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# Adsorption and Disproportionation of Ethylene on Supported Rhenium Oxide Catalysts

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The adsorption and disproportionation reaction of deuterated ethylene on various supported rhenium oxide catalysts have been studied. Silica gel and $\gamma$-alumina were used as supports with a rhenium oxide content ranging between 5 and 20%. Adsorption on the unreduced catalysts was found to be reversible with an isosteric heat that decreased slightly with increasing coverage. Entropy changes associated with the reversible adsorption were indicative of a somewhat mobile absorbate. For both the $SiO_2$ and $Al_2O_3$ supported catalysts, hydrogen reduction at 500°C for less than 5 hr created sites that absorbed ethylene irreversibly. After continued reduction for greater than 15 hr, ethylene adsorption on the $SiO_2$ supported samples became reversible again, whereas the $Al_2O_3$ samples retained a significant and constant level of irreversible adsorption even after 20 hr of reduction.

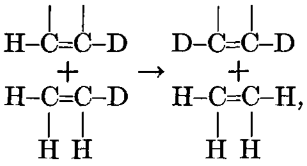
Initial kinetic studies with propylene indicated that the silica supported samples were inactive for the disproportionation reaction up to 180°C. By contrast, the reaction proceeded readily on the alumina supported catalysts even at room temperature.

The rate of disproportionation of monodeuterated ethylene on the unreduced catalyst was measured at 75 and 95°C with ethylene partial pressures between 300 and 760 Torr. The olefin surface concentration under these conditions was determined independently by measuring the extent of adsorption of light ethylene. Since the rate was found to vary as the square of the surface concentration, the results support the contention that the rate determining step involves the interaction of two adsorbed olefin molecules.

## INTRODUCTION

Since first discovered by Banks and Bailey (*1*) the olefin disproportionation reaction has been the subject of many investigations (*2*). Of particular interest has been the order of the rate determining step with respect to the adsorbed olefin. Although it is generally felt that the reaction proceeds through a four-centered intermediate, rate equations based on both a Langmuir–Hinshelwood (LH) model with two adsorbed olefin molecules and a Rideal (R) model with only one adsorbed species have been proposed (*3, 4*). In certain cases significant mass transfer limitations have obscured a detailed kinetic study of the reaction (*5–7*). Even in the absence of a diffusion controlled reaction, it is necessary to make several assumptions before interpreting the form of the rate equation, and of central importance is the nature of the assumed adsorption isotherm.

We report here an investigation of the disproportionation reaction of monodeuterated ethylene,



$$\begin{array}{ccc} \begin{array}{c} \mathrm{H\ \ H} \\ \mathrm{H{-}C{=}C{-}D} \\ + \\ \mathrm{H{-}C{=}C{-}D} \\ \mathrm{H\ \ H} \end{array} & \rightarrow & \begin{array}{c} \mathrm{H\ \ H} \\ \mathrm{D{-}C{=}C{-}D} \\ + \\ \mathrm{H{-}C{=}C{-}H,} \\ \mathrm{H\ \ H} \end{array} \end{array}$$

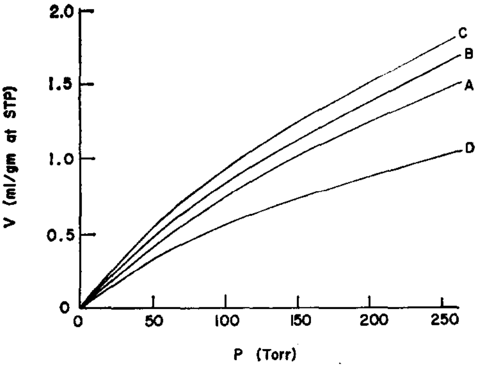


FIG. 1. Ethylene adsorption for various weight percentage Re–$Al_2O_3$ catalysts at 25°C (unreduced), (A) 0%; (B) 1.5%; (C) 5%; (D) 22%.

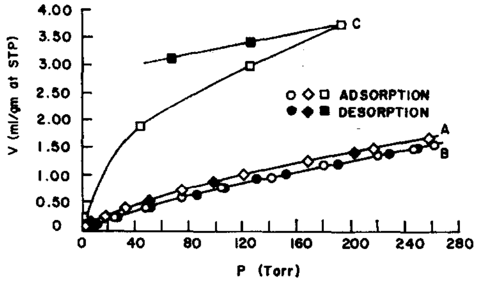


FIG. 3. Ethylene adsorption on reduced and oxidized Re–$Al_2O_3$ at room temperature; (A) alumina (reversible); (B) air oxidized (500°C) 10% Re–$Al_2O_3$ (reversible); (C) hydrogen reduced (15 hr at 500°C) 10% Re–$Al_2O_3$ (irreversible).

on supported rhenium oxide catalysts. The disproportionation reaction on rhenium oxide proceeds readily at or slightly above room temperature. By using light and deuterated ethylene, it is possible to monitor *independently* the disproportionation rate and the extent of adsorption under identical reaction conditions. Adsorption equilibrium is maintained throughout the course of the reaction and the dependence of the rate on surface coverage can be determined directly. Preliminary studies on the disproportionation of propylene were also performed to determine the relative levels of activity for the rhenium oxide catalysts of different weight percents on the two supports, $SiO_2$ and $Al_2O_3$ in both the oxidized and reduced forms.

## METHODS

### *Catalyst Preparation*

The catalysts were prepared by impregnating the supports (40–60 mesh) with aqueous ammonium perrhenate. The supports used were Davison grade 59 silica gel (435 $m^2/g$) and Harshaw γ-alumina (300 $m^2/g$). The catalysts contained from 5 to 20 wt% of the rhenium oxide (as $Re_2O_7$). The samples were activated in a mixture of $N_2$ and $O_2$ at 500°C for 2 hr followed by a 1 hr $N_2$ or He purge before being cooled to the desired temperature.

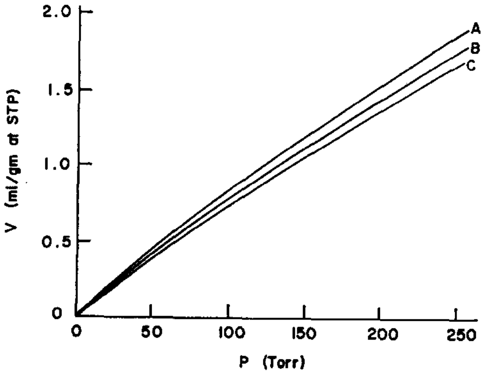


FIG. 2. Ethylene adsorption for various weight percentage Re–$SiO_2$ samples at 25°C (unreduced), (A) 0%; (B) 12%; (C) 21%.

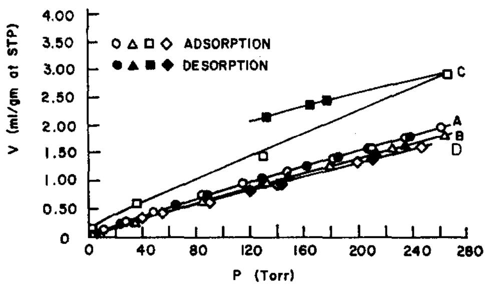


FIG. 4. Ethylene adsorption on reduced and oxidized Re–$SiO_2$ at room temperature; (A) $SiO_2$ (reversible); (B) air oxidized (500°C) 10% Re–$SiO_2$ (reversible); (C) hydrogen reduced (2.5 hr at 500°C) 10% Re–$SiO_2$ (irreversible); (D) hydrogen reduced (15 hr at 500°C) 10% Re–$SiO_2$ (reversible).

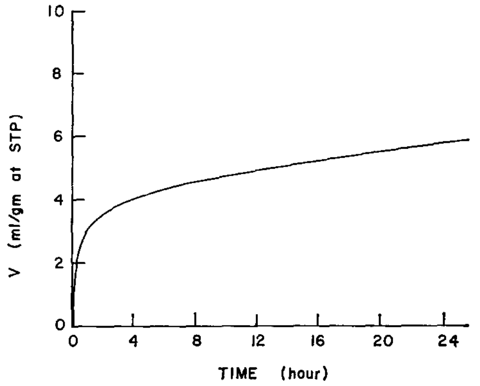


FIG. 5. Ethylene adsorption on 10% Re–$Al_2O_3$ at room temperature after a 15 hr reduction (500°C).

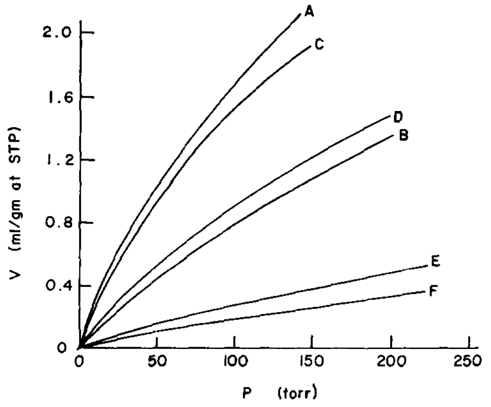


FIG. 7. Ethylene adsorption at various temperatures for the unreduced Re–$Al_2O_3$ catalysts. (A) $Al_2O_3$ (0°C); (B) $Al_2O_3$ (25°C); (C) 10% Re–$Al_2O_3$ (5°C); (D) 10% Re–$Al_2O_3$ (25°C); (E) 10% Re–$Al_2O_3$ (75°C); (F) 10% Re–$Al_2O_3$ (95°C).

*Adsorption Experiments*

The adsorption of ethylene was determined volumetrically in a Pyrex glass adsorption system. After the catalyst pretreatment, the system was evacuated for 3 hr at a pressure less than $5 \times 10^{-6}$ Torr using a two-stage mercury diffusion pump. The adsorption cell was isolated from the pumps with a liquid nitrogen cold trap and greaseless stopcocks or Teflon glass valves were used to minimize the extent of contamination. The volume of the adsorption cell was determined by introducing helium from a precalibrated constant volume bulb. Pressure measurements were made with a Model 145 Precision Pressure Gage manufactured by Texas Instruments, Inc. and the adsorption cell was immersed in a constant temperature oil bath for thermal control. High purity He, $N_2$, and $O_2$ were dried before use. $H_2$ was purified with a Serfass hydrogen purifier and a Matheson research grade ethylene (99.98% min) was used as the adsorbate.

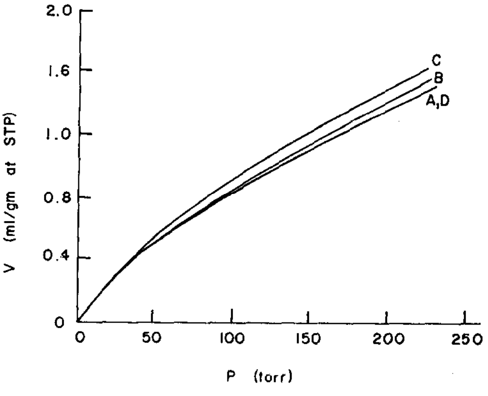


FIG. 6. Reversible component of the ethylene adsorption on the reduced 10% Re–$Al_2O_3$; (A) unreduced; (B) 2.5 hr reduction; (C) 7.5 hr reduction; (D) 15 hr reduction.

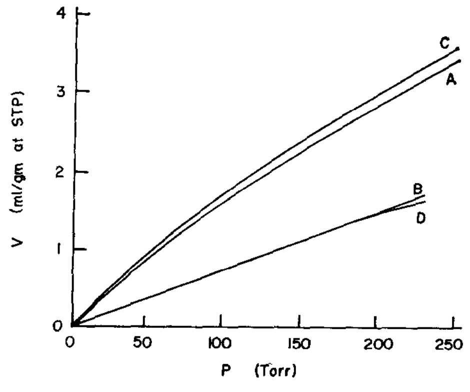


FIG. 8. Ethylene adsorption on the reduced and unreduced 11% Re–$SiO_2$ sample at 1 and 25°C. (A) Unreduced (1°C); (B) unreduced (25°C); (C) 15 hr reduction (1°C); (D) 15 hr reduction (25°C).

TABLE 1

The Heats of Adsorption and the Entropies of Adsorption of Ethylene on Alumina[a]

| $V$ (ml/g @STP) | 0.3 | 0.6 | 0.9 | 1.2 | 1.5 | |
|---|---|---|---|---|---|---|
| Equilibrium pressure (Torr) | | | | | | |
| (0°C) | 10 | 23 | 41 | 61 | 85 | |
| (25°C) | 31 | 74 | 124 | 178 | 245 | |
| $-\Delta H$ (kcal/mole) | 7.603 | 7.853 | 7.437 | 7.196 | 7.114 | 7.441 (av) |
| $-\Delta S$ (e.u.) | 19.23 | 21.80 | 21.43 | 21.33 | 21.69 | 21.10 (av) |

[a] $({}_2S_{trans} - {}_3S_{trans})$ at 300°K: −20.60 e.u.; $(S_{config} - {}_3S_{trans})$: −28.9 e.u.

*Disproportionation Experiments*

The disproportionation of propylene was studied in the adsorption cell described above. Phillips polymerization grade propylene (99%) was used as the reactant. The reaction products were analyzed chromatographically using 20% bis-2-methoxy ethyl adipate on Chromosorb P. For the experiments with monodeuterated ethylene, the reactant was passed over the catalyst for at least 20 min and then part of the effluent was collected in a glass sampling bulb. The products were analyzed mass spectrometrically at low ionization voltages (5–7 eV). The monodeuterated ethylene was purchased from Merck & Co. Canad.

## RESULTS

### *Adsorption Studies*

*A. Ethylene adsorption on unreduced samples at room temperature.* The isotherms for the adsorption of ethylene on the unreduced alumina and silica supported samples are given in Figs. 1 and 2. The isotherms were found to be reversible in all cases. For rhenium oxide catalysts supported on alumina (Re–$Al_2O_3$) the metal oxide content was between 2.5 and 20 wt%. The amount of olefin adsorbed at a given pressure was found to first increase with increasing wt% of the metal oxide. However, for catalysts with greater than 5% $Re_2O_7$, the extent of adsorption decreased with increasing rhenium oxide content. On the silica supported samples (Re–$SiO_2$) the extent of adsorption decreased monotonically with increasing wt% of the promoter. In addition, there was a slight color change for the Re–$SiO_2$ catalysts indicative of a partial reduction of the oxide in the presence of the olefin. For the alumina supported samples, there was no observable color change.

*B. Adsorption of ethylene on the reduced samples at room temperature.* The isotherms for the adsorption of ethylene on the Re–$SiO_2$ samples after varying periods of re-

TABLE 2

The Heats of Adsorption and the Entropies of Adsorption of Ethylene on 10.81% $Re_2O_7/Al_2O_3$ Catalyst

| $V$ (ml/g @ STP) | 0.05 | 0.1 | 0.15 | 0.2 | 0.25 | 0.30 | |
|---|---|---|---|---|---|---|---|
| Equilibrium pressure (Torr) at | | | | | | | |
| 75°C | 18 | 38 | 61 | 85 | 110 | 161 | |
| 95°C | 28 | 65 | 102 | 139 | 178 | 259 | |
| $-\Delta H$ (kcal/mole) | 5.621 | 6.821 | 6.540 | 6.257 | 6.123 | 6.048 | 6.203 (av) |
| $-\Delta S$ (e.u.) | 8.716 | 13.673 | 13.78 | 13.63 | 13.76 | 14.30 | 13.10 (av) |

TABLE 3

The Heats of Adsorption and the Entropies of Adsorption of Ethylene on the Unreduced 11.06% $Re_2O_7/SiO_2$ Catalyst

| $V$ (ml/g @ STP) | 0.3 | 0.6 | 0.9 | 1.2 | 1.5 | |
|---|---|---|---|---|---|---|
| Equilibrium pressure (Torr) at | | | | | | |
| 1°C | 16 | 35 | 54 | 74 | 95 | |
| 25°C | 38 | 75 | 118 | 160 | 202 | |
| $-\Delta H$ (kcal/mole) | 5.883 | 5.183 | 5.316 | 5.244 | 5.131 | 5.352 (av) |
| $\Delta S$ (e.u.) | 13.78 | 12.78 | 12.78 | 14.49 | 14.57 | 13.95 (av) |

duction are shown in Fig. 3. Reduction in hydrogen initially created sites which adsorbed ethylene irreversibly. However, after a 15 hr reduction at 500°C the adsorption again became reversible. The difference between the extents of adsorption on the unreduced and extensively reduced (15 hr) samples were found to be small.

Hydrogen reduction of the alumina supported catalyst also created sites which adsorbed ethylene both slowly and irreversibly. Unlike the silica supported catalysts, the amount of irreversibly held ethylene on the Re–$Al_2O_3$ samples became constant after about 15 hr of reduction. These results are shown in Fig. 4 with points on the ascending branch taken at 1 hr intervals and those on the descending branch every 10–15 min.

Pretreating both supports in hydrogen at 500°C had no appreciable effect on the amount of ethylene adsorption. The extent of adsorption as a function of time for the 10% Re–$Al_2O_3$ catalyst is shown in Fig. 5 The initial olefin pressure was 536 Torr and it took more than 1 day to reach the final value.

The extent of adsorption on the reduced catalyst after varying reduction times was also studied. After an oxidation–reduction cycle, ethylene was passed over the catalyst for 4 hr at 760 Torr in order to saturate the irreversible sites. The system was then evacuated and the adsorption–desorption experiments were repeated. The results shown in Fig. 6 indicate that the reversible component of the adsorption is essentially independent of the reduction time.

*C. Ethylene adsorption at elevated temperatures.* Figure 7 shows the results for the adsorption of ethylene at various temperatures on the 10% Re–$Al_2O_3$ catalyst and Fig. 8 gives the comparable results for the 10% Re–$SiO_2$ sample. In all cases the amount of adsorption decreased with increasing temperatures. The isosteric heats

TABLE 4

The Heats of Adsorption and the Entropies of Adsorption of Ethylene on the Reduced (15 hr) 11.06% $Re_2O_7/SiO_2$ Catalyst

| $V$ (ml/g @ STP) | 0.3 | 0.6 | 0.19 | 1.2 | 1.5 | |
|---|---|---|---|---|---|---|
| Equilibrium pressure (Torr) at | | | | | | |
| 1°C | 12 | 28 | 46 | 65 | 84 | |
| 25°C | 38 | 75 | 118 | 160 | 206 | |
| $-\Delta H$ (kcal/mole) | 7.801 | 6.668 | 6.375 | 6.096 | 6.071 | 6.602 (av) |
| $-\Delta S$ (e.u.) | 20.21 | 17.76 | 17.68 | 17.35 | 17.77 | 18.15 (av) |

TABLE 5

Adsorption of $C_2H_4$ and $C_2H_3D$ at 22°C on 10.81% $Re_2O_7/Al_2O_3$ Catalyst

| $C_2H_4$ | | $C_2H_3D$ | |
|---|---|---|---|
| Equilibrium pressure (Torr) | Vol adsorbed (ml/g @ STP) | Equilibrium pressure (Torr) | Vol adsorbed (ml/g @ STP) |
| 18.88 | 0.2360 | 18.92 | 0.2596 |
| 39.62 | 0.3931 | 44.15 | 0.4902 |
| 89.60 | 0.6857 | 89.89 | 0.8138 |
| 129.00 | 0.9909 | 129.79 | 1.0592 |
| 158.75 | 1.1406 | 162.66 | 1.2185 |
| 206.57 | 1.3265 | 207.03 | 1.4305 |
| 255.43 | 1.5304 | 255.51 | 1.6367 |
| $V_{C_2H_4} = 0.027126\, P^{0.730923}$ (by least square fitting) | | $V_{C_2H_3D} = 0.033077\, P^{0.708066}$ (by least square fitting) | |

and entropies of adsorption are given in Tables 1–4.

*D. Adsorption of monodeuterated ethylene.* The adsorption isotherms for $C_2H_3D$ were measured on the unreduced Re–$Al_2O_3$ catalysts at 22 and 95°C. The results are shown in Tables 5 and 6 along with the corresponding values for light ethylene.

TABLE 6

Adsorption of $C_2H_4$ and $C_2H_3D$ at 95°C on 10.81% $Re_2O_7/Al_2O_3$

| $C_2H_4$ | | $C_2H_3D$ | |
|---|---|---|---|
| Equilibrium pressure (Torr) | Vol adsorbed (ml/g @ STP) | Equilibrium pressure (Torr) | Vol adsorbed (ml/g @ STP) |
| 56.68 | 0.0471 | 30.89 | 0.0501 |
| 137.26 | 0.222 | 119.75 | 0.191 |
| 227.19 | 0.360 | 182.09 | 0.283 |
| 269.48 | 0.400 | 249.51 | 0.383 |
| 368.50 | 0.533 | 355.09 | 0.535 |
| 419.08 | 0.587 | 400.50 | 0.587 |
| 492.74 | 0.689 | 468.13 | 0.638 |
| 535.44 | 0.727 | 506.35 | 0.678 |
| 615.82 | 0.846 | 533.65 | 0.729 |
| 667.61 | 0.903 | 632.40 | 0.808 |
| 701.92 | 0.947 | 692.54 | 0.886 |
| 750.98 | 1.041 | 743.21 | 0.953 |
| 781.06 | 1.105 | 770.15 | 0.998 |
| $V_{C_2H_4} = 0.002571\, P^{0.903162}$ (by least square fitting) | | $V_{C_2H_3D} = 0.002237\, P^{0.922629}$ (by least square fitting) | |

### *Kinetic Studies*

*A. Reaction of propylene on the unreduced catalysts.* The Re–$SiO_2$ samples were found to be inactive for the disproportionation reaction even up to 180°C. By contrast the reaction proceeded readily at room temperature on alumina supported catalysts. In fact, it was found that the reaction on the 20% Re–$Al_2O_3$ catalyst was mass transfer limited. However, unlike the anomalous mass transfer effect for the $WO_3/SiO_2$ system (*5–7*), the mass transfer constraints in the rhenium oxide system could be removed by either a reduction in the temperature or the weight percent of the oxide. The rates on the 10% Re–$Al_2O_3$ catalyst were found to be free of both internal and external mass transfer limitations and all subsequent kinetic data was obtained with this sample. The activity was found to decay slowly with time and in all cases the products were equal moles of ethylene and 2-butenes. There was no appreciable change in the ratio of *trans*- to *cis*-2-butene with time but at higher flow rates this ratio was lowered. In all cases the ratio was less than the equilibrium value. A computer fit of the data indicated that the rate could be represented by the Langmuir–Hinshelwood equation. In the pressure and temperature range

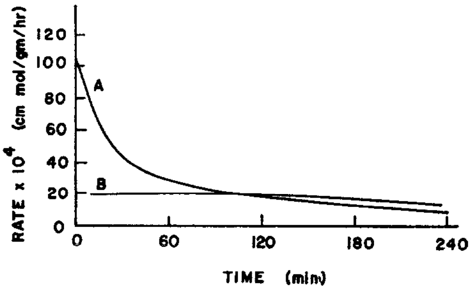


FIG. 9. Activity vs time for the Re–$Al_2O_3$ catalyst. (A) After a 15 hr hydrogen reduction; (B) unreduced.

TABLE 7

Effect of Time of Reduction on the Initial Rate of the Disproportionation of Propylene[a]

| Time of $H_2$ reduction (hr) | Initial rate (g mole/g/hr) | % with respect to the unreduced catalyst |
|---|---|---|
| 0 | 0.00260 | 100 |
| 2.5 | 0.00600 | 180 |
| 5 | 0.00220 | 65 |
| 10 | 0.0110 | 317 |
| 15 | 0.0130 | 360 |

[a] 10.95% $Re_2O_7/Al_2O_3$ at 25°C, and 1 atm.

TABLE 8

Effect of Preadsorption of Ethylene on the Initial Rate of the Disproportionation of Propylene at Room Temperature[a]

| Time of exposure to ethylene (hr) | Initial rate of propylene disproportionation (g mole/g/hr) | Initial ratio of *trans*-2-butene to *cis*-2-butene |
|---|---|---|
| 2.5 | 0.0081 | 2 |
| 7.5 | 0.0075 | 2 |
| 15.5 | 0.0021 | 1.5 |
| 22.5 | 0.0006 | 1.0 |

[a] 11.2% $Re_2O_7/Al_2O_3$ fresh catalysts reduced 15 hr.

studied, the apparent order with respect to the olefin partial pressure was 1.4 and the apparent activation energy was 11 kcal/mole.

*B. Reaction of propylene on the reduced catalyst.* The initial activity of the reduced 10% Re–$Al_2O_3$ catalyst was greater than that of the unreduced form under comparable conditions. However, the high initial activity decayed in time to the value of the unreduced sample as shown in Fig. 9. The relationship between the initial rate and reduction time at 500°C is given in Table 7. The effect of preadsorbed ethylene on the disproportionation rate of propylene over the reduced catalyst is shown in Table 8. After a 15 hr reduction in hydrogen the system was purged with helium for 1.5 hr. The system was then evacuated and the catalyst was exposed to $C_2H_4$ (12.4 ml/g) for varying periods of time. After evacuation the initial disproportionation rate of propylene was measured.

*C. Disproportionation of monodeuterated ethylene.* The results for disproportionation rate for $C_2H_3D$ are given in Table 9. The reaction was studied at 75 and 95°C. The rates were determined from the concentration of dideuterated ethylene. Light and dideuterated ethylene were the only products of this reaction.

TABLE 9

Results for the Disproportionation of $C_2H_3D$ over Unreduced 10.81% $Re_2O_7/Al_2O_3$ Catalyst at 75 and 95°C

| Temp (°C) | $P_{C_2H_3D}$ (atm) | $C_2H_3D$ flow rate (ml/min @ 1 atm 23°C) | Catalyst wt (g) | % Conversion of $C_2H_3D$ | Rate × $10^4$ (g moles/g/hr) |
|---|---|---|---|---|---|
| 75 | 1.0 | 7.21 | 3.1157 | 11.14 | 6.20 |
| | 0.826 | 4.10 | 3.1157 | 13.78 | 4.36 |
| | 0.667 | 2.54 | 3.1034 | 15.68 | 3.09 |
| | 0.435 | 2.67 | 3.1034 | 6.81 | 1.41 |
| 95 | 1.0 | 7.21 | 1.9841 | 7.94 | 6.94 |
| | 0.826 | 4.78 | 1.9787 | 8.51 | 4.94 |
| | 0.640 | 3.64 | 1.9787 | 7.04 | 3.11 |
| | 0.580 | 2.53 | 1.9726 | 8.86 | 2.74 |

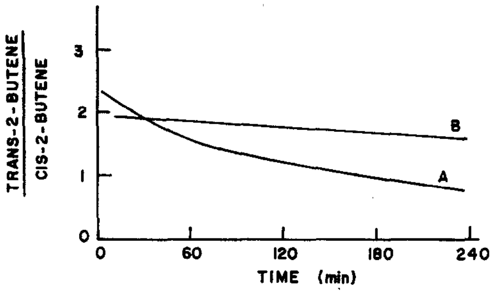


FIG. 10. Selectivity vs time for the Re–$Al_2O_3$ catalyst. (A) After a 15 hr hydrogen reduction; (B) unreduced.

## DISCUSSION

The results for both the adsorption of ethylene and the disproportionation of propylene indicate that the support can have a profound effect on the behavior of the rhenium oxide system. These results suggest that there is an interaction between rhenium oxide and alumina which stabilizes the oxide and limits the level of reduction relative to the silica supported catalyst. Similar results have been observed by Biolen and Pott (*8*) for supported tungsten oxide systems. Johnson and LeRoy (*9*) observed that for a Pt/Re/$Al_2O_3$ catalyst, rhenium, initially present as the heptoxide ($Re^{7+}$), is reduced only to the dioxide ($Re^{4+}$) in hydrogen at 482°C. It is also known (*10*) that despite the high volatility of the heptoxide, rhenium on alumina can be regenerated with oxygen at 500°C for 12 h without an appreciable loss of the oxide from the support. In the present study, it was found that for a moderate reduction period, either the alumina or silica supported oxide, sites were created that adsorbed ethylene slowly and irreversibly. These sites are most likely associated with anion vacancies in the rhenium oxide structure. After a more extensive period of reduction (i.e., 15–20 hr) these sites were destroyed on the Re–$SiO_2$ samples but were retained for catalysts using alumina as a support. In addition, both ethylene and propylene produced a change in the color of the silica catalysts from snow-white ($Re^{7+}$) to purple ($Re^{6+}$) even at room temperature. Under similar conditions the alumina supported samples retained their initial color. The color change and the absence of disproportionation activity for the silica supported oxide are indicative of the ease with which even the reactant olefin can reduce the oxide to an inactive state.

For the Re–$Al_2O_3$ catalysts, the reduced sample had initially a relatively large activity which, however, decayed in time to the level of its unreduced counterpart. The rate of decay in the activity was comparable to the slow rate of olefin adsorption on the reduced catalysts and, in general, the initial activity increased with an increase in the hydrogen reduction time as shown in Table 7. These results suggest that the anion vacancies, created by hydrogen reduction of the surface, can enhance the activity of neighboring disproportionation sites, but that the concentration of these vacancies is transitory, decreasing in time during the course of the reaction as the reactant olefin becomes irreversibly adsorbed on these sites. Ultimately, the activity of the reduced and unreduced catalysts become effectively identical. In addition it was observed that the product *trans*- to *cis*-2-butene ratio was a function of the anion vacancy concentration, decreasing as these vacancies become saturated (Fig. 10).

TABLE 10

Isotope Effect for the Adsorption of Ethylene at 22°C

| Pressure (Torr) | $V_{C_2H_3D}/V_{C_2H_4}$ |
|---|---|
| 760 | 1.0478 |
| 628 | 1.0524 |
| 456 | 1.0601 |
| 331 | 1.0679 |

The disproportionation of monodeuterated ethylene and the adsorption of light ethylene were studied independently at 75 and 95°C using the unreduced 10% Re–$Al_2O_3$ catalyst. To correct for the adsorption isotope effect, the ratio of the adsorptions of monodeuterated ethylene and light ethylene was also measured at a temperature sufficiently low to render the catalyst inactive (i.e., 22°C). For olefin partial pressures between 300 and 760 Torr, the ratio was found to be close to unity, with the values shown in Table 10 used to calculate the monodeuterated olefin surface concentration given in Tables 11–12, assuming that the ratio at a given pressure is independent of the temperature between 22 and 95°C.

In order to determine if the rate equation reproducing the results in Tables 11–12 can best be described in terms of a Langmuir–Hinshelwood or Rideal model, the disproportionation rates and olefin surface concentrations were correlated by

$$r = kV^n,$$

and

$$r = k'V^mP_o,$$

where $V$ is the volume of olefin adsorbed when the partial pressure is $P_o$. A value of $n = 2$ is consistent with a Langmuir–Hinshelwood model, whereas the Rideal equation would give $m = 1$. The results of a linear least squares analysis of the data at the two reaction temperatures are given in Tables 11–12. Thus, it was found that $m = 2$ to within about 2%, whereas the value of $m$ deviates from unity by about 14%. It is felt that these differences are significant and that the results support a rate determining step involving two adsorbed olefin molecules. The adsorption isotherms indicate that the heat of adsorption is small (≈6 kcal/mole) and that the surface species is somewhat mobile. The activation energy for the rate determining surface reaction was found to be 9.5 kcal/mole. Thus the apparent activation energy for the disproportionation of ethylene on the 10% Re–$Al_2O_3$ catalyst would be close to zero as compared with the value of 11 kcal/mole observed for the reaction of propylene on the same catalyst.

TABLE 11

Correlation of the Reaction Rate of the Disproportionation of $C_2H_3D$ with the Amount of Adsorption at 75°C on 10.81% $Re_2O_7/Al_2O_3$

| $P_{C_2H_3D}$ (atm) | Rate × $10^4$ (g moles/g/hr) | $V_{C_2H_3D}$ (ml/g @ STP) |
|---|---|---|
| 1.0 | 6.20 | 1.3343 |
| 0.826 | 4.36 | 1.1302 |
| 0.667 | 3.09 | 0.9249 |
| 0.435 | 1.41 | 0.6285 |

$$\ln(R) = -7.95391 + 1.95113 \ln(V)$$
$$\ln(R/P) = -7.63305 + 0.849196 \ln(V)$$

TABLE 12

Correlation of the Reaction Rate of the Disproportionation of $C_2H_3D$ with the Amount of Adsorption at 95°C on 10.81% $Re_2O_7/Al_2O_3$

| $P_{C_2H_3D}$ (atm) | Rate × $10^4$ (g moles/g/hr) | $V_{C_2H_3D}$ (ml/g @ STP) |
|---|---|---|
| 1.0 | 6.94 | 0.981 |
| 0.826 | 4.94 | 0.804 |
| 0.64 | 3.11 | 0.657 |
| 0.58 | 2.74 | 0.617 |

$$\ln(R) = -7.21145 + 2.03308 \ln(V)$$
$$\ln(R/P) = -7.24976 + 0.86197 \ln(V)$$

Thus, in conclusion, the rate equation for the disproportionation of ethylene on Re–$Al_2O_3$ was found to be consistent with a bimolecular surface reaction involving two adsorbed olefin molecules. Similar results were obtained by Lewis and Wills (*4*) for the disproportionation of propylene on a CO–$MO_3$–$Al_2O_3$ catalyst if it was assumed that the extent of adsorption of propylene was given by a Langmuir adsorption isotherm. In the present work, we have *independently* measured the extent of adsorption and the reaction kinetics and have thus related the reaction rate directly to the adsorbate surface concentration. Our conclusions are therefore independent of any assumptions with respect to the type of isotherm and in fact it was found that isotherms for the adsorption of ethylene could be more faithfully represented by a Freundlich equation than by the Langmuir isotherm.

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