Kinetics of Catalytic Disproportionation of Propylene*

by Tadao Takahashi**

Summary: The initial rates of the catalytic disproportionation of propylene were determined under controlled conditions in a closed circulating glass reactor. The catalysts used were MoO$_3$-Al$_2$O$_3$, WO$_3$-Al$_2$O$_3$, and WO$_3$-SiO$_2$, being typical combinations of promoters and supports. The initial rate data obtained are discussed and are correlated by a rate expression based upon a dual site Langmuir-Hinshelwood mechanism; the same expression is also derived from a mechanism involving a four center intermediate and a Langmuir type adsorption. The data obtained for the MoO$_3$-Al$_2$O$_3$ catalyst or the WO$_3$-Al$_2$O$_3$ catalyst are well correlated by this expression. It is considered that the adsorption of propylene on WO$_3$-SiO$_2$ catalyst obeys the Freundlich equation rather than the Langmuir isotherm. In the range of low pressure, however, the data obtained on the WO$_3$-SiO$_2$ are also correlated by the above mechanism. The activation energies for the surface reaction are evaluated to be 5.15 kcal/mol on the MoO$_3$-Al$_2$O$_3$, 14.8 kcal/mol on the WO$_3$-Al$_2$O$_3$, and 11.5 kcal/mol on the WO$_3$-SiO$_2$.

1 Introduction

Though it is well known that activities of catalysts for olefin disproportionation vary with their supports and promoters1), few kinetic studies on this reaction have been reported. The experimental results from an integral reactor with a tungsten oxide-silica catalyst were analyzed kinetically by Begley and Wilson2). They reported the data to be better correlated by a rate expression based upon a Rideal mechanism than by an expression based upon a Langmuir-Hinshelwood mechanism. Lewis and Wills showed that the initial rate3) and the differential rate4) data on a cobalt-molybdenum-alumina catalyst were well correlated by a Hougen and Watson type rate expression based upon a Langmuir-Hinshelwood mechanism.

In the present study, in order to compare the kinetic properties of several olefin disproportionation catalysts under controlled reaction conditions, the initial rates of the catalytic disproportionation of propylene were determined in a closed circulating glass reactor. The catalysts used were molybdenum oxide-alumina; tungsten oxide-alumina; and tungsten oxide-silica, being typical of combinations of promoters and supports. The initial rate data obtained are considered to be correlated with a rate expression based upon a dual site Langmuir-Hinshelwood mechanism, and the expression is also derived from a mechanism involving a four center intermediate and a Langmuir type adsorption.

2 Reaction Mechanism and Kinetics

On the mechanism of olefin disproportionation, Bradshaw et al.5) suggested that the reaction must proceed via a quasi-cyclobutane intermediate. Afterward, through the studies on the disproportionation of [2-14C]-propene6),7) and of [2-D]-propene8) etc.9) it has been virtually confirmed that olefins are disproportionated via the quasi-cyclobutane or a four center intermediate. On the other hand, olefin metathesis10),11), which is effected by homogeneous catalysts obtained from molybdenum or tungsten complexes, is considered to be essentially the same reaction as olefin disproportionation on the solid catalysts. Hughes12) suggested a cis-diolefin-molybdenum complex as a reaction intermediate in disproportionation in a homogeneous molybdenum complex catalyst system, and discussed the application of the Woodward-Hoffmann rule, which explained theoretically the catalytic transformation of the bis-olefin complex to a cyclobutane structure. A similar explanation was made for the reaction on a solid catalyst13).

On the surface of the solid catalyst, it is considered that an active metal atom is coordinated with two olefin molecules to form a four membered carbon ring intermediate. In other words,
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among the tungsten or molybdenum atoms existing on the surface of the catalyst, what can be coordinated by two olefin molecules only may become an active site for olefin disproportionation. If the adsorption of olefin on such sites is in equilibrium and the formation of the four center intermediate is a rate controlling step, the disproportionation of propylene is expressed by the following:

\[
\begin{align*}
M + C_3H_6 & \rightleftharpoons M(C_3H_6) \\
M(C_3H_6) + C_3H_6 & \rightleftharpoons M(C_3H_6) _2 \\
M(C_3H_6) _2 & \rightarrow \text{four center intermediate} \\
\text{four center intermediate} & \rightarrow M + C_3H_6 + C_2H_4 \\
\text{four center intermediate} & \rightarrow M + 2C_2H_4
\end{align*}
\] (1)

where \( M \) is an active site for the disproportionation, \( K_1 \) and \( K_2 \) are the adsorption coefficients, \( k_1 \) is the surface reaction rate constant for the formation of the intermediate, \( k_2 \) and \( k_3 \) are the rate constants for the products and for the reactant respectively from the dissociation of the intermediate. Having resolved into several steps, \( k_2 \) and \( k_3 \) are expressed as one step for simplification. Then, the rate constant for the surface reaction to form ethylene and butene-2 is given by

\[ k = k_1 \left( \frac{k_2}{k_2 + k_3} \right) \] (2)

At the initial stage of the reaction, where the adsorption of the products may be neglected, if both of first and second step adsorptions of propylene on the active sites obey the Langmuir adsorption isotherms, the surface fraction of the active sites adsorbing two molecules, \( \theta \) is given by

\[ \theta = \frac{K_1 K_2 P_0^2}{1 + K_1 P_0 + K_1 K_2 P_0^2} \] (3)

where \( P_0 \) is the initial pressure of propylene. The initial rate of the reaction is therefore

\[ r_0 = k \theta = \frac{k K_1 K_2 P_0^2}{1 + K_1 P_0 + K_1 K_2 P_0^2} \] (4)

If the ratio of \( K_1 / K_2 \) is about 4 and the geometric mean of \( K_1 \) and \( K_2 \) is written as \( K \), Eq. (4) is simplified to

\[ r_0 = \frac{kK_2 P_0^2}{(1 + K P_0)^2} \] (5)

This is the same equation derived from a Langmuir-Hinshelwood mechanism for a bimolecular surface reaction.

In Eq. (4), if \( K_2 \) is sufficiently small, the term \( K_1 K_2 P_0^2 \) can be neglected in comparison with \( 1 + K_1 P_0 \), and the initial rate becomes

\[ r_0 = \frac{k K_1 K_2 P_0^2}{1 + K_1 P_0} \] (6)

which is none other than the equation based upon a Rideal mechanism.

3 Experimental

3.1 Catalysts and Material

The catalysts used had been prepared by impregnation methods in our laboratory. The contents of the promoters and the properties of the supports are shown in Table 1.

The catalysts had been crushed, sieved to 32-60 mesh, and stored in a P2O5-desicator. A molybdenum oxide-silica catalyst was also tested, but since it showed poor reproducibility, kinetic data on it were not obtained.

Propylene was of 99.0 mol% purity. Propane and ethane were the principal impurities. The propylene had been dried by active alumina before use.

3.2 Apparatus and Procedures

A closed recycle system was used for the reaction. The system consisted of a U-shaped quartz reactor and a glass piston pump. An evacuating system, three gas holders, and a gas chromatograph for the analysis of the products were attached to the system. The inner volume of the reaction system was 812 ml. An electric tubular heater for higher temperature and a jacket heater for lower temperature were employed, so that the rapid change of reactor temperature was achieved by means of changing the heaters. A 4 m

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Content of MoO3 or WO3 (wt%)</th>
<th>Support</th>
<th>SSA (m²/g)</th>
<th>ABD (g/cc)</th>
<th>Size (mesh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoO3-Al2O3</td>
<td>9</td>
<td></td>
<td>192</td>
<td>0.76</td>
<td>12~24</td>
</tr>
<tr>
<td>WO3-Al2O3</td>
<td>14.5</td>
<td></td>
<td>270</td>
<td>0.37</td>
<td>10~20</td>
</tr>
<tr>
<td>WO3-SiO2</td>
<td>5.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

SSA : specific surface area, ABD : apparent bulk density
dimethylformamide column was used at 0°C for the gas chromatography.

One series of the experiments was carried out on the same catalyst without replacement. The catalysts were regenerated and activated before each experiment. About 300 mmHg of air was introduced into the system through a silica gel dryer, and while the air was recycled, the reactor was heated for 1 hour at 500°C or 550°C, following which the system was evacuated for 5 hours at the same temperature. After activation of the catalyst the heaters were exchanged. When the desired temperature of the reactor was achieved, propylene was introduced into the system, but U-shaped reactor remained vacuous. The quantity of propylene was determined from its pressure and volume. Then, the recycle pump was turned on, and the reaction was started by the opening of the stop cocks of the reactor. Three samples of the reaction mixture were introduced into the gas chromatograph through the sampling cocks at the intervals of 10 or 15 min. in each experiment.

The initial rate for Eq. (7) is defined by Eq. (8), and calculated by Eq. (9)\textsuperscript{14}

\[ \text{[C}_3\text{H}_6\text{]} = \text{C}_3\text{H}_6 + \text{C}_4\text{H}_8 \quad (7) \]

\[ r_0 = -\frac{1}{2} \left( \frac{d\text{[C}_3\text{H}_6\text{]}}{dt} \right)_{t=0} \quad (8) \]

\[ r_0 = \frac{1}{2dt} \left( 3x_1 - 3 \frac{x_1}{2} + \frac{x_3}{3} \right) \quad (9) \]

where \([\text{C}_3\text{H}_6\text{]}) is moles of propylene per unit weight of the catalyst, \(\Delta t\) is the time interval of the sampling, and \(x_1\), \(x_2\), and \(x_3\) are the moles of propylene converted per unit weight of catalyst in the first, second, and third samples, respectively.

By means of the reaction under various recycle speeds on molybdenum oxide-alumina which was the most active among the catalysts used, it was ascertained that the external diffusion did not affect the reaction rate. In order to prevent the effects of diffusion in the pores, small particles (32~60 mesh) of the catalysts were used. The activities of the catalysts remained essentially constant through a series of experiments.

4 Results

4.1 Molybdenum Oxide-Alumina Catalyst

The weight of molybdenum oxide-alumina catalyst used was 0.128 g. The catalyst was regenerated and activated at 500°C because MoO\textsubscript{3} was apt to sublime. The data obtained are shown in Table 2.

Eq. (5) may be rewritten as

\[ \frac{p_0}{Vr_0} = \frac{1}{K\sqrt{k}} + \frac{1}{Vk} p_0 \quad (10) \]

Therefore, if the data are correlated by Eq. (5), a plot of \(p_0/Vr_0\) vs. \(p_0\) must be linear. The plots are shown as being linear in Fig. 1.

\[ K_{M} \text{ and } k_{M} \text{ (subscript } M \text{ expresses "for MoO}_{3-x}Al_{2-x}O_{x}\text{"} \) at each temperature are evaluated from Fig. 1, and shown in Table 3.

The temperature dependencies of \(K_{M}\) and \(k_{M}\) are illustrated in Fig. 2. The Arrhenius plot of the rate constants is linear in the temperature range of 40°C to 60°C, but the deviation at
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100°C is quite large. Internal diffusion may have been a cause for the deviation at the higher temperature. The following expressions are obtained from Fig. 2 in the range of 40°C to 60°C,

\[ K_{MA} = 2.73 \cdot \text{exp} \left[ \frac{820}{RT} \right] \text{atm}^{-1} \]  
(11)

\[ k_{MA} = 2.15 \times 10^2 \cdot \text{exp} \left[ -\frac{5.15}{RT} \right] \text{mol g-cat}^{-1} \text{hr}^{-1} \]  
(12)

where \( R \) is the gas constant, 1.987 cal/mol-deg, \( T \) is absolute temperature (°K), and the activation energy for the surface reaction is 5.15 kcal/mol.

### 4.2 Tungsten Oxide-Alumina Catalyst

The weight of the catalyst used was 0.205 g. It was regenerated and activated at 550°C. The reactions were carried out at temperatures of 140, 150, and 170°C and in the pressure range of 80 to 280 mmHg. The results are shown in Table 4.

The plots of \( p_0 \sqrt{r_0} \) vs. \( p_0 \), shown in Fig. 3, are linear for each temperature. Thus, it is apparent that the data obtained on the tungsten oxide-alumina catalyst are correlated by Eq. (5).

The values of \( K_{WA} \) and \( k_{WA} \) (subscript WA expresses "for WO₃-Al₂O₃") are evaluated from Fig. 3, and shown in Table 5. The plots of \( \log K_{WA} \) and \( \log k_{WA} \) vs. reciprocal of the absolute temperature are shown in Fig. 4, from which following expressions are derived.

### 4.3 Tungsten Oxide-Silica Catalyst

The weight of the catalyst used was 0.150 g. The catalyst was also regenerated and activated at 550°C. The results of the reaction are shown in Table 6.

The plots of \( p_0 \sqrt{r_0} \) vs. \( p_0 \), shown in Fig. 5, are linear for each temperature. Thus, it is apparent that the data obtained on the tungsten oxide-silica catalyst are correlated by Eq. (5).

The values of \( K_{WA} \) and \( k_{WA} \) (subscript WA expresses "for WO₃-Al₂O₃") are evaluated from Fig. 3, and shown in Table 5. The plots of \( \log K_{WA} \) and \( \log k_{WA} \) vs. reciprocal of the absolute temperature are shown in Fig. 4, from which following expressions are derived.

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**Table 3.** \( K_{MA} \) and \( k_{MA} \)

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>( K_{MA} ) (atm⁻¹)</th>
<th>( k_{MA} ) (mmol/g-cat-hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>10.2</td>
<td>54.9</td>
</tr>
<tr>
<td>50</td>
<td>9.75</td>
<td>71.8</td>
</tr>
<tr>
<td>60</td>
<td>9.42</td>
<td>89.8</td>
</tr>
<tr>
<td>100</td>
<td>8.28</td>
<td>122.1</td>
</tr>
</tbody>
</table>

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**Table 4.** Results Obtained on WO₃-Al₂O₃ Catalyst

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>( p_0 ) (mmHg)</th>
<th>Conversion of Propylene (( r_0 ))</th>
<th>( r_0 ) (mmol/g-cat-hr)</th>
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<tbody>
<tr>
<td>140</td>
<td>83.7</td>
<td>4.20</td>
<td>7.53</td>
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<tr>
<td>140</td>
<td>133.2</td>
<td>3.71</td>
<td>6.91</td>
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<tr>
<td>140</td>
<td>190.8</td>
<td>3.68</td>
<td>7.08</td>
</tr>
<tr>
<td>140</td>
<td>225.9</td>
<td>3.52</td>
<td>6.73</td>
</tr>
<tr>
<td>140</td>
<td>257.9</td>
<td>3.32</td>
<td>6.52</td>
</tr>
<tr>
<td>150</td>
<td>7.88</td>
<td>5.38</td>
<td>7.97</td>
</tr>
<tr>
<td>150</td>
<td>132.9</td>
<td>5.55</td>
<td>10.1</td>
</tr>
<tr>
<td>150</td>
<td>182.0</td>
<td>5.24</td>
<td>8.88</td>
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<tr>
<td>150</td>
<td>230.9</td>
<td>4.60</td>
<td>8.55</td>
</tr>
<tr>
<td>150</td>
<td>279.5</td>
<td>4.54</td>
<td>8.83</td>
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<tr>
<td>170</td>
<td>85.6</td>
<td>9.01</td>
<td>14.5</td>
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<td>170</td>
<td>153.9</td>
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<td>15.6</td>
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<td>170</td>
<td>210.2</td>
<td>9.76</td>
<td>16.1</td>
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<td>170</td>
<td>241.9</td>
<td>8.36</td>
<td>14.5</td>
</tr>
<tr>
<td>170</td>
<td>281.8</td>
<td>8.60</td>
<td>15.5</td>
</tr>
</tbody>
</table>

---

**Table 5.** \( K_{WA} \) and \( k_{WA} \)

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>( K_{WA} ) (atm⁻¹)</th>
<th>( k_{WA} ) (mmol/g-cat-hr)</th>
</tr>
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<tbody>
<tr>
<td>140</td>
<td>9.57</td>
<td>6.07</td>
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<tr>
<td>150</td>
<td>9.02</td>
<td>8.82</td>
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<tr>
<td>170</td>
<td>7.06</td>
<td>20.5</td>
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</table>

**Table 6.** Results Obtained on WO₃-SiO₂ Catalyst

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>( p_0 ) (mmHg)</th>
<th>( r_0 ) (mmol/g-cat-hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>140</td>
<td>8.28</td>
<td>122.1</td>
</tr>
<tr>
<td>150</td>
<td>13.49</td>
<td>233.1</td>
</tr>
<tr>
<td>170</td>
<td>18.74</td>
<td>344.2</td>
</tr>
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</table>

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**Fig. 2.** Temperature Dependency of \( K_{MA} \) and \( k_{MA} \)

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**Fig. 3.** Plots of \( p_0 \sqrt{r_0} \) vs. \( p_0 \), WO₃-Al₂O₃ Catalyst

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**Fig. 4.** Plots of \( \log K_{WA} \) and \( \log k_{WA} \) vs. reciprocal of the absolute temperature

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**Fig. 5.** Plots of \( p_0 \sqrt{r_0} \) vs. \( p_0 \), WO₃-SiO₂ Catalyst

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**Fig. 6.** Temperature Dependency of \( K_{WA} \) and \( k_{WA} \)
220°C, the deviation is considerable, and the plot cannot be recognized as being straight. If the data are correlated by Eq. (6), the plots of $p_0^2/r_0$ vs. $p_0$, WO$_3$-SiO$_2$ Catalyst would be linear, but as shown in Fig. 6, the plots are not linear. Moreover, even if the plots would be regarded as being linear, they intersect the abscissa at the lower temperatures, and the values of $K_1$ would become negative. Thus, the data are not correlated by the Rideal mechanism.

The relations of $\log r_0$ to $\log p_0$ are shown in Fig. 7, which shows linear correlations. This fact may be evidence that the adsorption of propylene on the active sites of the WO$_3$-SiO$_2$ catalyst obeys the Freundlich equation

$$v = ap^{1/n}$$  \hspace{1cm} (15)

where $v$ is the adsorption amount, $a$ and $n$ are constants; it suggests that the active sites are not uniform.

As described above, the initial rates on the
Disproportionation of Propylene

Table 7  $K_{WS}$ and $k_{WS}$

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>$K_{WS}$ (atm$^{-1}$)</th>
<th>$k_{WS}$ (mmol/g-cat·hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>23.7</td>
<td>4.36</td>
</tr>
<tr>
<td>200</td>
<td>10.0</td>
<td>15.5</td>
</tr>
<tr>
<td>220</td>
<td>6.22</td>
<td>30.9</td>
</tr>
</tbody>
</table>

Fig. 8 Temperature Dependency of $K_{WS}$ and $k_{WS}$

MoO$_3$-Al$_2$O$_3$ catalyst and on the WO$_3$-Al$_2$O$_3$ catalyst were correlated by Eq. (5). In the case of the WO$_3$-SiO$_2$ catalyst, in the pressure region lower than about 200 mmHg, the plots in Fig. 5 may be regarded as being linear. From the straight lines in this region, $K_{WS}$ and $k_{WS}$ (subscript WS expresses “for WO$_3$-SiO$_2$”) are evaluated. The values of $K_{WS}$ and $k_{WS}$ are shown in Table 7, and their temperature dependencies are illustrated in Fig. 8.

The following expressions are obtained from Fig. 8.

$$K_{WS} = 1.96 \times 10^{-1} \exp\left[\frac{7,960}{RT}\right]$$

$$k_{WS} = 3.57 \times 10^{2} \exp\left[-\frac{11,500}{RT}\right]$$

5 Discussion

As described above, the initial rates of catalytic disproportionation of propylene may be accounted for in terms of a Langmuir-Hinshelwood equation. The facts show that the assumption that the ratio of $K_1$ to $K_2$ is about 4 is not a great error, though it is impossible to show that the ratio is very close to 4, since the ranges of experimental conditions have been comparatively narrow. Nakamura et al. have assumed that the rate of olefin disproportionation is given by

$$R = \frac{kK_1K_2[S]^2[C]}{1 + 2K_1[S] + K_2[S]^2}$$

where $[S]$ and $[C]$ are the concentrations of olefin and catalyst respectively. If $K_1$ is equal to $K_2$, Eq. (18) is simplified to the same type as Eq. (5). However, the reason why $K_1[S]$ is doubled in Eq. (18) seems ambiguous. It is more acceptable that $K_1/K_2$ should be about 4 than that $K_1$ equals $K_2$.

The data with the MoO$_3$-Al$_2$O$_3$ catalyst and the WO$_3$-Al$_2$O$_3$ catalyst as well as the data with a CoO-MoO$_3$-Al$_2$O$_3$ catalyst by Lewis et al. are correlated by the Langmuir-Hinshelwood equation, but the results on the WO$_3$-SiO$_2$ catalysts have deviated somewhat from the equation, both in the case of Begley et al. and ourselves. In order to explain the deviation Begley et al. have assumed a Rideal mechanism, but some problems still remain. In the present study, it is assumed that the adsorption of propylene obeys the Freundlich equation, however there is no certain basis for this.

Recently Moffat et al. pointed out the interphase mass transfer effects in propylene disproportionation with WO$_3$-SiO$_2$ catalysts. They have considered that the effects, although unexpected by classical consideration, can be explained by assuming that a small number of very active sites are widely separated on the catalyst surface and, hence, the reaction is limited by site-localized diffusion effects. The unusual kinetic data on the WO$_3$-SiO$_2$ catalysts may depend upon such mass transfer effects; these have not been examined in the present study.

The apparent activation energy estimated from the plot of the rate constants on the CoO-MoO$_3$-Al$_2$O$_3$ catalyst is about 3.5 kcal/mol. Clark et al. determined the value to be 7.7 kcal/mol on a similar catalyst. These values agree with the value obtained on the MoO$_3$-Al$_2$O$_3$ catalyst. The low apparent heat of adsorption on the MoO$_3$-Al$_2$O$_3$ is probably related to its high sensitivity to catalyst poison. Begley et al. determined the apparent activation energies to be 21.6 and 18.6 kcal/mol on WO$_3$-SiO$_2$ catalysts, and Moffat et al. obtained the values of 37-59 kcal/mol. Although the experimental conditions and assumed reaction mechanisms have been different, these values are considerably higher than the value in the present study.

The compensation effect, though it is not very accurate, is recognized between the frequency factors and the activation energies in the rate constants obtained. This suggests that the
reaction proceeds by essentially the same surface reaction mechanism in spite of the differences of promoters and supports.

References