

# Temperature-Programmed Desorption Study of Ammonia Desorption–Diffusion in Molecular Sieves

## I. Theory

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Different approaches are compared for the analysis of TPD curves of ammonia–zeolite systems. Desorption of the adsorbed base, either with no readsorption or with free readsorption, and intracrystalline diffusion of the desorbed ammonia through the zeolitic pores have been considered alternatively as the controlling step of the overall process and the corresponding model equations have been derived for the evaluation of the kinetic or thermodynamic parameters. The solution of such equations may be easily obtained numerically by means of the usual nonlinear regression–optimization procedures. The dependence on temperature of the amount of base, chemically held by the zeolitic acid centers, and of the apparent diffusion coefficient, has been discussed and some model equations are proposed, to be inserted in the main regression routine. © 1988 Academic Press, Inc.

### INTRODUCTION

Temperature-programmed desorption (TPD) is one of the most widely employed techniques for measuring the adsorption properties of solids. Two excellent reviews, by Falconer and Schwarz (1) and by Lemaitre (2), discuss the advantages and drawbacks of the method. For the characterization of surface acidity, in regard to both the amount and the strength of acid sites, many recent papers (3–12) confirm that TPD of preadsorbed ammonia has become very popular, so much so that it has been proposed by the Japanese Catalysis Society as a possible standard method for testing acid catalysts, particularly zeolites (13).

Most of the work on this subject is based on a procedure suggested in a well-known review by Cvetanovic and Amenomiya (14). These authors showed that, under well-defined conditions, i.e., energetically homogeneous surface sites, first-order desorption rate with respect to the adsorbed species, absence of intraparticle diffusion effects, and linear temperature increase, a

correlation among the rate of temperature increase  $\beta$ , the temperature  $T_M$  at peak maximum, and activation energy  $E_d$  of desorption is given by the equation

$$2 \ln T_M - \ln \beta = (E_d/RT_M) + C_1 \quad (1)$$

if readsorption of the adsorbate does not occur. If readsorption occurs freely, the following similar equation holds,

$$2 \ln T_M - \ln \beta = (\Delta H_d/RT_M) + C_2, \quad (2)$$

in which  $\Delta H_d$  is the enthalpy change associated with desorption. The constants  $C_1$  and  $C_2$  are determined mainly by the experimental conditions.

These two equations have been applied frequently (3, 4, 9–11) for the determination of  $E_d$  or  $\Delta H_d$  from the slope of the straight lines obtained by plotting  $(2 \ln T_M - \ln \beta)$  vs  $1/T_M$ . Unfortunately, first-order desorption processes under kinetic control are indistinguishable from diffusion-controlled ones on the basis of the TPD curve shape only. As a consequence, it has been pointed out (5, 15–19) that other criteria should be employed in order to establish

whether diffusion, particularly intraparticle diffusion, plays an important or a negligible role in the actual TPD experiment. For example, according to Ibok and Ollis (15), intraparticle diffusion is most likely to be controlling when

$$\beta R_p^2 > \frac{D_e C_g}{v_m (d\theta/dT)_{\max}}, \quad (3)$$

$R_p$  being the radius of the adsorbent particle, assumed as spherical,  $D_e$  the effective diffusion coefficient within the pores,  $C_g$  the concentration of adsorbate in the gaseous phase,  $v_m$  the concentration of active sites (of a given species) carrying the adsorbate, per unit volume of particle, and  $(d\theta/dT)_{\max}$  the maximum rate of desorption. However, when working with zeolites, the characteristic particle dimension to be taken into account should be the zeolitic microcrystal radius  $R_c$ , rather than the radius  $R_p$  of the bulk solid particle. Indeed, the diffusion within the zeolite pores is much more difficult than that in the intercrystalline voids within the particle, the effective diffusion coefficient being many orders of magnitude lower in the former than in the latter. As a consequence, according to the inequality (3), for the conditions usually encountered in TPD experiments on zeolites,  $D_e$  should be higher than ca.  $10^{-9}$  cm<sup>2</sup>/s in order to ensure a negligible influence of intracrystalline diffusion. In practice, lower values of  $D_e$  are not unusual for the diffusion within the zeolite pores. Hence it is probable that in many cases the overall desorption–diffusion process taking place during the TPD experiment on zeolites is controlled by diffusion, rather than by desorption.

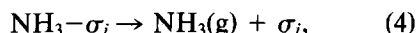
However, the values entering in these formulas are seldom available with the desirable reliability, so that the usefulness of such criteria is frequently poor. Furthermore, it is frequent practice, during the TPD experiment with NH<sub>3</sub> in zeolites (3–5, 7–11), to leave a rather short time for the desorption of the physically sorbed ammonia at the temperature of adsorption, before

starting the programmed temperature rise. This may easily lead to a lack of reproducibility and to serious errors in determining the amount of chemically adsorbed NH<sub>3</sub>. Indeed, especially for initial isothermal desorption temperatures lower than 450 K, many hours or even days may be required for all the physically adsorbed ammonia to leave the solid adsorbent.

In the present work, the sorption–diffusion of ammonia in zeolites has been studied by TPD, by comparing different approaches for the analysis of data, considering desorption (either with no readsorption or with free readsorption of the desorbed base) or diffusion within the zeolitic pores, as the controlling step of the overall process.

#### THEORY

*Desorption controlling with no readsorption.* According to one of the most recently proposed methods (11), the distribution of the strength of acid sites as a function of the activation energy for ammonia desorption may be evaluated by representing the desorption process from sites of different strength by a series of irreversible first-order reactions:



$\sigma_i$  being a surface site of  $i$ th strength. Every one of these surface reactions is characterized by a particular value of the kinetic constant  $k_d$ , expressed by an Arrhenius-type equation. Hence a different value of the frequency factor  $A$  and of apparent activation energy  $E_d$  may be assigned to each reaction. If the heating rate  $\beta$  ( $T = T_0 + \beta t$ ) is high enough to permit the neglect of readsorption, the ammonia desorption rate may be written as

$$-d(\Delta q)/dt = k_d \Delta q, \quad (5)$$

$\Delta q$  being the amount of ammonia held by acid sites, considered energetically homogeneous, at temperature  $T$ , so that  $\Delta q_0$  is the value of  $\Delta q$  for  $T = T_0$ . The desorption rate constant  $k_d$  is given by

$$k_d = A \exp(-E_d/RT). \quad (6)$$

After a series of TPD curves is recorded, by raising the starting temperature  $T_0$  by  $\Delta T$  each time, the difference curve  $-d(\Delta q)/dt$  vs  $t$  is calculated by evaluating, point by point, the difference between such experimental curves. This is made for each pair of curves, whose starting temperatures are  $T_0$  and  $T_0 + \Delta T$ .  $\Delta q$  is then calculated by integrating numerically such a difference curve. If  $\Delta T$  is sufficiently small, the integral curve so calculated represents the ammonia held by sites of uniform strength, characterized by a given pair of  $E_d$  and  $A$  values.

By combining Eqs. (5) and (6) we obtain

$$-d(\Delta q)/dt = A \Delta q \exp(-E_d/RT). \quad (7)$$

However,

$$dt = dT/\beta \quad (8)$$

so that

$$-d(\Delta q)/\Delta q = (A/\beta)\exp(-E_d/RT)dT \quad (9)$$

which can be integrated between the limits  $\Delta q_0$ ,  $\Delta q$  and  $T_0$ ,  $T$ , respectively, to give

$$\ln(\Delta q/\Delta q_0) = -(A/\beta)I, \quad (10)$$

where

$$I = \int_{T_0}^T \exp(-E_d/RT)dT. \quad (11)$$

Furthermore, from Eq. (7),

$$A = -\exp(E_d/RT)(1/\Delta q)d(\Delta q)/dt \quad (12)$$

and combining Eqs. (8), (10) and (12),

$$\Delta q \ln(\Delta q/\Delta q_0) \frac{1}{d(\Delta q)/dT} = \exp(E_d/RT)I. \quad (13)$$

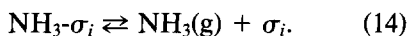
In Eq. (13), the left-hand side member contains only known data and may be defined as the "experimental" curve, while the right-hand side member can be considered the "calculated" curve and contains only  $E_d$  as an unknown parameter.

In the work by Hashimoto *et al.* (11) the

pair of values of  $E_d$  and  $A$  for each difference peak are obtained referring only to the temperature  $T_M$ , corresponding to the peak maximum, and the solution of the analytically unsolvable integral  $I$  is obtained on the basis of a previous graphical relationship (20). A less rough approach could be the following. First, starting from Eq. (13), a nonlinear regression procedure is employed, evaluating  $E_d$  numerically by minimizing the sum of the squares of the differences between the "experimental" and "calculated" values, i.e., between the two members of the equation. The sum is extended to the whole set of experimental points, forming the difference curve  $-d(\Delta q)/dt$  vs  $t$ . Then, by inserting the value of  $E_d$  so obtained in Eq. (12), the preexponential factor  $A$  is calculated for each of the experimental points. The final value of  $A$  is then obtained by averaging these "single-point" results.

However, a more reliable solution is possible. A nonlinear regression procedure (21) is applied directly to Eq. (7), for the simultaneous evaluation of both  $E_d$  and  $A$ , by minimizing the sum of the squares of the differences between the points forming the experimental and the calculated difference peaks, i.e., between the two members of the equation. The substantial improvement of this procedure, with respect to the previous one (11), is that it does not employ only one experimental datum (corresponding to  $T_M$ ), but it makes use of the whole set of experimental data for the calculation of  $E_d$  and  $A$ . Furthermore, the optimization is carried out directly on the experimental difference curve and the analytically unsolvable integral  $I$  no longer needs to be calculated.

*Desorption controlling with free readsorption.* If readsorption of the desorbed base occurs freely, i.e., if the ammonia desorption is reversible, the desorption process from sites of different strength may be represented once again by a series of first-order reactions, but considered at equilibrium:



Every one of these surface reactions is characterized by particular values of the kinetic constants.

The previous procedure then needs to be modified as follows. From Eq. (14) we have, at any temperature,

$$r_a(\text{adsorption rate}) = r_d(\text{desorption rate}), \quad (15)$$

where

$$r_a = k_a(\Delta q_0 - \Delta q)C_g \quad (16)$$

and

$$r_d = k_d\Delta q, \quad (17)$$

$k_a$  and  $k_d$  being the adsorption and desorption rate constants, respectively, and  $C_g$  the concentration of ammonia in the gaseous phase leaving the zeolite bed. The values of  $d(\Delta q)/dt$ ,  $\Delta q$ , and  $\Delta q_0$  are calculated as seen above. Furthermore, for the mass balance,

$$FC_g = -d(\Delta q)/dt, \quad (18)$$

$F$  being the volumetric flow rate of the carrier gas per unit mass of zeolite. By combining Eqs. (8), (16), and (18), we obtain

$$r_a = -(\beta/F)k_a(\Delta q_0 - \Delta q)d(\Delta q)/dT \quad (19)$$

and, by virtue of Eq. (15),

$$\begin{aligned} ((\Delta q_0 - \Delta q)/\Delta q)d(\Delta q) \\ = -(F/\beta)(k_d/k_a)dT. \end{aligned} \quad (20)$$

The desorption equilibrium constant

$$K_d = k_d/k_a \quad (21)$$

depends on temperature through a van't Hoff-type equation

$$K_d = K_0 \exp(-\Delta H_d/RT), \quad (22)$$

where  $K_0 = \exp(\Delta S_d/R)$ ,  $\Delta H_d$  and  $\Delta S_d$  being the enthalpy and entropy change, respectively, associated with the desorption process. Combining Eqs. (20) and (22),

$$\begin{aligned} ((\Delta q_0 - \Delta q)/\Delta q)d(\Delta q) \\ = -(F/\beta)K_0 \exp(-\Delta H_d/RT)dT, \end{aligned} \quad (23)$$

and integrating

$$\begin{aligned} \int_{\Delta q_0}^{\Delta q} ((\Delta q_0 - \Delta q)/\Delta q)d(\Delta q) \\ = -(F/\beta)K_0 \int_{T_0}^T \exp(-\Delta H_d/RT)dT \end{aligned} \quad (24)$$

or

$$\begin{aligned} \Delta q_0 \ln(\Delta q/\Delta q_0) + \Delta q_0 - \Delta q \\ = -(F/\beta)K_0 \int_{T_0}^T \exp(-\Delta H_d/RT)dT. \end{aligned} \quad (25)$$

Combining Eqs. (23) and (25),

$$\begin{aligned} \Delta q_0 \ln(\Delta q/\Delta q_0) + \Delta q_0 - \Delta q \\ = ((\Delta q_0 - \Delta q)/\Delta q)(d(\Delta q)/dT) \\ \exp(\Delta H_d/RT)I', \end{aligned} \quad (26)$$

where

$$I' = \int_{T_0}^T \exp(-\Delta H_d/RT)dT. \quad (27)$$

The integral  $I'$  is similar to that defined by Eq. (11). It may be solved numerically, e.g., by Simpson's rule, as a subroutine inserted in the nonlinear regression-optimization procedure for the evaluation of  $\Delta H_d$  by means of Eq. (26).

Equation (26) is implicit in  $\Delta H_d$ . Its solution gives the value of the enthalpy change associated with desorption from the sites corresponding to the difference peak examined. It is important to note that, in such an equation,  $T$  is any value of temperature within the range corresponding to the actual difference peak. As a consequence it is possible, by means of Eq. (26), to analyze the same peak in many points, which must lead to the same value of  $\Delta H_d$ . In this way, the validity of the model can be tested effectively.

*Intracrystalline diffusion controlling.* After desorption, the ammonia molecules coming from inside the zeolite pores must diffuse through the latter to reach the carrier gas, flowing outside the crystals. This diffusive process is much more difficult than the relatively free diffusion in the bulk gaseous phase, owing to the presence of the acid sites, in addition to the geometric restriction, due to the narrowness of the

pores. The process may be represented as a surface diffusion, further slowed down by the reversible acid–base chemical reaction.

Under isothermal conditions, the amount of substance that has diffused out of the zeolite from  $t = 0$  to  $t = t$  is given by (22)

$$M_t/M_\infty = 1 - (6/\pi^2) \sum_{n=1}^{\infty} (1/n^2) \exp(-D_e n^2 \pi^2 t/R_c^2), \quad (28)$$

where  $M_t$  and  $M_\infty$  represent the amount of ammonia which has come out of the crystal of radius  $R_c$  after time  $t$  or  $t = \infty$ , respectively, and  $D_0$  is the effective diffusion coefficient.

For nonisothermal conditions, Eq. (28) needs to be modified. Let us assume that the duration of the TPD experiment is divided into small time intervals  $\Delta t$ , so that, during each of them, the temperature of the system increases by 1 K. During each  $i$ th increment, the temperature is assumed constant and equal to  $T_i^* = T_{i-1} + 0.5$  K. Hence, the diffusion of the base may be described by the following modification of Eq. (28),

$$M_{\Delta t_i} = (N(T_i) - N_\infty(T_i^*)) (1 - (6/\pi^2) \sum_{n=1}^{\infty} (1/n^2) \exp(- (D_e/R_c^2)(T_i^*) n^2 \pi^2 \Delta t_i)), \quad (29)$$

where  $M_{\Delta t_i}$  is the amount of ammonia (mmol/g of solid) coming out of the zeolite during the time interval  $\Delta t_i$ ,  $N(T_i)$  is the amount of base present in the porous solid during the TPD experiment at temperature  $T_i$ , and  $N_\infty(T_i^*)$  is the amount of ammonia chemically held by the zeolite at temperature  $T_i^*$ . The latter quantity corresponds to the zeolitic acid sites still covered at temperature  $T_i^*$ .  $N(T_i)$  is given by

$$N(T_i) = N_\infty(T_i) \quad (i = 1) \quad (30)$$

or

$$N(T_i) = N(T_{i-1}) + M_{\Delta t_{i-1}} \quad (i > 1). \quad (31)$$

A mass balance, similar to Eq. (18), may be written by inserting finite differences for

differentials

$$-dN/dt = M_{\Delta t}/\Delta t. \quad (32)$$

In Eq. (32), the left-hand side member represents the experimental TPD peak, while the right-hand side member is the calculated peak.

An experimental approach is perhaps the safest procedure for obtaining the function

$$N_\infty = N_\infty(T) \quad (33)$$

describing the dependence on temperature of the parameter  $N_\infty$ . After collecting data, within the actual temperature range, on the amount of ammonia chemically held at varying temperatures, one may test some simple equations (e.g., a low-degree polynomial or a simple exponential) and evaluate the relative parameters by the usual optimization procedures.

As for  $D_e/R_c^2$ , an exponential form of the type

$$D_e/R_c^2 = A_a \exp(-E_a/RT) \quad (34)$$

has been suggested (23) for surface diffusion. However, it must be remembered that, in the present case,  $D_e$  also takes into account the additional slowing effect due to the reversible chemical reaction between sorbate and acid sites, as mentioned.

The analysis of the TPD experiment may then be carried out by drawing a calculated peak, by means of Eqs. (29) and (32), in which Eqs. (33) and (34) are inserted. This calculated peak is then compared with the experimental one and the parameters  $E_a$  and  $A_a$  of Eq. (34) are optimized, by the usual nonlinear regression routines (21).

It may be noted that, in Eq. (34), the parameters  $E_a$  and  $A_a$  may be considered apparent kinetic parameters for the intracrystalline diffusion process.

#### CONCLUSION

The equations obtained in the present work represent a starting point for the application of the TPD technique to the study of the desorption of bases, particularly ammonia, from microporous acid solids, par-

ticularly zeolites. By analyzing the experimental TPD data by means of these equations describing the characteristics of the thermogram, it is possible to obtain information on which of the various phenomena involved plays a significant role in the overall process. In Part II (24) this procedure is applied to the study of ammonia desorption from differently decationated Y-zeolites.

## NOMENCLATURE

$A$	preexponential factor ( $s^{-1}$ )
$C_g$	concentration of adsorbate in the gas phase ( $mmol/cm^3$ )
$D_e$	effective diffusion coefficient ( $cm^2/s$ )
$E_a, E_d$	apparent activation energy, of diffusion and of desorption ( $kcal/mol$ )
$F$	specific volumetric flow rate of carrier gas ( $cm^3/s$ g)
$\Delta H_d$	enthalpy change of desorption ( $kcal/mol$ )
$I, I'$	integral, defined by Eq. (11) or (27)
$k_a$	adsorption rate constant ( $cm^3 s^{-1} mmol^{-1}$ )
$k_d$	desorption rate constant ( $s^{-1}$ )
$K_d$	desorption equilibrium constant
$K_0$	thermodynamic parameter in Eq. (22)
$M_t, M_\infty$	ammonia released from the zeolite crystals at $t = t, \infty$ ( $mmol/g$ )
$M_{\Delta t}$	ammonia released from the zeolite crystals during the time interval $\Delta t$ ( $mmol/g$ )
$n$	integer in Eqs. (28), (32), (34)
$N_0, N_t, N_\infty$	ammonia present in the zeolite pores at $t = 0, t, \infty$ ( $mmol/g$ )

$\Delta q, \Delta q_0$	ammonia held by energetically homogeneous sites at $T = T, T_0$ ( $mmol/g$ )
$r_a, r_d$	adsorption and desorption rate ( $mmol/g s$ )
$R$	gas constant
$R_c, R_p$	radius, of crystal and of particle ( $cm$ )
$\Delta S_d$	entropy change of desorption (e.u.)
$t$	time (s)
$T, T_0, T_M, T^*$	temperature, initial, at peak maximum, mean value during a given time interval (K)
$\beta$	temperature increasing rate (K/s)
$\theta$	fraction of occupied sites
$\nu_m$	concentration of active sites of a given species per unit volume of particle ( $mmol/cm^3$ )

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