Dehydrogenation of Ethane to Ethylene via Radical Pathways Enhanced by Alkali Metal Based Catalyst in Oxysteam Condition

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The oxidative dehydrogenation (ODH) of ethane to ethylene in the presence of oxygen and water was conducted using Na2WO4/SiO2 catalyst at high temperatures. At 923 K, the conversion rate without water was proportional to ethane pressure and a half order of oxygen pressure, consistent with a kinetically relevant step where an ethane molecule is activated with dissociated oxygen on the surface. When water was present, the ethane conversion rate was drastically enhanced. An additional term in the rate expression was proportional to a quarter of the oxygen pressure and a half order of the water pressure. This attainable yield can be accurately described by taking the water contribution into consideration. At high conversion levels at 1073 K, the C2H4 yield exceeded 60% in a single-pass conversion. The C2H4 selectivity was almost insensitive to the C2H4 and O2 pressures. © 2016 The Authors AIChE Journal published by Wiley Periodicals, Inc. on behalf of American Institute of Chemical Engineers AIChE J, 63: 105–110, 2017

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Introduction

The oxidative dehydrogenation (ODH) of ethane to ethylene has some advantages over the non-oxidative counterpart because of the higher expected rates and fewer thermodynamic constraints.1 Detailed information of this catalytic reaction can be found in excellent review articles in the literature.2–6 The attainable yields are largely associated with the reactivity of oxygen species, which activates the C–H bonds of ethane and ethylene at different rates. The ethylene selectivity decreases with increasing ethane conversion because of the competitive ethylene oxidation to COx as a secondary reaction when the ethylene concentration increases. There are basically two types of catalysts: redox catalysts (mainly V- or Mo-based catalysts) and alkali-metal (halide) catalysts.5 In particular, when an alkali-metal catalyst is used (mainly Li-based catalysts),7 it is proposed that a complex reaction mechanism is involved, where the catalytic surface participates in radical formations in homogeneous gas phase reactions.

A similar heterogeneous (surface)-homogeneous (gas-phase) reaction pathway has been discussed during the oxidative coupling of methane (OCM).8–14 Our previous works on alkali-metal-based catalysts show the beneficial effects of water to improve the OCM rate and C2 selectivity.15–17 This water effect is exceptionally unique for Na2WO4/SiO2 catalysts, with which notably high OCM attainable yields have been reported (C2+ yields >25%).17 In the absence of water, the rates were proportional to PCH4P0.5O2.17 When H2O is present, the methane conversion rates were proportional to P0.25O2P0.5H2O consistent with the quasi-equilibrated OH radical formation from the O2–H2O mixture, which in turn subtracts hydrogen from CH4.18 Identical kinetics was obtained in both a recirculating-batch reactor and a fixed-bed reactor,14–17 which validates the obtained rate expressions. The selective OCM catalyst in this series of catalysts is required to paradoxically catalyze H2O instead of CH4 on the surface.

Kinetic analyses on the Na2WO4/SiO2, Na2WO4/Al2O3, K2WO4/SiO2, Na2MoO4/SiO2, and Na2CO3/SiO2 OCM catalysts suggest that Mn, W, Mo, and SiO2 are not essential to give water activation but alkali metals are.17 This result suggests that the redox properties of specific oxides (such as Mn) do not play an important role, but alkali metal peroxide-like intermediates are expected to be involved. For example, the presence of Mn in the catalyst component improves the OCM rate because it mildly combusts CH4 to generate H2O, which subsequently selectively catalyzes to produce C2.17 Such metals are not required if the water is co-fed to make an oxysteam condition. It should be noted that many alkali-metal-based salts such as Na2WO4 melt on the catalyst surface during high-temperature reactions because the melting point of the alkali salt is lower than the OCM reaction temperature. This melting makes the support material sinter (e.g., cristobalite formation in the case of SiO2),17 which reduces the surface area of the catalyst, prevents the bare support and/or impurity surface from exposure, and suppresses the combustion that is prevalent for the high-temperature reaction.17

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This study is an extension of the unique water effects that were found during the OCM to apply to the ODH of ethane. Therefore, the reaction is expected to proceed in radical homogeneous pathways. In this study, we intend to introduce the similar kinetic contribution of water in homogeneous gas phase reactions that are induced by the Na2WO4/SiO2 catalyst. The enhancement in rate by water was observed, which is consistent with the additional water term in the rate expression to convert hydrocarbons. This rate expression will provide new insight into the ODH reaction mechanism and an accurate description of the attainable ODH yield.

**Experimental**

For the catalyst preparation, SiO2 (Sigma-Aldrich, Silica Gel, Davasil Grade 646, 35–60 mesh) was used as a support to immobilize 10 wt % Na using Na2WO4·2H2O (Sigma-Aldrich, 99%) via wet impregnation. This sample was heated under a dry air flow at 1173 K for 8 h at a rate of 2 K min⁻¹.

The rates and selectivities of the CH₄–O₂–H₂O reactions were measured in flow reactors using a U-shaped quartz cell (4-mm I.D.). The samples (0.8 g) were held onto quartz wool without dilution and almost completely filled in the heated zone. The temperature was maintained using a Honeywell controller, which was coupled to a resistively heated furnace, and measured with a K-type thermocouple set outside the catalyst bed. C₂H₆ (99.995%), 20% O₂ in He, and He (99.999%) were purchased from Abdullah Hashim Industrial Gases & Equipment (AHG) and used after further purifying via filtration. The flow was regulated with mass flow controllers. A saturator with a well-controlled temperature (278–293 K) was used to introduce the H₂O gas.

The reactant and product concentrations were measured using a VARIAN gas chromatograph 450GC with a programmed system. This programmed system involves a molecular sieve 5A column, a HayeSep Q column with a thermal conductivity detector, and a VARIAN CP-Wax 52 CB capillary column with a flame ionization detector. This configuration enables the distinction of all C₁–C₄ hydrocarbons. The conversion, selectivities and yields are reported on a carbon basis as cumulative integral values as follows:

\[
X_{C_2H_6} (\%) = \frac{(\text{total mols of carbon in products})}{(\text{total mols of } C_2H_6 \text{ in})} \times 100
\]

or

\[
X_{C_2H_6} (\%) = \frac{(\text{total mols of carbon in products})}{(\text{total mols of carbon out incl. } C_2H_6)} \times 100
\]

\[
S_{C_2H_6} (\%) = \frac{(\text{mols of carbon in the specific product})}{(\text{total mols of carbon in products})} \times 100
\]

\[
Y_{C_2H_6} (\%) = X_{C_2H_6}(\%) \times S_{C_2H_6}(\%) / 100
\]

For rigorous kinetic analyses, linear regression was used to extrapolate the rates that were measured at various conversions to the rates at zero conversion. The obtained rates at zero conversion strictly reflect the input conditions with the given reactant pressures, which minimizes the contribution of the generated heat by the reaction at low conversion levels. The carbon balance was always close to unity during our measurements, suggesting that no carbon deposition or no formation of condensable products was observed.

The N₂ sorption studies were conducted using a Micromeritics ASAP 2420 to determine the Brunauer–Emmett–Teller (BET) surface area. Inductively coupled plasma (ICP) measurements were performed using an Agilent 720 Series ICP-OES instrument (Agilent Technologies). The material was digested in an ETHOS 1 microwave digestion system (Milestone Srl).

**Results and Discussion**

First, the Na2WO4/SiO2 catalyst was treated at 1173 K under flowing air for extended time. This treatment before ODH was found to be critical to achieve high selectivity to C₂H₄ from C₂H₆. The melting point of Na2WO4 is 971 K, which is substantially lower than this treatment temperature; the molten salt was generated, and excess salt was eluted to be ~4 wt % of Na. It is considered that the molten state generated at high temperature will decorate the surface of the non-selective sites and facilitate the crystal transformation of SiO₂ to the cristobalite phase. The catalyst with the resultant low surface area of ~5 m² g⁻¹ became stable for at least a week during the continuous kinetic measurements, which are reported below. Consistently, no loss of Na or surface area was measured before and after the kinetic analyses.

The effect of the water pressure on the C₂H₆ conversion rates using the Na2WO4/SiO2 catalyst at 923 K is evident in Figure 1A, where the rates are plotted as a function of residence time. The C₂H₆ conversion rate increased monotonically with the addition of water into the reactant stream. Figure 1B shows the corresponding C₂H₄ selectivity as a function of the C₂H₆ conversion. In all cases, the C₂H₄ selectivity was maintained high, and it was greater than 97% when the C₂H₆ conversion was ~5%. The measured products were CO₂ and CO (<2%), with minor hydrocarbon products of CH₄ (<1.5%), C₃H₆ (<0.05%), and n-C₄H₈ (<0.1%).

Considering this strong effect of the water pressure on the rates, kinetic analyses using the zero-conversion rates (rates extrapolated to zero conversion) were conducted to isolate the rates in the absence and presence of water. The partial pressure dependencies for C₂H₆ and O₂ on the C₂H₆ conversion rates are shown in Figures 2A, B. These figures show that the zero-conversion rates for C₂H₆ conversion in the absence of water were first order in C₂H₆ pressure and half order in O₂ pressure. The mechanism is consistent with the reaction of dissociated oxygen (reaction 1) with the C₂H₆ molecule, which is a kinetically relevant step (reaction 3), and is similar to the reported kinetics for CH₄ activation:\(^3\):

\[
2* + O_2 \xrightarrow{K_{O_2}} 2O(s) \quad (1)
\]

\[
s + C_2H_6 \xrightarrow{K_{C_2H_6}} C_2H_4(s) \quad (2)
\]

\[
C_2H_6(s) + O(s) \xrightarrow{k_{C_2H_6}} C_2H_5 + OH(s) + * \quad (3)
\]

where * and (s) indicate the empty surface site and surface species, respectively. The recombination of hydroxyls to generate H₂O is omitted from the scheme, which occurs after the kinetically relevant step. Next, Figure 1A shows that the presence of water drastically enhances the ODH rate. The incremental rate in the presence of water compared to that without water has a pressure dependency of \(P_{O_2}^{0.4}/P_{H_2O}^{0.5}\), as shown in Figure 3, which is consistent with the kinetically relevant mechanism of the quasi-equilibrated OH radical formation (reaction 4) and subsequent C–H bond activation of C₂H₆ (reaction 5).

\[
O_2 + 2H_2O \xrightarrow{P_{O_2}^{0.4}/P_{H_2O}^{0.5}} 4OH^- \quad (4)
\]

\[
C_2H_6 + OH^- \xrightarrow{k_{C_2H_6}} C_2H_5 + H_2O \quad (5)
\]

Thus, the overall rate can be described as...
In our previous study, we found that alkali metal is the essential component for the water term in the rate expression. We propose that the Na peroxide species is the critical component during the catalytic cycles, which was originally separately proposed for OCM by Otsuka et al. The difference of this study from the literature is that Na$_2$O$_2$ activates H$_2$O instead of CH$_4$:

$$2Na_2O_2(s) + H_2O \rightarrow 2Na_2O_2H_2O$$

In reaction 8, Na$_2$O$_2$ activates H$_2$O to generate the H$_2$O$_2$ species either on the surface or in the gas phase, and the generated H$_2$O$_2$ decomposes to form OH radicals (reaction 9). The significance of H$_2$O on the ODH rate suggests that the catalyst can preferentially activate H$_2$O compared to C$_2$H$_6$. It is reasonable to consider that H$_2$O has a higher adsorption capability than C$_2$H$_6$ does. In other words, the rate constants $k'$ and $k''$ in Eq. 6 have the term of adsorption of the reactant ($K_{C_2H_6}$ and $K_{H_2O}$ in reactions 2 and 7), which may account for this difference. It is reasonable to consider adsorption before the bond activation because the O–H bond in H$_2$O (497 kJ mol$^{-1}$) is stronger than the C–H bond in C$_2$H$_6$ (423 kJ mol$^{-1}$) and C$_2$H$_4$.

In our previous study, we found that alkali metal is the essential component for the water term in the rate expression. We propose that the Na peroxide species is the critical component during the catalytic cycles, which was originally separately proposed for OCM by Otsuka et al. The difference of this study from the literature is that Na$_2$O$_2$ activates H$_2$O instead of CH$_4$:

$$2Na_2O_2(s) + O_2 \rightarrow 2Na_2O_2(s)$$

(Figure 2. Zero C$_2$H$_6$ conversion rate as a function of the (A) C$_2$H$_6$ pressure and (B) O$_2$ pressure (923 K, Na$_2$WO$_4$/SiO$_2$ 0.8 g).)

Figure 1. (A) C$_2$H$_6$ conversion rate as a function of the residence time at various H$_2$O pressures and (B) C$_2$H$_4$ selectivity as a function of the C$_2$H$_6$ conversion at various H$_2$O pressures and residence time (923 K, Na$_2$WO$_4$/SiO$_2$ 0.8 g, C$_2$H$_6$ 10 kPa, O$_2$ 1.7 kPa, H$_2$O 0–2.3 kPa).
activate the C–H bond even in CH₄ below 673 K and generate methyl radicals. For the OH radical pathway, the enthalpy ΔH₀ of the quasi-equilibrated steps of OH radical formation (reaction 4) is 650 kJ mol⁻¹. The reported activation energy Eₐ,OH for the H-abstraction by OH radical from C₂H₆ (reaction 5) at 923 K is ~4 kJ mol⁻¹:

\[ E_{a,app}^{OH} = E_{a,OH} + \frac{1}{4} \Delta H_{OH} \]  

The expected apparent activation energy is ~167 kJ mol⁻¹, which is close to the measured value of 181 kJ mol⁻¹.

The attainable yield in a single-pass reactor was investigated by increasing the temperature to 1073 K as a set temperature, and H₂O was co-fed into the C₂H₆/O₂ mixture. Here, we did not attempt to isolate the surface kinetic pathways or avoid exotherms from the reaction; instead, we attempted to achieve high conversions in a single pass with concurrent homogeneous gas-phase pathways. Figures 5A, B show the C₂H₄ selectivity and yield, respectively, as a function of C₂H₆ conversion. The reaction conditions were 1073 K, 5–20 kPa C₂H₆, 2.3 kPa H₂O, and C₂H₆/O₂ = 1–6, and four different space velocities were set to vary the conversion. High C₂H₄ selectivity ~90% was achieved up to nearly 50% C₂H₆ conversion. Further increase in conversion reduced the C₂H₄ selectivity obviously because of the secondary reaction of C₂H₄, which is combusted to form CO and CO₂ (where CO selectivity > CO₂ selectivity in the investigated conditions). Under the investigated conditions, the highest C₂H₄ yield of ~61% was experimentally achieved at the C₂H₆ conversion of 82%, whose yield value is among the highest for single-pass conversions. The trend lines of the selectivity and yield in Figures 5A, B are based on the pseudo-first-order rate constants of the scheme, which is described in the figures, where the ratios of rate constants are k₂/k₃ = 0.28 and k₄/k₅ = 0.02.

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Reactions 15 and 16 show that the C₂H₄ conversions use identical oxidants (O(s) or OH•) to the C₂H₆ conversions.
(reactions 3 and 5). Thus, we consider that the oxygen membrane does not help improve the C₂H₄ selectivity but may benefit by controlling the reaction rate and resultant exotherms. It is worth noting that in the previous study, a high H₂O/O₂ ratio made the O₂ chemisorption step kinetically relevant for OCM.¹⁶ This argument should be applicable for ODH; however, the oxidant to activate the C–H bond in C₂H₆ and C₂H₄ is similar in this kinetic regime, which should not drastically perturb the selectivity.

The overall attainable yield was determined based on the ratio of rate constants $k_{2}/k_{1}$ in the pseudo-first-order scheme in Figures 5A, B. Because $k_{3}/k_{1}$ is negligibly small, we simplified $k_{2}/k_{1}$ to be the ratio of the overall conversion rate constants of C₂H₆ and C₂H₄ ($k_{C₂H₆}/k_{C₂H₄}$), i.e., the relative C–H bond activation for C₂H₆ vs. C₂H₄. The adsorption of hydrocarbons on the surface may affect the rate if the surface reaction pathway with adsorbed hydrocarbon species is involved in the reaction (compare reactions 2 and 14). C₂H₄ is expected to have a larger adsorption coefficient than C₂H₆ because C₂H₄ contains π-electrons ($K_{C₂H₄} > K_{C₂H₆}$, although experimental values are not available for the relevant catalyst surface). This difference accounts for the rapid combustion on the surface of C₂H₄ relative to C₂H₆, particularly when there is an acid site on the surface. The OH radical pathway in the gas phase is essentially beneficial to improve the C₂H₄ yield if the preferential adsorption of C₂H₄ as an unsaturated hydrocarbon is avoided. In homogeneous gas phase reactions, the rate constants of C₂H₆ and C₂H₄ activation are reported with various H-abstractors. Table 1 shows the rate constants and their ratios of representative reactants (O₂, OH, O, H) to activate the C–H bond from C₂H₆ and C₂H₄ at 923 and 1073 K.²² In all cases, C₂H₆ reacts more rapidly than C₂H₄, which apparently reflects the weaker C–H bond energy (C₂H₆: 423 kJ mol⁻¹, C₂H₄: 463 kJ mol⁻¹).²⁰ Generally, a weaker H-abstractor gives a higher $k_{C₂H₄}/k_{C₂H₆}$ ratio.¹⁵ The OH radical is one of the strongest H-abstractors, so it has a relatively high $k_{C₂H₄}/k_{C₂H₆}$ ratio of 0.37, which is not drastically perturbed with the change in reaction temperature (Table 1). The measured $k_{C₂H₄}/k_{C₂H₆}$ ratio of 0.28 during the ODH is close to this value, but the lower value certainly implies that the weaker H-abstractor is likely involved, which slightly reduces $k_{C₂H₄}/k_{C₂H₆}$. It is re-emphasized that the selective catalyst for the ODH of C₂H₆ to C₂H₄ should make less reactive O species without inducing a preferential adsorption of unsaturated hydrocarbon (C₂H₄) over saturated hydrocarbon (C₂H₆).

This study demonstrates detailed kinetic analyses and provides accurate description of the attainable product yield for a relatively high-temperature ODH of ethane reaction that involves radical chemistry. The unique characteristic of the Na-based catalyst (Na₂WO₄/SiO₂) is the large increase in C₂H₆ rates because of water, whose kinetics is consistent with the quasi-equilibrated formation of OH radicals and subsequent C–H bond activation of C₂H₆. Our careful kinetic analyses in this study suggest new insights to unite some discrepancies in the literature of the active sites and mechanistic aspects.

![Figure 5](image.png)

Table 1. Rate Constants and Their Ratio of C–H Bond Activation Using Various H-Abstractors for C₂H₆ and C₂H₄ at 923 and 1073 K²²

<table>
<thead>
<tr>
<th>H-abstractor</th>
<th>Hydrocarbon</th>
<th>$k$ at 923 K</th>
<th>$k_{C₂H₄}/k_{C₂H₆}$</th>
<th>$k$ at 1073 K</th>
<th>$k_{C₂H₄}/k_{C₂H₆}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>C₂H₆</td>
<td>$1.37 \times 10^{11}$</td>
<td>0.20</td>
<td>$3.53 \times 10^{13}$</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>C₂H₄</td>
<td>$2.37 \times 10^{10}$</td>
<td></td>
<td>$8.30 \times 10^{10}$</td>
<td></td>
</tr>
<tr>
<td>OH</td>
<td>C₂H₆</td>
<td>$6.11 \times 10^{12}$</td>
<td>0.36</td>
<td>$8.54 \times 10^{12}$</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>C₂H₄</td>
<td>$2.21 \times 10^{12}$</td>
<td></td>
<td>$3.13 \times 10^{12}$</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>C₂H₆</td>
<td>$2.11 \times 10^{3}$</td>
<td>0.15</td>
<td>$3.13 \times 10^{3}$</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>C₂H₄</td>
<td>$3.24 \times 10^{3}$</td>
<td></td>
<td>$4.29 \times 10^{3}$</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>C₂H₆</td>
<td>$1.86 \times 10^{3}$</td>
<td>0.46</td>
<td>$2.83 \times 10^{3}$</td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td>C₂H₄</td>
<td>$8.54 \times 10^{2}$</td>
<td></td>
<td>$1.56 \times 10^{3}$</td>
<td></td>
</tr>
</tbody>
</table>
Conclusions

Our rigorous kinetic analyses for the ODH of C2H6 using the Na2WO4/SiO2 catalyst unveil a predominant reaction pathway and a quantitative, mechanism-based description of the attainable C2H4 yield. The incremental rates for C2H6 conversion that are introduced by the presence of H2O are consistent with the mechanism of quasi-equilibrated OH radical formation and subsequent C–H bond activation of C2H6 as a kinetically relevant step. The C2H4 selectivity was insensitive to the C2H6 and O2 pressures, which universally describes the attainable yield by ratios of pseudo-first-order rate constants in hydrocarbons. The measured ratio of rate constants ($k_{C2H4}/k_{C2H6}$) was 0.28; the high C2H4 selectivity was $\sim$90% at 50% C2H6 conversion, and the maximum C2H4 yield was $\sim$61% at the C2H6 conversion of 82%. This study demonstrates the unique but consistent kinetic data for selective dehydrogenation reaction using radical reactions that are initiated by the catalyst surfaces. This information is benchmarking for similar hydrocarbon transformations using alkali-metal-based catalysts.

Acknowledgment

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Literature Cited