JOURNAL OF CATALYSIS 30, 430–437 (1973)

Estimation of Rate Coefficients from Pulsed Microcatalytic Reactors

Oxidation of Ethylene over Silver Catalyst

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Received January 31, 1973

The experimental conditions and requirements for the continuity equation to reduce to a total differential equation are analyzed. These lead to a simple method for obtaining rate coefficients from pulsed microcatalytic reactors, provided that the conversions are limited to differential conversions. Coefficients obtained this way, for ethylene oxidation over silver, are compared with estimations from steady state data.

The pulse microcatalytic technique, where small amounts of reactants are injected into a carrier gas stream before its entry into the reactor, has established itself in the field of heterogeneous catalysis as an important analytical tool. A brief survey of the fundamentals and operating principles is given by Galeski and Hightower (*1*) in a recent publication. However, since Kokes *et al.* (*2*) first introduced this technique, it has been mainly used as a qualitative tool in comparing a series of catalysts or in observing products distribution. This technique has found useful applications in situations where either the reactants or the catalyst are in short supply or are very expensive to be used in an ordinary steady state flow reactor. Its main advantage is that the experimental technique is so straightforward and consumes so little time that large numbers of catalysts can be screened in a single set of experiments.

Some workers have attempted to take advantage of these positive aspects of the pulse technique, in an effort to obtain quantitative kinetic information from experimental results. The necessary theoretical treatment is complicated by the fact that the system is essentially under unsteady state condition; the reactant concentrations vary with time and position in the catalyst bed. Bassett and Habgood (*3*) have obtained quantitative results for first order reactions and have observed the rate constants to be independent of pulse shape. Gaziev (*4*) has extended this work for kinetic equations other than first order, for square and triangular input pulses having no axial dispersion. Schwab and Watson (*5*) have confirmed Gaziev's equations experimentally for a first order reaction. However, Bett and Hall (*6*) have found a difference between the results obtained from microcatalytic technique and flow technique for a zero order reaction. In this case, they observed that the species adsorbed on the surface were not in adsorption equilibrium with the gas phase. Collins and Deans (*7*) have also reported a theoretical study for linear kinetics. Another theoretical study is due to Hattori and Murakami (*8*), who presented some data on catalytic cracking of cumene (*9*),

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obtained with a rectangular input pulse. This kind of pulse has the advantage of being identical to the steady state case, provided dispersion or reaction does not change its shape and adsorption equilibrium is reached instantaneously. Rectangular pulses, however, like triangular pulses, are quite difficult to obtain experimentally, whereas a Gaussian-shaped pulse is easily obtained. Keeping this in mind, Merrill and coworkers (*10, 11*) have recently extended the usefulness of the pulse technique to more general cases of non-first-order kinetics. In their treatment of the continuity equation for an isothermal bed of catalyst, they neglected the pulse dispersion. This assumption was made realistic by introducing a dispersion column upstream of the catalyst bed. Thus the Gaussian-shaped pulse was made broad enough so it could be assumed that axial dispersion in the bed had negligible effect on the width of the peak. This could be observed by placing concentration sensors immediately before and after the catalyst bed.

This approach was followed in the present work along with a further simplification of the continuity equation, which can be stated as follows: If the depth of the catalyst bed is very small, as compared to the total length that the pulse would occupy in a tube having the same diameter as the reactor, then at any time the gas phase concentration can be considered to be constant over the whole length of bed (see Fig. 1). The so defined concentration is thus only time dependent, an assumption which greatly simplifies the continuity equation, especially if conversion over the bed can be considered differential at any time (*17, 18*).

The validity of the theoretical equation has been further verified by using ethylene oxidation reaction over silver powder.

Theoretical Approach

Let n_o be the total number of moles of reactants fed in the pulse, q the volumetric flow rate of the carrier gas and $C(t)$ the concentration of the reactants at a particular point.

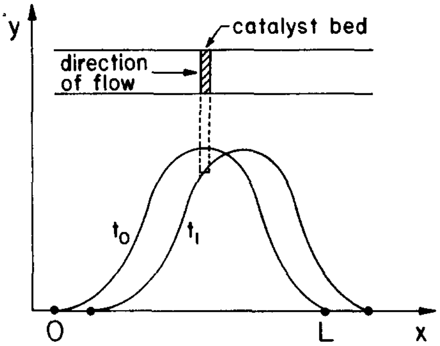

FIG. 1. Schematic representation of the necessary conditions of Eq. (9).

$$n_o = q \int_0^\infty C(t)\,dt. \tag{1}$$

The molar flux $N(t)$ is given by:

$$N(t) = qC(t). \tag{2}$$

The height y of the pulse may be represented as:

$$y = aqC(t), \tag{3}$$

where a is a proportionality constant. By integrating Eq. (3) with respect to time:

$$\int_0^\infty y\,dt = aq \int_0^\infty C(t)\,dt = \frac{1}{\beta}A \tag{4}$$

where A is the area of the pulse and β is the speed of the chart paper. Thus from Eqs. (1) and (4):

$$\frac{1}{\beta}A = an_o \tag{5}$$

Eliminating a between Eqs. (3) and (5),

$$C(t) = y\beta n_o/Aq. \tag{6}$$

If only one reactant is fed into the pulse, $C(t)$ will represent its concentration. If more than one reactant is injected, then $C(t)$ will represent total combined concentration. For a binary mixture,

$$C(t) = C_A + C_B.$$

Defining $\lambda = C_A/C_B$ in the injection pulse, the parameter λ is a constant when the pulse passes over the catalyst, assuming, as we have already mentioned, that conversion is differential and that back mixing is not taking place (perfect plug flow).

Consider a rate equation of the type:

$$r = kC_A{}^mC_B{}^n. \tag{7}$$

Then, under the conditions stated above,

$$\frac{dn_p}{w\,dt} = k\,\frac{\lambda^m}{(1+\lambda)^{m+n}}\,C(t)^{m+n}, \tag{8}$$

where w is the weight of the catalyst.

The total production for a given peak becomes:

$$n_p = kw\,\frac{\lambda^m}{(1+\lambda)^{m+n}}\int_0^\infty C(t)^{m+n}\,dt, \tag{9}$$

where the integral can be evaluated numerically from the pulse diagram traced on the chart paper.

EXPERIMENTAL APPROACH

Experiments were carried out using the ethylene oxidation reaction over silver metal (precipitated powder, obtained from Fisher Scientific Co.) at 221°C. The two reactions observed were the formation of ethylene oxide (i) and complete combustion to carbon dioxide and water (ii).

$$C_2H_4 + \tfrac{1}{2}O_2 \rightarrow C_2H_4O \tag{i}$$

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \tag{ii}$$

Both reactions are essentially irreversible under the operating conditions. A schematic diagram of the experimental setup is given in Figure 2. The reactor was made of a stainless steel tube (3/8 in. i.d. and 5 in. length), surrounded by a jacket through which a heating oil maintained at high temperature was kept circulating during the reaction period. The oil temperature was controlled to within 0.1°C. The reactor could be used as a pulse or as a flow reactor by proper positioning of valves A and B.

For use as a pulse reactor, the setup contained two major features as recommended by Galeski and Hightower (*1*). First, a device allowed precise control and measurements of pulse shape before and after the reactor. This included dispersion column D (3 ft 6 in. long, ½ in. copper tube, filled with −100 mesh pyrex glass beads), thermal conductivity cell TC, and coils C_1 and C_2 which were both immersed in the same water bath at room temperature (not shown in Fig. 2). Typical recording of pulse before and after reaction is presented in Fig. 3. Secondly, a system including valve V_2 (Perkin Elmer sampling valve) and liquid nitrogen trap T permitted the separation of reaction products and unreacted gases from the helium stream which was used as the carrier gas. Later, the trap was warmed and the trapped gases were carried by another helium stream to the gas chromatograph for analysis. This was done in order to be able to have a large range of variation for the flow rate of the carrier gas through the reactor. To check

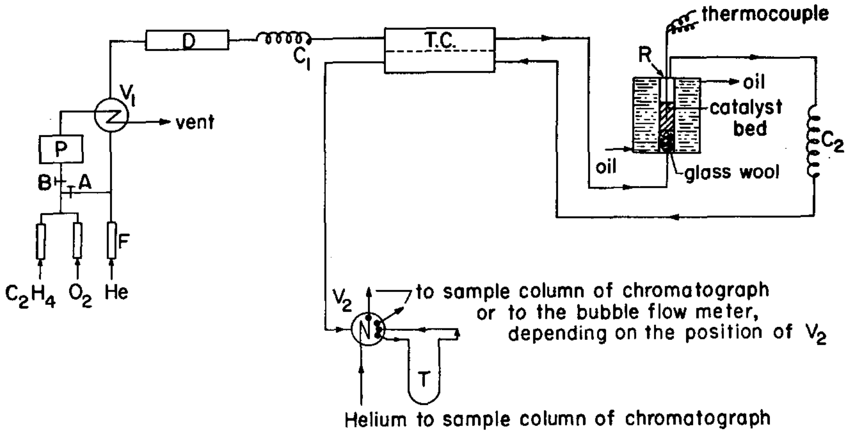

FIG. 2. Schematic diagram of the experimental set-up.

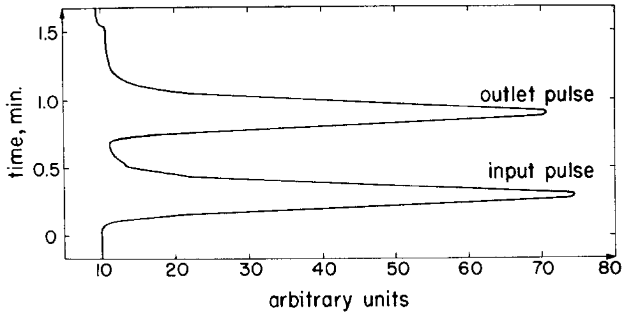

FIG. 3. Actual shapes of the pulse before and after the reactor.

the efficiency of the trap, a material balance was made by injecting a pulse of ethylene through the empty reactor while using helium as the carrier gas. In the first case the ethylene was taken directly to the chromatograph, bypassing the trap, and in the second case the ethylene was caught in the trap which was immersed in a liquid nitrogen bath. The efficiency was found to be close to 98% after repeated experiments to verify the reproducibility. The only difference observed between the two peaks of ethylene obtained by the above mentioned two methods was not in the area of the peak but in the height of the peak, a sharper peak being obtained when the trap was not used. Same efficiency was obtained using ethylene oxide instead of ethylene.

Pump P, placed before the loop in valve V_1, was a mixing device which could provide binary mixtures of gases at selected concentrations between 1% and 99% (Wösthoff).

When the setup was used as a flow reactor, pump P and sampling valve V_1 were not used and the nitrogen trap T was replaced by a 0.5 cc sampling loop in valve V_2. In this case the inlet flow was measured by flowmeters F, and samples of reaction gases were taken using valve V_2 and introduced into the gas chromatograph for analysis. Total flow rate through the reactor was finally measured by a bubble flow meter.

Helium (Canadian Liquid Air, 99.998% pure) was dried in a molecular sieve column before being used. Oxygen (Canadian Liquid Air, minimum purity 99.5%) and ethylene (Matheson, minimum purity 99.5%) were used without further purification.

EXPERIMENTAL RESULTS

Steady State Data

The catalyst was pretreated at 221°C with oxygen for 12 hr. This was found necessary for rapid achieving of constant activity of the catalyst during the steady-state experiments. After the steady state activity of the catalyst was achieved, reaction was carried out at 221°C at low conversions while varying the partial pressures of the reactants in the reaction mixture. The partial pressures of ethylene and oxygen were varied from 0.1 to 0.9 atm interdependently as well as independently by using helium as a diluent. Helium flow for these runs ranged from 0% to 70% of the total flow rate, which was varied from 1.5 to 4.0 liter/hr. The total pressure was maintained at 1 atm for every run.

For the steady state runs, the reactor was operated in a differential manner where the total maximum conversion (based on the limiting reactant) was kept in the range of 1–6% conversion.

The reaction rate was calculated from the product gas analysis and the exit gas flow rate, measured by the soap-bubble flow meter:

$$r = (F/w)(X), \tag{10}$$

where r is the rate of formation of ethylene oxide or carbon dioxide per hour per gram catalyst; F, the feed rate of ethylene in gram moles per hour; X represents the fraction of ethylene converted to ethylene oxide or the fraction converted to carbon dioxide and water; w, is the weight of the catalyst in grams.

By carrying out a regression analysis of the steady state data, the following expressions were obtained for the rates of production of ethylene oxide and carbon dioxide at 221°C:

$$r_{C_2H_4O} = 0.00044(p_E)^{-0.03}(p_O)^{0.91} \quad (11)$$

$$r_{CO_2} = 0.00015(p_E)^{-0.2}(p_O)^{1.1} \quad (12)$$

where $r_{C_2H_4O}$ and r_{CO_2} are expressed in moles of ethylene oxide and carbon dioxide per hour and per gram of catalyst, respectively. Partial pressures are in atmospheres.

The average deviation of these expressions from experimental data was ±6% with a maximum deviation of 15%. A sample of kinetic data, obtained without helium dilution, is shown in Fig. 4, along with the curves calculated from Eqs. (11) and (12).

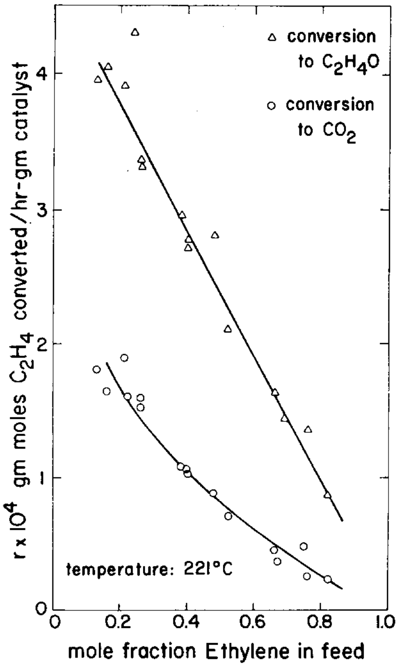

FIG. 4. Kinetic data from steady state experiments (without helium dilution).

Pulse Data

For the pulse experiments, the catalyst was treated with oxygen (66 cc/min) in the same manner as for the steady state experiments at 221°C and for a duration of 12 hr. Then the catalyst was maintained under a flow of helium (60 cc/min) for at least two hours before pulse runs were started. For injecting the pulses, valve V_1 with a sample loop of 0.5 cc was used.

It was found necessary that the catalyst be saturated with oxygen by injection of a series of four or five pulses of oxygen into the carrier stream before a mixture pulse of oxygen and ethylene was introduced into the system. Time between the injection of oxygen pulses and that of a mixture pulse was kept between 20–30 min. Only in this manner were the results found to be reproducible. In fact, when this procedure was not followed, the conversions were observed to be dependent on the number of pulses of mixture already passed over the catalyst bed. For example, when the first pulse of a 50% ethylene–50% oxygen was injected over a clean catalyst, no reaction was observed. This was attributed to the fact that initially the surface was not covered with chemisorbed oxygen to provide the active sites for the reactant gases to adsorb and react. This is consistent with the conclusions of Klugherz and Harriott (*12*) that the reaction takes place between an ethylene species and an oxygen species, both of which are competitively adsorbed over the top of a layer of oxygen chemisorbed by the silver catalyst. A similar observation has been made by Blome (*13*).

After the method of obtaining reproducible data was established, reaction from pulses of different ethylene–oxygen ratios was studied under three different flow rates of helium.

For Eq. (9) to be valid, it was essential that the conversions be low. The maximum total conversion was 5%, although the conversions varied from 1% to 5%. The exponents in Eq. (11) and (12), obtained from steady state data in the same reactor and on the same catalyst, were used as values of m and n in Eq. (9), from which values of constant k could be obtained for each run. The rate constants thus obtained are summarized in Table 1.

As can be noticed from this table, the rate constant for ethylene oxide does not change appreciably either with ethylene to oxygen ratio or with flow rate of the carrier gas. Moreover, the overall average value of this constant for all the experiments at 221°C is 41×10^{-5} mole/hr g atm$^{0.88}$. This is close to the value of 44×10^{-5} obtained from the steady state data.

By contrast, the rate constant for carbon dioxide is dependent on percent ethylene in the pulse as well as the flow rate of the carrier gas. The values of the constant are five to ten times more than those obtained from the steady state runs. To be able to throw more light on this behaviour, the catalyst was treated with oxygen for a period of 12 hr in the usual manner and then treated with helium for two hours under a continuous flow of gas at 221°C. After this, four pulses of ethylene were injected in helium flow over the catalyst, followed by a pulse of pure oxygen; no reaction products were observed at the reaction temperature of 221°C. This indicated that ethylene is not adsorbed on a clean silver surface, a view supported by many workers and mentioned in an extensive review by Klugherz (*16*).

In a reverse experiment, four pulses of oxygen were injected in the helium carrier gas, later followed by a pulse of ethylene. Very little or no ethylene oxide was observed in the reaction products; however, considerable carbon dioxide and water were observed. A similar behavior has been reported by Flank (*14*) where no ethylene oxide but considerable carbon dioxide and water were seen in the reaction products when the catalyst surface was saturated with air and then slugs of ethylene were sent over the silver catalyst in a helium carrier gas.

The presence of ethylene oxide along with CO_2 and H_2O in the reaction products when pulses of oxygen–ethylene mixture are sent into the system and the presence of only carbon dioxide and water when an ethylene pulse is sent over the catalyst covered with oxygen suggests reaction of ethylene with two types of oxygen. It should be noted that during the present experiments the catalyst was continuously purged with helium at 221°C. Therefore, it was not the weakly adsorbed oxygen which was involved in the formation of carbon dioxide and water but the strongly adsorbed one. On the other hand, ethylene to ethylene oxide formation possibly involves only gaseous or weakly adsorbed oxygen, e.g., oxygen physically adsorbed on top of the strongly chemisorbed oxygen film (*12*) on silver during

TABLE 1
Observed Rate Constants

% Ethylene in pulse	20	30	40	50	60	temp °C	Flow rate (liter/hr)
$k_{C_2H_4O}$ mole/hr g atm$^{0.88}$	0.00049	0.00039	—	0.00046 0.00039	0.000404	221.0	1.63
	—	—	—	0.00041	—	221.0	1.82
	—	0.00039	0.00037	0.00042	—	221.0	3.63
	—	—	—	0.00044 0.00045	—	232.0	1.82
k_{CO_2} mole/hr g atm$^{0.9}$	0.002	0.0011	—	0.0010 0.0012	0.0015	221.0	1.63
	—	—	—	0.0010	—	221.0	1.82
	—	0.00079	0.00078	0.00075	—	221.0	3.63
	—	—	—	0.0015 0.0016	—	232.0	1.82

the passage of the mixture pulse over the catalyst. This reasoning suggests that the oxygen available for the formation of carbon dioxide is actually more than what is available in the pulse mixture; this extra oxygen being available in the form of chemisorbed or strongly adsorbed oxygen already present due to the saturation of the catalyst because of oxygen pulses which were sent in, before a mixture pulse was injected, thus resulting in a much higher conversion and rate constant than would be expected. It has also been suggested by Moss and Thomas (*15*) and Flank (*14*) that ethylene oxide is produced by the interaction of ethylene with the weakly adsorbed oxygen.

Conclusions

The nearly quantitative agreement between the pulsed and steady state rate parameters for ethylene oxide formation establishes the validity of quantitative analysis of pulse results used in this work.

In the case of carbon dioxide formation, however, the disagreement between the values obtained from both experimental techniques underlines one of the major drawbacks of the pulse technique as a quantitative kinetic tool, namely the need for an instantaneous adsorption equilibrium. The strongly adsorbed oxygen species involved in this reaction are thought to have been in a concentration higher than the one of adsorption equilibrium under the partial pressure in the pulse. This led to a rate constant for conversion to CO_2 which was higher in the pulse experiments than in the steady state reactor.

However, the method proposed here is not free from serious limitations. The same "plug" flow pattern has to be followed by each reactant. This means not only that the bed has to be thin enough for back mixing to have a negligible effect on the width of the peak. Actually, the catalyst particles have also to be small enough for internal diffusion to be also negligible. Otherwise, the chromatographic effect would result in a time dependent parameter λ. The method is also restricted to differential conversions at every location in the pulse. A unique feature of the present analysis, however, is that it handles a two components pulse. In order to do so, steady state measurements have to be performed to establish the kinetic orders.

Despite all these restrictions, it is felt that the proposed method can be of some value in several situations. For example, the kinetic orders could be established with ordinary materials and the pulse studies done with expensive isotopes. This would give quantitative kinetic comparisons of the various isotopes, while preserving the advantage of using only small amounts of reactants. Another example could be a kind of study of catalyst decay and variation in selectivity through poisoning. If known concentrations of poison were continuously fed in the carrier gas stream to the reactor, pulses could be sent at various times. Our method applied to these data will provide quantitative information on the catalyst decay. Steady state measurements can be obtained on the system without any poison, and one could take advantage of the ease to obtain a large number of data, by screening various poisons, at various concentrations. Needless to state that such data would be of great help in industrial design of catalytic reactors.

NOMENCLATURE

a	proportionality constant as expressed by Eq. (3)
A	area of the pulse, sq. cm
C_A	concentration of reactant A, moles/liter
C_B	concentration of reactant B, moles/liter
$C(t)$	concentration of reactants at any time, moles/liter
F	feed rate of ethylene, g moles/hr
k	rate constant
m	exponent for reactant A as expressed by Eq. (7)
n	exponent for reactant B as expressed by Eq. (7)
n_o	total number of moles of reactant, moles
n_p	number of moles of the product, moles
$N(t)$	molar flux, moles/hr

p_E	partial pressure of ethylene, atm
p_O	partial pressure of oxygen, atm
q	volumetric flow rate of carrier gas, liters/hr
r	rate of reaction, moles/hr g catalyst
w	weight of catalyst, g
X	fraction of ethylene converted to ethylene oxide or CO_2 and H_2O
y	height of pulse, cm
x	length, cm
β	rate of chart paper; cm/hr
λ	molar ratio of reactant A to B in the pulse

References

1. Galeski, J. B., and Hightower, J. W., *Can. J. Chem. Eng.* **48,** 151 (1970).

2. Kokes, R. J., Tobin, H., and Emmett, P. H., *J. Amer. Chem. Soc.* **17,** 5860 (1955).

3. Bassett, D. W., and Habgood, H. W., *J. Phys. Chem.* **64,** 769 (1960).

4. Gaziev, G. A., Filinovskii, V. Yu, and Yanovskii, M. I., *Kinet. Katal.* **4,** 688 (1963).

5. Schwab, G. M., and Watson, A. M., *J. Catal.* **4,** 570 (1965).

6. Bett, J. A. S., and Hall, W. K., *J. Catal.* **10,** 105 (1968).

7. Collins, C. G., and Deans, H. A., *A.I.Ch.E.J.* **14,** 25 (1968).

8. Hattori, T., and Murakami, Y., *J. Catal.* **10,** 114 (1968).

9. Hattori, T., Murakami, Y., and Hattori, T., *J. Catal.* **10,** 123 (1968).

10. Blanton, Jr., W. A., Byers, C. H., and Merrill, R. P., *I & EC Fund.* **7,** 611 (1968).

11. Makar, K., and Merrill, R. P., *J. Catal.* **24,** 546 (1972).

12. Klugherz, P. D., and Harriott, P., *A.I.Ch.E.J.* **17,** 856 (1971).

13. Blome, D. W., Ph.D. Thesis, Univ. of Washington (1957).

14. Flank, W. H., Ph.D. Thesis, Univ. of Delaware (1965).

15. Moss, R. L., and Thomas, D. H., *J. Catal.* **8,** 151, 162 (1967).

16. Klugherz, P. D., Ph.D. Thesis, Cornell University (1969).

17. Germain, J. E., *C. R. Acad. Sci. Ser. C* **263,** 27 (1966).

18. Aliev, R. R., Berman, A. D., Zhomov, A. K., Lokteva, N. K., Roguinskii, S. Z., and Yanovskii, M. I., *Kinet. Katal.* **9,** 610 (1968).