SBA-15-supported Pd catalysts: The effect of pretreatment conditions on particle size and its application to benzyl alcohol oxidation

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A B S T R A C T

SBA-15-supported Pd catalysts were prepared by impregnation, thermal pretreatment, and H_2 reduction. The pretreatment conditions have an important influence on the resulting size (from 1.3 to 10.3 nm) of the Pd particles; the catalyst prepared under vacuum conditions possessed the smallest particles (size 1.3 nm). X-ray absorption spectra were used to analyze the transformation of the Pd precursor in each step of the preparation. These catalysts were applied to the oxidation of benzyl alcohol by molecular oxygen; the catalyst with the smallest Pd particles exhibited the highest turnover frequency (9684 h^{-1}). The catalyst was reusable three times without loss of activity (with conversion >96%). X-ray absorption spectra were recorded ex situ to monitor the oxidation and the coordination structure of Pd at varied temperatures of reaction; when the reaction temperature was above 100 °C, the Pd species were in the metallic state. This result indicates that metallic Pd might be the active phase in the oxidation of benzyl alcohol by molecular oxygen.

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1. Introduction

The oxidation of alcohols to aldehydes or ketones is an important reaction in the production of fine and specialty chemicals [1,2]. In contrast to a traditional method using stoichiometric oxidation with mineral oxidizing agents, a recently developed method using a noble metal (e.g., Ru, Pt, Pd, or Au) as a catalyst and molecular oxygen as the oxidant constitutes a sustainable and green process [1,2]. Among those catalysts, Pd-containing catalysts appear to be promising because both high activity and high selectivity can be obtained concurrently [3–11].

As Pd is recognized to be a scarce resource, the synthesis of a Pd catalyst with high dispersion and high efficiency is an attractive topic in catalytic research [12–15]. Among various methods of synthesizing a supported Pd catalyst are impregnation [7,12,16,17], a ligand-assisted method [14–16,18,19], and an ion-exchange method [4,12,17,20]. With the latter two methods and on improving the interaction of the Pd precursor and the support through grafting a hydrophilic or hydrophobic functional group (e.g., —NH, —SOH, —CH=CH₂, or —CH₃) or adjusting the surface charge of the support, catalysts consisting of Pd nanoparticles (size <2 nm) were synthesized [4,12,14–20], but the impregnation method yielded Pd catalysts that generally showed a broad distribution of size of Pd particles larger than 2 nm [7,12,16,17,19]. A synthesis of a Pd catalyst that possesses a narrow distribution of particle size <2 nm with a simple impregnation method is attractive [16].

When we synthesized SBA-15-supported copper catalysts by a vacuum-thermal method, we found that the vacuum condition was vital for preparing highly dispersed copper catalysts; the transformation of the copper species during the heat treatment was altered by the vacuum condition [21]. The atmosphere during the thermal decomposition is reported to be an important factor in tuning the resulting metal or metal-oxide size in supported catalysts [12,22–24]. Sietsma et al. found that gaseous dinitrogen monoxide prevented the rapid decomposition of $Ni_3(NO_3)_2(OH)_4$ that is observed in air, resulting in smaller NiO nanoparticles than those prepared in air [22]. Zou et al. discovered that, when the chemical structure of the adsorbed palladium complex is varied during the pretreatment (i.e., with H_2, O_2, or N_2), the resulting silica-supported Pd catalysts possessed varied particle sizes [23]. Yuranov et al. showed that reducing the adsorbed palladium species before oxidation gave the resulting SBA-15-supported PdO catalyst smaller PdO nanoparticles than without that reduction [24]. To the best of our knowledge, there is no report of supported Pd catalysts from a vacuum-thermal preparation.

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Here we report the preparation of SBA-15-supported Pd catalysts with an impregnation method and subsequent varied pretreatment conditions and H_2 reduction, and tests of oxidation of benzyl alcohol with molecular oxygen. SBA-15 was selected as a support because it has great chemical stability, a large surface area for metal dispersion, and porosity of nanometer size to facilitate molecular diffusion [18,21,25]. The pretreatment condition was found to have an important influence on the resulting Pd particle size (from 1.3 to 10.3 nm); among those catalysts the catalyst pretreated under vacuum conditions possessed the smallest particles (1.3 nm). X-ray absorption spectroscopy (XAS) served for analysis of the transformation of the Pd precursor in each preparation step. These catalysts were applied to the oxidation of benzyl alcohol with molecular oxygen, which showed that the catalyst with the smallest Pd particles exhibited the greatest activity. The catalyst was reusable three times without loss of activity (with conversion >96%). XAS measurements were recorded ex situ to monitor the oxidation and the coordination structure of Pd at varied reaction temperatures.

2. Experiments

2.1. Preparation of the catalyst

The synthesis of mesoporous SBA-15 silica involved the addition of tetraethoxysilane (TEOS) to a solution of triblock copolymer (Pluronic P123, $EO_{20}PO_{70}EO_{20}$) and zirconium oxychloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) in hydrochloric acid (HCl). The mixture was stirred at 35 °C for 24 h. After sulfuric acid (H_2SO_4) was added to the mixture in a calculated proportion to remove the triblock copolymer [26], the mixture was aged at 90 °C for 24 h. The molar proportions of the final mixture were 1 TEOS:0.017 P123:5.9HCl:193 H_2O:2.9 H_2SO_4:0.05ZrOCl$_2$. The solid product was washed with propanone, filtered, and dried in air. The product was heated further at 350 °C to produce the SBA-15 support.

To impregnate Pd nanoparticles, we loaded the SBA-15 support with a solution of dichlorobis(acetonitrile) palladium ($PdCl_2(MeCN)_2$) in propanone (nominally 1 mass% Pd by an incipient wetness method) and dried it. The sample was subsequently heated under varied gases (hydrogen, air, nitrogen), or vacuum, at 350 °C for 2 h with a ramp rate of 1 °C min^{-1}. The resulting samples are referred to as Sample X, in which X denotes the conditions of thermal treatment (with X = H_2, air, N_2, or Vac for treatment under hydrogen, air, nitrogen, or vacuum (ca. 0.1 Torr), respectively). Each sample X was further reduced under pure hydrogen at 350 °C for 2 h. After cooling to 23 °C, the resulting samples were stored under atmospheric conditions. The resulting samples are referred to as Sample X–H_2, in which X denotes the conditions of thermal treatment (with X = Air, N_2, and Vac for pretreatment in air, nitrogen or vacuum, respectively).

2.2. Characterization of the catalyst

X-ray diffraction (XRD) patterns were recorded on a diffractometer (Mac Science 18MPX) using Cu Kα radiation. N_2 physisorption isotherms were measured (QuantachromeAutosorb-1-MP) at 77 K. The isotherms were analyzed with nonlocal density-functional theory (NLDFT) to evaluate the pore sizes of the samples using the kernel of NLDFT equilibrium capillary condensation isotherms of nitrogen at 77 K on silica (adsorption branch, assuming cylindrical pore geometry). The BET surface areas were calculated from the adsorption branches in the relative pressure range 0.05–0.30; the total pore volumes were evaluated at relative pressure 0.95. Inductively coupled plasma mass spectral (ICP-MS) data were recorded (Perkin–Elmer SCIEX-ELAN 5000). Transmission electron microscopy (TEM) images were taken from ultramicrotomed samples (thickness 80–100 nm) with an electron microscope (JEOL JEM-ARM 200 FTH) equipped with an energy-dispersive X-ray (EDX) spectrometer and a high-angle annular dark-field (HAADF) detector. X-ray photoelectron spectra (XPS) were recorded on an Ulvac-PHI PHI Quantera device.

2.3. XAS

Pd K-edge XAS were recorded at beamline 01C1 at Taiwan Light Source (storage-ring energy 1.5 GeV, ring current 360 mA) in the National Synchrotron Radiation Research Center. In a typical experiment, the Pd catalyst (about 120 mg) was pressed to form self-supporting wafers and mounted on a sample holder for measurements. Spectra were recorded near 23 °C in a transmission
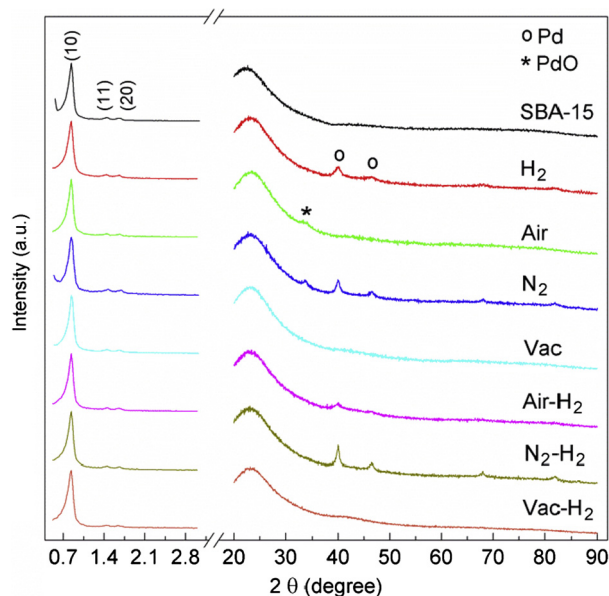

Fig. 1. Small-angle and wide-angle XRD patterns of SBA-15 and SBA-15-supported Pd materials.

Table 1
Physical properties of materials.[a]

Sample	a (nm)	D (nm)	W (nm)	S (m^2 g^{-1})	V_t (cm^3 g^{-1})	D_{Pd}[b] (nm)	D_{Pd}[c] (nm)
SBA-15	12.1	8.1	4.0	1023	1.38	—	—
H2	12.1	8.1	4.0	1001	1.31	5.6	6.6
Air-H2	12.1	8.1	4.0	1022	1.31	4.5	5.2
N2-H2	12.1	8.1	4.0	1008	1.31	10.2	10.3
Vac-H2	12.1	8.1	4.0	1024	1.31	—	1.3

[a] a: unit cell parameter; D: mesopore diameter; W: wall thickness; S: BET surface area; V_t: total pore volume.
[b] D_{Pd}: Pd particle size calculated from XRD pattern.
[c] D_{Pd}: average particle size observed by TEM.