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Improved catalytic performance of Pd/TiO$_2$ in the selective hydrogenation of acetylene by using H$_2$-treated sol-gel TiO$_2$

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Abstract

The anatase nanocrystalline TiO_2 samples were synthesized by a sol-gel method with a thermal treatment under air and H_2 atmospheres at 350°C and employed as the supports for preparation of Pd/TiO_2 catalysts by impregnation and electroless deposition methods. The surface Ti^{3+} defects on the TiO_2 significantly increased when treated under H_2, compared to air, with no changes in the average crystallite size, specific surface area, and pore structure. The CO chemisorption and IR of adsorbed CO results showed that the use of H_2-treated TiO_2 resulted in higher Pd dispersion and the formation of more isolated adsorption sites, hence improving the catalytic performance in terms of both acetylene conversion and ethylene selectivity.

1. Introduction

Selective hydrogenation of acetylene over Pd-based catalysts has been one of the most studied hydrogenation reactions over the last decades [1]. It is a major method used for purification of ethylene feedstocks obtained from thermal cracking of oil compounds in the ethylene-based polymerization reactions. Despite its long-term application in industry, Pd-based catalysts still suffer from poor selectivity of acetylene conversion to ethylene which leads to the production of a large amount of ethane and the waste of ethylene [2, 3] According to a recent review by Kim et al. [4], to achieve high selectivity and activity of Pd-based catalysts, recent trend has been (i) to add a second metal to form alloy with Pd or to suppress the number of multicoordination sites of the Pd surface and (ii) to induce the strong metal-support interaction (SMSI) effect so that the adsorption strength of ethylene is weakened [5]. A number of previous studies show that the presence of Ti^{3+} species that was in contact with Pd promotes the SMSI on Pd/TiO_2 catalysts, resulting in an improved catalyst performance in the selective acetylene hydrogenation [6-10].

The properties of TiO_2 such as crystallite size, crystalline phase composition, particle morphology, and surface defects (Ti^{3+}) can be controlled by synthesis method as well as post-synthesis treatment conditions [11]. The performance of Pd catalysts supported on novel TiO_2 prepared by hydrolysis-precipitation in the selective acetylene hydrogenation depended largely on the preparation conditions of the TiO_2 such as pH value, $Ti(OBu)_4$ addition rate, and calcination temperature [12]. Sol-gel method is an easy route to obtain high purity nano-sized TiO_2 at mild reaction conditions. However, the precipitated powders obtained are amorphous in nature and further heat treatment is required for crystallization. The properties of sol-gel derived TiO_2 nanoparticles were found to be influenced by the calcination atmosphere. For examples, rutile TiO_2 prepared under Ar and H_2 atmosphere showed higher photocatalytic activity than that prepared under air atmosphere [13]. Suriye et al. [14]

reported that the surface Ti^{3+} varied with the amount of oxygen fed during calcination. Huang et al. [15] showed that H_2-atmosphere calcination was important to give visible-region photocatalytic activity of TiO_2.

In the present study, the sol-gel derived TiO_2, which was calcined under H_2 or air, was employed as the supports for preparation of Pd/TiO_2 catalysts and studied in the selective hydrogenation of acetylene at 40-100°C. Deposition of Pd on the TiO_2 supports was done by two different methods (conventional impregnation and electroless deposition). The catalyst performance was correlated with the surface and structural properties of the Pd/TiO_2 according to the characterization results from X-ray diffraction (XRD), transmission electron microscopy (TEM), N_2 physisorption, electron spin resonance (ESR), CO pulse chemisorption, and infrared spectroscopy of adsorbed CO (CO-IR).

2. Experimental

2.1 Preparation of TiO$_2$ support

Titanium dioxide support was prepared by sol-gel method using 83.5 cm^3 of titanium isopropoxide (Aldrich Chemical Ltd.), 7.33 cm^3 of 70 vol.% nitric acid (Asia Pacific Specialty Chemical Limited), and 1000 cm^3 of distilled water. At first, 70 vol.% nitric acid was added to distilled water. The mixture was continually stirred using a magnetic stirrer. While the mixture was stirred, titanium isopropoxide was added slowly. The mixture was stirred continually for about 3 days at room temperature until clear sol was obtained. The clear sol was placed in dialysis tubing, which was submerged in distilled water. The water was changed daily for 3-4 days until the pH of water reached 3.5 from the initial pH at 1.1. The solvent was removed and then dried at 110°C overnight. The resulting materials were heated at a rate of 10°C/min in hydrogen or air to 350°C and calcined at this temperature for 2

h. The TiO$_2$ so prepared will be referred to as TiO$_2$-H$_2$ and TiO$_2$-Air for those calcined in hydrogen and air, respectively.

2.2 Preparation of Pd/TiO$_2$ catalysts

The 1 wt.% Pd/TiO$_2$ catalysts were prepared by electroless deposition and impregnation techniques. For the electroless deposition method, firstly, the TiO$_2$ support was activated in 14 vol.% HCl solution for 15 min and rinsed with deionized water. Then, the support was activated with SnCl$_2$ and PdCl$_2$ acidic solution for 20 min and the suspension was centrifuged and washed with deionized water. The TiO$_2$ support was dried at 110$^{\text{o}}$C overnight. After activated, the support was transferred to Pd electroless deposition bath. The electroless deposition bath was prepared using 0.0168 g of PdCl$_2$ as palladium precursor in 9.2 ml of HCl and the solution was diluted to 100 ml using DI water (deionized water). Ammonium chloride was added to stabilize the bath for extended use and lastly sodium hypophosphite was added with a molar ratio of PdCl$_2$: NaH$_2$PO$_2$.H$_2$O = 1:10. During electroless deposition at room temperature, the bath was continuously stirred and the pH was maintained at 10. After stirring for 1 h, the suspension was centrifuged and washed with deionized water. The catalyst was then dried at 110$^{\text{o}}$C overnight and calcined in air at 450$^{\text{o}}$C for 3 h.

For the impregnation method, the TiO$_2$ supports were impregnated with an acidic solution containing 0.0168 g of palladium chloride. The Pd/TiO$_2$ was left to stand for 6 h to assure adequate distribution of metal complex and subsequently dried at 110$^{\text{o}}$C in air overnight. The catalysts were then calcined in air at 450$^{\text{o}}$C for 3 h. In the following, the Pd/TiO$_2$ catalysts will be denoted as Pd/TiO$_2$-H$_2$ (I) and Pd/TiO$_2$-Air (ED) for those prepared by impregnation and electroless deposition, respectively.

2.3 Catalyst characterization

XRD patterns of the TiO_2 supports and Pd/TiO_2 catalysts prepared was obtained using a SIEMENS XRD D5000 X-ray diffractometer with Cu K_α radiation. The average crystallite size of TiO_2 was calculated using the Scherrer's equation. The BET surface areas of the TiO_2 supports were measured by N_2 physisorption using a Micrometritics ASAP 2000 automated system. The samples were degassed at 200^oC for 1 h prior to N_2 physisorption. The catalyst morphology and dispersion of Pd on the TiO_2 were observed using a JEOL-JEM 200 CX transmission electron microscope operated at 200kV. The surface Ti^{3+} on TiO_2 supports were detected by ESR using a JEOL JES-RE2X electron spin resonance spectrometer. The amounts of CO chemisorbed on the Pd/TiO_2 catalysts were measured at room temperature by using a Micromeritic Chemisorb 2750 automated system attached with ChemiSoft TPx software at room temperature. Prior the measurement, 30 cm^3/min of He gas was introduced into the sample cell in order to remove the remaining air. The system was switched to 50 cm^3/min of hydrogen and heated to 150^oC with a heating rate of 10^oC/min. The temperature was kept constant for 2 h and then cooled down to the room temperature. After that, 80 μL of carbon monoxide was injected into catalyst and repeated until the desorption peaks were constant at room temperature. The metal contents in the catalyst samples prepared were analyzed by the inductive coupled plasma-optical electron spectroscopy using the Optima 2100 DV spectrometer and determined to be ca. 0.9 wt%. The amounts of residual Cl on the catalyst surface were determined using an Amicus photoelectron spectrometer to be 1.0-1.2 atomic%.

The CO adsorbed species on the Pd/TiO_2 catalysts were measured using FTIR-620 spectrometer (JASCO) with a MCT detector at a wavenumber resolution of 2 cm^{-1}. He gas was introduced into the sample cell in order to remove the remaining air. The system was switched to hydrogen and heated to 150^oC. The temperature was kept constant for 30 min and

then cooled down to the room temperature with He gas. After that, carbon monoxide was flow to the system for 15 min. The IR spectrum of CO adsorbed onto the catalyst was recorded in the 4000‑600 cm^{-1} range after the gaseous CO had been removed from the cell by He flow.

2.4 Reaction study

Acetylene hydrogenation was performed in a pyrex tube reactor of 10 mm in diameter. Prior to the start of each experimental run, the catalyst was reduced with hydrogen by heating from room temperature to 150°C for 2 h at a heating rate of 10°C /min. Then the reactor was purged with argon and cooled down to the reaction temperature. The reactant gas mixture composed of 1.5% C_2H_2, 1.7% H_2, and balanced C_2H_4 (Rayong Olefin Co., Ltd). The flow rate of the reactant stream was 100 cm^{3}/min. The reaction products and feed were analyzed by a gas chromatograph equipped with TCD detector (SHIMADZU TCD GC 8A, molecular sieve-5A) and FID detector (SHIMADZU FID GC 9A, Carbosieve column S-2).

3. Results and discussion

3.1 Characterization of TiO$_2$ and Pd/TiO$_2$

The sol-gel method is an easy method for preparation of nano-sized TiO$_2$ but the precipitated powder obtained is amorphous in nature and further heat treatment is required for crystallization. In the present study, the TiO$_2$ supports were prepared by sol-gel and calcined under air or H$_2$ at 350°C. From the XRD results (**Figure 1**), the major phase of calcined TiO$_2$ samples was anatase TiO$_2$ as shown by the peaks at 25.36, 37.82, and 48.18 ^{o}2θ. A small peak at 30.81 ^{o}2θ corresponded to brookite phase TiO$_2$. A mixture of anatase/brookite polymorphs was often found on nano-TiO$_2$ powder prepared by a sol–gel method at a

sintering temperature of 350°C [16]. The average crystallite size of anatase phase TiO$_2$ was determined from the half-width of the XRD peak at 2θ = 25.36^o using the Scherrer equation and are reported in **Table 1**. The TiO$_2$ supports calcined in H$_2$ and air were similar in the structural properties, having crystallite size of ca. 4 nm, BET surface area of 187-198 m^2/g, pore volume of 0.3 cm^3/g, and average pore diameter of 4.7-4.8 nm. Both the TiO$_2$ supports and the TiO$_2$ supported Pd catalysts exhibited type-IV isotherm with hysteresis loop, describing the characteristic of mesoporous materials with pore diameters between 2 and 50 nm (results not shown). The shape of hysteresis loop of all the catalysts was type H1, which corresponded to narrow distribution of relatively uniform pores. The calcination atmosphere did not have any influence on the structural properties of the sol-gel derived TiO$_2$. Similar results have been reported by Wu et al. [17] on the TiO$_2$ nanoparticles prepared by a sol-gel method and calcined under different atmospheres including Ar, air, N$_2$, H$_2$, and vacuum.
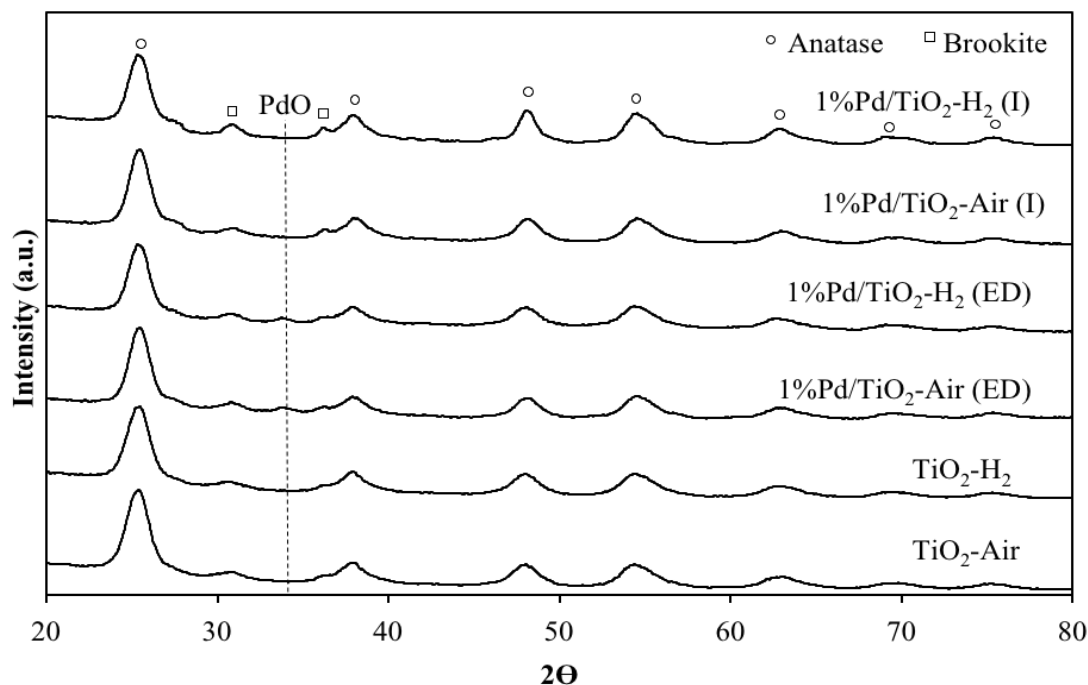

Figure 1 The XRD patterns of TiO$_2$ and 1%Pd/TiO$_2$ catalysts

Table 1 Physicochemical properties of TiO_2 and 1%Pd/TiO_2 catalysts

Catalysts	Crystallite size[a] of TiO_2 (nm)	BET surface area (m^2/g)	Pore volume (cm^3/g)	Avg. pore diameter[b] (nm)	wt% Pd[c]	CO Chemisorption (x 10^{23} molecule CO/ mole Pd.)	Pd dispersion (%)	d_P Pd^0 (nm)
TiO_2-H_2	4.0	198	0.30	4.8		-	-	-
TiO_2-Air	4.2	187	0.29	4.7		-	-	-
Pd/TiO_2-H_2-(ED)	4.2	126	0.19	3.8	0.94	4.3	70	1.0
Pd/TiO_2-Air-(ED)	4.6	124	0.21	4.4	0.92	3.4	56	1.9
Pd/TiO_2-H_2-(I)	4.3	144	0.23	4.4	0.87	3.9	65	1.7
Pd/TiO_2-Air-(I)	4.5	149	0.24	4.6	0.89	2.4	39	2.6

[a] Based on the XRD results.
[b] Determined from the Barret-Joyner-Halenda (BJH) desorption method.
[c] Based on the ICP-OES results.

The average TiO_2 crystallite size, surface area, pore volume, and average pore diameter of the 1 wt.% Pd/TiO_2 catalysts prepared by impregnation and electroless deposition methods are also shown in **Table 1**. There was no significant change of the average crystallite of anatase phase TiO_2 upon metal loading and calcination at 450^oC for 3 h. The calcination temperature at 450^oC, however, contributed to about 20% decrease in the surface area of the bare TiO_2 support (i.e., from 198 m^2/g to 156 m^2/g for the TiO_2-H_2). Upon metal loading, the BET surface area and pore volume of the TiO_2 supports decreased further by 20 and 7 % for the 1 wt.% Pd/TiO_2 catalysts prepared by electroless deposition and impregnation, respectively due to pore blockages. The Pd/PdO particles/clusters may be located deeper inside the pores of the TiO_2 when prepared by electroless deposition compared to those obtained by impregnation technique, leading to a lower amount of pore volume. Electroless deposition is a simple methodology to synthesize supported Pd catalyst with uniform and nano-sized Pd particles. Pd precursor can be interacted directly with the Sn^{2+} ions, and subsequently transformed into Pd nanoparticles deposited on the support. Okada et al. [18] has recently reported a comparison of Pd/SiO_2 catalysts prepared by electroless deposition and impregnation in the hydrogenation of nitrobenzene and the synthesis of H_2O_2. Smaller Pd metal particles ($\sim$ 4 nm) with a narrow size distribution were formed by utilizing electroless deposition method rather than impregnated technique. According to the XPS results (not shown here), palladium was found to be in the form of PdO (detected at binding energy 337.0 eV) for the catalysts prepared by electroless deposition method. The Pd 3d peaks were not observed for those prepared by impregnation due probably to the relatively low metal dispersion.

Electron spin resonance is a technique for studying chemical species that have one or more unpaired electrons. The ESR spectra of the TiO_2 supports are shown in **Figure 2**. According to Nakaoka and Nosaka [19, 20], there are six signals of ESR measurement

occurring on the TiO_2: (i) $Ti^{4+}O^-Ti^{4+}OH^-$, (ii) surface Ti^{3+}, (iii) adsorbed oxygen (O^{2-}), (iv) $Ti^{4+}O^{2-}Ti^{4+}O^{2-}$, (v) inner Ti^{3+}, and (vi) adsorbed water. It was found that the sol-gel TiO_2 calcined under air and H_2 exhibited only one ESR signal at g value of 1.997, which can be attributed to surface Ti^{3+} [7, 8]. The Ti^{3+} species are produced by trapping of electrons at defective sites of TiO_2 and the amount of accumulated electrons may therefore reflect the number of defective sites [21]. The intensity of ESR signal of the TiO_2-H_2 was found to be stronger than the TiO_2-Air, indicating a larger amount of Ti^{3+} defects on the surface of TiO_2-H_2.
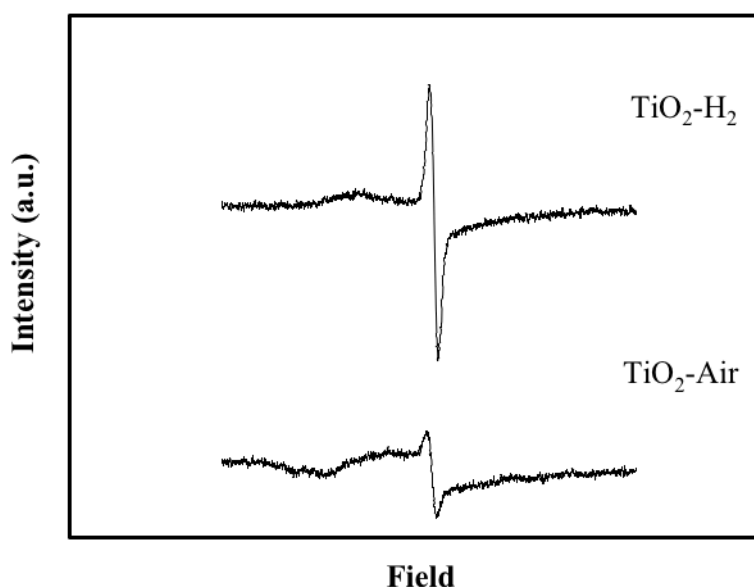

Figure 2 The ESR results of TiO_2 calcined under air and H_2 at 350^oC

The TEM images of 1 wt% Pd/TiO_2 catalysts are shown in **Figure 3**. The TiO_2 particles showed spherical shape with average size of around 4 to 6 nm, which were consistent to those obtained from the XRD results. It is quite difficult to distinguish Pd/PdO clusters from the TiO_2 supports especially for the electroless-made samples. However, some agglomeration of metal particles can be seen on the impregnation-made catalysts. The amounts of CO chemisorption on the 1 wt% Pd/TiO_2 catalysts reduced at 150^oC and the

percentages of palladium dispersion are also given **Table 1**. Regardless of the preparation method used, the Pd catalysts supported on TiO_2-H_2 exhibited larger amounts of CO chemisorption than those supported on TiO_2-Air. The Pd dispersion was increased in the order: Pd/TiO_2–H_2 (ED) > Pd/TiO_2–H_2 (I) > Pd/TiO_2–Air (ED) > Pd/TiO_2–Air (I). For the same TiO_2 support, a higher Pd dispersion and smaller Pd particle size were obtained on the catalysts prepared by electroless deposition than impregnation method. Generally, for the electroless deposition method, Pd obtained from the activation step is used to render catalytic sites for nucleation of metals in the subsequent electroless plating, and $SnCl_2$ serves as the reducing agent that induces the formation of Pd from Pd ions according to the redox reaction: $Pd^{2+} + Sn^{2+} \rightarrow Pd^0 + Sn^{4+}$ [22]. The presence of Sn^{4+} can stabilize the palladium metals via a strong Sn^{4+} adsorption so that very small Pd particles were obtained [23]. The results are similar to those reported by Okada et al. on a comparison of Pd/SiO_2 catalysts prepared by electroless deposition and impregnation techniques [18]. For the same preparation method, smaller Pd particles were obtained on TiO_2-H_2 than TiO_2-air.
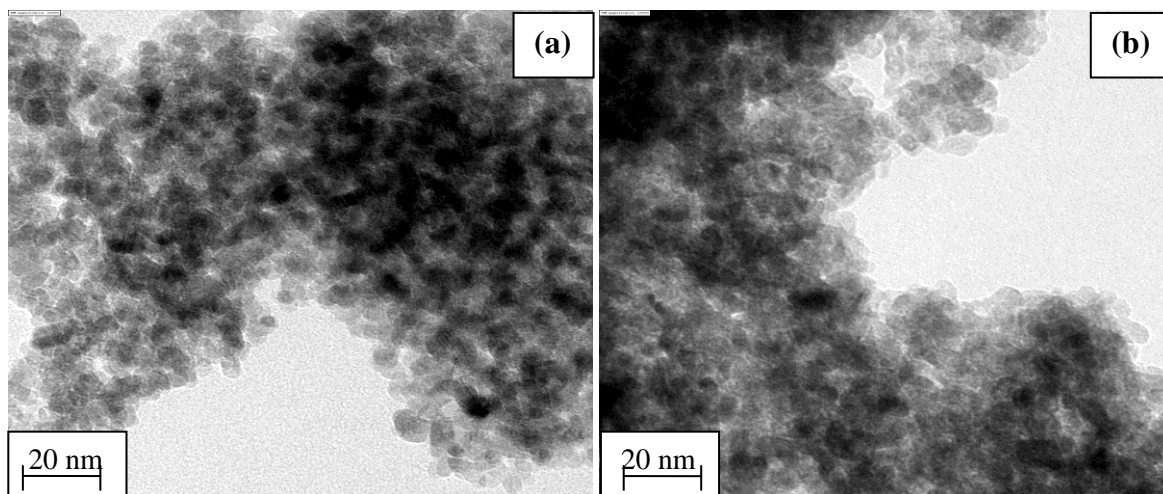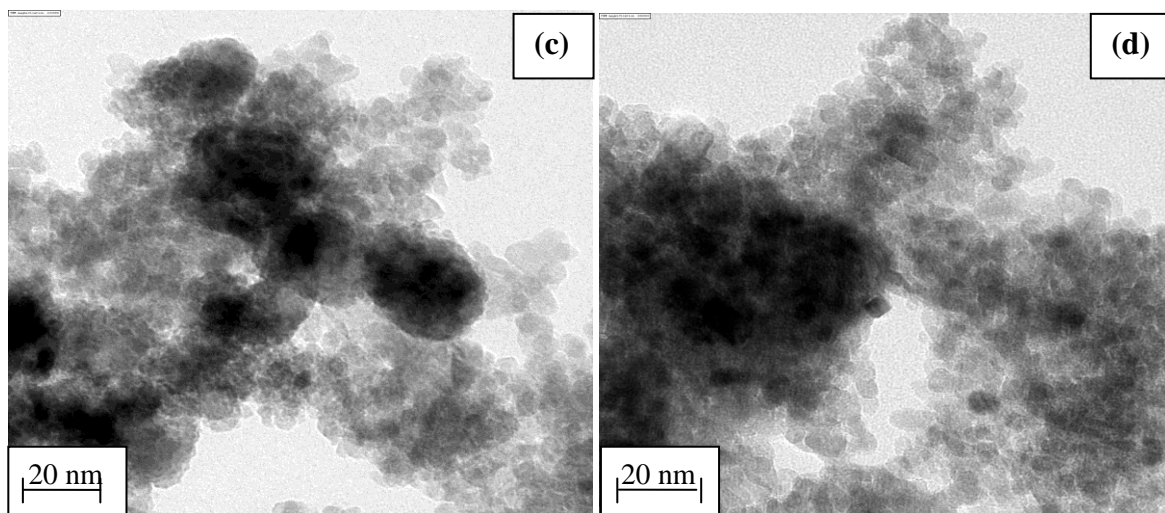
Figure 3 The TEM micrographs of 1%Pd/TiO$_2$–Air (ED) (a), 1%Pd/TiO$_2$–H$_2$-(ED) (b), 1%Pd/TiO$_2$–Air (I) (c), 1%Pd/TiO$_2$–H$_2$-(I) (d)

The amount of Pd active sites is usually calculated from chemisorption results based on the assumption that only CO molecule is adsorbed on one Pd site, however, various CO species are actually adsorbed on metallic Pd. From the literatures [24-26], the IR spectra of adsorbed CO show typical four peaks corresponding to different CO adsorbed species on Pd surface including linear (2100–2050 cm^{-1}), compressed-bridged (1995–1975 cm^{-1}), isolated-bridged (1960–1925 cm^{-1}), and tri-coordinated (1890–1870 cm^{-1}) species. **Figure 4** shows the IR spectra of adsorbed CO on the various Pd/TiO$_2$ catalysts in this study. The ratio of the peak areas corresponding to linearly and multiply bound CO are provided in **Table 2** as A_l/A_m. The A_l/A_m ratio increased in the order of Pd/TiO$_2$–H$_2$(ED) > Pd/TiO$_2$–H$_2$(I) > Pd/TiO$_2$–Air(ED) ≈ Pd/TiO$_2$–Air(I).
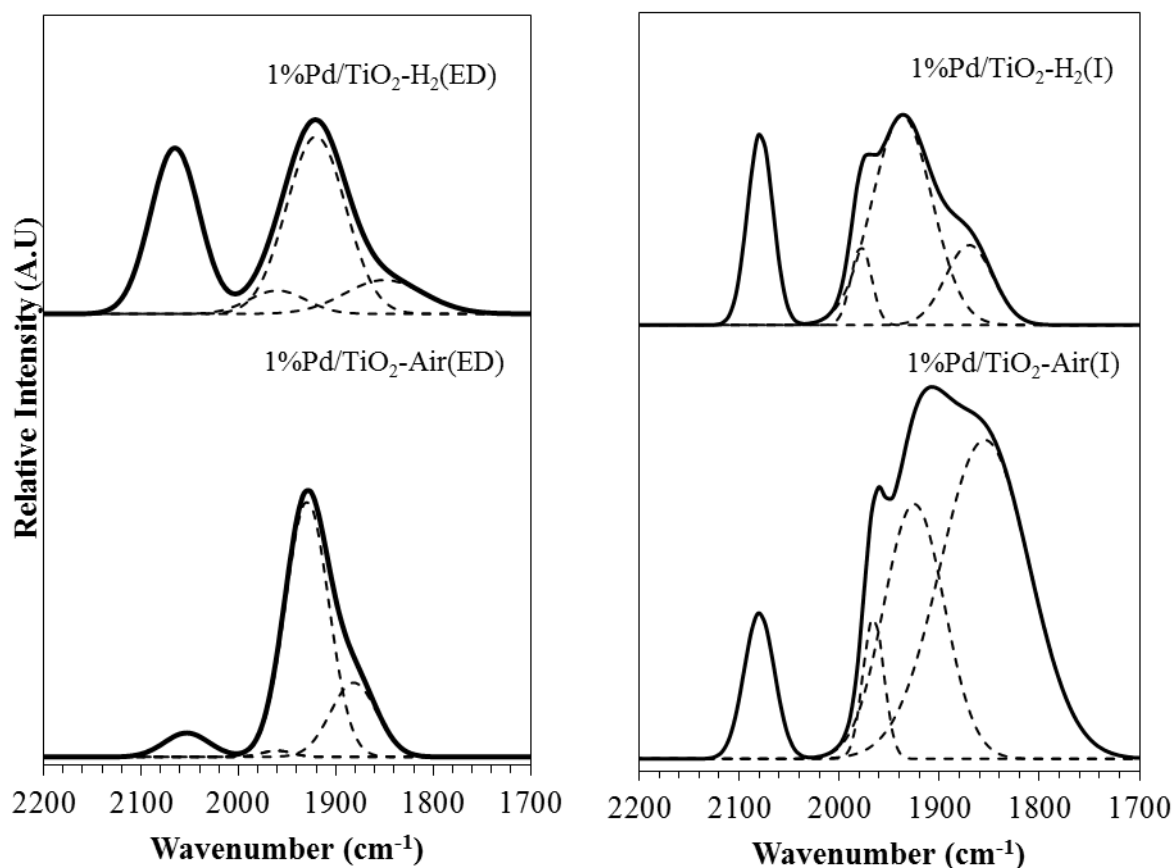
Figure 4 CO-IR spectra of 1%Pd/TiO$_2$ catalysts.

Table 2 Normalized peak area of various CO adsorbed species from the CO-IR results on 1% Pd/TiO$_2$ catalysts.

Catalyst	Tri-coordinated	Isolated-bridged	Compressed-bridged	Linear	A_l/A_m*
Pd/TiO$_2$-H$_2$-(ED)	0.12	0.46	0.06	0.36	0.52
Pd/TiO$_2$-Air-(ED)	0.19	0.6	0.15	0.06	0.06
Pd/TiO$_2$-H$_2$-(I)	0.17	0.55	0.07	0.21	0.27
Pd/TiO$_2$-Air-(I)	0.55	0.3	0.07	0.08	0.09

* A_l: peak area of linear-bound CO and A_m: peak area of multi-bound CO

3.2 Selective hydrogenation of acetylene

The catalytic performance of 1 wt% Pd catalysts supported on sol-gel derived TiO_2 calcined under H_2 and air were investigated in the selective hydrogenation of acetylene. Acetylene conversion is defined as moles of acetylene converted with respect to acetylene in feed. Ethylene selectivity is defined as the percentage of acetylene hydrogenated to ethylene over totally hydrogenated acetylene. The ethylene being hydrogenated to ethane (ethylene loss) is the difference between all the hydrogen consumed and all the acetylene which has been totally hydrogenated [27]. The catalyst performance plots are illustrated in **Figure 5(a)**. Since ethylene is produced as an intermediate in acetylene hydrogenation, which is a typical consecutive reaction, the ethylene selectivity decreases with acetylene conversion [3]. In this work, improved catalytic performance in terms of both acetylene conversion and ethylene selectivity was achieved using the Pd catalysts on the H_2-treated sol-gel derived TiO_2, regardless of the preparation methods used. High ethylene selectivity (~90%) can be obtained at complete acetylene conversion (100%) over 1 wt.% Pd/TiO_2-H_2-(ED) and 1 wt.% Pd/TiO_2-H_2-(I). The same effectiveness of H_2-treated TiO_2 was also confirmed for 0.5 wt.% Pd loaded samples (Figure 5(a)). Ethylene selectivity of Pd/TiO_2 catalysts from this study was relatively high comparing with those reported previously in the literature. For example, Kang et al. [5] showed that high ethylene selectivity (> 90%) can be obtained over Pd/TiO_2 and Pd/Si-modified TiO_2 when they were reduced at 500^oC due to the strong metal-support interaction (SMSI) effect at about 50% conversion of acetylene. In our previous studies, the solvothermal-derived TiO_2 supported Pd catalysts exhibited 40% selectivity of ethylene at complete conversion of acetylene [6]. Ethylene selectivity $\geq$ 80% has been reported over Pd catalysts supported on the mixed phase TiO_2 containing 44% rutile phase [7] and the sol-gel-derived TiO_2 at acetylene conversion < 50% [8].

It is well-known that operating temperature plays a large role in the activity of the supported Pd catalysts. As the temperature increased from 40-100°C, acetylene was completely hydrogenated to ethylene and ethane for all the catalysts except the Pd/TiO$_2$-Air-(ED). For the same preparation method, the 1 wt.% Pd/TiO$_2$-H$_2$ showed higher Pd dispersion than 1 wt.% Pd/TiO$_2$-Air and, as a consequence, they exhibited higher hydrogenation activity (**Figure 5(b)**). Because all the prepared TiO$_2$ supports possessed similar average crystallite size, BET surface area, pore volume, and pore diameter, the higher Pd dispersion on the catalysts supported on H$_2$-treated sol-gel TiO$_2$ was attributed to the larger amount of surface Ti^{3+} on the TiO$_2$ supports. The higher defects could lead to numerous crystal boundaries, where a larger number of Pd atoms can be deposited; hence higher Pd dispersion was obtained. The role of defects has gradually attracted the interest of researchers [28, 29]. The relationship between the defect sites of supported metal catalysts and their catalytic activities has been reported. For example, Blackmond et al. [30] showed that the defect sites at edges and corners on the surface of metal nanoparticles were the active sites for the Heck reaction. In the selective hydrogenation of acetylene, Li et al. [31] reported that the hydrogenation activity of the Pd nanowires increased because of the defect sites at crystal boundaries. In our previous work [32], a larger amount of Ti^{3+} surface defects on the solvothermal-derived nanocrystalline TiO$_2$ was also found to result in a stronger interaction between Co and TiO$_2$ and then a higher Co dispersion.

As can be seen from **Figure 5(c)**, ethylene selectivity was higher on the Pd catalysts supported on H$_2$-treated TiO$_2$ than Pd/TiO$_2$-Air, regardless of the preparation method used. Ethylene selectivity did not depend much on reaction temperature but rather affected by the nature of the adsorption sites of Pd. Ethylene selectivity over the Pd-based catalysts was found to increase with increasing A_l/A_m ratio. It has been rationalized that the presence of more isolated adsorption sites could be responsible for the increased selectivity to ethylene

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[33, 34]. The number of isolated adsorption sites was greatly enhanced on the H_2-treated sol-gel TiO_2 supports than the ones calcined in air. The presence of surface Ti^{3+} led to a higher dispersion of the active sites, probably via the covalent bonding between Pd and Ti. The growth of Pd crystallite size lowered the A_l/A_m ratio. In addition, diffusion of Ti^{3+} from the lattice of TiO_2 to surface Pd particles has shown to result in the SMSI effect so that the adsorption strength of ethylene is weakened [10]. Without promoters and alloying with other elements, Shao et al. [35] recently suggest the design methodology of transition-metal-supported catalyst systems to improve selectivity in the selective acetylene hydrogenation by 1) saturating the active transition metal and forming stable but selective phases; 2) choosing supports with suitable geometric structures; and 3) establishing an SMSI effect to regularly rearrange accumulated species and expose the reaction-active phase. Our work complies with such methodology by simply using H_2-treated sol-gel TiO_2 supported Pd catalysts. No catalyst deactivation was observed during the 8 h time-on-stream.
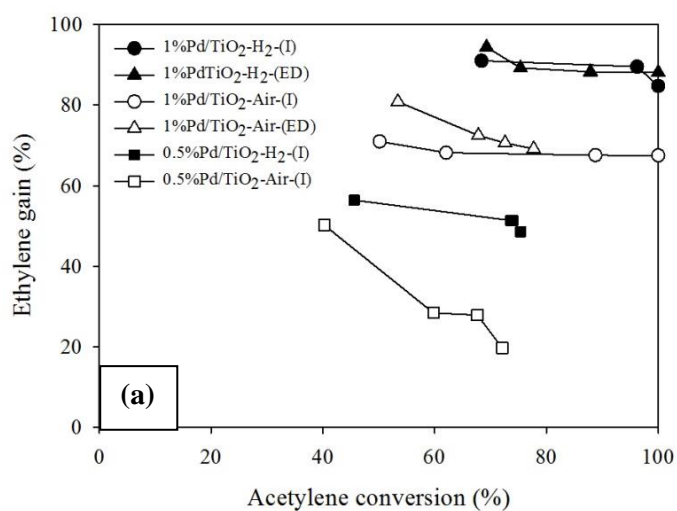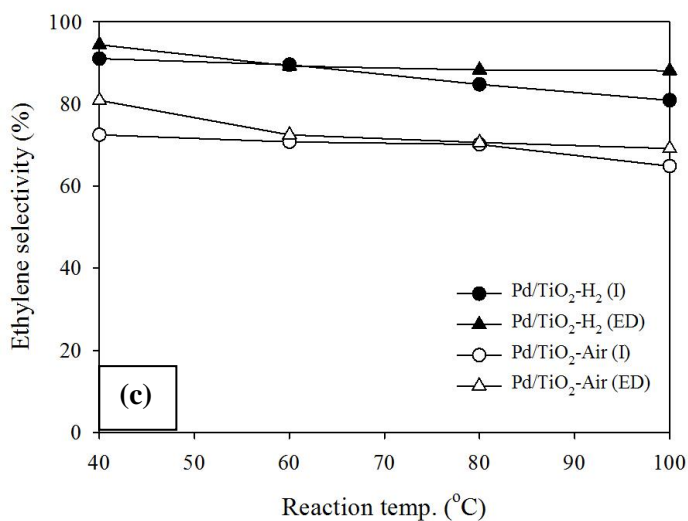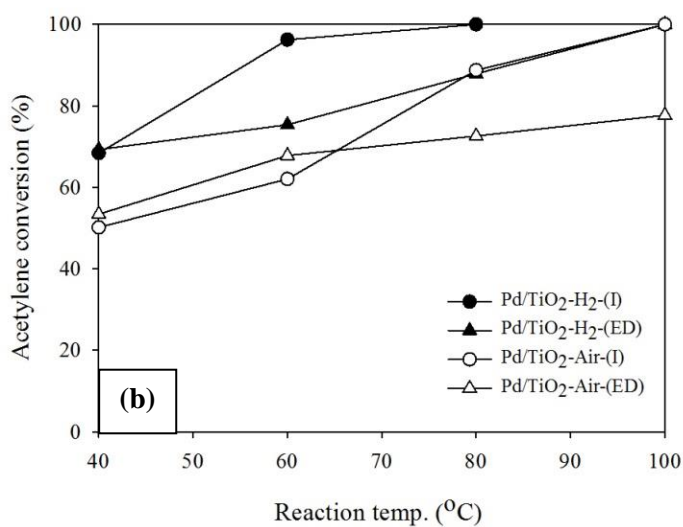
Figure 5 Results of acetylene hydrogenation: (a) catalytic performance plots for 1% and 0.5% Pd/TiO$_2$ catalysts, (b) and (c) acetylene conversion and ethylene selectivity as a function of reaction temperature for 1% Pd/TiO$_2$ catalysts

4. Conclusions

The use of H$_2$-treated sol-gel derived TiO$_2$ resulted in higher Pd dispersion and improved catalytic performance of Pd/TiO$_2$ catalysts in the selective hydrogenation of acetylene, compared to the TiO$_2$ calcined in air. As revealed by ESR results, calcination

under H_2 atmosphere led to more surface Ti^{3+} defective sites on the TiO_2, while there were no significant differences in the average crystallite size and specific surface area of the TiO_2. The presence of Ti^{3+} gives the higher Pd dispersion and promoted the formation of isolated Pd adsorption sites. In addition, higher Pd dispersion was obtained when the catalysts were prepared by electroless deposition technique, compared to conventional impregnation.

Acknowledgements

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