

Note**NON-ISOTHERMAL KINETIC STUDY OF CATALYTIC AMMONIA OXIDATION****M.M. GIRGIS***Department of Chemistry, Faculty of Science, University of Assiut, Assiut (Egypt)***D. LAZĂR***Department of Physical Chemistry, The Polytechnical Institute of Jassy, Jassy (Romania)***E. SEGAL***Department of Physical Chemistry and Electrochemical Technology, National Institute of Chemistry, Bucharest (Romania)*

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This paper aims to present the results of some non-isothermal kinetic studies of ammonia oxidation using atmospheric oxygen and $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$, $\text{NiO/Al}_2\text{O}_3$ and $\text{Pd-Ru/Al}_2\text{O}_3$ catalysts.

Previous work by the authors [1–3] has shown that if the reaction is being followed in a flow reactor in given conditions of temperature, volume and flowrate of ammonia, after an induction period a temperature peak appears. This peak is initially in the middle of the reactor, but shifts slowly against the gas-flow towards the reactor entrance. During this shift, the temperature peak becomes narrower and higher. Finally, the peak becomes steady with a maximal height and minimal width. The temperature value behind the moving temperature peak returns to its initial value T_i . During oxidation, no temperature increase of the reactor surroundings was observed. Thus, the peak exhibits adiabatic behaviour.

Taking into account the adiabatic character of the temperature peak, from the observed curve of its temperature changes in time, an attempt was made to evaluate the overall kinetic parameters of ammonia oxidation in non-isothermal conditions.

If the exothermic reaction responsible for the temperature increase of the temperature peak, is described by the Arrhenius equation, then

$$-\frac{dx}{dt} = Z e^{-E/RT} x^n \quad (1)$$

where x stands for the ammonia concentration in the gaseous mixture and T is the temperature which varies from the initial temperature, T_i , to T_{max} (the temperature corresponding to the steady temperature peak): the other nota-

tions have the usual meanings. The thermal balance equation corresponding to heating the gaseous mixtures is

$$Q_v d\alpha = C_v dT \quad (2)$$

where Q_v and C_v stand for the molar heat of reaction and the heat capacity at constant volume of the gaseous mixture in the region of the temperature peak, respectively, and α is the degree of conversion.

From the relationship

$$x = x_0(1 - \alpha) \quad (3)$$

where x_0 stands for the ammonia concentration at the reactor entrance.

$$dx = -x_0 d\alpha \quad (4)$$

and taking eqn. (2) into account

$$-dx = x_0 \frac{C_v}{Q_v} dT \quad (5)$$

Integration of eqn. (5) gives

$$x = x_0 \frac{C_v}{Q_v} (T_{\max} - T_x) \quad (6)$$

From eqns. (1) and (6)

$$\frac{dT_x}{dt} = \left[Z \left(x_0 \frac{C_v}{Q_v} \right)^{n-1} \right] (T_{\max} - T_x)^n e^{-E/RT_x} \quad (7)$$

which is similar to an equation given by Kondratiev [4] when given in the logarithmic form

$$\log \left(\frac{dT_x}{dt} \right) = \log \left[Z \left(x_0 \frac{C_v}{Q_v} \right)^{n-1} \right] + n \log(T_{\max} - T_x) - \frac{E}{2.303 RT_x} \quad (8)$$

For two close temperatures, $(T_x)_1$ and $(T_x)_2$, such that $x_0(C_v/Q_v)^{n-1}$ is practically independent of temperature, and using the difference operator, Δ , on eqn. (8), we get

$$\frac{\Delta \log(dT_x/dt)}{\Delta \log(T_{\max} - T_x)} = n - \frac{E}{2.303R} \times \frac{\Delta(1/T_x)}{\Delta \log(T_{\max} - T_x)} \quad (9)$$

or

$$A = n - \frac{E}{2.303R} B \quad (9')$$

where

$$A = \frac{\Delta \log(dT_x/dt)}{\Delta \log(T_{\max} - T_x)} \quad \text{and} \quad B = \frac{\Delta(1/T_x)}{\Delta \log(T_{\max} - T_x)}$$

According to eqns. (9) and (9'), the plot of A values vs. B values should be a

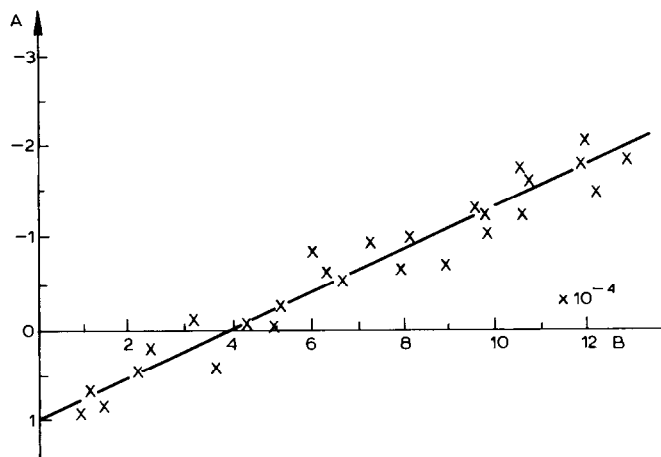


Fig. 1. Graphical illustration of eqn. (9') for the ammonia oxidation on $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$.

straight line whose slope and intercept allow estimation of the activation energy, E , and the reaction order, n , values. Then, the pre-exponential factor, Z , can be evaluated from eqn. (8).

The plots (A vs. B) for catalytic ammonia oxidation on $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$, $\text{NiO/Al}_2\text{O}_3$ and $\text{Pd-Ru/Al}_2\text{O}_3$, are given in Figs. 1, 2 and 3, respectively. In spite of a certain dispersion of the points, mainly due to the inaccuracy of the data obtained by graphical differentiation, straight lines, whose intercepts give a value of one for the reaction order, were obtained.

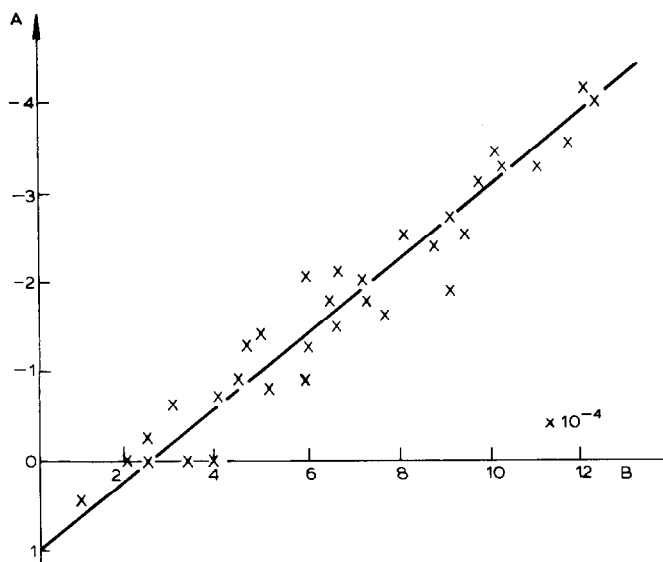


Fig. 2. Graphical illustration of eqn. (9') for the ammonia oxidation on $\text{NiO/Al}_2\text{O}_3$.

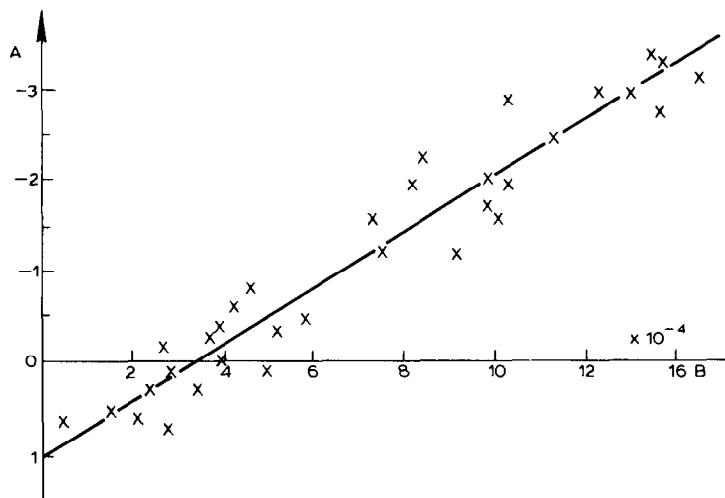


Fig. 3. Graphical illustration of eqn. (9') for the ammonia oxidation on Pd-Ru/Al₂O₃.

TABLE 1

Values of the overall activation energy and pre-exponential factor for the catalytic ammonia oxidation

Catalyst	E (kJ mole ⁻¹)	Z (min ⁻¹)
Fe ₂ O ₃ -Cr ₂ O ₃	44	2.5×10^4
Ni/Al ₂ O ₃	75	4.5×10^4
Pd-Ru/Al ₂ O ₃	55	1.9×10^4

The least-squares values of the activation energy and pre-exponential factor are given in Table 1.

In conclusion, a difference-differential method used in non-isothermal kinetics allowed estimation of the kinetic parameters of catalytic ammonia oxidation.

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