

THE BREAK-IN BEHAVIORS OF THE COBALT OXIDE-MOLYBDENA-
ALUMINA CATALYST AND THE TUNGSTEN OXIDE ON SILICA
CATALYST DURING PROPYLENE DISPROPORTIONATION

by

Solomon Hsing-Kuo Tang

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APPROVED:

G. B. Wills, Chairman

T. C. Ward

P. R. Rony

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Blacksburg, Virginia

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I. INTRODUCTION

It has been known for over 150 years that many reactions can be accelerated in the presence of certain substances called catalysts. Good catalysts are those which can induce the rapid transformation of a reactant molecule while themselves apparently suffering little alteration in character or quantity. If the catalyst exists in the same phase as the reactants, it is said to be homogeneous; otherwise it is heterogeneous. Most commercial chemicals are prepared by converting raw materials via chemical reactions. Such reactions usually require catalysts, and these are normally solids. Since the temperatures must be high for rapid reaction rates, the reacting fluid commonly is in the gas phase. Examples of large-scale catalytic reactions are the major hydrocarbon transformations: cracking, reforming, dehydrogenation, isomerization, and desulfurization. In practice, the term heterogeneous catalysis usually refers to systems in which the reactants and products are gases and the catalyst is a solid.

One important demand society makes upon chemical engineers is that they successfully make specifically desired products at the fastest possible rate to attain an overall economic optimum. This demand leaves chemical engineers with the question of how to make or select the right catalyst for a given reaction.

The economic value of a catalyst resides in three characteristics--activity, selectivity, and life--but these may not function independently, and the activity and selectivity of a catalyst may change with time

through its life. It is well known that three regimes usually exist in the temporal history of a catalyst:

1. A break-in period, during which the activity of the catalyst increases or decreases. The time involved in this regime depends on the nature of catalytic reaction and can be as long as days or as short as seconds.
2. A steady-state period, during which the catalyst is in its fully activated state and the rate of reaction does not change appreciably with time.
3. A breakdown or deactivation period during which the activity of the catalyst decreases with time.

Although the existence of break-in phenomena has been noted, there has not been many studies performed on such phenomena during the past several years. In the search for a new catalyst, a clear understanding of the nature of break-in phenomena has become increasingly important, because ignorance of the existence of break-in period may lead to the erroneous selection of catalysts. Catalysts with long break-in periods may well be discarded in a regular catalyst screening program, even though they may actually be superior catalysts in many other respects once the existence of break-in is clearly understood and eliminated.

The study of break-in phenomena is quite different from studies of the usual "transient kinetics" in which the full activity of the catalyst is supposed to be present and consequently the observed transients are solely due to dispersion, mass transport delays, and to displacement of the adsorption-desorption equilibria. In the studies of time-dependent effects of "break-in," the elimination of residual

effects due to mass transfer or to displacement of adsorption-desorption equilibria is essential. The possibilities which may be considered being responsible for the break-in behavior include:

1. The purging of physisorbed or weakly chemisorbed poisons, formed during the activation procedures, from the catalyst surface.
2. Changes in surface structure and/or composition due to either reactant-surface or product-surface interactions.
3. Formation of intermediate complexes from reactants or products that are catalytically active sites for the reaction.

The objective of this investigation was to study the break-in with two similar heterogeneously catalyzed systems. The first system was a cobalt-molybdenum-alumina catalyst that efficiently promoted olefin disproportionation at relatively low temperatures. The other system was tungsten oxide supported on silica which was also reported to be an efficient catalyst for propylene disproportionation. The plan of investigation will be given later in Section III.

II. LITERATURE REVIEW

It was reported in 1964 by Banks and Bailey⁽⁴⁾ that linear olefins containing three to eight carbon atoms could be converted to homologs of shorter and longer carbon chains over certain catalysts. The catalysts for the so-called olefin disproportionation reaction consisted of molybdenum hexacarbonyl, tungsten hexacarbonyl, and molybdenum oxide supported on alumina. Since then, many varieties of solid materials have been reported to be active for olefin disproportionation.⁽²⁾ They fall into the category of supported heterogeneous catalysts, comprising a high-surface-area refractory support upon which a promotor is deposited. Among these catalyst systems, tungsten oxide on silica and cobalt-molybdena-alumina have received considerable attention.^(9,23)

Olefin Disproportionation

Cobalt Oxide-Molybdena-Alumina Catalysts. Two types of molybdena-alumina catalysts were described in the first paper on olefin disproportionation;⁽⁴⁾ one catalyst contained cobalt oxide and the other did not. It was reported that the cobalt oxide reduced coke formation during use, but did not affect the initial activity. The cobalt molybdate catalyst was used for the disproportionation of a variety of olefins, from propylene to 1-octene, over a temperature of 90 to 300°C, 450 psig, and 3-4 weight hourly space velocity (WHSV which has units of grams reactant/hour/gram catalyst). Propylene was further tested over a range of space velocities from about 4 to 110. Propylene

conversion near thermodynamic equilibrium (about 43%) was obtained at 160-205°C and space velocities of 4-8.

The effect of the molybdena content of the catalyst was studied over laboratory prepared molybdena-alumina catalysts containing up to 13.2 percent molybdena.⁽⁴⁾ Propylene conversions were highest with 7 to 12 percent molybdena catalysts. When the temperature was increased stepwise from 90 to 300°C, propylene conversion increased with increasing temperature to a maximum value for each catalyst and then decreased with further increases in temperature.

Bradshaw, Howman, and Turner,⁽⁹⁾ who used a commercial cobalt-molybdena-alumina catalyst in their work, reported that the activity of the catalyst for double-bond isomerization had a marked influence on the course of the reaction. Selectivity of the catalyst was increased by poisoning the isomerization sites with sodium ions. The sodium ions were added by treating the catalysts with solutions of sodium bicarbonate. Workers at Shell International⁽⁴³⁾ also showed that adding alkaline metal ions to cobalt molybdate and molybdena-alumina catalyst reduced isomerization and increased selectivity. According to their work, the order of increasing ionic effectiveness was sodium, potassium, rubidium and cesium.

The activity of a molybdena-alumina catalyst could be increased by treating the alumina support with a strong inorganic or organic acid before impregnating with the promoter.⁽¹⁰⁾

Tungsten Oxide on Silica Catalysts. In 1968 Heckelsburg, Banks and Bailey⁽²²⁾ reported that tungsten oxide on silica catalysts had excellent disproportionation activity. Such catalysts were reported

to be more desirable for olefin disproportionation than the cobalt molybdate catalysts. For commercial applications, this catalyst operated best in the temperature range of 260 to 550°C and offered resistance to common poisons such as air and water. In addition, operation in this temperature range also reduced or eliminated costly and time consuming cooling and heating periods during regeneration.

Water, air, acetone, carbon monoxide, hydrogen and methanol in the feed were reported to be temporary poisons.⁽²³⁾ They decreased the catalyst activity; however, on reintroduction of pure feed, the original activity was recovered. The effect of a feed saturated with water is shown in Figure 1. In this example, the activity of catalyst is reduced by the poisons present in feed, but increases to 44 to 45% propylene conversion in about one hour upon the reintroduction of dry feed. No special pretreatment is needed to use this catalyst for olefin disproportionation; however, a 5 hour activation in air at 590°C followed by a one hour purge with nitrogen at same temperature is highly recommended.

Catalysts that were deactivated during use could be regenerated by repeating the activation procedure with a controlled amount of oxygen to burn off accumulated coke.⁽²²⁾ Heckelsberg reported that over 110 regenerations in a period of about one year the activity of tungsten oxide-silica catalyst was only slightly lower than that of fresh catalyst, but the disproportionation selectivity was even higher. Heckelsberg⁽²¹⁾ also reported that selectivity of tungsten oxide-silica for disproportionating propylene could be increased by adding Na, K, Ba and Cs to the catalyst.

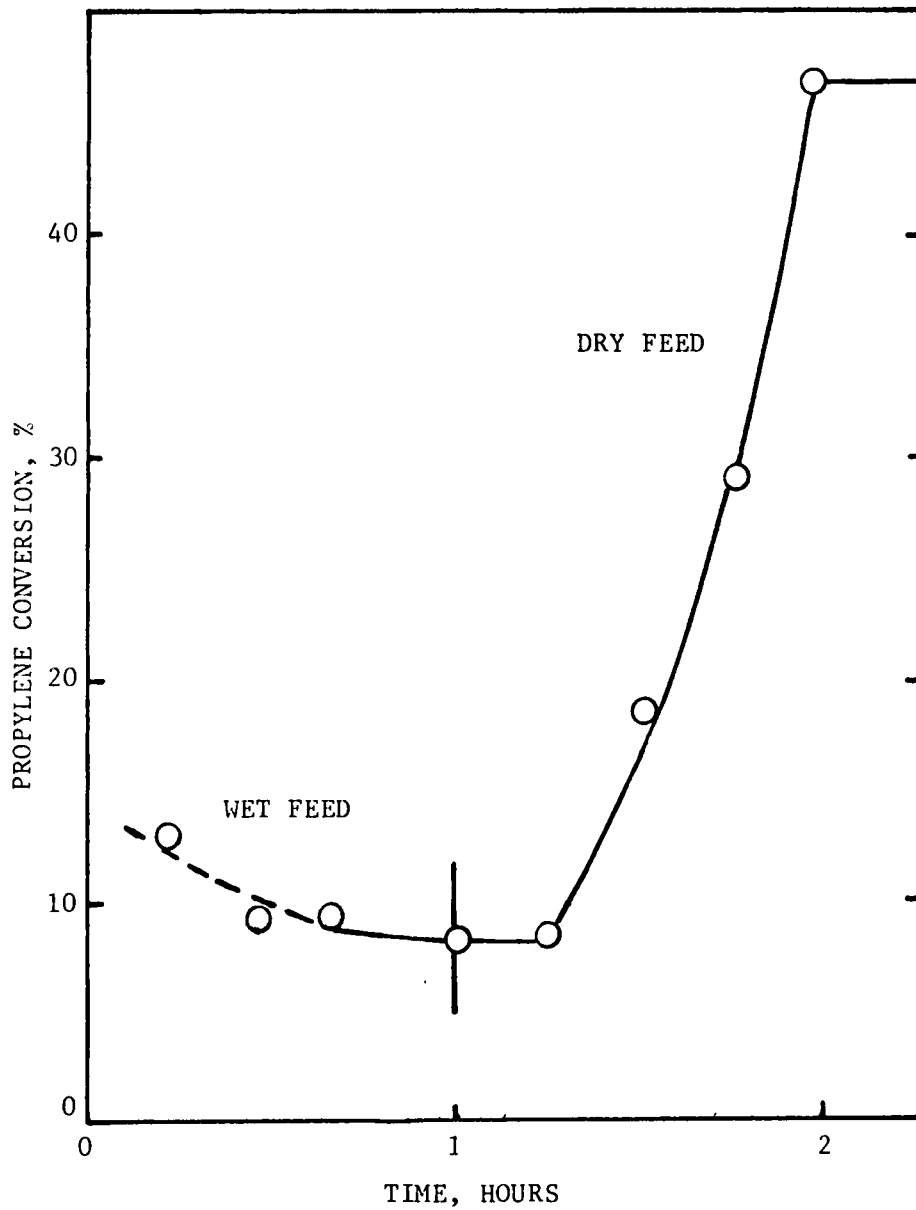
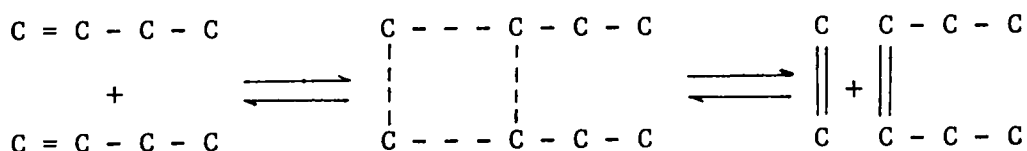
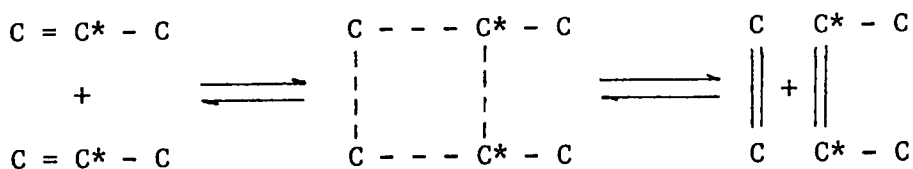


Figure 1. Effect of Water-Saturated Feed on Propylene Conversion. (Helckelsberg, L. F., R. L. Banks, and G. C. Bailey, Ind. Eng. and Prod. Res. and Devel., 7, (1) 29-31 (1968).

Mechanism of Disproportionation. The observed results of olefin disproportionation could be caused by either the cleavage of a carbon-carbon single bond adjacent to the double bond (transalkylation) or the cleavage of the double bond itself (transalkylidenation). Bradshaw, Howman, and Turner⁽⁹⁾ studied the disproportionation of 1-butene over cobalt molybdate catalyst in detail. They suggested that the reaction occurs via a "quasi-cyclobutane" intermediate formed by the correct alignment of the carbon atoms at the double bonds of two reacting olefins. Applied to 1-butene, the reaction was pictured as follows:

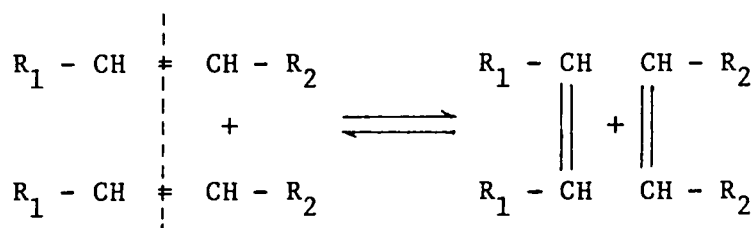


Tracer experiments were employed to support this reaction scheme. Mol et al.⁽³⁸⁾ disproportionated (2-C¹⁴) propylene over a Re₂O₇-Al₂O₃ catalyst and found that the ethylene formed had no radioactivity, while the 2-butene showed a specific radioactivity twice as high as that of the starting material. This result is completely consistent with a transalkylidenation scheme, and excludes a transalkylation reaction. Similar results were obtained by Clark and Cook⁽¹⁵⁾ in experiments with radioactive (1-C¹⁴) propylene and (2-C¹⁴) propylene on a cobalt molybdate catalyst at lower temperature. The reaction was reported to proceed as:



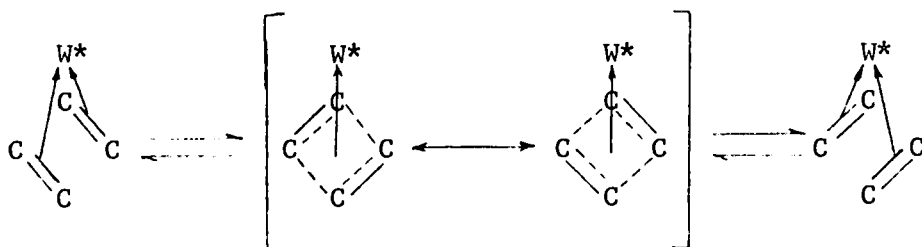
At higher temperatures, Woody, Lewis, and Wills⁽⁴⁸⁾ reported that the double bond in the olefin could be quite mobile as a result of the observation that radioactive propylene (1-C¹⁴) gave a mixture of C¹⁴ products with radioactivity in both ethylene and 2-butene.

In 1967, Calderon, Chen, and Scott⁽¹²⁾ proposed a similar mechanism for olefin disproportionation catalyzed by the homogeneous complex obtained from the interaction of WCl₆, C₂H₅OH, and C₂H₅AlCl₂. They pictured a transalkylidenation reaction as follows:



Later Calderon and co-workers⁽¹¹⁾ pictured the transition state as:

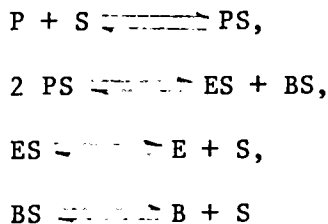
as:



where W* denotes the transition metal atom plus the remaining ligands.

Kinetic Studies of Propylene Disproportionation

For the heterogeneously catalyzed disproportionation of propylene, the Langmuir-Hinshelwood model, in which the reaction occurs between two chemisorbed molecules, was examined by several investigators. In this model, the following reactions are assumed:



These equations represent the adsorption-desorption reactions and the surface reaction; E, P and B are, respectively, ethylene, propylene, and 2-butene, and S represents an active site. If the surface reaction is rate determining, the following rate equation can be derived:

$$\begin{aligned}
 r &= -\frac{1}{2}d[P]/dt \\
 &= kK_P^2([P] - [E][B]/K_{eq})/(1 + K_E[E] + K_P[P] + K_B[B])^2
 \end{aligned}$$

where k is a reaction rate constant, K_{eq} is the equilibrium constant and K_E , K_P , and K_B are the adsorption-equilibrium constants of ethylene, propylene, and 2-butene, respectively. This rate equation leads to the following expression for the initial rate of the reaction: (28)

$$r_o = KK_P^2 [P]_o^2 / (1 + K_P [P]_o)^2$$

Several other rate expressions can be developed based on various controlling mechanisms. Table I contains a partial list of the mechanisms considered and the initial rate form for each mechanism.

The Langmuir-Hinshelwood, dual-site surface reaction proved to be successful in correlating the initial rate data obtained by several investigators. Lewis and Wills⁽²¹⁾ obtained initial differential rate data for the disproportionation of propylene over a cobalt molybdate catalyst in the temperature range of 394-478°K and pressure range of 1

Table I

PARTIAL LIST OF POSSIBLE CONTROLLING⁽³¹⁾
MECHANISMS AND INITIAL RATE FORMS

Controlling Mechanism	Initial Rate Form
1. Dual site surface reaction	$r_o = \frac{kP_p^2}{(1+K_p P_p)^2}$
2. Single site surface reaction	$r_o = \frac{kP_p^2}{1+K_p P_p}$
3. Adsorption of propylene	$r_o = kP_p$
4. Adsorption of propylene with dissociation	$r_o = kP_p^2$
5. Desorption of ethylene	$r_o = k$
6. Desorption of 2-butene	$r_o = k$

to 9 atmospheres. They reported that the experimental data were well correlated when it was assumed that a dual site surface reaction was the controlling step in the mechanism. Moffat and Clark⁽³⁴⁾ also found that a Langmuir-Hinshelwood model applied to a heterogeneous surface could be used to describe both the general kinetics and the rate-temperature maxima reported by Banks and Bailey⁽⁵⁾ for olefin disproportionation in the same catalytic system. With a $\text{Mo}(\text{Co})_6\text{-Al}_2\text{O}_3$ catalyst at low pressures (0.5 to 20 KNm^{-2}) and temperatures between 290 and 350°K, Davie et al.⁽¹⁸⁾ arrived at the same conclusion. Expressions for the reaction rate based on adsorption- or desorption-controlling mechanisms or derived from other common Langmuir type models were found to be unsuccessful in correlating the data.

Several studies were performed for the propylene disproportionation over tungsten oxide-on-silica catalyst. Earlier, Begley and Wilson⁽⁶⁾ studied the kinetics of propylene disproportionation in this catalyst system under different conditions (20 to 60 atmospheres and 590 to 730°K) and reported that the controlling mechanism was the reaction between a chemisorbed molecule and a gas phase molecule (Rideal model). At lower pressures, 3.4 and 7.3 atmospheres, the rate constants were higher and they suggested that this was because of a change in the linear gas velocity in the catalyst bed. Although they provide empirical evidence that interphase and intraparticle mass transfer were not the rate controlling steps in their system, Clark⁽¹³⁾ subsequently reported experimental evidence that severe interphase diffusional effects were observed in the system used by Begley and Wilson. Moffat et al.^(35,36) have also shown that their reaction conditions could not

have eliminated the effects of interphase mass transfer.

Luckner et al.⁽³³⁾ obtained initial rate data for the disproportionation of propylene using a WO_3-SiO_2 catalyst at flow rates where mass transfer effects were negligible. Their experimental data at 1 to 9 atmospheres and 672 to 727°K could be well correlated with the dual site reaction mechanism. Mol⁽³⁷⁾ conducted propylene disproportionation on a $Re_2O_7-Al_2O_3$ catalyst at 313-343°K and atmospheric pressures and found that a Langmuir-Hinshelwood model gave a good correlation of the experimental results. The experimental results obtained by Hattikdur et al.⁽²⁵⁾ for a WO_3-SiO_2 catalyst system at pressures up to 50 atmospheres also correlate to a dual site reaction mechanism.

Break-in Phenomena

Many catalysts have been reported to undergo dramatic increases in activity during initial contacting with the reactants. This phenomena was labeled "break-in" by Baddour,⁽¹⁾ to be distinguished from the usual term, "transient kinetics." The induction period before reaching maximum activity is solely due to an essential change in catalytic activity, although the residual effects due to mass transfer or displacement of adsorption-desorption equilibria should be corrected for. Very few quantitative studies have been made of break-in, and hence the phenomena involved are still not clearly understood. A review in this area is classified into three general categories:⁽³¹⁾

Purging of a Temporary Poison from the Catalyst Surface. The presence of a catalyst poison in reactor feed streams results in the reduction of catalyst activity. Depending upon the strength of the

poison-surface interaction, this reduction in activity may be either permanent or temporary. Heckelsberg et al.⁽²³⁾ presented an example of temporary poison which also served to illustrate the rate at which a poison was purged from the catalyst surface. The reaction system was propylene disproportionation over a tungsten oxide-on-silica catalyst with water in the reactor feed. A reproduction of their data is shown in Figure 1.

A Modification of the Surface Due to Reactant-Surface Interactions.

Several examples exist of reactant-surface interactions which result in physical modifications of the surface. Schmidt and Luss⁽⁴²⁾ report significant increases in catalyst surface area during the oxidation of ammonia over a platinum-rhodium gauze. Scanning electron microscope studies demonstrated that the increase in surface area is due to the formation of randomly oriented crystal facets and the catalyst activity was increased as a result.

Another kind of reactant-surface interaction is the chemical reduction of the catalyst surface. Dimitrov and Leach⁽¹⁶⁾ studied the isomerization of 1-butene over Cu-X zeolite catalyst. They reported that the initial activity period observed was due to the reduction of Cu^{++} to Cu^+ by hydrogen.

The desulfurization of thiophene over a cobalt molybdate catalyst was studied by Lipsch et al.⁽³⁰⁾ They found that the chemical reduction of catalyst during the initial contacting with reactants was responsible for the induction period. The results of the studies done by Luckner and Wills⁽³²⁾ on propylene disproportionation over a tungsten oxide-on-silica catalyst have shown that the oxidation state of the tungsten is

a factor in catalyst activity. The initial WO_3 gives modest rates of disproportionation while stable $WO_{2.9}$ gives very much faster rates, and WO_2 yields even higher rates of disproportionation. The reductions reduce but do not eliminate the break-in period completely. It was also reported by these authors that the irreversible adsorption of propylene accompanies the period of transient activity.

Formation of Reactant-Surface Complexes. It is possible that the formation of polymeric hydrocarbons which adsorb on the catalyst surface occurs during the initial exposure of a catalyst to the feed. These polymeric complexes may have little or nothing to do directly with the catalysis of reactions on the catalyst surface, or they may be directly involved in the reaction either as an active center or as a reaction intermediate.⁽¹⁴⁾ It was shown by Peri⁽⁴⁰⁾ that a polymeric species did form during the isomerization of linear olefins over a silica-alumina catalyst. Blomfield⁽⁸⁾ has also given evidence for the formation of polymeric hydrocarbons which remain adsorbed on the surface during the isomerization of 1-butene. Propylene polymerization over silica-alumina was studied by Finch and Clark.⁽¹⁷⁾ They employed a deuterium tracer and ammonia blocking techniques to reveal the formation of a polymeric complex and the fact that this complex remains adsorbed on the catalyst sites. Reactant-surface complexes were also observed on non-metal oxide catalysts. Heinemann⁽²⁴⁾ used palladium chloride-on-alumina to vinylize acetic acid and copper chloride-on-alumina to conduct the oxychlorination of ethylene. In both cases, reactant-metal complexes must have been formed prior to the reaction. Such complexes made the reactant more readily available for metal attack according

to the evidence that the break-in period was eliminated when the catalysts were pretreated with reactants.

Rate Expression of Break-in during Propylene Disproportionation.

Luckner⁽³¹⁾ correlated the rates of propylene disproportionation during break-in by the following equations.

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

$$k = k_o e^{-E/RT} \quad (2)$$

where r_{ss} = steady state rate of disproportionation

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

r_o = rate of disproportionation at $t=0$

k = break-in rate constant

By combining the effect of partial pressure of propylene with equation (2), Luckner found that the activation energy is 47.2 Kcal in the expression,

$$k = k_o e^{-E/RT} P_{C_3H_6}$$

for the system propylene-WO₃-SiO₂. Similar results were obtained for the propylene-CoO-MoO₃-Al₂O₃ system but the activation energy was much smaller (~7Kcal) and the break-in period was much shorter. Typically, steady state activity in the Co-MoO₃-Al₂O₃ system was achieved in 5-20 minutes while as long as eight hours were required in the WO₃-SiO₂ system. Generally WO₃-SiO₂ was active in the 400°C range and CoO-MoO₃-Al₂O₃ in the 150-200°C range.

Qualitative Studies of Break-in Behavior of Tungsten Oxide-on-Silica Catalyst during Propylene Disproportionation. Fathi⁽¹⁹⁾ studied the influence of various changes in reaction conditions on the break-in behavior and activity of a tungsten oxide-on-silica catalyst in propylene disproportionation. In studies involving helium purges of various durations, he found that a ten minute purge with helium reduced the activity of the catalyst to a point which was indistinguishable from a fresh sample of the catalyst. Figure 2 is a reproduction of his data.

In order to "freeze" the surface of a fully activated catalyst for later inspection by X-ray diffraction, ESCA, and the scanning electron microscope, Fathi⁽¹⁹⁾ cooled down the reactor to room temperature and shut it down for 8, 9, and 11 hours respectively while the propylene flow was maintained. Upon reheating to the original temperature the break-in periods were not eliminated, although they were much shorter than that of a fresh catalyst. Fathi concluded that to maintain the catalyst in its essential fully activated state required the reaction temperature to be maintained as well as the propylene flow.

The effects of the product gases of propylene disproportionation on break-in were examined by interrupting the flow of propylene with a mixture of 55.5 percent ethylene and 44.5 percent 2-butene for thirty or seventy minutes. Fathi⁽¹⁹⁾ found that the interruption of propylene with the mixture reduced the activity of the catalyst to a point where another break-in period was needed to restore the full activity of the catalyst.

The review of the literature suggested that both cobalt molybdate catalyst and tungsten-oxide-on-silica catalyst undergo drastic change

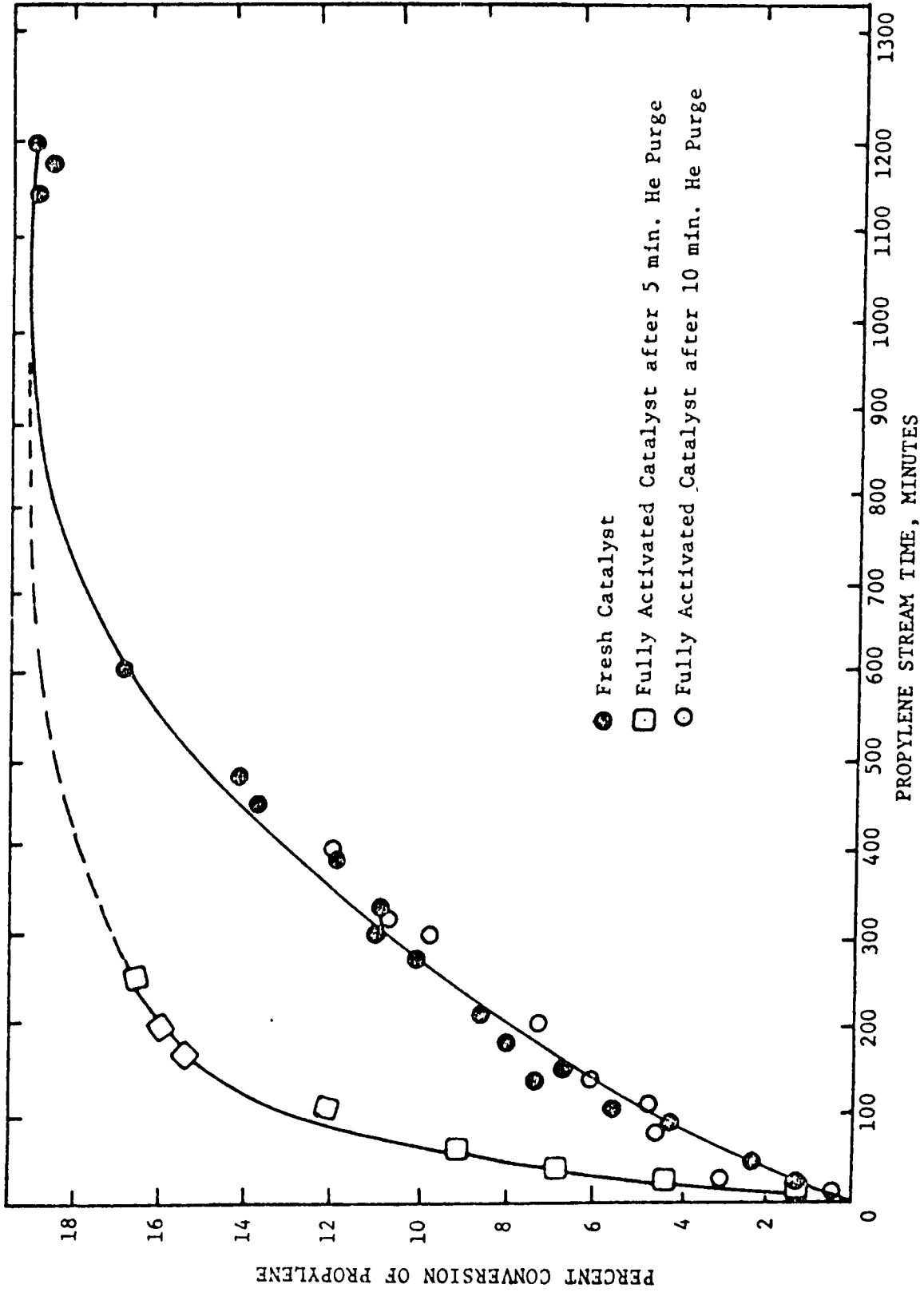


Figure 2. Effect of Purging with an Inert on Break-in of the Catalyst. (19)

during initial contacting with reactant. The primary products of propylene disproportionation and the heavy hydrocarbons may play an important role in the time-dependent initial activity of these catalysts.

Discussion of Literature

Olefin disproportionation is a process in which unsymmetric n-olefins are converted into olefins of longer and shorter carbon chain length. This process was first reported in 1964 by Banks and Bailey,⁽⁴⁾ who demonstrated that several molybdenum compounds such as molybdenum hexacarbonyl, molybdenum oxide-alumina catalyzed this reaction. In 1968, Heckelsberg⁽²³⁾ reported a catalyst of tungsten oxide-on-silica for disproportionation of olefins. Since then, a number of catalysts have been reported. The cobalt oxide-molybdenum-alumina catalyst and the tungsten oxide-on-silica catalyst have received the most attention because of their high resistance to common poisons such as air and water and their low coke formation.^(4,23)

Olefin Disproportionation Catalysts

The most active catalysts for olefin disproportionation contain molybdenum, tungsten, or rhenium. Rhenium oxide on alumina is an outstanding catalyst because it is very active under very mild conditions, viz. room temperature and pressure, yielding exclusively the primary disproportionation products.

In their earlier studies of olefin disproportionation, Banks and Bailey^(4,5) reported that the cobalt oxide-molybdena-alumina catalyst

was the most effective of the catalysts studied and gave a propylene conversion approaching thermodynamic equilibrium in the temperature range of 150° to 200°C. Bradshaw, Howman, and Turner⁽⁹⁾ reported a significant rate of decay of the cobalt oxide-molybdena-alumina catalyst at 180°C. Their results show a considerable loss of activity within a thirty minute period. This decay was found to be considerably less significant below 160°C. This agrees with the results of the Lewis investigation,⁽²⁸⁾ in which catalyst activity decay was found to be quite rapid at 200°C and relatively slow at 120°C. The visual inspection made on these catalysts revealed the catalyst at 120°C to have the blue color of the original active catalyst while the catalyst at 200°C was black. It was therefore suggested that the catalyst decay was due to coke formation.

Heckelsberg, Banks and Bailey⁽²³⁾ reported that tungsten oxide on silica was an excellent disproportionation catalyst when operated at a relatively high temperature, 350°C or above. Good propylene conversions were obtained using catalysts containing from 2 to 10 % tungsten oxide. Near equilibrium conversion, (about 44%) were obtained at 425°C, 450 psig, and a 60 weight hourly space velocity. The major advantage of this catalyst was its resistance to common poisons. Banks and Bailey reported the loss of feed to coke to be about 0.2 percent of the feed, indicating very little coke formation on the tungsten oxide-silica catalyst.

Olefin isomerization has been known for many years. Pines and Haag⁽⁵⁰⁾ were among the first to report stereo-selectivity over sodium dispersed on alumina, and Lucchesi et al.⁽⁴⁹⁾ noted that the thermo-

dynamically unfavored cis-2-butene was kinetically favored in 1-butene isomerization over silica-alumina. Since then a number of investigators^(20,21,41,45) have found such catalyst-dependent selectivity to be quite general over most oxides. Selectivity for primary disproportionation products were increased by adding small amounts of alkali metal or alkaline earth metal ions to the cobalt oxide-molybdena-alumina catalyst⁽⁹⁾ and tungsten oxide on silica catalyst.⁽²¹⁾

Break-in Behavior of Catalysts During Propylene Disproportionation

Generally, a disproportionation catalyst is activated by passing a stream of inert gas or dry air over the catalyst at elevated temperature. In a few cases it has been shown⁽⁴⁷⁾ that the actual activation procedure does not yield a catalyst with maximum initial activity; rather the activity gradually increases when the activated catalyst is brought into contact with the reactants. The time needed for catalyst to become fully activated is labeled "break-in." Both cobalt oxide-molybdena-alumina catalyst and tungsten-oxide-on-silica catalyst fall into this category; the former was found to have a break-in period of thirty minutes in the present investigation while the latter was found to have break-in periods of up to 24 hours.

Luckner and Wills⁽³²⁾ studied the break-in behavior of the tungsten oxide on silica catalyst and reported that the rate of catalyst approach to steady state activity was first order in propylene and had a 47.1 Kcal per mole activation energy. The rate of break-in can be expressed as follows:

$$\frac{r_{ss} - r}{r_{ss} - r_0} = e^{-kt} \quad \text{and}$$

$$k = 1.99 \times 10^{-10} e^{-47.1/RT_P} \text{C}_3\text{H}_6 \text{ Min}^{-1}$$

The pre-reduction of the tungsten trioxide (yellow, characteristic of the fresh catalyst) was found to substantially increase the rate of catalyst break-in but not to eliminate the period of transient activity. Pulse studies showed a defective mass balance and Luckner et al. (32) concluded that the break-in period was related to the strong adsorption of an olefin and that this adsorption is at least partly reversible.

(19)
Fathi also studied the break-in behavior of a tungsten oxide-on-silica catalyst. In his work he presented the effect of an inert purge, cooling and reheating, and propylene flow interruption on catalytic activity and break-in of this catalyst during propylene disproportionation. In each case the activity was seen to decrease and then increase during another break-in period. He concluded that steady state activity requires maintenance of both the reaction temperature and the propylene flow. It was suggested that propylene initially reacted with the catalyst surface to form an unstable organic fragment which acted as an active site. It was thought that these active sites were constantly formed and destroyed during the break-in period and as break-in progressed, these active sites increased in number until at steady state an equilibrium situation was reached between production and destruction. This equilibrium then continued so long as there was no disturbance in reaction conditions.

III. EXPERIMENTAL SECTION

This section summarizes the plan of investigation, the experimental equipment and its operation, the materials used, and the results obtained. Also included are methods of procedures.

Plan of Investigation

The overall plan followed in this investigation consisted of two parts. The first part was to establish a reaction system and to investigate the transient activity initially exhibited by the $\text{CoO-MoO}_3\text{-Al}_2\text{O}_3$ catalyst upon introduction of propylene. This was followed by the study of the phenomena associated with the break-in behavior of $\text{WO}_3\text{-SiO}_2$ during propylene disproportionation. The following phenomena were studied.

Part 1. Quantitative studies of the transient activity period of a $\text{CoO-MoO}_3\text{-Al}_2\text{O}_3$ catalyst during propylene disproportionation.

(a) Determine the time constant associated with the transient activity of this catalyst.

(b) Determine the response of catalytic activity to a unit step input of an inert gas after the catalyst had obtained full activity.

(c) Determine the effects of a purge of a fully activated catalyst by an inert gas.

Part 2. Studies of the phenomena associated with the break-in behavior of $\text{WO}_3\text{-SiO}_2$ catalyst during propylene disproportionation.

(a) Using a split bed reactor, determine the effects of products from the first bed on the activity of second bed.

(b) Determine the effects of different product concentration levels in the feed on the activity of the catalyst.

(c) Dose the catalyst with sodium ions and search for possible effects on the distribution of products.

(d) Determine the effects of dosing with oxidizing and/or reducing gases on the activity of the catalyst.

(e) "Freeze" a fully activated catalyst in a stagnant atmosphere of propylene for possible study following removal from the reactor system.

In somewhat more detail, the plan included system construction and calibration, catalyst activation, and collection of data. A detailed description of each part of the plan of investigation is given in the following sections.

Studies of Break-in Phenomena

A 5- to 20-minute break-in period of the $\text{CoO-MoO}_3\text{-Al}_2\text{O}_3$ catalyst during propylene disproportionation was reported in the proposal by Wills⁽⁴⁷⁾ to the American Chemical Society. The first goal of this investigation was to confirm that this transient activity of $\text{CoO-MoO}_3\text{-Al}_2\text{O}_3$ catalyst really existed and that it was not solely due to mass transport delays. Preliminary studies were performed to demonstrate the existence of transients with the $\text{CoO-MoO}_3\text{-Al}_2\text{O}_3$ catalyst. These were followed by the purging studies with an inert gas at full catalyst activity. The flow of propylene was stopped as soon as the catalyst had obtained full activity and a steady flow of nitrogen gas was introduced into the reactor. Data were taken to determine the

possible presence of another transient and its order of magnitude. A literature review revealed that a polymeric complex was possibly formed on the surface of the catalyst during propylene disproportionation.⁽⁸⁾ A fully activated catalyst was purged with nitrogen to determine if the decay of activity was due to the slow purge of such an adsorbed species.

It was reported by Fathi⁽¹⁹⁾ that the replacement of a propylene feed with a mixture of products (55.5% ethylene and 44.5% 2-butene) reduced the activity of the WO_3-SiO_2 catalyst to a point where another break-in period was needed to restore the full activity of the catalyst. Therefore, a split-bed reactor was employed to study the effects of products from the upper bed on the activity of the lower bed. Mixtures with different concentrations of products in propylene were used as feed to interrupt the propylene disproportionation reaction after the catalyst had been fully activated.

The nature of possible adsorbed polymeric compounds is still unclear. If it were possible to freeze the surface of a fully activated catalyst in the presence of propylene, it might be possible to inspect the surface changes during break-in by using instruments such as X-ray diffraction, ESCA and the scanning electron microscope. Attempts to maintain the activity of catalyst upon reducing the operating temperature to room temperature in the presence of propylene flow were unsuccessful. It was then proposed that reducing the operating temperature to room temperature by fast cooling in the presence of stagnant propylene might prevent or at least hinder those processes that deactivated the catalyst.

Sodium dispersed on the catalyst support was shown to be capable of inhibiting isomerization of 2-butene to 1-butene. An effort was made

to pretreat the $\text{WO}_3\text{-SiO}_2$ catalyst with weak sodium hydroxide solution so that the sodium-incorporated catalyst would have higher selectivity through suppression of the double bond isomerization reaction.

Reducing gas (hydrogen) and oxidizing gas (dry air) were dosed into the reactor separately and both were found to be temporary poisons. We tried to restore the activity of a fully activated catalyst by dosing a reducing gas immediately after an oxidizing gas, and vice versa.

Experimental Equipment

The equipment used in this investigation consisted of a feed preparation section, a microcatalytic reactor, and a product analysis section. This section of the thesis is restricted to the equipment specially constructed for this investigation. Figure 3 shows a schematic diagram of the complete system. The complete specification of the equipment and materials shown in this figure are presented in Appendix B.

System Selection and Design

The microcatalytic reactor used in the investigation of transient activities of the $\text{CoO-MoO}_3\text{-Al}_2\text{O}_3$ catalyst was that used by Fathi⁽¹⁹⁾ in the investigation of the break-in behavior of $\text{WO}_3\text{-SiO}_2$ catalyst during propylene disproportionation. Details of this reactor were reported by Fathi.⁽¹⁹⁾ Figure 4 is a sketch of the reactor. The feed section was constructed such that it allowed an accurately metered feed, free of poisons, to be fed into the reactor.

In order to avoid deactivation of the dryer and to reduce the dead volume when one gas was replaced with another in the system, two

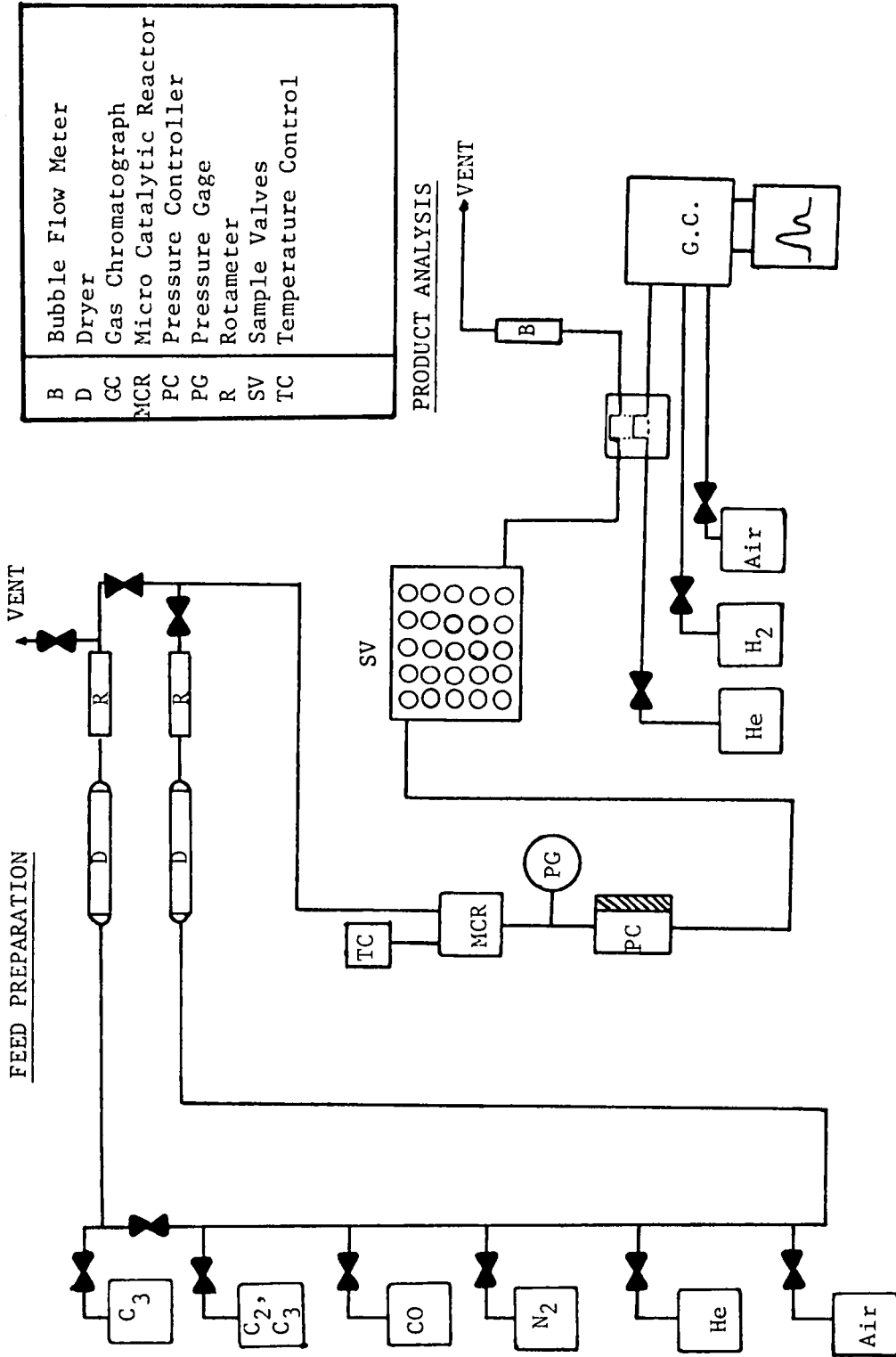


Figure 3. Schematic Diagram of the Reactor.

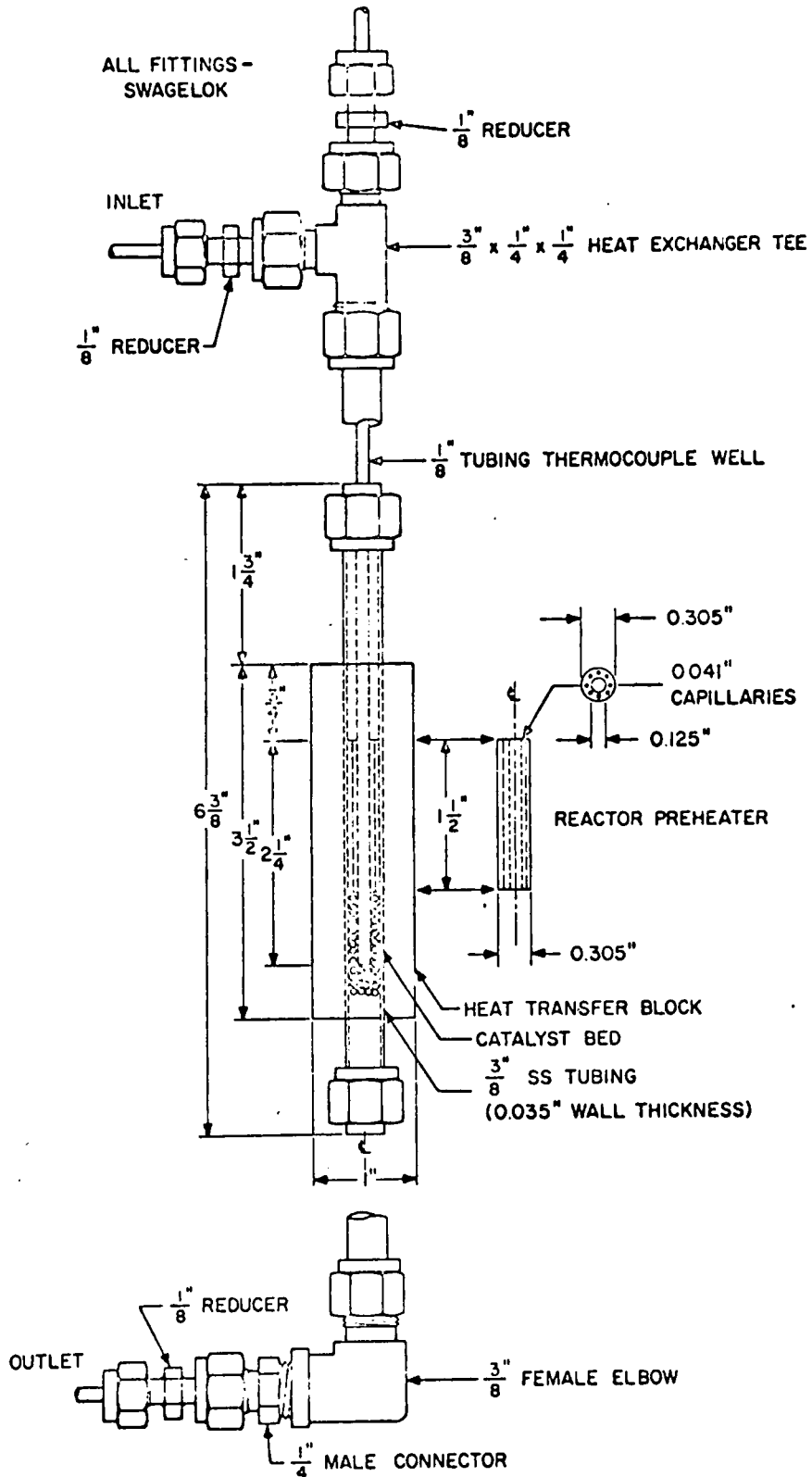


Figure 4. Details of Micro-Reactor.

identical inlet lines were constructed to the reactor. To achieve isothermal conditions, the temperature in the middle of the bed was controlled. The product analysis section consisted of a series of sample valves and a gas chromatograph fitted with a dual flame ionization detector, a soap bubble flow meter and a wet test flow meter.

In the studies of the effects of products on the catalytic activity of the $\text{WO}_3\text{-SiO}_2$ catalyst, the microcatalytic reactor was replaced by a split-bed reactor and the outlet of reactor was connected directly to the gas chromatograph instead of to the sample valves. Details of the split-bed reactor are shown in Figure 5. The two outlets of the reactor were connected to the same three-way valve so that the stream from between the beds as well as that having passed through both beds could be analyzed.

The microcatalytic reactor used in the studies associated with the transient activity of $\text{CoO-MoO}_3\text{-Al}_2\text{O}_3$ catalyst was also used in the remaining studies concerning the $\text{WO}_3\text{-SiO}_2$ catalyst except that the reactor preheater was replaced by a piece of stainless steel wire gauze. A sample valve with two identical loops, which was used as a gas injector, was connected between the rotameter and the microcatalytic reactor. Any gas that was used for dosing was allowed to flow through one loop of the dosing valve while propylene was flowing through the other loop and the plunger was in the "in" position. As soon as the plunger was pulled "out," the dosing gas flowed directly through the valve while the propylene switched to the other loop and carried the dosing gas, which had been trapped in the loop, into the reactor. Details of the dosing valve are shown in Figure 6.

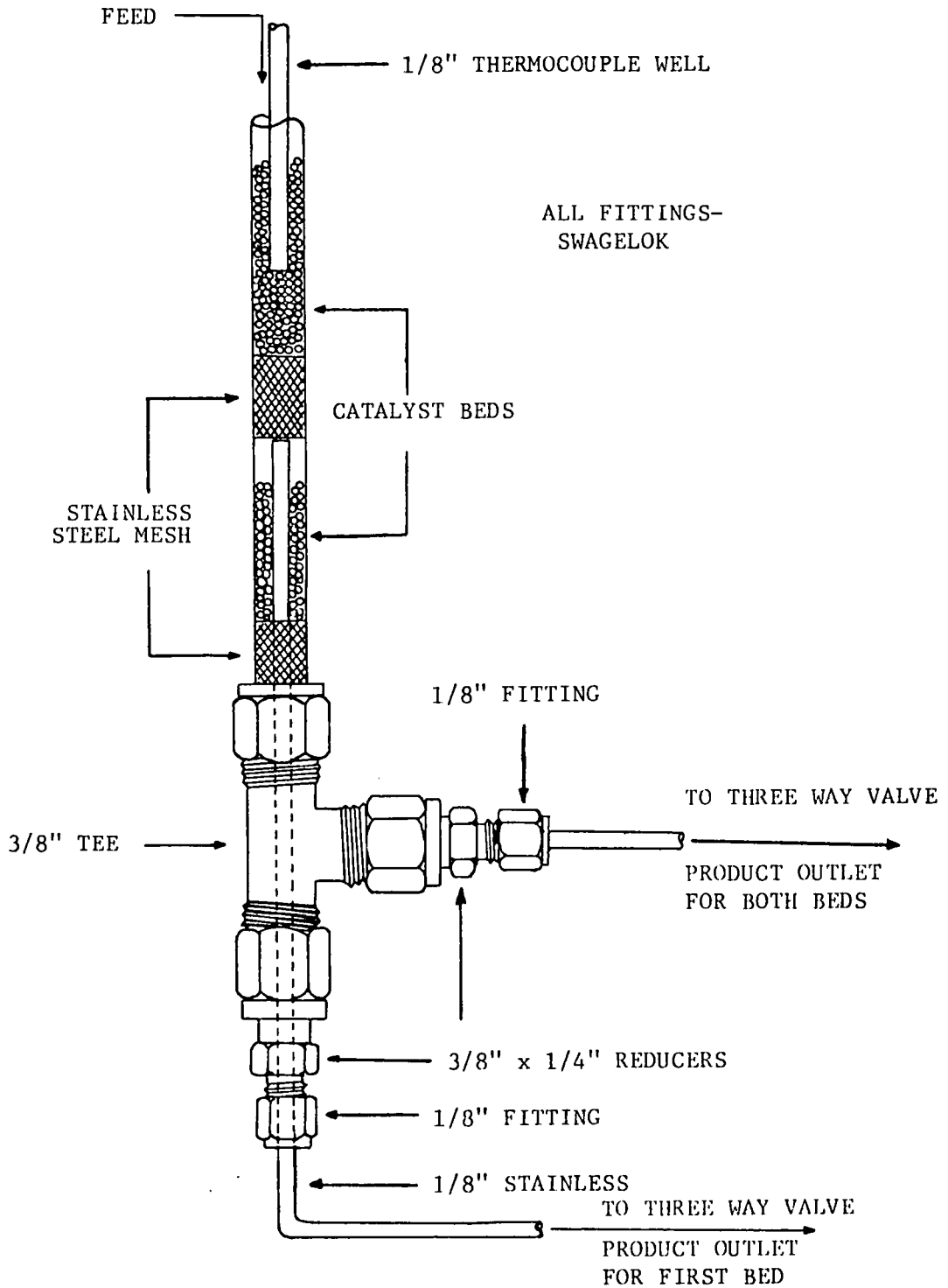


Figure 5. Details of the Split-Bed Reactor.

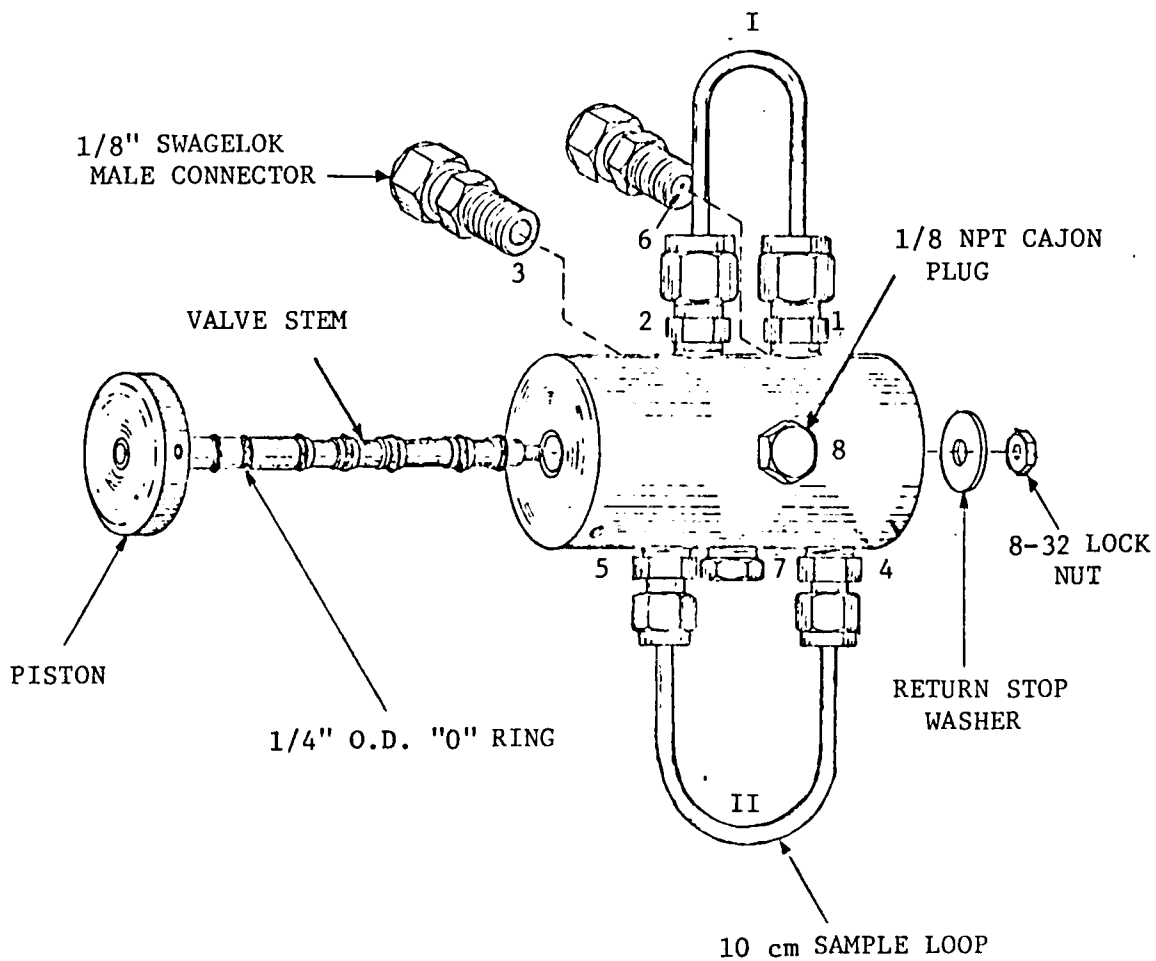


Figure 6. Details of Sampling Valve.

Feed Preparation. This section consisted of gas cylinders of chemically pure feeds that were connected to a gas manifold. All the gases from the manifold were passed through a rotameter, a Moore differential pressure controller, and a dryer filled with molecular sieves before entering the reactor. This provided an accurately metered feed stream to the reactor that was free of a known catalyst poison, water.

Microcatalytic Reactor

Single Bed Reactor. The reactor was constructed of 3/8-inch o.d. 6-inch long 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"). This tee provided fittings for the inlet line and the reactor thermowell. The bottom of the reactor was fitted with a 3/8 inch "Swagelok" male connector to which a 1/4 inch "Whitey" KEL-F valve was attached. A preheater was formed by winding a 4 foot section of 1/16 inch o.d., 316 stainless steel tubing around a heater block. Figure 4 shows the details of the microcatalytic reactor. The single bed reactor was fitted with temperature and pressure controllers. To minimize variations in temperature, the reactor was surrounded by a heavy metal cylinder. This method was used in all of the studies. It is important to bring the reactor gases to the same temperature as the bed before entering the bed. This was achieved by preheating the gases in a 4-foot section of 1/16-inch 316 stainless steel tubing wound around the heat block as a coil and by the reactor preheater which was placed just before the bed. The combination of the preheaters, low heat of reaction, and the small size of the bed essentially eliminated temperature gradients in

the bed. Isothermal conditions were achieved by controlling the mid-bed temperature at the desired temperature. A thermowell was placed in the reactor such that the tip of it was at the center of the bed.

In addition to isothermal operation, it is important to distribute the reactant gases over the bed uniformly. This was achieved by seven capillaries of 0.04 inch diameter drilled in the reactor preheater. This single-bed reactor was used in all of the studies involving the $\text{CoO-MoO}_3\text{-Al}_2\text{O}_3$ catalyst and those involving poisoning, dosing, and fast cooling of the $\text{WO}_3\text{-SiO}_2$ catalyst except that the reactor preheater was replaced by a stainless steel wire plug in the studies of the $\text{WO}_3\text{-SiO}_2$ catalyst just mentioned.

Split-bed Reactor. As shown in Figure 5, the split bed reactor used in the studies to determine the effects of products on the activity of the $\text{WO}_3\text{-SiO}_2$ catalyst was constructed of a single 3/8-inch o.d., 316 stainless steel tube that was six inches long. 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"). This tee provided fittings for the inlet line and the reactor thermowell. The bottom of the reactor was fitted with a 3/8-inch "Swagelok" male connector which was connected to a 3/8-inch tee. This fitting provided two outlets for the reactor. One outlet was made by inserting a 10 inch long 1/8-inch 316 stainless steel tubing in the reactor. The tip of the tubing touched the bottom of the stainless steel wire plug supporting the upper half bed. The other outlet collected the products from the whole bed. Both outlets were connected to the same three way valve, which allowed the products from either outlet to be analyzed.

Dosing Valve. The dosing valve was installed by adapting one of the sample valves used to collect sample products. The 4-inch long 1/8-inch stainless steel sample loops were replaced by two identical 1/4-inch copper tubes each of which had a volume of about 13 cm³. Details of the dosing valve are shown in Figure 6. The openings on the valve are numbered from 1 to 8. When the plunger was in the "in" position, the dosing gases would go via the route 7 → 2 → loop I → 1 → 8 → to the soap bubble flow meter and the reactant gases would go through 3 → 5 → loop II → 4 → 6 → to the G.C. With the plunger pulled out, openings 4 and 5 would be sealed and the dosing gas would pass from 7 directly to 8, and then to the soap bubble flow meter, but the reactant gases would go through loop I instead of loop II and thus carry the dosing gas, which had been trapped in loop I, into the reactor. The path which reactant gases would take is as follows: 3 → 2 → loop I → 1 → 6 → to G.C.

Reactor Furnace. During each experiment, the reactor was placed in a six-inch long, tubular resistance heating furnace. The desired reactor temperature was maintained by controlling the mid-bed temperature. One bank of the resistance elements in the furnace was connected through a powerstat to the power line. The voltage to this bank was adjusted so that, if used alone, it would maintain the reactor approximately 10°C below the desired temperature. This bank was on continuously. The second bank of resistance elements was connected through a powerstat to a thermo-regulator whose sensor was an iron-constantan thermocouple in the reactor thermocouple well. This bank was activated at a reduced power level by the thermo-regulator. Temperature control

was a sinusoid of 0.5°C amplitude about the desired temperature.

Product Gas Analysis. This section consisted of an in-line gas chromatograph equipped with a 0.5 cubic centimeter sampling valve and a dual flame ionization detector. The detector was calibrated using pure and prepared mixtures and all components present in the reactor effluent. This section also contained a bubble flow meter and a wet test meter for the exact determination of the flow rate. High flow rates were measured by the wet test meter and low flow rates with the bubble flow meter.

Dryers. Three dryers were constructed from a one-inch carbon steel pipe that was fourteen inches long. These were packed with 5A type molecular sieves. Both ends were fitted with a pipe cap which had a 1/8 inch "Swagelok" male connector installed in the end.

Methods and Procedures

This section contains procedures for calibrating various pieces of equipment and the procedures for each individual experiment.

Calibration of Pressure Gages. All the pressure gages used in this investigation were calibrated against a twelve-inch U. S. standard test gage by Fathi.⁽¹⁹⁾ The gage being calibrated was connected to the test gage and was pressurized by nitrogen gas. An individual calibration curve was prepared for each gage.

Reactant Gases. All the reactant gases used were purchased in cylinders and were reported to be a minimum of 99% pure. A check was made by gas chromatography to confirm this claim. In studying the effects of products in the feed stream on the activity of the $\text{WO}_3\text{-SiO}_2$

catalyst, mixtures of different concentrations of reactant gases were prepared and the compositions were measured by gas chromatography.

Gas Chromatograph Calibration. Since in this study all of the reactant gases and product gases were analyzed by gas chromatography, the chromatograph detector calibration factors for ethylene, propane, 1-butene, 2-butene and 1.3-butadiene reported by R. C. Luckner⁽³¹⁾ were used in the calculations. The F and M Scientific Research Chromatograph used during this study was equipped with a 0.5 cubic centimeter gas sampling valve and a 30-foot column of dimethyl sulfolane on chromosorb W (-30/+60). The following procedure for calibration of the gas chromatograph was described by Luckner.⁽³¹⁾

For calibration purposes the gas sampling loop was connected to a vacuum system. The loop and auxiliary components could be evacuated, with the pressure monitored by a mercury U-tube manometer. The initial step in any calibration was the evacuation of the system. Then the olefin for which the detector was being calibrated was allowed to fill the system to some predetermined pressure. This sample was injected and the peak area determined as the product of the peak height, and the chromatograph attenuation factor for the recorder detector output.

The flame-ionization detector has an output which is proportional to the number of moles of a particular compound being ionized,

$$n_i = f_i A_i \quad (3)$$

where

n_i = number of moles of component i in the sample

A_i = peak area for detector response to component i

f_i = proportionality factor for component i

By summing all of the components present in the sample, the total moles can be determined as

$$N = \sum_{i=1}^m n_i = \sum_{i=1}^m f_i A_i \quad (4)$$

The total number of moles injected can also be calculated by,

$$N = \frac{P_L V_L}{\bar{Z} R T_L} \quad (5)$$

where

P_L = pressure in the sample loop

\bar{Z} = average compressibility factor of the sample

T_L = temperature in the sample loop

V_L = volume of the sample loop

and R = gas constant

Upon combining equations (4) and (5) and rearranging, the following equation is obtained,

$$\sum_{i=1}^m \frac{f_i}{V_L} A_i = \frac{P_L}{\bar{Z} R T_L} \quad (6)$$

Pure samples and prepared mixtures of known compositions were injected into the chromatograph and component areas determined. Using multiple regression, the best least squares estimates of the f_i/V_L factor of each component were obtained.

To eliminate the scale factor of the recorder and the constant but unknown sample loop volume, the f_i/V_L factors were normalized

by dividing each by the f_i/V_L of propylene,

$$f_i^* = \frac{f_i/V_L}{f_{C_3H_6}/V_L}$$

since propylene was expected to be present in every sample analyzed during this investigation.

For all experimental runs, the chromatograph conditions used during calibration were maintained. These were: oven temperature, 25°C; detector temperature, 120°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, fourteen pounds per square inch gage. Calibration factors along with their 95 percent confidence interval reported by Luckner⁽³¹⁾ are listed in Table II.

Preparation of Catalyst. The CoO-MoO₃-Al₂O₃ catalyst used in the first part of this study was furnished by Girdler Catalyst Department of Chemetron Chemical Company, Louisville, Kentucky. These catalysts were 1/8 inch extrudates containing 3.5 percent CoO and 10.0 percent MoO₃ on an alumina support. The initial step in the preparation of this catalyst was to crush and screen several grams of the pellets. This gave fractions from 1/8 inch pellets to -20/+30 mesh (0.028 inches).

The WO₃-SiO₂ catalyst used in the second part of this study was supplied by the Davidson Chemical Division of W. R. Grace and Company and was designated SMR7-3322. It contained 10% tungsten oxide on silica gel and was prepared by impregnating 3/16 inch silica extrusions with ammonium tungstate. This catalyst was crushed and screened to

Table II

GAS CHROMATOGRAPH DETECTOR COMPONENT CALIBRATION FACTORS

<u>Component</u>	<u>Calibration factor, f_i^* and 95% confidence, interval</u>
Ethylene	1.587 \pm .601
Propane	1.007 \pm .425
Propylene	1.000 \pm .226
1-Butene	.7169 \pm .309
2-Butene	.8221 \pm .335
1-3 Butadiene	.4390 \pm .372

-20/+30 mesh (0.028 inches) and -30/+40 mesh (0.020 inches). The catalysts of these two sizes were used in this study separately. All the catalysts were dried for ten hours at 120° and then were stored in a dessicator until needed.

Catalyst Activation. A standard method of catalyst activation was employed in all of the studies. A description of this procedure is given here and it will not be repeated in the description of the procedures of each experiment conducted. The first step of this procedure was to charge a known weight of catalyst ($\text{WO}_3\text{-SiO}_2$ or $\text{CoO-MoO}_3\text{-Al}_2\text{O}_3$) to the reactor. A plug of stainless steel mesh was inserted to support the catalyst charge and the thermocouple well tip was placed at the midpoint of the catalyst bed. In the case of the split-bed reactor, the top of the thermocouple well was at the midpoint of the first catalyst bed. The reactor was then placed in the reactor furnace and the ends of the tube furnace were wrapped with glass wool in order to minimize heat losses from the protruding inlet and outlet of the reactor. The catalyst was heated to 600° centigrade for five hours while dry air was passed over the catalyst at a rate of two to three cubic centimeters per second. At the end of the five hour activation period, dry nitrogen was passed over the catalyst at 600° centigrade for thirty minutes at a rate of two or three cubic centimeters per second. After these treatments, the temperature of the bed was reduced to the desired temperature. At this point the catalyst was ready for use and was termed "freshly activated" in order to be differentiated from "fully activated" catalysts which had achieved stable activity. Usually, the reactant gases were not introduced

until the required temperature was stabilized for fifteen minutes.

Part 1. The Studies of the Transient Activity of the Cobalt
Oxide-Molybdena-Alumina Catalyst

Time Constant Determination of Transient Activity. To determine the time constant of the transient activity of $\text{CoO-MoO}_3\text{-Al}_2\text{O}_3$ catalyst, 0.5 grams of -20/+30 mesh dry catalyst were placed in the single bed reactor and a sampling system containing twenty four sampling valves was connected between the reactor outlet and the gas chromatograph. The standard activation procedure outlined above was followed, and the temperature in the reactor was cooled down to 120°C . After the catalyst had equilibrated at 120°C for fifteen minutes, the nitrogen purge was stopped and propylene feed started at a rate of 4.2 cubic centimeters per second (WHSV=46.87) and atmospheric pressure. The plunger of the first sampling valve was pulled out ten seconds after the propylene flow had been started; a sample was taken in this way every ten seconds over a period of four minutes. The outlet of the sampling system was connected to the auxiliary inlet of the gas chromatograph and the trapped samples were analyzed by gas chromatography by pushing back the plungers one by one.

The same experiments were repeated twice at the same flow rate but different temperatures; 121°C and 160°C , respectively.

The Response to a Unit Step Input of an Inert Gas. The response of the catalytic activity to a unit step input of an inert gas was studied after the catalyst had obtained stable activity. As soon as steady state activity had been established at 160°C , 0.94 atm., and a

flow rate of 4.2 c.c./sec (WHSV=46.87), the propylene flow was stopped and nitrogen gas was introduced at the same pressure and a flow rate of 3 cm³/sec. A sample was taken every ten seconds over a period of two minutes after the nitrogen flow had been started. Some experiments were repeated.

Effects of an Inert Gas Purge. The effects of a purge of a "fully activated" catalyst with an inert gas was also studied with the same batch of catalyst. After the standard activation period, the reactor was cooled down to 165°C and left at this temperature for fifteen minutes. Propylene feed was introduced at the same flow rate and pressure as in the previous experiment and transient activity data were taken as before. After a steady state activity had been established, the propylene flow was stopped and nitrogen gas was introduced at the same pressure and a flow rate of 1.4 cm³/sec for a period of fifteen minutes. At the end of fifteen minutes, the nitrogen gas flow was stopped and propylene was reintroduced at the same flow rate and pressure. After reintroduction of propylene, the conversion of propylene was determined over a period of two minutes, with a sample taken every ten seconds.

Part 2. Break-in Behavior of the Tungsten Oxide on Silica Catalyst

Effects of Products from the First Bed on the Second Bed in a Split Bed Reactor. A split bed reactor, as shown in Figure (5), was used to study the effects of products on the catalytic activity of the WO₃-SiO₂ catalyst during propylene disproportionation. 0.303 Grams of -20/+30 mesh dry catalyst particles were mixed with 0.300 grams dry

quartz of the same size to make the first catalyst bed. After this bed was pushed into place, a loosely twisted piece of fine stainless steel gauze one inch long was placed under the bottom of the bed. The position of the gauze was such that the tip of the thermocouple well was in the middle of the first catalyst bed. Another 0.302 grams of -20/+30 mesh dry catalyst particles were also mixed with 0.337 grams dry quartz of the same size to make the second catalyst bed. This catalyst bed was also supported by a twisted stainless steel wire gauze and a 1/16-inch stainless steel tubing was inserted half way in, up to the bottom of first stainless steel gauze, to provide a sampling port opening for the products from the first bed.

The standard activation procedure was followed to obtain the freshly activated catalyst. After the temperature of the reactor had stabilized at 430°C for 15 minutes, the propylene feed was introduced into the reactor at a flow rate of 2.174 c.c./sec (WHSV=20.14) and atmospheric pressure. An approximate steady state of catalyst activity was established after 20 hours. The extent of reaction throughout the whole reactor was first determined by gas chromatographic analysis. After the three-way valve had been switched to the outlet of upper half bed for forty seconds, the products from the first bed were analyzed. The three-way valve was then switched back to the outlet of the whole bed and data were taken again. The same procedure was repeated several times. Products from the whole bed--before and after switching the three-way valve to the outlet of the first bed for thirty seconds--were compared to see if the switching procedure caused any back-mixing problem.

Effects of Products on Catalyst Activity. The effects of different product concentration levels in the reactant feed on the activity of WO_3-SiO_2 catalyst were studied by giving the fully activated catalyst a step input of mixtures of propylene, ethylene and 2-butene. The catalysts in the split-bed reactor were regenerated by the standard activation procedure and were brought to the fully activated state after introducing propylene under the same conditions as before for twenty hours, but with the reaction temperature was increased to $430^\circ C$. Pure propylene flow was stopped and the prepared mixture was introduced at the same flow rate and pressure. Samples were analyzed periodically on the gas chromatograph. Two mixtures of approximately equal molar ethylene and 2-butene in propylene were used in this study. The total concentrations of ethylene and 2-butene in the mixtures were 0.573 percent and 3.604 percent respectively. The methods used to prepare these mixtures were given by Fathi⁽¹⁹⁾ and the compositions of the mixtures were determined by gas chromatography.

Product Distribution of a Sodium Ion Incorporated Catalyst. In order to incorporate the catalyst with sodium ions, which we hoped would increase the selectivity of catalyst, a batch of 2 grams of -30/+40 mesh WO_3-SiO_2 catalyst particles used by Luckner⁽³¹⁾ in previous experiments were regenerated by the standard activation procedure. 0.3 Grams of catalyst were taken from this batch of catalyst and were mixed with quartz of the same weight and size. The product distribution data, both during break-in and at steady state, were taken on this non-pretreated catalyst at $429^\circ C$, 0.94 atm, and a propylene flow rate of 2.174 c.c./sec (WHSV=40.28) for later comparison with the

sodium-dosed catalyst.

To prepare the sodium-dosed catalyst, 2 cm³ of catalyst (bulk density=0.385 grams/cm³) from the same batch was put into a 50 cm³ beaker. 1 cm³ of a 0.02 N aqueous solution of sodium hydroxide was added to convert ten percent of the tungsten oxide in the catalyst to sodium tungstate. The catalyst, together with the sodium hydroxide solution, was dried in an oven at 120° for fourteen hours. 0.3 Grams of the catalyst pretreated in this way was mixed with dry quartz of the same quantity and size and the diluted catalyst bed was placed in a single-bed reactor. The maximum conversion of propylene obtained from this catalyst was found to be approximately one percent after fifteen hours of propylene flow under the same conditions as were used in the preceding experiment. To test for moisture that might still exist in the catalyst after the drying and activation procedures (and might be responsible for the low catalytic activity of this pretreated catalyst), 1 cm³ of catalyst from the same batch of regenerated catalyst was moisturized with 1 cm³ of distilled water and was then dried in an oven at 110°C for twelve hours. 0.3 Grams of this dried catalyst was then mixed with 0.3 grams dry quartz of the same size. After the standard activation procedure and twelve hours propylene flow at the same flow rate, temperature, and pressure, the steady-state activity obtained from this catalyst bed was as high as that of the non-pretreated catalyst.

Attempts were also made to revitalize the inactive pretreated sodium-dosed catalyst. 1 cm³ of a 0.04 N aqueous solution of hydrochloric acid was added to the sodium-dosed catalyst; the wet catalyst was then

dried in an oven at 200°C for twelve hours. The break-in data were taken for this catalyst and the reaction conditions were set as before. The activity of this catalyst was still found to be very low; therefore, it was washed with 100 ml distilled water for two hours by use of a 50 ml burette. After being dried in an oven at 200°C for twelve hours this catalyst was again placed in the single bed reactor and was activated by the standard procedure. The highest propylene conversion obtained on this catalyst was approximately one percent twelve hours after propylene had been started under the same conditions as before.

Effects of the Dosing of an Oxidant Followed by that of a Reduc-
tant and Vice Versa. It was speculated that the catalyst activity decreased by an oxidizing poison could be recovered by introducing a reducing poison, or vice versa. The non-pretreated catalyst used in the preceding study was used in this dosing experiment. A dosing valve was connected between rotameter and reactor inlet. The details of this dosing valve are shown in Figure 5. Two cylinders for supplying air and hydrogen were connected to the same three way valve respectively. One dryer was connected between each cylinder and the valve to remove the moisture in the gas streams and the outlet of the three way valve was connected to the inlet of the dosing valve. The same procedures used to establish a steady state catalyst in the previous sodium dosing studies were also employed in all of the experiments concerning dosing gases.

Air and hydrogen were dosed into the reactor for one minute respectively after the stable catalyst activity was established. The time for one dosing gas to be replaced by another in the dosing system

was calculated to be fifteen seconds. The composition of products was analyzed on the gas chromatograph periodically after the air or hydrogen pulse was fed to the reactor. Another experiment was conducted by dosing air into the fully activated catalyst bed first for one minute and then switching the three way valve to permit hydrogen to enter into the reactor. One minute after the introduction of hydrogen, products from the reactor were analyzed by the gas chromatographic method. The same experiment was repeated but the order of dosing of air and hydrogen was reversed.

The Effect of Fast Cooling. The catalyst bed was allowed to establish a steady state activity first. Then the propylene flow was stopped while the temperature of the reactor was reduced from 430°C to 50°C in thirty minutes. It took another half hour to cool the reactor from 50°C down to room temperature (20° centigrade). The catalyst bed was then undisturbed for eight hours. After the eight hour shut-down, the reactor was reheated to 430°C over a thirty minute period. As soon as the temperature reached the desired temperature, the propylene was reintroduced into the reactor and the products from the reactor were analyzed periodically on the gas chromatograph.

Data and Results

This section contains the results of transient activity studies of the cobalt oxide-molybdena-alumina catalyst and those of the various studies of the break-in behavior of the tungsten oxide-on-silica catalyst.

Part 1. Transient Activity of the Cobalt Oxide-
Molybdena-Alumina Catalyst

The data tables for all studies concerning the transient activity of the cobalt molybdate catalyst are in Appendix C. The results of these studies are presented graphically in this section. Each graph or closely related series of graphs is introduced and briefly interpreted.

Time Constant Determination of Catalytic Transient Activity.

Figures 7 and 8 are plots of percent propylene conversion versus time on stream at 120°C and 160°C respectively.

Both figures show that the propylene conversion increased very fast during the first one hundred seconds of the contacting of the catalyst and the reactants, and then it increased very slowly with time.

Response of the Fully Activated Catalyst to a Step Input of an Inert. Figure 9 is a plot of the relative concentration of organic materials versus the on stream time of nitrogen using average amount of the organic materials in 24 samples taken previously at the steady state catalytic activity. It can be seen in this figure that after propylene flow had been stopped for over one hundred seconds there were still some products and reactants detectable by gas chromatography. Table IX shows that the propylene conversion increased.

The Effect of Purging with an Inert Gas on the Transient Activity of the Catalyst. Figure 10 is a plot of percent conversion of propylene versus the on stream time of propylene. A short break-in period of one hundred seconds and a long break-in period of about twenty-five minutes

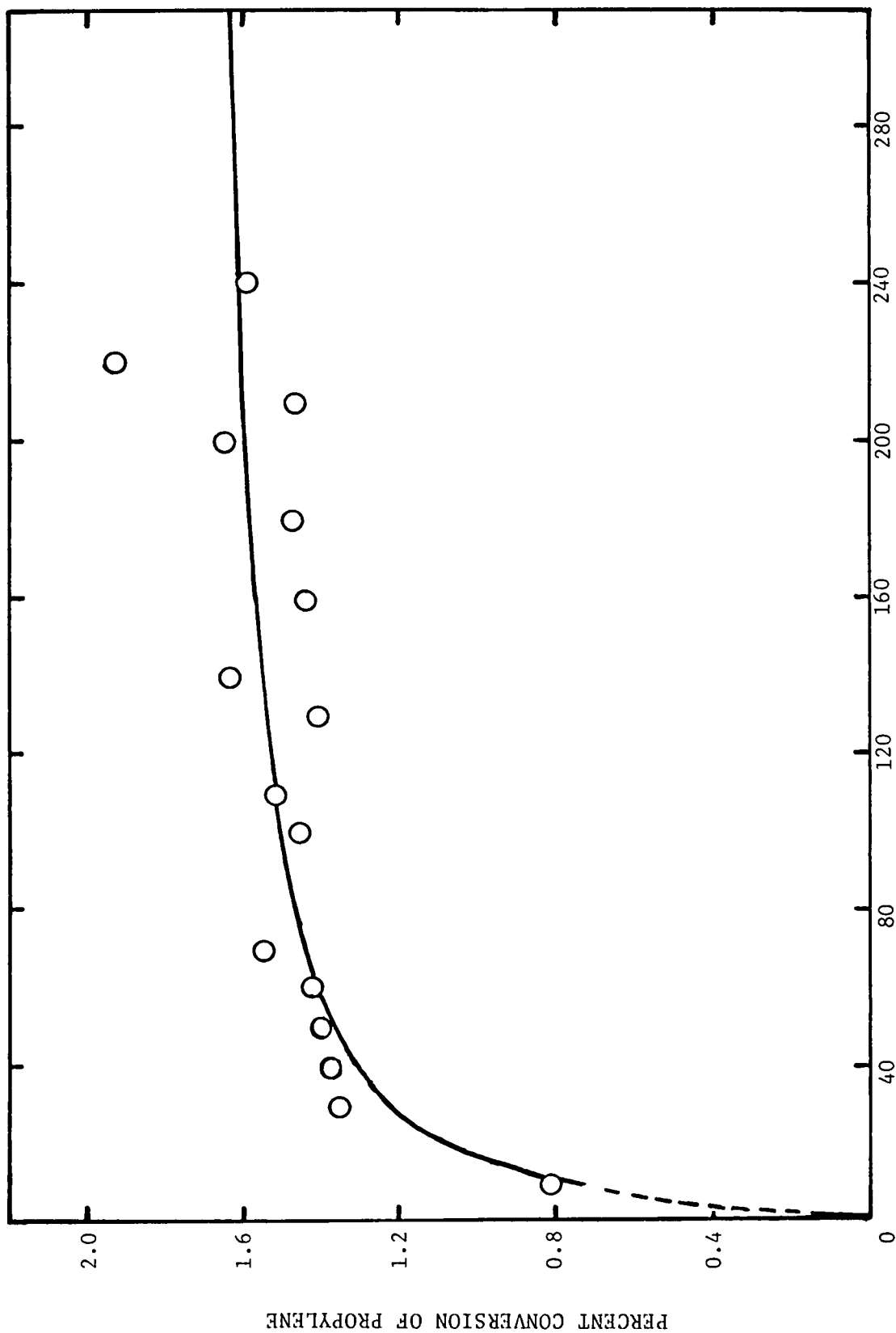


Figure 7. Break-in Behavior of the $\text{CoO-MoO}_3\text{-Al}_2\text{O}_3$ Catalyst at 120°C , $.94 \text{ atm}$.

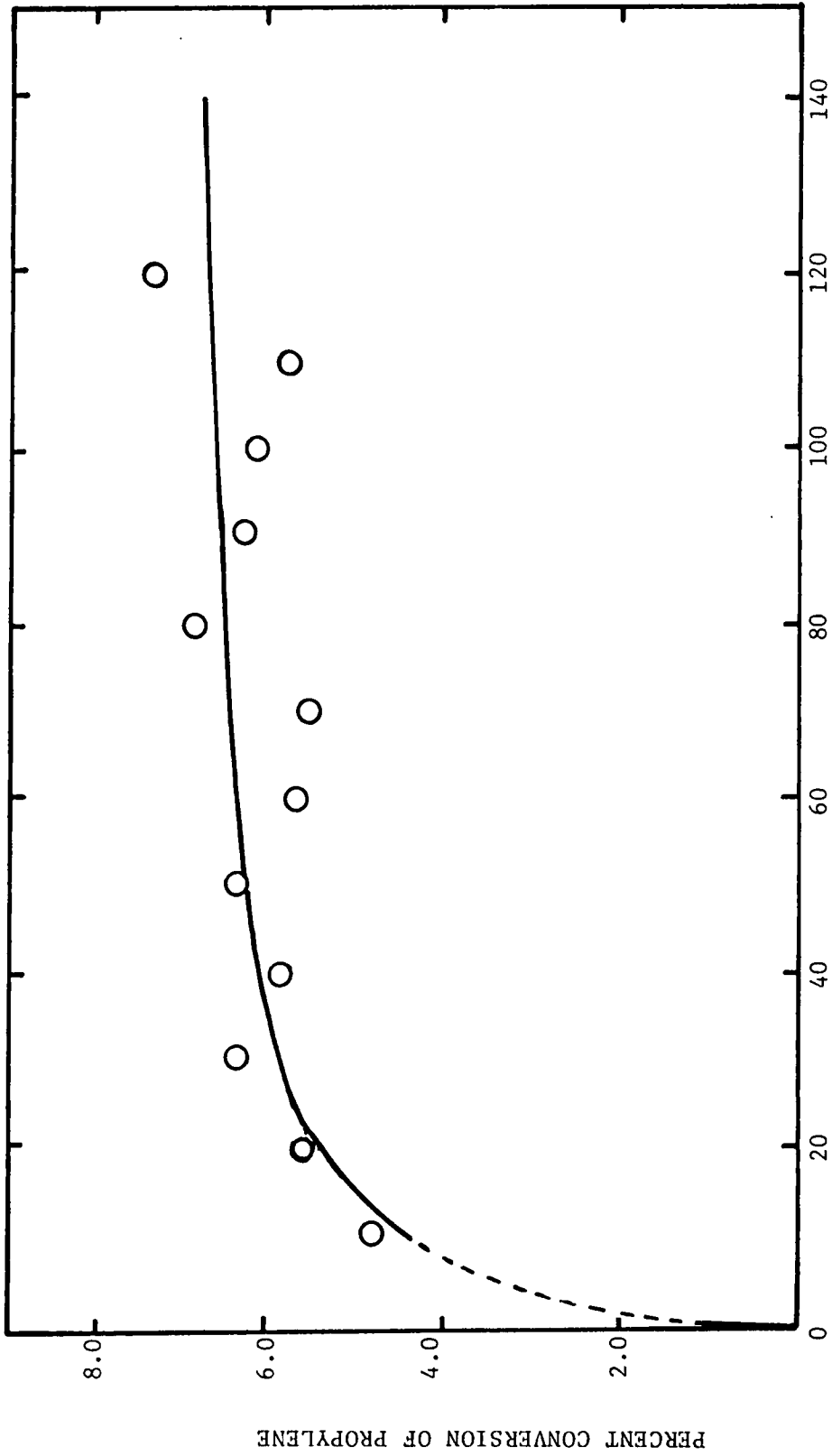


Figure 8. Break-in Behavior of $\text{CoO-MoO}_3\text{-Al}_2\text{O}_3$ Catalyst at 160°C , 0.94 atm.

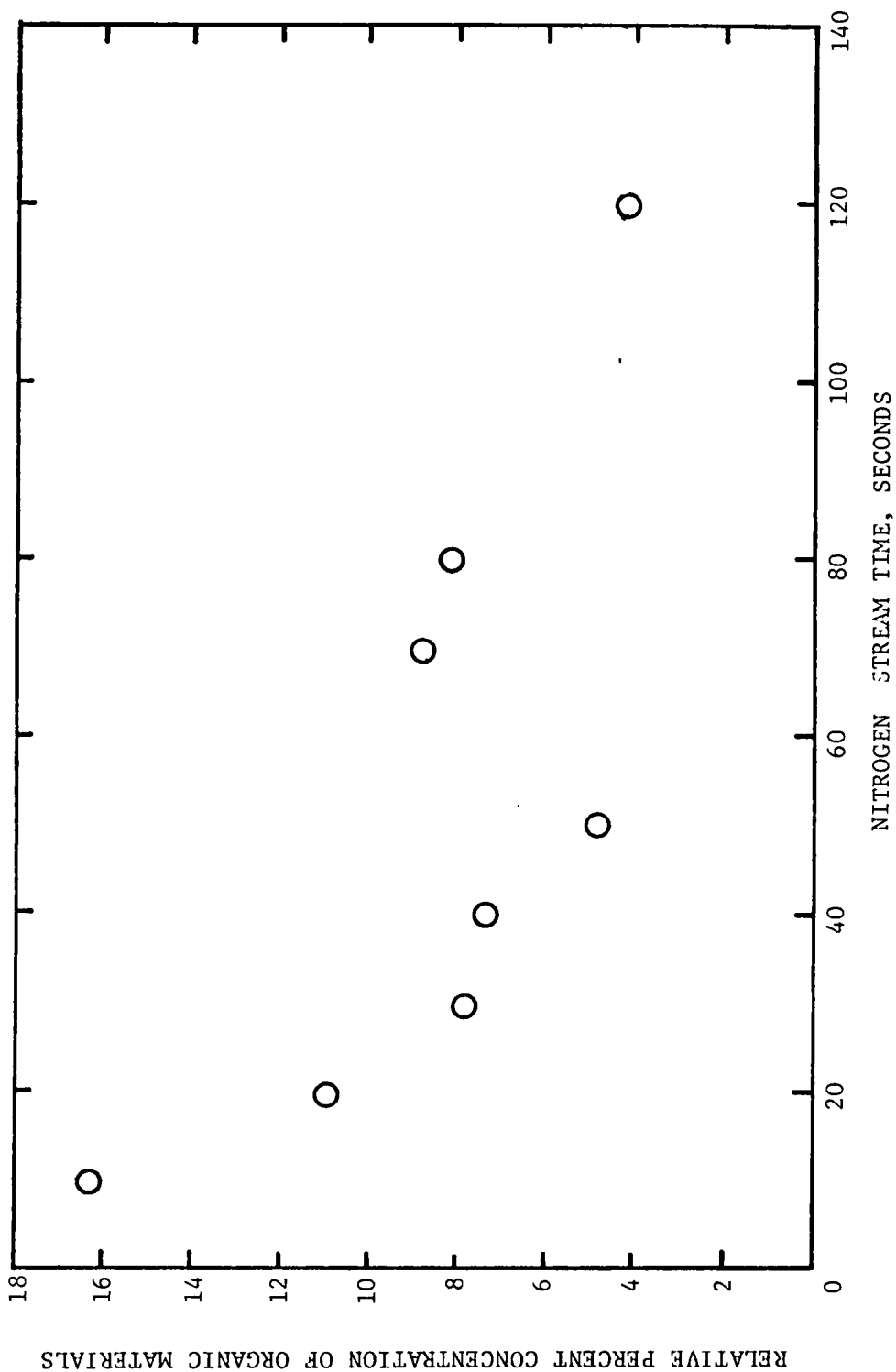


Figure 9. Response of Catalytic Activity of CoO-MoO₃-Al₂O₃ Catalyst to a Step Input of an Inert at 165°C, 0.94 atm.

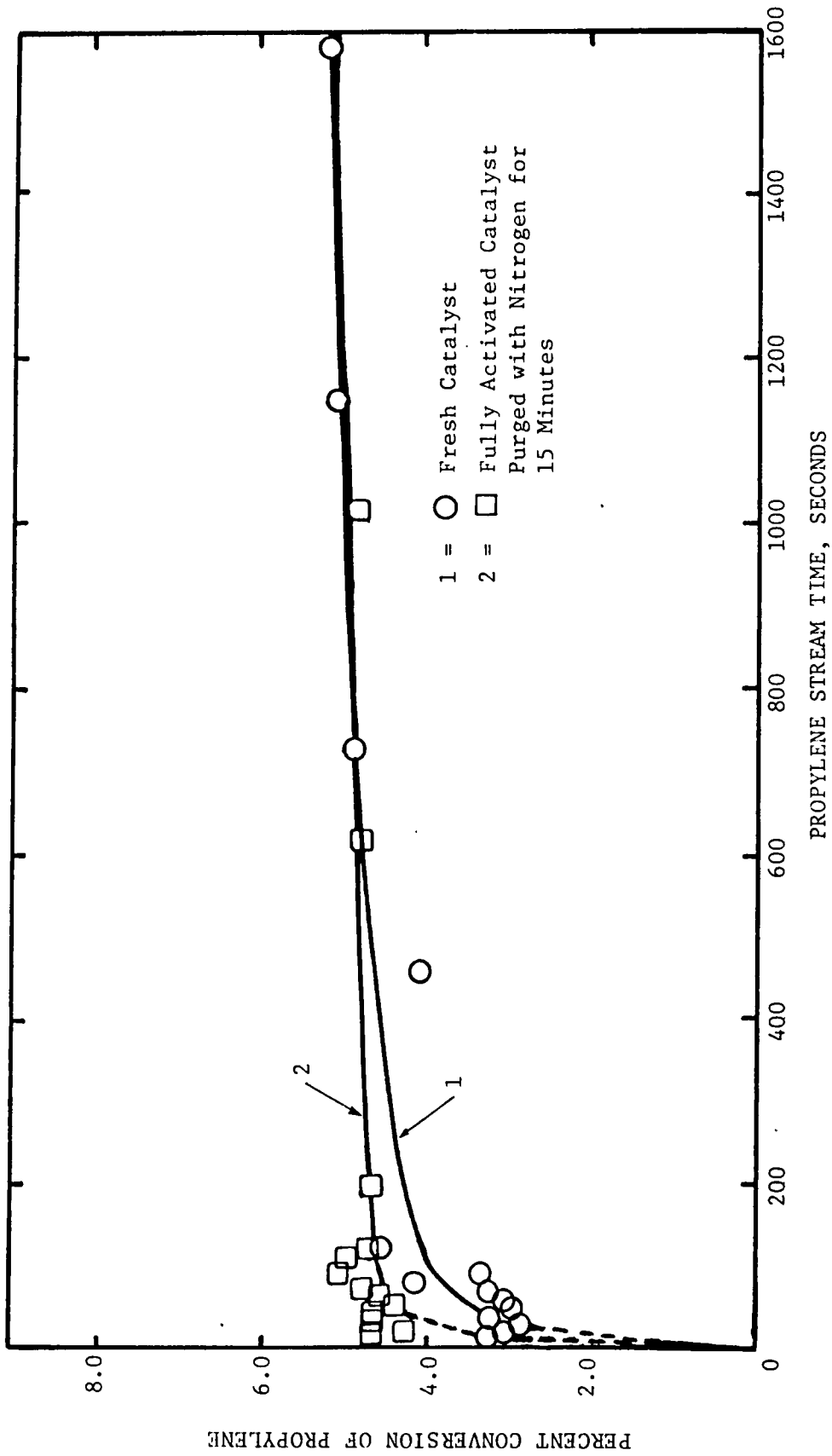


Figure 10. Effect of Purging with an Inert on Break-in of the $\text{CoO-MoO}_3\text{-Al}_2\text{-O}_3$ Catalyst at 165°C , 0.94 atm.

were found for freshly activated catalyst. As can be seen in the same figure the nitrogen purge caused another break-in period for the catalyst to restore full activity.

Part 2. Break-in Behavior of the Tungsten Oxide-
On-Silica Catalyst

The Effect of the Products from First Bed on the Catalytic
Activity of the Second Bed. Table III shows the data obtained from the split-bed reactor. The propylene conversion from whole bed is less than the expected value based on the propylene conversion from the upper half bed. The calculation of these expected propylene conversions is shown in Appendix A, sample calculations. Table IV contains the conversion data taken both before and after the switching of the three way valve from two beds to one bed for thirty seconds. These data show that this switching process did not affect the propylene conversion from the whole bed.

The Effect of Products in the Reactant Feed Stream on the Activity
of the Catalyst. We suspected that products in the reactant stream might cause deactivation of the catalyst. Experiments were performed by introducing mixtures with different concentration levels of products in the propylene feed. Table V shows the data obtained from three runs with a total product concentration of 0.573 percent in the feed stream. Figures 11 and 12 are plots of percent conversion of propylene versus stream time with a mixture containing 3.604 percent ethylene and 2-butene. The data tables for Figures 11 and 12 are in Appendix C.

Table III

EFFECTS OF THE PRODUCTS FROM THE FIRST BED ON THE
CATALYTIC ACTIVITY OF THE SECOND BED

T = 430°C

P = 0.94 atm

WHSV = 20.14

Catalyst Wt. = 0.6 grams

RUN	NUMBER OF BEDS	FRACTION OF COMPONENTS				PERCENT Conversion	
		Ethylene	Propane	Propylene	2-butene	Observed	Expected
1	2	11.887	1.611	208.8	14.342	11.084	13.424
1	1	7.665	1.410	219.6	8.758	6.917	
2	2	14.997	1.586	208.8	17.348	13.326	14.738
2	1	9.109	1.435	212.4	10.817	8.524	
3	2	13.109	1.586	200.6	15.480	12.388	13.219
3	1	7.832	1.410	220.5	8.846	6.990	

Table IV

EFFECT OF SWITCHING THREE WAY VALVE TO THE OUTLET
OF ONE BED FOR THIRTY SECONDS ON THE ACTIVITY OF
THE SECOND CATALYST BED

T = 430°C

P = 0.94 atm

WHSV = 40.28

Catalyst Wt. = 0.3 grams

NUMBER OF RUNS	SWITCH- ING TO ONE BED	FRACTION OF COMPONENTS				PERCENT
		Ethylene	Propane	Propylene	2-butene	Conversion from whole bed
1	before	3.511	0.631	91.580	4.278	7.789
	after	3.650	0.624	91.640	4.087	7.737
2	before	3.882	0.653	90.904	4.561	8.443
	after	3.967	0.623	91.240	4.170	8.138
3	before	3.668	0.619	91.380	4.334	8.002
	after	3.770	0.645	91.291	4.293	8.064

Table V

EFFECT OF A MIXTURE CONTAINING 0.573 PERCENT ETHYLENE
AND 2-BUTENE ON THE ACTIVITY OF CATALYST

T = 430°C

P = 0.94 atm

WHSV = 20.14

Catalyst Wt. = 0.6 grams

<u>RUN</u>	<u>STATE</u>	<u>FRACTION OF COMPONENTS</u>				<u>PERCENT Conversion</u>
		<u>Ethylene</u>	<u>Propane</u>	<u>Propylene</u>	<u>2-butene</u>	
1	Steady state activity	13.267	1.737	217.6	20.199	13.238
1	2 min. after switching	14.775	1.850	223.2	17.441	12.104
1	10 min. after switching	17.886	1.853	218.7	21.564	14.791
2	Steady state activity	17.886	1.853	221.4	21.428	14.973
2	2 min. after switching	16.697	1.692	219.3	21.205	14.307
2	10 min. after switching	16.917	1.737	223.2	26.962	15.819
3	Steady state activity	13.513	1.762	236.3	16.380	11.156
3	2 min. after switching	13.410	1.692	232.9	15.824	10.694
3	10 min. after switching	13.823	1.692	217.6	17.042	12.002

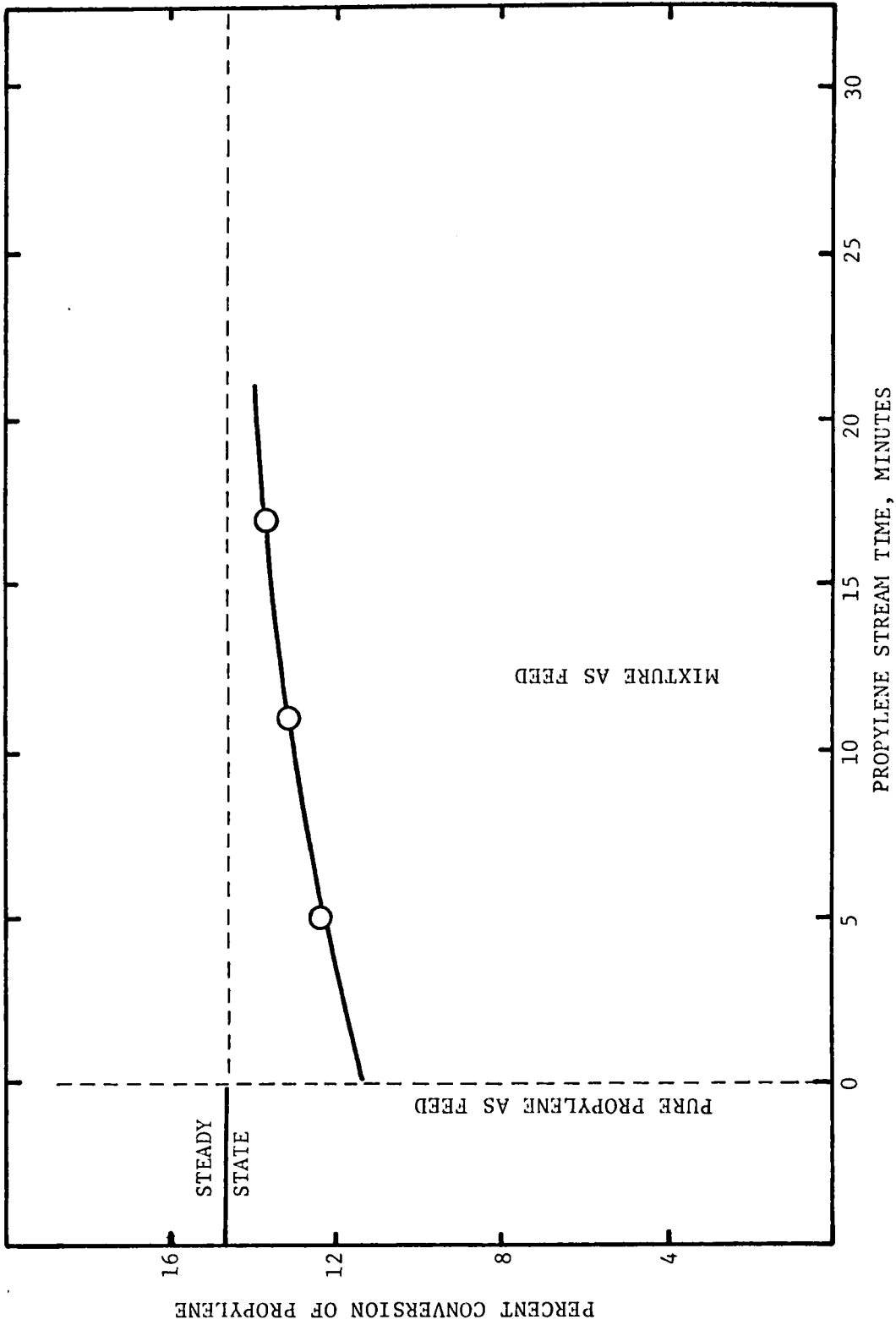


Figure 11. Effect of a Mixture Containing 3.60 Percent Ethylene and 2-Butene on the Break-in of the WO_3-SiO_2 Catalyst at $430^\circ C$, 0.94 atm. (First Run)

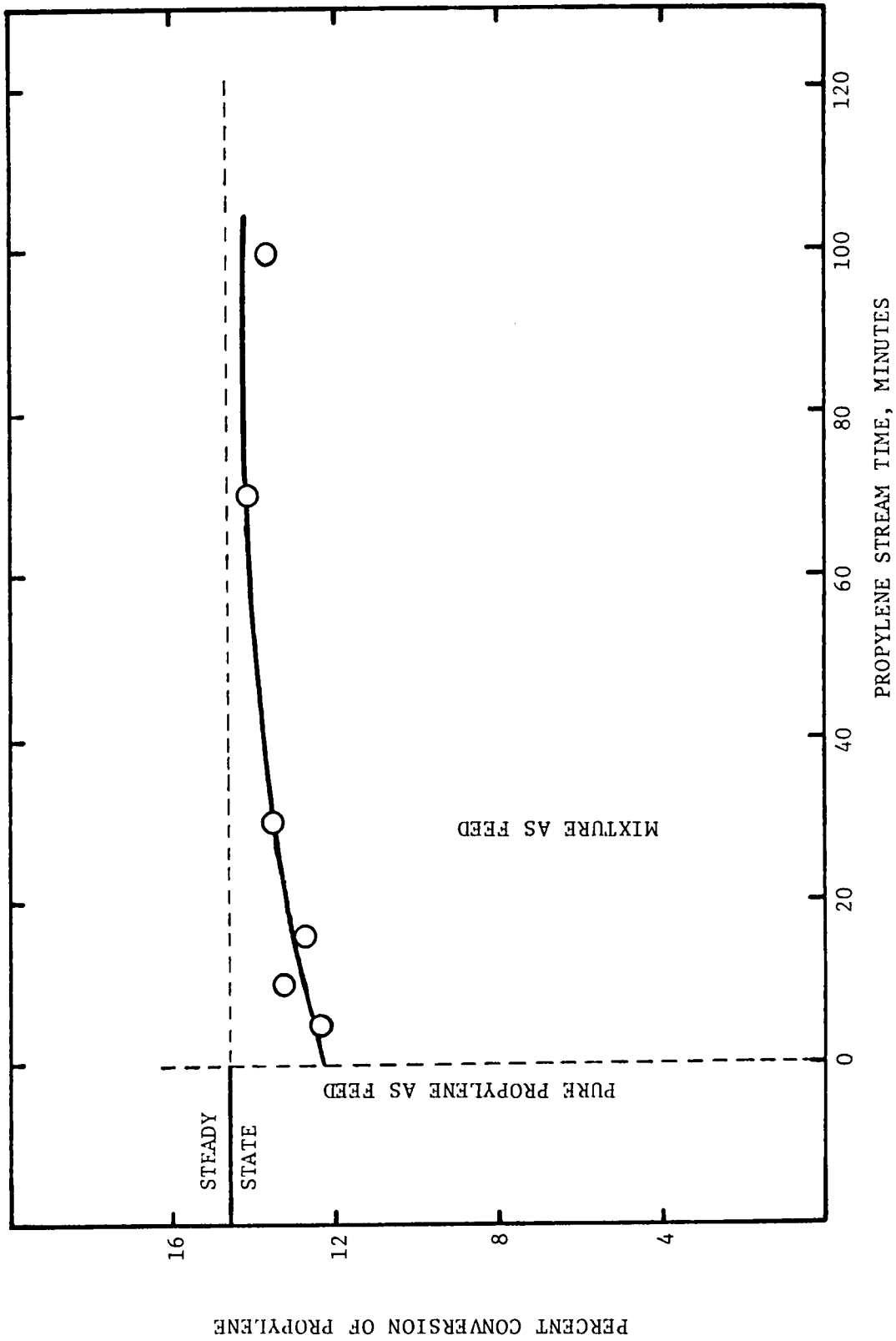


Figure 12. Effect of a Mixture Containing 3.60 Percent Ethylene and 2-Butene on the Break-in of the WO_3-SiO_2 Catalyst at $430^\circ C$, 0.94 atm. (Second Run)

Products Distribution from a Sodium-Incorporated Catalyst.

Attempts made to dose a WO_3-SiO_2 catalyst were not successful. Figure 13 is based on break-in data collected from 0.3 grams of non-pretreated catalyst from the same batch. The steady state conversions of propylene for a sodium-dosed catalyst in various experiments were found to be approximately one percent. Figure 14 is a plot of percent conversion of propylene versus on stream time. Data for this figure were taken from the experiment done on the catalyst pretreated with hydrochloric acid after being incorporated with sodium ions. A table of these data is shown in Appendix C.

The Effect of Dosing an Oxidizing Gas after the Dosing of a Reducing Gas, and Vice Versa. The data tables for the figures are in Appendix C. Figures 15 and 16 are plots of percent conversion of propylene versus stream time after the dosing of hydrogen and dry air for one minute respectively. A break-in period of 18 minutes was found for hydrogen dosing and 80 minutes for air dosing. Figures 17 and 18 are plots of break-in data of dry air dosing followed by hydrogen dosing and hydrogen dosing followed by dry air dosing respectively. Each gas was dosed for one minute. A break-in period of 60 minutes was needed in each case.

The Effect of Fast Cooling in the Presence of Stagnant Propylene on Break-in. Figure 19 is a plot of percent conversion of propylene versus stream time after a 8-hour shut down. A break-in period of 60 minutes was needed for the catalyst to resume the original steady state activity.

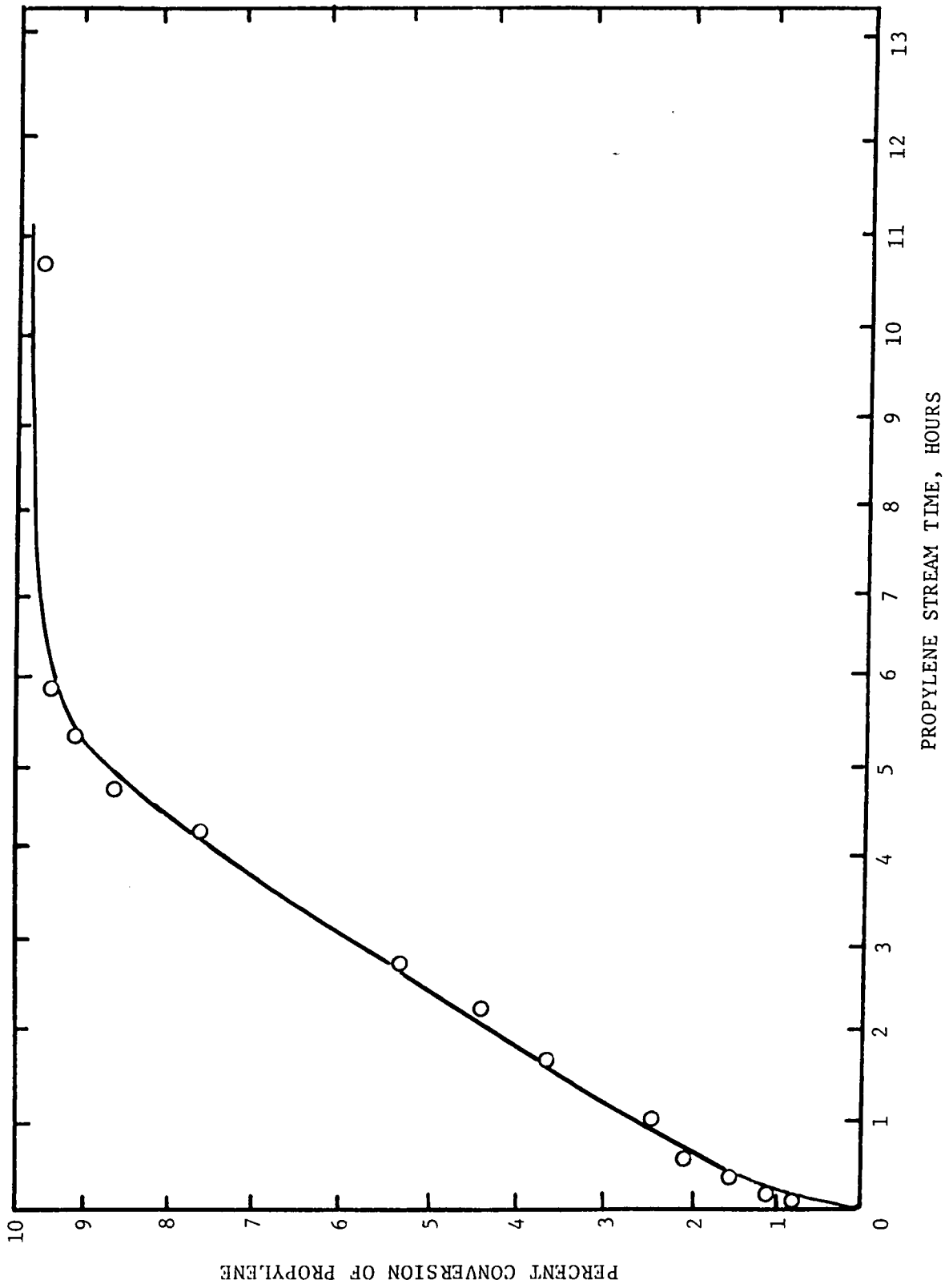


Figure 13. Break-in Behavior of the $\text{WO}_3\text{-SiO}_2$ Catalyst at 430°C , 0.94 atm.

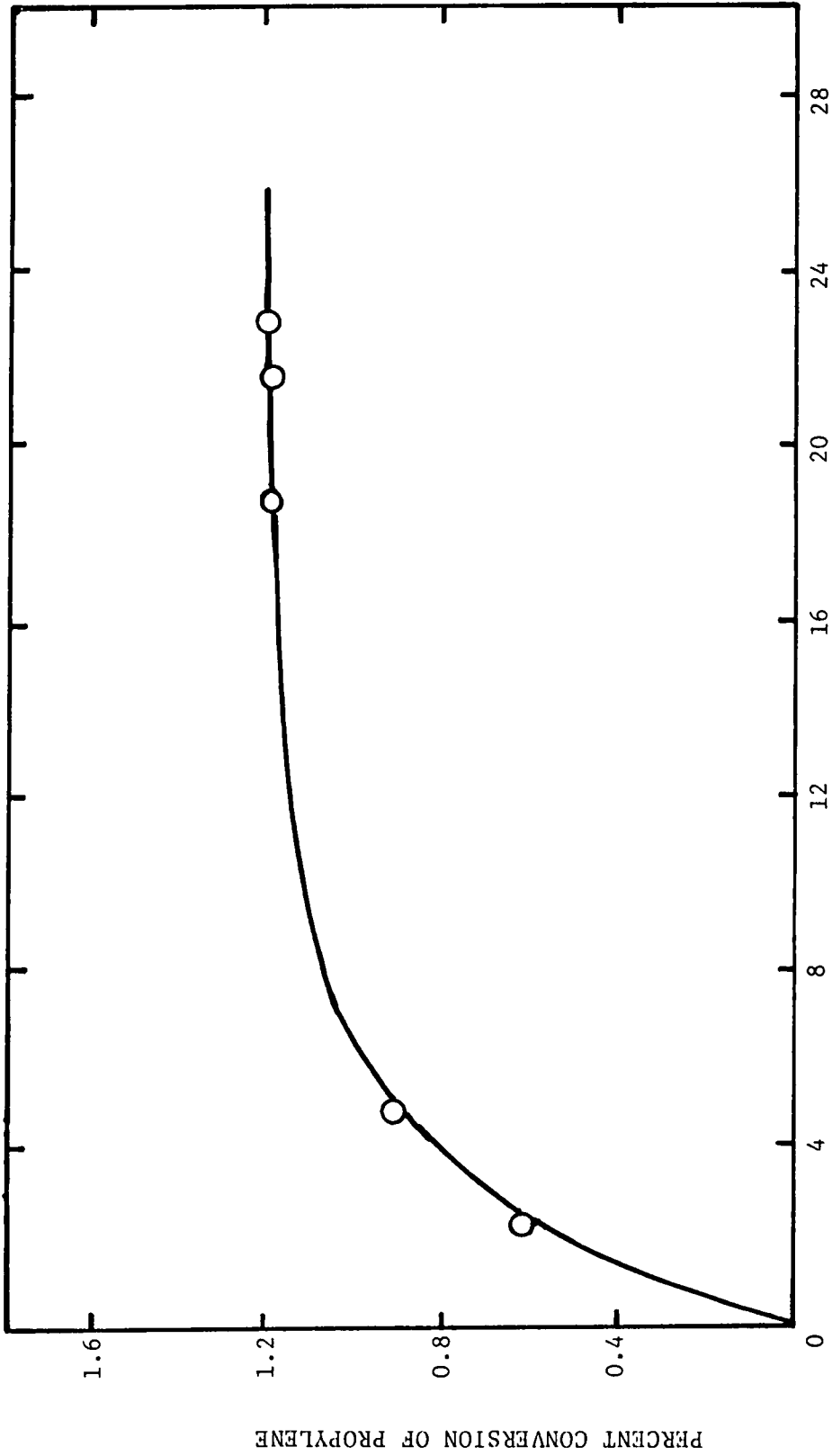


Figure 14. Break-in Behavior of the Sodium-dosed $\text{WO}_3\text{-SiO}_2$ Catalyst at 430°C , 0.94 atm.

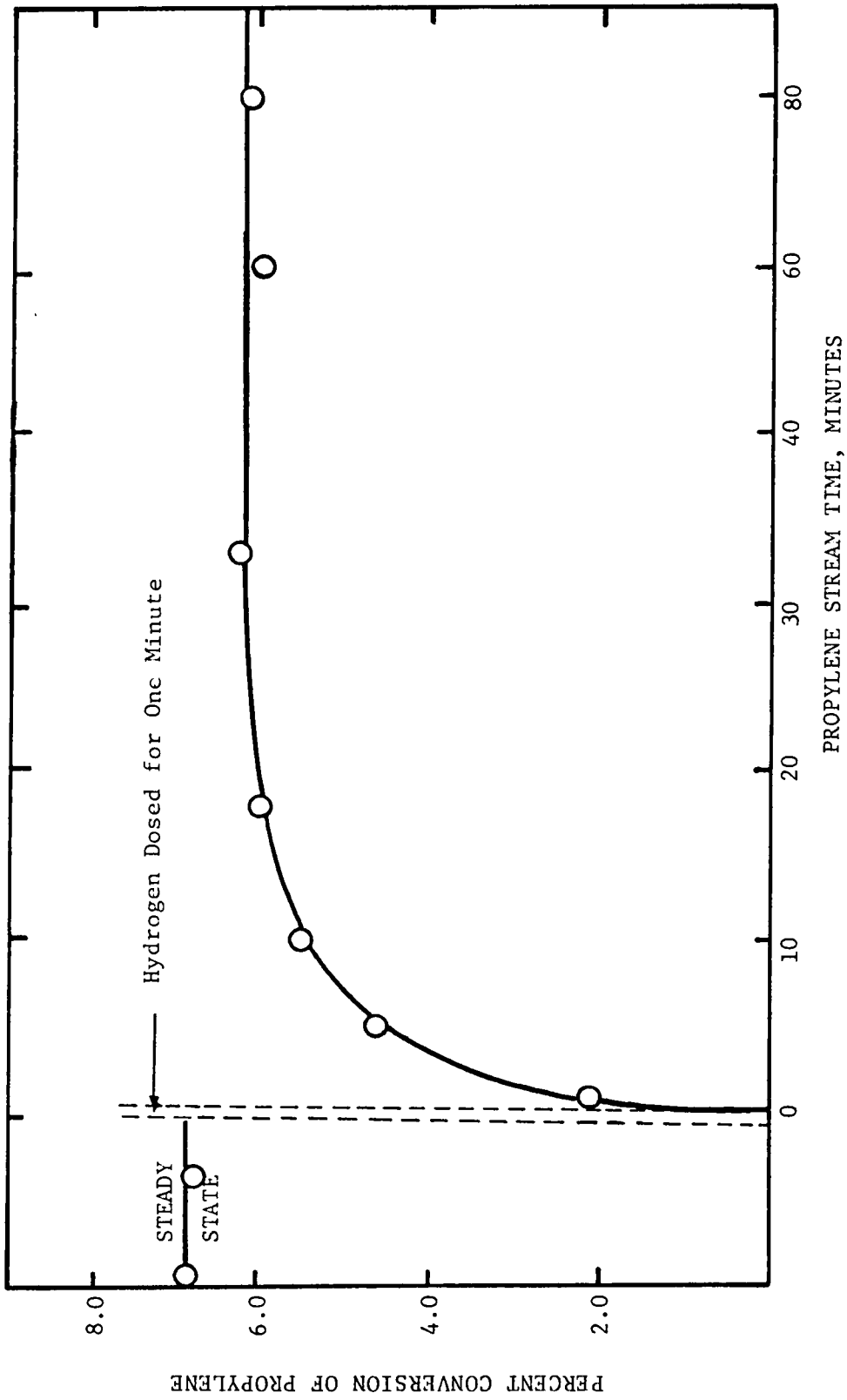


Figure 15. Effect of Hydrogen Dosing on the Break-in of the $\text{WO}_3\text{-SiO}_2$ Catalyst at 430°C , 0.94 atm.

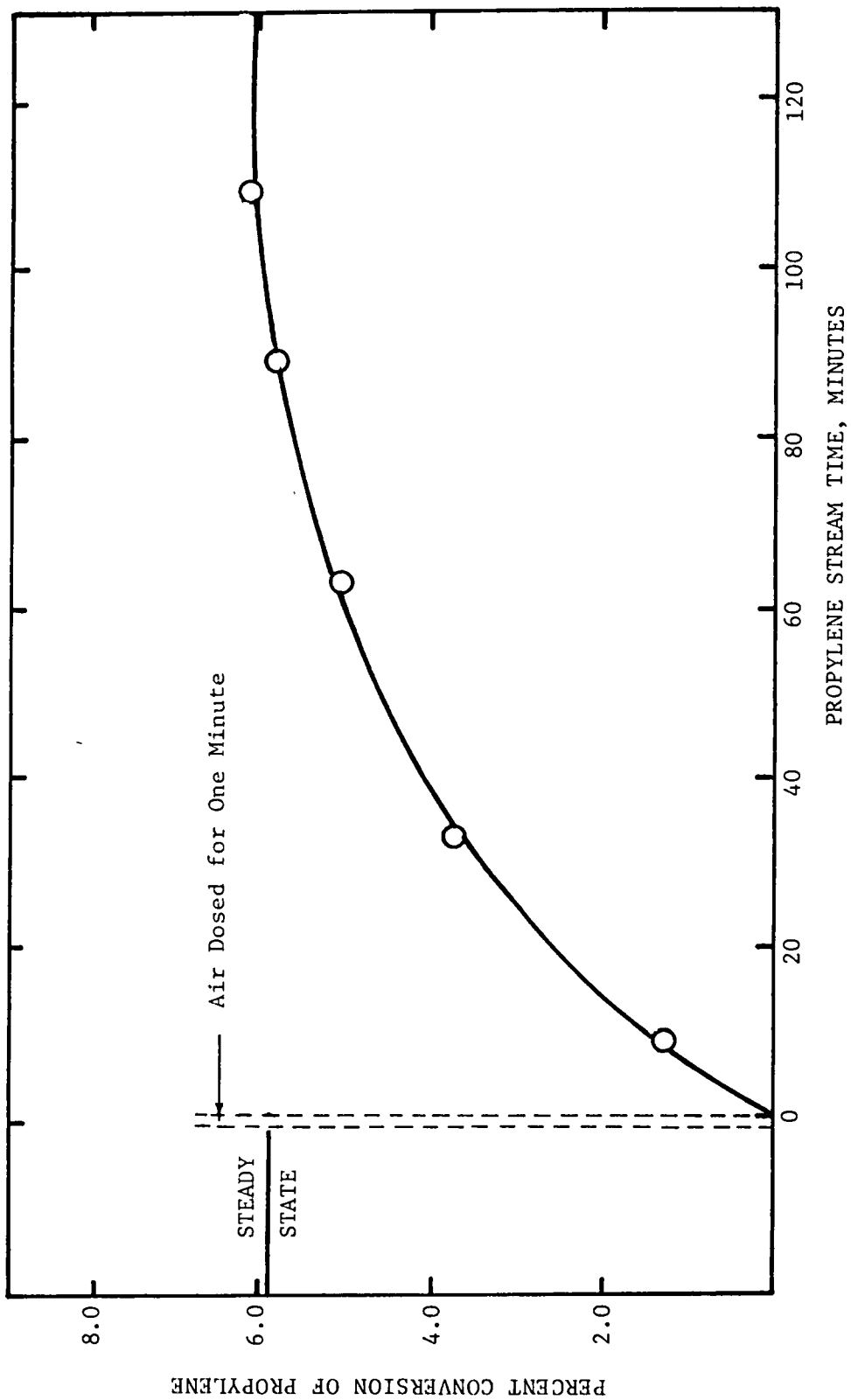


Figure 16. Effect of Air Dosing on the Break-in of the $W_0_3-SiO_2$ Catalyst at $430^\circ C$, 0.94 atm.

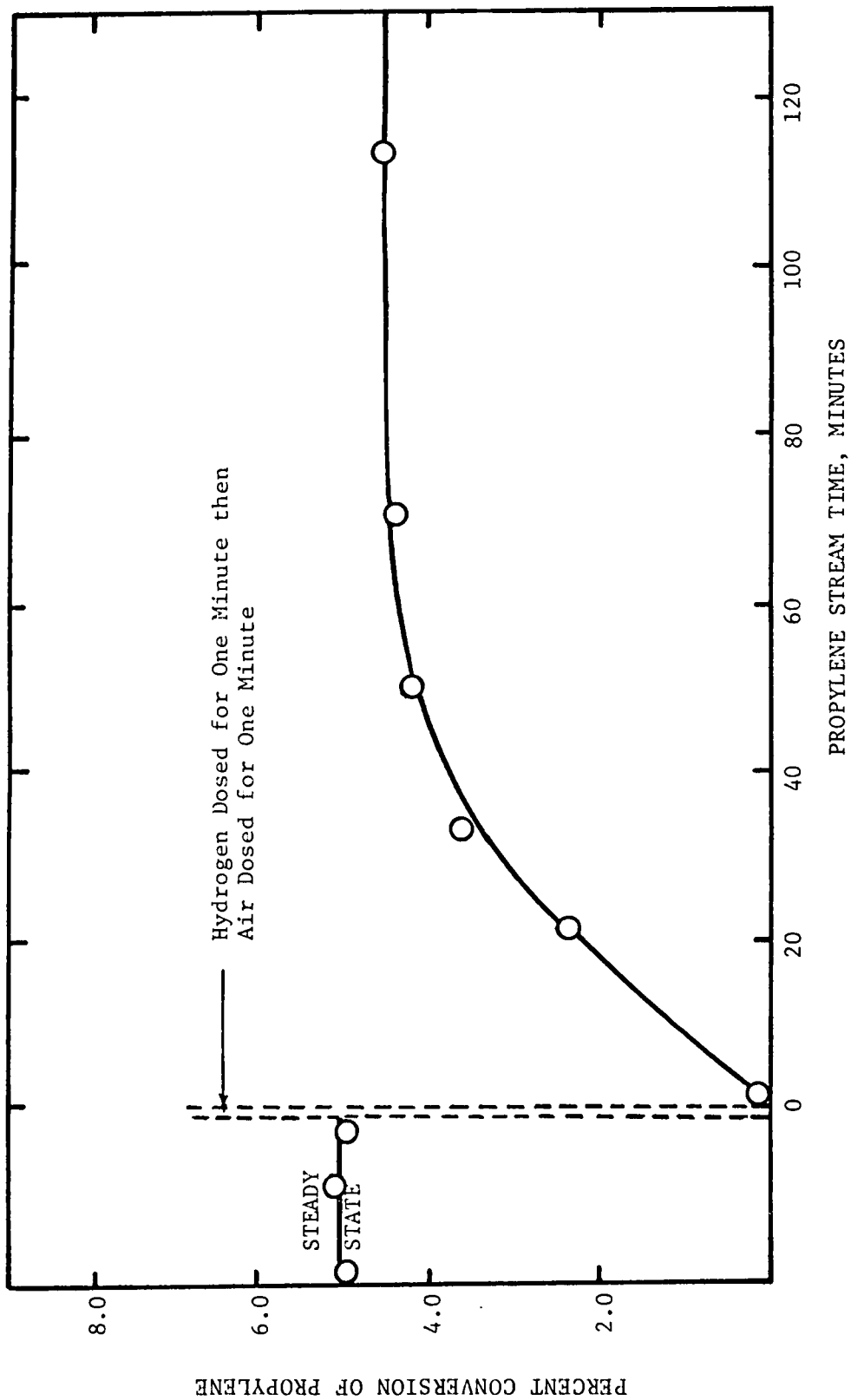


Figure 17. Effect of Hydrogen-Air Dosings on the Break-in of the WO_3-SiO_2 Catalyst at $430^\circ C$, 0.94 atm.

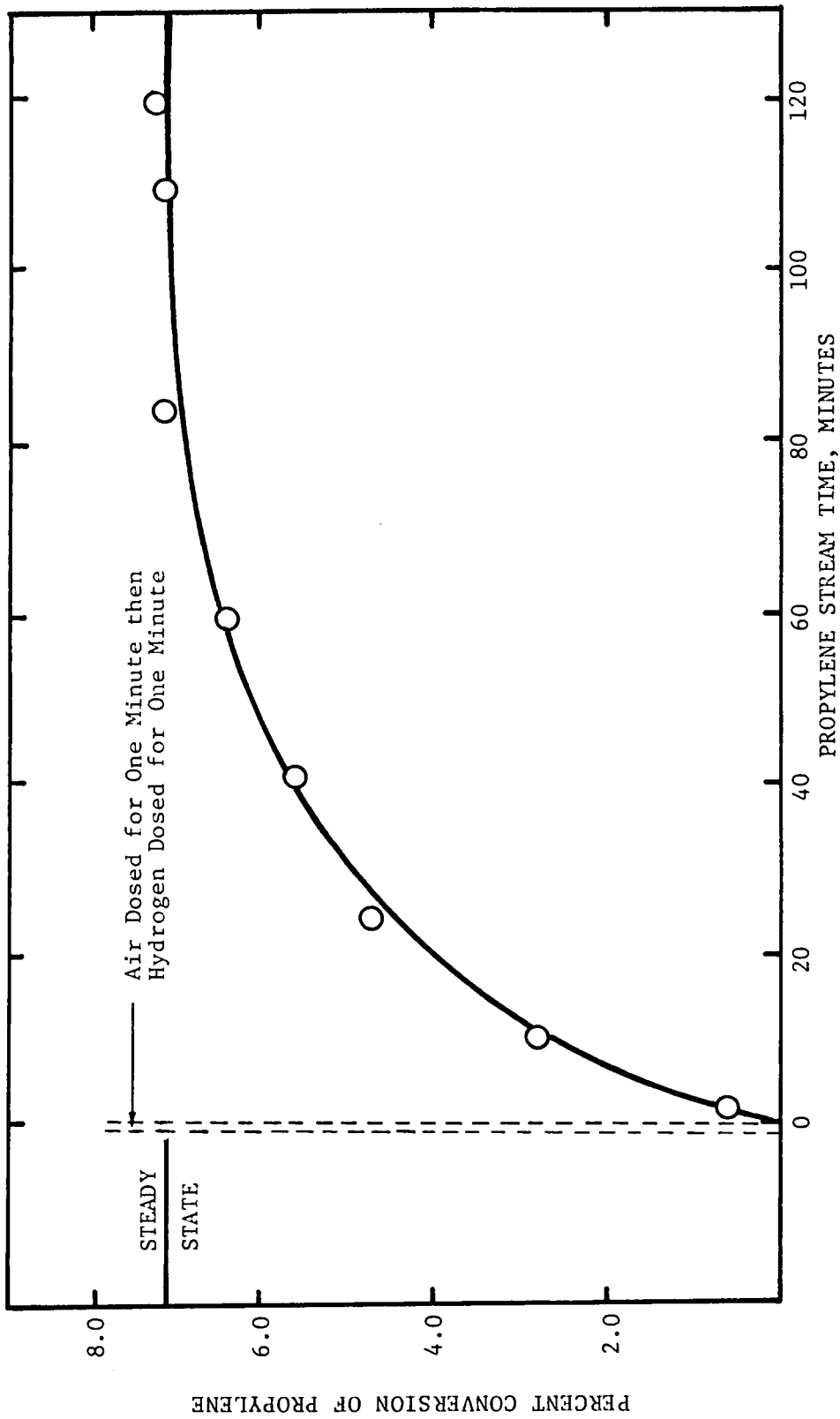


Figure 18. Effect of Air-Hydrogen Dosings on the Break-in of the WO_3-SiO_2 Catalyst at $430^\circ C$, 0.94 atm.

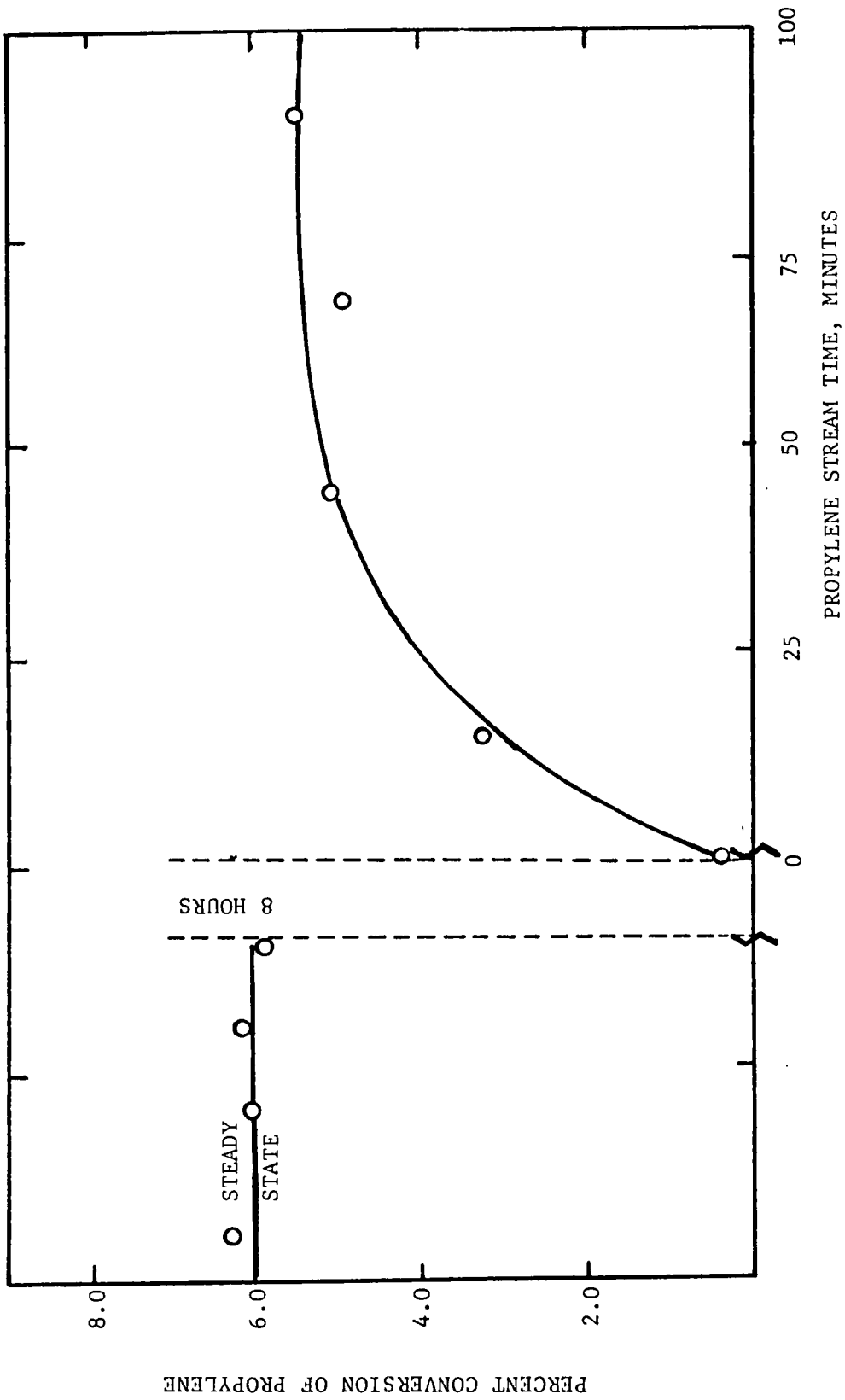


Figure 19. Effect of Cooling and Reheating in the Presence of Stagnant Propylene on the Break-in of the $W_0_3-SiO_2$ Catalyst at $430^\circ C$, 0.94 atm. (Eight Hours Shutdown)

IV. DISCUSSION

Discussion of Experimental Procedures

Discussed in this section are the catalyst activation procedure, the disproportionation reactor system and its operation, and the product analysis procedure.

Catalyst Activation Procedure

The activation procedure employed throughout this study was suggested by several investigators. (25,31,35) The major advantage of this procedure was that the activation took place in the reactor and the catalyst was exposed in situ to propylene afterwards. This minimized the chance of contamination of the catalyst. A tubular furnace was used to supply heat to the reactor during the period of activation. Measurements showed that these furnaces heated non-uniformly along their length, with the center more than 5°C hotter than the two ends. A heat transfer block made of heavy metal was placed around the reactor to eliminate this problem. The catalyst bed was placed in the center of the reactor and the tip of the thermocouple well was positioned in the middle of the catalyst bed in this way the temperature of the bed could be controlled within $\pm 2^{\circ}\text{C}$. A four-foot long 1/16 inch I.D. 316 stainless steel tubing was made into a coil to surround the heat block so that the propylene was preheated before entering the reactor. The activation procedure was followed either to regenerate a used catalyst or to prepare a freshly activated catalyst. Anhydrous air was passed through the catalyst bed and this oxidized the coke which might be deposited on the catalyst during the previous experiment. The

temperature required for the activation procedure was above the ignition point of carbon (about 500°C). Usually the activation temperature was between 550°C and 600°C. In this study, the activation temperature was kept at 600°C. Normally, activation was followed with a one-hour nitrogen purge to remove traces of air, moisture, and other polar compounds known to be temporary poisons to these catalysts.

This method of catalyst activation proved to be very reproducible and little trouble was experienced not only in this study but also in the investigations performed by others. (19,28,31)

Disproportionation Reactor Procedures

Three factors which affect the rate of reaction are temperature, pressure and flow rate. Careful control of these factors is essential to obtain reproducible data during each experiment. As a regular procedure, the reactor was cooled down to the required temperature at the end of each six-hour activation period. The propylene flow was not introduced to the reactor until the temperature of the reactor had stabilized for at least fifteen minutes. To eliminate channeling and temperature gradients along the catalyst bed, the size of the bed was made very small and crushed quartz was mixed with the catalyst particles to improve feed distribution.

The reactor pressure was controlled by a "Mity-mite" back pressure controller. Since only atmospheric pressure was used throughout this study, the pressure was set at the desired value at the beginning of this study, and this gave very good pressure control over a wide range of flow rates. By using this equipment, it was possible to control

the reactor pressure and product flow rate independently, and the necessity of using more complicated pressure sensors and feed back control instrumentation was thus eliminated.

Isothermal conditions in the reactor were maintained by independently activating two banks of resistance elements around the reactor. The continuous source of energy from one bank was combined with an intermittent source of energy at a reduced level from the other bank to give a good control of temperature. Continuous observation of the reactor temperature was made possible by connecting a digital temperature indicator directly to the thermocouple in the reactor. During all studies, care was taken to sample the product stream only when the temperature was within 2°C of the desired temperature. Due to sensitivity to the ambient temperature, it was very difficult to control the temperature to better than $\pm 1^{\circ}\text{C}$.

Since the flow rate control was independent of the pressure control, it was the last to be adjusted. Through the combination of a two-stage regulator on each gas cylinder, a Moore differential flow controller, and a needle valve, a stable, accurately metered reactor feed was maintained throughout this investigation. During each experiment direct measures were made of the reactor flow rate using an in-line soap bubble flow meter. This procedure provided an accurate measure of the reactor flow rate and eliminated the necessity of accurate rotameter calibrations in each experiment.

Product Analysis Procedures

The composition of effluent gases was measured by using a calibrated

gas chromatograph. The calibration factors given by Luckner⁽³¹⁾ and Fathi⁽¹⁹⁾ were used throughout this investigation. The detector gas supplies were maintained at the same pressure as were used by the above-mentioned investigators. The performance of the gas chromatograph was satisfactory. A straight base line was easy to set prior to the recording of each sample. The recorder was operated at a proper chart speed, and the peaks of low concentration components were enlarged by varying the attenuation so that the integration of the peaks was accurate.

A complete sample analysis on the gas chromatograph usually took at least seven minutes. Because of the rather short break-in period of the cobalt oxide-molybdena-alumina catalyst, the in-line gas chromatographic analysis was not practical. An auxiliary sampling system containing twenty-four sample valves was used during the studies associated with the transient activities of this catalyst. Once the propylene was introduced to the freshly activated catalyst, one sample valve was actuated every ten seconds. Although the quantity of products trapped in the sample loop depended on the speed at which the plunger of sample valve was pulled out, the data obtained in this manner was still very reliable because the gas chromatographic method did not depend upon the quantity of sample being analyzed. There was a possible disturbance of product flow while the plunger of sample valve was being pulled out. Checks on the product flow rate were made before and after each plunger was pulled out. No substantial change of product flow rate was found.

Discussion of Results

This section contains a discussion of the results obtained for each experiment on the break-in behavior of the cobalt oxide-molybdena-alumina catalyst and the tungsten oxide-on-silica catalyst during propylene disproportionation.

Part 1. Transient Activities of the Cobalt Oxide-Molybdena-Alumina Catalyst

In the following paragraphs the results obtained from each experiment concerning the transient activities of the cobalt oxide-molybdena-alumina catalyst are discussed.

Time Constant Determination of the Catalytic Transient Activity.

Since no quantitative information about the transient activities of this catalyst was available when this study was started, the first several experiments were performed to observe this phenomena. Break-in data obtained at different temperature levels are shown graphically in Figures 7 and 8. A long break-in period of more than ten minutes following a short one of about one hundred seconds can be observed in each case. The break-in rate constants are not available for these two cases because the steady-state activity of the catalyst was not obtained.

Response of the Fully Activated Catalyst to a Step Input of Nitrogen. In order to verify that the transient activities observed in the previous experiments were not solely due to the mass transfer effects or the displacement of adsorption-desorption equilibria, an inert gas was introduced to the reactor after the catalyst had reached steady-state activity. Figure 9 shows the results of this experiment. Using the average quantities of organic compounds at steady state in

the 24 sample valves, the quantity of organic compounds was still detectable on gas chromatograph after the propylene flow had been stopped for about one hundred seconds. Theoretically the time needed for propylene to diffuse into or out of the pores of this catalyst in nitrogen atmosphere was estimated to be 0.15 seconds by a nonsteady-state approach. The calculation of this diffusion time is shown in Appendix A, sample calculations. As can be seen in Figure 9, the time needed for the reactor system to purge the organic materials is of the same order of magnitude as the first short induction period found in previous experiments. The propylene conversions of these purged organic materials were found to jump to a higher level after the propylene had been stopped (Table IX, Appendix C). This indicates that these organic materials must have come from the pores of the catalyst and they have anomalously long residence times. If they had been coming from the dead volume of the system, the propylene conversion would have been less. Therefore, the first short induction period is believed to be due to pore diffusion effects.

The Effect of Purging with an Inert Gas on the Transient Activity of the Catalyst. In the previous studies of the break-in behavior of tungsten oxide on silica catalyst, ^(19,31) it was believed that the reduction of WO_3 to $WO_{2.9}$ together with some other phenomena were responsible for break-in. It was thought that this might also be true for the cobalt oxide-molybdena-alumina catalyst. Shown in Figure 9 are the break-in data of a freshly activated catalyst and the same catalyst previously purged with nitrogen for fifteen minutes after full activity had been achieved. This figure shows that a short break-in

of one hundred seconds is followed by a longer break-in of about twenty-five minutes for the fresh catalyst. The same type of break-in period was needed for the catalyst to restore full activity after the nitrogen purge, although the first break-in period was shorter than that of the fresh catalyst. This implies that some phenomena other than the reduction of the catalyst is responsible for the break-in behavior of the catalyst. Figure 21 shows that the break-in periods of this catalyst involves two first order processes, although the data for first break-in period are scattered. The second break-in period has a rate constant of $8.0 \times 10^{-5} \text{ second}^{-1}$.

Part 2. Break-in Behavior of Tungsten Oxide-on-Silica Catalyst

This section contains a discussion of the results obtained in the experiments concerning the break-in behavior of the tungsten oxide-on-silica catalyst during propylene disproportionation.

The Effect of Products from the First Bed on the Catalytic Activity of the Second Bed. In the studies of the reverse reaction of propylene disproportionation over tungsten oxide-on-silica catalyst, Fathi⁽¹⁹⁾ used a mixture of approximately equal moles of ethylene and 2-butene as a reactant to determine the roles of the product gases of propylene disproportionation in the break-in of the catalyst. Unexpectedly, he found that this catalyst ($\text{WO}_3\text{-SiO}_2$) was not an effective catalyst for producing propylene from ethylene and 2-butene, although it had a high selectivity for propylene disproportionation. His experimental results indicated that as the time of contact of reactants increased, the activity of the catalyst decreased. In the same study, Fathi interrupted

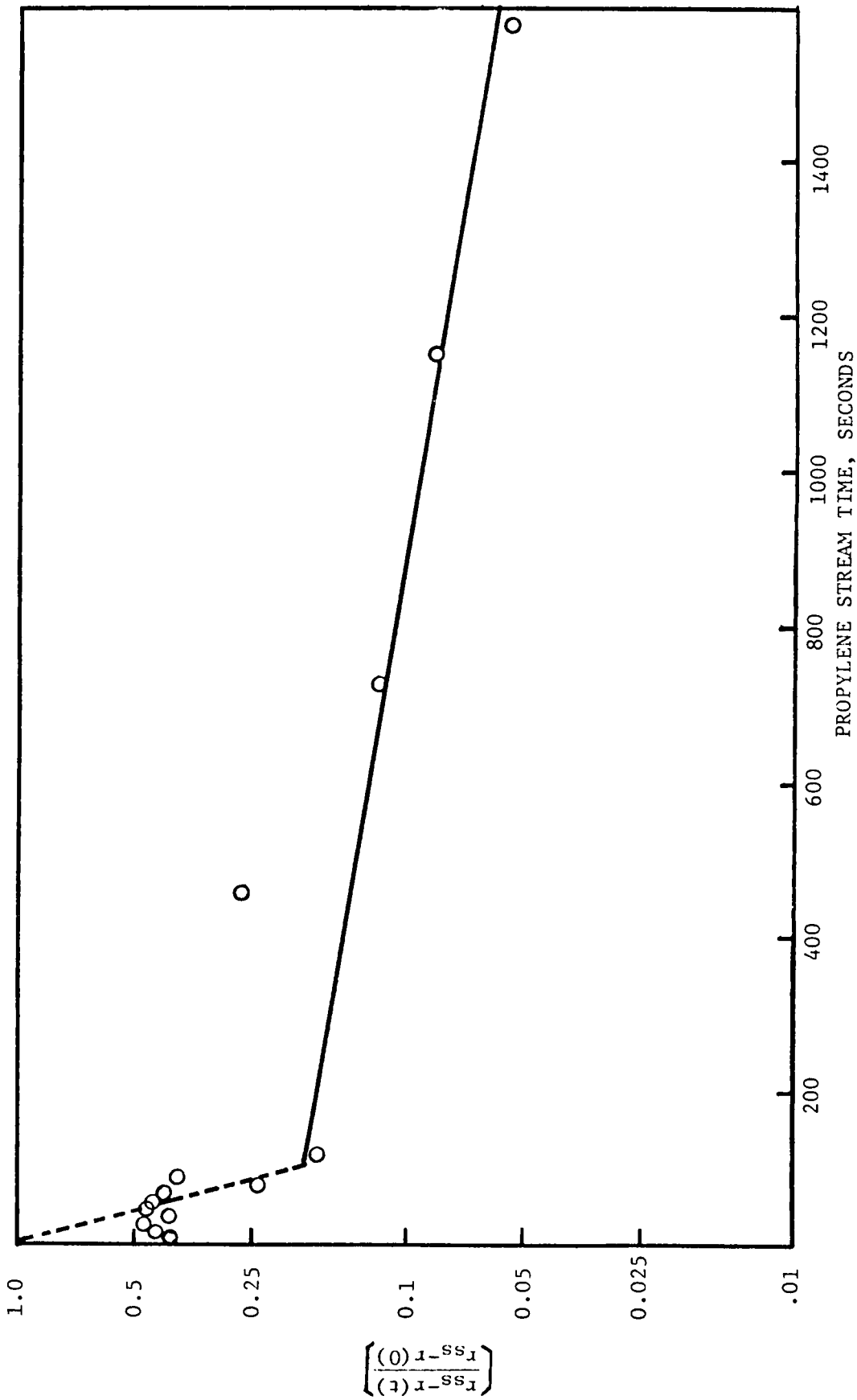


Figure 20. Rate of Fractional Approach to Steady-State for Fresh CoO-MoO₃-Al₂O₃ Catalyst at 165°C, 0.94 atm.

the propylene flow with a mixture of 55.5% ethylene and 44.5% 2-butene for 30 minutes and for 70 minutes. The results showed that the interruption of propylene with the mixture reduced the activity of the catalyst to a point where another break-in period was needed to restore the fully activity of the catalyst.

It was therefore expected that in a split-bed reactor, the products from first bed might deactivate the second catalyst bed. A split-bed reactor was built to check this speculation and the product gases from both the upper half of the bed and the whole bed were analyzed chromatographically. The results shown in Table III indicate that the products from the first bed have some deactivating effect on the second bed since the propylene conversion in two beds is 1-2 percent less than expected in each case. The calculation of the expected propylene conversion is shown in Appendix A, Sample Calculations.

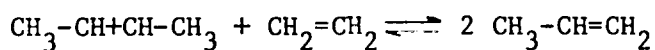
The Effects of Different Product Concentration Levels in the Feed on the Activity of the Catalyst. In these experiments, the pure propylene flows were replaced by different mixtures containing propylene and approximately equal moles of ethylene and 2-butene. This switch was made after the catalyst had reached full activity. The total concentrations of ethylene and 2-butene in the two mixtures used are 0.573 percent and 3.604 percent, respectively. Table V shows the mixture containing 0.573 percent ethylene and 2-butene initially deactivated the catalyst a little in the first two minutes after switching, but full catalyst activity was restored within ten minutes. Figures 11 and 12 show the results obtained from the experiments using mixture containing 3.604 percent ethylene and 2-butene as feed. Both figures show

that this mixture had a suppressing effect on the activity of the catalyst. The product concentrations in the feed were far below their thermodynamical equilibrium values; therefore, they did not show drastic effects on the activity of the catalyst as reported by Fathi.⁽¹⁹⁾

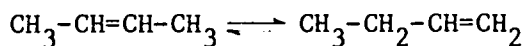
The Effect of the Sodium-Incorporation on the Product Distribution of Propylene Disproportionation. Bradshaw et al.⁽⁹⁾ studied the disproportionation of n-butenes over a cobalt oxide-molybdena-alumina catalyst and reported that the product distribution was markedly affected by double-bond isomerization which accompanied the disproportionation. They also reported that the reaction could be made highly selective for the production of either ethylene plus 3-hexene, or propylene plus n-pentenes, by suitable choice of the reaction conditions or by dosing the catalyst with controlled amounts of sodium ions. The reversibility of this reaction was confirmed and 2-butene reacted with ethylene to give propylene with a selectivity of over 90%. Heckelsberg⁽²¹⁾ used Na, K, Ba and Cs with tungsten oxide on silica catalyst to increase selectivity for the disproportionation of propylene.

In the studies of the reverse reaction of propylene disproportionation, Fathi⁽¹⁹⁾ found that this catalyst (WO_3-SiO_2) was deactivated as the time of contact with the mixture of product gases increased. This suggested that this phenomena might be either due to the presence of oxygen in the mixture prepared in the laboratory or due to the isomerization of 2-butene to 1-butene and the heavy hydrocarbons resulting from reaction of these butenes. The proposed reactions are as follows:

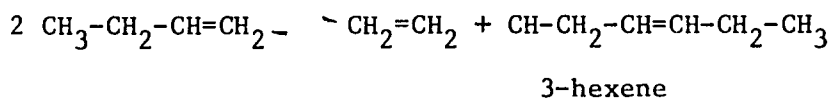
1. Reverse reaction



2. Isomerization



3. Disproportionation



etc.

In order to increase the selectivity of the catalyst for the disproportionation reaction and to eliminate the isomerization and secondary disproportionation, an attempt was made to incorporate small amounts of sodium ions into the catalyst. The attempt to alter the ten percent WO_3 catalyst by adding 0.02N sodium hydroxide aqueous solution followed by drying at 120°C for twelve hours was not successful. As shown in Figure 10, the non-pretreated catalyst reached a steady-state activity of approximately ten percent conversion after a break-in period of ten hours. The sodium-incorporated catalyst of the same quantity gave a propylene conversion of only about one percent under the same conditions after ten hours. Another attempt was made to revitalize the catalyst by adding 0.04N aqueous hydrochloric acid to the pretreated catalyst followed by twelve hours of drying at 120°C afterwards. As can be seen in Figure 14, the maximum propylene conversion was only 1.2% after a break-in period of ten hours. No 1-butene was detected by gas chromatography. This may be due to the low propylene conversion or to the sodium incorporation.

An alternative is to pretreat the catalyst with a weaker acid such as sodium bicarbonate and use higher temperatures (e.g. 400°C) to get rid of the water of hydration.

Effect of Cooling and Reheating upon Catalyst Activity in the Presence of Stagnant Propylene. A defective mass balance in previous pulse studies⁽³¹⁾ revealed the strong adsorption of organic species during break-in. Attempts made to "freeze" the fully activated catalyst for possible studies of the surface changes during break-in were not successful.

It was hoped that the surface of a fully activated catalyst might remain undisturbed upon cooling and reheating in stagnant propylene instead of flowing propylene. If successful this could serve as a technique to remove the catalyst from the reactor during break-in for surface inspections by the instruments such as X-ray diffraction, ESCA, and the scanning electron microscope.

In this experiment, the catalyst was fully activated and the reactor temperature was reduced to room temperature in less than one hour with the propylene flow stopped. After eight hours the reactor was reheated to the previous reaction temperature in thirty minutes and the propylene flow was reintroduced. If the "freezing" procedure had been successful, there should have not been any break-in or reduction of catalyst activity upon reintroduction of propylene at normal reaction temperatures. But as can be seen in Figure 16, the initial conversion was increased slightly after cooling and reheating. Also the induction time was reduced from ten hours to sixty minutes but still not eliminated.

It is therefore evident that the reduction in reaction temperature results in large reductions in activity, and this freezing technique does not allow surface inspection of a fully active surface.

Effects of Alternating Dosing of Hydrogen and Air on Catalyst Activity. A reducing gas, hydrogen, and an oxidizing gas, dry air, are reported to be temporary catalyst poisons. Figures 12 and 13 show the results of hydrogen dosing and oxygen dosing, respectively. A break-in period of 18 minutes was needed following hydrogen dosing while 80 minutes was necessary for oxygen dosing. Heckelsberg⁽²²⁾ treated activated catalysts with reducing gases, such as hydrogen and carbon monoxide, at relatively high temperature (600°C) and increased the activity of these catalysts.

It was hoped that the activity of a fully broken-in catalyst, whose activity was decreased by the dosing of a reducing gas, could be restored to full activity by the dosing of an oxidizing gas or vice versa. Both the dosing of hydrogen followed by oxygen and the dosing of oxygen followed by hydrogen were tried, but as can be seen in Figures 14 and 15, the break-in periods were not eliminated. A break-in period of sixty minutes is needed in each case to restore full activity.

Thus it is evident from the results that to maintain the fully activated catalyst in its essential condition, it is not sufficient just to dose the reactor with an oxidizing gas after the catalyst is poisoned by a reducing gas, and vice versa. Procedures to recover catalyst activity after being poisoned by reducing gas or oxidizing gas are still open to question.

Luckner and Wills⁽³²⁾ studied the catalyst break-in phenomena. Their data were correlated with both temperature and pressure and a first-order propylene partial pressure dependency was found.

$$\frac{r_{ss} - r(t)}{r_{ss} - r(0)} = e^{-kt}$$

$$\text{and } k = 1.993 \times 10^{12} e^{-47.2/RT} P_{C_3H_6}$$

A check of this correlation was made with the break-in data obtained from the studies of the tungsten oxide on silica catalyst. The break-in rate constant together with the induction time in each case is listed in Table VI.

Recommendations

The following are recommendations for further studies that are suggested by the results of this investigation.

Quantitative Studies of the Break-in of the Cobalt Oxide-Molybdena-Alumina Catalyst. A short break-in period was observed for this catalyst (CoO-MoO₃-Al₂O₃). A quantitative study is proposed to correlate the break-in data with temperature and pressure.

Preparation of Sodium-dosed Catalyst. To prepare a sodium-dosed tungsten oxide-on-silica catalyst for possible study of the reverse reaction, it is proposed here that a weaker base such as sodium bicarbonate be used to incorporate sodium ions into the catalyst. A high temperature (about 400°C) is also recommended for drying the wet catalyst in order to get rid of all traces of water.

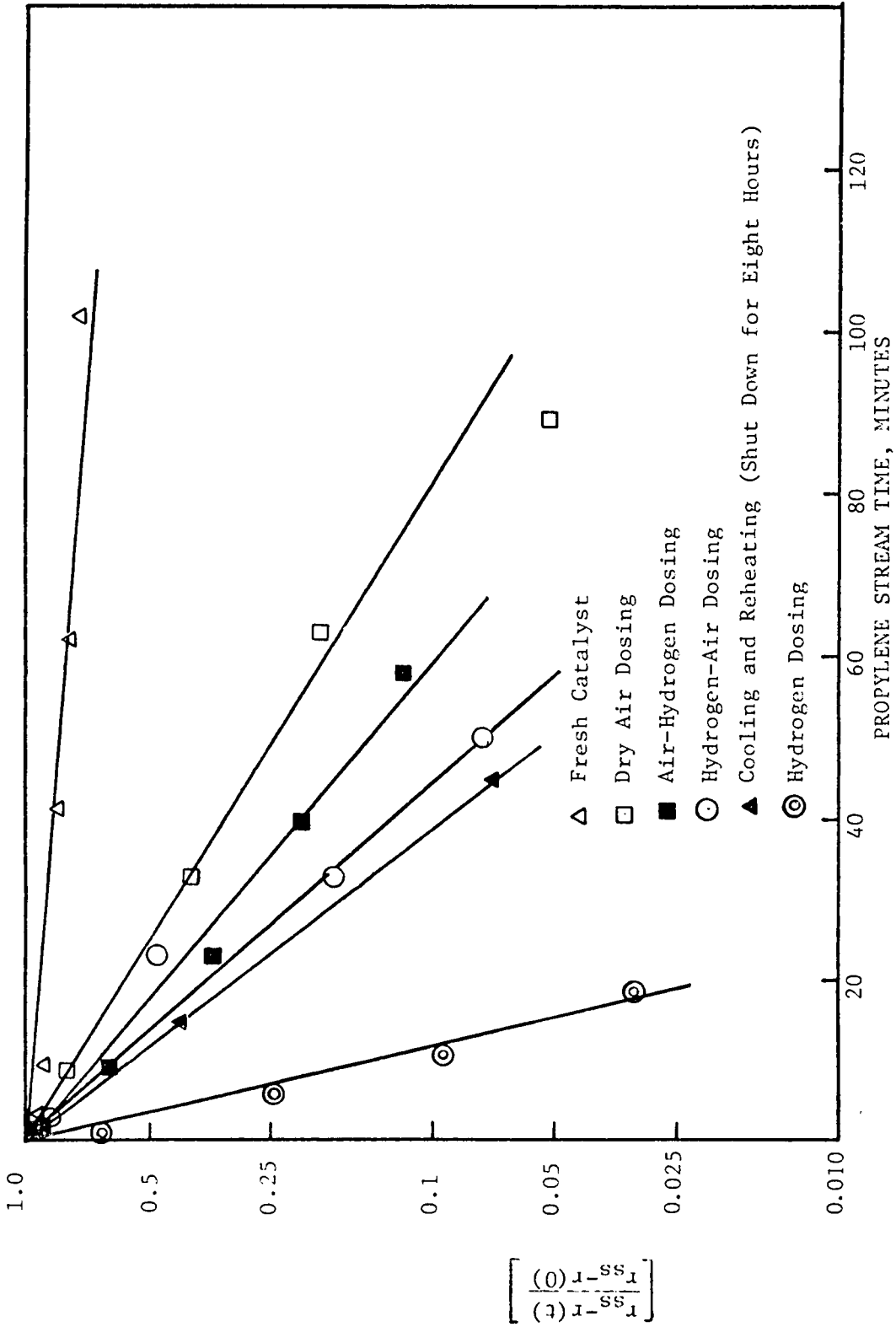


Figure 21. Rate of Fractional Approach to Steady-State for Fresh $\text{WO}_3\text{-SiO}_2$ Catalyst and the Steady-State $\text{WO}_3\text{-SiO}_2$ Catalyst with Different Treatments at 430°C , 0.94 atm.

Table VI

BREAK-IN PERIOD AND RATE CONSTANTS

T = 430°C

P = 0.94 atm

WHSV = 40.28

Catalyst Wt. = 0.3 grams

<u>TREATMENT</u>	<u>BREAK-IN PERIOD (min.)</u>	<u>RATE CONSTANT (min⁻¹)</u>
Predicted by Luckner's rate expression		0.0039
Freshly activated	600	0.0034
Cooling and reheating (Shut down for 8 hours)	45	0.0584
Dosing, hydrogen	18	0.189
Dosing, dry air	80	0.0268
Dosing, hydrogen after air	60	0.0391
Dosing, air after hydrogen	60	0.0506

Limitations

This investigation was conducted under the following limitations:

1. A single commercial cobalt oxide-molybdena-alumina catalyst and a single commercial tungsten oxide-on-silica catalyst were used in the first part and the second part of this study, respectively.
2. Temperatures ranging from 120°C to 165°C were used for the studies of the cobalt oxide-molybdena-alumina catalyst, while 430°C was used for the studies concerning the tungsten oxide-on-silica catalyst.
3. Atmospheric pressure was used for all reactions.
4. A standard activation procedure was employed. Both catalysts were activated at 600°C in anhydrous air for five hours and this was followed by an hour of nitrogen flow. This single activation procedure was used to minimize initial activity variations.
5. All of the calculations were based on near-differential conversions in the near-absence of reaction products.
6. Only laboratory prepared mixtures were used to study the effects of product gases on the activity of the tungsten oxide-on-silica catalyst.
7. Only the disproportionation of propylene was studied.

V. CONCLUSIONS

As a result of this study of the break-in behaviors of the cobalt oxide-molybdena-alumina catalyst and the tungsten oxide-on-silica catalyst during propylene disproportionation, the following conclusions were made:

1. Two induction periods were involved in the break-in period of the cobalt oxide-molybdena-alumina catalyst. The first short induction period was thought to be caused by mass transport delays.
2. The second, longer break-in period of the cobalt oxide-molybdena-alumina catalyst involves a first order process which has a rate constant of $8.0 \times 10^{-5} \text{sec}^{-1}$. This first order process is reversible in an inert atmosphere.
3. The products at low concentration levels (less than ten percent) in the feed have little suppressing effect on the activity of the tungsten oxide-on-silica catalyst during propylene disproportionation.
4. Adding sodium hydroxide aqueous solution to the catalyst and drying at 120°C for twelve hours greatly reduces the steady-state activity of the catalyst.
5. Cooling and reheating the catalyst in the presence of stagnant propylene does not eliminate the break-in period of the tungsten oxide-on-silica catalyst upon the re-introduction of the propylene flow, but this break-in period

is much shorter than that observed in the presence of flowing propylene.

6. Among the gas-dosing experiments, hydrogen dosing has the shortest break-in period. The relatively long break-in period of air-dosing was reduced by the dosing of hydrogen but was not eliminated.
7. All of the break-in data obtained from the experiments concerning tungsten oxide-on-silica catalyst fit Luckner's⁽³¹⁾ break-in rate expression.

VI. SUMMARY

This investigation consisted of a preliminary study of the period of transient activity of a cobalt oxide-molybdena-alumina catalyst (216 square meter per gram B.E.T. surface area) and a continued study of the break-in behavior of a tungsten oxide-on-silica catalyst (223 square meter per gram B.E.T. surface area) during propylene disproportionation. The former contains 3.5 percent cobalt oxide and 10 percent molybdena while the latter contains 10 percent tungsten oxide. In the study concerning the cobalt oxide-molybdena-alumina catalyst, break-in periods at temperatures varying from 120°C to 165°C were found to involve two first order processes. The propylene conversion increased very quickly during the first one hundred seconds of propylene contacting and then increased gradually over the next thirty minutes. After a step input of an inert gas was introduced to the full activated catalyst, traces of reactants and products were still found after the propylene had been stopped for one hundred seconds. The time needed for propylene to diffuse into or out of the pores of the catalyst was calculated to be less than one second by a nonsteady-state theoretical approach. However, the first induction period is believed to be caused by mass transport delays. Effects of purging the fully activated catalyst with nitrogen were studied and it was found that a fifteen minute purge with nitrogen reduced the activity of the catalyst to a point another break-in period was needed to restore full activity. This indicates that a reversible process was involved during the

break-in period. This process is thought to be the adsorption of an organic species to the catalyst.

The influence of the products from propylene disproportionation on the activity of the tungsten oxide-on-silica catalyst was studied by using a split-bed reactor and mixtures of products and reactants. In the experiments with the split-bed reactor, some suppressing effects of the products from first catalyst bed were observed on the activity of the second catalyst bed. This was further confirmed by using mixtures with different product concentrations as reactants in a single bed reactor. The total concentration of the products in the mixtures was 0.573 percent and 3.604 percent, respectively. These mixtures also showed some suppressing effects on the steady-state activity of the catalyst.

In order to prevent the isomerization of 2-butene to 1-butene for possible studies of the reverse reaction of the propylene disproportionation, we dosed the tungsten oxide-on-silica catalyst with sodium ions. We found that the steady-state activity of this catalyst, which was pretreated with 0.02N sodium hydroxide aqueous solution and dried at 120°C for twelve hours, dropped to less than one percent propylene conversion. Although hydrochloric aqueous solution was used to neutralized catalyst, the propylene conversion never increased to more than 1.2 percent.

The fully activated catalyst was cooled from 430°C to room temperature in the presence of stagnant propylene. We hoped that if this effort to "freeze" the catalyst was successful, it would allow us to inspect the surface changes occurring during break-in using instruments

such as X-ray diffraction, ESCA, and the scanning electron microscope. After an eight hour shut-down, the activity of the catalyst dropped to a point at which another break-in period was necessary to restore full activity, but it was much shorter than that observed in the presence of flowing propylene. This indicated that maintaining the reaction temperature is essential to maintain the catalyst in its fully activated state.

A reducing gas, hydrogen, and a oxidizing gas, dry air, were dosed into the propylene flow both individually and alternately after the tungsten oxide-on-silica catalyst was fully activated. In each case, a break-in period was observed after the dosing, with hydrogen dosing alone having the fastest break-in. All of the break-in rates followed the equation reported by Luckner⁽³¹⁾ with different rate constants.

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APPENDIX A

Sample Calculations

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

Calculation of Reactant Feed Rates. Reactant feed rates were calculated from experimentally measured product flow rates and were expressed in terms of a unit gram of catalyst charge. Under the name of "weight hour space velocity" (WHSV), the calculation was carried out according to the relationship

$$\text{WHSV} = \frac{PV}{ZRT} \times \frac{C}{W} \times M = \frac{\text{grams reactant}}{\text{gm catalyst-hour}} \quad (8)$$

where:

P = pressure at which the flow rate was measured, atm.

V = volumetric flow rate of product gas, cm³/hr, measured
by bubble flow meter

M = molecular weight of product gas

Z = compressibility factor of product gas = 0.99

R = 82.06 $\frac{\text{cc-atm}}{\text{gm-mole-}^\circ\text{K}}$

T = temperature at which flow rate was experimentally
measured, ^oK

C = correction for water saturation of gas prior to measurement = 0.966

W = weight of catalyst charge, grams

Calculation of Product Composition from Chromatographic Analysis

Data. The peak height and the peak width at half the peak height were

obtained for each component from the recorded chromatographic analysis of a sample. These data, plus the range and attenuation used to record each peak, together with the detector calibration factors reported by Luckner⁽³¹⁾ were used to calculate the mole fraction of the four components: ethylene, propane, propylene, and 2-butene according to the relationship

$$M_i = \frac{A_i f_i}{\sum_{i=1}^4 A_i f_i} \quad (9)$$

in which M_i = mole fraction of component "i" in the sample

f_i = detector calibration factor of component "i"

A_i = area of detector response to component "i"

and

$$A_i = h_i w_i a_i r_i \quad (10)$$

where h_i = height of the peak recorded for component "i"

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

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

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

Calculation of Conversion. The percentage conversion X_A of a given reactant A is calculated according to the following equation:

$$X_A = \frac{N_{A0} - N_A}{N_{A0}} \times 100 \quad (11)$$

where

X_A = percentage conversion of propylene

N_{A0} = initial moles of propylene

N_A = final moles of propylene

N_{A0} was calculated by adding the product of peak area and ionization factor of each gas (ethylene, propane, propylene and 2-butene). N_A was calculated by adding the product of peak area and ionization factor of ethylene and 2-butene.

Prediction of Propylene Conversion from Two Beds in a Split-Bed Reactor. Propylene reaction rates in first bed was calculated in each run according to the relationship

$$r = \frac{\text{WHSV}}{42.08 \frac{\text{gm C}_3\text{H}_6}{\text{gm-mole C}_3\text{H}_6}} \times = \frac{\text{gm-moles}}{\text{gm catalyst-hr}} \quad (12)$$

where

WHSV = weight hourly space velocity of C_3H_6 , gm/gm cat-hr.

X = observed fractional conversion of C_3H_6

From run 1, Table III, we obtain

$$\text{WHSV} = 40.28 \text{ (1 bed)}$$

$$T = 703^\circ\text{K}$$

$$X = 6.917\%$$

$$P = 0.94 \text{ atm}$$

$$r_{ca} = \frac{40.28}{42.08} \times 6.917\% = 0.0662 \frac{\text{gm-moles}}{\text{gm cat.-hr.}}$$

For the catalytic disproportionation of propylene in a system where the reaction rate is controlled by a dual site surface reaction, and for conversion less than ten percent, the rate equation is given in Table I.

$$r_p = \frac{K P_p^2}{(1 + K P_p)^2} \quad (13)$$

where

r_p = predicted rate of reaction, $\frac{\text{gm-mole}}{\text{gm cat-hr}}$

K = rate constant, $\frac{\text{gm-moles}}{\text{gm cat-hr-atm}^2}$

K_p = propylene adsorption coefficient, atm^{-1}

P_p = partial pressure of propylene, atm

$$P_p = (1 - X_p)P = (1 - 0.0692) \times 0.94 = 0.875 \text{ atm}$$

$$K = 8.196 \times 10^7 e^{-24730/RT} \quad (14)$$

$$K_p = 11.50 e^{-4550/RT} \quad (15)$$

$$R = 1.987 \quad T = {}^\circ\text{K}$$

Using these two relationships for K and K_p we obtain

$$K = 1.678$$

$$K_p = 0.443$$

$$r_p = \frac{(0.875)^2 (1.678)}{(1 + 0.443 \times 0.875)^2}$$

$$r_p = 0.667 \frac{\text{gm-moles}}{\text{gm cat-hr}}$$

The observed propylene conversion is lower than predicted because of its unknown history.

Define

$$C_f = \text{correction factor} = \frac{\text{observed reaction rate}}{\text{predicted reaction rate}}$$

$$C_f = \frac{0.0662}{0.667} = 0.0992$$

The difference of propylene conversion between first bed and second bed can be calculated by the relationship

$$r_1 - r_2 = \frac{WHSV}{42.08} (X_1 - X_2) \quad (16)$$

where

r_1 = reaction rate in bed 1

r_2 = reaction rate in bed 2

X_1 = propylene conversion in bed 1

X_2 = propylene conversion in bed 2

Equation (16) can be re-written as

$$\Delta X = \frac{r_1 - r_2}{[WHSV/42.08]} \quad (17)$$

P_1 = propylene partial pressure in bed 1 = 0.94 atm

P_2 = propylene partial pressure in bed 2 = 0.875 atm

Using equations (13), (14), (15), and the correction factor

$$\begin{aligned} r_1 &= \frac{(0.94)^2(1.678)}{(1+0.443 \times 0.94)^2} \times 0.0992 \\ &= 0.0733 \end{aligned}$$

$$\begin{aligned} r_2 &= \frac{(0.875)^2(1.678)}{(1+0.443 \times 0.875)^2} \times 0.0992 \\ &= 0.0662 \end{aligned}$$

Using equation (17) we get

$$\Delta X = \frac{0.0733 - 0.0662}{(40.28/42.08)}$$

$$\Delta X = 0.0041 = 0.41\%$$

Propylene conversion from two beds

$$= 6.917\% \times 2 - 0.41\%$$

$$= 13.424\%$$

The propylene conversions from two beds are predicted for run 2 and run 3 in the same way.

Calculation of Pore Diffusion Time. Since Lennard-Jones parameters are not available for C_3H_6 , the diffusivity of propylene in nitrogen was calculated by the equation given by (7):

$$\frac{D_{PN}}{(P_{cp} P_{cN})^{1/3} (T_{cp} T_{cN})^{5/12} \left(\frac{1}{M_p} + \frac{1}{M_N}\right)^{1/2}} = a \left(\frac{T}{\sqrt{T_{cp} T_{cN}}}\right)^b \quad (18)$$

where

P_{cp} = critical pressure of propylene = 45.5 atm

P_{cN} = critical pressure of nitrogen = 33.5 atm

T_{cp} = critical temperature of propylene = 365.0°K

T_{cN} = critical temperature of nitrogen = 126.2°K

M_p = molecular weight of propylene = 42.08 $\frac{\text{gms}}{\text{gm-mole}}$

M_N = molecular weight of nitrogen = 28.02 $\frac{\text{gms}}{\text{gm-mole}}$

T = temperature of reactor = 393.0°K

P = total pressure in the reactor = 0.94 atm

For non-polar gas-pairs

$$a = 2.745 \times 10^{-4}$$

$$b = 1.823$$

We get

$$D_{pN} = 0.2165 \text{ cm}^2/\text{sec}$$

The effective diffusivity was calculated by the equation given by⁽⁴⁴⁾

$$D_e = \bar{D}_M \epsilon_M^2 = \frac{\epsilon_\mu^{2(1+\epsilon_M)}}{1 - \epsilon_M} \bar{D}_\mu \quad (19)$$

where

ϵ_M = void fraction of macropores (800 Å)

ϵ_μ = void fraction of micropores (140 Å)

$$\text{and } \bar{D}_M = \left(\frac{1}{D_{PN}} + \frac{1}{(\bar{D}_K)_M} \right)^{-1} \quad (20)$$

$$\bar{D}_\mu = \left(\frac{1}{D_{PN}} + \frac{1}{(\bar{D}_K)_\mu} \right)^{-1} \quad (21)$$

$(\bar{D}_K)_M$, $(\bar{D}_K)_\mu$ could be obtained by the equation given in the same book⁽⁴⁴⁾

$$(\bar{D}_K)_A = 9.70 \times 10^3 a \left(\frac{T}{M_A} \right)^{1/2} \quad (22)$$

where

a = radius of micropore or macropore

T = temperature of reactor = 393°K

M_A = molecular weight of propylene = 42.08 $\frac{\text{gms}}{\text{gm-mole}}$

From (22) we get

$$(\bar{D}_K)_M = 0.0415 \text{ cm}^2/\text{sec}$$

$$(\bar{D}_K)_\mu = 0.237 \text{ cm}^2/\text{sec}$$

From equations (20) and (21), we get

$$\bar{D}_M = 0.1130 \text{ cm}^2/\text{sec}$$

$$\bar{D}_\mu = 0.237 \text{ cm}^2/\text{sec}$$

Substituting the values of \bar{D}_M and \bar{D}_μ into equation (19), we get the effective diffusivity as

$$D_e = 7.31 \times 10^{-3} \text{ cm}^2/\text{sec}$$

The concentration of propylene in bulk fluid could be calculated from the equation

$$C_{ps} = \frac{P}{zRT} = \text{gm-moles/cm}^2 \quad (23)$$

where

$$z = \text{compressibility factor} = 0.99$$

therefore

$$C_{ps} = \frac{0.94}{82.05 \times 393 \times 0.99} = 2.93 \times 10^{-5} \frac{\text{gm-moles}}{\text{cm}^3}$$

The size of the cobalt oxide-molybdena-alumina catalyst was 0.071 cm (-20/+30 mesh). The catalyst particle was assumed to be a sphere having an effective radius of 0.071 cm. The effective radius of the particle was used to calculate the diffusion time.

The pore diffusion time was calculated as that needed for the center of particle to have a propylene concentration equal to 80 percent of the bulk propylene concentration.

The variables were put in dimensionless form:

$$\tau = \frac{D_e t}{R^2} \quad (24)$$

$$n = \frac{r}{R} = 0 \quad (25)$$

$$Y = \frac{C_{ps} - C_p(t)}{C_{ps} - C_{po}} = 0.2 \quad (26)$$

where

t = time, sec

R = radius of the sphere

r = distance from the center of the sphere, cm

C_{ps} = bulk concentration of propylene gm-moles/cm³

$C_p(t)$ = concentration of propylene in pores at time t

C_{po} = initial concentration of propylene in pores

Figure 9, Appendix F in⁽⁴⁶⁾ was used to find τ .

For $n = 0$, $m = 0$ (no convective resistance)

$$\tau = \frac{D_e t}{R_2} = 0.22$$

$$t = \frac{0.22 \times (0.071)^2}{7.31 \times 10^{-3}} = 0.15 \text{ sec.}$$

APPENDIX B

MATERIALS AND APPARATUS

Materials

This section contains a list of materials used, their source and specifications:

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

Butene-2. No-2 cylinder of C.P. grade cis- and trans-2-butene, minimum 99.0 percent purity. Obtained from Matheson Company, East Rutherford, New Jersey. Used as a reactant to the reactor in the study of the effects of products in the feed stream on propylene disproportionation.

Catalysts. 1/8-Inch tablets of cobalt oxide-molybdena-alumina catalyst with the following specifications:

Cobalt oxide	3.5%
Molybdena	10.0%
Surface area	216 m ² /gm
Void fraction of 140 Å pores	0.18
Void fraction of 800 Å pores	0.21

This catalyst was furnished by Girdler Catalysts Department, Chemetron Chemicals, Louisville, Kentucky, and was used in the studies of its break-in during propylene disproportionation. 3/16-Inch

extrudates of tungsten oxide on silica with the following specifications:

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

This catalyst was furnished by Davidson Chemical Division of W. R. Grace and Company, Baltimore, Maryland and was designated SMR-7-3322. Used in the studies of its break-in during propylene disproportionation.

Chromatographic Column Packing. 20 Percent dimethyl sulfolane on chromasorb W, 30-60 mesh obtained from Avondale Division, Hewlett-Packard. Used as a chromatographic column packing to separate product gases for analysis.

Ethylene. 1.604 ft³ cylinder of pure grade ethylene minimum purity 99.0 percent. Obtained from Phillips Petroleum Company, Bartlesville, Oklahoma. Used as a reactant in studying the effects of products in feed stream on propylene disproportionation.

Helium. Size 1-A cylinder 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 and as a dosing agent in the studies of the effect of oxidant and reductant on activity of catalyst.

Molecular sieves. 1/16-Inch pellets, lot 5277, type 5A. Obtained from Linde Air Products Company. 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, as a carrier gas in disproving the break-in behavior of cobalt oxide-molybdena-alumina catalyst during propylene disproportionation, and to provide back pressure to the reactor.

Propylene. 2.14 and 3.74 ft³ cylinders of polymerization grade propylene, minimum purity 99.0 percent. Obtained from Phillips Petroleum Company, Bartlesville, Oklahoma. Used as a feed to the reactor and to check the calibration of the chromatograph.

Apparatus

This section is descriptive of all the apparatus used during this investigation.

Balance. Mettler, type H15, No. 263600, 160 grams capacity. Obtained from the Mettler Instrument Corporation, Hightstown, New Jersey. Used to weigh catalyst samples and quartz.

Chromatograph. F and M, Model 810-29 analytical gas chromatograph equipped with a 30 foot dimethylsulfolane on chromosorb-W column, manufactured by F and M Scientific Corporation, Avondale, Pennsylvania. Used to analyze the reactor effluent gases.

Desiccator. A desiccator with coors plate, 25.0 cm inside diameter, catalog No. 8-615. Obtained from Scientific Inc., Raleigh, North Carolina. Used to store catalyst samples.

Digital Thermocouple Indicator. Model 2809-C digital readout meter, serial No. 00914, five different calibrations of thermocouples. R, K, J, T and E conforming to ANSl standards. J type thermocouple (iron-constantan) was used. Range 0 to 800°C, AC 115V, 50-60Hz, cali-

brated for iron-constantan, maximum deviation of 2°C. Obtained from Omega Engineering, Inc. Stanford, Connecticut. Used to measure the temperature of the reactor.

Dryer. Three dryers, constructed from one inch carbon steel pipe, fourteen inches long. They were packed with 5A type molecular sieves. Both ends were fitted to the pipe caps, which had 1/8 inch "Swagelok" male connector installed in the ends. Used to remove the water content of the feed gases and purging gases.

Electric Furnaces. A 6-inch tubular furnace, type 123-1 115V, 422W, serial No. 67875, maximum temperature 1850°F, safe working temperature 1850°F. Manufactured by Heavy Duty Electric Company, Milwaukee, Wisconsin. Used to supply heat to the reactor. Another twelve inches tubular furnace, type 123-3, 115V, 720W, serial No. 67877, maximum temperature 1850°F, safe working temperature 1850°F. Manufactured by Heavy Duty Electric Company. Used to activate the dryer tube.

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

Moore Flow Controller. Constant differential type flow controller, type 63 BU.L. Obtained from Moore Products Company, Philadelphia, Pennsylvania. Used to control feed flow rate to the reactor.

Mortar and Pestle. Coors porcelain, fitted, size No. 2, 90 mm o.d., catalog No. 12-961. Obtained from Fisher Scientific Company, Raleigh, North Carolina. Used to crush catalyst pellets and quartz.

Motor. A-C motor, manufactured by General Electric Company, 1/3 horsepower, 115V/230V, Model No. 5KC47AB8996, 1725 r.p.m., 60 cy.

4.8/4.2 amp. Used to drive vacuum pump.

Oven. Stabil-therm gravity oven, Model No. OV-18A, serial No. RPA 6173, 120V, 1PH, 60 cy. A.C., 1.91 KW, temperature range 38-280°C. Obtained from Blue M Electric Company, Blue Island, Illinois. Used to dry catalysts.

Powerstat. Two variable transformers, type No. 116 primary voltage 120V, 50.60 cy. A.C. output voltage 0 to 140, maximum 7.5 amp. Manufactured by the Superior Electric Company, Bristol, Connecticut. Obtained from Fisher Scientific Company, Inc., Pittsburgh, Pennsylvania. Used to regulate current to electric furnace surrounding the reactor.

Pressure Gauge. 400 psig range, five psi subdivision. Obtained from Champion Gauge Company, New York. Used to measure the reactor back pressure.

Pressure Regulator. Obtained from Grove Valve and Regulator Company, subsidiary of Walworth Company, Oakland, California, control range 25 to 400 psi, maximum temperature 200°F, model No. 706077-3. Used to regulate the reactor pressure.

Vacuum Pump. Patent No. 2337849, serial No. 16593-0. Manufactured by W. M. Welch Manufacturing Company, Chicago, Illinois. Used to evacuate the sampling loop.

Pyrometer. Sim-ply-trol automatic temperature controller 0 to 1000°F range, catalog No. 1635, model No. 100. Manufactured by Assembly Products, Inc., Chesterland, Ohio. Used to control mid-bed temperature.

Reactors, Two. A six-inch tubular, fixed bed catalytic reactor and a split-bed reactor of the same kind were used during this

investigation. A detailed description of these two reactors is given in the experimental equipment section of this thesis.

Rotameters, Two. Dual float rotameters, tube Nos. 601 and 603, 0.09 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 sieves 20, 30, 40, brass frame, inside diameter eight inches, sides two inches high, catalog No. 4-881. Obtained from Fisher Scientific Company, Inc., Pittsburgh, Pennsylvania. Used to screen catalyst and quartz.

Soap Bubble Flow Meter, Two. Two schellbach burets, 50 ml capacity, catalog No. 3-70. Obtained from Fisher Scientific Company, Inc., Raleigh, North Carolina. They were modified into two bubble flow burets 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 and purging gas streams.

Stop Watch. Electric direct reading stop watch, 1/10 second divisions, reading up to 10,000 second, 115V, 60 cy. A.C., catalog No. 69230, second model. Obtained from Fisher Scientific Company, Inc., Raleigh, North Carolina. Used to time flows measured with the bubble flow meter.

Thermocouple. Quick disconnect thermocouple assemblies iron-constantan thermocouple, catalog No. 1C55-18U, 12 inches. Obtained from Omega Engineering, Inc., Stamford, Connecticut. Used as a sensor to the thermo-regulator.

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

APPENDIX C

Table VII

BREAK-IN BEHAVIOR OF THE $\text{CoO-MoO}_3\text{-Al}_2\text{O}_3$ CATALYST

T=120°C

P=0.94 atm

WHSV=46.87

Catalyst Wt. = .5 grams

<u>TIME</u> Sec.	<u>PERCENTAGE OF COMPONENTS</u>				<u>PERCENT</u>
	<u>Ethylene</u>	<u>Propane</u>	<u>Propylene</u>	<u>2-Butene</u>	<u>Conversion</u>
10	.514	.638	98.554	.294	.808
30	.740	.662	98.000	.609	1.350
40	.744	.616	98.013	.628	1.371
50	.736	.648	97.962	.654	1.390
60	.763	.654	97.925	.657	1.421
70	.787	.675	97.779	.760	1.547
100	.765	.624	97.920	.690	1.456
110	.745	.638	97.844	.772	1.518
130	.772	.640	97.960	.628	1.400
140	.809	.643	97.721	.827	1.636
160	.700	.620	97.942	.738	1.438
180	.810	.655	97.873	.662	1.472
200	.796	.674	97.672	.858	1.654
210	.772	.624	97.915	.688	1.461
220	.980	.622	97.454	.945	1.925
230	.823	.627	97.790	.761	1.583

Table VIII

BREAK-IN BEHAVIOR OF $\text{CoO-MoO}_3\text{-Al}_2\text{O}_3$ CATALYST

T=160°C

P=0.94 atm

WHSV=46.87

Catalyst Wt.=.5 grams

<u>TIME</u>	<u>PERCENTAGE OF COMPONENTS</u>				<u>PERCENT</u>
	<u>Ethylene</u>	<u>Propane</u>	<u>Propylene</u>	<u>2-Butene</u>	<u>Conversion</u>
10	2.946	.939	94.207	1.908	4.854
20	2.973	.873	93.486	2.668	5.640
30	3.125	1.062	92.587	3.226	6.351
40	3.293	.872	93.221	2.614	5.907
50	3.365	.731	93.001	2.904	6.269
60	3.164	.909	93.380	2.548	5.711
70	2.903	.635	93.821	2.640	5.544
80	3.670	.729	92.425	3.176	6.847
90	3.557	.640	92.975	2.828	6.385
100	3.431	.664	93.152	2.753	6.184
110	3.247	.601	93.608	2.544	5.790
120	3.575	.673	91.914	3.838	7.413

Table IX

RESPONSE OF CATALYTIC ACTIVITY OF $\text{CoO-MoO}_3\text{-Al}_2\text{O}_3$ CATALYST TO
A STEP INPUT OF AN INERT

T=165°C

P=0.94 atm

WHSV=46.87

Catalyst Wt.=.5 grams

<u>TIME</u> Sec.	<u>PERCENT</u> Conversion	<u>TOTAL PEAK AREA</u> $\sum_{i=1}^4 A_i f_i$	<u>RELATIVE PERCENT</u> Concentration
10	13.488	42.854	16.350
20	14.540	28.491	10.870
30	12.591	20.815	7.942
40	12.456	20.367	7.771
50		12.957	4.944
70	11.190	23.321	8.898
80	13.001	21.673	8.268
120	11.203	11.204	4.274

*Use the average total peak area of the previous samples taken at steady state of catalytic activity

$$\left(\sum_{i=1}^4 A_i f_i \right)_{\text{ave}} = 262.113.$$

Table X

EFFECT OF PURGING WITH AN INERT ON BREAK-IN OF THE

CoO-MoO₃-Al₂O₃ CATALYST

T=165°C

P=.94 atm

WHSV=46.87

Catalyst Wt.=.5 grams

TIME Sec.	PERCENTAGE OF COMPONENTS				PERCENT
	Ethylene	Propane	Propylene	2-Butene	Conversion
10	2.01	.73	96.02	1.24	3.26
20	1.78	.71	96.24	3.05	3.05
30	1.66	.62	96.53	1.20	2.86
40	1.81	.69	96.08	1.41	3.22
50	1.74	.67	96.38	1.21	2.95
60	1.79	.66	96.29	1.26	3.05
70	1.87	.67	96.12	1.34	3.21
80	2.14	.77	95.06	2.03	4.17
90	1.79	.66	96.00	1.56	3.35
120	2.50	.62	94.83	2.05	4.54
460	1.82	.62	95.34	2.21	4.03
730	2.24	.65	94.52	2.58	4.82
1150	2.27	.60	94.37	2.76	5.03
1580	2.42	.63	94.18	2.78	5.20
AFTER FIFTEEN MINUTES NITROGEN PURGE.					
10	2.65	.78	94.58	1.98	4.64
20	2.55	.74	95.02	1.70	4.24
30	2.69	.80	94.55	1.96	4.65
40	2.61	.74	94.62	2.03	4.64
50	2.34	.76	94.90	2.00	4.34
60	2.34	.75	94.72	2.19	4.53
70	2.49	.68	94.56	2.27	4.76
90	2.78	.74	94.21	2.27	5.05
110	2.48	.70	94.34	2.48	4.96
120	2.33	.73	94.62	2.32	4.65
200	2.16	.63	94.73	2.48	4.64
620	2.19	.64	94.61	2.56	4.75
1020	2.23	.64	94.55	2.58	4.81

Table XI

EFFECT OF A MIXTURE CONTAINING 3.60 PERCENT ETHYLENE AND
2-BUTENE ON THE BREAK-IN OF THE WO_3-SiO_2 CATALYST (FIRST RUN)

T = 430°C

P = 0.94 atm

WHSV = 20.14

Catalyst Wt. = 0.6 grams

<u>TIME</u>	<u>PERCENTAGE OF COMPONENTS</u>				<u>PERCENT</u>	
	<u>Min.</u>	<u>Ethylene</u>	<u>Propane</u>	<u>Propylene</u>	<u>2-Butene</u>	<u>Conversion*</u>
Mixture		1.66	0.56	95.83	1.95	
0		6.733	0.734	84.540	7.988	14.722
5		7.148	0.682	84.037	8.134	12.308
11		7.756	0.660	83.219	8.365	13.160
17		0.393	0.651	82.790	8.575	13.609

$$*\text{Percent Conversion} = \frac{(N_p)_o - (N_p)_f}{(N_p)_o} \times 100$$

$(N_p)_o$ = Initial percentage mole fraction of propylene in feed.

$(N_p)_f$ = Final percentage mole fraction of propylene in products.

Table XII

EFFECT OF A MIXTURE CONTAINING 3.60 PERCENT ETHYLENE AND
2-BUTENE ON THE BREAK-IN OF THE WO_3-SiO_2 CATALYST (SECOND RUN)

T=430°C

P=0.94 atm

WHSV=20.14

Catalyst Wt.=0.6 grams

TIME Sec.	PERCENTAGE OF COMPONENTS				PERCENT
	Ethylene	Propane	Propylene	2-Butene	Conversion
Mixture	1.66	0.56	95.83	1.95	
0 (Steady state)	6.804	0.683	84.676	7.837	14.641
5	7.320	0.700	83.928	8.052	12.421
10	7.759	0.636	83.044	8.562	13.344
16	7.440	0.398	83.316	8.318	12.790
31	8.115	0.616	82.868	8.402	13.527
70	8.277	0.689	82.344	8.805	14.074
100	8.021	0.652	82.719	8.608	13.509

$$\text{*Percent Conversion} = \frac{(N_p)_o - (N_p)_f}{(N_p)_o} \times 100$$

$(N_p)_o$ = Initial percentage mole fraction of propylene in feed.

$(N_p)_f$ = Final percentage mole fraction of propylene in products.

Table XIII

BREAK-IN BEHAVIOR OF THE $\text{WO}_3\text{-SiO}_2$ CATALYST

T=430°C

P=0.94 atm

WHSV=40.28

Catalyst Wt.=0.3 grams

<u>TIME</u>	<u>PERCENTAGE OF COMPONENTS</u>				<u>PERCENT</u>
<u>Min.</u>	<u>Ethylene</u>	<u>Propane</u>	<u>Propylene</u>	<u>2-Butene</u>	<u>Conversion</u>
3	0.034	0.651	98.478	0.826	0.861
10	0.148	0.663	98.257	0.921	1.069
41	0.443	0.639	98.215	1.126	1.570
62	0.682	0.666	97.247	1.405	2.086
102	0.893	0.632	96.933	1.541	2.434
159	1.499	0.663	95.698	2.126	3.625
223	1.841	0.617	95.109	2.523	4.364
287	2.218	0.612	94.033	3.121	5.339
407	3.276	0.676	91.674	4.359	7.629
457	3.873	0.687	90.548	4.870	8.744
525	4.074	0.655	86.197	5.001	9.075
579	4.052	0.652	89.978	5.293	9.348
1071	4.602	0.514	89.903	4.958	9.560

Table XIV

BREAK-IN BEHAVIOR OF SODIUM-DOSED $\text{WO}_3\text{-SiO}_2$ CATALYST

T=430°C

P=.94 atm

WHSV=40.28

Catalyst Wt.=0.3 grams

<u>TIME</u>	<u>PERCENTAGE OF COMPONENTS</u>				<u>PERCENT</u>
<u>Min.</u>	<u>Ethylene</u>	<u>Propane</u>	<u>Propylene</u>	<u>2-Butene</u>	<u>Conversion</u>
144	0.272	0.688	98.701	0.338	0.6104
304	0.431	0.667	98.425	0.477	0.9083
408	0.507	0.665	98.163	0.665	1.1716
571	0.540	0.670	98.160	0.630	1.1702
1356	0.514	0.572	98.248	0.667	1.1806

Table XV

EFFECT OF HYDROGEN-DOSING ON THE BREAK-IN OF THE $\text{WO}_3\text{-SiO}_2$ CATALYST

T=430°C

P=0.94 atm

WHSV=40.28

Catalyst Wt.=0.3 grams

<u>TIME</u> Min.	<u>PERCENTAGE OF COMPONENTS</u>				<u>PERCENT</u>
	<u>Ethylene</u>	<u>Propane</u>	<u>Propylene</u>	<u>2-Butene</u>	<u>Conversion</u>
0	3.061	0.641	92.496	3.801	6.862
1	0.984	0.656	97.200	1.160	2.144
6	2.154	0.616	94.691	2.539	4.693
11	2.580	0.660	93.718	2.509	5.622
19	2.756	0.602	93.394	3.249	6.004
34	2.895	0.580	93.112	3.413	6.308
51	2.781	0.663	93.278	3.278	6.059
61	2.841	0.613	93.197	3.349	6.189

Table XVI

EFFECT OF AIR DOSING ON THE BREAK-IN OF THE WO_3-SiO_2 CATALYST

T=430°C

P=0.94 atm

WHSV=40.28

Catalyst Wt.=0.3 grams

<u>TIME</u>	<u>PERCENTAGE OF COMPONENTS</u>				<u>PERCENT</u>
<u>Min.</u>	<u>Ethylene</u>	<u>Propane</u>	<u>Propylene</u>	<u>2-Butene</u>	<u>Conversion</u>
0 (Steady state)	2.504	0.690	93.420	3.385	5.890
9	0.11	0.717	98.015	0.702	1.267
33	1.709	0.713	95.540	2.039	3.747
63	2.288	0.753	94.229	2.730	5.018
89	2.684	0.733	93.381	3.202	5.886
109	2.828	0.727	93.070	3.375	6.203

Table XVII

EFFECT OF HYDROGEN-AIR DOSINGS ON THE
BREAK-IN OF THE $\text{WO}_3\text{-SiO}_2$ CATALYST

T=430°C

P=0.94 atm

WHSV=40.28

Catalyst Wt.=0.3 grams

<u>TIME</u>	<u>PERCENTAGE OF COMPONENTS</u>				<u>PERCENT</u>
<u>Min.</u>	<u>Ethylene</u>	<u>Propane</u>	<u>Propylene</u>	<u>2-Butene</u>	<u>Conversion</u>
0 (Steady state)	2.415	0.612	94.209	2.764	5.179
1	0.052	0.648	99.256	0.045	0.097
23	1.299	0.620	96.950	1.131	2.430
33	1.727	0.654	95.547	2.073	3.800
50	1.933	0.645	95.145	2.319	4.252
72	2.079	0.626	94.972	2.323	4.402
108	2.167	0.602	94.809	2.422	4.589

Table XVIII

EFFECT OF AIR-HYDROGEN DOSINGS ON THE BREAK-IN
OF THE $\text{WO}_3\text{-SiO}_2$ CATALYST

T=430°C

P=0.94 atm

WHSV=40.28

Catalyst Wt.=0.3 grams

<u>TIME</u>	<u>PERCENTAGE OF COMPONENTS</u>				<u>PERCENT</u>
<u>Min.</u>	<u>Ethylene</u>	<u>Propane</u>	<u>Propylene</u>	<u>2-Butene</u>	<u>Conversion</u>
0 (Steady state)	2.999	0.751	92.692	3.558	6.557
1	0.279	0.749	98.709	0.263	0.541
9	1.240	0.719	96.462	1.559	2.799
23	2.211	0.693	94.544	2.553	4.764
40	2.635	0.665	93.657	3.043	5.678
58	2.981	0.665	92.908	3.442	6.423
82	3.313	0.642	91.464	3.824	7.191
108	3.323	0.632	92.210	3.836	7.159

Table XIX

EFFECT OF COOLING AND REHEATING IN THE PRESENCE OF STAGNANT
 PROPYLENE ON THE BREAK-IN OF THE WO_3-SiO_2 CATALYST
 (EIGHT HOURS SHUTDOWN)

T=430°C

P=0.94 atm

WHSV=40.28

Catalyst Wt.=0.3 grams

<u>TIME</u>	<u>PERCENTAGE OF COMPONENTS</u>				<u>PERCENT</u>
<u>Min.</u>	<u>Ethylene</u>	<u>Propane</u>	<u>Propylene</u>	<u>2-Butene</u>	<u>Conversion</u>
0 (Steady state)	2.781	0.663	93.278	3.237	6.059
0.5	1.220	0.759	98.876	0.145	0.365
15	1.424	0.640	96.147	1.788	3.213
45	2.246	0.585	94.349	2.820	5.066
68	2.170	0.609	94.498	2.724	4.893
90	2.419	0.615	93.928	3.038	5.457
119	2.381	0.611	94.019	2.990	5.371

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THE BREAK-IN BEHAVIORS OF THE COBALT OXIDE-MOLYBDENA-
ALUMINA CATALYST AND THE TUNGSTEN OXIDE ON SILICA
CATALYST DURING PROPYLENE DISPROPORTIONATION

by

Solomon Hsing-Kuo Tang

(ABSTRACT)

The break-in behaviors of two similar heterogenously catalyzed systems were studied during propylene disproportionation. A cobalt oxide-molybdena-alumina ($\text{CoO-MoO}_3\text{-Al}_2\text{O}_3$) catalyst was found to undergo a rapid increase in the catalytic activity during the first 100 seconds of contacting with the reactants and this was the order of magnitude of the mass transport delays. A slower first order process was observed with a break-in period of about 30 minutes, and this process is reversed by inert purge.

The effects of the products of propylene disproportionation on the activity of a tungsten oxide on silica ($\text{WO}_3\text{-SiO}_2$) catalyst were studied by using a split-bed reactor and using mixtures containing low concentrations of products in propylene as feed. In both experiments the products were found to have some suppressing effects on the activity of this catalyst. The activity of the $\text{WO}_3\text{-SiO}_2$ catalyst was reduced to one tenth of the original by adding 0.02N NaOH aqueous solution to the catalyst and drying at 120°C for twelve hours. Dosing hydrogen (a reductant) and oxygen (an oxidant) to the fully activated $\text{WO}_3\text{-SiO}_2$ catalyst individually

or alternatively reduced the activity of this catalyst to a point where another break-in period was needed to restore full activity. The break-in period of cooling and reheating the steady-state $W\text{O}_3\text{-SiO}_2$ catalyst in stagnant propylene was much shorter than that observed in propylene flow.