

Note**NON-ISOTHERMAL KINETICS IN THERMAL DESORPTION**

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To point out the similarity between working data techniques applied in thermal desorption, namely, in thermal programmed desorption (TPD), and in non-isothermal kinetics, one of us [1] used a typical method for thermal desorption [2] to evaluate the kinetic parameters of calcium oxalate dehydration. To illustrate the same similarity, in this paper, the data concerning the thermal desorption of hydrogen from an ammonia-synthesis catalyst are treated by the Coats–Redfern method [3], which is widely used in non-isothermal kinetics.

EXPERIMENTAL

The TPD method is based on the fact that while the surface temperature is increased desorption of adsorbed species on the surface occurs. Experimentally, the sample is heated with a linear heating programme and from the total pressure vs. temperature curves the kinetic parameters can be calculated.

A 1 g promoted and reduced iron catalyst for ammonia synthesis was used. The hydrogen was obtained by vacuum desorption from spongy palladium. The sample was submitted to a treatment consisting of activation in high vacuum at 773 K, pumping out at the same temperature to remove gaseous impurities, hydrogen exposure at various doses at room temperature, pumping out the excess hydrogen, and, finally, TPD measurement. A heating rate of $\beta = 0.16 \text{ K s}^{-1}$ was used.

RESULTS AND DISCUSSION

In order to evaluate the kinetic parameters of hydrogen thermal desorption from the catalyst, we used the Coats–Redfern method, based on the relationships

$$\left. \begin{aligned} n = 1 \ln \frac{-\ln(1-\alpha)}{T^2} \\ n = 2 \ln \frac{\alpha}{(1-\alpha)T^2} \end{aligned} \right\} = \ln \frac{AR}{\beta E_d} \left[\left(1 - 2 \frac{RT}{E_d} \right) - \frac{E_d}{RT} \right] \quad (1)$$

where α stands for the conversion degree at temperature T , and n , E_d and A stand for the kinetic order of desorption, activation energy and pre-exponential factor, respectively. R stands for the gas constant and β for heating rate. The method is suitable for TPD kinetics, the degree of surface coverage being related to α by the relation, $\theta = 1 - \alpha$. A plot of the first member of eqn. (1) vs. $1/T$, for the correct value of n , should give a straight line whose slope and intercept allow the activation energy and pre-exponential factor to be obtained.

Our results concerning the TPD of hydrogen desorption from the the iron ammonia-synthesis catalyst, given in Fig. 1, are described by eqn. (1) for $n = 2$. This reaction order value suggests an associative desorption mecha-

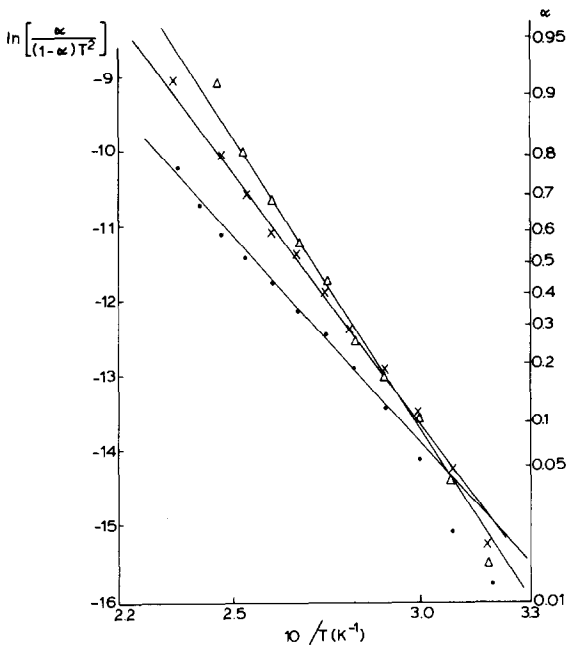


Fig. 1. Linearization of experimental data according to eqn. (1) for $n = 2$. Δ , run 4; \times , run 8; \bullet , run 9.

TABLE 1

Kinetic parameters for hydrogen TPD

Run	D (L) ^a	E_d (kcal mole ⁻¹)	A (sec ⁻¹)	E_d ^b (kcal mole ⁻¹)
1	2×10^0	17.8	8.9×10^7	16.0
2	3×10^{-1}	16.6	2.0×10^7	13.5
3	2×10^{-2}	16.0	1.2×10^7	15.6
4	3×10^{-2}	16.1	1.2×10^7	15.0
5	8×10^{-2}	14.3	1.3×10^6	12.8

^a H₂ exposure given in Langmuir: 1 L = $10^{-6} \times 1$ torr \times 1 sec.^b Values calculated using eqn. (2).

nism. The values of the activation energy for hydrogen desorption in the first five runs are given in Table 1: values of E_d calculated for the hyperbolic heating programme after Kelly and Laubitz [4,5] are given in the last column. These values were calculated using the formula

$$E_d = \frac{3.52 RT_1 T_2}{\omega} \quad (2)$$

where T_1 and T_2 are the two temperatures corresponding to the half width of the TPD peak, and $\omega = T_2 - T_1$. (A hyperbolic programme according to the equation $1/T = 3.36 \times 10^{-3} - 5.25 \times 10^{-7}t$ was used). Quite good agreement was obtained between the two sets of activation energy values.

A linear dependence between the activation energy and the logarithm of hydrogen exposure was obtained (Fig. 2).

Considering the maximum desorption rate for $n = 2$, we obtain [1,2]

$$(1 - \alpha)_m = \frac{E_d/RT_m + 4}{2(E_d/RT_m + 2)} \quad (3)$$

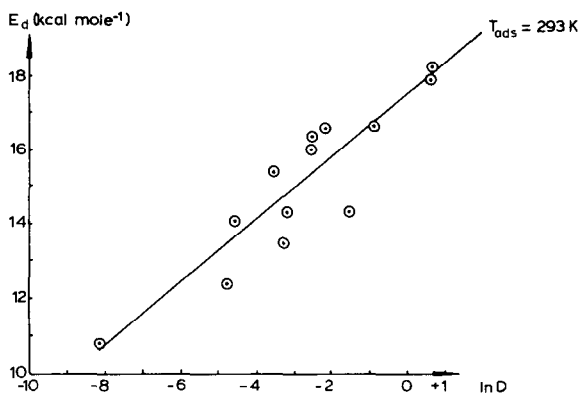
Fig. 2. Changes of the activation energies with H₂ exposure.

TABLE 2

Experimental values of $(1 - \alpha)_m$ and those calculated using eqn. (3)

Run	$(1 - \alpha)_m$	
	Exp.	Calcd.
1	0.675	0.650
2	0.635	0.670
3	0.622	0.542
4	0.580	0.540
5	0.536	0.547

where subscript m indicates the maximum conditions.

From the data given in Table 2, the experimental values of $(1 - \alpha)_m$ could be compared with the calculated ones obtained by eqn. (3). The quite satisfactory agreement between the two sets of values can be considered as proof of the validity of eqn. (3) as well as the value of the kinetic desorption order which equals two.

CONCLUSIONS

A kinetic study of the TPD of hydrogen from an iron catalyst for ammonia synthesis was performed. The value $n = 2$ for kinetic desorption order is assigned to the associative desorption of hydrogen. An activation energy decrease with the logarithm of the hydrogen dose was put in evidence.

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