JOURNAL OF CATALYSIS **114**, 377–387 (1988)

Development of a Supported Molten-Salt Wacker Catalyst for the Oxidation of Ethylene to Acetaldehyde

VENKATESH RAO AND RAVINDRA DATTA[1]

Department of Chemical and Materials Engineering, University of Iowa, Iowa City, Iowa 52242

Received June 22, 1987; revised June 24, 1988

A modified supported molten-salt Wacker catalyst involving palladium chloride/copper chloride is developed by replacing the conventional aqueous reaction medium (H_2O + HCl) with a eutectic melt of cuprous chloride and potassium chloride and supporting it on a porous support. Experimental studies for the oxidation of ethylene to acetaldehyde over the supported molten-salt catalyst (SMSC) show the kinetics to be similar to the aqueous-phase Wacker process and the SMSC diffusion-reaction characteristics to be well predicted by the theoretical model of R. Datta and R. G. Rinker (*J. Catal.* **95**, 181 (1985)). The SMS catalyst was found to be extremely stable owing to the essentially nonvolatile nature of the molten salt whereas the aqueous-phase supported liquid-phase catalyst deactivated rapidly due to the evaporation of the solvent. The developed supported molten-salt catalyst appears to have substantial advantages over the commerical liquid-phase Wacker process. Further, the SMSC technique utilized here should prove to be useful in developing efficient catalysts for many other processes. © 1988 Academic Press, Inc.

1. INTRODUCTION

The Wacker process (*2*) for the manufacture of acetaldehyde by air oxidation of ethylene using an aqueous $PdCl_2$–$CuCl_2$ solution along with HCl is among the earliest and still one of the major industrial processes catalyzed by homogeneous transition-metal compounds. While it is gradually being displaced as the major route in the production of acetic acid from acetaldehyde oxidation by the methanol carbonylation process based on rhodium complex catalyst with methyl iodide as co-catalyst, it is still the major industrial route for producing acetaldehyde. The catalyst is also useful in the oxidation of higher olefins (*3, 4*).

There are, however, some major engineering concerns associated with the conventional liquid-phase Wacker process. These include inefficient catalyst utilization in the gas sparged bubble-column or tubular reactors containing inert packing, the required separation of catalyst solution from the product, and the very significant corrosion problems associated with the catalyst solution owing to its low pH (*3*). The catalyst recirculation system in the the original industrial Wacker process was constructed with expensive titanium alloys (*3*). For these reasons, several investigators have attempted to "heterogenize" the Wacker catalyst so as to use it for vapor-phase reaction but these efforts have been met with varying degrees of success. Smidt *et al.* (*5*) briefly describe a process in which an ethylene–oxygen mixture saturated with water vapor is passed over a fixed bed of porous particles containing the palladium–copper catalyst solution within the pores. Komiyama and Inoue (*6, 7*) studied the performance of a supported liquid-phase catalyst (SLPC) analog of the aqueous catalyst solution. In the SLPC technique, the liquid catalyst solution is coated as a thin film on the pore walls of the porous support, much like a chromatographic packing containing a liquid phase. The ethylene–oxygen mixture

---

[1] To whom correspondence should be addressed.

0021-9517/88 $3.00
Copyright © 1988 by Academic Press, Inc.
All rights of reproduction in any form reserved.

was bubbled through a water saturator in order to compensate for the vaporization of the solvent in SLPC at the reaction temperature. However, this procedure can result in complete filling of the pores with water with a resultant loss in activity due to increased diffusional resistance. Katz and Pismen (*8*) also mention that such a catalyst is very sensitive to humidity and that pore filling causes a decrease in activity. Desai *et al.* (*9*) have studied the aqueous Wacker supported catalyst for CO oxidation. Even at 60°C, they experienced stability problems due to solvent evaporation and, therefore, a water vapor saturator was used. Evnin *et al.* (*10*) describe a solid heterogeneous catalyst based on palladium-doped vanadium pentoxide with Ti, Ru, Pt, or Ir as a third component and supported on α-Al_2O_3. They report good reactivity under relatively mild conditions (383 to 440 K and 0.1 to 3 MPa). The catalyst containing Pd^{2+}, Ru^{3+}, and V_2O_5 showed good stability while most other formulations deactivated rapidly. Rony (*11*) has briefly described the use of molten salts as the solvent for a supported Wacker catalyst.

It is our objective here to describe the development of a supported molten-salt (SMS) Wacker catalyst (formulated along Rony's suggestion) for ethylene oxidation to acetaldehyde. The catalyst developed by us is extremely stable, active, and selective under relatively mild conditions (468 K and 0.16 MPa), makes extremely effective utilization of the $PdCl_2/CuCl_2$ catalyst (almost complete utilization) since the catalyst is coated as a film approximately 30–70 Å thick on the walls of the porous support, and essentially eliminates corrosion problems. The developed catalyst consists of $PdCl_2/CuCl_2$ solution in a eutectic of 65 mol% cuprous chloride and 35 mol% potassium chloride (melting point = 423 K) that is supported on a porous silica support. The kinetics of this catalyst are described here as are the SMS transport and reaction characteristics. The results of reaction rate for SMSC are compared with the theoretical model of Datta and Rinker (*1*) for transport and reaction in SLPC.

2. CHOICE OF SOLVENT

It is evident from the above discussion that while a number of investigators have attempted to use the Wacker process in the SLPC mode, evaporation of the aqueous solvent (H_2O + HCl) and consequent loss of activity have been the major stumbling blocks. Thus, in our search for an appropriate low-volatility solvent, the supported Wacker reaction was initially studied using the conventional aqueous solvent. This SLP catalyst was observed to deactivate almost completely within 2 h. The addition of ethylene glycol to the solvent improved the stability of the catalyst somewhat, but still almost complete deactivation occurred in less than 1 day. It was the continuing problem of deactivation due to the evaporation of the solvent that subsequently led us to test molten-salt eutectics as possible solvents.

Molten salts are versatile and often better solvents than water and many other room temperature liquids, being capable of dissolving such diverse substances as water, metals, oxides, and other salts (*12*). These should, thus, make ideal solvents for the supported liquid-phase catalysis technique for many catalyst systems over a wide range of temperatures, since an almost infinite variety of eutectic mixtures with melting points in the range below 100 to above 1000°C is available (*13*). Molten salts possess a number of other advantages. For example, molten salts have nonelectrolyte properties similar in magnitude to those of room temperature liquids, despite the obvious temperature differences, and have very low volatility. However, very few industrial catalytic systems use molten salts as the reaction media, the two major exceptions being the V_2O_5 catalyst dissolved in a melt of potassium pyrosulfate for the industrial SO_2 oxidation reaction and the Deacon process (*14*). The reason that molten salts have not attracted much attention as reaction medium may be due to the fact that molten electrolytes are very corrosive and readily corrode reactors when used as a bath. However, this problem is obviously circumvented by operating in the SMSC mode. Further, it should be apparent that even many conventional heterogeneous catalysts could be converted into SMSC.

In an attempt to find an appropriate eutectic melt, three different melts were tested, namely, (i) 60 mol% $CuCl_2$ and 40 mol% KCl (m.p. approximately 723 K); (ii) 54 mol% $ZnCl_2$ and 46 mol% KCl (m.p. 503 K); and (iii) 65 mol% CuCl and 35 mol% KCl (m.p. 423 K). The zinc chloride system displayed no activity. Since the melting point of the $CuCl_2$–KCl system is high (723 K), substantial amounts of undesirable products (CO_2 + H_2O), as a result of the combustion of ethylene, were produced along with the desired product, acetaldehyde. On the other hand, the eutetic melt of CuCl and KCl was found to produce acetaldehyde at high rates while producing only a small amount of combustion products (selectivity of acetaldehyde was about 95%) at about 468 K. This selectivity is no lower than that obtained with the aqueous-phase catalyst (*3*). This was, therefore, the solvent of choice for further study.

3. EXPERIMENTS

(*a*) *Materials*

The catalyst, $PdCl_2/CuCl_2$, and the solvent components (CuCl, KCl, HCl) were used directly as purchased from Aldrich Chemical Co. The porous support used, Silica T-1571 (see Table 1 for its characteristics) in the form of 4- to 5-mm spherical pellets, was obtained from United Catalysts. The gases used were purchased from Air Products, Inc., and were of high-purity grade.

(*b*) *Catalyst Preparation*

The catalyst used is a mixture of $PdCl_2$ and $CuCl_2$ while the solvent is a eutetic melt of CuCl and KCl. The catalyst preparation involved dissolving the required amounts of all of these substances in an appropriate aqueous liquid, impregnating the porous support, and then drying off the liquid thereby leaving only the catalyst and solvent salt mixture in the support. Known amounts of catalyst and salt mixture were dissolved in a dilute, warm, aqueous solution of hydrochloric acid in order to dissolve all the salts. Gentle stirring of this mixture for 24 h resulted in a homogeneous, dark green solution.

TABLE 1

Physical Characteristics of United Catalyst T-1571 Spherical, Silica Support

BET surface area	1.3×10^5 m²/kg
Average pellet diameter	4.5×10^{-3} m
Pellet bulk density	9.62×10^2 kg/m³
Average pore diameter	1.8×10^{-8} m
Porosity of dry support	0.71
Estimated dusty-gas constants	
C_0^0	5.1×10^{-18} m²
C_1^0	3.1×10^{-9} m
C_2^0	0.5041

The liquid-loaded pellets were prepared as follows: (a) the catalyst and solvent were dissolved in the dilute acidic solution, as described above, in a volumetric ratio corresponding to the desired liquid loading; (b) the pellets were kept under vacuum overnight to remove air from the pores; (c) the vacuum pump was then shut off and the catalyst solution was added, breaking the vacuum and immersing the pellets; (d) the pellets remained immersed in the solution for about 24 h; and (e) the pellets were finally removed from the solution and placed in a vaccum oven at 110°C for about 12 h to evaporate the hydrochloric acid and water from the pores. Final weight gain of support confirmed the amount of catalyst–salt mixture remaining in the pore space. Liquid loading, q, at the reaction temperature was then calculated using the melt density (1103 kg/m³ at 468 K). The maximum possible loading thus achievable experimentally with repeated impregnations was about 85%.

(*c*) *Apparatus and Procedure*

The reaction was conducted in a continuous 3-in. Berty catalytic reactor, equipped with a variable speed magnetic drive assembly, obtained from Autoclave Engineers. Gas feed mixtures of ethylene and air entered the reactor at the bottom on one side and were removed at the bottom on the other side. A sparging unit containing water was included in the apparatus. This permitted the moisture content of the gas feed stream to be varied for those experiments in which the effect of water concentration on reaction rate was studied. A Teledyne Hastings–Raydist mass flow meter provided accurate measurement of ethylene flow rate while a rotameter, calibrated with a soap bubble-film meter, provided the total flow rate measurements. A large excess of air with respect to ethylene was always maintained in the feed.

For studies of reaction kinetics without any diffusional limitations, a carefully weighed sample of well-ground supported catalyst (the pellets were loaded to a liquid loading of about 20% and pulverized using a mortar and pestle in order to minimize intrapellet diffusion and obtain an effectiveness factor of unity) was spread in a thin layer in a crucible which, in turn, was placed in the catalyst basket of the reactor. The reactant gas mixture was continuously passed through the reactor (the impeller in the reactant was kept spinning at a constant rate of about 1000 rpm to minimize any gas-phase resistance to mass and heat transfer) and the resulting product stream was passed through a heated line (to avoid condensation of acetaldehyde) leading to a gas chromatograph for analysis. An average run lasted approximately 6 h, and the conversion obtained for each run represents the average value of five measurements taken 4 to 5 h after starting the run. No change in reaction rate or selectivity was detected for the entire duration. The crushed catalyst particles with an average diameter of approximately 0.1 mm were confirmed to be free of diffusional retardation by using the Weisz–Prater criterion (*15*). Some kinetic runs were also made with only the catalyst melt contained in a crucible which was placed in the reactor. After accounting for the diffusional retardation within the melt pool, the rate of homogeneous reaction was found to be the same as that in the supported melt. It was, therefore, concluded that the support had no effect on the catalyst and was chemically inert. For runs to study the interaction of diffusion and reaction in SLPC, a similar procedure was followed except that the pellets were loaded to a desired value and used intact. Typical operating conditions for kinetic runs are shown in Table 2 while the typical operating conditions for intact SMSC runs are shown in Table 3. Continuous sampling was done on all reactant and product gas streams using an on-line HP5840A gas chromatograph equipped with an automatic gas sampling valve. A $\frac{1}{8}$-in. by 6-ft Porapak Q column was used with temperature programming from 323 to 408 K at the rate of 20 K per minute.

TABLE 2

Operating Conditions for Reaction Kinetics Runs

Solvent (m.p. 423 K)	35 mol% KCl/65 mol% CuCl
$PdCl_2$ concentration	7.2 mol/m^3
$CuCl_2$ concentration	123.4 mol/m^3
Temperature	468 K
Pressure (absolute)	0.16 MPa
Gas flow rate (STP)	1.2×10^{-6} to 1.7×10^{-6} m^3/s
Volume of 20% loaded crushed catalyst (V_{cat})	0.15 cm^3
Feed composition (M)	
Ethylene	5%
Air	95%
Stirrer speed	1000 rpm

4. RESULTS AND DISCUSSION

(*a*) *Reaction Kinetics*

The mechanism of the Wacker ethylene oxidation in the aqueous phase is well studied (*4*, *16*). For the overall reaction given by

TABLE 3

Operating Conditions for SMSC Runs

Solvent (molten-salt eutectic)	35 mol% KCl/65 mol% CuCl
$PdCl_2$ concentration	7.3 mol/m^3
$CuCl_2$ concentration	130 mol/m^3
Temperature	468 K
Pressure (absolute)	0.12 MPa
Gas flow rate (STP)	2×10^{-7} m^3/s
No. of pellets in reactor	6
Feed composition (*M*)	
Ethylene	6%
Air	94%
Stirrer speed	1000 rpm

$$C_2H_4 + \tfrac{1}{2}O_2 \xrightarrow[CuCl_2]{PdCl_2} CH_3CHO$$

this mechanism leads (*3*) to the following rate expression at concentrations of palladium below 0.04 *M* and assuming that water is present in large excess:

$$r = \frac{k[Pd^{2+}]}{[Cl^-]^2[H^+]}[C_2H_4] = k'[C_2H_4]. \quad (1)$$

It was decided to experimentally study the reaction kinetics for the catalyst in the melt as against this expression. The experimental results corroborated this form for the developed catalyst as well. The experimental reaction rate was calculated using

$$r = F(C_{A0} - C_A)/V_{cat}. \quad (2)$$

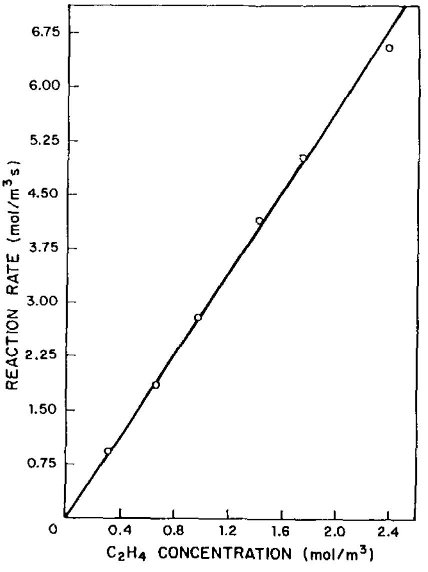

FIG. 1. The effect of ethylene concentration on the rate of reaction under conditions given in Table 2.

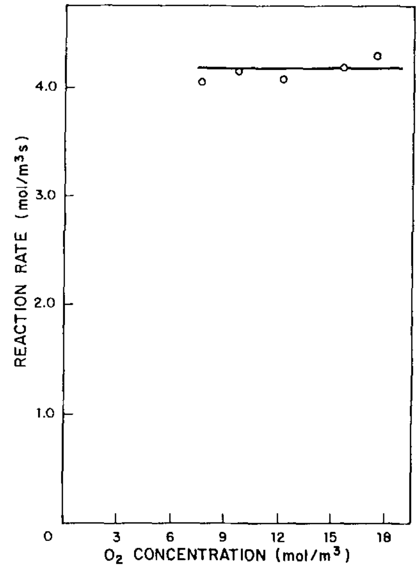

FIG. 2. The effect of oxygen concentration on the rate of reaction under conditions given in Table 2.

Figures 1 and 2 were obtained by using the condition shown in Table 2 while varying the ethylene and oxygen concentrations, respectively. Figure 1 is the result of varying the mole fraction of ethylene in the feed between 1 and 8%, while Figure 2 is the result of varying the mole fraction of oxygen (the tank of air was replaced with a tank of oxygen and nitrogen was used as an inert for just this series of runs) in the feed between 15 and 48%. These results, in the range tested, confirm the fact that the rate is first-order in ethylene concentration and zero-order in oxygen concentration, in agreement with Eq. (1).

Figures 3 and 4 were obtained by using the conditions shown in Table 2 while varying the $PdCl_2$ and $CuCl_2$ concentrations in the melt, respectively. Figure 3 is the result of varying the concentrations of $PdCl_2$ in the melt between 1 and 10 mol/m^3, while Fig. 4 is the result of varying the concentra-

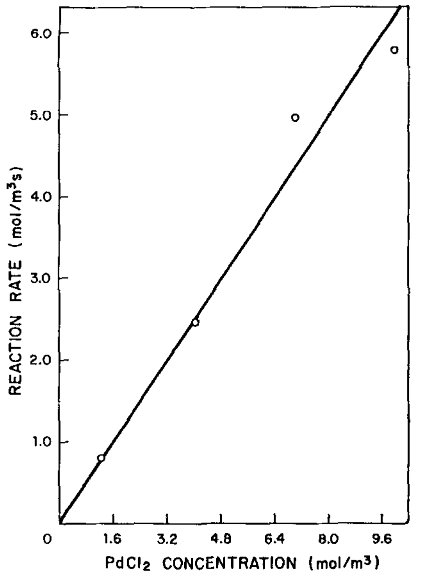

FIG. 3. The effect of $PdCl_2$ concentration on the rate of reaction under conditions given in Table 2.

tion of $CuCl_2$ in the melt between 10 and 1000 mol/m^3. By replotting the data in Fig. 3 on log–log coordinates, it was found that the rate is proportional to $[Pd^{2+}]^{0.89}$. This result agrees reasonably well with Eq. (1) and has also been confirmed by Komiyama and Inoue (*6*) for aqueous catalyst systems. While the results from Fig. 4 cannot be compared directly to Eq. (1), because it only correlates the rate to the total chloride concentration, the result is in good agreement with the observation (*3*) that varying amounts of $CuCl_2$ in the solvent has no appreciable effect on the rate of reaction in the industrial Wacker process.

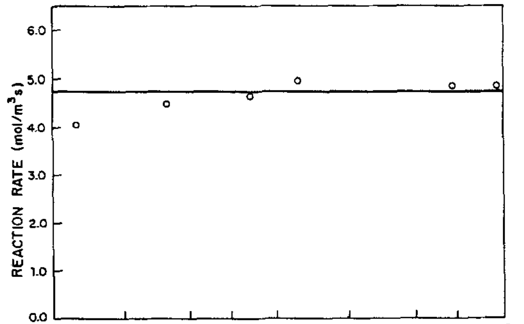

FIG. 4. The effect of $CuCl_2$ concentration on the rate of reaction under conditions given in Table 2.

Figure 5 was obtained by using the conditions in Table 2 while varying the amount of water in the feed stream. The feed mixture of ethylene and air was bubbled through a sparging system containing water. By variation of the temperature of the water in the sparger, different amounts of water vapor could be introduced in the feed stream. It was assumed here that at any given sparger temperature, the gas stream is saturated with water vapor as it passes through the sparger. Figure 5 is plotted as total vapor concentration (amount of water introduced plus a constant amount produced by the side reaction) versus reaction rate. It can be seen that after an initial increase in the reaction rate at small amounts of water in the feed, the rate becomes constant as the catalyst becomes diluted by the water and even starts to decrease. The small maximum in the reaction rate corresponds to about 6 mol% water in the feed. These results are not totally unexpected, as Komiyama and Inoue (*7*) found similar results, using water

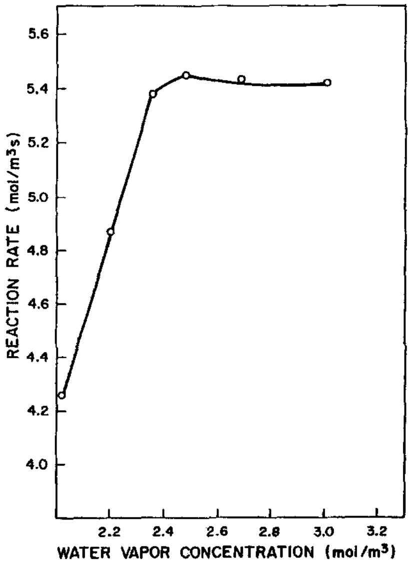

FIG. 5. The effect of water concentration on the rate of reaction under conditions given in Table 2.

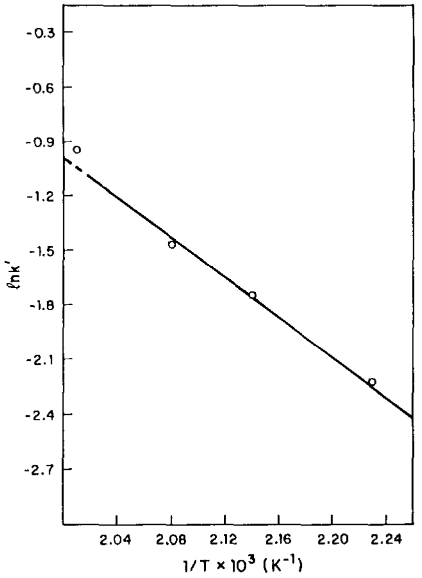

FIG. 6. An Arrhenius plot of the pseudo-first-order rate constant, k', under the conditions given in Table 2.

as the solvent, except that the initial increase in reaction rate noted by them was much greater. The initial slope of Fig. 5 corresponds to the rate being proportional to $[H_2O]^{0.2}$ and then, eventually, the rate of reaction is essentially independent of the amount of water in the feed. It may be mentioned here that all other runs, except for this series, were done using a dry feed (only ethylene and air), although some small, constant amount of water is produced due to combustion of ethylene as a side reaction. This side reaction is, thus, not altogether undesirable since the presence of a certain amount of water is essential for the reaction to occur (*3*). No other products were detected.

Figure 6 was obtained by using the conditions in Table 2 while varying the temperature of the reaction over the narrow range between 448 and 498 K. In Fig. 6 the reciprocal of the absolute temperature is plotted against ln k'. From the slope and intercept of this plot, it was determined that the apparent activation energy and the preexponential factor for the pseudo-first-order rate constant k' are 10.5 kcal/mol and 1.45×10^4 s^{-1}, respectively. The activation energy of the 10.5 kcal/mol thus obtained compares well with the value of 9.6 kcal/mol reported by Komiyama and Inoue (*6*) at lower temperatures in the aqueous phase. The low value for the apparent activation energy may possibly be explained by the fact that the pseudo-first-order rate constant k' actually involves several equilibrium constants of intermediate steps (*3*) as well as concentrations. No reaction was observed below 423 K, the melting point of the eutectic.

Finally, it must be mentioned that the reaction kinetics for the developed catalyst are remarkably similar to that for the aqueous-phase catalyst despite the obvious differences.

(*b*) *Diffusion and Reaction in SMSC*

While the reaction kinetics reported in the above section were not influenced by diffusion as ensured by utilizing pulverized catalysts, the conversion obtained over intact SMSC pellets is likely to be influenced by diffusion. This section describes analysis of diffusion and reaction in SMS Wacker catalyst and calculation of effectiveness factor. The analysis is also useful in studying the effect of liquid loading, q, on the observed rate of reaction.

A few different models have been proposed in the literature for the transport and chemical reaction of gaseous species in SLPC (*19–21*) in which catalytic liquids are dispersed within inert porous supports. The latest of these is based on the dusty-gas model as developed by Datta and Rinker (*1*). This is the model that will be used in our analysis here.

If we represent C_2H_4, CH_3CHO, and air by A, B, and C, respectively, then the oxidation reaction can be written as

$$A + C \rightarrow B.$$

By assuming the pellet as essentially isobaric ($dP/dz \rightarrow$ zero within the pellets), the overall flux of A in SLPC can be shown (*1*, *22*) to be adequately described by

$$N_A = -(D^G_{Ae} + D^L_{Ae}) \frac{dC^G_A}{dz} = -D_{Ae} \frac{dC^G_A}{dz}. \quad (3)$$

The overall diffusivity of A, D_{Ae}, takes the form (22)

$$D_{Ae} = C^0_2(1-q)^2 \Big/ \left\{ \frac{x_C}{D_{AC}} + \frac{x_B}{D_{AB}} - x_A \left(\frac{1}{D_{AC}} - \frac{1}{D_{AB}} \right) + \frac{1}{(1-q)^{1/3} D_{kA}} \right\} + C^0_2 H_A D^L_A q^2, \quad (4)$$

where D_{kA}, the Knudsen diffusivity of A, is given by

$$D_{kA} = \frac{C^0_1}{C^0_2} \left(\frac{8R_gT}{\pi M_A} \right)^{1/2}. \quad (5)$$

Further, since A and B are present in trace amounts in C under our experimental conditions, we may use average values for their mole fractions within the catalyst, thus yielding an invariant effective diffusivity. Then, for spherical geometry the effectiveness factor becomes

$$E_p = \frac{3}{\phi_p^2} (\phi_p \coth \phi_p - 1), \quad (6)$$

where ϕ_p, the Thiele modulus for a SLPC pellet for a pseudo-first-order, irreversible reaction is given by

$$\phi_p = R \left(\frac{q\theta H_A k'}{D_{Ae}} \right)^{1/2}. \quad (7)$$

The theoretical reaction velocity, defined as the ratio of reaction rate to concentration of A in the gas phase at the surface, is given by (*1*)

$$\frac{r_A}{C^G_{As}} = \frac{R}{3} \theta H_A q k' E_p. \quad (8)$$

The experimental reaction velocity is calculated by

$$\frac{r_A}{C^G_{As}} = \frac{F}{A_p} \left\{ \frac{X}{(1-X)} \right\}, \quad (9)$$

where X is the conversion of ethylene and A_p is the total external surface area of SMSC pellets exposed to reactants in the stirred reactor.

TABLE 4

Values of Constant Parameters Employed in the Calculations for Oxidation of Ethylene in SMSC at 468 K

Parameter	Value
D_{AB}	1.23×10^{-5} m²/s
D_{AC}	2.29×10^{-5} m²/s
D_{kA}	3.57×10^{-6} m²/s
D^L_A	1.58×10^{-9} m²/s
H_A	1.25
k'	0.17 s^{-1}

The parameters used in the above equations are presented in Table 4 and were obtained as follows: The binary gas diffusion coefficients were calculated from the Chapman–Enskog formula (*23*); the Knudsen diffusion coefficient was calculated by Eq. (5); the liquid-phase diffusion coefficient was calculated using the Wilke–Chang equation (*24*); and the partition coefficient, H_A, was estimated by extrapolating the vapor pressure curve for ethylene. The pseudo-first-order rate constant was obtained from kinetic experiments described in the last section. The dusty-gas structural parameters given in Table 1 were estimated by comparing the flux relationship in DGM to the parallel pore model which results in the following expressions (*1*) (where tortuosity is estimated by $1/\theta$):

$$C^0_0 = \frac{\theta^2 a^2}{8} \quad (10)$$

$$C^0_1 = \frac{2}{3} \theta^2 a \quad (11)$$

$$C^0_2 = \theta^2. \quad (12)$$

In Fig. 7, the theoretical reaction velocity, calculated using Eq. (8) and the parameter values listed in Table 4, is plotted versus the liquid loading along with experi-

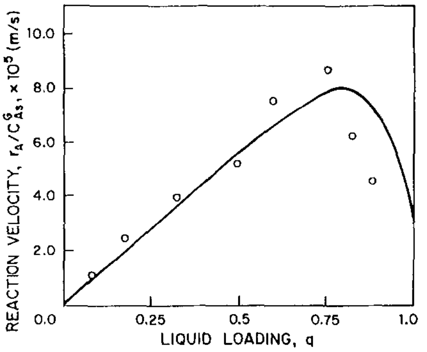

FIG. 7. Experimental points and the theoretical reaction velocity curve for the oxidation of ethylene in SMSC under conditions given in Table 3.

mental points obtained by using Eq. (9). As predicted, the data verify a maximum in the reaction rate for an optimum liquid loading. The experimental points are scattered and deviate somewhat from the theoretical curve. However, the overall agreement is quite good considering that (i) the model involves no adjustable parameters, and (ii) the dusty-gas parameters estimated as above cannot be expected to be very accurate.

(c) *Stability of SMS Catalyst*

Finally, the stability of the supported molten-salt catalyst developed was checked by allowing the reaction to run continuously for approximately 1 week. These results are also compared to the stability of a SLPC pellet using an aqueous (50% ethylene glycol and 50% water) solvent. The data for both these systems are plotted simultaneously in Fig. 8 as reaction rate versus time. From this plot the advantages of the supported molten-salt catalyst developed here are evident. With the aqueous-phase SLPC the reactivity becomes nearly zero (even though it is initially somewhat higher than the reactivity for the molten-salt system) within a 24-h time period due to the evaporation of water. When no ethylene glycol was present in the aqueous phase catalyst, the catalyst deactivated within 2 h. On the other hand, however, the molten-salt system was found to be extremely stable throughout the 150-h time frame.

5. CONCLUSIONS

It was the objective of this study to develop a stable supported molten-salt Wacker catalyst for the production of acetaldehyde by the air oxidation of ethylene. After investigating some alternatives, we were led to the choice of a eutectic melt of CuCl and KCl (m.p. 423 K) as an excellent solvent for the $PdCl_2$–$CuCl_2$ catalyst mixture supported on a silica support. This supported molten-salt catalyst overcomes the major disadvantages of the conventional Wacker process, namely, inefficient use of the catalyst in a sparged or bubble-column commercial reactor, corrosion problems of the catalyst solution, and the problem of separating catalyst from product, while at the same time maintaining a 95% selectivity of the product, acetaldehyde. The melt provides a very stable me-

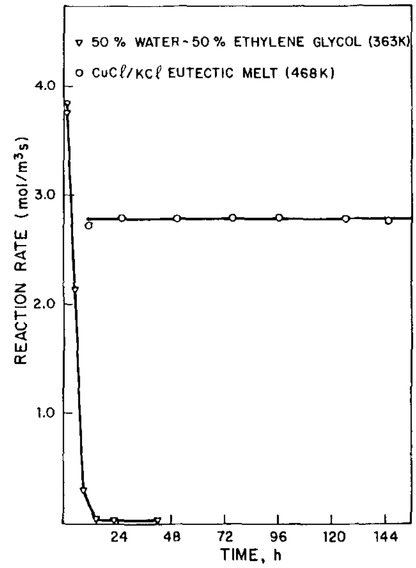

FIG. 8. A comparison of the stability of SLP catalyst using an aqueous-phase (50% water and 50% ethylene glycol) solvent (liquid loading of about 27%) and SMSC (liquid loading of about 30%) under the following conditions: $[PdCl_2]$ = 7.7 mol/m^3, $[CuCl_2]$ = 130 mol/m^3, a pressure of 0.16 MPa, and a total flow rate of 1.2 × 10^{-6} m^3/s.

dium in which this reaction can proceed. The kinetics and SMSC diffusion-reaction characteristics of this process also agree well with the theoretical predictions. It is apparent that this SMS catalyst has potential for commercial application. Further, the SMSC technique described here should find considerable application in developing efficient catalysts from homogeneous and even heterogeneous catalysts.

APPENDIX: NOMENCLATURE

A	gaseous component A (ethylene)
A_p	total external surface area of pellets exposed to reactants (m^2)
a	mean pore radius of pellet (m)
B	gaseous component B (acetaldehyde)
C	gaseous component C (air)
C_A	outlet concentration of A from the reactor
C_{A0}	inlet concentration of A to the reactor
C_{As}^G	concentration of A in the gas phase at the pellet surface (mol/m^3)
C_0^0	D'Arcy permeability for the dry support (m^2)
C_1^0	dusty-gas Knudsen diffusion constant for the dry porous support (m)
C_2^0	dusty-gas molecular diffusion constant for the dry porous support (dimensionless)
C_2^L	dusty-gas constant for liquid-phase diffusion (dimensionless)
C_A^G	concentration of A in gas phase (mol/m^3)
C_{As}^G	gas-phase concentration of A at the pellet surface (mol/m^3)
D_A^L	molecular diffusivity of A in liquid phase (m^2/s)
D_{ij}	binary molecular diffusivity in gas phase (m^2/s)
D_{kA}	Knudsen diffusivity (Eq. (5); m^2/s)
D_{Ae}	overall effective diffusivity of A in liquid-loaded support (m^2/s)
D_{Ae}^G	effective diffusivity of A in the gas phase (m^2/s)
D_{Ae}^L	effective diffusivity of A in the liquid phase (m^2/s)
E_p	effectiveness factor for SLPC (dimensionless)
F	volumetric gas flow rate through reactor (m^3/s)
H_A	gas–liquid partition coefficient for A (mol/m^3 liquid)/(mol/m^3 gas)
k'	pseudo-first-order homogeneous reaction rate constant Eq. (1) (s^{-1})
M_A	molecular weight of A
N_A	molar flux of A in pellet (mol/m^2 s)
P	total pressure (Pa)
q	liquid-loading parameter representing the ratio of the pore volume occupied by the liquid (dimensionless)
R	pellet radius (m)
R_g	gas constant = 8.314 J/mol · K
r	rate of reaction per unit volume of molten catalyst solution (mol/m^3 s)
r_A	rate of reaction per unit external surface area of pellet (mol/m^2 s)
T	temperature (K)
V_{cat}	volume of molten catalyst solution (m^3)
X	conversion of ethylene
x_i	mole fraction of species i in gas phase
z	radial distance in SLPC pellet (m)

Greek Symbols

ϕ_p	Thiele modulus for SLPC (dimensionless)
θ	porosity of dry support (m^3/m^3)

REFERENCES

1. Datta, R., and Rinker, R. G., *J. Catal.* **95,** 181 (1985).

2. Parshall, G. W., "Homogeneous Catalysis." Wiley, New York, 1980.

3. Gates, B. C., Katzer, J. R., and Shuit, G. C. A., "Chemistry of Catalytic Processes." McGraw–Hill, New York, 1979.

4. Henry, P. M., "Palladium Catalyzed Oxidation of Hydrocarbons." Reidel, Boston, 1980.

5. Smidt, J., Hafner, W., Jira, R., Sedlmeir, J., Sieber, R., Ruttinger, R., and Kojer, H., *Angnen. Chem.* **71,** 176 (1959).

6. Komiyama, H., and Inoue, H., *J. Chem. Eng. Japan* **8,** 310 (1975).

7. Komiyama, H., and Inoue, H., *J. Chem. Eng. Japan* **10,** 124 (1977).

8. Katz, G., and Pismen, L. M., *Chem. Eng. J.* **18,** 203 (1979).

9. Desai, M. N., Butt, J. B., and Dranoff, J. S., *J. Catal.* **79,** 95 (1983).

10. Evnin, A. B., Rabo, J. A., and Kasai, P. H., *J. Catal.* **30,** 109 (1973).

11. Rony, P. R., *Ann. N.Y. Acad. Sci.* **172,** 238 (1970).

12. Bloom, H., "The Chemistry of Molten Salts." Benjamin, New York, 1967.

13. Janz, G. J., "Molten Salts Handbook." Academic Press, New York, 1967.

14. Kenney, C. N., *Catal. Rev. Sci. Eng.* **11,** 197 (1975).

15. Weisz, P. B., and Prater, C. D., "Advances in Catalysis" (W. G. Frankenburg, V I. Komarewsky, and E. K. Rideal, Eds.), Vol. 6, p. 144. Academic Press, New York, 1954.

16. Schultz, R. G., and Rony, P. R., *J. Catal.* **16,** 133 (1970).

17. Henry, P. M., *J. Amer. Chem. Soc.* **86,** 3246 (1964).

18. Moiseev, J. I., Levanda, O. G., and Vargaftik, M. N., *J. Amer. Chem. Soc.* **96,** 1003 (1974).

19. Rony, P. R., *Chem. Eng. Sci.* **23,** 1021 (1968).

20. Abed, R., and Rinker, R. G., *J. Catal.* **91,** 119 (1973).

21. Chen, O. T., and Rinker, R. G., *Chem. Eng. Sci.* **33,** 1201 (1978).

22. Datta, R., and Rinker, R. G., *J. Catal.* **95,** 202 (1985).

23. Bird, R. B., Stewart, W. E., and Lightfoot, E. N., "Transport Phenomena." Wiley, New York, 1960.

24. Reid, R. C., Prausnitz, J. M., and Sherwood, T. K., "The Properties of Gases and Liquids," 3rd ed. McGraw–Hill, New York, 1977.