Gravimetric Study of the Dynamics of Adsorption and Desorption of Ammonia on γ-Alumina*

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In the earlier study of the adsorption of propylamines on alumina it was suggested that the catalytic decomposition of propylamines on γ-alumina accompanied by stop-effect involves the blockage of the adsorbing centres by ammonia and by propylene formed. The present work contributes to the elucidation of this complex phenomenon by the study of the adsorption of ammonia on γ-alumina, using electronic recording microbalances CAHN D-200. The kinetic model was suggested, taking into account that the ammonia molecule may be bound to basic centres by one, two, and even by three hydrogen bonds consecutively, and to the acidic centres by its lone electron pair on the nitrogen atom. This model has been used for the evaluation of the experimental data. The fitting of the model to the isothermal parts of the adsorption-desorption curves was joined with the deconvolution of the temperature-programmed desorption data. The results suggest that ammonia occupies both acidic and basic sites during the desorption stage, so supporting the previous assumptions.

Electronic recording microbalances, which are destinated primarily for the experimental evaluation of equilibrium adsorption capabilities of various sorbents, we are using also for the study of the dynamic behaviour of slower processes, which are accompanied by weight changes. From the previous work [1], which was aimed at the study of the adsorption and desorption of propylamines on alumina, we know that at temperatures above 300 °C the catalytic decomposition of propylamines to propylene and ammonia occurs. The aim of the present work is to contribute to the elucidation of this complex phenomenon accompanied by the stop-effect [2] by the study of the adsorption of one of the reaction products of this process, namely, the sorption of ammonia on γ-alumina. For this purpose, this model describing the whole process, *i.e.* adsorption and desorption at 320 °C, followed by the temperature-programmed desorption (TPD) has been suggested and tested experimentally.

The course of the adsorption-desorption curve has atypical shape. The prevailing amount of the ammonia is adsorbed (and desorbed later on) during the initial 5 min. Then, both adsorption and desorption slow down distinctly, and the equilibrium is not achieved within the reasonable time period. Only part of ammonia adsorbed is removed during the desorption. It is possible to remove the strongly bound remainder of ammonia only during the heating up to 450 °C when performing TPD.

THEORETICAL

According to the published results [3—6], IR spectra obtained during studies of the adsorption of ammonia on γ-alumina suggest the existence of at least three different types of species adsorbed on basic Broensted sites and of one adsorbed on Lewis acid sites. Regarding these results, the model is here suggested, taking into account that the ammonia molecule may be bound to basic sites **B** by one, two, and even by three hydrogen bonds consecutively, and to the acidic sites **A** by its lone electron pair on the nitrogen atom

$$\mathrm{NH_3 + B = NH_3B} \qquad (A)$$

$$\mathrm{NH_3B + B = NH_3B_2} \qquad (B)$$

$$\mathrm{NH_3B_2 + B = NH_3B_3} \qquad (C)$$

$$\mathrm{NH_3 + A = NH_3A} \qquad (D)$$

The kinetics of these four chemical reactions is expressed by the following differential equations

$$\mathrm{d[NH_3B]}/\mathrm{d}t = k_1\mathrm{[NH_3][B]} - k_{b1}\mathrm{[NH_3B]} - k_2\mathrm{[NH_3B][B]} + k_{b2}\mathrm{[NH_3B_2]} \qquad (1)$$

$$\mathrm{d[NH_3B_2]}/\mathrm{d}t = k_2\mathrm{[NH_3B][B]} - k_{b2}\mathrm{[NH_3B_2]} - k_3\mathrm{[NH_3B_2][B]} + k_{b3}\mathrm{[NH_3B_3]} \qquad (2)$$

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$$d[NH_3B_3]/dt = k_3[NH_3B_2][B] - k_{b3}[NH_3B_3] \quad (3)$$

$$d[NH_3A]/dt = k_4[NH_3][A] - k_{b4}[NH_3A] \quad (4)$$

The concentrations of the adsorbing sites on the surface of the alumina are bound by mass balances

$$[B] = c_B - [NH_3B] - 2[NH_3B_2] - 3[NH_3B_3] \quad (5)$$

$$[A] = c_A - [NH_3A] \quad (6)$$

The integration of the set of eqns (*1*) to (*6*) may be done under the initial conditions

$$t = 0,\ [NH_3B] = 0,\ [NH_3B_2] = 0,$$

$$[NH_3B_3] = 0,\ [NH_3A] = 0 \quad (7)$$

For the description of the transient isothermal adsorption-desorption experiments used, ammonia pulse should be defined as

$$0 < t < 2\ \text{h},\ [NH_3] = \text{const} > 0;$$

$$t \geqq 2\ \text{h},\ [NH_3] = 0 \quad (8)$$

This MODEL I has been used for the evaluation of the experimental data.

EXPERIMENTAL

Procedure

The measurement of adsorption and desorption of ammonia on γ-alumina was performed using the recording microbalances CAHN D-200. The measuring range up to 150 mg was used, ensuring the precision of the measurement to 0.1 μg. The initial sample mass of alumina was chosen near the maximum of the range, *i.e.* at 150 mg. The temperature of the sample was measured by thermocouple of type K positioned near the sample pan in a sample tube of balances. The mass, temperature, and time data were recorded by personal computer in 10 s intervals.

The activation of the sorbent has been performed in a manner usual in studies of the stop-effect of alkylamines on alumina [2]. The γ-alumina sample was heated to 450 °C in a stream of the wet air (freed from carbon dioxide by bubbling through the saturated solution of barium hydroxide) and maintained at this temperature for 30 min (*cf.* Fig. 1, area A). After switching from air to pure dried argon stream (15 to 15.5 $dm^3\ h^{-1}$), the activation of the sample continued for next 3 h keeping the temperature unchanged (Fig. 1, area B). Then the temperature was lowered to 320 °C (using the industrial temperature controller, Model T48, Red Lion Controls, U.S.A.), the value which was used throughout the whole study.

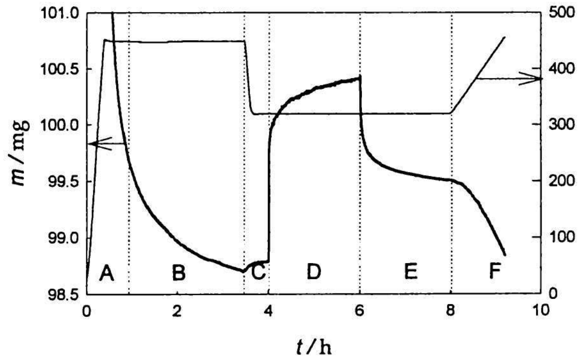

Fig. 1. The whole course of the mass (*m*) and temperature (*θ*) changes with time (*t*).

After reaching stable weight reading (Fig. 1, area C), the adsorption of ammonia was started (Fig. 1, area D). Using the four-way valve, the stream of pure argon was switched to the one of a mixture of argon and gaseous dry ammonia. The flow of the mixture was kept at the same value as that of pure argon used before. Partial pressure of ammonia in the mixture was kept at 41 kPa. After 2 h of adsorption, the desorption was started by replacing the mixture by pure argon, again of the same flow. The desorption was performed for 2 h (Fig. 1, area E). Then, the upper limit of 450 °C and the heating rate 2 °C min^{-1} was set at the temperature controller, and TPD continued under the stream of pure argon, its flow unchanged (Fig. 1, area F).

Theoretical models were fitted to the experimental data using the software package Scientist version. 2.01 for Windows, MicroMath Research, U.S.A.

RESULTS AND DISCUSSION

The above model of the isothermal adsorption and desorption involves 10 adjustable parameters. By fitting the model to experimental data, the values of these parameters were found with good precision, with the exception of the rate constant of desorption from Lewis acid centres, k_{b4} (see Table 1). The uncertainty in determining this constant is obviously due to almost horizontal course of the curve describing the desorption of the component concerned (see Fig. 3, part A).

The values of the equilibrium constant (calculated from the ratio of rate constants as given in Table 2) suggest that the strength of the bound of ammonia molecule to alumina increases with increasing number of its hydrogen bonds, and, moreover, that the strength of the bound to Lewis acid centre is even higher.

Further information about the bound of ammonia to alumina may be obtained from the TPD experimental data. First, we tried to interpret the TPD data alone. Usually, the peaks of individual components are obtained during the following of the process of their

Table 1. Parameter Values Found according to the MODEL I

Parameter	Numerical value^a	Error/%^{b}
k_1	3.753317	2.10
k_{b1}	0.052728	2.99
k_2	4.992086	4.99
k_{b2}	0.00195	3.68
k_3	0.30273	6.13
k_{b3}	0.000115	10.30
k_4	0.045037	3.03
k_{b4}	$<5.5 \times 10^{-6}$	see the text
c_A	0.000334	0.79
c_B	0.001663	0.77
q_3	0.000108	12.1
q_4	0.000312	4.18

a) For value units see Symbols. *b*) = 100 × standard deviation of the numerical value/numerical value.

Table 2. Equilibrium Constants of Adsorption

Parameter	Numerical value^a	Error/%^{b}
K_1	71.18	3.65
K_2	2560.11	6.68
K_3	2623.52	11.98
K_4	>8200	see the text

a) $K_i = k_i/k_{bi}$. *b*) For value units see Symbols. *c*) See Table 1.

desorption, *e.g.* by a chromatograph or mass spectrometer. In our case where the decrease of the sum of masses of sorbent and sorbate during the programmed heating is experimentally followed, similar peaks could be obtained by the derivating the summary curve obtained. As it can be seen from Fig. 2, the summary TPD curves are fairly smooth. Their derivating, however, yielded the peaks almost lost in the noise. That noise was not feasible to remove by the Fourier filtration, since ambiguous results were obtained, depending on the threshold of the filtration chosen. Therefore, the models describing the TPD process were fitted directly to the summary experimental data, and the peaks of individual components were obtained during the numerical integration of the models.

Generally, the summary TPD curve may be deconvoluted in several ways. First, the simplest model assuming the desorption of only one component (MODEL II) was compared with the model assuming two components being desorbed under TPD experiments (MODEL III). In the former case, the rate of desorption of the component 1, R_1 is given by the equation

$$R_1 = -\mathrm{d}q/\mathrm{d}t = -b(\mathrm{d}q_1/\mathrm{d}T) = \\ = A_1 q_1 \exp(-E_1/(\boldsymbol{RT})) \qquad (9)$$

which may be numerically integrated at initial conditions

$$t = 0,\ T = 593\ \mathrm{K},\ q_1 = q_{01} \qquad (10)$$

And in the second case, where *e.g.* components 3 and 4 are desorbed under TPD, the system of the following differential equations describes the situation

$$R_3 = -\mathrm{d}q_3/\mathrm{d}t = -b(\mathrm{d}q_3/\mathrm{d}T) = \\ = A_3 q_3 \exp(-E_3/(\boldsymbol{RT})) \qquad (11)$$

$$R_4 = -\mathrm{d}q_4/\mathrm{d}t = -b(\mathrm{d}q_4/\mathrm{d}T) = \\ = A_4 q_4 \exp(-E_4/(\boldsymbol{RT})) \qquad (12)$$

where the total observed desorption rate R is given by the sum of rates R_3 and R_4

$$R = R_3 + R_4 \qquad (13)$$

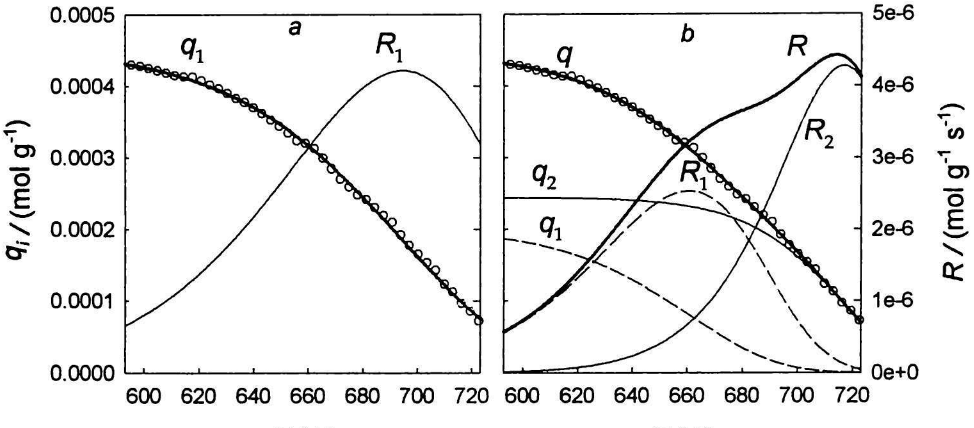

Fig. 2. *a*) Fit of MODEL II; *b*) fit of MODEL III. Circles – experimental data, lines – calculated. Some experimental points omitted for the sake of legibility.

Table 3. Parameters Calculated

according to MODEL II			according to MODEL III		
Parameter	Numerical value^a	Error/%^{b}	Parameter	Numerical value^a	Error/%^{b}
A_1	5.41×10^3	13.27	A_3	1.084×10^6	45.07
E_1	9.14×10^4	0.81	E_3	1.142×10^5	2.17
q_{01}	4.51×10^{-4}	0.22	A_4	1.045×10^{11}	673.13
			E_4	1.902×10^5	20.78
			q_{03}	1.875×10^{-4}	12.49
			q_{04}	2.446×10^{-4}	9.58

a) For value units see Symbols. *b*) See Table 1.

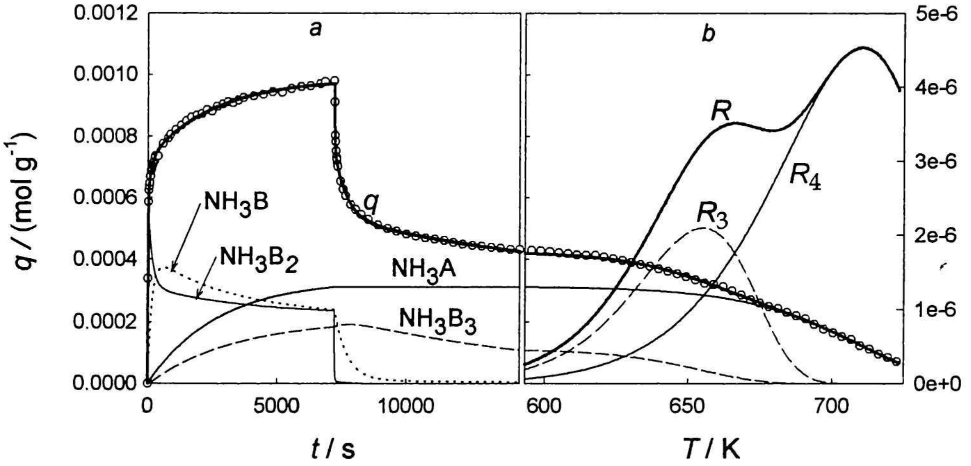

Fig. 3. The joint fit of MODEL I (*a*) and of MODEL III (*b*). Circles – experimental data, lines – calculated. Some experimental points omitted for the sake of legibility.

and the system is integrated under initial conditions

$$T = 593\ \text{K},\ q_3 = q_{03},\ q_4 = q_{04},\ q = q_3 + q_4 \qquad (14)$$

The former one showed to be more appropriate from the point of view of statistical reliability, as it might be expected, since the latter model has twice as high the number of adjustable parameters (see Table 3).

Besides of purely statistical approach to TPD curves, it is possible also to utilize the knowledge obtained during the previous, isothermal stage of the adsorption-desorption experiment. As it can be seen in Fig. 3, part A, after 2 h of the desorption at 320 °C, two components remained evidently on the sorbent. The two-component MODEL III of the deconvolution of the summary TPD curve is therefore more appropriate with regard to these findings. In order to decrease the uncertainties following from increased number of the parameters in this model, the values of concentrations of the components, q_{03}, q_{04} (as they were found by the MODEL I at the end of the second hour of desorption), were overtaken into the MODEL III. Only four unknown parameters were now fitted using this model.

The results so obtained are listed in Table 4. The values of the preexponential factor are still statistically uncertain. Nevertheless, the orders of the values themselves are much nearer to that expected from the literature [7—10] than those obtained for the single peak MODEL II. This observation seems to support the two-component model of the TPD process.

Table 4. Results according to MODEL III with Reduced Number of Parameters^a

Parameter	Numerical value^b	Error/%^{c}
A_3	7.03×10^{10}	288.49
E_3	1.71×10^5	8.87
A_4	2.26×10^8	268.26
E_4	1.53×10^5	10.15

a) Numerical values $q_{03} = 1.08 \times 10^{-4}$ and $q_{04} = 3.12 \times 10^{-4}$ used (see the text). *b*) For value units see Symbols. *c*) See Table 1.

The values of preexponential factor and of activation energy of the desorption process allow to calculate the values of desorption constants at 320 °C, the temperature of isothermal adsorption-desorption experiment. The values so obtained, *i.e.* $k_{b3} = 5.71 \times$

10^{-5} s^{-1} and $k_{b4} = 6.85 \times 10^{-6}$ s^{-1} are in fair agreement with those obtained according to MODEL I (*cf.* Table 1). The agreement between the MODEL I and MODEL III is further illustrated in Fig. 3, where both the isothermal adsorption-desorption process (part A) and the TPD data (part B) are given.

Apart from the experiments described, various other influences on the system were investigated. The adsorption-desorption isothermal and TPD curves were recorded after various manners of the activation of sorbent, during the repeated adsorption on alumina reactivated several times, at various temperatures (in the range 130 to 400 °C) of the isothermal adsorption-desorption, at ammonia partial pressure ranging from 3 to 98 kPa. The MODEL I together with MODEL III fitted well to all the experimental data so obtained.

CONCLUSION

The model for the adsorption, isothermal desorption, and TPD of ammonia on γ-alumina was suggested, involving both the consecutive formation of bounds between basic Broensted sites of the adsorbent *via* hydrogen bonding with H atoms of ammonia molecule, and the formation of the bound between the lone electron pair of ammonia molecule and Lewis acid sites. The model fits well to the experimental data.

The results obtained are of importance for the understanding of the mechanism of the catalytic deamination of aliphatic amines on γ-alumina, accompanied with the so-called stop-effect. Namely, here it was proved that ammonia is present at the surface of alumina even after its removal from the gas phase. Moreover, the present results suggest that ammonia occupies both acidic and basic sites during the desorption stage. The presence of ammonia during the deamination reaction on the surface of the sorbent we assumed earlier [1] when trying to interpret our observations on stop-effect. The present results support this opinion.

SYMBOLS

$[A]$	concentration of free acid centres	mol g^{-1}
A_1, A_2, A_3, A_4	preexponential factor of desorption of components	s^{-1}
$[B]$	concentration of free basic centres	mol g^{-1}
$[NH_3]$	concentration of ammonia in a gas phase	mol dm^{-3}
b	rate of heating	K s^{-1}
c_A, c_B	maximal concentration of acid and basic centres, respectively	mol g^{-1}
E_1, E_2, E_3, E_4	energy of desorption of components	J mol^{-1}
K_1, K_4	equilibrium adsorption constants	dm^3 mol^{-1}
K_2, K_3	equilibrium constants	g mol^{-1}
k_1, k_4	adsorption rate constants of components 1, 4	dm^3 mol^{-1} s^{-1}
k_2, k_3	rate constants of components 2, 3	g mol^{-1} s^{-1}
k_{b1}, k_{b2}, k_{b3}, k_{b4}	desorption rate constants of components 1, 2, 3, 4	s^{-1}
$[NH_3B]$, $[NH_3B_2]$, $[NH_3B_3]$	concentration of ammonia sorbed at one, two or three basic centres	mol g^{-1}
$[NH_3A]$	concentration of ammonia sorbed at acid centre	mol g^{-1}
q_{01}	initial concentration of adsorbed component 1	mol g^{-1}
q_1	concentration of adsorbed component 1	mol g^{-1}
q_{03}, q_{04}	initial concentrations of strongly adsorbed components	mol g^{-1}
q_3, q_4	concentrations of strongly adsorbed components	mol g^{-1}
R_1	desorption rate of adsorbed component 1	mol g^{-1} s^{-1}
R_3, R_4	desorption rates of strongly adsorbed components	mol g^{-1} s^{-1}
$\boldsymbol{R}$	gas constant (8.31451 J mol^{-1} K^{-1})	
t	time	s
T	thermodynamic temperature	K
θ	Celsius temperature	°C

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