CHINESE JOURNAL OF CATALYSIS
Volume 31, Issue 11, 2010
Online English edition of the Chinese language journal

Cite this article as: Chin J Catal, 2010, 31: 1342–1346.

RESEARCH PAPER

The Effect of Preparation Procedure on the Performance of Pd-SiW$_{12}$/SiO$_2$ Catalysts for the Direct Oxidation of Ethylene to Acetic Acid

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Abstract: Pd-SiW$_{12}$/SiO$_2$ catalysts were investigated to elucidate the effect of preparation procedure on the direct oxidation of ethylene to acetic acid. Pd-SiW$_{12}$/SiO$_2$ catalysts with a fixed amount of Pd and SiW$_{12}$ were prepared in various ways. The order in which Pd and SiW$_{12}$ were loaded on the SiO$_2$ support and the treatment conditions for the supported Pd have a significant influence on the dispersion of Pd on the Pd-SiW$_{12}$/SiO$_2$ catalysts, but no influence on the concentration of B acid sites. The Pd-SiW$_{12}$/SiO$_2$ catalyst prepared by simultaneously loading Pd and SiW$_{12}$ on the SiO$_2$ support showed the best catalytic activity. The dispersion of Pd was the main factor in the catalytic activity.

Key words: preparation procedure; palladium; silicotungstic acid; silica; ethylene oxidation; acetic acid

Acetic acid is a very important organic acid, which is used in a broad range of applications. It is mainly produced from methanol carbonylation and acetaldehyde oxidation, but both these processes give rise to many problems of corrosion and waste disposal [1–4]. The use of Pd-$H_4SiW_{12}O_{40}$(SiW$_{12}$)/SiO$_2$ for the direct catalytic oxidation of ethylene to acetic acid, developed by Showa Denko [1], has considerable interest. SiW$_{12}$ heteropoly acid has several advantages as a Brönsted acidic catalyst, which makes it economically and environmentally attractive [5,6]. The Pd-SiW$_{12}$/SiO$_2$ catalyst is a promising material for reactions such as the isomerization of *n*-pentane and *n*-heptane [7–9]. Both the palladium catalyst and an acidic support are common features of the catalysts used for the selective oxidation of ethylene to acetic acid [10–13]. With the Pd-SiW$_{12}$/SiO$_2$ catalyst, Pd and SiW$_{12}$ act as the redox and acidic active sites, respectively.

Various parameters, including the Pd precursor [14] and the nature of the support [15], are factors that influence the catalytic activity of Pd-SiW$_{12}$/SiO$_2$. Besides these factors, the importance of the preparation procedure should also be emphasized. It has been found that the procedure for the preparation of the Pd-SiW$_{12}$/SiO$_2$ catalyst, such as the order of application of Pd and SiW$_{12}$ on the SiO$_2$ support, led to big differences in catalytic performance [7,10,16–18]. Therefore, new experimental data on the preparation procedures are needed to elucidate these differences. Furthermore, in the preparation process, the role of treatment conditions for the supported Pd is significant for the dispersion of the active phase. According to the literature [17,18], before loading the SiW$_{12}$, reduction of Pd/SiO$_2$ by H_2 led to a lower catalytic activity than reduction by hydrazine hydrate ($N_2H_4 \cdot H_2O$). Despite extensive research work on the design and characterization of the Pd-SiW$_{12}$/SiO$_2$ catalyst, the effect of preparation procedure on the catalytic performance for the selective oxidation of ethylene to acetic acid is still unclear. In this report, we describe the influence of the preparation procedure on the catalytic activity of Pd-SiW$_{12}$/SiO$_2$ for the direct oxidation of ethylene to acetic acid. The catalyst was characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) of adsorbed pyridine, and H_2-pulse chemical adsorption. The

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Received date: 12 May 2010.

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DOI: 10.1016/S1872-2067(10)60123-4

relationship between Pd dispersion, surface acidity, and catalytic properties of the Pd-SiW_{12}/SiO_2 catalyst is discussed.

1 Experimental

1.1 Preparation of the catalysts

Pd-SiW_{12}/SiO_2 catalysts with fixed amounts of SiW_{12} and Pd, mass loadings 30.0 wt% and 1.0 wt%, respectively, were prepared by various procedures. Commercially available SiO_2 (A_{BET} = 384.7 m^2/g) was used as the support. The Pd-SiW_{12}/SiO_2 catalysts were prepared according to the following different procedures shown in Fig. 1.

For procedure (A), Pd was first impregnated onto SiO_2 using a solution of $PdCl_2$ dissolved in 0.1 mol/L HCl. The mixture was stirred vigorously for 3 h, then dried at 343 K until the wet sample became colloidal. Then the Pd/SiO_2 sample was dried in an oven at 383 K overnight. The resulting dry solid was calcined at 523 K in static air for 3 h. Subsequently, SiW_{12} was supported on the Pd/SiO_2 by the incipient wetness method from aqueous $H_4SiW_{12}O_{40}$. After vigorously stirring for 3 h, the same procedures as those used in preparing the Pd/SiO_2 sample were used for drying and calcination. This catalyst was denoted as Pd-SiW_{12}/SiO_2(A).

For procedure (B), Pd was first impregnated onto SiO_2 with the preparation process being the same as procedure (A) but the sample was reduced in an aqueous solution of 5% hydrazine hydrate at room temperature for 24 h. The resulting mixed sample was filtered and washed until no $N_2H_4\cdot H_2O$ was detected. The reduced Pd/SiO_2 sample was dried in an oven at 383 K overnight. Finally, SiW_{12} was supported by the same incipient wetness method as that in procedure (A). This catalyst was denoted Pd-SiW_{12}/SiO_2(B).

For procedure (C), Pd was first impregnated onto SiO_2 with the preparation process the same as that of procedure (A) but the sample was reduced in a flow of 5% H_2-95% Ar (30 ml/min) at 523 K for 3 h. Finally, SiW_{12} was supported by the same incipient wetness method as used in procedure (A). This catalyst was denoted Pd-SiW_{12}/SiO_2(C).

For procedure (D), first, SiO_2 was added to an aqueous solution of $H_4SiW_{12}O_{40}$ in the appropriate concentration. The mixture was stirred vigorously for 3 h, then dried at 343 K until the wet sample became colloidal. Then the sample SiW_{12}/SiO_2 was dried in an oven at 383 K overnight. The resulting dry solid was calcined at 523 K in static air for 3 h. Subsequently, Pd was supported using the incipient wetness method from a solution of the $PdCl_2$ dissolved in 0.1 mol/L HCl. The same procedures were used for drying and calcination as used in procedure (A). This catalyst was denoted Pd-SiW_{12}/SiO_2(D).

For procedure (E), simultaneously, Pd and SiW_{12} were supported onto SiO_2 using a mixed solution of $PdCl_2$ dissolved in 0.1 mol/L HCl and an aqueous solution of $H_4SiW_{12}O_{40}$. The mixture was stirred vigorously for 3 h, then dried at 343 K until the wet sample became colloidal. After impregnation, the sample was dried in an oven at 383 K overnight and then calcined at 523 K in static air for 3 h. This catalyst was denoted Pd-SiW_{12}/SiO_2(E).

1.2 Characterization of the catalysts

Powder XRD patterns were recorded with a Rigaku D/Max-2500 diffractometer employing Cu K_α radiation (λ = 0.154 2 nm) in the 2θ range 5°–70° with a scan rate of 0.02°/s at 40 kV and 200 mA.

FT-IR spectra of adsorbed pyridine were obtained using an FT-IR spectrometer. The samples were pressed into a self-supporting wafer (~10 mg/cm^2) and mounted into an in situ quartz IR cell with CaF_2 windows. The nature of the acid sites was investigated using pyridine as the probe molecule. Prior to the experiment, the sample was degassed at 523 K at a pressure of 10^{-3} Pa. Pyridine was introduced to the evacuated samples for 10 min at room temperature, followed by evacuation at a fixed temperature (room temperature, 423 K, or 523 K) for 0.5 h. Then, a difference IR spectrum was recorded at room temperature.

The palladium dispersion was measured by a H_2-pulse chemical adsorption method using an Autosorb-1/C system at 313 K. In a typical experiment, the sample was first pretreated

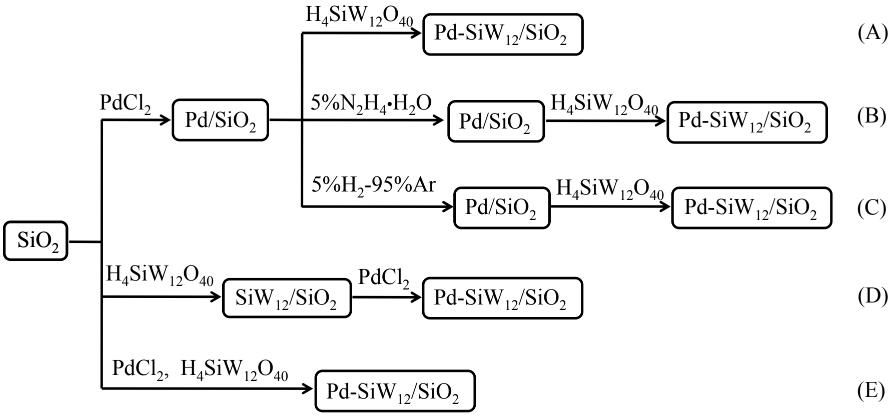

Fig. 1. Schematic of the preparation procedures for Pd-SiW_{12}/SiO_2 catalysts.

in a flow of He at 523 K for 6 h and subsequently reduced in H_2 at 523 K for 1 h. Hydrogen was removed from the system by evacuating for 2 h. The adsorption isotherm was obtained by measuring the amount of H_2 adsorbed as a function of pressure at 313 K.

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 the 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.

1.3 Catalytic reaction

The direct oxidation of ethylene to acetic acid was performed in a fixed-bed flow reactor (stainless steel, 10 mm i.d.). The catalyst (2 ml, 40–60 mesh) was placed in the reactor and pretreated at 523 K for 1 h under a mixed stream of H_2/He (1:1, vol%) at a flow rate of 60 ml/min. After cooling in a flow of He to the reaction temperature of 423 K, a mixture of the reactant gases (C_2H_4:O_2:H_2O:He = 50:7:30:13, vol%) was fed into the reactor at a total flow rate of 100 ml/min (SV = 3 000 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 by 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 online TCD-GC (Agilent 6890) with 13X (3 m × 2 mm) and Porapak Q (3 m × 2 mm) columns.

2 Results and discussion

The XRD patterns of the Pd-SiW_{12}/SiO_2 catalysts prepared using the various procedures are shown in Fig. 2. No diffraction peak of Pd appeared for all the catalysts, which suggested that Pd was well dispersed on the surface of the catalysts. The samples displayed a wide peak at $2\theta = 8^{\circ}$ (d = 1.1 nm) that can be attributed to X-ray scattering by non-ordered hydrated SiW_{12} polyanions present on the surface as isolated molecular moieties or small clusters containing a few Keggin units [7]. The absence of signals from bulk SiW_{12} suggested that it was also well dispersed on the surface of the silica support. This observation is significant because the acidity of supported SiW_{12} was related to its dispersion on the support [7,10]. It was reasonable to consider that with a higher SiW_{12} dispersion, there are more protons present on the surface of the support.

In order to investigate the nature of the surface acid sites (Brönsted and Lewis) of the catalyst, the FT-IR spectra of adsorbed pyridine on the Pd-SiW_{12}/SiO_2 catalysts were recorded. As shown in Fig. 3, pyridine molecules bonded to Lewis acid sites give a peak at 1 450 cm^{-1}, while those that interact with Brönsted acid sites (pyridinium ions) displayed absorbance at 1 540 cm^{-1}. The concentration of the Lewis and Brönsted acid sites, obtained from the integrated absorbance peaks of pyridine at 1 450 and 1 540 cm^{-1} [19], is shown in Table 1. As can be seen in Table 1, the Pd-SiW_{12}/SiO_2 catalysts prepared using the various procedures possessed mainly Brönsted acid sites although small numbers of Lewis acid sites were also observed. It can be seen that the preparation procedure had little influence on the concentration of B acid sites on the Pd-SiW_{12}/SiO_2 catalysts, but had significant influence on the L acid sites. It has been reported [20–22] that the appearance of Lewis acid sites on Pd-SiW_{12}/SiO_2 catalysts was due to the presence of Pd^{2+} electron-deficient metal sites, which exhibited Lewis acidity as a result of the interaction between the metal sites and the acid sites. The difference in preparation procedures can lead to different interactions between the metal sites and acid sites, which explained the difference in the

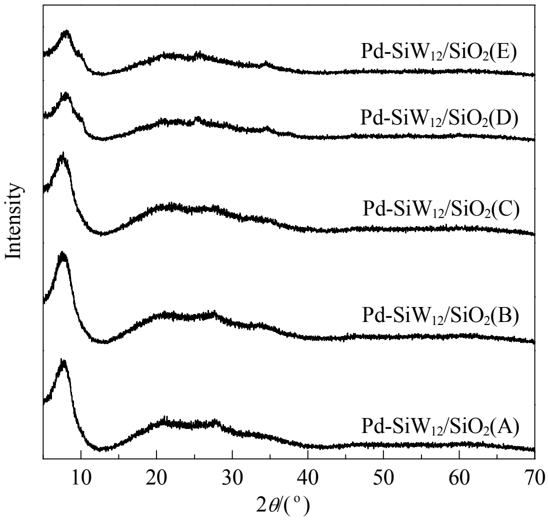

Fig. 2. XRD patterns of Pd-SiW_{12}/SiO_2 catalysts prepared by various procedures.

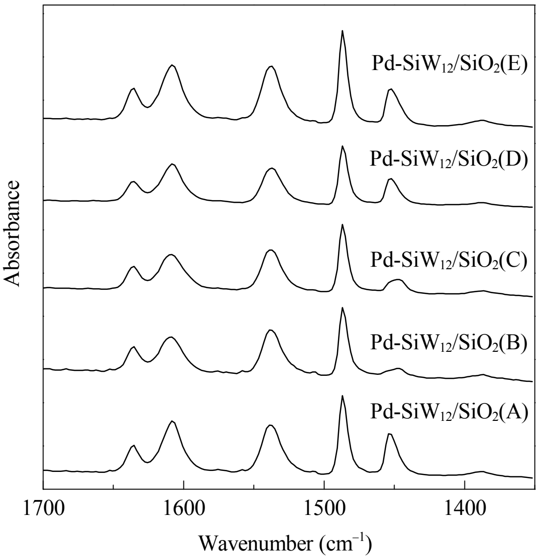

Fig. 3. FT-IR spectra of pyridine adsorbed on Pd-SiW_{12}/SiO_2 catalysts prepared by various procedures.

Table 1 Concentrations of B and L acid sites on Pd-SiW_{12}/SiO_2 catalysts prepared by various procedures

Catalyst	Acid site concentration (mmol/g)	
	B acid	L acid
Pd-SiW_{12}/SiO_2(A)	0.23	0.067
Pd-SiW_{12}/SiO_2(B)	0.24	0.024
Pd-SiW_{12}/SiO_2(C)	0.28	0.054
Pd-SiW_{12}/SiO_2(D)	0.22	0.075
Pd-SiW_{12}/SiO_2(E)	0.26	0.089

concentration of L acid sites listed in Table 1.

Table 2 shows the specific surface areas measured by the BET method, and the dispersion of Pd determined from H_2-chemical adsorption. On comparing the different Pd-SiW_{12}/SiO_2 catalysts, no significant variation of the surface area was observed. This result indicated that the preparation procedures had little effect on the bulk physical structure of the catalysts. However, it is found that the Pd-SiW_{12}/SiO_2(E) catalyst prepared by simultaneously supporting Pd and SiW_{12} on the SiO_2 support showed a better dispersion than those catalysts prepared by the other procedures. This clearly indicated that the dispersion of the Pd metal was strongly dependent on the preparation procedures, and decreased in the following order: (E) > (D) > (B) > (A) > (C). It is obvious that impregnating Pd first on the SiO_2 support or reduction of supported Pd was unfavorable for the dispersion of Pd on the Pd-SiW_{12}/SiO_2 catalysts.

Table 3 shows the catalytic performance for the oxidation of ethylene to acetic acid on the various Pd-SiW_{12}/SiO_2 catalysts after 2 h reaction time. The catalytic properties strongly depended on the preparation procedure. The conversion of ethylene, space-time yield (STY) of acetic acid, and selectivity for acetic acid decreased in the order: Pd-SiW_{12}/SiO_2(E) > Pd-SiW_{12}/SiO_2(D) > Pd-SiW_{12}/SiO_2(C) > Pd-SiW_{12}/SiO_2(A) > Pd-SiW_{12}/SiO_2(B). The Pd-SiW_{12}/SiO_2(E) catalyst prepared by simultaneously loading Pd and SiW_{12} on the SiO_2 support gave the best catalytic activity. The Pd-SiW_{12}/SiO_2(D) catalyst, which was obtained by first impregnating SiW_{12} on the SiO_2 support, also exhibited better catalytic properties than those prepared by impregnating Pd first. As was concluded about the Pd dispersion, it can be seen that impregnating Pd first on the SiO_2 support or reduction of supported Pd was unfavorable for the catalytic performance of the Pd-SiW_{12}/SiO_2 catalysts.

Table 2 Specific surface area and Pd dispersion of Pd-SiW_{12}/SiO_2 catalysts prepared by various procedures

Catalyst	$A_{BET}{}^a$/ (m^2/g)	$A_{Pd}{}^b$/ (m^2/g)	Pd dispersion^b (%)	Pd crystallite size^b (nm)
Pd-SiW_{12}/SiO_2(A)	206.2	1.96	44.04	2.5
Pd-SiW_{12}/SiO_2(B)	203.5	2.40	53.91	2.1
Pd-SiW_{12}/SiO_2(C)	189.1	1.60	35.97	3.1
Pd-SiW_{12}/SiO_2(D)	210.0	2.97	66.64	1.7
Pd-SiW_{12}/SiO_2(E)	210.1	3.44	77.22	1.5

^{a}Measured by nitrogen adsorption.

^{b}Measured by H_2-pulse chemical adsorption.

In the literature [8–10], it was suggested that the direct oxidation of ethylene on Pd-SiW_{12}/SiO_2 catalysts take place bifunctionally by cooperation between Pd species and the acid sites of the support. In the present study, the B acid sites of the catalysts prepared by various procedures were rather similar. It is well known that Pd itself plays a vital role in the selective oxidation of ethylene to acetic acid [23,24]. Usually, the catalytic properties of supported Pd catalysts were dependent on the Pd dispersion. Thus, the catalytic performance of the Pd-SiW_{12}/SiO_2 catalysts prepared by the various procedures was mainly controlled by the dispersion of palladium for similar concentrations of B acid sites. This is in agreement with the result of our experiment, which showed that the catalytic performance of the Pd-SiW_{12}/SiO_2 catalysts prepared by the various procedures was dependent on the dispersion of palladium.

3 Conclusions

A series of Pd-SiW_{12}/SiO_2 catalysts prepared by various procedures and their catalytic performance in the selective oxidation of ethylene to acetic acid was investigated. The numbers of B acid sites of the catalysts were similar. The order in which Pd and SiW_{12} were supported on SiO_2 and the treatment conditions for the supported Pd catalysts had a significant influence on the dispersion of Pd. The catalytic activity was dependent on the dispersion of palladium. The Pd-SiW_{12}/SiO_2 catalyst prepared by simultaneously supporting Pd and SiW_{12} on SiO_2 gave the best catalytic performance for the selective oxidation of ethylene. This was attributed to the better dispersion of palladium. For fixed amounts of SiW_{12} and Pd, the

Table 3 Catalytic performance of Pd-SiW_{12}/SiO_2 catalysts prepared by various procedures

Catalyst	Conversion of ethylene (%)	STY of acetic acid (g/(L·h))	Selectivity (%)					
			Acetic acid	Acetaldehyde	Ethanol	Ethyl acetate	CO_2	CO
Pd-SiW_{12}/SiO_2(A)	3.8	79.0	53.5	10.5	3.0	5.2	24.5	3.3
Pd-SiW_{12}/SiO_2(B)	3.2	64.4	52.4	12.1	3.4	5.0	24.9	2.1
Pd-SiW_{12}/SiO_2(C)	4.2	90.6	56.2	9.3	3.3	5.9	22.4	2.8
Pd-SiW_{12}/SiO_2(D)	5.4	134.0	63.9	7.0	3.6	7.9	15.0	2.7
Pd-SiW_{12}/SiO_2(E)	5.8	145.2	64.0	5.6	2.5	6.5	18.7	2.7

Reaction conditions: $C_2H_4:O_2:H_2O:He = 50:7:30:13$, GHSV = 3 000 h^{-1}, 150 °C, p = 0.6 MPa, 2 h.

preparation procedures mainly influenced the dispersion of palladium and did not influence the concentration of surface acid sites. Thus, the high activity of the Pd-SiW_{12}/SiO_2 catalyst can be assigned to the high dispersion of Pd.

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