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Synthesis, characterization, and catalytic properties of Pd and Pd–Ag catalysts supported on nanocrystalline TiO_2 prepared by the solvothermal method

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Nanocrystalline titania have been prepared by thermal decomposition of titanium (IV) *n*-butoxide in two different solvents (toluene and 1,4-butanediol) at 320 °C and employed as supports for Pd and Pd–Ag catalysts for selective acetylene hydrogenation for the first time. The titania products obtained from both solvents were pure anatase phase with relatively the same crystallite sizes and BET surface areas. However, due to different crystallization pathways, the number of Ti^{3+} defective sites as shown by ESR results of the titania prepared in toluene was much higher than the ones prepared in 1,4-butanediol. It was found that the use of anatase titania with higher defective sites as a support for Pd catalysts resulted in lower activity and selectivity in selective acetylene hydrogenation. However, this effect was suppressed by Ag promotion.

KEY WORDS: nanocrystalline titania; solvothermal method; acetylene hydrogenation; supported Pd catalysts.

1. Introduction

The solvothermal method has been used to successfully synthesize various types of nanosized metal oxides with large surface area, high crystallinity, and high thermal stability [1–7]. For example, thermal decomposition of titanium (IV) *n*-butoxide in organic solvents yields nano-sized pure anatase titania without bothersome procedures such as purification of the reactants or handling in an inert atmosphere. These nanocrystalline titanias have been shown to exhibit high photocatalytic activities [8, 9]. However, the thermal stability as well as photocatalytic activity of the solvothermal-derived titania were found to be strongly dependent on the organic solvent used as the reaction medium during crystallization [7]. The titania products synthesized in toluene showed lower thermal stability and lower photocatalytic activities than the ones synthesized in 1,4-butanediol. The authors suggested that the amount of defect structures in the titania prepared by this method was different depending on the solvent used due to the different crystallization pathways.

Due to their unique properties, it is interesting to investigate the characteristics and catalytic properties of the solvothermal-derived nanocrystalline titania supported noble metal as another exploitation of such materials. It is well known that metal catalyst supported on titania exhibits 'the strong metal-support interaction' (SMSI) phenomenon after reduction at high temperatures due to the decoration of the metal surface by partially reducible metal oxides [10, 11] or by an electron transfer between the support and the metals [12, 13]. In selective hydrogenation of acetylene to ethylene on Pd/TiO_2 catalysts, the charge transfer from Ti species to Pd weakened the adsorption strength of ethylene on the Pd surface hence higher ethylene selectivity was obtained [14].

In this study, nanocrystalline titanias were synthesized by the solvothermal method in two different solvents (1,4-butanediol and toluene) and employed as supports for Pd and Pd–Ag catalysts for selective hydrogenation of acetylene for the first time. The physicochemical properties of the titania and the titania supported catalysts were analyzed by means of X-ray diffraction (XRD), N_2 physisorption, scanning electron microscopy (SEM), electron spin resonance (ESR), and CO chemisorption. Moreover, the effect of defective structures in titania on the catalytic performance of the titania supported Pd and Pd–Ag catalysts in acetylene hydrogenation was investigated.

2. Experimental

2.1. Preparation of TiO_2 by the solvothermal method

TiO_2 was prepared according to the method described in Payakgul *et al.* [7] using 25 g of titanium(IV) *n*-butoxide (TNB) 97% from Aldrich. The starting material was suspended in 100 ml of solvent

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(1,4-butanediol or toluene) in a test tube and then set up in an autoclave. In the gap between the test tube and autoclave wall, 30 ml of solvent was added. After the autoclave was completely purged with nitrogen, the autoclave was heated to 320 °C at 2.5 °C/min and held at that temperature for 6 h. Autogenous pressure during the reaction gradually increased as the temperature was raised. After the reaction, the autoclave was cooled to room temperature. The resulting powders were collected after repeated washing with methanol by centrifugation. They were then air-dried at room temperature.

2.2. Preparation of TiO_2 supported Pd and Pd–Ag catalysts

1%Pd/TiO_2 were prepared by the incipient wetness impregnation technique using an aqueous solution of the desired amount of $Pd(NO_3)_2$ (Wako). The catalysts were dried overnight at 110 °C and then calcined in N_2 flow 60 cc/min with a heating rate of 10 °C/min until the temperature reached 500 °C and then in air flow 100 cc/min at 500 °C for 2 h. 1%Pd–3%Ag/TiO_2 catalysts were prepared by sequential impregnation of the 1%Pd/TiO_2 with an aqueous solution of $Ag(NO_3)$ (Aldrich) and were calcined using the same calcination procedure as for 1%Pd/TiO_2.

2.3. Catalyst characterization

The BET surface areas of the samples were determined by N_2 physisorption using a Micromeritics ASAP 2000 automated system. Each sample was degassed under vacuum at $<10\mu$m Hg in the Micromeritics ASAP 2000 at 150 °C for 4 h prior to N_2 physisorption. The XRD spectra of the catalyst samples were measured from 20–80° 2θ using a SIEMENS D5000 X-ray diffractometer and CuK_α radiation with a Ni filter. Electron spin resonance (ESR) spectra were taken at −150 °C using a JEOL JES-RE2X spectrometer. Relative percentages of palladium dispersion were determined by pulsing carbon monoxide over the reduced catalyst. Approximately 0.2 g of catalyst was placed in a quartz tube in a temperature-controlled oven. CO adsorption was determined by a thermal conductivity detector (TCD) at the exit. Prior to chemisorption, the catalyst was reduced in a flow of hydrogen (50 cc/min) at room temperature for 2 h. Then the sample was purged at this temperature with helium for 1 h. Carbon monoxide was pulsed at room temperature over the reduced catalyst until the TCD signal from a pulse was constant.

The ethylene-TPD profiles of supported palladium catalysts were obtained by temperature programmed desorption from 35 to 800 °C. Approximately 0.05 g of a calcined catalyst was placed in a quartz tube in a temperature-controlled oven and connected to a thermal conductivity detector (TCD). The catalyst was first reduced in H_2 flow 100 cc/min for 1 h at 500 °C (using a ramp rate of 10 °C/min) and cooled down to room temperature before ramping up again to 70 °C in helium flow. The catalyst surface was saturated with ethylene by applying a high purity grade ethylene from the Thai Industrial Gas, Co., Ltd. at 60 ml/min for 3 h. Then the samples were flushed with helium while cooling down to room temperature for about 1 h. The temperature-programmed desorption was performed with a constant heating rate of ca. 10 °C/min from 35 to 800 °C. The amount of desorbed ethylene was measured by analyzing the effluent gas with a thermal conductivity detector.

2.4. Selective hydrogenation of acetylene

Approximately 0.2 g of catalyst was packed in a quartz tubular reactor in a temperature-controlled furnace. Prior to reaction, the catalyst was reduced in H_2 at 500 °C for 2 h. The reactor was then cooled down to 40 °C and the reactant gas composed of $C_2H_2/H_2 = 1{:}2$ (2/4 cc) balance with N_2 total flow of 200 ml/min was fed to the reactor to start the reaction. The product samples were taken at 30 min intervals and analyzed by GC.

3. Results and discussion

3.1. Physicochemical properties of the solvothermal-derived TiO_2

Figure 1 shows the XRD patterns of the TiO_2 particles prepared by thermal decomposition of titanium *n*-butoxide in organic solvents. It was found that nano-sized anatase titania was produced without any contamination of other phases. The crystallite sizes (d) and BET surface areas of the TiO_2 products synthesized in 1,4-butanediol and toluene were found to be essentially the same ($d = 9$–10 nm and BET S.A. 65 m^2/g). However, the morphology of the TiO_2 particles was different as shown by SEM micrographs (figure 2). The products synthesized in toluene agglomerated into spherical micron-sized particles whereas irregular aggregates of nanometer particles were observed for the ones prepared in 1,4-butanediol. The effect of reaction medium on the synthesis of TiO_2 nanocrystals by solvothermal method has recently been reported by Praserthdam *et al.* [7]. It was suggested that anatase titania synthesized in 1,4-butanediol was the result from direct crystallization while titania synthesized in toluene was transformed from precipitated amorphous intermediate.

Due to the different crystallization pathways, degree of crystallinity of the TiO_2 synthesized in 1,4-butanediol and toluene may be different. In this study, the number of defective sites of TiO_2 was determined using electron spin resonance spectroscopy technique and the results are shown in figure 3. ESR has been shown to be a powerful tool to detect Ti^{3+} species in TiO_2 particles. Such Ti^{3+} species are produced by trapping of electrons at defective sites of TiO_2 and the amount of

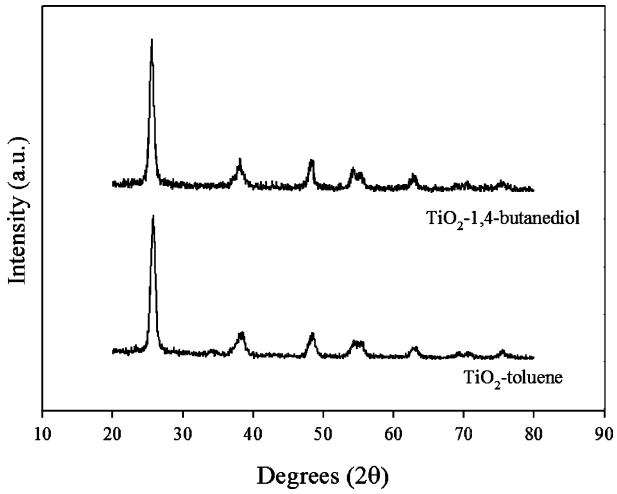

Figure 1. XRD patterns of the solvothermal-derived TiO_2 prepared in two different solvents.

accumulated electrons may therefore reflect the number of defective sites [15]. The signal of g value less than 2 was assigned to Ti^{3+} ($3d^1$) [16]. Both TiO_2-1,4-butanediol and TiO_2-toluene show Ti^{3+} ESR signal at $g = 1.9979$–1.9980 with TiO_2-toluene exhibited much higher intensity. The results clearly show that TiO_2-toluene possessed more Ti^{3+} defective sites than TiO_2-1,4-butanediol.

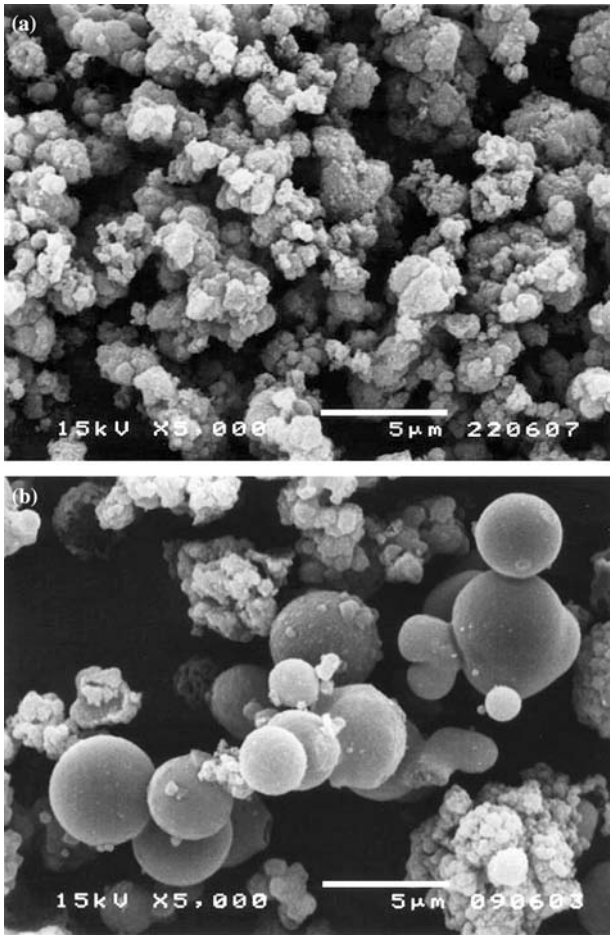

Figure 2. SEM micrographs of (a) TiO_2-1,4-butanediol and (b) TiO_2-toluene.

3.2. Characteristics of Pd/TiO_2 and $Pd–Ag/TiO_2$ catalysts

Table 1 shows the physicochemical properties of the Pd/TiO_2 and $Pd–Ag/TiO_2$ catalysts. It was found that BET surface areas of the TiO_2 were slightly decreased after impregnation Pd and Pd–Ag suggesting that the metals were deposited in some of the pores of TiO_2. The pulse CO chemisorption technique was based on the assumption that one carbon monoxide molecule adsorbs on one palladium site [17–19]. It was found that Pd/TiO_2-1,4-butanediol exhibited higher amount of CO chemisorption than Pd/TiO_2-toluene. Since both TiO_2 supports possess similar BET surface areas and crystallite sizes, the differences in the amount of active surface Pd were probably induced by the different degrees of crystallinity of the TiO_2 particles.

Addition of Ag to Pd/TiO_2 catalysts resulted in lower amount of active surface Pd. The bimetallic Pd–Ag catalyst has been reported to show many beneficial effects in selective hydrogenation of acetylene to ethylene, for examples, suppression of oligomers formation and improvement of ethylene selectivity [20]. These beneficial effects are due to the altered surface arrangement of Ag atoms on the Pd surface. Roder *et al.* [21] suggested that Ag atoms are likely to stay at the surface in segregated form with Pd rather than forming an alloy.

3.3. Catalytic performance in selective acetylene hydrogenation

The conversion and selectivity of Pd and Pd–Ag catalysts supported on TiO_2-1,4-butanediol and TiO_2-toluene in selective acetylene hydrogenation as a function

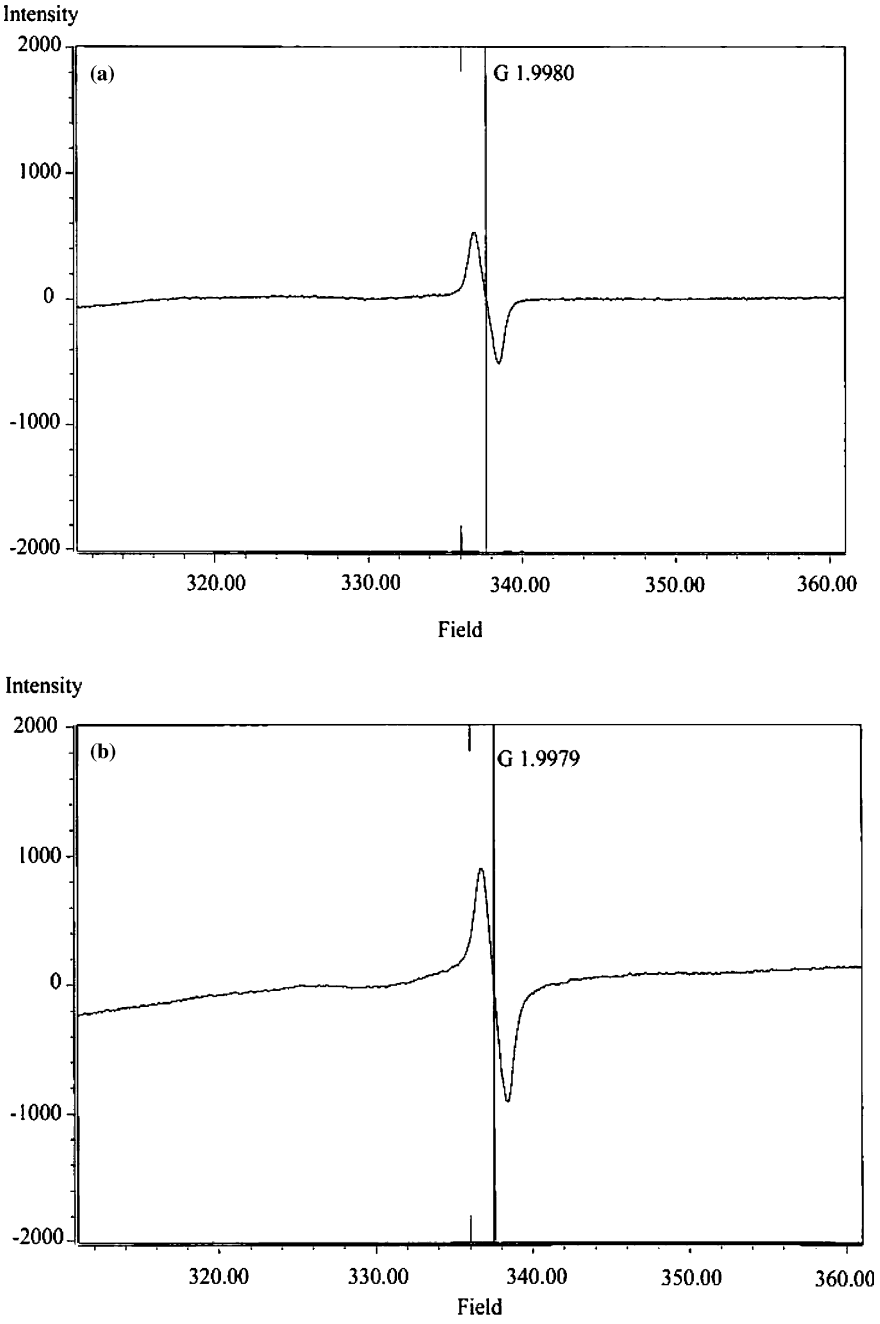

Figure 3. ESR results of (a) TiO_2-1,4-butanediol and (b) TiO_2-toluene.

Table 1
Characteristics of Pd and Pd–Ag catalysts supported on solvothermal-derived TiO_2 prepared in different solvents

Catalyst	BET S.A.[a] (m^2/g)	CO chemisorption[b] (molecule CO $\times 10^{18}$/g catalysis)	Pd dispersion (%)	d_p Pd^0 (nm)[c]
1%Pd/TiO_2 (1,4-butanediol)	52	5.65	10.0	11.2
1%Pd/TiO_2 (toluene)	60	4.69	8.3	13.5
1%Pd–3%Ag/TiO_2 (1,4-butanediol)	42	2.18	3.8	29.1
1%Pd–3%Ag/TiO_2 (toluene)	47	2.05	3.6	30.9

[a]Error of measurement = ± 10 %.
[b]Error of measurement = ± 5 %.
[c]Based on $d = 1.12/D$ (nm), where D = fractional metal dispersion [17].

of reaction temperature are shown in figures 4 and 5, respectively. The use of TiO_2-1,4-butanediol as the supports for Pd or Pd–Ag catalysts resulted in higher acetylene conversions than the ones supported on TiO_2-toluene. Acetylene conversion of the single metal catalysts reached 100% at ca. 70 °C while those for the bimetallic catalysts showed only 40% (for Pd–Ag/TiO_2-toluene) and 80% (for Pd–Ag/TiO_2-1,4-butanediol) conversions at 90 °C. The ethylene selectivity for all the catalysts at the temperature ranges 40–50 °C were not significantly difference and were found to be ca. 80–90%. However, at 60–70 °C, ethylene selectivity of Pd/TiO_2-1,4-butanediol was much higher than those of Pd/TiO_2-toluene. Ethylene selectivity for the Ag-promoted catalysts were similar for all the reaction temperature used in this study and were higher than those of the non-promoted ones. It was reported that SMSI effect occurs for Pd/TiO_2 catalysts after reduction at high temperature lowering the adsorption strength of ethylene on catalyst surface thus high ethylene selectivity is obtained [10]. Recently, Fan *et al.* [22] reported that diffusion of Ti^{3+} from the lattice of anatase TiO_2 to surface Pd particle can lower the temperature to induce SMSI. However, in this study we have found that use of TiO_2 with higher concentration of Ti^{3+} as a support for Pd catalyst resulted in lower acetylene conversion and selectivity for ethylene after reduction at 500 °C. The turnover frequencies were calculated to be ca. 0.50–0.95 s^{-1} based on the reaction rates at 50 °C. Since the TOFs for all the catalysts were quite similar, it would appear that there was no support effect on the specific activity.

The characteristics of the surface active sites of the catalysts were studied by means of the temperature programmed desorption of ethylene from 30–800 °C. The results are shown in figure 6. The TiO_2-toluene support was found to exhibit two main desorption peaks at ca. 460–680 °C while the TiO_2-1,4-butanediol showed only one desorption peak at 680°C. The results suggest that there were two different active sites on the TiO_2-toluene support, probably Ti^{3+} and Ti^{4+} sites. The high temperature peak for both TiO_2 supports disappeared after Pd loading as shown in the profiles of the Pd catalysts. However, desorption peak at ca. 460 °C was still apparent for Pd/TiO_2-toluene. Since lower ethylene

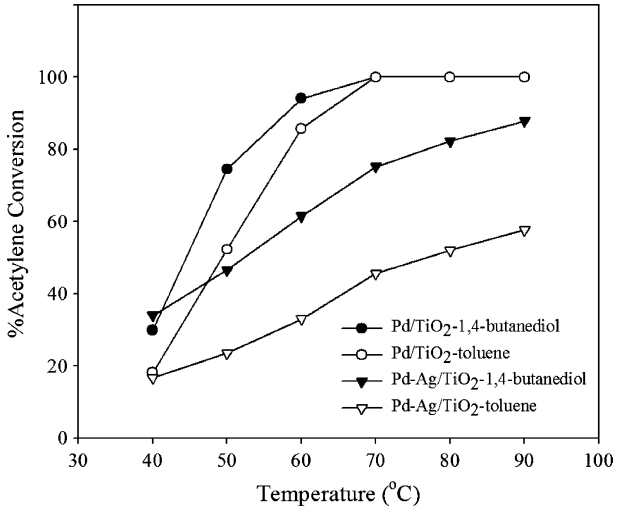

Figure 4. Acetylene conversion as a function of temperature for various TiO_2 supported catalysts.

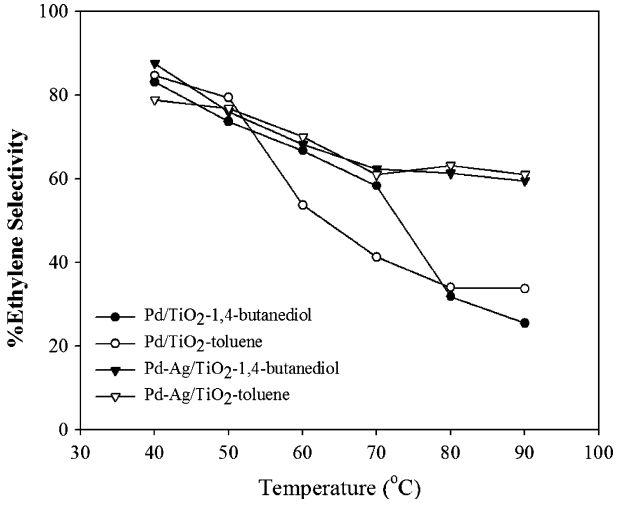

Figure 5. Ethylene selectivity as a function of temperature for various TiO_2 supported catalysts.

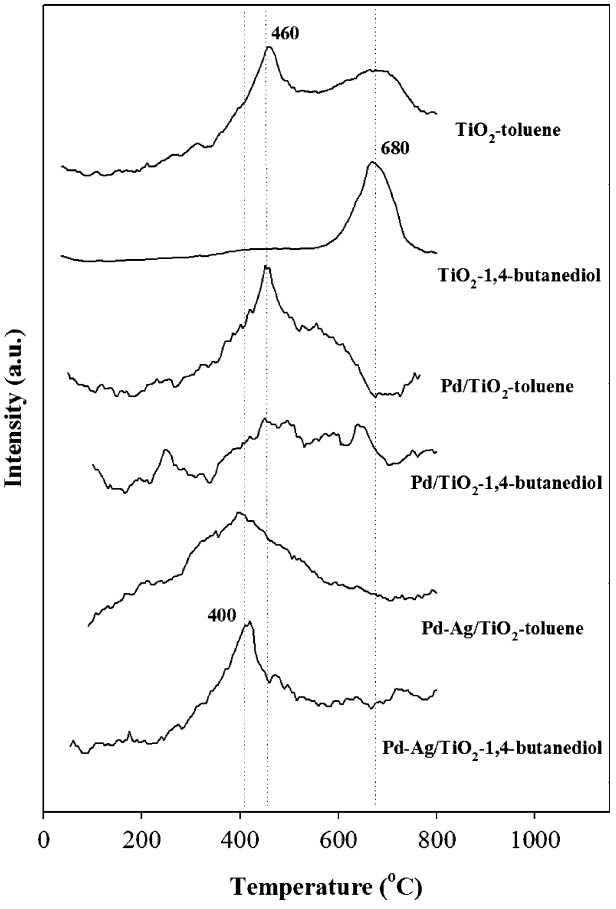

Figure 6. Ethylene-TPD results.

selectivity was found for Pd/TiO_2-toluene than Pd/TiO_2-1,4-butanediol for similar acetylene conversion, this peak can be assigned to the sites for ethylene hydrogenation to ethane. Ethylene hydrogenation is usually believed to take place on the support by means of a hydrogen transfer mechanism [23]. Since only Ti^{3+} species that were in contact with palladium surface promoted SMSI effect [22], ethylene hydrogenation could take place on the Ti^{3+} defective sites that were not in contact with palladium resulting in lower acetylene conversion and selectivity for ethylene as observed in the case of Pd/TiO_2-toluene in this study. The Ag-promoted Pd catalysts exhibited only one ethylene desorption peak at ca. 400 °C suggesting that the Pd catalyst surface on both TiO_2 supports was modified by Ag atoms. The presence of Ag probably blocked the sites for ethylene hydrogenation to ethane for both catalysts thus a significant improvement in ethylene selectivity was observed especially for high acetylene conversion at high temperature. Further study on the titanium defective sites using more sophisticated characterization techniques such as XPS and SIMS is recommended in order to obtain more information on other titanium oxidation states that might be involved in the defective sites, oxygen to titanium ratio, etc. However, in term of catalyst deactivation, we did not observe a decrease in activity or ethylene selectivity for all the catalyst after 12 h on stream. Therefore, there was no effect of carbonaceous deposits involved in the mechanism of acetylene hydrogenation in this study.

4. Conclusions

Nanocrystalline anatase titania prepared by the solvothermal method were successfully used as supports for Pd and Pd–Ag catalysts for selective hydrogenation of acetylene to ethylene. However, Pd supported on titania synthesized in toluene (higher defective sites) exhibited lower activity and selectivity for selective acetylene hydrogenation than the ones supported on titania synthesized in 1,4-butanediol (lower defective sites). Ethylene hydrogenation probably took place on the Ti^{3+} defective sites that were not in contact with palladium surface. These sites were blocked by promotion of Pd/TiO_2 with Ag metal.

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