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THE EFFECT OF CATALYST PRETREATMENT ON THE OLEFIN METATHESIS CATALYZED BY ALUMINA-SUPPORTED RHENIUM-OXIDE.

THE UNIVERSITY OF OKLAHOMA, PH.D., 1979

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THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

THE EFFECT OF CATALYST PRETREATMENT ON THE OLEFIN METATHESIS CATALYZED BY ALUMINA-SUPPORTED RHENIUM OXIDE

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

JAAN-CHYI HSU

Norman, Oklahoma

1979

THE EFFECT OF CATALYST PRETREATMENT ON THE OLEFIN METATHESIS CATALYZED BY ALUMINA-SUPPORTED RHENIUM OXIDE

APPROVED BY

DISSERTATION COMMITTEE

ABSTRACT

The kinetics of olefin (propene and cis-2-butene) metathesis over 9% Re_2O_7/Al_2O_3 catalysts pretreated with various conditions have been studied. The selectivity (i.e. ratio of ethylene to butenes (E/B); ratio of trans-2-butene to cis-2-butene (TB2/CB2)) and the catalytic nature of the catalyst have also been concerned.

A kinetic model has been developed to express the time-on-stream profile of the activity that may involve catalyst break-in and deactivation depending upon the pretreatment conditions and reaction temperature. The experimental data can be correlated better through the kinetic model based on break-in at the second-order and deactivation at an order between one and two of the residual activity.

Usually, the catalyst break-in of propene metathesis (at 0°C) can be observed on an oxygen-activated catalyst, a dispersion-treated catalyst, and a hydrogen-reduced catalyst. The break-in could be attributed to the fact that the initial metathesis rate is limited by the slow reduction step by propene or its metathesis products for creation of metathesis sites, or by site-localized diffusion effect. The decay in metathesis

activity may be due to the generation of a surface polymer, the impurities in the feedstock (e.g. water), and coke, etc. The observed changes in metathesis activity with different pretreatment procedures may be explained through changes in coordination number and the type of ligand associated with the metal of the catalyst.

Part of Re of a fresh impregnation-prepared catalyst can be lost due to sublimation in oxygen-heated conditions. The catalyst activity is proportional to the oxygen-activated temperature starting from about 200°C, but sharply increases after 500°C. About 10% or more of the metathesis sites available are reversible. In the catalyst activation, oxygen is an important factor to maintain a mesoperrhenate-like structure. Oxygen-free helium may destroy the structure (at 500°C) and create more metathesis sites and/or their strength.

By varying evacuation temperature (T_{ev}) in pretreating an oxygen-activated catalyst (for 11 hrs), the catalyst exhibits two regimes of different characteristics centered in the neighborhood of 320°C. At $T_{ev} < 320°C$, the metathesis activity is low and no break-in but decay. At $T_{ev} > 320°C$, the activity pronouncedly increases with increasing T_{ev}, and the break-in reappears but the deactivation is less T_{ev}-dependent. It is suggested that a dispersed phase is formed starting from 320°C and has high activity for metathesis.

Similar results were obtained for the catalysts treated with hydrogen at various temperature. But at 500°C, the activity

is low and the break-in is protracted. This result may imply that the catalyst can not be completely reduced by hydrogen at 500°C. At a temperature between 200°C and 350°C the reduced catalyst is inactive.

An oxygen pulse into the propene metathesis system can be an activator. The increase of the activity due to the oxygen activator is dependent upon the reduction level of the catalyst. It is suggested that metathesis activity is associated with rhenium in a particular oxidation state or narrow distribution of oxidation levels and proper ligand coordination.

Isolating an oxygen-activated catalyst in static propene for a long time and evacuating overnight at room temperature increases the initial activity up to 4 times greater than the normal but decays more rapidly. The initial activity and the deactivation rate are a function of not only the isolation but the evacuation time.

In a flowing system, no 1-butene or higher olefins were observed from propene or cis-2-butene metathesis, but propene from cis-2-butene (CB2). In a static system, from CB2 metathesis, a very trace of 1-butene but large propene and higher olefins are observed; from propene metathesis, 1-butene and polymers are observed. In general, the TB2/CB2 ratio increases proportionally to metathesis activity but the E/B ratio increases inversely. However, there is an exception on a hydrogen reduced catalyst (at 500°C) that the TB2/CB2 ratio decreases in the

period of break-in. CB2 is the initial product in propene metathesis. The transformation from CB2 to TB2 is, in part, limited by the stereoselectivity. Some of ethylene product may be converted to propene or butenes.

The alkylidene-carbene complex mechanism is found better correlated with the experimental data.

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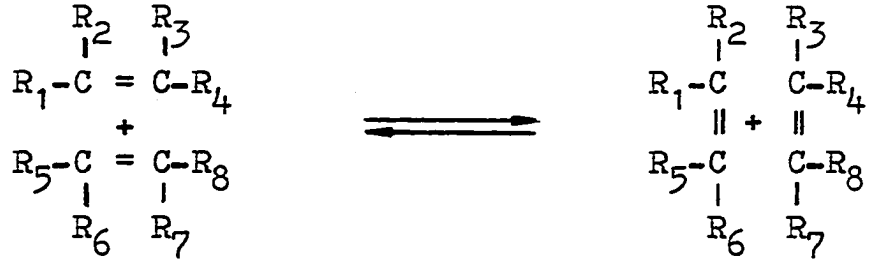
CHAPTER I

INTRODUCTION

A wide variety of efforts has been devoted to the investigation of the heterogeneously and homogeneously catalyzed metathesis of olefins (1,2). For acyclic olefins the reaction stoichiometry of olefin metathesis can be characterized by:



Where the R_1--R_8 are either hydrogen or hydrocarbon groups (3).

Of more interest is the heterogeneous metathesis of olefins. The heterogeneous catalysts are mainly transition metal oxides, carbonyls, or sulfides deposited on high surface area carriers like alumina or silica. Most studies of the heterogeneous metathesis have been carried out with WO_3/SiO_2, MoO_3/Al_2O_3, and $MoO_3/CoO/Al_2O_3$ catalysts. In recent years there has been increased interest in Re_2O_7/Al_2O_3 catalysts. The Re_2O_7/Al_2O_3 catalyst is a selective metathesis catalyst, active even

at subatmospheric pressures and at ambient temperature, and therefore suited for kinetics and spectroscopic studies (1,8, 25). Rhenium-containing supported catalysts are also used in the reforming of petroleum feedstocks (26) and three-way automotive exhaust catalysts (27) etc.

The pretreatment conditions and composition of the catalyst, operating temperature, pressure, space velocity, and the impurities of the reactant, etc., are factors to be concerned for the kinetic study and the investigation of the characteristics of a catalyst. Usually, a catalyst exhibits a maximum relationship between the activity and the activation temperature (28,29,30). Teichner et al.(29,30) found that there are two maxima (470°C and 650°C) and two minima (520°C and 750°C) in their studies of the effect of the activation temperature on the initial activity of amorphous alumina in the isomerization of butene-1. Whan et al. (31,32) observed that the activity of the supported molybdenum hexacarbonyl catalyst depended markedly on the pretreating temperature of the support, the activation temperature after addition of the hexacarbonyl and the storage conditions and time. N.Giorano et al. (33) also found that the bulk and structure of the alumina supported molybdena catalyst differed considerably depending upon the activation temperature. They studied about the factor of catalyst reduction and found that the changes of surface structure were a function of the

acidity of the support, the molybdenum concentration and the conditions of reduction. Lin et al.(15) observed the dependency of ethylene adsorption irreversibility on the reduction time and the kind of support. It was suggested that H_2 reduction created anion vacancies which enhanced the activity and selectivity of the catalyst, but the enhancement was transitory, decreasing in time as reactant became irreversibly adsorbed on those sites. Minachev et al. (5) concluded from the XPS study that the reducibility of Re on γ-Al_2O_3 is much less than that of Re on SiO_2 and can be attributed to a stronger interaction of Re^{7+} with the γ-Al_2O_3 surface. Yao and Shelef (7) have shown the co-existence of two aggregation states of Re on the surface of γ-Al_2O_3: a dispersed, two-dimensional phase of Re interacts strongly with the γ-Al_2O_3 and can be reduced to Re^0 by H_2 only at temperatures in excess of 500°C; the crystalline, three-dimensional phase can be oxidized to Re^{7+} and reduced to Re^0 by H_2 at 350°C. The dispersion treatment creates anion vacancies on the surface which are electron traps and sites for hydrogen adsorption. Olsthoorn and Boelhouwer also observed that their catalyst could, in part, be reduced to the metallic state of Re, but the reduction was not complete (8).

Many heterogeneous catalytic reactions show a maximum in rates as a function of reaction temperature. Clark and Moffat (22) suggested that the rate-temperature maximum observed in the system of propene metathesis over a cobalt-molybdate-

alumina catalyst was caused by the reversible deactivation of sites superimposed on the irreversible poisoning of sites. They successfully applied the Langmuir-Hinshelwood model to a heterogeneous surface and found that it is a neccessary condition for the existence of a rate temperature maximum that the absolute magnitude of the heat of adsorption should be greater than one half of the Arrhenius activation energy.

There are three kinds of mass transfer effects, i.e., the interphase, the intraparticle, the site-localized diffusional effects, proposed for the olefin metathesis on the catalysts, (34,35). If there exists mass transfer effects in the reaction system, the reaction rate will be a function of the amount of the catalyst used, the particle size etc. Interphase mass transfer effects have been observed (35) in propene metathesis with WO_3/SiO_2 catalysts but not with $MoO_3/CoO/Al_2O_3$ catalysts. Lin et al. (15) found that the mass transfer effects were significant on a 20% Re_2O_7/Al_2O_3 catalyst but negligible on a 10% Re_2O_7/Al_2O_3 for propene metathesis at room temperature in a flowing system.

The observation that the cis-trans ratio of the products of the metathesis is equal to the thermodynamic equilibrium value suggests that the reaction is not highly stereoselective. However, under certain conditions the product distribution is influenced by kinetic factors (2). For instance, at short contact times the formation of cis-2-butene is favored in the

system of propene metathesis over some solid catalysts (36). Many authors have observed that when starting from alpha-olefins a high degree of stereoselectivity of metathesis was in favor of cis-isomers especially at low temperature (14). The selectivity to primary metathesis products can be improved by adding small amounts of alkali, alkaline earth metal ions, or thallium copper, or silver ions (1, 38). Swift and Kobylinski (39) also reported that the olefin treatment of molybdena-alumina at 200°C resulted in a decrease in conversion with a significant increase in selectivity. The selectivity increase by olefin is in the order: iso-butylene >1-butene >1-octene >propene.

It is accepted that olefin metathesis proceeds through a transalkylidenation reaction involving cleavage and scrambling of the double bonds (1,2). Three kinds of metathesis mechanisms have been proposed: (a) pairwise, concerted quasi-cyclobutane-metal complex mechanism; (b) pairwise, nonconcerted metallocyclopentane complex mechanism; or (c) nonpairwise carbene chain carrier mechanism. Mathematic models of the olefin metathesis rate were also developed to correlate the experimental data from kinetic studies. The Rideal model based upon the interaction of an adsorbed species and species from gas phase. The Langmuir-Hinshelwood model postulates that the reaction occurs between two chemisorbed molecules. The carbene-complex model is based on alkene- or alkylidene-metal complexes as active sites. Recently, the carbene-complex mechanism has

been examined and found to be more agreeable to experimental data (40, 41) (details shown in Appendix A).

The chemical nature of catalytic active sites has been characterized by various approaches (20). In the studies of n-butene isomerization on acid catalysts, Ozaki and Kimura (43) observed that the deuterium concentration of 2-butene decreased with the rise in the evacuation temperature of catalysts even as the conversion of butene increased and at 500°C little hydrogen exchanged between butene and the catalyst. They suggested that n-butene isomerization on the acid catalysts proceeded at least partly through a proton donor-acceptor mechanism with either Bronsted acids on the surface or the carbonium ions formed by adsorption of olefins on Lewis acid sites serving as proton donors. Applying selective poisoning techniques, Teichner et al. concluded that catalytic activity is simultaneously due to acid sites with oxidizing character and to basic sites with reducing character (29,30). By varying evacuation temperature they found two maxima of activity in the isomerization of butene-1. At 470 °C, acid sites were ascribed to Lewis centers whereas basic sites to surface hydroxyls; at 650 °C acid sites to adjacent aluminum ions (Al^{3+}) whereas basic sites to O^{-2} ions. Similarly, Rosynek et al.(43) suggested that the exposed aluminum ions on γ-alumina functioned as active sites for the isomerization reaction. Running cyclopropane reactions over molybdena-alumina, Hall et al. (44) found that the isomerization

reaction correlated linearly with the sum of the concentrations of anion vacancies and hydroxyls introduced as Mo-OH during the reduction with hydrogen, and olefin metathesis could be correlated with anion vacancy. Using the temperature-programmed desorption method (TPD) Engelhardt(45) observed four types of adsorbed hydrogen on the molybdena-alumina catalyst reduced with hydrogen. He also found that the low temperature adsorption of hydrogen increased the activity and stability of the catalyst for propene metathesis but activity decreased with the high temperature adsorption hydrogen.

Olsthoorm and Boelhouwer (8) concluded from I.R studies that the reduction step of the activated Re_2O_7/Al_2O_3 catalyst with propene or products was a prerequisite to metathesis activity. Nakamura and Echigoya suggested that there were three types of active sites on the similar catalyst treated in vacuo (23). They classified these sites to K-, L-, and M-region for the ratio of $Re/Al < 1/99$, $1/99 < Re/Al < 3/97$, $Re/Al > 3/97$ respectively. The catalystic activity for olefin metathesis increased in the order: $M \gg L > K$. At K-region, the X-ray spectrum was similar to that of the alumina, whereas at M-region it appeared a sharp peak which is a characteristic of a relatively large crystal of Re_2O_7 which has no activity for the metathesis. According to those data, they suggested that the active sites at M-region comprized Re-O-Re bond, the strength of which was so weak that it could be easily converted to active species

by the activation at elevated temperatures and the reduction and complexation with olefins at the reaction temperature; at L-region the active sites comprized Re-O-Al bonds which did not have the doubly promoting effects; at K-region the activity could be enhanced by reduction with hydrogen. Many authors have applied EPR techniques to investigate alumina-supported rhenium oxides (7,23,24). They found the same result that the catalyst treated in vacuo had a sharp line at $g = 2.00$ which could be attributed to free electrons trapped in anion vacancies of the alumina (F center defined by Andreev (24)). This fact is observed at the L-region defined by Naramura et al. (23). Finding F centers, Andreev et al. (24) proposed a "shuttle" mechanism in which the elementary steps involved a shuttle cycle between two oxidation levels(Re^{7+} and Re^{6+}) with the anion vacancy serving as an electron sink and source (F center).

The activity of a freshly prepared catalyst usually exhibited three regimes with time in use; the first, a "break-in" regime characterized by a steady increase in the catalyst activity; the second, a "steady-state" regime with activity relatively constant and the third, a "deactivation" regime associated with the decay in catalyst activity (13,45, 46,47). The break-in phenomena may be due to the reactant-surface interactions which result in a modification of the nature of the active sites responsible for catalytic activity. Luckner and Wills (47) suggested that break-in of the silica supported

tungsten oxide catalyst resulted in the strong adsorption of an organic intermediate or fragment which played an important role in propene metathesis and the oxidation state of the tungsten was also an important factor in the break-in. Pennella and Banks (49) proposed that the catalytic activity of olefin metathesis may be as a function of the energy levels of metal ion which could be adjusted by changes in the oxidation state of the metal and by changes in the nature of the ligands, in their number, or in their geometry. They suggested that the catalyst break-in period, shortened by reduction of the surface, could be attributed to an increase in the number of active sites through modification by the polyolefins of the energy level distribution in the tunsten oxide centers. On the other hand, catalyst deactivation could be defined as any phenomenon which lowered the overall rate of a catalytic reaction below the value which could be obtained with a fresh catalyst and uncontaminated reagents (48). Deactivation may be caused by impurities deposited on the catalyst surface, changes of crystalline form, loss of surface area, sintering, deposition of residues on active sites, pore plugging, etc. (4, 48).

To eliminate mass transfer effects, according to the conclusion of Lin et al., we prepared an alumina(γ-)-supported rhenium oxide containing 9% Re_2O_7 for the studies of kinetics and investigation of its catalytic charateristics. The kinetic study of olefin metathesis over the catalyst is

achieved by using a differential reactor (conversion less than 10%). Propene is, usually used as a probe molecule. Unless otherwise stated, the amount of the catalyst used is about 0.5 gram, the reaction temperature is 0 °C, and the propene partial pressure is about 760 torr. The variation of the catalytic activity is performed over the catalysts treated with various pretreatments including varying activation temperature (in O_2), evacuation temperature, and H_2 reduction temperature etc. The effect of the activity by the impurities contained in the feedstock, and pretreating with olefins (e.g. ethylene, butenes) is also studied. Meanwhile, the selectivity (e.g. the ratios of ethylene to butenes, and trans-2-butene to cis-2-butene) profile is also taken into consideration. We hope to characterize the catalytic activity and the active centers of the catalyst in the olefin metathesis reaction from the activity and selectivity profiles.

CHAPTER II

METHODS

A. Materials

The catalyst used for the studies of olefin metathesis was an alumina-supported rhenium oxide catalyst containing 8.96%wt. Re_2O_7 and was prepared by impregnation. In order to make the catalyst uniform, the mixture of γ-alumina (99.% purity, Harshaw Chemical Co., Type 0104, 40-60 mesh) and the aqueous ammonium perrhenate (99.% purity, Apache Chemicals Inc.) was stirred in excess distilled water at temperature below boiling point of water in a three-neck flask for two days and the water was evaporated. The product was dried in oven at 150°C for one day.

The olefins used for studies were: (1): research grade ethylene (99.95% purity); (2): polymerization grade (p.g.) propene (99.%min); (3): research grade (r.g.) propene(99.99%). (4): research grade cis-2-butene (99.96% purity). All olefins were purchased from Philips Petroleum Co..

B. Apparatus

The apparatus used in these studies is shown schematically in Fig. 1. This apparatus is similar to that used by Lin et al. (15), with some modifications.

The inert gas (He, N_2), oxygen and olefins are separately dried with molecular sieve 4A, 4A, and 3A respectively. All molecular sieve columns are in the size of 3/4" x 34". The driers were provided with some accessories for regeneration of molecular sieve with nitrogen at high temperature. Hydrogen was purified through a Serfass Hydrogen Purifier (Milton Roy Co.).

A reduced cupric oxide column with water condenser was built and connected upstream of the molecular sieve driers for removing trace amounts of oxygen contained in the gases. This system was arranged to be evacuated and to reduce cupric oxide with helium-dilute hydrogen at temperature about 200°C

An Aero-Vac Model 702 Monitor Mass Spectrometer was also added to the system. A Keithley Instruments Model 147 nanovolt null detector and Model 260 nanovolt source was used for thermal emf measurements.

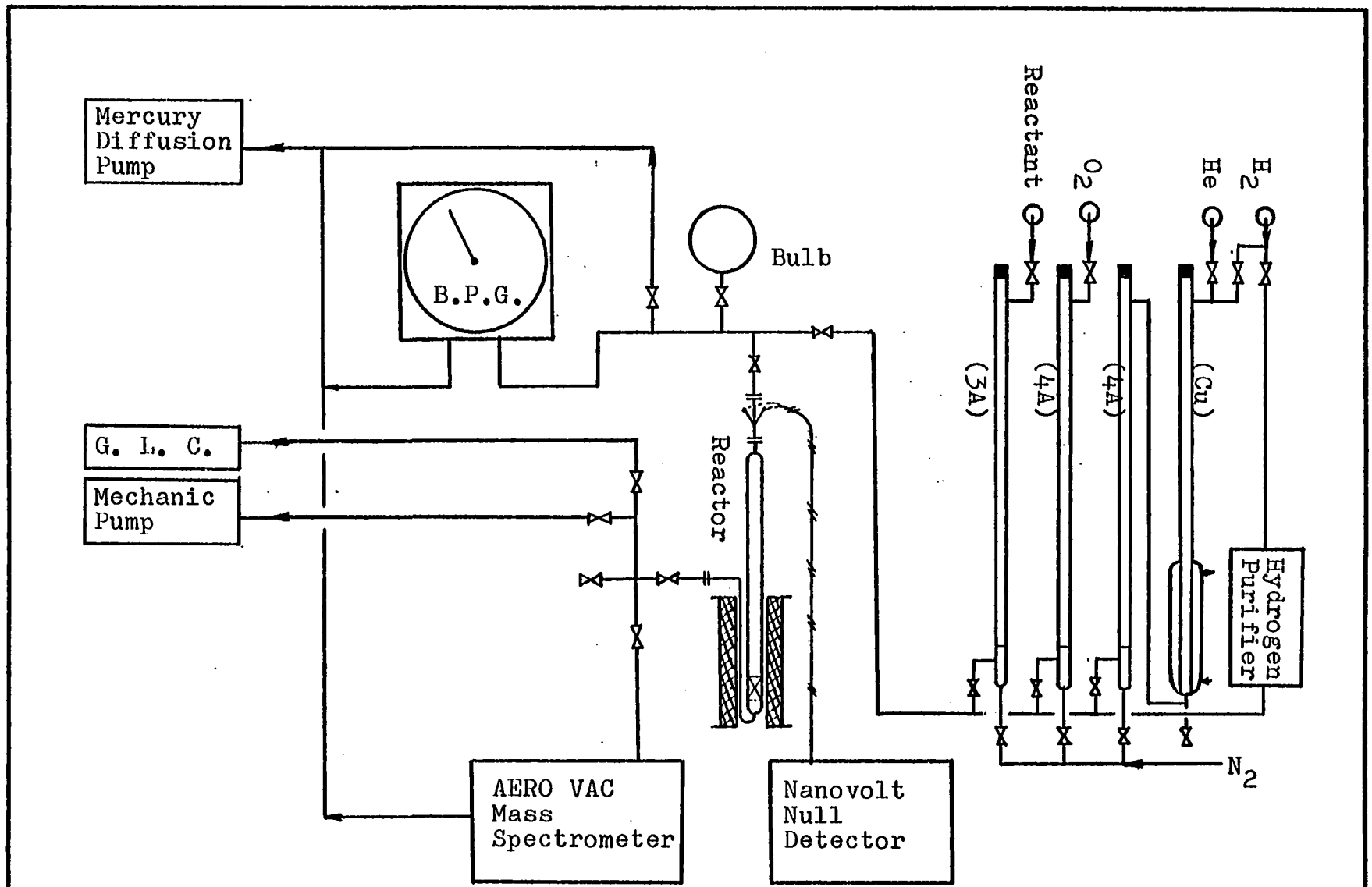


Fig. 1 Flow Diagram for Olefin Metathesis

C. Experimental Procedure

Because the effects of pretreatment on the characteristics of the catalyst was to be studied, different types of catalyst pretreatments were executed. The standard procedure of catalyst pretreatment was to activate the catalyst with dry oxygen for about 17 hours at about 500 °C and 300 ml/min. The catalyst was then cooled to the reaction temperature in a static oxygen atmosphere. This pretreatment is designated as follows: O_2/17 @500°C Rxn T. ***°C

Before running the metathesis reaction the whole system except the reactor was treated by evacuation and purged with reactant to make sure no oxygen detectable in the system and to rid the system of possible poisons from the stagnant reactant (16). The bulk of the oxygen was then pumped out of the reactor. The reactant was introduced and controlled in the range of ±5% of the desired flow rate. Using an on-line injector the reaction products could be analyzed with an F & M Model 810 Analytical Gas chromatograph in an interval of about 10 minutes.

A 'static experiment' was also done. After a kinetics experiment the reactor was isolated in static reactant or its products at room temperature and evacuated at the same temperature for the desired time, respectively, and made ready for the kinetics experiment of metathesis reaction at 24 °C.

CHAPTER III

RESULTS

A. Typical Time-Dependence of Propene Metathesis

Figure 2 shows kinetic curves to illustrate the time-dependence of the reaction rate and product distribution of propene metathesis run over a Re_2O_7/Al_2O_3 catalyst pretreated with the standard procedure (Ch.II). It was made at 0 °C where it was more convenient to investigate variation of metathesis rate and product distribution in the period of break-in. In this typical case the metathesis activity of the catalyst exhibited a "break-in" regime, a maximum rate ($R_{max.}$), and a "deactivation" regime.

The olefin metathesis rate in vapor is calculated with the following equation suggested by Milanovic et al.(14):

$$R = X(V/22400)(273/T)(P/760)(3600/W) \quad (g\text{-}mol\text{-}g^{-1}hr^{-1}) \quad (1)$$

Where, X = fractional conversion.

V = total volume flow rate, ml/sec.

T = absolute reaction temperature, °K.

P = the partial pressure of the reactant, torr.

W = catalyst weight, gm.

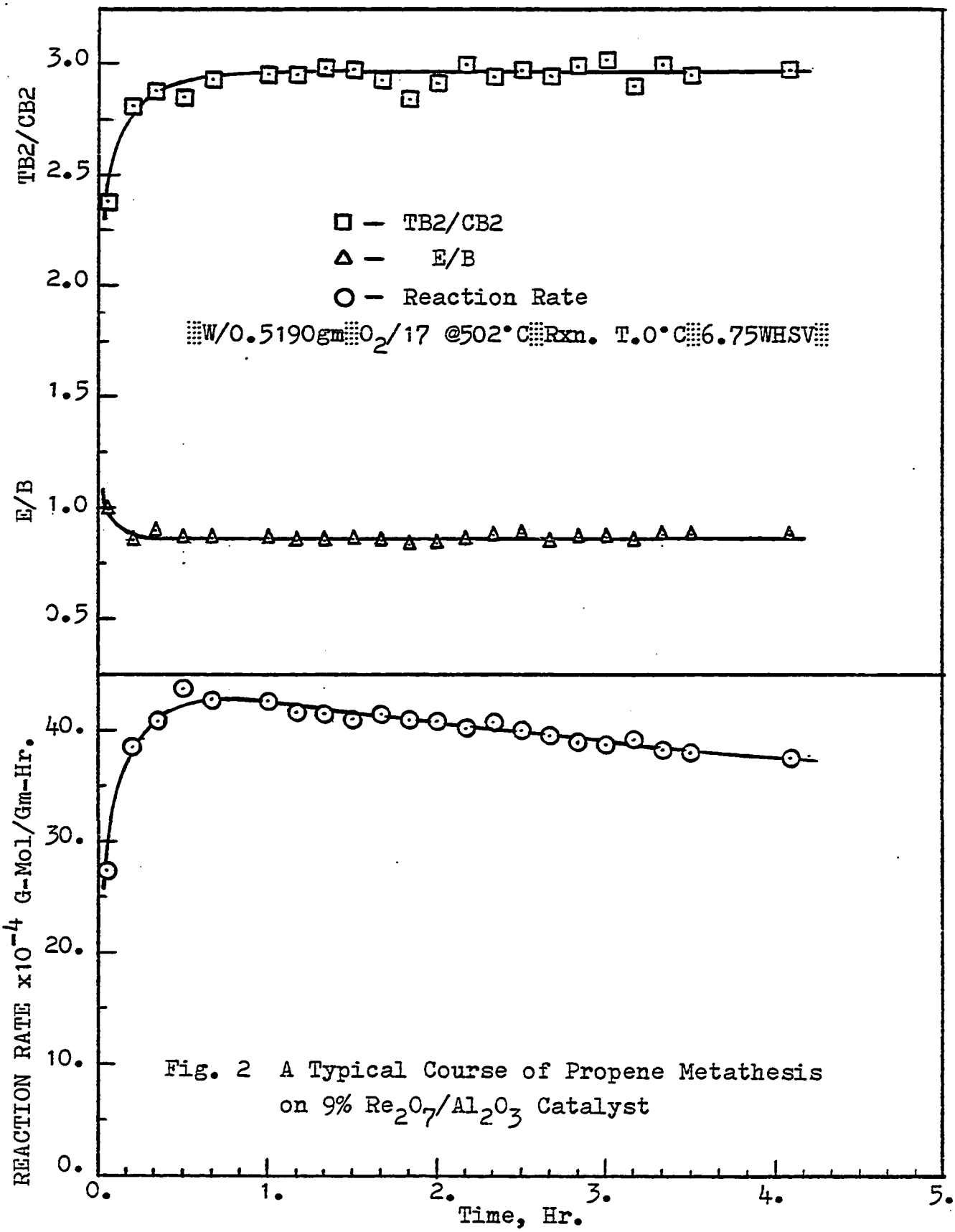


Fig. 2 A Typical Course of Propene Metathesis on 9% Re_2O_7/Al_2O_3 Catalyst

A model to express the kinetic curve of olefin metathesis reaction has been developed and will be discussed later. This model is successfully consistent with the experimental rate data. It can be simply expressed as follows:

$$R(t) = At(1 + Bt)^{-1}(1 + Gt)^{-N} \qquad (2)$$

Where A,B,G,N are parameters characterizing the catalytic activity of a metathesis catalyst during break-in and deactivation. Equation 2 shows that the variation in the rate of propene metathesis with time during break-in can be represented by a second-order rate equation with respect to the residual activity. But it is difficult to determine the deactivation order for reaction at ice temperature by regression of experimental data. For example, the typical rate equation of propene (r.g.) metathesis at 0°C (Fig. 2) and space velocity at 6.75 WHSV can be expressed as:

$$R(t) = 0.13626t(1 + 29.610t)^{-1}\exp(-0.05156t) \qquad (3)$$

with average error ($\Delta R\%$) between theoretical and experimental data 0.883%; or,

$$R(t) = 0.13469t(1 + 29.092t)^{-1}(1 + 0.05829t)^{-1} \qquad (4)$$

with $\Delta R\% = 0.889\%$. Where t is reaction time in hours. However, at room temperature, the second order expression for deactivation seems better (see discussion).

A ratio of ethylene (E) to butenes (B) higher than the stoichiometric value (i.e. 1.) was observed in the initial metathesis reaction of olefins (17,18). A ratio of trans-2-butene (TB2) to cis-2-butene (CB2) lower than the equilibrium value

was observed for gas propene metathesis in flowing system (13), but the reverse results obtained for propene metathesis in a pulse analytical system (18). Fig. 2 also elucidates the typical variation of product distributions of propene metathesis with time. Those results were similar to that obtained by O'Neill and Rooney (17). Fig. 2 shows that:(a) the very initial yield of ethylene is higher than that of butenes, and both increase with time, that of butenes faster, and reach a maximum and then both decrease in the same rate so that the ratio of E/B is initially high but decreases to a constant value (0.85) lower than the stoichiometric value; (b) the ratio of TB2/CB2 increases with time but after about one hour of reaction time it becomes constant (3.0) which is lower than the equilibrium value (i.e. 3.92 @ 0°C). The time course of the percentage of TB2 in the total conversion is similar to that of the ratio of TB2/CB2.

The selectivity of propene metathesis to ethylene and butenes in a flowing system on a Re_2O_7/Al_2O_3 catalyst is about 100%. 1-Butene and higher olefins are undetectable, the only detectable products are ethylene , trans-2-butene and cis-2-butene. However, in a static case, small amounts of 1-butene and higher olefins are observed.

B. The Activation of the Catalyst

In general, a catalyst is activated after drying in certain conditions to maximum activity. For example, the metal oxides for metathesis reactions are activated in a stream of dry air, oxygen or inert gas at temperature around 500-600°C for several hours(1--18hrs), and purged with inert gas for a few hours and then cooled down to the desired reaction temperature.

The activation of the Re_2O_7/Al_2O_3 catalyst has been carried out with certain carrier gases such as dry oxygen, commercial helium, oxygen-free helium and hydrogen, at certain temperature. The metathesis activity of the activated catalyst was examined by r.g. propene running in a flow system.

(a) Dry Oxygen

The metathesis activity of a used catalyst can be restored by treating at a temperature about 500°C in dry oxygen except when the catalyst has been reduced with hydrogen or by evacuation at the same or higher temperature. The color of the oxygen-heated catalyst is light-yellow at high temperature (e.g. 500 °C) but white at room temperature. Once a zeolite adsorber was used to measure the water content (7%wt) in the fresh catalyst (never exposed to propene). Keeping the zeolite adsorber in liquid nitrogen temperature and evacuating the reactor containing 1 gram of the catalyst at 470 °C for a few hours, we found that there was a silvery grey ring formed on the wall of glass tubing at the inlet of the adsorber,

and that the color of the catalyst turned greyish-violet. When oxygen was introduced to the reactor, the temperature of the catalyst bed increased by about 43 °C. This suggests that the catalyst had been reduced at 470 °C by evacuation. We could ascribe the silvery-grey ring formed on the glass wall to the decomposition of ammonium perrhenate or some other rhenium compound which was weakly adsorbed on the surface, but most of rhenium was still strongly held on the support because the recovery of the metathesis activity of the catalyst was observed after treating with oxygen at about 500 °C.

After running the "static experiment", we treated the catalyst in the following way and ran with propene:

O_2/3 @ 236°C Ev./1 @ 0°C Rxn T. 0°C

a trace of ethylene but no butenes was observed. Even when kept in static propene at 0°C for 5.5 hours, the total conversion was about 0.85%.

With the following treatment:

O_2/12 @ 355°C Ev./1 @ 0°C Rxn T. 0°C

initially no butenes were observed but ethylene was 0.08%. After half an hour, the total conversion increased to about 0.21% (E: 0.11%, B: 0.1%). Treating the catalyst again via:

O_2/9 @ 512°C Ev./0.5 @ 0°C Rxn T. 0°C

we obtained a similar kinetic curve and product distribtution to that shown in Fig. 2 with a maximum total conversion about 2.20%.

The above results suggest that: (a) the active sites responsible for propene metathesis are attributed to some kinds of organometallic complexes; (b) the oxidation reaction occurred on the used catalyst treated with oxygen at increasing temperature, and produced water which was strongly adsorbed on the catalyst surface and destroyed the metathesis sites. The fact that the metathesis activity of the catalyst increased with increasing activation temperature might imply that the number of active sites were associated with the removal level of water from the surface.

The kinetic studies of the effects of activation temperature on the rates of break-in and deactivation of propene metathesis activity are shown in Fig. 3. The data show that the higher the activation temperature, the higher the break-in rate, the reaction rate, and the deactivation rate. The plot of the maximum metathesis rate versus activation temperature shows that the creation of active sites for olefin metathesis begins from about 200°C, slowly increases with the activation temperature, but increases sharply after 500°C. Also the maximum rate versus the time required to reach maximum rate is plotted in Fig. 4. There is a linear relationship between them. Extrapolating this straight line to zero time gives a value of maximum rate at 126×10^{-4} g-mol-gm^{-1}hr^{-1}. This indicates that a Re_2O_7/Al_2O_3 catalyst treated in oxygen at certain temperatures and provided the propene metathesis over 126×10^{-4} g-mol-gm^{-1}hr^{-1}

Fig. 3 The Effect of Activation Temperature in Oxygen

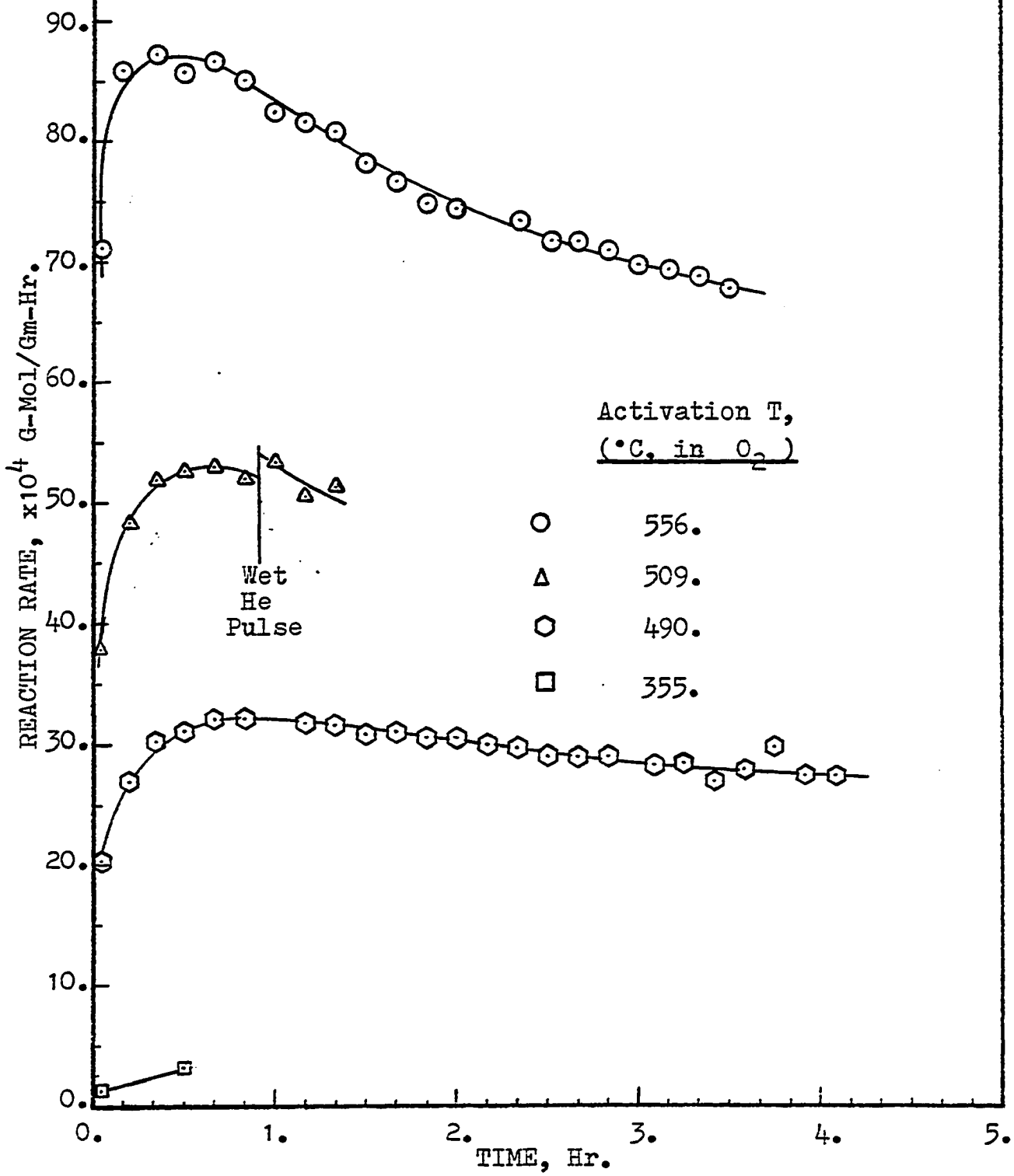


Fig. 4 Effect of Activation Temperature on the Activity of the Catalyst

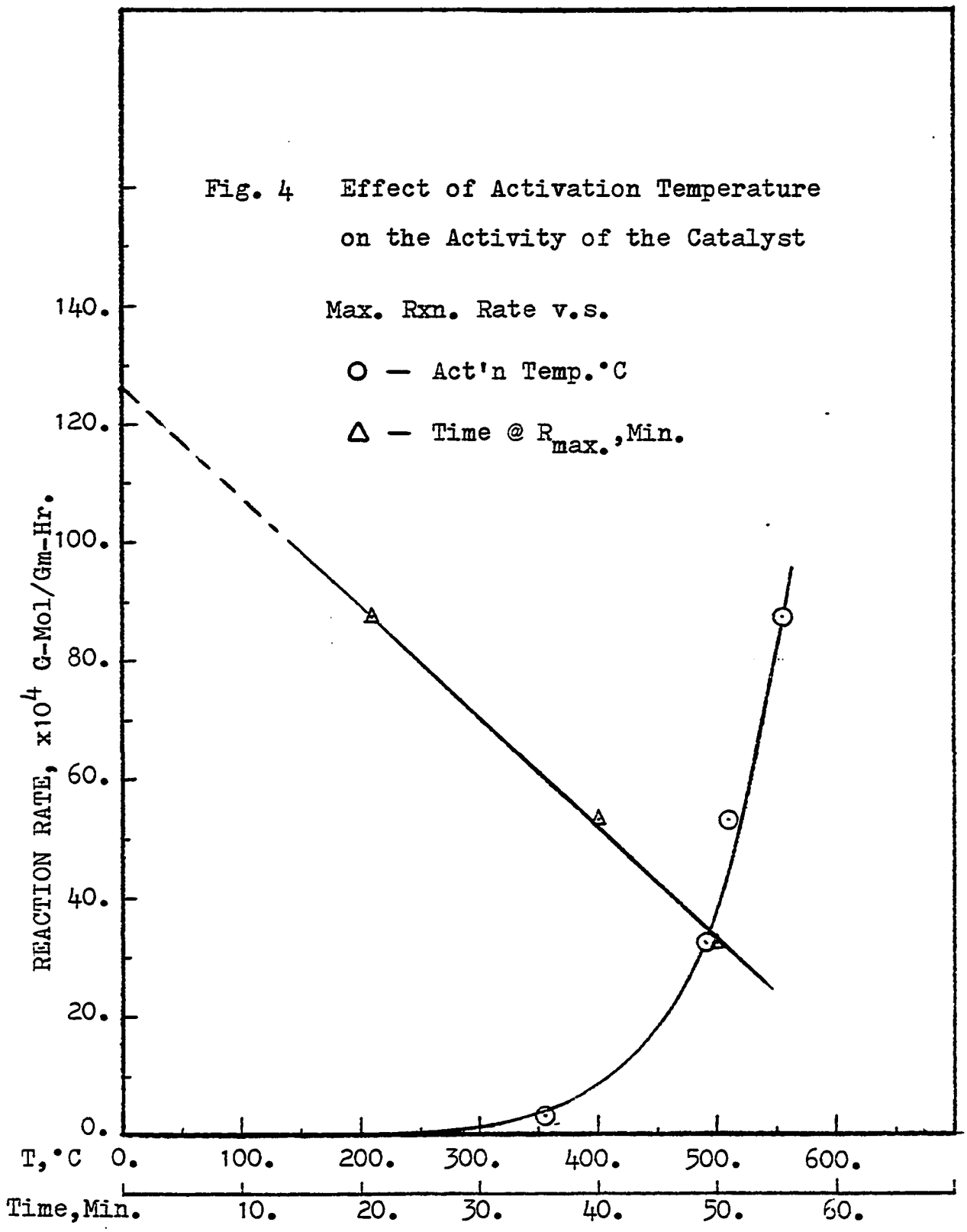
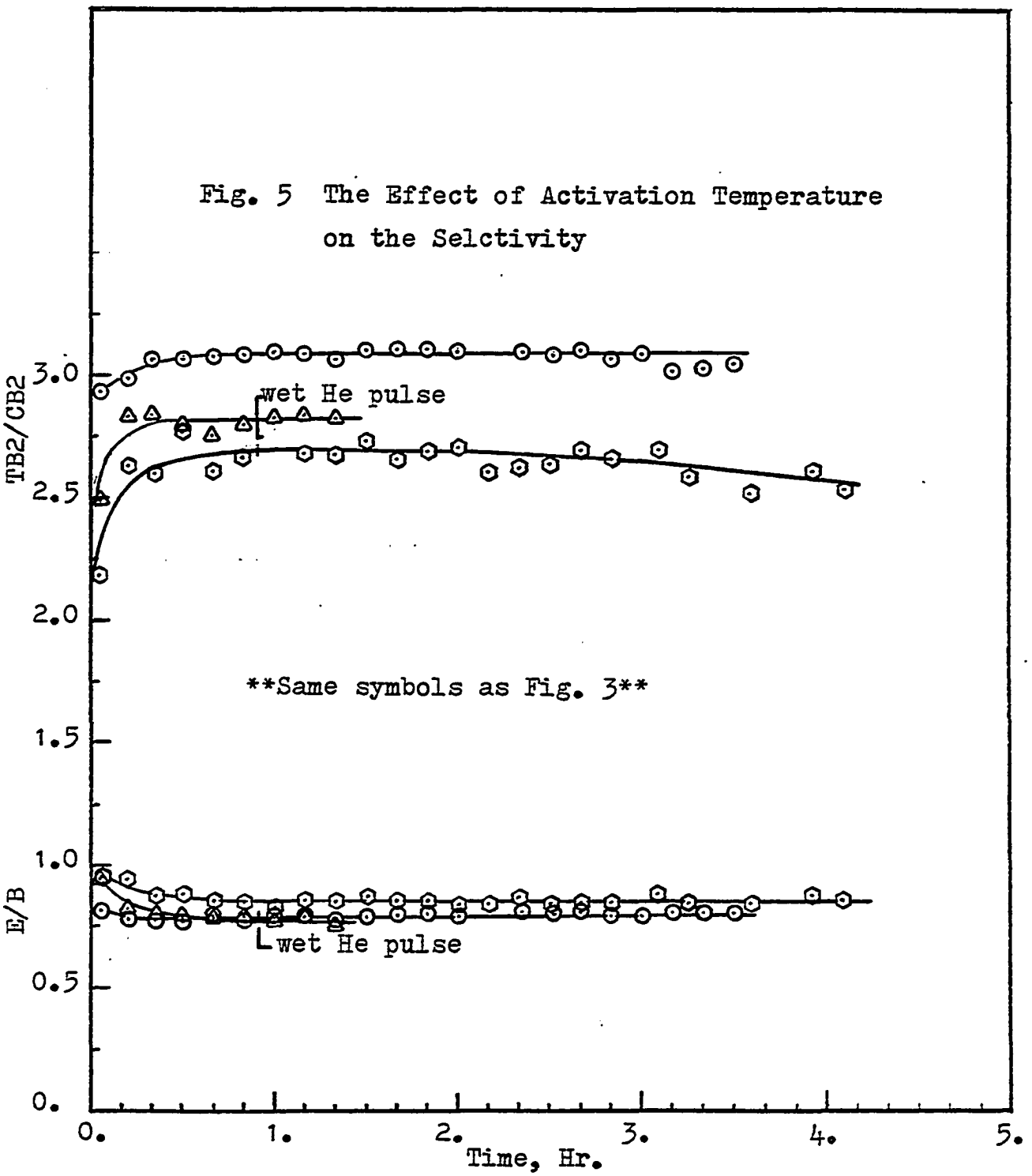


Fig. 5 The Effect of Activation Temperature on the Selctivity



at certain reaction temperatures(which may not be only at 0°C) would not exhibit break-in phenomenon. The break-in may be associated with the reduction level of the surface by reaction products and also the reversibility of active sites, and will be discussed later.

Fig. 5 shows that increasing activation temperature makes propene metathesis reaction on the catalyst favor the production of butenes, especially trans-2-butene, but not 1-butene. However, above 500°C the ratio of E/B would be less affected although the metathesis activity increased sharply.

(b) Dry Helium

Two kinds of helium are available. Usually, a commercial helium contains a trace of oxygen (designate as He). The trace of oxygen in He can be removed by reduced cupric oxide at about 330°C and become oxygen-free helium (He(Cu)).

On a fresh catalyst, heating the catalyst at about 500°C in He(Cu) could activate more pronounced metathesis sites than heating in oxygen or He, with greater stability (Fig. 9). However, on a used catalyst not reactivated with oxygen, it was quite different.

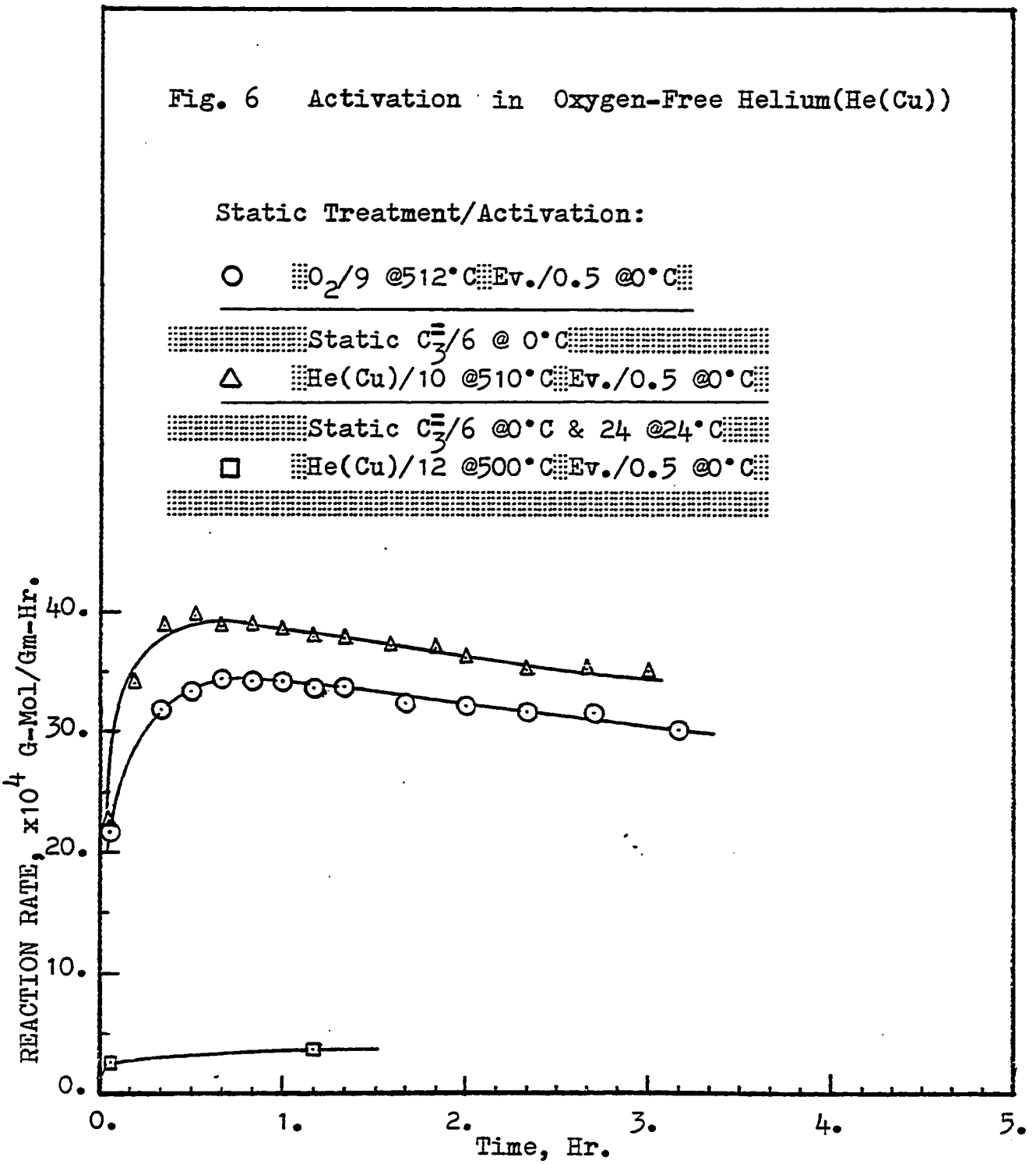
After a flowing run of propene metathesis, purging with dry He at a low temperature (e.g. 46°C) for a few hours and

then introducing propene again, it was found that the initial activity was very high, but decayed rapidly and continuously to a value slightly lower than that of the last run.

A used catalyst, e.g. after a static experiment at room temperature, truned black color when it was flushed with dry He or He(Cu) and heated in a static helium environment for a few hours at about 500°C. Following introduction of oxygen the temperature of the catalyst bed increased by about 115 C° and the catalyst turned light-yellow again. Compared to the temperature increases of fresh catalyst after similar treatment (i.e. 43 C°) it was thought that propene or other reaction products may be strongly adsorbed on the surface of the catalyst and partly cracked to coke at high temperature. The coke was deposited on the surface and burned when oxygen was introduced, resulting in the larger increase in reactor temperature.

After a static experiment the used catalyst was treated with He and tested with dry polymerization grade propene as follows: ⁞He/18 @ 500°C⁞He/1 @ 0°C⁞Rxn T. 0°C⁞. The results show that the propene metathesis rate is only about 48% of that with the standard treatment (in oxygen). This partial recovery of activity could be attributed to the very long exposure to the trace of oxygen in He resulting in removal of strongly adsorbed polymers or deposited coke. It can be proved by the following experiments (Fig. 6).

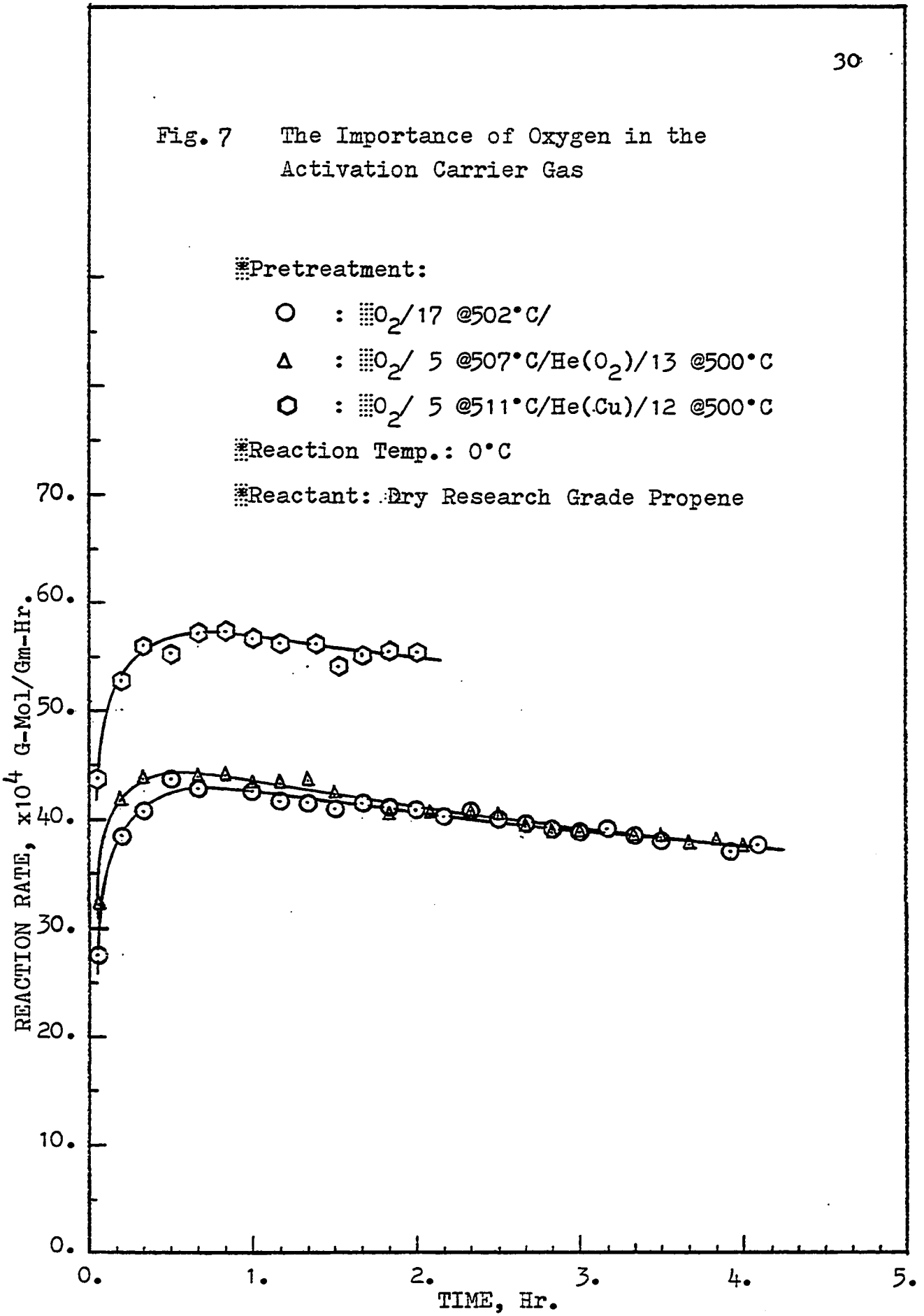
Fig. 6 Activation in Oxygen-Free Helium(He(Cu))



Activating a used catalyst with the standard procedure and running with research grade propene at 0°C, the catalyst was isolated in static propene and its metathesis products at 0°C for 6 hours. Following heating in flowing He(Cu) at 510°C for about 10 hours, the propene metathesis reaction was run again. A reaction rate profile higher by about 13% than that of the standard run but same product distribution was observed. Then, the reactor was isolated again at 0°C for 6 hours and at 24°C for 24 hours followed by heating in He(Cu) at 500°C for 12 hours.In this run a small propene metathesis activity of about 10% of the previous run was observed. At ice temperature, the static products were: E: 15.15%; 1-butene: 0.16%; TB2: 6.51%; CB2: 1.62%; E/B: 1.83; TB2/CB2: 4.02; at room temperature, they were: E: 18.21%; 1-B: 0.96%; TB2: 10.16%; CB2: 3.07%; E/B: 1.28; TB2/CB2: 3.31. These results suggest that: (a) in a flowing inert environment, more active sites responsible for propene metathesis can be created, (b) at ice temperature, quite small amounts of polymers form on the surface which are strongly adsorbed and not removed by inert gas even at high temperature, so the deactivation at ice temperature is quite small. At room temperature, more polymers form and are strongly adsorbed on the surface which are not removed from the surface before cracking to coke, and (c) the olefins of less than four carbons could be removed from metal-olefin complexes before cracking by heating in an inert gas.

Now, the importance of a trace of oxygen in the helium used for activation to the effect of metathesis active sites or the structure of the catalyst will be shown; later, we will show the importance of a trace of oxygen to metathesis activity. Since for each run, the used catalyst has been treated with oxygen first at about 505°C for at least 5 hours, the metathesis rate profile of the catalyst treated with He is the same as that with standard procedure but less by about 30% than that with He(Cu). These results (Fig. 7) are in accord with the suggestion that He(Cu) could create more active sites. With He(Cu), the color of the catalyst turned greyish-violet; but with He, it was still white. By heating in inert gas the surface may be rid of oxygen (atoms or ions) so that the structure of Re_2O_7/Al_2O_3 has been changed.

Fig. 7 The Importance of Oxygen in the Activation Carrier Gas



C. The Effect of Impurity

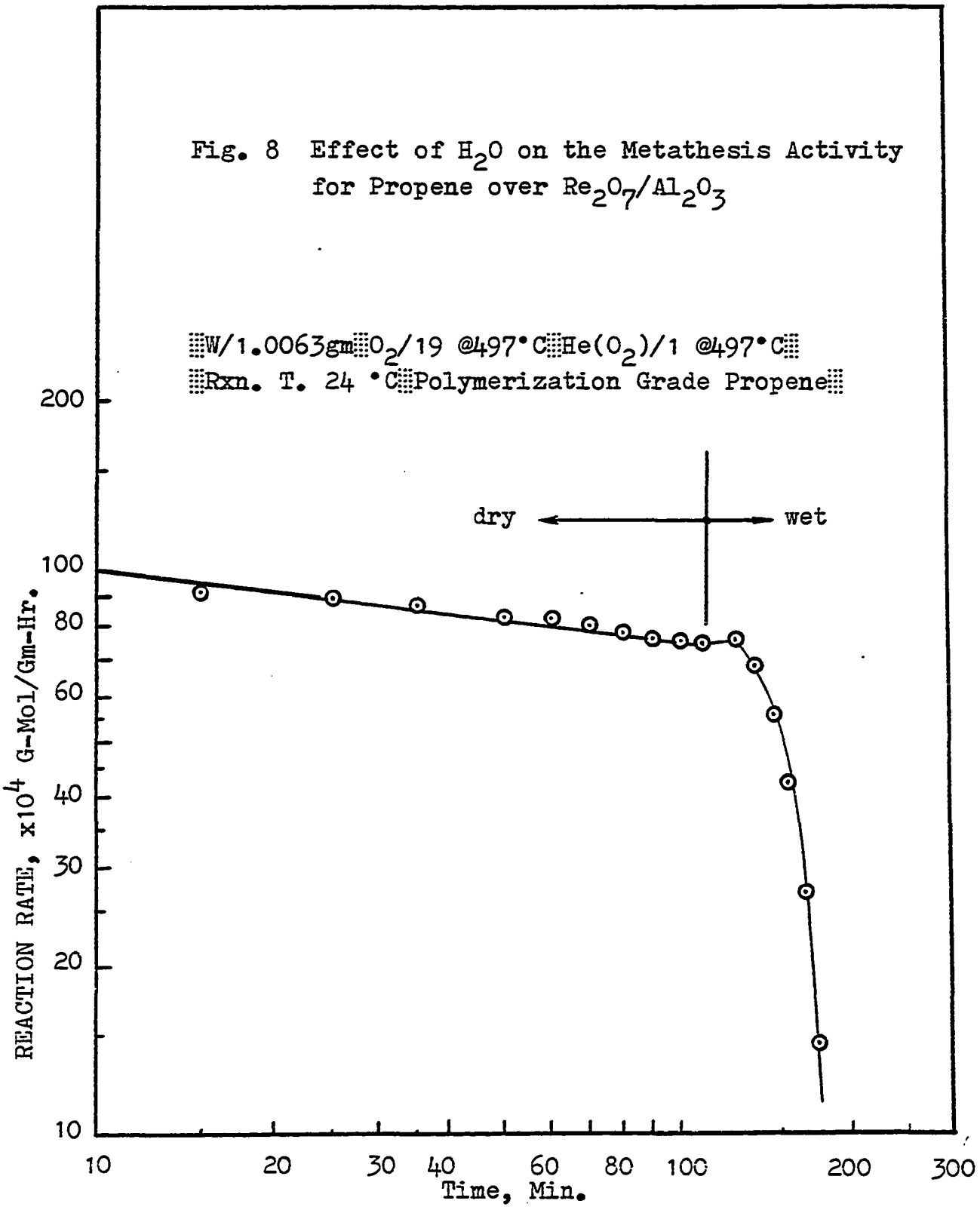
The impurities existing in a flowing reaction system are water, air (oxygen), and carbon dioxide etc. The presence of water, oxygen, or both (1, 2, 11, 12), and carbon dioxide (19) on an oxide catalyst surface could effectively reduce the catalytic activity, but on the other hand, promotional effects have also been observed (20).

(a) Water

Water is a severe metathesis poison. A used catalyst was activated with the standard procedure and cooled down to ice temperature and evacuated for 5 minutes. Then, a wet helium saturated with distilled water at room temperature was introduced passing through the catalyst for about 5 minutes at a flow rate of 2.5 ml/sec. After the introduction of wet helium, the temperature of the catalyst bed increased from 0°C to 24°C. Then the system was evacuated and tested with dry propene. No metathesis activity was observed. In order to test its reversibility the reactor was evacuated at room temperature for 2.5 hours, and tested with dry propene again. Still no activity was observed. These results might imply that the creation of active metathesis sites would be associated with the removal of water from the catalyst surface such as that of Lewis acidic sites. etc.

The effect of a propene feed saturated with water at room temperature on the catalyst activity is shown in Fig. 8.

Fig. 8 Effect of H_2O on the Metathesis Activity for Propene over Re_2O_7/Al_2O_3



In this experiment, dry polymerization grade propene was passed over 1. gm Re_2O_7/Al_2O_3 catalyst, which was activated with the standard pretreatment and purging with He for 2 hours, at 24 °C and atmosphere pressure for two hours. Upon introduction of a water-saturated feed the acti ity was reduced by about 81% in about one hour. Correspondingly, the ratios of E/B and TB2/CB2 were significantly decreased. This information may suggest something which would help the later discussion about the lower ratio of TB2/CB2 at the beginning of reaction and lower value of E/B than the stoichiometric value during deactivation.

Table 1 shows how well the molecular sieve 3A functions as a drier for propene. The catalyst was treated similar to the above experiment but tested with two kinds of polymerization grade propene: one was raw; the other was dried using zeolite 3A. From the experimental data or the rate equation in Table 1 , we found that with the dry propene, the break-in rate was slightly higher but the deactivation was improved significantly and also the metathesis activity was enhanced about 16%.

Unfortunately, we have no moisture detector available, so that we can not quantitatively determine the relationship between deactivation of the olefin metathesis activity and the water content in the olefin feedstock.

Table 1. Efficiency of Zeolite 3A on Drying Reactant

R.G. $C_3^=$	WHSV	R(t) [a]	ΔR% [b]	t_{max} (min	$R_{max.} \times 10^4$	E/B [c]	TB2/CB2
Dry	7.21	$0.07152t(1 + 15.549t)^{-1} *(1 + 0.07157t)^{-1}$	0.81	56.9	40.33	0.84	2.68
Raw	7.02	$0.06124t(1 + 14.945t)^{-1} *(1 + 0.1072t)^{-1}$	0.68	47.4	34.83	0.84	2.69

a. Catalyst and pretreatment: W/0.508gm O_2/13 @500°C He/2 @500°C Rxn T. 0°C; Metathesis rate R(t) is expressed in g-mol-$g^{-1}hr^{-1}$, time, t, in hour.

b. ΔR% = ABS(R(calulated)-R(experimental)/R(calculated))*100

c. The corresponding value at t_{max}.

(b) Oxygen

In the investigation of active sites on some alumina-supported tungsten metathesis catalysts, Pott et al. (12) concluded that in the presence of both oxygen and water the metathesis catalyst was deactivated very rapidly but the loss in activity was partly reversible. The presence of oxygen without water in the propene feed deactivated the catalyst completely and irreversibly, but relatively slow.

However, we found that a pulse of dry oxygen could increase the propene metathesis activity quite pronouncedly depending upon the reduction level and pretreating conditions of the catalyst. Shown in Fig. 9 is the effect of a small O_2 pulse on the activity of the catalyst pretreated in different ways. A record was taken of the temperature of the catalyst bed after an oxygen pulse was injected. This temperature profile is very dependent upon the pretreatment of the catalyst. For instance, to the catalyst activated with the standard procedure, the O_2pulse caused the temperature of the catalyst bed to decrease about 2 C° and then return to a temperature slightly higher than the reaction temperature (about .5 C°). This indicates that something desorbed from the surface and a simultaneously oxidation reaction occurred on the surface when O_2 pulse passed over the catalyst. However, in this example, an O_2 pulse had a negligible effect on the activity.

Fig. 9 Effects of Oxygen Pulse

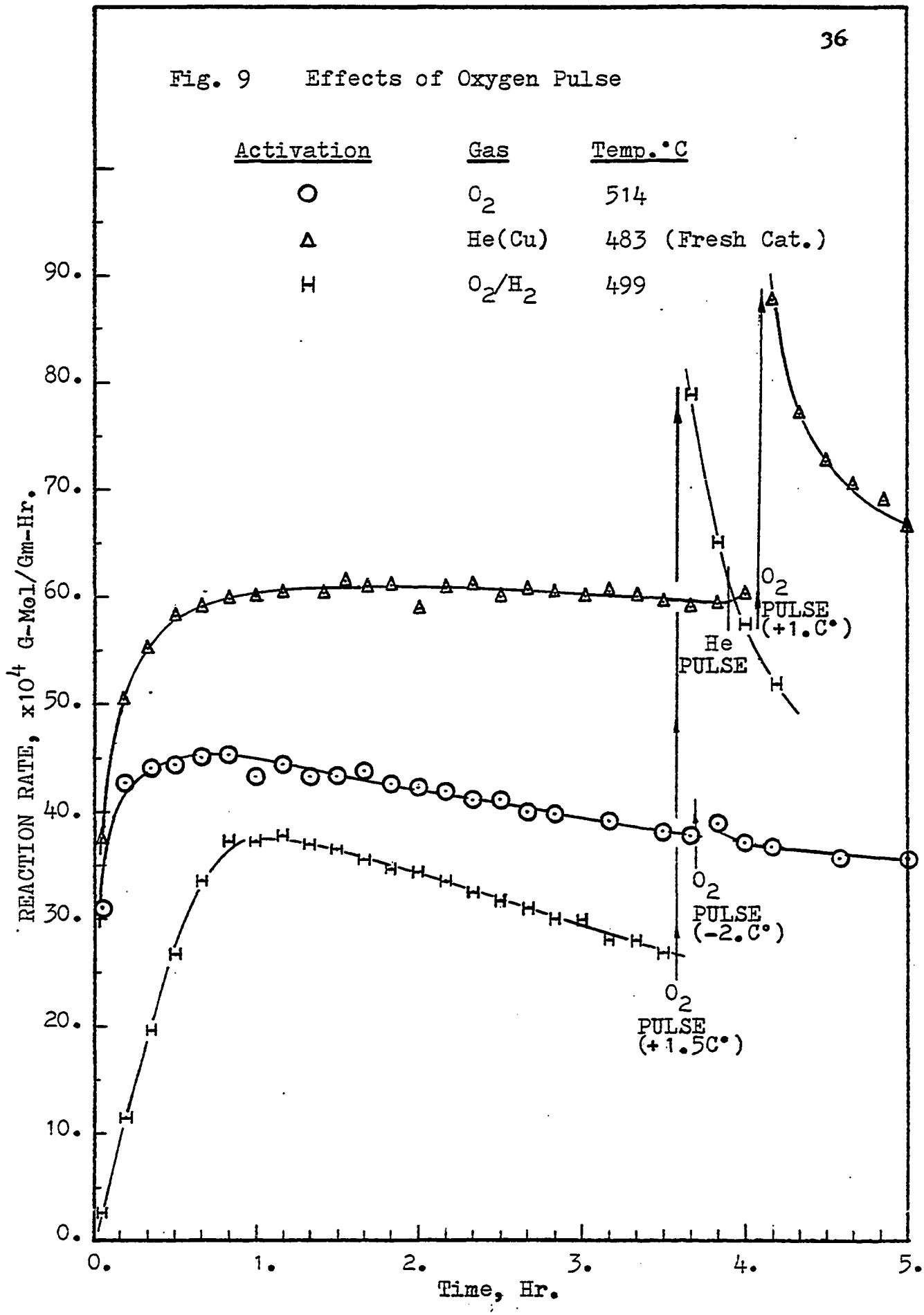
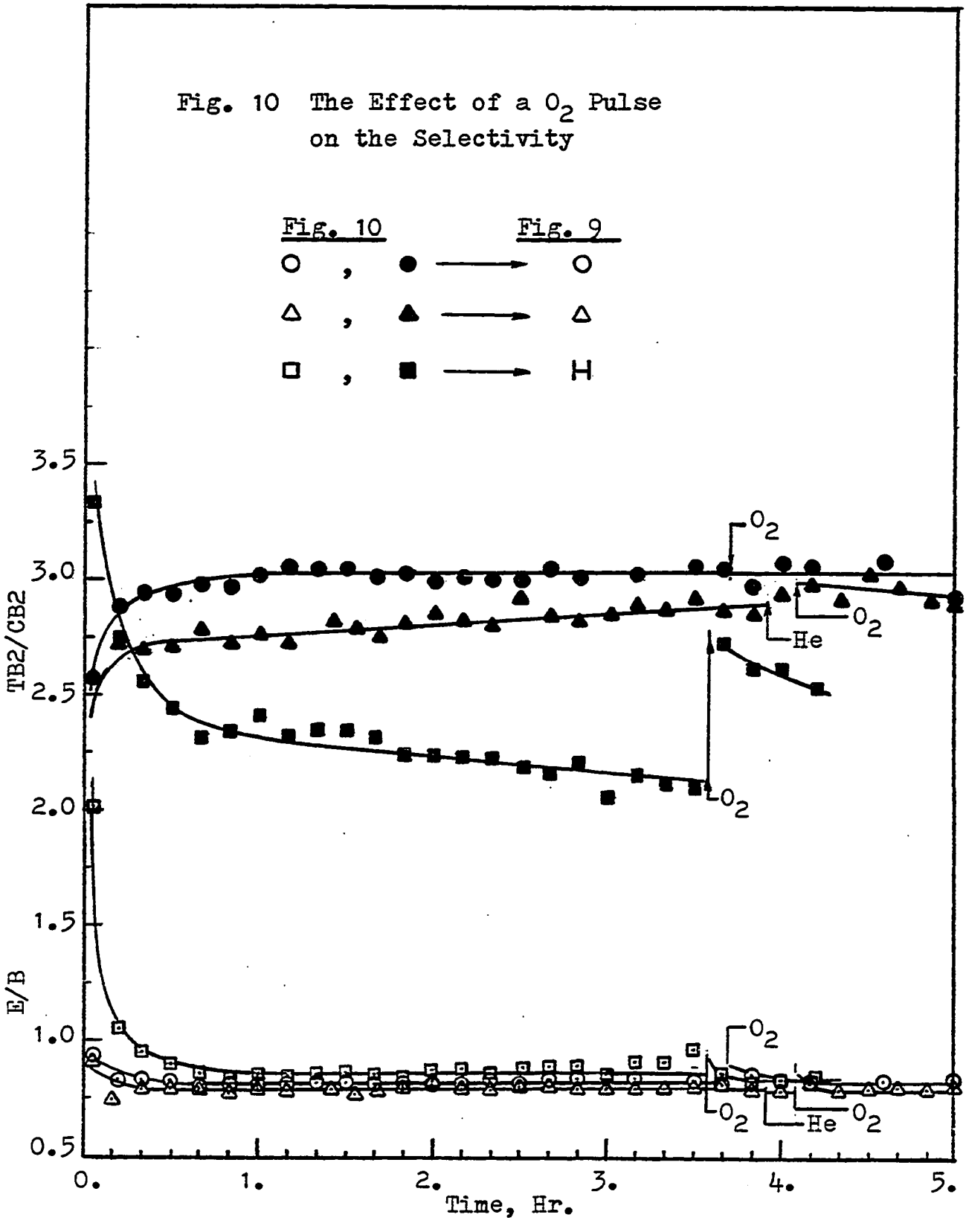


Fig. 10 The Effect of a O_2 Pulse on the Selectivity



On a fresh catalyst pretreated only in He(Cu) at about 500°C, a dry He(Cu) pulse increases the activity very slightly. This observation indicates the reversibility of part of the metathesis sites. A dry O_2 pulse caused a catalyst temperature increase of only 1. °C, but enhanced the activity over 50%. To a used catalyst activated with oxygen and reduced with hydrogen at about 500 °C, an O_2 pulse caused the activity to jump up over 200%, while the catalyst temperature increased about 1.5 °C. In the other cases an O_2 pulse increased the catalyst temperature up to 20--38 °C depending upon the reduction temperature in H_2 (see later).

It is worth mentioning an experiment with r.g.propene inadvertently contaminated with air (about 0.5% O_2). The catalyst was pretreated as: O_2/7 @ 516°C H_2/11 @ 365°C Rxn T. 0°C The product sample taken at 3 minutes of reaction time showed a negligible initial activity, but at 12 minutes, it was about $130.\times10^{-4}$ g-mol-$g^{-1}hr^{-1}$ and the activity increased with time to $175.\times10^{-4}$ g-mol-$g^{-1}hr^{-1}$ at 40 min.(about 5 times of the maximum activity of the catalyst pretreated with the standard procedure).

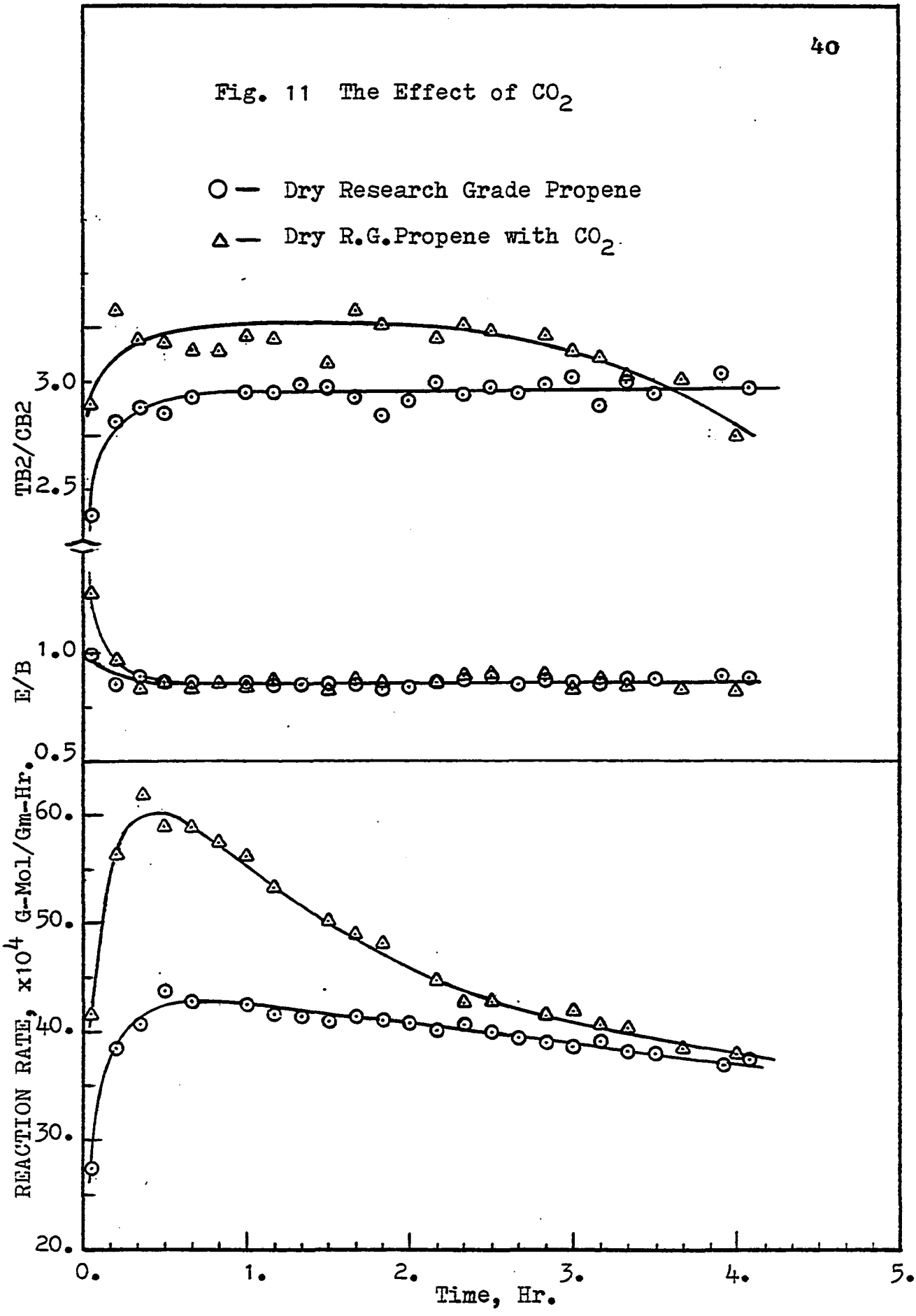
Concerning the effect of an O_2 pulse to product distribution, the experimental data show that on a reduced catalyst the ratio of TB2/CB2 is increased but E/B become less; on an unreduced one the effect is negligible (Fig. 10).

(c) Carbon Dioxide

Carbon dioxide poisons alumina for vaious reactions but a proportional effect has been observed on toluene disproportionation and benzene alkylation over X and Y zeolites (19,20).

Cuprous oxide is a catalyst for the selective oxidation of propene to acrolein (21). In our system the reduced cupric oxide bed, oxygen trap, is a multiphase (Cu-CuO-and/or Cu_2O) system. After research grade propene was passed through reduced cupric oxide bed at 320°C and through molecular sieve 3A at room temperature, a small amount of CO_2 (about 0.7%) was seen in the gas phase. A dry CO_2-containing propene stream was diverted through the catalyst activated by the standard pretreatment. Comparing the kinetic results with those of dry propene without CO_2 contamination (Fig.11), it was found that the $R_{max.}$ was increased by about 42%, but the activity decayed to that characteristic of the standard pretreatment in about 3 hours. CO_2 enhanced not the activity, the break-in rate but also the ratio of TB2/CB2 and the initial value of E/B.

Fig. 11 The Effect of CO_2



D. Mass Transfer Effects

Lin et al. (15) concluded that the mass transfer effect was significant on a 20% Re_2O_7/Al_2O_3 catalyst but negligible on a 10% Re_2O_7/Al_2O_3 for propene metathesis reaction at room temperature in a flowing system.

The catalyst used in our studies was 9% Re_2O_7/Al_2O_3. The catalyst that was used to test mass transfer effect was treated with the standard pretreatment. Fig. 12 shows the results of interphase diffusional effect on propene metathesis at ice and room temperature. The catalysts used for reaction at 0°C were activated at about 490°C, the others at about 510°C. From the data it was concluded that interphase diffusonal effect was negligible on the catalyst used for kinetic studies of propene metathesis at a linear velocity about 6.6 WHSV, although the deviation between both runs at 0°C was about 10%. Also their product distributions were about the same for the same reaction temperature.

E. Activation Energy for Propene Metathesis

We attempted to use the Arrhenius relation to measure the activation energy for propene metathesis on the alumina supported rhenium oxide catalyst from our kinetic data. But

Fig. 12 Mass Transfer Effect

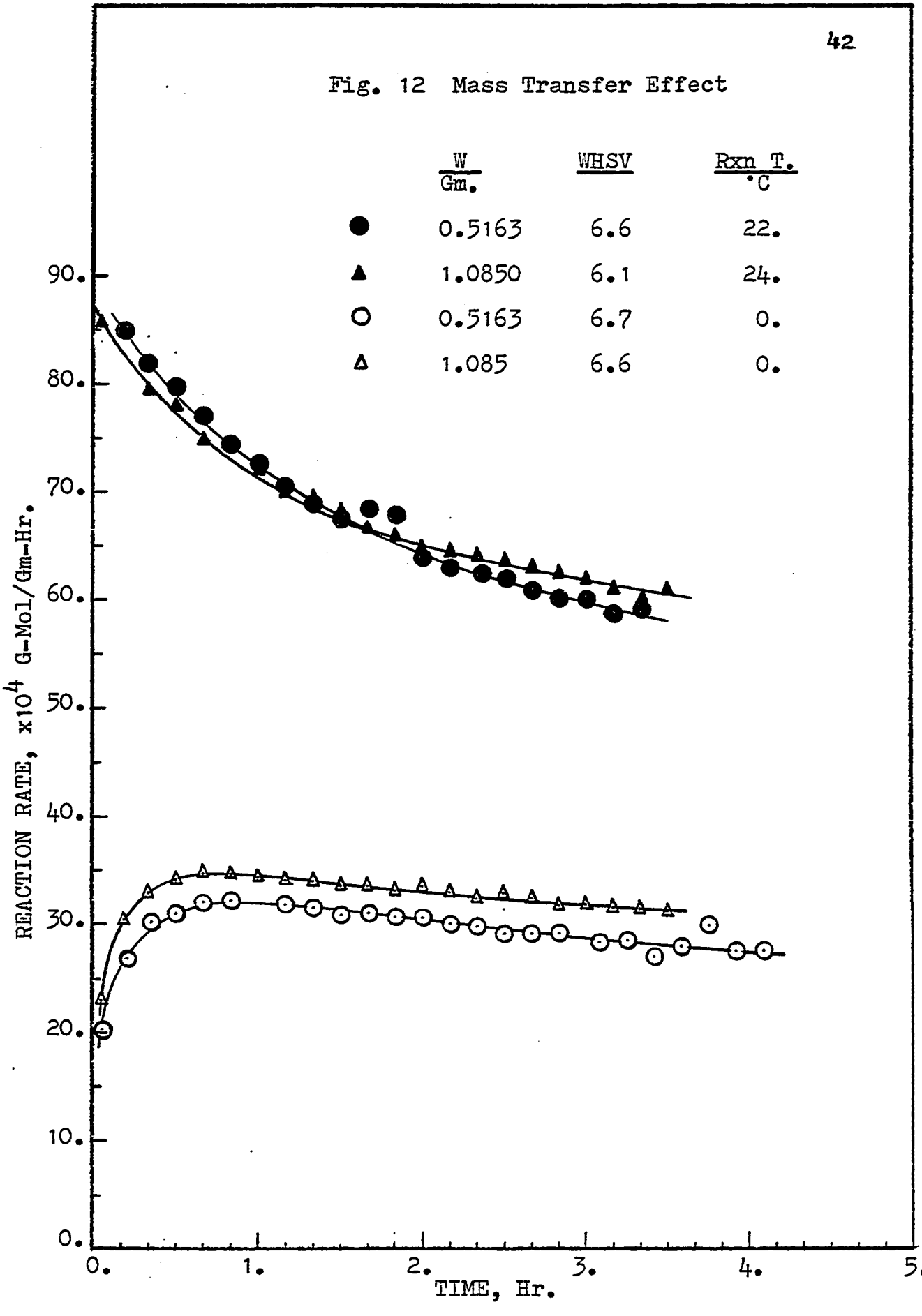


Table 2. The Activation Energy of Propene Metathesis on Re_2O_7/Al_2O_3

T °C	W gm	WHSV	Pretreatment	R(t)	ΔR%	$R_{max.} \times 10^4$	E. kcal.
0	0.5190	6.75	O_2/17 @ 502 °C	$0.13469t(1 + 29.092t)^{-1} *(1 + 0.0583t)^{-1}$	0.89	42.42	5.00
24.	0.5163	6.61	O_2/16 @ 513 °C	$0.008934 *(1 + 1.013t)^{-0.29438}$	0.82	89.34	
0	1.0850	6.55	O_2/19 @ 490 °C	$0.12082t(1 + 32.724t)^{-1} *(1 + 0.0494t)^{-1}$	0.75	34.21	6.28
24.	1.0850	6.09	O_2/18 @ 507 °C	$0.008723 *(1 + 2.033t)^{-0.17715}$	0.50	87.23	
0	0.5190	6.70	O_2/8 @ 514 °C Ev./11@ 24 °C	$0.003940 *(1 + 0.2573t)^{-0.55358}$	0.92	39.40	5.88
24.	0.5190	6.54	O_2/6 @ 515 °C Ev./11@ 24 °C	$0.009467 *(1 + 8.628t)^{-0.21747}$	1.06	94.67	
0	0.5190	6.76	O_2/7 @ 516 °C Ev./11@ 496 °C	$0.96462t(1 + 85.605t)^{-1} *(1 + 0.0849t)^{-1}$	0.60	105.91	2.82
24.	0.5190	6.57	O_2/7 @ 516 °C Ev./11@ 499 °C	$0.016114 *(1 + 6.9628t)^{-0.21416}$	1.98	161.14	

it was difficult to achieve the measurement because, with standard pretreatment, the catalyst exhibits a break-in of the propene metathesis rate at 0°C but not (explicitly) at 24°C. The exhibition of break-in at 0°C is dependent upon the pretreatment conditions of the catalyst (see later).For example, the catalyst activated with standard procedure followed by evacuation at room temperature for 11 hours, did not exhibit break-in again but decay. If the maximum point of reaction rate for the case having break-in and the initial value (at $t = 0$, by regression) for the case having no break-in are used and the Arrhenius relation is plotted, the activation energy is obtained for the catalysts activated differently and is shown in Table 2. The activation energy of propene metathesis on the catalyst pretreated with standard procedure is about 5 kcal. Significantly, with dispersion pretreatment after oxidation, the activation energy is very low, i.e. the sites created by the pretreatment are very active even at 0°C.

F. Reversibility of Metathesis Activity

Clark and Moffat (22) found that there was a reversible deactivation of sites superimposed on the irreversible poisoning of sites in the system of propene metathesis over a cobalt-molybdenate-alumina catalyst. A run was made of propene metathesis to test the reversibility of metathesis sites by varying the reaction temperature between ice and room temperature (Fig. 13).

The catalyst was pretreated as:

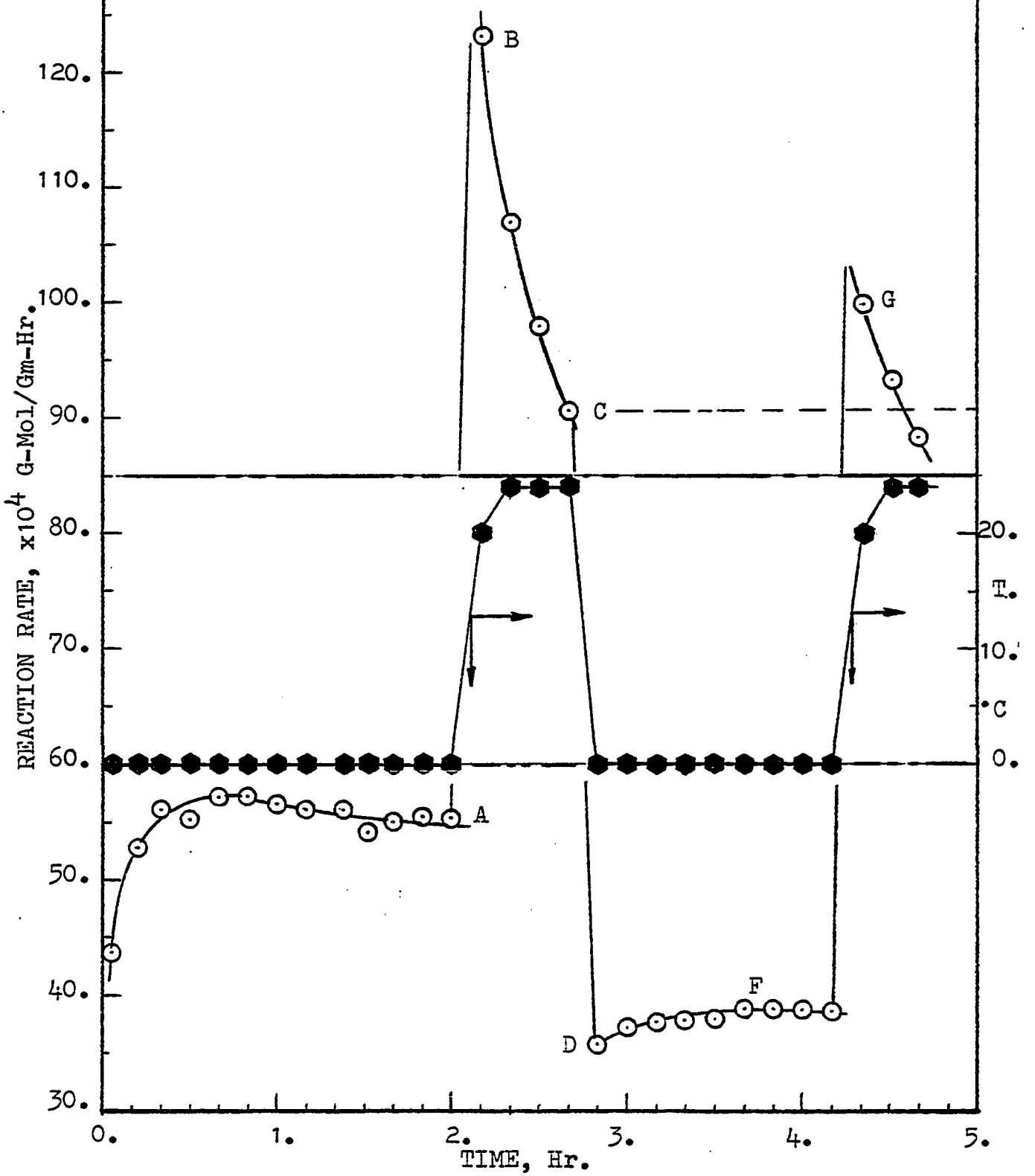
O_2/5 @ 511 °C He(Cu)/12 @ 500 °C

And then propene metathesis reaction was started at 0 °C; as usual, break-in and deactivation were observed. Two hours later, the ice bath was removed and the reaction temperature and activity increased. Because of the rapid deactivation, the ac activity was decaying even while the reaction temperature was increasing. This decay was more pronounced than that while running initially from room temperature. With reference to the points given on the curve, the ratio of the activities between B and A,(R(B/A)), is 2.22. After 30 minutes the temperature was readjusted to 0 °C. Over this 30 minute period, R(C/B) = 0.74. As the sample cooled, the activity decreased and R(D/A) = 0.65. The interesting point is that the catalyst at 0 °C went through a break-in phase, and had a second maximum F. The rate ratio between F and A, R(F/A), is 0.70, so that

Fig. 13 Reversibility of Metathesis Activity

Pretreatment:

O_2/5 @511°C/He(Cu)/12 @500°C



by reacting at 24°C for 30 minutes the activity lost about 30% irreversibly. After 80 minutes, the temperature was again readjusted to 24°C, the activity increased to a value higher than point C, (R(G/C) = 1.10). Because the deactivation of the activity at 0°C is negligible, we could conclude that the reversible sites for propene metathesis is about 10% or more of the metathesis sites available.

The occurrence of the second break-in phase is not fully understood and further study is needed. However, a hypothesis is presented here to interpret this observation. The rate ratio of F/D is 1.09. This value is very close to that of G/C (see above). The second break-in may be attributed to the phase change of butenes adsorbed on the surface during which the catalyst was quenched. The phase change of butenes may block the metathesis sites temporarily. These butenes could be removed from the reversible sites by the introduction of fresh propene reactant. This revival of reversible sites caused the increase of the activity.

G. The Effect of Linear Space Velocity

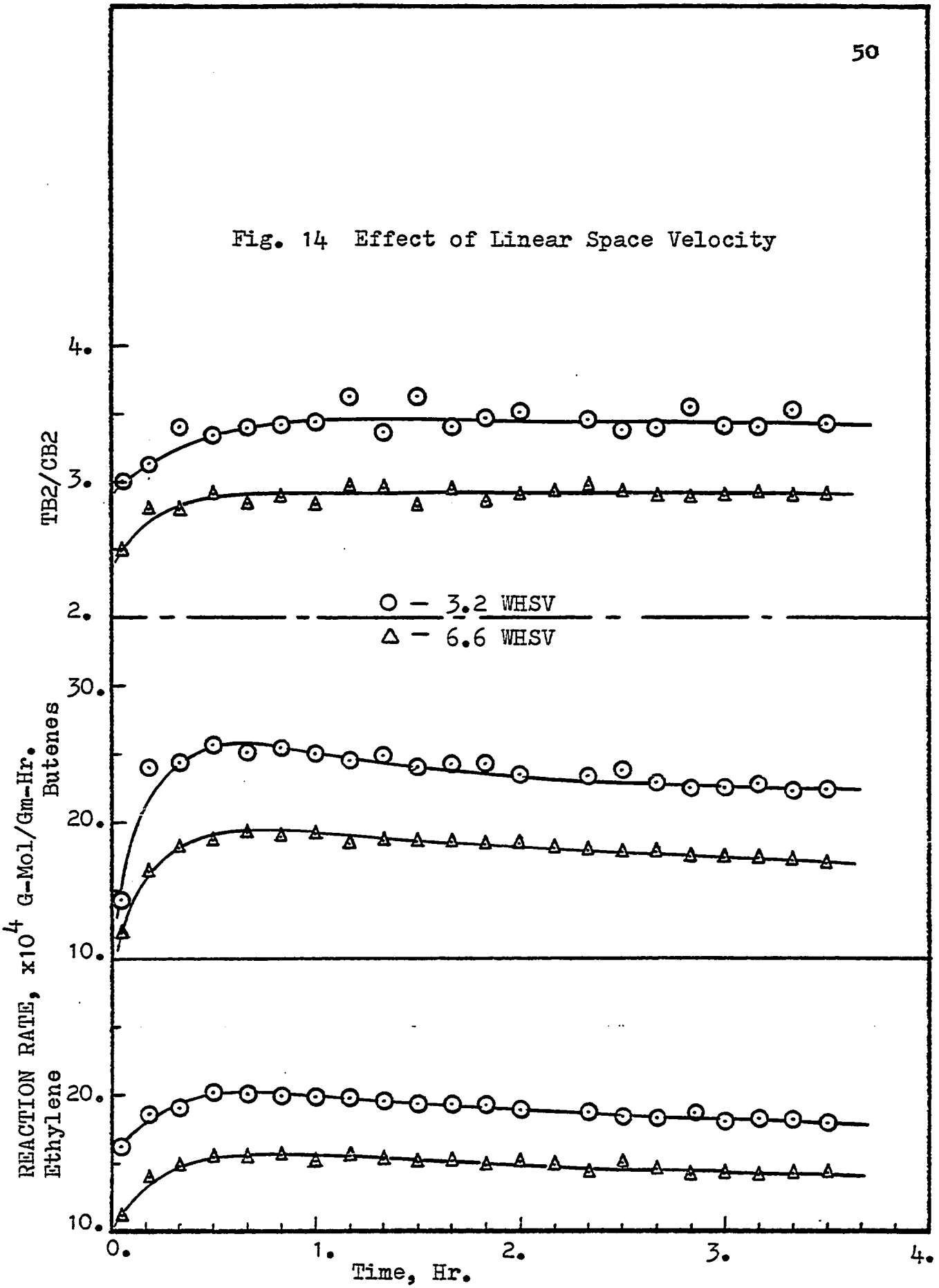
The linear space velocity (WHSV) is a significant factor affecting the reaction rate and the selectivity of propene metathesis on the catalyst. The results of the experiments with different grade of propene and at different space velocities are summarized in Table 3, and the time-dependence of product selectivity is given in Fig. 14.

With a given reactant the experiments were run through the same catalyst activated with the same procedure with a fixed space velocity for each run. Besides the results mentioned in section A, we also found that:(a) using p.g. propene, a higher space velocity accelerated both the break-in and the deactivation rates; but reverse results were obtained for r.g. propene (Table 3). The results suggest that the activity profile of propene metathesis is affected by the impurities (e.g. CO_2 in p.g.propene) and products (e.g. polymers). The polymers may act as a poison on the surface and may be too strongly bound to the surface to escape. But using p.g. propene, the impurities may act more significantly for break-in and deactivation than the surface polymers ;(b) a higher space velocity gave a smaller TB2/CB2 ratio suggesting that the CB2 isomer may be the initial product; (c) a lower space velocity increased both the yields of ethylene and butenes; using r.g. propene the increase of butenes was more pronounced; but the p.g. propene the ethylene. In other words, a lower space

Table 3. Effect of Linear Space Velocity

WHSV	$C_3^=$	W gm	Pretreatment	R(t)	ΔR%	t_{max} (min)	$R_{max} \times 10^4$	E/B	TB2/ CB2
4.58	p.g.	.508	O_2/15 @ 514°C He/2 @ 495°C	$0.05756t(1 + 12.163t)^{-1}$ $*(1 + 0.0679t)^{-1}$	1.30	66.0	41.0	0.95	2.99
7.20	p.g.	.508	O_2/13 @ 501°C He/2 @ 500°C	$0.07152t(1 + 15.549t)^{-1}$ $*(1 + 0.0716t)^{-1}$	0.81	56.9	40.3	0.83	2.72
4.77	r.g.	.511	O_2/5 @ 502°C	$0.10709t(1 + 22.518t)^{-1}$ $*(1 + 0.0937t)^{-1}$	1.13	41.3	42.0	0.81	3.08
6.75	r.g.	.519	O_2/17 @ 502°C	$0.13469t(1 + 29.092t)^{-1}$ $*(1 + 0.0583t)^{-1}$	0.89	46.1	42.4	0.86	2.94
3.20	r.g.	1.085	O_2/21 @ 493°C	$0.16563t(1 + 33.670t)^{-1}$ $*(1 + 0.0645t)^{-1}$	0.82	40.7	45.2	0.79	3.43
6.55	r.g.	1.085	O_2/19 @ 490°C	$0.12082t(1 + 32.724t)^{-1}$ $*(1 + 0.0494t)^{-1}$	0.75	47.2	34.2	0.81	2.86

Fig. 14 Effect of Linear Space Velocity



velocity gave a lower E/B for r.g. propene but higher for p.g. propene. The r.g. propene used contained small amounts of carbon dioxide (about 1.%), so we may conclude (see sction C-c) that the selectivity may be affected by the type of the ligands added to the transition metal of the catalyst.

A qualitative test to show the variation of temperature of the catalyst bed when the flow rate is changing was made. The following figure shows the temperature profile when the flow rate of propene is changing from static to about 1.5 ml/ sec. at room temperature.

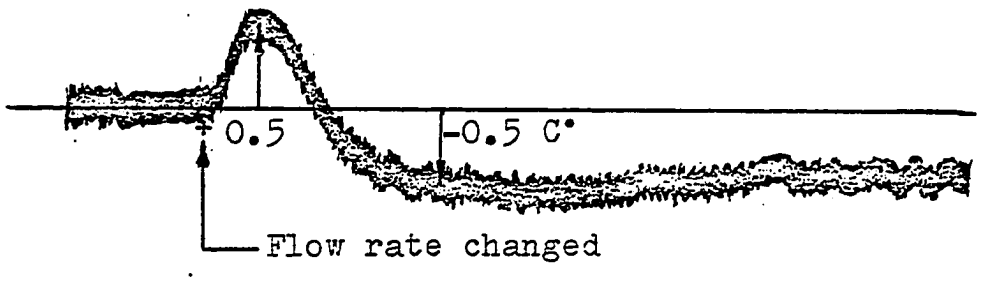


Fig. 14A Effect of Flow rate on the Catalyst Temperature

The temperature changed by about 0.5 C° above the normal (room temperature) and then dropped below the normal about 0.5 °C and then increased very slowly. This observation indicates that part of sites are reversible and the hydrocarbon attached on the sites can be replaced by the incoming propene.

From another run in which the space velocity was changed during reaction and dry polymerization grade propene was used, we found that the higher the space velocity, the faster the deactivation, with product selectivity varying in the same way mentioned above. However, the yield (not conversion) of both ethylene and butenes varied proportionally with the space velocity. This discrepancy between the above results (see part c, this section) can be explained that during reaction the poisons already adsorbed on the reversible sites at a certain space velocity may not be removed at a lower space velocity.

H. The Effect of Evacuation Temperature

In the following is shown kinetic studies about the effect of pretreatment on the activity and the selectivity of the Re_2O_7/Al_2O_3 catalyst.

Yao and Shelef (7) have applied the dispersion treatment (i.e. an evacuation at 500 °C for more than 5 hours or heating at 500 °C under flowing N_2 for 16 hours) to investigate the surface interactions in the Re/Al_2O_3 system. A series of experiments using the catalyst treated by various evacuation temperature were designed to investigate the association of the characteristics of the catalyst with propene metathesis activity.

The pretreatment of the catalyst was:

O_2/6--8 @ 515 °C Ev./11 @ T_{ev} °C Rxn T. 0 °C

Where T_{ev} is the evacuation temperature in centigrade. After heating in oxygen, the reactor was cooled to T_{ev} before evacuation. Evacuation is achieved by mechanic vacuum pump to a pressure about 10^{-2} torr. Dry research grade propene is used as the probe for metathesis reaction. And the space velocity is kept at about 6.7 WHSV for every run. The plot of reaction rate versus evacuation temperature is shown in Fig. 15; and the time course of the product selectivity at the corresponding T_{ev} in Fig. 16, and the rate profiles in Fig. 17 and 18.

The most interesting sequence of these experiments is that the activity of the catalyst shows two regimes of quite different characteristics centered in the neighborhood of 320 °C (T_{ev}), (Fig. 15). For $T_{ev} < 320$ °C (and 334 °C) there was no break-in, only decay; but with the standard pretreatment (i.e. short evacuation time about 5 minutes at room temperature) break-in was noted (solid points in Fig. 17). The data showed that at $T_{ev} = 147$ °C the decay was rather pronounced with the initial activity being anomalously large. Fig. 15 also showed that the initial activity and the level of deactivation increased with T_{ev} and reached a maximum in the neighborhood of 100 °C. At $T_{ev} \doteq 320$ °C, it can be predicted from Fig. 15 and Fig. 17, that negligible amounts of

Fig. 15 Effects of Evacuation Temperature

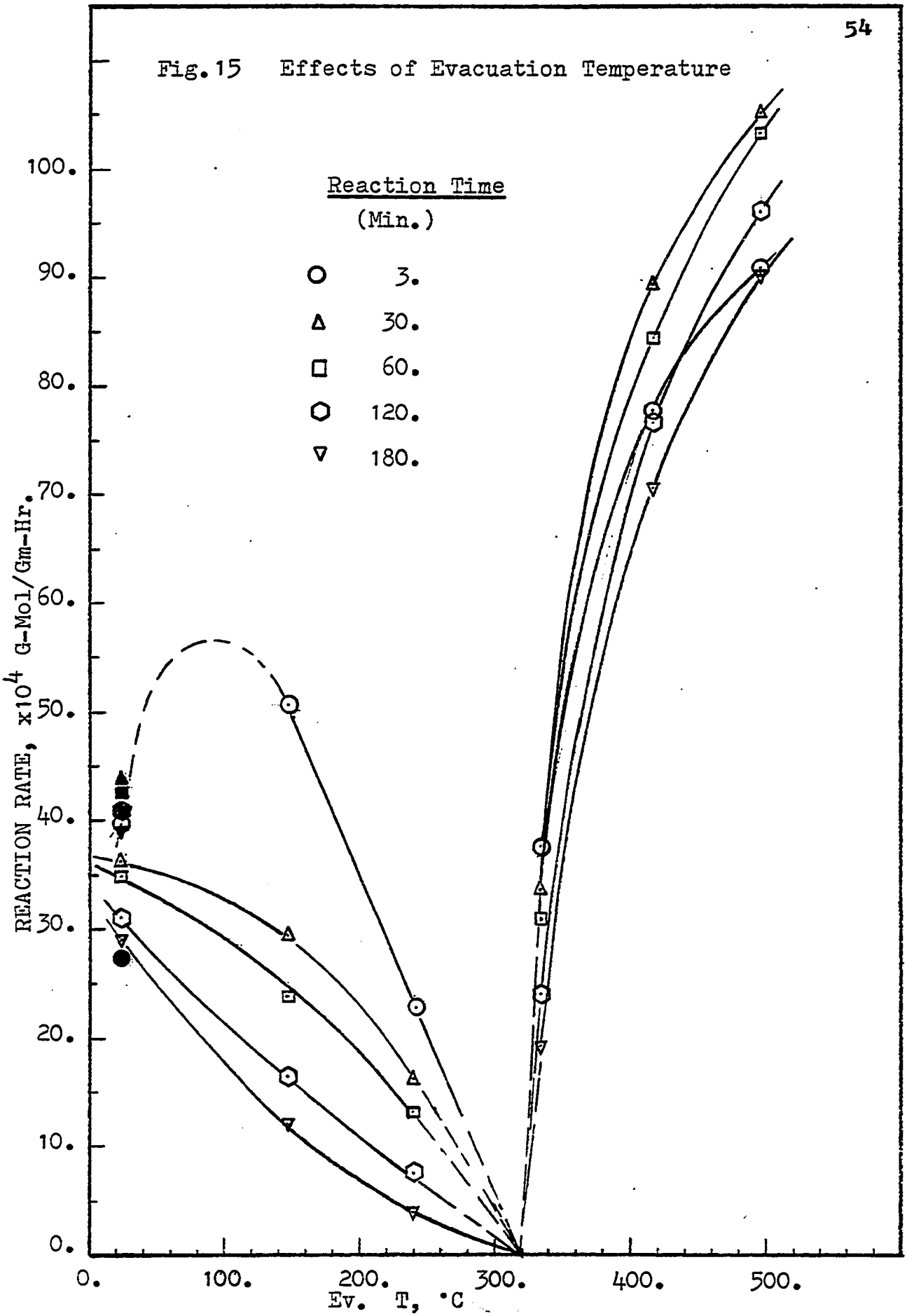
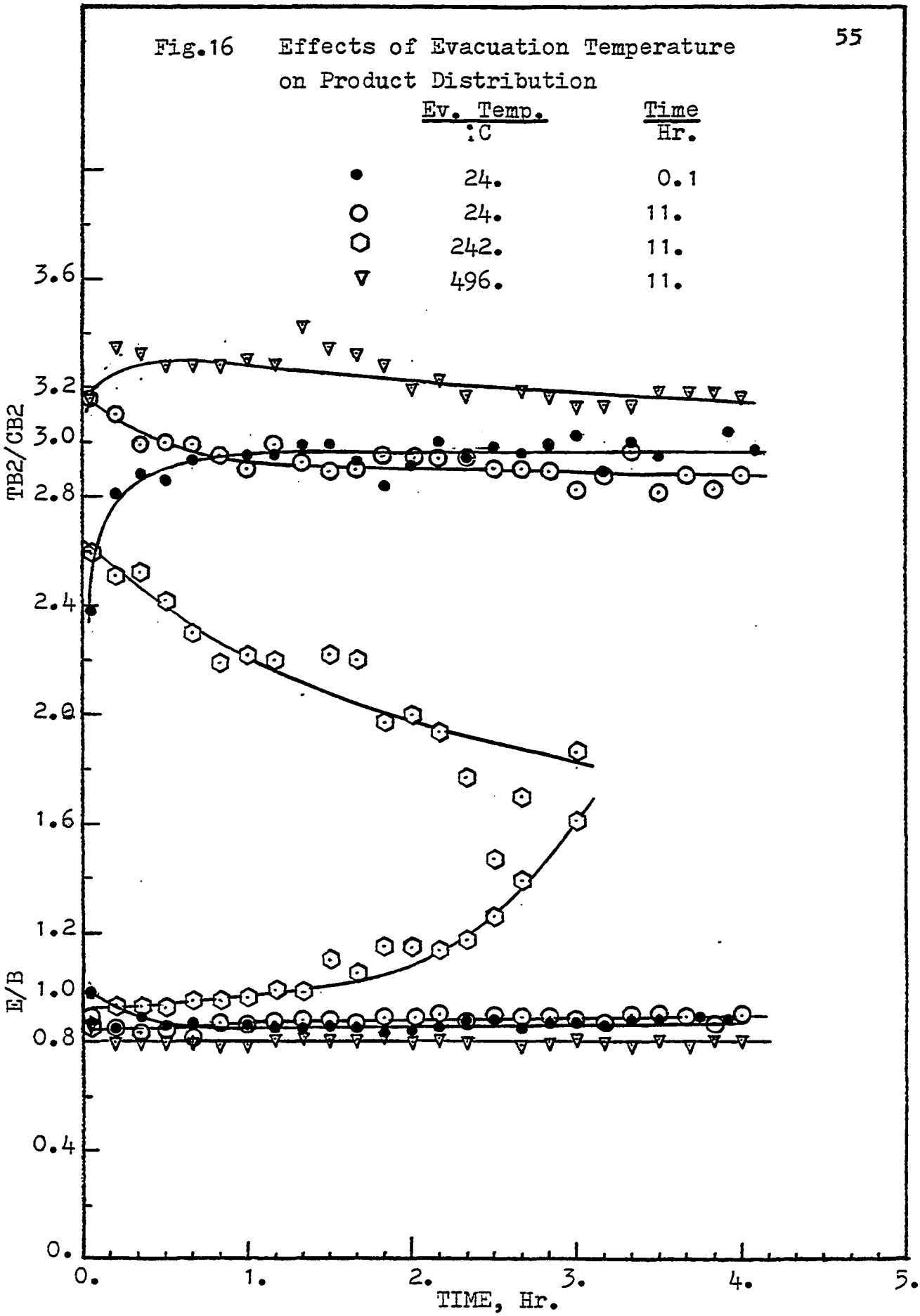


Fig.16 Effects of Evacuation Temperature on Product Distribution



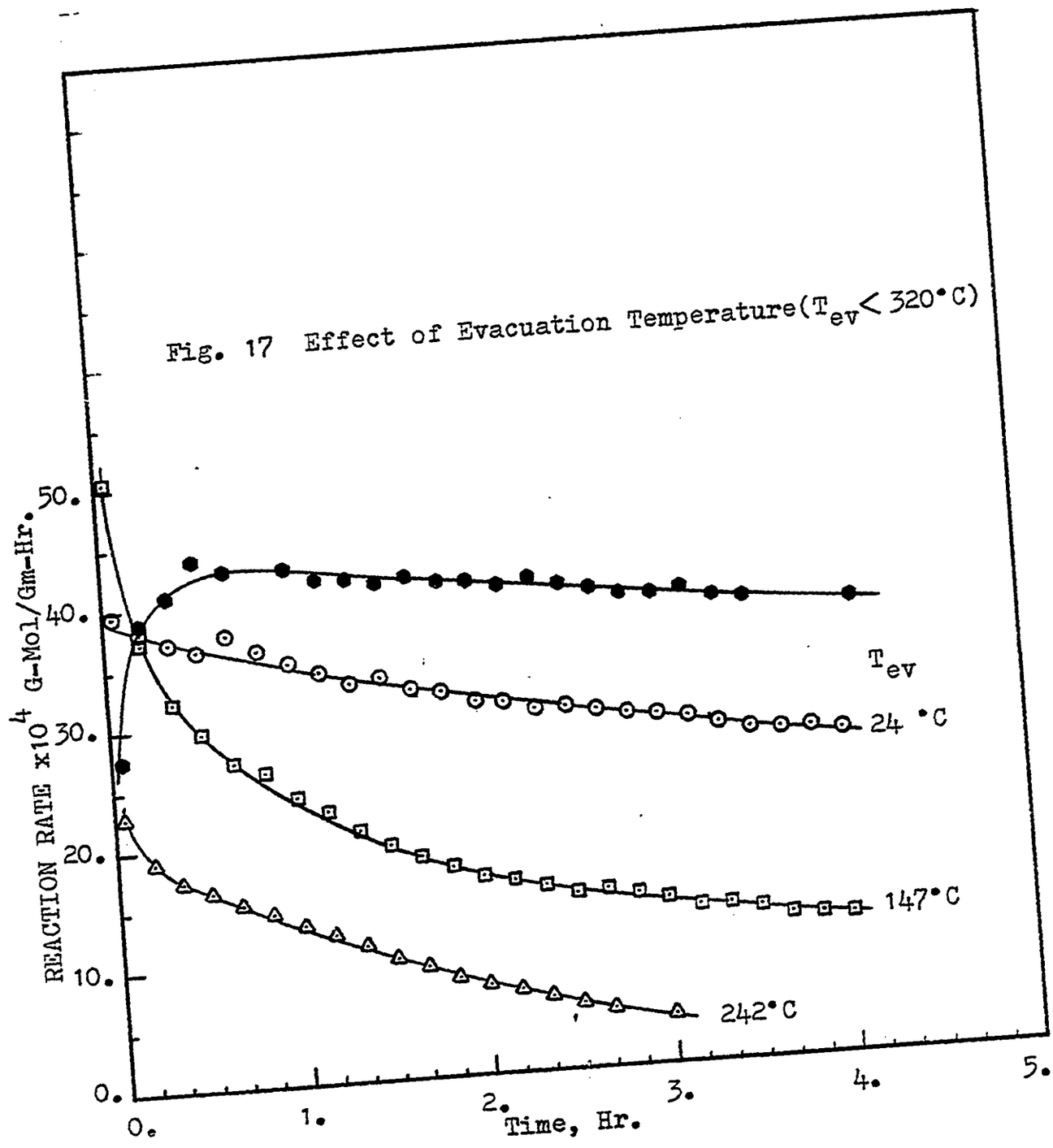
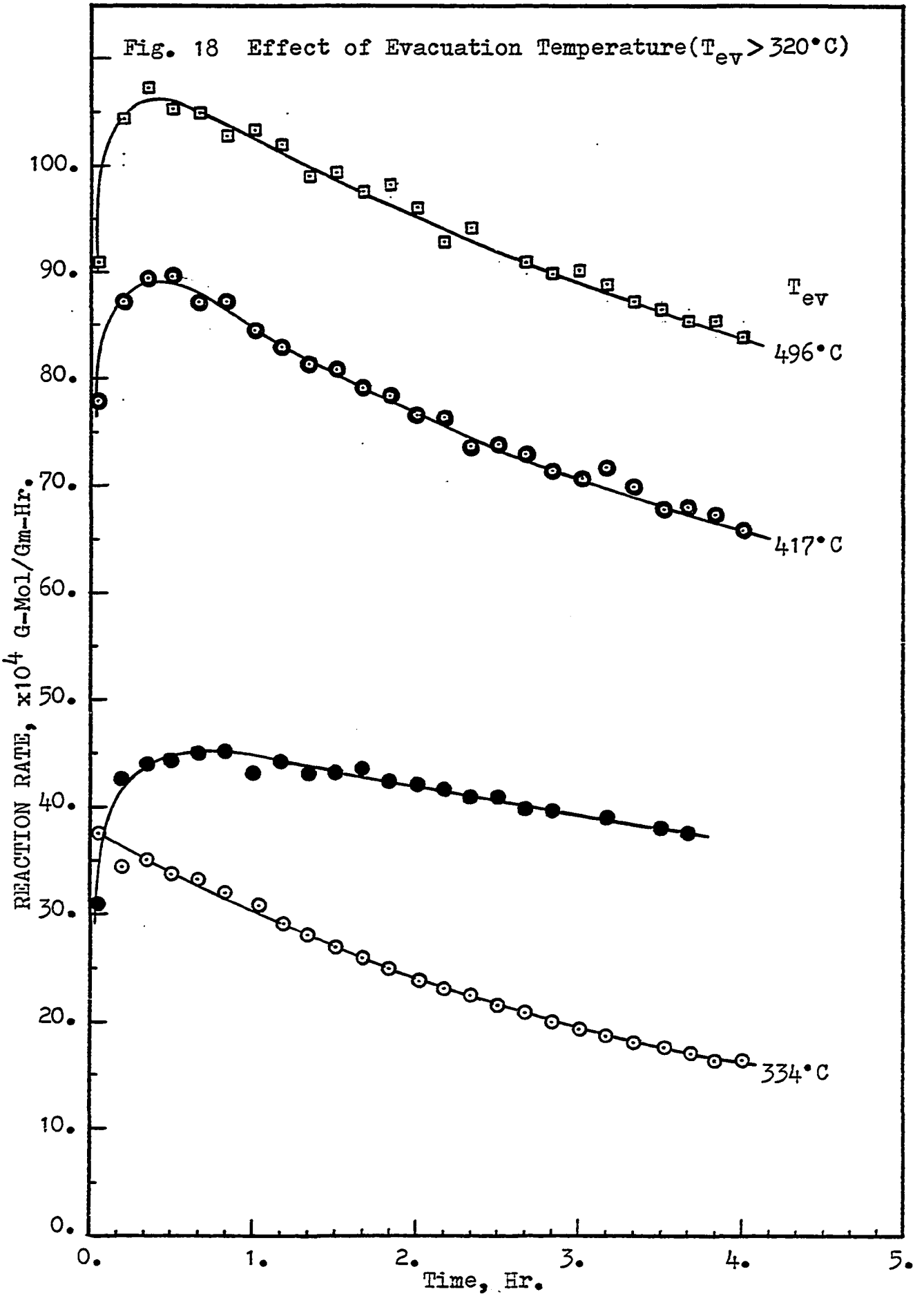


Fig. 17 Effect of Evacuation Temperature($T_{ev} < 320°C$)

Fig. 18 Effect of Evacuation Temperature(T_{ev} > 320°C)



products would be found at that reaction conditions. So, in the range of T_{ev} between 100 and 320 °C the activity decreased with increasing T_{ev}. But for $T_{ev} > 320$ °C the activity sharply increased with increasing T_{ev}. Curiously, the break-in was observed again in this regime and the break-in rate also increased with increasing T_{ev} but the level of deactivation was little affected by evacuation treatment (Fig. 18).

The evacuation temperature also affects the product selectivity of propene metathesis (Fig. 16). For $T_{ev} < 320$ °C the ratio of E/B slightly increased (but the reaction rate decreased) but the ratio of TB2/CB2 decreased with increasing T_{ev}; especially the effect was rather pronounced in the range of low activity around 320 °C (T_{ev}). In this T_{ev} range, because there was no break-in, the ratio of E/B was about constant through out that run, but when the activity was less than certain value the E/B ratio increased with decreasing activity (i.e. with increasing time because of deactivation) more pronouncedly. For instance, at T_{ev}= 242 °C, at 3 minutes the rate was about 22.8×10^{-4} g-mol/gm-hr and the E/B ratio was 0.85; at 90 minutes, they became $10. \times 10^{4}$ and 1.10, respectively; at 180 minutes, they significantly changed to 4.0×10^{-4} and 1.61, respectively. On the other hand, the TB2/CB2 ratio decreased with reaction time up to about one hour and then became constant later on for the range of mild activity; Similar to the variation of E/B, less than a certain activity,

the decrease of TB2/CB2 ratio became significant; for example, at T_{ev}= 242°C, at 3 minutes the ratio of TB2/CB2 was 2.59; at 90 minutes, 2.22; at 180 minutes it dropped to 1.77. The results may imply some kind of connection with the break-in of the activity, because in the period of break-in, the E/B ratio decreased and the TB2/CB2 increased with increasing activity.

For T_{ev}> 320 °C, the E/B ratio slightly decreased and the TB2/CB2 ratio increased with increasing temperature. The variation of the selectivity (E/B and TB2/CB2) during the break-in is similar to that with the standard pretreatment.

When this series of experiments was finished, the used catalyst was reactivated with the standard pretreatment at 514°C (Fig. 18, solid points). If we take account of the effect of activation temperature, the activity loss was about 15%, but the rate profile is similar. Therefore, we may conclude that most of the activity of the catalyst can be restored by the standard pretreatment, in other words, most of the rhenium and/or its compounds (oxides) were not removed from the surface even when the catalyst was treated at 500 °C by a long evacuation.

Peri(6), in the study of dehydration of alumina arogel measured the residual water content on the surface as a function of the evacuation temperature and time. His results

showed that after about 4 hours of evacuation the residual water was less dependent on the evacuation time. The effect of the evacuation time on the activity profile was examined in our system. The catalyst was pretreated at about 500 °C in O_2 for a few hours and then evacuated at about the same temperature for only 4 hours. Using research grade propene we obtained the same profile as above. However, using polymerization grade propene the rate profile shows no break-in, only decay. In both cases, the activities are higher than the standard. The results suggest other clues about the effect of carbon dioxide on the activity profile.

The measurement of propene adsorption on the catalysts treated by varying evacuation temperature has also been carried out. The results are summarized in Table 4 . After pretreatment, the whole system was evacuated and dry r.g. propene was introduced into the space before the reactor to a pressure about 700 torr for every run, and then expanded into the reactor at room temperature.One hour later, the pressure of the system was recorded and using the ideal gas law the adsorption amounts could be measured. The dead space of the reactor was measured by using He(Cu). And the static product was analyzed by gas chromatography.

At $T_{ev} = 24$ °C, longer evacuation time made the adsorption amounts smaller, but the conversion higher. The propene adsorption amounts decreased with increasing T_{ev} down to a minimum in the neighborhood of 300°C and then increased with

Table 4. Propene Adsorption on the Re_2O_7/Al_2O_3 [a] Treated at T_{ev} and Studied at 24 °C

T_{ev} °C	Adsorption x10^4 mol.	$C_3^=$ ad./Re	Total Conv.%	E/B	TB2/CB2
24. [b]	3.38	0.844	26.1	3.75	4.24
24.	2.80	0.698	32.7	3.56	3.50
248.	1.19	0.296	33.8	3.40	3.29
483.	2.89	0.720	35.3	4.07	3.38

a. 9% Re_2O_7/Al_2O_3, W=1.085 gm(Re 4.008×10^{-4} mol.)

b. Evacuated for only 5 minutes; the others, 11hrs.

increasing T_{ev}, but the conversion very slightly increased with increasing T_{ev}.

The above kinetic and adsorption results suggests that the Re_2O_7/Al_2O_3 catalyst is heterogeneous and provides different kinds of sites (two, at least) active for olefin metathesis.

I. The Effect of Reduction with Hydrogen

It has been found that the reducibility of Re on γ-Al_2O_3 is much less than that of Re on SiO_2 is due to a stronger interaction of Re^{7+} with the γ-Al_2O_3 surface; and reduction at relatively low temperatures (200-300 °C) results in transition of some Re^{7+} into an intermediate oxidation state, (5, 15). The dispersed phase of Re strongly interacts with the γ-Al_2O_3 and can be reduced to zero-valent state by H_2 only at >500 °C, but the crystalline, three-dimensional phase can be reduced to Re^0 by H_2 at 350 °C (7). Lin et al. (15) found that in measuring the propene metathesis activity at room temperature, the H_2 treated catalyst was initially more active (about 5 times higher), but the activity rapidly (in 1.5 hrs) decayed to the same as that the air treated sample. The propene used by Lin et al. was polymerization grade.

Next, we would like to show the effect of varying H_2

reduction temperature and dispersion pretreatment on the activity and also the surface interactions between the dry oxygen and the reduced catalyst.

(a). The Effect of H_2 Reduction Temperature

The hydrogen reduction pretreatment of the catalyst was:

O_2/6--7 @ 515 °C H_2/10--12 @ T_H Rxn T. 0 °C

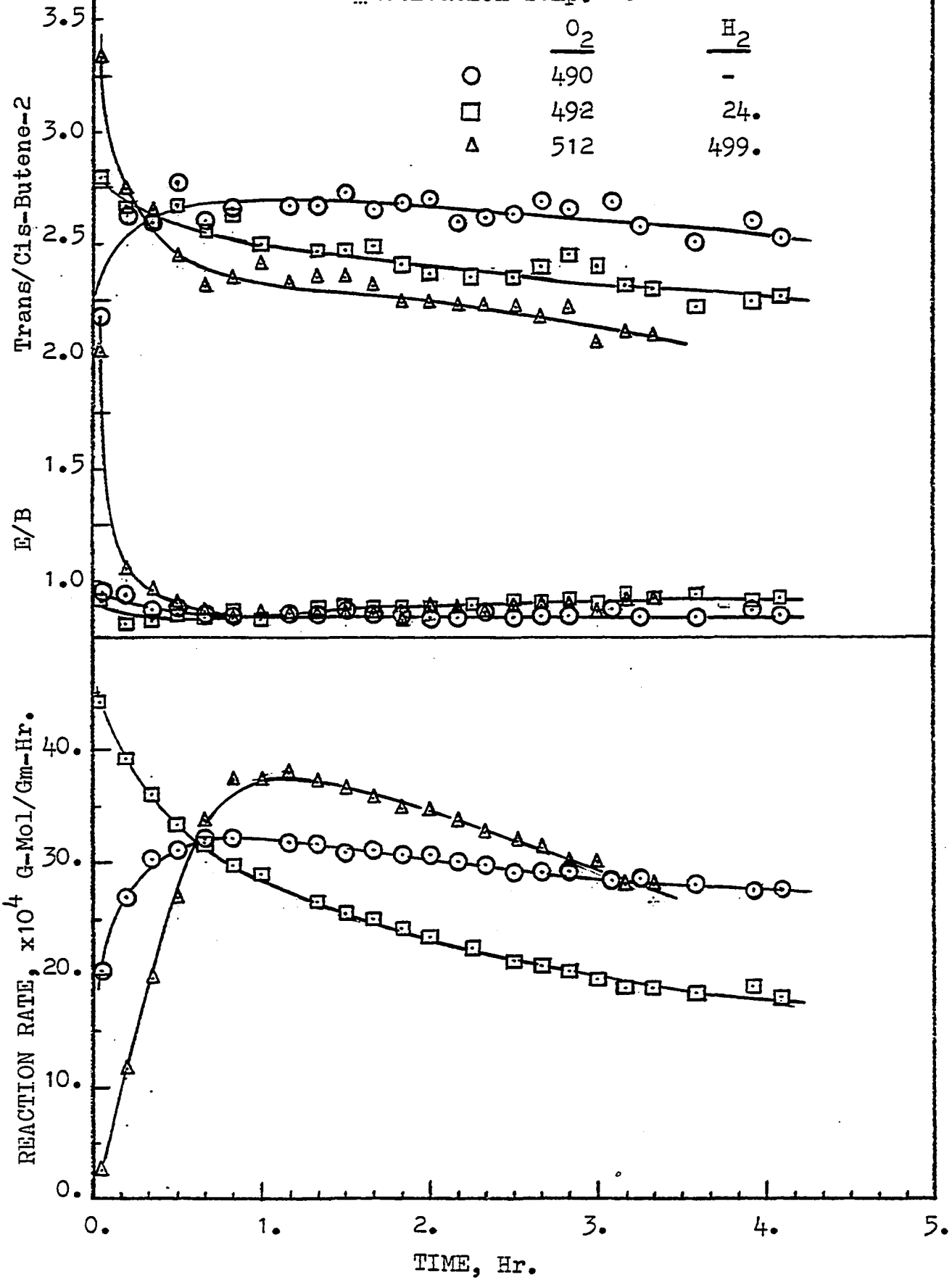
Where T_H is the hydrogen pretreatment temperature in °C. After oxygen activation the reactor is cooled to T_H and evacuated for a few minutes before introducing hydrogen. Commercial hydrogen is purified by a Serfass Hydrogen Purifier for use. The hydrogen pretreatment is achieved in flowing hydrogen at a flow rate about 120 ml/min. Before introduction of the reactant (dry research grade propene) the reactor was evacuated at 0 °C for about 5 minutes. The space velocity was kept at about 6.9 WHSV for every run. The results are shown in Fig. 19.

After treating in H_2 at 24°C, the catalyst has the activity profile similar to that for a T_{ev} of 24 °C, i.e., no break-in, only decay, with a higher deactivation rate and also the TB2/CB2 ratio continuously decreasing with time. Catalysts treated in H_2 at 244 °C and 335 °C were inactive until they were exposed to an O_2 pulse (see later). This may be due to unsufficient dehydroxylation at this temperature. If hydrogen treatment temperature was over 500°C, the catalyst became active again, but had a negligibly small initial activity and a protracted break-in and high deactivation rate. The interesting result of experiment for T_H=500°C is that the initial TB2/CB2 ratio

Fig. 19 Effects of Reduction Temperature w. H_2

Activation Temp. °C

	O_2	H_2
○	490	-
□	492	24.
△	512	499.



is about the equilibrium value(3.9) and rapidly decreases with time and to a value less than that for a T_H of 24 °C, although the break-in is observed. Recall that the catalyst activated with the standard pretreatment shows the break-in but the TB2/CB2 ratio increases with time during the break-in. Also the initial E/B ratio is anomalously large and rapidly drops to the same value as that for T_H at 24 °C (0.85). We also observed that the catalyst treated at 500 °C in H_2 could not recover its structure and its activity by heating at 500 °C in oxygen, since the catalyst still had grey spots and the activity was less (see later).

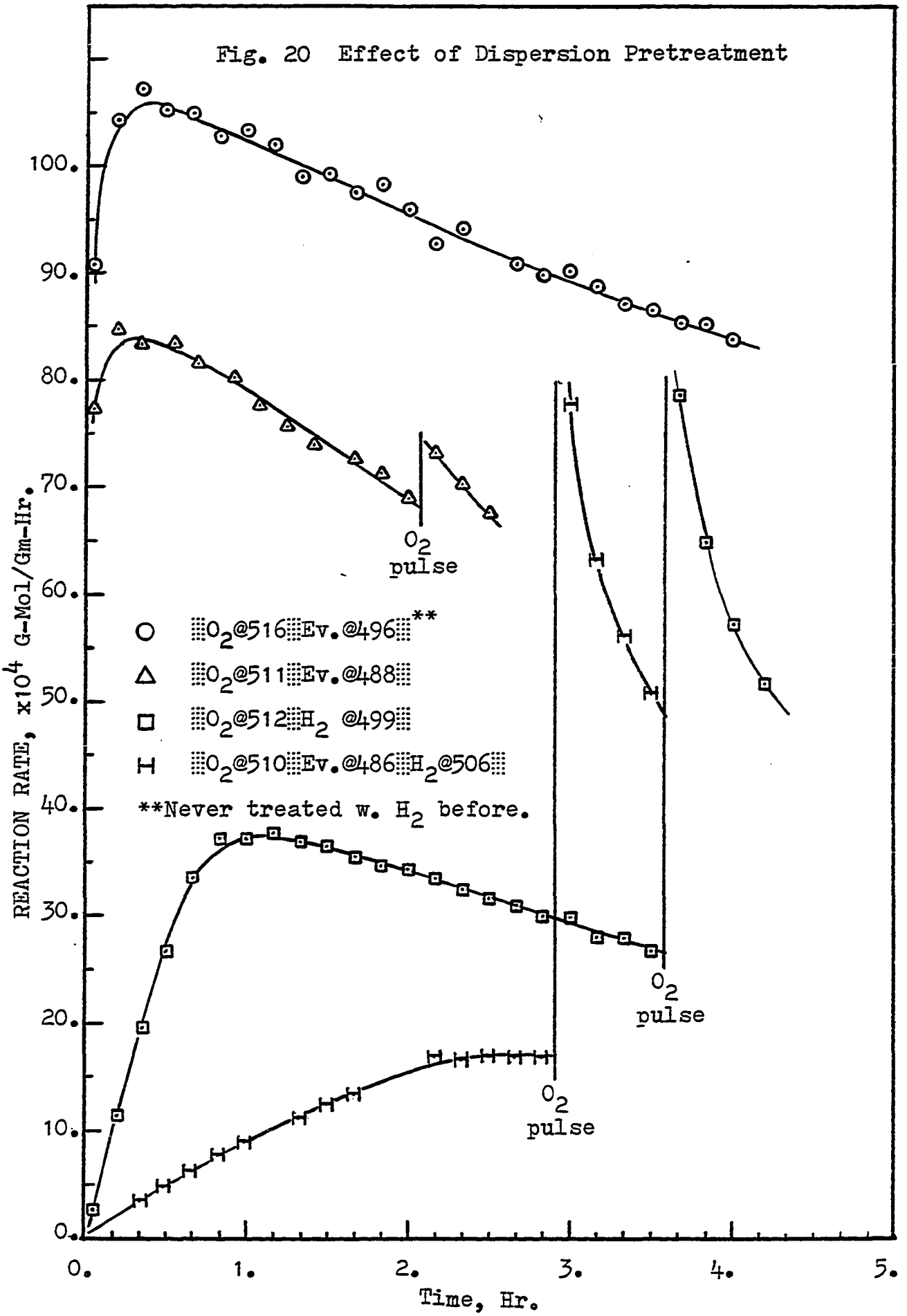
(b) The effect of Dispersion Pretreatment

It has been found that the crystalline, three-dimensional phase (reduced to Re^0 by H_2 at 350 °C) in the Re/Al_2O_3 system can be dispersed into the two-dimensional phase (reduced to Re^0 by H_2 only at >500 °C) by oxidation followed by vacuum or inert gas treatment at >500 °C (7). It was shown that the dispersion pretreatment (see section H) has a pronounced effect on the catalytic activity (increase about 1.4 times more than the standard). In order to know the effect of the hydrogen reduction with dispersion pretreatment on the activity, the catalyst was pretreated as:

O_2/6 @ 510 °C Ev./4 @ 486 °C H_2/1 @ 506 °C Rxn T. 0°C

The results are shown in Fig.20 . By contrast, the H_2 reduced catalyst with dispersion pretreatment has less activity and a

Fig. 20 Effect of Dispersion Pretreatment



slower break-in rate, and the profiles of the ratios of E/B and TB2/CB2 are respectively, similar to that without dispersion pretreatment although the values are smaller.

In the following, it is shown that the activity of the H_2 reduced (at 500°C) catalyst can not be completely recovered. In Fig. 20, the circles correspond to the case where the catalyst has <u>never</u> been treated with H_2, whereas the triangles correspond to the case where the sample was treated with H_2 at 500°C just before the run. Both catalysts were pretreated with the dispersion after oxidation at about 510°C. The results show that about 26% of the sites (assuming the total sites created by oxidation/dispersion treatment to be unity) were permanently reduced by hydrogen at 500°C.

(c) Surface Interaction on the H_2 reduced catalyst

In section B-b, the importance of a trace of oxygen in the helium used for activation of an unreduced catalyst on the metathesis activity was shown. Here, the effect of small amount of oxygen in the inert activation gas on the activity of a reduced catalyst will be discussed. Dry polymerization grade propene was used. After a static experiment the catalyst was purged with dry N_2 and then treated at 496°C in flowing H_2 for about 17 hours followed by a purge with dry nitrogen (containing small amount of oxygen) at the same temperature for about one hour. The propene metathesis

reaction was carried out at room temperature. The color of the catalyst just after reduction by H_2 was black, but after purging with N_2 it became white-black-spots. The activity was about 10% less than that with the standard pretreatment. Compared with the results shown in the previous sections,it is noted that the high recovery of the activity of the used catalyst pretreated by H_2/N_2 at about 500 °C is due to the oxidation which occurred on the surface by the samll amount of oxygen contained in the N_2.

It was shown in section C-b that an H_2 reduced catalyst "thirsts" for oxygen to revive the active sites for propene metathesis. Now, let us see the dependence of the level of thirst for oxygen on the surface reduced by varying reduction temperature in H_2. The results are summarized in Table 5 .

An O_2 pulse has negligible effect on the activity for T_H at 24 °C and also the temperature of the catalyst bed (actually the temperature decreased first (about 2. C°) and slowly increased to a value slightly higher the reaction temperature(about 0.5 C°)). At T_H= 500 °C, the effect is anomalously large on the activity (increased about 3. times) but little on the temperature of the catalyst bed. (+ 1.5C°). The increase of the activity causes the drop of E/B ratio and the increase of TB2/CB2 ratio.A similar effect is observed on the catalyst having dispersion/reduction pretreatment (activity increased about 4.6 times, temperature increased about 2. C°). The

Table 5. Effect of O_2 pulse on the Catalyst Treated @ T_H

T_H(°C)	R_b[a] g-mol-$g^{-1}hr^{-1}$	T(C°)[b]	R_a[a] g-mol-$g^{-1}hr^{-1}$	$R_a - R_b$
24.[c]	18.4×10^{-4}	- 2.	20.3×10^{-4}	1.9×10^{-4}
244.[c]	0.	+20.	115.2×10^{-4}	115.2×10^{-4}
335.[d]	0.	+38.2	263.2×10^{-4}	263.2×10^{-4}
499.[c]	26.8×10^{-4}	+ 1.5	78.8×10^{-4}	52.0×10^{-4}

a. R_b is the rate before O_2 pulse; R_a, the rate at 5 min. after O_2 pulse.

b. The maximum temperature change of the catalyst by O_2 pulse.

c. W = 0.5080 gm.

d. W = 0.5163 gm.

results of the above two cases show an interesting fact that in spite of having dispersion pretreatment the activity profiles are the same after injection of O_2 pulse (Fig.20).

It was shown that at T_H= 244 °C and 335 °C the catalysts were inactive, but the injection of O_2 pulse caused a very high jump in the activity and the temperature of the bed. At T_H = 244 °C and 335 °C, the activity increased to $115.\times10^{-4}$ g-mol-$g^{-1}hr^{-1}$ and $263.\times10^{-4}$ g-mol-$g^{-1}hr^{-1}$, respectively; and the temperature of the bed increased from 0°C to 20. °C and 38. °C respectively. Because of the temperature increase of the catalyst part of the increased activity can be attributed simply to a greater reaction temperature. However, the temperature recovered very quickly (about 5 min.) whereas the high activity and the high deactivation persisted.

In summary, the Re_2O_7/Al_2O_3 catalyst became inactive when the catalyst was treated by H_2 at a temperature around 300 °C; but it thirsts abnormally high for oxygen to revive the catalyst and the activity after revival is much higher than for the other cases. The H_2 reduced catalyst had the selectivity of TB2/CB2 decreasing with time throughout that run. At T_H = 500 °C, the initial TB2/CB2 ratio reached the equilibrium value (3.9) but rapidly decreased with time.

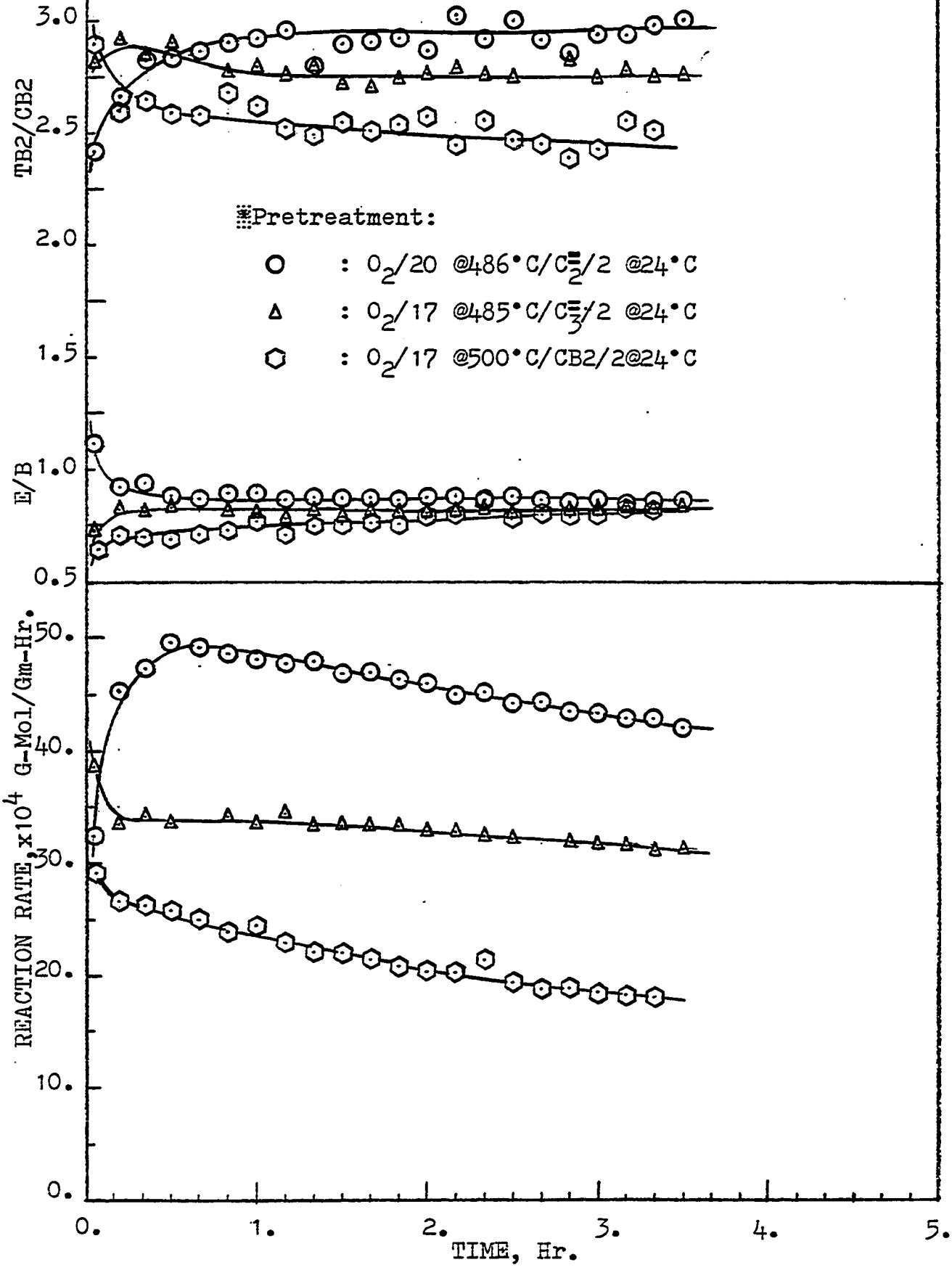
J. The Effect of Olefin Pretreatment

Swift and Kobylinski (39) found that olefin pretreatment of MoO_3/Al_2O_3 at 200 °C for 15 minutes resulted in a very selective catalyst for olefin (1-octene) metathesis, for example, treated with isobutylene, the total conversion dropped from 90.8% (no olefin treatment) to 26.3%, but the selectivity to tetradecene and ethylene increased from 28.2% to 91.2%. The effect of olefin treatment was found to be pronounced in the order: iso-butylene > 1-butene > 1-octene > propylene > ethylene. Water evolved during butene treatment.

Similar experiments were conducted on the Re_2O_7/Al_2O_3 catalyst (0.5163 gm). Dry research grade ethylene, propene, cis-2-butene were used for treating the catalyst. The catalyst was pretreated with the standard procedure and then exposed to static olefin at room temperature and a pressure of about 700 torr for two hours. Before starting the propene metathesis reaction, the bulk gas of olefin in the system was pumped out. The results are shown in Fig. 21 .

When the olefin used for pretreatment was introduced, the temperature variation of the catalyst was recorded. The maximum increase of the temperature was 2.5, 7., and 11. °C, for ethylene, propene, and cis-2-butene, respectively. The temperature increase of the catalyst by olefin pretreatment was attributed not only to the heat of adsorption but chemical reaction from which the heat evolved also depended on

Fig.21 Effects of Olefin Treatment



the type of olefin. The chemical reactions on the surface may involve the reduction of metal oxides. The degree of reduction by the olefins increases in the order: ethylene<propene<CB2. Lin et al. (15) have found that the reduction on the Re_2O_7/Al_2O_3 by ethylene had negligible capacity at ambient temperature. Now, based on the information, let us look at the activity profiles of propene metathesis (at 0 °C) on the catalysts pretreated with different olefins (Fig. 21).

Consistent with the results of Lin et al.(15), the ethylene pretreatment has no effect on the profiles of the activity and the selectivity, i.e. having break-in, high initial E/B ratio but low initial TB2/CB2 ratio (see section A). Assume the number of metathesis sites at the maximum rate of the activity profile using ethylene pretreatment is unity. The propene pretreatment caused the activity leveling out (with very slight decay) to a value less than ethylene pretreatment about 31% , i.e. 31% metathesis sites were poisoned due to reduction or other reasons. The high activity at the first point (3 minutes)was due to the effect of evacuation by reviving part of the reversible sites (see section B-b). About 46% of the active metathesis sites were lost after cis-2-butene pretreatment. By contrast, inverse profiles of the selectivity were observed for the pretreatments with propene or cis-2-butene, i.e. no break-in, low initial E/B ratio but high TB2/CB2 ratio. The results may suggest something connected to the break-in

and deactivation.

K. The effect of Isolation and Evacuation Time in the Static Propene Pretreatment

The procedure of a "static experiment" has been described in chapter II. Fig.22 shows the results of the static experiments. The following results were obtained: (a) there was no break-in; (b) the initial activity was up to 4 times greater than that of the fresh or freshly regenerated catalyst, depending upon the period of isolation and evacuation; (c) the rate rapidly decayed within the first hour to a value slightly lower than the fresh catalyst (d) not only the initial activity, but the rate of deactivation also increased proportionally to the isolation time (Fig. 23). Also the rate of deactivation was affected by the evacuation time. With the same isolation time (about 44 hours) but different evacuation time, (i.e. 24 hrs, and 0 hr), The initial activity and the deactivation power (N in eqn.20) were 494.6 $x10^{-4}$ g-mol-$g^{-1}hr^{-1}$ and 0.48; 132.5$x10^{-4}$ g-mol-$g^{-1}hr^{-1}$ and 0.20, respectively. This indicates that the 'evacuation' treatment could increase not only the metathesis activity but the deactivation rate of the catalyst; (e) Fig.24 shows how the initial activity increases with the period of isolation of the catalyst in the static polymerization grade propene at room temperature. The increasing trend of the activity implies that beyond 10 days' isolation

Fig. 22 Effect of Static Propene Pretreatment

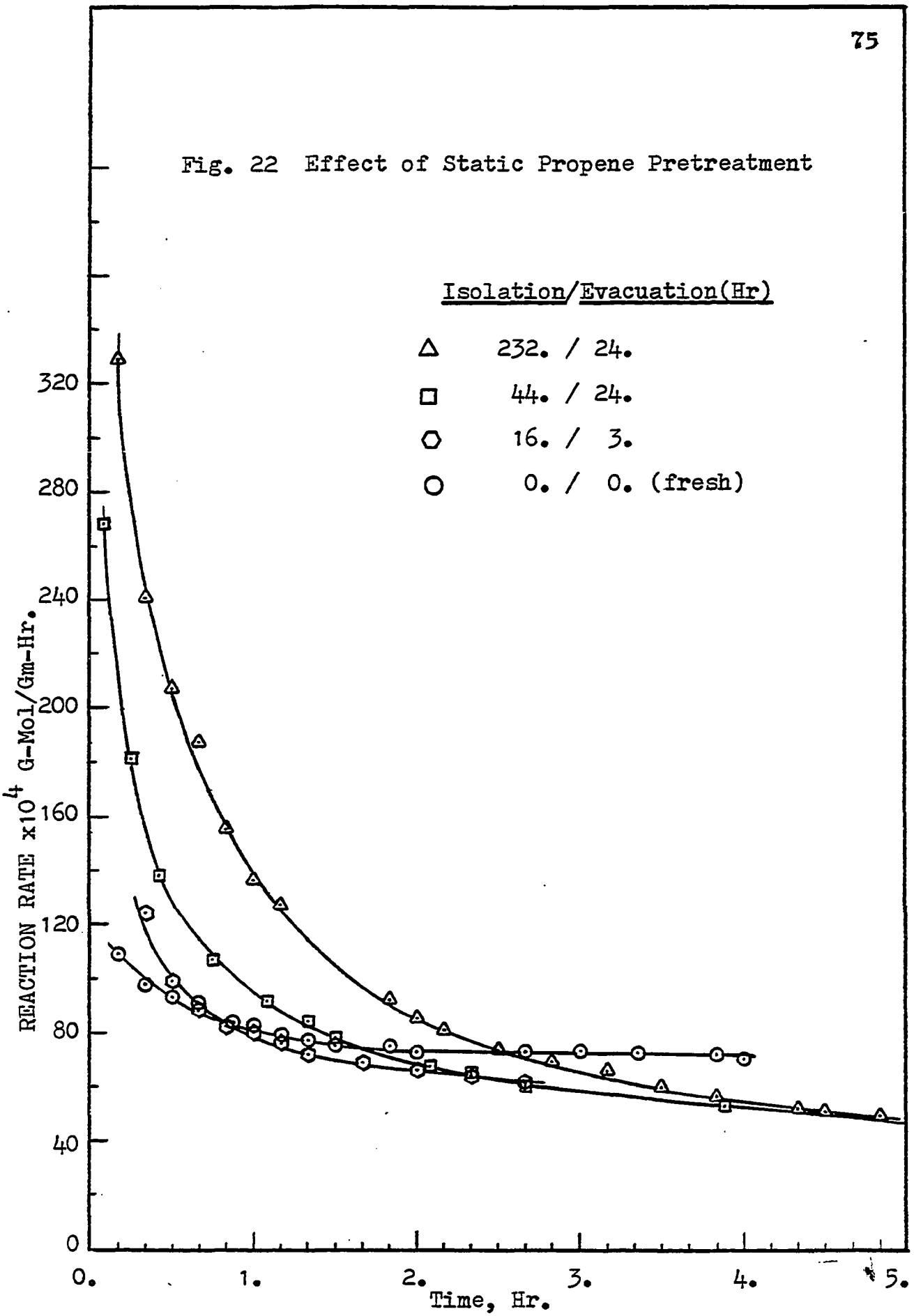


Fig. 23 Effect of Evacuation Time and Reactant

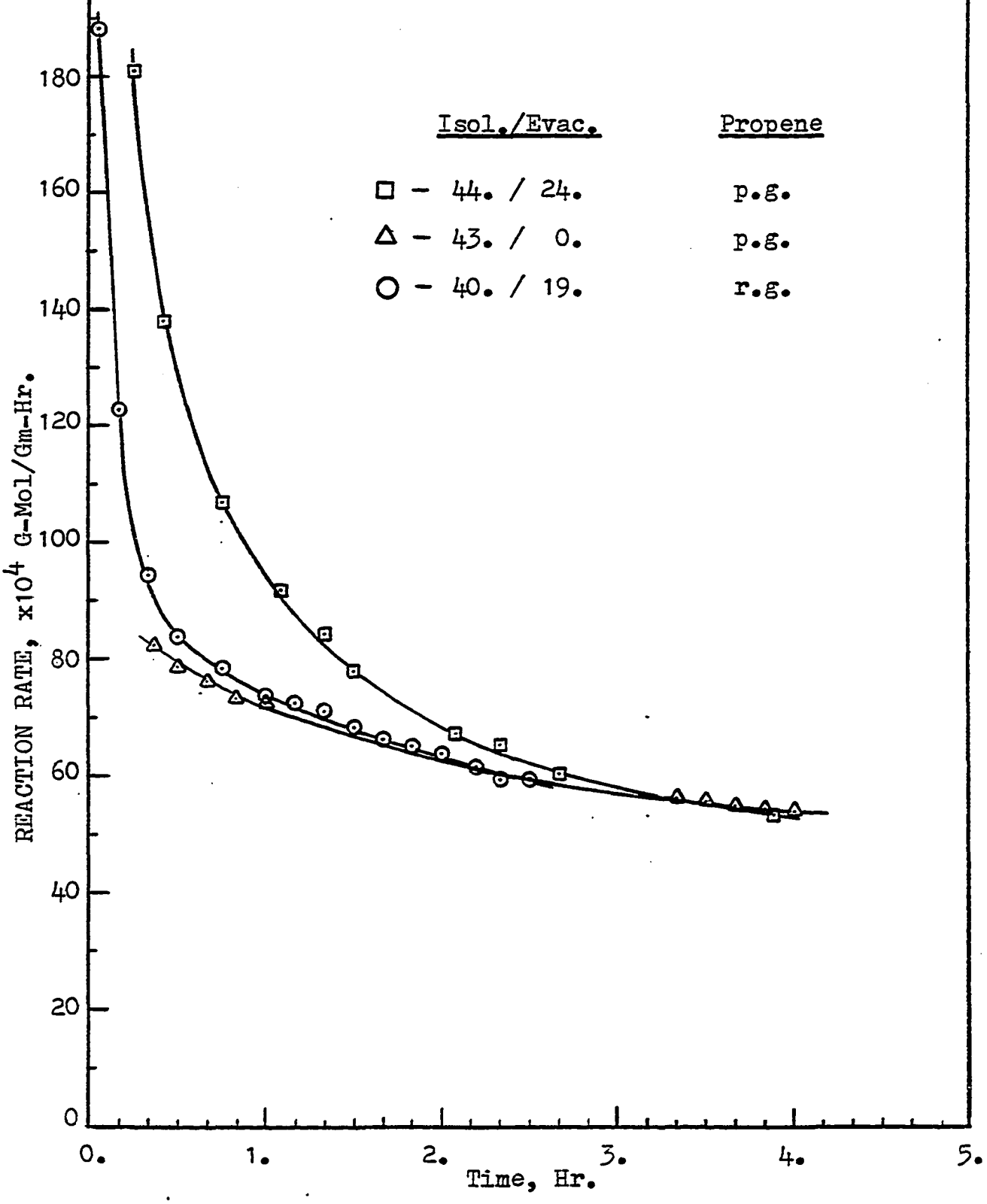
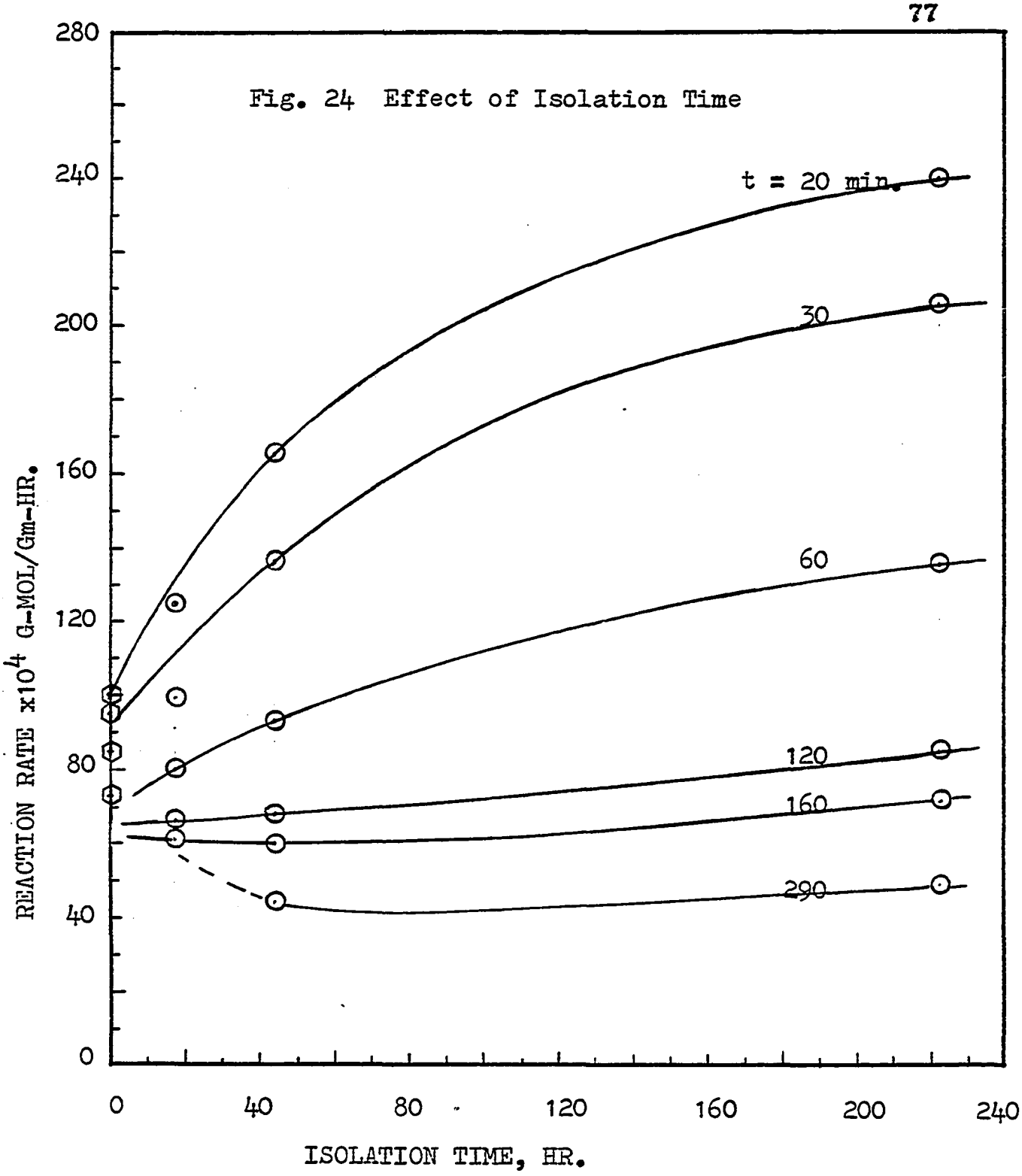
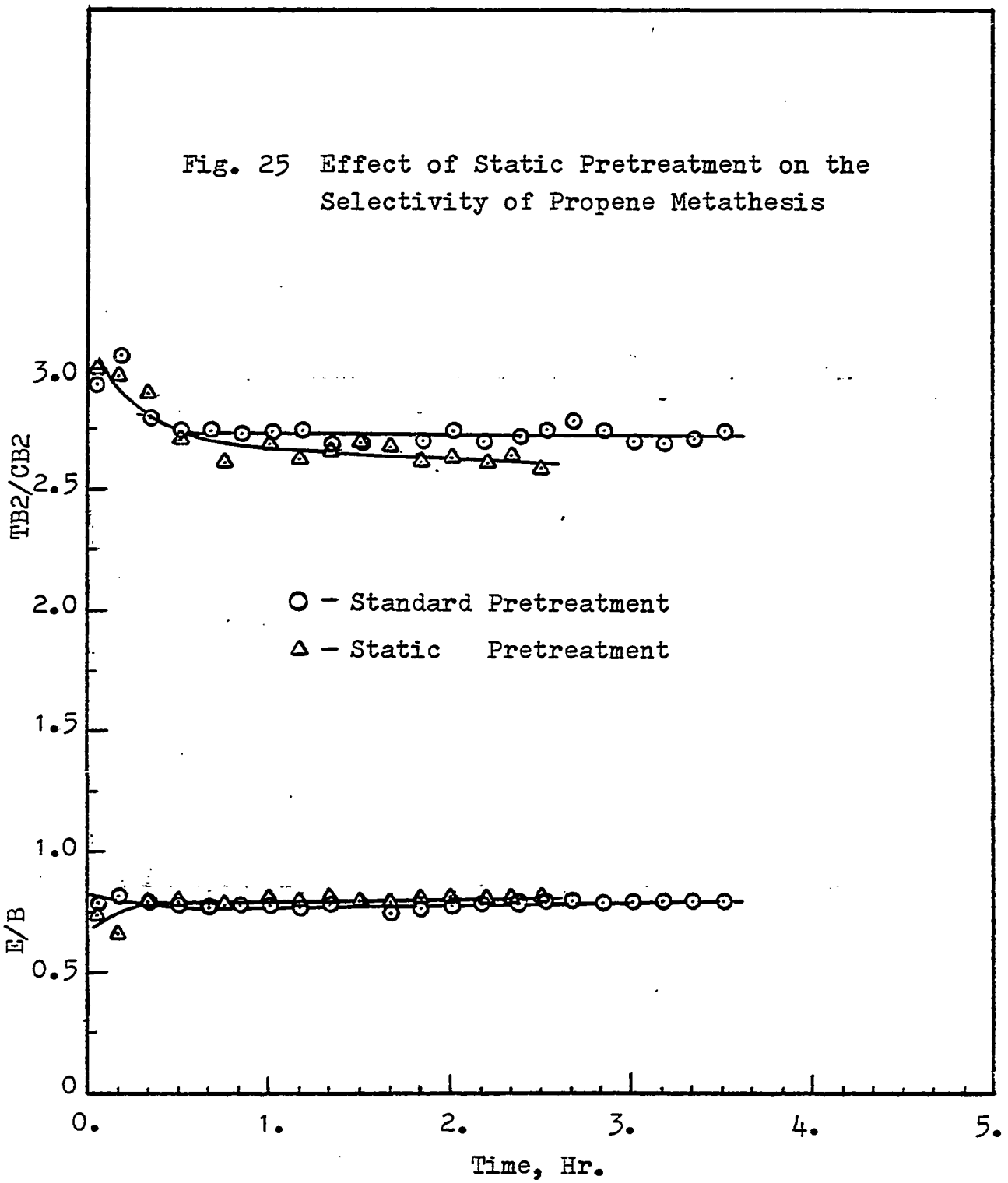


Fig. 24 Effect of Isolation Time



the creation of the activity by evacuation may be independent of isolation time; (f) however, after a static experiment and further treatment (without activation in O_2) similar to that in the last one, the activity profile (i.e. the second static experiment) was lower than the last one, but the initial activity is higher than the final activity of the last run. This indicates that part of sites were poisoned, but part of them is reversible; (g) with about the same periods of isolation and evacuation (e.g. 40 hrs and 20 hrs, respectively) the initial activity and the deactivation rate of olefin metathesis using r.g. propene were less (about 40% and 50%, respectively) than that using p.g. propene. This difference may be ascribed to the presence of carbon dioxide in the p.g. propene (Fig.23); (h) The E/B ratio was less time dependent except for the case of shorter isolation and evacuation time on a fresh catalyst (e.g. 16.5 hrs and 3 hrs, respectively) in which it was initially high but decayed rapidly (in 1.5 hrs) to the same level as the others; (i) the TB2/CB2 ratio decreased with reaction time (Fig. 25).

Fig. 25 Effect of Static Pretreatment on the Selectivity of Propene Metathesis



L. Propene Metathesis on γ-Al_2O_3 alone

To test the metathesis activity (of propene) on the carrier of the Re_2O_7/Al_2O_3 catalyst, i.e. γ-Al_2O_3, the carrier was treated by many ways. The size of γ-Al_2O_3 used was 40--60 mesh. Pretreatments performed were:

(a). O_2/15 @ 493 °C Rxn T. 0°C

(b). O_2/10 @ 504 °C static $C_3^=$/80 @ 24 °C

(c). O_2/ 4 @ 491 °C Ev./5 @ 481°C Rxn T. 0°C

(d). O_2/11 @ 495 °C H_2/1 @ 497 °C Rxn T. 0°C

The results were simple: whatever the pretreatment, there was not any kind of reaction on the γ-Al_2O_3, when propene was used as the reactant.

M. Metathesis of Ethylene and Cis-2-Butene on the Re_2O_7/Al_2O_3 catalyst

Only a trace of propene was observed in the case of ethylene metathesis at room temperature in static reactant, on the catalyst activated with the standard pretreatment.

The activity (conversion) profiles of cis-2-butene metathesis on the Re_2O_7/Al_2O_3 catalyst and γ-alumina alone are shown in Fig. 26 (pretreatment of the catalyst is also shown). It was observed that:(a) a small amount of propylene was produced and its concentration decreased with time to a negligible value in about one hour, (b) no 1-butene was observed (trace in static cases), (c) the initial activity was very large with conversion

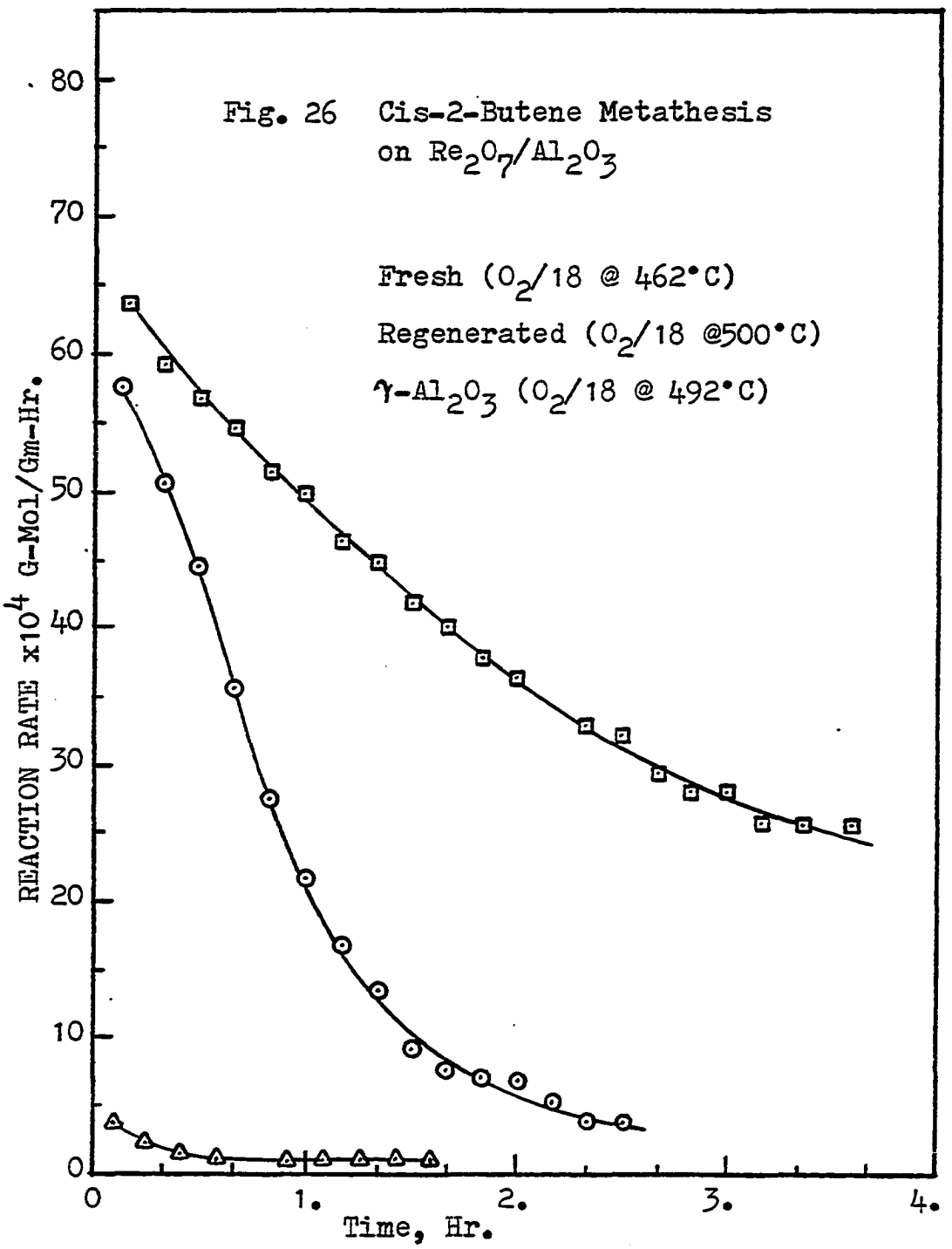


Fig. 26 Cis-2-Butene Metathesis on Re_2O_7/Al_2O_3
Fresh (O_2/18 @ 462°C)
Regenerated (O_2/18 @500°C)
γ-Al_2O_3 (O_2/18 @ 492°C)
REACTION RATE x10^4 G-Mol/Gm-Hr.
Time, Hr.
0
10
20
30
40
50
60
70
80
0
1.
2.
3.
4.

approaching equilibrium for a WHSV of 8.3, (d) there was a rapid decay in the activity, and (e) the catalyst could be regenerated in oxygen at 500°C with a slightly higher initial activity and a less pronounced activity decay (relative to the fresh sample activated in oxygen at 462°C).

CHAPTER IV

DISCUSSION

A. The Rate Equation of Propene Metathesis on Re_2O_7/Al_2O_3

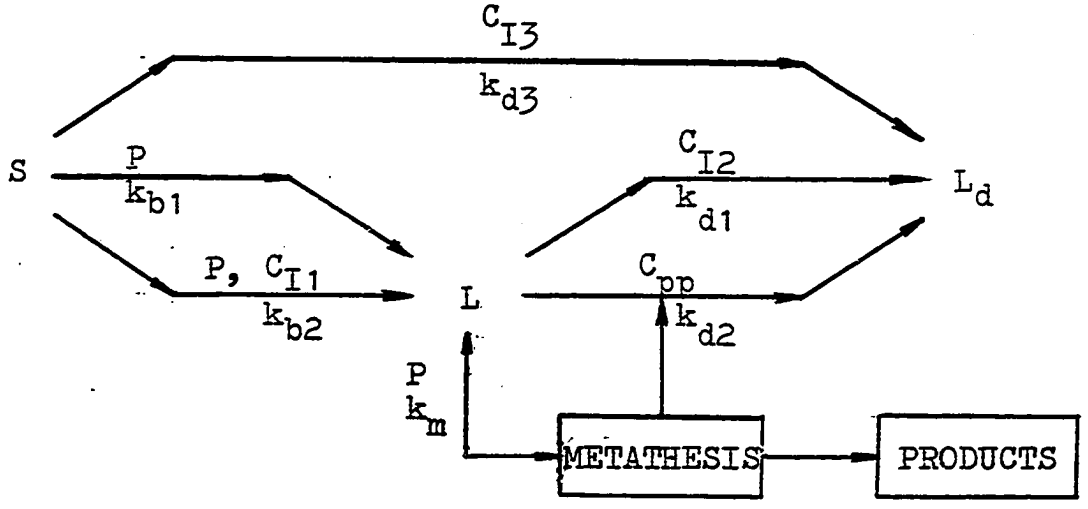
In the kinetics studies we observed that the catalytic activity of propene metathesis over Re_2O_7/Al_2O_3 catalyst exhibited a "break-in" regime, a maximum, and a "deactivation" regime. The activity profile depended upon the activation temperature in oxygen, the reduction level of the catalyst, the reaction temperature, and the impurities contained in the feedstock, etc. This profile may result from superposition of the time-dependent deactivation curve upon the break-in curve. The active sites which are responsible for metathesis may be generated upon introducing olefin (8). However, the deactivation may be caused by the impurities contained in the feed (i.e. side-by-side deactivation) or by the products (e.g. water or polymers) formed from reactions (i.e. series deactivation) (4). If the catalytic reaction occurred on the surface of the catalyst in a region of low surface coverage where the reaction is dependent on the concentration of propene in the gas phase and on unpoisoned active sites on the catalyst, the

catalyzed-reaction rate can be written as

$$R = k_m P^a L \qquad (5)$$

Where P is the partial pressure of propene reactant. L is an activity which corresponds to the density of available (unpoisoned) active sites. k_m is a rate constant for metathesis.

Whatever the mechanism is for olefin metathesis, the generation and poisoning of the active sites for metathesis L can be sketched as follows:



After activation, the S sites are <u>not</u> directly responsible for metathesis but for generation of L sites as active metathesis sites with olefins. The S sites may be poisoned before becoming L sites by the impurities or the products (I3). However, the density or the activity strength of the L sites may be promoted by some kinds of impurities (e.g. CO_2, I1), with or without the presence of olefins. As mentioned above, some impurities (I2), or the metathesis products (pp) may cause the deactivation of L sites.

For constant reaction temperature, partial pressure of the reactant, and space velocity, the reaction rate R, would be a function of L only; i.e. from equation 5,

$$R = k_c L \tag{6}$$

Where, $k_c = k_m P^a$ (7)

Therefore, the time-dependence of L or R could be classified into the following three cases:

(a) Break-in

In this regime, we assume no deactivation occurred, the concentration of L would increase with time in the following way:

$$\frac{dL}{dt} = (k_{b1} + k_{b2} C_{I1}^{i1})\, S^b = k_b' S^b \tag{8}$$

And,

$$\frac{dS}{dt} = -(k_{b1} + k_{b2} C_{I1}^{i1} + k_{d3} C_{I3}^{i3})\, S^b = -k_b S^b \tag{9}$$

If, C_{I1}, C_{I3} are constants, then k_b and k_b' are constants, too. Where k_b includes the factor of olefin partial pressure P. Integration of equations 8 and 9, yields a time function $L_b(t)$ for L in the break-in regime:

$$L_b(t) = S_0'(1 - (1 + (b-1)S_0^{b-1} k_b t)^{-(1/(b-1))}) \tag{10}$$

With b = 2, the metathesis rate is,

$$R_b(t) = k_c k_b' S_0^2 t/(1 + k_b S_0 t) \tag{11}$$

For b = 1,

$$R_b(t) = k_c S_0'(1 - e^{-k_b t}) \tag{12}$$

Where S_0 is the initial number of S; $S_0' = (\frac{k_b'}{k_b}) S_0$, b, the number of break-in order.

Equations 11 and 12 are the metathesis break-in rate equations expressed with the second-order and the first-order of the residual active sites S, respectively. If C_{I1} or C_{I3} is also a function of L or S , for instance, I1 or I3 may be some products formed from the reaction affecting the order of break-in and making the rate equation more complex.

(b) Deactivation

Running the propene metathesis over the catalyst activated with certain types of pretreatments or at high temperature may make k_b in equation 10 large and therefore, S sites are rapidly converted to L so that no break-in is observed. Side-by-side and series deactivations are observed, therefore the activity of the catalyst decreases with time may be written as:

$$\frac{dL}{dt} = - (k_{d1}C_{I2}^{i2} + k_{d2}C_{pp}^{pi})L^m \qquad (13)$$

There are two cases for discussion of equation 13:
First, if side-by-side deactivation is predominant, (i.e. $k_{d1}C_{I2}^{i2} \gg k_{d2}C_{pp}^{pi}$), and C_{I2} is constant, then,

$$L_{d1}(t) = L_{max}(1 + (m-1)L_{max}^{m-1}k_{d1}C_{I2}^{i2}t)^{-(1/(m-1))} \qquad (14)$$

With m = 2, the deactivation rate is:

$$R_{d1}(t) = L_{max}(1 + L_{max}k_{d1}C_{I2}^{i2}t)^{-1} \qquad (15)$$

For m = 1,

$$R_{d1}(t) = L_{max}e^{-k_{d1}C_{I2}^{i2}t} \qquad (16)$$

Second, if the series deactivation is predominant, the time function of L becomes more complex and difficult to solve, because the concentration of the product C_{pp} is also a function of L. At a constant reactant pressure, for simplicity, we may assume that there is a relationship between C_{pp} and L as follows:

$$C_{pp} = k_{pp} L^{cp} \tag{17}$$

Substituting equation 17 into 13 and integrating:

$$L_{d2}(t) = L_{max}(1 + (n-1)L_{max}^{n-1} k'_{d2} t)^{-(1/(n-1))} \tag{18}$$

Where, $n = m + m'$; $m' = (cp)(pi)$; $k'_{d2} = k_{d2} k_{pp}^{pi}$

When decay proceeds simultaneously by a number of parallel reactions, the general expression for the deactivation of L may be written as:

$$\frac{dL}{dt} = -\sum_{i} k_{di} L^{i} \qquad (i = 0 \text{ -- } i) \tag{19}$$

And the deactivation rate could be expressed as:

$$R_d(t) = \sum_{i} A_i (1 + G_i t)^{-N_i} \tag{20}$$

(c) Model for the Activity Profile

When the activity profile of propene metathesis over alumina-supported rhenium oxides includes break-in and deactivation, according to the sequence mentioned above the variation of L with time may be written as:

$$\frac{dL}{dt} = k_b' S^b - \sum_i k_{di} L^i \qquad (21)$$

We could apply numerical methods (power series) to solve equation 21 by computer. However, in order to investigate the characteristics of the catalyst from the activity profile, it is physically more meaningful to express an approximate solution for equation 21 as follows:

$$R(t) = k_c L$$
$$= K(1 - (1 + Bt)^{-M})(\sum_i A_i (1 + G_i t)^{-N_i}) \qquad (22)$$

in which $K = k_f k_c S_0'$; $B = (b-1) S_0^{b-1} k_b$; $M = 1/(b-1)$; A_i, G_i and N_i are the same meaning as in equation 20, and k_f is a correction factor.

If $Bt \gg 1$, the break-in would be too fast to be observed. If there is no deactivation, then the metathesis rate would reach a steady-state and equal K/B, and G or N should be zero. In the case of $Gt \gg 1$, one obtains a power function deactivation. So, K,B,N,and G are the parameters characterizing the olefin metathesis rate during break-in and deactivation. The model testing will be shown in the following .

(d). Model Testing:

The models developed for the activity profiles of olefin metathesis over Re_2O_7/Al_2O_3 catalyst will be tested with the experimental data. And the parameters characterizing the rates of break-in and deactivation will also be measured. A regression program applying the least-square method has been designed for the IBM 370 computer (see Appendix B).

Table 6 shows the cases that only deactivation is observed. Equations 14, 15, and 16 have been tested for the deactivation with m-th, 2nd, and 1st order of the activity, respectively (the mth order of deactivation will be designated as m-D). Table 6 shows that the value of k_{d1} is correlated with the value of m, so unless one of these values stays constant, no definitive statement can be made regarding their relative size in various systems and k_{d1} may be not the true kinetic constant. The true order of deactivation can not be obtained from the regression information, however, it could be located in a certain range. For example, the number of m-D versus $\Delta R\%$ can be plotted to locate the minimum point or regime. The true value of m-D may locate in the minimum regime. Narrowing the range of m-D may facilitate searching for the true m-D by other techniques. However, because of the heterogeneity of the catalyst, deactivation may proceed simultaneously by a number parallel reactions and the deactivation order becomes more complex and difficult to be determined.

Table 6. Model Testing: Deactivation Only

Pretreatment	Order	R(t)	ΔR%
W/0.5163gm O_2/16@513°C Rxn. T. 22°C R.G.Propene 6.61 WHSV	1	$0.008244\exp(-0.11233t)$	1.894
	2	$0.008400(1 + 0.14169t)^{-1}$	1.527
	4.4	$0.008934 * (1 + 1.0130t)^{-0.29438}$	0.822
W/0.5112gm Static Exp't Isol./40. Ev./19 @24°C Rxn. T. 24°C 6.36 WHSV R.G.Propene	1	$0.011238\exp(-0.29465t)$	10.19
	2	$0.012673(1 + 0.53794t)^{-1}$	9.224
	4.8	$0.031665 * (1 + 218.76t)^{-0.26612}$	2.788

Table 7 shows the cases that break-in and deactivation are observed. The b-B denotes that the activity increases with time in the b-th order of the residual S sites. Equation 22 was tested according to the following five types extended from that equation:

1). 2-B and 1-D: $K(1 + Bt)^{-1}\exp(-Gt)$ (23)

2). 2-B and 2-D: $K(1 + Bt)^{-1}(1 + Gt)^{-1}$ (24)

3). 1-B and 1-D: $K(1 - \exp(-Bt))(\exp(-Gt))$ (25)

4). 1-B and 2-D: $K(1 - \exp(-Bt))(1 + Gt)^{-1}$ (26)

5). 2-B and m-D: $K(1 + Bt)^{-1}(1 + Gt)^{-N}$ (27)

The five stars shown in Table 7 denote that no solution can be obtained from the regression program. Equations 23--27 have been tested and the regression results are shown in Table 7.

From these regression results we may conclude that: (a) a second-order expression (2-B) for metathesis break-in rate better fits the experimental data than a first-order one. (b) at ice temperature, the deactivation order is in the range between one and two depending upon the surface characteristics of the catalyst. (c) at room temperature, the break-in rate may be too fast to be detected, and the other poisoning reactions may simultaneously occur on the surface and cause the deactivation order increase, so at high reaction temperature(e.g. room temperature) the deactivation order may be higher than two. (d) the rates of break-in and deactivation are very dependent on the reaction temp-

Table 7. Model Testing: Break-in and Deactivation

Pretreatment	order		R(t)	ΔR%
	B	D		
W/0.5190gm O_2/17@502°C Rxn. T. 0°C R.G.Propene 6.75 WHSV	2	1	$0.13626t(1 + 29.610t)^{-1} * \exp(-0.05156t)$	0.883
	2	2	$0.13469t(1 + 29.092t)^{-1} * (1 + 0.05829t)^{-1}$	0.889
	1	1	*****	*****
	1	2	*****	*****
	2	10.4	$0.11128t(1 + 15.988t)^{-1} * (1 + 63.912t)^{-0.1060}$	1.411
W/0.5190gm O_2/7 @516°C Ev/1.1@496°C Rxn. T. 0°C R.G.Propene 6.76 WHSV	2	1	$1.01981t(1 + 91.474t)^{-1} * \exp(-0.07166t)$	0.640
	2	2	$0.96462t(1 + 85.605t)^{-1} * (1 + 0.08487t)^{-1}$	0.600
	1	1	*****	*****
	1	2	*****	*****
	2	3.6	$0.84069t(1 + 72.862t)^{-1} * (1 + 0.3088t)^{-0.3823}$	0.728
W/0.5080gm O_2/7 @512°C H_2/10@499°C Rxn. T. 0°C R.G.Propene 6.76 WHSV	2	1	$0.00643t(1 + 0.0713t)^{-1} * \exp(-0.5621t)$	6.176
	2	2	$0.00723t(1 + 0.4923t)^{-1} * (1 + 0.5986t)^{-1}$	10.01
	1	1	*****	*****
	1	2	$0.00527(1-\exp(-1.3291t) * (1 + 0.22412t)^{-1}$	8.053
	2	1.3	$0.08968t(1 + 0.0933t)^{-1} * (1 + 0.2494t)^{-3.3830}$	3.064

erature and the pretreatment conditions of the catalyst etc.

B. Olefin Metathesis on the surface of Re_2O_7/Al_2O_3

As shown in the previous Chapter, we have kinetic data of propene metathesis over Re_2O_7/Al_2O_3 catalyst treated with various pretreatments. Those pretreatments can be classified into four cases:

(a) activated in oxygen at various temperature.

(b) oxidized at about 500°C and further treated in inert environment or in vacuo at various temperature.

(c) oxidized at about 500°C and further treated with hydrogen reduction at various temperature.

(d) oxidized at about 500°C and further treated with various olefins at room temperature.

We would like to discuss the dependence of the characteristics of the catalyst on the pretreatments and its relation to the activity of olefin metathesis, etc., in the light of current literatures and our kinetics results (see Table 8).

In general, the alumina-supported rhenium oxide exhibits break-in in the activity of propene metathesis as long as it is pretreated in the dry, flowing oxygen at high temperature (250°C). And the period of break-in decreases linearly proportional to activation temperature (see Fig. 4).

Table 8. Effect of Pretreatment Conditions on the Selectivity *

Pretreatment **		$R_{max.}$ $\times 10^4$	$t_{max.}$ min.	E/B				TB2/CB2				O_2 pulse			
												E/B		TB2/CB2	
				3 min.	20 min.	60 min.	200 min.	3 min.	20 min.	60 min.	200 min.	*** b	*** a	b	a
Ev./0.1@0°C		45.2	50.	.93	.83	.80	.83	2.57	2.93	3.02	3.04	.82	.86	3.05	2.97
Ev./11	@ 24°C	39.5	0	.89	.85	.86	.88	3.16	2.99	2.91	2.87	-	-	-	-
	@ 242	23.	0	.85	.93	.96	@180 1.61	2.59	2.53	2.22	@180 1.76	-	-	-	-
	@ 496	107.3	21.	.86	.80	.79	.79	3.16	3.33	3.30	3.14	-	-	-	-
H_2/10	@ 24.	49.	0	.91	.82	.83	.92	2.80	2.59	2.49	2.30	.94	.97	2.21	2.35
	@ 244	0.	-	-	-	-	-	-	-	-	-	-	.79	-	2.87
	@ 499	37.8	70.	2.02	.95	.86	.92	3.33	2.57	2.42	2.12	.97	.86	2.11	2.73
E./2 @ 24°C		49.6	30.	1.12	.93	.89	.85	2.42	2.82	2.92	2.98	-	-	-	-
CB2/2@ 24°C		30.	0.	-	.70	.77	.82	-	2.65	2.63	2.51	-	-	-	-

*The metathesis reaction was run over 9%Re_2O_7/Al_2O_3 with r.g.propene at 0 °C.

**The catalyst was activated at about 510°C in oxygen before further pretreatment.

***b'means 'before' injection of oxygen pulse; 'a' means 'after'.

By extrapolation, at an activation temperature higher than 590°C the break-in may not be observed because the break-in time is too short.

It is generally accepted that Re interacts more strongly with γ-Al_2O_3 than with SiO_2 (5,15). Heating the Re_2O_7/Al_2O_3 catalyst in oxygen at about 500°C may lead to form a compound providing a mesoperrhenate structure with the participation of surface aluminum ions (24). The equilibrium high temperature oxidation state of this structure is Re(+7)-d^0 in ReO_5^{3-} (24,7). The color of this oxygen-heated sample is light-yellow. And anion vacancies are probably not available on the surface of the sample because of complete oxidation of the catalyst.

Olsthoorm and Boelhouwer (8) has concluded that the metathesis activity is generated by the reduction of the catalyst (Re_2O_7/Al_2O_3) with olefins (propene or higher alkenes). Simultaneously, water is generated which is, for the greater part, associatively adsorbed at room temperature. The initial reduction of Re^{7+} by olefin (e.g. propene) probably occurs according to the reaction proposed by Peacock et al.(9):

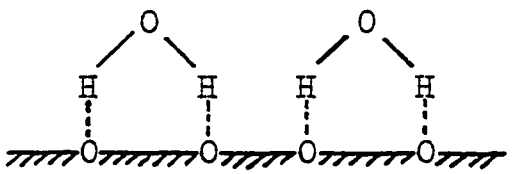
$$mC_3H_6 + Re^{7+} + O^{2-} \longrightarrow ((C_3H_5)_m\text{-}Re)^{7+} + mOH^- + me^- \quad (28)$$

Where m is the number of propene molecules attacking the Re (it may be between zero and three (7,24));and the neighboring Re(+7) is reduced by the free electron(s) as follows:

$$me^- + Re^{7+} \longrightarrow Re^{(7-m)+} \quad (29)$$

And water may be generated simultaneously in the reduction and

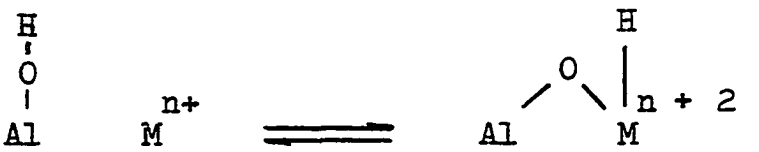
perhaps during or after the formation of the hydroxyl groups. The water generated may be partly adsorbed and block the sites, thus preventing the metal from the attachment of olefins. Part of the water may be removed (38). However, before introduction of the olefin, purging with wet He(Cu) (saturated with water at room temperature) exhausted entirely the metathesis activity (see chapter II-C-a). The abnormally high temperature jump upon introduction of wet helium (about 24 C°) suggests that some of the molecules reacted with the surface and probably became hydroxyl groups, but the greater part was associatively adsorbed (8). Such a molecule will bond to two surface oxygen ions by very strong hydrogen bonds as (62):



(30)

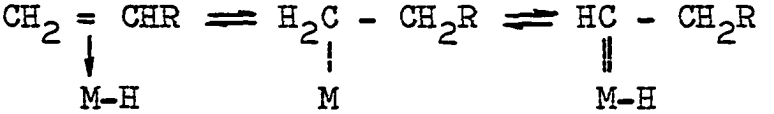
The hydroxyl groups formed or the strong hydrogen bonds between water molecules and the surface oxygen ions may be strong enough to resist the reduction of the catalyst by olefins introduced.

Rooney et al.(10) have proposed a metal hydide mechanism for the initiation and the termination of carbene-chain carriers. The carbene-chain carriers are supposed to be responsible for olefin metathesis. The metal hydride is formed by an oxidative addition of hydrogen from adjacent hydroxyl group to the metal ion in a low or intermediate oxidation state, i.e.



(31)

The metal-carbene is formed by the subsequent reaction of an olefin with the hydride involving sequentially a β-addition and α-elimination:



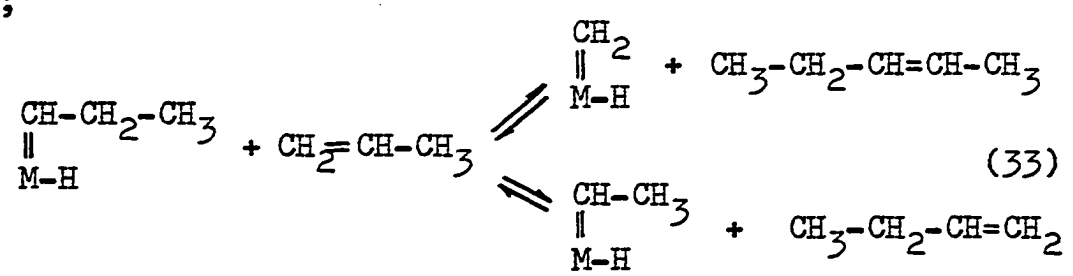
(32)

On the other hand, Banks et al. (49,50) proposed that olefin metathesis occurs through promotion of electrons from molecular orbitals comprising metal d-orbitals and olefin pi-orbitals to levels comprising metal d-orbitals and olefin anti-bonding pi-orbitals. The enhancement of the pi-olefin-metal bonding also follows this concept. Whatever it is, the necessary criterion for the olefin metathesis activity is to provide the filled d-orbitals in the transition metal of the catalyst. The filled d-orbitals of the metal may be available by partial reduction.

It is recognized that to create free electron(s) from reduction should consume some reactants (equation 28). The free electrons provide the source to fill the metal d-orbitals (e.g. Re^{7+}). Compared to the case that the catalyst, pretreated in prolonged evacuation at room temperature after oxidation, exhibited no break-in (Fig. 17), and less adsorption of propene (Table 4), it may be surmised that:

there are anion vacancies created by the prolonged evacuation (the color of the catalyst is bright-pink) which are also responsible for olefin metathesis, but part of active metathesis sites are still coming from reduction by olefin. However, those anion vacancies created by prolonged evacuation at low temperature have much less ability to resist poisons (otherwise, adsorb more strongly to impurities or olefins), and thus, the profile of metathesis activity resulting from the anion vacancy exhibits much higher deactivation power. For convenience, we designate the anion vacancies created by prolonged evacuation as A sites, the sites by olefin reduction as B sites. The apparent activity profile is the superposition of the activity profiles due to A sites and B sites. Because B sites are increasing with time, and A sites are always deactivated by olefins, the appearance of break-in in the apparent activity profile would be determined on whether B sites are predominant over A sites. Before the structure of the catalyst is changed or destroyed, increasing T_{ev} could increase the number of A sites (29,30), and the predominance of A sites over B sites. Because of the high deactivation of A sites due to poisons, increasing T_{ev} could increase the initial deactivation rate. The predictions arising from these considerations are shown to be in accord with existing experimental data (shown in Fig. 17 and Table 4). The high deactivation of A sites may be attributed to their ability to strongly adsorb the reactant or products during

the initiation of normal carbene complexes. For example, using propene;



(33)

Those products, e.g. butene-1 or pentenes etc. (observed in static system, but not in flowing system) may be formed and strongly adsorbed by A sites and block them. Or A sites may be reduced further by olefins to an inactive or less-active oxidation-state. The water generated from creation of B sites is also probably strongly adsorbed and blocks the A sites.

Usually, the period of break-in is less than one hour. By exposing the oxidized catalyst in flowing hydrogen at room temperature overnight, the active sites (C-sites) would be already created to a saturated level. So the slow elementary steps (eqn 28 and 29) for creation of B sites would be skipped and break-in would not be observed. The experimental data shown in Fig. 19 are in agreement with the above predictions. Similar results are obtained for the catalyst pretreated with olefins (except for ethylene pretreatment) and static pretreatment in propene (see Fig. 21, 22,23). Because ethylene shows hardly any reduction capacity at room temperature over Re_2O_7/Al_2O_3 (8,15), the creation of B sites should be achieved by introducing propene and break-in should be observed.

However, it is interesting, shown in Fig. 15, that T_{ev} is higher than 320°C, the olefin metathesis activity is pronouncedly increasing with increasing T_{ev} and break-in is observed again as $T_{ev} > 350$°C. Following the conclusions by Yao and Shelef (7), we may ascribe the active sites created by evacuation at $T_{ev} < 320$ °C to the crystalline three-dimensional phase. The results also suggest that at $T_{ev} < 320$°C, dispersion of the crystalline phase into two-dimentional phase could not occur. Other evidence to support this idea is that the catalyst exhibits no activity when it is reduced by H_2 at 244°C. In this case rhenium would be reduced to an oxidation level which is inactive to olefin metathesis. The crystalline phase can be reduced to Re^0 by H_2 at 350°C (7).

When T_{ev} increases to a value higher than 320°C, the crystalline phase could be dispersed on the surface and more active sites could be created for olefin metathesis. Although there are F centers observed (7,23,24) and a "shuttle" cycle mechanism has been proposed (24) in which the oxidation state of Re is changed between 6+ and 7+, it is still not certain that the F centers are responsible for olefin metathesis. In Fig. 15, 18 and Table 4, the results show that at a higher T_{ev} (>320°C) break-in is observed again and the adsorption amount of propene is larger. The results may suggest that part of sites in the dispersed phase may be not directly responsible for olefin metathesis but need the reduction and complexation

with olefins, or the site-localized diffusion effect becomes significant in this situation. Dispersion treatment probably increases the number of sites and the activity per site.

Figs.22, 23, and 24 show that the activity or the number of active sites of the catalyst is dependent on the period of isolation in static olefins and evacuation. It is noted that the reduction of the catalyst with olefins is a slow elementary step and the reduction ability of olefin is different. So, isolating the catalyst in static propene and its metathesis products (e.g. ethyelene, butenes etc.) could give certain situations of Re accessible to reduction by the high concentration (comparing to the flowing system) and high reduction ability of products like cis-butene-2 or trans-butene-2. The reduction may generate more metal-olefin complexes which are reversible sites and can be created as active sites for olefin metathesis by prolonged evacuation. However, those active sites have a strong ability to adsorb impurities or olefins, especially the higher olefins (than butenes) produced during reaction, so that the deactivation order is high.

On reduction with H_2 or NH_3 , Re crystals are formed; therefore, a sintering must occur (8).A mechanism for reduction of MoO_3/Al_2O_3 catalysts with H_2 has been proposed (42). It is generally accepted that the Re_2O_7/Al_2O_3 catalyst can not be completely reduced to Re^0 metal by H_2 at 500°C (7). According to the hydrogen reduction mechanism (42, 63, 65, 66),

anion vacancies could be created by H_2 reduction at 500°C. Because greater part of Re may be sintered and hydroxyl groups may be formed which are not removed as water, the anion vacancies are probably scarce on the surface. The slow break-in rate of the reduced catalyst (by H_2 at 500°C) shown in Fig. 19 could be ascribed to a reaction controlled by site-localized diffusion effects (34). The result of high initial ratio of TB2/CB2 close to the equilibrium value could support the above consideration; it will be discussed latter. Fig. 20 shows that the dispersed phase could be reduced by H_2 at about 505°C and the active sites of the reduced catalyst are situated on the Re which is hard to be reduced by H_2 only (without dispersion pretreatment).

The pronounced increase of the metathesis activity of a partially reduced catalyst by an O_2 pulse (Fig. 9 and Table 5) could be ascribe to the fact that oxidation reaction has occurred in the presence of olefins and changes the Re to an oxidation state at which it is active for olefin metathesis, in other words, the sintered Re is spread out again by oxidation.

In general, the ratio of TB2/CB2 increases proportionally to the metathesis activity (reaction rate) but the ratio of E/B increases inversely (Fig. 5, and 16). However, there is an exception on the reduced (by H_2 at 500°C) catalyst in which the ratio of TB2/CB2 decreases proportionally to the activity in the period of break-in (Fig. 19).

It has been shown that the CB2 isomer is the initial product of propene metathesis. Combination with the above results suggests that the transformation from CB2 to TB2 is a function of the concentration of CB2-metal complex, and/or controlled by the steric factors. Shown in Fig. 19, the high initial TB2/CB2 ratio could be attributed to no steric effects on the reaction because the reduced catalyst has few sites on the surface. On an oxidized catalyst, the low value of TB2/CB2 at the begining may be due to the steric factors caused by the products generated during the initiation of carbene complexes such as 1-butene, or pentenes etc. In the other cases, when the activity is decaying, the poisoned sites are perhaps occupied by some kinds of polymers and provide a steric network to prevent CB2 transformation to TB2. So, we may conclude that the TB2/CB2 ratio is limited by the steric configuration of complexes around the sites.

On the other hand, the high initial ratio of E/B was ascribed by many authors to butenes being more strongly adsorbed (65,67) (We also observed that butenes were more strongly adsorbed than ethylene). But it may be, in part, attributed to the fact that the yield of butenes is a function of the concentration of metal-butenes complexes, because below a level of activity the yield of butenes decreased pronouncedly with the activity. At a level higher than a certain activity, the ratio of E/B is less time-dependent even when the activity is decreasing.

In this range, the apparent E/B ratio is less than the stoichiometric value (i.e. unity). This fact may result from part of ethylene product being converted to propene or butenes. Therefore, the E/B ratio can not reach the stoichiometric value but depends upon the kinetic factors (see next section).

C. The Elementary Steps in Olefin Metathesis

The results suggest that our kinetic experimental data can be correlated better through the alkylidene-carbene complex mechanism. That is, there are, at least two different carbene complexes on the catalyst surface responsible for olefin metathesis in the propagation steps. In general, these two complexes will react with propene at different rates. The following elementary steps could be proposed:

(a). Initiation:

1). $P + S = L$ .....(34)

2). $P + L = PL$ .....(35)

3). $PL = EL + A_1$ .....(36)

4). $PL = BL + A_2$ .....(37)

(b). Propagation:

5). EL + P = PEL .....(38)

6). PEL = EBL .....(39)

7). EBL = E + BL .....(40)

8). BL + P = PBL .....(41)

9). PBL = BEL .....(42)

10). BEL = TBEL .....(43)

11). BEL = CB2 + EL .....(44)

12). TBEL = TB2 + EL .....(45)

(c). Side Reaction:

13). 2E + EL = P + BL .....(46)

14). E + EL + P = B + BL .....(47)

(d). Termination:

15). L + I = LI .....(48)

16). EL + I = ELI .....(49)

17). BL + I = BLI .....(50)

Where P is propene; S is the site which can be reduced by propene to create the metathesis sites L; EL, $M{=}CH_2$; BL, $M{=}CH{-}CH_3$; A_1, A_2 the olefin metathesis products (see eqn.33).

From the experimental results, it is concluded that: (a) in the case of no impurity in the feedstock, step 1 is the slowest step in the initiation; step 9 is the rate-determining step in the propagation. The presence of ligands may increase the rate constant of the elementary step 1 or/and step 9 and cause the break-in rate high; (b) in the termination, I is

the impurity from reactant or products of reaction; the presence of the impurity could diminish the available metathesis sites and cause deactivation; (c) in equation 43, the rate constant for butene isomers transformation is controlled by the configuration of complexes around the site; (d). at a certain activity level, the side reaction may proceed and cause the E/B ratio less than unity; and (e) at a low level of activity, the concentration of BL is so low that the rate of the rate-determining step (eqn. 42) is negligible comparing with that of step 6 (eqn.39), and thus the E/B ratio is high ($\geqslant$1.0) in this range of activity.

CHAPTER V

CONCLUSION

The kinetics of olefin (propene, and cis-2-butene) metathesis over 9%Re_2O_7/Al_2O_3 catalysts pretreated with various conditions were studied. A kinetic model was developed to elucidate the time-on-stream profile of the activity that may involve catalyst break-in and deactivation depending upon the pretreatment conditions and reaction temperature. The metathesis rate, break-in rate, and deactivation rate of the catalyst activity are dependent upon activation temperature, pretreatment conditions, reaction temperature, reactant and its partial pressure, and impurities containing in the feedstock etc. The experimental data can be correlated better through the developed kinetic model based on break-in at the second-order and deactivation at an order between one and two of the residual activity.

The phenomenon of break-in in propene metathesis on the catalyst studied can be observed only at 0°C reaction temperature. Usually, it appears on an oxidized catalyst (without any further treatment), on a catalyst treated with dispersion

pretreatment (ev. at 500°C), or on a reduced catalyst (with H_2 at 500°C). The occurrence of break-in could be due to the fact that the necessary reduction step by propene to create anion vacancies for metathesis is a slow elementary step (for oxidized, or dispersed catalysts), or that the metathesis rate is limited by site-localized diffusion effects (for H_2 reduced catalyst). The maximum metathesis rate (R_{max}) of an oxidized catalyst is proportional to activation temperature, whereas the period of break-in decreases linearly with increasing R_{max}. Catalysts reduced in H_2 at 500°C are initially inactive with a protracted break-in phase. Thus, the generation of a coordinatively unsaturated metal probably of an intermediate oxidation level (for Re, may be between 2+ and 6+) is a prerequisite step for olefin metathesis. However, the activity can be affected by the type of ligand associated with the metal. For instance, CO_2 could promote the break-in rate and the activity (R_{max}) of propene metathesis over supported rhenium oxide catalysts.

The decay in metathesis activity may be due to the generation of a surface polymers (e.g. pentenes) and impurities in the feedstock etc. The metathesis sites may adsorb the polymers or impurities too strongly to be active. Thus, the deactivation may depend on the adsorptive capacity of the sites to the poisons, whose adsorptive ability is determined by the type of the metathesis sites which are

dependent upon pretreatment conditions. Also the reaction temperature is an important factor on the activity decay. Water is a severe metathesis poison. Carbon dioxide can not only promote break-in rate but deactivation.

Usually, a catalyst studied is activated at about 500°C in dry oxygen. The metathesis activity of a used catalyst can be restored by treating at the same activation temperature in dry oxygen except that the catalyst has been reduced with H_2 or by dispersion pretreatment at the same or higher temperature. When the catalyst is activated with oxygen at increasing temperature starting from 200°C, the activity of propene metathesis at 0°C can be detected but become large after 500°C.

During activation at 500°C, oxygen is an important factor to maintain a mesoperrhenate structure of rhenium oxides on the catalyst surface. Even a trace of oxygen in the activation gas (e.g. He) can not destroy or change the structure in this activation condition. After oxidation, purging with oxygen-free helium increases the activity significantly, but the same is not true with the commercial helium containing a small amount of oxygen. To a fresh catalyst, heating the catalyst at about 500°C in oxygen-free helium could activate more pronounced metathesis sites and stability. However, to a used catalyst, with the same activation (without oxidation pretreatment) the activity can not be restored but depends on its history.

On an oxygen-activated catalyst the interphase diffusional effect was negligible at ice and room temperatures.

The activation energy of propene metathesis over the catalyst activated with the standard procedure is about 5 kcal., but varies depending on the pretreatment conditions. For example, with dispersion pretreatment it is about 2.8 kcal.

About 10% or more of the sites available for propene metathesis are reversible.

Using p.g. propene, a higher space velocity accelerated both the break-in and deactivation rates, but reverse results were obtained for r.g. propene. This observation shows that deactivation is resulted not only from the imurities in the feed but from the polymer products.

If the oxidized catalysts are pretreated by evacuation at various temperature, the activity shows two regimes of quite different characteristics centered in the neighborhood of 320°C. When $T_{ev} < 320°C$, no break-in but decay was observed and the activity decreased with increasing T_{ev}. At $T_{ev} > 320°C$, the activity sharply increased with increasing T_{ev} and break-in appeared again, but the deactivation was less dependent on T_{ev}. Also the adsorption amount of propene at room temperature decreases with increasing T_{ev} to a minimum at about 320°C, and increases again with increasing T_{ev}. The results suggest that the active sites created by evacuation at $T_{ev} < 320°C$ are located on the crystalline three-dimensional phase and have weak

resistance to poisons and dispersion of the crystalline phase into the two dimensional phase can not occur. When $T_{ev} > 320°C$, the dispersion can be accomplished and increase the number of sites or the metathesis activity per site.

Similar results were obtained for the catalysts treated with H_2 at various temperature. But at 500°C, the activity is low and the break-in is protracted. At a temperature between 200 and 350°C, the catalyst is inactive. Perhaps dehydroxylation can not be accomplished at this temperature. The metathesis activity of the H_2 reduced catalyst (at 500°C) may be associated with a small number of sites that resist complete reduction. With dispersion pretreatment, more sites can be reduced to inactivity under the same reduction conditions.

An O_2 pulse into the propene metathesis system pronouncedly increases the activity of a partial reduced catalyst (by dispersion or H_2 reduction). In this case, oxidation reaction may occur even at 0°C in the presence of O_2 and propene and changes the oxidation level of Re to an active one.

Isolating an activated catalyst in static propene for a long time and evacuating overnight at room temperature increases the initial activity up to 4 times greater than the normal but decays rapidly within one hour to a value slightly lower than the normal. The initial activity and the deactivation rate are a function of not only the isolation time but the evacuation time.

In propene metathesis studies, 1-butene or higher olefins were not observed in a flowing system, but in a static system. In CB2 metathesis, propene was observed in either system, but 1-butene and higher olefins were only observed in static system. The initial activity of CB2 metathesis was large with conversion approaching equilibrium, but decays rapidly.

In general, the TB2/CB2 ratio increases proportionally to the metathesis activity but the E/B ratio increases inversely. However, there is an exception on the H_2 reduced catalyst (at 500°C) in which the TB2/CB2 ratio decreases proportionally to the activity in the period of break-in. CB2 is the initial product in propene metathesis system. The transformation may be, in part, limited by the steric configuration of complexes formed around the sites. The TB2/CB2 ratio is usually less than the equilibrium value. The E/B ratio at the begining depends upon the pretreatment conditions of the catalyst but rapid becomes constant even the catalyst activity is decaying; where the constant E/B ratio is less than the stoichiometric value. This may result from some of ethylene product being converted to propene or butenes. At a very low activity, the yield of butenes is limited by the rate-determining step so that the E/B ratio is higher than unity.

The alkylidene-carbene complex mechanism is found better correlated with the experimental data.

CHAPTER VI

RECOMMENDATIONS

Further studies of the catalytic properties of supported rhenium oxide catalysts as a function of pretreatment conditions are needed to investigate the relationships of metathesis activity, the structure, and the oxidation state of Re, etc. The structure of the catalyst and the oxidation state of Re can be changed in terms of pretreatment conditions. The important pretreatments include heating in the environment of oxygen, purely inert gas, vacuum, olefins, and hydrogen at various temperature. Based on those pretreatments, some special techniques may be applied and different reactants used as probes to charaterize the catalytic properties of the catalyst.

The following general types of experiments classified in terms of experimental techniques are recommended for further understanding of the properties of the catalyst:

A. Kinetic Studies

(a) Use various light olefins as reactant to determine the variation in the activity of supported rhenium oxide from break-in through decay as a function of pretreatment variables,

reaction temperature (below room temperature) , and partial pressure of reactant. Also changes in selectivity must be monitored.

(b) Determine propene and butene yield from ethylene as a function of reduction level of the catalyst reduced by various olefins.

(c) Simlar to a, and b, but as a function of Re loadings.

(d) Determine mass transfer effects.

(e) Using TGA to determine the kinetics of reduction with various olefins and hydrogen as a function of pretreatment conditions (42). (f). Similar to Section III-F.

B. Volumetric Adsorption Study

(a) Using ethylene, and TB2 to determine adsorption isotherms as a function of pretreatment variables. Also monitor changes of composition and selectivity.

(b) Determine dependence of olefin adsorption on the reduction level of the catalyst reduced by olefins and hydrogen.

(c) Use oxygen and hydrogen to determine adsorption isotherms and figure out oxidation level as a function of pretreatment variables.

C. DGA, DTA, and TPD.

(a). Quantitatively determine Re loss during pretreatment by DGA (differential gravimetric analyzer) or qualitatively by liquid nitrogen trap.

(b) Determine temperature change profiles of the catalysts

during pretreatment and reaction by DTA (differential thermal analyzer).

(c) Determine the heterogeneity of the catalysts by TPD (temperature-programmed desorption).

(d) Use moisture analyzer to quantitatively determine water generation during reaction and water removal during pretreatment and its relation to the activity.

(e) Similar to the work presented by Hall et al. (63, 65), determine the number of anion vacancies as a function of pretreatment variables and reduction level of the catalysts and connect the information with the variation of the activity to determine their relationships.

D. Pulse-Technique Analysis

(a) Use oxygen-free helium as carrier gas and apply pulse technique to inject olefins (ethyelene, propene or TB2) as probe reactant and quantitatively determine the water produced, the composition and selectivity of products. Information on the elementary steps and their rate constants can thereby be obtained.

(b) Pulses of activators (e.g. O_2) and poisons (e.g. H_2O) can be introduced and the response of the system followed to assess the nature of the active sites.

(c) Pulses of O_2 and H_2 can be introduced and monitored to determine the level of oxidation and reduction of the surface after various pretreatment.

E. Mass Spectrometry

(a) Pulses of isotopically labelled oxygen can be used to assess the role and exchangability of lattice oxygen during the reaction. Also pulses of deuterated ethylene can be used to monitor the metathesis activity under adsorption equilibrium conditions after various pretreatment.

(b) Isotopically labelled trans-2-butene can be used to determine the mechanism of metathesis and to explain how propene is produced in the TB2 metathesis system.

F. Specific Poisoning Techniques.(8,20,29,30,37)

(a) With the help of IR, determine the active sites responsible for metathesis, and isomerization and the Bronsted acidic sites and Lewis acidic and basic sites etc.

(b) Determine the mechanism of transformation of CB2 and TB2.

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APPENDICES

A. Mechanisms and Kinetic Models of Olefin Metathesis

There are two plausible reactions which lead to the observed products of olefin metathesis (2). One possibility involves cleavage of a carbon-carbon single bond adjacent to the double bond and transfer of alkyl groups. This case is a transalkylation reaction. Another involves cleavage and scrambling of the double bonds, a transalkylidenation reaction. A transalkylidenation reaction of propene metathesis is shown in page 123.

Mol et al.(51) and Clark et al.(3) analyzed the products formed in the heterogeneously catalyzed metathesis of propene labeled with ^{14}C. From (2-^{14}C)-propene, the radioactive carbon was found in the butene product not in the ethylene, from (1-^{14}C)-propene the radioactivity was found in the ethylene, and from (3-^{14}C)-propene the butenes product was radioactive. Calderon et al (52) obtained analogous results from the reactions of 2-butene and 2-butene-d_8, the only new product was 2-butene-d_4. All the information ruled out the transalkylation mechanism and the pi-allylic intermediate mechanism (2). So, the transalkylidenation mechanism would be more acceptible to

account for the disproportionation of olefins.

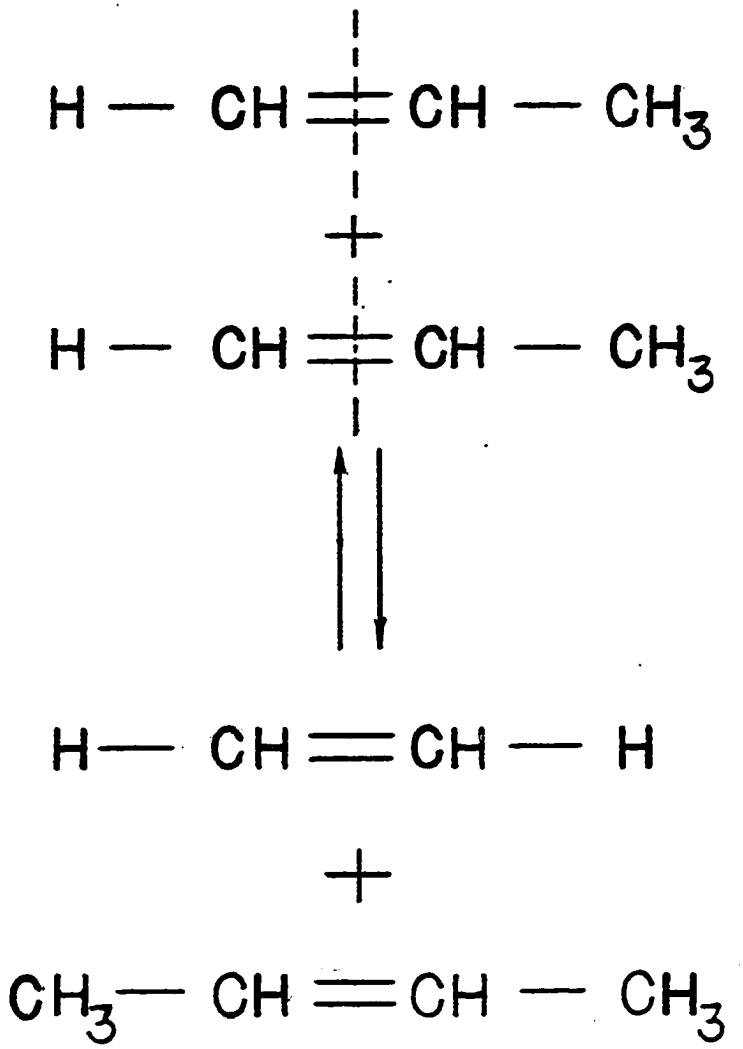
Bradshaw et al.(53) proposed that the olefin metathesis proceeded via a "quasi-metal-cyclobutane complex" intermediate. Mango et al. (54) suggested from calculations and orbital symmetry considerations that the reaction could proceed by the same mechanism in a concerted fashion with a low activation energy. This mechanism is shown in page 124.

Due to the difficulty of finding evidence to support the concerted, diolefin, pairwise scheme, other mechanisms were considered. One of these was a pairwise, nonconcerted scheme (shown in page124) (55). This mechanism required a tetramethylene metallocycle as an intermediate. Evidence for the rearrangement of metallocycle came from the investigation of 1,4-dilithiobutane with tungsten hexachloride. However, as with any model study or mechanistic study involving the preparation of intermediates, the results only demonstrate what is possible but may have no relationship to the reaction under study (40).

The other mechanism, non-pairwise chain reaction, (shown in page 125) involved a chain reaction in which a carbene-metal complex was the active sites. Herisson and Chauvin (56) proposed this carbene mechanism in 1970 and suggested that this scheme would account for the products and general characteristics equally well as the pairwise schemes. This mechanism has been examined by Grubbs et al. (40) using mixtures of 1,7-octadiene and 1,7-octadiene-1,1,8,8-d_4 as the olefins and three basically

MECHANISM

I. TRANSALKLIDENATION

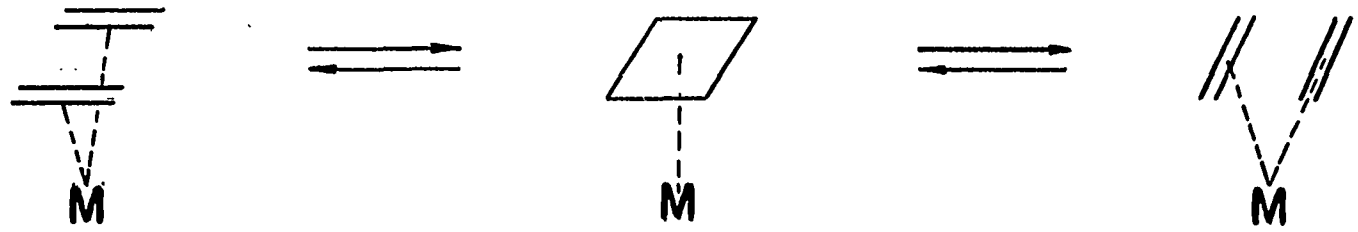


A. MOL.et al. (2-^{14}C)$C_3^=$/Re_2O_7-Al_2O_3

B. Clark et al. (1-/2-^{14}C)$C_3^=$/MoO_3-CoO-Al_2O_3

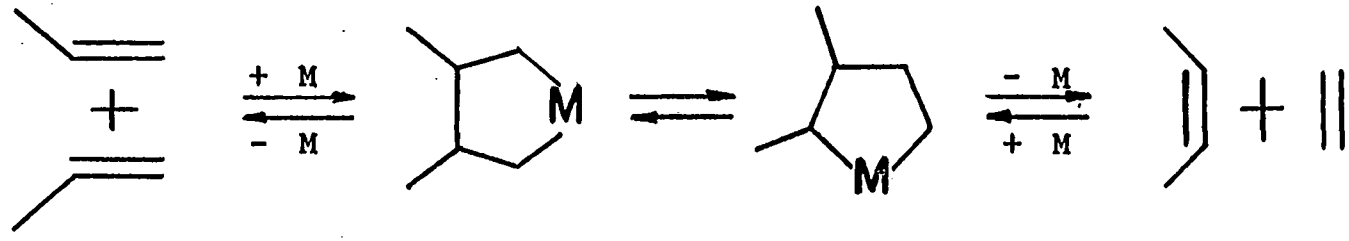
C. Calderon et al. 2-B/2-B-D_8/W-Complex.

2. PAIRWISE/CONCERTED (QUASI-CYCLOBUTANE)



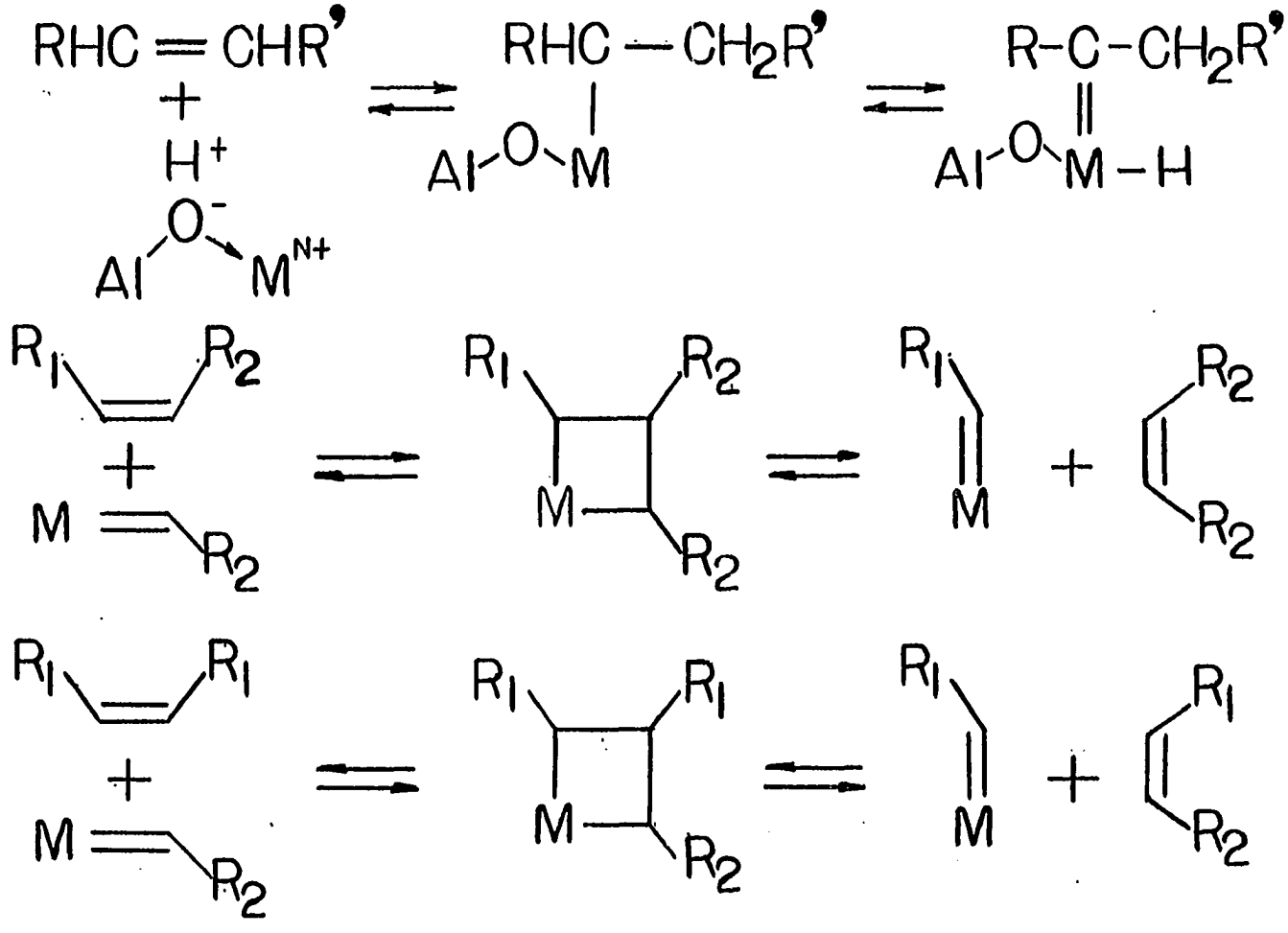
*Pettit et al (Tetramethylene Complex) * Bradshaw et al.

3. PAIRWISE/ NON-CONCERTED (METALLOCYCLOPENTANE COMPLEX)



Grubbs & Brunck

4. NON-PAIRWISE CHAIN M. (CARBENE-COMPLEX)



*Herrison & Chauvin (Carbene);*Rooney et al.(M-H);*Rijn & Mol(Kinetic Model);*Grubbs et al.(Exp'T Test)

different catalyst systems. They concluded that the results obtained were most consistent with this mechanism. From kinetic studies, Mol and Rijn (41) obtained analogous conclusion to support this carbene mechanism.

Even though much evidence has been obtained that olefin metathesis and ring-opening polymerization of cycloalkenes are chain reactions, with carbene as the chain carrier reversibly reacting with complexed alkenes to generate new carbenes and alkenes via intermediate metallocyclobutanes, the next problem being raised is the initiation of carbene complexes. Rooney et al. (10) obtained good evidence that metal hydides were responsible for ring-opening polymerization and dimerization reactions of norbornene catalyzed by several transition metal halides. Using the same techniques they detected hydridotungsten complexes in a tungsten complex metathesis catalyst in benzene solution. They concluded that the role of hydride was to isomerize olefin reversibly to carbene complexes via metal alkyl formation, thereby providing carbene initiation.

The kinetic study is a formal method of investigating the characteristics and the mechanism of a chemical reaction system. From that we could develop a mathematic model to the observed fact and reasonably predict the properties of another similar reaction system.

If a catalytic chemical reaction on a solid surface is free of the diffusion limitation, there are three steps in the

overall process of catalysis. They are:(1) the adsorption of the reactant on the catalyst surface, (2) the surface reaction of the adsorbed reactant, and (3) the desorption of the products from the surface.

In the adsorption studies, Brunauer et al. (57) has classified adsorption isotherms into five types (shown in page 130). Lin et al. (15) found that isotherms for adsorption of ethylene on alumina supported rhenium oxides under 300 torr pressure could be more faithfully represented by the Freundlich equation than by the Langmuir isotherm.

There are three kinds of kinetic models proposed;

(a) Rideal Model (page 133)

It is based upon the assumed interaction of an adsorbed species and species from the gas phase striking the surface or species in a state of physical adsorption. Begley and Wilson (58) concluded from their kinetic studies of propene metathesis over tungsten-silica catalyst at high pressure range (up to 900 psia) that the Rideal model fitted the data better than others.

(b) Langmuir-Hinshelwood Model (L-H) (page 134 and 135)

It is postulated that the reaction occurs between two chemisorbed molecules. It is conceivable that the two chemisorbed molecules are either adsorbed on the two active sites which are localized at the same active center (L-H B) or individually at two neighboring active centers (L-H A). The L-H model of

reaction rate is developed on the assumption that the surface reaction step is the rate determining step.

(c) Carbene-Complex Model (page 136 and 137)

It is based on alkene (CMC A) or alkylidenation (CMC B) complexes as active sites, the number of these being independent of the alkene pressure in the gas phase.

Wills et al. (59,60) utilized the initial differential rate models as a method for testing the metathesis mechanism of propene over a $CoO-MoO_3-Al_2O_3$ catalyst in the temperature range 394-478°K and pressure 1--9 atm. The experimental data were well correlated by the L-H dual site surface reaction model. They also studied the metathesis of propene over 10%WO_3 on silica gel catalyst using the same techniques. Reaction temperature ranged from 399--454°C and pressure from 1---9 atm. Similar results were obtained and they concluded that the L-H model was correlated with the data better than the Rideal model over the range of variables studied.

In the study of the rate temperature maximum for olefin metathesis on $CoO-MoO_3-Al_2O_3$ catalyst, Moffat and Clark (22) concluded that the L-H model applied better to the heterogeneous surface reaction and could be used to describe both the general kinetics and other characteristics such as the observed kinetics below T_{max}, the observed rate-temperature maximum; the shift in T_{max} with decreasing propene pressure; the decrease in T_{max} with decreasing catalyst activity and the abnormally low apparent heat of adsorption.

Davie et al.(31) found that the rate controlling step was a surface reaction between two adjacently adsorbed propene molecules, i.e. the L-H mechanism. This conclusion was obtained from a study of the kinetics of propene metathesis on a alumina-supported molybdenum hexacarbonyl catalyst in a static system at temperature between 290--350°K with propene pressures in the range 0.5--20. kNm^{-2}(3.75--150 torr).

Lin et al. (15) studied the kinetics of propene metathesis on 10.95% Re_2O_7/Al_2O_3 catalyst at low temperatures (25--68°C). They concluded that the rate of reaction was proportional to the partial pressure of propene to the 1.4th power for pressures equal to or less than one atmosphere and the L-H model fitted the data better than the Rideal model. Hughes (61) found the order with respect to 2-pentene to be between 0.7--1.7, depending on the alkene to catalyst ratio.

On the basis of the data of Lewis et al. (62) and Hattikudur and Thodos (63), Rijn and Mol (41) compared the kinetic models of L-H A and B, and carbene-complex A and B, applying nonlinear regression to the initial rate equations and their integrated forms. By comparing the Rideal model and L-H model, Lewis et al. and Thodos et al. concluded that the L-H dual-site mechanism was followed. However Rijn and Mol demonstrated that the experimental literature data can be correlated just as well or even better through kinetic models based on the carbene complex single-site mechanism.

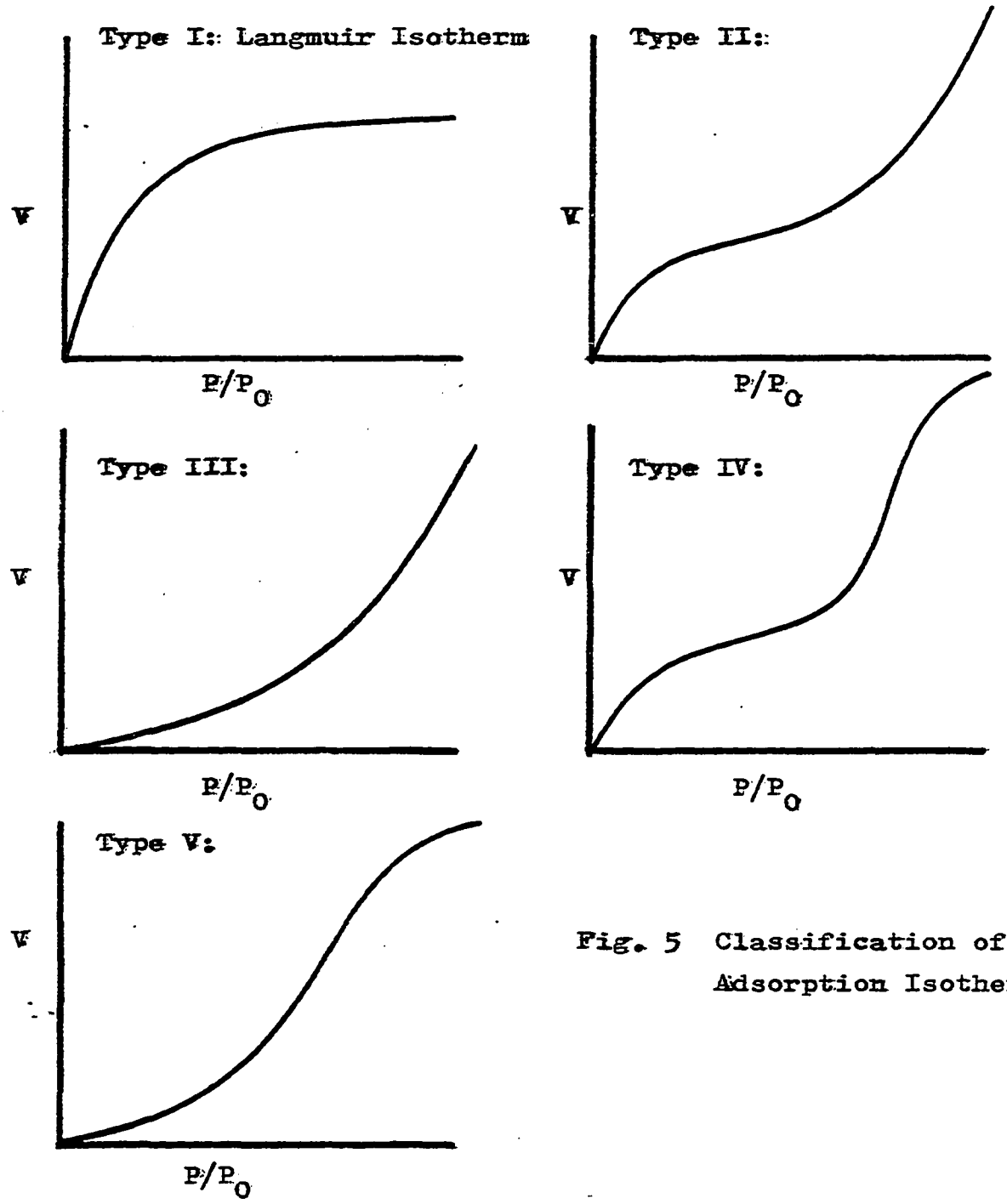


Fig. 5 Classification of Adsorption Isotherms

ADSORPTION ISOTHERMS

I. LANGMUIR ISOTHERM:

$$\theta = \frac{KP}{1 + KP} \quad ; \quad \frac{P}{V} = \frac{1}{KV_m} + \frac{P}{V_m}$$

II. BRUNAUER, LOVE, KEENAN ISOTHERM:

$$E_a = E_a^0 + a\theta \; ; \quad E_d = E_d^0 - b\theta \; ; \quad q = q_0 - c\theta \; ; \quad c = a+b$$

$$\theta = \frac{RT}{c} \operatorname{Ln} \frac{1 + k_0 P}{1 + k_0 P \exp(-c/RT)} \; ; \quad k_0 = A\exp(q_0/RT)$$

III. FREUNDLICH ISOTHERM:

$$\theta = KP^{1/n} \quad ; \quad \operatorname{Ln} V = \operatorname{Ln} K + (1/n)\operatorname{Ln} P$$

IV. TEMKIN ISOTHERM:

$$\theta = \frac{1}{f}\operatorname{Ln} KP \quad ; \quad V = \frac{V_m}{f}(\operatorname{Ln} K + \operatorname{Ln} P)$$

V. BET ISOTHERM:

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m c} + \frac{(c-1)P}{V_m c P_0}$$

VI. HENRY ISOTHERM:

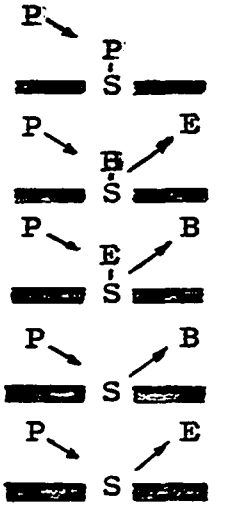
$$V = KP$$

KINETIC MODELS

I. RIDEAL MODEL

##INTERACTION OF ADSORBED MOLECULES WITH MOLECULES FROM THE GAS PHASE ##########

1. $P + S \rightleftharpoons PS$
2. $P + PS \rightleftharpoons E + BS$
3. $P + PS \rightleftharpoons B + ES$
4. $BS \rightleftharpoons B + S$
5. $ES \rightleftharpoons E + S$



RATE DETERMINING STEP: 2 & 3

INITIAL RATE EQUATION:

$$R_0 = (k_2 + k_3)K_P P_P^2 / (1 + K_P P_P) \qquad (14)$$

REACTION RATE EQUATION:

$$R = \frac{(k_2+k_3)K_P P_P^2 - (k_{-2}K_E + k_{-3}K_B)P_E P_B}{1 + K_P P_P + K_B P_B + K_E P_E + \sum K_I P_I} \qquad (15)$$

P/Propene; S/Acive Center; E/Ethylene; B/Butenes.

KINETIC MODELS

II. LANGMUIR-HINSHELWOOD MODEL A

##THE REACTION OCCURS BETWEEN TWO MOLECULES CHEMISORBED ON THE TWO NEIGHBORING ACTIVE CENTERS####

1. $P + S \rightleftharpoons PS$



2. $2\,PS \rightleftharpoons ES + BS$



3. $ES \rightleftharpoons E + S$

4. $BS \rightleftharpoons B + S$



RATE DETERMINING STEP: 2

INITIAL RATE EQUATION:

$$R_0 = k_2 K_P^2 P_P^2 / (1 + K_P P_P)^2 \qquad (16)$$

REACTION RATE EQUATION:

$$R = \frac{k_2 K_P^2 (P_P^2 - P_B P_E / K_{eq})}{(1 + K_P P_P + K_B P_B + K_E P_E + \sum K_I P_I)^2} \qquad (17)$$

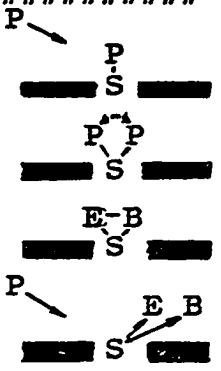
P/Propene; S/Active Center; E/Ethylene; B/Butenes.

KINETIC MODELS

III. LANGMUIR-HINSHELWOOD MODEL B

##THE REACTION OCCURS BETWEEN TWO MOLECULES CHEMISORBED ON THE TWO ACTIVE SITES AT THE SAME ACTIVE CENTER ##

1. $P + S \rightleftharpoons PS$
2. $P + PS \rightleftharpoons P_2S$
3. $P_2S \rightleftharpoons EBS$
4. $EBS \rightleftharpoons E + BS$
5. $BS \rightleftharpoons B + S$



RATE DETERMINING STEP: 3

INITIAL RATE EQUATION:

$$R_0 = k_3K_PK_2P_P^2 / (1 + K_PP_P + K_PK_2P_P^2) \qquad (18)$$

REACTION RATE EQUATION:

$$R = \frac{k_3K_PK_2(P_P^2 - P_EP_B/K_{eq})}{1+K_PP_P+K_PK_2P_P^2+K_EP_E+K_BP_B+K_{EB}P_EP_B+\sum K_IP_I} \qquad (19)$$

RATE DETERMINING STEP: 4

INITIAL RATE EQUATION:

$$R_0 = k_3K_PK_2P_P^2 / (1 + K_PP_P + K_PK_2P_P^2)$$

REACTION RATE EQUATION:

$$R = \frac{k_3K_PK_2(P_P^2 - P_EP_B/K_{eq})}{1 + K_PP_P + K_PK_2P_P^2 + K_EP_E + K_BP_B + \sum K_IP_I} \qquad (20)$$

P/Propene; S/Active Center; E/Ethylene; B/Butenes.

KINETIC MODELS

IV. CARBENE-COMPLEX MODEL A

##BASED ON ALKENE COMPLEXES AS ACTIVE CENTERS #####

1. $P + PS \rightleftharpoons P_2S$



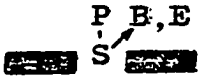
2. $P_2S \rightleftharpoons EBS$



3. $EBS \rightleftharpoons E + BS$



4. $P + BS \rightleftharpoons B + PS$



RATE DETERMINING STEP: 2

INITIAL RATE EQUATION:

$$R_0 = k_2K_1P_P / (1 + K_1P_P) \qquad (21)$$

REACTION RATE EQUATION:

$$R = \frac{k_2K_1(P_P^2 - P_EP_B/K_{eq})}{P_P + K_1P_P^2 + K_EP_E + K_BP_B + K_{EB}P_EP_B + \Sigma K_IP_I} \qquad (22)$$

RATE DETERMINING STEP: 3

INITIAL RATE EQUATION:

$$R_0 = k_3K_1P / (1 + K_1P_P)$$

REACTION RATE EQUATION:

$$R = \frac{k_3K_1(P_P^2 - P_EP_B/K_{eq})}{P_P + K_1P_P^2 + K_EP_E + K_BP_B + \Sigma K_IP_I} \qquad (23)$$

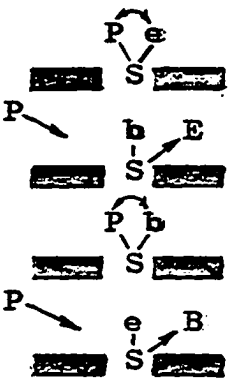
P/Propene; S/Active Center; E/Ethylene; B/Butenes.

KINETIC MODELS

V. CARBENE-COMPLEX MODEL B

##BASED ON ALKYLIDENE COMPLEXES AS ACTIVE CENTERS#

1. $P + eS \rightleftharpoons PeS$
2. $PeS \rightleftharpoons EbS$
3. $EbS \rightleftharpoons bS + E$
4. $P + bS \rightleftharpoons PbS$
5. $PbS \rightleftharpoons BeS$
6. $BeS \rightleftharpoons eS + B$



RATE DETERMINING STEP: 2 & 5

INITIAL RATE EQUATION:

$$R_0 = (k_2 + k_5)K_1P_P / (1 + K_1P_P) \qquad (24)$$

REACTION RATE EQUATION:

$$R = \frac{(k_2 + k_5)K_1(P_P^2 - P_EP_B/K_{eq})}{P_P+K_1P_P^2+K_EP_E+K_BP_B+K_{EB}P_EP_B+K_{PE}P_PP_E+K_{PB}P_PP_B+\Sigma K_IP_I} \qquad (25)$$

RATE DETERMINING STEP: 3 & 6

INITIAL RATE EQUATION:

$$R_0 = (k_3 + k_6)K_1P_P / (1 + K_1P_P)$$

REACTION RATE EQUATION:

$$R = \frac{(k_3 + k_6)K_1(P_P^2 - P_EP_B/K_{eq})}{P_P+K_1P_P^2+K_EP_E+K_BP_B+K_{PE}P_PP_E+K_{PB}P_PP_B+\Sigma K_IP_I} \qquad (26)$$

P/Propene; S/Active Center; e/CH_2= ; b/CH_3-CH= ;

E/Ethylene; B/Butenes.

B. Least-Square Regression Program:

A computer program has been designed for calcuations of product compositions and metathesis rate and selectivity from gas chromatograph analysis data and regression of the experimental metathesis rate to the kinetic model (Ch. IV-A). The least-square curve fitting method is applied (64). The following is the list of this program:

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```
// EXEC FORTGCLG
//FORT.SYSIN DD *
CC MAIN PROGRAM ***********************************************************************
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*4 AX(100), BX(100,2)
      REAL MW
      DIMENSION XF(10), B(35),NC(50),LABL(5,2), WHSV(50)
      DIMENSION TIME(50), RATE(50), REB(50), RTCB(50), TBCV(50)
      DIMENSION X(34,5),Y(34),WEIGHT(34),YFIT(34)
      DIMENSION Z(35), ETHENE(50), BUTENE(50)
      DIMENSION A(5),ITERM(5),SIGMAA(5)
      DIMENSION AG(5), PG(5), CG(5), RG(5)
      DATA A/0.1, 5., 1., 1. , 1./
      READ (5,51) CF11, CF22, CF33
   51 FORMAT(3F10.5)
      READ(5,71) W, T, P, MW, NNPT , NCHECK
   71 FORMAT(4F10.4, 2I10)
      READ(5,80) AG, PG, CG, RG
   80 FORMAT(4(5A4))
      READ(5,81)      DT, AT, PT, ATM, PTM, CTM
   81 FORMAT(     6F7.2)
      WRITE(6,76)W, T, P, MW, DT
   76 FORMAT (1H1, / 2X, 'CAT.WT/GM', F7.4, 5X, 'TEMP/C', F6.2, 5X,'PRES
     1 /TORR', F6.2, 5X, 'MOL.WT', F6.2, 5X, 'NO:  ',F10.2)
      WRITE(6,73)
   73 FORMAT(  / , 3X, 'TIME', 6X, 'RATE,GM/GH', 4X,'ETHYLENE', 3X, 'PRO
     1PENE', 3X, '1-BUTENE',4X,  'T82',  7X, 'C82', 6X, 'CONV', 7X, 'REB
     2', 5X, 'RTCB',  5X, 'TBCV', 7X, 'WHSV', 5X,'BUTENE')
      N=1
      TMAX=60
      DO 75 I=1, NNPT
      READ(5,72)TM, S, Q1,P1,Q2,P2, Q3,P3,P4,P5
   72 FORMAT(F7.1, 9F7.3)
      TIME(I)=TM
      PAR22=CF11*P1*Q1
      PAR33=P2*Q2
      PARTT=CF22*P4*Q3
      PARCC=CF33*P5*Q3
      PAR44=CF33*P3*Q3
      TOTAL=PAR22+PAR33+PARTT+PARCC+PAR44
      C2=PAR22/TOTAL
      C3=PAR33/TOTAL
      TB2=PARTT/TOTAL
      CB2=PARCC/TOTAL
      C41=PAR44/TOTAL
      BU    =C41+CB2+TB2
      REB(I)=C2/BU
      RTCB(I)=TB2/CB2
      CONV=1.-C3
      DDT=C2 - BU
      FR=20./S
      WHSV(I)=MW*(FR/22400.)*(273./(273.+T))*(P/760.)*(3600./W)
      RATE(I)=CONV*WHSV(I)/MW
      ETHENE(I)=C2*WHSV(I)/MW
      BUTENE(I)=BU*WHSV(I)/MW
      C2CV=C2/CONV
      TBCV(I)=TB2/CONV
      CBCV=CB2/CONV
      WRITE(6,74)TM,RATE(I),C2   ,C3, C41, TB2, CB2, CONV, REB(I),
     3 RTCB(I), TBCV(I), WHSV(I), DDT
   74 FORMAT(/ , 2X, F7.2, 3X, E13.6, 3X, 6(F7.5,3X), 2(F6.3, 3X), F7.5,
     4 3X, F6.2, 1X, F8.5)
   75 CONTINUE
```

```
      NPTS=0
      SWV=0.
      DO 35 I=1, NNPT
   35 SWV=SWV + WHSV(I)
      AGWV= SWV /NNPT
      DO 36 I=1, NNPT
      PEWV=DABS((WHSV(I)-AGWV)/AGWV)
      IF(PEWV .GE. 0.05 ) GO TO 36
      NPTS=NPTS + 1
      X(NPTS, 1)=TIME(I)/60.
      Y(NPTS)=RATE(I)
      NC(NPTS)=I
   36 CONTINUE
      YMAX=Y(1)
      MM=1
      DO 21 I=1,NPTS
      IN=I+1
      ERR=YMAX - Y(IN)
      IF(ERR .GE. 0) GO TO 21
      YMAX=Y(IN)
      MM=IN
   21 CONTINUE
      NR=NPTS
      XM=X(MM,1)*60.
      WRITE(6,150) XM, Y(MM)
  150 FORMAT(//,2X,'MAX. METATHESIS*******TIME/MIN.=', F10.2, 5X,
     1 'REACTION RATE=', E15.6)
C
      FLAMDA=0.001D0
      II=1
      IMAX=25
  222 CONTINUE
      FFF=FLAMDA
      EPS=0.0001D0
      CHISQ1=1.D+60
      SUMAD1=2000.
      NCODE=3
      NDIM=N + NPARM
      IF(MM.EQ.1) GO TO 63
      GO TO (61,62), NCHECK
   61 CONTINUE
      ISIGN=1
      GGGG=1.D0
      ITERM(1)=1
      ITERM(2)=2
      ITERM(3)=3
      ITERM(4)=4
      ITERM(5)=5
      NTERMS=4
      NPARM=5
      NPN=N+NPARM
      NIT=1
      GO TO 64
   62 CONTINUE
      GGGG=3.D0
      ISIGN=1
      A(1)=0.01
      A(2)=2.
      A(3)=2.63
      ITERM(1)=1
      ITERM(2)=2
      ITERM(3)=3
      NPARM=3
      NTERMS=3
      NPN=N+NPARM
      NIT=1
```

```
      GO TO 64
   63 CONTINUE
      GGGG=2.D0
      ISIGN=1
      NCHECK=3
      ITERM(1)=1
      ITERM(2)=3
      ITERM(3)=4
      ITERM(4)=2
      NPARM=4
      NTERMS=3
      NPN=N+NPARM
      NIT=1
   64 CONTINUE
      CALL CPUTIM
      DO 7 II=II, IMAX
CC    EVALUATE WEIGHTS
CC
CC    NCODE - DETERMINES METHOD OF WEIGHTING LEAST-SQUARES FIT
C               1  (STATISTICAL) WEIGHT(I) = 1/Y(I)
C               2  (NO WEIGHTING) WEIGHT(I) = 1
C               3  (INSTRUMENTAL) WEIGHT(I) = 1/Y(I)**2
C               4  GOSMAN'S WEIGHTING FUNCTION
CC                              PERCENT ERROR WEIGHT
CC
CC    AND CALCULATE AVERAGE AND VARIANCE OF Y
      DO 41 J=1,NPARM
      B(J)=A(J)
41    XF(J+N)=A(J)
      SUMW=0.
      SUMWY=0.
      DO 40 I=NIT, NPTS
      XF(1)=X(I,1)
      XF(2)=X(I,2)
      PPTS=Y(I)
      GO TO (1,2,3),NCODE
1     IF(Y(I) .EQ. 0.) GO TO 2
      WEIGHT(I) = 1./DABS(Y(I))
      GO TO 30
2     WEIGHT(I)=1.
      GO TO 30
3     CONTINUE
      IF(Y(I) .EQ. 0.) GO TO 2
      WEIGHT(I)=1./Y(I)**2
      GO TO 30
30    CONTINUE
      SUMW=SUMW + WEIGHT(I)
      SUMWY=SUMWY + WEIGHT(I)*Y(I)
40    CONTINUE
      YBAR=SUMWY/SUMW
      SUMV=0.
      DO 50 I=NIT, NPTS
      SUMV=SUMV + WEIGHT(I)*(Y(I) - YBAR)**2
50    CONTINUE
      YVAR=SUMV
      CALL CURFIT(X,N,Y,WEIGHT,NPTS,NTERMS,A,  SIGMAA,FLAMDA,YFIT,
     1            CHISQR,NPARM,ITERM,ISIGN,NCHECK)
      SUMAD=0.
      DO 23 K=NIT, NPTS
      PERC=(Y(K) - YFIT(K))/Y(K)*100.
      SUMAD=SUMAD + DABS(PERC)
23    CONTINUE
      SUMAD=SUMAD/NPTS
      IF(II .EQ. 1) CALL CPUTIM(TFIRST)
      CALL CPUTIM(TLAST,TTOTL)
      WRITE(6,10) II
```

```
10    FORMAT(////T47,'*****  ITERATION  *****'/,I58)
      WRITE(6,28) TFIRST,TLAST,TTOTL
28    FORMAT(//T5,'CPU TIME FOR THE 1ST ITER =',F 8.4,'   FOR THE LAST I
     1TER =',F 8.4,'   TOTAL ELASPED TIME =',F 8.3)
      WRITE(6,5) CHISQR,FLAMDA
5     FORMAT(//T5,'OBJECTIVE FUNCTION',9X,'FLAMDA'/,G19.6,G20.4)
      WRITE(6,6) (SIGMAA(L),L=1,NTERMS)
6     FORMAT(//T5,'PARAMETER VARIANCE'/,5X,10G12.6)
      WRITE(6,24) SUMAD
24    FORMAT(//T5,'AVERAGE ABSOLUTE DEVIATION %'/,G22.4)
      WRITE(6,4) (A(L),L=1,NPARM)
4     FORMAT(//T5,'NEW PARAMETERS'/,3X,10G12.6)
      IF(SUMAD .GE. SUMAD1) GO TO 33
      IF(CHISQ1 .LT. CHISQR) GO TO 12
      IF(DABS(CHISQ1 - CHISQR) .LT. EPS*CHISQR) GO TO 13
      IF(FLAMDA .GT. 100. .AND. CHISQ1 .GT. 1D+50) GO TO 14
      SUMAD1=SUMAD
      CHISQ1=CHISQR
      IF( II .EQ. 1 .AND. (2*TFIRST) .GT. TMAX) GO TO 27
      IF((TLAST+TFIRST) .LT. TMAX .AND. (TLAST+TTOTL) .LT. TMAX) GO TO 7
27    WRITE(6,9) TTOTL
9     FORMAT(//T5,'REMAINING TIME NOT ENOUGH FOR ONE MORE ITERATION ***
     1TOTAL ELASPED TIME =',F7.2)
      GO TO 8
7     CONTINUE
      WRITE(6,11)
11    FORMAT(//T5,'NO CONVERGENCE WITHIN MAXIMUM ITERATION')
      GO TO 811
12    WRITE(6,18)
18    FORMAT(//T5,'OBJECTIVE FUNCTION INCREASED')
      GO TO 8
13    WRITE(6,19) EPS
19    FORMAT(///T5,'RATIO OF CHANGE IN OBJECTIVE FUNCTION IS LESS THAN',
     1F6.3)
      GO TO 8
14    WRITE(6,20)
20    FORMAT(//T5,'NO IMPROVEMENT OVER INITIAL')
      GO TO 8
33    WRITE(6,34)
34    FORMAT(//T5,'AVERAGE ABSOLUTE DEVIATION INCREASED')
      DO 94 L=1,NPARM
      A(L)=B(L)
 94   Z( L+N)=A(L)
      DO 93 I=NIT,NPTS
      Z(1)=X(I,1)
 93   YFIT(I)=FUNCN(Z,NPN,NPARM,NCHECK)
      SUMAD=0.
      SWV=0.
      DO 38 K=NIT, NPTS
      PERC=(Y(K)-YFIT(K))/Y(K)*100.
      SUMAD=SUMAD+DABS(PERC)
      JJ=NC(K)
      SWV=SWV + WHSV(JJ)
 38   CONTINUE
      AGWV= SWV /NPTS
      SUMAD=SUMAD/NPTS
8     CONTINUE
      IF(SUMAD.LE.GGGG) GO TO 811
      FLAMDA=FFF
      IF(FLAMDA .GE. 1000.) GO TO 811
      FLAMDA=FLAMDA*10.
      II=II+1
      GO TO 222
811   CONTINUE
      CHI1=1.
      NFREE=NPTS-NTERMS
```

```
      CHIN=CHISQR*NFREE
      FR=(1.-CHIN/YVAR)*(NFREE-1)*YVAR/(CHIN*NTERMS)
      FCHI=(CHI1-CHIN)*(NFREE-1)/CHIN
      CHI1=CHIN
      WRITE(6,29)
29    FORMAT(//,9X,'NUMBER',9X,'PARAMETER',9X,'STANDARD ERROR',9X,
     1 'VARIANCE')
      DO 16 J=1,NTERMS
      JJ=ITERM(J)
      SE=DSQRT(SIGMAA(JJ)*CHISQR)
      WRITE(6,17) JJ,A(JJ),SE,SIGMAA(JJ)
17    FORMAT(/,I13,G22.6,G20.6,G20.6)
16    CONTINUE
      WRITE(6,31) SUMAD
31    FORMAT(//T27,'AVERAGE ABSOLUTE DEVIATION %'/,G44.4)
      WRITE(6,32)
  32  FORMAT(//,2X,'NPTS',2X, 'TIME/MIN', 4X, 'EXPMT RATE', 7X, 'CALCD
     1RATE', 2X, 'PER. ERR. %')
      SUM=0.
      DO 100 I=NIT, NPTS
      PERC=(Y(I)-YFIT(I))/Y(I)*100.
      SUM=SUM+DABS(PERC)
      TMM=X(I,1)*60.
      WRITE(6,25) I, TMM,      Y(I), YFIT(I), PERC
  25  FORMAT (I5, F10.1, 2E16.6, F15.3)
100   CONTINUE
      ASUM=SUM/NPTS
      WRITE(6,67) ASUM
   67 FORMAT(/,5X,'AVE. ABS. DEV. %=',F10.4)
  110 CONTINUE
   57 FORMAT(5A4)
      DO 59 J=1,2
   59 READ(5,57)  (LABL(I,J), I=1,5)
      DO 55 I=1, NPTS
      AX(I)=X(I,1)*60.
      BX(I,1)=Y(I)
      BX(I,2)=YFIT(I)
   55 CONTINUE
      CALL PRPLOT(AX,BX,100,2,NPTS,2,LABL)
      IF(A(4).GT.1.0D-4) GO TO 116
      TREX=1.0D+20
      TTMA=1.0D+20
      GO TO  106
  116 CONTINUE
      GO TO (77,78,79), NCHECK
   77 TABC=A(3)*(1.-A(4))
      TAA=A(2)*A(3)*A(4)
      TBBB=DABS(TABC)
      TASQ=(TBBB)**2. + 4.*TAA
      TART=TASQ**(0.5)
      TTMA=60.*(TABC+TART)/(2.*TAA)
      GO TO 105
   78 TTMA=1.0D 20
      TREX=1.0D 20
      GO TO 106
   79 TTMA=0.
      TREX=0.
  106  YY=1.3D+20
      RELXR=1.0D+20
      GO TO 103
  105 Z(1)=TTMA/60.
      DO 66 I=1, NPARM
   66 Z(I+1)=A(I)
      YY=FUNCN(Z,NPN,NPARM,NCHECK)
      RELXR=YY/DEXP(1.D0)
      Z(1)=3.
```

```
      YRX=FUNCN(Z,NPN,NPARM,NCHECK)
  113 AAA=A(4)
      GO TO 115
  115 CONTINUE
      AK=YRX*(Z(1)**AAA)
      TREX= (AK/RELXR)**(1./AAA)
      Z(1)=TREX
      CALL RELTM(RELXR, Z, NPN,NPARM,NCHECK)
      TREX=Z(1)
  103 CONTINUE
      WRITE(6,82)
   82 FORMAT(1H1,///, 110('*'))
      WRITE(6,83) DT, W
   83 FORMAT(//,10X,'SUMMARY',//,10X,'NO:  ', F7.2, 10X,
     1 10X,'CAT.WT./GM', F7.4)
      WRITE(6,84)
   84 FORMAT(// ,33X,'GAS', 9X, 'TEMP/C', 10X, 'TIME/HR')
      WRITE(6,85) AG, AT, ATM
   85 FORMAT(// , 10X, 'ACTIVATION', 5X, 5A4, F7.2, 10X, F7.2)
   86 FORMAT(// , 10X, 'PURGE     ', 5X, 5A4, F7.2, 10X, F7.2)
   87 FORMAT(// , 10X, 'COOLING   ', 5X, 5A4,17X, F7.2)
      WRITE(6,86) PG, PT, PTM
      WRITE(6,87) CG, CTM
      RTM=TIME(NNPT)/60.
      WRITE(6,88) RG, T, RTM
   88 FORMAT(// ,10X, 'REACTION', 7X, 5A4, F7.2, 10X, F7.2)
C
      GO TO (42,119,43),NCHECK
   42 WRITE(6,92) A(1),A(2),A(5),A(3),A(4)
   92 FORMAT(///,10X, 'RATE EQTN  R(G-MOL/G-HR)= (', E13.6, '*(1. - (1.
     1 + ', E13.6, '*(TIME(HR)))**( - ',E13.6,'))', /, 37X,'*(1. + ',
     2E13.6, '(TIME(HR)))**(- ',E13.6, ' )')
      GO TO 44
  119 WRITE(6,120) A(1),A(2),A(3)
  120 FORMAT(///,10X, 'RATE EQTN  R(G-MOL/G-HR)= (', E13.6, '*(1. - (1.
     1 + ', E13.6, '*(TIME(HR)))**( - ',E13.6,'))')
      GO TO 44
   43 WRITE(6,89) A(1),A(3),A(4)
   89 FORMAT(///,10X, 'RATE EQTN  R(G-MOL/G-HR)=  ', E13.6, ' * ',
     1  /, 37X,'*(1. + ',E13.6, '(TIME(HR)))**(- ',E13.6, ' )')
   44 CONTINUE
      WRITE(6,90) ASUM, AGWV
   90 FORMAT(//, 10X, 'AVG. ERR. %', F7.4, 20X, 'AVG. WHSV', F7.3)
      WRITE(6,68) TTMA, YY, RELXR, TREX
   68 FORMAT(///,10X,'TIME(MAX.RATE)/MIN.=', E13.5,10X,'MAX.RATE=',
     1 E13.6,//, 10X, 'RELAXATION RATE=', E13.6, 10X,'RELAXATION TIME/HR
     1 ', E13.6)
      WRITE(6,91)
   91 FORMAT(///, 110('*'), 1H1)
      IF(MM.EQ.1) GO TO 65
   26 CONTINUE
   65 CONTINUE
      STOP
      END
CC*****************************************************************************
C   SUBROUTINE CURFIT
C
C
C
C
C   PURPOSE
C     MAKE A LEAST-SQUARES FIT TO A NON-LINEAR FUNCTION
C       WITH A LINEARIZATION OF THE FITTING FUNCTION
C
C   USAGE
C     CALL CURFIT (X,N,Y,WEIGHT,NPTS,NTERMS,A,
```

```
C       SIGMAA,FLAMDA,YFIT,CHISQR,NPARM,ITERM,ISIGN)
C
C   DESCRIPTION OF PARPMETERS
C      X       - ARRAY OF DATA POINTS FOR INDEPENDENT VARIABLE
C      Y       - ARRAY OF DATA POINTS FOR DEPENDENT VARIABLE
C      WEIGHT  - ARRAY OF WEIGHTS FOR DATA POINTS
C      N       - NUMBER OF INDEPENDENT VARIABLES
C      NPTS    - NUMBER OF PAIRS OF DATA POINTS
C      NTERMS  - NUMBER OF PARAMETERS TO BE FITTED .LE. NPARM
C      A       - ARRAY OF PARAMETERS
C      SIGMAA  - ARRAY OF STANDARD DEVIATIONS FOR PARAMETERS A
C      FLAMDA  - PROPORTION OF GRADIENT SEARCH INCLUDED
C      YFIT    - ARRAY OF CALCULATED VALUES OF Y
C      CHISQ1  - REDUCED CHI SQUARE FOR FIT
C      NPARM   - TOTAL NUMBERS OF PARAMETERS
C      ITERM   - PARAMETER NUMBERS IN ORDER TO BE FITTED
C      ISIGN   - PARAMETER CONSTRAINT MODE FOR ALLOWANCE OF SIGN CHANGE AS
C                0   UNCONSTRAINED
C                1   CONSTRAINED AGAINST SIGN CHANGES
C
C   SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED
C      FUNCN (X,NDIM,NPARM)
C         EVALUATES THE FITTING FUNCTION
C      FCHISQ (Y,WEIGHT,NPTS,NFREE,YFIT)
C         EVALUATES REDUCED CH SQUARE FOR FIT TO DATA
C      FDERIV (X,I,NDIM,NPARM)
C         EVALUATES THE DERIVATIVES OF THE FITTING FUNCTION
C         WITH RESPECT TO THE ITH VARIABLE
C      GJEL(ARRAY,NTERMS,NTERMS+1,DET,IER)
C      SOLVES A SYSTEM BY THE GAUSS JORDAN METHOD RETURNING THE
C        DETERMINANT AND THE INVERSE IN PLACE
C
C
C   COMMENTS
C      DIMENSION STATEMENT VALID FOR NTERMS UP TO 35
C      SET FLAMDA =0.001 AT BEGINNING OF SEARCH
CCCC
      SUBROUTINE CURFIT(X,N,Y,WEIGHT,NPTS,NTERMS,A,  SIGMAA,FLAMDA,
     1                  YFIT,CHISQR,NPARM,ITERM,ISIGN,NCHECK)
      IMPLICIT REAL*8(A-H,C-Z)
      DIMENSION X(NPTS,N),Y(NPTS),WEIGHT(NPTS),YFIT(NPTS)
      DIMENSION SIGMAA(NPARM),A(NPARM),ITERM(NPARM)
      DIMENSION ALPHA(630),BETA(35),DERIV(35),ARRAY(1260),B(35)
      DIMENSION Z(45)
      FACT=.9900
      IF(NTERMS.LE.35) GO TO 6000
      PRINT 600
  600 FORMAT(1X,10('*'),' MORE THAN 35 PARAMETERS FITTED.  ONLY 35' ,
     1 ' USED.  ',10('*'))
 6000 CONTINUE
      NPN=N+NPARM
   11 NFREE =NPTS-NTERMS
      IF (NFREE) 13,13,20
   13 CHISQR=0.
      GO TO 110
C
C       EVALUATE ALPHA AND BETA MATRICES
C
   20 CONTINUE
   31 DO 34 J=1,NTERMS
      BETA(J)=0.
      DO 34 K=1,J
   34 ALPHA(K+J*(J-1)/2)=0.
C
C      NOTE - 1ST N OF Z ARE VARIABLES
C      (N+1) TO (NPARM+N+1) ARE PARAMETERS
```

```
C
      DO 44 L=1,NPARM
   44 Z(L+N)=A(L)
      DO 230 J=1,NTERMS
      ARRAY(J)=0.
  230 CONTINUE
   41 DO 50 I=1,NPTS
      DO 45 L=1,N
   45 Z(L)=X(I,L)
   62 YFIT(I)=FUNCN(Z,NPN,NPARM,NCHECK)
      DO 43 L=1,NTERMS
      JJ=ITERM(L)+N
      DERIV(L)=FDERIV(Z,JJ,NPN,NPARM,NCHECK)
      IF(DABS(DERIV(L)).LT.1.D-30) DERIV(L)=0.
   43 CONTINUE
      DO 46 J=1,NTERMS
      BETA(J)=BETA(J)+WEIGHT(I)*(Y(I)-YFIT(I))*DERIV(J)
      DO 46 K=1,J
      ALPHA(K+J*(J-1)/2)=ALPHA(K+J*(J-1)/2)+WEIGHT(I)*DERIV(J)*DERIV(K)
   46 CONTINUE
   50 CONTINUE
C
C      EVALUTAE CHI SQUARE AT STARTING POINT
C
   63 CHISQ1 = FCHISQ(Y,WEIGHT,NPTS,NFREE,YFIT)
C
C      INVERT MODIFIED CURVATURE MATRIX TO FIND NEW PARAMETERS
C
   71 DO 74 J=1,NTERMS
      IF(ALPHA(J*(J+1)/2).GT.0.) GO TO 280
      IF(ALPHA(J*(J+1)/2).EQ.0.) PRINT 200,J
  200 FORMAT(1X,I5,'  DERIVATIVE IS ZERO',60('*'))
      IF(ALPHA(J*(J+1)/2) .EQ. 0.) GO TO 105
      JJ=ITERM(J)
      PRINT 300,J,JJ
  300 FORMAT(1X,I5,' DERIVATIVE IS NEGATIVE FOR PARM ',I5,20('*'))
  105 ALPHA(J*(J+1)/2)=1.D-20
  280 CONTINUE
      ARRAY(NTERMS**2+J)=BETA(J)/DSQRT(ALPHA(J*(J+1)/2))
      DO 73 K=1,J
      ARRAY(J+(K-1)*NTERMS)=ALPHA(K+J*(J-1)/2)/DSQRT(ALPHA(J*(J+1)/2)
     1 *ALPHA(K*(K+1)/2))
      ARRAY(K+(J-1)*NTERMS)=ARRAY(J+(K-1)*NTERMS)
   73 CONTINUE
   74 ARRAY(J+(J-1)*NTERMS)=1.+FLAMDA
      IF(NTERMS.GT.1) GO TO 80
      ARRAY(1)=1/ARRAY(1)
      ARRAY(2)=ARRAY(2)*ARRAY(1)
      GO TO 81
   80 CALL GJEL(ARRAY,NTERMS,NTERMS+1,DET,IER)
   81 DO 84 J=1,NTERMS
      JJ=ITERM(J)
      B(J)=A(JJ)+ARRAY(NTERMS**2+J)/DSQRT(ALPHA(J*(J+1)/2))
      IF(ISIGN .EQ. 0 .OR. B(J)*A(JJ) .GT. 0.) GO TO 84
      WRITE(6,100) B(J),A(JJ),JJ
  100 FORMAT(/T10,'OLD,NEW,PARM SIGN CHANGE',2G20.6,I10)
      B(J)=A(JJ)*(1.-FACT)
   84 CONTINUE
C
C      IF CHI SQUARE INCREASED, INCREASE FLAMDA AND TRY AGAIN
C
      DO 94 L=1,NTERMS
      JJ=ITERM(L)
   94 A(JJ)=B(L)
      DO  5 K=1,NPARM
    5 Z(K+N)=A(K)
```

```
   91 DO 92 I=1,NPTS
      DO 96 L=1,N
   96 Z(L)=X(I,L)
   93 CHISQR = FCHISQ(Y,WEIGHT,NPTS,NFREE,YFIT)
   92 YFIT(I)=FUNCN(Z,NPN,NPARM,NCHECK)
      IF(FLAMDA.EQ.0.) GO TO 101
      IF (CHISQ1-CHISQR) 95,101,101
  135 DO 140 L=1,NPARM
  140 Z(L+N)=A(L)
      DO 150 I=1,NPTS
      DO 160 L=1,N
  160 Z(L)=X(I,L)
  150 YFIT(I)=FUNCN(Z,NPN,NPARM,NCHECK)
      CHISQR=CHISQ1
      GO TO 110
   95 FLAMDA =10.*FLAMDA
      FACT=FACT/2.
      IF(FLAMDA.GT.1000.) GO TO 135
      IF(FLAMDA.GT.0.01D0) GO TO 71
  115 DO 125 I=1,NTERMS
  125 SIGMAA(I)=DSQRT(ARRAY(I+(I-1)*NTERMS)/ALPHA(I*(I+1)/2))
      GO TO 71
  260 CONTINUE
      DO 270 J=1,NTERMS
      SIGMAA(J)=DSQRT(ARRAY(J+(J-1)*NTERMS)/ALPHA(J*(J+1)/2))
  270 CONTINUE
      CHISQR=CHISQ1
      RETURN
C
C      EVALUATE PARAMETERS AND UNCERTAINTIES
C
  101 DO 103 J=1,NTERMS
      JJ=ITERM(J)
      A(JJ)=B(J)
      IF(ARRAY(J+(J-1)*NTERMS).GT.0.) GO TO 103
      JJ=ITERM(J)
      PRINT 400,J,JJ
  400 FORMAT(1X,10('*'),' VARIANCE ',I3,' FOR PARAMETER',I3,
     1 ' IS NEGATIVE.  CORRECTION TAKEN.',2X,10('*'))
      ARRAY(J+(J-1)*NTERMS)=0
  103 SIGMAA(J)=DSQRT(ARRAY(J+(J-1)*NTERMS)/ALPHA(J*(J+1)/2))
      FLAMDA =FLAMDA/10.
  110 RETURN
      END
CC*****************************************************************************
C   FUNCTION FCHISQ
C
C   PURPOSE
C       FCHISQ = SUM((Y-YFIT)**2/SIGMA**2)/NFREE
C     EVALUATE REDUCED CHI SQUARE FOR FIT TO DATA
C
C   USUAGE
C     RESULT = FCHISQ(Y,WEIGHT,NPTS,NFREE,YFIT)
C
C   DESCRIPTION OF PAFAMETERS
C     Y       - ARRAY OF DATA POINTS
C     WEIGHT - ARRAY OF WEIGHTS FOR DATA POINTS
C     NPTS    - NUMBER OF DATA POINTS
C     NFREE   - NUMBER OF DEGRES OF FREEDOM
C     YFIT    - ARRAY OF CALCULATED VALUES OF Y
C
C   SUBROUTINES AND VUNCTION SUBPROGRAMS REQUIRED
C     NONE
C
      FUNCTION FCHISQ (Y,WEIGHT,NPTS,NFREE,YFIT)
      IMPLICIT REAL*8(A-H,O-Z)
```

```
      DIMENSION Y(NPTS),WEIGHT(NPTS),YFIT(NPTS)
   11 CHISQ=0.
   12 IF (NFREE) 13,13,20
   13 FCHISQ =0.
      GO TO 40
C
C       ACCUMULATE CHI SQUARE
C
   20 DO 30 I=1,NPTS
   30 CHISQ = CHISQ + WEIGHT(I)*(Y(I)-YFIT(I))**2
C
C       DIVIDE BY NUMBER OF DEGREES OF FREEDOM
C
   31 FREE =NFREE
   32 FCHISQ=CHISQ/FREE
   40 RETURN
      END
CC*********************************************************************
C    SUBROUTINE GJEL(A,ND,MD,DETD,IER)
C
C    PURPOSE
C       SIMULTANEOUS SOLUTION OF LINEAR EQUATIONS BY GAUSS-JORDAN
C    USUSGE
C      CALL GEJEL(A,ND,MD,DETD,IER)
C
C    DESCRIPTION OF PARAMETERS
C     A  IS THE ND BY MD AUGMENTED MATRIX
C     THE FIRST ND COLUMNS RETURNS THE INVERSE MATRIX
C     THE LAST MD-ND COLUMNS CONTAIN THE SOLUTION VECTORS
C     DETD RETURNS THE DETERMINANT
C
C    SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED
C      NONE
C
      SUBROUTINE GJEL(A,ND,MD,DETD,IER)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION A(ND,MD)
      DATA EPS/1.D-20/
      IER=0
      N=ND
      M=MD
      DET=1.
      DO 4 I=1,N
      IF(A(I,I))1,2,1
    2 DET=0.
      IER=N+1
      RETURN
    3 DET=0.
      IER=I
      GO TO 8
    1 IF(DABS(A(I,I)).LT.EPS) GO TO 3
    8 DET=A(I,I)*DET
C     FORM DETERMINANTS
      FACT=A(I,I)
      A(I,I)=1.
      DO 5 J=1,M
C     NORMALIZE
      A(I,J)=A(I,J)/FACT
    5 CONTINUE
      DO 6 J=2,N
      L=MOD(I+J-2,N)+1
      IF(A(L,I).EQ.0.)GO TO 6
      FACT=A(L,I)
      A(L,I)=0.
      DO 7 K=1,M
      LL=MOD(I+K-2,M)+1
```

```
      IF(A(I,LL).EQ.0.)GO TO 7
C     REDUCE
      A(L,LL)=A(L,LL)-A(I,LL)*FACT
    7 CONTINUE
    6 CONTINUE
    4 CONTINUE
      DETD=DET
      RETURN
      END
CC*****************************************************************************
C     FUNCTION FDERIV
C
C     PURPOSE
C        EVALUATE NUMERICALLY DERIVATIVE OF FUNCTN WITH RESPECT
C        TO THE ITH VARIABLE
C
C     USUAGE
C       RESULT = FDERIV(X,I,NDIM,NPARM)
C
C     DESCRIPTION OF PARAMETERS
C       X     - ARRAY OF INDEPENDENT VARIABLE VALUES
C       I     - NUMBER OF VARIABLE FOR DERIVATIVE
C       NDIM  - NUMBER OF INDEPENDENT VARIABLES
C       NPARM- NUMBER OF PARAMETERS
C
C     SUBROUTINES NEEDED
C       FUNCN(X,NDIM,NPARM)
C         EVALUATES THE FUNCTION AT POINT X
C
      FUNCTION FDERIV (X,I,NDIM,NPARM,NCHECK)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION X(NDIM)
      EPS=.01D0
      N=3
      ITR=0
      SAVE=X(I)
      DEL=DABS(EPS*SAVE)
   14 CONTINUE
      IF(DEL .LT. 1.D-6) DEL=EPS
      X(I)=SAVE+DEL
      F2=FUNCN(X,NDIM,NPARM,NCHECK)
      X(I)=SAVE-DEL
      F1=FUNCN(X,NDIM,NPARM,NCHECK)
      DFDX=(F2-F1)/(2.*DEL)
C
C       TESTS PRECISION OF DERIVATIVE
C
      IF(DABS(F1-F2)*(10**(6-N)).GT.DABS(F1)) GO TO 40
      ITR=ITR + 1
      IF(ITR .GE. 4) GO TO 12
      EPS=EPS*3.
      DEL=DABS(SAVE*EPS)
      GO TO 14
   12 IF(DABS(F1-F2).LT.DABS(F1)*1.D-5) DFDX=0.
   40 FDERIV=DFDX
      X(I)=SAVE
      RETURN
      END
CC*****************************************************************************
      SUBROUTINE RELTM(RELXR, Z,NPN,NPARM,NCHECK)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION A(5), B(30),Z(5)
      DO 10 J=1,NPARM
   10 A(J)=Z(J+1)
      B(1)=Z(1)
      DO 4 I=1,20
```

```
      FN=FUNCN(Z,NPN,NPARM,NCHECK)
      FX=FN-RELXR
      GO TO (1,2), NCHECK
    1 DD=A(1)*(1.+A(3)*(1.-A(4))*B(I) - A(2)*A(3)*A(4)*(B(I)**2.))
      EE=((1.+A(2)*B(I))**2.)*((1.+A(3)*B(I))**(A(4)+1.))
      FDX=DD/EE
      GO TO 3
    2 DD=A(1)*(1.+A(2)*(1.-A(3))*B(I))
      EE= (1.+A(2)*B(I))**(A(3)+1.)
      FDX=DD/EE
    3 CONTINUE
      DELTA=FX/FDX
      B(I+1)=B(I)-DELTA
      FX=DABS(FX)
      WRITE(6,117) FX, B(I), I
  117 FORMAT(//,10X, 'DELTAOF RELAXATION RATE=', E15.6,10X, 'TREX=',
     1 E15.6, 10X,'I=', I10)
      IF (FX .LE. 0.5D-5 ) GO TO 5
      Z(1)=B(I)
    4 CONTINUE
    5 CONTINUE
      Z(1)=B(I)
      RETURN
      END
CC*****************************************************************************
      FUNCTION FUNCN(X,NPN,NPARM,NCHECK)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION X(NPN),A(35)
      N=NPN-NPARM
      DO 10 I=1,NPARM
   10 A(I)=X(N+I)
      GO TO (1,2,3), NCHECK
C     GENERAL METATHESIS RATE EQUATION
    1 AN=(1.+A(2)*X(1))*A(5)
      BN=A(1)*(1. - (1./AN))
      CN=(1.+A(3)*X(1))**A(4)
      FUNCN=BN/CN
      GO TO 9
CC    METATHESIS RATE EQUATION FOR BREAK-IN ONLY
    2 AN=(1.+A(2)*X(1))**A(3)
      FUNCN=A(1)*(1.-(1./AN))
      GO TO 9
CCC   METATHESIS RATE EQUATION FOR DEACTIVATION ONLY
    3 AN=A(1)
      CN=(1.+A(3)*X(1))**A(4)
      FUNCN=AN/CN
    9 RETURN
      END
//GO.SYSIN DD *
0.8407    1.6657    1.6658
0.519      0.        760.     42.                23          1
OXYGEN                ---                  OXYGEN                R.G.PROPENE
12.04  502.   0.      17.    0.     2.
3.     39.7   4.      20.2    256.  29.8   2.     0.     14.5   6.1
12.    39.1   4.      25.8   256.    29.5  2.     0.     22.5   8.
21.    38.6   4.      28.5   256.   30.5    2.     0.     23.9   8.3
30.    38.4   4.      29.7    256.  30.2   2.     0.     25.7    9.
40.    38.4   4.      29.4    256.   30.5   2.     0.     25.5   8.7
60.    38.3   4.      29.1   256.   30.5    2.     0.     25.4   8.6
70.    38.8   4.      28.6   256.    30.6   2.     0.     25.4   8.6
80.    38.8   4.      28.2   256.   30.2   2.     0.     25.1   8.4
90.    37.5    4.     27.    256.    30.2   2.     0.     23.8   8.
100.   38.2   4.      28.1   256.   30.6   2.     0.     24.9   8.5
110.   38.4   4.      27.6   256.   30.5   2.     0.     24.7   8.7
120.    38.4   4.     27.1   256.   30.    2.     0.     24.2   8.3
130.   38.2   4.      27.5   256.   30.6   2.     0.     24.    8.
```

140.	38.4	4.	28.1	256.	30.5	2.	0.	24.1	8.2
150.	38.5	4.	27.4	256.	30.1	2.	0.	23.5	7.9
160.	38.3	4.	26.7	256.	30.4	2.	0.	23.6	8.
170.	38.4	4.	26.8	256.	30.5	2.	0.	23.3	7.8
180.	38.5	4.	26.7	256.	30.6	2.	0.	23.3	7.7
190.	38.5	4.	26.7	256.	30.5	2.	0.	23.4	8.1
200.	39.5	4.	27.2	256.	30.5	2.	0.	23.4	7.8
210.	37.8	4.	25.9	256.	30.5	2.	0.	22.1	7.5
235.	38.9	4.	26.1	256.	30.6	2.	0.	22.2	7.3
245.	38.6	4.	26.1	256.	30.5	2.	0.	22.3	7.5

EXPT RATE/GM/GH/0 C
CALD RATE/GM/GH/0 C

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