An Active Catalyst for the Oxidation of Acetic Acid Solutions

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This note presents new experimental data for the oxidation of aqueous solutions of acetic acid. For this relatively refractory substance, oxidation catalysts normally give low rates. For example, Levec and Smith (1976) using iron oxide found no diffusion retardation for 3.2 × 1.6 mm pellets, even though diffusivities in liquid filled pores are much less than for gas filled pores. Recently (Box and Farha, 1974) a specially designed oxidation catalyst consisting of copper, manganese, and lanthanum oxides on a zinc aluminate spinel has been patented. Data given here show sharply higher rates for this catalyst and also diffusion retardation for 0.18 cm particles.

The data were obtained in an upflow packed bed operated as a differential, liquid full reactor at 250° to 280°C. Oxygen and acetic acid (concentrations from 50 to 500 mg/l) were predissolved in distilled water at atmospheric pressure. Then the liquid was compressed to 68 atm before it was heated (and entered the reactor) in order to prevent vaporization. Data were obtained at various temperatures, concentrations, and for three catalyst particle sizes as indicated in Table 1. The reactor (25 cm length of 0.93 cm I.D. stainless steel), auxiliary apparatus, operating procedure, and analytical methods were the same as described in detail in the earlier work (Levec and Smith, 1976). The catalyst bed was diluted with about equal volumes of 70 mesh glass beads.

The catalyst composition and physical properties (before final calcination) are given in Table 2. Metals were added by impregnation of soluble salts and then calcined in air to produce the oxides. Details of the preparation procedure are given by Box and Farha (1974). The larger particle sizes were cylinders 0.18 cm × 0.18 cm. These cylinders were crushed and sieved, retaining the 35 to 42 and 28 to 32 mesh size ranges (average sizes 0.038 and 0.054 cm) for the smaller sizes. Pretreatment with oxygen-saturated distilled water, as described earlier (Levec and Smith, 1976), was necessary to achieve constant activity over the operating period (110 hr) of each bed. Mass balances of carbon and oxygen based on the reaction

$$CH_3COOH + 2O_2 \rightarrow 2CO_2 + 2H_2O \qquad (1)$$

were within 2 to 12% of the carbon dioxide produced.

RATE EQUATION

Rates calculated from the differential reactor data show a half-order dependency on oxygen and a mixed (zero to first) order effect of acetic acid concentration. The results are illustrated in Figure 1 which shows the effect of acetic acid at constant oxygen concentration. The data are for a catalyst particle size of 0.054 cm for which intraparticle diffusion does not retard the rate appreciably. These results indicate the same type of kinetics as found by Levec and Smith (1976) using an iron oxide catalyst and can be represented by

$$R_{CO_2} = -R_{O_2} = \frac{K' C_{HA}}{1 + K'' C_{HA}} C_{O_2}{}^{1/2} \qquad (2)$$

The straight lines in Figure 1 are a plot of the linearized form of Equation (2).

Figure 2 shows the effects of temperature and catalyst particle size on the rate at constant feed concentrations of acetic acid and oxygen. When the feed rate was varied from 0.60 to 1.09 cm³/s, the reaction rate did not change significantly, indicating that external diffusion resistances

TABLE 1. REACTOR OPERATING CONDITIONS

Conversions: 3 to 15% for acetic acid, 15 to 40% for oxygen

Mass of catalyst, g	1.0(d_p = 0.038), 1.0(d_p = 0.054), and 1.2(d_p = 0.18)
Catalyst particle size, d_p, cm	0.038*, 0.054†, 0.180**
Liquid flow rate (at 25°C, 1 atm; cm³/s)	0.60, 0.80, 0.95, 1.09
Temperature, °C	250, 260, 270, 280
Pressure, atm	68.0
Feed concentration:	
Oxygen (mole/cm³) × 10^7	2.32, 4.51, 7.00, 10.40
Acetic acid (mole/cm³) × 10^7	8.33, 16.66, 33.33, 83.33

* 35 to 42 mesh size.
† 28 to 32 mesh size.
** 0.18 cm diameter cylindrical extrudate cut into 0.18 cm lengths.

TABLE 2. PROPERTIES OF CATALYST PARTICLES

Composition of support, wt. %	
Al_2O_3	51.5
ZnO	48.5
Metals deposited on support, wt. %	
Cu	4.0
Mn	2.0
La	1.0
Surface area (BET) S_g, m²/g	89
Solid phase density, ρ_s, g/cm³	4.2
Pore volume, V_g, cm³/g	0.31
Porosity (from ρ_s and V_g)	0.55
Mean pore radius (2 V_g/S_g), Å	70*

* After final calcination, all small pores are converted into pores with radii greater than 100A.

Janez Levec is on leave from the University of Ljubljana, Yugoslavia.

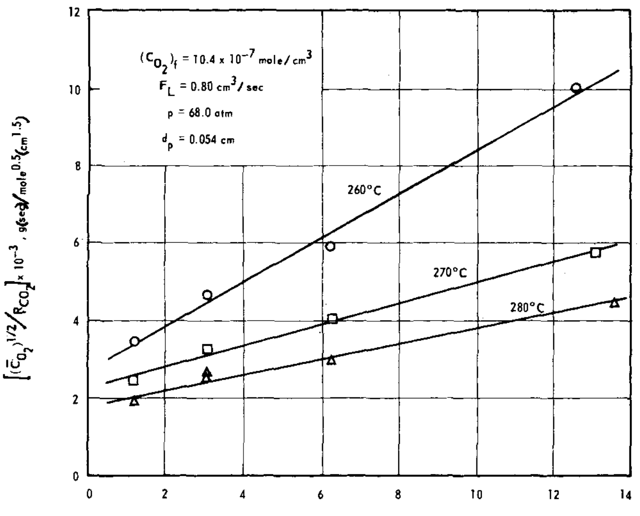

Fig. 1. Effect of acetic acid concentration on rate.

TABLE 3. INTRINSIC RATE CONSTANTS AND EFFECTIVENESS FACTORS

°C	$K' \times 10^{-2}$ (cm)$^{4.5}$/(mole)$^{0.5}$(g)(s)	$K'' \times 10^{-5}$ cm^3/mole	E_f*
250	1.10	3.69	0.78
260	1.93	5.17	0.70
270	3.22	7.10	0.64
280	5.39	9.76	0.59

* For the larger (d_p = 0.18 cm) particles.

were negligible. However, the data do show that intraparticle diffusion sharply retards the rate in the liquid-filled pores for particles of 0.18 cm size.

RATE CONSTANTS AND EFFECTIVENESS FACTORS

The coincidence of the data in Figure 2 for the 0.038 and 0.054 cm particles indicates that the effectiveness factor is near unity for the 0.054 cm particles. Hence, Equation (2) can be used with the rate vs. concentration data in Figure 1 to obtain K' and K'' for each temperature. The values of these intrinsic constants, as read from lines drawn through the data points on a plot of K' or K'' vs. $1/T$, are given in Table 3. The slope of the line in Figure 2 for the smallest particle sizes gives an overall activation energy of 17 kcal/mole. The apparent overall activation energy indicated by the line for 0.18 cm particles is less, 12 kcal/mole, providing supplementary evidence that intraparticle diffusion hinders the rate.

The ratio of the rates in Figure 2 for the 0.18 cm and 0.054 particles gives an effectiveness factor for the larger particles. The effective diffusivity D_e can be calculated from these E_g values and the intrinsic kinetics, Equation (2) with K' and K'', from Table 3. This was done by using the approximation procedure of Bischoff (1965). This procedure eliminates the iterative numerical solution of the mass conservation equation and requires only a closed-form integration of the product of $R\ D_e$ with respect to the concentration of the limiting reactant (oxygen). The value of $(D_e)_{O_2}$ so obtained was about 2×10^{-5} cm^2/s. As estimated by Levec and Smith (1976), the molecular diffusivity is 2×10^{-4} cm^2/s. For a particle porosity of 0.55 (Table 2), these values correspond to a tortuosity factor ($\delta = \epsilon D/D_e$) of about 5, in reasonable agreement with $\delta = 3.9$ found by Satterfield et al. (1968) for the liquid phase hydrogenation of α-methyl styrene on a Pd/Al$_2$O$_3$ catalyst. However, this is not consistent with the much lower values noted by Baldi et al. (1974) and by Kenney and Sedricks (1972). Effective diffusivity measurements under nonreactive conditions, and at conditions where the molecular diffusivity is accurately known, are needed to resolve the question of tortuosity factors in liquid filled catalyst pores.

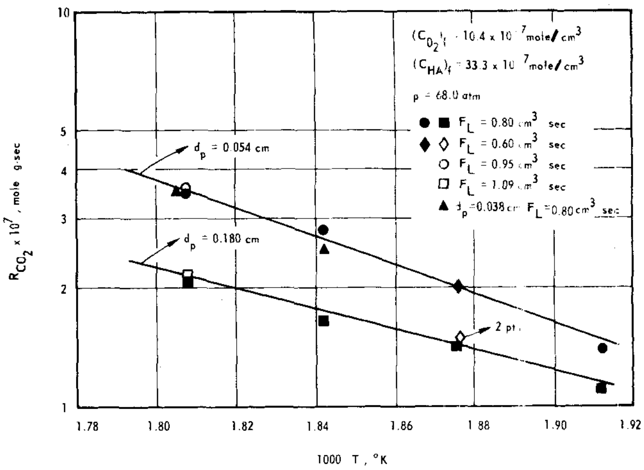

Fig. 2. Effect of temperature and particle size on rate.

NOTATION

C = concentration in liquid; $\overline{C}$, average of feed and effluent values, mole/cm^3
D = molecular diffusivity of component in water, cm^2/s
D_e = effective diffusivity of component in liquid filled pores, based upon total void plus nonvoid area, cm^2/s
d_p = equivalent spherical particle diameter, cm
E_f = effectiveness factor
F_L = volumetric flow rate of liquid at reactor conditions, cm^3/s
K' = kinetic constant in Equation (3), (cm)$^{4.5}$/(mole)$^{0.5}$(g)(s)
K'' = kinetic constant in Equation (3), cm^3/mole
R = rate of production, mole/(g)(s)
W = mass of catalyst in reactor, g
ϵ = porosity
δ = tortuosity factor

Subscripts

O$_2$, HA = oxygen or acetic acid
e = reactor effluent
f = reactor feed
s = outer surface of catalyst particle

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