

## Low-Temperature Oxidation of CO by a Heterogenized Wacker Catalyst

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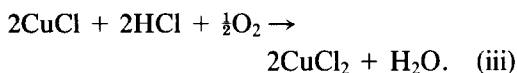
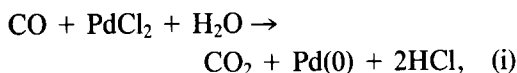
### INTRODUCTION

Low-level (ppm) stationary emissions of CO are a continuing problem in many processes involving partial oxidation of hydrocarbons. Control of such emissions via catalytic oxidation has potential advantages over other methods in terms of equipment size and operating characteristics, however, there are problems which arise from the nature of the process streams involved. In addition to the low concentrations of CO, these streams are often water saturated and at low temperature, 40–60°C. Hence specific catalysts must be active at low temperature and water tolerant; the latter requirement rules out low-temperature oxidation catalysts such as Hopcalite (1), although SnO<sub>2</sub>-CuO gels may be a possibility (2). In this study we report the investigation of a heterogenized form of Wacker catalyst for CO oxidation under these conditions (3).

The Wacker process for manufacture of acetaldehyde, utilizing a PdCl<sub>2</sub>-CuCl<sub>2</sub> (aq) homogeneous catalyst, has been industrialized on an extensive scale. Lloyd and Rowe (4) claim that Cu(NO<sub>3</sub>)<sub>2</sub> serves as a promoter for this catalyst when supported on alumina and used for CO oxidation. Further studies in this laboratory (5, 6) indicated high activity at reasonably low temperatures (ca. 60°C), and reasonable activity maintenance in the presence of water vapor.

The overall chemistry of CO oxidation is

similar to that detailed for ethylene oxidation in the Wacker process (4):



In (i) the Pd(II) is reduced to Pd(0) by the CO, then Pd(0) is reoxidized in (ii) by CuCl<sub>2</sub> and the resulting CuCl is reoxidized by molecular oxygen in (iii). No apparent role of Cu(NO<sub>3</sub>)<sub>2</sub> as a promoter, other than the incorporation of additional Cu(II) in the system, is apparent from this scheme.

Detailed mechanistic studies of Wacker oxidation of C<sub>2</sub>H<sub>4</sub> (7, 8) enlarge considerably upon the picture above. These postulate (PdCl<sub>4</sub>)<sup>2-</sup> as initiating the reaction sequence with ethylene and yield a kinetic correlation of the form

$$(-r) = \frac{k[(\text{PdCl}_4)^{2-}][\text{C}_2\text{H}_4]}{[\text{Cl}^-]^2[\text{H}_3\text{O}^+]}. \quad (1)$$

Studies of CO oxidation in aqueous media by various palladium complexes have also been reported (9–13). While these investigations have not yielded as complete a picture of the mechanism and kinetics of this reaction as in the case of C<sub>2</sub>H<sub>4</sub> oxidation, they do indicate that formation of a palladium chloride carbonyl complex is involved and first-order dependence of the

rate on palladium chloride and CO concentrations is expected.

In the present experiments on the heterogenized Wacker catalyst with water-saturated feed streams, we believe that under reaction conditions the active ingredients are contained in a liquid phase within the internal pore structure of the support. There are several descriptions in the patent literature (14–16) of supported Wacker oxidation catalysts which were used in the presence of water vapor or acetic acid; it is not clear from those descriptions whether the catalysts contained a liquid phase under reaction conditions. However, more recent studies of ethylene oxidation by heterogenized Wacker catalysts have clearly involved a liquid-phase catalyst (17, 18). A general discussion of various aspects of supported liquid-phase catalysts has been given by Rony (19).

#### EXPERIMENTAL

**Catalysts.** Catalysts were prepared by impregnation to incipient wetness of Harshaw alumina (Al-0104), 80–140 mesh, 100 m<sup>2</sup>/g, or Fisher neutral alumina (A-950) of the same mesh size, 150 m<sup>2</sup>/g. These supports were washed repeatedly with 0.1 N HCl, thoroughly rinsed with distilled water, and dried at 300°C for 3 hr before impregnation. Various compositions of impregnating solution were used, but a typical composition was 2.38% CuCl<sub>2</sub> (as the dihydrate), 0.435% PdCl<sub>2</sub>, and 7.85% Cu(NO<sub>3</sub>)<sub>2</sub> (as the trihydrate). PdCl<sub>2</sub> was initially dissolved in an aqueous solution of the CuCl<sub>2</sub>. Total loading on the support (on the above basis) was 6.75%. In terms of metals alone, loading was 0.29% Pd and 4.13% Cu. After impregnation the catalyst was air-dried overnight, then oven-dried at 75°C for 9 hr. Prior to use in a reaction experiment, the catalyst was packed in the reactor (see below) and exposed *in situ* to flowing Cl<sub>2</sub> at room temperature for 15 min and then heated in air at 130°C for 20 min.

**Reactor.** Experimental studies were carried out with a conventional bench scale

flow reactor system consisting of a gas feed manifold and purification train, a water vapor saturator enclosed in a constant temperature bath, the reactor (similarly thermostatted), and a LIRA 202 Luft-type CO infrared analyzer. The reactor was simply a ½-in. glass tube containing ca. 0.05 g catalyst held in place by calcined glass wool plugs. Cold finger traps were placed between the reactor and the analyzer to prevent the intrusion of water vapor into the ir cells. Further details of the experimental apparatus are given by Desai (20).

**Chlorination.** Early studies of 0.15% PdCl<sub>2</sub>, 1.61% (CuCl<sub>2</sub> + Cu(NO<sub>3</sub>)<sub>2</sub>) catalyst on Fisher alumina revealed that conversion decreased from 90 to 26% over a period of 35 hr for an experiment at 330°K and space velocity of 50,000 vol/vol-cat-hr. It was felt that this apparent deactivation would be due to the loss of small amounts of HCl from the liquid phase on the support under reaction conditions, with consequent loss of activity for reoxidation of Pd(0) to Pd(II), since a similar phenomenon occurs in homogeneous Wacker oxidation. The chlorination procedure described above was developed more or less on a trial basis, and resulted in a significant increase in catalyst durability. Comparison of unchlorinated and chlorinated catalysts is shown in Fig. 1.

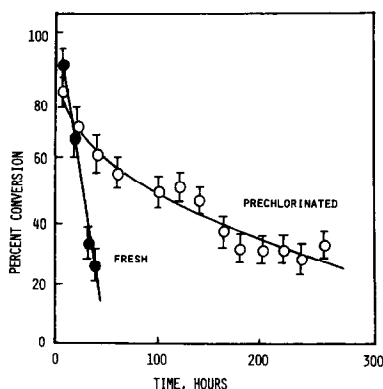


FIG. 1. Comparison of the stability of prechlorinated catalyst with an untreated sample. Experiment conducted at 50,000 hr<sup>-1</sup>, 333°K, CO inlet  $5.5 \times 10^{-8}$  g mol/cm<sup>3</sup> (1500 ppm), O<sub>2</sub> inlet  $1.3 \times 10^{-3}$  g mol/cm<sup>3</sup>, 0.0712 g catalyst. Feed water saturated at 313°K.

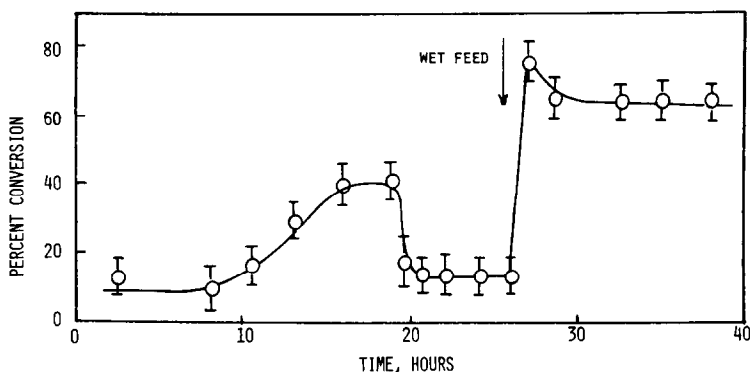


FIG. 2. Conversion for the standard catalyst with dry and water-saturated (313°K) feeds. Experiment conducted at  $58,000 \text{ hr}^{-1}$ ,  $333^\circ\text{K}$ ,  $0.0584 \text{ g}$  catalyst.

Total chlorine dosage amounted to ca.  $250 \text{ m}^3 \text{ Cl}_2/\text{m}^3$  catalyst; treatment much in excess of this amount resulted in a depression of initial activity.

*Experimental conditions.* The primary experimental variables were temperature ( $40\text{--}80^\circ\text{C}$ ), feed composition (including degree of saturation with water vapor), and catalyst composition. The "standard" catalyst was the  $0.29\%$  Pd/ $4.13\%$  Cu formulation described above supported on the Harshaw alumina. Experimentation on reaction kinetics encompassed a wide range of conversions, hence both differential and integral analyses of data were performed. Experimental conditions were such as to eliminate inter- and intraparticle gradient disguises of results.

*The importance of water.* The supported Wacker catalyst exhibits enhanced activity in the presence of water vapor. Typical results are shown in Fig. 2 for the base catalyst. For dry feed there is an initial induction period followed by ignition to a steady conversion of approximately  $40\%$ . The decrease in conversion at about  $20 \text{ hr}$  was thought to be the result of evaporation of the liquid phase from the catalyst. This was tested by saturating the feed with water at  $29^\circ\text{C}$ , shown at  $27 \text{ hr}$ , and a resultant increase to a high, steady level of conversion was measured.

The behavior of the supported Wacker catalyst is somewhat more complicated

than for some other types where the liquid phase under reaction conditions is a melt. Here the presence of water vapor in the reaction mixture results in an equilibration of water on the surface which will be dependent upon the temperature of saturation prior to reaction. Differing amounts of adsorbed water lead to differing concentrations of active catalytic ingredients in the supported liquid phase, hence apparent activity may vary with feed saturation temperature. A series of experiments was run with the standard catalyst at  $58,000 \text{ hr}^{-1}$  and conversion was measured as a function of saturation temperature and reaction temperature. As shown in Fig. 3, an optimum water content exists which increases and becomes more diffuse as reaction temperature increases. The maximum conversion observed over the range of  $45$  to  $80^\circ\text{C}$  is the same, possibly indicating some compensation between reaction temperature and dilution of the liquid-phase catalyst. The fraction of pore volume occupied by liquid,  $\delta$ , was determined gravimetrically in a separate series of experiments with variable saturation temperature. (Nominal support pore volume was  $0.3 \text{ cm}^3/\text{g}$ .) These data were then correlated with corresponding conversion measurements at  $60^\circ\text{C}$ , with the results shown in Fig. 4. Low activity of the catalyst at low water content was seen previously in Fig. 2; the decrease in activity at high water contents probably results from

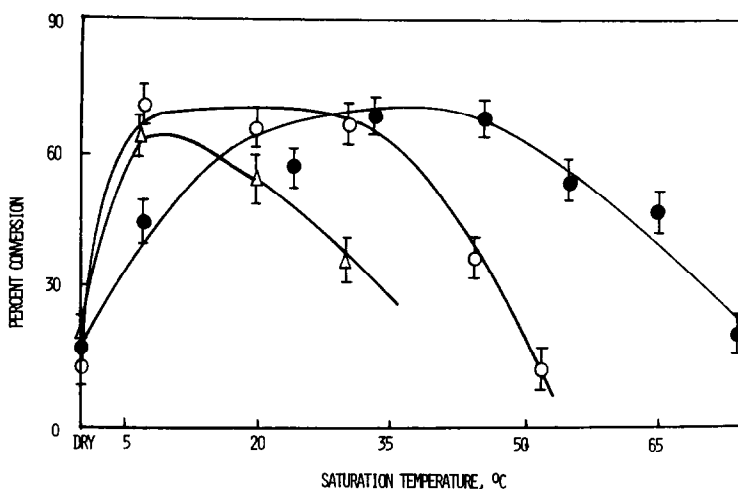


FIG. 3. Effect of saturation temperature on conversion. Reaction temperatures: ●—45°C; ○—60°C; △—80°C.

the combination of dilution of the liquid phase and pore filling with liquid, decreasing the gas-liquid interfacial surface area available. Similar results have been presented by Komiyama and Inoue (17) for ethylene oxidation at 70°C on an alumina-supported Wacker catalyst containing differing amounts of liquid in the pores.

These results suggest that pore size distribution can be an important factor in de-

termining apparent activity in supported liquid phase catalysts—not only for the normal pore diffusion reasons but also for access to the liquid-phase surface within the pore structure. One can estimate a rough range of useful pore sizes based on a simplified Kelvin equation analysis (20). The results are in qualitative agreement with experimental results to be presented later in which the Fisher support with an average pore diameter of 58Å resulted in a less active catalyst than the Harshaw support at 100Å, even though the respective surface areas were 150 vs 100 m<sup>2</sup>/g. Under the experimental conditions here, more pore filling apparently occurred in the smaller pore support, reducing the access to effective surface.

*Activation energies.* The importance of catalyst concentration as affected by water content here also has implications in kinetic studies, particularly in the determination of activation energy. In addition to corresponding to the kinetically controlled regime, activation energy data taken at different temperatures ideally should be for catalysts with the same liquid content,  $\delta$ , in the pores. Even for feeds saturated at the same temperature, different reaction temperatures will result in different values of  $\delta$

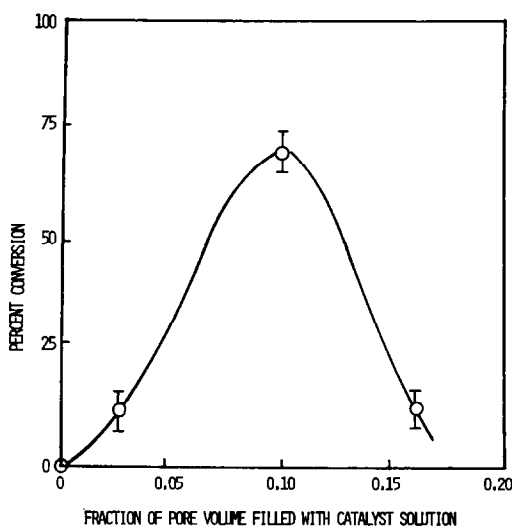


FIG. 4. Conversion as a function of  $\delta$  at 60°C. Other conditions as for Fig. 2.

for the catalyst corresponding to different volumes of the catalyst solution on the support. Since reaction rate should be proportional to the concentration of the Pd complex in solution (see Eq. (1)), it is expected that the apparent rate constant for the reaction will vary with reaction temperature because of concentration changes as well as the normal temperature dependence of the intrinsic rate constant.

As a result, for determination of true activation energy the saturation temperature of the feed should be adjusted with the reaction temperature to obtain the same  $\delta$ , something which has apparently not been a controlled variable in the past. Katz and Pismen (18) report an apparent activation energy of  $-20.7$  kcal/mol for ethylene oxidation over a heterogenized Wacker catalyst. Typical experimental conditions were feed composition 70% (mol)  $\text{H}_2\text{O}$ , 10%  $\text{C}_2\text{H}_4$ , and 20%  $\text{O}_2$ , at temperatures of 90–130°C. With the large excess of water vapor, but with varying temperature,  $\delta$  was an uncontrolled variable in their experiments and the reported activation energy probably represents a combination of factors.

#### CATALYST COMPOSITION EFFECTS

It is well accepted that the Wacker catalyst contains  $(\text{PdCl}_4)^{2-}$  species in acidic aqueous solution (21). Addition of  $\text{CuCl}_2$  results in a color change from brown to dark green; further addition of  $\text{Cu}(\text{NO}_3)_2$  as carried out here resulted in no further change in color, suggesting that the complex formed with  $\text{CuCl}_2$  is not substantially altered upon incorporation of  $\text{Cu}(\text{NO}_3)_2$ . After impregnation of this solution upon the support, one obtains a light-green material which changes to a rather vivid yellow after exposure to chlorine. This is probably the result of oxidation of Pd(II) to Pd(IV) (21); the  $(\text{PdCl}_6)^{2-}$  complex so formed could be decomposed with the evolution of  $\text{Cl}_2$  upon heating to 200°C, as has been reported previously (22). It is also likely that such Pd(IV) complexes will be rapidly converted

to the more stable Pd(II) complexes when reaction begins.

Independent experiments were carried out to investigate the effects of changes in the molar ratio of  $\text{CuCl}_2$  in the complex with  $\text{PdCl}_2$  and of composition on catalyst activity. A series of catalysts was prepared with constant  $\text{CuCl}_2$  (1.25%),  $\text{Cu}(\text{NO}_3)_2$  (4.04%), and variable  $\text{PdCl}_2$ , and the activity at 45,000  $\text{hr}^{-1}$ , 60°C, and inlet CO of ca. 2700 ppm was examined as a function of  $\text{PdCl}_2$  loading. The results, shown in Fig. 5, indicate that steady-state activity is essentially directly proportional to  $\text{PdCl}_2$  loading. Similar results have recently been reported by Rakitskaya *et al.* (23). Other experiments under conditions as above indicated that the activity of catalyst containing the standard amount of  $\text{PdCl}_2$  but no other ingredients was about a factor of 5 lower than the standard formulation. Catalysts prepared from  $\text{PdCl}_2$ – $\text{CuCl}_2$  and  $\text{PdCl}_2$ – $\text{Cu}(\text{NO}_3)_2$  were similar in activity; it would appear that the nitrate is converted into the chloride complex during chlorination, and there is no particular promotional effect of  $\text{Cu}(\text{NO}_3)_2$  that we observe. This was further investigated in a series of experiments, also at the conditions above, in which Cu loading from the nitrate was varied from zero to the maximum 4.13% corresponding to the standard catalyst; conversion was unaffected.

In the experiments in Fig. 5, the catalyst contained a large excess of  $\text{CuCl}_2$  and  $\text{Cu}(\text{NO}_3)_2$ . A further series of catalysts was prepared with constant Pd (0.31%) but differing  $\text{CuCl}_2$ . The results, again at the experimental conditions given above, are shown in Fig. 6. Activity increased up to Cu of 0.49%, then remained constant. The breakpoint corresponds to a 2:1 molar ratio of  $\text{CuCl}_2$  to  $\text{PdCl}_2$ , suggestive of the stoichiometry of the overall reactions (i)–(iii). Matreev *et al.* (24) have also reported rate dependency on Cu(II) concentration, and have postulated the existence of a Pd(II)–Cu(II) complex.

Finally, there was no positive control ex-

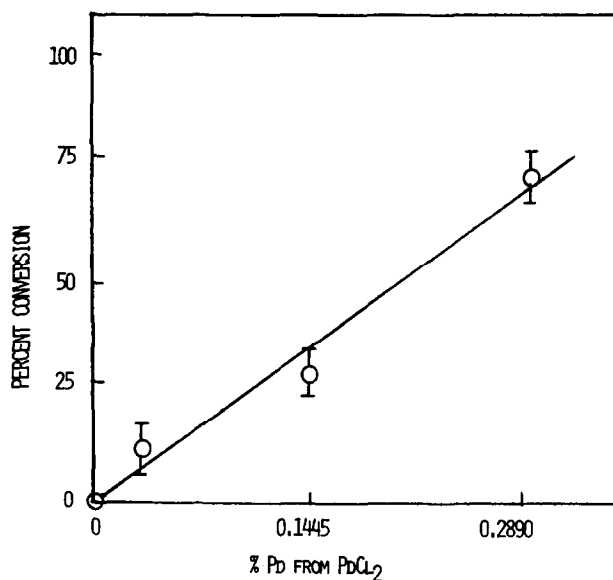


FIG. 5. Activity dependence on PdCl<sub>2</sub> concentration.

erted in these experiments over the chloride content in the active catalyst, since the chlorination procedure resulted in contact with chlorine in great excess. Assuming equilibration in



the [Cl<sup>-</sup>] is estimated to be ca.  $5.9 \times 10^{-6} M$  upon saturation at 29°C and 1 (20). One might expect gradual loss of Cl<sub>2</sub> over extended operation to be a major factor in the activity maintenance of these catalysts.

#### KINETICS OF CO OXIDATION ON SUPPORTED LIQUID PHASE WACKER CATALYST: EXPERIMENTAL RESULTS

In the initial analysis of kinetic results, we seek a simple power law expression of the form

$$(-r) = k[\text{CO}]^m[\text{O}_2]^n. \quad (2)$$

Both differential and integral conversion experiments were conducted, although the bulk of the data was obtained at high conversions and differential experiments were

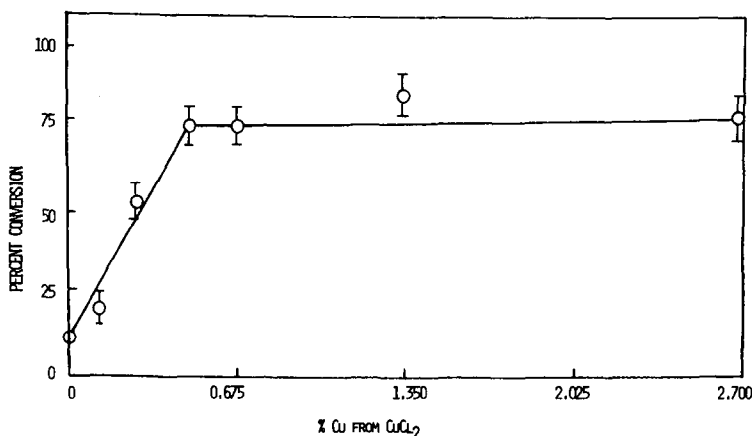


FIG. 6. Activity dependence on CuCl<sub>2</sub> loading.

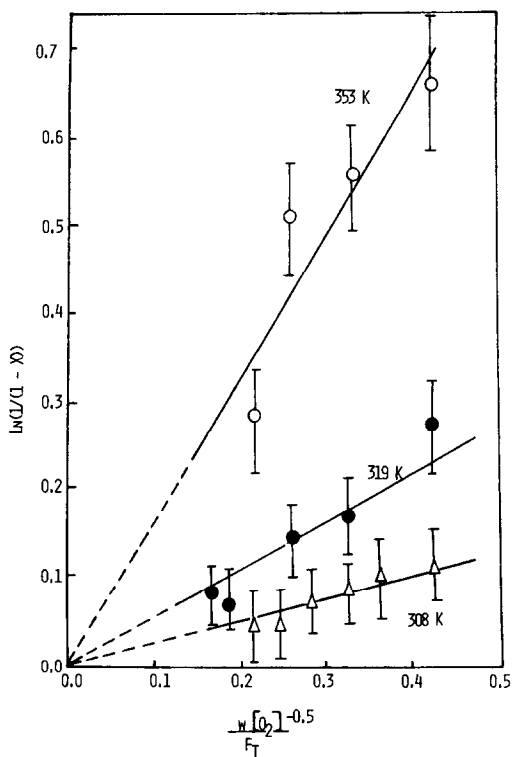


FIG. 7. Integral analysis of kinetic data at different temperatures. Standard catalyst composition; Fisher alumina support.

used primarily to determine initial estimates of  $m$ ,  $n$ , and  $k$ . In all experiments oxygen was present in large excess, although it was varied over a sevenfold range in the overall experimental program. Because  $[O_2] \gg [CO]$ ,  $[O_2]^n$  was approximately constant in any experiment and consequently the following simple forms apply for analysis of integral conversion data:

$$m = 1: \frac{W}{F_T} [O_2]^n = \frac{1}{k} \ln(1/(1-x)), \quad (3)$$

$$m \neq 1: \frac{W}{F_T} [O_2]^n = \frac{(1-x)^{1-m} - 1}{k(m-1)}, \quad (4)$$

where  $W$  is the weight of catalyst,  $F_T$  is the total feed rate (vol/time), and  $x$  is fractional conversion.

Analysis of differential conversion data for the standard catalyst composition (but Fisher support) at 60°C indicated  $m \approx 1.15$  and  $n \approx -0.45$ , so integral data were ana-

lyzed with  $m = 1.0$  and  $n = -0.5$ . The results are shown in Fig. 7 for the temperature range 308–353°K with feeds saturated with water vapor at 298°K. Satisfactory fit is obtained (the lines shown are linear least-squares fits) with  $m = 1$ ,  $n = -0.5$ , independent of temperature. (A series of experiments at 333°K not shown in Fig. 7 gave similar results.) An Arrhenius plot of  $k$  in Eq. (3) is shown in Fig. 8. In the lower temperature range results are consistent with an activation energy of 14.2 kcal/mol.

Corresponding studies of the standard catalyst composition supported on the Harshaw support resulted in similar kinetics,  $m = 1$ ,  $n = -0.5$ , and a similar temperature dependence (see Fig. 9), with activation energy of about 16 kcal/mol<sup>-1</sup> in the lower temperature range. We consider this value to be the same (within experimental error) as that for Fisher support. However, the absolute values of the rate constant are somewhat higher here; at 333°K the ratio is about 3.5. In view of the equivalent activation energies on the two supports, this difference in rates may be the result of the larger average pore diameter of the Harshaw alumina providing a better "dispersion" of the liquid-phase catalyst distributed within. This point requires further

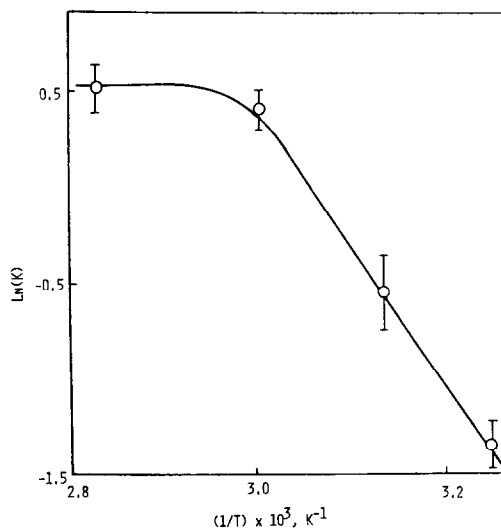


FIG. 8. Arrhenius plot—Fisher support.

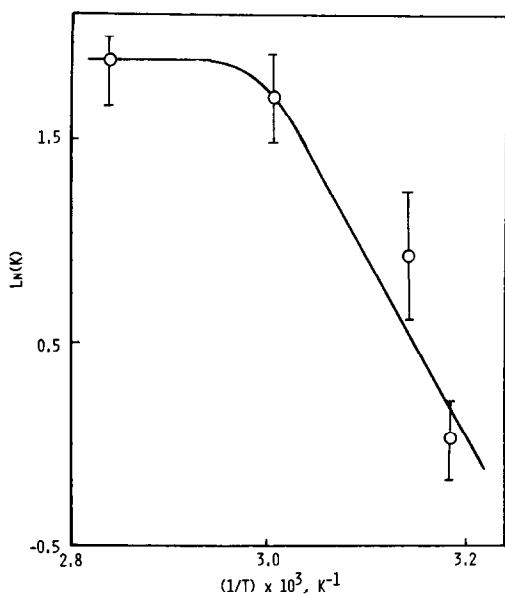


FIG. 9. Arrhenius plot—Harshaw support.

investigation but indicates an important role of pore structure in determining the properties of such supported liquid-phase catalysts.

Interpretation of the Arrhenius plots is difficult because of the compositional effects mentioned previously. Nonetheless, it should be noted that the Arrhenius correlation is nonlinear at higher temperatures for both supports; such a decrease in apparent activation energy is normally the fingerprint of diffusional intrusions into the kinetic regime. However, the conditions of experimentation employed were analyzed by a number of criteria which have been proposed (25) for estimation of the extent of diffusional disguises of various types from observed experimental quantities. In all cases, these were satisfied to better than an order of magnitude (20), so it is difficult to believe that the decrease in rate observed at 353°K is a diffusional effect. Partial evaporation of the supported liquid phase is more likely, resulting in discrete areas of liquid rather than a continuous film in the internal surface of the support. Such "partially dried" catalyst would have substantially

lower activity, as shown by the results of Fig. 2.

#### DISCUSSION

The kinetic model determined in this work, Eq. (5), contains some expected and some unexpected features:

$$(-r) = k[\text{CO}][\text{O}_2]^{-0.5}. \quad (5)$$

The first-order dependence on CO concentration is in agreement with the customary Wacker oxidation process model, as indicated in Eq. (1). Furthermore, the apparent rate constant has been shown to be proportional to the PdCl<sub>2</sub> content of the catalyst solution and essentially independent of CuCl<sub>2</sub> content as long as Cu is present in sufficient excess relative to Pd (>2:1) to ensure that all of the latter is continuously reoxidized. This is also expected in view of Eq. (1) and other research on CO oxidation (9, 11). Temperature dependence of *k* is somewhat uncertain in view of the factors discussed previously, but the apparent activation energy of approximately 16 kcal/mol is reasonable.

What is unexpected, however, is the inhibitory effect of oxygen on the rate. No satisfactory mechanistic explanation for this effect has appeared as yet. Apparently, oxygen is involved in some kind of competitive reaction with the catalytic Pd complex, but the possible form of this reaction is still unclear.

The precise role of the chlorine treatment of the impregnated catalyst particles in improving catalyst life is also not clear. While it seems likely that the presence of excess Cl<sub>2</sub> minimizes the loss of Cl<sup>-</sup> from the liquid phase, thereby ensuring the presence of enough Cl<sup>-</sup> to maintain the palladium chloride complex in solution, what is unclear is how this excess Cl<sub>2</sub> is stored in the catalyst; one possibility is that the alumina support reacts with Cl<sub>2</sub> to form aluminum-chloro compounds which serve as a reservoir of chloride until needed to replace that which is volatilized. This must, however, remain



speculation in the absence of further experimental data on this system.

#### CONCLUSIONS

The heterogenized Wacker catalyst prepared in this study is active for oxidation of CO in the range of  $10^3$  ppm at temperatures near  $60^\circ\text{C}$ . Satisfactory maintenance of activity seems to be associated with retention of sufficient  $\text{Cl}^-$  in the supported liquid phase, as well as with the presence of sufficient water vapor in the reaction mixture to maintain the liquid phase. These can be controlled by prechlorination of the catalyst and humidification of the feed. Pore structure is also important in obtaining maximum activity of the catalyst.

The reaction rate is proportional to CO concentration and inversely proportional to the square root of  $\text{O}_2$  concentration. The apparent rate constant varies directly with Pd content of the catalyst solution and exhibits an effective activation energy of 16 kcal/mol.

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