Depletion of Reactants on a Catalytic Surface During Reaction

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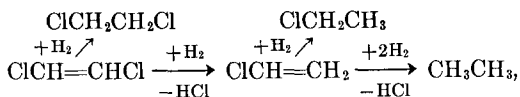*Worcester, Massachusetts 01609*

The steady state reactions of a mixture of physically adsorbed *cis-* and *trans-*dichloroethylenes with H_2 on Pt peripherally deposited on alumina pellets were terminated abruptly by flooding the reactor with CCl_4 to permit direct measurement of species on the catalyst at that instant. It was found that products—ethane, vinyl chloride, ethyl chloride, and 1,2-dichloroethane—were present on the catalyst during reaction in quantities proportional to boiling points and in an order opposite to production rates. At constant partial pressure of 485 Torr H_2 and 10.8 Torr $C_2H_2Cl_2$ at 32°C, the amounts of reactants on the surface decreased from 370 to 122 μmoles/g of catalyst as conversion ranged from 0 to 2.5%. We believe that the observation of depletion of the amounts of reactant on the surface as a function of conversion at constant partial pressure is a consequence of a required surface diffusion process from the inert alumina surface (190 m^2/g) to the catalyst's active Pt sites (1.34 m^2/g). Observed adsorption data are a function of the large inert surface rather than the small active site area. Surface diffusion effects are marked when using catalysts with dispersed active sites. Not only activity but also selectivity is affected.

INTRODUCTION

Langmuir–Hinshelwood rate expressions involve surface coverage terms which are related to concentrations in the bulk gas. Kinetic expressions are formulated on information obtained from the gas phase, rather than the working state of the catalyst, especially in case of multicomponent reaction systems. Experimental methods that have been used for adsorption measurements during the process of surface catalysis include gravimetric, volumetric, gas chromatographic (*1, 2*) and temperature programmed desorption techniques (*3*). Tools such as ESR, NMR, IR, LEED, field ionization, and UV spectroscopy have been adapted for surface studies of catalytic reactions. By use of such techniques, information on adsorbed species—their quantity, and their reactivity—is now

becoming available. Such simultaneous measurements are useful for elucidating reaction mechanisms and identifying intermediates present on the catalyst. In the present paper, a flooding technique is described to measure the amounts of different species present on catalyst in a flow reactor at steady state, both when reaction is in progress and when no reaction is taking place. Hydrodechlorination of *cis-* and *trans*-dichloroethylenes on 0.5% Pt peripherally deposited on η-Al_2O_3 catalyst is used as a model reaction. Isomerization of *cis-* and *trans*-dichloroethylenes is negligible in the system; and the major reaction is conversion of dichloroethylenes to vinyl chloride, which in turn is hydrodechlorinated and rapidly hydrogenated to ethane as an observed product. Side hydrogenation reactions also occur in the system to produce ethyl chloride and 1,2-dichloroethane. The zero order reaction scheme is as follows:

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$$ClCH_2CH_2Cl \qquad ClCH_2CH_3$$

$$ClCH{=}CHCl \xrightarrow[-HCl]{+H_2 \nearrow \quad +H_2} ClCH{=}CH_2 \xrightarrow[-HCl]{+H_2 \nearrow \quad +2H_2} CH_3CH_3,$$

and kinetics are provided by Weiss and Krieger (4). They showed that Pt was the active catalytic agent and that the alumina only served as an inert surface carrier.

EXPERIMENTAL METHODS

Materials

All gases used for this work were obtained from the Matheson Co. and had purities greater that 99.5%. Hydrogen was passed over palladium Deoxo catalyst and then over Houdry Process and Chemical Co. Type K nickel on alumina catalyst at 250°F to remove traces of oxygen. Water and carbon dioxide present in the gas streams were removed by serial passage over Drierite and Ascarite. Except for the Deoxo catalyst, helium diluent gas and gases going to the gas chromatograph received the same treatment as hydrogen.

Both *cis*- and *trans*-dichloroethylenes were purchased as the practical grades from Eastman Kodak Organic Chemical Department of Distillation Product Industries, Inc., CCl$_4$ of reagent grade from Matheson Co. Prior to use, *cis*- and *trans*-dichloroethylenes, and CCl$_4$ after pretreatment with analytical P$_2$O$_5$ (reagent grade) were each fractionated at 30:1 reflux ratio in a packed distillation column with dry N$_2$ bubbled into the still pot. Middle fractions were collected at the appropriate boiling points and stored in the dark in a freezer until used. Distilled CCl$_4$ was >99.9% pure. The analysis of dichloroethylenes, designated "*cis*" and "*trans*" for their major components were as follows:

	cis	trans
Mole fraction *cis*-C$_2$H$_2$Cl$_2$	0.993	0.0067
Mole fraction *trans*-C$_2$H$_2$Cl$_2$	0.004	0.996

The catalyst used was 0.5% Pt (by wt) peripherally deposited on η-Al$_2$O$_3$. The η-Al$_2$O$_3$ pelleted support, supplied by Houdry Process and Chemical Co., had a bulk density of 0.77 g/cm^3, and was in the form of extruded pellets, $\frac{1}{16}$ in. in diameter and of variable length, nominally

$\frac{1}{8}$ in. A single batch of catalyst was prepared by impregnating the dried support with aqueous chloroplatinic acid solution, the volume of the solution being that just sufficient to wet the pellets. Five to 6 g batches were reduced in flowing H$_2$ and He (20 cm^3/min each) at 190°C for 10 hr. For each run, the reactor was loaded with the appropriate amount of the catalyst and reduced a second time for 2 hr. After the second reduction, the catalyst was maintained under positive hydrogen pressure to avoid air leakage into the reactor.

Equipment

The experimental setup of the flow reaction system used for the study was basically the same as employed by Weiss *et al.* (6) except for the reactor, which is shown in Fig. 1. The reactor was a U tube fabricated from 6 mm i.d., 8 mm o.d. Pyrex glass, with a 5 mm pyrex glass rod inserted on the effluent side (after the catalyst bed) of the reactor. The reactor was connected to the rest of the system by $\frac{1}{8}$ in. o.d. Teflon tubing. Beginning with the point of dichloroethylenes addition, only Pyrex and Teflon were used as materials of construction. Gas flow rates ranged from 37 to 560 ml/min. Liquid dichloroethylenes feed was pumped by a Sage syringe pump equipped with 1, 2.5, 5, or 50 ml Hamilton Teflon plunger gastight syringes. Air dissolved in the liquid feed was purged by back-flushing hydrogen from the unit through the capillary line to the syringe and then through the liquid contained in the syringe. For all the runs, catalyst loadings of 0.3005 ± 0.0005 g corresponding to L/D (length:diameter ratio of the catalyst bed) of 2.30 was used. The reactor effluent stream, after the system had reached steady state (which usually required 2.5 hr) or the charge stock (if the reactor were bypassed) then passed through a 1.96 ml Teflon sample loop and then to a vent. The sample was trapped in the loop by a nylon sampling valve and passed into the gas chromatograph for analysis. To measure the amounts of adsorbed species on the catalyst or support at steady state (at
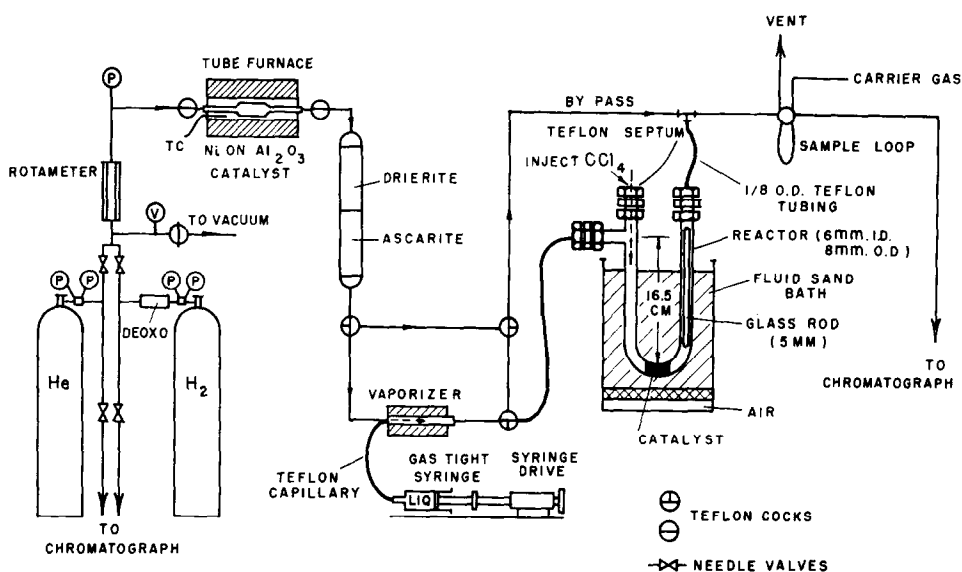
FIG. 1. Flow reaction system.

least 3 hr operation) the feed stream to the reactor was bypassed and, simultaneously, 3.5 ml of CCl_4 were injected with a 5 ml Hamilton gastight syringe into the reactor through a Teflon septum (Fig. 1). The reactor was simultaneously withdrawn from the constant temperature fluid sand bath. The CCl_4 displaced and dissolved the various species present on the catalyst and terminated the reaction at the instant of flooding. The contents of the reactor (CCl_4 solution and catalyst) were then transferred to a sampling bottle which was stored at $-8°C$ in the dark. Samples of CCl_4 solution were analyzed gas chromatographically.

N_2 BET isotherms were obtained in a Benson constant volume system (7) at liquid nitrogen temperature. The modified McBain-Bahr sorption balance unit described in detail by Chang (8) was used for obtaining static adsorption isotherms at 32°C with pure cis- and trans-dichloroethylenes on both catalyst and support. Before measuring static isotherms, the support or catalyst was activated in vacuo at 190°C.

H_2 chemisorption at 190°C was used to determine the Pt dispersion and the specific surface area following the procedure outlined by Spenadel and Boudart (9). The

ratio of hydrogen atoms adsorbed to atoms of Pt on the catalyst was 0.975. The metal surface area was 1.34 m^2/g.

Flow adsorption–desorption experiments were also made; and, for these, catalyst activation was in flowing helium at 190°C for 2 hr. Adsorbent temperature was then fixed at 32°C in flowing helium and vaporized cis- and trans-dichloroethylenes adsorbate at fixed vapor pressure in flowing helium (74.1 cc/min) was abruptly passed over the catalyst. Sequential effluent analyses were made until the effluent analysis matched that of the feed. At this point, the adsorbate feed stream was abruptly switched to pure He at the same linear rate over the adsorbent. The desorbate analysis and quantity was sequentially measured as a function of time chromatographically to the limit of detection. While the sequential analysis flow method (because of the required integration of the composition–time curve) does not have the inherent accuracy of the gravimetric static adsorption procedure, it does permit ready observation of the time behavior of adsorption–desorption phenomena in multicomponent (rather than single component) systems—in this case mixed cis- and trans-dichloroethylenes. The integrated amount of adsorbates on the adsorbent at adsorp-

tion steady state was also determined directly by the flooding technique described for the reaction studies; and this provides an inherently accurate direct measure of adsorption quantity, with no need for integration of time-dependent analyses.

Analysis

A Varian Acrograph Series 1200 flame ionization detector gas chromatograph with a 10% squalane on Chromosorb PAW 80/100 mesh, 10 ft × ⅛ in. o.d. SS column was used for analyses. Helium was used as a carrier gas. For product gas stream analyses, C_2H_6, C_2H_3Cl, and C_2H_5Cl separated at room temperature. The column temperature was then raised to 70°C at a rate of 33°C/min to separate the *cis*- and *trans*-dichloroethylenes and 1,2-$C_2H_4Cl_2$. For the CCl_4 flooding solution analysis, isothermal separation at 70°C of all the species was had.

To test for heavier species in the flooding samples, a Perkin–Elmer gas chromatograph with dual flame ionization detectors and a 50 ft SCOT *meta*-bisphenoxy phenoxy benzene–Apiezon L column was used at a column temperature of 150°C.

RESULTS

Static adsorption and desorption isotherm data at 32°C for both pure *cis*- and *trans*-$C_2H_2Cl_2$ on both catalyst and support are plotted in Fig. 2. There is no observable hysteresis on desorption and therefore, there is no activated adsorption in this system. Adsorption isotherms at 32°C were also measured in the flow mode (by the flooding procedure), passing pure *cis*- and *trans*-$C_2H_2Cl_2$ individually at partial pressures ranging from 0–33 Torr and a fixed liquid hourly space velocity (LHSV) of 0.52. Appropriate blank corrections were applied by subtracting the amounts of *cis*- and *trans*-$C_2H_2Cl_2$ adsorbed by the empty reactor from the adsorption quantities measured when catalyst was in the reactor.

Figure 2 shows a close agreement between the flow and static adsorption results for pure species over the catalyst, except that for *trans*-$C_2H_2Cl_2$ at higher
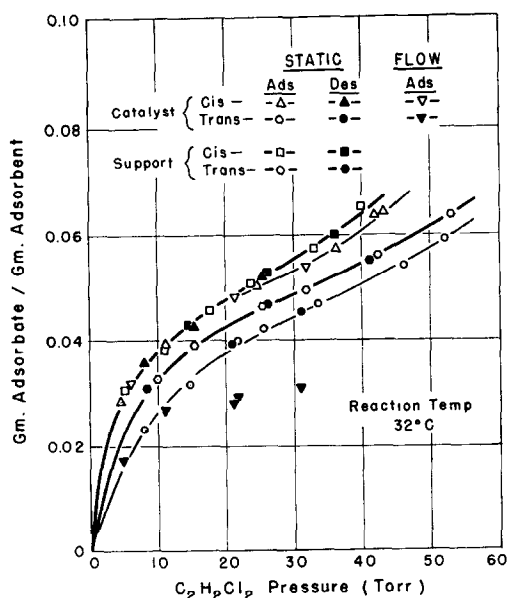
FIG. 2. Flow and static adsorption results for pure species over catalyst agree closely: Absence of hysteresis suggests no significant chemisorption in the system.

partial pressures, flow adsorption quantities fall below those measured by the static isotherms.
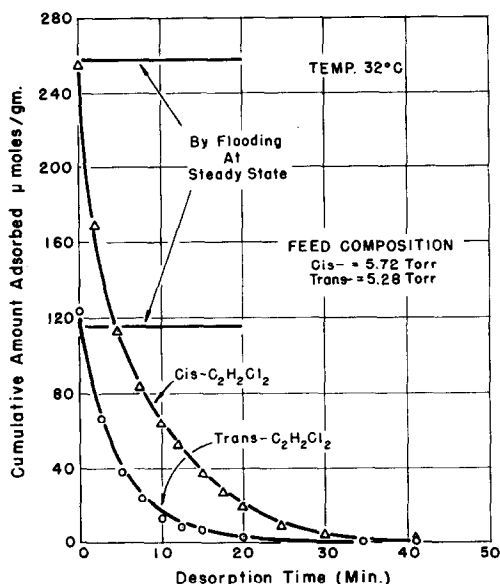
Figure 3 shows a plot of the 32°C desorp-

FIG. 3. Adsorbate quantity in a flow system can be measured either by sequential analysis of desorbates or by flooding the reactor with CCl_4 and dissolving adsorbate off the catalyst.

tion dynamics from catalyst brought to adsorption steady state by passing 52% *cis*- and 48% *trans*-C₂H₂Cl₂ feed mixture over it. The cumulative amount of each desorbing species is plotted as a function of the desorption time and the value measured by a separate flooding experiment is also shown in Fig. 3. Agreement between the methods is excellent.

Cis- and *trans*-dichloroethylene adsorption isotherms on support (without Pt) are unaffected by whether the diluent gas is helium or hydrogen, in the absence of HCl. Catalyst pretreatment temperature does have an effect. We do not know whether the HCl generated in the reaction affects the adsorption–desorption behavior of reactants on catalyst and/or support; and we have not yet directly measured the adsorption–desorption properties of HCl. The effect of Pt dispersion also remains to be characterized. Data published previously (*4*) showed that wide variations of activity and selectivity were possible depending on the mode of preparation of 0.5% Pt on η-Al₂O₃, a probable result of Pt dispersion differences.

Adsorption isotherms for the 52.0 mole % *cis*-, 48.0 mole % *trans*-dichloroethylene mixture were measured in the flow mode and fitted to the Langmuir equation for two-component adsorption (*10, 11*). Figure 4 shows these data, from which monolayer capacities and adsorption equilibrium constants were calculated. These values are tabulated in Table 1; and results from
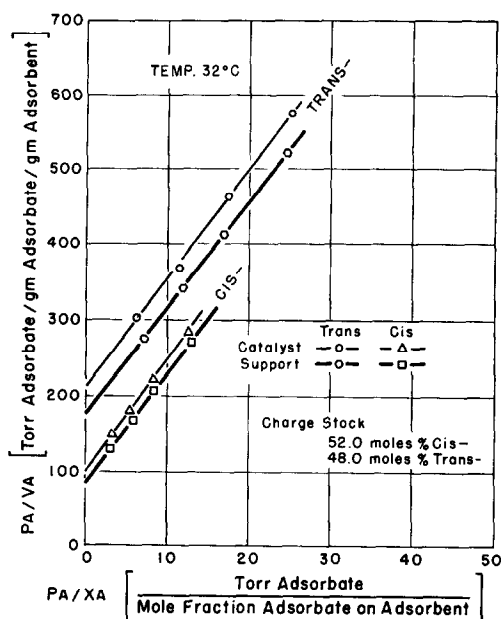

Fig. 4. *Cis*- and *trans*-C₂H₂Cl₂ mixture adsorption data obtained in the flow mode fit well to the Langmuir criteria for two-component physical adsorption.

the flow experiments with the *cis*- *trans*-mixture are compared with flow and static results for pure *cis*- and *trans*-. Table 1 also lists N₂ BET results.

Table 1 shows a close agreement of monolayer capacities and Langmuir coefficients measured with the mixture by the flow technique and for the single species by both flow and static adsorption. All adsorbents were heat treated at 190°C. The flooding procedure quantitatively recovers

TABLE 1

COMPARISON OF FLOW AND STATIC ADSORPTION RESULTS

190°C heat treatment

| | | Temp (°C) | Monolayer capacity [liquid adsorbate (ml/g)] | | | Langmuir K (Torr⁻¹) | | |
| | | | Pure species | | Mixture | Pure species | | Mixture |
			Static	Flow	Flow	Static	Flow	Flow
Support	*cis*	32	0.061	—	0.067	0.175	—	0.174
	trans	32	0.061	—	0.069	0.115	—	0.085
	N₂	−195	0.067	—	—	0.0426	—	—
Catalyst	*cis*	32	0.061	0.060	0.066	0.183	0.183	0.160
	trans	32	0.071	0.069	0.069	0.053	0.053	0.068
	N₂	−195	0.067	—	—	0.0426	—	—

the species on the adsorbent, giving valid results for a mixture and results equivalent in reliability (if not accuracy) to those obtained for individual species by static techniques. The important point is that, for the reaction studies which will now be discussed, the reliability of the flooding method for measuring quantitatively the species on a catalyst has been established.

Measurement of Adsorbed Species During Reaction

Having shown that the flooding method used is reliable and that the system is physically adsorbed, a mixture of H_2 and He was then used over the catalyst as the carrier gas in place of He at $32 \pm 0.2°C$, $p_{H_2} = 48.5 \pm 0.5$ Torr, $p_{C_2H_2Cl_2} = 10.8 \pm 0.2$ Torr, $p_{total} = 745 \pm 5$ Torr, LHSV = 0.25–3.85, and using a 50.3% cis-, 49.7% $trans$-$C_2H_2Cl_2$ feed mixture. After the reaction reached steady state, as indicated by constant product analysis, the reactor was flooded with CCl_4. The reaction is highly exothermic, 64.9 kcal/mole heat of reaction (12), so, to avoid any severe inter-particle and intraparticle temperature gradients, experiments were confined to low conversion ranges. Figure 5 is a plot of total fractional cis- plus $trans$-$C_2H_2Cl_2$ conversion and the reaction rate of each species vs space time at the fixed conditions. Reaction rate is independent of conversion level at fixed temperature and partial pressures.

Relative mole fractions of all products and unreacted species are plotted as a function of dichloroethylenes conversions in the gas phase in Fig. 6. The order of production is $C_2H_6 > C_2H_3Cl > C_2H_5Cl > 1,2\text{-}C_2H_4Cl_2$ (except for C_2H_3Cl beyond 10% conversion), which is in inverse relation to increasing boiling points.

The amounts (μmoles/g of catalyst) of the different species measured on the catalyst are plotted against the average total fractional feed conversion in Fig. 7. Cis- and $trans$-$C_2H_2Cl_2$ were the major species present on the catalyst—all other product species were found in minute quantities only. In the conversion range studied (0.6–20%), the gas analyses of Fig. 6 showed that the influent and effluent ratio of cis-
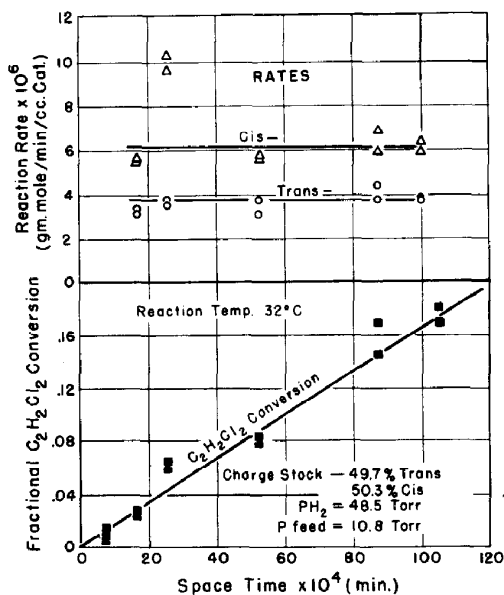

FIG. 5. Both cis- and $trans$-$C_2H_2Cl_2$ reaction rates remain independent of conversion level at fixed temperature and fixed $C_2H_2Cl_2$ and H_2 partial pressures.
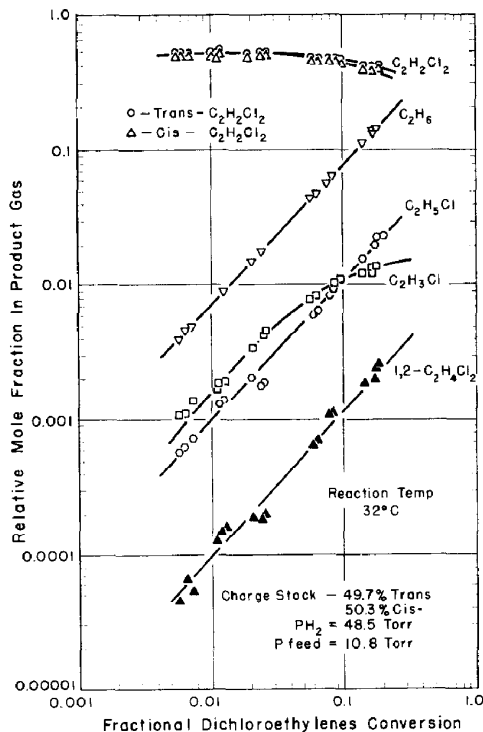

FIG. 6. The order of production in the $C_2H_2Cl_2$ hydrodechlorination reaction is $C_2H_6 > C_2H_3Cl > C_2H_5Cl > 1,2\text{-}C_2H_4Cl_2$ (except for C_2H_3Cl beyond 0.10 fractional $C_2H_2Cl_2$ conversion). This is an order opposite to increasing boiling points.
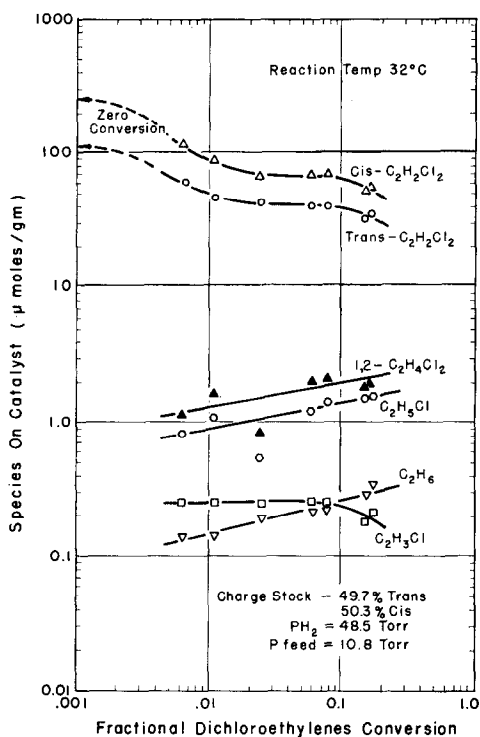
FIG. 7. The amounts of $C_2H_2Cl_2$ reactants on the catalyst are a function of conversion at fixed partial pressure and temperature: The quantities of product species on the catalyst rank in the order of boiling points and in opposite order to production rates.

to trans-$C_2H_2Cl_2$ remained almost constant at 1:1 and 0.95 ± 0.05:1 respectively. On the other hand, Fig. 7 shows that a dramatic decrease with conversion (far beyond that accountable by reaction alone) in the amounts of cis- and trans-$C_2H_2Cl_2$ actually adsorbed on the catalyst occurs. At conversions as low as 2.5%, for example, both cis- and trans-$C_2H_2Cl_2$ adsorbed on the catalyst fall to 27 and 38% of their respective values measured at zero conversion in helium. Since the partial pressure of total reactants was practically constant, the amount of reactants on the catalyst is a function of extent of reaction, rather than the partial pressures.

Anderson's criterion (13) was used to compute the possible effect of intraparticle (within the catalyst pellet) and interphase (between the catalyst surface and the bulk gas phase) temperature gradients for the purpose of establishing that high surface temperatures were not the reason that the amounts on the catalyst were a function of extent of reaction. It was found that the possible deviation of the measured reaction rate could be no more than 5% from the true isothermal rate. Interphase gradients were calculated to be between 0.03–0.17°C for the entire conversion range studied. The method suggested more recently by Bercovich and Jaine (14) was also used to calculate the possible temperature gradients. They only amounted to 0.26–0.53°C, still too small to account for the observed differences in the quantities of species on the catalyst.

A second explanation for the reduced quantities of the reactants measured on the reactive surface as a function of conversion at constant reactant partial pressure could be attributed to the possibility that dichloroethylenes react during the time CCl_4 competitively displaces them from the surface and terminates the reaction. If such a time lag is assumed to be 5 sec, the total cis- + trans-$C_2H_2Cl_2$ that reacted would be of the order of only 1.2 μmoles/g, while the observed decrease in dichloroethylenes is on the order of 250 μmoles/g.

Product species (C_2H_6, C_2H_3Cl, C_2H_5Cl and 1,2-$C_2H_4Cl_2$) on the catalyst were found to be present in only minute quantities. The amounts on the catalyst are proportional to increasing boiling points, the opposite of production rates. The CCl_4 solutions were analyzed for heavier species and no measurable quantities could be detected.

Even though CCl_4 has been found to react at a comparable rate of 5×10^{-6} g mol/min/cm^3 of cat at 32°C to $CHCl_3$ and CH_4 (6) on 0.5% Pt on η-Al_2O_3 catalyst (the same catalyst as used for this study), no $CHCl_3$ and CH_4 were detected in the CCl_4 quench solutions. The amounts of H_2 on the catalyst surface could not, therefore, be inferred from the yield of these species and must have been quite small.

Figure 8 is a plot of both the ratio of cis- and trans-reaction rates and the ratio of adsorbed cis- and trans- on the catalyst
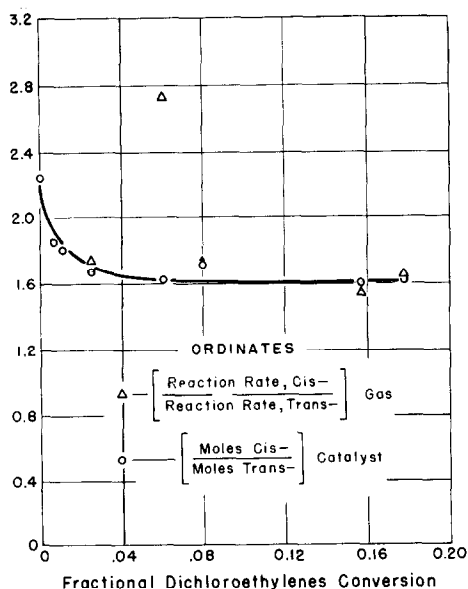
FIG. 8. Approximate 1:1 correlation between the observed (cis/trans) reaction rate ratio and measured (cis/trans) surface coverage ratio.

the species involved. Ideal gas and solution behavior were assumed. Results calculated for the lowest and highest conversions are compared with those obtained from direct measurement (assuming that the surface covered by H_2 and HCl is small in comparison with the rest of the species) in Table 2. The measured amounts on the catalyst rank in the same order but different quantities from those predicted by the relative volatility calculations. Note that the quantities of trace species are not related to the reaction rates to produce them.

To ensure that surface phenomena, rather than transport phenomena were being observed, effectiveness factor was experimentally determined and found to be unity. Cis- plus trans-conversions (at 11.0 Torr mixed feed, 45.5 Torr H_2, 32°C, and 0.00175 min space time) were practically a standoff for the $\frac{1}{16} \times \frac{1}{8}$ in. pellets (1.16%) and pellets ground and screened to −150 mesh (1.15%). Quan-

TABLE 2

CORRELATION OF QUANTITIES ON THE CATALYST WITH RELATIVE VOLATILITY

	Relative mole fraction on the catalyst			
	0.65% Total feed conversion		17.7% Total feed conversion	
Component	From equilibrium calculations	Measured	From equilibrium calculations	Measured
C_2H_6	0.0000403	0.000722	0.00166	0.00336
C_2H_3Cl	0.000110	0.00132	0.00161	0.00216
C_2H_5Cl	0.000141	0.00445	0.00621	0.0147
trans-$C_2H_2Cl_2$	0.380	0.346	0.404	0.366
cis-$C_2H_2Cl_2$	0.619	0.641	0.578	0.596
1,2-$C_2H_4Cl_2$	0.000175	0.00579	0.0084	0.0179

vs total feed conversion. Figure 8 shows that in the conversion range of 2–20% there is approximately a 1:1 correlation between the observed reaction rate ratio to the corresponding surface coverage ratio. For conversions less than 2%, since the individual cis- and trans-reaction rates are a difference of two large numbers, ratios cannot be calculated with accuracy.

The composition of the liquid which was in equilibrium with the gas phase was calculated from the composition of the gas phase and from vapor pressure data for

tities adsorbed on the catalysts were also independent of particle size:

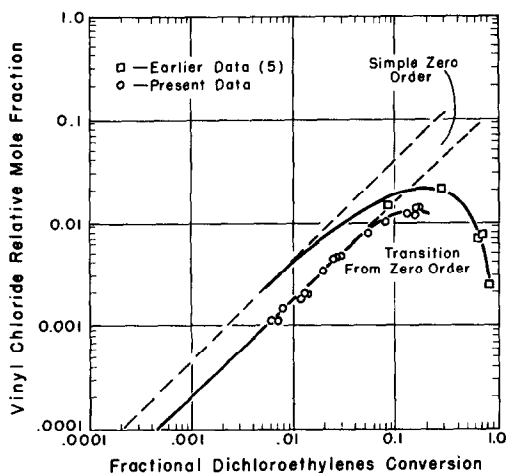| Component	μmoles/g on catalyst	
	Pellets	Powder
C_2H_6	0.20	0.27
C_2H_3Cl	0.27	0.25
C_2H_5Cl	0.37	0.37
trans-$C_2H_2Cl_2$	49.3	55.9
cis-$C_2H_2Cl_2$	99.0	100.3
1,2-$C_2H_4Cl_2$	0.34	0.46

FIG. 9. Comparison of earlier selectivity data (5) with the present data: Depletion in amounts of the reactants on the surface with conversion may account for the shift from zero order kinetics at higher conversions.

Figure 9 is a selectivity plot of vinyl chloride relative mole fraction vs dichloroethylenes fractional conversion. Selectivity data reported earlier (5) on a similarly prepared catalyst are compared with the present data. Difference in the two curves is probably due to the different preparations. It was shown earlier that the deviation at higher conversions from the zero order straight-line relationship corresponded to neither a transition to first order surface controlled behavior nor a transition to pore diffusion controlled regimes. The present study corroborates this behavior, and the depletion of the quantity of reactants on the catalyst surface with conversion (at constant gas phase partial pressures) is probably the explanation for the observed shift in kinetics of the consecutive reaction system.

DISCUSSION OF RESULTS

To explain the phenomena that have been observed, consider the fact that the active sites of this catalyst only occupy 1.34 m^2/g as measured by H_2 chemisorption, compared to the total physical adsorption area of 190 m^2/g, measured by N_2 BET. Langmuir theory states that at ad-
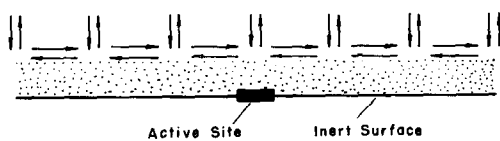

FIG. 10. Uniform surface coverage, no reaction.

sorption–desorption equilibrium, there is no difference in the rate of each process for a physically adsorbed nonreacting system. Similarly, at any point on the surface, net lateral surface diffusion rates must be identical at equilibrium. The schematic below indicates two-dimensionally the small fraction of surface occupied by the active site and adsorption–desorption and surface diffusion rates in a nonreacting equilibrium system. In such a nonreacting system, the amounts of species that will be measured to be adsorbed will be mainly a function of the much larger inert surface, rather than the active site. On the other hand, rate phenomena will be mainly a function of the active site (Fig. 10).

If, in a reacting system, the area of the active site is so small that the adsorption rate of reactant from the gas stream to that site cannot satisfy the reaction demands, then lateral surface migration of the species mobilely adsorbed in the inert surface to the site will occur. In such a case, there will be, in a flow system, a steady state net flux of reactant to the site, both from the gas stream and from the surrounding inert surface. Equilibrium rates of reactant adsorption–desorption and surface migration will only be had at the equivalent of infinite distance from the site. Adsorption of the reactant on the total surface from the gas stream above is the only means for replenishment of reactant lost by reaction. Figure 11 indicates the rate vectors around the active sites and suggests, by the density gradient of adsorbed
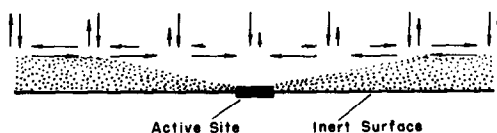

FIG. 11. Reactant concentration gradients due to reaction at site.

reactant molecules, the depletion of reactant in the vicinity of the site.

In a recent study of propylene disproportionation, Moffat et al. (15) pointed out that highly active cobalt–alumina–molybdate catalyst exhibited no diffusion limitation, while WO_3 on silica catalyst, which was less active, did. They suggested that the explanation could have been that the cobalt catalyst had a large number of moderately active sites distributed over its entire surface, while the tungsten catalyst had very few sites, which were highly active and disperse. The WO_3 amounted to only 5% of the catalyst external surface area. Aris (16) has considered the case of an irreversible first order reaction taking place at the boundary of an isolated reaction site in a plane. The flux to the site by surface diffusion was assumed equal to the reaction rate if there were no limitation of mass transfer from the gas to the surface. Effectiveness factors are presented for the situation where concentrations fall below adsorption–desorption equilibrium levels.

The experimental observations for the zero order hydrodechlorination system support the type of behavior inferred by these investigators. The amounts of all species on the catalyst rank in order of boiling points—even that of vinyl chloride which, as an intermediate, should be present in significantly higher quantities—rather than in order of production rates. This follows if reactants and products are generated at only the limited active site area rather than over the entire surface. The measured depletion of reactants on the surface as a function of conversion at constant partial pressure and temperature could indeed be a manifestation of the required surface diffusion process.

It was fortunate in this study involving physically adsorbed species that reaction rates were slow enough to allow use of the flooding technique. Surface diffusion is apparently so important a process that it should not be neglected when fitting kinetics of reactions on catalysts with dispersed active sites, as not only activity but also selectivity is affected.

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