# Initial Rates of Propylene Disproportionation Over WO₃ on Silica Catalysts

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Initial rate data were obtained for the disproportionation of propylene over a 10% WO₃ on silica gel catalyst. Temperatures of 399–454°C and pressures from 1 to 9 atm were used. The experimental data were well correlated by assuming that a dual-site surface reaction was the rate-controlling step in the reaction mechanism. The mechanism parameters and their temperature dependence were extracted from the experimental data using a least-squares technique.

Anomalously high linear velocities through the reactor were necessary for the elimination of interphase mass-transport limitations, and this was attributed to particle-to-particle variations in promoter level.

## INTRODUCTION

In 1964, Banks and Bailey (1) reported a new catalytic reaction that they called olefin disproportionation. Several catalytic systems have been reported to be active for olefin disproportionation (2). In all cases where the surface reaction mechanisms have been studied, a second-order reaction between adjacently adsorbed olefins has been proposed (3–6), except in the tungsten oxide–silica system (7).

In this latter system, Begley and Wilson (7) conducted a kinetic study of propylene disproportionation over a silica catalyst containing 9 wt % WO₃, using an integral reactor. Data were taken over a pressure range of 2–60 atm at temperatures between 320 and 440°C. Two rival models were proposed: (1) a model based on a second-order reaction between adjacently adsorbed propylene molecules (Langmuir–Hinshelwood), and (2) a model based on a second-order reaction between an adsorbed propylene molecule and a propylene molecule in the gas phase (Rideal). Model discrimination was made on the basis of the ability of the integrated forms of the two proposed mechanisms to correctly predict the observed changes in conversion as a function of total pressure. The Rideal model was found to correlate the data better than the Langmuir–Hinshelwood over the range of variables studied. Recently, others (8, 9) have shown that the system of Begley and Wilson had severe mass-transfer limitations.

The object of this work was to use initial rate data to obtain a reliable rate equation for propylene disproportionation over a catalyst consisting of 10 wt % WO₃ on a silica gel support. However, before seeking this initial rate data, it was necessary to determine experimentally the minimum reactor operating conditions needed to insure negligible interphase and intraparticle mass transfer effects.

## EXPERIMENTAL

Interphase mass transfer studies were made using a split bed reactor similar to that described by Moffat *et al.* (9). This type of reactor design allows two separate catalyst charges to be prepared with exactly the same activation history. The reactors were constructed of two 3⁄8 in. o.d., 316 stainless-steel tubes 6 in. long. The two reactors were connected in series with valves installed to direct the feed

over both beds or only over the first. The preheater was prepared by winding a 7-ft section of ⅛ in. o.d., 316 stainless-steel tubing into a coil of approximately 1 in. diameter. The reactor and the preheater were placed in a tubular resistance-heating furnace.

Intraparticle mass-transfer studies were made by determining the specific reaction rate as a function of catalyst particle diameter. Care was taken to choose reactor operating conditions such that interphase mass transfer would be negligible.

Initial rates were measured at 399, 427, and 454°C and at pressures ranging from 1 to 9 atm in a near-differential fixed bed reactor. The catalyst was prepared by the Davidson Chemical Division of W. R. Grace and Company. It consisted of 10% $WO_3$ on silica gel prepared by impregnating 3/16-in. silica extrusions with ammonium tungstate. This catalyst was found to have a BET surface area of 223 $m^2/g$. It was activated in dry air for 5 hr at 600°C.

The reactor for the initial rate studies was a section of ⅜ in. stainless steel tubing placed in a tubular resistance-heating furnace. A more detailed description of this system can be found elsewhere (10). A tuft of stainless-steel wire gauze supported the catalyst charge of from 0.07 to 0.3 g. The catalyst particle size was −40/+50 mesh (387 $\mu$m).

Product analysis was made using an in-line Hewlett–Packard 5754-B gas chromatograph fitted with a 30-ft dimethyl sulfolane on chromosorb W(−30/+60) column operated at room temperature.

## RESULTS

Figure 1 shows the effects of interphase mass transport. The curves marked Set 1 are data from a high-activity catalyst, and the lower pair marked Set 2 are for a less active catalyst. The lower set of curves were obtained at reduced activity by bypassing the feed dryers and allowing the slightly moist feed to contact the catalyst. This depression of catalyst activity by moisture is a reversible effect which has been reported elsewhere (12). Each curve in a set represents conversion versus space
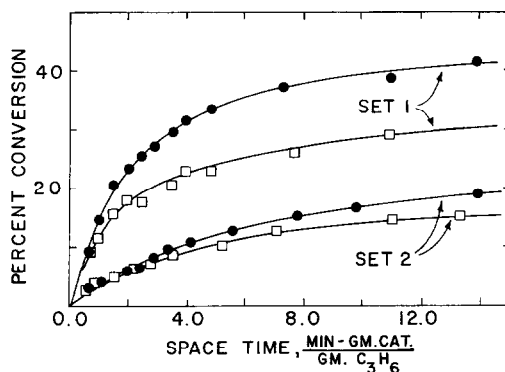


FIG. 1. Percent conversion vs space time for two levels of catalyst activity (□ = 1.0 g of catalyst, ● = 1.5 g of catalyst).

time for a particular weight catalyst charge. The upper curve in each set are data for a catalyst charge 50% greater in weight than that used to generate the associated lower curve. Thus, at a particular space time, the linear velocity in the upper curve is 1.5 times that in the associated lower curve. This difference in linear velocity has an effect on conversion only if interphase mass transfer effects are significant. It will be observed that space times of the order of two min or less are needed to gain substantial convergence of the curves in each set.

Data were obtained using different particle sizes to determine the effects of intraparticle mass transfer. A feed stream of pure propylene was used and typical data are shown in Fig. 2.
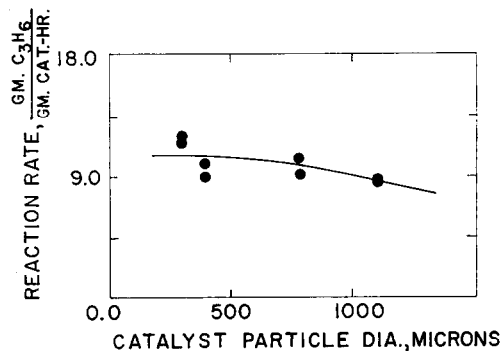


FIG. 2. Effect of catalyst particle diameter on reaction rate (space time = 0.67 min, 1.5 g of catalyst).

The initial rate data are shown in Fig. 3. Conversion levels were in the range of 4–12% and space times were in the range of 0.01–0.2 min with most measurements in the 0.02–0.06-min range.

For the catalytic disproportionation of propylene with the rate controlled by a dual-site surface reaction, the complete rate equation is given by:

$$r_1 = \frac{k(P_P^2 - P_E P_B/K_{Eq})}{(1 + K_E P_E + K_P P_P + K_B P_B)^2}. \quad (1)$$

Applying the initial rate assumption of near-zero partial pressures of products, Eq. (1) reduces to:

$$r_1 = k P_P^2/(1 + K_P P_P)^2. \quad (2)$$

Equation (2) may be rearranged to give

$$P_P/r_1 = (1/k) + (K_P/k)P_P. \quad (3)$$

Thus a plot of $P_P/r_1$ versus propylene partial pressure should be linear if Eq. (1) represents the rate-controlling mechanism step. Figure 4 illustrates the data of Fig. 3 correlated by Eq. (3). Using linear least squares, the rate constant and the propylene adsorption coefficient were determined. Figure 5 illustrates the temperature dependency of these two parameters.

## Discussion

Figure 1 shows that space times of the order of 0.5–2.0 min are required to eliminate the effects of interphase mass transport. Since these effects depend upon catalyst activity as well as the linear velocity over the particle surface, the higher activity catalyst required a higher linear veloc-
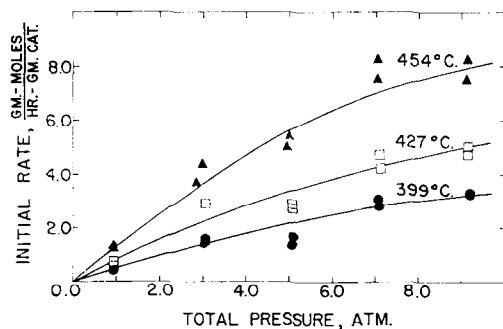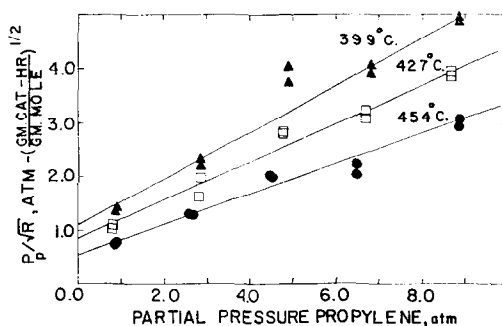


Fig. 4. Langmuir Hinshelwood model with initial rate assumptions.

ity. This is of course reflected by the lower required space time.

It should also be pointed out that while the conditions for the elimination of interphase mass transport effects have been experimentally demonstrated, these conditions are significantly more severe than the currently accepted mass transfer correlation would predict (13). Thus these data confirm the anomalous interphase mass transfer effects reported by Moffat et al. (8, 9) for this same system. A possible reason for this anomalous behavior may be nonuniform impregnation of the original silica support. Assuming such an anistotropic distribution of promoter, the observed anomalous mass transfer effects become reasonable. Upon crushing and screening of the 3/16 in. diameter pellets to prepare the small particles used in this investigation, a random distribution is obtained of the original pellet, some particles coming from the center of the pellet, some coming from the regions nearer to
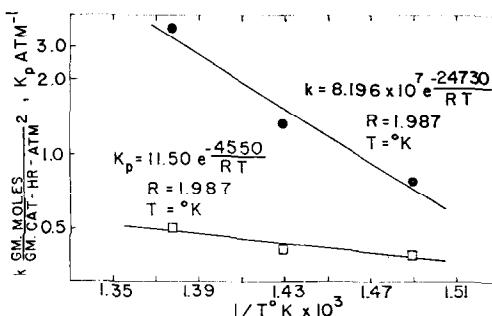


Fig. 3. Initial rate vs total pressure.



Fig. 5. Temperature dependency of $k$ and $K_P$.

the surface, and some particles actually containing a portion of the original pellet surface. For a reactor bed of these particles, there would result a distribution of activity within the bed, since some particles would contain relatively large quantities of promoter while others would perhaps contain little or no promoter. This would be reflected by a difference in activity from particle to particle. To eliminate interphase mass transfer effects, the space time would need to be adjusted to eliminate interphase mass-transfer effects at the periphery of the most active particles. This would be a much shorter space time than one would predict using existing mass-transfer correlation and assuming that the promoter were uniformly distributed.

To check the possibility of anisotropic promoter distribution within the original $\frac{3}{16}$ in. diameter extrudates, two pellets were cleaved and an electron probe scan was made of the cloven surface. It was found that areas near the original pellet surface contained about 30% $WO_3$, while at the center of the original pellet there was but 6.5% $WO_3$. Thus, at least a portion of the observed anomalous interphase mass transfer effects would appear to be attributable to anisotropy in the distribution of promoter. This variation in activity from particle to particle would have an effect on mechanism studies only if changes in promoter level induced a change in the mechanism of the surface reaction.

When intraparticle mass transfer is a significant factor, changes in particle diameter result in substantial changes in the observed reaction rate. In regions in which intraparticle mass-transfer is not an important factor, changes in particle diameter have essentially no effect on the observed reaction rate. While some scatter exists in the data presented in Fig. 2, it is apparent that although particle diameters were varied by almost an order of magnitude, there was only a slight, if any, increase in observed reaction rate with decreasing particle size. Thus, for particle diameters below 400 $\mu$m, intraparticle mass-transfer effects appear negligible, and an effectiveness factor of 1 can be assumed.

The preceding analysis of the initial rate data shows that initial rates of propylene disproportionation over tungsten oxide on silica gel are well correlated by a rate expression based upon a Langmuir–Hinshelwood mechanism in which the rate-controlling step in the reaction is assumed to be a dual-site surface reaction.

Begley and Wilson (7) have proposed a rate expression based upon a Rideal mechanism in which the rate-controlling step in the reaction has been assumed to be a reaction between an adsorbed molecule and a gas phase molecule. The complete Rideal rate equation is given by:

$$r_2 = \frac{k(P_P{}^2 - P_E P_B / K_{\text{Eq}})}{(1 + K_E P_E + K_P P_P + K_B P_B)}. \quad (4)$$

Again applying the initial rate assumption of near-zero partial pressure of products, Eq. (4) becomes:

$$r_2 = k P_P{}^2 / (1 + K_P P_P). \quad (5)$$

Equation (5) may be rearranged to give:

$$P_P{}^2 / r_2 = (1/k) + (K_P/k) P_P. \quad (6)$$

Thus a plot of $P_P{}^2/r_2$ vs $P_P$ should be linear. Figure 6 illustrates the data of Fig. 3 correlated by Eq. (6). Using linear least-squares, the rate constant and the propylene adsorption coefficient were determined.

Model discrimination between two rival models has been reviewed by Kittrell (11). He outlines both qualitative and quantitative methods of model discrimination. Qualitative methods generally are most successful when applied to the simplest possible model form, such as initial rate
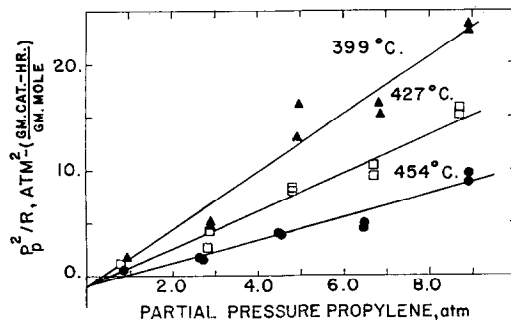


FIG. 6. Rideal model with initial rate assumptions.

data. One qualitative method is based on examining the linearized forms of the two rival models such as Eqs. (3) and (6). In comparing Figs. 4 and 6 using this criterion, the Langmuir–Hinshelwood form appears to correlate the data better. A second qualitative criterion is that the rate and adsorption constants estimated using these linearized forms should be positive. These are given in Table 1 for the two models under consideration. The Langmuir–Hinshelwood form, Eq. (3), correlates the data with positive rate and adsorption constants at each temperature studied. The Rideal form, Eq. (6), correlates the data with negative rate and adsorption constants at each temperature. Thus the Rideal form yields unreasonable values based on this second criterion.

Kittrell (11) also describes a quantitative method of model discrimination based upon a nonintrinsic discrimination parameter. This method involves the definition of a new dependent variable as:

$$z = r - [(r_1 - r_2)/2], \qquad (7)$$

where $r$ is the observed reaction rate at a given set of conditions and $r_1$ and $r_2$ are predicted reaction rates of the two rival models at the same conditions, using the least-squares estimates of the parameters within each model. This variable is then used to estimate the discrimination parameter, $\lambda$, by least-squares using the following model:

$$z = \lambda(r_2 - r_1). \qquad (8)$$

If $r_1$ is the correct model, $\lambda$ should equal $-\frac{1}{2}$, while if $r_2$ is the correct model, $\lambda$

### TABLE 2
DISCRIMINATION BETWEEN THE LANGMUIR–HINSHELWOOD MODEL AND RIDEAL MODEL

| Temperature, °C | Discrimination parameter |
|---|---|
| 454 | $-0.4932 \pm 0.2136$[a] |
| 427 | $-0.4480 \pm 0.3236$[a] |
| 399 | $0.2788 \pm 1.0105$[a] |

[a] 95% confidence interval.

should equal $+\frac{1}{2}$. Table 2 contains the discrimination parameter found by this method at each temperature studied together with 95% confidence intervals. Although no discrimination can be made at the lowest temperature studied by this method, the Langmuir–Hinshelwood is unequivocally the better model at the two higher temperatures.

These results are at variance with the disproportionation kinetics proposed by Begley and Wilson (7). Others have since shown (8, 9) that severe mass-transfer effects existed in the study. Such effects make the model discrimination made by Begley and Wilson somewhat in question. Also, the data of Begley and Wilson were obtained in an integral reactor, and such data would be expected to be less sensitive to the reaction model than the differential data given here.

This work brings the reaction model of propylene disproportionation over tungsten oxide on silica into agreement with the reaction models obtained by others (3–6) on similar systems used for propylene disproportionation and substantiates the concept of a quasicyclobutane-type interme-

### TABLE 1
LEAST-SQUARES ESTIMATES OF THE RATE CONSTANT AND PROPYLENE ADSORPTION COEFFICIENT FOR THE LANGMUIR–HINSHELWOOD AND RIDEAL MODELS

| Temperature °C | Langmuir–Hinshelwood | | Rideal | |
|---|---|---|---|---|
| | $k$ g-moles / g cat-hr-atm$^2$ | $K_P$ atm$^{-1}$ | $k$ g-moles / g cat-hr-atm$^2$ | $K_P$ atm$^{-1}$ |
| 399 | 0.7928 | 0.3933 | $-1.0052$ | $-2.7243$ |
| 427 | 1.3279 | 0.4087 | $-1.0501$ | $-1.6937$ |
| 454 | 3.2876 | 0.5116 | $-1.1704$ | $-0.9054$ |

diate as is now generally accepted (*2*) for this reaction.

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