

## FORMULATION OF APPARENT REACTION ORDER AND ITS APPLICATION

S. Kagawa

Department of Industrial Chemistry, Faculty of Engineering,  
Nagasaki University, Nagasaki 852, Japan

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The apparent reaction order  $\alpha_i$  with respect to component  $i$  was shown to be described as  $\alpha_i = \partial \ln R / \partial \ln p_i$ , where  $R$  and  $p_i$  are the reaction rate and the partial pressure of component  $i$ , respectively. This equation makes it possible to compare the parameters in the power functional rate equation and those in the fractional rate equation with each other. An application was illustrated on a steady-state two-step kinetics.

Кажущийся порядок реакции  $\alpha_i$  по отношению к компоненту  $i$  может быть выражен как  $\alpha_i = \partial \ln R / \partial \ln p_i$ , где  $R$  и  $p_i$  являются скоростью реакции и парциальным давлением компонента  $i$ , соответственно. Это уравнение позволяет производить сравнения параметров в уравнении скорости, выраженной в степенной форме, с параметрами в фракциональных уравнениях скорости. Применение было продемонстрировано в двухступенчатой кинетике стационарного состояния.

### INTRODUCTION

Rate equations for heterogeneous catalytic reactions are usually written either by power functional expressions or by fractional expressions. The latter have the advantage of permitting a more detailed discussion of the reaction mechanism. However, a great deal of measurements and a very high accuracy of kinetic data are required to select correctly a specific fractional expression from a lot of plausible ones. When the data are considered not to be satisfactorily precise, a power functional expression is adopted out of sheer necessity. These circumstances result in the appearance of both types of expressions for the same reaction in the literature. Hitherto, however, we have had no means of comparing the parameters in both types of expressions with each other. The present paper will propose a method making such comparison possible.

## FORMULATION OF APPARENT REACTION ORDER

Let us consider the power functional rate equation

$$R = k p_1^{\alpha_1} p_2^{\alpha_2} \dots \quad (1)$$

Apparent reaction orders  $\alpha_1, \alpha_2, \dots$  are not always integers, but often take a numerical value containing decimal fractions for complicated catalytic reactions. One of the usual methods for determining reaction orders experimentally are as follows. By using a differential tubular reactor, a series of reaction rates are measured at a variety of partial pressures of one reactant, while those of other reactants are kept constant, and the reaction order with respect to that reactant is determined from the slope of log-log plots of the reaction rates against the partial pressures of the reactant.

Since eq. (1) is one of the approximate expressions used to correlate kinetic data, the plot does not always give a straight line over a wide range of partial pressures. It seems reasonable to consider that the reaction order is determined from data covering a specified range of partial pressures. Thus the reaction order will be written as

$$\alpha_i = (\partial \ln R / \partial \ln p_i)_{p_j} \quad (2)$$

$$j = 1, 2, \dots \neq i$$

## APPLICATION

On the basis of eq. (2), values of parameters in two types of rate expressions can be estimated from one another. As an example, take the steady-state two-step (SSTS) kinetic model

$$R = \frac{k_A k_B p_A p_B}{k_A p_A + n k_B p_B} \quad (3)$$

which is gathering support in some heterogeneous catalytic reactions /1-4/. This model assumes that the rate of chemisorption of molecule A on the catalyst surface is equal to the rate of consumption of chemisorbed A by the reaction with molecule B, and that both steps are first order with respect to A and B. Here,  $k_A$  and  $k_B$  are the rate constants of respective steps and  $n$  is the stoichiometric coef-

ficient of A per mole of B. In the steady state, the fraction of surface covered by substance A is given by

$$\Theta_A = \frac{k_A p_A}{k_A p_A + n k_B p_B} \quad (4)$$

Substituting the right-hand side of eq. (3) for R in eq. (2) and carrying out the differentiation, we obtain

$$\alpha_A = \frac{n k_B p_B}{k_A p_A + n k_B p_B} \quad (5)$$

and

$$\alpha_B = \frac{k_A p_A}{k_A p_A + n k_B p_B} \quad (6)$$

Both apparent reaction orders  $\alpha_A$  and  $\alpha_B$  will be seen to take values in the range between zero and unity as a function of  $k_A p_A / n k_B p_B$ . Interestingly, in this case the relations of  $\alpha_A + \alpha_B = 1$  and  $\alpha_B = \Theta_A$  are valid.

Next we deal with a practical example. In Table 1 are shown the apparent reaction orders with respect to oxygen ( $\alpha_{O_2}$ ) and ethylene ( $\alpha_{ET}$ ) in the complete oxidation of ethylene over various metal and metal oxide catalysts, which were measured by Seiyama et al. /5/. The different reaction temperatures for each catalyst,  $T_{1.8}$ , were taken to allow us to treat all kinetic data as a differential reaction. It is noticeable that every reaction order takes a value in the range from zero to unity, and that the sum of  $\alpha_{O_2}$  and  $\alpha_{ET}$  for each catalyst is close to unity. These facts suggest that the SSTS model is applicable to the complete oxidation of ethylene. Thus the values of  $k_{O_2}$  (the rate constant of oxygen adsorption) and  $k_{ET}$  (the rate constant of surface reaction) for each catalyst were calculated from eqs. (3, 5, and 6) by inserting the numerical values of  $\alpha_{O_2}$ ,  $\alpha_{ET}$ ,  $p_{O_2}$  (0.207 atm),  $p_{ET}$  (0.017 atm), R ( $2.35 \times 10^{-4}$  atm cm<sup>3</sup> g<sup>-1</sup> s<sup>-1</sup>) and n (3), and are given in the last two columns of Table 1.

In Table 1, catalysts are listed in order of the magnitude of the enthalpy of formation of the metal oxide per g-atom of oxygen, which has been proposed as an indication of the metal-oxygen bond strength in the oxide /8/. Obviously, with increasing  $-\Delta H_f^\circ$ /g-atom of oxygen,  $k_{O_2}$  systematically increases, whereas  $k_{ET}$  decreases. This result is in accord with the expectations based on the SSTS model, that is, the stronger the metal-oxygen bond in the catalyst, the easier the adsorp-

Table 1  
Rate parameters in the complete oxidation of ethylene over various metals and metal oxides

	$-\Delta H_f^{\circ a}$ (kJ mol <sup>-1</sup> O <sub>2</sub> )	T <sub>1.8</sub> <sup>b</sup> (°C)	$\alpha_{O_2}$	$\alpha_{ET}$	$10^3 k_{O_2}$ (cm <sup>3</sup> g <sup>-1</sup> s <sup>-1</sup> )	$10^2 k_{ET}$ (cm <sup>3</sup> g <sup>-1</sup> s <sup>-1</sup> )
Au <sub>2</sub> O <sub>3</sub> <sup>c</sup>	-26.9	463	0.63	0.20	4.8	4.7
PdO <sup>c</sup>	90.8	120	0.50	0.20	5.5	3.6
CuO	156	224	0.40	0.30	6.7	2.8
NiO	241	314	0.45	0.30	6.2	3.1
Cr <sub>2</sub> O <sub>3</sub>	377	540	0.25	0.65	11.7	2.0
CeO <sub>2</sub>	544	382	0.30	0.50	9.7	2.1
CaO	634	545	0.05	0.90	51.0	1.5

<sup>a</sup>The enthalpy of formation of metal oxide per g-atom of oxygen taken from Refs. /6/ and /7/ for Au<sub>2</sub>O<sub>3</sub> and others, respectively.

<sup>b</sup>The temperature at which the extent of conversion of ethylene reached 1.8% under standard reaction conditions (catalyst = 4.1 g, flow rate = 3.2 cm<sup>3</sup> s<sup>-1</sup>, P<sub>O<sub>2</sub></sub> = 0.207, p<sub>N<sub>2</sub></sub> = 0.776, and p<sub>C<sub>2</sub>H<sub>4</sub></sub> = 0.017 atm).

<sup>c</sup>In the working state, these were metallic.

tion of oxygen, and the more difficult the removal of chemisorbed oxygen by ethylene. Further, the catalyst may be expected to be most active, of which the metal-oxygen bond shows an appropriate (neither too strong nor too weak) strength. For the complete oxidation of ethylene, palladium, exhibiting the lowest value of T<sub>1.8</sub> appears to be just such a catalyst.

Very recently Vayenas et al. /4/ confirmed on platinum catalyst that the SSTS model is applicable to the complete oxidation of ethylene, supporting the approach proposed in the present paper.

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