

Particle size effects in vinyl acetate synthesis over Pd/SiO₂

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Abstract

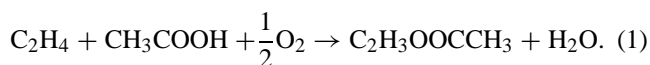
Pd catalysts with varying particle size supported on a high-surface-area (600 m²/g) SiO₂ were prepared by wet impregnation. The kinetics of vinyl acetate (VA) synthesis at atmospheric pressure was investigated in a fix-bed microreactor. With transmission electron microscopy (TEM), the average diameter of the Pd particles was estimated to be 4.0 ± 0.2 and 2.5 ± 0.1 nm over the reduced Pd(5.0 wt%)/SiO₂ and Pd(1.0 wt%)/SiO₂ catalysts, respectively; limited sintering of the Pd particles during the reaction was observed for both catalysts. X-ray diffraction (XRD) showed primarily metallic Pd crystallites on the reduced catalyst and the formation of Pd carbide (PdC_x) on the reacted catalyst. The Pd kinetics shows that the apparent activation energy increases with a decrease in the Pd particle size, varying from 17.0 kJ/mol over Pd(5.0 wt%)/SiO₂ to 39.0 kJ/mol over Pd(1.0 wt%)/SiO₂, and the rate of VA formation was significantly enhanced. On the other hand, the reaction orders (i.e., negative order with respect to ethylene and positive order with respect to oxygen) showed very little dependence on the Pd particle size.

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Keywords: Vinyl acetate synthesis; Kinetics; Size dependence; Palladium; XRD; Pd/SiO₂ catalyst

1. Introduction

Since the first report by Moiseev et al. [1] of the catalytic synthesis of vinyl acetate (VA) from ethylene (C₂H₄), acetic acid (AcOH), and oxygen (O₂) in the homogeneous phase with palladium chloride, significant advances have been made in the process. Currently, production of VA by the vapor-phase oxyacetylation of ethylene over Pd-based catalysts is a very important industrial process [2–4]. The overall reaction can be written as



Because this reaction has been commercialized for several decades, improving the catalysts with respect to rate and VA selectivity is a challenge, particularly given that the nature of the active site and mechanism for VA synthesis on Pd-based catalysts have not been established. Previous studies of VA synthesis in the vapor phase were conducted pri-

marily on supported Pd catalysts, such as Pd/SiO₂, Pd/Al₂O₃ [5], and Pd/Al₂O₃ promoted by K⁺ [6,7] and Pd/C [8]. Approximately 80–90% selectivity for VA has been observed over a Pd(2.0 wt%)/SiO₂ catalyst [5]. The catalytic performance of Pd-only catalysts can be improved considerably with the addition of Au. For instance, over Pd–Au/SiO₂ catalysts [2,9], selectivity can be increased to 94.0%, and the VA synthesis rate can be enhanced by a factor of 2 [9] compared with a Pd-only catalyst. In theoretical studies, Neurock et al. [9,10] have suggested that VA synthesis over a Pd-only catalyst requires a relatively large ensemble and therefore is structure-sensitive; dilution of surface Pd atoms with inert Au atoms modifies the active sites (ensembles) required for the structure-sensitive reactions [11,12]. Generally, the high reactivity of Pd–Au alloy catalyst has been assumed to be related to the modification of the electronic and geometric properties of Pd particles by the formation of a Au_xPd_y alloy [11–19].

In the present study, VA synthesis over Pd/SiO₂ catalysts with two Pd particle sizes supported on a high-surface-area (600 m²) SiO₂ has been studied. The kinetics study was car-

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ried out at 413 K at atmospheric pressure by online GC analysis. To determine the reaction order with respect to C_2H_4 and O_2 and the selectivity for VA formation, we obtained the pressure-dependent reaction rates by fixing the pressure of C_2H_4 or O_2 while changing the pressure of the other reactant; the apparent activation energies (E_a), were measured concurrently in the temperature range of 393–433 K over the different Pd/SiO₂ catalysts. The detailed kinetics of VA synthesis over nanosized Pd catalysts as prepared here has not been addressed, with the exception of a preliminary kinetic study over Pd(2.0 wt%)/SiO₂ reported by Samanos et al. [5]. The change in the Pd morphology before and after reaction was characterized by TEM and XRD.

2. Experimental

2.1. Catalyst preparation and the reactants

Pd/SiO₂ catalysts with a loading of 5.0 wt% and Pd 1.0 wt% metal, denoted Pd-5 and Pd-1, respectively, in the text, were prepared by the incipient wet-impregnation method. High-surface-area (600 m²/g) SiO₂ (Aldrich no. 7631-86-9), with a mesh size of 230–400 and a pore volume of 1.1 ml/g, was used as the support. We first prepared a Pd²⁺ solution by dissolving Pd(NO₃)₂ (C.P., commercial sources) in deionized water. The Pd²⁺ solution, with an equal volume of SiO₂, was then added to the SiO₂ powder with stirring to wet the support; the impregnated catalyst was allowed to stand for 4 h in a covered beaker. Finally, the precursor was dried under vacuum at 393 K overnight before it was used. N₂, C₂H₄, O₂(10%)/N₂, and air (Messer MG Industries) were purified with gas filters (Chrompack) to remove trace amounts of water, oxygen, and hydrocarbons. The partial pressure of AcOH was 2.0–3.5 kPa, which we achieved by bubbling the reactant gas stream through AcOH (Aldrich C.P.).

2.2. Catalyst characterization

2.2.1. X-ray diffraction (XRD)

The X-ray powder diffraction data were acquired with a Bruker D8 diffractometer and Cu-K α radiation. Samples were scanned over the 2θ range from 30° to 50°; the step size was 0.2° and 0.04° for the Pd-5 and Pd-1 catalysts, respectively.

2.2.2. Transmission electron microscopy (TEM)

TEM measurements were performed on a 200-keV microscope (JOEL 2010). 200–300 particles were counted to evaluate the particle size (diameter) distribution.

2.3. Activity measurements

All kinetics measurements were carried out at atmospheric pressure in a quartz tube microreactor with a 0.8-cm inner diameter and a catalyst bed (1–2 cm length) containing

approximately 1.0–2.0 g. The reactants and products were analyzed by online gas chromatography (GC) (HP 5890). A HayeSep R column (80/100 mesh and 2 m long) connected to a flame ionization detector (FID) was used to detect VA and AcOH; a Porapak column RT (80/100 mesh and 1.5 m long) connected to a thermal conductance detector (TCD) was used to determine the CO₂, C₂H₄, VA, and mixtures of O₂ and N₂. The flow rates of the gases were controlled by mass flow meters.

Before the kinetic measurements, 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. (This catalyst is referred to as a freshly reduced catalyst in the text.) Subsequently the reactor was cooled to reaction temperature in N₂. The kinetics measurements were performed under differential flow conditions, with the conversion of ethylene kept below 5%. In the extended reaction tests ($p_{C_2H_4}$: 7.5 kPa, p_{O_2} : 1.0 kPa, p_{AcOH} : 2.0 kPa, the rest N₂, at 413 K), approximately 30% of reactivity was lost between 1.7 and 16.7 h. All data were acquired after 4 h of reaction time. The method used to calculate the reaction rates and selectivity for VA formation has been described in detail previously [20].

3. Results and discussion

3.1. Catalyst characterization

3.1.1. X-ray diffraction data

X-ray diffraction scans of the reduced and reacted catalysts are shown in Fig. 1 for Pd-5 (Fig. 1, curves a and b) and Pd-1 (Fig. 1, curves c and d). The diffraction features at Bragg angles of 40.2° and 46.9° were detected for the reduced Pd-5 corresponding to the Pd <111> and <200> planes, respectively [21,22]. The peak intensities were significantly reduced for the reacted catalyst, and the features correspond-

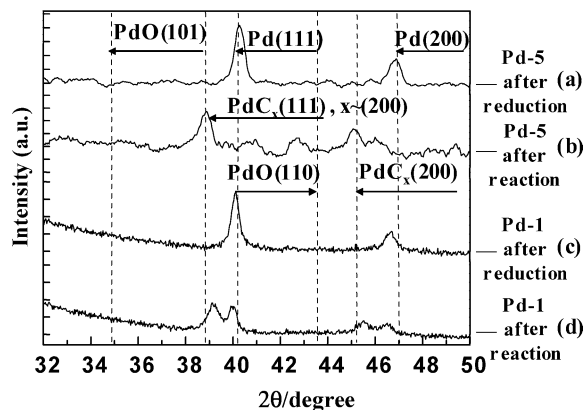


Fig. 1. (a) XRD of the Pd-5 catalyst after reduction at 673 K in 20 ml/min O₂(10%)/N₂, 30 min, then 573 K in 20 ml/min H₂ for 30 min; (b) after reaction for 10 h, at $p_{C_2H_4}$ = 7.5 kPa, p_{O_2} = 1.0 kPa, p_{AcOH} = 2.0 kPa, with remainder N₂; flow rate: 60 ml/min, at 413 K; (c) XRD of the Pd-1 catalyst after reduction; and (d) after reaction per above for 16.7 h.

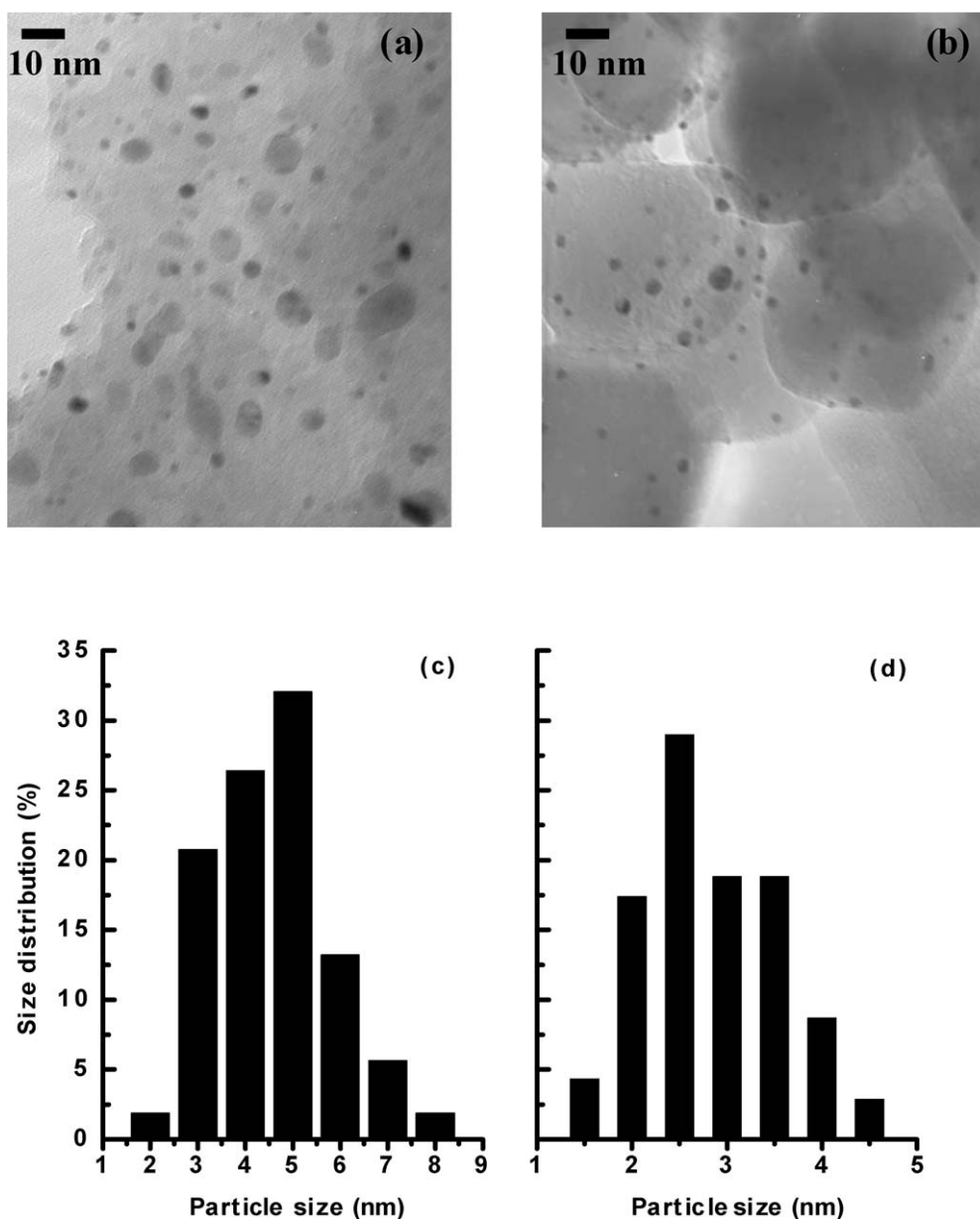


Fig. 2. Micrograph of the reduced Pd-5 (a) and the reduced Pd-1 (b) treated as in Fig. 1. Size distribution of Pd particles over the reduced catalysts, Pd-5 (c) and Pd-1 (d).

ing to the $\langle 111 \rangle$ and $\langle 200 \rangle$ planes shifted downward to 38.9° and 45.0° , respectively.

For the Pd-1 catalyst, as shown in Fig. 1, curves c and d, the features for Pd $\langle 111 \rangle$ centered at $2\theta = 40.1^\circ$ and Pd $\langle 200 \rangle$ at 46.8° were detected for the reduced Pd-1; these were lower by 0.1° than the corresponding values for the Pd-5 catalyst. However, splitting of each of the features was observed for the reacted Pd-1, that is, two distinct peaks at 40.0° and 39.1° were apparent at the Pd $\langle 111 \rangle$ reflection. Also, in contrast to the reduced Pd-1 catalyst, this feature was sharpened in the reacted Pd-1, consistent with an increase in the Pd particle size.

As shown in Fig. 1, curves b and d, the downward shift of all reflections for the reacted catalysts can be ascribed primarily to the formation of Pd carbides (PdC_x ($x \approx 0.13$))

[6,8,23–25]. On the other hand, in comparison to the Pd-5 catalyst, the slight downshift of the peaks for the reduced Pd-1 may very well be due to a decrease in the Pd particle size (see Table 1), as indicated by TEM in Fig. 2. Recently, Kaszkur [21,22] also observed a similar downshift caused by the decrease in the Pd particles size from 3.5 to 1.5 nm with a simultaneous reduction in the peak intensity. In addition, the peaks at 34.0° and 42.5° , assigned to the $\langle 101 \rangle$ and $\langle 110 \rangle$ planes of PdO, are not evident for either catalyst.

3.1.2. TEM images

The TEM image in Figs. 2a and 2b clearly shows the Pd particles to be highly dispersed on the SiO_2 surface. The Pd particle sizes are distributed over the range of 1.5–8.5 and 1.5–4.5 nm for the reduced Pd-5 and Pd-1 catalysts (see

Table 1
Pd particle sizes measured by TEM before^a and after reaction^b

Sample	XRD		TEM	
	Diameter (nm)	Dispersion (%)	Diameter (nm)	Dispersion (%)
Pd-5 reduced	3.8	37.5	4.2	30
Pd-5 reacted	4.2	30	5.5	22
Pd-1 reduced	2.8	40	2.5	40
Pd-1 reacted	3.7	32	3.5	36

^a Treated in O₂(10%)/N₂ mixture at 673 K for 30 min, then reduced in H₂ at 573 K for 30 min.

^b p_{C₂H₄}: 7.5 kPa, p_{O₂}: 1.0 kPa, p_{AcOH}: 2.0 kPa, the remainder N₂, at 413 K; 10 h for Pd-5 and 16.7 h for Pd-1.

Figs. 2c and 2d), yielding an average size of 4.0 ± 0.2 and 2.5 ± 0.1 nm, respectively. Growth of the Pd particles size was observed by TEM for the two reacted catalysts as indicated in Table 1. In general, the Pd particle sizes obtained by TEM were close to the sizes determined by XRD, and the trends exhibited by the catalysts before and after the reaction were identical, as indicated in Table 1.

3.2. Kinetics of the synthesis of VA over Pd/SiO₂ catalyst

The temperature-dependent rates in the range of 393–433 K are shown in Fig. 3. The rate over the Pd-1 is higher than that for Pd-5 by a factor of 2 at 393 K and by a factor of 5 at 433 K. The activation energy (E_a) of 39.0 kJ/mol for the Pd-1 decreases to 17.3 kJ/mol for the Pd-5 catalyst. The selectivities (S) for VA formation for the two catalysts were very close [96 versus 95% at 393 K; see Fig. 4]; however, a more significant difference in S was observed at 433 K. For Pd-1, S was reduced from 95% at 393 K to 93% at 413 K and changed little with a temperature increase to 433 K; similarly, over Pd-5, S dropped from 95% at 393 K to 90% at 413 K and then to 86% at 433 K. These data show that with an increase in temperature CO₂ formation occurs preferentially for Pd-5 compared with Pd-1.

For comparison, the E_a and the corresponding reaction rates (r_{VA}) in the temperature range of 373–433 K obtained for the Pd-only and the promoted Pd catalysts are listed in Table 2. The E_a measured for Pd-1, 39.0 kJ/mol, is very close to the values previously measured for Pd-only (30.5 kJ/mol for Pd(2.0 wt%)/SiO₂) [5] and promoted (29.3 kJ/mol for Pd(5.0 wt% and K⁺)/Al₂O₃) Pd [6] catalysts. The r_{VA} for the Pd-5 catalyst was less than 0.5 μmol/(g_{Pd} s), which is significantly lower than the rates measured over other Pd catalysts listed in Table 2 (TOFs not available), perhaps because of the relatively low pressures used in the present experiments.

The pressure-dependent r_{VA} and S at 413 K are displayed in Figs. 5 and 6. As shown in Fig. 5, with varying p_{C₂H₄} in the range of 5.0–15.0 kPa and the p_{O₂} fixed at 1.0 kPa, the rates over the Pd-1 decreased from 0.35×10^{-3} to 0.24×10^{-3} s⁻¹ and the corresponding S was reduced from 95 to 84%; a similar change in reactivity occurred for Pd-5

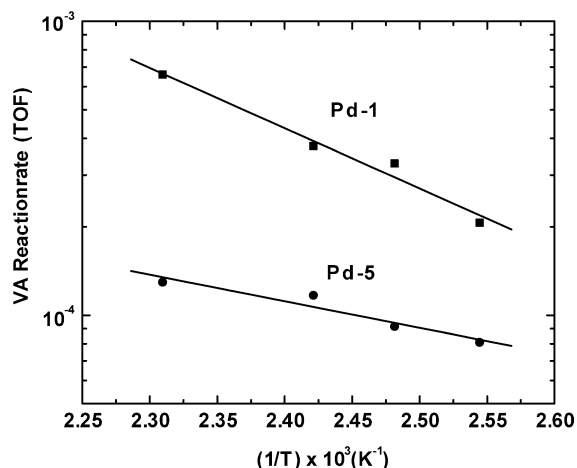


Fig. 3. VA synthesis versus temperature over Pd-1 and Pd-5 catalysts: (●) Pd-5; (■) Pd-1, gas: p_{C₂H₄} = 7.5 kPa, p_{O₂} = 1.0 kPa, p_{AcOH} = 2.0 kPa, the remainder N₂; flow rate: 60 Nml/min. Catalyst wt: 1.2 g.

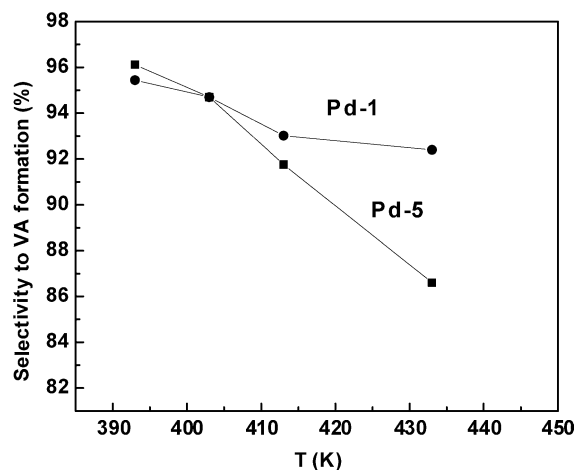


Fig. 4. VA selectivity versus temperature over Pd-5 and Pd-1 catalysts. (■) Pd-5; (●) Pd-1, reaction conditions as in Fig. 3.

for relatively low rates, from 0.14×10^{-3} to 0.08×10^{-3} s⁻¹ with S falling from 94 to 80%. In contrast, with p_{C₂H₄} fixed at 7.5 kPa and p_{O₂} increased from 1.0 to 8.4 kPa, the r_{VA} increased from 0.34×10^{-3} to 0.51×10^{-3} s⁻¹ and the S decreased from 94 to 86% for Pd-1; under the same conditions r_{VA} over Pd-5 increased from 0.11×10^{-3} to nearly 0.14×10^{-3} s⁻¹, and S decreased from 92 to 76%. The corresponding kinetic parameters are summarized in Table 3; the reaction orders with respect to C₂H₄ and O₂ were fit to a power law as follows:

$$r_{VA} = k p_{C_2H_4}^\alpha p_{O_2}^\beta \quad (2)$$

As listed in Table 3, similar negative orders with respect to C₂H₄ and positive order with respect to O₂ have been obtained for the two catalysts studied, in agreement with the results for a Pd(2.0 wt%)/SiO₂ catalyst [5]. In contrast, at approximately 500 kPa over a Pd(5.0 wt%)/Al₂O₃ catalyst, Nakamura et al. reported [6] that the reactivity was enhanced with an increase in p_{C₂H₄} from 50 to 200 kPa but

Table 2
Comparisons of rate parameters for VA synthesis over Pd catalysts

Catalyst	Reaction conditions	E_a (kJ/mol)	Reaction rate ($\mu\text{mol}/(\text{gPd s})$)	Ref.
1.0 wt% Pd/SiO ₂	7.5% C ₂ H ₄ , 2% AcOH, and 1% O ₂ , rest N ₂ , SV: 1400 h ⁻¹ , 101.3 kPa	39.0 ± 2.0	0.9–3.0	This study
5.0 wt% Pd/SiO ₂	7.5% C ₂ H ₄ , 2% AcOH, and 1% O ₂ , rest N ₂ , SV: 1400 h ⁻¹ , 101.3 kPa	17.3 ± 2.0	0.3–0.5	This study
2.0 wt% Pd/SiO ₂ promoted by 15 wt% sodium acetate ^a	52% C ₂ H ₄ , 13.8% AcOH, 14.2% O ₂ and 20% H ₂ O, SV: 2250 h ⁻¹ , 101.3 kPa	30.5	2.0–8.5 ^b	[5]
5.0 wt% Pd/Al ₂ O ₃ promoted by potassium acetate	80% C ₂ H ₄ , 3% AcOH, 9% O ₂ , TPD	29.3	2.0–20.0 ^b	[26]
1.0 wt% Pd/Al ₂ O ₃ promoted by 3.0 wt% potassium acetate	80% C ₂ H ₄ , 10% AcOH, 10% AcOH and 393 K, SV: 600 h ⁻¹ , 500 kPa		9.3 ^b	[6]

^a Initial rate since no differential flow rate data are available.

^b Data based on total Pd.

Table 3

Kinetic parameters for the synthesis of VA over Pd/SiO₂ catalysts, power law functionality: $r_{\text{VA}} = k(p_{\text{C}_2\text{H}_4}/P_{\text{Total}})^\alpha (p_{\text{O}_2}/P_{\text{Total}})^\beta$

Catalysts	Rate constant (k) ($\mu\text{mol}/(\text{gPd s})$)	α	β	γ_{VA}^a ($\mu\text{mol}/(\text{gPd s})$)	γ_{VA}^b (10^{-4} s^{-1})
Pd-1	1.32	-0.34 ± 0.02	0.18 ± 0.01	1.1–2.3	2.4–5.1
Pd-5	0.15	-0.60 ± 0.02	0.12 ± 0.01	0.3–0.5	0.8–1.4

^a Mass-based reaction rates at $p_{\text{C}_2\text{H}_4}$: 13.5 kPa, p_{O_2} : 1.0 kPa, p_{AcOH} : 2.0 kPa, the remainder N₂, at 413 K (low) and $p_{\text{C}_2\text{H}_4}$: 7.5 kPa, p_{O_2} : 8.4 kPa, p_{AcOH} : 2.0 kPa, the remainder N₂, at 413 K (high).

^b Turnover frequencies (TOF) calculated based on: $r_{\text{TOF,VA}} = r_{\text{VA}} m_{\text{Pd}}/D$, m_{Pd} = Pd atom weight, D = Pd dispersion, determined using the Pd particle size measured by XRD and TEM.

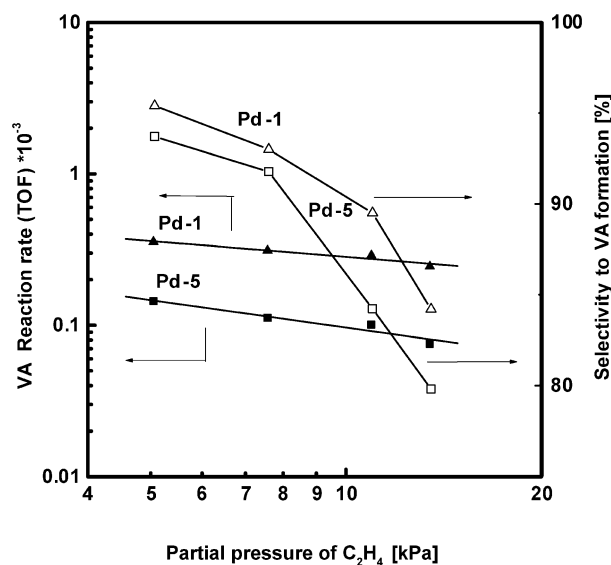


Fig. 5. VA reaction rates (\blacktriangle : Pd-1, \blacksquare : Pd-5) and selectivities (\triangle : Pd-1, \square : Pd-5) as a function of the C₂H₄ partial pressure at 413 K. $p_{\text{C}_2\text{H}_4}$ = 5.0–15.0 kPa, p_{O_2} = 1.0 kPa, p_{AcOH} = 2.0 kPa, the remainder N₂; flow rate = 30–60 ml/min. Catalyst: 1.2–2.0 g.

decreased slightly with a further increase in $p_{\text{C}_2\text{H}_4}$. In addition, it is noted that the reactivity was observed to be almost independent of the p_{AcOH} in the range of 2.0–3.5 kPa (not shown here for the sake of brevity). A zero-order dependency with respect to AcOH has been measured and dis-

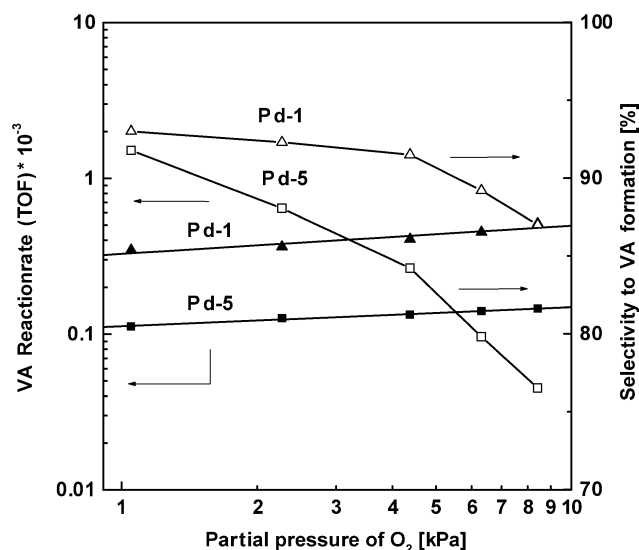


Fig. 6. VA reaction rates (\blacktriangle : Pd-1, \blacksquare : Pd-5) and selectivities (\triangle : Pd-1, \square : Pd-5) as a function of the O₂ partial pressure at 413 K. $p_{\text{C}_2\text{H}_4}$ = 7.5 kPa, p_{O_2} = 1.0–10.0 kPa, p_{AcOH} = 2.0 kPa, the remainder N₂; flow rate = 30–60 ml/min. Catalyst: 1.2–2.0 g.

cussed for Pd(5.0 wt%)/Al₂O₃ [26] and a Pd(2.0 wt%)/SiO₂ catalyst [5].

The negative order with respect to C₂H₄ suggests that saturation on Pd of C₂H₄ and its dehydrogenated species (e.g., ethylidene (CH=CH₂) and/or ethylidyne (C≡CH₃) [27–31])

may block the dissociative adsorption of oxygen, thought to play an important role in the cleavage of the O–H bond of acetic acid and promoting the surface stability of the acetate species [32]. It is noteworthy that the negative reaction order with respect to C_2H_4 and the positive reaction order with respect to O_2 have also been observed in ethylene combustion in the presence and absence of AcOH over the Pd-5 catalyst [20].

As discussed by us previously [20], CO_2 in this reaction is formed mainly via combustion of ethylene and its dehydrogenated species. The decrease in selectivity with an increase in temperature (see Fig. 4) indicates that the combustion reaction is favored at elevated temperatures. A decline in selectivity was also observed with an increase in the partial pressure of O_2 (see Fig. 6). However, a drop in selectivity was also observed with an increase in the partial pressure of C_2H_4 . This can be ascribed to the fact that the rate of VA synthesis is inhibited more than is CO_2 formation upon the adsorption of additional C_2H_4 .

As this study shows, the Pd-1 catalyst exhibited a relatively high reactivity and selectivity for VA synthesis compared with Pd-5. The improvement can be generally ascribed to the change in the morphology and unique electronic structure of metal particles less than 3 nm in diameter [33–36]. The special electronic structure of these small particles can lead to altered catalytic reactivity, demonstrated in the extreme for nanosized Au clusters on titania for CO oxidation [34].

4. Conclusions

A kinetic study of VA synthesis over Pd particles with varying size, supported on a high-surface-area SiO_2 , has been carried out at atmospheric pressure. Pd/ SiO_2 catalysts have been characterized before and after reaction by TEM and XRD. Reducing the Pd particle size leads to an increase in the reactivity, the selectivity, and apparent activation energy with little change in the other kinetic parameters, such as negative order with respect to C_2H_4 and positive order with respect to O_2 . VA synthesis is determined to be a structure-sensitive reaction that is best carried out over small rather than large Pd particles.

Acknowledgments

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