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Journal of Catalysis 230 (2005) 353–358
JOURNAL OF CATALYSIS
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Particle size effects in vinyl acetate synthesis over Pd/SiO_2

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Received 29 September 2004; revised 15 December 2004; accepted 17 December 2004

Available online 25 January 2005

Abstract

Pd catalysts with varying particle size supported on a high-surface-area (600 m^2/g) SiO_2 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%)/SiO_2 and Pd(1.0 wt%)/SiO_2 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%)/SiO_2 to 39.0 kJ/mol over Pd(1.0 wt%)/SiO_2, 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.

Keywords: Vinyl acetate synthesis; Kinetics; Size dependence; Palladium; XRD; Pd/SiO_2 catalyst

1. Introduction

Since the first report by Moiseev et al. [1] of the catalytic synthesis of vinyl acetate (VA) from ethylene (C_2H_4), acetic acid (AcOH), and oxygen (O_2) 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

$$C_2H_4 + CH_3COOH + \frac{1}{2}O_2 \rightarrow C_2H_3OOCCH_3 + H_2O. \quad (1)$$

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 primarily on supported Pd catalysts, such as Pd/SiO_2, Pd/Al_2O_3 [5], and Pd/Al_2O_3 promoted by K^+ [6,7] and Pd/C [8]. Approximately 80–90% selectivity for VA has been observed over a Pd(2.0 wt%)/SiO_2 catalyst [5]. The catalytic performance of Pd-only catalysts can be improved considerably with the addition of Au. For instance, over Pd–Au/SiO_2 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/SiO_2 catalysts with two Pd particle sizes supported on a high-surface-area (600 m^2) SiO_2 has been studied. The kinetics study was car-

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0021-9517/$ – see front matter
doi:10.1016/j.jcat.2004.12.018

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/SiO_2 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%)/SiO_2 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/SiO_2 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 m^2/g) SiO_2 (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 Pd^{2+} solution by dissolving $Pd(NO_3)_2$ (C.P., commercial sources) in deionized water. The Pd^{2+} solution, with an equal volume of SiO_2, was then added to the SiO_2 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. N_2, C_2H_4, $O_2(10\%)/N_2$, 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 CO_2, C_2H_4, VA, and mixtures of O_2 and N_2. 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% O_2/N_2 mixture at 673 K (30 min, 20 Nml/min), followed by reduction in 100% H_2 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 N_2. 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 N_2, 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-

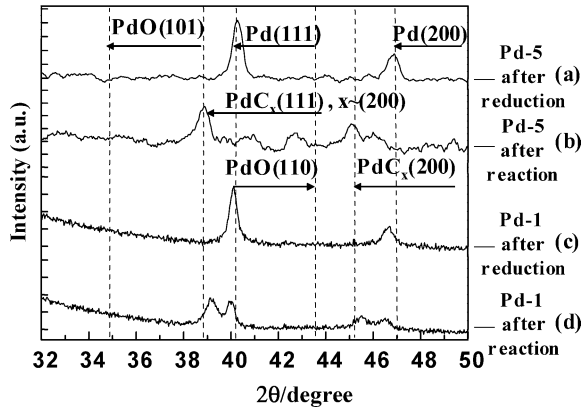

Fig. 1. (a) XRD of the Pd-5 catalyst after reduction at 673 K in 20 ml/min $O_2(10\%)/N_2$, 30 min, then 573 K in 20 ml/min H_2 for 30 min; (b) after reaction for 10 h, at $p_{C_2H_4} = 7.5$ kPa, $p_{O_2} = 1.0$ kPa, $p_{AcOH} = 2.0$ kPa, with remainder N_2; flow rate: 60 ml/min, at 413 K; (c) XRD of the Pd-1 catalyst after reduction; and (d) after reaction per above for 16.7 h.