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Initial Rates of Propylene Disproportionation

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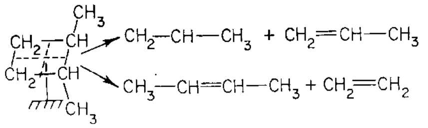
Initial differential rate data was obtained for the disproportionation of propylene over a $CoO–MoO_3–Al_2O_3$ catalyst. Temperatures of 394–478°K and pressures of from 1 to 9 atmospheres were used. The experimental data were well correlated by assuming a dual site surface reaction was the controlling step in the reaction mechanism. The mechanism parameters and their temperature dependence were extracted from the experimental data using a least squares technique.

INTRODUCTION

Since the original publication (*1*) on the catalytic disproportionation of olefins by workers at Phillips Petroleum Company, results of several other studies on such systems have been reported. Bradshaw *et al.* (*2*) proposed that olefin disproportionation proceeds via a "quasi-cyclobutane" intermediate. Disproportionation of propylene on a tungsten oxide–silica catalyst was studied by Begley and Wilson (*3*). They reported their kinetic data for disproportionation to be better correlated by a rate expression based upon a Rideal mechanism than by an expression based upon a Langmuir–Hinshelwood mechanism. Several investigators (*2, 4, 6*) have postulated the existence of a four-membered carbon ring intermediate which can be represented as



with the product pair obtained depending upon where the above intermediate breaks. Using propylene-2-^{14}C it was found that the butene formed was radioactive while the ethylene did not exhibit radioactivity. Mol *et al.* (*4*) suggest that a four-membered cyclobutadiene ring intermediate is the '"quasi-cyclobutane" intermediate suggested by Bradshaw *et al.* (*2*).

METHODS

No investigation of propylene disproportionation reported to date has utilized initial rates to obtain information as to the rate controlling step in the reaction mechanism. The initial rates reported below are the result of an investigation directed toward developing a reliable rate equation for propylene disproportionation over a catalyst consisting of 3.5% CoO and 10% MoO_3 on an alumina support. The catalyst was manufactured by the Girdler Catalyst Department of Chemetron Chemical Company of Louisville, Kentucky, and is reported to have a surface area of 216 m^2/g and a pore volume of about 0.18–0.21 cm^3/cm^3. The catalyst was activated in dry nitrogen for 5 hr at 840°K. Initial rates were measured at 394, 436, and 478°K and at pressures ranging from 1 to 9 atm in a differential fixed-bed reactor. Space velocities ranged from 1.5 to 5.25 g moles/hr g catalyst. The reactor was a section of ⅜ in. stainless steel tubing surrounded by a heated oil jacket. A tuft of wire gauze supported the catalyst charge of from 0.15 to 0.60 g. The catalyst particle size was $-20 + 30$ mesh (0.028 in.), a particle size such that the effects of mass and heat transfer were demonstrated to be negligible in preliminary tests. Propylene conversions were in the 4–8% range at each temperature level.

TABLE 1
INITIAL RATES AT 436°K

Total pressure (atm)	Catalyst wt. (g)	Space velocity (g moles/hr g cat.)	Conversion (g moles C_3 converted/g moles C_3 in feed)	Initial rate ($\times 10^2$; g moles/hr g cat.)
0.939	0.30	3.44	0.038	13.0
0.939	0.30	2.86	0.054	15.5
0.939	0.25	5.15	0.024	12.4
2.939	0.30	3.44	0.081	27.7
2.939	0.30	3.44	0.087	29.9
2.939	0.25	5.15	0.051	26.3

RESULTS

The results of a typical set of tests are shown in Table 1. The complete data are presented graphically in Fig. 1. These data were well correlated by a simplified form of a Hougen and Watson (*5*) type rate expression based upon a Langmuir-Hinshelwood mechanism. For the catalytic disproportionation of propylene the complete rate expression for a reaction rate controlled by a dual site surface reaction is given by

$$r = \frac{k(P_p^2 - P_e P_b/K_{eq})}{(1 + K_e P_e + K_p P_p + K_b P_b)^2}, \quad (1)$$

in which k is the reaction rate constant, K_{eq} is the equilibrium constant, K_e, K_p, and K_b, and P_e, P_p, and P_b are the adsorption coefficients and partial pressures of ethylene, propylene, and 2-butene. Applying the initial rate assumption of near zero partial pressure of products, Eq. (1) reduces to

$$r = \frac{kP_p^2}{(1 + K_p P_p)^2}, \quad (2)$$

Equation (2) may be rearranged to give

$$P_p^2/r = (1 + K_p P_p)^2/k, \quad (3)$$

or

$$P_p/r^{1/2} = a + bP_p, \quad (4)$$

where $a = 1/k^{1/2}$ and $b = K_p/k^{1/2}$. Thus a plot of $P_p/r^{1/2}$ versus total pressure ($\simeq P_p$) should be linear if Eq. (1) represents the rate controlling mechanism step. Figure 2 illustrates the data of Fig. 1, (av values plotted) correlated by Eq. (4) by least squares. Figure 3 illustrates the temperature dependency of the rate constant, k, and the propylene adsorption coefficient, K_p, determined by Eq. (4).

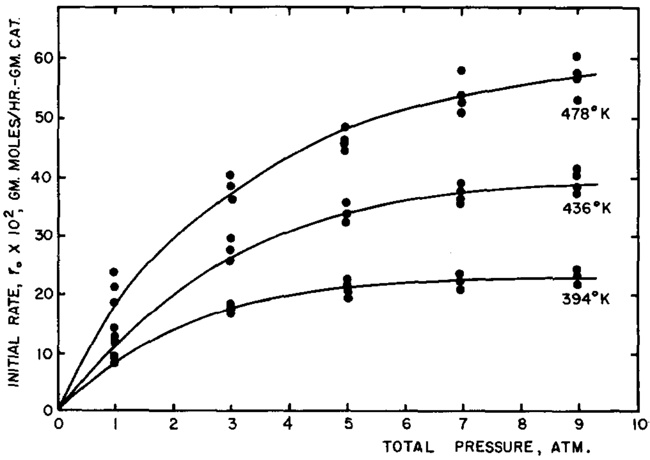


FIG. 1. Initial rates of propylene disproportionation as a function of total reactor pressure ($\approx P_p$).

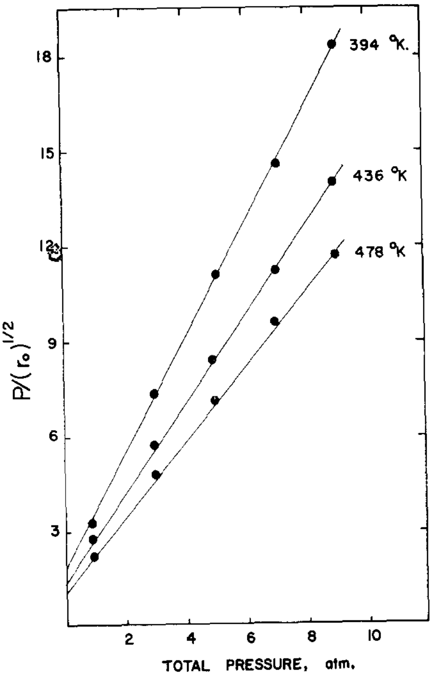


FIG. 2. Least squares correlation of initial rate with linearized form of initial rate equation. points are averages of those in Fig. 1 for clarity.

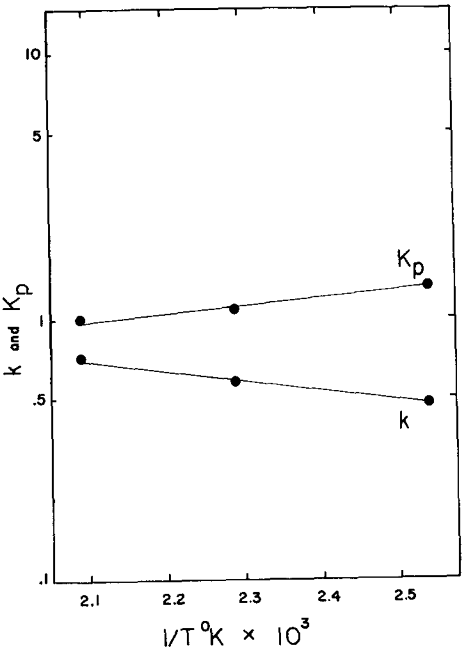


FIG. 3. Temperature dependency of parameters from least squares analysis of initial rates.

DISCUSSION

The preceding data and analysis show that initial rates of propylene disproportionation are well correlated by a rate expression based upon a Langmuir-Hinshelwood mechanism in which the controlling step in the reaction has been assumed to be a dual site surface reaction. While a number of possible mechanisms were considered, only the dual site mechanism proved successful in correlating the data. Other possible mechanisms were ruled out on the basis of improper pressure dependency of the initial rates.

For example, the single site mechanism suggested by Begley and Wilson (*3*) gives Eq. (5) which predicts that a plot of $P_p/r^{1/2}$ versus P_p will be nonlinear.

$$P_p/r^{1/2} = [(1 + K_pP_p)/k]^{1/2}. \quad (5)$$

However, it is still possible that over the experimental range of this investigation that one is simply observing an effectively linearized form of the right side of Eq. (5). To check this further, the right hand side of Eq. (5) was linearized and a linear least squares analysis was made. Analysis of these results showed unequivocally that the data were better correlated by the dual site mechanism than by the single site mechanism.

The present results are somewhat at variance with the disproportionation kinetics proposed by Begley and Wilson (*3*). But in comparing results it should be noted that a different catalyst system and much higher pressures and temperatures were used in the Begley and Wilson investigation. Also, Begley and Wilson correlated data from an integral reactor, and such data would be expected to be less sensitive to the reaction model than the differential data given here due to the integration process inherent in integral data.

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