Kinetics of ethylene combustion in the synthesis of vinyl acetate over a Pd/SiO₂ catalyst

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Abstract

The kinetic parameters of ethylene combustion in the presence of acetic acid, i.e., during the synthesis of vinyl acetate and in the absence of acetic acid, have been measured in the temperature range 413–453 K over Pd supported on a high surface area SiO₂ (600 m²/g) at pressures ranging from 5.0 to 15.0 kPa of C₂H₄ and 1.0 to 10.0 kPa of O₂. CO₂ formation as a function of the partial pressures of C₂H₄ and O₂ exhibited a negative reaction order with respect to C₂H₄ and a positive order with respect to O₂. The kinetic parameters of ethylene combustion in the presence and absence of acetic acid were essentially the same, consistent with ethylene combustion being primarily responsible for CO₂ formation in the synthesis of vinyl acetate from ethylene and acetic acid over unpromoted Pd within the pressure regime investigated.

Keywords: Ethylene combustion; Vinyl acetate synthesis; Reaction kinetics; Pd/SiO₂ catalyst

1. Introduction

The synthesis of vinyl acetate (VA) from ethylene, acetic acid (ACOH), and oxygen over Pd-based catalysts is an important industrial process [1]. The reaction occurs ideally as

\[ \text{C}_2\text{H}_4 + \text{CH}_3\text{COOH} + \frac{3}{2}\text{O}_2 \rightarrow \text{C}_2\text{H}_3\text{OOCCH}_3 + \text{H}_2\text{O} \]  

However, CO₂ production via combustion of ethylene and/or acetic acid [2] lowers the selectivity.

Previous work has shown that the synthesis of VA depends upon several factors [2] including Pd dispersion, partial pressures of reactants, catalyst additive(s), and contact time. VA selectivities as low as 80% have been observed over a Pd/SiO₂ catalyst [2], whereas selectivities as high as 94% have been measured for Pd–Au/SiO₂ catalysts [1]. Obviously a key to improvement in selectivity to VA is an understanding of the origin and mechanism of CO₂ formation.

Although the kinetics of VA synthesis has been addressed [2–4], the relative contributions to the CO₂ product by ethylene and acetic acid remain in dispute. Some three decades ago, Samanos et al. [3], reported no differences in the apparent activation energies measured for ethylene combustion in the presence and absence of AcOH over unpromoted Pd/SiO₂ and Pd/Al₂O₃ catalysts and concluded that CO₂ was formed primarily from ethylene. For unsupported Pd, Pd/Al₂O₃, and alkali-promoted Pd/Al₂O₃ catalysts, Nakamura and Yasui [4] concluded that CO₂ is produced mainly via oxidation of C₂H₄. More, recently in the most comprehensive study of VA synthesis to date, Crathorne et al. [2], using isotopic transient kinetics and Pd/Cd/SiO₂/K⁺ and Pd/Au/SiO₂/K⁺ catalysts, concluded that CO₂ was derived equally from ethylene and acetic acid.

In the work reported here, the kinetic parameters for ethylene combustion in the synthesis of VA have been measured over an unpromoted Pd catalyst supported on a high surface area SiO₂ (600 m²/g) as a first step in a comprehensive study of VA synthesis over catalysts ranging from supported Pd and Pd/Au to Pd and Pd/Au single crystals. Specifically this study addresses the reaction of ethylene (5.0–15.0 kPa) with O₂ (1.0–10.0 kPa) in the presence and absence of acetic acid (AcOH, 2.0 kPa) and vinyl acetate (2.0–3.5 kPa) between 423 and 453 K. By fixing either the partial pressure of ethylene or oxygen, the reaction orders with respect to oxygen and ethylene were measured with differential flow and with the ethylene conversion maintained at less than 5%. For comparison, experiments were carried out under similar con-
conditions with and without AcOH. A model is developed that explains these kinetics as well as previous data for ethylene combustion over a Pd single-crystal surface [5–7].

2. Experimental

2.1. Catalyst preparation and reaction conditions

The kinetic measurements were carried out over a Pd (5 wt%)/SiO2 catalyst prepared by the incipient wetness method. High surface area SiO2 (Aldrich No. 7631-86-9) with a surface area of 600 m2/g, a particle size of 230–400 mesh, and a pore volume of 1.1 ml/g was used. A Pd2+ solution was first prepared by dissolving Pd(NO3)2 (C.P., commercial source) into deionized water. The Pd2+ solution was then added with an equal volume of SiO2 powder. The impregnated catalyst was allowed to stand for approximately 4 h in a covered beaker. The precursor was dried extensively under vacuum at 393 K prior to use. N2, C2H4, O2 (10%/N2), and air (Messer MG Industries) were purified with gas filters (Chrompack) to remove trace amounts of water, oxygen, and hydrocarbon. Partial pressures of AcOH were maintained by bubbling N2 through a AcOH (Aldrich C.P.) bath at a preset and regulated temperature.

2.2. Catalyst characterization

2.2.1. X-ray diffraction (XRD)

X-ray powdered diffraction data were obtained with a Bruker D8 diffractometer using Cu-Kα radiation. The samples were scanned over the 2θ range from 30 to 75° in either 0.2 or 0.4° steps. Pd particle sizes were estimated using the Scherrer formula [8],

\[ D = \frac{k\lambda}{\Delta \cos \theta}, \]

where \( \lambda \) (0.15 nm) is the wavelength of the X-rays, \( k \) is a constant (0.94), \( \theta \) is the Bragg angle of the peak maximum, and \( \Delta \) is the full width at half-maximum (FWHM).

2.2.2. Transmission electron microscopy (TEM)

Pd(5 wt%)/SiO2 were ultrasonically dispersed in an ethanol solvent and then dried over a carbon grid. The Pd were imaged using a Jeol 2010 microscope; at least 200–300 particles were measured to obtain the average particle-size distributions reported.

2.2.3. X-Ray photoelectron spectroscopy (XPS)

XPS measurements were performed using a XPS-5500 Perkin-Elmer spectrometer. The samples were pressed onto an indium foil (Aldrich) and high-resolution scans carried out using a Mg-Kα source and a pass energy of 58.7 eV. The signal from the Si (2p) feature at 103.1 eV, present in all measurements, was used as a reference. The C(1s) was acquired after all surface contaminants were removed by ion sputtering (PHI Model 11-065 ion gun) for 30 min with a beam voltage of 3.4 kV.

2.3. Catalytic activity

The catalytic activity was measured in a conventional-flow quartz tube reactor with 0.8 cm inner diameter and a catalyst bed of approximately 1.0–1.6 g (2–3 cm length) at atmospheric pressure. The reactor temperature was regulated with an Omega temperature controller. The reactants and products were analyzed by an online gas chromatograph (GC, HP 5890). A HayeSep-R column (80/100 mesh, 2 m) and a flame ionization detector (FID) were used to detect VA and AcOH; a Porapak column (RT, 80/100 mesh, 1.5 m), with a thermal conductance detector (TCD), was used to measure CO2, C2H4, and mixtures of O2 and N2. The gasflow rates were controlled by mass-flow meters.

Prior to use, the catalysts were conditioned by calcination in a 10% O2/N2 mixture at 673 K (30 min, 20 Nml/min), followed by reduction in 100% H2 at 573 K. Subsequently the reactor was cooled to reaction temperature in N2. Reaction kinetics of ethylene (5.0–15.0 kPa) with O2 (1.0–10.0 kPa) in the presence and absence of acetic acid (AcOH, 2.0 kPa) and vinyl acetate (2.0–3.5 kPa) were measured between 423 and 453 K. The kinetic measurements were performed under differential flow conditions, with the conversion of ethylene maintained below 5%. VA combustion was carried out in a mixture of VA (2.0–3.5 kPa) + O2 (1.0–10.0 kPa) and C2H4 (7.5 kPa) + VA (3.5 kPa) + O2 (10.0 kPa). In the absence of C2H4, CO2 was not detected at 413 K; however, combustion increased significantly at temperatures greater than 433 K, becoming comparable to that found in the presence of ethylene. At temperatures > 433 K, VA combustion was essentially quenched upon the addition of C2H4; the rate of CO2 formation increased by less than 5% in the presence of VA (3.5 kPa). Due to the very low concentration of VA (> 0.07 kPa) under VA synthesis conditions, the CO2 contribution from VA combustion under these conditions is negligible.

2.4. Calculations of the reaction rates and selectivities

C2H4 conversion, \( X_{C2H4} = \frac{(p_{C2H4, in} - p_{C2H4, out})}{p_{C2H4, in}} \), was calculated from the CO2 concentration at the reactor exit:

\[ X_{C2H4 \rightarrow CO2} = \frac{0.5p_{CO2, out}}{p_{C2H4, in}}. \]

Under differential flow conditions the mass-normalized reaction rates \( r_{C2H4} \) can be calculated directly from the average C2H4 partial pressure \( \bar{p}_{C2H4} \) at the entrance and exit of the reactor, normalized to the atmospheric pressure \( p_0 \), the metal mass in the catalyst bed, \( m_{Me} \), and the total molar flow rate \( \dot{V}_{tot} \).

\[ r_{C2H4} = \frac{\bar{p}_{C2H4} X_{C2H4} \dot{V}_{tot}}{p_0 m_{Me}} \quad (\text{mol s}^{-1} \text{g}^{-1} \text{Me}). \]

Consequently,

\[ r_{C2H4 \rightarrow CO2} = \frac{\bar{p}_{C2H4} X_{C2H4 \rightarrow CO2} \dot{V}_{tot}}{p_0 m_{Me}} \quad (\text{mol s}^{-1} \text{g}^{-1} \text{Me}). \]
The VA formation rate is expressed as

\[ r_{C_2H_4 \rightarrow VA} = \frac{p_{C_2H_4} X_{C_2H_4 \rightarrow VA} \dot{V}_{tot}}{p_0 m_{Me}}, \]  

while

\[ X_{C_2H_4 \rightarrow VA} = \frac{p_{VA, out}}{p_{C_2H_4, in}}. \]  

It should be noted that \( r_{C_2H_4 \rightarrow CO_2} \) only reflects the conversion rate of \( C_2H_4 \) to \( CO_2 \). The rate at which ethylene converts to \( CO_2 \) is equal to half the \( CO_2 \) formation rate, or 0.5\( r_{CO_2} \). In the present study, all \( CO_2 \) formation rates are expressed as \( r_{CO_2} \).

In the absence of AcOH, \( r_{C_2H_4} \) should be equal to \( r_{C_2H_4 \rightarrow CO_2} \) and 0.5\( r_{CO_2} \), consistent with only ethylene combustion occurring; in the synthesis of VA, the selectivity \( S \) to \( CO_2 \) formation, expressed as the fraction of \( C_2H_4 \) consumed for \( CO_2 \) formation vs the total amount of \( C_2H_4 \) consumed, is shown in

\[ S = \frac{0.5 p_{CO_2, out}}{p_{C_2H_4, in} - p_{C_2H_4, out}} = \frac{r_{C_2H_4 \rightarrow CO_2}}{r_{C_2H_4}}. \]  

Finally, all the mass-based reaction rates were converted into turnover frequencies, s\(^{-1}\) (TOF), according to

\[ r_{TOF} = \frac{r_{mass \ based} M_{Me}}{D} (s^{-1}). \]

3. Results

3.1. Characterization of the Pd(5 wt%)/SiO\(_2\) catalyst

3.1.1. X-ray diffraction

The X-ray diffraction data for the Pd(5 wt%)/SiO\(_2\) catalyst are shown in Fig. 1. The freshly reduced catalyst (as pretreated before reaction, heated in O\(_2\) at 673 K for 30 min, and then reduced in H\(_2\) at 573 K for 30 min) reveal several diffraction features at Bragg angles of 40.2, 46.2, and 67.9°, corresponding to polycrystalline Pd(111), (200), and (220), respectively [9,10]. In contrast, the peak intensities were significantly reduced for the used catalyst following VA synthesis \( (p_{C_2H_4} = 7.5 kPa; p_{O_2} = 1 kPa; p_{AcOH} = 2.0 kPa, \) with the remainder N\(_2\), at 413 K, 600 min); the (220) feature was no longer present while the (111) and (200) features shifted to 38.1 and 45.0°, respectively. According to Eq. (2), the average Pd particle size is estimated to be approximately 3.8 nm for the freshly reduced catalyst and approximately 4.2 nm for the used catalyst.

3.1.2. Transmission electron microscopy

As shown in Fig. 2, the Pd particles for the 5 wt% Pd/SiO\(_2\) catalyst are distributed between 1.5 and 8.5 nm in the freshly reduced catalyst and 2.0 and 18.0 nm for the used catalyst (see Fig. 3). As shown in Table 1, the Pd particle size ob-
Fig. 2. TEM micrograph of SiO₂-supported Pd particles. (A) Fresh reduced, (B) after reaction; the samples are the same as in Fig. 1.

Fig. 3. Size distribution of Pd particles for the Pd(5 wt%)/SiO₂ catalyst.

tained via TEM is somewhat higher than that found by XRD. In the present study the 40% dispersion of Pd subsequently used in determining the reaction rate (TOF) is based on the XRD analysis for the freshly reduced catalyst.

3.1.3. X-ray photoelectron spectroscopy

Pd(3d) core level shifts for the fresh and used catalysts are shown in Table 2 according to peak position, peak widths, and Pd⁰/Pd²⁺ peak area ratios. Over the freshly reduced sample, Pd 3d 5/2 and 3/2 features were observed at 335.0 and 340.1 eV binding energy (BE), respectively. Deconvolution of these features shows two features corresponding to Pd 3d 5/2 BEs of 335.0 and 336.5 eV, corresponding to Pd⁰ and Pd²⁺ [11–13], respectively. Similar data were observed for the used catalyst; however, a significant shift of approximately 2.0 eV toward higher BE was observed. Noticeably, the ratios of the peak area (Pd⁰ 3d 5/2/Pd²⁺ 3d 5/2), qualitatively representing the percentage of Pd⁰ and oxidized Pd²⁺ on the surface of Pd particles, indicate that the Pd⁰ is a predominant species on the Pd surface for the freshly reduced catalyst (Pd⁰/Pd²⁺ = 7.6) whereas after reaction the surface is essentially completely oxidized (Pd⁰/Pd²⁺ = 0.05). It should be noted, however, that the samples were temporarily exposed to air before measurement; therefore, the XPS results are only qualitative. C(1s) data show a broad peak centered at 285.1 eV for the freshly reduced and used catalysts, with the peak intensity (area) for the used catalyst being appreciably larger, consistent with moderate carbon deposition during reaction.

3.2. Synthesis of VA over a Pd (5 wt%)/SiO₂ catalyst

The stability of the catalyst was measured for 600 min under differential flow conditions as shown in Fig. 4. The rate of CO₂ formation versus time shows that catalyst stability was achieved after 100 min. The data used for kinetic analysis were those measured after 2.5 h time on stream unless otherwise noted. As shown in Fig. 5, variation of the reaction rates, rVA and rCO₂, with the partial pressure of O₂ (P₂O₂) was determined at 413 K with the P₃H₄ fixed at 7.5 kPa, and

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>XRD</th>
<th>TEM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Diameter (nm)</td>
<td>Dispersion (%)</td>
</tr>
<tr>
<td>Fresh reduced</td>
<td>3.8</td>
<td>37.5</td>
</tr>
<tr>
<td>After reaction</td>
<td>4.2</td>
<td>30</td>
</tr>
</tbody>
</table>

a Treated in O₂ (10%)/N₂ mixture at 673 K for 30 min, then reduced in H₂ at 473 K for 30 min.
b P₃H₄ 7.5 kPa, P₂O₂ 1.0 kPa, P₃AcOH 2.0 kPa, with remainder N₂ at 413 K, 600 min.
p_{\text{AcOH}} held at 2.0 kPa. With an increase in \( p_{\text{O}_2} \) from 1.0 to 8.4 kPa, \( r_{\text{CO}_2} \) increased by a factor of 7, from \( 0.13 \times 10^{-4} \) to \( 0.9 \times 10^{-4} \) \( \text{s}^{-1} \); concurrently, a 20% increase of \( r_{\text{VA}} \) from 1.1 \( \times 10^{-4} \) to 1.3 \( \times 10^{-4} \) \( \text{s}^{-1} \) was observed. The corresponding selectivity toward \( \text{CO}_2 \) increased from \(< 10\%\) at \( p_{\text{O}_2} = 1.0 \) kPa to nearly 25% at \( p_{\text{O}_2} = 8.4 \) kPa. Obviously, ethylene combustion is enhanced more than \( \text{VA} \) synthesis by an increase in \( p_{\text{O}_2} \).

### 3.3. Kinetics for ethylene combustion

#### 3.3.1. Dependence of \( r_{\text{CO}_2} \) on \( p_{\text{C}_2\text{H}_4} \) at 413, 433, and 453 K

In the presence and absence of \( \text{AcOH} \), the dependence of \( r_{\text{CO}_2} \) on \( p_{\text{C}_2\text{H}_4} \) was measured in the range 5.0–15.0 kPa at 413, 433, and 453 K, respectively. While \( p_{\text{O}_2} \) was held constant at 6.3 kPa. As shown in Fig. 6, in the presence of \( \text{AcOH} \) \( (p_{\text{AcOH}} = 2.0 \) kPa) (see the dashed-line plots) a similar small decrease of \( r_{\text{CO}_2} \) with an increase in \( p_{\text{C}_2\text{H}_4} \) was observed over the entire temperature range. At 413 K, \( r_{\text{CO}_2} \) drops from 0.72 \( \times 10^{-4} \) \( \text{s}^{-1} \) at \( p_{\text{C}_2\text{H}_4} = 5.0 \) kPa to 0.53 \( \times 10^{-4} \) \( \text{s}^{-1} \) at \( p_{\text{C}_2\text{H}_4} = 15.0 \) kPa; a slope of \(-0.27\) was measured from regression of the data at 413 K. Parallel plots at 433 and 453 K exhibited slopes of \(-0.31\) and \(-0.27\), respectively. Furthermore, \( r_{\text{CO}_2} \) increases significantly with an increase in temperature for the same reactant composition. For example, with reactant pressures of \( p_{\text{C}_2\text{H}_4} = 5.0 \) kPa, \( p_{\text{O}_2} = 6.3 \) kPa, \( p_{\text{AcOH}} = 2.0 \) kPa (\( \text{N}_2 \) balance), \( r_{\text{CO}_2} \) is 0.72 \( \times 10^{-4} \) \( \text{s}^{-1} \) at 413 K and increases to 1.07 \( \times 10^{-4} \) \( \text{s}^{-1} \) at 433 K and 1.35 \( \times 10^{-4} \) \( \text{s}^{-1} \) at 453 K, an approximately 50% increase for a 20 K rise in the reaction temperature.

The behavior of \( r_{\text{CO}_2} \) versus \( p_{\text{C}_2\text{H}_4} \) in the absence of \( \text{AcOH} \) is essentially the same as that in the presence of \( \text{AcOH} \) (see solid line in Fig. 6). Slopes of \(-0.15\), \(-0.17\), and \(-0.19\) were measured at 413, 433, and 453 K, respectively. The absolute value of the slopes in the absence of \( \text{AcOH} \) is lower than those in the presence of \( \text{AcOH} \). Furthermore, at 413 K \( r_{\text{CO}_2} \) in the absence of \( \text{AcOH} \) is significantly higher than \( r_{\text{CO}_2} \) in the presence of \( \text{AcOH} \) with the same \( p_{\text{C}_2\text{H}_4} \). The difference between these two reaction conditions changes from 20\% at \( p_{\text{C}_2\text{H}_4} = 5.0 \) kPa to nearly 50\% at \( p_{\text{C}_2\text{H}_4} = 15.0 \) kPa. However, this difference was minimal at 433 K; nearly equal \( r_{\text{CO}_2} \)’s were measured at 533 K for both reaction compositions.

#### 3.3.2. Dependence of \( r_{\text{CO}_2} \) on \( p_{\text{O}_2} \), \( 413, 433, \) and 453 K

In the presence and absence of \( \text{AcOH} \), with a fixed \( p_{\text{C}_2\text{H}_4} \) of 7.5 kPa, the change in \( r_{\text{CO}_2} \) with \( p_{\text{O}_2} \) was investigated at 413, 433, and 453 K. As illustrated in Fig. 7, in the presence of \( \text{VA} \) (shown as dashed lines), \( r_{\text{CO}_2} \) increases rapidly with an increase in \( p_{\text{O}_2} \); the plot corresponding to 413 K is the same as the one shown in Fig. 5 and parallels the plots at 433 and 453 K. A least-squares fit of the lines yields slopes of 0.88, 0.82, and 0.89, respectively. An increase of \( r_{\text{CO}_2} \) with an increase in temperature was measured as well as shown in Fig. 6. A reactant composition of \( p_{\text{C}_2\text{H}_4} = 7.5 \) kPa, \( p_{\text{O}_2} = 1.0 \) kPa, and \( p_{\text{AcOH}} = 2.0 \) kPa, (residual \( \text{N}_2 \)), is optimum for the synthesis of \( \text{VA} \) [1,2]. \( r_{\text{CO}_2} \) increased from \( 0.08 \times 10^{-4} \text{ s}^{-1} \) at 413 K to \( 0.11 \times 10^{-4} \text{ s}^{-1} \) at 433 K and \( 0.13 \times 10^{-4} \text{ s}^{-1} \) at 453 K. Comparatively, a similar behavior of the variation of \( r_{\text{CO}_2} \) versus \( p_{\text{O}_2} \) in the absence of \( \text{AcOH} \) (see the solid line in Fig. 6) was also observed. Slopes of 1.22, 1.18, and 1.16 were obtained at 413, 433, and 453 K, respectively. It is noteworthy that \( r_{\text{CO}_2} \) versus \( p_{\text{O}_2} \) in the absence of \( \text{AcOH} \) grows faster than in the presence of \( \text{AcOH} \). At \( p_{\text{O}_2} = 1.0 \) kPa, \( r_{\text{CO}_2} \) was lower in the presence of \( \text{AcOH} \); however, this behavior was reversed with an increase in \( p_{\text{O}_2} \) to 8.4 kPa.

### 3.4. Kinetic parameters and the ethylene combustion mechanism

To calculate the reaction orders with respect to ethylene (\( \alpha \)) and oxygen (\( \beta \)), a simple power-law functionality is assumed:

\[
r_{\text{CO}_2} = kp_{\text{C}_2\text{H}_4}^\alpha p_{\text{O}_2}^\beta. \tag{10}\]

By fitting Eq. (10) to the results in Figs. 5–6, reaction orders and apparent activation energies, \( E_a \), were calculated and are tabulated in Table 3. The \( E_a \) for ethylene combustion in the absence of \( \text{AcOH} \) is 17.0 kJ/mol, lower than 21.0 kJ/mol measured in the presence of \( \text{AcOH} \); whereas variation in reaction order was apparent in the two reaction mixtures. This is contrary to the results previously reported by Samanos et al. [3] and demonstrates that \( \text{AcOH} \) has essentially no

65

(a)

(b)

Fig. 4. (a) Catalytic stability of Pd/SiO₂ catalyst in the synthesis of vinyl acetate: feed gas, \( p_{C_2H_4} = 7.5 \) kPa, \( p_{O_2} = 1.0 \) kPa, \( p_{AcOH} = 2.0 \) kPa, rest N₂; flow rate, 60 N ml/min, at 413 K (■) reaction rate for VA formation; (●) reaction rate for CO₂ formation; (△) selectivity toward VA formation. (b) Catalytic stability of Pd/SiO₂ catalyst in the absence of VA: feed gas, \( p_{C_2H_4} = 7.5 \) kPa, \( p_{O_2} = 6.3 \) kPa, rest N₂; flow rate, 60 N ml/min, at 413 K (●) and 453 (■).

influence under these reaction conditions on ethylene combustion during the synthesis of VA.

Two possible pathways have been assumed for the catalytic ethylene combustion over a Pd(100) surface [6]. One is indirect combustion, in which C₂H₄ dissociates into C(a) and H(a) on the Pd surface; the carbon then reacts with O(a) to form CO, CO₂, and H₂O. An alternative pathway is oxygen-activated combustion, in which adsorbed O assists

Fig. 5. Variation of reaction rates (vinyl acetate (■) and CO₂ formation (●)) and selectivity of CO₂ (△) with the partial pressure of O₂ at 413 K over Pd(5 wt%)/SiO₂ catalyst: feed gas, \( p_{C_2H_4} = 7.5 \) kPa, \( p_{O_2} = 1.0–10 \) kPa, \( p_{AcOH} = 2.0 \) kPa, rest N₂; flow rate, 60 N ml/min; catalyst weight, 1.6 g.

Fig. 6. Dependence of CO₂ formation rate on partial pressure of C₂H₄ in the presence of acetic acid: (□) at 413 K, (○) 433 K, and (△) 453 K; feed gas, \( p_{O_2} = 6.3 \) kPa, \( p_{C_2H_4} = 5.0–15.0 \) kPa, \( p_{AcOH} = 2.0 \) kPa, rest N₂; flow rate, 60 N ml/min; catalyst weight, 1.6 g; in the absence of acetic acid, (■) at 413 K, (●) at 433 K, (▲) at 453 K; feed gas, \( p_{O_2} = 6.3 \) kPa, \( p_{C_2H_4} = 5.0–15.0 \) kPa, rest N₂; flow rate, 60 N ml/min; catalyst weight, 1.2 g.

in the removal of H from ethylene via formation of O–H and/or O–C bonds, yielding CO, CO₂, and H₂O. Guo and Madix [6] failed to detect CO or CO₂ within the temperature range 200–900 K for ethylene combustion over Pd(100); however, Jia et al. [7] detected a CO product at 230 K over Pd{001}–c(2×2)–O. In the present work, no CO was de-
exposure shows CO₂ evolution due to reaction of O(a) and

4.1. Pd cluster restructuring and catalyst stability

Analysis of the XRD and TEM data suggests that the Pd particles on the freshly reduced catalyst are highly dispersed. The XRD data of Fig. 1 indicate a Pd particle diameter of approximately 3.8 nm for the freshly reduced catalyst, corresponding to approximately 500 atoms per cluster. However, moderate aggregation of the Pd to particles to approximately 4.2 nm in diameter occurs during reaction. Growth of the Pd particles during reaction was also apparent in the TEM images; however, the Pd particle sizes deduced by TEM were substantially larger than those found by XRD (see Table 1). Particle sizes below 1.0 nm were not visible in the TEM images likely because of intrinsic resolution; therefore, some discrepancy between XRD and TEM regarding particle size is anticipated. Recently, Kaszkur [9,10] has used powder diffraction to determine the size of Pd particles within 1.5–3.5 nm by monitoring the shift and peak intensity of the Pd(111) feature. This approach was applied to the data found for the freshly reduced and used catalyst in this study. As shown in Fig. 1, from the freshly reduced catalyst to the used catalyst, the 2θ of Pd(111) peak shifted from 40.2 to 38.1° with a concomitant change in peak intensity. In particular, the disappearance of the Pd(220) phase in XRD was observed for the used catalyst, suggesting a phase transformation of the Pd particles during reaction. It should be emphasized here that the downshift of the Pd(111) feature may also be ascribed to the formation of PdC₃ [14].

The XPS results shown in Table 2 indicate that a layer of PdO₃ may cover the used catalyst. This result is consistent with previous results for a Pd single crystal as well as supported Pd catalysts [14,15,19–30]. Klötzer et al. [15] reported an oxygen-induced surface-phase transformation on Pd(111) between 0.25 and 1.0 ML (ML: monolayer) and between 300 and 600 K; above 900 K and at higher O₂ pressures (>10⁻³ Pa), formation of bulk PdO was reported on Pd(111) [16–20]. Voogt et al. [12] showed that a surface oxide was produced on Pd(111) at temperatures greater than 470 K and at pressures greater than 2 × 10⁻⁴ Pa. Recently, however, Leisenberger et al. [11] failed to observe PdO₃ species on Pd(111) at temperatures below 525 K and an oxygen pressure of 2 × 10⁻⁷ Pa. Although the lack of oxide formation may be due to the lower oxygen pressure, clearly the formation of a surface oxide is more facile on the low-index planes of Pd, e.g., Pd(100) and Pd(110), compared to Pd(111) [21–23]. Huang et al. [21] produced a surface oxide on Pd(100) at 430 K and an oxygen pressure of 1.1 × 10⁻⁵ Pa. On the other hand, Graoui et al. [24], after depositing Pd particles onto a MgO single crystal under UHV conditions, observed the formation of PdO at the edges of the particles by HRTEM at 723 K and 10⁻³ Pa of O₂. Furthermore,
formation of an oxide phase as well as restructuring of supported particles has been reported by Yang et al. [25], who detected the formation of PdO alone on Pd catalysts supported on Al2O3, ZrO2, and ZrO2–SiO2 during methane combustion between 473 and 873 K.

XRD and TEM show the Pd particles in this study to be highly dispersed and therefore likely to have a higher concentration of defect sites relative to Pd single crystals. PdO, may very well be more easily formed on these small clusters upon exposure to 1.0–10.0 kPa O2 at 413–453 K. Also under reaction conditions AcOH-induced Pd oxidation during VA synthesis may be an alternative pathway to PdO oxidation. Pd(OAc)2 has been proposed as an intermediate in the formation of VA [2]. Although a surface oxide may be present under reaction conditions, the formation of bulk PdO can be excluded based on the XRD data (see Fig. 1). No features related to bulk PdO are present for the used catalyst.

4.2. Adsorption of ethylene and O2 on Pd

The positive reaction order wrt O2 and negative order wrt C2H4 (see Table 3) suggest that C2H4 adsorption plays a key role in ethylene combustion on Pd. Adsorbed ethylene, C2H4(a), or its dehydrogenated product may block the dissociative adsorption of O2. Previous experimental [26–28] and theoretical [29–32] studies of the adsorption of C2H4 and O2 on Pd single crystals and clusters show two kinds of adsorption sites on Pd surface: (i) atop adsorption site on a Pd atom, the so-called π-type; and (ii) bridge adsorption sites called di σ-type, related to adsorption of a rehybridized (sp2 → sp3) C2H4 molecule. However, molecular C2H4 adsorbed on Pd(111), (110), and (100) has only been detected at low adsorption temperatures (< 150 K) [26–28,33–36]. With an increase in temperature, the adsorbed ethylene C2H4(a) apparently isomerizes to ethylidene (CH=CH2), followed by dehydrogenation to ethyldiene (C=CH2) [27,30,35–39], then finally decomposition to CHx fragments at temperatures between 400 and 500 K [36,37]. It is noteworthy that different Pd surfaces exhibit different adsorption–desorption behavior with respect to C2H4. Ethyldiene forms on Pd(111) at room temperature [40–42] and desorbs below 350 K [27]; however, C2H4 was found to adsorb reversibly on Pd(100) at room temperature [38] and directly dehydrogenate to CHx [36] at x > 400 K. Similarly, by IR spectroscopy, Frank et al. [43] could not detect any molecular ethylene on Pd clusters at 300 K. Ethylene is known to exhibit a range of binding energies on various Pd surfaces [44].

On the other hand, as noted above, the adsorption of O2 on Pd surface may lead to the oxidation of the Pd surface. In fact, molecular O2 likely dissociates on a Pd surface. Within the temperature range 100–650 K, dissociation of molecular O2 on Pd(111) [45,46] and Pd(110) [47,48] has been demonstrated. Voogt et al. [12] confirmed that there were three stages in the interaction of oxygen with Pd(111): (1) dissociative adsorption of oxygen where the saturation coverage of oxygen, θsat, was estimated to be 0.25 ML > 470 K;

(2) the diffusion of oxygen atoms into Pd; and (3) oxide nucleation and growth. For Pd(111) the formation of a new surface phase, consisting of islands of high-density oxygen acting as a reservoir for O, was observed between 300 and 623 K [15]. However, diffusion of oxygen atom into the bulk or subsurface layers was not observed.

4.3. Proposed mechanism for ethylene combustion

As shown in Table 3, the kinetic parameters at 413, 433, and 453 K suggest a single mechanism for ethylene combustion within the temperature range 413–453 K. The slight negative order wrt ethylene and the positive order wrt oxygen indicate that ethylene or dehydrogenation/decomposition derivatives cover to a large extent the Pd surface and occupy most of the adsorption sites, therefore blocking oxygen adsorption. The adsorption of ethylene on Pd single crystals under UV conditions has been briefly discussed in terms of the adsorbed ethylene desorbing from Pd at or above room temperature and the remaining ethylene being dehydrogenated to a CHx species above 400 K. Assuming this to be the case, suppression of oxygen very well may occur above 400 K. However, in the present studies ethylene is adsorbed on a high surface area supported catalyst under atmospheric conditions where the di-σ and π-bonded ethylene species have been reported [49–51]. The π-bonded ethylene species, proposed to be adsorbed at the atop site on a single Pd atom, has been identified on single crystals of Pd in UV at room temperature. Because ethylene dominates the surface, the dissociative adsorption of oxygen may be suppressed and may become the rate-determining step in ethylene combustion. Ethylene combustion on a supported Pd/SiO2 catalyst likely proceeds via the mechanism of oxygen-activated combustion proposed by Guo and Madix [6], whereby an oxygen atom abstracts a hydrogen atom from an ethylene molecule and attacks the C atom of ethylene. On the other hand, the mechanism of indirect combustion, in which the adsorbed oxygen reacts with an adsorbed C and H to form CO2 and H2O, cannot be completely ruled out. It is likely, however, that only a small fraction of the CO2 is produced via this mechanism since in this case the reaction rate would not depend upon the ethylene partial pressure.

Nevertheless, the mechanism of ethylene combustion may very well be more complex than suggested here, particularly under typical VA synthesis conditions. The influence of AcOH on the reaction rates is apparent in Fig. 4. Studies are currently underway to assess the role of AcOH in ethylene combustion and the role of adsorption site blocking by C2H4(a) on the overall reaction mechanism.

5. Conclusions

The kinetic parameters of ethylene combustion in the presence of acetic acid, i.e., during the synthesis of vinyl ac-
etate, and in the absence of acetic acid have been measured in the temperature range 413–453 K over Pd supported on a high surface area SiO₂ (600 m²/g). CO₂ formation as a function of the partial pressures of C₂H₄ and O₂ exhibits a negative reaction order with respect to C₂H₄ and a positive order with respect to O₂. The ethylene combustion kinetics in the presence and absence of acetic acid were essentially the same, suggesting that ethylene combustion is primarily responsible for CO₂ formation in the synthesis of vinyl acetate from ethylene and acetic acid over unpromoted Pd within the temperature and pressure regime investigated.

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References