



Influence of Pd precursors on the catalytic performance of Pd–H₄SiW₁₂O₄₀/SiO₂ in the direct oxidation of ethylene to acetic acid

Shuliang Xu^{a,b}, Lixia Wang^{a,b}, Wenling Chu^{a,*}, Weishen Yang^{a,*}

^a State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, P.O. BOX 110, Dalian 116023, China

^b Graduate School of the Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:

Received 11 October 2008

Received in revised form 21 May 2009

Accepted 5 June 2009

Available online 16 June 2009

Keywords:

Ethylene oxidation

Acetic acid

Pd–SiW₁₂/SiO₂

Pd dispersion

ABSTRACT

The effects of palladium precursors (PdCl₂, (NH₄)₂PdCl₄, Pd(NH₃)₂Cl₂, Pd(NO₃)₂ and Pd(CH₃COO)₂) on the catalytic properties in the selective oxidation of ethylene to acetic acid have been investigated for 1.0 wt% Pd–30 wt% H₄SiW₁₂O₄₀/SiO₂. The structures of the catalysts were characterized using X-ray diffraction, N₂ adsorption, H₂-pulse chemical adsorption, infrared spectrometry of the adsorbed pyridine, H₂ temperature-programmed reduction and X-ray photoelectron spectroscopy. The present study demonstrates that the different palladium precursors can lead to the significant changes in the dispersion of palladium. It is found that Pd dispersion decreases as follows: PdCl₂ > (NH₄)₂PdCl₄ > Pd(NO₃)₂ > Pd(NH₃)₂Cl₂ > Pd(C₂H₃O₂)₂, which is nearly identical to the catalytic activity. This indicates that the dispersion of palladium plays an important role in the catalytic activity. Furthermore, density of Lewis (*L*) and Brønsted (*B*) acid sites are also strongly dependent on the palladium precursors. It is also demonstrated that an effective catalyst should possess a well combination of Brønsted acid sites with dispersion of palladium.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Acetic acid is one of the most important organic acids since it is used in a broad range of applications. It is used primarily as a raw material for the synthesis vinyl acetate monomer (VAM) and acetic anhydride, and as a solvent for the production of pure terephthalic acid (PTA) [1]. Commercially, acetic acid is mainly produced from methanol carbonylation and acetaldehyde oxidation, which can give rise to many problems concerning handling, corrosion and waste disposal [1–4]. Therefore, considerable efforts have been made to develop alternative means of the acetic acid production, among which the direct oxidation of ethylene to acetic acid has shown promise. The development of a catalyst for this environmentally friendly reaction has attracted considerable attention. As an example, a process over palladium-based heteropolyacid catalysts for ethylene oxidation to acetic acid was commercialized by Showa Denko in 1997 [5–7] to give approximately 80% acetic acid selectivity at low temperature (~420 K). Moreover, the lower capital costs and the easy treatment of wastewater mean that this route, to some extent, has advantages over methanol carbonylation and the other processes.

* Corresponding authors. Tel.: +86 411 84379073/84379301; fax: +86 411 84694447.

E-mail addresses: cwl@dicp.ac.cn (W. Chu), yangws@dicp.ac.cn (W. Yang).

URL: <http://yanggroup.dicp.ac.cn/> (W. Yang).

A common feature of the catalysts for selective ethylene oxidation is that the bifunctional catalysts composed of palladium and an acidic support favor the selective formation of acetic acid [5–12]. Although the beneficial role of palladium is an important fact, little knowledge exists concerning the nature of its action and its chemical oxidation state. In particular, few reports exist on the effects of different palladium precursors for the catalysts except those for PdCl₂ and Pd(NH₃)₄Cl₂.

In the present study, the catalytic performance of Pd–H₄SiW₁₂O₄₀/SiO₂ with different palladium precursors was evaluated with respect to the selective oxidation of ethylene. The results are discussed in conjunction with the palladium dispersion and/or the oxidation state and the acidic properties of SiW₁₂ with the aim of contributing to better understanding of the correlation between the catalytic performance and catalyst properties.

2. Experimental

2.1. Catalyst preparation

Silica-supported H₄SiW₁₂O₄₀ samples (H₄SiW₁₂O₄₀/SiO₂) were prepared by a wetness impregnation method (excess water). Commercially available SiO₂ (384.7 m²/g) was used as the support.

Firstly, SiO₂ was added to an aqueous solution of H₄SiW₁₂O₄₀ with the appropriate concentration. The mixture was stirred vigorously for 3 h and then dried at 343 K till the wet sample became

Table 1

The corresponding solvents for different palladium precursors.

Pd precursors	Pd(C ₂ H ₃ O ₂) ₂	Pd(NO ₃) ₂	Pd(NH ₃) ₂ Cl ₂	(NH ₄) ₂ PdCl ₄	PdCl ₂
Solvents	CH ₃ COOH	1 M HNO ₃	NH ₃ ·H ₂ O	H ₂ O	0.1 M HCl

colloidal. After impregnation, the sample was dried in an oven at 383 K overnight and then calcined at 523 K in static state air for 3 h. This sample is denoted as SiW₁₂/SiO₂.

SiW₁₂/SiO₂ was impregnated with Pd using a solution of a compound containing Pd. To dissolve the Pd compound with different Pd precursors, different solvents as shown in Table 1 were added to the corresponding palladium solutions. After the solid was dried at 383 K, the sample was calcined at 523 K in static state air for 3 h. The loading amount of Pd was adjusted to 1.0 wt%. These catalysts are denoted as Pd-SiW₁₂/SiO₂.

2.2. Catalytic reaction

The direct oxidation of ethylene to acetic acid was performed in a fixed-bed flow reactor (stainless steel, 10 mm i.d.). 2 cm³ (40–60 mesh) of the catalyst was placed in the reactor and pretreated at 523 K for 1 h under a mixture stream of H₂/He (1:1, in vol%) at a flow rate of 60 cm³/min controlled by a mass flow controller. After cooled under a flow of He to the reaction temperature of 423 K, a mixture of the reactant gas (C₂H₄:O₂:H₂O:He = 50:7:30:13, in vol%) was fed into the reactor at a total flow rate of 100 cm³/min (SV = 3000 h⁻¹) and a total pressure of 0.6 MPa. A cooling trap filled with water and ice (~273 K) was used to collect the liquid products, which were later analyzed using an FID-GC (Agilent 6890) equipped with an FFAP column (30 m × 0.25 mm, film thickness 0.3 μm). The outlet gaseous compounds were analyzed by an on-line TCD-GC (Agilent 6890) operating with 13X (3 m × 2 mm) and Porapak Q (3 m × 2 mm) columns. The catalytic performance was expressed by the conversion of ethylene (X_{C₂H₄}), space-time yield (STY) of acetic acid and selectivity of the products after 2 h reaction time, which were defined as follows:

$$X_{C_2H_4} = \frac{\sum nP_i}{\sum nP_i + Q} \times 100\% \quad (1)$$

$$\text{Sel.} = \frac{nP_i}{\sum nP_i} \times 100\% \quad (2)$$

where P_i is the formation rate (C-mol/min) of each product, n is the carbon number and Q is the flow rate of ethylene remaining (C-mol/min).

2.3. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were recorded with a Rigaku D/Max-2500 diffractometer employing Cu K α radiation ($\lambda = 0.1542$ nm) in the 2θ range of 5–70° with a scanning step of 0.02°/s at 40 kV and 200 mA.

Fourier-transform infrared (FT-IR) spectra of the catalysts were obtained using a Nicolet Impact 410 FT-IR spectrometer. A sample disk (13 mm diameter, 50 mg) was prepared from the sample powder mixed with KBr (2 wt% catalyst). The spectrum was recorded at room temperature with 32 sample scans and a spectral resolution of 4 cm⁻¹.

The IR study of the pyridine adsorption was conducted by the same FT-IR spectrometer. The sample was pressed into a self-supporting wafer (~10 mg/cm²) and mounted into an in situ quartz IR cell with CaF₂ windows. The nature of the acid sites was investigated using pyridine as a probe molecule. Prior to each experiment, the sample was degassed at 523 K in vacuum to a pressure of 10⁻³ Pa. Then pyridine was applied to the evacuated samples for

10 min at room temperature, followed by evacuation at a fixed temperature (RT, 423 and 523 K) for 0.5 h. Then, a difference IR spectrum was recorded at room temperature.

The palladium dispersion was measured by a H₂-pulse chemical adsorption method using an Autosorb-1/C system at 313 K. In a typical experiment, the sample was firstly pretreated in a flow of He at 523 K for 6 h and subsequently reduced in a H₂ atmosphere at 523 K for 1 h. Then, hydrogen was purged from the system by evacuation for 2 h. The adsorption isotherm was established by measuring the amount of H₂ adsorbed as a function of pressure at 313 K.

X-ray photoelectron spectroscopy (XPS) measurements were carried out on a VG ESCALAB MK2 spectrometer by using an Al K α ($h\nu = 1486.6$ eV) radioactivity source and operating at 11 kV and 220 W. The photoelectron kinetic energy was measured by a hemispherical analyzer, with a pass energy of 20 eV. The vacuum in the spectrometer chamber was 0.9–1.5 × 10⁻⁶ Pa. The binding energy (BE) was calibrated against the Si_{2p} signal (103.4 eV) as a reference.

H₂-TPR was performed using an AutoChem II 2920 manufactured by Micromeritics. The analysis was carried out on all freshly prepared catalysts to identify reducible species present on the catalyst surface. In a typical experiment, 70 mg of sample was purged by flowing Ar at 523 K for 1 h and cooled down to 323 K. Then, the temperature was ramped from 323 to 1213 K at 10 K/min in a mixture of 10 mol% H₂/Ar. The rate of hydrogen consumption was detected with a TCD detector and recorded as the H₂-TPR profile of the catalyst.

The specific surface area and pore size distribution of the catalysts were derived from nitrogen adsorption/desorption isotherms at 77 K using a Counter Omnisorp-100CX apparatus, using BET and BJH methods, respectively. The samples were pretreated at 523 K under high vacuum (1.33 × 10⁻⁴ Pa) for 3 h before the isotherms were recorded.

3. Results

3.1. Catalytic performance

Table 2 shows the catalytic activity for the oxidation of ethylene to acetic acid on the Pd-SiW₁₂/SiO₂ catalysts prepared from the different Pd precursors. It is evident that the catalytic properties strongly depend on the palladium precursors. The conversion of ethylene decreases in the order PdCl₂ > (NH₄)₂PdCl₄ > Pd(NO₃)₂ > Pd(CH₃COO)₂ > Pd(NH₃)₂Cl₂. The catalyst with PdCl₂ as Pd precursor exhibits the highest catalytic activity for the selective oxidation of ethylene, showing 5.4% ethylene conversion and 134 g L⁻¹ h⁻¹ yield of acetic acid. As shown in Table 2, no significant differences in the selectivity to acetic acid are observed for any of the Pd-SiW₁₂/SiO₂ catalysts except that from Pd(CH₃COO)₂, which shows very low selectivity to acetic acid. These results suggest that the surface structure of palladium and/or the nature of the catalytically active sites are different, depending on the palladium precursors.

3.2. Characterization

3.2.1. XRD

The XRD patterns of Pd-SiW₁₂/SiO₂ catalysts with different palladium precursors are shown in Fig. 1. It is clear that no diffraction peak for Pd appears for any of the catalysts with 1.0 wt% Pd. From Fig. 1, it can be seen that a broad diffraction peak appears at $2\theta = 8^\circ$,

Table 2
Catalytic activity of Pd-SiW₁₂/SiO₂ prepared from different palladium precursors^a.

Pd precursors	X _{C₂H₄} (%)	STY _{AcOH} (g/(Lh))	Selectivity to products ^b (%)					
			AcOH	AcH	EtOH	EtAc	CO ₂	CO
Pd(CH ₃ COO) ₂	3.0	62.9	54.5	14.9	3.2	3.7	21.6	2.1
Pd(NO ₃) ₂	3.9	90.2	60.3	9.6	2.8	4.6	20.6	2.0
Pd(NH ₃) ₂ Cl ₂	2.2	56.4	65.9	7.2	0.1	0.1	23.7	3.0
(NH ₄) ₂ PdCl ₄	4.8	120.0	65.4	6.9	0.9	1.8	21.7	3.3
PdCl ₂	5.4	134.0	63.9	7.0	3.6	7.9	15.0	2.7
Pd-free	0.1	0.0	0.0	0.9	99.1	0.0	0.0	0.0

^a Reaction conditions: C₂H₄:O₂:H₂O:He = 50:7:30:13, GHSV = 3000 h⁻¹, temperature 423 K, and pressure 0.6 MPa.

^b AcOH = acetic acid, AcH = acetaldehyde, EtOH = ethanol, EtAc = ethyl acetate.

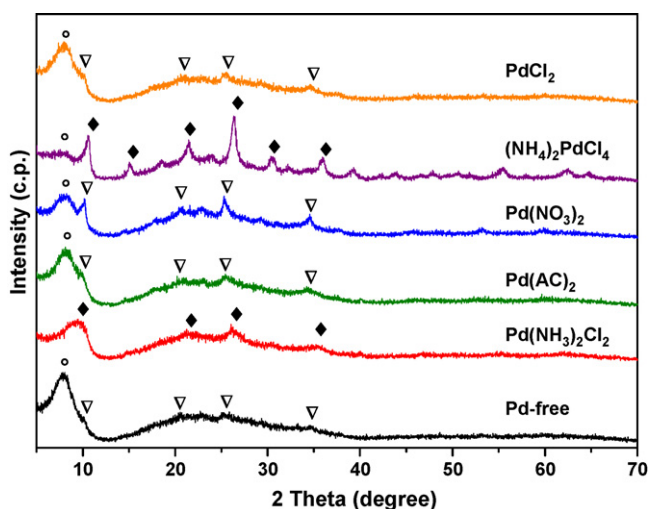


Fig. 1. XRD patterns of the Pd-SiW₁₂/SiO₂ catalysts prepared from different palladium precursors.

characteristic of solid state 12-tungstosilic acid [13], for all of the samples except that from the Pd(NH₃)₂Cl₂ precursor, where this characteristic peak is absent. This difference may be mainly attributed to the formation of the salt (NH₄)₄SiW₁₂O₄₀ [14] resulting from the reaction between H₄SiW₁₂O₄₀ and NH₃·H₂O solvent during the impregnation.

3.2.2. FT-IR

FT-IR spectra for the Pd-SiW₁₂/SiO₂ catalysts prepared from different palladium precursors are illustrated in Fig. 2, together with that for the Pd-free SiW₁₂/SiO₂ sample. SiW₁₂/SiO₂ gave peaks due to the characteristic Keggin structure at 977 cm⁻¹ (ν_{as}(W–O_t)), 926 cm⁻¹ (ν_{as}(Si–O_j)), 880 cm⁻¹ (ν_{as}(W–O_b–W)), and 802 cm⁻¹ (ν_{as}(W–O_c–W)) [13]. All the SiW₁₂/SiO₂ catalysts containing Pd also exhibit the peaks due to a Keggin structure with similar shape and intensity, indicating that the polyanion of the Keggin structure is retained during the loading with all of the different palladium precursors.

3.2.3. Pyridine adsorption

The adsorption of pyridine as a base on the surface of solid acids is one of the most frequently applied methods for the characterization of surface acidity. The FT-IR pyridine adsorption spectra of the different Pd-SiW₁₂/SiO₂ catalysts are shown in Fig. 3. The spectra show sharp pyridine adsorption bands at 1448 and 1540 cm⁻¹. As can be seen in Fig. 3, pyridine molecules bonded to Lewis acid sites give rise to a peak at about 1448 cm⁻¹, whereas those that interact with Brønsted acid sites (pyridinium ions) display an absorbance at 1540 cm⁻¹. The concentration of Lewis (L) and Brønsted (B) acid sites, obtained from the absorbance at 1448 and 1540 cm⁻¹ [15] and the calculated L/(B+L) ratios are presented in Table 3. The results

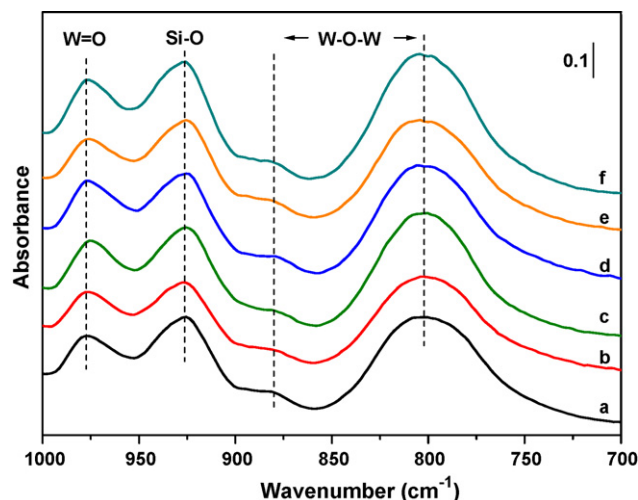


Fig. 2. IR spectra of the Pd-SiW₁₂/SiO₂ catalysts prepared from different palladium precursors: a, Pd(C₂H₃O₂)₂; b, Pd(NO₃)₂; c, Pd(NH₃)₂Cl₂; d, (NH₄)₂PdCl₄; e, PdCl₂; f, Pd-free.

show that Pd-free SiW₁₂/SiO₂ catalyst possesses mainly Brønsted acid sites with only a weak absorbance for Lewis acid sites. The loading of palladium result in an increase in the Lewis acidity on all the samples except that from the Pd(NH₃)₂Cl₂ precursor, in which NH₄⁺ may occupy the Lewis acid sites. Furthermore, the IR spectra of the Pd-SiW₁₂/SiO₂ catalyst from the PdCl₂ precursor show a more intense adsorption band for Lewis acidity compared with

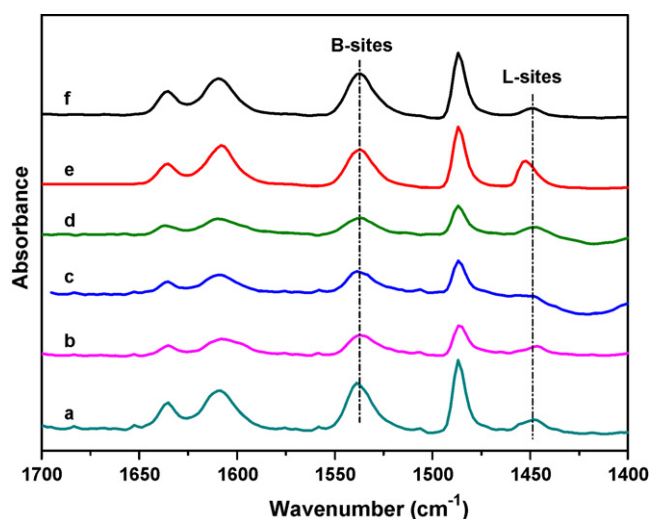


Fig. 3. IR spectra of pyridine adsorption on the Pd-SiW₁₂/SiO₂ catalysts prepared from different palladium precursors: a, Pd(C₂H₃O₂)₂; b, Pd(NO₃)₂; c, Pd(NH₃)₂Cl₂; d, (NH₄)₂PdCl₄; e, PdCl₂; f, Pd-free.

Table 3
Amount of acid sites determined by FT-IR of pyridine adsorption.

Pd precursors	Brønsted acid sites (mmol g ⁻¹)	Lewis acid sites (mmol g ⁻¹)	L/(B+L) ratio
Pd(CH ₃ COO) ₂	0.30	0.042	0.12
Pd(NO ₃) ₂	0.14	0.023	0.14
Pd(NH ₃) ₂ Cl ₂	0.14	0.014	0.09
(NH ₄) ₂ PdCl ₄	0.12	0.022	0.15
PdCl ₂	0.22	0.075	0.25
Pd-free	0.28	0.022	0.07

Table 4
The surface area, Pd dispersion^a and crystallite size of Pd-SiW₁₂/SiO₂ catalysts with different palladium precursors.

Pd precursors	S _{BET} (m ² /g)	S _{Pd} (m ² /g)	Pd disp. (%)	Pd crystallite Size (nm)
Pd(CH ₃ COO) ₂	202.0	0.87	19.57	5.7
Pd(NO ₃) ₂	211.5	1.18	26.36	4.2
Pd(NH ₃) ₂ Cl ₂	199.5	1.06	23.78	4.7
(NH ₄) ₂ PdCl ₄	217.6	2.31	51.86	2.2
PdCl ₂	210.0	2.97	66.64	1.7
Pd-free	217.5	–	–	–

^a Measured by H₂-pulse chemical adsorption.

other samples, indicating that the palladium precursors have an important influence on the relative amount of Brønsted and Lewis acid sites.

3.2.4. BET and H₂ chemical adsorption

Table 4 shows the specific surface areas measured by the BET method, and the dispersion of palladium determined from H₂-chemical adsorption. Compared with SiW₁₂/SiO₂ samples, no significant changes of the surface area are observed for any of the SiW₁₂/SiO₂ catalysts containing Pd. This result indicates that the precursors have little effect on the bulk physical structure of the catalysts. However, it is found that Pd-SiW₁₂/SiO₂ catalysts prepared from (NH₄)₂PdCl₄ and PdCl₂ show greater dispersion than those from other palladium precursors, clearly indicating that dispersion of Pd metal is strongly dependent

Table 5
The atomic ratio of surface element to silicon obtained with XPS for the Pd-SiW₁₂/SiO₂ catalysts with different palladium precursors.

Pd precursors	Atomic ratio of surface element to Si					
	C	O	W	Pd	N	Cl
Pd(CH ₃ COO) ₂	0.16	1.66	0.05	0.002	–	–
Pd(NO ₃) ₂	0.18	1.91	0.03	0.004	0.01	–
Pd(NH ₃) ₂ Cl ₂	0.22	1.92	0.04	0.003	0.02	0.004
(NH ₄) ₂ PdCl ₄	0.29	1.89	0.04	0.011	0.02	0.02
PdCl ₂	0.26	2.22	0.04	0.009	–	0.01
Pd-free	0.15	1.73	0.04	–	–	–

upon the palladium precursors, decreasing in the following order: PdCl₂ > (NH₄)₂PdCl₄ > Pd(NO₃)₂ > Pd(NH₃)₂Cl₂ > Pd(CH₃COO)₂. This result indicates that the dispersion is related to the nature of Pd precursors.

3.2.5. XPS

To investigate the state of Pd in the Pd-SiW₁₂/SiO₂ catalysts with different Pd precursors, an XPS test was carried out with the results shown in Fig. 4A. The intense peaks of Pd3d_{5/2} can be deconvoluted into two peaks at 335.5 and 336.1 eV which show the presence of Pd⁰ and Pd²⁺, respectively. The result indicates that the palladium species on the surface of the catalysts are not only in the zero-valent state but also present as Pd²⁺ species. Table 5 lists the surface atomic ratio of each component obtained by integration of the corresponding element and the Si2p peak according to the literature [16,17]. Table 5 shows that the concentration of the surface palladium is strongly dependent on the palladium precursors and decreases in the following order: (NH₄)₂PdCl₄ > PdCl₂ > Pd(NO₃)₂ > Pd(NH₃)₂Cl₂ > Pd(CH₃COO)₂, which is nearly identical to the Pd dispersion results (Table 4).

Fig. 4B shows a comparison of the O1s X-ray photoelectron spectra of all the Pd-SiW₁₂/SiO₂ catalysts. No significant differences in the O1s spectra of the catalysts are observed except that from the Pd(CH₃COO)₂ precursor, which is attributed to the oxygen in the carboxyl group (533.8 eV). This also provides further explanation of the distinctly high proportion of Brønsted acid sites on the sur-

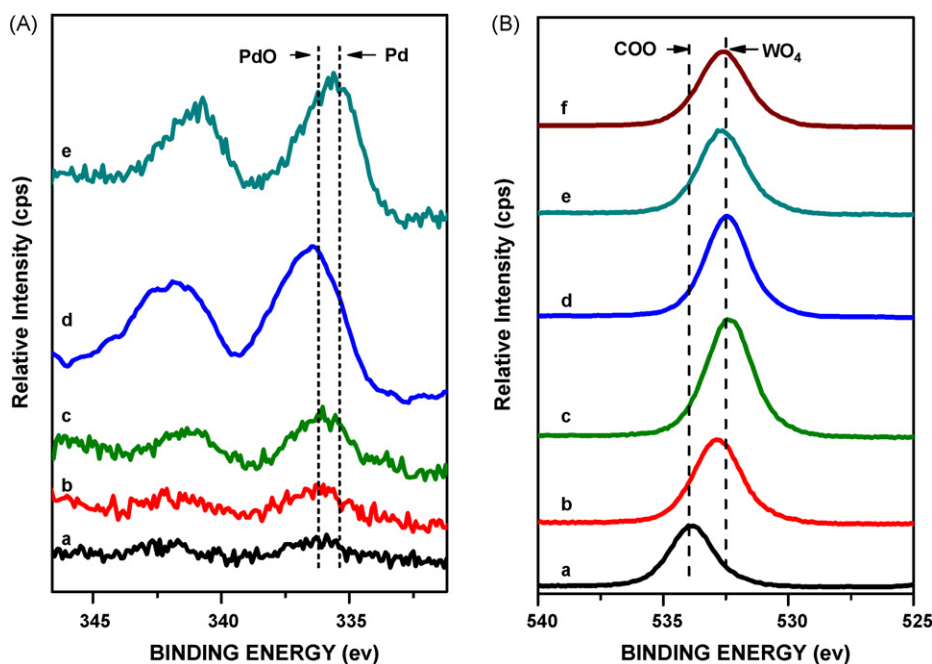


Fig. 4. Evolution of Pd3d (A) and O1s (B) XPS spectra of the Pd-SiW₁₂/SiO₂ catalysts prepared from different palladium precursors: a, Pd(C₂H₃O₂)₂; b, Pd(NH₃)₂Cl₂; c, Pd(NO₃)₂; d, PdCl₂; e, (NH₄)₂PdCl₄; f, Pd-free.

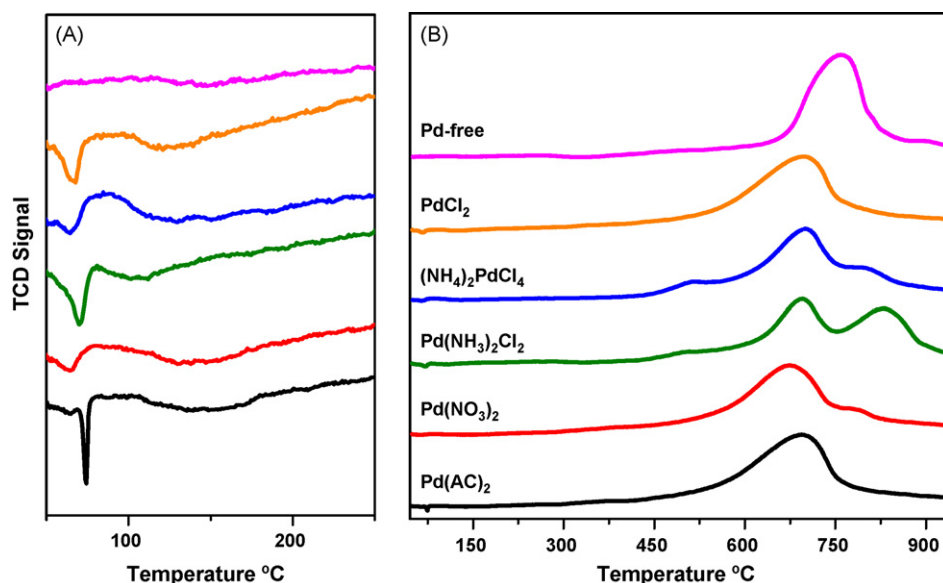


Fig. 5. TPR profiles of the Pd-SiW₁₂/SiO₂ catalysts prepared from different palladium precursors. (A) is a partial enlarged figure of (B).

face of the catalyst from the Pd(CH₃COO)₂ precursor (Table 3), in that some of Brønsted acid sites may originate from the carboxyl itself.

3.2.6. H₂-TPR

The H₂-TPR profiles of the Pd-SiW₁₂/SiO₂ catalysts from different palladium precursors are shown in Fig. 5. The patterns reveal important information about the nature of the palladium species. For all the samples containing Pd, the catalysts exhibit a negative peak in the region of 338–348 K, which is characteristic of the decomposition of the β-PdH phase that forms before the start of the H₂-TPR run. It has been widely accepted that the formation of β-PdH is favored by the existence of large Pd particles, which are easily reducible to metallic Pd [18–20]. It is important to observe the sharper negative peaks in the catalysts from the Pd(CH₃COO)₂ and Pd(NH₃)₂Cl₂ precursors, possibly due to an increase in particle size. The evidence for the formation of large Pd particles can be implied from the low dispersion values obtained by H₂ chemisorption (Table 4). The positive reduction peak with its maximum at approximately 360 K can be ascribed to the reduction of Pd²⁺ species that are well dispersed on the support. It can be clearly seen that the amounts of Pd²⁺ species in the catalysts from Pd(CH₃COO)₂ and Pd(NO₃)₂ precursors are far lower than those from the other precursors. The high-temperature reduction peaks at approximately 950 K could be a result of the reduction of metal oxides originating from the decomposition of Keggin polyanions, as shown in the H₂-TPR profile of the Pd-free SiW₁₂/SiO₂ catalyst.

4. Discussion

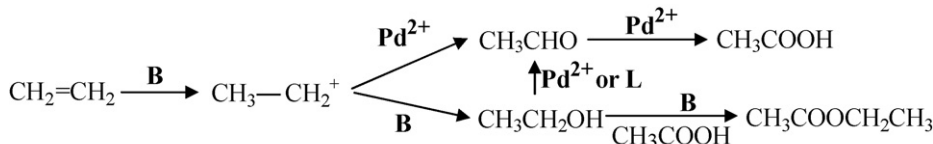
According to the literature [11,21,22], it is possible that the selective oxidation of ethylene on Pd-SiW₁₂/SiO₂ catalysts can take place bifunctionally by co-operation between Pd species and the acid sites of the support. A comparison of the catalytic activity of Pd-SiW₁₂/SiO₂ prepared from different palladium precursors for the direct oxidation of ethylene to acetic acid shows that there is a significant difference in the conversion of ethylene and yield of acetic acid. This result suggests that using different palladium precursors may produce acid sites with different acidic properties as well as palladium species with different dispersion, both of which are directly related to the catalytic properties.

It is well known that Pd itself plays a vital role in the selective oxidation of ethylene to acetic acid [23,24]. For example, Pd-free SiW₁₂/SiO₂ is inactive for the formation of acetic acid (Table 2). Usually, the catalytic properties of Pd supported catalysts have been found to be dependant on the palladium dispersion and/or the oxidation state of the noble metal. Regarding the first point, it has been shown, from H₂ chemisorption data, that the Pd dispersion over SiW₁₂/SiO₂ decreases as follows: PdCl₂ > (NH₄)₂PdCl₄ > Pd(NO₃)₂ > Pd(NH₃)₂Cl₂ > Pd(CH₃COO)₂, which is nearly identical to the order of catalytic activity. This indicates that the dispersion of palladium plays an important role in the catalytic activity. The reason for high activity of PdCl₂-loaded catalysts may be attributed to the higher dispersion of Pd as displayed in Table 4. Regarding the oxidation state of palladium, H₂-TPR results have clearly shown that the amounts of Pd²⁺ species in the catalysts from Pd(CH₃COO)₂ and Pd(NO₃)₂ precursors are far lower than those from other precursors, leading to a poor selectivity for acetic acid. In particular, for the catalyst from the Pd(CH₃COO)₂ precursor, the presence of a sharp negative peak at 347 K suggests that Pd²⁺ agglomeration has occurred, leading to the formation of large particles that are easily reduced to metallic Pd, for which the lowest selectivity to acetic acid is observed. For the catalysts from three other precursors, the better selectivity for acetic acid can be due to the presence of the Pd²⁺ species.

Considering the acidity of the support, it has been found that both Lewis and Brønsted acid sites are observed in the pyridine-IR spectra, the number of which is different for different palladium precursors. This provides clear evidence that the acidic properties of Pd-SiW₁₂/SiO₂ catalysts are strongly dependent on the palladium precursors. Interestingly, the total concentration of Brønsted or Lewis acid sites did not show a correlation with the dispersion of palladium, which has been found to play an important role in catalytic activity. A good correlation, however, is found for the L/(B+L) ratio (Tables 2 and 3). With increasing ratios of Lewis to Brønsted acid sites, the dispersion of palladium increases. The results from the FT-IR pyridine adsorption have demonstrated the appearance of new Lewis acid sites in the SiW₁₂/SiO₂ catalysts containing Pd. This is due to the existence of electron-deficient metal sites Pd²⁺ which exhibit Lewis acidity as a result of the interaction between the metal sites and the acid sites [25–27], which is in good agreement with the coherence of Pd dispersion and the ratio of L/(B+L). As shown in Table 3, the catalyst from the PdCl₂ precursor

with the highest $L/(B+L)$ ratio gives the highest dispersion of palladium, indicating that the $L/(B+L)$ ratio is related to the Pd dispersion, that is, to the catalytic activity for the selective oxidation of ethylene.

The mechanism of ethylene oxidation and the role of the metal and acid sites on the bifunctional Pd-SiW₁₂/SiO₂ catalyst remain unclear. Sano et al. [1] reported a route where ethanol is formed by the hydration of ethylene and then it is oxidized to acetic acid. However, Okuhara et al. [28] and other researchers [29] tended to favor another route where ethylene is first converted into acetaldehyde by the Wacker type reaction, and the acetaldehyde is oxidized into acetic acid. According to the literature and product distribution observed in the present catalytic system (Table 2), we propose that two pathways are concurrent in the Pd-SiW₁₂/SiO₂ catalytic oxidation of ethylene to acetic acid, as follows:



B: Brønsted acid sites; L: Lewis acid sites; Pd²⁺: Pd²⁺ species

It is obvious that Brønsted acid sites are indispensable in order to obtain carbocation intermediates. But if the proportion of Brønsted acid sites is too high, especially, if Pd²⁺ species are absent, for example, for the Pd-free SiW₁₂/SiO₂ catalyst, then the route of hydration of ethylene to ethanol is absolutely predominant and no acetic acid is observed in the products.

For Pd-containing catalysts, it is obvious that the production of acetic acid is dominating with rather low selectivity to ethanol, suggesting that the presence of Pd²⁺ species is indispensable in order to obtain acetic acid. It is well known that palladium oxide in a well dispersed state can increase the concentration of oxidizing sites with redox properties. These are responsible for the chemisorption and O insertion of carbocations adsorbed on the B acid sites to form acetaldehyde, which can be further oxidized to acetic acid on the well-dispersed Pd²⁺ sites. As a result, for SiW₁₂/SiO₂ catalysts containing Pd, for which the formation of carbocations results from Brønsted acid sites, the higher is the dispersion of palladium, the easier are the carbocations conversion into acetaldehyde and further to acetic acid. As for Brønsted acid sites, from the results above, it can be found that it is necessary to obtain carbocation intermediates. According to the literature [11], it seems that Brønsted acid sites are also responsible for the re-oxidation of Pd²⁺ species. Accordingly, it can be concluded that efficient catalytic reactivity are realized by the combination of Brønsted acid sites from heteropolyacid with high dispersion of palladium.

5. Conclusion

Samples of Pd-SiW₁₂/SiO₂ prepared from different palladium precursors were used as catalysts for the selective oxidation of ethylene to acetic acid. Among these catalysts, Pd-SiW₁₂/SiO₂ from

the PdCl₂ precursor shows the best catalytic properties, yielding approximately 134 g L⁻¹ h⁻¹ of acetic acid. This higher performance for the selective oxidation of ethylene is attributed to a significantly better dispersion of palladium, which is related to the high $L/(B+L)$ ratio. Furthermore, we conclude that the palladium precursors have a significant influence on the acidic properties and palladium dispersion of the Pd-H₄SiW₁₂O₄₀/SiO₂ catalysts, and that a well combination of Brønsted acid sites with dispersion of palladium has been found to be responsible for the catalytic activity.

Acknowledgments

The authors gratefully acknowledge financial support from the National Science Foundation for Distinguished Young Scholars

(Grant No. 20725313) and the Ministry of Science and Technology of China (Grant No. 2005CB221404).

References

- [1] K. Sano, H. Uchida, S. Wakabayashi, Catal. Surv. Jpn. 3 (1999) 55.
- [2] M.J. Howard, M.D. Jones, M.S. Roberts, S.A. Taylor, Catal. Today 18 (1993) 325.
- [3] R. Jira, W. Blan, D. Grimm, Hydrocarbon Process. (March) (1976) 97.
- [4] N. Yoneda, S. Kusano, M. Yasui, P. Pujado, S. Wilcher, Appl. Catal. A 221 (2001) 253.
- [5] Japan Kokai Tokkyo Koho 9-48744 (1997), to Showa Denko K.K.
- [6] Japan Kokai Tokkyo Koho 9-100254 (1997), to Showa Denko K.K.
- [7] Japan Kokai Tokkyo Koho 9-151158 (1997), to Showa Denko K.K.
- [8] W. Chu, T. Echizen, Y. Kamiya, T. Okuhara, Appl. Catal. A 259 (2004) 199.
- [9] W. Chu, Y. Ooka, Y. Kamiya, T. Okuhara, Catal. Lett. 101 (2005) 225.
- [10] W. Chu, Y. Ooka, Y. Kamiya, T. Okuhara, H. Hattori, Chem. Lett. 34 (2005) 642.
- [11] T. Kawakami, Y. Ooka, H. Hattori, W. Chu, et al., Appl. Catal. A 350 (2008) 103.
- [12] Y. Yuan, P. Xu, Z. Zhu, J. East China Univ. Sci. Technol. 26 (2000) 126.
- [13] A. Miyaji, T. Echizen, K. Nagata, Y. Yoshinaga, T. Okuhara, J. Mol. Catal. A 201 (2003) 145.
- [14] H. Hayashi, J.B. Moffat, J. Catal. 83 (1983) 192.
- [15] C.A. Emeis, J. Catal. 141 (1993) 347.
- [16] Y. Boudeville, et al., J. Catal. 58 (1979) 52.
- [17] J.H. Scofield, J. Elec. Spec. 8 (1976) 129.
- [18] H. Lieske, J. Volter, J. Phys. Chem. 89 (1985) 1841.
- [19] M. Boudart, H.S. Hwang, J. Catal. 39 (1975) 44.
- [20] J.E. Benson, H.S. Hwang, M. Boudart, J. Catal. 30 (1973) 146.
- [21] A. Miyaji, R. Ohnishi, T. Okuhara, Appl. Catal. A 262 (2004) 143.
- [22] T. Okuhara, J. Jpn. Petrol. Inst. 47 (2004) 1.
- [23] X.-B. Li, E. Iglesia, Angew. Chem. Int. Ed. 46 (2007) 8649.
- [24] J.-H. Xie, Q.-L. Zhang, K.T. Chuang, Catal. Lett. 93 (2004) 181.
- [25] H. Yasuda, T. Sato, Y. Yoshimura, Catal. Today 50 (1999) 63.
- [26] F. Garin, G. Maire, S. Zyade, M. Zauwen, A. Frennet, P. Zielinski, J. Mol. Catal. 58 (1990) 185.
- [27] J. Zielinski, J. Chem. Soc. Faraday Trans. 93 (1997) 3577.
- [28] A. Miyaji, T. Hamada, Y. Kamiya, T. Nakajo, T. Okuhara, Catal. Lett. 119 (2007) 252.
- [29] J.-L. Zhang, X.-P. Wang, X.-Y. Su, T.-X. Cai, Chin. J. Catal. 23 (2002) 309.