

BREAK-IN BEHAVIOR OF A TUNGSTEN OXIDE ON SILICA
CATALYST DURING PROPYLENE DISPROPORTIONATION

by

Jamshid Fathi-Kalajahi

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APPROVED:

G. B. Wills, Chairman

/ G. H. Beyer

P. R. Rony ✓

D. L. Michelson

T. C. Ward

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Blacksburg, Virginia

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I. Introduction

It has been known for over 150 years that many chemical reactions are affected by materials that are neither reactants nor products. Such materials are called catalysts. The importance of a catalyst in a chemical reaction is that it increases the rate of the desired reaction by a thousandfold or millionfold by making possible an alternative mechanism each step of which has a lower free energy of activation than that for the uncatalyzed process. Recently, with the increasing use of catalyst industrially, a significant amount of research has been directed toward a better understanding of fundamental processes involved in catalytic reactions. Even though the nature of the selectivity of a catalyst for promoting a given reaction is not well understood, understanding of the steady-state kinetics and transport processes have advanced well.

The activity of a freshly prepared catalyst almost invariably changes with time. One could imagine all temporal studies in heterogeneous catalysis to fall into one of three classes:

1. A break-in period during which the activity of the catalyst increases or decreases. The time involved in this regime, depending on the nature of catalytic reaction, could be as long as days or as short as seconds.
2. A steady-state regime during which the catalyst is in a fully activated state. This regime is the basis of almost all studies of catalysts kinetic and transport phenomena behavior.

3. A break-down or deactivation period during which the activity of the catalyst decreases with time.

In spite of the importance of understanding of break-in phenomena in the selection of a catalyst, until recently this regime has been given very little attention and the phenomena involved have been clearly understood. Recent literature contains examples of a number of widely different catalyst systems that exhibit catalyst break-in. Although the initial steps toward understanding of the break-in phenomena have been taken, the question of the exact cause or causes of break-in remains to be answered.

While there exist uncertainties as to the phenomena involved in break-in, the length of the time involved in the transition of a fresh catalyst to a steady state catalyst usually eliminates mass transfer effects as the major phenomena. Consequently, other alternatives must be considered responsible for break-in behavior. These include:

1. purging of physisorbed or weakly chemisorbed poisons, introduced in the activation procedure, from the surface;
2. changes in the 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.

The object of this investigation was to study the break-in behavior of a tungsten-oxide-on-silica catalyst during propylene disproportionation.

II. Literature Review

In 1964, Banks and Bailey (4) reported that linear olefins of three to eight carbon atoms could be catalytically converted to homologs of shorter and longer carbon chains. Reported catalysts for the reaction consisted of molybdenum hexacarbonyl, tungsten hexacarbonyl, and molybdenum oxide, all supported on alumina. Since then, a wide variety of solid materials have been reported to be active for olefin disproportionation (3). One of these catalysts is tungsten oxide on silica, which operates best in temperature range of 260° to 550° Centigrade (21). This catalyst, compared to other active catalysts, behaves quite anomalously. Severe mass transfer effects have been discussed by several investigators (36,61). Also, significant periods of time are required for transition from a freshly activated catalyst to a steady-state catalyst. This is the phenomenon of interest in this study. The following literature review is of the quantitative studies of the break-in behavior of catalysts in general. These studies will be classified into three categories:

1. Purging of contaminants or foreign species from the surface.
2. Changes in surface structure and/or composition due to either reactant-surface or product-surface interaction.
3. Formation of polymeric surface species.

Purging of Contaminants or Foreign Species from the Surface. The presence of a poison in the feed stream to the reactor causes a reduction in the activity of the catalyst. Depending on the poison-

surface interaction this reduction can be permanent or temporary. Permanent reductions are the result of chemisorption on the active sites, and in general these poisons can be removed by a flash desorption at high temperature or by chemical reaction with an activating species. Temporary poisons, on the other hand, are weakly chemisorbed or physisorbed species that occupy some of the active sites when they are present in the feed. They cause a drastic reduction in the activity, but when the poison is eliminated from the feed, the poison is quickly purged from the surface. Once the poison is removed from the surface, the activity of the catalyst return to its normal value. Helckelsberg and coworkers (21) have demonstrated this phenomenon by studying propylene disproportionation with the feed saturated with water, a known poison.

Figure 1 illustrates the typical transient activity exhibited by a freshly activated tungsten oxide on silica catalyst upon introduction of propylene. To insure that the phenomenon in Figure 1, which is associated with "normal" activation, was not due to the purging of temporary poisons from the catalyst, inadvertently introduced during the activation procedure, Luckner and Wills (32) have studied two variations in the activation procedure. First, they followed the normal activation in dry air at 600C° with a 3-hour purge in dry helium at 600C° . In the second variation, they followed the normal air activation and 30 minutes nitrogen purge with a 3-hour evacuation at $100\ \mu\text{m}$ total pressure. The results of these variations in the activation procedure, along with the result of a normal activation,

are shown in Figure 1. From this figure it is clear that the changes in the activation procedure do not affect the break-in period of this catalyst, and thus the observed transient activity cannot be due to the purging of poisons from the surface.

Change in Surface Structure and/or Composition Due to Either Reactant-Surface or Product-Surface Interaction.

While the catalytic surface promotes reaction, the reactants or products may also cause changes in the structure of the surface. It has been suggested that break-in is due, at least in part, to some sort of reactant-surface interaction. There are various ways that reactants or products could affect the surface of the catalyst. A review has been made of the literature for quantitative studies in this area.

Changes in Catalyst Surface Area. Increases in the surface of a platinum 10% rhodium gauze catalyst during commercial oxidation of NH_3 have been reported by Schmidt and Luss (47).

Distribution of the Promoter on the Catalyst Support. Baddour et al. (1) have studied the break-in period for CO oxidation over a pressed-disk catalyst of silica supported palladium by monitoring the infrared spectra of the adsorbed CO. They have proposed that the break-in phenomenon results from a structural rearrangement of the palladium catalyst. The structural rearrangement is most likely associated with a redistribution of crystallographic planes resulting from surface diffusion of palladium atoms or palladium oxygen complexes.

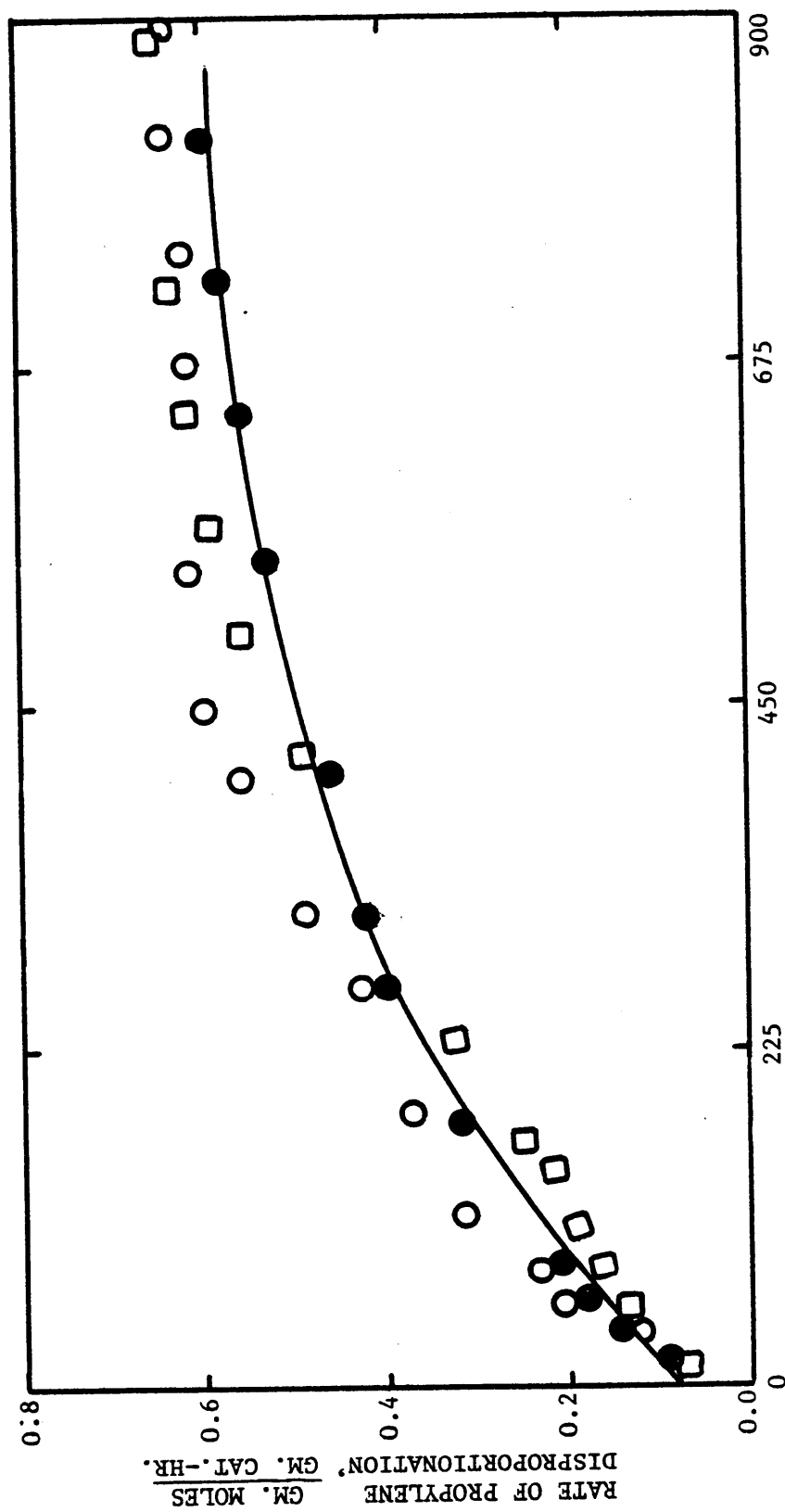
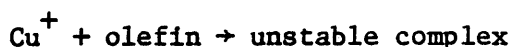
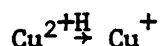


Figure 1. Effect of Activation Procedure on catalyst Break-In.

(427°C, 0.94 ATM, ● 30 min N₂, ○ 180 min He, □ 180 min Evacuation)

(Luckner, R. L. and G. B. Wills, J. Catalyst, 28, 63-68 (1973)).

Chemical Reduction of the Catalyst. Chemical reduction of the catalyst has been reported in several cases to be at least in part responsible for the break-in behavior of the catalyst. The isomerization of n-butene over a copper catalyst has been studied by Dimitrou and Leach (13) and they have reported that the initial activity period observed is due to the reduction of the catalyst and they have postulated that:



Through a prereduction of the catalyst with hydrogen they found that the induction period is solely due to the reduction of the catalyst. Lipsch et al. (30) have reported that the chemical reduction of the catalyst is responsible for the induction period in desulfurization of thiophene over $\text{CoO-MoO}_3\text{-Al}_2\text{O}_3$. Luckner et al. (32) have reduced the break-in period during propylene disproportionation over tungsten oxide on silica catalyst by reducing WO_3 to $\text{WO}_{2.9}$ with hydrogen.

Formation of Polymeric Surface Species. During the initial exposure of a catalyst to feed, it is sometimes possible to complex a small amount of the feed with the surface and form a tightly absorbed residue. These complexes can play an important role in the catalytic reactions. The formation of polymeric hydrocarbon species that remains adsorbed to the surface in 1-butene isomerization has been reported by Blomfield (6). The nature of the sites on silica-alumina for propylene polymerization has been investigated by Finch and coworkers (16). Their studies have revealed that propylene, like

1-butene, rapidly undergoes polymeric complex formation and remains tightly adsorbed on the catalyst sites. From conventional pulse studies of break-in, Luckner and Wills (32) have found that approximately 35% of the first few pulses were irreversibly adsorbed by the fresh catalyst, and this percentage steadily declined with increasing number of pulses. From this study, they concluded that the period of transient activity exhibited by the tungsten oxide on silica catalyst during propylene disproportionation was related to the strong adsorption of an olefin species during this period.

Interphase and Intraparticle Transport Effects. In the experimental studies of heterogeneously catalyzed reactions, one must account for the various processes that may impede the reaction. Interpretation of experiments becomes difficult when a mass-transfer resistance affects the rate. To avoid this problem, one of the first objectives should be to determine whether the investigation is concerned with catalytic kinetics or with the interaction between the kinetics and transport phenomena. To insure that the data obtained in an experiment reflect true chemical kinetics, it is necessary first to find the limits of operation beyond which mass transfer resistances become important.

Since in our study of propylene disproportionation over tungsten oxide on silica our concern is with the chemical events on the surface, operating conditions should be selected such that both interphase and intraparticle mass transfer effects can be eliminated. For the

WO_3-SiO_2 catalysis of propylene disproportionation, interphase and intraparticle mass transfer effects have been studied by several investigators. Moffat et al. (36) have reported that interphase mass transfer limitations exist in propylene disproportionation with WO_3-SiO_2 catalysts in spite of the fact that calculations based on the external catalyst area predicts the mass transfer rate required for significant mass transfer effects to be several orders of magnitude greater than the observed rate of product formation.

Luckner (31) has studied the interphase mass transfer effects for this catalytic reaction experimentally. Using a split-bed reactor charged with two different amounts of catalyst, he has conducted a series of experiments and has determined the conversion as a function of reactant flow rate over the range of 1.2 to 120 WHSV with reactant flowing over both beds. Then these experiments were repeated with the reactant flowing over only the first bed. In this way he was able to measure experimentally the effects of changing the Reynolds number while maintaining a constant space time. The reactor Reynolds number, or linear bed velocity, has an effect on conversion only if interphase effects are significant. Luckner found significant interphase mass transfer effects at all but the highest linear velocities.

One explanation of why conversion is a function of linear bed velocity at a constant space time is that each particle is surrounded by a gaseous film through which reactants must diffuse to reach the catalyst surface. Increasing the linear velocity decreases this film thickness and thereby decreases the difference between the bulk gas

reactant composition and composition of the external surface of the catalyst. At the limit of sufficiently high velocity, the composition of the particle surface becomes essentially the bulk gas stream composition. In Figure 2 (reproduction of Luckner's data) below a space time of approximately 0.4 minutes the level of conversion is the same for the single-bed and for split-bed. This suggests that below this space time interphase mass transfer effects can be neglected.

Intraparticle Mass Transfer Studies. The measure of how much the reaction rate is lowered because of pore diffusion is usually expressed as an effectiveness factor ($\epsilon = \frac{\text{actual reaction rate within pore}}{\text{rate if not slowed by pore diffusion}}$). When intraparticle mass transfer resistance is significant, a change in the particle diameter results in substantial changes in the observed reaction rate. In a region where the effectiveness factor approaches one, a change in particle diameter has no effect on the observed reaction rate. This region, for propylene disproportionation over $\text{WO}_3\text{-SiO}_2$, has been determined by Luckner (31). His study of the effect of particle size on reaction rate in the region of negligible interphase mass transfer effects have revealed that for a particle diameter below 400 microns, the intraparticle mass transfer effects appear negligible and an effectiveness factor of one can be assumed.

Break-In Phenomena

In the temporal history of a catalyst, several regimes exist. One of these regimes is the transient period of activity, which has been labelled "break-in". This type of transient is so commonly

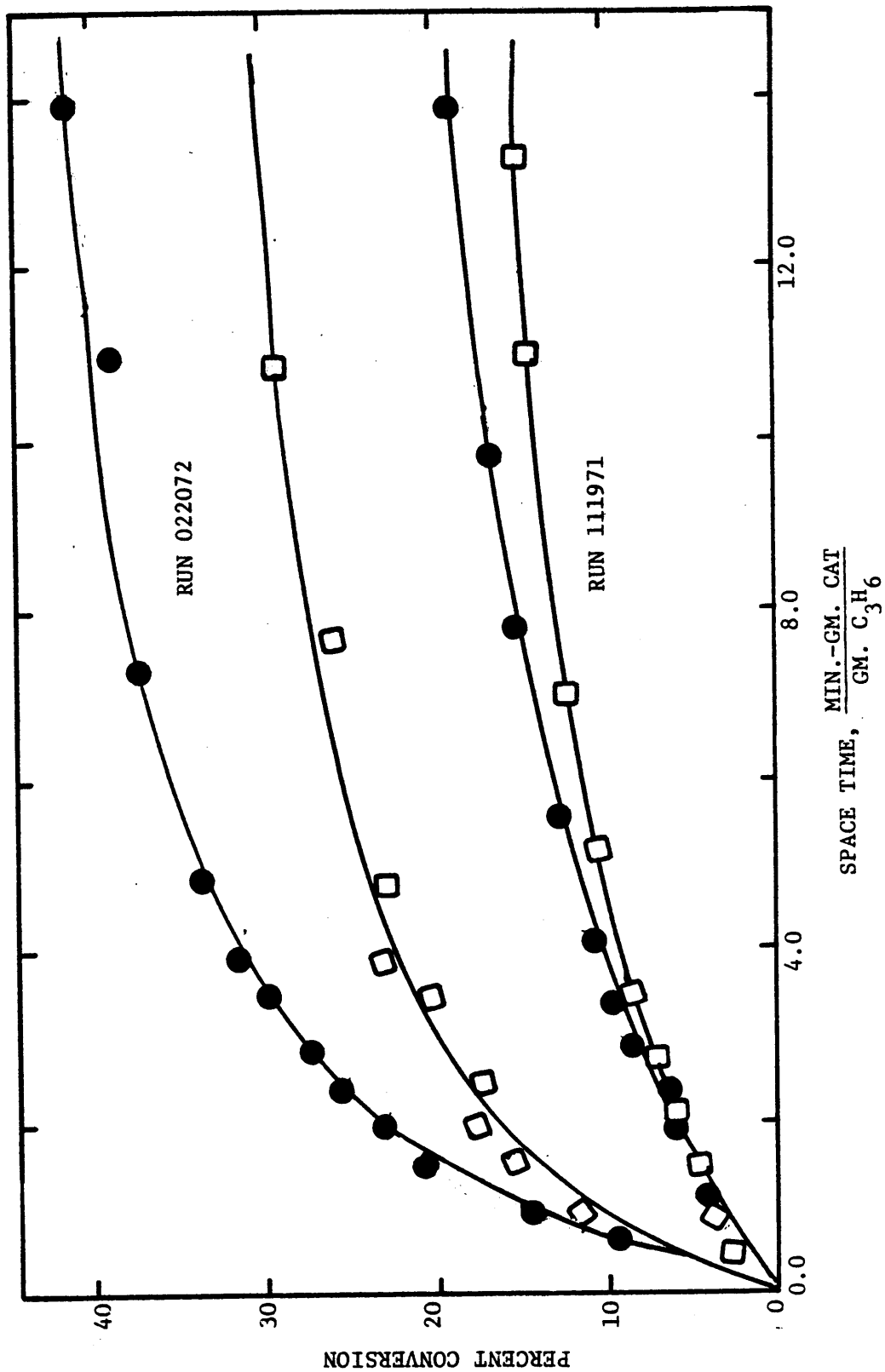
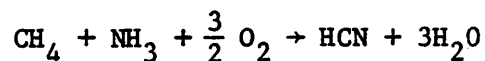


Figure 2. Interphase Mass Transfer Studies in the Split-Bed Reactor at 427°C, 0.94 ATM,

(□ 1.0 GM. CAT, ● 1.5 GM. CAT) (31).

exhibited by freshly activated catalyst that it is not always reported in the literature. There has been very little quantitative study of this subject and the phenomena involved are not always clearly understood. There are examples of a number of widely differing catalyst systems that exhibit catalyst break-in in the literature. Baddour (1) has reported a relatively slow break-in period of 5 days for oxidation of carbon monoxide over a platinum catalyst. Pan and Roth (42) have reported 60-65 hours before reaching steady state activity for the following reaction catalyzed by a platinum-and-rhodium gauze catalyst.



Lipsch et al. (30) have studied desulfurization of thiophene over a $\text{CoO-MoO}_3\text{-Al}_3\text{O}_3$ catalyst and reported the existence of an induction period for this catalyst. Several investigators (32,14,20) reported a break-in period of 15-20 hours for propylene disproportionation over a tungsten-oxide-on-silica catalyst. Thus, the concept of catalyst break-in appears to be a fairly general phenomenon about which there is only qualitative understanding.

Quantitative Studies of the Break-In Phenomena of Tungsten-Oxide-on-Silica and Similar Catalysts During Olefin Disproportionation

The first quantitative study of the break-in period for tungsten catalyst was carried out by Luckner and Wills (31,32). In a fixed bed microcatalytic reactor operated as a near differential reactor, they found that the steady state rate of propylene disproportionation

was some 750% greater than that of the freshly activated catalyst and that the transition to a steady state catalyst system required some 900 min. (at $T = 427^{\circ}\text{C}$, $P = 0.94$ atm.) of propylene contact. They reported that the variation in the rate of propylene disproportionation with time during break-in may be represented by a first order expression, which is given mathematically as,

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

where r_{ss} is the steady-state rate, r_0 is the rate at $t = 0$, and k is the break-in rate constant.

At constant pressure, but at different temperatures, they found an Arrhenius correlation with an activation energy of 47.2 kcal/mole. They studied the dependence of the rate of break-in on pressure at a constant temperature and reported that the rate of break-in was directly proportional to the partial pressure of the propylene. The combined effect of pressure and temperature on the rate of break-in constant was given as:

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

Another major study on the break-in period of propylene disproportionation over this catalyst was performed by Pennella and coworkers (43). They have based their discussion on the electronic configuration of the carbon-carbon double bond of the olefin molecule. In the structure of the carbon-carbon double bond, there is a cloud

of π electrons, in the bonding of the carbon-carbon nuclei. These loosely held π electrons are particularly available to a reagent that is seeking electrons. Since the promoter in this catalyst (WO_3 , W^{+6}) has empty d orbitals, it is expected that some stabilization of energy by coordination of electrons donated by the ligand (propylene) takes place. The olefin contributes some electron density from the π -bonding orbital to the vacant d orbitals of the metal. The rigidity of the system forces some overlap of filled d orbitals of the metal with the π^* antibonding orbitals of the olefin. As a result, some electron density is transferred from the metal to the antibonding π^* orbitals of the olefin (back donation). They have proposed that olefin disproportionation over this catalyst occurs through promotion of electrons from molecular orbitals comprising metal d orbitals and olefin π orbitals to levels comprising metal d orbitals and olefin antibonding π^* orbitals.

Pennella et al. (44) have also investigated the influence of chelating di- and triolefins (polyenes) on propylene disproportionation. Their experimental results have revealed that the addition of a small amount (0.5 cc liquid/hr) of 1,5 cyclooctadiene (1,5 COD) both at atmospheric and higher pressure (21.4 atm.) reduced the induction period of this catalytic reaction system and enhanced the reaction following the induction period. In addition to 1,5 COD, they have added several other polyenes to test their influence on propylene disproportionation over tungsten oxide on silica. They found that the tests fell into three groups:

1. Compounds, which did not affect the course of reaction, such as n-octane and benzene.
2. Compounds which enhanced significantly propylene conversion such as 1,4 cyclohexadiene, 1,5,9 cyclododecatriene, 1,5 COD.
3. Compounds which produced moderate increase in propylene conversion such as 1,5 hexadiene and dicyclopentadiene.

It should be noted that all of these effects were temporary, and that continuous addition was necessary to maintain enhanced activity.

Takahashi (50) has reported that in the disproportionation of olefins an improvement in the selectivity was affected by adding PHNH_2 , $\text{C}_5\text{H}_5\text{N}$ or their alkyl derivatives to $\text{WO}_3\text{-SiO}_2$ catalyst, or by treating the catalyst with PHNH_2 , $\text{C}_5\text{H}_5\text{N}$ or their alkyl derivatives. Olefins disproportionated were, 1-butene, trans 2-butene and isobutene. Takahashi also has reported that, in the WO_3 catalyzed disproportionation of olefins, addition of NH_3 increased the selectivity. The addition of NH_3 is reported to decrease the isomerization of the double bond and to increase the activity of the catalyst.

Response of the Catalyst Activity to Different Atmospheres. In the last several years, the following studies have been carried out in this laboratory to obtain a clearer understanding of the phenomena involved in the break-in period of propylene disproportionation over a tungsten-oxide-on-silica catalyst.

Helium Purges of Various Duration. Purging a steady state catalyst with helium for 5 and 10 minutes at 3.32 atm. reduces the catalytic

activity upon readmission of the propylene. After a 5 minute purge, a break-in period is observed, but it is of shorter duration than that observed for a freshly activated catalyst. Purging for 10 minutes with helium reduces the activity of the catalyst to a point where the observed break-in is indistinguishable from that of a freshly activated catalyst (14). In studies at a lower pressure (0.94 atm.), purging of the fully activated catalyst with helium for both 5 and 30 minutes resulted in a reduced break-in period in comparison to that observed for a freshly activated catalyst (18). From these results it appears that the activity loss during helium purging is affected by both the duration and the pressure level of the purge.

Successive Reduction and Increase in Temperature with Propylene Flow

Maintained Through the Reactor. In order to study the surface changes taking place during break-in through use of x-ray diffraction or the scanning electron microscope, one must maintain a fully activated catalyst in its essential condition far removed from reaction conditions by "freezing" the surface. In three successive coolings of the reactor to room temperature in presence of propylene followed by reheating to the reaction temperature, it was found that although this cooling and reheating reduces the break-in period, it does not eliminate it (14). This suggested that maintaining a fully activated catalyst in its essential condition not only requires the presence of reaction gases but it also requires maintenance of the reaction temperature level.

The Reverse Reaction of Propylene Disproportionation. We have studied (14) the break-in behavior of a WO_3-SiO_2 catalyst using a reactant gas consisting of a mixture of approximately equal moles of ethylene and 2-butene. The result of this study has revealed that the number of moles of ethylene in the product gases was greater than initial moles, even though a significant amount of 2-butene was consumed. This excess ethylene was explained by postulating that the disproportionation reaction is accompanied by isomerization of the 2-butene to 1-butene followed by disproportionation of 1-butene to form ethylene and hexene. It was also found that in the reverse reaction there is a drastic decrease in the amount of propylene (product) as the time of contact increased, and after about six hours the catalyst is almost inactive for the reverse reaction. This deactivation in the reverse reaction was thought to be either due to the formation of heavy hydrocarbons such as 3-hexene or due to the contamination of the catalyst by oxygen in the feed.

The Effect of Products in the Reactant Feed Stream on the Activity of the Catalyst. Tang (51) has studied the effect of a small amount of ethylene and 2-butene in the propylene feed. Replacing the pure propylene feed to a steady state catalyst with a mixture which contained about 1% each of ethylene and 2-butene and 99% propylene reduces the catalytic activity upon initial contact. However, the original steady state activity is regained after 20 minutes of contact with the mixture. Similar effects were noted when a mixture containing about 4% each of ethylene and 2-butene were introduced. On the other

hand, when the propylene flow was interrupted with a mixture of approximately 50% ethylene and 50% 2-butene for 30 minutes, the activity of the catalyst drastically decreases upon reestablishing propylene flow (14). In these types of experiments, which required preparing a mixture in the laboratory, one should always consider the possibility that the results were altered by presence of a small amount of oxygen in the feed.

Effect of Dosing Small Amounts of Chemicals During the Break-In Period.

Small amounts of different chemicals have been dosed to the reactor both during the break-in and during steady-state activity regimes (19). The most interesting result was obtained when a small amount of NH_3 was dosed into the reactor. A substantial increase in activity was obtained both during break-in and during steady-state by the addition of ammonia. Table I is the list of the chemicals and their effects on activity when dosed into the system. From this list one generalization is that amines that decreased activity have no N-H bonds while the amines that increased the activity have at least one N-H bond.

Catalyst Activity Response to Reactant Flow Changes. It was mentioned earlier that the $\text{WO}_3\text{-SiO}_2$ catalyst exhibits two types of unusual and incompletely understood behavior. The first anomalous effect is the break-in period involving the transition from a freshly activated catalyst to a steady state catalyst. The second anomalous behavior of this system is its unusual response to changes in reactant flow

Table I
Effect of Dosed Chemicals on Activity

Chemicals	Initial Effects	Long-Term Effects
Ammonia	Increased	Constant
Tri-Ethyl Amine	Decreased	Decreased
Pyridine	Decreased	Decreased
Aniline	Increased	Decreased
n-Butyl Amine	Increased	Decreased
Di-n-Butyl Amine	Increased	Decreased
Hexyl Amine	Increased	Decreased
Air	Decreased	Constant
Nitrogen	None	None
1-Butene	None	None
2-Butene	Slight Increase	None
Ethylene	Slight Decrease	None
Hydrogen	Decrease	None
HCl	Decrease	None

rate. Moffat et al. (34,61) has reported that the activity of this catalyst increased with increased flow rate, and suggested that very unusual mass transfer existed. Moffat (37) later suggested that the anomaly could be explained if there was very few, but very active sites. This explanation was based on the observation that some catalysts had extremely low site densities (38). Luckner et al. (33) have reported similar results for the tungsten catalyst. They suggested that this unusual behavior was partly due to a non-uniform impregnation of the silica gel support.

Fletcher (15) studied the effect of change of reactant flow rate on the catalytic activity. Her results show that the catalytic activity decrease with decreasing flow rate. Furthermore, her results indicate that effect is reversible with activities increasing with increasing flows. It has been suggested that these anomalous results are not easily explained by an analysis of mass transfer.

Structure and Activity of the Tungsten Oxide on Silica Catalyst During the Disproportionation Reaction. Most of the research results for the tungsten-silica catalyst have been limited to phenomenological studies such as measurements of rates and of factors which influence the rates. Less attention has been paid to the nature of the active sites. Recently, there have been some studies directed toward understanding the nature of the active sites in this catalytic reaction system. Kerkhof et al. (25) have tried to identify the specific tungsten species formed during preparation and activation of the tungsten oxide/silica catalyst and then to correlate these species in a given

catalyst with its activity in the disproportionation reaction. In their study, they have considered the following interactions between promoter and support:

- a. Diffusion of the promoter into the supporting material (solid solution).
- b. Formation of a new bulk compound between the supported material and the carrier.
- c. Creation of a molecular dispersion of the promoter on the carrier (monolayer).
- d. Growth of promoter crystallites on the carrier.

They have studied these possibilities by preparing a number of tungsten-oxide-on-silica catalysts and then investigating them by chemical and spectroscopic methods. From these studies, they concluded that the activity of unsupported WO_3 was negligible in spite of a surface area comparable to the exposed area of the crystallites present in the WO_3-SiO_2 catalyst. The catalyst showed a maximum in turnover number for catalyst with 6-20% WO_3 . In comparing a low tungsten content with high tungsten content, they found that at low tungsten content, a major part of the tungsten is present as a surface compound that was difficult to reduce. On the other hand, at higher tungsten contents, the crystalline WO_3 present was converted to $W_{20}O_{58}$ during disproportionation. They also observed that immediately after introduction of hydrogen a reduction of WO_3 to $W_{20}W_{58}$ took place, which was followed by a slower reduction during the first 2000 seconds of the experiments. Further reduction proceeded quite slowly.

Thomas et al. (52) have measured infrared and Raman spectra of a number of tungsten oxide on silica catalysts and have concluded that at least two tungsten compounds were present: crystalline WO_3 and a polymeric tungstate species. On a $WO_3/\gamma-Al_2O_3$ catalyst only the polymeric species was observed.

Structure Chemistry of Some Oxidic Tungsten Compounds Active as Disproportionation Catalysts.

Stork and Pott (49) have tested a number of oxidic tungsten compounds for propylene disproportionation activity. In their study, they tried to obtain information on the nature of the active site, i.e. the valency and coordination of the W ion. Attention was also paid to the marked dependence of the catalytic activity of the supported WO_3 catalyst on the nature of the carrier. Table II is the partial list of the compounds that were tested. Their studies reveal that all of the tungsten compounds exhibit catalytic activity for disproportionation when used at temperatures of about $500^\circ C$, and those tungsten compounds containing tungsten ions of a valency lower than six did not have a higher activity than those which prior to activation contained only W^{6+} (compare WO_3 , $WO_{2.9}$, $WO_{2.72}$ and WO_2). Also, in this study they found that $Al_2(WO_3)_3$ had a marked activity at lower temperature ($200^\circ C$). By comparing the activity of the $Al_2(WO_4)_3$ with $CaWO_4$, Na_2WO_4 and Li_2WO_4 , they ruled out the fact that this activity was solely due to the tetrahedral surroundings of the tungsten.

The nature and number of active sites of an alumina-supported tungsten disproportionation catalyst was investigated by

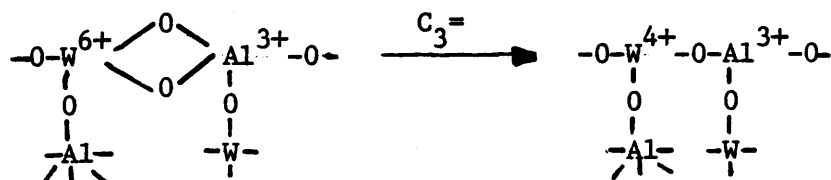
Table II

Activity of Unsupported Tungsten Compounds in Propylene Disproportionation (49)

Catalyst	Specific surface area m^2/g	Amount of cat., g	Temp., $^{\circ}C$	WHSV $g.g.^{-1}.h^{-1}$	Conversion to Ethylene %	Activity of cat., arb. units	Activity/ m^2 surface area arb. units
WO_3	3	12.4	440	.03	2.5	13.2	4.4
$WO_{2.9}$	2	4	457	.02	.4	1.6	.8
$WO_{2.72}$	1.25	8	352	.005	.75	.65	.5
WO_2	.09	18	461	.004	.5	.32	3.6
Na_6WO_3	.59	20	376	.007	.04	.028	.05
Na_2WO_4	.12	21	400	.004	.08	.05	.4

de Vries and Pott (12). In this study they have attempted to elucidate the nature and determine the number of active sites for propylene disproportionation on $WO_3/\gamma-Al_2O_3$ type catalysts by selective poisoning. They have given special attention to the influence of the catalyst preparation and activation used and the effects of poisons such as H_2O and O_2 on the catalytic activity. Their studies revealed that a considerable amount of water was released during activation, and the amount of water released increases with increasing activation temperature. From the amount of H_2O in the off gas for different temperatures, they showed that the release of water from the calcined catalyst is a slow process with a high activation energy. From this fact, together with the observation that the dry air is just as effective in activating the catalyst as dry nitrogen, they suggested that the activation is an ordinary dehydroxylation process. They also investigated the effect of a step temperature change on the activity of the activated catalyst and observed that when the reaction temperature is raised from $170^\circ C$ to $235^\circ C$ it takes more than one hour for the activity to reach its maximum steady-state value at $235^\circ C$. After a decrease in reaction temperature to $140^\circ C$, the catalyst deactivates, and when the reaction temperature is brought back to $235^\circ C$, another, but much shorter, break-in period is required to restore the original activity. From these types of experiments, they postulated that during the break-in period the sites active for the disproportionation reaction are being formed. In order to understand what was happening during break-in, they analyzed the off-gas formed

during this period and they flushed the fully activated catalyst for half an hour with nitrogen at elevated temperature (550°C). By cleaning the surface and analyzing the gases, they were not able to detect any trace of CO, CO₂, acrolein or acetone. Also, with a break-in reaction at 250°C, the amount of water in the off-gas was below detection limits. They assumed that during the break-in some kind of chemical change took place at the catalyst surface that resulted in the formation of a product that is volatile at 550°C. However, they concluded that the number of active sites formed was very small, and thus the amount of the products was below their detection limits. They postulated that active sites during the break-in period were formed according to the following scheme:



In this scheme, propylene could be oxidized to acetone or CO₂ and H₂O in such small amounts as to be undetectable.

In a catalyst deactivation experiment at 250°C, de Vries and Pott (12) observed that the conversion of propylene to ethylene decreased with time. At two different flow rates, the rate of decrease with time was approximately proportional to the flow rate. From this they suggested that a poison in the feed was responsible for deactivation. In another experiment, this deactivation was interrupted by a flow of nitrogen for 3 hours, and when propylene flow was reinstated, they

found that the deactivation of the catalyst had continued during the purge with nitrogen. From these experiments, they concluded that at least part of the deactivation was due to presence of inorganic impurities in the feed. They further studied the role of poisons on the activity of the catalyst. Their findings were as follows:

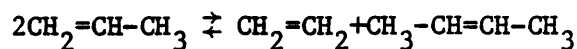
1. Catalyst poisoning can be mainly attributed to inorganic impurities such as O_2 and H_2O present in the feed;
2. H_2O alone, in the complete absence of oxygen, deactivates the catalyst very slowly and incompletely;
3. O_2 without H_2O in the propylene feed deactivates the catalyst completely and irreversibly, but the deactivation rate is relatively low;
4. O_2 in the presence of some water deactivates the catalyst very rapidly and the deactivation is partly reversible;
5. Oxygen acts only as a poison in the presence of the propylene feed.

Relation Between Kinetic Models and the Mechanism of the Propylene Disproportionation.

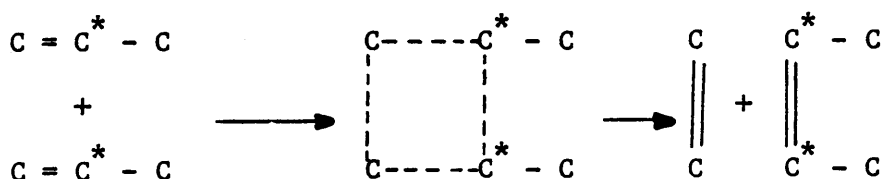
The most important question to be answered in heterogeneous system is the kinetic behavior of reactants in the presence of the solid catalyst. The concept that a catalyst provides an alternate mechanism for accomplishing a reaction, and that this alternate path is the more rapid one, provides the necessary information to understand the kinetic behavior. Because of the great industrial importance of catalytic reactions, considerable effort has been expended developing mechanisms from which kinetic equations can

rationality be developed. In heterogeneous systems, there are several possible controlling mechanisms and each mechanism leads to different kinetic model. Frequently, it is difficult to determine with reasonable confidence the correct mechanism.

With regard to the disproportionation of olefins, most of the kinetic studies in this field have been concerned with the heterogeneous disproportionation of propylene,



over solid catalysts such as WO_3-SiO_2 , MoO_3 , $\text{CoO}-\text{Al}_2\text{O}_3$ and $\text{R}_2\text{O}_7-\text{Al}_2\text{O}_3$. Clark and Cook (11) have disproportionated $[1-^{14}\text{C}]$ and $[2-^{14}\text{C}]$ over a cobalt molybdate catalyst and they have reported that the reaction proceeds as follows:



This result was in agreement with the four-center mechanisms that were proposed by Bradshaw and coworkers (7) for the n-butene disproportionation. The four center mechanisms were supported by the fact that all of the radioactivity was found only in the 2-butene product at lower temperatures. At higher temperatures, Woody and Wills (57) have reported that isomerization of the radioactive propylene gave a mixture of ^{14}C products with activity in both the ethylene and the 2-butene. A partial list of possible controlling mechanisms and initial forms for the propylene disproportionation reaction are

listed in Table III. The four-center mechanisms mentioned above suggest that the disproportionation of olefins occurs between two molecules which are adsorbed on adjacent catalyst sites (24) (Langmuir-Hinshelwood).

Several investigators have shown that a dual-site mechanism, involving two adjacently adsorbed molecules, is the controlling step. Lewis and Wills (27) have studied the kinetics of propylene disproportionation over a cobalt-molybdenum catalyst and have reported that their experimental data were well correlated by assuming a dual site surface reaction. Moffat et al. (35) have supported Lewis' conclusion for the same catalytic reaction system.

Several studies have been published for propylene disproportionation on a tungsten-oxide-on-silica catalyst. Luckner et al. (31,32) have studied the propylene disproportionation reaction over this catalyst. Their initial rate data were well correlated with the dual-site reaction mechanism. Hattikdur et al. (20) have supported Luckner's conclusion for the same system. Early work on this catalyst system by Begley and Wilson (5) showed that the controlling mechanism of propylene disproportionation reaction in an integral reactor is a second order reaction between an adsorbed molecule and a gas phase (Rideal). Recently considerable attention has been given to another mechanism called the carbene mechanism. In this mechanism there is a chain reaction but not a bimolecular surface step. van Rijn and Mol (54) have correlated literature data on the kinetics of the propylene disproportionation on the basis of a number of kinetic

Table III

Partial List of Possible Controlling
Mechanisms and Initial Rate Forms

<u>Controlling Mechanism</u>	<u>Initial Rate Form</u>
1. Dual site surface reaction	$r_o = \frac{K P_p^2}{(1 + K_p P_p)^2}$
2. Single site surface reaction	$r_o = \frac{K P_p^2}{1 + K_p P_p}$
3. Adsorption of propylene	$r_o = K P_p$
4. Adsorption of with dissociation	$r_o = K P_p^2$
5. Desorption of ethylene	$r_o = K$
6. Desorption of 2-butene	$r_o = K$
7. Carbene mechanism	$r_o = \frac{K K^* P_p}{1 + K^* P_p}$

where:

K is the reaction rate constant

K_p is the equilibrium constant for the propylene adsorption

K^* represents a combination of reaction rate constants of an elementary process (or processes).

models, more or less different from the classical Langmuir-type models. With this investigation they have demonstrated that the experimental literature data can be correlated just as well or even better through other kinetic models, based on a mechanism in which only one metal atom is involved in the actual disproportionation step. From this investigation they were not able to draw definite conclusion for the reaction mechanism, but from the considerations about parameter values for the several models, they were able to conclude that the carbene mechanism is the most probable mechanism.

III. Experimentation

This section contains the plan of investigation, the materials and experimental equipment used, and the methods of procedure.

Plan of Investigation

This investigation was concerned with the break-in behavior of a tungsten oxide on silica catalyst during propylene disproportionation. As mentioned earlier, break-in is the term applied to the period of transient activity that is observed following initial catalyst-reactant contact. A steady-state catalyst is one that is fully broken-in, while "freshly activated" is the term applied to a catalyst activated in air at an elevated temperature prior to its use in propylene disproportionation. The studies of break-in can be divided into groups as follows:

- a. In the first group, freshly activated catalysts were exposed to repetitive pulses of the reactant and product gases. These were: propylene, ethylene, and 2-butene respectively. The inlet and outlet gases were analyzed for each pulse, and from these analyses, a material balance was made around the reactor for each pulse.
- b. Following apparent saturation of the catalyst by pulsing in (a), the propylene disproportionation activity of the saturated catalyst was determined at two pressure levels.

- c. Relaxation of break-in was studied quantitatively in two series of experiments. In the first set, the catalyst was brought to steady-state activity and then the reactor temperature level was reduced to room temperature. The reactor was held at room temperature for varying periods of time, following which the reactor was brought back to the original reaction temperature. This cooling, holding at room temperature, and reheating was done with and without flow and in the presence and absence of propylene. In the experiments with the propylene absent during cooling and reheating, helium was substituted. In all cases, a relaxation of break-in was observed and this effect was measured quantitatively.
- d. A second set of relaxation experiments involved subjecting steady-state catalysts to an inert purge (helium) for varying periods while maintaining the reaction temperature level. Again, a relaxation of break-in was observed and this was quantified by measuring the rate of break-in observed following the relaxation of the original break-in. These experiments were performed at two temperature levels so that an estimate could be made of the activation energy of the relaxation of break-in. Also, relaxation of the catalyst during purging with helium at reaction temperature was investigated at two pressure levels to determine the effects of the pressure of the purging gas on the relaxation of break-in.

- e. In a final set of experiments, the propylene feed to a steady-state catalyst was pulsed with a small dose of ammonia gas, and the effect of this upon the steady-state catalytic activity was measured. Then the propylene disproportionation reaction was studied using a catalyst which had been pre-treated with ammonia. In other experiments, break-in was measured using a propylene feed which contained a small amount of ammonia. Finally, the effect on break-in of passing the reactant gas through a magnesium oxide bed was determined.

System Selection and Design. A microcatalytic reactor was used in this investigation. Details of this reactor are shown in Figure 4. The feed section was constructed such that it allowed an accurately metered feed, free of poisons, to be fed to the reactor. To avoid deactivation of the dryer, and to reduce the dead volume during the pulsing experiments or when one gas was replaced with another, two identical, parallel inlet lines were constructed to the reactor.

For temperature control, the temperature of the mid-point of the bed was monitored. The product analysis section consisted of a gas chromatograph fitted with a dual-flame ionization detector. A soap bubble flow meter and a wet test flow meter were used to measure flow rates.

Experimental Equipment

The equipment used in this investigation consisted of three major sections: feed preparation, a microcatalytic reactor, and a product analysis section. This discussion is restricted to the detailed description of these. Figure 3 shows a schematic diagram of the complete system. The complete specification of the equipment and materials in this figure together with their functions are presented in Appendix A.

Feed Preparation. This section consisted of gas cylinders of chemically pure feeds connected to a gas manifold. The gases from the manifold were passed through a rotameter, a Moore differential flow control, and through a dryer before entering the reactor. This provided an accurately metered feed stream to the reactor which was free of the known catalyst poison, water.

Micro-catalytic Reactor. The reactor was constructed from a 6 inch section of 3/8 inch o.d., 316 stainless steel tubing. The top of the reactor was fitted with a 3/8 inch "Swagelok" male connector which was connected to a heat exchanger tee (3/8", 1/4", 1/4"). This tee provided fittings for the inlet line and for the reactor thermowell. The bottom of the reactor was fitted with a 3/8 inch "Swagelok" male connector to which was attached a 1/4 inch "Whity" KEL-F tip valve. A preheater was formed by winding a 4 foot section of 1/16 inch o.d., 316 stainless steel tubing around the heat block which surrounding the reactor.

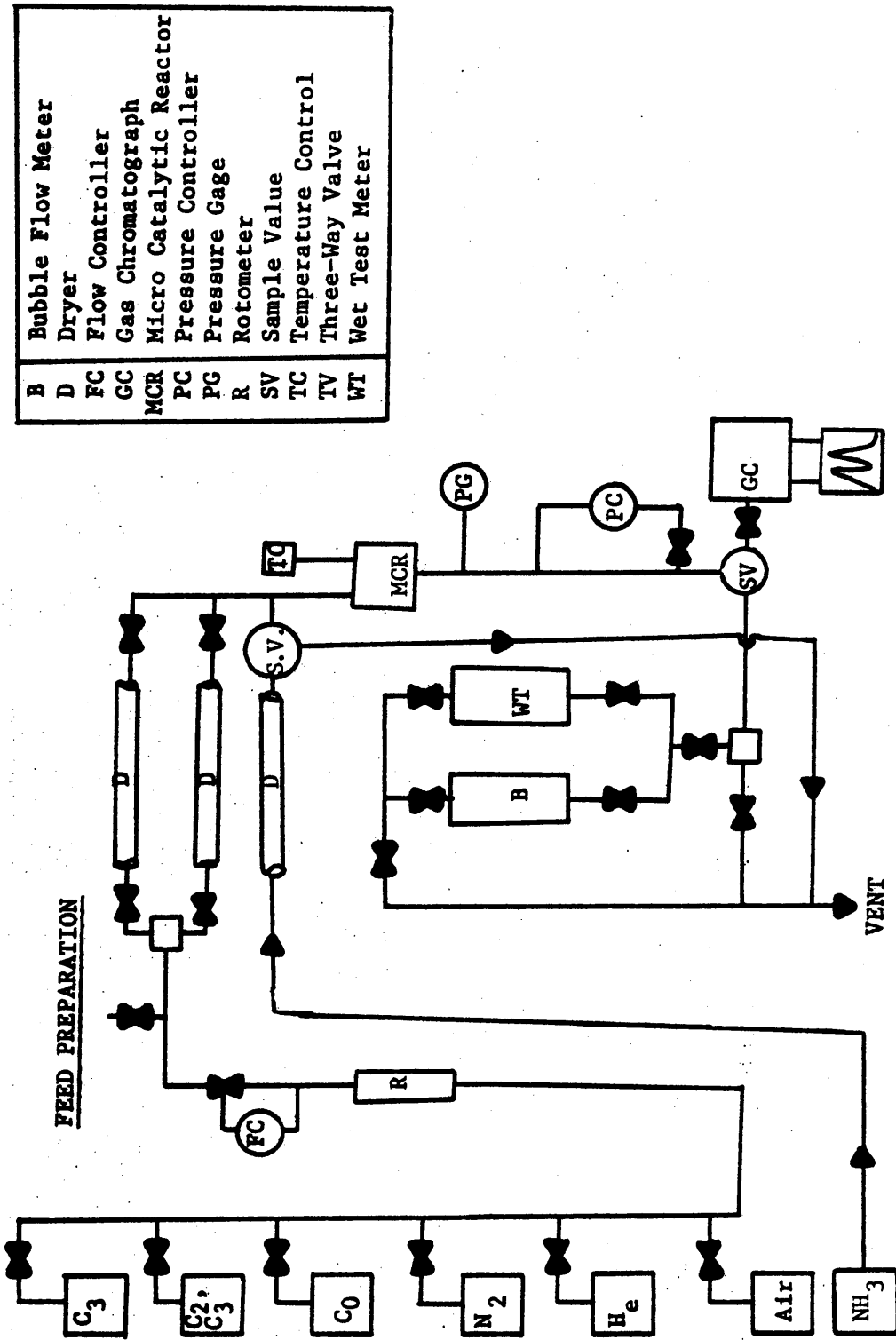


Figure 3. Schematic Diagram of the Reactor System.

The micro-catalytic reactor was fitted with a temperature and pressure control which was selected for accuracy and control performance. Several methods were used to eliminate variations in temperature. One of these methods was to surround the reactor with a heavy metal cylinder, which is shown as the "heat transfer block" in Figure 4. In this method, heat was supplied to the outer cylinder and the high conductivity and heat capacity of the heat block improved the temperature control within the reactor. This method was used in all of the studies. It is also important to bring the reactant gases to nearly 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 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 preheater, the 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 temperature of the middle of the bed at the desired temperature levels. For this purpose, a thermowell was placed in the reactor such that the tip was at the center of the bed.

In addition to isothermal conditions, it is important to distribute the reactant gases over the bed uniformly to avoid channelling. This was achieved by 7 capillaries of 0.04-inch diameter drilled in the reactor preheater. This was further improved by mixing the catalyst with quartz.

Reactor Furnace. During each experiment, the reactor was placed in a six-inch long, tubular resistance heating furnace. One bank of the resistance elements in the furnace was connected to the power line through a powerstat. The voltage to this bank was adjusted to maintain the reactor approximately 10°C below the desired temperature if used alone. This bank was on continuously. The second bank of the 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 in order to maintain the reactor at the desired temperature level. Temperature control within the reactor 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 mixture of all the components present in the reactor effluent. This section also contained a bubble flow meter and a wet test meter for exact determination of the flow rate. Higher flow rates were measured by the wet test meter and the lower ones with the bubble flow meter.

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

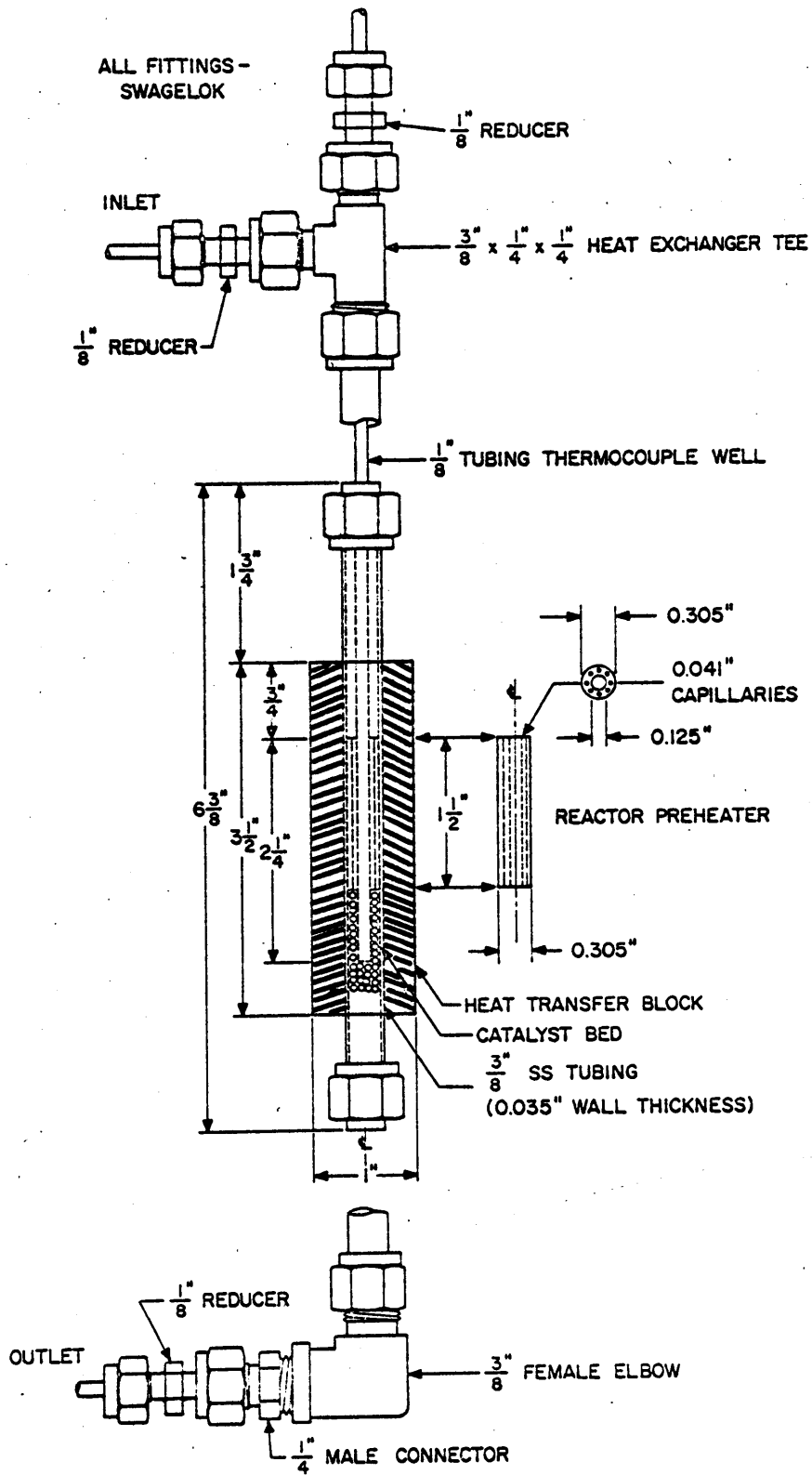


Figure 4. Details of Micro-Reactor.

Magnesium Oxide Bed. To add a MgO bed in the feed line, a 1/4-inch copper tubing, 10 inches long, was filled with magnesium oxide powder. This bed was activated at 300°C for 2 hours while passing nitrogen through it and it was saturated with propylene before further use.

Methods of Procedure

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

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. The major impurity found was propane at about a 0.5% level in the propylene. When the reactant was more than one gas, the mixture was prepared and the composition was measured by gas chromatography.

Preparation of the Mixtures. To prepare an oxygen-free mixture of two gases, the gas cylinders were connected to an empty tank and to a vacuum pump. Then the empty tank and all the lines were filled to 5 atm. with one of the gases in the mixture. After checking the system for leaks under pressure, the tank was evacuated to 10 mm. Hg. This cycle of filling and evacuating was repeated until the estimated partial pressure of residual oxygen was less than a few parts per million. At this point the tank was filled to the appropriate pressure with each individual gas. Figure 5 shows the schematic diagram of the system for preparing the mixtures.

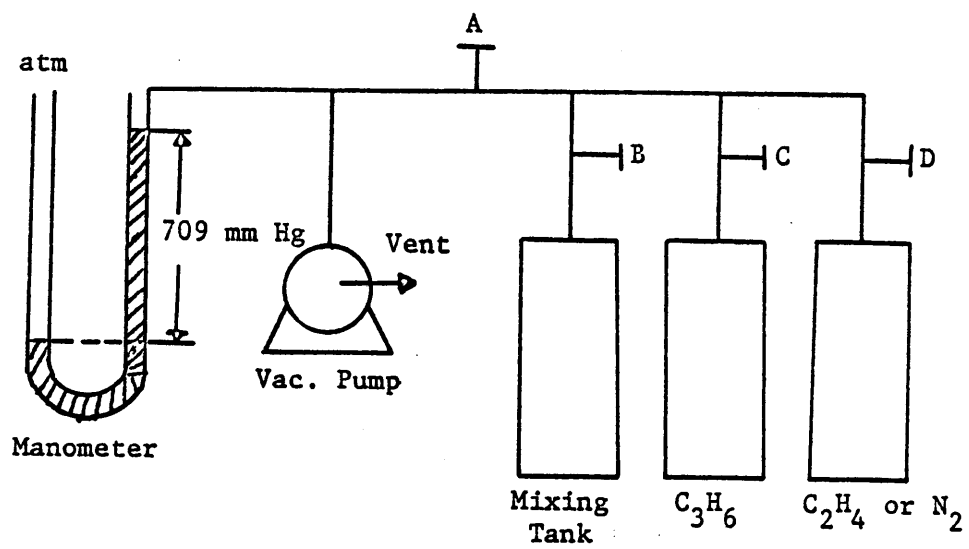


Figure 5. Schematic Diagram of Preparing Mixture.

Preparation of Catalyst. The catalyst used in this study was supplied by the Davidson Chemical Division of W. R. Grace and Company and was designated SMR 7-3322 and SMR 7-5381. It was reported to be 10% tungsten oxide on silica gel, prepared by impregnating 3/16 inch silica extrusions with ammonium tungstate. Luckner (31) confirmed that it was 10% tungsten oxide and he reported a B.E.T. surface area of $223 \text{ m}^2/\text{g}$.

The catalyst was prepared by crushing and screening several grams of the pellets. The crushed catalyst was first screened in a U. S. Standard sieve No. 30. Then it was screened in a U. S. Standard sieve No. 40. This gave a fraction from 28 mesh (595 microns) to 35 mesh (420 microns). The catalyst was dried for 10 hours at 120°C and then was stored in a dessicator until needed.

Catalyst Activation. A standard method of catalyst activation was employed in all of the following experiments. In this method, catalyst ($\text{WO}_3\text{-SiO}_2$) of known weight was charged to the reactor. A plug of stainless steel mesh supported the catalyst in the reactor such that a thermocouple well tip was at the midpoint of the catalyst bed. The reactor was 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 to the reactor. The catalyst was heated to 590°C over a period of about 1 hour and then was held at that temperature for 4 hours. Dry air at atmospheric pressure was passed through the catalyst bed at a flow rate of two to three cubic centimeters per second during this treatment. At the end of four hours

the air flow was replaced with a nitrogen flow at atmospheric pressure. Nitrogen was passed through the catalyst bed for a half an hour with the temperature held at 590°C. After these treatments the temperature of the bed was reduced to the desired reactor temperature. Usually, the reactant gases were not introduced until the temperature was stabilized for fifteen minutes.

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

Gas Chromatograph Calibration. In this study all of the 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 all calibrations was 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, the peak width at half the peak height, and the chromatograph attenuation factor for the recorder detector output.

The flame-ionization detector has an output that is proportional to the number of moles of a particular compound being ionized. Mathematically this is given by the equation,

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

where

n_i = number of moles of component i in sample

A_i = area of detector response to component i

f_i = proportionality factor for component i

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

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

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

$$N = \frac{P_L V_L}{ZRT_L} \quad (5)$$

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.

Combining equation 4 and 5 and rearranging gives:

$$\sum_{i=1}^n \frac{f_i}{V_L} A_i = \frac{P_L}{\bar{Z}RT_L}$$

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

$$f_i^* = \frac{f_i/V_L}{f_{C_3H_6}/V_L} \quad (6)$$

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

In all the experiments, the conditions used during calibration were maintained on the chromatograph. These conditions were: oven temperature 25° Centigrade, detector temperature 250° Fahrenheit, helium carrier gas pressure of 40 pounds per square inch gage at a

flow rate of 60 cubic centimeters per minute, air pressure 30 pounds per square inch gage, and hydrogen 14 pounds per square inch gage. Calibration factors along with their 95% confidence limit reported by Luckner are listed in Table IV.

At times it was necessary to change the calibration conditions slightly. Whenever there was a change of the calibration conditions, the validity of the factors were checked by analyzing samples of known composition.

Pulse Studies with Propylene, Ethylene and 2-Butene. Pulse studies were carried out to determine the product distribution and the extent of any irreversible, or difficulty reversible, adsorption of hydrocarbons during exposure of freshly activated catalyst samples to pulses of propylene, ethylene and 2-butene. In these studies the experimental set up was modified so that it was possible to follow pulsing with a step function of propylene. The first step in the pulse study was to develop the skill of injecting equal amounts of gas in each pulse. This was accomplished by admitting gas into the sample loop to a known and constant pressure. The chromatograph's detector was calibrated prior to each run by injecting several pulses of each gas while bypassing the reactor. This calibration was used in the analysis of the total moles in the exit pulse from the reactor and the composition of each exit pulse.

In the calibration procedure the system was set up so that it was possible to enter the carrier gas of the G. C. through two different paths: in the first path, which was used for calibration

Table IV

Gas Chromatograph Detector Component Factors

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

purposes, the reactor was bypassed. The second path, which included the reactor, was used in actual experimentation. The initial step in all calibrations was evacuation of the sample loop and auxiliary components. Then the olefin for which the detector was being calibrated was allowed to fill the system to a predetermined pressure of 68.7 cmHg, measured by a U type manometer. This sample was injected directly into the G. C. by activating a sample valve with a .5 cc sample loop. The peak area was determined as the product of peak height, the peak width at half the peak height, and the chromatograph attenuation factor. This procedure was repeated several times and the average of these values was used as a calibration value. These calibration values are listed in Table V.

When the actual experiments were performed, the same amount of gas was injected into the carrier gas by activating the sample valve. However, in this case, the injected sample was carried by carrier gas through the reactor and then into the G. C. column. Peak areas were determined as before. To do a material balance for each pulse, the difference in the areas for the calibration and for the actual experiment were calculated.

To determine how the break-in behavior of the catalyst was affected by each gas involved in this reaction, the disproportionation reaction was studied on a surface saturated first with propylene, then with ethylene, and finally with 2-butene. These experiments were done at pressures of 2.7 atm. or at 0.94 atm.

Table V
Calibration Values for Pulse Studies

Amount of gas injected = 2×10^{-5} moles

Sample	Propylene	Ethylene	2-Butene
No.	$A_{p p}^f$	$A_{E E}^f$	$A_{2B 2B}^f$
1	68.64	67.37	65.84
2	68.67	66.16	67.504
3	67.4	67.84	67.105
4	66.00	67.84	67.104
5	66.6	66.25	67.401
6	65.6	66.39	67.57
Average	67.15	66.98	67.07

Effect of Cooling and Reheating Upon the Catalyst Activity. To determine the surface changes taking place during break-in using instruments such as x-ray diffraction or the scanning electron microscope, it is necessary to develop a method which maintains the fully activated catalyst at its essential condition far removed from experimental conditions. To do this, an attempt was made to prevent or greatly hinder those processes that deactivate the catalyst upon simple loss of contact with propylene by quickly cooling the fully activated catalyst. For this purpose a freshly activated catalyst was brought to steady-state activity at 431°C and then it was cooled to room temperature without interruption of the flow. Immediately after cooling, the reactor temperature was raised to the initial reaction temperature. A loss in activity was observed and the break-in behavior of the catalyst was determined after this cooling and reheating. Other cooling and reheating experiments were carried out as described above, except that during the cooling and reheating the propylene flow was stopped (stagnant condition). In other experiments the cooling and reheating was carried out in the absence of propylene. In these experiments the propylene flow was replaced by helium gas during the cooling and reheating. In all cases, a relaxation of break-in was observed. Following these studies, a series of runs were made at stagnant conditions and in presence of helium flow to measure quantitatively the relaxation of the catalyst upon cooling and reheating.

Purge of Fully Activated Catalyst with an Inert. To determine the extent of reversibility of the break-in, a sample of catalyst was

allowed to reach a steady-state level of conversion. The propylene flow was then stopped and the catalyst was purged with dry helium for several periods of time. The rate of propylene disproportionation was determined as a function of time after this purging.

Keeping the pressure and temperature constant, a fully activated catalyst was purged with dry helium for 5 and 30 minutes and activity of the catalyst after these purges was determined. Then, keeping the temperature constant, a fully activated catalyst was purged with helium at a low and at a high pressure to determine how the activity after purging was affected by the pressure of the purging gas. Then at a constant pressure, but at different temperatures, the fully activated catalyst was purged to determine the activation energy for the deactivation process. Also, the effects of small amounts of propylene and hydrogen in the inert purging gas were studied.

Following the above studies, the effect of cooling and reheating upon the catalyst activity was determined in the presence of helium. In these experiments, after establishing steady-state, the propylene flow was replaced with helium and then the reactor was allowed to cool to room temperature. Immediately after cooling, the reactor was reheated to the reaction temperature. After reaching the reaction temperature, propylene flow was reinstated and the rate of reaction was determined as a function of contact time. The cooling and reheating in presence of helium experiments were repeated in the same manner as described, except that instead of immediately reheating after cooling, the catalyst was purged with helium for various time periods at

room temperature before reheating to the reaction temperature. Finally, a freshly activated catalyst was brought to steady-state activity and then, without altering the experimental conditions, the propylene flow was replaced with inert helium for a certain period of time. The activity of the catalyst for propylene disproportionation was determined at the end of the purging times by replacing the helium flow with the original flow of propylene.

The Effects of Ammonia Upon the Activity of the Catalyst. Following the normal activation procedure, the catalyst was treated with ammonia at the activation temperature of 590°C and 0.94 atm. for 90 minutes. After 90 minutes of ammonia treatment, the reactor was allowed to cool to the reaction temperature of 450°C while nitrogen flow was maintained. After establishing the reaction temperature, the nitrogen flow was stopped and propylene was started and the extent of the reaction was determined as a function of contact time. In another experiment, after activating the catalyst and cooling to the reaction temperature of 430°C , ammonia was passed into the reactor for 30 minutes at 430°C and 0.94 atm. At the end of 30 minutes of ammonia treatment, the propylene flow was started and the extent of the reaction was determined. In other studies, the effect of a small amount of ammonia in the propylene feed was studied by exposing a freshly activated catalyst to a mixture of 1.5% ammonia and 98.5% propylene. Also studied were the effects of injecting a small quantity of ammonia into a steady-state system and purging a fully activated catalyst with ammonia for 10 minutes at reaction temperature.

Data and Results

The results of the experimental procedures outlined in the previous section are presented in this section.

Pulse Reactor Studies. Microcatalytic pulse studies were made on freshly activated catalyst samples at 437°C and 3.5 atmospheres. For each pulse of propylene, ethylene, and 2-butene, a mass balance was made around the reactor to determine the extent of any irreversible or strong adsorption of hydrocarbons by the catalyst. Figure 6 illustrates the results of these mass balances made during exposure of a fresh catalyst to a number of pulses of propylene. It should be noted that approximately 30% of the first few propylene pulses were irreversibly adsorbed and that this fraction steadily declined as the total catalyst exposure to propylene increased. The product analysis for each propylene pulse indicated that the amount of ethylene decreased with continued catalyst exposure to propylene. Figure 7 shows the percent of ethylene in the product versus the total moles of propylene pulsed. A mass balance around the reactor for the ethylene pulses revealed that ethylene does not absorb to a significant extent on a freshly activated catalyst. A maximum difference of 3.6% was noticed between the calibration value and the value from the pulse which had passed over the catalyst. When 2-butene was pulsed over a freshly activated catalyst, the chromatograph analysis of the reaction products indicated that the product consisted of ethylene, 1-butene, 1,3 butadiene, and 2-pentene.

From the chromatographic analysis of the reaction products for each pulse it will be noted that the dominating reaction was the isomerization of 2-butene to 1-butene. Eventhough there was no detectable quantity of 1-butene in the feed, it was found that 15% of each pulse was isomerized to 1-butene upon contact with a freshly activated catalyst and the amount of 1-butene produced was approximately the same for each pulse. There was also a significant amount of 1,3 butadiene produced from each pulse. The activity for the production of 1,3 butadiene declined with continued exposure of the catalyst to 2-butene. Simultaneously, the amount of ethylene increased and the amount of propylene and 2-butene remained constant. Figures 8 and 9 illustrate the product distribution of each pulse as a function of total moles of 2-butene.

The Effect of Saturation of a Freshly Activated Catalyst with the Gases Involved in Propylene Disproportionation on the Break-in Behavior of the Catalyst. During the initial exposure of a catalyst to feed, it is sometimes possible to complex a small amount of the feed with the surface and form a tightly adsorbed residue. Such complexes may have little or nothing to do directly with the catalysis of reactions on the surface, or they may be directly involved in the reaction either as an active center or as a reaction intermediate (10). To determine to what extent the break-in exhibited by this catalyst was effected by the defective mass balances observed in the previous pulse studies, and to determine which one of these gases played an important role in the break-in behavior, the disproportionation reaction was studied

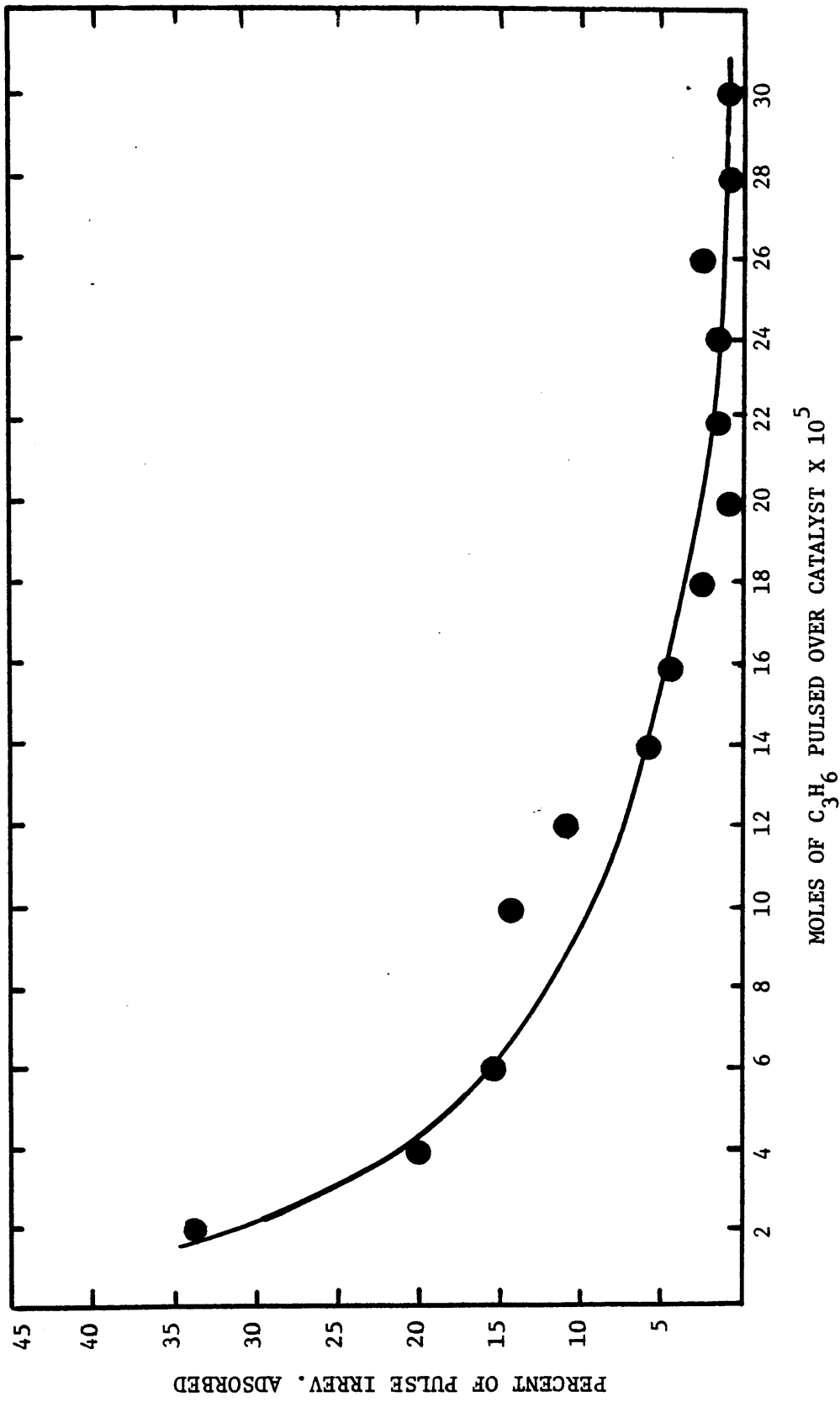


Figure 6. Adsorption of Propylene by a Fresh Catalyst During Pulse Studies at 437°C and 3.5 ATM.

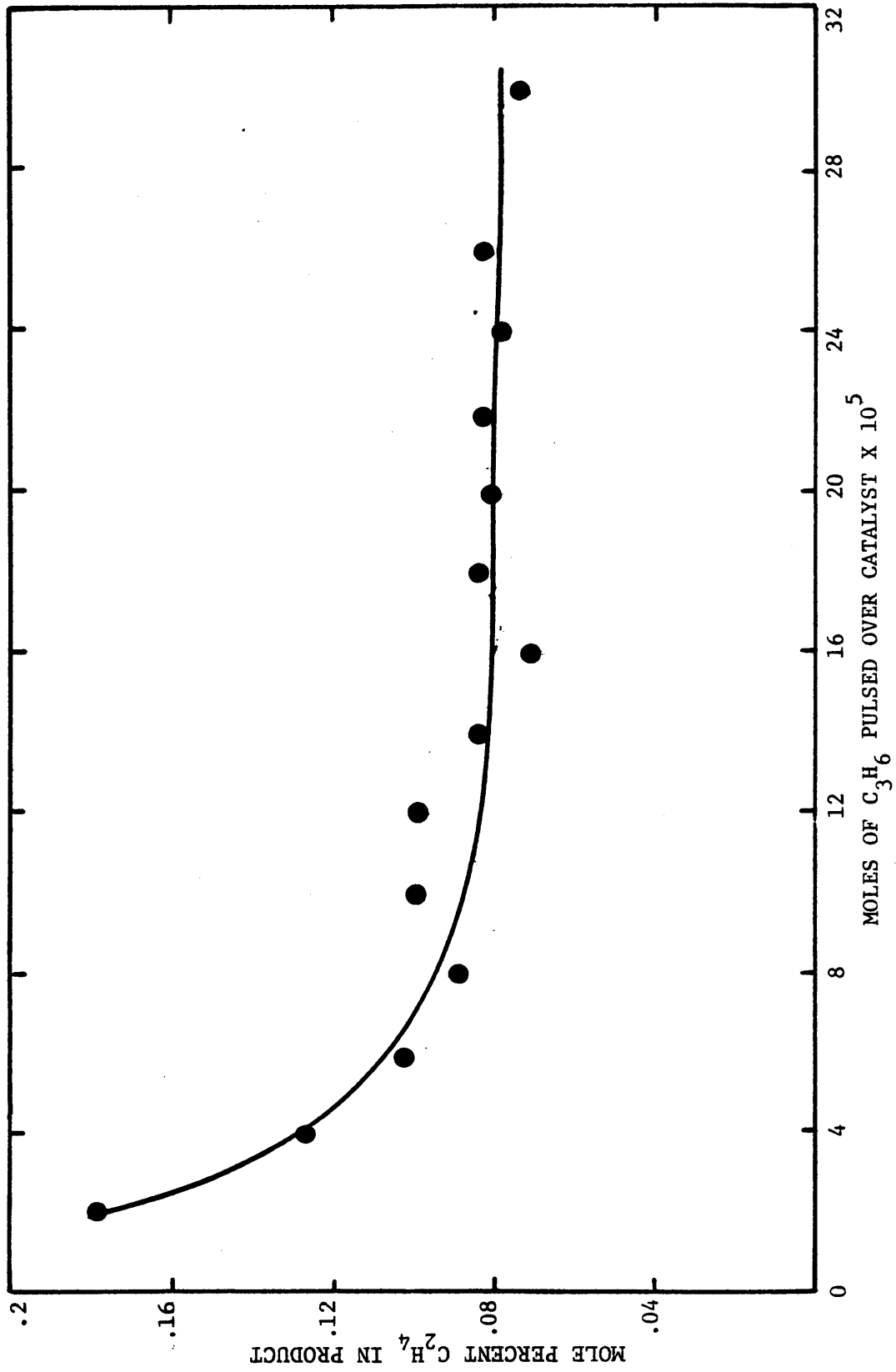


Figure 7. Ethylene Production as a Function of Catalyst Propylene Exposure in Pulse Studies at $437^\circ C$ and 3.5 ATM.

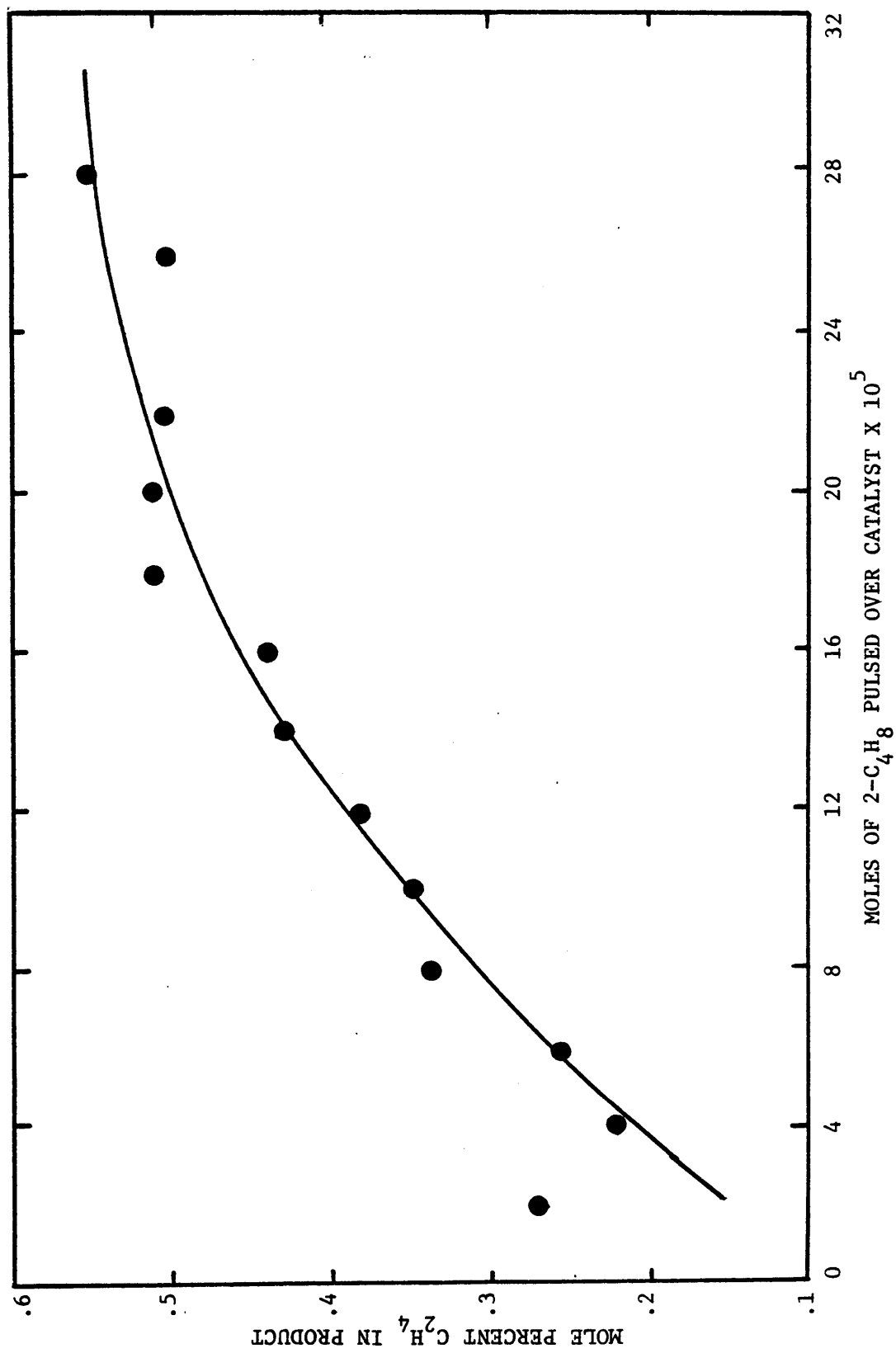


Figure 8. Ethylene Production as a Function of Catalyst Exposure to 2-Butene in Pulse Studies at 437°C and 3.5 ATM.

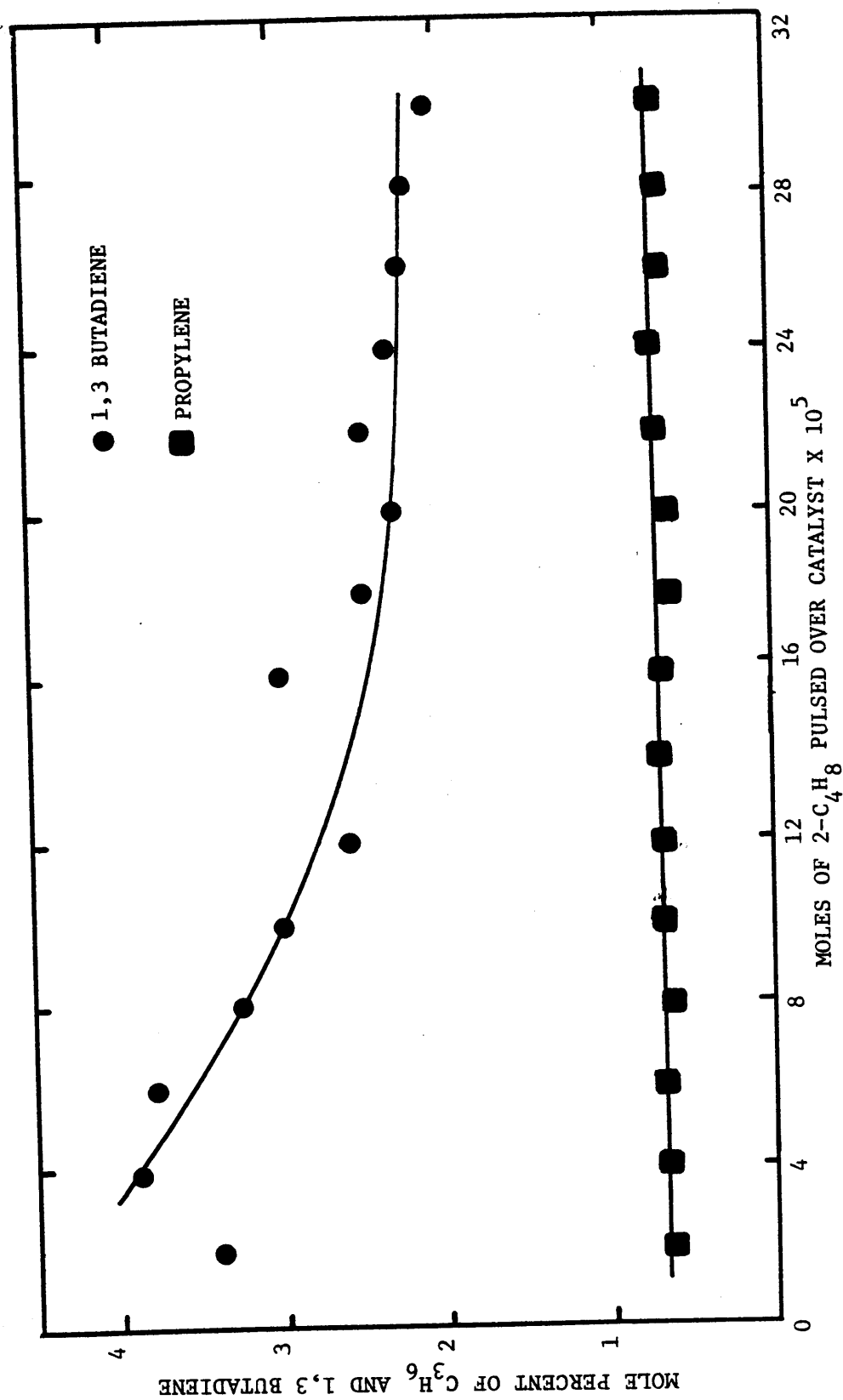


Figure 9. Propylene and 1,3 Butadiene Production as a Function of Catalyst Exposure to 2-Butene in Pulse Studies at 437°C and 3.5 ATM.

using surfaces that were first saturated at 440°C and 0.94 atm. with each gas involved in this reaction. To do this, a freshly activated catalyst was separately exposed to repetitive pulses of either propylene, or ethylene, or 2-butene. These saturated catalysts were then used to disproportionate propylene. Figure 10 illustrates the approach to steady-state activity after saturation of surface with each of these gases. It appeared that after saturating with ethylene and 2-butene the rate of approach to steady-state activity was initially slightly slower than that when the surface was saturated with propylene. In another set of experiments, freshly activated catalysts were saturated with each of the gases at a higher pressure (2.7 atm) before carrying out the disproportionation reaction. The results of these studies are shown in Figure 11. Table X through Table XVII in Appendix B contains the tabulated results of these runs.

Effect of Cooling and Reheating Upon Catalyst Activity. In the studies here, almost any change that disturbs the steady-state reaction has been found to cause at least a temporary loss in catalytic activity. Studies were conducted to determine the factors that influence this decay of steady-state activity and to find a mechanism for deactivation. To this purpose, a sample of the catalyst was brought to steady-state activity at 431°C and 0.94 atm. After establishing steady-state activity, the reactor was allowed to cool to 35°C with propylene flow maintained. In 20 minutes the temperature of the reactor fell from 431°C to 35°C. Immediately after cooling, the reactor was reheated to the reaction temperature in 20 minutes without

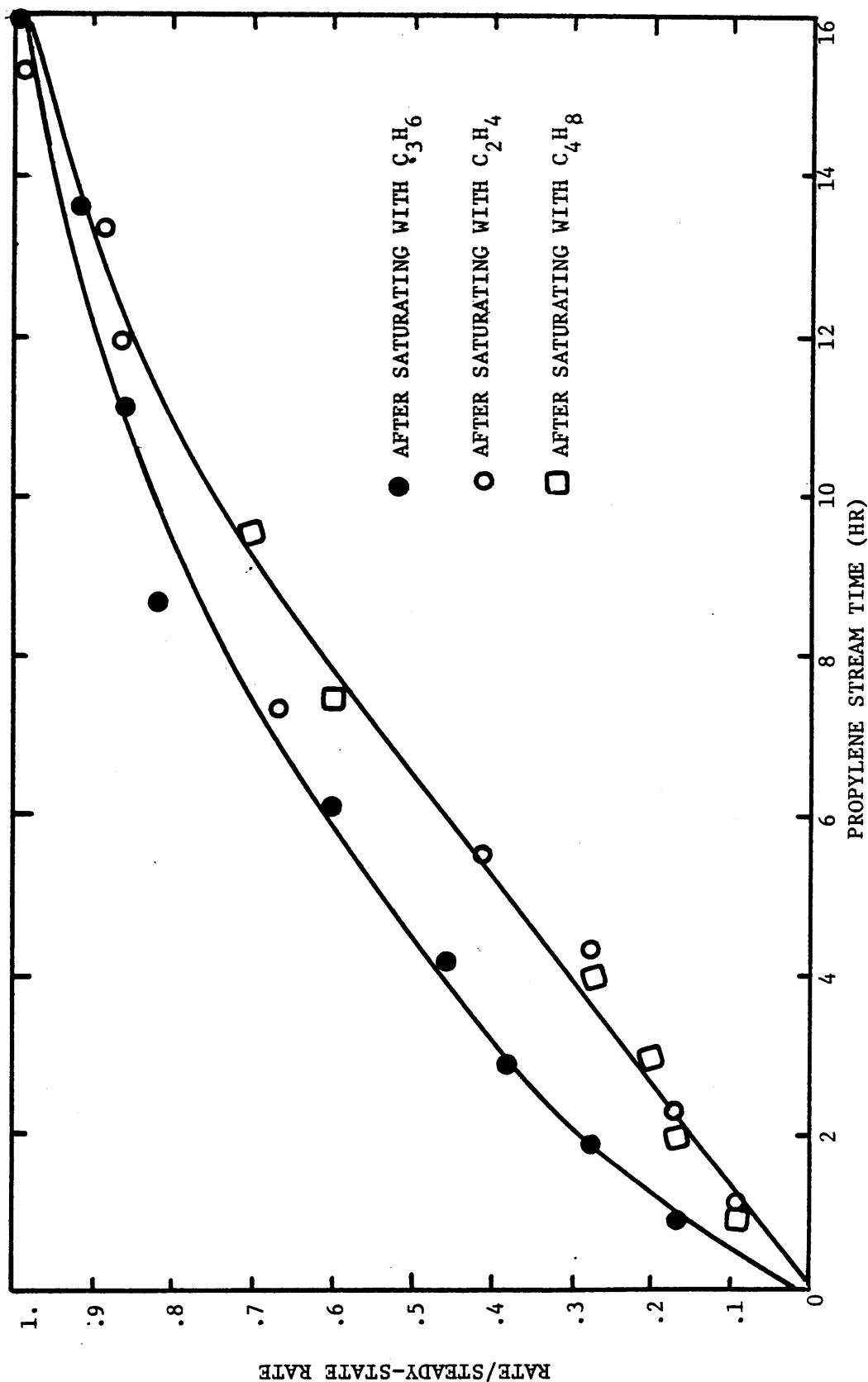


Figure 10. Effect of Saturation of Freshly Activated Catalyst with Propylene, Ethylene, and 2-Butene on Break-in at 440°C and .94 ATM.

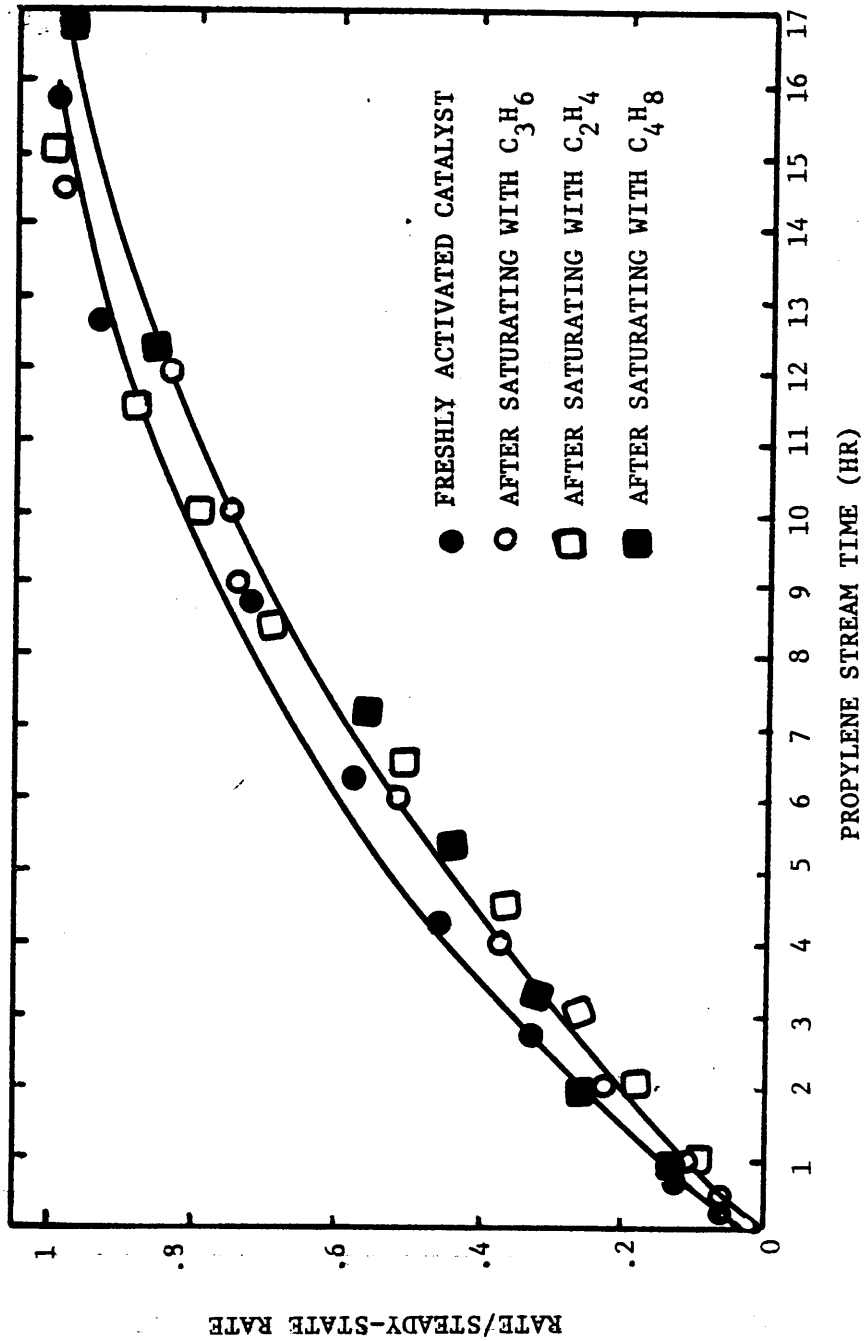


Figure 11. Effect of Saturation of a Freshly Activated Catalyst with Propylene, Ethylene, and 2-Butene on Break-in at 421°C and 2.7 ATM.

Table VI

WO₃-SiO₂ Break-in Rate Constant for Propylene Disproportionation
for Various Catalyst Pretreatments

Pretreatment after normal activation	Reaction T, C°	Reaction P, atm.	Break-in rate constant min ⁻¹
Saturating with C ₃ H ₆	440	.94	.00317
Saturating with C ₂ H ₄	440	.94	.00166
Saturating with 2-C ₄ H ₈	440	.94	.00216
Passing helium for half hour	421	2.7	.00231
Saturating with C ₃ H ₆	421	2.7	.00237
Saturating with C ₂ H ₄	421	2.7	.00253
Saturating with 2-C ₄ H ₈	421	2.7	.00201

any disturbance in the propylene flow. As soon as the reaction temperature was reached (431°C), an effluent sample was injected into the gas chromatograph for analysis to determine the initial activity of the catalyst after cooling and reheating ($t=0$). From then on the reactor temperature was kept constant at 431°C and periodically the product gases were analyzed until steady-state was reached. To compare the extent of deactivation for flow and stagnant conditions, the experiment was repeated exactly in the manner as described, except that during cooling and reheating, the propylene flow was stopped. Figure 12 illustrates these results. From the results of these studies it can be noted that there is less deactivation with flow than without flow. To determine how the deactivation is related to the time at which the catalyst is purged with propylene at low temperature, another set of tests were conducted. After cooling the reactor to 35°C under both flow and stagnant conditions, the reactor was left unattended for 8 hours at room temperature before reheating to 431°C . During this eight-hour period, propylene flow was maintained. Figure 13 shows the results of these experiments. By comparison of the results in Figures 12 and 13, it is evident that the extent of deactivation of the catalyst does not change drastically due to purging with propylene at room temperature between the cooling and the reheating cycle. It will be noted that the rate of approach to steady-state activity after cooling and reheating at stagnant conditions is slower than that observed for flow conditions. To investigate this, tests were conducted in which the reactor was cooled both at

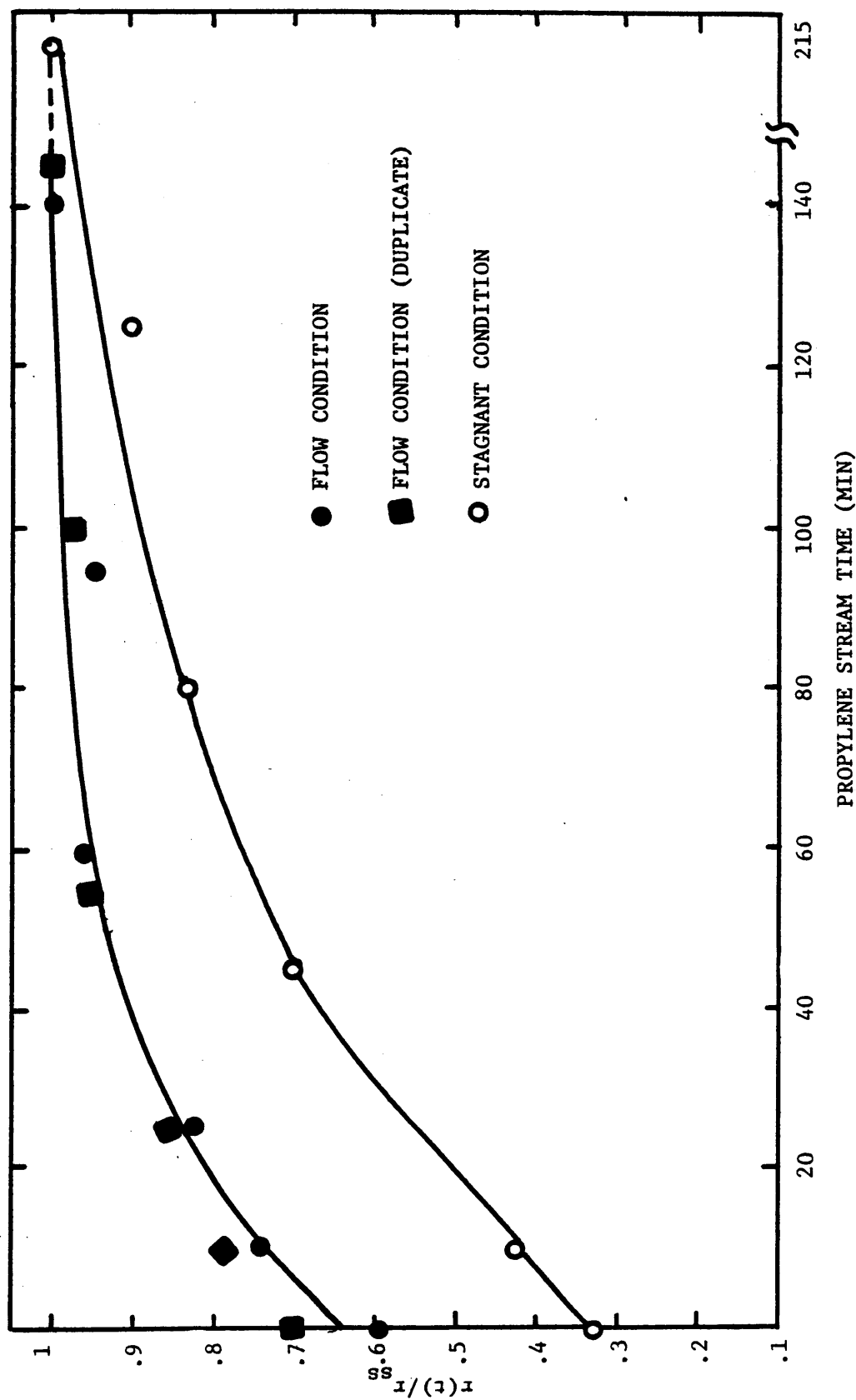


Figure 12. Activity of the Catalyst After Cooling and Immediately Reheating at 431°C and .94 ATM.

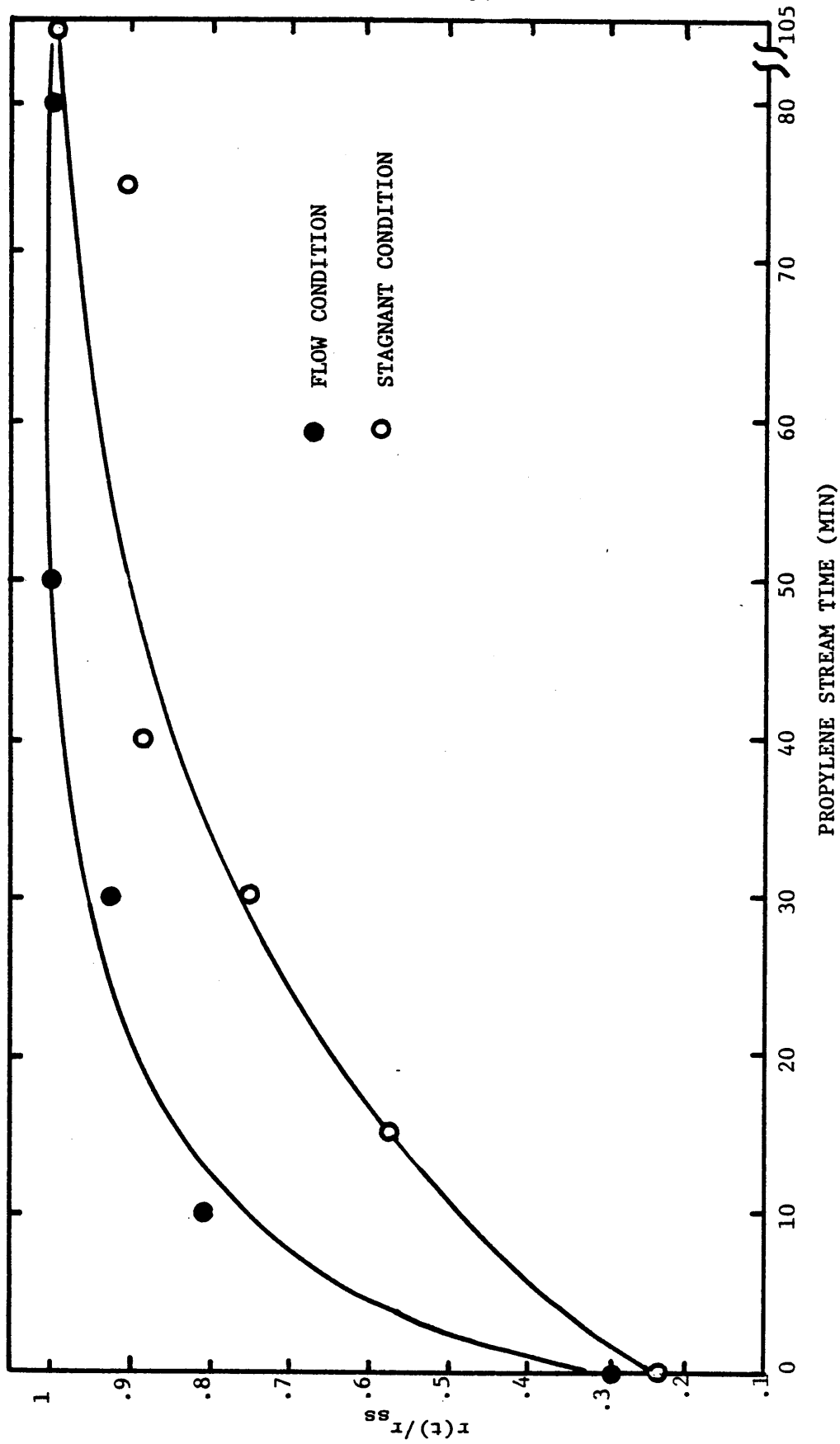


Figure 13. Activity of the Catalyst after Cooling and Reheating at 431°C and .94 ATM. (8 hours purge with C_3H_6 at 25°C).

stagnant and flow conditions. It was then left unattended for eight hours before reheating without propylene flow. Figure 14 illustrates the results of these studies. From comparison of results of Figure 14 Figure 13, it will be noted that the major part of deactivation is taking place during the shut down period in which there was no propylene flow.

The results of the proceeding experiments revealed that the major part of deactivation in the process of cooling and reheating occurs during the time that the reactor was left unattended without flow. This was deduced from Figures 13 and 14 and from the fact that when cooling and reheating was carried out with flow, the decay of activity was less than when it was carried out at stagnant conditions. It should be mentioned that at stagnant conditions, even though the flow was stopped, the catalyst bed was bathed in a propylene atmosphere, and to avoid back diffusion of air or vapor to the system during shut down period, both ends of the reactor were closed.

Finally, in order to determine quantitatively the decay of activity of the catalyst as a function of time at room temperature, the steady-state catalyst was allowed to cool from 431°C to 35°C in 20 minutes with propylene flow maintained. Then it was left unattended for different periods of time without flow. At the end of each shut down period, propylene flow was started and the reactor was reheated to 431°C in approximately 20 minutes. Propylene flow was maintained at all times except during the shut down periods at room temperature. The catalyst was not air activated between experiments. Figure 15

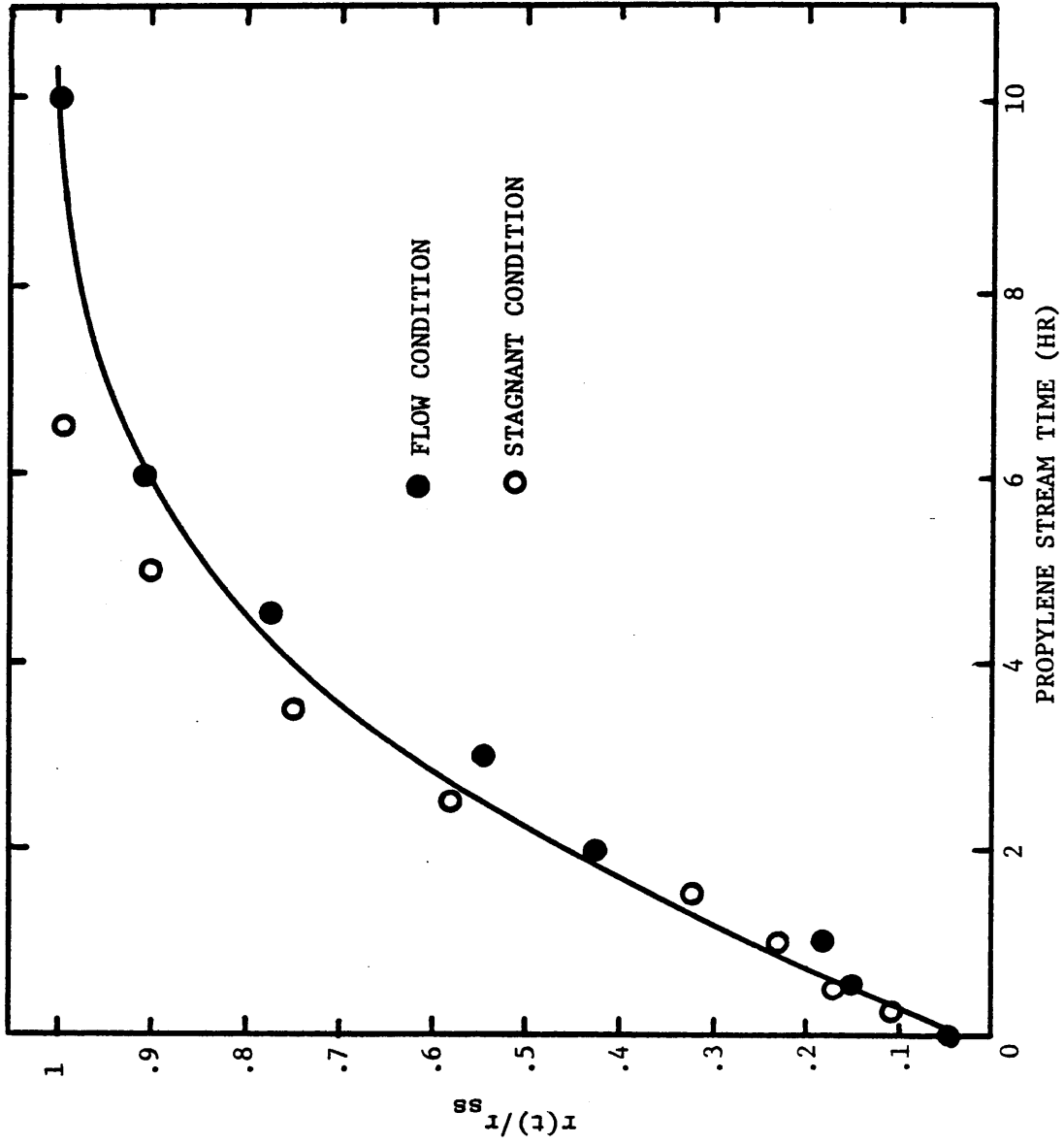


Figure 14. Activity of the Catalyst after Cooling and Reheating at 431°C and .94 ATM. (8 hours shut down without flow between cooling and reheating cycle).

shows the results of 0, 1, 3, 8, and 11 hours of shut down between cooling and reheating without flow. These results clearly indicate that the level of deactivation is a function of the length of time the system was left unattended without flow at room temperature. The form of the data in Figure 16 suggests that the variation in the initial rate of propylene disproportionation with time may be approximated by a first order expression which is mathematically given as:

$$\frac{r_{ss} - r(t)}{r_{ss} - r_0} = e^{-kt} \quad (7)$$

Thus, a plot of the logarithm of the left side of equation 7 versus time should be linear and the rate of catalyst break-in, k , may be obtained from the slope of this plot. Figure 17 contains the variation in the rate of propylene disproportionation with time as correlated by equation 7 during break-in for some of the cooling and reheating experiments at 431° Centigrade and 0.94 atmosphere. Table VII contains the break-in rate constants which were obtained from the slopes of Figure 17 by using least square method to fit the best straight line through the experimental points. It will be observed from these slopes that as the shut down time increases, the break-in rate constant decreases. Figure 18 is a plot of break-in rate constants versus shut down time. Appendix B contains the tabulated results of these runs.

Purging of a Steady-State Catalyst with an Inert Gas. Another disturbance of steady-state rate of reaction, which causes a temporary loss in activity, is that which occurs when a steady-state catalyst

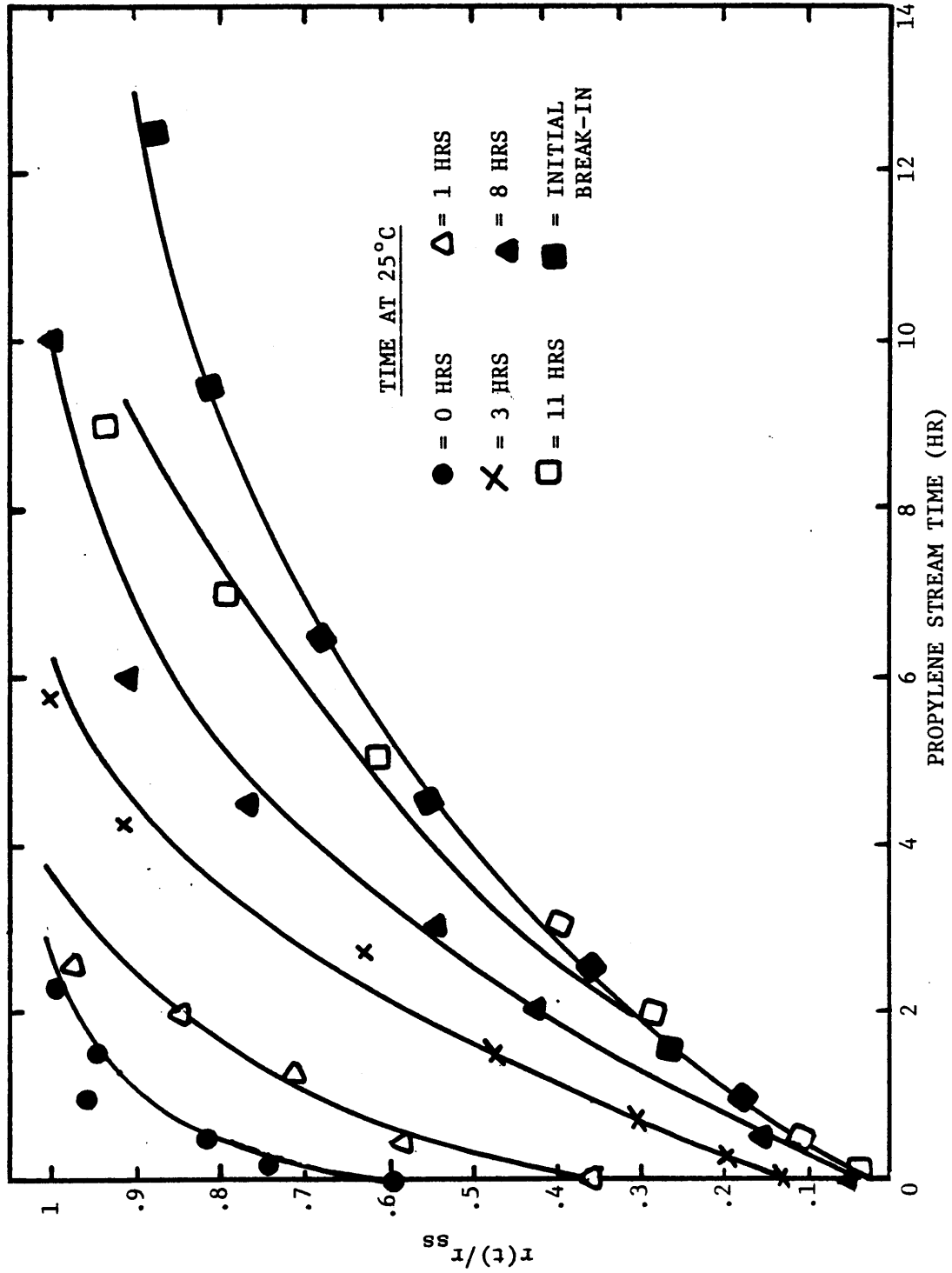


Figure 15. Activity of the Catalyst after Cooling and Reheating at 431°C and .94 ATM.

Table VII

WO₃ Catalyst Activity and Break-in Rate Constant During Propylene Disproportionation in Cooling and Reheating Studies at 431°C and .94 atm.

Experimental Condition	Steady-state conversion of propylene	Initial Rxn rate $\frac{\text{gm moles}}{\text{gm cat-hr}}$	Steady-state Rxn rate	Break-in rate constant min^{-1}
Freshly activated catalyst	.115	0	.0591	.00284
Cooling and reheating immediately in flow condition	.1133	.0343	.0583	.0542
1 hour shut down at 25°C stagnant	.1006	.0188	.0545	.00864
3 hours shut down at 25°C stagnant	.105	.007	.054	.00644
8 hours shut down at 25°C stagnant	.118	.0028	.0607	.00423
11 hours shut down at 25°C stagnant	.109	.0027	.0559	.00352
Cooling and reheating immediately at stagnant conditions	.1177	.0207	.0605	.0149
Cooling and heating at stagnant conditions + 8 hours shut down with flow	.117	.0139	.0602	.0284

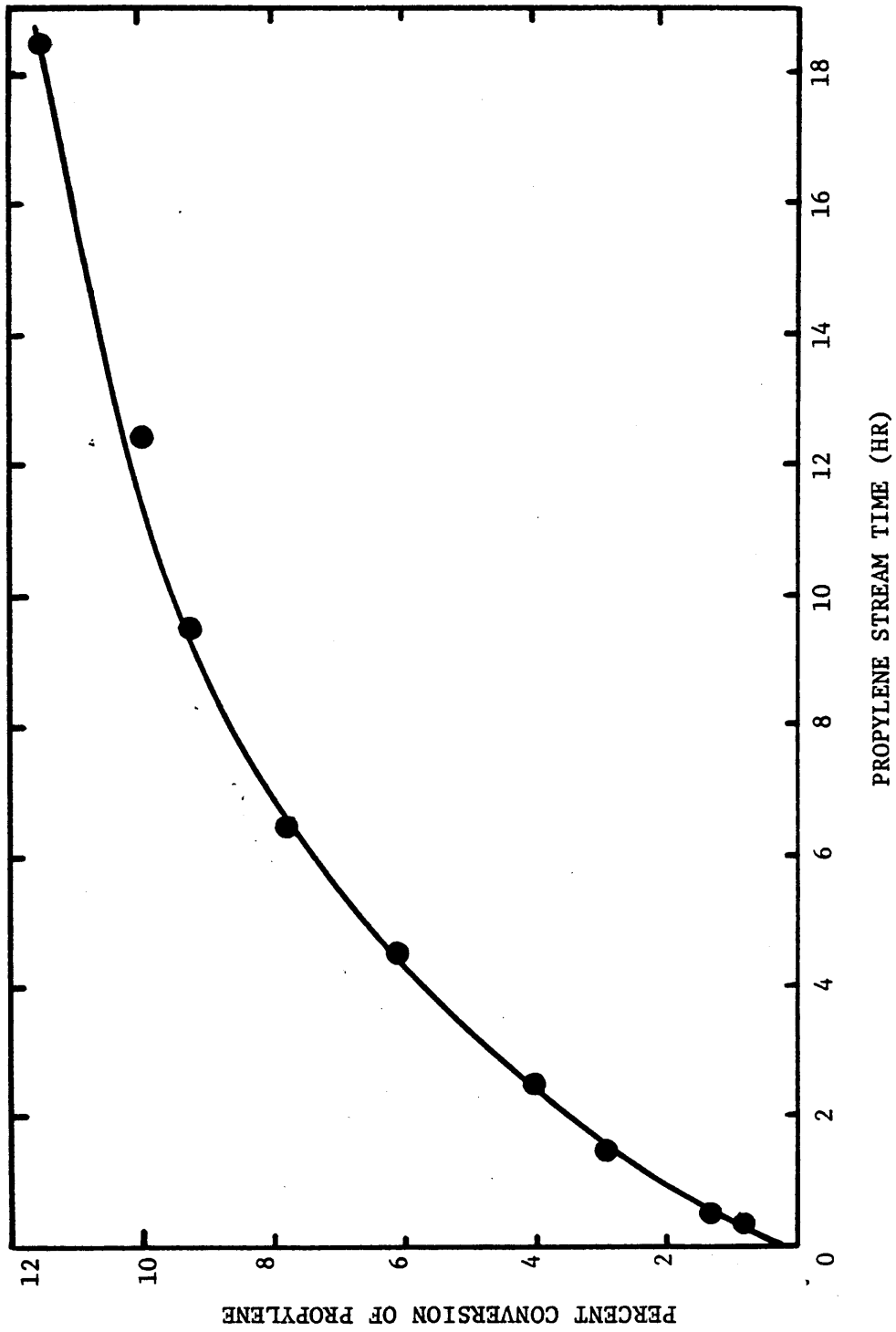


Figure 16. Break-In Behavior of Freshly Activated Catalyst at 431°C and .94 ATM.

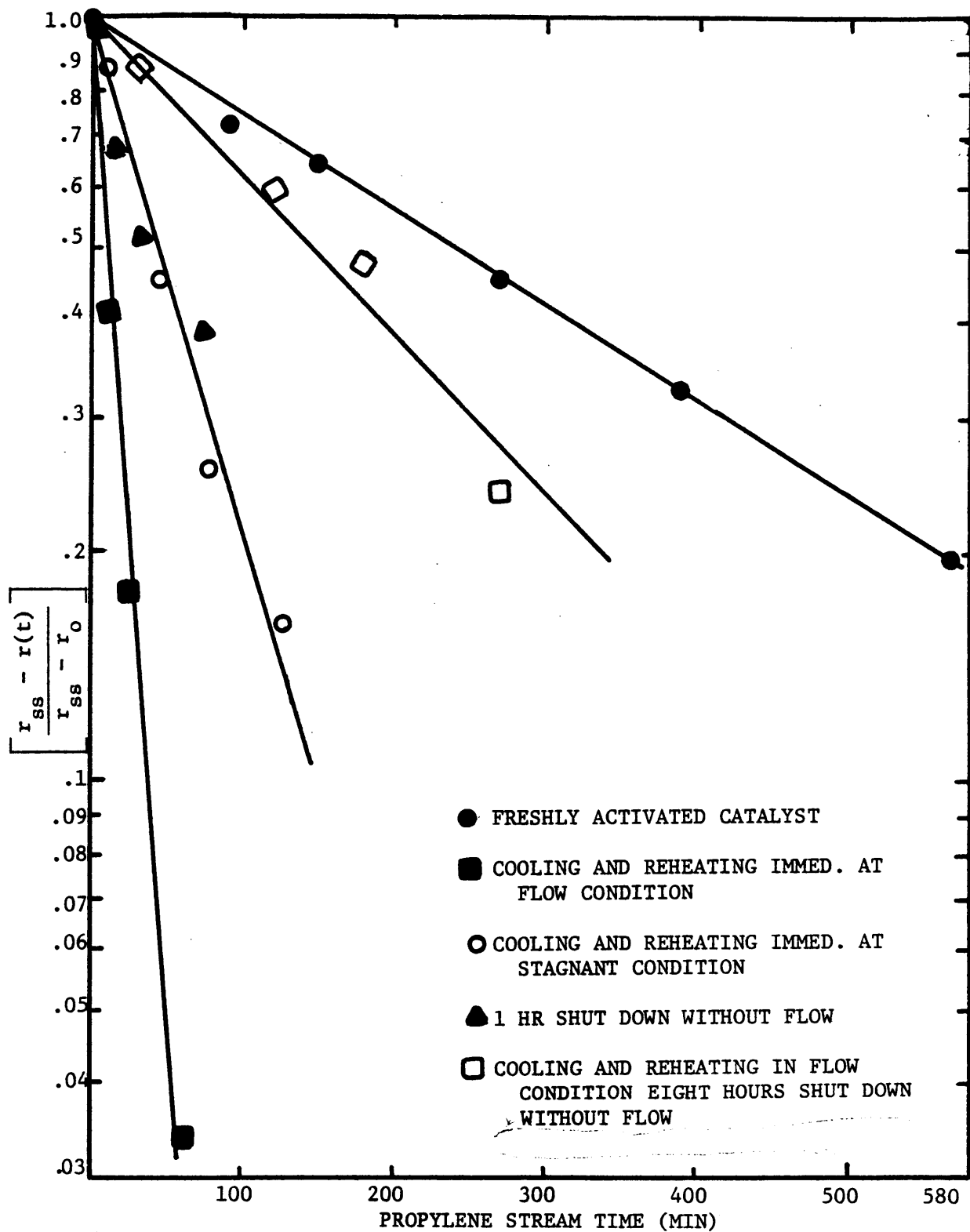


Figure 17. Rate of Fractional Approach to Steady-State Activity at 431°C and .94 ATM.

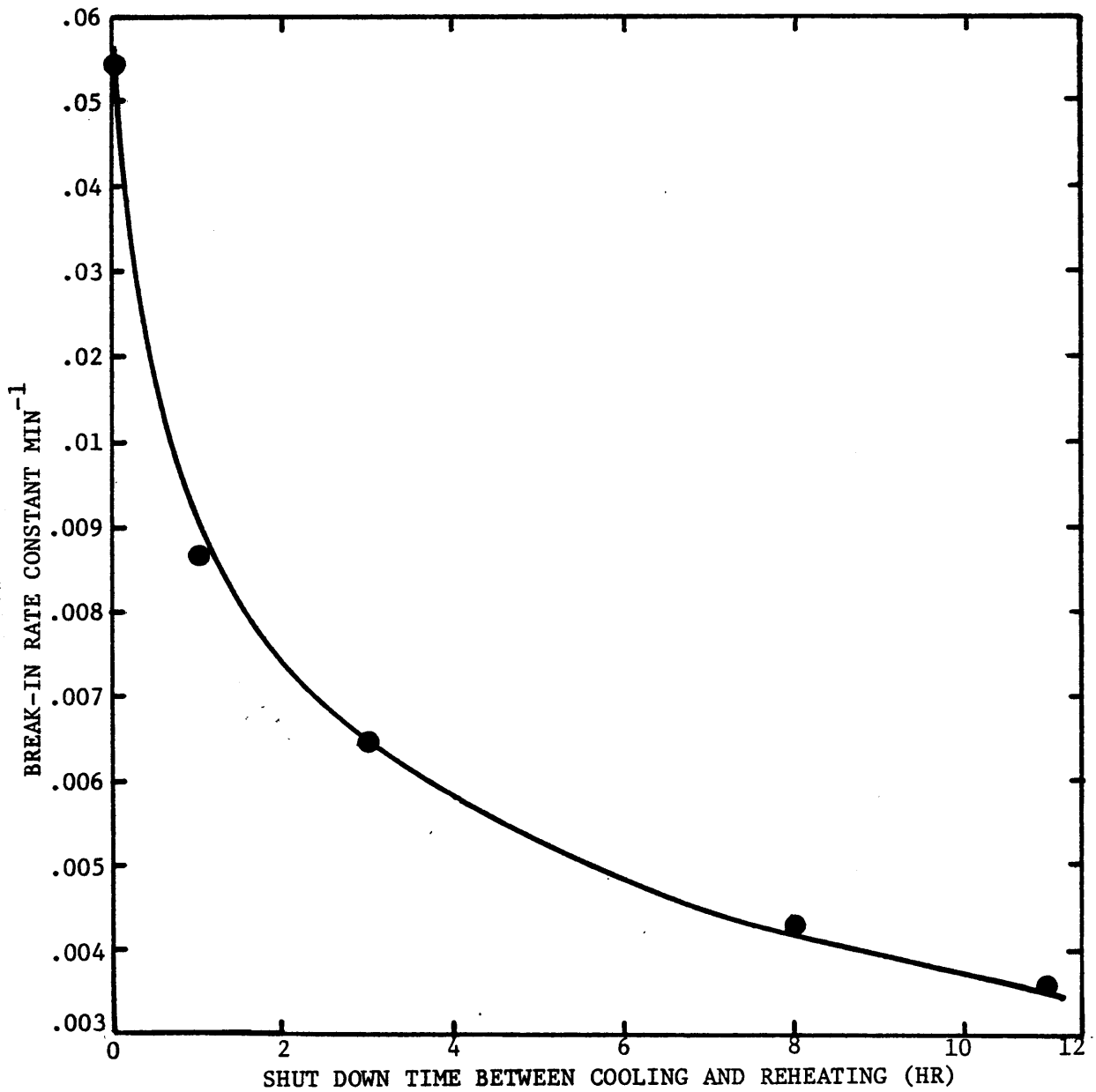


Figure 18. Break-In Rate Constant as a Function of Shut Down Time at 431°C and .94 ATM.

is placed in an inert atmosphere. To determine the reversibility of the break-in in an inert atmosphere, and the mechanism of decay in activity in an inert atmosphere, a freshly activated catalyst was first brought to steady-state activity at 429°C and 0.94 atm. After reaching steady-state, the propylene flow was stopped and the fully activated catalyst was purged with dry helium for 5 and then 30 minutes at 429°C. Following each purge with helium, the propylene flow was reintroduced. Figure 19 illustrates the effects of the 5 and 30 minute helium purges on the initial activities displayed by these catalysts upon reintroduction of propylene. Shown for comparison is the break-in of a freshly activated catalyst.

It will be noted that the initial activities of these catalysts, upon reintroduction of the propylene, were reduced by some 80% from the steady-state activity. The catalyst, however, returned to steady-state at a rate and order of magnitude greater than that for a freshly activated catalyst. To determine whether or not the decay of activity upon purging with an inert was a function of the reactor pressure, a fully activated catalyst was again purged with helium for 5 and then 10 minutes at 429°C but at 3 atmospheres rather than at 0.94 atmospheres. Figure 20 illustrates the break-in behavior of the catalyst after purging, and again, for comparison, the break-in behavior of a freshly activated catalyst is shown. It will be noted that even though the rate of approach to steady-state activity after purging at high pressure is faster than that observed for a freshly

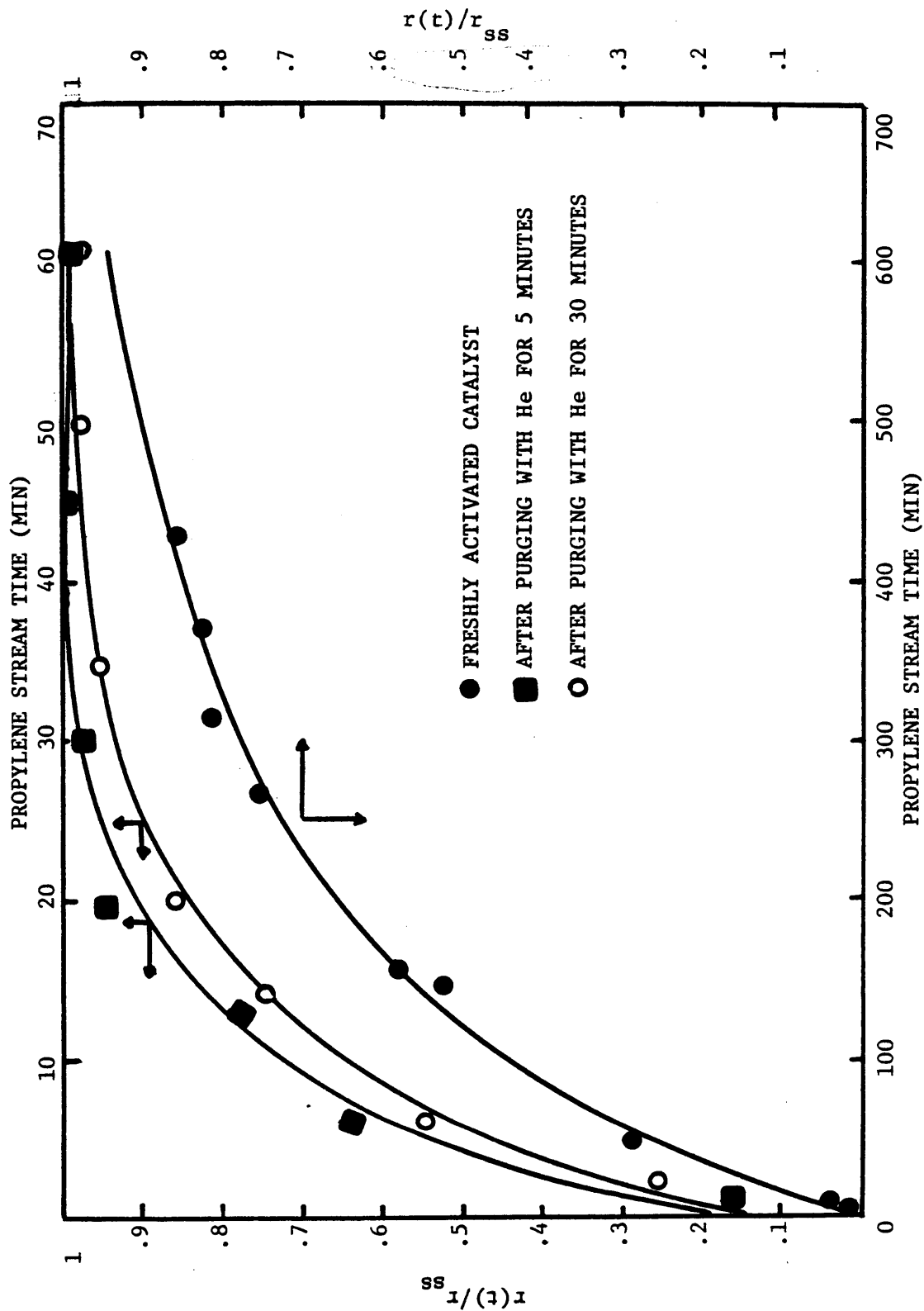


Figure 19. Activity of the Catalyst after Purging with Helium at 429°C and .94 ATM.

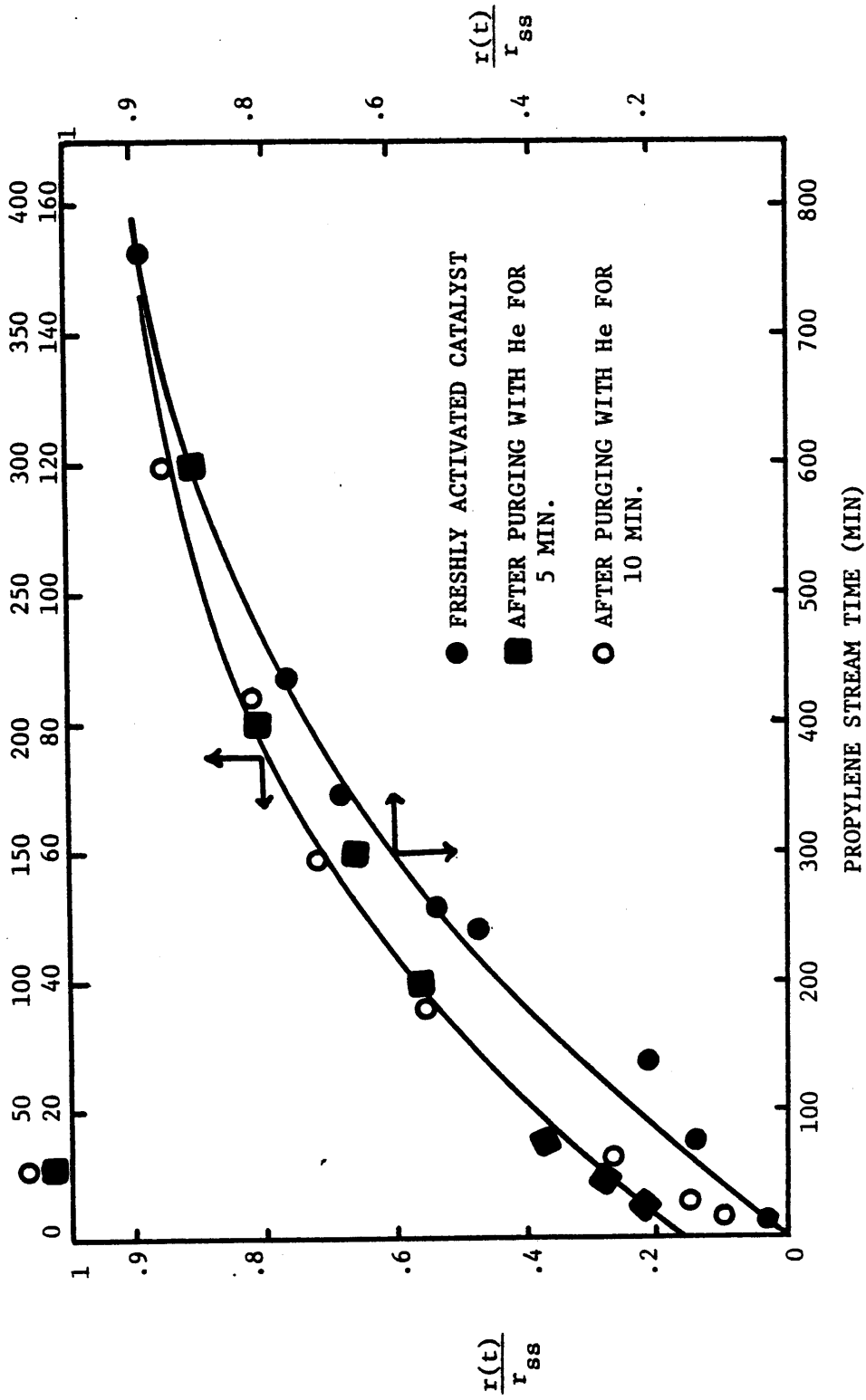


Figure 20. Activity of the Catalyst after Purging with Inert at 429°C and 3 ATM.

activated catalyst, it is much slower than that observed at the lower pressure of 0.94 atmospheres. Thus, the decay of steady-state activity upon purging is a strong function of the reactor pressure.

Tests were conducted to determine if the decay of steady-state catalyst during purging was a function of temperature. Figure 21 contains the variation in approach to steady-state after purging a fully activated catalyst with helium for 10 minutes at 405°C and then at 431°C. Figure 22 contains the variation in the rate of propylene disproportionation with time correlated by equation 7 after purging with helium. It can be observed that the deactivation of the catalyst during purging is not a strong function of temperature. Assuming an Arrhenius type of correlation for the rate constant of catalyst break-in after purging, an activation energy of 6300 calories per gram mole was calculated.

To determine how the break-in rate was related to the length of the purging, a fully activated catalyst was purged with helium for 5, 270, and 720 minutes at 452°C and 0.94 atm. Figure 23 illustrates the effects of purging a fully activated catalyst for the different lengths of time at 452°C and compares the ensuing break-in with that of a freshly activated catalyst. It can be observed that the break-in rate constant decreases with increasing purging time. Table VIII contains additional data on these tests and the break-in rate constants obtained from correlating the data with equation 7.

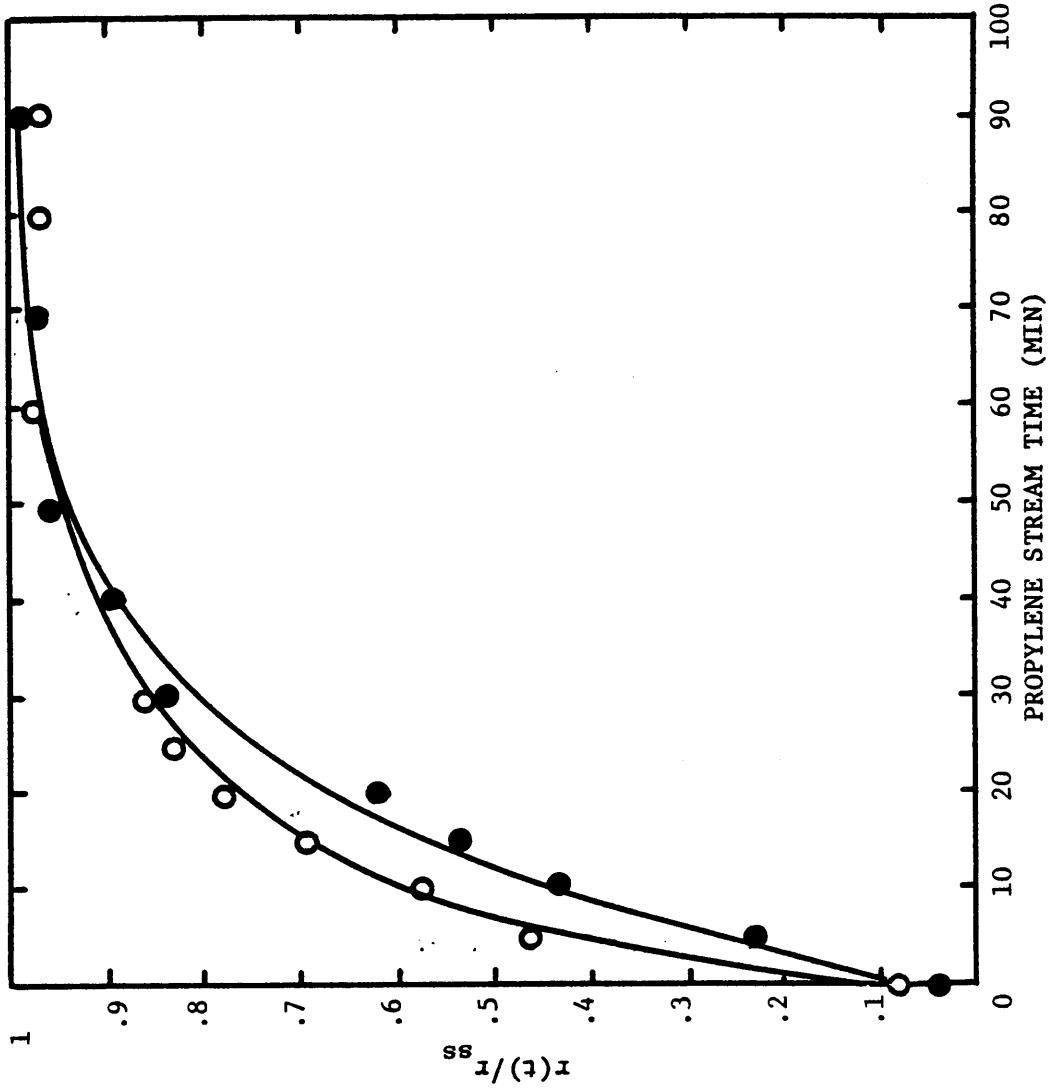


Figure 21. Activity of the Catalyst after Purging with 10 MIN Helium at .94 ATM. (● 405°C, ○ 431°C).

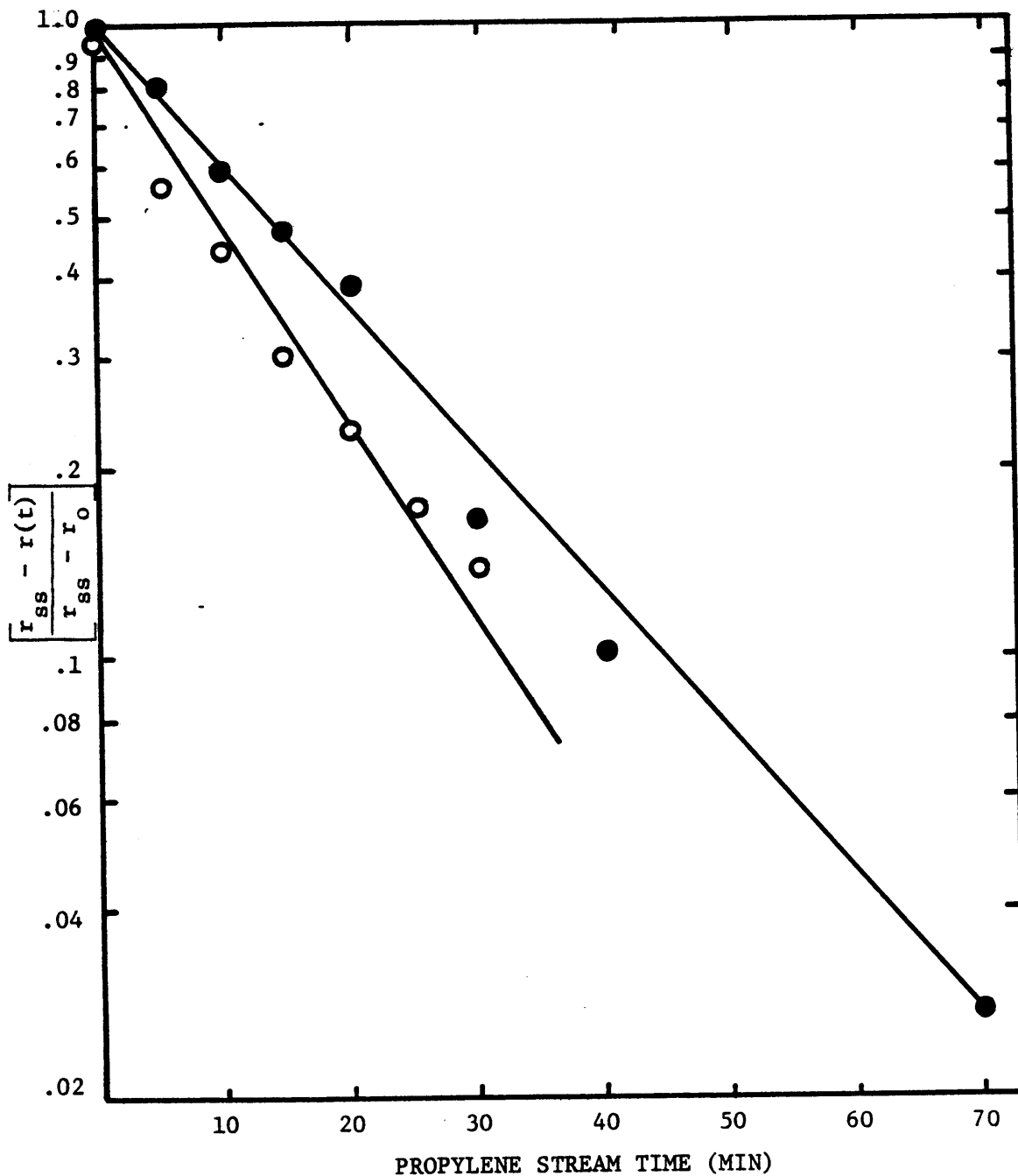


Figure 22. Rate of Fractional Approach to Steady-State at .94 ATM. (● 405°C, ○ 431°C) After Purging with Helium for 10 Minutes.

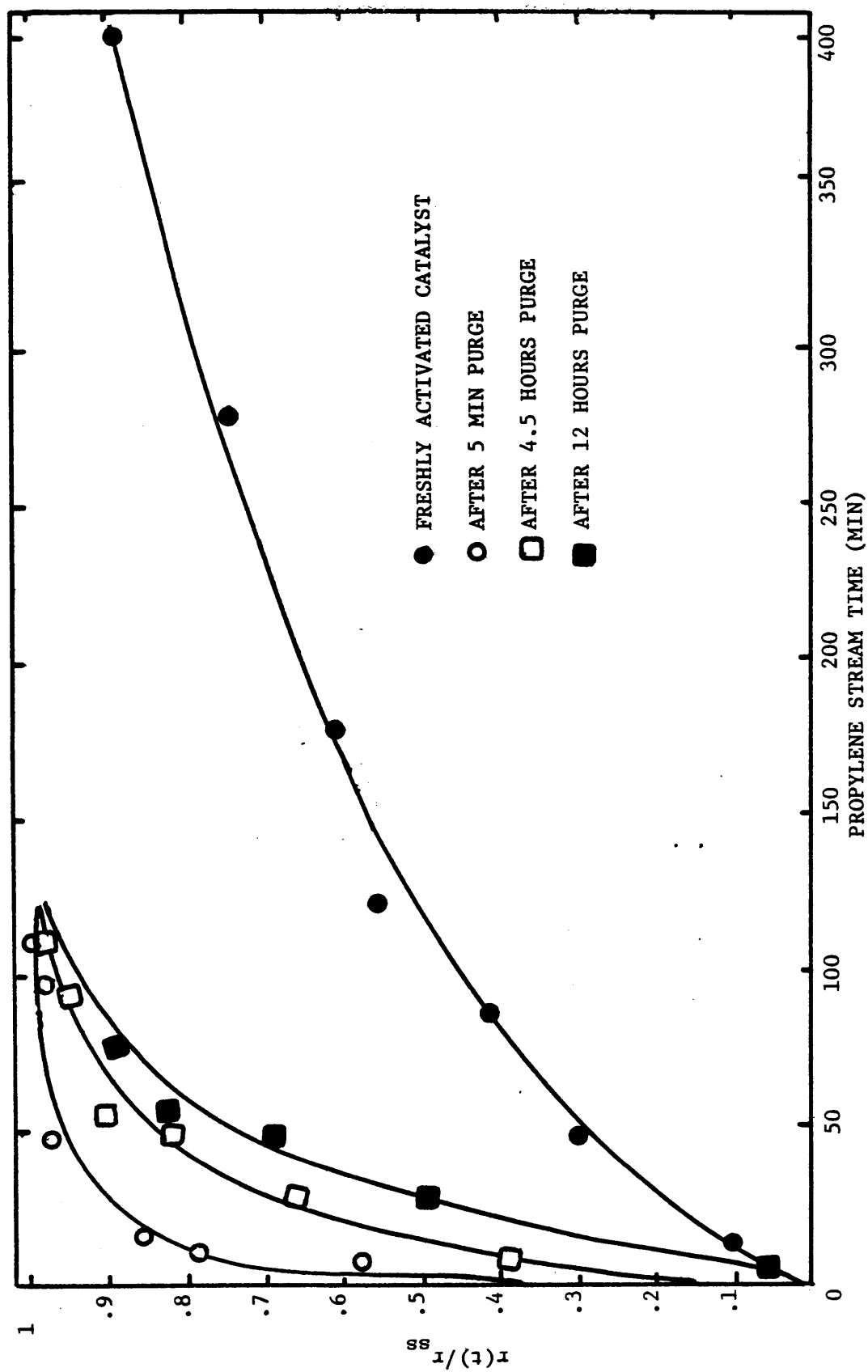


Figure 23. Activity of the Catalyst after Purging with Helium at 452°C and .94 ATM.

Table VIII

W₃ Catalyst Activity and Break-in Rate Constant During Propylene
Disproportionation in Purging with Helium

T = 452°C

P = .94 atm.

WHSV = 78

Catalyst Wt. = 3 grams

Experimental Condition	Steady-state conversion of propylene	Initial Rxn rate $\frac{\text{g moles}}{\text{gm cat-hr}}$	Steady-state Rxn rate	Break-in rate constant min^{-1}
Freshly activated catalyst	.157	0	.291	.00523
After 5 min. He purge	.181	.0408	.336	.0795
After 10 min. He purge	.181	.0408	.336	.0614
After 4.5 hours He purge	.186	.037	.346	.0348
After 8 hours He purge	.186	.037	.346	.033
After 12 hours He purge	.166	0	.308	.0333

Tests were conducted to determine the extent of decay of activity during purging at room temperature. After establishing steady-state activity using sample of a fresh catalyst, propylene flow was replaced with helium and then the reactor was allowed to cool to room temperature. After cooling, it was immediately reheated. After reaching the reaction temperature of 452°C , the helium flow was replaced with propylene and the extent of the reaction was determined periodically until steady-state activity was reached. The cooling and reheating experiments were repeated with the difference that, instead of reheating immediately after cooling, the reactor was held at room temperature for 5, 8, and 12 hours with helium flow maintained. At the end of each shut down period, the reactor was reheated to reaction temperature. Figure 24 illustrates the break-in behavior of the catalyst after cooling and reheating. Table IX contains additional data about these tests. It can be noted that the deactivation processes is slow at room temperature. Regardless of the length of the purging time, the rate of approach to steady-state activity remains about constant. Figure 25 illustrates the break-in rate constant versus length of helium purge time at 452°C and 25°C . It appears that the same processes are responsible for deactivation of the catalyst at reaction temperature and at room temperature with a major difference that the processes are more faster at higher temperatures. Furthermore, the major portion of the deactivation is taking place during a short time at the beginning of the purging. It should be noted that 0 hours

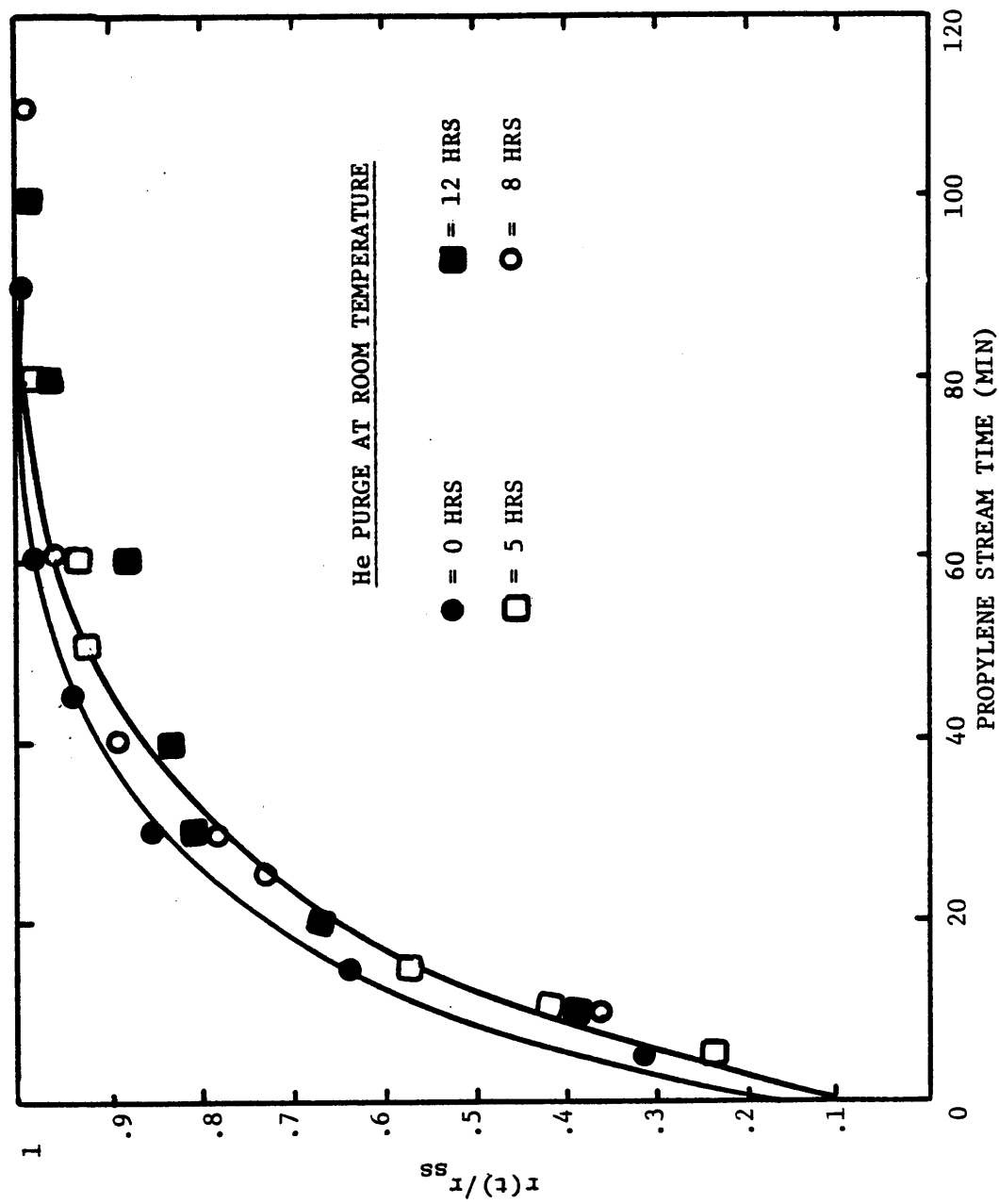


Figure 24. Activity of the Catalyst after Purging with He at Room Temperature and .94 ATM.

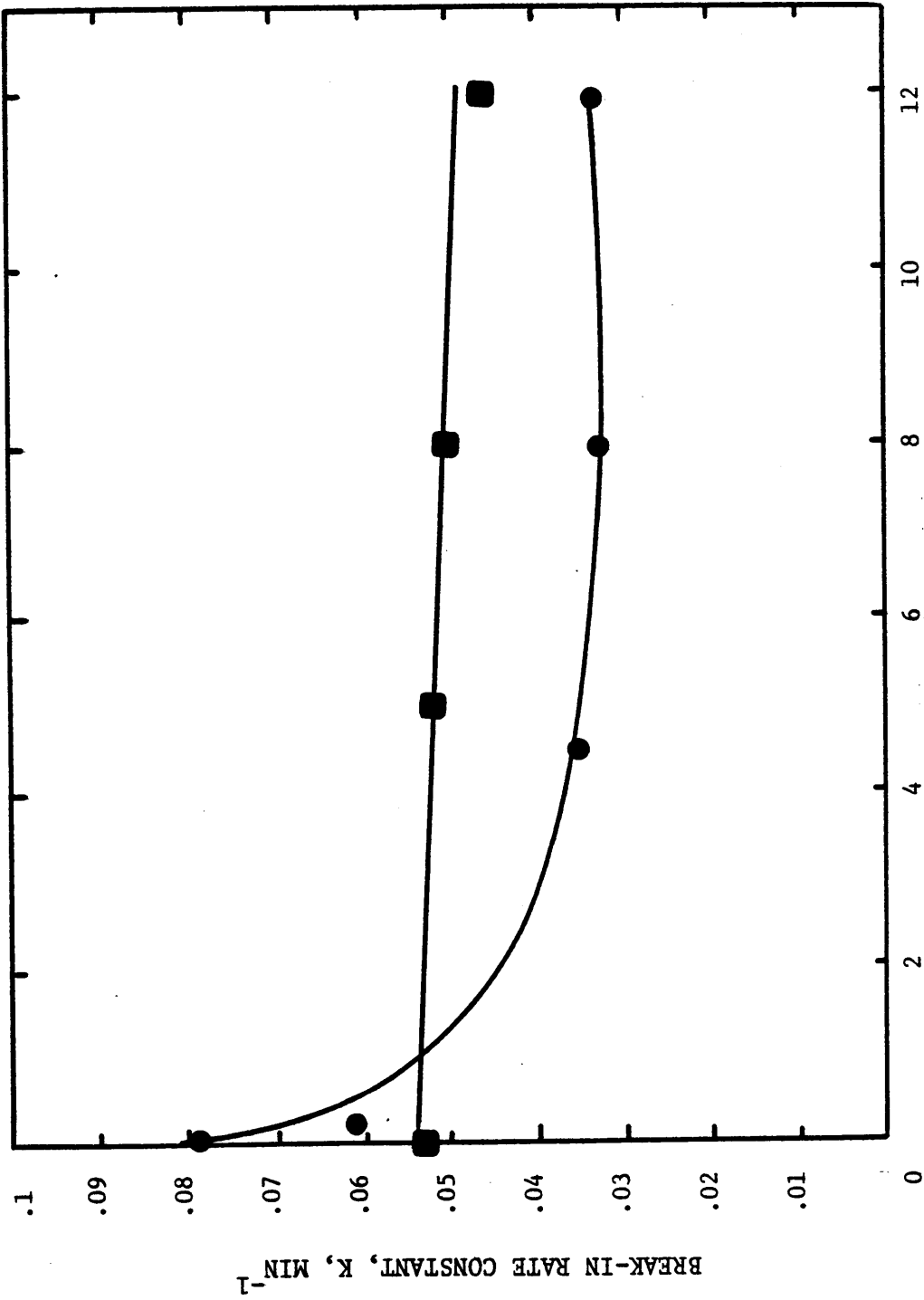


Figure 25. Length of Helium Purge Hours (● at 452°C and .94 ATM., ■ at 25°C and .94 ATM.).

Table IX

W_3 Catalyst Activity and Break-in Rate Constant During Propylene
Disproportionation in Purging with Helium at 25 C

T = 452°C P = .94 atm.
WHSV = 78 Catalyst Wt. = .3 grams

Experimental Condition	Steady-state conversion of propylene	Initial Rxn rate $\frac{\text{g moles}}{\text{g cat-hr}}$	Steady-state Rxn rate	Break-in rate constant $\frac{-1}{\text{min}}$
Freshly activated catalyst	.157	0	.291	.00523
After 0 hour purge with He	.18	.037	.345	.05345
After 5 hours purge with He at 25°C	.1616	.037	.300	.05255
After 8 hours purge with He at 25°C	.164	.037	.304	.0502
After 12 hours purge with He at 25°C	.159	.037	.295	.0451

of purging at 25°C includes about 1 hour of purging with helium during the cooling/reheating time.

Effect of a Small Amount of Propylene in the Helium Purging Gas. To determine the role of a small amount of propylene in the helium purging gas on the subsequent catalyst activity, a mixture consisting of 1.5% propylene and 98.5% helium was prepared. After establishing steady-state activity, the fully activated catalyst was purged for 10 minutes with the mixture at the reaction temperature of 421°C. Even though the mixture was accurately prepared, there existed uncertainty as to the percentage of propylene in the mixture as it reached to the reactor after passing through a drier which was previously saturated with propylene. It was noted that when pure helium was passed through the drier, the effluent gases from the drier contained small amounts of propylene.

Other tests were conducted to determine if the presence of a small amount of reducing gas would hinder those processes which are deactivating the catalyst during purging. For this purpose a fully activated catalyst was purged for 10 minutes with a mixture which consisted of 98% helium and 2% hydrogen. Figure 26 illustrates the rates of approach to steady-state when a fully activated catalyst was purged with a mixture of helium and 2% hydrogen, 98.5% helium and 1.5% propylene, and pure helium. It will be noted that the presence of a small quantity of propylene in the purging gas greatly hinders the deactivation processes. On the other hand, the presence of 2%

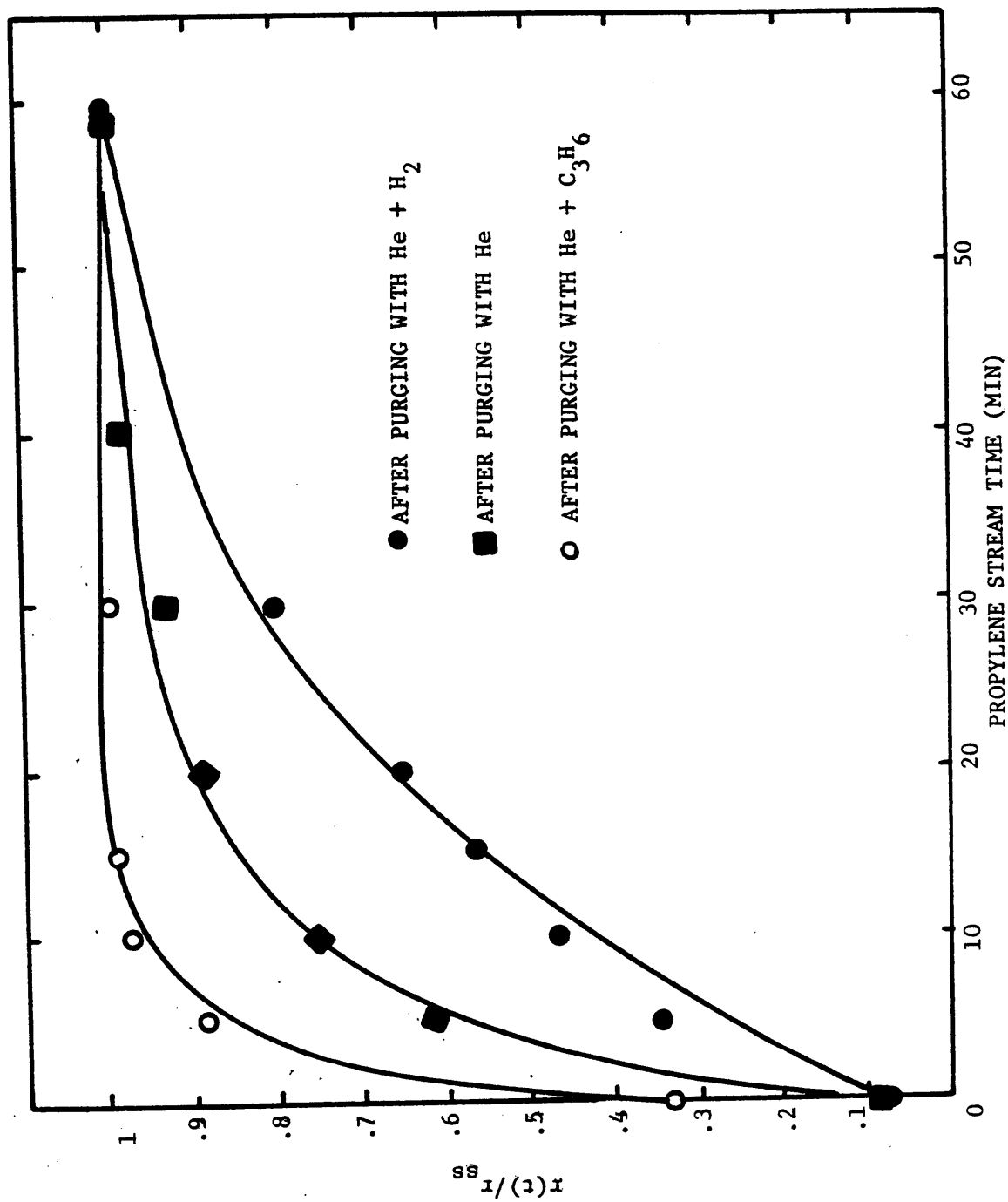


Figure 26. Activity of the Catalyst after Purging with Mixtures at 421°C and .94 ATM.

hydrogen increases the rate of deactivation. Appendix B contains the tabulated results of these runs.

Characterization of the Effect of Ammonia on the Activity of the

Catalyst. It was mentioned earlier that the addition of a small amount of ammonia, either during break-in or at steady-state, drastically enhances the rate of propylene disproportionation. To explain such dramatic effects, the disproportionation reaction was studied using a sample of catalyst that was activated according to the normal procedure at 450°C and 0.94 atm. The same sample of catalyst was exposed to the ammonia gas for 90 minutes, following the normal activation procedure, but before cooling the reactor to the reaction temperature. After stabilizing the reaction temperature, the propylene disproportionation reaction was studied using this pre-treated catalyst.

In another experiment, after activation of the catalyst and cooling the reactor to the reaction temperature of 430°C, the catalyst was exposed to 30 minutes of ammonia at 430°C before introducing propylene. Figures 27 and 28 illustrate the effects of the pretreatments of the catalyst at activation and reaction temperature, respectively. It will be noted that these treatments leave the catalyst nearly inactive for the disproportionation reaction.

A test was conducted to study the relaxation of the catalyst activity in an ammonia atmosphere. For this purpose, a sample of freshly activated catalyst was brought to steady-state activity and then the propylene flow was replaced with ammonia without altering

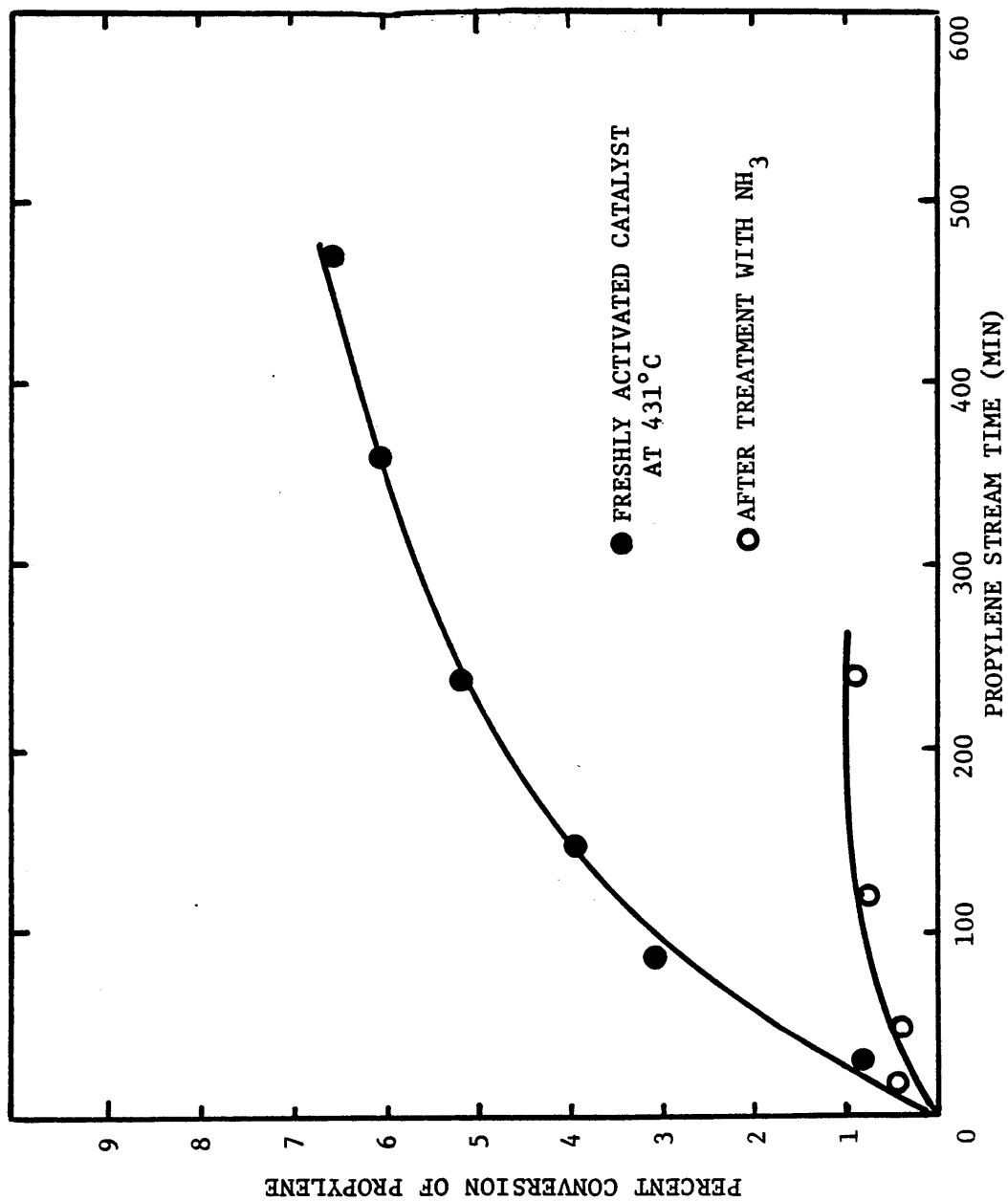


Figure 27. Effect on Activity of Pretreatment of the Catalyst at 430°C with Ammonia for 30 Minutes.

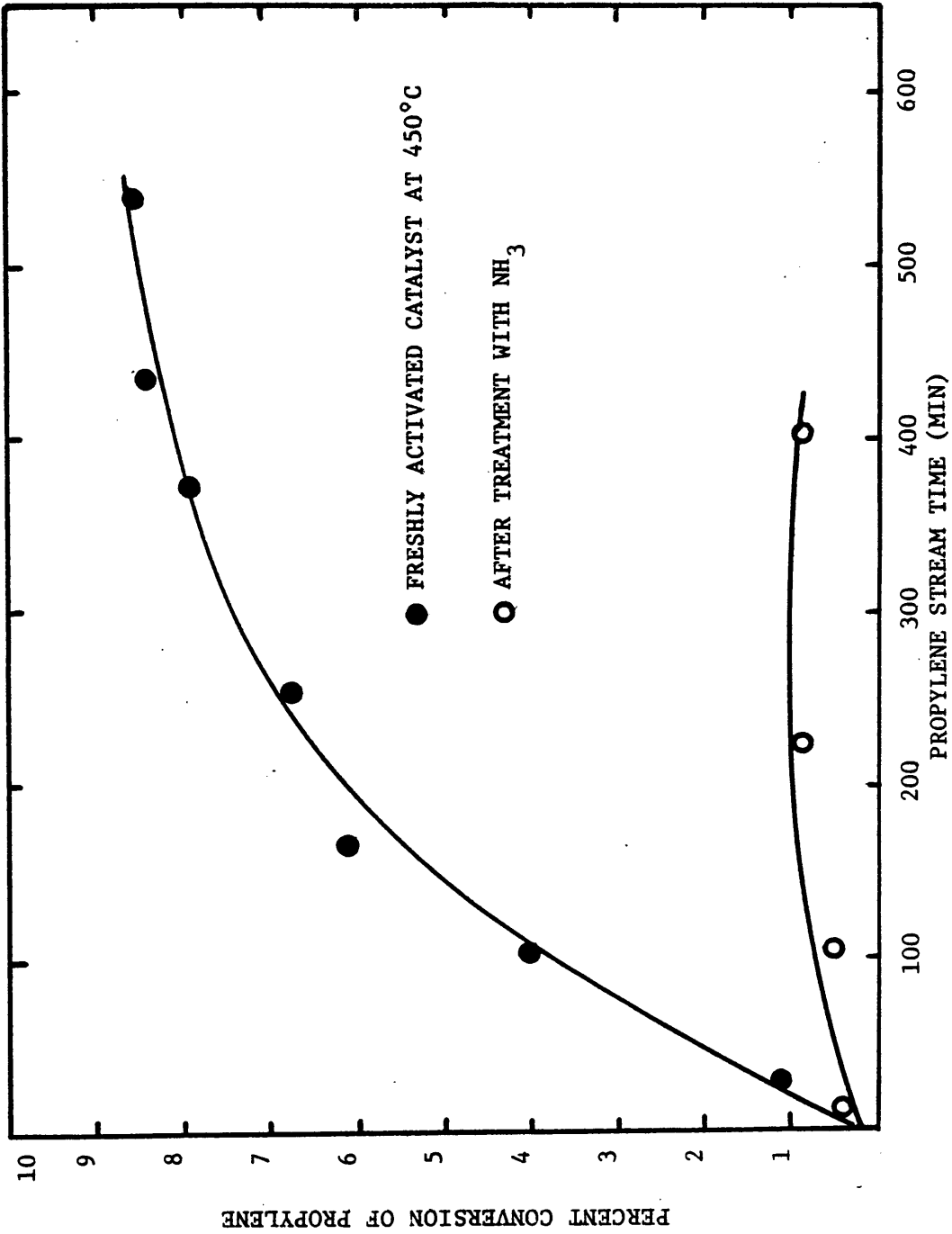


Figure 28. Effect on Activity of Pretreatment of the Catalyst at 590°C with Ammonia for 90 Minutes.

any other experimental conditions. At the end of 10 minutes, the propylene flow was reintroduced and the rate of reaction was measured. Figure 29 contains the variation in the activity of the catalyst after purging with ammonia for 10 minutes. It can be observed that in the first few minutes of propylene contact, the catalyst reaches a maximum activity that is some 45% greater than the original steady-state activity. However, the activity declines with increasing contact time and returns to the original steady-state value. In a different experiment, a small quantity of ammonia was dosed into the propylene feed. For this experiment, a gas sampling valve was placed in the propylene feed line and the dosing gas was placed in the sample loop of 13 ml. Upon activating the valve, the dosing gas was introduced into the propylene feed as a square wave pulse. Figure 30 illustrates the activity of the catalyst after pulsing with ammonia. A rapid and dramatic, though temporary, increase is seen immediately following ammonia injection.

Effects of a Small Amount of Ammonia in the Feed. A test was conducted to determine the effects on break-in of a small amount of ammonia in the feed. For this study, a sample of catalyst was activated according to the normal procedure and the propylene disproportionation reaction was studied using a mixture consisting of 98.5% propylene and 1.5% ammonia at 430°C and .94 atm. Periodically, the extent of the reaction was measured until a steady-state activity was reached; at this time the feed was changed to 100% propylene and the conversion

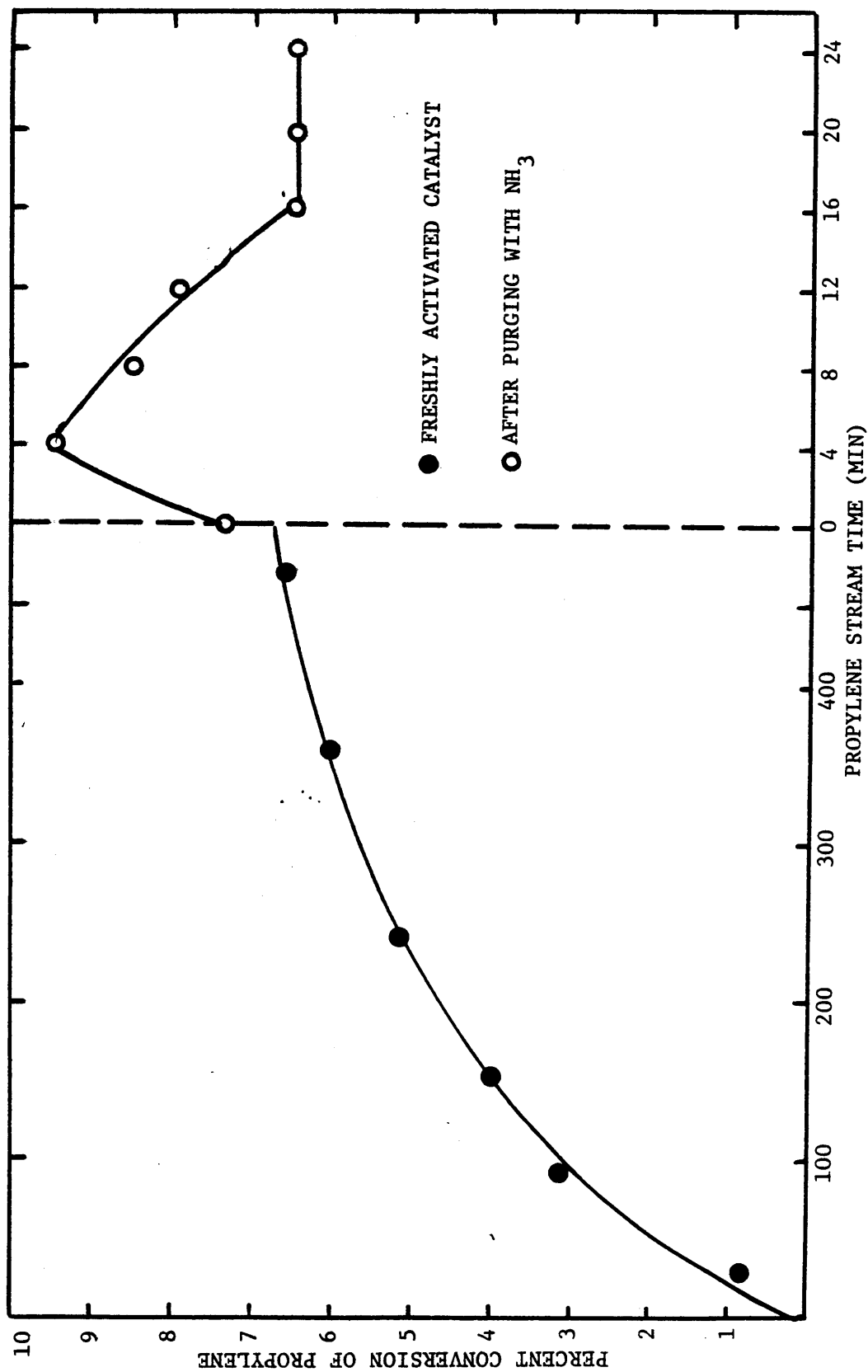


Figure 29. Effect of Purging a Fully Broken-In Catalyst with NH_3 for 10 Minutes at 430°C and $.94\text{ ATM}$.

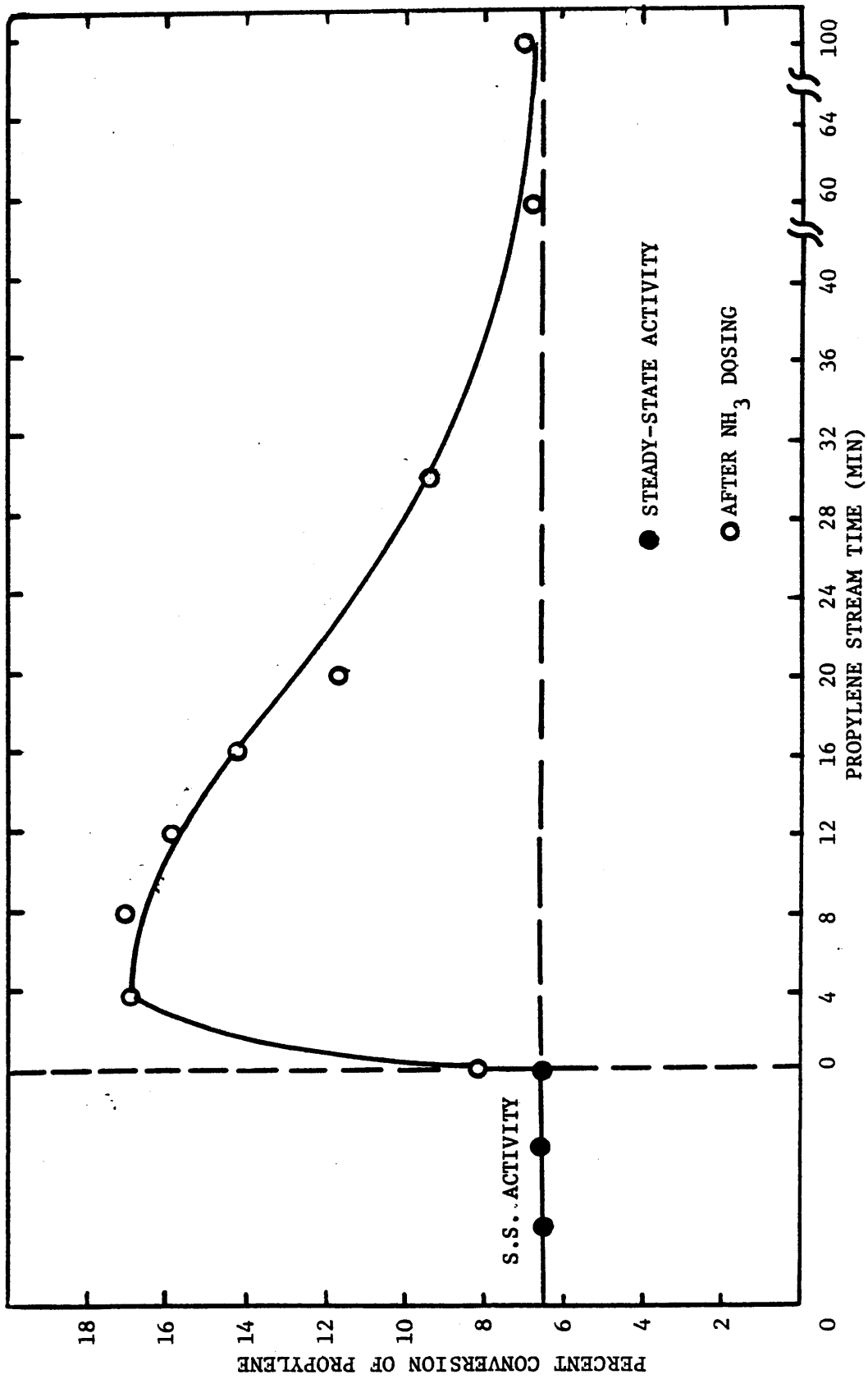


Figure 30. The Effect of NH₃ Dosing on Catalytic Activity with a Fully Broken-In Catalyst at 430°C and .94 ATM.

was measured until the catalyst reached full activity. After the catalyst reached steady-state activity with 100% propylene, the mixture was introduced to the reactor, and the rate of disproportionation was measured. Figure 31 illustrates the results of these investigations. It will be seen that by the addition of 1.5% NH_3 to the feed, the break-in period was drastically decreased, and the level of steady-state conversion increased some 150% over that for pure propylene. However, the break-in behavior and the steady-state conversion resumed normal behavior upon changing the feed to 100% propylene. Switching the feed from pure propylene to the mixture resulted in a rapid and dramatic increase in the activity and in a new level of steady-state conversion that was significantly higher than the previous steady-state conversion. Appendix B contains the tabulated results of these runs.

Effect of a Magnesium Oxide Bed in the Feed Line on the Break-in Behavior of the Catalyst. It was reported (62) that addition of a magnesium oxide bed to the feed line improves propylene disproportionation reaction in some systems for an unexplained reason. To determine if the addition of such bed to the feed line has any effect on the conversion, the propylene disproportionation reaction was studied in a system with a magnesium oxide bed and without such a bed. In the first experiment, after activating .4 grams of catalyst, the reactor temperature was set at 421°C and the propylene was introduced at a flow rate of 3.5 cc/sec. Periodically the extent of the reaction was determined through chromatographic analysis until

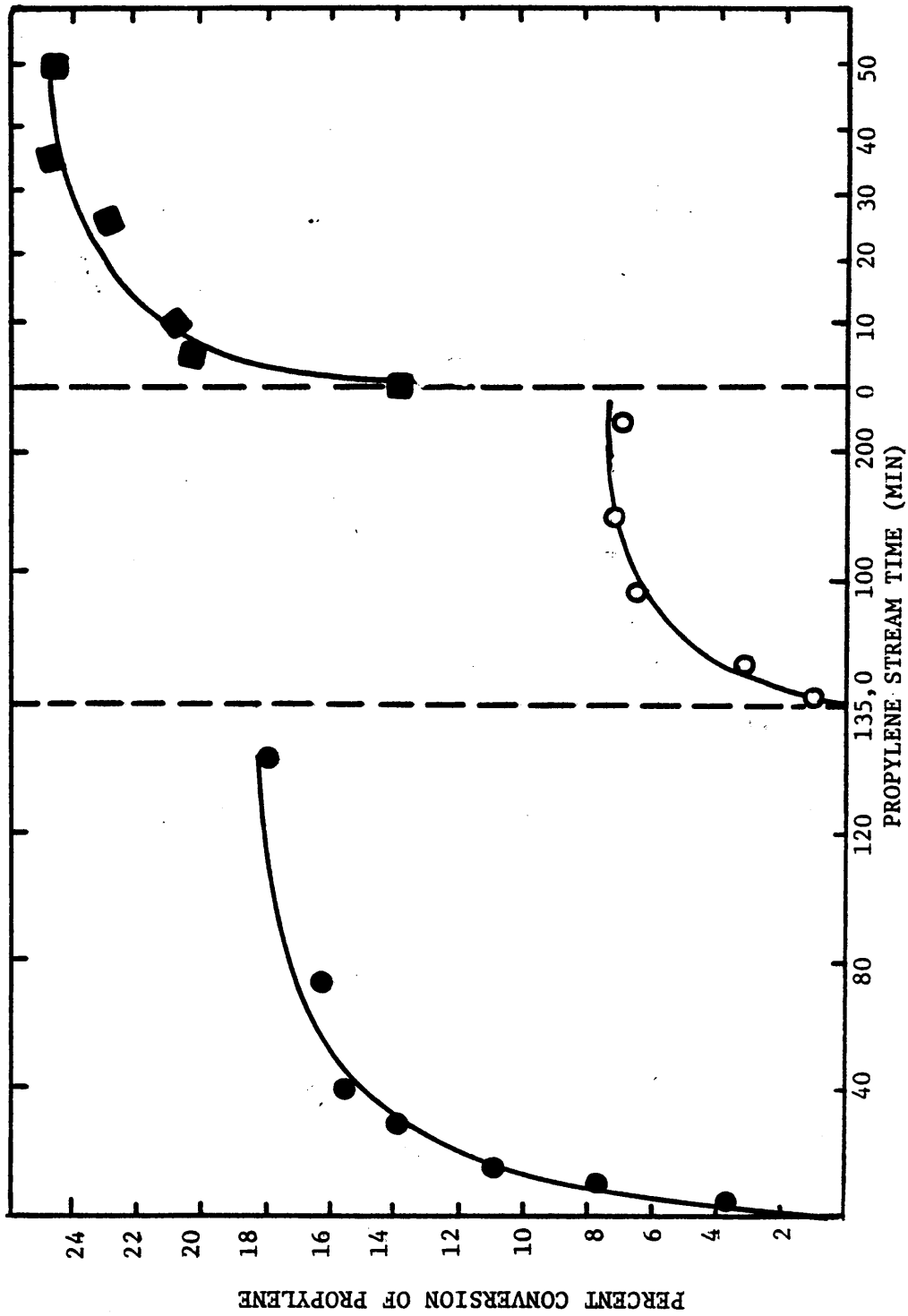


Figure 31. Break-In Behavior of the Catalyst at 430°C and .94 ATM.
 (● 98.5% C₃H₆ + 1.5% NH₃, ○ 100% C₃H₆, ■ 98.5% C₃H₆ + 1.5% NH₃).

steady-state activity was reached. In this experiment propylene was fed to the reactor after passing through a flow controller and a dryer. In the second experiment the same catalyst bed was activated, and after establishing all the experiment conditions to the same as in the previous experiment, propylene was fed to the reactor after passing through a flow controller, a dryer, and a magnesium oxide bed which was placed on the top of the reactor. Periodically, the extent of the reaction was determined for this system. Figure 32 illustrates the results of these two experiments. As can be seen from this figure, the presence of a magnesium oxide bed in the feed line does not improve the reaction rate in this system. The magnesium oxide bed was constructed from a 10 inch long copper tube of 1/4 inch diameter, inside of the tube was packed with stainless steel wire gauze and then the magnesium oxide, in powder form, was used to fill the void spaces in the tube. Stainless steel gauze was used in packing the tube to reduce the pressure drop across the bed. The magnesium oxide bed was activated for two hours at 300°C while passing dry nitrogen over it. Appendix B contains the tabulated results of these runs.

Sample Calculations

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

Reduction of Chromatographic Analysis Data. The peak height and the peak half width were measured for each component from the recorded

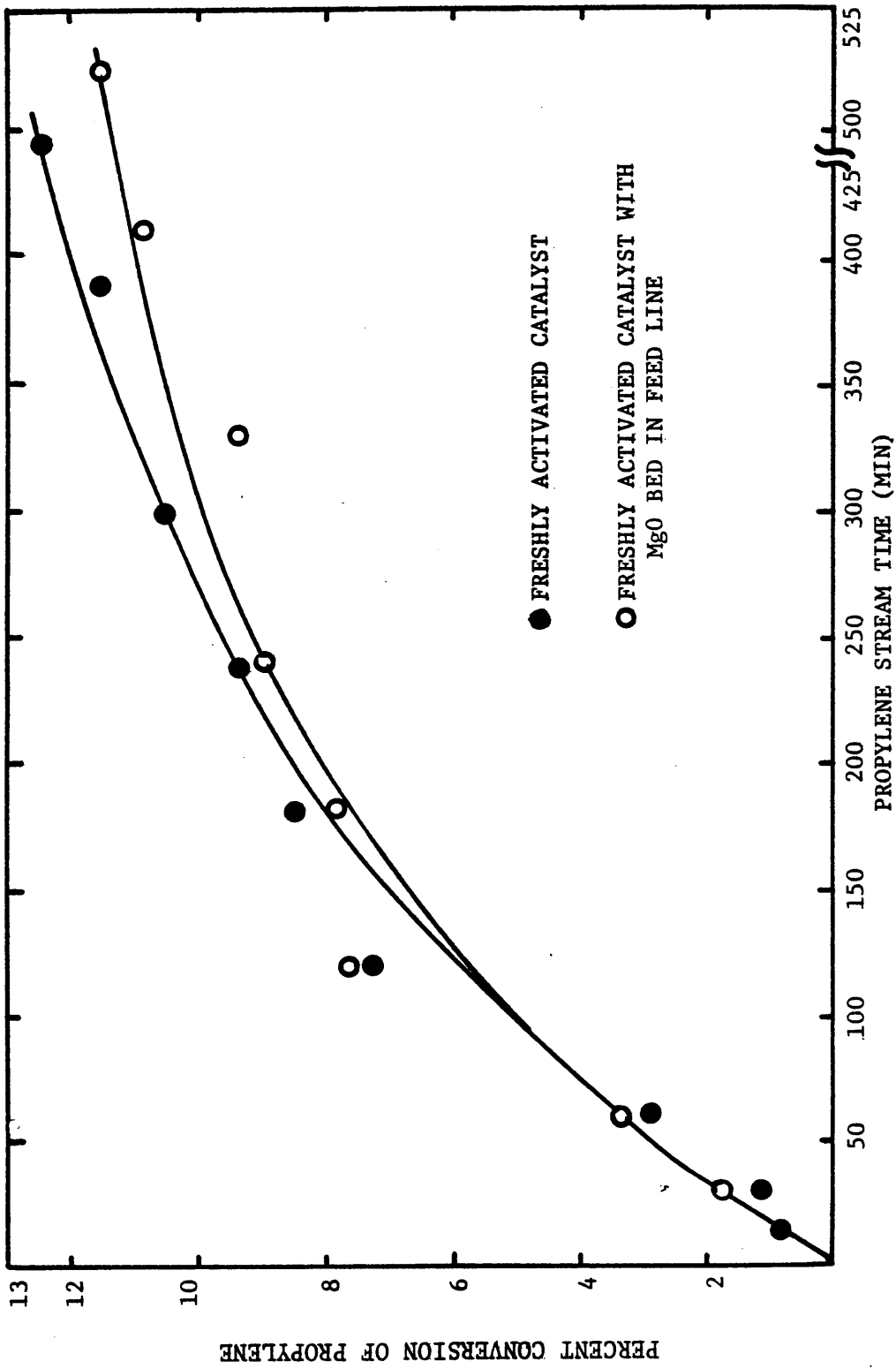


Figure 32. Break-In Behavior of the Catalyst at 421°C and .94 ATM.

chromatographic analysis of a sample. These data, plus the range and attenuation used to record each peak, together with the detector calibration factor reported by Luckner (31), were used to calculate the moles of the three components that existed in the product gases (ethylene, propylene, and 2-butene) according to the relationship

$$M_i = \beta_i h_i \Omega_i A_i R_i \quad (8)$$

where

M_i = moles of component "i"

β_i = detector calibration factor for component i

A_i = recorder attenuation used to record the detector response to component i

h_i = height of the peak for component i

Ω_i = width of the peak at half height

R_i = recorder range used to reach the detector response for component i

Equation 8 can be deduced from the fact that the flame ionization detector has an output which is proportional to the number of moles of a particular compound being ionized. Mathematically speaking this is

$$M_i = \beta_i A_i \quad (9)$$

where

M_i = number of moles of component i in the sample

A_i = area of detector response to component i

β_i = proportionality factor for component i

Conversion Calculations. Using the definition of conversion given by Levenspiel (29), "conversion X_A of given reactant A is defined as the fraction of reactant converted into products" or

$$X_A = \frac{N_{A_0} - N_A}{N_{A_0}} \quad (10)$$

where

X_A = conversion of propylene

N_{A_0} = initial moles of propylene

N_A = final moles of propylene

N_{A_0} was calculated by adding the product of the peak and ionization factors of each gas (ethylene, propylene, 2-butene). N_A was calculated by subtracting the product of the peak area and the ionization factor of ethylene and 2-butene from N_{A_0} .

Reactant Feed Rate Calculations. Reactant feed rates were calculated from the experimentally measured flows using a bubble meter, and were expressed in terms of flow per gram of catalyst charge. The calculation was carried out according to the definition of "weight hourly space velocity" (WHSV).

$$\text{WHSV} = \frac{\dot{m}}{W}, \text{ where } \dot{m} = \text{mass flow rate of propylene}$$

W = weight of catalyst charged

using the gas law,

$$PV = ZnRT \text{ where } n = \frac{m}{M} \text{ so } \dot{m} = \frac{PV}{ZRT} \times M \text{ now}$$

$$\text{WHSV} = \left(\frac{PV}{ZRT}\right) \left(\frac{1}{W}\right) (C) (M) \quad (11)$$

where

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

V = volumetric flow rate of product gas, cm^3/hr , measured by bubble flow meter

M = molecular weight of product gas

Z = compressibility factor of product gas

$R = 82.06 \frac{\text{cm}^3 \text{ atm.}}{\text{gm. mole } ^\circ\text{K}}$

T = temperature at which flow rate was experimentally measured, $^\circ\text{K}$

C = a constant which corrects the experimentally measured flow rate

When the bubble flow meter is used to measure the flow rate, the gas is passed through water. As a result, the measured flow contains some water vapor. From the mole fraction of water vapor in the mixture one can calculate the value of C.

Reaction Rate Calculations. Propylene reaction rates were calculated in each run according to the relationship

$$r = \left[\frac{\text{WHSV}}{42.08 \frac{\text{gm. C}_3\text{H}_6}{\text{g. mole C}_3\text{H}_6}} \right] [X] \quad (12)$$

where

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

X = observed fractional conversion of C_3H_6

IV. Discussion

Discussion of Literature

Since the discovery of tungsten-oxide-on-silica gel as an active catalyst for olefin disproportionation by Heckelsberg and Banks (21), a number of experimentalists have given considerable attention to this heterogeneous catalytic reaction system. Most of these research studies have been directed towards understanding the following three fundamental subjects:

- a. mechanism of propylene disproportionation over the tungsten oxide on silica catalyst;
- b. anomalous mass transfer effects exhibited by this catalyst;
- c. the break-in period, a rather protracted period of transient catalyst activity that occurs on the contacting of a freshly activated catalyst with propylene.

Mechanism and Kinetics of Reaction. From conversion of n-butene into olefins of lower and higher carbon number on catalysts containing cobalt molybdenum and aluminum oxides, Bradshaw and coworkers (7) concluded that the disproportionation reaction must proceed via a "quasi-cyclobutane" intermediate. Clark and Cook (11) performed experiments [1-¹⁴C] propylene and [3-¹⁴C] propylene and found that no double bond migrations occurred during the course of reaction. They also obtained reaction products that supported the four-center reaction mechanism. Contrary to the Clark and Cook conclusion,

Woody et al. (57) have reported in the disproportionation of [1- ^{14}C] propylene that a large amount of the ^{14}C was found in the ethylene, but about one-third of the isotope was found in 2-butene. This experimental result implies migration of the propylene double bond. Thus, there exists a discrepancy between these results; this discrepancy may be attributed to the difference in experimental procedures and conditions. For example, the study by Woody and coworkers was performed at a higher temperature than that by Clark and coworkers (11). Further support of the adequacy of the four-center mechanism has been reported by Mol and coworkers (39). Although there have been abundant data for a four-center mechanism in olefin disproportionation, it is not at all clear how the olefin molecules are arranged with respect to the metal atom. Pennella and Banks (43) have proposed that within the concept of a four-center mechanism, the role of metal is mainly that of providing a suitable framework for the transfer of electron from the Π orbitals of the reactant olefins to their antibonding Π^* -orbitals from which the incipient σ bonds of the product molecules are formed.

The kinetics of propylene disproportionation over tungsten oxide on silica catalyst and cobalt-molybdate-alumina catalysts has been studied by several authors. Begley and Wilson (5) have reported that the results of their kinetic investigation of propylene disproportionation over a tungsten oxide catalyst indicates that the reaction mechanism to be of a Rideal-Ely type. This mechanism requires only one of the reacting molecules to be chemically adsorbed while the

other molecule is either physically adsorbed or is in the gas phase.

Luckner (31) has studied propylene disproportionation over a tungsten oxide on silica catalyst at temperatures ranging from 399°C to 450°C and pressure up to 9 atmospheres and he has reported that the results of his kinetic investigation indicates that the mechanism to be a Langmuir Hinshelwood Model. In this model both molecules are chemically adsorbed on the surface. Hattikudur and coworkers (20) have supported Luckner's conclusion by studying propylene disproportionation over a tungsten oxide catalyst at temperatures ranging from 650°F to 850°F and pressures up to 1000 psi. This discrepancy in the literature data can be attributed to two reasons: first, the discrimination made by Begley and Wilson was based upon integral data, and such data would be expected to be less sensitive to the reaction model than the near-differential data of the others due to the integration process inherent in integral data. Secondly, severe interphase mass transfer effects were present in the Begley and Wilson data and this casts doubt on the Rideal model.

Recently another possible model has been considered by van Rijn and coworkers (54). In this study they have correlated the data from the literature to a carbene mechanism. In this mechanism there is a chain reaction but not a bimolecular surface step. They have demonstrated that the experimental literature data can be correlated as well, or even better, through models other than Langmuir Hinshelwood, namely through mechanisms in which only one metal atom is involved in

the actual disproportionation step. Although they have failed to draw definite conclusion concerning the reaction mechanisms, from considerations about the parameters value for several models, they concluded that there exists a preference for the carbene mechanism. Disagreements in the kinetic models suggests that the derivation of reaction rate expressions in a classical way may be acceptable for chemical engineering purposes, but it does not necessarily give an adequate description of the real chemical reaction mechanism. In other words, one must be careful in drawing conclusions from model discrimination, because the best model obtained may not really be the best model if not all possible models were taken into account.

Mass Transfer Effects in Propylene Disproportionation. Moffat et al. (35) have reported that the mass transfer effects existed in propylene disproportionation over tungsten oxide on silica catalyst in spite of the fact that calculations made on the basis of generalized equations for diffusion predicts no limitation in the reaction rate. In this study they found an increase in catalyst efficiency with increasing flow rate which clearly indicates a mass transfer or interphase diffusional effect. A study by Fletcher (15) has revealed that when the flow rate is decreased below a critical value, there is a dramatic reduction in activity with decreasing flow rate. The activity appears to fall to a near zero value even though the corresponding conversion levels are far below equilibrium values. Later Moffat and coworkers (36) reported that interphase mass transfer effects have been observed

in propylene disproportionation with WO_3-SiO_2 catalyst, although calculations based on the external catalyst area predicted little or no mass transfer limitations. These diffusional effects were noted at all levels of conversion. They accounted for this unexpected mass transfer effects by assuming that reaction occurs on a small number of very active sites which are widely separated on the catalyst surface and that the reaction may be limited by site localized diffusion effects which are a function of Reynolds number and WO_3 concentration. Luckner et al. (33) have reported that the interphase mass transfer effects can be eliminated for this system at very high Reynolds numbers. One explanation of why conversion is a function of linear bed velocity at constant space time is that each catalyst particle is surrounded by a gaseous film through which reactants must diffuse to reach the catalyst surface. Increasing the linear velocity decreases this film thickness and thereby decreases the difference between the bulk gas reactants composition and the composition of the external surface of the catalyst. In the limit of sufficiently high velocity, the composition at the particle surface becomes essentially the bulk gas stream composition. Recently it has been suggested that anomalous response of catalyst activity to the flow rate is due to a reversible poison which is introduced into the feed stream ahead of the catalyst bed at a rate independent of the flow rate, thus the partial pressure of the poison decreases with an increase in activity, as the flow rate increases at constant total pressure.

Break-in Behavior of Tungsten Oxide on Silica Catalyst During Propylene

Disproportionation. A third area of anomalous behavior of the tungsten oxide on silica catalyst to which this study directed itself was the rather protracted period of transient catalyst activity which occurs on the contacting of a freshly activated catalyst with propylene. The freshly activated sample of the catalyst has very little or no initial activity. A period of the order of 15 hours is required to achieve full activity once contact with the reactant propylene is instituted. The review of the literature in this area yielded a number of examples of catalyst which exhibited such a transient activity. In fact, this type of phenomenon is so commonly observed that it is rarely reported in the literature. Although there have been several suggestions that what might be the cause of break-in, this phenomenon is not clearly understood. In the case of propylene disproportionation, the length of time involved alone seems to eliminate transport delays or transient in adsorption and desorption as possible explanation of this phenomenon. However, there are some other possible explanations for the transient activity which were put forward in the introduction section. Luckner and Wills (32) have considered the possible explanation of purging of temporary poisons from the catalyst, these poisons being introduced during the activation procedure. Their results indicated that variations in the activation procedure has little effect on the transient activity of this catalyst. This suggests that the purging of a temporary poison from the catalyst during its initial exposure to propylene can not be responsible for the observed transient activity

of the catalyst. The literature contains examples of heterogeneous catalytic reaction systems in which the reduction of the catalyst during the course of the reaction is solely responsible for the transient activity, i.e. the isomerization of n-butene over copper catalyst in which the initial activity period observed is due to the reduction of the catalyst. A change of color from yellow to blue during break-in observed in propylene disproportionation suggests that the reduction of the catalyst from WO_3 to $WO_{2.9}$ might be responsible for the transient activity. The partial reduction of catalyst from WO_3 to $WO_{2.9}$ during break-in has been confirmed by x-ray diffraction (43). This hypothesis has been investigated by reduction of the catalyst prior to the admission of propylene by hydrogen or carbon monoxide (31). This study has shown that although reduction of the catalyst increases the rate of catalyst break-in it does not eliminate it. Reduction of the catalyst surface, while a necessary step in catalyst break-in, does not appear to be only phenomenon involved. It should be mentioned that this study did not rule out the possibility that the transient activity may be determined by the rate at which the surface is being reduced. Pennella et al. (43) have proposed that, if in fact, the reduction plays a direct role in promoting activity it may be needed mainly to form vacant coordination sites on the tungsten by removal of oxygen atoms, or to produce active metal species such as pentavalent tungsten. In a recent study, Kerkhof and coworkers (25) have published that when the WO_3-SiO_2 catalyst was reduced by hydrogen,

immediately after introduction of hydrogen a reduction of WO_3 to $W_{20}O_{58}$ takes place. This is followed by a slower reduction during the first 2000 seconds of the contact with hydrogen. Because WO_3 is known to have a reasonably fast reduction at $873^\circ K$, they have attributed the fast reduction in the beginning to the reduction of crystalline WO_3 and the slow reduction later on to the reduction of difficulty reducible material.

Luckner and Wills (32) have shown that the rate of propylene disproportionation with time during break-in may be represented by,

$$(r_{ss} - r)/(r_{ss} - r_0) = e^{-kt} \quad (7)$$

Although such an expression is an approximation to reality, the approximation is surprisingly good. Equation 7 allows the rate of catalyst break-in to be expressed quantitatively. The rate constant of catalyst break-in, k , may be obtained from the slope of a plot of the logarithm of the fractional approach to steady-state versus time. Such an estimation of the rate constant of catalyst break-in is, however, only the best least squares estimate of the logarithmically transformed data. Because of the asymptotic approach of this data to steady-state, such a transformation tends to weigh too heavily the data obtained at long times.

Discussion of Experimental Procedures

This section contains a discussion of the catalyst activation procedure and the disproportionation reactor procedure.

Catalyst Activation. The method of activation described previously was based upon experimental techniques reported in the literature (31,20,14) for this catalyst system. The advantage of this procedure was that activation takes place in the reactor, hence, minimizing the chance of contamination of the catalyst. Since in activation of the catalyst heat was supplied by a tubular furnace, disadvantages become obvious. These furnaces seldom heat uniformly along their length; usually the center gets hotter than the ends, and control of temperature to better than ± 5 Centigrade becomes difficult. In order to overcome such disadvantages a heat block was positioned at the center of the reactor, and the catalyst bed was positioned at the center of the reactor.

Air, water vapor, and several polar compounds are known to be temporary poisons for this catalyst. This combined with the required activation temperature of 590° Centigrade were strong factors in the developed method of catalyst activation. Normally, activation was followed with a nitrogen purge of at least 30 minutes in order to remove traces of the air from the system. Reproducibility of this method was satisfactory and there were few problems in obtaining uniform initial activity.

Disproportionation Reactor Procedure. During experimentation the first goal was to fix and control the conditions which would affect the rate of reaction. Normally after activating the catalyst by standard method, the reactor was allowed to cool to the desired

temperature while nitrogen flow was maintained. Propylene feed was not started until the temperature was stabilized for at least fifteen minutes. On those experiments which were conducted at pressures other than atmospheric, the reactor back pressure was set to the desired value during cooling with nitrogen. Before introducing propylene feed, the pressure and temperature were stabilized. Since pressure and flow rate were controlled independently, the flow rate was the last to be fixed. In most of the studies the first sample was taken at least fifteen minutes after starting propylene; during this time, the flow rate was periodically measured by a bubble flow meter to insure that it had been stabilized. In these types of experiments conversion was measured about every hour over a long period of time. Before injecting each sample into the chromatograph, temperature, pressure, and flow rate were checked to make sure that there had been no change in operating conditions during the experiment. On the other hand, when a experiment involved a shorter break-in, the initial conversion was determined as soon as propylene feed was introduced. In this case there was little difficulty in controlling the flow rate before the first sample, but usually the original conditions were reset after the first few minutes of propylene contact. Overall, this method of fixing the operation conditions was very satisfactory.

For achieving isothermal conditions, it was necessary to independently activate two banks of resistance elements around the reactor. The continuous sources of energy from one bank, which was on continuously, and an intermittent source of energy at reduced level from

the other bank, resulted in a good control of temperature. During all experiments care was taken to sample the product stream only when the temperature was $\pm 1^\circ$ Centigrade from the set temperature. A digital temperature indicator connected directly to the thermocouple in the reactor allowed continuous observation of the temperature of the reactor. In spite of all attempts to maintain a constant temperature, it was very difficult to control the temperature to better than $\pm 1^\circ\text{C}$.

The pressure of the reactor was controlled by a "Mity Mite" back pressure controller. This was a very simple, rugged piece of equipment which gave excellent pressure control over a wide range of flow rate. This ability to set the reactor pressure independently of product flow rates eliminated a problem normally associated with this type of micro-catalytic system.

The flow rate was controlled by the combination of a two-stage regulator on each gas cylinder, a Moore differential flow controller, and a needle valve. This combination provided accurately metered reactor feed during this study. The exact flow rate of gases was measured with an in-line bubble flow meter. This procedure provided an accurate measure of the flow rate and eliminated the necessity of a rotameter calibration for each operating condition.

The composition of effluent gases was measured by using a calibrated gas chromatograph. The calibration factors given by Luckner (31) were checked by analyzing samples of known composition. The performance of the gas chromatograph was satisfactory, a constant base line was easy to set, and different combinations of range and

attenuation allowed detection of very low concentrations of gases in the mixtures. A suitable recorder speed and magnification of peaks by changing the attenuation resulted in accurate integration of the peaks.

In all of the studies of catalyst break-in, the same methods of activation, reactor pressure, temperature, and flow control were used. Temperature and pressure control proved very satisfactory, but some difficulty was encountered with the flow rate control, and continued measurement of flow rate was necessary to eliminate slow drifts in the reactor feed rate during the catalyst break-in period. In part of this study it was necessary to stop or to replace propylene flow for a certain time; it was important to readmit the propylene at the original flow rate and then to analyze a sample as soon as possible. In these cases, without altering the set points of the regulators and the rotameter, flow was stopped by a valve on top of the reactor; when the valve was re-opened, the original flow rate was obtained within a few minutes. When propylene flow was replaced with another gas, two identical feed lines to the reactor were used so that the substitution could be made as fast as possible, so that an accurate measurement was obtained of the time that the flow was interrupted. In studies which involved disturbing the steady-state rate of reaction, such as cooling and reheating or purging with an inert, maximum care was taken to repeat the same procedure. When a study was done with a mixture of gases, it was important to prepare a mixture that was free of oxygen poison, because oxygen is a known

poison. To achieve this goal, the feed tank was evacuated and refilled with one of the gases several times until the estimated partial pressure of oxygen in the feed was less than few parts per million.

During pulse studies of catalyst break-in, which involved a material balance around the reactor for each pulse of propylene, or ethylene, or 2-butene, the experimental apparatus allowed the calibration of the gas sampling valve prior to each run by routing the flow of carrier gas around the catalyst bed. In this case, the sample loop was connected to a vacuum pump and a U-type manometer. This allowed evacuation of the loop and auxiliary component. Then the olefin for which the detector was being calibrated was allowed to fill the sample loop to some predetermined pressure. Several pulses at a predetermined sample loop pressure of propylene, or ethylene, or 2-butene were injected into the carrier gas and the total area of the detector output for each pulse was recorded. When actual pulse experiments were carried out, the carrier gas was routed over the catalyst bed before entering the G.C. column. The product of total area and the proportionality factor of the detector for each pulse which passed over the catalyst, compared to that from the initial calibration pulses, gave an accurate measure of the percentage of each pulse lost upon passing over a freshly activated catalyst. Knowing the pressure of the gas in the loop and the volume of the loop allowed a reasonably accurate calculation of the absolute amount of gases to which the catalyst was exposed in each pulse. It should be noted that

these pulse studies allowed no discrimination to be made as to whether the apparent loss of olefin was due to an irreversible adsorption of olefin or to a strong adsorption of the olefin which resulted in considerable tailing in the exit pulse. However, it was found that when propylene gas was pulsed over the catalyst at room temperature, the total area under the peak was approximately 10% less than that of the calibration value. This deficiency was at least in part due to tailing; for when the area under the peak was measured by dividing the peak into several sections, which included the tailing part of the peak, a closer value to the calibration value was obtained. No attempt was made to calculate the activity of the catalyst during these pulse studies because of the wide distribution of products found and the inability to differentiate between the amount of olefin which was adsorbed on the catalyst and the amount which disappeared or appeared due to the reaction.

When pulse studies were followed with a step change, a freshly activated catalyst was exposed to several pulses of a particular gas and then, without disturbing the system, the propylene was introduced into the reactor. Periodically, the extent of the reaction was determined until steady-state activity was reached. Between saturation of surface with different gas, the catalyst was air activated at elevated temperature to eliminate the initial activity as a variable in the study.

Discussion of Results

This section contains a discussion of the results obtained in the four phases of this investigation. These phases consisted of pulse studies of catalyst break-in, cooling and reheating a fully activated catalyst, purging a steady-state catalyst with an inert, and characterization of the effect of ammonia gas on the activity of the catalyst.

Pulse Studies of Catalyst Break-in. The pulse studies made during this investigation were aimed at determining which one of three gases (propylene, ethylene, 2-butene) was primarily involved in the break-in phenomenon. Furthermore, these studies made possible a direct observation of any irreversible, or difficulty reversible, adsorption of hydrocarbons during break-in. The pulse studies of propylene revealed that some 30% of the first few pulses were either irreversibly or strongly adsorbed by the freshly activated catalyst, and that this strong adsorbing steadily declined with continued exposure. Because of the unusual distribution of products during these initial pulses, it was not possible to relate the catalyst activity to either the total amount of exposure or to the amount of the hydrocarbon absorbed. The observed defective mass balance during propylene pulsing could be attributed either to the irreversible adsorption of the olefin by the catalyst or to a strong adsorption of the olefin, which resulted in considerable tailing in the exit pulse. It should be noted that these pulse studies did not allow a discrimination to be made between

irreversible adsorption of the olefin or merely strong adsorption of the olefin. The products observed in the reactor effluent did indicate that the amounts of ethylene produced from each pulse declined as the total moles of propylene exposure increased. In most of the pulses the amount of 2-butene was detectable but was not present in sufficient quantity to be measured. According to the stoichiometry of the reaction and the step change studies of propylene disproportionation over this catalyst, ethylene and 2-butene should be produced in a one to one ratio. This suggests that either some of the 2-butene is irreversibly adsorbed or else it is disappearing by reaction. It is very important for the clear understanding of the processes occurring during initial catalyst reactant contact to be able to account for all reactants and products in these kind of pulse studies. An attempt was made to remove the irreversibly or strongly adsorbed olefin by injecting a second pulse of ammonia gas, which is known to be strongly adsorbed, after the initial pulse of propylene passed through the bed of catalyst. After injecting the second pulse the flow of carrier gas was slowed momentarily. In this way the equilibrium was shifted to favor desorption of strongly adsorbed reactant residuals, while at the same time allowing the concentration of this fraction in the gas space or near the catalyst bed. If this method were successful, a second effluent pulse should be detected after the normal flow of carrier gas was reinstated. From this study nothing was detected even at highest possible sensitivity of the gas chromatograph.

When a freshly activated catalyst was exposed to pulses of ethylene it was found that there is very little or no interaction between the surface and the reactant. In each pulse more than 96% of the gas was recovered in the product stream. The product observed in the reactor effluent did not indicate any gas other than ethylene. This result was expected because in cases where the reactant is a symmetric olefin, i.e. ethylene and 2-butene, the product will be the same as the reactant, if disproportionation is only reaction taking place. The fact that ethylene does not irreversibly or strongly adsorbed on the catalyst might, in part, explain why more ethylene than 2-butene was observed during the propylene pulsing.

When the pulse studies were carried out with 2-butene, the product observed in the reactor effluent consisted of 2-butene, ethylene, propylene, 1-butene, 1,3 butadiene, and 2-pentene. This suggested that the tungsten on silica catalyst does not disproportionate 2-butene with high selectivity. Because 2-butene is a symmetrical olefin, and according to the mechanism of olefin disproportionation, if the selectivity of the catalyst was high for disproportionation, the product should be mainly 2-butene. The results of these studies revealed that several other reactions are taking place simultaneously. A partial list of possible reactions may include

1. 2-butene \rightleftharpoons 1-butene (isomerization)
2. 2-butene \rightleftharpoons 1,3 butadiene + hydrogen
3. 1-butene + 2-butene \rightleftharpoons propylene + 2-pentene
4. 2(1-butene) \rightleftharpoons ethylene + 3-hexene

5. 1-butene + 2-pentene \rightleftharpoons propylene + hexene
6. ethylene + 2-pentene \rightleftharpoons propylene + 1-butene
7. ethylene + 2-butene \rightleftharpoons 2 propylene

In each pulse of 2-butene it was found that 15% isomerizes to 1-butene, and this percentage remained approximately constant as the total 2-butene exposure increased. From the product analysis for each pulse it was found that the isomerization reaction is the dominating one. The percentage of 2-butene in the reactor effluent was observed to remain constant as the total moles of 2-butene exposure increased. On the other hand, an increase in the percentage of ethylene, and a decline in the percentage of 1,3 butadiene in product stream with increasing exposure of 2-butene, signaled that the activity of the catalyst changes for some of the reactions as the exposure of 2-butene increases. It should be noted that during 2-butene pulsing, because of the wide distribution of products found and the inability to detect some of the products quantitatively, made it impossible to carry out a material balance around the reactor. Furthermore, no attempt was made to calculate the activity of the catalyst during these pulse studies for any of the reactions.

One of the questions concerning propylene disproportionation over a tungsten oxide on silica catalyst is whether or not one of the product gases of this reaction in any way hinders or enhances the rate of propylene disproportionation. In other words, does one of these three gases play an important role in the break-in behavior of the catalyst? In a split bed reactor, where the product gases from the first bed

pass through the second bed, the activity of the second bed catalyst was found to be lower than expected. Figure 10 illustrates the break-in behavior of the catalyst after saturating the freshly activated catalyst with either ethylene, propylene, or 2-butene at .94 atmosphere and 440°C. It appears that after saturating the catalyst with either ethylene or 2-butene, that there is a slight decrease in the rate of break-in upon introducing propylene. Since the shift of the curve in Figure 10 was not significant enough to draw a definite conclusion, the same studies were repeated at a higher pressure (2.7 atm.) but at the same temperature. When the surface is saturated at higher pressure with the gases, one would expect that the effect of the saturation of the catalyst upon break-in will be magnified, and as a result, the difference in the rate of approach to steady-state would be increased, if in fact, the saturation of the surface with ethylene or 2-butene slows the rate of approach to steady-state. Figure 11 illustrates the effect of saturation of the surface on rate of approach to steady-state. As one can see from this figure, there is a slight difference in the rate of approach to steady-state after pretreatment of the catalyst with either propylene, or ethylene, or 2-butene. However, the results of these studies show that the effects of the product gases can not be considered to be very significant.

Cooling and Reheating of Steady-state Catalysts. Figure 12 shows the results of cooling a steady-state catalyst to room temperature and immediately reheating up to the reaction temperature at two different

conditions: the upper curve corresponds to the result of cooling and reheating immediately with propylene flow maintained, and the lower curve corresponds to the results of cooling and reheating immediately with no flow (stagnant condition). At both conditions, it is evident that the catalyst undergoes a relaxation of break-in, and the extent of this relaxation is greater under stagnant conditions than under flow conditions. These results show that maintaining the catalyst in its fully activated state requires not only the temperature of the reaction to be kept constant but the propylene flow to be maintained as well.

Figure 13 shows the results of cooling the reactor to room temperature, both at flow and stagnant conditions, and then leaving the reactor system unattended for eight hours while maintaining propylene flow. At the end of the eight hours, the system was reheated to the reaction temperature. Again, these results indicate a relaxation of the break-in and this is more significant in the case of the nonflow cooling and reheating than in flow condition cases. When the results of Figures 12 and 13 are compared, it becomes clear that leaving the catalyst at room temperature with flow maintained does not lead to much further relaxation of break-in. This suggests that the relaxation of break-in is a phenomenon in which maintaining flow plays an important role.

Figure 14 illustrates the results of cooling the reactor to room temperature at both stagnant and flow conditions, and then leaving the system unattended for eight hours with no propylene flow at room temperature. This was followed by reheating the reactor to the reaction

temperature. When the results of Figures 14 and 13 are compared, two important points can be noted: first, leaving the reactor at room temperature for eight hours at stagnant conditions causes a nearly complete deactivation of the catalyst to a point where a break-in period of seven to eight hours is needed to regain the full activity. On the other hand, when the catalyst is left at room temperature for eight hours with flow, the catalyst only partially deactivates and only a short break-in period of 40 to 50 minutes is required to regain the full activity. The second point is that leaving the system for eight hours without flow, and then reheating to the reaction temperature, gave results which do not distinguish whether the cooling and reheating was carried out at stagnant or at flow conditions.

We have also found that a momentarily (30 seconds) interruption of flow during steady-state at the reaction temperature reduces the activity of the catalyst to a point where a break-in period of about 10 minutes is needed to regain full activity. Stopping the propylene flow for longer periods of time was not feasible because of a coking reaction at high temperature. These studies demonstrated that relaxation occurs at both room temperature and at the reaction temperature in the absence of flow, and this relaxation involves two factors: flow and temperature. When the system was left unattended for eight hours, the extent of the deactivation was much more than that observed in cooling and then reheating immediately. This suggests that decreasing the temperature from the reaction temperature

to room temperature contributes to a constant extent to the relaxation and that this portion of relaxation is independent of length of time that the catalyst is held at the lower temperature. On the other hand, a significant portion of relaxation can be due to the absence of flow, and this appears to be a strong function of the length of time during which the flow was stopped.

Based on the results of the proceeding studies, the relaxation of the break-in was investigated in detail by cooling a fully activated catalyst to room temperature and holding at room temperature for various time periods before reheating. The results in Figure 15 were obtained in this order: initial break-in, then cooling/reheating experiment in the order of 0, 1, 8, 11, 3 hours of holding at 25°C. The same sample of catalyst was used throughout, with air activation at 590°C carried out before the initial break-in but not between the cooling and reheating experiments. Propylene flow was maintained at all times except during the holding periods at room temperature. The trend of data in Figure 15 shows clearly that interrupting the disproportionation reaction through cooling causes a relaxation of break-in. One characteristic of this relaxation is the parameter r_o/r_{ss} listed in Table VII. This is a measure of the initial activity upon reheating to the reaction temperature. The other characteristic parameters of relaxation is the break-in rate constant, K, given in Table VII. These two parameters appear to be clearly related, with a larger value of r_o/r_{ss} associated with an increase in the break-in constant, K. The parameter, K, is perhaps the more reliable index of

relaxation since its determination weights all of the data, while the parameter r_o/r_{ss} relies primarily upon points obtained near the zero reference time, and the reference time itself is somewhat uncertain in this type of experiment. Furthermore, the best estimate of K is relatively insensitive to changes in the estimate of r_o/r_{ss} . Thus, errors in assigning an effective initial time causes significant errors in r_o/r_{ss} , but only a small error in the determination of K .

Before considering the trend of the data in Figure 15, the question comes to mind, "What is the effect of repeated cycles of cooling and reheating for a fixed holding time at 25°C?" This data has been obtained (14). The results show that repeated cycling (through three cycles) leads to a small increase in both the break-in rate constant, K , and the initial activity parameter r_o/r_{ss} . Undoubtedly, this effect of repeated cycling is superimposed on the effects seen in Figure 15, namely, a decrease in the break-in parameter K and r_o/r_{ss} with increasing holding time at 25°C. However, the effect of repeated cycling is such as to transpose the curves slightly to the left, and this in no way alters the conclusions to be drawn from Figure 15, which is that relaxation must be occurring at a significant rate even at 25°C. This is substantiated by the increase in relaxation as the holding time at 25°C is progressively increased from 0 to 11 hours. The fact that relaxation continues to occur at 25°C at a measurable rate signals that the relaxation process must have a small activation energy. Break-in is known to have a large activation energy of 47 K cal; furthermore, break-in has been shown to have a

first order dependence upon the reactant propylene pressure (31). This suggests, but of course does not prove, that break-in is a chemical reaction involving propylene and the promoter WO_3 . On the other hand, the relaxation process appears to be either a physical process or else a reaction with a very low activation energy. The results of these studies directed the investigation toward finding answers to questions such as: is the propylene gas flow important because of the interaction between the catalyst and gas at room temperature, (recalling the difference in the relaxation of break-in for stagnant and flow conditions) or is flow important because it blocks the catalyst from foreign species which would be available due to back diffusion in the absence of flow? What type of physical or chemical processes are responsible for the relaxation, and what is the activation energy of relaxation? How does the pressure and temperature of the gas effect the relaxation? To provide answers to these types of questions and further elucidate the relaxation phenomenon, the following studies were conducted.

Purging a Fully Activated Catalyst with an Inert. Figure 19 shows the results of purging steady-state activity with helium for 5 and 30 minutes at the reaction temperature of $429^\circ C$ and at a pressure of .94 atmospheres. These results clearly indicate that the catalyst undergoes relaxation upon purging with an inert at the reaction temperature. Furthermore, the break-in time required upon reinstating the propylene flow is of the same order of magnitude as that obtained

during cooling and reheating immediately (0 hr. holding time at 25°C). Figure 20 shows the results of purging a fully activated catalyst at the same temperature as before, but at a higher pressure (3 atm.). A comparison of results in Figures 20 and 19 clearly indicates that the relaxation of the catalyst at reaction temperature is strongly influenced by the pressure of the purging gas. This is deduced from the break-in periods observed when a fully activated catalyst was purged at .94 and 3 atmospheres.

Figure 21 shows the results of relaxation of the catalyst at two different reaction temperatures. These data allowed an estimate of the activation energy of the relaxation process. Based on a Arrhenius type of correlation, an activation energy of 6.3 kcal was calculated. This low activation energy supported the idea that relaxation occurs at 25°C at a measurable rate is an indication of a relaxation process having a small activation energy. It was mentioned earlier that the relaxation of the catalyst involved two factors: temperature and flow.

To determine whether propylene flow was needed at room temperature, because of interaction between the gas and catalyst, or because of merely protecting the catalyst from the foreign species such as oxygen or water vapor, which could reach the catalyst in absence of flow, the cooling and reheating experiments were carried out in the absence of propylene. In these experiments, helium gas replaced the propylene during cooling and reheating. The results in Figure 24 were obtained in order of 0, 8, 12, 5 hours of holding the system at

25°C while maintaining helium flow. The same sample of catalyst was used throughout, with air activation at 590°C carried out before the initial break-in, but not between the cooling/reheating experiments.

Also purging a fully activated catalyst at the reaction temperature for longer periods of time were studied. These results are shown in Figure 23 and they were obtained in order of 5, 270, 720 minutes. When the results of cooling, holding at 25°C, and reheating with helium are compared to those which were obtained in absence of any flow and propylene flow, it becomes clear that, as far as the relaxation is considered at room temperature, there is practically not much difference. Propylene flow and helium flow at 25°C give similar results. The magnitude of break-in times required after reestablishing the propylene flow at the reaction temperature are almost the same. This suggests that the flow at 25°C is needed mainly either to protect the catalyst from contacting with species which could reach the surface if flow was stopped or flow is needed to purge poisons which could be formed during the reaction from the surface. Further support of the role of flow in the relaxation can be provided from results of Figure 15, where as the holding time of the catalyst at 25°C increases without flow, the catalyst deactivation increases. This can be attributed to the fact that the longer the system is left without flow, the more chance there is of contamination of the catalyst by foreign species. This means when the flow is stopped at 25°C there is an interaction between a foreign species and the catalyst which results in a deactivation of the catalyst. These

conclusions are a direct result of considerations of two characteristic parameters of the relaxation, namely, r_0/r_{ss} , and the break-in rate constant, K , which are listed in Table VIII. It is clear that both of these parameters remain approximately constant during purging at room temperature, regardless of length of purging times. This means that relaxation has been stopped or greatly slowed at room temperature. However, the data in Figure 23 clearly indicates that when a fully activated catalyst is purged with helium at reaction temperatures, the relaxation is occurring at a significant rate. The fact that relaxation occurs at reaction temperature in the presence of helium may indicate that at least a part of the deactivation is caused by the presence of inorganic impurities in the feed. These results for deactivation of the catalyst in a helium flow at reaction temperatures are similar to the results of de-Vries (12) and coworkers, who carried out studies using nitrogen as purging gas with a tungsten oxide-alumina catalyst.

Considering the characteristic parameters of relaxation during purging, one can see that an increase in the purging period is associated with a decrease in the break-in rate constant, K . Figure 25 shows a plot of break-in rate constant after purging versus time of purging of the catalyst at room temperature and at the reaction temperature.

When the results of Figure 25 are compared with the results of Figure 18 (which illustrates the break-in rate constant after holding at room temperature versus holding time at 25°C without propylene

flow), two conclusions can be made: the cause of the relaxation during purging with helium has been hindered by lowering the reaction temperature to room temperature. Secondly, the trend of data of the relaxation for purging the fully activated catalyst at the reaction temperature with helium is the same as the trend of data which were obtained from cooling, holding at 25°C, and reheating. This suggests that the same processes are occurring during cooling and reheating and purging with the inert. However, the temperature plays an important role in interaction and thus the processes takes place much more rapidly at reaction temperature. In the cases of cooling the freshly activated catalyst and holding at 25°C without flow, the foreign species assume present are playing an important role. Keep in mind that holding the catalyst at room temperature while helium flow is maintained does not result in further deactivation of the catalyst with increasing the length of holding time.

In summary, we have in hand a process which involves a small activation energy. Its effect on deactivation of the catalyst is greatly influenced by the reactor pressure. At reaction temperatures its effect is increased by increasing contact time, and at room temperature its effect is eliminated by flow but is significant at stagnant conditions. There are two possible explanations for the relaxation of catalyst break-in. First, the relaxation observed during the cooling/reheating experiments could be due to some temporary poisons which are physically absorbed to the surface upon interrupting the steady-state rate of reaction. These poisons do not cause changes

in the structure of the catalyst, and the break-in period observed after reestablishing flow is merely the time needed to remove these weakly absorbed species from the surface. A second explanation could be that during the normal break-in period two competitive processes are taking place. One of these processes is causing the increase in the activity of the catalyst which is most probably the reduction of the catalyst surface. The second process is the one causing deactivation of the catalyst which is most probably the oxidation of the catalyst surface to some intermediate tungsten oxide by impurities in the feed. As long as the steady-state reaction conditions are maintained the activation process is the dominating factor, but when there is a disturbance in the system, such as cooling the reactor to room temperature or purging the steady-state catalyst, the deactivation process becomes significant. This is why transition times are observed during the cooling/reheating and the purging studies. The transition time observed is the time needed to restore the original state of the catalyst. From the results obtained in this investigation, the second explanation seems the more reasonable. If the physically absorbed contaminants at 25°C during cooling, holding at 25°C, and reheating were responsible for the relaxation, then one would expect the physical desorption to take place at a much faster rate at the reaction temperature, and a break-in period of 7 or 8 hours would not be necessary to restore the full activity.

With regard to the second explanation, the question comes to mind "Can small amounts of impurities in the feed cause the relaxation?" Recently, de Vries and coworkers (12) have shown that when a pulse of a mixture of nitrogen and oxygen, which contained only 0.1% oxygen, was injected into the feed, a very rapid decline in activity was observed.

This has been justified by calculating the number of active sites, which turned out to be only about 10^{16} sites per gram of the catalyst, and this corresponded to only one active site per 50,000 tungsten ions. From this argument, it is feasible to assume that small amounts of oxygen in the feed can be responsible for the relaxation. To prove this matter further, an attempt was made to counteract the effect of small amounts of oxygen in the feed by adding a small amount of a reducing gas to the feed. In this way one would expect to reduce the effect of oxygen in the feed. Figure 26 illustrates the effects of purging a fully activated catalyst with a mixture of helium plus 1.5% hydrogen and with a mixture of helium plus 2% propylene for 10 minutes at the reaction temperature. It is evident from these results that the addition of 2% propylene reduces the extent of the relaxation of the catalyst after purging, compared with the results for purging with pure helium. The rate of approach to the steady-state after purging with the mixture is much faster than that obtained during purging with helium alone. In contrast, the presence of 1.5% hydrogen in the purging gas results in a further deactivation of the catalyst, and a longer break-in period is needed to restore the original steady-state activity. The effects of hydrogen in the mixture were expected, because hydrogen is a known temporary poison. The effect of the presence of the propylene in the purging mixture is attributed to the fact that the oxidation of the catalyst by the small amount of oxygen in the helium is counteracted to some extent by the presence of the propylene. This supports the idea that the relaxation during purging with helium, is at least in part, due to oxidation of the catalyst to some intermediate tungsten oxide.

It is also interesting to note that both during the cooling/reheating and during the purging of a fully activated catalyst with an inert at the reaction temperature, it appears that the break-in rate constant declines rapidly in the first 60 minutes of the disturbance and then declines more slowly as the disturbance period is increased (Figures 18 and 25). In a recent study, Kerkhof and coworkers (25) have found that when WO_3 is reduced with hydrogen, immediately after introduction of the hydrogen, a reduction of WO_3 to $W_{20}O_{58}$ takes place, which is followed by a fast, although slower, reduction in the next 2000 seconds of the experiment. The remaining reduction proceeds slowly and at a decreasing rate. From these studies, they concluded that the fresh catalyst contains at least two tungsten species, viz, tungsten trioxide crystallites and a difficult-to-reduce material. This might explain why the dramatic decrease in the break-in rate constant was observed during the first 60 minutes of disturbance. Perhaps the relaxation of the catalyst during these disturbances involves a two step process.

The Effects of Ammonia Upon the Activity of the Catalyst. Figures 27 and 28 illustrate the results of propylene disproportionation reaction over freshly activated catalysts and catalysts that were pretreated with ammonia at reaction and activation temperatures respectively. It is clear that after pretreatment with ammonia the freshly activated catalyst becomes nearly inactive for the propylene disproportionation reaction. In contrast, dosing small amounts of ammonia into the feed causes a dramatic, though temporary, increase in the activity. Also, interrupting propylene flow for 10 minutes with ammonia at the reaction temperature results in a temporary increase in

the activity. These results reveal that ammonia is effective in increasing the activity only in presence of the reactant propylene, and this effect can not be due to direct interaction between the catalyst and ammonia, otherwise, an increase in the activity of the catalyst should be observed after pretreatment of a freshly activated catalyst with ammonia. During dosing experiments, continuous addition of ammonia was necessary to keep the catalyst at the higher activity level.

Figure 31 shows the break-in behavior of the freshly activated catalyst during disproportionation of propylene which contained 1.5% NH_3 . It is evident from this figure that the addition of a small amount of ammonia to the feed decreases the break-in period and increases the steady-state level of conversion significantly. When the feed to the reactor is switched from the mixture to pure propylene, after establishing the steady-state activity with the mixture, it appears that the catalyst exhibits normal break-in and reaches a steady-state level of conversion as usual. This means that ammonia in the feed is not a long lasting effect. However, when the feed to a fully activated catalyst with 100% propylene is switched to the mixture, a rapid increase in activity is observed. With increasing contact time with the mixture, the catalyst reaches a new steady-state conversion level in a short transition time, and this steady-state conversion is much higher than the steady-state conversion which was obtained during disproportionation with a freshly activated catalyst. The results of Figure 31 indicates that the activity increase due to

NH_3 in the feed is proportional to the activity already generated by break-in. The increase in activity is practically instantaneous and temporary. This increase in activity is quite different from the increase due to normal break-in, which is permanent but slow in developing. It appears that the break-in is independent of the processes which are occurring during NH_3 addition. On the other hand, it is most likely that NH_3 in the system affects only those sites already partially activated by normal break-in processes.

Recommendations.

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

Purification of the Reactor Feed. This thesis proposes that the relaxation of break-in of this catalyst upon disturbing the steady-state reaction is at least in part due to the presence of inorganic chemicals, such as oxygen and water vapor in the feed. It is recommended that the oxygen content of the feed to the reactor be reduced by passing the gases through a column packed with activated copper gauze wire before reaching the catalyst bed. By adding such a column one would expect to reduce the amounts of oxygen in the feed by oxidizing the copper. For best results, this column should be activated by passing hydrogen at a temperature around 300°C before placing it in the feed line, and the column should be operated at a temperature

range of 250-300°C in order to achieve oxidation of copper by the small amounts of oxygen in the feed.

Investigation of Relaxation of the Break-in in a Split Bed Reactor.

It is recommended that the relaxation of the break-in during purging a fully activated catalyst with helium be studied in a split bed reactor. Here, the reactor should contain two different sizes of catalyst charge. The first bed should be larger than the second bed so as to reduce the inorganic impurities in the feed before it reaches the second bed. After establishing steady-state activity in both beds, the catalyst in both beds should be purged with helium for a short period. Studying the propylene disproportionation reaction after purging, and monitoring the conversion in each bed independently, should reveal the extent of the relaxation of the break-in in both beds. From comparison of the relaxation in the first and the second bed one should be able to determine the extent of deactivation caused by these inorganic impurities.

Modification of the Equipment for Detecting Trace Amounts of Water

and Oxygen. In order to be able to monitor the water and oxygen content of the effluent gases from the reactor during purging of a fully activated catalyst both at reaction and room temperatures, it is recommended that a conventional Hersch cell and a trace moisture analyzer to be placed in line at downstream of the reactor. These would allow monitoring of the oxygen and water content of the effluent gases from the reactor during purging.

Studies of the Relaxation of the Break-in Under Vacuum During the Cooling and Reheating Experiments. It is recommended that the cooling and reheating experiments to be carried out under a similar condition to those in this thesis, except that during holding the catalyst at 25°C, the reactor system should be placed under a vacuum. The results of this thesis proposes that the relaxation of the break-in at room temperature without flow is mainly due to the foreign species which become available in absence of flow. By placing the system under a vacuum, one might be able to protect the catalyst from contacting with foreign species during the holding time at 25°C.

Limitations

This study was conducted under the following limitations:

1. A single commercial tungsten-on-silica-gel catalyst, provided by Davidson Chemical Division of the W. R. Grace and Company was used in all studies.
2. Temperatures ranging from 406° to 452° Centigrade were used. No higher temperatures were feasible due to cooking reactions.
3. The maximum pressure used was 35 psig.
4. A single method of activation was used. The catalyst was activated at 590°C in a dry air flow for 4 hours and this was followed with 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 reactor operations.
6. Only the disproportionation of propylene was studied.

V. Conclusions

As a result of this study of the break-in behavior of a tungsten oxide on silica gel catalyst during propylene disproportionation, the following conclusions were made:

1. Saturation of the catalyst with product gases (ethylene and 2-butene) prior to the propylene disproportionation do not alter the break-in behavior or the steady-state activity of the catalyst.
2. Relaxation of the break-in is occurring during cooling and reheating experiments at a significant rate even at 25°C in absence of propylene flow. This relaxation is more dramatic in stagnant conditions than in flow conditions. The relaxation increases as the holding time at 25°C is progressively increased from 0 to 11 hours without propylene flow. Propylene flow reduces the relaxation of break-in by protecting the catalyst bed from foreign species at room temperature.
3. Disturbing the steady-state rate of the reaction with helium for a short period of time causes a relaxation similar to that noticed during the cooling and reheating experiments. These effects are strong functions of the reactor pressure and weakly dependent on the reactor temperature. The effects of purging fully activated catalyst with helium are more drastic at the reaction temperature

than at room temperature. The presence of a small amount of propylene in the purging gas greatly hinders those processes which are responsible for the temporary loss of activity during purging.

4. An apparent activation energy of 6300 cal/g mole was found for the relaxation of the break-in during purging of the fully activated catalyst with helium.
5. Based on the results of this study it is concluded that, the deactivation of the catalyst upon disturbance of the steady-state rate of reaction is due to the interaction of the catalyst with foreign species which are either in the feed (during purging with helium) or they become available from back diffusion (during cooling and reheating) studies. Furthermore, it is concluded that at least in part the deactivation of the catalyst upon disturbance is due to the oxidation of the catalyst to an intermediate oxide of tungsten.
6. From the quantitative measurements of the break-in rate constants after purging a fully activated catalyst with helium, and the cooling/reheating experiments, it was found that the major portion of the deactivation is caused in the initial period of disturbances. This was followed by a gradual decline as the length of time of the disturbance increased.

7. Pretreatment of the catalyst with ammonia at reaction and at activation temperatures, prior to the propylene feed, leaves the catalyst nearly inactive for the disproportionation reaction. However, dosing a small amount of ammonia into the feed during the steady-state regime enhances the rate of reaction by some 150%, and the addition of 1.5% ammonia to the propylene feed not only reduces the break-in behavior of the freshly activated catalyst significantly, but also the steady-state level of conversion obtained for this mixture is significantly higher than the one for pure propylene feed.
8. Passing the reactant through a magnesium oxide bed does not improve the rate of the propylene disproportionation in this reaction system.

VI. Summary

This investigation consisted of a study of the break-in behavior of a tungsten oxide on silica catalyst during propylene disproportionation. A catalyst of 10 percent WO_3 on silica gel (223 square meters per gram B.E.T. surface area) was used in a microcatalytic reactor. During the initial contacting of freshly activated samples of this catalyst with propylene, significant increases in disproportionation activity were observed for periods of up to 20 hours. The object of this study was to investigate the phenomenon responsible for this break-in.

The rate of approach to steady-state activity data were obtained using catalyst samples which were first saturated with each of the three gases involved in this reaction (propylene, ethylene, and 2-butene) by pulsing at .94 and 2.7 atmospheres before starting the propylene flow. Effects of each gas on the break-in behavior of the catalyst were determined. A material balance around the reactor was made for each gas by pulse reactor techniques.

In general, it was found that, almost any change that disturbs the steady-state reaction causes a relaxation of the break-in. Relaxation of the break-in was studied quantitatively under two different conditions. In the first condition the temperature of the reactor during the steady-state regime was lowered to room temperature level and then the reactor was held at room temperature for varying periods of time, following which, the reactor was brought back to the original

reaction temperature. Data were obtained for the relaxation of the break-in for cases in which the catalyst was cooled, held at room temperature, and reheated, both with and without flow, and in the presence and absence of propylene. The break-in rate constants, as well as initial activities, exhibited by these catalysts were determined. The relaxation of the break-in was studied by subjecting a fully activated catalyst to an inert purge (helium) for varying periods while maintaining the reaction temperature level. Again, the break-in rate constants and the initial activities were determined by measuring the rate of the break-in observed following the relaxation of the original break-in. The relaxation of the catalyst break-in was found to depend on both the reactor temperature and pressure with an activation energy of 6300 cal/g mole.

Data for the rate of approach to steady-state activity was obtained using a freshly activated catalyst which was pretreated with ammonia at the reaction and at activation temperatures. Catalysts so treated had little activity for disproportionation. The influence of injecting small quantities of ammonia into the propylene feed during the steady-state regime was studied. Ammonia was found to give a large increase in catalytic activity and the effect was found to be reversible with continuous injection of ammonia necessary to maintain high catalytic activity. When the disproportionation reaction was studied with a propylene feed which contained 1.5% ammonia, it was found that the rate of approach to steady state and the steady-state conversion level were increased significantly.

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APPENDIX A
MATERIALS AND APPARATUS
Materials

The following section is a list of the materials used, their sources, and their specifications:

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

Ammonia. No. 2 cylinder of Matheson ammonia, obtained from Matheson Gas Products, a division of Will Ross, Inc., East Rutherford, New Jersey. Used in pretreatment of the catalyst, dosing experiments, and to prepare a mixture of propylene and ammonia.

Butene-1. Lecture bottle of C.P. grade 1-butene, minimum purity 99 percent, obtained from Matheson Company, East Rutherford, New Jersey. Used to determine the retention time in the gas chromatograph.

Butene-2. No. 2 cylinder of C.P. grade Cis and trans 2-butene, minimum 99 percent purity. Obtained from Matheson Company, East Rutherford, New Jersey. Used to saturate the catalyst prior to propylene feed.

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

tungsten oxide	10%
surface area	223 m ² /gram
pore volume	1 cm ³ /gram

This catalyst was furnished by Davidson Chemical Division of W. R. Grace and Company, Baltimore, Maryland, and was designated SMR-7-3322 or SMR-7-5381. Used in all studies involving the disproportionation reaction.

Chromatographic Column Packing. 20% dimethyl sulfolane on chromosorbed W, 45, 60 mesh obtained from Avondale Division, Hewlett-Packard. Used as a chromatographic column to separate product gases for analysis.

Ethylene. Twelve gallon cylinders of pure grade ethylene minimum purity 99 percent. Obtained from Phillips Petroleum Company, Bartlesville, Oklahoma. Used in pulse studies and catalyst pretreatment.

Helium. Size 1-A cylinder of Airco Commercial grade helium. Obtained from Industrial Supply Company, Bluefield, West Virginia. Used as a carrier gas for chromatograph and as an inert in purging the steady-state activity of the catalyst.

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.

Magnesium Oxide. Powder form, lot D293C168, obtained from Chemistry Department of VPI&SU, Blacksburg, Virginia. Used in the feed line for improvement of the reaction rate.

Molecular Sieves. 1/16 inch pellets, part number 5943350233, type 5A.

Obtained from Linder Air Products Company. Used to dry all gases entering to 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 and provide back pressure to the reactor.

Propane. 5 gallon cylinder of pure grade propane, minimum purity of 99 percent. Obtained from Phillips Petroleum Company, Bartlesville, Oklahoma. Used to determine impurity of propylene.

Propylene. 16 and 28 gallon cylinders of polymerization grade propylene, minimum purity 99 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, 2.5 cm inside diameter, catalog No. 8-615. Obtained from Scientific, Inc., Raleigh, North Carolina. Used to store catalyst samples.

Digital Thermocouple Indicator. Model 400 JC, digital thermocouple indicator, Serial No. 1750, Range -200 to 933°C. 115V, 60 cy, AC, calibrated for-iron-constantan, maximum deviation of 1°C. Obtained from Omega Engineering, Inc., Stamford, Connecticut. Used to measure the temperature of the reactor.

Dryer. Three dryers, constructed from one inch stainless 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.

Electric Furnaces. A six 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 ten inches tubular furnance, type 128-8, 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 charging 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, fotted, 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. Single wall transition oven, manufactured by Blue M Electric Company, 0-200°C range, serial No. XA-14746, 120V/1PH/50-60 Hz. Used to dry catalyst.

Powerstat. Two variable transformer, 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 Gage. 400 psi range, 5 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.

Reactor. A six inches tubular, fixed bed catalytic reactor used during this investigation. A detailed description of the reactor is given in the experimental equipment section of this thesis.

Rotameter. Dual float rotameter, tube No. 601, 9.09 to 268.5 scc/min, manufactured by Matheson Company, Inc., East Rutherford, New Jersey. Used to indicate flow rate to the reactor.

Sieves. U. S. Standard sieves No. 20, 25, 30, 40, 50, 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. A schell bach buret, 50 ml. capacity, catalog No. 3-70. Obtained from Fisher Scientific Company, Inc., Raleigh, North Carolina. It was modified into a bubble flow buret 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.

Stop Watch. Electric direct reading stop watch, 1/10 second divisions, reading up to 10,000 seconds, 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. ICSS-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, .1 cubic feet per revolution, .001 cubic feet subdivision. Used to measure flow rates of gas streams leaving the reactor.

APPENDIX B

Table X

Products Distribution of Propylene Pulses on a Freshly Activated
Tungsten Oxide on Silica Catalyst

T = 437°C

P = 3.5 atm.

Sample Size = 20×10^{-6} moles

Catalyst Weight = .4 grams

Sample No.	Component Ethylene	Peak Areas Propylene	$\sum f_i^*$ 2-Butene	$A_i f_i$	% Fraction Adsorbed
1	0.08	44.53	----	44.61	33.56
2	0.067	53.55	.017	53.59	20.19
3	0.056	56.67	.016	56.74	15.503
4	0.059	67.54	----	67.6	0
5	0.058	57.24	----	57.3	14.67
6	0.059	59.77	----	59.83	10.90
7	0.056	63.14	----	63.20	5.88
8	0.044	63.87	----	63.92	4.81
9	0.055	65.44	----	65.49	2.47
10	0.054	66.6	----	66.65	0.74
11	0.056	66.08	----	66.13	1.51
12	0.052	65.81	----	65.86	1.92
13	0.055	65.18	----	65.23	2.86
14	----	66.89	----	66.89	0.39
15	0.049	66.6	----	66.65	0.744

* f_i = detector calibration factor.

Table XI

Product Distribution of the Ethylene Pulses on a Freshly Activated
Tungsten Oxide on Silica Catalyst

T = 437°C

P = 3.5 atm.

Sample Size = 20×10^{-6} moles

Catalyst weight = .4 grams

Sample No.	Component Peak Area X f_i	% Difference from Calibration Value
1	65.13	2.7
2	64.86	3.16
3	65.33	2.46
4	64.55	3.62
5	66.86	0.179
6	64.91	3.06
7	65.73	1.86
8	65.87	1.65
9	65.76	1.82
10	66.23	1.12
11	66.57	.61

Table XII

Products Distribution of the 2-Butene Pulses over a Freshly

Activated Tungsten Oxide on Silica Catalyst

Temperature = 437°C

P = 3.5 atm.

Sample Size = 20×10^{-6} moles

Catalyst Weight = .4 grams

Sample No.	PERCENTAGE OF COMPONENTS					
	Ethylene	Propylene	2-Butene	1,3 Butadiene	1-Butene	2-Pentene
1	0.271	0.633	80.656	3.469	14.83	-----
2	0.222	0.654	80.477	3.89	14.757	-----
3	0.258	0.660	78.775	3.80	15.492	-----
4	0.342	0.660	79.864	3.28	15.721	0.132
5	0.347	0.672	80.63	3.05	15.192	0.11
6	0.381	0.654	79.584	2.633	16.23	0.117
7	0.433	0.656	81.3	2.696	14.81	0.097
8	0.437	0.656	80.01	3.065	15.63	0.152
9	0.514	0.636	80.17	2.474	15.964	0.241
10	0.510	0.635	80.451	2.291	15.941	0.16
11	0.502	0.662	79.591	2.55	16.438	0.251
12	0.539	0.661	81.208	2.379	14.863	0.333
13	0.504	0.653	82.24	2.266	14.111	0.232
14	0.454	0.644	81.272	2.114	15.3	0.22
15	0.453	0.645	80.924	2.077	15.48	0.221

Table XIII

Break-In Behavior of a Tungsten Oxide on Silica Catalyst
After Saturating Freshly Activated Catalyst with Propylene

T = 440°C

P = .94 atm.

WHSV = 17.8

Catalyst Wt. = .4 grams

Propylene Stream Time Hr.	Percent Conversion of Propylene	Rate Steady-State Rate r/r_{ss}	Fractional Approach to Steady-State $(r_{ss} - r(t))/(r_{ss} - r_0)$
0	0	0	1
0.33	.39	0.047	0.953
0.88	1.372	.172	0.827
1.88	2.2	.276	0.723
2.88	3.04	.384	0.616
4.13	3.62	.457	0.543
6.13	4.83	.608	0.391
8.63	6.58	.827	0.172
11.13	6.8	.856	0.143
13.63	7.318	.92	0.0783
16.13	7.94	1	0

Table XIV

Break-In Behavior of a Tungsten Oxide on Silica Catalyst
After Saturating a Freshly Activated Catalyst with Ethylene

T = 440°C

P = .94 atm.

WHSV = 17.8

Catalyst Wt. = .4 grams

Propylene Stream Time Hr.	Percent Conversion of Propylene	Rate Steady-State Rate r/r_{ss}	Fractional Approach to Steady-State $(r_{ss} - r)/(r_{ss} - r_0)$
0	0	0	1
0.5	0.306	0.04	0.961
1.16	0.656	0.09	0.909
2.33	1.35	0.176	0.824
4.33	2.04	0.278	0.722
7.33	4.91	0.673	0.326
8.33	4.103	-----	0.437
12.33	6.35	0.87	0.130
13.33	6.47	0.886	0.113
15.33	7.3	1	0

Table XV

Break-In Behavior of a Tungsten Oxide on Silica Catalyst
After Saturating a Freshly Activated Catalyst with 2-Butene

T = 440°C

P = .94 atm.

WHSV = 17.8

Catalyst Wt. = .4 grams

Propylene Stream Time Hr.	Percent Conversion of Propylene	Rate Steady-State Rate r/r_{ss}	Fractional Approach to Steady-State $(r_{ss} - r)/(r_{ss} - r_0)$
0.0	0	0	1
0.25	0.38	0.066	0.933
0.5	0.385	0.0678	0.933
1	0.52	0.0916	0.908
2	0.98	0.172	0.83
3	1.13	0.197	0.803
4	1.58	0.277	0.722
5.5	2.37	0.416	0.584
7.5	3.41	0.598	0.401
9.5	4.03	0.71	0.292
10.5	4.06	0.71	0.292
16.5	5.15	0.907	0.095
17.5	5.68	1	0

Table XVI

Break-In Behavior of a Tungsten Oxide on Silica Catalyst During
Disproportionation of Propylene (Freshly Activated Catalyst)

T = 421°C

P = 2.7 atm.

WSHV = 28.3

Catalyst Wt. = .35 grams

Propylene Stream Time Hr.	Percent Conversion of Propylene	Rate Steady-State Rate r/r_{ss}	Fractional Approach to Steady-State $(r_{ss} - r)/(r_{ss} - r_0)$
0	0	0	1
0.08	0.97	0.025	-----
0.25	2.28	0.06	0.97
0.75	5.51	0.144	0.883
1.75	8.55	0.223	0.800
2.75	12.71	0.332	0.688
4.25	17.72	0.46	0.553
6.25	22.14	0.578	0.434
8.75	27.42	0.717	0.292
10.75	31.08	0.812	0.193
12.75	36.48	0.94	0.047
15.9	38.25	1	0

Table XVII

Break-In Behavior of a Tungsten Oxide on a Silica Catalyst After Saturating a Freshly Activated Catalyst with Propylene, Ethylene, and 2-Butene

T = 421°C

P = 2.7 atm.

WHSV = 28.3

Catalyst Wt. = .35 grams

Propylene Stream Time Hr.	Percent Conversion of Propylene	Rate Steady-State Rate r/r_{ss}	Fractional Approach to Steady-State $(r_{ss}-r)/(r_{ss}-r_0)$
0	0	0	1
0.25	1.25	0.037	0.986
0.5	2.13	0.063	0.959
1	3.73	0.111	0.909
2	7.52	0.225	0.793
4	12.31	0.37	0.646
6	17.28	0.517	0.494
9	24.82	0.744	0.262
10	25.16	0.755	0.252
12.25	28.1	0.84	0.161
14.5	32.02	1	0
Ethylene			
0	0	0	1
0.5	0.96	0.032	0.967
1	2.87	0.096	0.903
2	5.55	0.186	0.814
3	7.58	0.254	0.746
4.5	10.97	0.367	0.632
6.5	14.87	0.498	0.501
8.5	20.4	0.684	0.3155
10	24.1	0.808	0.1914
11.5	26.6	0.89	0.1072
15	29.8	1	0
2-Butene			

Table XVII (Continued)

Propylene Stream Time Hr.	Percent Conversion of Propylene	Rate Steady-State Rate r/r_{ss}	Fractional Approach to Steady-State $(r_{ss} - r)/(r_{ss} - r_0)$
0	0	0	1
0.25	1.41	0.053	0.947
0.5	1.83	0.068	0.931
1	3.37	0.126	0.873
2	6.7	0.25	0.748
3.25	8.6	0.323	0.676
5.25	11.4	0.43	0.57
7.25	14.84	0.558	0.442
9.25	18.63	0.701	0.298
12.25	23	0.86	0.134
17	26.56	1	0

Table XVIII

Break-In Behavior of a Tungsten Oxide on Silica Catalyst During
Propylene Disproportionation (Freshly Activated Catalyst and Cooling/
Reheating Immediately In Flow Conditions)

T = 431°C

P = .94 atm.

WHSV = 20.9

Catalyst Wt. = .4 grams

Propylene Stream Time Min.	Percent Conversion of Propylene	Rate Steady-State Rate r/r_{ss}	Fractional Approach to Steady-State $(r_{ss}-r)/(r_{ss}-r_0)$
0	0	0	1
15	0.863	0.075	0.925
30	1.42	0.123	0.876
90	3.06	0.266	0.734
150	4.05	0.352	0.648
270	6.32	0.55	0.45
390	7.78	0.676	0.323
570	9.3	0.808	0.1912
780	10.06	0.874	-----
1110	11.5	1	0
-----Cooling and reheating immediately			
0	6.68	0.59	1
10	8.4	0.743	0.416
25	9.32	0.824	0.1784
60	10.95	0.966	0.0338
95	10.7	0.944	0.056
140	11.33	1	0

Table XIX

Break-In Behavior of a Tungsten Oxide on Silica Catalyst During Propylene Disproportionation for Cooling and Reheating at Stagnant Conditions. (0 hrs. and 8 hrs. holding at 25°C with propylene flow)

T = 431°C

P = .94 atm.

WHSV = 20.9

Catalyst Wt. = .4 grams

Propylene Stream Time Min.	Percent Conversion of Propylene	Rate Steady-State Rate r/r_{ss}	Fractional Approach to Steady-State $(r_{ss} - r)/(r_{ss} - r_o)$
0	3.94	0.334	1
10	5.0	0.425	0.874
45	8.23	0.7	0.457
80	9.77	0.83	0.259
125	10.5	0.89	0.163
215	11.77	1	0
-----Holding 8 hrs. at 25°C with propylene flow			
0	2.7	0.23	1
15	6.7	0.573	0.557
30	8.75	0.748	0.328
45	10.37	0.886	0.149
75	10.63	0.91	0.119
105	11.7	1	0

Table XX

Break-In Behavior of a Tungsten Oxide on Silica Catalyst During
Propylene Disproportionation for Cooling/Reheating at Flow Conditions.
(8 hrs. holding at 25°C with propylene flow and stagnant conditions)

T = 431°C

P = .94

WHSV = 20.9

Catalyst Wt. = .4 grams

Propylene Stream Time Min.	Percent Conversion of Propylene	Rate Steady-State Rate r/r_{ss}	Fractional Approach to Steady-State $(r_{ss} - r)/(r_{ss} - r_0)$
0	3.4	0.291	1
10	9.512	0.81	0.265
30	10.75	0.92	0.115
50	11.7	1	0
80	11.68	1	---
-----8 hrs. holding at 25°C without propylene flow			
0	0.544	0.046	1
30	1.83	0.155	0.886
60	2.14	0.18	0.858
120	5.06	0.43	0.599
180	6.43	0.545	0.478
270	9.15	0.775	0.237
360	10.73	0.91	0.095
600	11.8	1	0

Table XXI

Break-In Behavior of a Tungsten Oxide on Silica Catalyst During Propylene Disproportionation for Cooling/Reheating at Stagnant Conditions. (8 hrs. and 3 hrs. holding at 25°C without flow)

T = 431°C

P = .94 atm.

WHSV = 20.9

Catalyst Wt. = .4 grams

Propylene Stream Time Min.	Percent Conversion of Propylene	Rate Steady-State Rate r/r_{ss}	Fractional Approach to Steady-State $(r_{ss}-r)/(r_{ss}-r_0)$
0	0.46	0.045	1
15	1.12	0.11	0.934
30	1.76	0.172	0.869
60	2.42	0.237	0.802
90	3.32	0.325	0.675
150	5.97	0.585	0.436
210	7.63	0.75	0.266
300	9.3	0.911	0.094
390	10.2	1	0
-----3 hrs. holding at 25°C without flow			
0	1.36	0.14	1
15	1.84	0.19	0.94
45	2.93	0.3	0.695
90	4.48	0.465	0.534
165	6.04	0.627	0.434
255	8.9	0.92	0.075
345	9.63	1	0

Table XXII

Break-In Behavior of a Tungsten Oxide on Silica Catalyst During Propylene Disproportionation for Cooling/Reheating at Stagnant Conditions. (1 and 11 hrs. holding at 25°C without flow)

T = 431°C

P = .94 atm.

WHSV = 20.9

Catalyst Wt. = .4 grams

Propylene Stream Time Min.	Percent Conversion of Propylene	Rate Steady-State Rate r/r_{ss}	Fractional Approach to Steady-State $(r_{ss} - r)/(r_{ss} - r_0)$
0	3.65	0.36	1
15	5.8	0.584	0.652
35	6.98	0.693	0.48
75	7.2	0.715	0.441
115	10.02	0.99	0
145	10.06	1	0
-----11 hrs. holding at 25°C without flow			
0	0.544	0.05	1
15	1.04	0.095	0.951
30	1.23	0.113	0.933
60	1.99	0.183	0.86
120	3.07	0.283	0.755
180	4.35	0.4	0.631
300	6.73	0.62	0.40
420	8.65	0.796	0.215
540	10.38	0.96	0.047
660	10.87	1	0

Table XXIII

Break-In Behavior of the Catalyst ($\text{WO}_3\text{-SiO}_2$) When a Fully Activated Catalyst was Purged for 5 and 30 Minutes with Helium

T = 429°C

P = .94 atm.

WHSV = 42.3

Catalyst Wt. = .29 grams

Propylene Stream Time Min.	Percent Conversion of Propylene	Rate Steady-State Rate r/r_{ss}	$\frac{\text{C}_2\text{H}_4}{2\text{-C}_4\text{H}_8}$
1	0.927	0.165	0.843
6	3.58	0.64	0.845
13	4.36	0.778	0.822
19	5.32	0.95	0.823
30	5.46	0.975	0.835
45	5.66	-----	0.826
55	5.6	1	0.825
-----30 minutes purge with helium			
2	1.433	0.26	0.804
6	3.03	0.555	0.804
14	4.18	0.766	0.828
20	4.72	0.866	0.828
34	5.25	0.963	0.833
49	5.42	1	0.82
62	5.45	1	0.833

Table XXIV

Break-In Behavior of a Freshly Activated Catalyst ($\text{WO}_3\text{-SiO}_2$) During
Propylene Disproportionation and After Puring For
5 and 10 Minutes with Helium

T = 429°C

P = 3 atm.

WHSV = 147.3

Catalyst Wt. = .3 grams

Propylene Stream Time Min.	Percent Conversion of Propylene	Rate		$\frac{\text{C}_2\text{H}_4}{2\text{-C}_4\text{H}_8}$
		Steady-State	Rate r/r_{ss}	
15	0.6		0.04	1.00
30	0.93		0.062	1.44
75	2.02		0.135	1.20
135	3.16		0.211	1.25
240	7.13		0.477	1.18
255	8.06		0.539	1.08
345	10.28		0.69	1.20
435	11.59		0.775	1.00
765	14.95		1	1.316
-----After purging with helium for 5 minutes				
5	3.29		0.223	1.24
10	4.01		0.273	1.24
15	5.46		0.371	1.10
25	6.45		0.44	1.15
40	8.25		0.56	1.06
60	9.57		0.651	1.01
90	12.1		0.823	1.25
120	13.11		0.89	1.04
150	13.1		0.89	1.03
210	14.7		1	1.06
-----After purging with helium for 10 minutes				
10	1.5		0.103	1.28
15	2.26		0.155	1.09
30	3.93		0.27	0.98
90	8.16		0.56	1.12
150	10.5		0.721	1.00
210	11.91		0.82	0.981
300	13.88		0.954	1.15
420	14.55		1	0.996

Table XXV

Break-In Behavior of the Catalyst ($\text{WO}_3\text{-SiO}_2$) When a Fully
Activated Catalyst was Purged with 10 Minutes Helium

T = 405°C

P = .94 atm.

WHSV = 28

Catalyst Wt. = .4 grams

Propylene Stream Time Min.	Percent Conversion of Propylene	Rate Steady-State Rate r/r_{ss}	Fractional Approach to Steady-State $(r_{ss}-r)/(r_{ss}-r_o)$
285	6.68	0.95	0.05
690	7.07	1	0
840	6.9	1	0
-----10 minutes purge with helium			
0	0.25	0.034	1
5	1.7	0.23	0.797
10	3.2	0.432	0.587
15	4.00	0.54	0.475
20	4.6	0.621	0.391
30	6.24	0.843	0.162
40	6.67	0.901	0.10
50	7.1	0.959	0.041
70	7.2	0.973	0.027
90	7.4	1	0

Table XXVI

Break-In Behavior of the Freshly Activated Catalyst ($\text{WO}_3\text{-SiO}_2$) and
When a Fully Activated Catalyst was Purged for 10 Minutes with Helium)

T = 431°C

P = .94 atm.

WHSV = 28

Catalyst Wt. = .4 grams

Propylene Stream Time Min.	Percent Conversion of Propylene	Rate Steady-State Rate r/r_{ss}	Fractional Approach to Steady-State $(r_{ss}-r)/(r_{ss}-r_0)$
0	2.0	0.011	1
15	6.1	0.216	0.843
30	8.6	0.305	0.748
60	12.64	0.448	0.593
105	17.87	0.634	0.394
180	20.1	0.713	0.309
225	21.75	0.772	0.245
300	21.84	0.775	0.242
375	24.83	0.88	0.128
525	26.02	0.923	0.084
840	28.18	1	0
-----10 minutes purge with helium			
0	1.18	0.045	1
5	12.35	0.466	0.559
10	15.26	0.576	0.444
15	18.52	0.699	0.301
20	20.67	0.78	0.230
25	22.09	0.834	0.174
30	22.94	0.865	0.141
40	23.2	0.87	0.130
60	25.77	0.972	0.035
90	26.5	1	0

Table XXVII

Break-In Behavior of the Freshly Activated Catalyst ($\text{WO}_3\text{-SiO}_2$) and
When a Fully Activated Catalyst was Purged for 5 and 10 Minutes
With Helium at 452°C

T = 452°C

P = 194 atm.

WHSV = 77.8

Catalyst Wt. = .3 grams

Propylene Stream Time Min.	Percent Conversion of Propylene	Rate Steady-State Rate r/r_{ss}	Fractional Approach to Steady-State $(r_{ss}-r)/(r_{ss}-r_0)$
15	1.05	0.067	0.933
45	4.75	0.302	0.697
75	6.54	0.416	0.584
120	8.69	0.553	0.446
165	9.6	0.611	0.388
285	11.66	0.742	0.257
405	14.07	0.896	0.103
525	14.33	0.91	0.086
615	15.7	1	0
-----5 minutes purge with helium			
15	10.57	0.58	0.474
20	14.32	0.791	0.237
30	15.64	0.86	0.156
45	17.67	0.976	0.027
60	17.65	0.976	0
90	17.75	0.98	0
120	18.1	1	0
-----10 minutes purge with helium			
0	3.5	0.193	1
15	9.94	0.55	0.511
25	12.91	0.71	0.329
35	16.45	0.908	0.105
45	17.65	0.975	0.0305
80	18.1	1	0

Table XXVIII

Break-In Behavior of the Catalyst ($\text{WO}_3\text{-SiO}_2$) When a Fully Activated Catalyst was Purged for 4.5 and 8 Hours at the Reaction Temperature

T = 452°C

P = .94 atm.

WHSV = 77.8

Catalyst Wt. = .3 grams

Propylene Stream Time Min.	Percent Conversion of Propylene	Rate Steady-State Rate r/r_{ss}	Fractional Approach to Steady-State $(r_{ss}-r)/(r_{ss}-r_0)$
0	2.0	0.107	1
15	7.25	0.39	0.685
30	12.37	0.665	0.373
45	15.43	0.829	0.191
60	16.9	0.908	0.1
90	17.75	0.954	0.052
120	18.6	1	1
-----8 hours purging with helium			
0	2.0	0.107	1
15	6.1	0.33	0.753
30	10.93	0.58	0.461
60	17.99	0.967	0.0357
90	18.71	1	0
120	18.6	1	0
-----12 hours purging with helium			
0	0	0	1
10	0.84	0.05	-----
30	8.33	0.496	0.5
45	11.59	0.69	0.302
60	14.13	0.84	0.149
75	15.2	0.905	0.085
105	16.78	1	0
120	16.55	-----	0

Table XXIX

Break-In Behavior of the Catalyst ($\text{WO}_3\text{-SiO}_2$) after Cooling/ReheatingIn Presence of Helium (0 and 8 hours holding at 25°C)T = 452°C

P = .94 atm.

WHSV = 77.8

Catalyst Wt. = .3 grams

Propylene Stream Time Min.	Percent Conversion of Propylene	Rate Steady-State Rate r/r_{ss}	Fractional Approach to Steady-State $(r_{ss}-r)/(r_{ss}-r_0)$
0	2.00	0.11	1
5	5.71	0.32	0.795
15	11.56	0.64	0.425
30	15.46	0.857	0.188
45	17.03	0.944	0.094
60	17.83	0.989	-----
90	18.03	1	0
-----8 hours holding at 25°C			
0	1.5	0.091	1
10	6.01	0.366	0.711
25	11.96	0.729	0.301
30	12.81	0.78	0.247
40	14.63	0.891	0.138
60	16.1	0.98	-----
90	15.3	0.933	0.075
110	16.4	1	0

Table XXX

Break-In Behavior of the Catalyst (WO_3-SiO_2) after Cooling/Reheating
In Presence of Helium (12 and 5 hours holding at 25°C)

T = 452°C

P = .94 atm.

WHSV = 77.8

Catalyst Wt. = .3 grams

Propylene Stream Time Min.	Percent Conversion of Propylene	Rate Steady-State Rate r/r_{ss}	Fractional Approach to Steady-State $(r_{ss} - r)/(r_{ss} - r_0)$
0	1.5	0.094	1
10	6.2	0.39	0.697
20	10.78	0.678	0.368
30	12.95	0.814	0.213
40	13.28	0.834	0.18
60	13.9	0.87	0.143
80	15.73	0.989	0.012
100	15.85	0.996	0
120	15.9	1	0
-----5 hours holding at 25°C			
0	1.5	0.093	1
5	3.9	0.24	0.867
10	6.8	0.42	0.661
15	9.25	0.57	0.346
50	15.1	0.93	0.076
60	15.1	0.93	0.076
70	16.7	-----	-----
80	16.16	1	0

Table XXXI

Break-In Behavior of the Catalyst ($\text{WO}_3\text{-SiO}_2$) When a Fully Activated Catalyst was Purged with a Mixture of Helium and 2% Hydrogen and Helium for 10 Minutes at Reaction Temperature

T = 421°C

P = .94 atm.

WHSV = 48.6

Catalyst Wt. = .4 grams

Propylene Stream Time Min.	Percent Conversion of Propylene	Rate Steady-State Rate r/r_{ss}	$\frac{\text{C}_2\text{H}_4}{2\text{-C}_4\text{H}_8}$
0	0.843	0.078	1.29
5	3.73	0.345	0.987
10	5.14	0.476	0.925
15	6.07	0.562	0.954
20	7.1	0.657	0.927
30	8.68	0.803	0.951
40	9.86	0.91	0.91
60	10.8	1	0.95
-----10 minutes purge with pure helium			
0	0.981	0.086	1.14
5	6.93	0.613	1.00
10	8.49	0.751	0.979
15	9.48	0.839	0.91
20	10.00	0.885	0.877
30	10.5	0.929	0.895
40	11.16	0.987	0.90
60	11.3	1	0.89

Table XXXII

Break-In Behavior of the Catalyst ($\text{WO}_3\text{-SiO}_2$) When a Fully Activated Catalyst was Purged with a Mixture of Helium + 1.5% Propylene and Pure Helium for 10 Minutes at Reaction Temperature

T = 430°C

P = .94 atm.

WHSV = 27.8

Catalyst Wt. = .4 grams

Propylene Stream Time Min.	Percent Conversion of Propylene	Rate Steady-State Rate r/r_{ss}	$\frac{\text{C}_2\text{H}_4}{2\text{-C}_4\text{H}_8}$
0	4.17	0.339	1
5	10.96	0.891	1
10	11.96	0.972	0.89
15	12.28	0.998	0.88
20	13.0	-----	-----
30	12.3	1	0.87
-----10 minutes purge with pure helium			
0	0.45	0.035	1
5	5.29	0.412	0.894
15	7.74	0.603	0.95
25	8.56	0.667	0.923
40	9.91	0.773	0.97
80	12.83	1	0.93

Table XXXIII

Effect of a Magnesium Oxide Bed in the Feed Line on the Break-In

Behavior of the Freshly Activated Catalyst ($\text{WO}_3\text{-SiO}_2$)

T = 421°C

P = .94

WHSV = 48.6

Catalyst Wt. = .4 grams

Without Mgo Bed

Propylene Stream Time Min.	Percent Conversion of Propylene	Rate Steady-State Rate r/r_{ss}	$\frac{\text{C}_2\text{H}_4}{2\text{-C}_4\text{H}_8}$
15	0.86	0.069	1
30	1.19	0.095	1.13
60	2.89	0.231	1.008
120	7.38	0.59	0.905
180	8.56	0.685	0.911
240	9.34	0.75	0.923
300	10.51	0.84	0.86
390	11.52	0.92	0.92
480	12.5	1.00	0.907
-----with magnesium oxide bed			
15	0.74	0.064	1
30	1.7	0.146	0.90
60	4.37	0.376	0.95
120	7.73	0.666	1.03
180	7.95	0.685	1.00
240	8.9	0.767	1.00
330	9.34	0.805	1.04
420	10.9	0.94	0.988
520	11.6	1	0.963

Table XXXIV

Break-In Behavior of a Freshly Activated Catalyst ($\text{WO}_3\text{-SiO}_2$) and
 After Pretreatment with Ammonia for 30 Minutes at the Reaction
 Temperature and Purging Fully Activated Catalyst with Ammonia
 for 10 Minutes

T = 430°C

P = .94 atm.

WHSV = 27.8

Catalyst Wt. = .4 grams

Propylene Stream Time Min.	Percent Conversion of Propylene	$\frac{\text{C}_2\text{H}_4}{2\text{-C}_4\text{H}_8}$
30	0.846	1.26
90	3.1	0.904
150	3.95	1.03
240	5.2	0.901
360	6.02	0.933
470	6.56	0.897
1000	6.7	0.881
-----After treating with NH_3 for 30 minutes		
10	0.53	1.00
15	0.41	1.00
50	0.41	1.00
120	0.78	1.39
240	0.97	1.00
-----After purging with ammonia for 10 minutes		
0	7.36	1
4	9.58	0.863
8	8.5	0.906
12	7.95	0.694
16	6.45	0.915
20	6.47	0.988
24	6.42	0.945

Table XXXV

Break-In Behavior of the Freshly Activated Catalyst ($\text{WO}_3\text{-SiO}_2$) and
After Pretreatment with Ammonia for 90 Minutes at Activation Temperature

T = 450°C

P = .94 atm.

WHSV = 63

Catalyst Wt. = .3 grams

Propylene Stream Time Min.	Percent Conversion of Propylene	$\frac{\text{C}_2\text{H}_4}{2\text{-C}_4\text{H}_8}$
15	0.51	1.15
30	1.16	0.90
60	2.47	0.85
105	4.07	1.29
165	6.15	0.93
255	6.73	1.117
375	7.99	1.02
435	8.44	1.26
540	8.57	0.91
-----After Treatment with ammonia		
5	0.35	1.23
10	0.39	1.06
15	0.42	1.169
105	0.55	0.926
225	0.83	0.85
405	0.92	0.911

Table XXXVI

Activity of the Catalyst ($\text{WO}_3\text{-SiO}_2$) After Dosing a Small Amount of NH_3 into the Propylene Feed During the Steady-State Regime

T = 430°C

P = .94 atm.

WHSV = 27.8

Catalyst Wt. = .4 grams

Propylene Stream Time Min.	Percent Conversion of Propylene	$\frac{\text{C}_2\text{H}_4}{2\text{-C}_4\text{H}_8}$
1000	6.6	0.89
-----Steady-state conversion		
0	8.28	0.674
4	16.99	0.801
8	17.07	0.796
12	15.9	0.885
16	14.2	0.902
20	11.67	0.898
30	9.43	0.853
60	6.83	0.94
100	7.2	0.808

Table XXXVII

Break-In Behavior of Freshly Activated Catalyst ($\text{WO}_3\text{-SiO}_2$) During
Propylene Disproportionation (Using 98.5% C_3H_6 + 1.5% NH_3 as a Feed)

T = 430°C

P = .94 atm.

WHSV = 27.8

Catalyst Wt. = .4 grams

Propylene Stream Time Min.	Percent Conversion of Propylene	$\frac{\text{C}_2\text{H}_4}{2\text{-C}_4\text{H}_8}$
.5	3.76	0.78
10	7.86	0.856
15	11.0	0.836
25	10.6	0.926
30	13.98	0.844
40	15.67	0.869
75	16.27	0.815
105	17.95	0.803
135	18.00	0.82
-----Switched to 100% C_3H_8		
5	1.15	1
15	2.44	0.959
30	3.3	0.865
90	6.63	1.037
150	7.32	0.894
225	7.1	0.963
-----Switched to the mixture		
0	14.017	0.978
5	20.44	0.823
10	20.86	0.887
15	19.66	0.86
25	23.22	0.86
35	24.75	0.8
50	24.34	0.83

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BREAK-IN BEHAVIOR OF TUNGSTEN OXIDE ON SILICA
CATALYST DURING PROPYLENE DISPROPORTIONATION

by

Jamshid Fathikalajahi

(ABSTRACT)

This investigation consisted of a study of the break-in behavior of a tungsten oxide on silica catalyst during propylene disproportionation. A catalyst of 10 percent WO_3 on silica gel (223 square meters per gram B.E.T. surface area) was used in a microcatalytic reactor. During the initial contacting of freshly activated samples of this catalyst with propylene, significant increases in disproportionation activity were observed for periods of up to 20 hours. The object of this study was to investigate the phenomena responsible for this break-in.

The rate of approach to steady-state activity data were obtained using catalyst samples which were first saturated with each of the three gases involved in this reaction (propylene, ethylene, and 2-butene) by pulsing at .94 and 2.7 atmospheres before starting the propylene flow. Effects of each gas on the break-in behavior of the catalyst were determined. A material balance around the reactor was made for each gas by pulse reactor techniques.

In general, it was found that almost any change that disturbs the steady-state reaction causes a relaxation of the break-in. That is, a sharp decrease in the rate of reaction was observed, and following

this, there was another period of transient activity which ultimately returned the catalyst to steady state activity. Relaxation of the break-in was studied quantitatively under two different conditions. In the first condition, the temperature of the reactor during the steady-state regime was lowered to room temperature level and then the reactor was held at room temperature for varying periods of time, following which the reactor was brought back to the original reaction temperature. In the second condition the relaxation of the break-in was studied by subjecting a fully activated catalyst to an inert purge (helium) for varying periods while maintaining the reaction temperature level. The break-in rate constants and the initial activities were determined by measuring the rate of the break-in observed following the relaxation of the original break-in. The relaxation of the catalyst break-in was found to depend on both the reactor temperature and pressure with an activation energy of 6300 cal/g mole. From these studies it was concluded that, during the normal break-in period, two competitive processes are taking place. The processes probably are

- a. reduction of the catalyst surface which increases the activity of the catalyst
- b. oxidation of the catalyst surface to some intermediate tungsten oxide by impurities in the feed, which decreases the activity of the catalyst.

Data for the rate of approach to steady-state activity was obtained using a freshly activated catalyst which was pretreated

with ammonia at the reaction and at activation temperatures. Catalysts so treated has little activity for disproportionation. The influence of injecting small quantities of ammonia into the propylene feed during the steady-state regime was studied. Ammonia was found to give a large increase in catalytic activity and the effect was found to be reversible with continuous injection of ammonia necessary to maintain high catalytic activity. When the disproportionation reaction was studied with a propylene feed which contained 1.5% ammonia, it was found that the rate of approach to steady state and the steady-state conversion level were increased significantly.