{-1}}\right) \cdot 10^{-3}$	NH_3, % (100 g)	$\left(\frac{P_{H_2O}}{atm}\right) \cdot 10^4$	$\frac{k}{h^{-1}\,atm^{0.5}} \cdot 10^{-3}$
425	25,4	0,0136	4,10	9,80
425	14,6	0,0173	6,85	9,25
450	36,1	0,138	0	24,4
450	21,2	0,160	0	25,0
450	35,7	0,0325	1,0	24,2
450	20,9	0,0405	1,77	23,9
450	51,5	0,0286	0,69	25,2
450	52,7	0,0137	3,32	26,0
450	36,2	0,0149	5,60	26,0
450	21,2	0,0211	8,40	26,8
475	36,7	0,1275	0	57,5
475	36,7	0,0260	3,7	57,7
475	14,4	0,0376	10,0	55,7
475	36,7	0,0945	0,1	54,3
475	14,2	0,0710	1,97	53,8
475	87,0	0,0266	0,55	54,5
475	59,5	0,0301	0,87	53,2
500	87,0	0,1005	0	54,0
500	36,7	0,0370	3,65	127
500	21,5	0,0435	6,85	125
500	36,7	0,0765	0,46	137
500	86,0	0,0352	0,77	129
500	86,0	0,0960	0	129
500	86,0	0,0133	6,9	136
500	123,0	0,0885	0	128
500	138,0	0,0162	2,44	142
525	124,0	0,0636	0,104	270
525	86,0	0,0496	0,620	260
525	124,0	0,0795	0	254
525	124,0	0,0418	0,620	284
525	152,0	0,0407	0,433	280
525	124,0	0,0239	2,44	277
525	86,0	0,0291	3,30	284

of 0.01) of the gas stream of the additional cycle, controlled by a rotameter, was saturated with water vapor at room temperature, after which part of the vapor was condensed at a lower temperature maintained to an accuracy of 0.05°. The humidified gas returned to the main cycle. The water-vapor content in the main cycle was determined from the dew point.

The experiments were carried out on an iron catalyst containing 3.8% Al_2O_3 and

2.1% K_2O, and on an iron catalyst containing 3.8% Al_2O_3, 0.97% K_2O, 3.4% CaO, and 1.0% SiO_2 (the weight content of promoters is given for the unreduced catalyst). Reduction was carried out with a gradual rise in temperature from 200 to 550°. The specific surface area (from low-temperature adsorption of nitrogen) was 13.6 m^2/g for the catalyst with 2 promoters and 13.7 m^2/g for the catalyst with 4 promoters. Catalyst grains of size 0.1-0.25 mm were used.

Control determinations of the reaction rate with a dry nitrogen-hydrogen mixture showed that the activity of the catalysts remained constant throughout the entire set of measurements. Thus, the poisoning was reversible.

To test equation (18), the usually used constant $k = ({}^4/_3)^{3(1-\alpha)} k_-$ was calculated. Taking $\omega = Vz$, where V is the space velocity (reduced to 0°) and z is the mole fraction of NH_3, we obtain

$$k = \frac{V z^{1+2\alpha} P^{1-\alpha} \left[1 + R({}^3/_4)^2 P_{H_2O}/z^2\right]^{\alpha}}{z_{eq}^2 - z^2}. \tag{19}$$

Here z_{eq} is the value of z at equilibrium. The value $\alpha = 0.5$, usual for iron catalysts, was adopted. The values of R for the catalyst with 2 promoters were determined by fitting; they are given in Table 3, where the values of z_{eq} used in calculating k are also given.

Table 3

Temp., °C	400	425	450	475	500	525
$(R/\text{atm}^{-1})\cdot 10$	7.4	4.6	2.8	2.0	1.4	0.85
$z_{eq}\cdot 10^2$	0.415	0.298	0.218	0.163	0.124	0.097

The data of Table 3 are satisfactorily represented by the equation

$$R = 1.30 \cdot 10^{-6} \exp \frac{8930}{T}. \tag{20}$$

Hence, for reaction (16), $\Delta H = -17.7$ kcal.

The experimental data and the values of k for the catalyst with 2 promoters are given in Table 1. The data for the catalyst with 4 promoters are described by equation (19) with the value of R obtained by multiplying the values of Table 3 by 6 (consequently, this catalyst is more sensitive to the poisoning action of water vapor than the catalyst with 2 promoters). These data are given in Table 2. The constants k in Tables 1 and 2 are sufficiently constant.

Calculations of k were made using equation (18), integrated for a flow system, on the basis of literature data for catalysts with 2 promoters, using the values of

R from Table 3. These data cover pressures of 1 atm (3), 31.6 atm (1), 300 atm (5), and 330 atm (4). In all cases satisfactory constancy of k was obtained. This makes it possible to regard equation (18) as applicable also at high pressures.

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