JOURNAL OF CATALYSIS 28, 83-91 (1973)

Transient Kinetics of the Disproportionation of Propylene Over a Tungsten Oxide on Silica Catalyst

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Received June 6, 1972

During the initial contacting of WO_3 on silica gel with propylene, significant increases in disproportionation activity were observed for periods of up to 24 hr. The rate of approach to steady state activity was found to depend on both temperature and pressure. The rate of activation was found to have an activation energy of 47.2 kcal and to be first order in propylene partial pressure.

Data are presented to establish that both a reduction of the catalyst and the irreversible adsorption of propylene accompany this period of transient activity.

INTRODUCTION

In the past several years, there have been a number of studies of olefin disproportionation, a new catalytic reaction first reported in 1964 (*1*). By this reaction linear olefins were converted into equimolar homologs of shorter and longer linear olefins in a highly specific and efficient manner. Several catalyst systems have been reported for propylene disproportionation (*2*). Most consist of a high surface-area refractory support on which a promoter has been deposited. One of these is a tungsten oxide on silica gel system (*3*).

During the initial contacting of freshly activated tungsten oxide catalysts with propylene, there exists (*4, 5*) a regime characterized by steady increases in catalyst activity and varying product distributions. These transients may last for up to 24 hr of contact time. This type of transient phenomenon is so commonly exhibited by freshly activated catalysts that it is not always reported in the literature. Furthermore, very few quantitative studies have been reported of such phenomena, and thus the mechanisms involved are not always clearly understood. In the past several years there has been mounting evidence of the importance of understanding these transient phenomena and of the role they play in subsequent catalyst activity. While uncertainty exists as to the nature of the phenomena involved in the transient, it is clear that the observed effects involve changes in the essential character of the surface reaction and are not merely temporal effects expected as a result of transport delays or transients involved in adsorption–desorption phenomena. Baddour (*6*) has recently studied a different catalyst system which also exhibits a regime of initial transient activity and selectivity and has used the term "catalyst break-in" to generally identify such transients.

Recent literature contains examples of a number of widely differing catalyst systems which exhibit catalyst break-in. It has been shown that frequently this break-in is due, at least in part, to various reactant–surface interactions which result in a chemical or physical change in the catalyst surface or in a modification of the nature of the sites responsible for catalytic activity. These reactant–surface interactions may result in changes in the catalyst surface area (*7, 8*), a redistribution of the promoter on the catalyst support (*6*), a chemical reduction of the catalyst surface (*9, 10*), a change in the electronic character or conductivity of the catalyst (*11*, *12*), or the formation of polymeric surface species which are active sites (*13–18*). In some systems, such reactant–surface interactions have been found to occur only at temperatures substantially above the normal operating temperature (*19*), and that high temperature conditionings of these fresh catalysts are necessary to obtain stable catalytic activity at normal operating temperatures.

The object of this study was to make a quantitative study of the catalyst break-in phenomenon exhibited by a tungsten oxide on silica catalyst during propylene disporportionation. The effects of pressure and temperature on catalyst break-in, the reversibility of break-in, and the effects of various catalyst pretreatments were studied using both fixed-bed flow and pulse reactors.

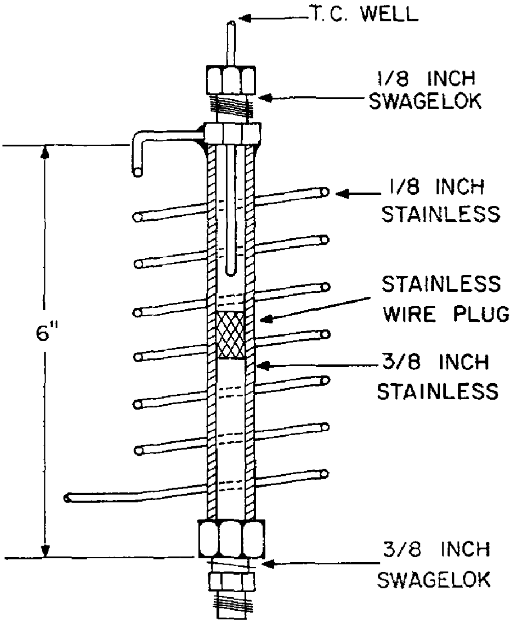

FIG. 2. Detailed section of the single-bed reactor.

EXPERIMENTAL

The reactor system used in this investigation was a fixed bed, microcatalytic reactor operated as a near-differential reactor. A schematic of the system is shown in Fig. 1. The feed preparation section consisted of cylinders of chemically pure (>99% pure) reactant and activation gases connected to a gas manifold system. All gases were metered through a rotameter and a differential flow controller to insure constant feed rates. Prior to contacting the catalyst, the gases were passed through a bed of 5-Å molecular sieves to remove water, a known catalyst poison.

The microcatalytic reactor was a section of ⅜-in. stainless-steel tubing. A preheater was constructed of 7 ft of ⅛ in. diameter stainless-steel tubing wound into a 1 in. coil and welded into the top of the reactor. Figure 2 contains a detailed schematic of this reactor. The reactor pressure was controlled by pressurizing the dome of a Grove back-pressure regulator to the desired pres-

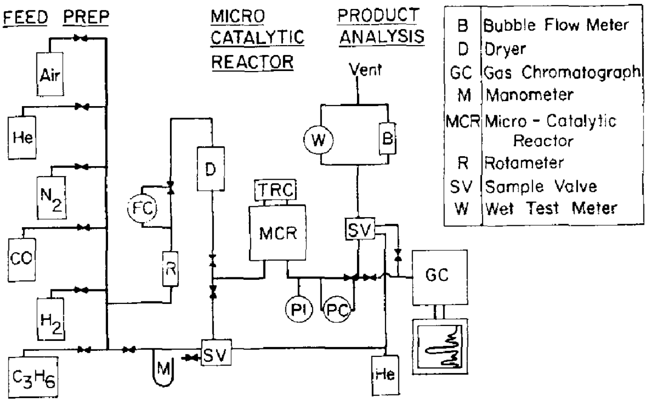

FIG. 1. Schematic of the reactor system.

sure. The reactor and preheater were placed in a tubular resistance heating furnace. A thermocouple at the middle of the catalyst bed was used as a temperature sensor for monitoring and control purposes.

Product analysis was by an in-line Hewlett Packard 5754-B gas chromatograph fitted with a 30-ft dimethyl sulfolane on chromosorb W(−30/+60) column operated at room temperature. An in-line wet test meter or bubble flow meter (depending on the magnitude of the flow rate) was used to measure product flow rates.

The catalyst was prepared by the Davison Chemical Division of W. R. Grace and Co. It consisted of 10% WO_3 on silica gel prepared by impregnating 3/16-in. silica extrusions with ammonium tungstate. This catalyst was ground and screened to give 387 μm (−40/+50) particles which were found to have a BET surface area of 223 m^2/g. All catalyst samples used in this study were initially activated *in situ* for 5 hr in dry air at 600°C. This was normally followed by a 30-min purge in dry nitrogen at 600°C and a slow cooling to the desired operating temperature in dry nitrogen.

In all flow experiments, the microcatalytic reactor was operated as a near-differential reactor on feeds of pure propylene to observe catalyst break-in in the near-absence of reaction products.

In all pulse experiments, the microcatalytic reactor was operated using techniques developed by Koges, Tobins, and Emmett *(21)*. The reactor was installed directly in the He carrier gas stream of the chromatograph. A sample valve fitted with a 0.5 cm^3 sample loop was installed upstream from the catalyst bed. This sample loop was used to introduce pulses of propylene into the carrier gas flowing over the catalyst sample. After leaving the catalytic reactor, the carrier gas flowed directly into the gas chromatograph, described above, for analysis.

RESULTS

Figure 3 illustrates the typical transient activity or catalyst break-in exhibited by freshly activated WO_3 on silica upon introduction of propylene at 427°C and 0.94 atm total pressure. The results for air activation followed by a 30-min nitrogen purge are shown as circles and the curve is the best fit of this data. Using this "normal" procedure, the steady-state rate of propylene disproportionation was found to be some 750% greater than that of the freshly activated catalyst, and the transition to a steady-state catalyst system required some 900 min of propylene contact.

To insure that the phenomenon in Fig. 3 associated with "normal" activation was not due to the purging of temporary poisons from the catalyst which were inadvertently introduced during the activation procedure, two variations in the activation procedure were made. The first was to follow the normal activation in dry air at 600°C with a

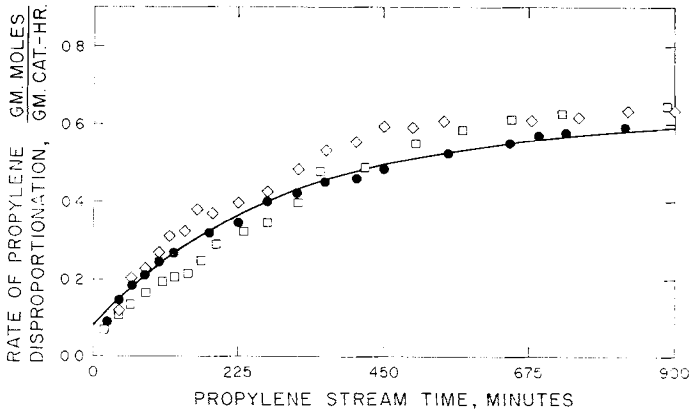

FIG. 3. Effect of activation procedure on catalyst break-in, 427°C, 0.94 atm, (● 30 min N_2, ◇ 180 min He, □ 180 min evacuation).

3-hr purge in dry helium at 600°C. Then the system was slowly cooled to the desired operating temperature in dry helium prior to the introduction of propylene. The second variation was to follow the normal air activation and 30-min nitrogen with a 3-hr evacuation at 100 μm total pressure. Following this, the system was slowly cooled to the desired operating temperature in dry helium. The results of these two variations in the activation procedure are shown in Fig. 3 as diamonds and squares, respectively.

The form of the data in Fig. 3 suggests that the variation in the rate of propylene disproportionation with time during break-in may be represented by a first-order expression which is given mathematically as:

$$(r_{ss} - r)/(r_{ss} - r_0) = e^{-kt}, \qquad (1)$$

where r_{ss} is the steady-state rate, r_0 is the rate at $t = 0$, and k is the break-in rate constant. A plot of the logarithm of the left side of Eq. (1) versus time should be linear, and the catalyst break-in constant, k, may be obtained from the slope of this plot. Next, tests were conducted to determine if the rate of catalyst break-in, k, was a function of temperature or reactant pressure. Figure 4 shows the variation in the rate of propylene disproportionation with time as correlated by Eq. (1) during break-in at 399, 427, and 454°C and at 0.94 atm pressure. Table 1 contains additional data on these tests. Figure 5 is an Arrhenius correlation of the temperature dependency of the rate of catalyst break-in, and an activation energy of 47.2 kcal/g mole is predicted.

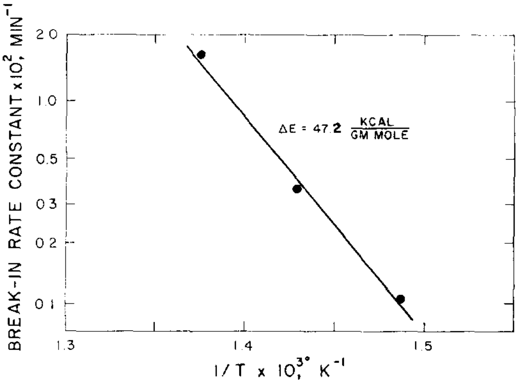

FIG. 5. Temperature dependency of the rate of catalyst break-in.

Figure 6 shows the variation in the rate of propylene disproportionation with time as correlated by Eq. (1) during the break-in of freshly activated catalyst at 427°C at various pressures in the range of 0.94–8.08 atm. Figure 7 demonstrates that the rate of catalyst break-in is directly proportional to the propylene partial pressure. Combining the results of these two series of tests gives the following expression for the rate of catalyst break-in:

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

A definite change in the color of the catalyst was associated with the catalyst break-in. The freshly activated catalyst was yellow, characteristic of the presence

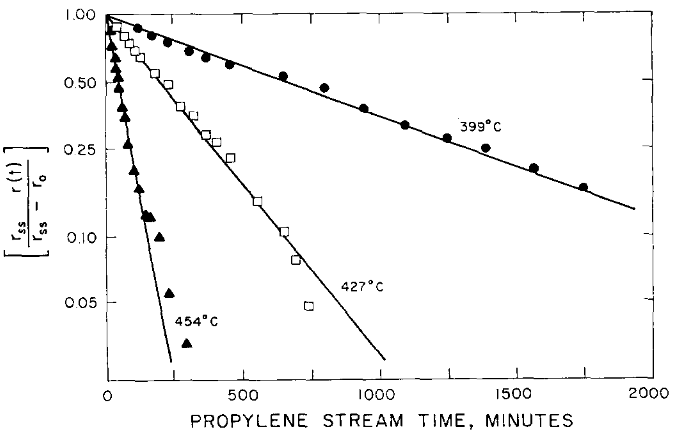

FIG. 4. Rate of fractional approach to steady-state for fresh catalyst at 0.94 atm as a function of temperature.

TABLE 1

WO_3 CATALYST ACTIVITY AND BREAK-IN RATE DURING PROPYLENE DISPROPORTIONATION FOR VARIOUS REACTION CONDITIONS AND CATALYST PRETREATMENT

Pretreatment after air activation	Reaction T (°C)	Conditions P (atm)	Steady-state conversion of propylene	Initial reaction rate	Steady-state reaction rate	Break-in rate (min^{-1})
				$\left(\frac{\text{g moles}}{\text{g cat hr}}\right)$		
30 min N_2 purge	427	0.94	0.0869	0.0790	0.6060	0.00351
120 min vacuum	427	0.94	0.0932	0.0766	0.6500	0.00347
120 min He purge	427	0.94	0.0914	0.0734	0.6371	0.00358
30 min N_2 purge	399	0.94	0.0293	0.0712	0.3800	0.00107
30 min N_2 purge	454	0.94	0.1025	0.0473	1.3240	0.01556
30 min N_2 purge	427	0.94	0.0869	0.0790	0.6060	0.00351
30 min N_2 purge	427	1.95	0.0872	0.3158	1.5606	0.00768
30 min N_2 purge	427	2.98	0.0952	0.5723	2.4026	0.01067
30 min N_2 purge	427	4.00	0.1194	0.7996	3.0601	0.01342
30 min N_2 purge	427	8.08	0.1089	0.7068	4.6840	0.02844
12 hr C_3H_6 + 180 min He	427	0.94	0.0883	0.2745	0.6155	0.02500
120 min CO at 400°C	427	0.94	0.0861	0.0134	0.6070	0.01538
120 min H_2 at 400°C	427	0.94	0.0865	0.0125	0.6100	0.01504
240 min H_2 at 600°C	427	0.94	0.1145	0.0203	0.8075	0.01245

of WO_3 (*20*), while the steady-state catalyst was blue, characteristic of $WO_{2.9}$ (*20*). It appears, therefore, that a reduction of the tungsten promoter may play an important role in catalyst break-in. In a reducing atmosphere at 400–540°C, conversion of WO_3 to $WO_{2.9}$ is reported with total conversion requiring approximately 120 min (*20*). In this temperature range, further reduction to a brown oxide, WO_2, is thermodynamically unfavorable. Reduction to WO_2 will proceed only at temperatures greater than 600°C and requires approximately 240 min in a reducing atmosphere.

If in fact catalyst reduction is the phenomenon responsible for catalyst break-in, then a reduction of the surface to $WO_{2.9}$ prior to the admission of propylene should eliminate the catalyst break-in as has been suggested (*2*). Figure 8 shows the variation in the rate of propylene disproportionation with time during the break-in of freshly

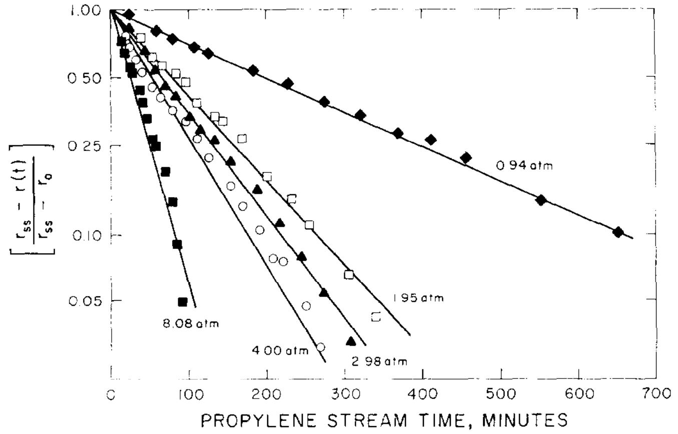

FIG. 6. Rate of fractional approach to steady-state for fresh catalyst at 427°C as a function of propylene partial pressure.

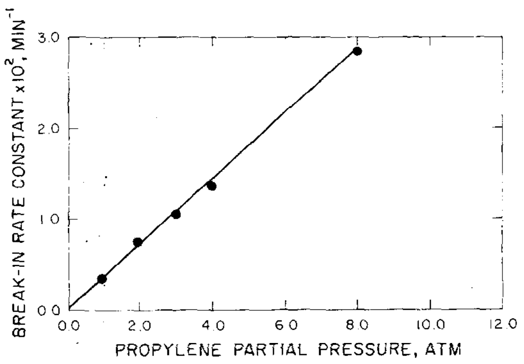

FIG. 7. Propylene partial pressure dependency of the rate of catalyst break-in.

activated catalyst samples which were reduced at 400°C for 120 min with either CO or H_2 prior to the introduction of propylene. Table I contains supplementary data concerning these runs. Prior reduction of the catalyst to $WO_{2.9}$ substantially increases the rate of catalyst break-in but neither eliminates the catalyst break-in nor influences the steady-state catalyst activity.

Reduction of the catalyst suggests the interesting possibility of converting the catalyst to WO_2 by prior reduction at 600°C with H_2. This is an oxidation state of tungsten not attainable when freshly activated catalyst is contacted with propylene. Thermodynamics restrict catalyst reduction to the $WO_{2.9}$ state over the normal operating range of temperatures used in propylene disproportionation while excessive coking restricts attempts to reach the WO_2 oxidation state by the exposure of the fresh catalyst to propylene at 600°C. Figure 8 illustrates the variation in the rate of propylene disproportionation with time during the break-in of a freshly activated catalyst sample which was previously reduced at 600°C for 240 min with H_2 to the brown oxide WO_2. It will be noted that prior reduction of the catalyst to WO_2 substantially increases the rate of catalyst break-in, but does not eliminate the catalyst break-in phenomenon. This prior reduction of the catalyst also results in more than a 30% increase in the steady-state catalytic activity when compared to the normal steady-state activity of the unreduced catalyst at similar conditions.

Data presented thus far suggest that reduction of the catalyst surface is a necessary step in the transition of fresh catalyst samples to steady-state catalysts. As was noted above, prior reduction of the catalyst surface did not, in itself, eliminate catalyst break-in. Thus, the next series of studies were directed towards establishing whether another phenomenon was also associated with catalyst break-in. Since a simple reduction of the catalyst surface should be unaltered in an inert atmosphere at normal operating conditions, an inert purge of a fully activated catalyst at 427°C using helium should not result in a catalyst break-in regime on readmission of propylene. Figure 9 illustrates the variation in

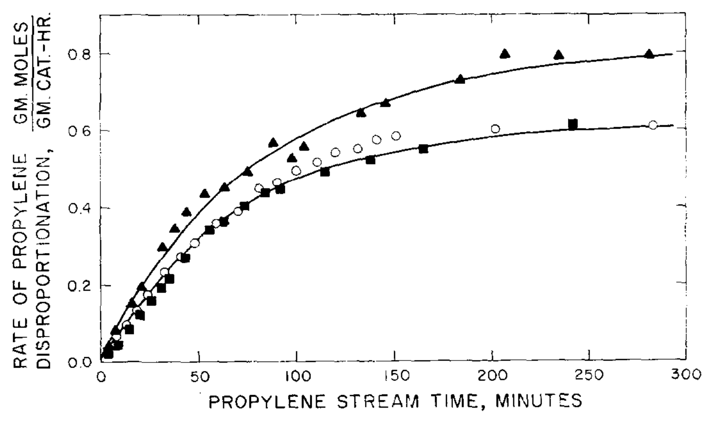

FIG. 8. Effect of catalyst reduction on catalyst break-in at 427°C, 0.94 atm (○ 120 min in CO at 400 °C, ■ 120 min in H_2 at 400°C, ▲ 240 min in H_2 at 600°C).

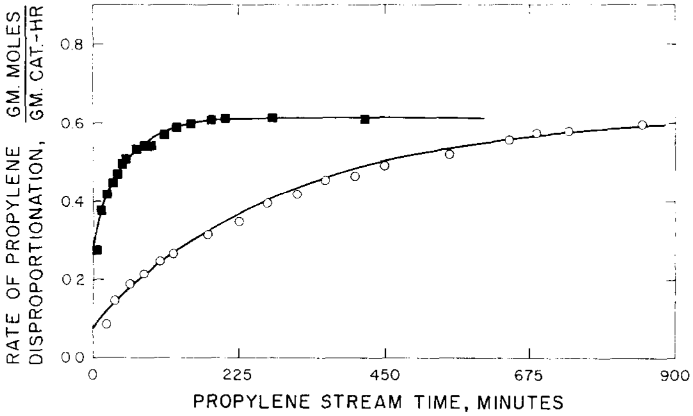

Fig. 9. Partially reversible nature of catalyst break-in at 427°C, 0.94 atm (○ fresh catalyst, ■ steady-state catalyst after a 180-min He Purge).

the rate of propylene disproportionation with time upon readmission of propylene following purging of a fully activated catalyst with He for 180 min. It was independently observed that no change in catalyst color was associated with the helium purge. While a catalyst break-in regime still existed, the initial activity was greater. The rate of break-in was the same as that of a freshly reduced catalyst sample. The steady-state activity was the same in both cases.

Microreactor pulse studies of break-in were made on normally activated catalyst samples using propylene pulses introduced into a stream of He flowing over the catalyst. A mass balance around the reactor was made on each pulse to determine if propylene was irreversibly adsorbed. These data are shown in Figs. 10–12. Figure 10 shows that approximately 30% of the first few propylene pulses were irreversibly adsorbed by the fresh catalyst, and this percentage steadily declined with increasing number of pulses. Figures 11 and 12 give the changes in the mole fractions of ethylene, 2-butene, and 1,3-butadiene as a function of the amount of propylene pulsed over the catalyst. After each series of pulse tests, the catalyst was exposed *in situ* to propylene at 427°C to fully activate the catalyst. The reactor was then reconnected to the chromatograph. A pulse of propylene was passed over the catalyst to obtain the final point in these figures which indicates the mole fraction of each component after

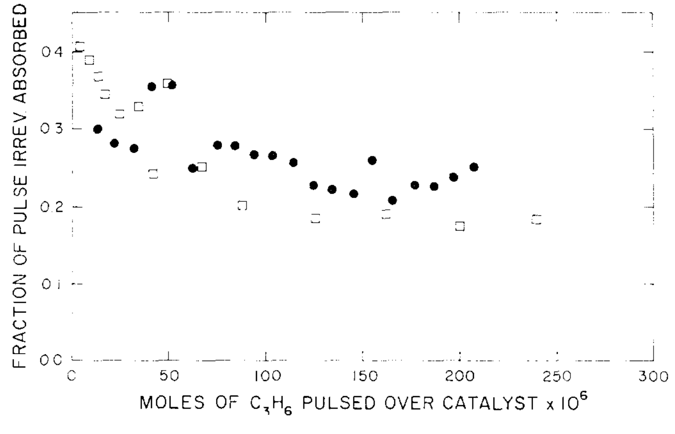

Fig. 10. Strong adsorption of olefins by a fresh catalyst during pulse studies at 427°C, 3.0 atm (●□ duplicate runs).

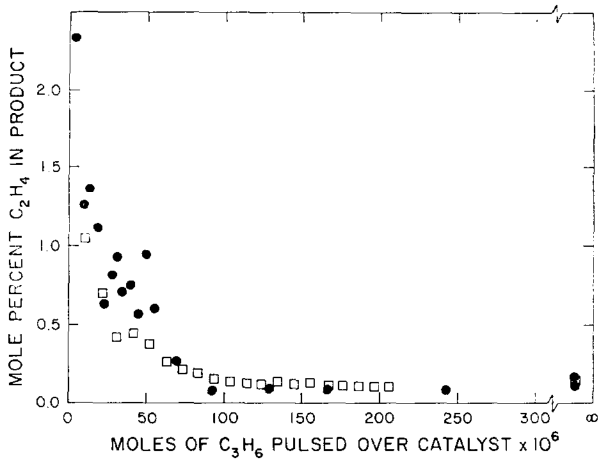

Fig. 11. Ethylene production as a function of catalyst propylene exposure in pulse studies at 427°C, 3.0 atm (●□ duplicate runs).

exposure to a fully activated catalyst. These final points indicate approximately equal molar production of ethylene and 2-butene and the absence of any 1,3-butadiene.

Discussion

It has been shown that the rate of catalyst break-in is first order in unaccomplished break-in (i.e., $r_{ss} - r$). The break-in rate constant is first order in propylene pressure, and has an Arrhenius temperature dependency with an activation energy of about 47 kcal. These results suggest that the break-in phenomenon is a second-order reaction involving potentially active sites and propylene. A break-in rate expression of the form of Eq. (1) would be consistent with such a mechanism, giving a first order dependency on the number of unactivated sites with a break-in rate constant proportional to the propylene partial pressure.

Studies of the break-in of prereduced catalysts show that the initial oxidation state of the tungsten influences the rate of break-in, but that break-in is not merely a result of reduction. That break-in is not simply a change in surface oxidation state

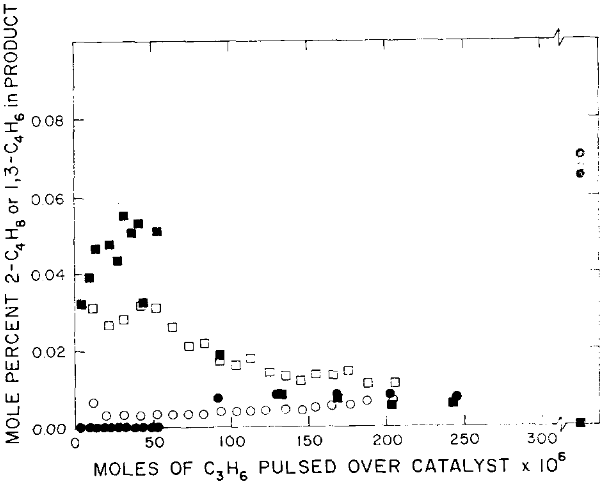

Fig. 12. 1,3-Butadiene (□ ■) and 2-butene (○ ●) production as a function of catalyst propylene exposure during pulse studies at 427°C, 3.0 atm.

is further indicated by the results of the helium purge of a fully broken-in catalyst shown in Fig. 9. These data, together with the pulse data shown in Fig. 10, suggest that break-in results in the strong adsorption of an organic intermediate or fragment which plays an important role in propylene disproportionation. However, the results of the studies with prereduced catalysts do show that the oxidation state of the tungsten is an important factor in catalyst activity, the initial WO_3 giving modest rates of disproportionation, the stable $WO_{2.9}$ giving very much faster rates, and WO_2 yielding even higher rates of disproportionation.

The appearance of butadiene in the initial reactor effluent is perhaps not essential to break-in, since this product appears only during the first few seconds of contacting, while break-in occurs over a protracted time interval. However, this may well be a product of the reduction of WO_3 to $WO_{2.9}$.

Another point is the formation of water, implied by the appearance of butadiene and by the reduction of the WO_3 to $WO_{2.9}$. Water is known to be a temporary poison and substantial purging with a dry feed is required for its removal (*3*). A qualitative explanation of break-in could be based on the formation of water upon reduction of the WO_3 to $WO_{2.9}$ during first contacting with propylene. The slow break-in could be attributed to slow displacement of the strongly chemisorbed water by adsorbed propylene. However, the reversal of break-in by an inert purge of helium, and the presence of break-in even by prereduced catalysts would make such an explanation seem unlikely.

Finally, as a note of caution, it should be mentioned the identification of the oxides of tungsten as WO_3, $WO_{2.9}$, and WO_2 is based upon the observed colors and the known behavior of unsupported oxides. However, it has been pointed out that the behavior of supported oxides does not always parallel that of the bulk oxides (*24*), and it may be that the actual structures are more complex than those given.

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