

EFFECTS OF FLOW ON THE ACTIVITY OF A WO_3-SiO_2
OLEFIN DISPROPORTIONATION CATALYST,

by

Seala Louise Fletcher,

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APPROVED:

G. B. Wills, Chairman

R. A. Mischke

J. P. Wightman

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I. INTRODUCTION

In the chemical and petroleum refining industries many of the important chemical reactions involve the use of catalysts. Catalysts play an important role in many industrial processes because they can accelerate the rate of desired reactions to form predominately the desired products. Annually millions of dollars are spent on the development and improvement of catalysts and catalytic processes. The economics of these processes are largely dependent on the proper selection and use of the catalyst. However, there is an incomplete understanding of what is occurring at the catalyst surface, because of the coupling of physical and chemical phenomena, and much of the research is predominately empirical.

The reaction of propylene disproportionation on a tungsten oxide-silica catalyst has been the subject of considerable research aimed at clarifying its mechanism. This catalytic reaction system has been observed to exhibit some unusual and unexplainable behavior. One area of anomalous behavior for this catalyst is the protracted period of transient activity exhibited on initial exposure to propylene or following most disturbances in the steady state activity regime [34]. This catalyst also exhibits

an apparent gas mass transfer effect which is not explainable through classical considerations [38,39].

The main purpose of this investigation was to study the phenomena associated with the anomalous mass transfer behavior of the tungsten oxide-silica catalyst during propylene disproportionation.

II. LITERATURE REVIEW

Banks and Bailey [5] reported in 1964 a new catalytic reaction that they called olefin disproportionation. By this reaction linear olefins were converted into homologs of shorter and longer chain olefins in a highly specific and efficient manner. The initial catalysts disclosed for olefin disproportionation were molybdenum and tungsten hexacarbonyls and oxides supported on alumina. Since then, several catalytic systems have been reported active for disproportionating olefins [3,4,25]. These catalysts are generally metal oxides deposited on a high surface area support such as silica or alumina.

One of the catalysts reported active for disproportionating olefins is tungsten oxide on silica which operates best in the temperature range 260 to 550°C [24]. Its high selectivity and resistance to common poisons and to coke formation makes it an excellent disproportionation catalyst. This catalyst has been the subject of considerable research activity stemming from experimental observations of unusual and unexplainable behavior. One area of anomalous behavior for this catalyst is the protracted period of transient activity exhibited on initial exposure to propylene or following most disturbances in the steady state activity regime [34]. A second area of

anomalous behavior is the severe mass transfer effects exhibited by the catalyst [38,39].

A review of the literature was conducted to obtain information on the disproportionation of olefins by heterogeneous catalysts with particular emphasis placed on the disproportionation catalyst tungsten oxide on silica.

Preparation of Tungsten Oxide-Silica Catalysts

The preparation of tungsten oxide-silica catalysts have been described by Heckelsberg, Banks, and Bailey [25]. The catalyst was prepared by conventional impregnation methods. The preparation of a catalyst by impregnation involves filling the pores of a preformed support with a solution of the metal salt, evaporating the solvent, and then decomposing or reducing the metal salt [43]. The concentration of the metal may be increased by carrying out several successive impregnations. When the desired amount of metal has been added to the support, the catalyst is activated. The most common form of activation is calcination in air or nitrogen to a temperature higher than that at which the catalyst is to be used [19]. The catalyst must be heated to at least the decomposition temperature of the salt.

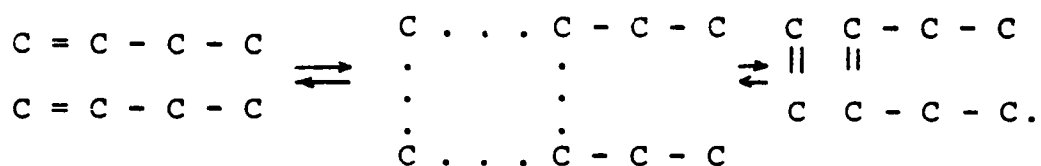
Specifically, Heckelsberg et al. [25] prepared the tungsten oxide-silica catalysts by incrementally adding

an aqueous ammonium metatungstate solution to silica gel. Between additions the catalyst was dried over a steam bath. The catalyst was activated with dry air at 540 to 600°C for one hour before use. A similar procedure is used for preparing molybdena-alumina catalysts [29].

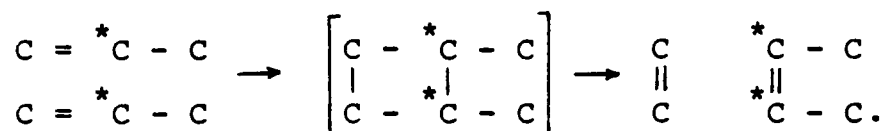
Mechanism of Disproportionation

Since the olefin disproportionation reaction was recognized as a transalkylidenation reaction which involves the cleavage of the double bond, several possible reaction mechanisms have been proposed. Presently a detailed mechanism for this reaction cannot be given with certainty. This section presents several of the more recognized reaction mechanisms.

Bradshaw, Howman, and Turner [9] were the first to propose that the disproportionation reaction proceeds via a four-center type of intermediate. Their study of the disproportionation of n-butenes using a cobalt molybdate catalyst lead to the theory that disproportionation occurs via a "quasi-cyclobutane" intermediate which is formed by correct alignment of the carbon atoms at the double bonds of two reacting olefins. They pictured the following mechanistic scheme for the 1-butene reaction



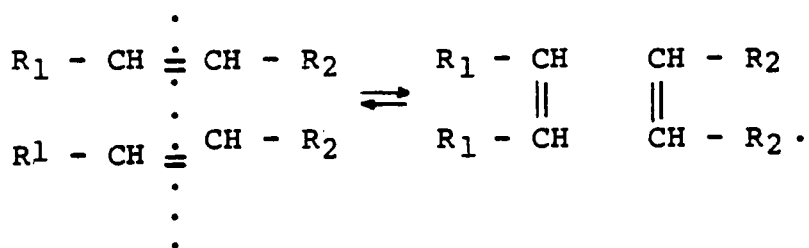
Studies with ^{14}C -labeled propylene were made by several groups of investigators in order to determine whether the position of the carbon atoms in the products conform to the four-center mechanism. Mol, Moulijn, and Boelhouwer [41] reacted propylene with ^{14}C in each of the three positions over a rhenium oxide-alumina catalyst at moderate temperatures. Their experiments supported that a four-center type of intermediate is involved in the reaction mechanism. They proposed the following mechanistic scheme



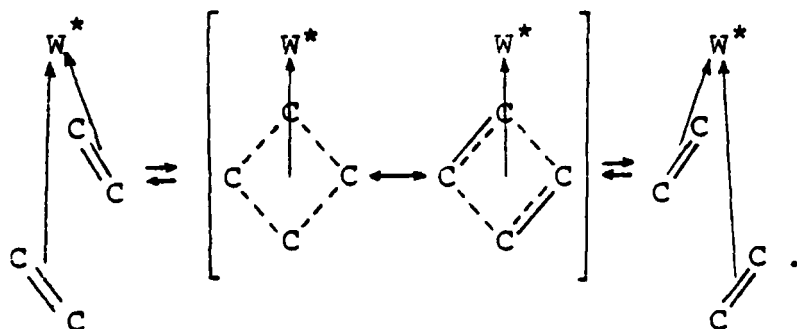
Clark et al. [12] and Woody et al. [56] also report tracer experiments on propylene disproportionation over a cobalt-molybdenum catalyst which support a four-center mechanism.

Other investigators have made studies with heterogeneous catalysts and have reported product distributions which are consistent with the four center mechanism. Mol, Moulijn, and Boelhouwer [42] proposed that a four center intermediate forms with the abstraction of hydrogen atoms by the catalyst, so that a cyclobutadiene intermediate is formed. Experiments by Crain [13] supported the four center mechanism, but indicated that a cyclobutadiene intermediate was not likely to occur with heterogeneous catalysts. Similarly Adams et al.[1] and Banks et al.[6] cite experimental evidence in support of the four center mechanism.

Calderon, Chen, and Scott [10] proposed a similar mechanism for the disproportionation of internal olefins in the presence of a homogeneous catalyst derived from the interaction of tungsten hexachloride, ethanol, and ethylaluminum dichloride. They proposed a transalkylidenation reaction as follows

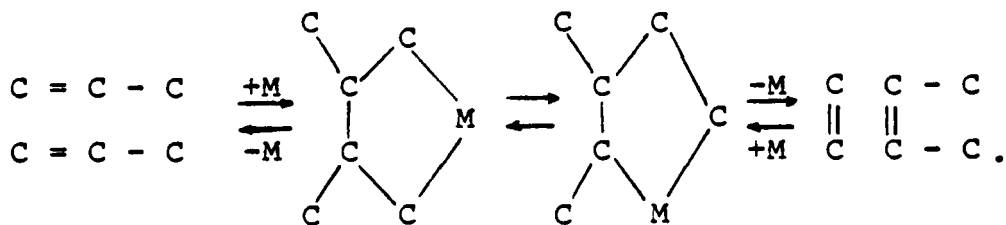


Later Calderon et al. [11] pictured the transition state as



where W^* is the transition metal atom plus the remaining ligands.

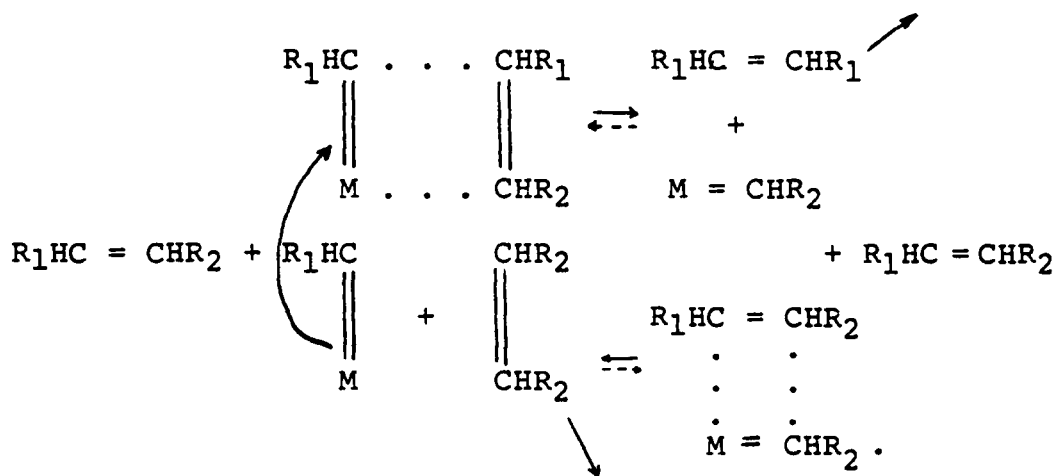
Another proposed mechanism for disproportionation involves a five-membered metallocyclic intermediate which can be visualized as follows



Experimental evidence supporting this mechanism was recently reported by Grubbs and Brunck [22].

Recently, Herisson and Chauvin [26] proposed that the mechanism involved a non-pairwise chain mechanism, in which the reaction takes place between an alkene molecule and a carbene-metal complex. They proposed the following

mechanistic scheme based on kinetic studies



Contradictory to a carbene mechanism is the high selectivity which is typical for the disproportionation reaction [40]. Side reactions, such as addition and insertion, can be expected with the carbene complexes. Since the selectivity is nearly 100% for most disproportionation catalyst systems, a carbene mechanism seems unlikely.

Rates of Disproportionation

Several kinetic studies of the disproportionation of propylene have been carried out to correlate conversion data with reaction rate equations in order to obtain a kinetic model for the reaction. A number of kinetic models and rate controlling mechanisms have been examined. Table 1 contains a partial list of initial rate equations for different models with indication of the rate controlling mechanism.

Table 1

Initial Rate of Reactions for Proposed Kinetic Models
for the Disproportionation of Propylene

Kinetic Model	Controlling Mechanism	Initial Rate Form	Reference
LANGMUIR-HINSHELWOOD $ \begin{aligned} &P + * \rightleftharpoons P^* \\ &2P^* \rightleftharpoons E^* + B^* \\ &E^* \rightleftharpoons E + * \\ &B^* \rightleftharpoons B + * \end{aligned} $	Dual Site Surface Reaction	$r = \frac{k_P P^2}{(1 + K_P P)^2}$	[40]
RIDEAL $ \begin{aligned} &P + * \rightleftharpoons P^* \\ &P^* + P \rightleftharpoons EB^* \\ &EB^* \rightleftharpoons E + B^* \\ &B^* \rightleftharpoons B + * \end{aligned} $	Single Site Surface Re- action	$r = \frac{k_P P^2}{1 + K_P P}$	[27]
LANGMUIR ADSORPTION $ \begin{aligned} &P + * \rightleftharpoons P^* \\ &P + P^* \rightleftharpoons P_2^* \\ &P_2^* \rightleftharpoons EB^* \\ &EB^* \rightleftharpoons B^* + E \\ &B^* \rightleftharpoons B + * \end{aligned} $	Single Site Surface Reaction or Desorption of Ethylene	$r = \frac{k K_2^* P^2}{1 + K_1^* P + K_2^* P^2}$	[52]
CARBENE $ \begin{aligned} &P + e^* \rightleftharpoons Pe^* \\ &Pe^* \rightleftharpoons Eb^* \\ &Eb^* \rightleftharpoons b^* + E \\ &P + b^* \rightleftharpoons Pb^* \\ &Pb^* \rightleftharpoons Be^* \\ &Be^* \rightleftharpoons e^* + B \end{aligned} $	Single Site Surface Reaction or Desorption of Ethylene	$r = \frac{k K^* P P}{1 + K^* P P}$	[52]

Table 1 (Continued)

Where P_p = initial propylene pressure

k = reaction rate constant

K_p = equilibrium constant for propylene adsorption

K^* = combination of rate constant of an elementary process (or processes)

Begley and Wilson [7] conducted a kinetic study using a tungsten-silica catalyst in an integral bed reactor for pressures up to 62.25 atmospheres and temperatures from 315 to 450°C. They concluded that their data were best correlated with a Rideal model, in which the reaction rate is controlled by the surface reaction between an adsorbed propylene molecule and a propylene molecule in the gas phase. However, Moffat et al. [38] reported experimental evidence that for the conditions involved interphase mass transfer is the rate controlling step. This casts some doubt on the validity of the Rideal model proposed by Begley and Wilson.

A number of investigators have shown that the rate equation is described by the Langmuir-Hinshelwood model, in which the reaction rate is controlled by the surface reaction between two adjacent chemisorbed propylene molecules. Lewis and Wills [30,31] used a differential bed reactor to obtain initial rates over a cobalt molybdate-alumina catalyst. Temperatures of 120-200°C and pressures from 1 to 9 atmospheres were used. They reported that their data were well correlated by the Langmuir-Hinshelwood model with the dual-site surface reaction as the controlling step. Moffat and Clark [37] also did experiments over a cobalt molybdate catalyst at 120-180°C and pressures up to 5.5 atmospheres to establish the validity of the Langmuir-Hinshelwood model.

They found the model can be used to describe both the general kinetics and the reversible rate-temperature maxima which they observed.

Davie et al. [14] investigated this reaction over a molybdenum hexacarbonylalumina catalyst in a static reactor for temperatures between 17 and 80°C with propylene pressures in the range 0.005 to 0.197 atmospheres. Their results also indicated that the rate controlling step is a surface reaction between two adjacently adsorbed propylene molecules.

Luckner et al. [35] obtained initial rate data for the disproportionation of propylene using a tungsten oxide-silica catalyst at flow rates where mass transfer effects were found to be negligible. Their experimental data for temperatures of 399 to 454°C and pressures up to 9 atmospheres were consistent with the Langmuir-Hinshelwood model. Similarly, Hattikudur and Thodos [23] found the Langmuir-Hinshelwood model gave a good correlation of their experimental results for the disproportionation of propylene over a tungsten oxide-silica catalyst at 354 to 455°C and pressures up to 50 atmospheres.

Mol [40] examined several kinetic models with initial rate data for the disproportionation of propylene on a rhenium oxide on alumina catalyst at 40-70°C and atmospheric pressure. He found good correlations for the

experimental results with rate equations of both the Langmuir-Hinshelwood model and the Langmuir adsorption model, in which the reaction rate is controlled by the surface reaction between two propylene molecules which are chemisorbed on the same active site. It was impossible to discriminate between the two models. Recently, van Rijn and Mol [52] correlated literature data on the kinetics of propylene disproportionation with several kinetic models. They reported the disproportionation reaction may be represented equally well or even better by kinetic models other than the Langmuir-Hinshelwood model. They were unable to draw definite conclusions for the reaction mechanism. However, based on a comparison of parameter values for the several models, they stated a preference for a model based upon a carbene mechanism.

From the kinetic studies mentioned above, evidence has been given that several kinetic models can represent the disproportionation reaction. Discrepancies in the kinetic models suggest that reaction rate expressions derived in the classical manner may be acceptable for chemical engineering purposes, but do not necessarily provide an adequate description of the real chemical reaction mechanism. Therefore in drawing conclusions from model discrimination one must be careful because unless all possible models are examined the best model may not be obtained.

Disproportionation Catalyst Break-in Phenomenon

The disproportionation catalyst tungsten oxide on silica has been reported to exhibit a regime of transient activity and selectivity following initial exposure with propylene [7,36,39]. The term "catalyst break-in" is generally used to identify such transients [2]. Begley and Wilson [7] present data for a freshly regenerated tungsten oxide on silica catalyst indicating a steady increase in catalyst activity during the first two hours of propylene exposure. During this break-in period significant changes in the product distribution were noted. Similarly, Moffat et al. [38] and Luckner et al. [36] report break-in periods of up to 24 hours were necessary to assure constant activity in a freshly activated catalyst.

Several studies have been made in order to investigate the phenomena responsible for catalyst break-in. The length of time involved in these transients seems to eliminate the possibility that transport delays or transients in adsorption or desorption are responsible for the phenomenon [34]. In other catalyst systems which exhibit catalyst break-in, it has been shown the transient phenomenon is frequently due to various reactant-surface interactions which result in a physical or chemical change in the catalyst surface or in a modification of the nature of the sites responsible for catalytic activity. These

reactant-surface interactions may result in changes of the catalyst surface area [45,49], a redistribution of the promoter on the catalyst support [2], a chemical reduction of the catalyst surface [15,33], or the formation of polymeric surface species which are active sites [8,18,44,47].

One possible explanation for the catalyst break-in which has been investigated is the possible purging of a temporary poison from the catalyst surface. Known temporary poisons include water, air, carbon monoxide, hydrogen, acetone, and methanol [24]. Luckner [34], to insure the phenomenon was not due to the purging of temporary poisons from the catalyst surface which were inadvertently introduced during the activation procedure, made variations in the procedure in an attempt to eliminate the period of transient activity. He found those variations in the activation procedure did not produce a significant change in the rate of catalyst break-in or in the steady-state activity of the catalyst which suggests the period of transient activity is not due to the purging of temporary poisons from the catalyst surface.

The observation of a color change for the catalyst during break-in has led to studies to determine if reduction of the tungsten promoter is responsible for the initial transient activity. Freshly activated catalyst is yellow which is characteristic of WO_3 [48]. During

break-in the catalyst turns blue, characteristic of $WO_{2.9}$ [48]. Bailey [3] reported catalyst break-in could be reduced or eliminated with controlled treatment with carbon monoxide or hydrogen at about 810 K. Luckner and Wills [36] pretreated the catalyst with hydrogen and carbon monoxide to reduce the tungsten promoter. They reported prior reduction of the catalyst to $WO_{2.9}$ substantially increases the rate of catalyst break-in, but does not eliminate the break-in phenomenon nor influence the steady-state activity. However, prior reduction of the catalyst with hydrogen to WO_2 resulted in more than a 30 percent increase in the steady-state catalytic activity when compared to the steady-state activity of an unpretreated catalyst at similar conditions. This pretreatment also increased the rate of catalyst break-in, but did not eliminate break-in.

Recently Westhoff and Moulijn [53] investigated the reduction process for this catalyst gravimetrically to determine its effect on catalyst activity. They found a very slight reduction of the catalyst results in a maximum for catalytic activity. Therefore, the most active catalyst sample must have a stoichiometric composition of tungsten oxide between WO_3 and $WO_{2.95}$. Kerhof, Thomas, and Moulijn [28,51] examined the disproportionation activity of a series of tungsten oxide-silica catalyst in an attempt to

identify the specific tungsten species formed during catalyst preparation and activation. From the reduction rates and the Raman spectra of the catalysts, they concluded that at least two tungsten species are present on the catalyst surface. These tungsten species are crystalline WO_3 and a polymeric tungsten compound. Their investigation also found the activity of unsupported WO_3 is negligible in spite of a comparable surface area with that of supported WO_3 catalysts. They concluded that an interaction between tungsten oxide and silica must be a prerequisite for disproportionation activity.

Another explanation for the break-in phenomenon which has been investigated is the possible formation of high molecular weight organic species on the catalyst surface which enhance the catalytic activity. Microcatalytic pulse studies were made on freshly activated catalyst by Luckner [34] and Fathikalajahi [17]. Both investigators reported that approximately 30 percent of the first few pulses of propylene were irreversibly adsorbed by the fresh catalyst and this percentage steadily declined with increasing number of pulses. Fathikalajahi [17] also investigated the effect of prior saturation of the freshly activated catalyst with either propylene or one of the reaction products on the break-in behavior of the catalyst. He found there is a slight difference in the rate

of catalyst break-in following pretreatment of the catalyst with either propylene, ethylene, or 2-butene, but the effect is not very significant.

Luckner and Wills [34,36] reported that the increase in the rate of propylene disproportionation during break-in could be approximated by a first order expression which is mathematically given as

$$\frac{(r_{ss} - r(t))}{(r_{ss} - r_0)} = e^{-kt} \quad (1)$$

where

k = break-in rate constant

r_{ss} = steady-state disproportionation rate

$r(t)$ = disproportionation rate at time t

r_0 = initial disproportionation rate.

The rate of approach to steady-state activity was found to depend on both temperature and pressure. They found the break-in rate constant has an Arrhenius temperature dependency with an activation energy of approximately 47 kcal and is first order in propylene partial pressure. The combined effect of pressure and temperature on the break-in rate constant has been given as

$$k = 1.993 \times 10^{12} e^{(-47.2/RT)} P_{C_3H_6} \text{ min}^{-1}. \quad (2)$$

Wills et al. [55] proposed that break-in is a chemical reaction involving propylene and the promoter WO_3 since break-in has a large activation energy and a first order dependence upon the reactant propylene pressure.

Investigations aimed at determining factors that influence the decay of steady-state activity for this catalyst have been made in an attempt to elucidate the mechanism of break-in. A temporary loss in activity is exhibited for almost any change that disturbs the steady-state rate of reaction. Fathikalajahi [17] investigated the effect on catalyst activity of a temporary reduction of the reaction temperature level for varying periods. He found that interrupting the disproportionation reaction through cooling causes a relaxation of break-in. The extent of relaxation increased as the length of holding time at room temperature was increased. Since relaxation continued to occur at room temperature at a measurable rate, this indicates the relaxation process must have a small activation energy. A physical process such as diffusion was proposed as the mechanism for relaxation since the process seems to have a low activation energy. A similar relaxation in break-in occurs when the disproportionation reaction is interrupted by a purge with an inert at reaction temperature [16,17,36]. Fathikalajahi [17] reported an apparent activation energy of 6 kcal/gmole for the relaxation of

break-in caused by a helium purge of a fully activated catalyst. He concluded that deactivation of the catalyst upon disturbance of the steady-state rate of reaction is due to the interaction of the catalyst with foreign species which are either in the feed or become available due to back diffusion.

Interphase and Intraparticle Transport Effects

Interphase mass transfer effects have been observed in the propylene disproportionation reaction over tungsten oxide-silica catalysts. Moffat, Johnson, and Clark [38,39] found the reaction to be limited by interphase diffusional effects in spite of calculations which predict no diffusional limitations should occur. They postulated that this anomalous behavior is due to a small number of very active and widely separated sites on the catalyst surface which cause the reaction to be limited by site-localized diffusional effects. In a similar study, Luckner et al. [35] reported that anomalously high linear velocities through the reactor were necessary for the elimination of interphase mass transport limitations. Space times of the order of 0.5 - 2.0 minutes were reported necessary to eliminate interphase mass transfer effects. They suggested that particle-to-particle variations in promotor levels may be partially responsible for the anomalous behavior.

Intraparticle mass transfer studies were made by Luckner et al. [35] and Hattikudur et al. [23] to determine whether or not the effects of pore diffusion could be eliminated in the propylene disproportionation reaction over tungsten oxide-silica catalysts. They reported that for particle diameters below 400 microns intraparticle mass transfer effects appear negligible.

Effect of Dosing Small Amounts of Chemicals

Several investigators have dosed small amounts of organic and inorganic chemicals into the reactor during both the break-in and the steady-state activity regimes [17,20,21,46,50]. The majority of these studies focus on the break-in phenomenon of the tungsten oxide-silica catalyst. Pennella and Banks [46] found the addition of small amounts of polyolefins (i.e., 1,5 cyclooctadiene) to the propylene feed significantly increased catalytic activity and reduced the break-in period as long as they were present in the feed. These results were attributed to an increase in the number of active sites through a modification of the energy level distribution in the tungsten oxide centers by the polyolefins.

The dosing of ammonia and certain amines have given similar results as those obtained by Pennella and Banks using polyolefins. Gangwal [21] observed an instantaneous

and temporary increase in catalytic activity when ammonia and certain amines were dosed into the system. He found amines with no N-H bonds reduced the activity while amines with at least one N-H bond increased the activity. Fathikalajahi [17] observed that the addition of a small amount of ammonia to the propylene feed dramatically increased catalytic activity and reduced the break-in period. However, the break-in behavior and the steady-state conversion resumed normal behavior when the feed was changed to pure propylene. From these experiments it appears that break-in is independent of the processes occurring with ammonia dosing. However, the initial state of the catalyst plays a role as it appears that the ammonia dosed only affects sites already partially activated by the normal break-in processes.

The dosing of known temporary poisons such as hydrogen, air, and water resulted in a temporary decrease in catalytic activity. A short break-in period was necessary to restore full activity following the dosing [24,50].

Dosing experiments have also been employed in studying the anomalous mass transfer behavior of the tungsten oxide-silica catalyst. One possibility for the anomalous behavior is inhibition of the disproportionation reaction due to the presence of products. Gangwal [20] dosed the propylene feed with small amounts of ethylene, 2-butene,

and 1-butene. He found 1-butene did not affect the activity, while 2-butene and ethylene caused small temporary changes in activity. Similarly, Tang [50] studied the effects of a small addition of ethylene and 2-butene in the propylene feed. The catalytic activity of a steady-state catalyst was initially reduced when pure propylene feed was replaced by a mixture containing a total product concentration of 3.6 percent. However, after 20 minutes of contact with the mixture, the original steady-state activity was restored. These experiments seem to indicate that the products do not inhibit the disproportionation reaction to any significant extent and thus does not offer an adequate explanation for the anomalous mass transfer effects.

III. EXPERIMENTAL

The following section contains the plan of investigation, the materials and equipment used, the methods of procedure, and the results obtained in this investigation.

Plan of Investigation

This investigation was principally a study of the phenomena associated with the anomalous mass transfer behavior of a tungsten oxide on silica catalyst during propylene disproportionation. The following phenomena were studied:

1. The effect of reactant flow rate on catalyst activity.
2. Hysteresis effect due to flow rate variations of reactant.
3. The effect of reactant flow rate through the dryer on catalyst activity.
4. The effect of reactant flow rate on the recovery from exposure to a temporary poison.

This study also investigated the effect of carbon monoxide dosing of a fully activated catalyst and the preparation and testing of olefin disproportionation catalysts.

In somewhat more detail the plan included system construction and calibration, catalyst preparation and

activation, and collection of data. A detailed description of each part of the plan of investigation is given in the following sections.

Experimental Equipment

The reactor system used in this investigation was that used by Fathikalajahi in his investigation of the break-in behavior of $\text{WO}_3\text{-SiO}_2$ catalyst during propylene disproportionation [16,17]. The system consists of three major parts- a feed preparation section, a microcatalytic reactor, and a product analysis section. Given here is a detailed description of each major section. Figure 1 shows a schematic diagram of the basic system. Some modifications in the system were necessary for certain studies, as indicated in Figure 2. The complete specifications of the equipment and materials are presented in Appendix C.

Feed Preparation This section was constructed such that it provided an accurately metered feed stream to the reactor which was free of a known catalyst poison, water. Gas cylinders of chemically pure feeds were connected to a gas manifold. These gases were then passed through a rotameter, a differential flow controller, and a dryer filled with 5A molecular sieves before entering the reactor. Two identical inlet lines were constructed to the

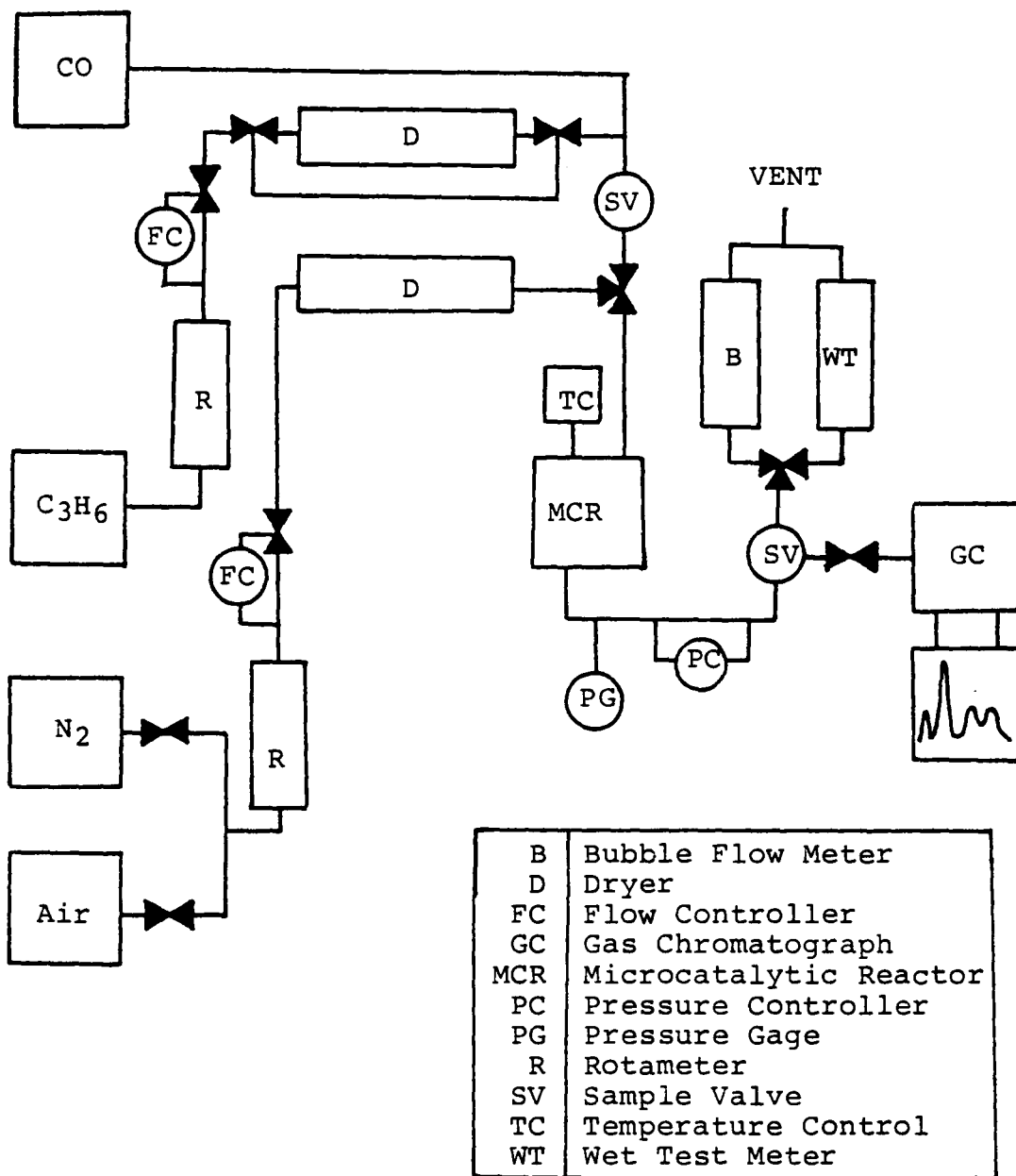


Figure 1. Schematic Diagram of the Reactor System.

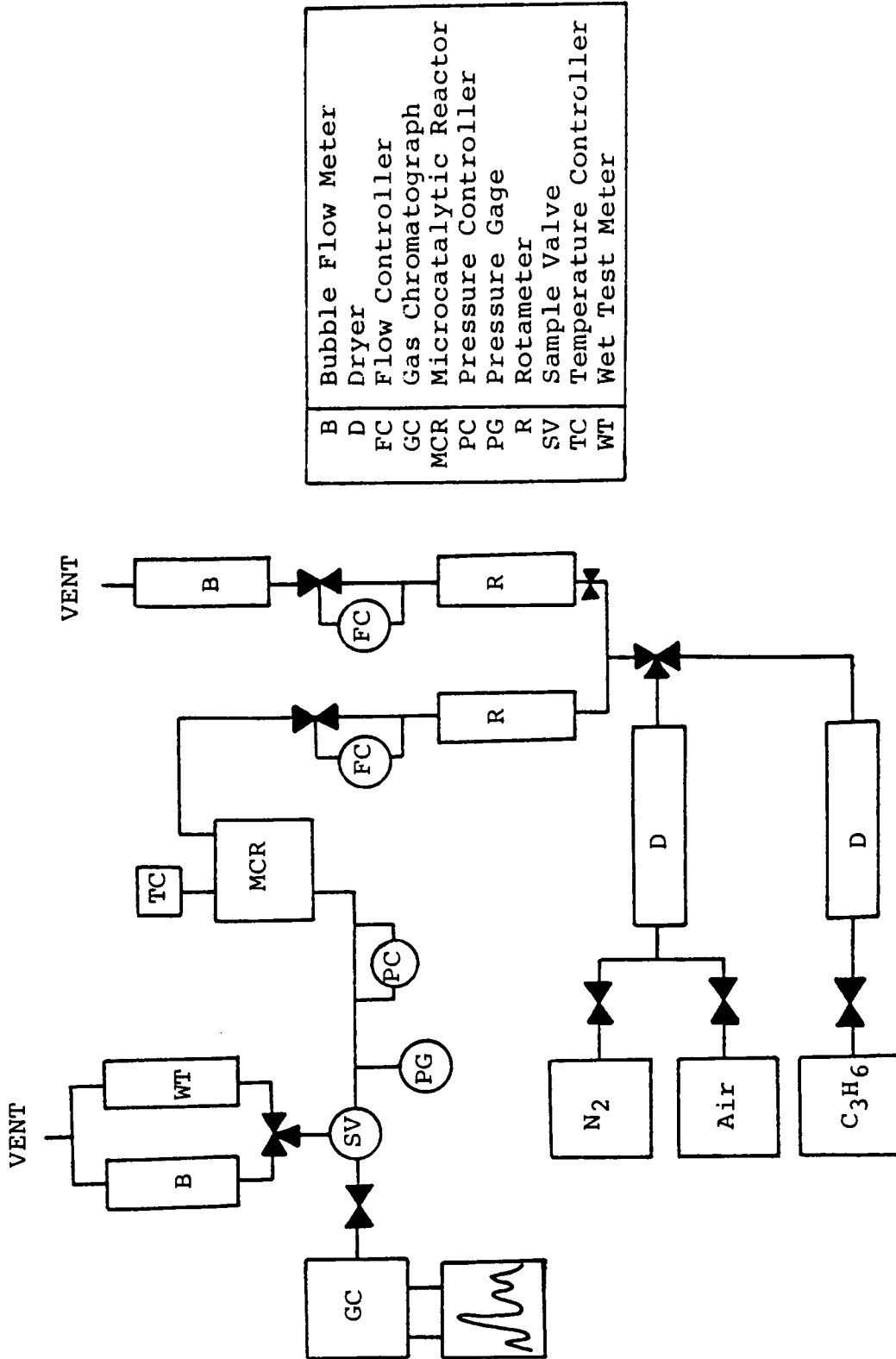


Figure 2. Schematic Diagram of the Modified Reactor System.

reactor. One of the inlet lines was used for the propylene feed and the other for the gases used during activation. This helped to retard deactivation of the dryers and to reduce the dead volume in the system when one gas was replaced with another.

Microcatalytic Reactor The reactor used in this investigation was constructed from a 6-inch section of 3/8 inch o.d., 316 stainless steel tubing. The top of the reactor was fitted with a 3/8 inch "Swagelok" male connector which was connected to a heat exchanger tee (3/8", 1/4", 1/4"). The tee provided fittings for the reactor thermowell and for the inlet line. The inlet line was connected to a preheater which was formed by winding a 4-foot section of 1/16 inch o.d., 316 stainless steel tubing around the heat transfer block which surrounded the reactor. The bottom of the reactor was fitted with a 3/8" "Swagelok" male connector which was connected to a 3/8" "Swagelok" female elbow. A detailed drawing of this reactor is shown in Figure 3.

The microcatalytic reactor was fitted with temperature, pressure, and flow control systems which were selected for accuracy and control performance. The temperature control system consisted of a combination of a long spiral preheater, a metal heat transfer block, a small catalyst charge, and a low heat of reaction which essentially eliminated temperature gradients in the catalyst bed. The temperature of the

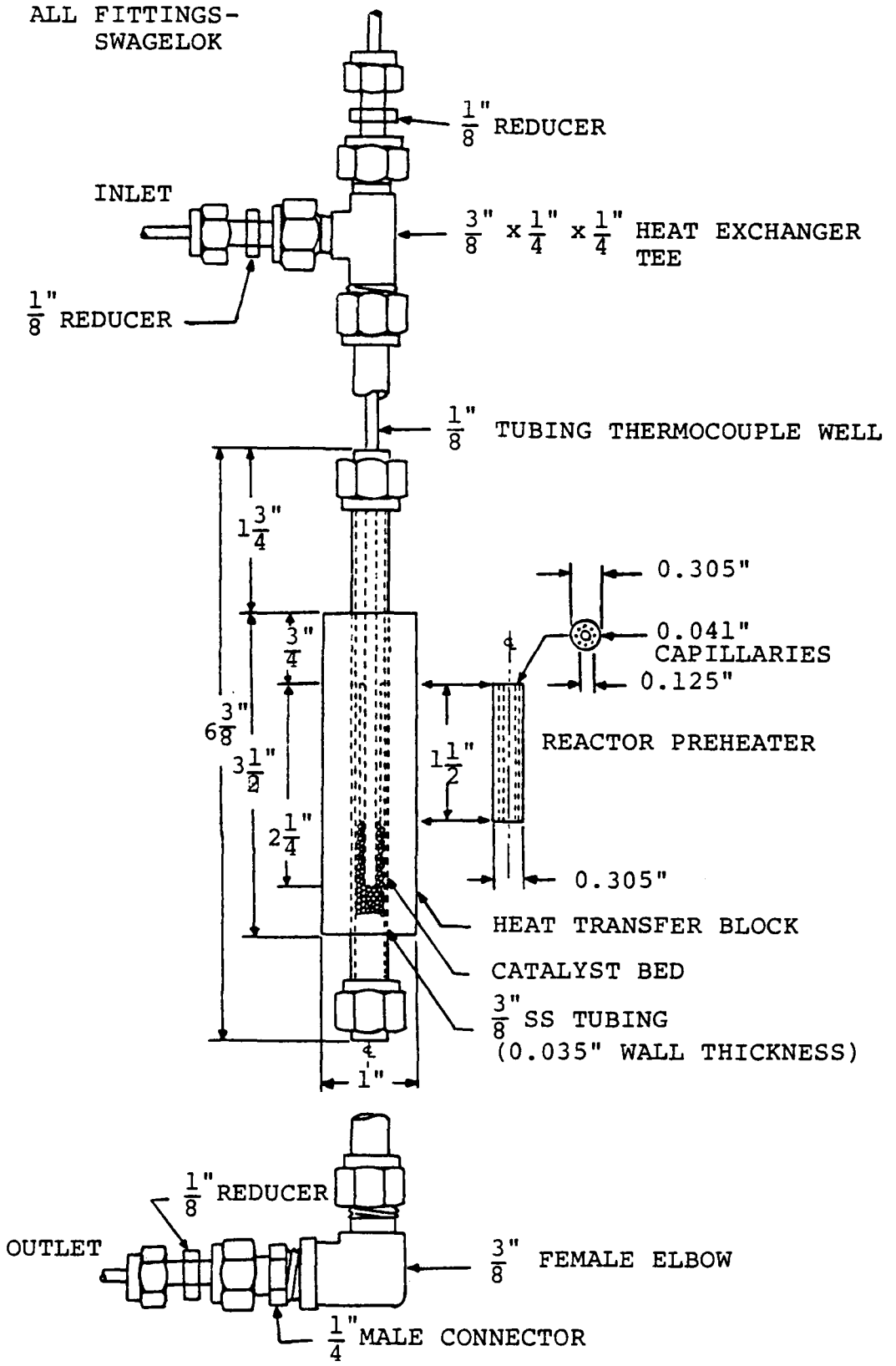


Figure 3. Details of Microcatalytic Reactor.

middle of the bed was monitored and controlled by placing the tip of the sensor of the pyrometer at the center of the bed. The pyrometer controlled the voltage input to one bank of resistance elements of the tubular furnace in which the reactor was placed. The voltage input to the second bank of resistance elements was adjusted so that if used alone it would maintain the reactor temperature approximately 10°C below the desired temperature. This bank remained on continuously. Temperature control was oscillatory with approximately a 0.5°C maximum deviation about the desired temperature.

The pressure control system consisted of a back pressure regulator which could be used to control reactor pressure in the range of 25 to 400 pounds per square inch, gage. A pressure gage was used to indicate the reactor back pressure.

The flow control system consisted of a Moore differential flow controller which controlled the flow of gases entering the reactor. Uniform distribution of the reactant gases over the catalyst bed is important. Channelling was eliminated by mixing the catalyst with quartz and distributing the reactant gases through eight 0.041 inch diameter capillaries in the reactor preheater. The flow rate through the system was monitored using the soap bubble flow meter or the wet test meter.

Product Gas Analysis In this section the effluent from the reactor was analyzed by an in-line gas chromatograph. The gas chromatograph was fitted with a 30 foot dimethylsulfolane on Chromosorb W column (-45/+60 mesh) which operated at room temperature with a flame ionization detector. The detector was calibrated using samples of the components in the reactor effluent individually and in a prepared mixture. This section also contained a bubble flow meter and a wet test meter for exact determination of the flow rate. The bubble flow meter was used to measure the lower flow rates and the wet test meter was used to measure the higher ones.

Methods of Procedure

This section contains calibration procedures for various pieces of equipment and operation procedure in each type of experiment.

Calibration of Pressure Gages All the pressure gages used in this investigation were calibrated against a twelve inch U.S. Standard test gage. The gage being calibrated was connected to the test gage and was pressurized by nitrogen gas. An individual calibration curve was prepared for each pressure gage.

Calibration of Gas Chromatograph During this investigation all olefin analyses were performed by gas chromatography using a F and M Scientific Research Chromatograph which was equipped with a 0.5 cubic centimeter gas sampling valve and a 30 foot column of dimethylsulfolane on Chromosorb W (-45/+60 mesh). The chromatograph's flame ionization detector was calibrated for ethylene, propylene, and butenes using the calibration procedure reported by Luckner [34].

For calibration purposes the gas sampling valve was connected to a vacuum system so the sampling loop and auxiliary components could be evacuated. The pressure in the system was monitored by a mercury U-tube manometer. The initial step in all calibrations was the evacuation of the system. After evacuation the olefin for which the detector was being calibrated was allowed to fill the system to some predetermined partial pressure. This sample was then injected into the chromatograph and the detector output was recorded. Pure samples and prepared mixtures of known composition were injected into the chromatograph and their component areas determined.

The flame ionization detector has an output which is proportional to the number of moles of a particular compound being ionized. Mathematically this relationship is

$$n_i = f_i A_i \quad (1)$$

where

n_i = number of moles of component i in the sample

A_i = area of detector response to component i

f_i = proportionality factor for component i .

The total number of moles in the sample can be determined by summing the number of moles of each component in the sample,

$$N = \sum_{i=1}^j n_i = \sum_{i=1}^j f_i A_i \quad (2)$$

where

N = total number of moles in the sample.

From the volume, temperature, and pressure in the sample loop the total number of moles injected can also be calculated by

$$N = \frac{P_L V_L}{\bar{z} R T_L} \quad (3)$$

where

P_L = pressure in the sample loop

R = ideal gas law constant

T_L = temperature of the sample loop

V_L = volume of the sample loop

\bar{z} = average compressibility factor of the sample.

Combining equations (2) and (3) and rearranging gives

$$\sum_{i=1}^j \frac{f_i}{V_L} A_i = \frac{P_L}{ZRT_L} \quad (4)$$

The best least square estimate of the f_i/V_L factor of each component was obtained. The f_i/V_L factors were normalized to eliminate the scale of the recorder and the unknown, but constant, sample loop volume. Since propylene was expected to be present in every sample analyzed during this investigation each factor was divided by the f_i/V_L factor of propylene,

$$f_i^* = \frac{f_i/V_L}{f_{C_3H_6}/V_L} \quad (5)$$

where

f_i^* = normalized proportionality factor for component i .

Periodically the validity of these factors were checked by injecting samples of a mixture of known composition. Slight adjustments in these factors were occasionally necessary.

For all experimental runs, the control positions used during calibration were maintained on the chromatograph. These were detector temperature 120°C, oven temperature 25°C, helium carrier gas pressure forty pounds per square inch gage at a flow rate of sixty cubic centimeters per

minute, air pressure thirty pounds per square inch gage, and hydrogen pressure fourteen pounds per square inch gage.

Preparation of Mixtures A mixture of the components found in the effluent from the reactor was prepared. An empty tank was connected to a vacuum pump and to gas cylinders containing the individual components of the mixture. The system was pressurized to 5 atm using one of the components in the mixture. After the system was checked for leaks under pressure, the tank was evacuated to 10 mm Hg. This cycle of filling and evacuating was repeated until the estimated partial pressure of residual impurities was less than a few parts per million. At this point the tank was filled to the appropriate pressure with each individual component of the mixture.

Preparation of Reactant Gases All of the reactant gases used were purchased in cylinders and were reported by the distributors to be a minimum 99% pure. A check to confirm this claim was made using the gas chromatograph. The major impurity found was a 0.5% level of propane in the propylene.

Preparation of the Commercial Catalyst The catalyst used in this investigation was furnished by the Davidson Chemical Division of W. R. Grace and Company and was

designated SMR 7-5381. It was reported to be 10% tungsten oxide on silica gel prepared by impregnating 3/16 inch silica extrusions with ammonium tungstate. Luckner [34] confirmed that it was 10% tungsten oxide and he reported a B.E.T. surface area of 233 m²/g.

The initial step in catalyst preparation was to crush and screen several grams of pellets to give (-30/+40 mesh) particles. The catalyst was dried for ten hours at 120°C and then stored in a dessicator until needed.

Catalyst Activation A standard method of catalyst activation was employed in all of the studies. A known weight of catalyst was charged to the reactor. This catalyst was mixed with an equal amount of quartz particles (-30/+40 mesh) to eliminate channeling. A plug of stainless steel wire gauze supported the catalyst charge so the tip of the thermocouple well was at the midpoint of the catalyst bed. The reactor was placed in the reactor furnace and glass wool was used to wrap the protruding inlet and outlet sections of the reactor to minimize heat losses. The catalyst was heated to 590°C while dry air at atmospheric pressure was passed through the catalyst bed at a flow rate of two to three cubic centimeters per second. These conditions were maintained for 5 hours at which point the system was purged with nitrogen for a half hour under

the same conditions. The temperature of the catalyst bed was then slowly reduced to the desired operating temperature. Propylene was introduced into the system when the temperature had stabilized at the operating temperature. At this point the catalyst was termed "freshly activated" and was ready for the various experiments outlined below.

Preparation and Testing of Laboratory Prepared Catalysts Two olefin disproportionation catalysts, tungsten oxide on silica and tungsten oxide on silica-alumina, were prepared in the laboratory. Approximately five grams of each catalyst were prepared using conventional impregnation methods. An aqueous solution of the metal salt ammonium metatungstate was prepared by dissolving approximately one gram of the salt in 100 milliliters of distilled water. This solution was added in 5 milliliter increments to the preformed support of either silica or silica-alumina. Between additions of the solution, the catalyst was dried in an oven at 120°C. When the desired amount of metal salt had been added to the support the catalyst was activated in dry air at 810 to 870°C for one hour. The prepared catalyst pellets were then crushed and screened to give (-30/+40 mesh) particles. The catalyst was dried for 10 hours at 120°C and then stored in a desiccator until needed.

The laboratory prepared catalysts were tested to determine their effectiveness as catalysts for the disproportionation of propylene. For comparison, a commercially prepared tungsten oxide-silica catalyst was also tested. For each catalyst tested, a catalyst charge of 0.3 grams was activated according to the procedure outlined above. The reactant gas, propylene, was passed through the catalyst bed at a WHSV of 70 g C₃H₆/g cat-hr. Reaction conditions of atmospheric pressure and 410°C were used. Propylene conversion was determined as a function of propylene contact time until the level of conversion was observed to be invariant with time.

Carbon Monoxide Dosing The effect of carbon monoxide on the catalytic activity of tungsten oxide-silica for the disproportionation of propylene was studied by dosing a fully broken-in catalyst with carbon monoxide. A catalyst charge of 0.4 grams was prepared and activated according to the procedures outlined above. The reactant gas, propylene, was then admitted at a flow rate of approximately 2.5 cubic centimeters per second. The catalyst was allowed to become fully broken-in at reaction conditions of 412°C and atmospheric pressure. The catalyst was classified as "fully broken-in" when analysis of effluent samples showed the level of conversion remained constant for an extended period of time. Carbon monoxide was then dosed into the

system using a gas sampling valve equipped with a 13 milliliter sample loop which had been placed in the propylene feed line. The carbon monoxide was introduced into the feed line in the form of a square wave pulse. Effluent samples from the reactor were periodically analyzed to determine the effect of carbon monoxide on the catalytic activity. Samples were analyzed until the conversion returned to the conversion level of the system before the dosing.

Effect of Reactant Flow Rate on Catalyst Activity

One area of anomalous behavior for this system is its unusual response to changes in reactant flow rate. It has been reported that the activity of this catalyst increases with increased flow rates [38,39]. An investigation was made to determine the relationship between the reactant flow rate and the catalyst activity. In this study a catalyst charge of 0.3 grams was prepared and activated according to the procedures outlined above. Propylene was then admitted to the system at a flow rate of approximately 2.5 cubic centimeters per second. When the catalyst was fully broken-in the propylene flow rate was decreased to approximately 0.5 cubic centimeters per second. The system was allowed to stabilize at the reaction conditions of 418°C and atmospheric pressure. Effluent samples from

the reactor were then analyzed to determine the activity of the catalyst. The propylene flow rate was then incrementally increased until the flow rate was approximately 15 cubic centimeters per second. At each flow rate, effluent samples were analyzed to determine the catalyst activity after the system stabilized at the reaction conditions.

Hysteresis Effect Due to Flow Rate Variations of Reactant The unusual response of this catalyst system to changes in reactant flow rate has led to an investigation to determine if this system exhibits a hysteresis effect due to variations in the reactant flow rate. A catalyst charge of 0.4 grams was prepared and activated according to the procedures outlined above. The reactant gas, propylene, was then admitted to the system at a flow rate of approximately 2.5 cubic centimeters per second. When the catalyst was fully broken-in, the propylene flow rate was increased to approximately 5 cubic centimeters per second. The system was allowed to stabilize at reaction conditions of 407°C and atmospheric pressure. Effluent samples from the reactor were then analyzed to determine the percent conversion of propylene. The propylene flow rate was then decreased. After the system stabilized at the previous reaction conditions, effluent samples were again analyzed

to determine the percent conversion of propylene. This procedure was repeated until the flow rate to the reactor was approximately 0.5 cubic centimeters per second. At this point the propylene flow rate was incrementally increased until the flow rate returned to approximately 5 cubic centimeters per second. At each flow rate to the reactor, effluent samples were analyzed to determine the percent conversion of propylene.

This procedure was repeated using a propylene feed which bypassed the dryer so it contained traces of water. The dryer was removed from the system when the catalyst was fully broken-in. Reaction conditions of 421°C and atmospheric pressure were used.

Effect of Reactant Flow Rate Through Dryer on Catalyst Activity It has been speculated that the anomalous mass transfer exhibited by this catalyst system may be a poisoning phenomenon rather than a mass transfer phenomenon [54]. The anomalous behavior could be due to a reversible poison being introduced into the propylene feed from the dryer that is used to remove traces of water in the feed. An experiment was designed to determine the effect of reactant flow rate through the dryer on the catalytic activity.

The reactor system was modified so it would be possible to split the exit stream from the dryer into two

streams. One of the streams went to the microcatalytic reactor and product gas analysis section of the system while the other stream bypassed these sections and was directly vented. A schematic of the system is given in Figure 2.

Preliminary studies were conducted to determine whether the activation procedure should be modified to include a nitrogen purge for the line bypassing the reactor. A catalyst charge of 0.4 grams was prepared according to the procedure outlined above. The entire system was flushed with air for 5 minutes before beginning the catalyst activation procedure outlined above. After activation, propylene was introduced to the system at a flow rate of two to three cubic centimeters per second. When the catalyst was fully broken-in, the flow rate was decreased to approximately 0.9 cubic centimeters per second. The system was allowed to stabilize at reaction conditions of 410°C and atmospheric pressure. Effluent samples from the reactor were analyzed to determine the percent conversion of propylene. At this point the flow rate of propylene was increased approximately 2.5 cubic centimeters per second. The exit stream from the dryer was split into two streams so the flow rate to the reactor was held constant. Percent conversion of propylene was determined periodically until the level of conversion was observed to be invariant

with time. The above procedure was repeated, but a nitrogen purge for the line bypassing the reactor during the last fifteen minutes of activation. The nitrogen flow rate during the purge was approximately one cubic centimeter per second. The flow through the bypass was terminated before propylene was introduced into the system.

The first portion of this study investigated the effect on catalytic activity from variations in the flow through the dryer when the feed rate is held constant. A catalyst charge of 0.3 grams was prepared and activated according to procedures outlined above. During the last fifteen minutes of activation a portion of the nitrogen flow was split off to flush the lines of the reactor bypass. Nitrogen flow through the bypass was terminated before propylene was introduced into the system at a flow rate between two and three cubic centimeters per second. When the catalyst was fully broken-in, the propylene flow rate to the reactor was decreased to 1.25 cubic centimeters per second. The system was allowed to stabilize at reaction conditions of 418°C and atmospheric pressure. Effluent samples from the reactor were then analyzed to determine the percent conversion of propylene. At this point the flow rate of propylene through the dryer was increased. The exit stream from the dryer was split into two streams so the flow rate to the reactor was held constant. After

the system stabilized at the previous reaction conditions, reactor effluent samples were again analyzed to determine the percent conversion of propylene. This procedure was repeated for several reactant flow rates through the dryer. The study was also conducted using a catalyst charge of 0.4 grams and reaction conditions of 410°C, reactant flow rate at 0.9 cubic centimeters per second and atmospheric pressure.

The second portion of this study investigated the effect of the reactant flow rate through the dryer on the relationship between the flow rate through the reactor and catalyst activity. The catalyst charge from the first portion of this study was reactivated and the above procedure was followed until the catalyst was fully broken-in. When the catalyst was fully broken-in the flow rate to the reactor was increased to approximately 5 cubic centimeters per second. The system was allowed to stabilize at reaction conditions of 418°C and atmospheric pressure. Effluent samples from the reactor were then analyzed to determine the percent conversion of propylene. The flow rate of propylene to the reactor was then decreased. After the system stabilized at the previous reaction conditions, reactor effluent samples were again analyzed to determine the percent conversion of propylene. This procedure was repeated for several flow rates to the reactor until the

flow rate was approximately 5 cubic centimeters per second. The percent conversion of propylene was determined from effluent samples after the system stabilized. The flow rate to the reactor was decreased while maintaining a constant flow of 5 cubic centimeters per second to the inlet of the dryer by adjusting the flow rate in the reactor bypass to handle the excess propylene. The system was again allowed to stabilize, at which point the percent conversion of propylene was determined. This procedure was repeated for several flow rates to the reactor until the flow rate was approximately 0.5 centimeters per second.

Effect of Reactant Flow Rate on the Recovery from Exposure to a Temporary Poison An investigation was made to determine the effect the reactant flow rate has on the recovery from exposure to a temporary poison, water. The catalyst charge from the experiment to determine the hysteresis effect due to flow rate variations when the reactant contained traces of water was used in this study without regeneration. At the end of the flow hysteresis experiment, the dryer was placed back into the system. This experiment was started approximately 12 hours after the completion of the flow hysteresis experiment. The system was allowed to stabilize at reaction conditions of 422°C, atmospheric pressure, and a reactant flow rate of 2.5 cubic centimeters per second. Effluent samples from

the reactor were then analyzed to determine the percent conversion of propylene. The dryer was then removed from the system so that the feed would contain traces of water. Effluent samples were analyzed until the level of conversion was observed to be invariant with time. At this point, the dryer was reconnected and effluent samples were again analyzed until the level of conversion was invariant with time. The reactant flow rate was then lowered to approximately 0.7 cubic centimeters per second and the above procedure was repeated.

Data and Results

The results of the experimental studies outlined in the previous section are presented in this section. The data tables for all studies are presented in Appendix A.

Catalytic Activity of Laboratory Prepared Catalysts

Two laboratory prepared catalysts, tungsten oxide on silica and tungsten oxide on silica-alumina, were tested to determine their effectiveness as catalysts for the disproportionation of propylene. These catalysts and a commercial tungsten oxide on silica catalyst were tested under similar reaction conditions of 410°C, atmospheric pressure, and a WHSV of 70.5 g C₃H₆/g cat-hr. The break-in behaviors of these catalysts are presented in Figure 4. The

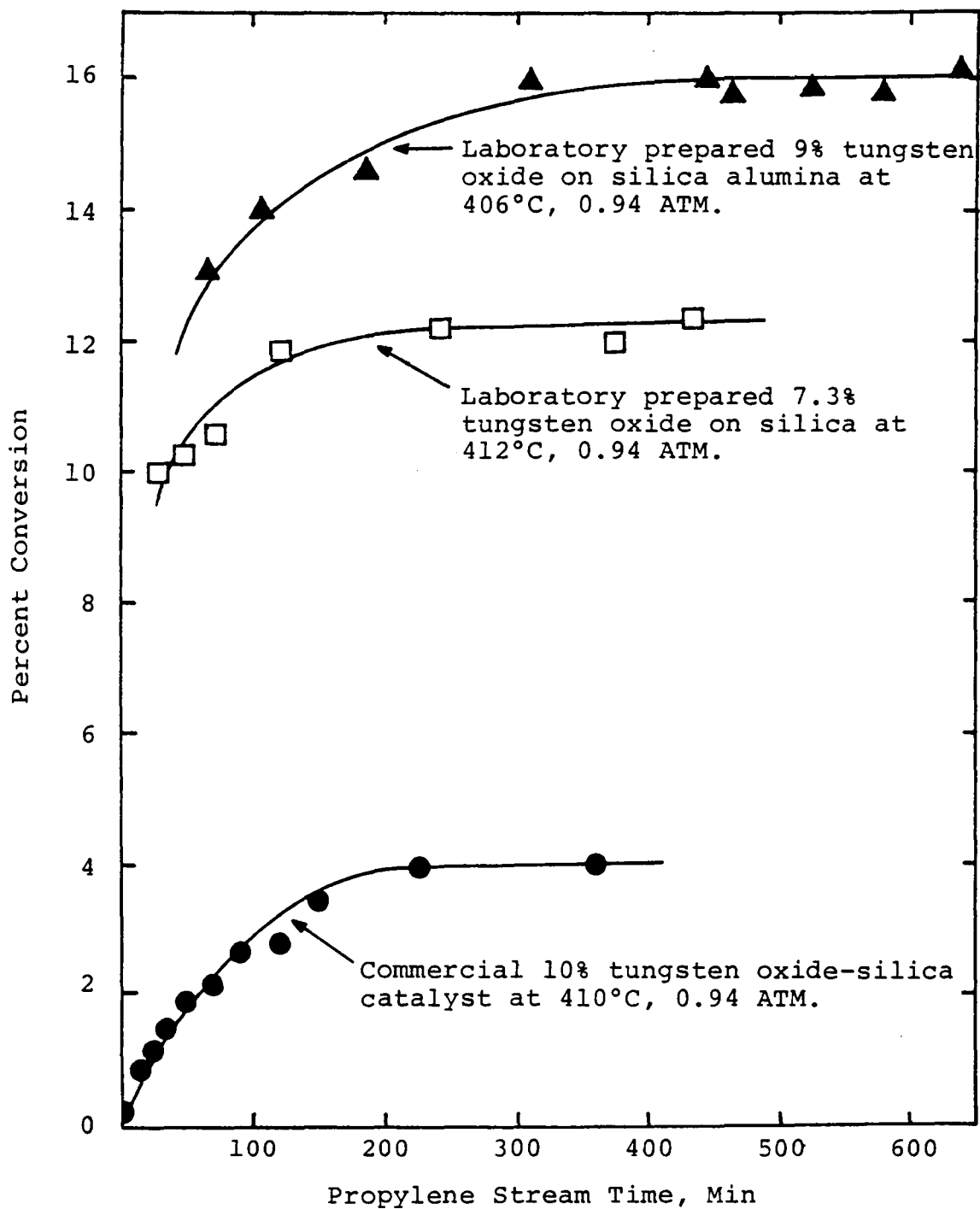


Figure 4. Break-in Behavior of Laboratory Prepared and Commercial Catalysts.

break-in period for the commercial and laboratory prepared tungsten oxide on silica catalysts was approximately 250 minutes, while the laboratory prepared tungsten oxide on silica-alumina catalyst had a break-in period of approximately 450 minutes.

The percent conversion of propylene for activated laboratory prepared catalyst was significantly higher than that of the commercial catalyst. However, the selectivity of the commercial catalyst was much greater since approximately 25% of the 2-butene formed using the laboratory prepared catalysts isomerized to 1-butene. Table 2 presents a typical product distribution for each catalyst when fully activated.

Effect of Carbon Monoxide Dosing on Catalytic Activity

The results of the experiment to determine the effect of carbon monoxide on the catalytic activity of tungsten oxide on silica for the disproportionation of propylene are given in Figure 5. A temporary decrease in the conversion level is observed immediately following the introduction of carbon monoxide in the propylene feed. The conversion returned to the conversion level of the system prior to dosing in approximately 110 minutes.

Effect of Reactant Flow Rate on Catalyst Activity

The results of the study to investigate the relationship between the reactant flow rate and the catalyst activity

Table 2

Typical Product Distributions for the Laboratory Prepared and Commercial Catalysts When Fully Broken-in

Catalyst	Product Distribution				Percent Conversion
	% C ₂ H ₄	% C ₃ H ₆	% 1-C ₄ H ₈	% 2-C ₄ H ₈	
9% Tungsten Oxide on Silica Alumina, Laboratory Prepared	8.08	83.86	1.80	6.26	16.14
7.3% Tungsten Oxide on Silica, Laboratory Prepared	6.01	88.01	1.48	4.50	11.99
10% Tungsten Oxide on Silica, Commercial	1.94	96.07	--	2.00	3.94

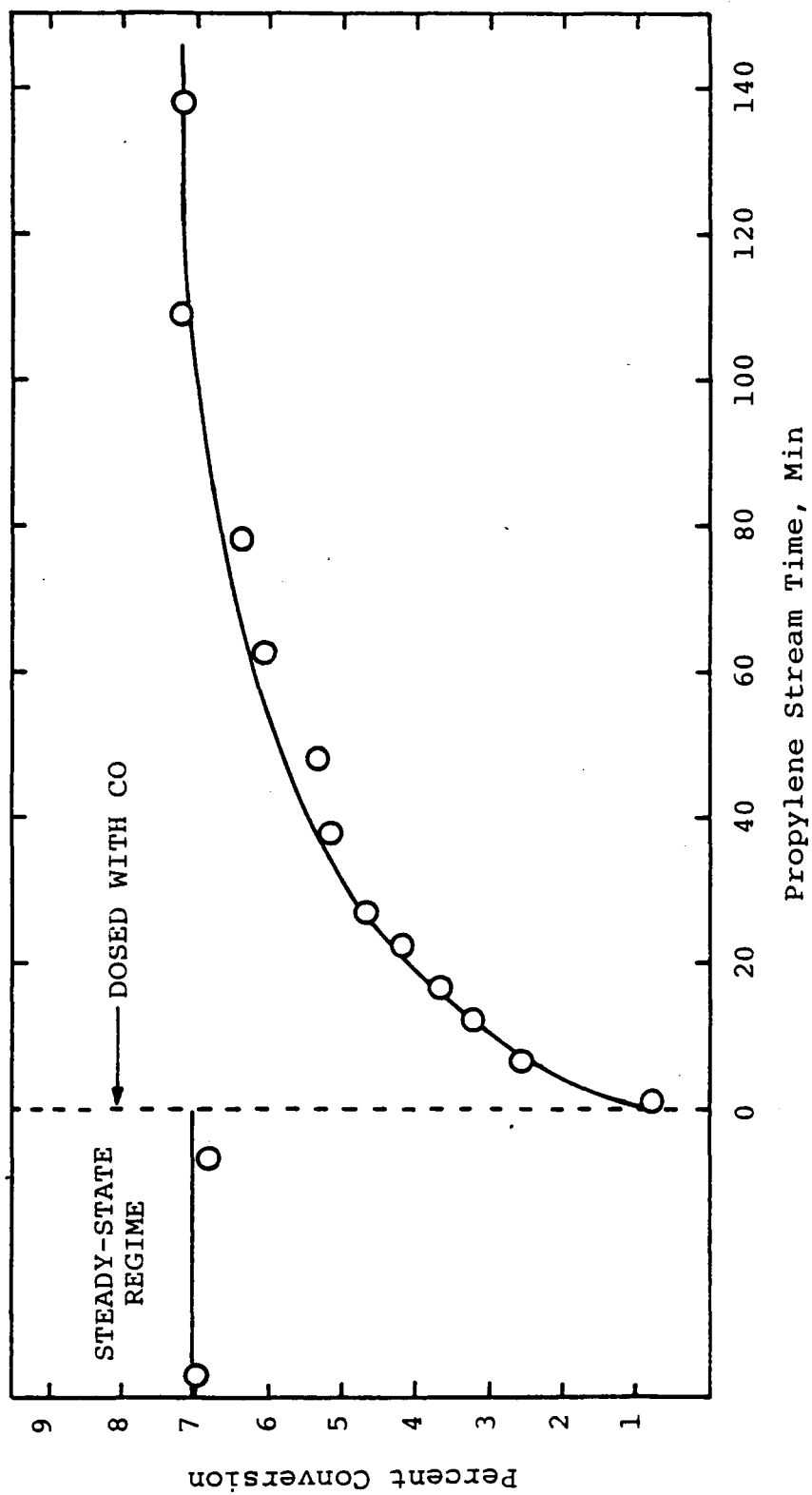


Figure 5. Effect of Carbon Monoxide Dosing on the Catalytic Activity of a Fully Broken-in Catalyst at 412°C and 0.94 ATM.

are given in Figures 6 and 7. Propylene flow rates between 0.5 and 16.9 cubic centimeters were used. Figure 6 is a plot of activity versus the propylene flow rate through the reactor. The activity increases when the flow rate is increased. A plot of percent conversion versus the propylene flow rate is given in Figure 7. Over the flow rate range of 0 to 4 cubic centimeters per second the conversion decreases as the flow rate is increased. However, for flow rates greater than 4 cubic centimeters per second the conversion appears to remain constant or increase when the flow rate is increased.

Hysteresis Effect Due to Flow Rate Variations of Re-

actant The results of the study to determine if this system exhibits a hysteresis effect due to variations in the reactant flow rate are given in Figures 8 and 9. Figure 8 is a plot of catalyst activity versus the flow rate of propylene to the reactor. The activity appears to be independent of the flow rate history. This feature is also evident in Figure 9 which is a plot of percent conversion of propylene versus the propylene flow rate. At any given flow rate the difference in the level of conversion between the first and second exposure to that flow rate is negligible. However, when the propylene feed contained traces of water, the flow rate history affects the catalytic activity. Following exposure to low flow rates the

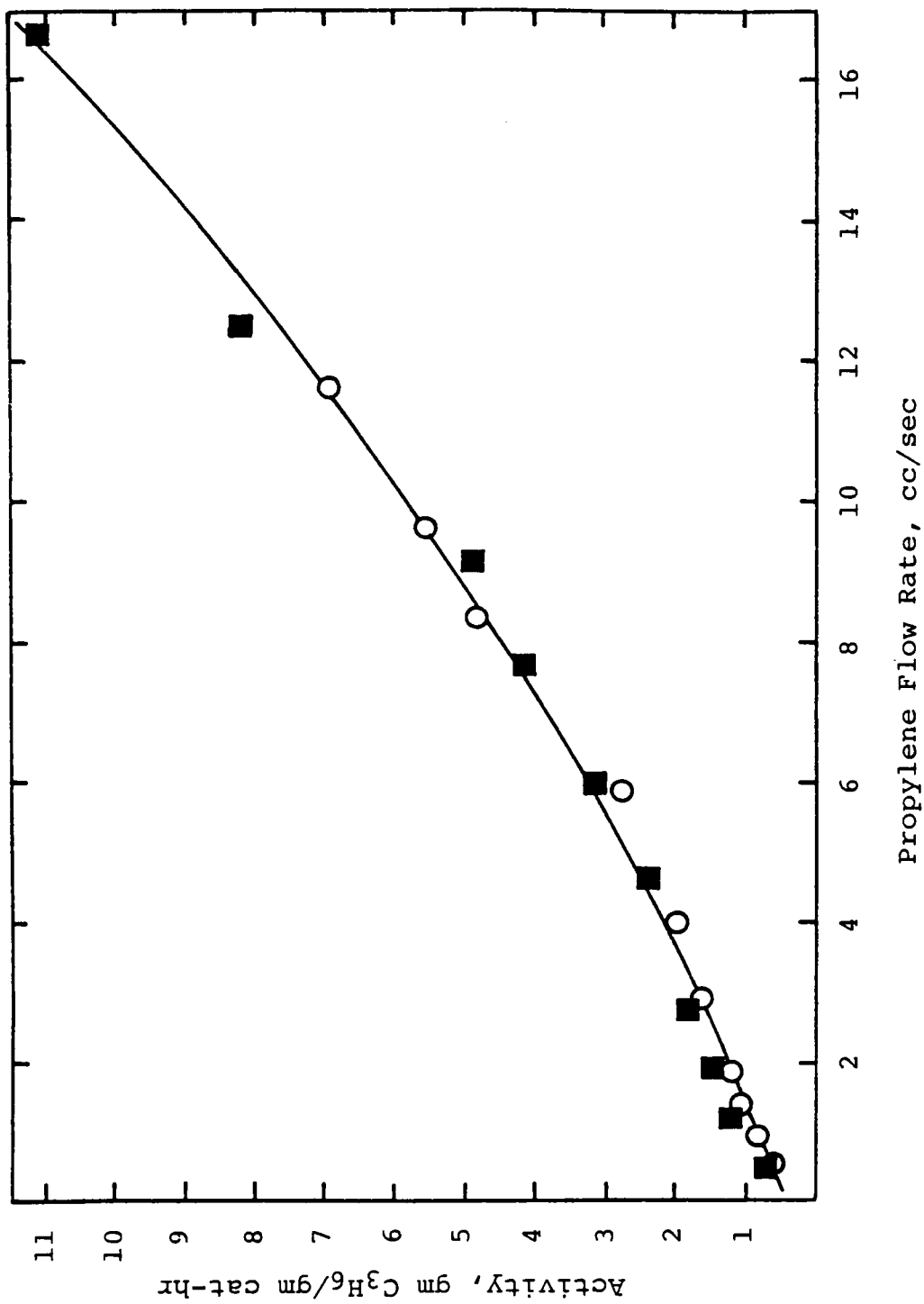


Figure 6. Effect of Reactant Flow Rate on Catalyst Activity at 418°C and 0.94 ATM (O duplicate run).

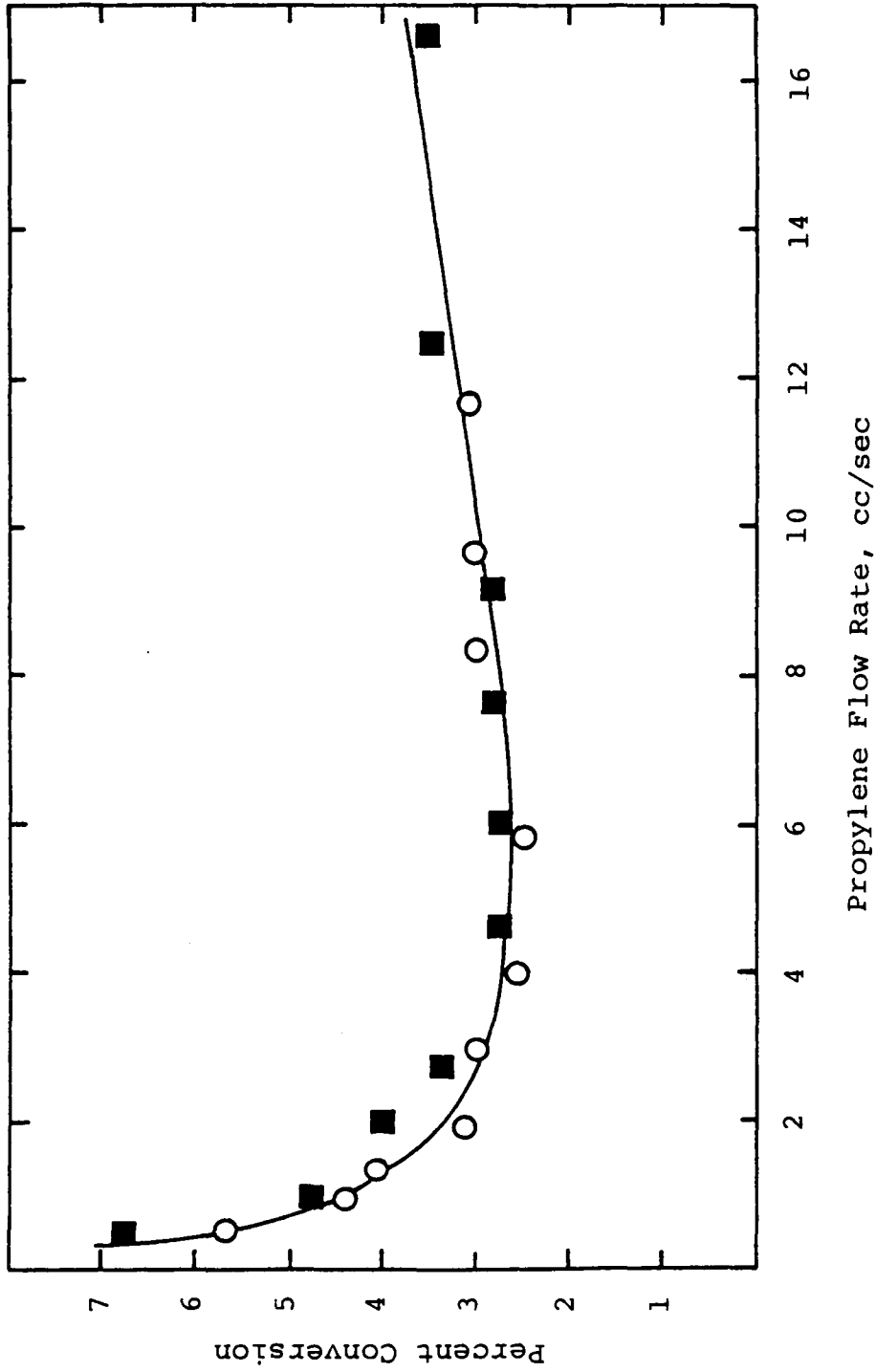


Figure 7. Effect of Reactant Flow Rate on Catalyst Conversion at 418°C and 0.94 ATM (O duplicate run).

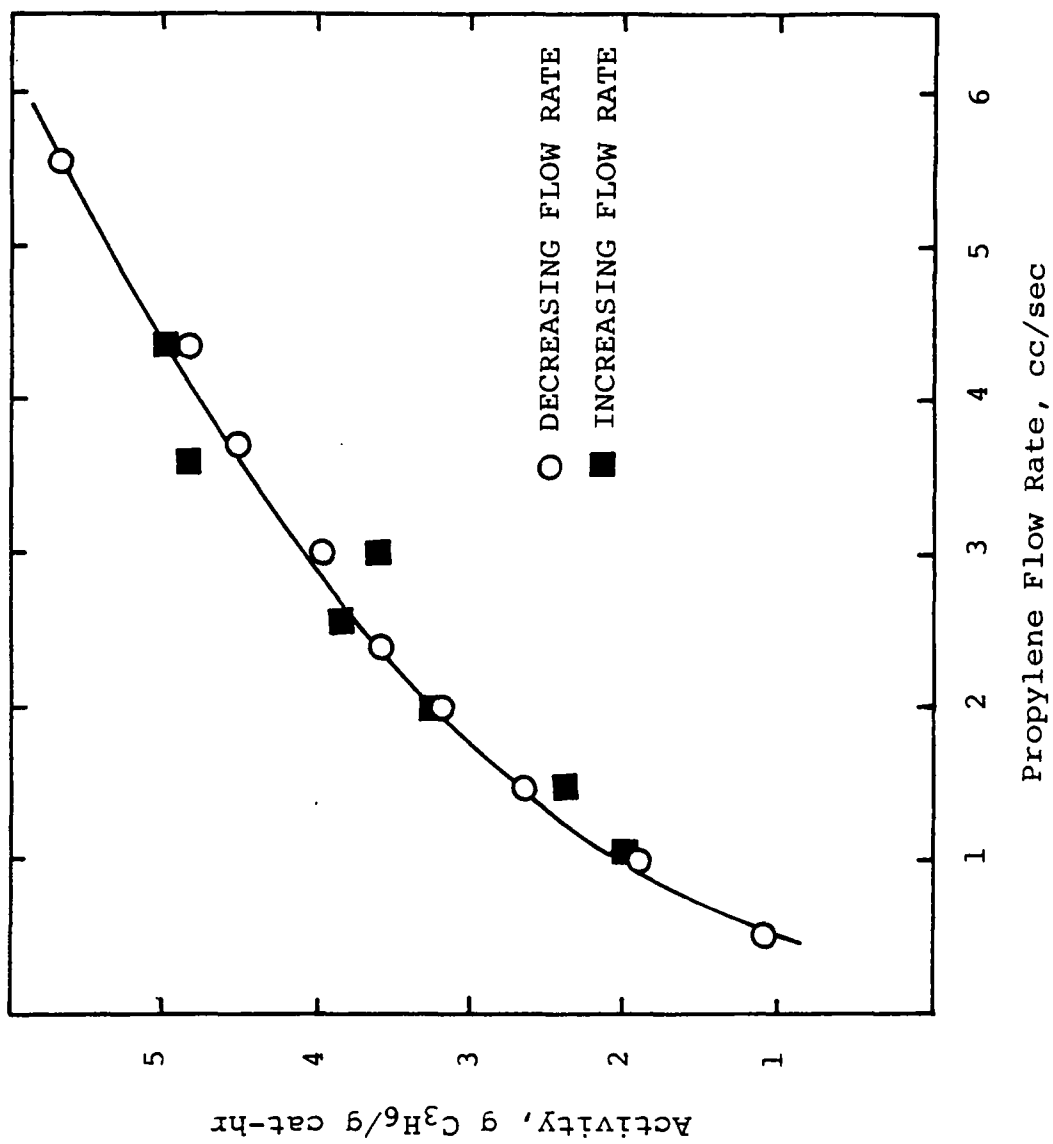


Figure 8. Response of Catalyst Activity to Variations in Reactant Flow Rate at 407°C and 0.94 ATM.

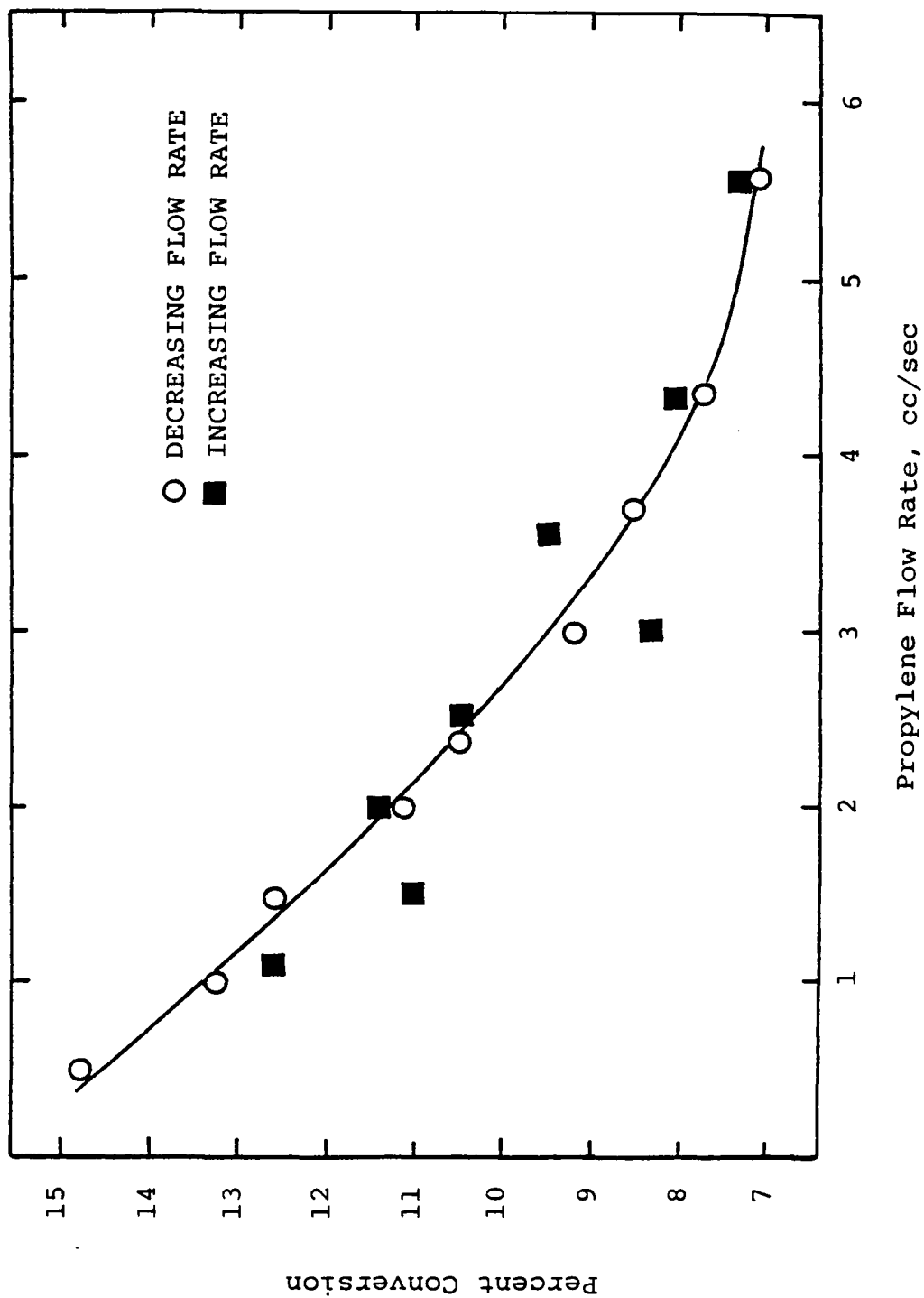


Figure 9. Response of Propylene Conversion to Variations in Reactant Flow Rate at 407°C and 0.94 ATM.

catalyst activity is decreased as shown in Figure 10. As shown in Figure 11, a plot of percent conversion of propylene versus the flow rate, the conversion is decreased for a given flow rate after contact with low flow rates.

Effect of Reactant Flow Rate Through Dryer on Catalyst Activity Results for the preliminary studies which were aimed at determining whether the activation procedure should be modified to include a nitrogen purge for the line bypassing the reactor are given in Figure 12. When the activation procedure did not include a nitrogen purge an increase in the level of conversion was observed following an increase in the flow rate through the dryer while maintaining the same flow rate to the reactor. This was not observed when the activation procedure included a nitrogen purge.

The results of the study to determine the effect on catalytic activity due to variations in the flow through the dryer when the feed rate to the reactor is held constant are given in Figures 13 and 14. There appears to be no effect on the conversion from splitting off some of the propylene feed leaving the dryer as the conversion was constant over the range studied.

This study also investigated the effect of the reactant flow rate through the dryer on the relationship

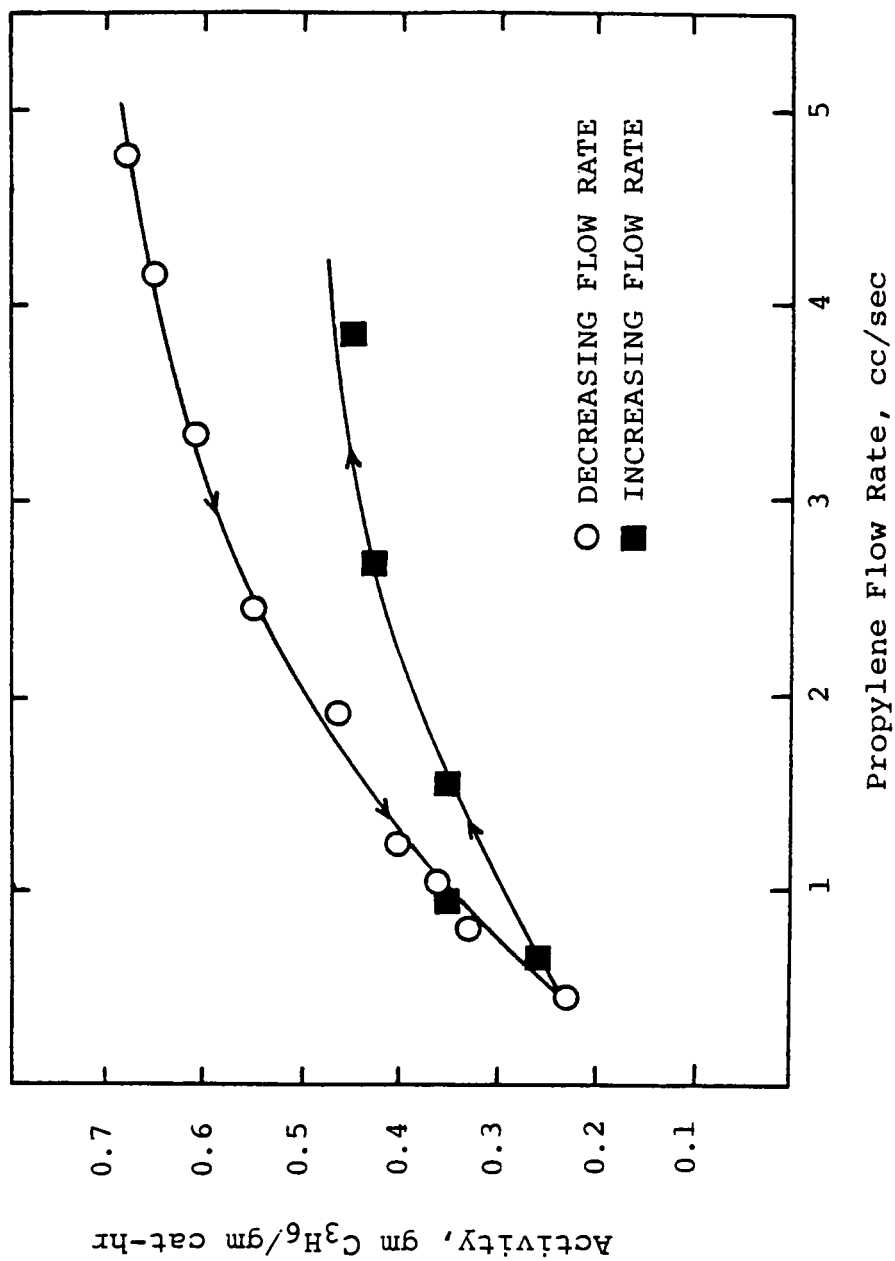


Figure 10. Response of Catalyst Activity to Variations in Reactant Flow Rate for Feed Containing Traces of Water at 421°C and 0.94 ATM.

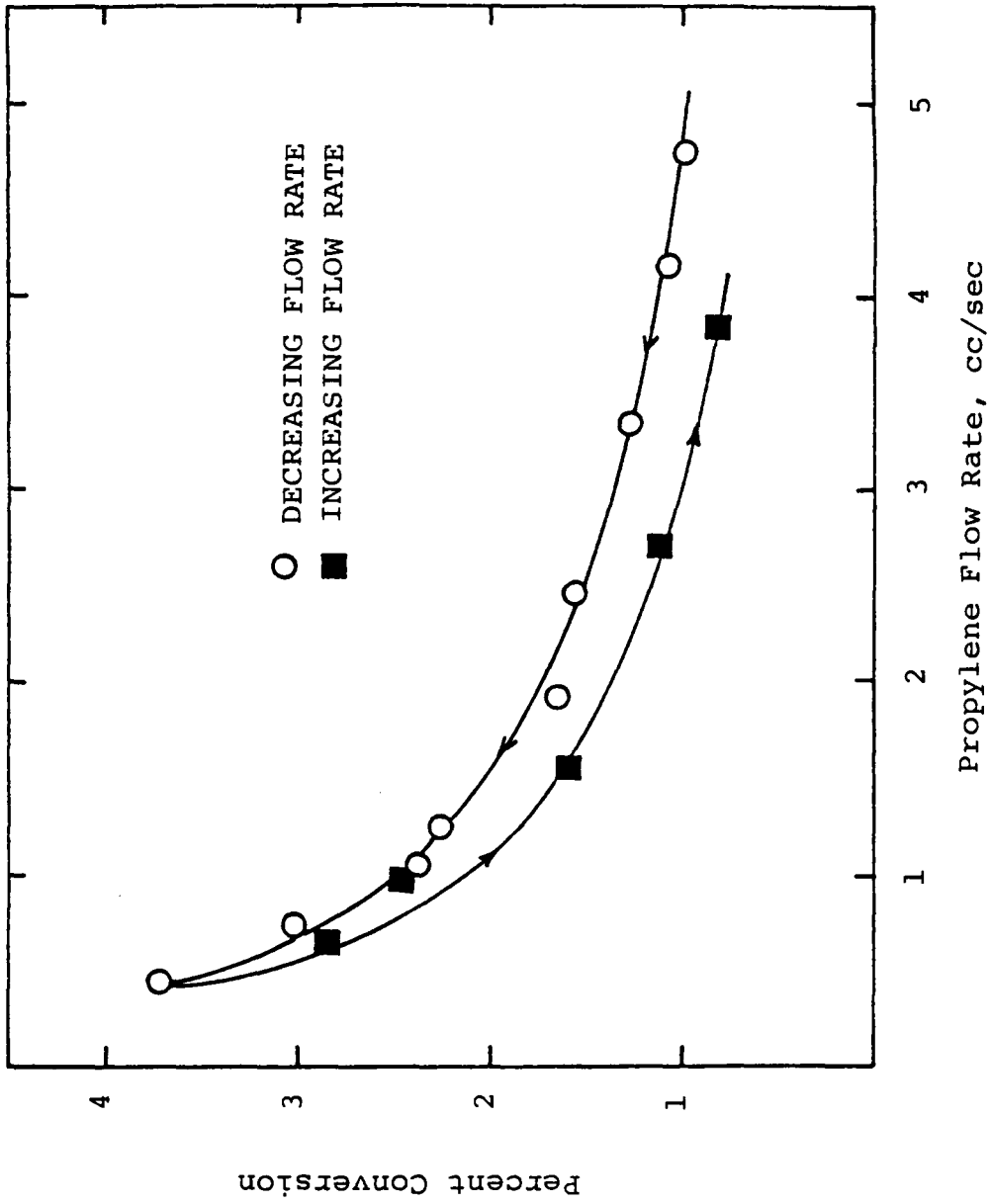


Figure 11. Response of Propylene Conversion to Variations in Reactant Flow Rate for Feed Containing Traces of Water at 421°C and 0.94 ATM.

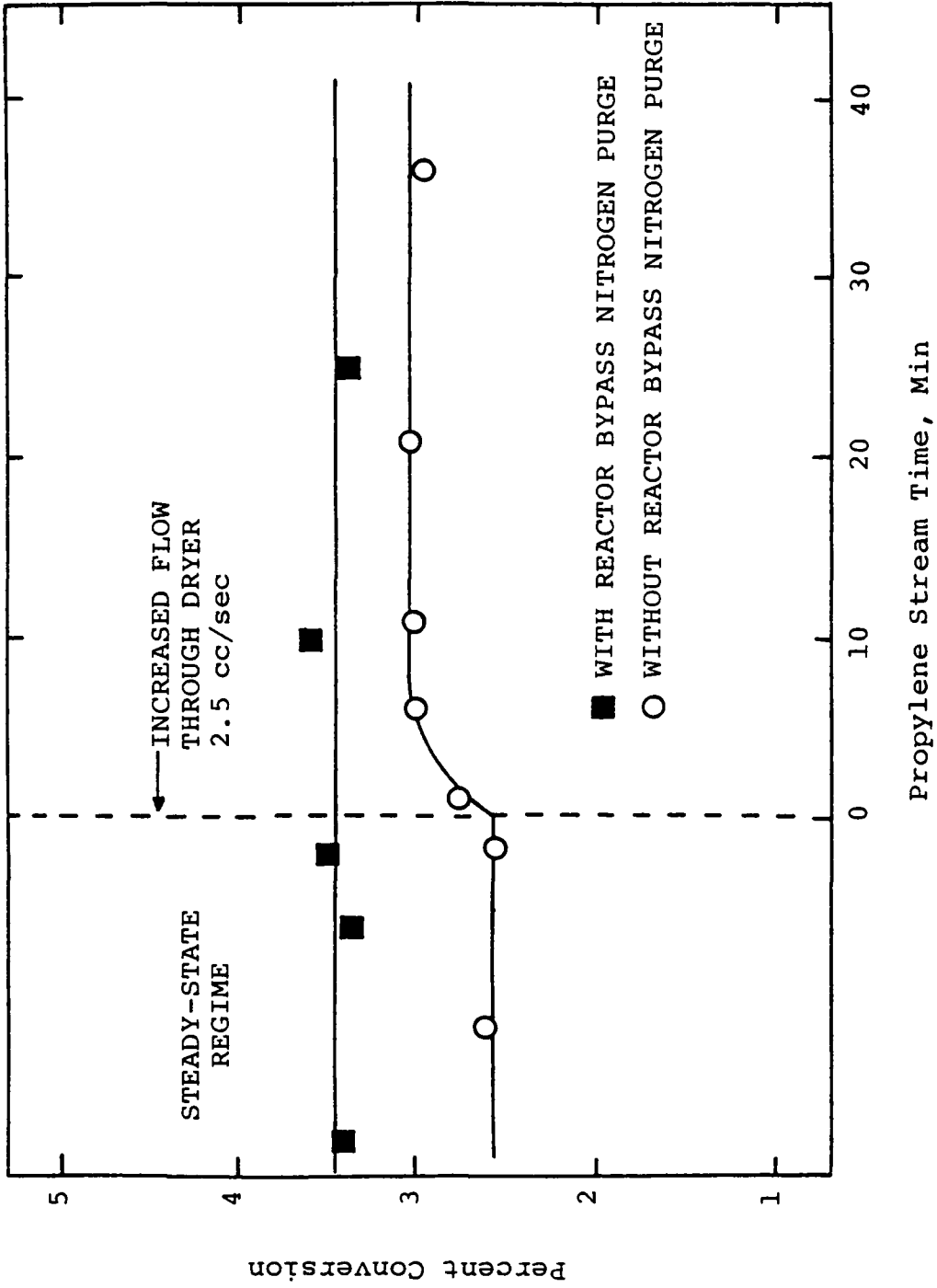


Figure 12. Effect of Reactor Bypass Nitrogen Purge on the Relationship Between Excess Reactant Flow Through Dryer and Catalyst Activity at 410°C, 0.94 ATM, and Reactor Feed Rate of 0.9 cc/sec.

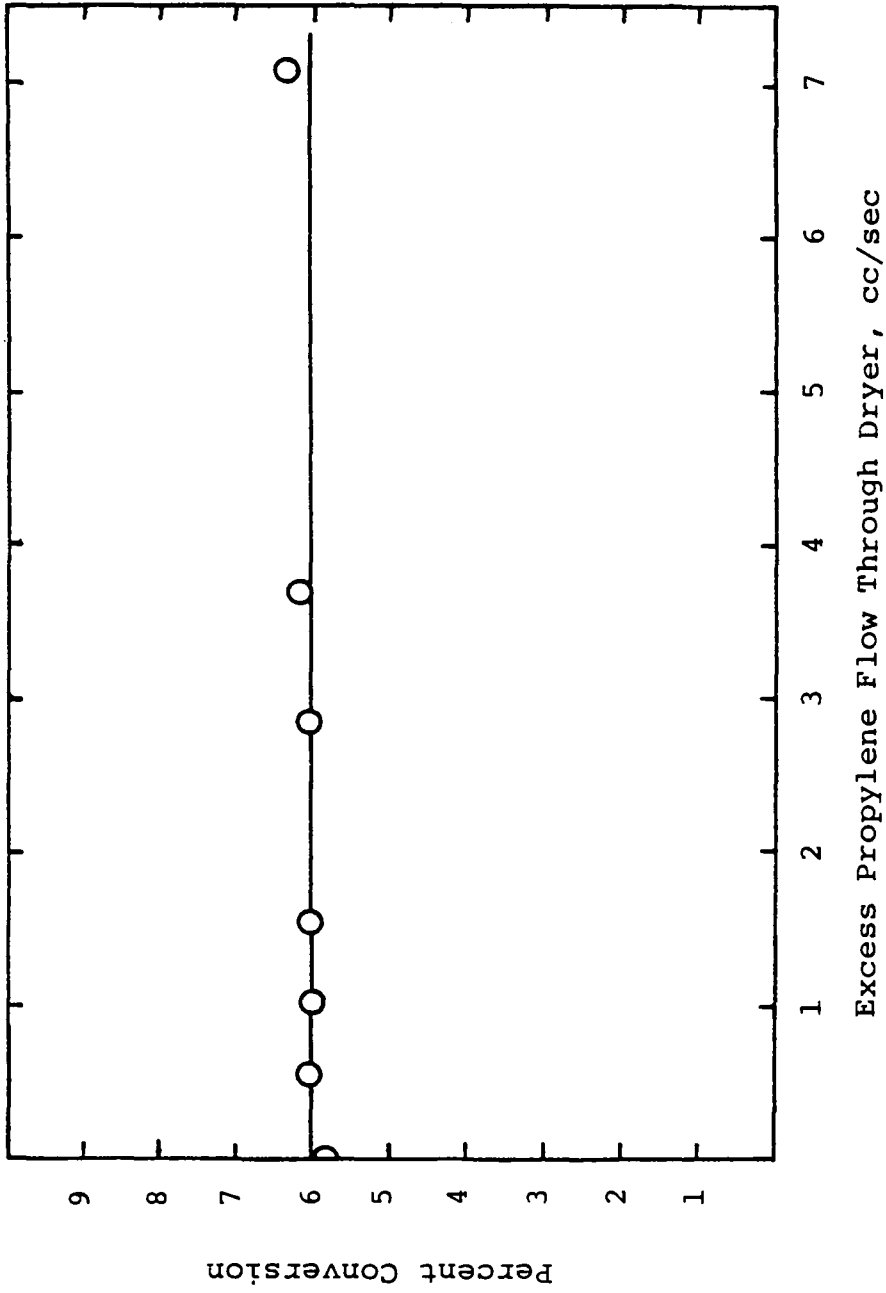


Figure 13. Effect of Excess Reactant Flow Through Dryer on Catalyst Activity when Reactor is Operated at 418°C, 0.94 ATM, and Reactor Feed Rate of 1.25 cc/sec.

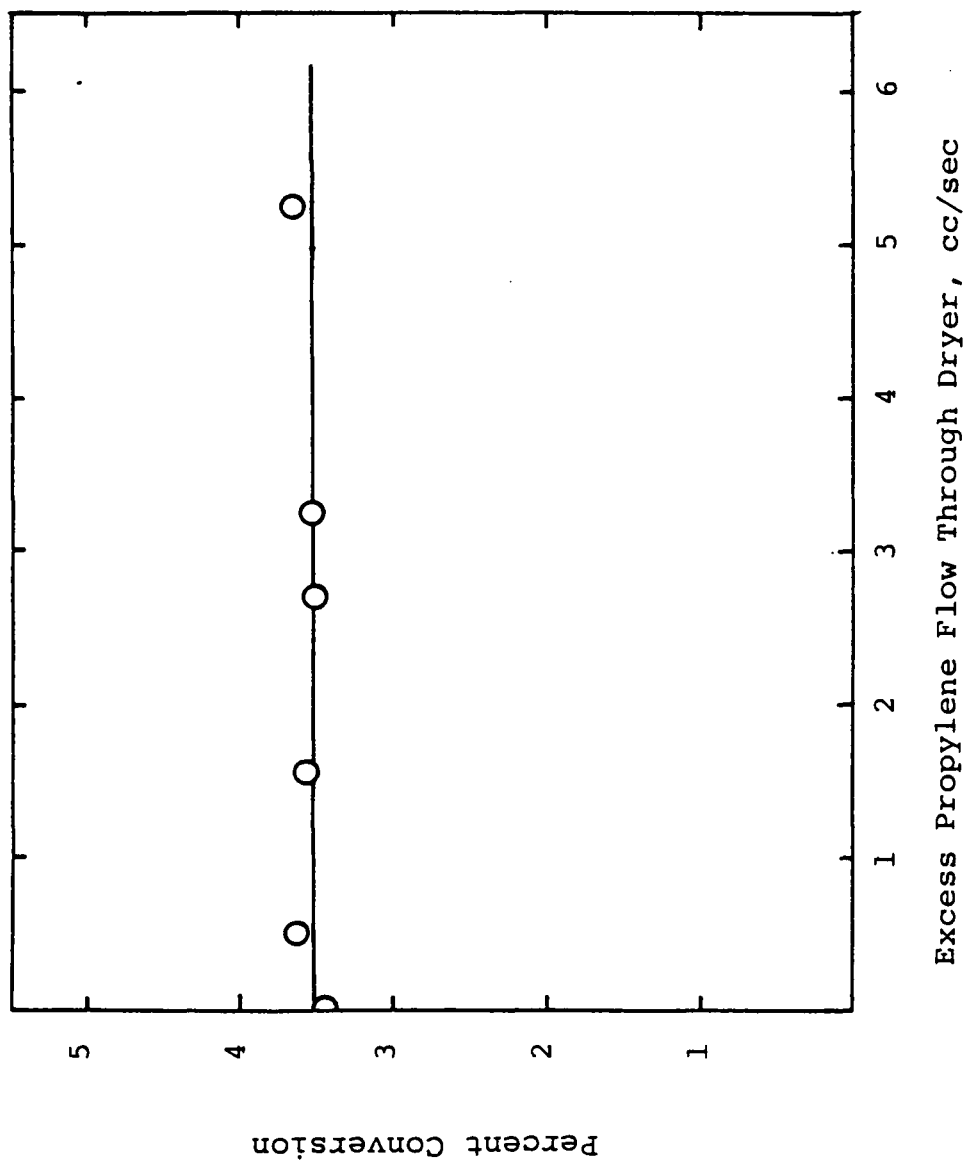


Figure 14. Effect of Excess Reactant Flow Through Dryer on Catalyst Activity When Reactor is Operated at 410°C, 0.94 ATM, and Reactor Feed Rate of 0.9 cc/sec.

between the reactor flow rate and catalyst activity. Figures 15 and 16 are plots of activity and conversion versus reactant flow rate respectively. These figures suggest that there is no effect on the catalyst activity from the flow rate in the dryer.

Effect of Reactant Flow Rate on the Recovery from Exposure to a Temporary Poison The results of the experiment to investigate the influence of reactant flow rate on catalyst recovery from exposure to a temporary poison, water, are given in Figures 17 through 20. Immediately following the introduction of water in the feed the level of conversion decreases as shown in Figures 17 and 19. Upon removal of the water in the feed the conversion gradually returns to the level achieved before the exposure to water. It took approximately 375 minutes for the system to recover from exposure to water when the reactant flow rate was 2.5 cubic centimeters per second, as shown in Figure 18. Similarly, for a reactant flow rate of 0.7 cubic centimeters per second a recovery period of 120 minutes was necessary as shown in Figure 20.

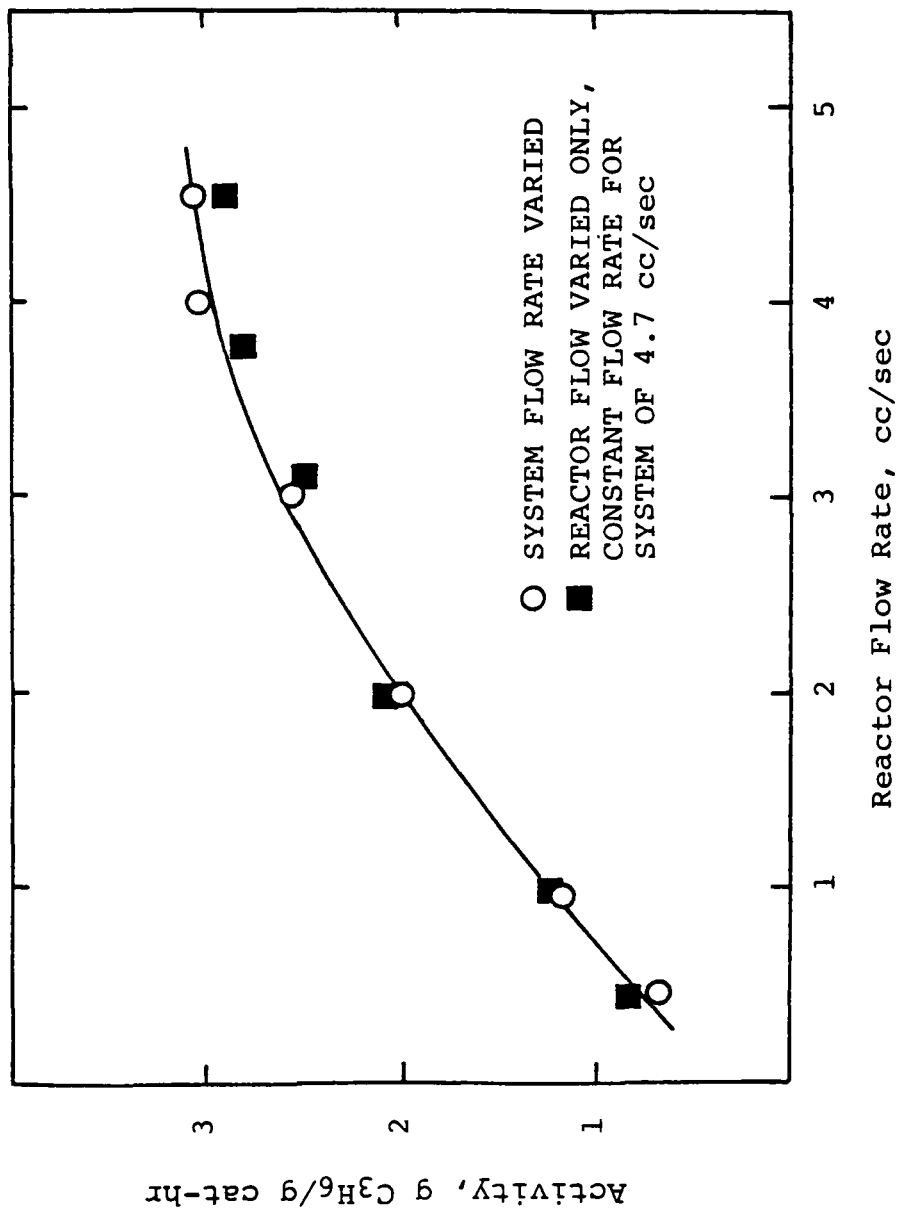


Figure 15. Effect of Reactor Flow Rate on Activity when Flow Rate in System Varied or Kept Constant at 418°C and 0.94 ATM.

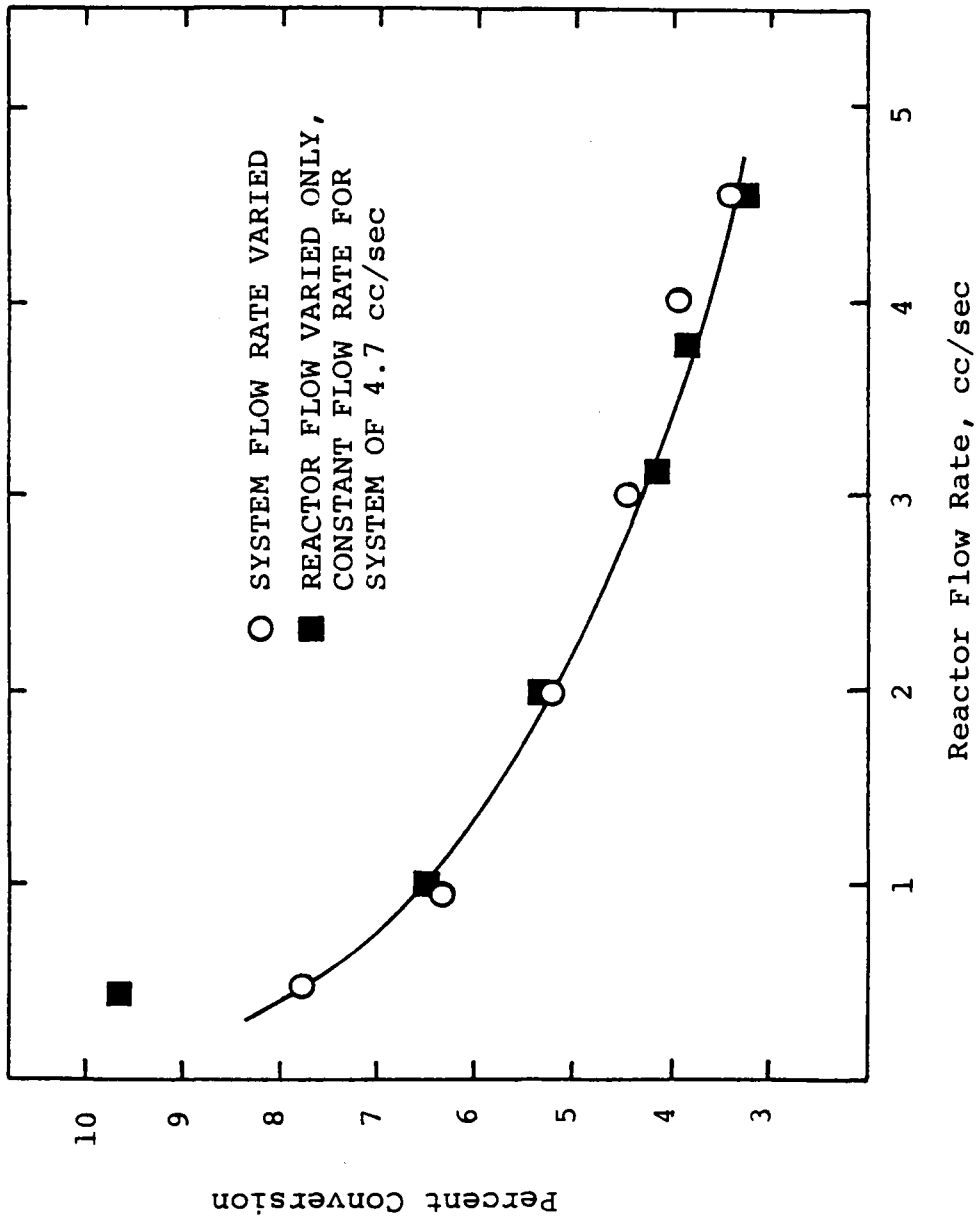


Figure 16. Effect of Reactor Flow Rate on Conversion when Flow Rate in System Varied or Kept Constant at 418°C and 0.94 ATM.

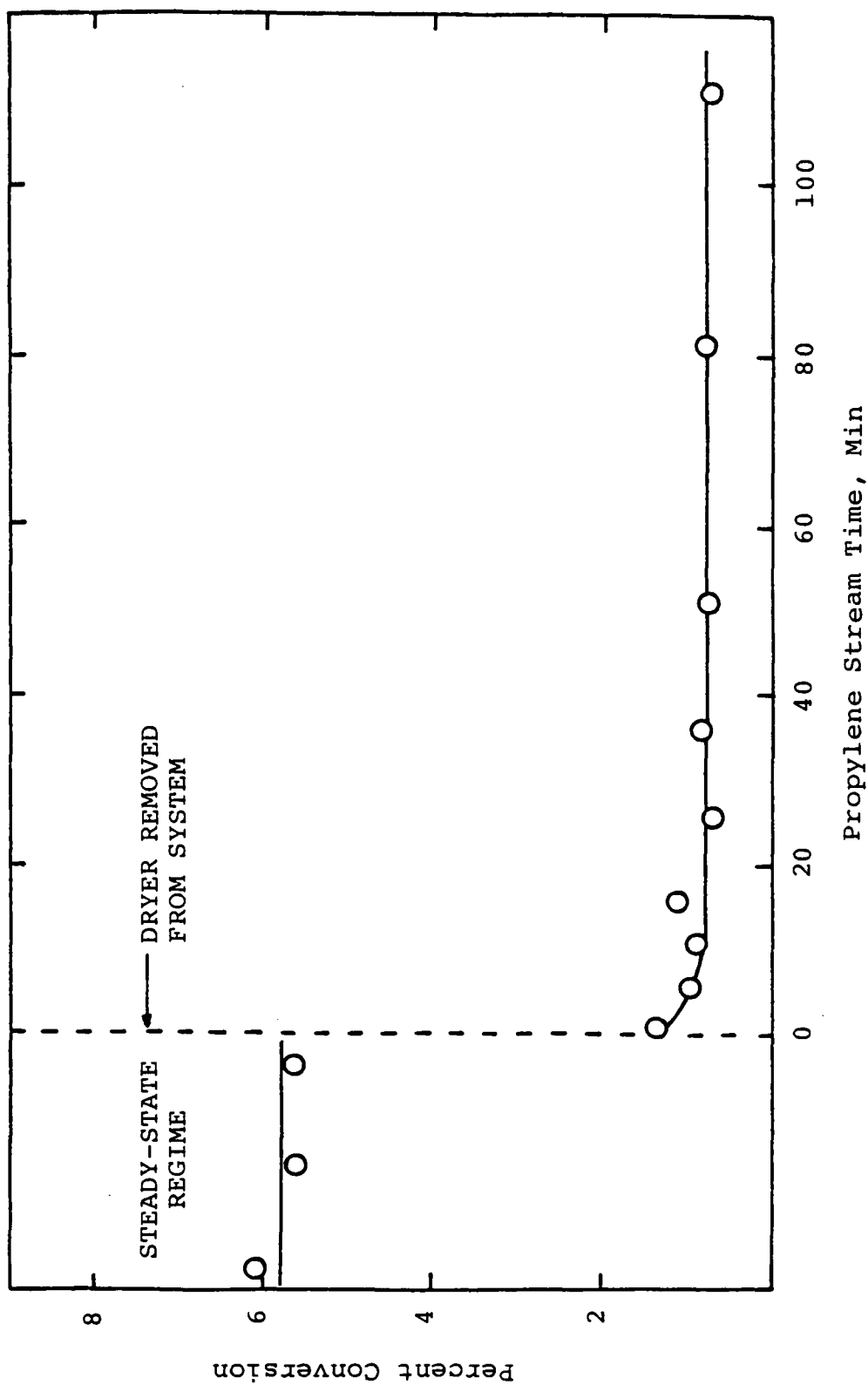


Figure 17. Effect of Water in Feed Stream on the Catalytic Activity of a Fully Broken-in Catalyst at 422°C, 0.94 ATM, and Reactant Flow Rate of 2.5 cc/sec.

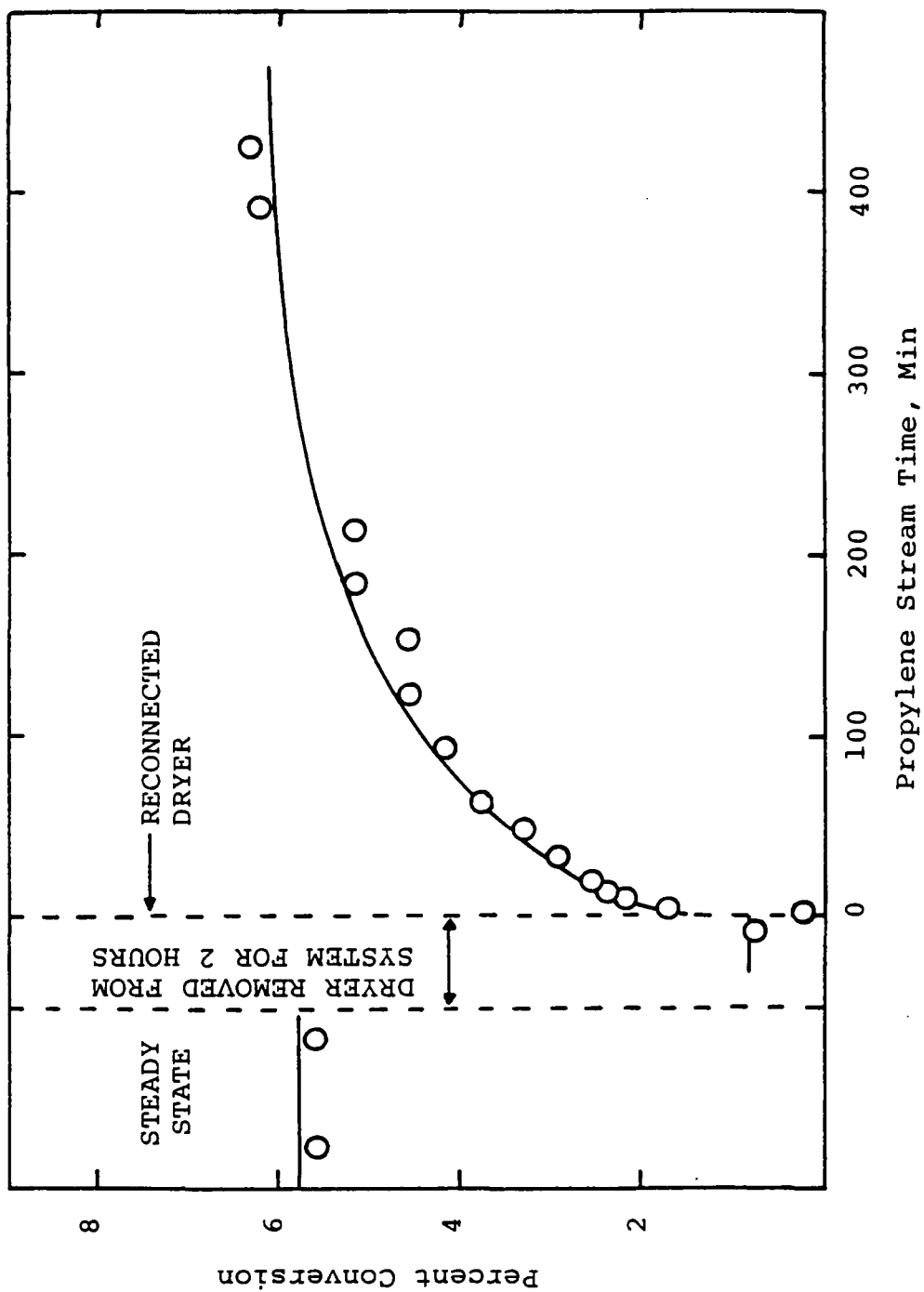


Figure 18. Transient Behavior of a Tungsten Oxide-Silica Catalyst Following a Two Hour Exposure to Propylene Feed Containing Water at 422°C, 0.94 ATM, and Reactant Flow Rate of 2.5 cc/sec.

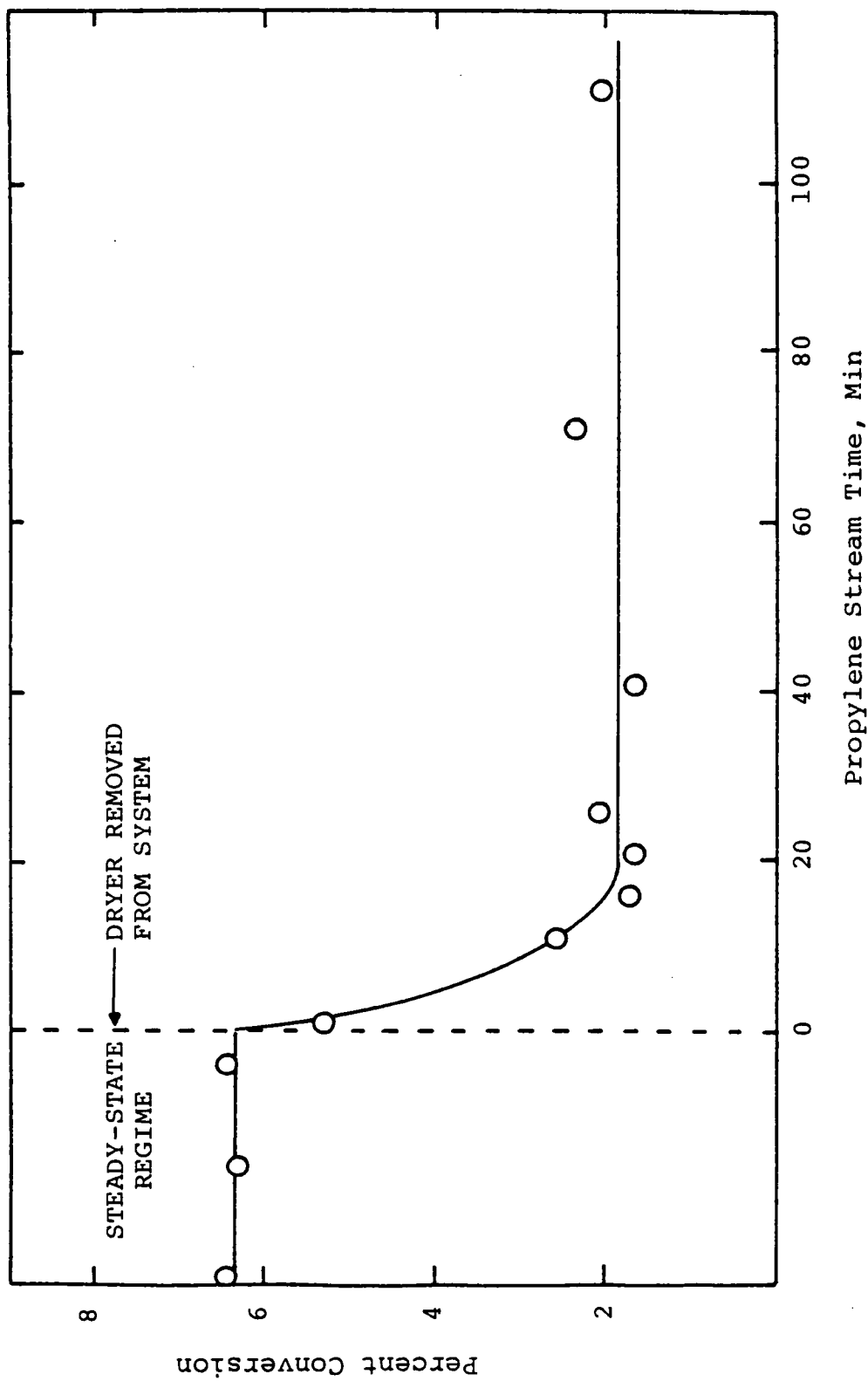


Figure 19. Effect of Water in Feed Stream on the Catalytic Activity of a Fully Broken-in Catalyst at 422°C, 0.94 ATM, and Reactant Flow Rate of 0.7 cc/sec.

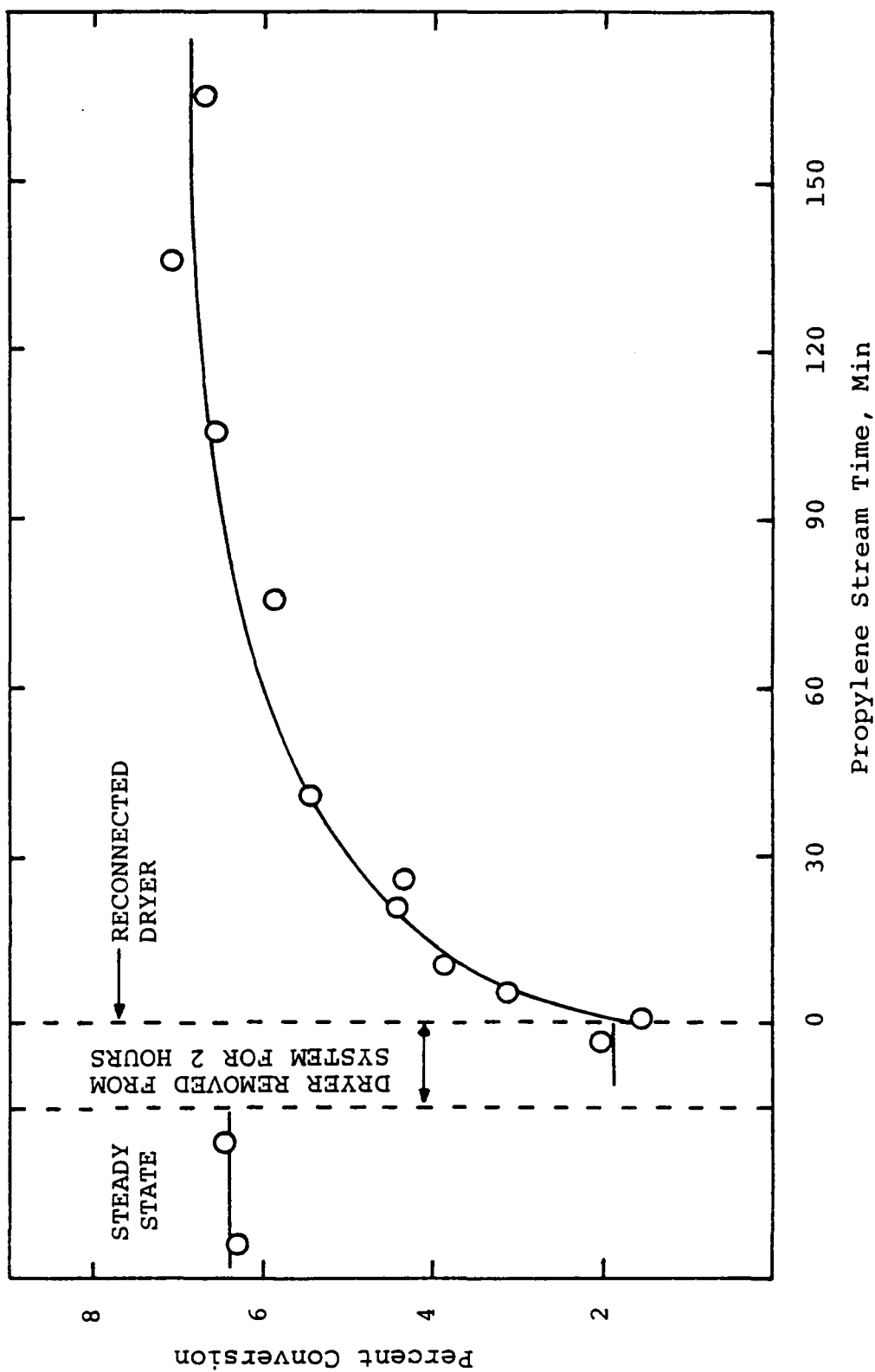


Figure 20. Transient Behavior of a Tungsten Oxide-Silica Catalyst Following a Two Hour Exposure to Propylene Feed Containing Water at 422°C, 0.94 ATM, and Reactant Flow Rate of 0.7 cc/sec.

IV. DISCUSSION

This section contains a discussion of the procedures used in this investigation, a discussion of the results obtained and comparison with published results, a listing of the limitations imposed upon this investigation, and recommendations for further studies.

Discussion of Experimental Procedures

A discussion of the experimental procedures followed in this investigation is presented in the following paragraphs.

Catalyst Activation The catalyst activation procedure used in this investigation was based upon the experimental techniques reported in the literature [17,24,34] for prior work on this catalyst system. The elevated activation temperature of 590°C and possible contamination of the catalyst with temporary poisons, air and water vapor, were strong factors in the development of an in situ catalyst activation procedure. Following activation, the catalyst was normally purged for at least sixty minutes with anhydrous nitrogen to remove any traces of air in the reactor system. Other investigators using this procedure reported the reproducibility of this procedure was

satisfactory and there were few problems in obtaining a uniform initial activity [17,34,50]. However, periodically there was difficulty in obtaining an active catalyst. The exact cause of this problem was never resolved. The problem was often corrected by replacing the molecular sieves in the dryers with fresh molecular sieves.

Reaction System In this investigation a reaction system equipped with temperature, pressure, and flow controllers was used. In order to obtain reproducible data during an experiment it is essential to carefully control these factors as they influence the rate of reaction. The overall performance of these control systems was satisfactory once the desired operating conditions were set, but it was difficult to achieve the desired setting for each.

Isothermal conditions in the reactor were maintained by independently activating the two banks of resistance elements within the tubular furnace. The continuous source of energy from one bank combined with an intermittent source of energy at a reduced level from the other bank resulted in temperature control which was oscillatory. The temperature in the reactor could be continuously monitored using the digital temperature indicator which was directly connected to the thermocouple in the reactor. In spite of attempts to maintain a constant temperature, it was

difficult to control the temperature to better than $\pm 1^\circ\text{C}$ from the set temperature. Care was taken to sample the effluent stream only when the temperature was $\pm 1^\circ\text{C}$ from the set temperature. The major difficulty with the temperature control was achieving the desired temperature setting. This often required thirty to sixty minutes of manipulating the set point on the temperature controller and the input voltages to both banks of resistance elements in the furnace to achieve the proper settings needed to maintain a particular temperature.

Flow control was achieved using a two-stage regulator on each gas cylinder, a Moore differential flow controller, and a needle valve. This provided a stable, accurately metered reactor feed throughout this investigation. The major difficulty with the flow control system was achieving the desired setting. It was difficult to make fine adjustments using the resistance value in the differential flow controller loop. During all experiments the reactant flow was measured using an in-line bubble flow meter. This procedure provided an accurate measure of the flow rate and eliminated the necessity of accurate rotameter calibrations at each operating condition.

Atmospheric pressure was used in all experiments for this investigation. This eliminated the need to use the back pressure regulator to control the pressure. Hence,

no comments can be made on the performance of the pressure controller.

Product Analysis The composition of the reactor effluent was measured using an on-line gas chromatograph. This provided an accurate and easy method of analysis. The overall performance of the gas chromatograph was satisfactory. Care was taken to always maintain the operating conditions used during calibration. The detector circuit was balanced and zeroed prior to the recording of each sample to eliminate any recorder non-linearities. A reference detector was not necessary since column bleeding was essentially eliminated due to the low temperature isothermal operation of the chromatograph oven. The recorder was operated at a fairly high chart speed and at various attenuations to magnify the peaks for low concentration components to provide an accurate integration of the chromatograms. The complete analysis of a sample took approximately six minutes which posed some limitation on studies interested in the transient behavior of the catalyst.

Experimental Errors In developing the equipment and operating procedures used in this investigation, considerable time was devoted to minimizing the experimental error.

One of the prime objectives of any experiment involving chemical reactions is the attainment of isothermal

conditions. The combination of a long spiral preheater, a metal heat transfer block, a small catalyst charge, and a low heat of reaction essentially eliminated temperature gradients within the catalyst bed for most operating conditions. The effect of the temperature variations due to the temperature controller has been previously discussed.

The gas flow rate measurements made with the bubble flow meter is a possible source of error. The principal error in the experimental determination of the flow rate is the error in the time recorded for a specific volume of flow from the reactor. The error due to the experimental determination of time was within 0.1 seconds. The measurement of a specific volume of flow from the reactor could be measured to the nearest 0.1 cubic centimeter. With care used in taking these measurements the flow measurements were believed to be accurate within an average of ± 3 percent.

The analysis of the reactor effluent sample is another source of error. The recorder was operated at a fairly high chart speed and at various attenuations to magnify the peaks to improve the accuracy of the integration of the chromatograms. Duplicate analyses of a sample with typical effluent composition were usually in agreement within 2 percent.

Errors attributable to weighing catalyst samples were believed to be negligible. The catalyst samples were dried and weighed on an analytical balance to the nearest 0.0005 grams prior to charging to the reactor.

Discussion of Results

This section contains a discussion of the results obtained in this investigation.

Catalytic Activity of Laboratory Prepared Catalysts

A tungsten oxide on silica catalyst and a tungsten oxide on silica-alumina catalyst were prepared in the laboratory using conventional impregnation methods. These catalysts were tested to determine their effectiveness as catalysts for the disproportionation of propylene. The break-in behavior for these catalysts and a commercial tungsten oxide on silica catalyst were determined under similar conditions. The results from this experiment show:

1. A break-in period of approximately 250 minutes was necessary for the commercial and laboratory prepared tungsten oxide on silica catalysts. The laboratory prepared tungsten oxide on silica-alumina catalyst has a break-in period of approximately 450 minutes.

2. The activity of a fully broken-in catalyst which was prepared in the laboratory was significantly higher than that of the commercial catalyst.
3. A significant portion of the 2-butene formed using the laboratory prepared catalysts isomerized to 1-butene. The product distribution of the commercial catalyst did not indicate 1-butene as a major product.

Two criteria in the evaluation of the suitability of a catalyst for use in a particular reaction are the activity and selectivity of the catalyst. The laboratory prepared catalysts were more active for the propylene disproportionation reaction than the commercial catalyst. However, these catalysts were not as selective as the commercial catalyst. The product distribution for the laboratory prepared catalysts indicated double bond isomerization was occurring. It has been reported that the addition of a small amount of alkali or alkaline earth metal in the disproportionation catalyst can reduce double bond isomerization [4]. Heckelsberg [4] increased the selectivity of tungsten oxide-silica and molybdena-silica catalysts for propylene disproportionation using Na, K, Ba, and Cs. The laboratory prepared catalysts were not treated with alkali or alkaline earth metal ions to improve their selectivity. The selectivity of the commercial catalyst

was nearly 100% which indicates possible treatment with alkali or alkaline earth metal ions to reduce double bond isomerization. This treatment also provides a possible explanation for the commercial catalyst being less active as the addition of the alkali or alkaline metal ions blocked some of the active disproportionation sites.

Effect of Carbon Monoxide Dosing on Catalytic Activity A fully broken-in tungsten oxide-silica catalyst was dosed with carbon monoxide to determine its effect on the catalytic activity for propylene disproportionation. The results for this experiment show a temporary decrease in the conversion level immediately following the introduction of carbon monoxide in the propylene feed. The conversion returned to the conversion level of the system prior to the dosing in approximately 110 minutes.

Carbon monoxide is reported to be a temporary poison to the catalyst [24]. The response of the catalyst to the carbon monoxide was similar to the results reported for the dosing of other known temporary poisons on this catalyst. Tang [50] reported the catalyst exhibited transient activity following the dosing of hydrogen and air. He reported the level of conversion returned to the prior level in 18 minutes when hydrogen was dosed and 100 minutes when air was dosed.

Effect of Reactant Flow Rate on Catalyst Activity

One area of anomalous behavior for this catalyst system is its unusual response to changes in the reactant flow rate. It has been reported that the activity of this catalyst increases when the flow rate is increased [38,39]. This experiment investigated the relationship between the reactant flow rate and the catalyst activity. The results from this experiment show:

1. The activity increases with increasing reactant flow rate over the entire range of reactant flow rates employed.
2. The conversion decreases with increasing reactant flow rate when the flow rate is below 4 cubic centimeters per second. Beyond this value, the conversion remains constant or increases when the flow rate is increased.

The plots of catalyst activity and conversion versus the reactant flow rate, given in Figures 6 and 7, suggest the presence of interphase mass transfer limitations on the reaction rate. When interphase mass transfer does not limit the reaction rate catalyst activity is independent of the reactant flow rate [27]. Therefore, the conversion will decrease with increasing reactant flow rate. The results of this experiment indicate the activity of the catalyst is a strong function of reactant flow rate. This

is usually indicative of significant interphase diffusional effects. However calculations predict that no limitation should exist [7].

The anomalous relationship between activity and reactant flow rate can not be easily explained as a mass transfer phenomenon [54]. It has been suggested that a poisoning phenomenon is responsible for the anomalous behavior [54]. It has been speculated that the poison is reversible and that it is introduced in the feed stream ahead of the catalyst bed at a rate independent of the flow rate. Hence as the reactant flow rate increases at constant pressure, the partial pressure of the poison decreases, and this results in an increase in the catalyst activity. It has been suggested that the poison is introduced from the system's dryer train and that a correlation exists between the flow rate through the dryer train and the activity. This phenomenon was investigated and will be discussed in greater detail in a subsequent section.

During this experiment difficulty was encountered in maintaining the set reaction temperature following an increase in the reactant flow rate. This effect became more pronounced at higher flow rates where it took several hours to reestablish the temperature to the set level with as much as a 30°C drop in temperature observed after a

flow rate increase. The energy input required to maintain the set reaction temperature was significantly higher at the higher flow rates. The catalyst bed was assumed to be isothermal so the temperature was only monitored at the middle of the catalyst bed. An increase in the energy input will result in a larger temperature gradient in the catalyst bed. Since activity is a function of temperature, this will result in an increase in activity for the catalyst bed. However, it is not known whether the energy input encountered in this experiment would cause a temperature gradient significant enough to be responsible for the observed increases in activity at the higher flow rates.

Hysteresis Effect Due to Reactant Flow Rate Variations

A study was made to determine if this catalyst system exhibits a hysteresis effect in the activity versus the reactant flow rate curves. This study was carried out for an anhydrous propylene feed and a propylene feed containing a trace amount of water. The results from this experiment show:

1. The activity of the catalyst is independent of the flow rate history when an anhydrous propylene feed is used.
2. The activity of the catalyst is influenced by the flow rate history for the catalyst when the

propylene feed contains a trace amount of water. The activity is decreased for a given flow rate following contact with low flow rates.

3. Over the range of flow rates used in this study, the activity increased steadily with increasing flow rate.

The catalyst activity was observed to be dependent on the reactant flow rate. The results from the experiment using an anhydrous propylene feed indicate this phenomenon is not influenced by the flow rate history of the catalyst. Several explanations have been proposed to explain the anomalous mass transfer phenomenon exhibited by this catalyst system. One explanation for this behavior is that it is due to catalyst poisoning [54]. The effect of the poisoning is more pronounced at lower flow rates. The results of this experiment indicate that if the relationship between activity and reactant flow rate is due to catalyst poisoning, the poisoning mechanism is reversible since a hysteresis effect due to flow rate variations was not observed. The concentration of the poison must be relatively small since it is reported the number of active sites is small [53] and no foreign species were detected chromatographically.

The principal difference between the two segments of this experiment was the propylene feed used in each

study. When an anhydrous propylene feed was used there was no evidence that the activity was affected by the previous flow rate history of the catalyst. However, when the propylene feed contained traces of water the catalyst activity was influenced by the flow rate history of the catalyst. Prior exposure to low flow rates decreased the catalyst activity. This hysteresis effect may be related to the extent of catalyst poisoning by the water. The prolonged period of exposure to water (approximately 30 hours) may have caused significant poisoning deep down in the catalyst pores. The rate of this poisoning phenomenon may be relatively slow and was not detected in these studies.

Effect of Reactant Flow Rate Through Dryers on Catalyst Activity It has been speculated that the anomalous behavior exhibited by this catalyst may be a poisoning phenomenon rather than a mass transfer phenomenon [54]. A reversible poison introduced in the feed stream from the system's dryer train has been reported to be responsible for this behavior. An investigation was made to determine if a correlation exists between catalyst activity and reactant flow rate through the dryer. The results from this study show:

1. An increase in the level of conversion was observed following an increase in the flow rate

through the dryer while maintaining the same flow rate to the reactor when the activation procedure did not include a nitrogen purge of the line to vent the excess propylene flow from the dryer. This effect was not observed when the activation procedures included a nitrogen purge for the line.

2. Increasing the flow rate through the dryer while maintaining the same reactant flow rate to the reactor has no effect on the conversion level.
3. Excess reactant flow through the dryer does not affect the relationship between catalyst activity and the reactant flow rate to the reactor.

The results of the experiments from this study indicate the catalyst activity is not affected by the reactant flow rate through the dryer. The only instance where any change in the conversion level was noticed was immediately following the initial increase of reactant flow through the dryer when the activation procedure did not include a nitrogen purge for the entire system. This suggests that dead volume in the system may be responsible for the introduction of oxygen in the feed which is a known poison to the catalyst. This would explain why the activity increases when the flow through the dryer is increased.

Effect of Reactant Flow Rate on Catalyst Recovery from Exposure to a Temporary Poison

An investigation was made to determine the effect the reactant flow rate has on the recovery of the catalyst from exposure to a temporary poison, water. The results of the study show:

1. Following the introduction of water in the feed stream the level of conversion decreased quickly and stabilized at a reduced level in approximately 10 minutes.
2. Upon removal of the water in the feed the conversion gradually returned to the level observed prior to the exposure to the water. A recovery time of approximately 375 minutes was necessary when the reactant flow rate was 2.5 cubic centimeters per second. For a reactant flow rate of 0.7 cubic centimeters per second, the recovery period was 120 minutes.

The results of this experiment are similar to those reported by Heckelsberg et al. [24] for the effect of water-saturated feed on propylene conversion. On the introduction of dry feed he reports the activity returned to the original level in about one hour after a one hour exposure to water-saturated feed.

The results of this experiment indicate a longer recovery time is required when higher reactant flow

flow rates are used. The catalyst was exposed to water-saturated feed for two hours when each reactant flow rate was used. However, this may not have resulted in the same extent of catalyst poisoning for the two cases studied. The catalyst was exposed to more water when the higher flow rate was used and the extent of poisoning may have been greater and this would result in a longer recovery period.

Recommendations

This section contains recommendations for further study that are suggested by the results of this investigation.

Modification of Equipment for Detection of Trace

Amounts of Water and Oxygen It is recommended that a conventional Hersch cell and a trace moisture analyzer be placed downstream of the reactor to monitor the oxygen and water content of effluent gases from the reactor. This information would supplement experimental results as well help to diagnose the problem when an active catalyst is not obtained following activation.

Addition of Alkali or Alkaline Earth Metal Ions to

Laboratory Prepared Catalysts It is recommended that the procedure for the preparation of laboratory prepared

catalysts be modified to include the treatment of the catalyst with small amounts of alkali or alkaline earth metal ions. Bradshaw et al. [9] outlined a procedure for treating the catalyst with sodium ions. The addition of a small amount of alkali or alkaline earth metal ions has been reported to improve the selectivity of disproportionation catalysts [4]. The effect of this treatment on the catalyst's activity and selectivity could be investigated with respect to the degree of treatment.

Effect of Catalyst Charge Size on Catalyst Activity

It is recommended that the relationship between the amount of catalyst charge and catalyst activity be determined. This experiment is a variation of this investigation's experiment to determine the relationship between the reactant flow rate and the catalyst activity. Catalyst activity at low conversion levels, can be taken as the product of the weight hourly space velocity, WHSV, and the fractional conversion of the reactant. Varying the reactant flow rate for a given catalyst charge changes the WHSV. An alternative way to vary the WHSV is to change the amount of catalyst charge for a given reactant flow rate. This alternative procedure should eliminate most of the variations in the energy input requirements to the reactor furnace observed in this investigation. This would

determine the significance of changing the temperature profile in the catalyst bed on the activity.

Limitations

This investigation was conducted under the following limitations:

1. A single commercial tungsten oxide on silica gel catalyst, obtained from the Davidson Chemical Division of the W. R. Grace Company was used in all studies.
2. Temperatures ranging from 406 to 422°C were used.
3. Atmospheric pressure was used in all studies.
4. Reactant flow rates from 0.5 to 16.8 cubic centimeters per second were used.
5. All calculations were based on the near-differential conversions in the near-absence of reaction products.
6. Only the disproportionation of propylene was studied.

V. CONCLUSIONS

As a result of this investigation, the following conclusions were made:

1. The catalysts prepared in the laboratory, tungsten oxide on silica and tungsten oxide on silica alumina, were active catalysts for the disproportionation of propylene. These catalysts were not as selective as the commercial tungsten oxide on silica catalyst used in this investigation.
2. The dosing of a fully broken-in tungsten oxide on silica catalyst with carbon monoxide caused a temporary decrease in catalyst activity. The activity returned to the level prior to the dosing in approximately 110 minutes.
3. The activity increased with increasing reactant flow rate over the range of reactant flow rates (0.5 to 16.4 cubic centimeters per second) used in this investigation.
4. The catalyst's response to the reactant flow rate was independent of the flow rate history when an anhydrous propylene feed was used. However, when the propylene feed contained traces of water the activity of the catalyst was influenced by the

flow rate history. The activity was decreased for a given flow rate following the contact with lower flow rates.

5. The activity is not affected by the reactant flow rate through the system's dryer.
6. Exposure of the catalyst to trace amounts of water in the feed resulted in an immediate decrease in activity. The rate of poisoning was small following the initial poisoning.

VI. SUMMARY

This investigation consisted of a study of the effects of the reactant flow rate on the activity of a tungsten oxide on silica catalyst during propylene disproportionation. A 10 percent tungsten oxide on silica catalyst (223 square meters per gram B.E.T. surface area) was used in a microcatalytic reactor. The catalyst activity was found to increase when the reactant flow rate was increased. The phenomenon responsible for the anomalous behavior was investigated.

The relationship between reactant flow rate and activity was found to be independent of the flow rate history when an anhydrous propylene feed was used. A hysteresis effect was observed when the feed contained traces of water. The activity decreased for a given flow rate following exposure at lower flow rates.

The explanation that a contaminant introduced in the dryers was responsible for the anomalous behavior of the catalyst to the reactant flow rate was investigated. However, it was found that reactant flow rate through the dryer had no effect on the catalyst activity.

This investigation also included studies of the effects of temporary poisons on a fully broken-in tungsten oxide on silica catalyst. The dosing of carbon monoxide

caused a temporary decrease in the catalyst activity. The activity returned to the level prior to the dosing in approximately 110 minutes. Trace amounts of water in the feed resulted in an immediate decrease in activity. Following the initial poisoning, the rate of poisoning was slower.

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APPENDIX A

EXPERIMENTAL DATA

Table 3

Break-in Behavior of a 9% Tungsten Oxide on
Silica-Alumina Catalyst Prepared
in Laboratory

T = 406°C

P = 0.94 ATM

WHSV = 70.8 g C₃H₆/g cat-hr

Catalyst = 0.31 grams

C ₃ H ₆ Stream Time, Min	Analysis of Reactor Effluent				Percent Conversion
	% C ₂ H ₄	% C ₃ H ₆	% 1-C ₄ H ₈	% 2-C ₄ H ₈	
67	6.65	86.93	1.52	4.89	13.07
107	7.11	86.02	1.70	5.16	13.98
190	7.44	85.42	1.65	5.49	14.58
310	8.07	84.05	1.85	6.03	15.95
445	8.08	84.04	1.81	6.06	15.94
465	7.76	84.31	1.86	6.08	15.69
525	7.83	84.21	1.86	6.11	15.79
580	7.76	84.28	1.82	6.14	15.72
640	8.08	83.86	1.80	6.26	16.14

Table 4

Break-in Behavior of a 7.3% Tungsten Oxide-Silica
Catalyst Prepared in Laboratory

T = 412°C

P = 0.94 ATM

WHSV = 70.7 gm C₃H₆/gm cat-hr

Catalyst = 0.3 grams

C ₃ H ₆ Stream Time, Min	Analysis of Reactor Effluent				Percent Conversion
	% C ₂ H ₄	% C ₃ H ₆	% 1-C ₄ H ₈	% 2-C ₄ H ₈	
30	4.83	90.29	1.29	3.59	9.71
45	5.34	89.82	1.24	3.59	10.18
70	5.41	89.36	1.36	3.88	10.54
120	6.07	88.20	1.44	4.29	11.80
240	6.28	87.87	1.38	4.46	12.13
375	6.01	88.01	1.48	4.50	11.99
435	6.35	87.68	1.40	4.57	12.32

Table 5

Break-in Behavior of a 10% Tungsten Oxide-Silica Catalyst
Obtained from W. R. Grace and Company

T = 410°C

P = 0.94 ATM

WHSV = 70.1 gm C₃H₆/gm cat-hr

Catalyst = 0.3 grams

C ₃ H ₆ Stream Time, Min.	Analysis of Reactor Effluent			Percent Conversion
	% C ₂ H ₄	% C ₃ H ₆	% 2-C ₄ H ₈	
5	0.11	99.78	0.10	0.22
15	0.43	99.17	0.40	0.83
25	0.58	98.88	0.54	1.12
35	0.75	98.52	0.73	1.48
50	0.99	98.15	0.86	1.85
70	1.09	97.88	1.03	2.12
90	1.29	97.36	1.35	2.64
120	1.45	97.26	1.34	2.79
150	1.66	96.57	1.77	3.43
225	1.94	96.06	2.00	3.94
360	1.87	96.07	2.06	3.93

Table 6

Transient Behavior of a Tungsten Oxide-Silica Catalyst
Following Carbon Monoxide Dosing

T = 412°C

P = 0.94 ATM

WHSV = 35.8 gm C₃H₆/gm cat-hr

Catalyst = 0.4 grams

C ₃ H ₆ Stream Time, Min	<u>Analysis of Reactor Effluent</u>			Percent Conversion
	% C ₂ H ₄	% C ₃ H ₆	% 2-C ₄ H ₈	
Steady State	3.33	93.05	3.62	6.95
	3.25	93.21	3.53	6.79
0	----- Dosed with Carbon Monoxide -----			
1	0.36	99.27	0.36	0.73
7	1.27	97.46	1.26	2.54
12	1.62	96.79	1.59	3.21
17	1.84	96.35	1.87	3.65
22	2.07	95.86	2.07	4.14
27	2.32	95.33	2.35	4.67
38	2.57	94.82	2.61	5.18
48	2.64	94.70	2.67	5.30
63	2.99	93.97	3.04	6.03
78	3.18	93.66	3.16	6.34
109	3.54	92.81	3.65	7.19
138	3.47	92.84	3.70	7.16

Table 7

Effect of Reactant Flow Rate on Catalyst Activity

T = 418°C

P = 0.94 ATM

Catalyst = 0.3 grams

Feed Rate cc/sec	Percent Conversion of Propylene (1)	Rate of Reaction (2) gm C ₃ H ₆ /gm cat-hr
0.52	6.74	0.67
1.27	4.74	1.15
1.96	3.93	1.47
2.78	3.34	1.77
4.65	2.68	2.38
6.00	2.73	3.13
7.69	2.80	4.11
9.18	2.80	4.91
12.50	3.44	8.21
16.67	3.47	11.04

- Notes: (1) Percent conversion of propylene reported is the average of three samples. Maximum deviation of any one sample from the average value was $\pm 4\%$.
- (2) Rate of reaction based on percent conversion of propylene average.

Table 8

Effect of Reactant Flow Rate on Catalyst Activity

T = 418°C

P = 0.94 ATM

Catalyst = 0.3 grams

Feed Rate cc/sec	Percent Conversion of Propylene (1)	Rate of Reaction (2) gm C ₃ H ₆ /gm cat-hr
0.51	5.65	0.55
0.92	4.38	0.77
1.32	4.02	1.01
1.89	3.10	1.12
2.94	2.96	1.66
4.00	2.54	1.94
5.88	2.42	2.72
8.33	3.03	4.82
9.62	3.00	5.51
11.63	3.09	6.86

- Notes: (1) Percent conversion of propylene reported is the average of three samples. Maximum deviation of any one sample from the average value was + 5%.
- (2) Rate of reaction based on percent conversion of propylene average.

Table 9

Effect of Flow Rate History on Catalyst Activity

T = 407°C

P = 0.94 ATM

Catalyst = 0.4 grams

Feed Rate cc/sec	Percent Conversion of Propylene (1)	Rate of Reaction (2) gm C ₃ H ₆ /gm cat-hr
----- Flow Rate Incrementally Decreased -----		
5.56	7.10	5.65
4.35	7.75	4.83
3.70	8.50	4.50
3.00	9.20	3.95
2.38	10.50	3.58
2.00	11.10	3.18
1.47	12.60	2.65
1.00	13.25	1.90
0.50	14.80	1.06
----- Flow Rate Incrementally Increased -----		
1.09	12.60	1.97
1.49	11.00	2.35
2.00	11.20	3.21
2.56	10.45	3.83
3.03	8.30	3.60
3.57	9.50	4.86
4.34	8.00	4.97
5.56	7.30	5.81

Notes: (1) Percent conversion of propylene reported is the average of three samples. Maximum deviation of any one sample from the average value was ± 5%.

(2) Rate of reaction based on percent conversion of propylene average.

Table 10

Effect of Flow Rate History on Catalyst Activity When
Propylene Feed Contains Traces of Water

T = 421°C

P = 0.94 ATM

Catalyst = 0.4 grams

Feed Rate cc/sec	Percent Conversion of Propylene (1)	Rate of Reaction (2) gm C ₃ H ₆ /gm cat-hr
----- Flow Rate Incrementally Decreased -----		
4.76	1.00	0.68
4.17	1.09	0.65
3.33	1.29	0.61
2.44	1.57	0.55
1.92	1.66	0.46
1.25	2.23	0.40
1.07	2.36	0.36
0.77	3.00	0.33
0.43	3.70	0.23
----- Flow Rate Incrementally Increased -----		
0.64	2.82	0.26
0.97	2.41	0.33
1.56	1.57	0.35
2.70	1.12	0.43
3.84	0.82	0.45

Notes: (1) Percent conversion of propylene reported is the average of three samples. Maximum deviation of any one sample from the average value was ± 5%.

(2) Rate of reaction based on percent conversion of propylene average.

Table 11

Effect of Excess Reactant Flow Through Dryer When
Activation Procedure Does Not Include a Nitro-
gen Purge for Reactor Bypass

T = 410°C

P = 0.94 ATM

WHSV = 14.1 g C₃H₆/g cat-hr

Catalyst = 0.4 grams

C ₃ H ₆ Stream Time, Min	<u>Analysis of Reactor Effluent</u>			Percent Conversion
	% C ₂ H ₄	% C ₃ H ₆	% 2-C ₄ H ₈	
Steady State	1.29	97.49	1.22	2.51
	1.32	97.40	1.28	2.60
	1.30	97.44	1.27	2.56
0 ---Increased Flow Rate Through Dryer 2.5 cc/sec -----				
1	1.45	97.25	1.31	2.76
6	1.51	97.02	1.48	2.99
11	1.52	97.00	1.48	3.00
21	1.52	96.97	1.51	3.03
36	1.53	97.04	1.44	2.96

Table 12

Effect of Excess Reactant Flow Through Dryer When
Activation Procedure Includes a Nitrogen Purge
for Reactor Bypass

T = 410°C

P = 0.94 ATM

WHSV = 14.1 g C₃H₆/g cat-hr

Catalyst = 0.4 grams

C ₃ H ₆ Stream Time, Min	<u>Analysis of Reactor Effluent</u>			Percent Conversion
	% C ₂ H ₄	% C ₃ H ₆	% 2-C ₄ H ₈	
Steady State	1.72	96.59	1.69	3.41
	1.70	96.54	1.67	3.36
	1.77	96.52	1.72	3.48
0---Increased Flow Rate Through Dryer 2.5 cc/sec -----				
10	1.82	96.42	1.76	3.58
25	1.71	96.62	1.67	3.38
60	1.91	96.22	1.87	3.78
130	1.77	96.50	1.73	3.50

Table 13

Effect of Reactant Flow Through Dryer When
Flow Rate to Reactor is Constant

T = 418°C

P = 0.94 ATM

Catalyst = 0.3 grams

Reactant Flow Rate = 1.25 cc/sec

Excess Reactant Flow Rate Through Dryer, cc/sec	Percent Conversion of Propylene (1)
0.00	6.88
0.54	7.05
1.04	6.98
1.59	6.99
2.85	7.04
3.85	7.17
7.14	7.47

Note: (1) Percent conversion of propylene reported is the average of three samples. Maximum deviation of any one sample from the average was ± 5%.

Table 14

Effect of Reactant Flow Through Dryer When
Flow Rate to Reactor is Constant

T = 410°C

P = 0.94 ATM

Catalyst = 0.4 grams

Reactant Flow Rate = 0.9 cc/sec

Excess Reactant Flow Rate Through Dryer, cc/sec	Percent Conversion of Propylene (1)
0.00	3.42
0.50	3.63
1.54	3.55
2.70	3.49
3.26	3.55
5.26	3.68

Note: (1) Percent conversion of propylene reported is the average of three samples. Maximum deviation of any one sample from the average was ± 6%.

Table 15

Effect of Flow Rate to Reactor when Flow Rate for
Entire System Varied and Kept Constant

T = 418°C

P = 0.94 ATM

Catalyst = 0.3 grams

Reactant Flow Rate cc/sec	Excess Reactant Flow Rate cc/sec	Percent Con- version of Propylene (1)	Rate of Reaction (2)
----- Flow Rate Varied for Entire System -----			
4.65	--	3.44	3.06
4.00	--	3.97	3.03
3.03	--	4.42	2.56
2.00	--	5.21	1.99
0.96	--	6.37	1.17
0.46	--	7.77	0.68
----- Constant Flow Rate for Entire System -----			
4.65	--	3.25	2.89
3.77	1.03	3.88	2.79
3.13	1.59	4.14	2.47
2.00	2.70	5.39	2.06
0.99	3.71	6.54	1.24
0.46	4.35	9.66	0.85

- Notes: (1) Percent conversion of propylene reported is the average of three samples. Maximum deviation of any one sample from the average was $\pm 5\%$.
- (2) Rate of reaction based on percent conversion of propylene average.

Table 16

Transient Behavior of a Tungsten Oxide-Silica Catalyst
Following a Two Hour Exposure to Propylene
Feed Containing Water

T = 422°C

P = 0.94 ATM

WHSV = 35.8 g C₃H₆/g cat-hr Catalyst = 0.4 grams

C ₃ H ₆ Stream Time, Min	Analysis of Reactor Effluent			Percent Conversion
	% C ₂ H ₄	% C ₃ H ₆	% 2-C ₄ H ₈	
Steady State	2.99	93.94	3.07	6.06
	2.91	94.21	2.88	5.79
	2.86	94.20	2.94	5.80
0	----- Dryer Removed From System -----			
1	1.33	97.29	1.37	2.71
6	0.50	99.04	0.46	0.96
11	0.50	99.09	0.41	0.91
16	0.51	98.92	0.57	1.08
26	0.37	99.32	0.30	0.67
36	0.45	99.20	0.36	0.80
51	0.43	99.24	0.33	0.76
81	0.46	99.20	0.34	0.80
111	0.43	99.23	0.34	0.77
0	----- Dryer Reconnected to System -----			
1	0.19	99.69	0.12	0.31
6	0.93	98.29	0.77	1.71
11	1.14	97.86	0.99	2.14
16	1.22	97.62	1.16	2.38
21	1.28	97.50	1.22	2.50
36	1.58	97.13	1.29	2.87
51	1.68	96.69	1.64	3.31
66	1.89	96.28	1.82	3.72
96	2.09	95.83	2.08	4.17
126	2.25	95.45	2.30	4.55
156	2.35	95.49	2.57	4.51
186	2.60	94.83	2.57	5.17
216	2.61	94.87	2.52	5.13
396	3.21	93.75	3.08	6.25
426	3.12	93.61	3.27	6.39

Table 17

Transient Behavior of a Tungsten Oxide-Silica Catalyst
Following a Two Hour Exposure to Propylene
Feed Containing Water

T = 422°C

P = 0.94 ATM

WHSV = 12.9 g C₃H₆/g cat-hr

Catalyst = 0.4 grams

C ₃ H ₆ Stream Time, Min	Analysis of Reactor Effluent			Percent Conversion
	% C ₂ H ₄	% C ₃ H ₆	% 2-C ₄ H ₈	
Steady State	3.30	93.56	3.14	6.44
	3.14	93.73	3.13	6.27
	3.38	93.57	3.05	6.43
0	----- Dryer Removed from System -----			
1	2.66	94.72	2.62	5.28
11	1.41	97.44	1.15	2.56
16	0.95	98.31	0.74	1.69
21	0.86	98.36	0.78	1.64
26	1.13	97.96	0.91	2.04
41	0.87	98.36	0.77	1.64
76	1.29	97.63	1.09	2.34
111	1.13	97.93	0.94	2.07
0	----- Dryer Reconnected to System -----			
1	0.92	98.33	0.76	1.67
6	1.71	96.87	1.42	3.13
11	2.03	96.18	1.80	3.82
16	2.18	95.79	2.02	4.21
21	2.28	95.60	2.13	4.40
26	2.25	95.63	2.12	4.37
41	2.82	94.59	2.59	5.41
76	3.08	94.12	2.80	5.88
106	3.32	93.42	3.26	6.58
136	3.60	92.90	3.51	7.10
166	3.35	93.27	3.37	6.73

APPENDIX B
SAMPLE CALCULATIONS

Sample Calculations

This section contains examples of the calculations made in the course of this investigation.

Calculation of Product Composition From the recorded chromatographic analysis of a sample, the peak height and the peak width at half the peak height were obtained for each component in the sample. Together with the range and the attenuation used to record each peak and the detector calibration factors reported by Luckner [34], these data were used to calculate the mole fraction of the three components in the effluent from the reactor (ethylene, propylene, and 2-butene) according to the relationship

$$m_i = \frac{f_i h_i w_i a_i r_i}{\sum_{i=1}^3 f_i h_i w_i a_i r_i} \quad (1)$$

where

a_i = recorder attenuation used to record the detector response to component "i"

f_i = detector calibration factor for component "i"

h_i = height of peak recorded for component "i"

m_i = mole fraction of component "i" in the sample

r_i = recorder range used to record the detector response to component "i"

w_i = width at half the peak height of the peak recorded for component "i".

Calculation of Conversion Conversion of the pure propylene feed was calculated using the definition of fractional conversion given by Levenspiel [32]. According to Levenspiel, fractional conversion X_A of a given reactant A is "the fraction of reactant converted into products" or

$$X_A = \frac{N_{A0} - N_A}{N_{A0}} = 1 - \frac{N_A}{N_{A0}} \quad (2)$$

where

N_A = final moles of propylene

N_{A0} = initial moles of propylene

X_A = fractional conversion of propylene

N_{A0} was calculated by summing the product of the peak area and ionization factors for each component in the product stream (ethylene, propylene, and 2-butene). N_A was calculated as a product of the peak area and ionization factors for propylene. So equation (2) becomes

$$X_A = 1 - m_A \quad (3)$$

where

m_A = mole fraction of propylene in the sample.

Calculation of Reactant Feed Rates Reactant feed rates were calculated from experimentally measured product

flow rates and were expressed in terms of mass flow rate of reactant per gram of catalyst charge. The calculation was carried out according to the definition of "weight hourly space velocity" (WHSV) by using the relationship

$$\text{WHSV} = \left[\frac{PM}{ZRT} \right] \left[\frac{C}{W} \right] [Q] \quad (4)$$

where

C = correction for water saturation of gas prior to measurement

M = molecular weight of product gas, gm/gm mole

P = pressure at which the flow rate was experimentally determined, atm

Q = volumetric flow rate experimentally measured, cm³/hr

R = ideal gas law constant, 82.06 cm³-atm/gmole-°K

T = temperature at which the flow rate was experimentally determined, °K

W = weight of catalyst charge, gm

WHSV = weight hourly space velocity, gm reactant/gm catalyst-hour

Z = compressibility factor of products.

In some of the studies, reactant flow rates were expressed in terms of space time by the relationship

$$\text{Space time} = \left[60 \frac{\text{minutes}}{\text{hour}} \right] \left[\frac{1}{\text{WHSV}} \right], \frac{\text{gm cat min}}{\text{gm reactant}} \quad (5)$$

where

WHSV = weight hourly space velocity, $\frac{\text{gm reactant}}{\text{gm cat-hr}}$.

Reaction Rate Calculations The rate of reaction or activity was calculated according to the relationship

$$r = \frac{\text{WHSV}}{42.08 \text{ gm C}_3\text{H}_6/\text{gmole C}_3\text{H}_6} [x] \quad (6)$$

where

r = rate of reaction, gmoles C₃H₆/g cat-hr

WHSV = weight hourly space velocity, gm C₃H₆/gm cat-hr

x = observed fractional conversion of C₃H₆.

APPENDIX C
MATERIALS AND APPARATUS

Materials

The following section contains a list of materials used, their source, and their specifications.

Air, Breathing Size 1-A cylinders of Airco commercial grade breathing air. Obtained from Industrial Supply Company, Bluefield, West Virginia. Used in activation of catalyst, in calcination of catalyst prepared, in activation of the dryers, and to supply oxygen to the flame ionization detector of the chromatograph.

Ammonium Metatungstate Powder form, lot no. 11478. Obtained from K & K Laboratories, Inc., Plainview, New York. Used in preparation of catalyst.

Butene-2 No. 2 cylinder of C.P. grade cis and trans 2-butene, minimum purity 99.0 percent. Obtained from Matheson Company, East Rutherford, New Jersey. Used to calibrate chromatograph.

Carbon Monoxide No. 3 cylinder of C.P. grade carbon monoxide, minimum purity 99.5 percent. Obtained from Matheson Company, East Rutherford, New Jersey. Used as a dosing agent.

Catalyst 3/16 inch extrudates of tungsten oxide on silica with the following specifications:

Tungsten oxide	10%
Surface area	223 m ² /gram
Pore volume	1 cm ² /gram

This catalyst was furnished by Davidson Chemical Division of W. R. Grace and Company, Baltimore, Maryland and was designated SMR 7-5381. Used in all studies involving the disproportionation reaction.

Chromatographic Column Packing 20 percent dimethyl sulfolane on Chrosorb W, NAW, 45-60 mesh. Obtained from Hewlett-Packard, Avondale Division, Avondale, Pennsylvania. Used as a chromatographic column packing to separate product gases for analysis.

Ethylene 12 gallon cylinder of pure grade ethylene, minimum purity 99.0 percent. Obtained from Phillips Petroleum Company, Bartlesville, Oklahoma. Used to calibrate chromatograph.

Helium Size 1-A cylinders of Airco commercial grade helium. Obtained from Industrial Supply Company, Bluefield, West Virginia. Used as a carrier gas for the chromatograph.

Hydrogen Size 1-A cylinders of Airco commercial grade hydrogen. Obtained from Industrial Supply Company, Bluefield, West Virginia. Used as a combustion gas in the flame ionization detector of the chromatograph.

Molecular Sieves 1/16 inch pellets, type 5A, part no. 5943350233. Obtained from Union Carbide Corporation-Linde Division. Used to dry all gases entering the reactor.

Nitrogen Size 1-A cylinders of Airco dry nitrogen. Obtained from Industrial Gas Supply, Bluefield, West Virginia. Used to purge the reactor system.

Propylene 28 gallon cylinders of polymerization grade propylene, minimum purity 99.0 percent. Obtained from Phillips Petroleum Company, Bartlesville, Oklahoma. Used as feed to the reactor and to calibrate the chromatograph.

Silica 3/16 inch pellets, designated as SMR 7-2047. Obtained from Grace-Davidson Chemicals, Baltimore, Maryland. Used in preparation of catalyst.

Silica Alumina 3/16 inch pellets, grade 979 with the following specifications:

Composition	87% silica
	13% Al ₂ O ₃
	0.3% Impurities
Surface area	400 sq. m/gram
Pore volume	1.0
Bulk density	24 lbs/cu.ft

Obtained from Grace-Davidson Chemicals, Baltimore, Maryland and was designated as SMR 7-1171.

Apparatus

The following section contains a list of the apparatus used in this investigation.

Balance Mettler, type H15, 160 gram capacity, serial no. 263600. Obtained from the Mettler Instrument Corporation, Hightstown, New Jersey. Used to weigh materials used in catalyst preparation and to weigh catalyst and quartz samples.

Chromatograph F and M, Model 810-29 analytical gas chromatograph equipped with a 30-foot dimethylsulfolane on Chromosorb W column, serial no. B-922. Manufactured by F and M Scientific Corporation, Avondale, Pennsylvania. Used to analyze effluent gases from reactor.

Desiccator Desiccator with coors plate, 25.0 cm inside diameter, catalog no. 8-615B. Obtained from Fisher Scientific Company, Inc., Raleigh, North Carolina. Used to store catalyst samples.

Digital Thermometer Omega digital readout thermometer, model 2809-C, serial no. 00914, AC 115V, 50-60 Hz, calibrations for type R, K, J, T and E thermocouples. Type J thermocouple, iron-constantan, was used so temperature range was 0 to 800°C with maximum deviation of 2°C. Obtained from Omega Engineering, Inc., Stamford, Connecticut. Used to measure the temperature of the catalyst bed.

Dryers Three dryers, constructed from one inch stainless steel pipe and packed with type 5A molecular sieves. Dryers were fourteen inches in length with both ends fitted with pipe caps which had 1/8-inch "Swagelok" male connectors installed in the end. Used to remove the water content of the feed gases.

Electric Furnaces A 6-inch tubular furnace, type 123-1, 115V, 422W, serial no. 67875, maximum temperature 1950°F, safe working temperature 1850°F. Manufactured by Heavy Duty Electric Company, Milwaukee, Wisconsin. Used to supply heat to the reactor. Also a 12-inch tubular furnace, type 123-3, 115V, 720W, serial no. 67877, maximum temperature 1950°F, safe working temperature 1850°F. Manufactured by Heavy Duty Electric Company, Milwaukee, Wisconsin. Used to activate the dryers and to calcine catalyst samples.

Flow Controllers Two constant differential type flow controllers, type 63BU-L, B/M 1074653. Obtained from Moore Products Company, Spring House, Pennsylvania. Used to control feed flow rates to the reactor.

Manometer U-tube manometer prepared by bending glass tubing and filling with mercury. Used to measure pressure in sampling system during charging of the sample loop.

Mortar and Pestle Coors porcelain, 90 mm outside diameter, footed bottom with pour lip, catalog nos. 12-961-A and 12-961-5A. Obtained from Fisher Scientific Company, Raleigh, North Carolina. Used to crush catalyst pellets and quartz.

Motor A-C motor, model no. 5KC47AB8996, 1/3 horsepower, 115/230V, 1725 rpm, 60 cy, 4.8/2.4 amp. Manufactured by General Electric Company. Used to drive the vacuum pump.

Oven Single wall transition oven, 0-200°C, 120V/1PH/50-60 Hz, serial no. XA-14746. Manufactured by Blue M Electric Company, Blue Island, Illinois. Used to dry catalyst.

Powerstats Two variable transformer powerstats, type no. 116, primary voltage 120V, 50/60 cy AC, output voltage 0-140V, maximum 7.5 amp. Manufactured by the Superior Electric Company, Briston, Connecticut and

obtained from Fisher Scientific Company, Inc., Pittsburgh, Pennsylvania. Used to regulate current input to electric furnace surrounding reactor.

Pressure Gage 0-400 psig, five psig subdivisions. Obtained from Champion Gauge Company, New York, New York. Used to measure the reactor back pressure.

Pressure Regulator Back pressure regulator, control range 25 to 400 psi, model no. S-91LW, maximum temperature 200°F, serial no. 706077-3. Obtained from Grove Valve and Regulator Company, subsidiary of Walworth Company, Oakland, California. Used to regulate reactor pressure.

Pyrometer Sim-Ply-Trol automatic temperature controller, 0-1000°F, model no. 100, catalog no. 1635. Manufactured by Assembly Products, Inc., Chesterland, Ohio. Used to control temperature of catalyst bed.

Reactor A 6-inch tubular, fixed bed catalytic reactor. A detailed description of the reactor is given in the experimental equipment section of this thesis.

Rotameters Two dual float rotameters, tube nos. 601 and 603, 9.09 to 268.5 cc/min. Manufactured by Matheson Company, Inc., East Rutherford, New Jersey. Used to indicate flow rate to the reactor.

Sieves U.S. standard sieve nos. 20, 30, and 40, brass frame, 8-inch inside diameter, 2-inch high sides, catalog no. 4-881. Obtained from Fisher Scientific Company, Inc., Pittsburgh, Pennsylvania. Used to screen catalyst and quartz samples.

Soap Bubble Flow Meters Two Schellbach burets, 50 ml capacity, 0.1 ml subdivisions, catalog no. 3-730B. Obtained from Fisher Scientific Company, Inc., Raleigh, North Carolina and were modified into bubble flow meters

by Research Division of Glass Shop, Davidson Hall, Virginia Polytechnic Institute and State University, Blacksburg, Virginia. Used to measure flow rates of gas streams leaving the reactor.

Stopwatch Electric, direct reading stopwatch, 0.1 second divisions, 0-10,000 seconds, 115V, 60 cy AC, catalog no. 69230. Obtained from Fisher Scientific Company, Inc., Raleigh, North Carolina. Used with soap bubble flow meter to determine flow rates.

Thermocouple Quick Disconnect Thermocouple Assemblies, type J thermocouple (iron-constantan), 12-inch length, catalog no. ICSS-18U. Obtained from Omega Engineering, Inc., Stamford, Connecticut. Used to measure temperature of catalyst bed.

Vacuum Pump Duo seal type vacuum pump, patent no. 2337849, serial no. 16593-0. Manufactured by W. M. Welch Manufacturing Company, Chicago, Illinois. Used to evacuate the sampling loop.

Wet Test Meter 0.1 cubic foot per revolution, 0.001 cubic foot subdivisions. Manufacturing by Precision Scientific Company, Chicago, Illinois. Used to measure flow rates of gas streams leaving the reactor.

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EFFECTS OF FLOW ON THE ACTIVITY OF A WO_3-SiO_2
OLEFIN DISPROPORTIONATION CATALYST

by

SEALA LOUISE FLETCHER

(ABSTRACT)

This investigation consisted of a study of the effects of the reactant flow rate on the activity of a tungsten oxide on silica catalyst during propylene disproportionation. A 10 percent tungsten oxide on silica catalyst (223 square meters per gram B.E.T. surface area) was used in a microcatalytic reactor. The catalyst activity was found to increase when the reactant flow rate was increased. The phenomenon responsible for the anomalous behavior was investigated.

The relationship between reactant flow rate and activity was found to be independent of the flow rate history when an anhydrous propylene feed was used. A hysteresis effect was observed when the feed contained traces of water. The activity decreased for a given flow rate following exposure at lower flow rates.

It has been suggested that a contaminant was being introduced in the driers and that the anomalous behavior of the catalyst to the reactant flow rate was due to this.

However, the reactant flow rate through the dryer was found not to affect the activity.

This investigation also included studies on the effects of temporary poisons on a fully broken-in tungsten oxide on silica catalyst. The dosing of carbon monoxide caused a temporary decrease in the catalyst activity. The activity returned to the level prior to the dosing in approximately 110 minutes. Trace amounts of water in the feed resulted in an immediate decrease in activity. Following the initial poisoning, the rate of poisoning was slowed.