

The Effect of Preparation Procedure on the Performance of Pd-SiW₁₂/SiO₂ Catalysts for the Direct Oxidation of Ethylene to Acetic Acid

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Abstract: Pd-SiW₁₂/SiO₂ catalysts were investigated to elucidate the effect of preparation procedure on the direct oxidation of ethylene to acetic acid. Pd-SiW₁₂/SiO₂ catalysts with a fixed amount of Pd and SiW₁₂ were prepared in various ways. The order in which Pd and SiW₁₂ were loaded on the SiO₂ support and the treatment conditions for the supported Pd have a significant influence on the dispersion of Pd on the Pd-SiW₁₂/SiO₂ catalysts, but no influence on the concentration of B acid sites. The Pd-SiW₁₂/SiO₂ catalyst prepared by simultaneously loading Pd and SiW₁₂ on the SiO₂ 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-H₄SiW₁₂O₄₀(SiW₁₂)/SiO₂ for the direct catalytic oxidation of ethylene to acetic acid, developed by Showa Denko [1], has considerable interest. SiW₁₂ heteropoly acid has several advantages as a Brønsted acidic catalyst, which makes it economically and environmentally attractive [5,6]. The Pd-SiW₁₂/SiO₂ 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-SiW₁₂/SiO₂ catalyst, Pd and SiW₁₂ 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-SiW₁₂/SiO₂. Besides these factors, the importance of the preparation procedure should also be empha-

sized. It has been found that the procedure for the preparation of the Pd-SiW₁₂/SiO₂ catalyst, such as the order of application of Pd and SiW₁₂ on the SiO₂ 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 SiW₁₂, reduction of Pd/SiO₂ by H₂ led to a lower catalytic activity than reduction by hydrazine hydrate (N₂H₄·H₂O). Despite extensive research work on the design and characterization of the Pd-SiW₁₂/SiO₂ 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-SiW₁₂/SiO₂ 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 H₂-pulse chemical adsorption. The

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relationship between Pd dispersion, surface acidity, and catalytic properties of the Pd-SiW₁₂/SiO₂ catalyst is discussed.

1 Experimental

1.1 Preparation of the catalysts

Pd-SiW₁₂/SiO₂ catalysts with fixed amounts of SiW₁₂ and Pd, mass loadings 30.0 wt% and 1.0 wt%, respectively, were prepared by various procedures. Commercially available SiO₂ ($A_{\text{BET}} = 384.7 \text{ m}^2/\text{g}$) was used as the support. The Pd-SiW₁₂/SiO₂ catalysts were prepared according to the following different procedures shown in Fig. 1.

For procedure (A), Pd was first impregnated onto SiO₂ using a solution of PdCl₂ 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/SiO₂ 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, SiW₁₂ was supported on the Pd/SiO₂ by the incipient wetness method from aqueous H₄SiW₁₂O₄₀. After vigorously stirring for 3 h, the same procedures as those used in preparing the Pd/SiO₂ sample were used for drying and calcination. This catalyst was denoted as Pd-SiW₁₂/SiO₂(A).

For procedure (B), Pd was first impregnated onto SiO₂ 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 N₂H₄·H₂O was detected. The reduced Pd/SiO₂ sample was dried in an oven at 383 K overnight. Finally, SiW₁₂ was supported by the same incipient wetness method as that in procedure (A). This catalyst was denoted Pd-SiW₁₂/SiO₂(B).

For procedure (C), Pd was first impregnated onto SiO₂ with the preparation process the same as that of procedure (A) but the sample was reduced in a flow of 5% H₂-95% Ar (30 ml/min) at 523 K for 3 h. Finally, SiW₁₂ was supported by the same incipient wetness method as used in procedure (A). This catalyst was denoted Pd-SiW₁₂/SiO₂(C).

For procedure (D), first, SiO₂ was added to an aqueous solution of H₄SiW₁₂O₄₀ 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 SiW₁₂/SiO₂ 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 PdCl₂ 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-SiW₁₂/SiO₂(D).

For procedure (E), simultaneously, Pd and SiW₁₂ were supported onto SiO₂ using a mixed solution of PdCl₂ dissolved in 0.1 mol/L HCl and an aqueous solution of H₄SiW₁₂O₄₀. 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-SiW₁₂/SiO₂(E).

1.2 Characterization of the catalysts

Powder XRD patterns were recorded with a Rigaku D/Max-2500 diffractometer employing Cu K_α radiation ($\lambda = 0.154 \text{ nm}$) 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/cm²) and mounted into an in situ quartz IR cell with CaF₂ 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 H₂-pulse chemical adsorption method using an Autosorb-1/C system at 313 K. In a typical experiment, the sample was first pretreated

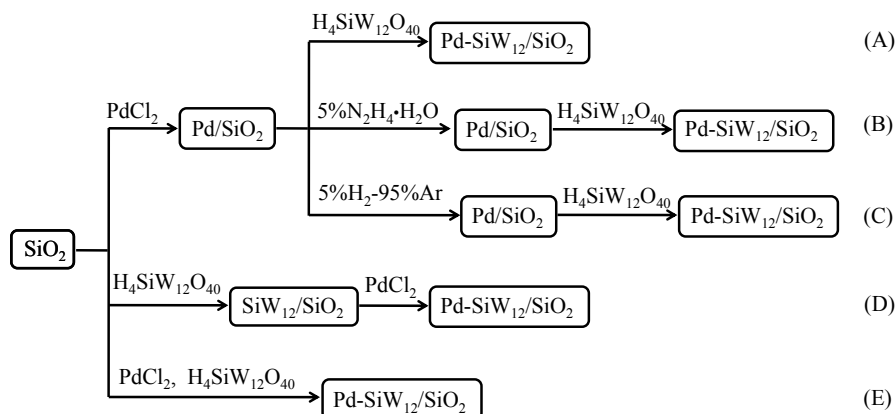


Fig. 1. Schematic of the preparation procedures for Pd-SiW₁₂/SiO₂ catalysts.

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