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REVISED

The effect of TiO₂ particle size on the characteristics of Au-Pd/TiO₂ catalysts

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Abstract

The nanocrystalline TiO₂ materials with average crystallite sizes of 9 and 15 nm were synthesized by the solvothermal method and employed as the supports for preparation of bimetallic Au/Pd/TiO₂ catalysts. The average size of Au-Pd alloy particles increased slightly from sub-nano (< 1 nm) to 2-3 nm with increasing TiO₂ crystallite size from 9 to 15 nm. The catalyst performances were evaluated in the liquid-phase selective hydrogenation of 1-heptyne under mild reaction conditions (H₂ 1 bar, 30°C). The exertion of electronic modification of Pd by Au-Pd alloy formation depended on the TiO₂ crystallite size in which it was more pronounced for Au/Pd on the larger TiO₂ (15 nm) than on the smaller one (9 nm), resulting in higher hydrogenation activity and lower selectivity to 1-heptene on the former catalyst.

Keywords: 1-heptyne, selective hydrogenation, TiO₂, Pd-Au bimetallic catalysts

1. Introduction

Bimetallic catalysts have attracted much attention because of their markedly different properties from either of the constituent metals, and their enhanced catalytic stabilities, activities and/or selectivities. Important examples are AuPd catalysts which have been found to be effective in many catalytic reactions such as CO oxidation, vinyl chloride synthesis, hydrodesulfurization, selective oxidation of alcohols to aldehydes or ketones and alkenes to epoxides, oxidation of hydrogen to hydrogen peroxide, and selective hydrogenation [1]. The selective hydrogenation of alkyne to the corresponding alkene is a very valuable reaction in synthetic organic chemistry. The alkyne hydrogenation over Pd–Au bimetallic catalysts focused on the gas-phase selective hydrogenation of low molecular weight substrates, mostly acetylene. In the present research, 1-heptyne a relatively long chain alkyne is used as the model reactant.

The promotional effect of Au in Au–Pd catalysts has been attributed to the synergistic effects arisen from both ligand effect and ensemble effect of the Au–Pd alloy [2, 3]. In hydrogenation reactions, a number of studies showed that electron transfer between Pd and Au species resulted in the modification of catalyst activity and selectivity [4-7]. However, it appears that the exertion of electronic interaction between Pd and Au species depend on several factors such as the molar ratio of Au to Pd, the preparation method, the particle morphology, and/or the particle size of Au–Pd alloys [8-11]. In our previous study, the formation of small size Au-Pd bimetallic particle (< 10 nm) could enhance the second step hydrogenation of 1-heptyne in the liquid-phase selective hydrogenation of 1-heptyne [12].

Despite the variety of supports being used for preparation of supported Au-Pd catalysts such as γ -Al₂O₃ [4], SiO₂ [5], TiO₂ [6, 13], SiO₂-Al₂O₃ [14], zeolite [15], CeO₂ [16], α -Fe₂O₃ [17], and carbon [18, 19], only a few studies systematically

reported the influence of support nature on the interaction of Au-Pd species and their corresponding catalytic behavior. Smolentseva et al. [16] showed that $Pd-Au/Al_2O_3$ exerted more pronounced interaction between gold and palladium species than Pd-Au/CeO₂ but the Pd-Au/CeO₂ manifested higher activity and selectivity in the selective oxidation of arabinose to arabinonic acid. The interaction of Au and Pd with reducible ceria coexisted with the mutual interaction between these metals.

TiO₂ is one of reducible metal oxides that have received considerable attention as catalyst supports. In the liquid-phase selective hydrogenation of alkyne to alkene, Pd/TiO₂ exhibited the strong metal-support interaction (SMSI) effect, resulting in an improvement of the catalytic performances [20]. However, the SMSI effect in Pd/TiO₂ depended on the properties of the TiO₂ such as the crystalline phase composition and the crystallite size [21, 22]. The TiO₂ supports used for preparation of Au–Pd catalysts in many research works were mostly the commercially available Degussa P25. For example, Enache and co-workers [7] studied the effect of Au–Pd ratio on the Au– Pd/TiO₂ catalyst performance in the oxidation of benzyl alcohol.

In the present study, the solvothemal method was employed to synthesize the nanocrystalline anatase TiO₂. Solvothemal method is an alternative route for direct (one step) synthesis of pure anatase TiO₂. Particle morphology, crystalline phase, and surface chemistry of the solvothemal-derived TiO₂ can be controlled by regulating precursor composition, reaction temperature, pressure, solvent property, and aging time [20]. The effect of TiO₂ crystallite size on the catalytic behavior of Au–Pd/TiO₂ catalysts was investigated in the selective hydrogenation of 1-heptyne to 1-heptene under mild reaction conditions. The catalysts were also characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transformed

infrared spectroscopy of adsorbed CO (CO-IR), and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1 Catalyst preparation

The TiO₂ support used in this work was synthesized by the solvothemal method as described in Ref. [20] using titanium (IV) tert-butoxide (97%TNB) and 1,4butanediol (Aldrich) as titanium precursor and solvent, respectively. Twenty five g of TNB was suspended in 100 ml of 1,4-butanediol. After the autoclave was completely purged with nitrogen, it was heated to 300°C at a rate of 2.5° C/min and held at this temperature for 30 min and for 6 h to prepare TiO₂_of 9 nm and 15 nm, respectively. After the reaction, the autoclave was cooled to room temperature. The resulting powder that collected from the test tube was centrifuged in methanol five times and then dried in air at room temperature overnight. The final product obtained were TiO₂ powders, which were denoted as TiO₂_9 and TiO₂_15.

The monometallic catalysts (ca. 0.5 wt% of Pd) were prepared by the incipient wetness impregnation technique using 1 M HCl solution of PdCl₂ (Aldrich). The catalysts were dried overnight at 110°C and calcined in air at 500°C for 2 h. The monometallic catalysts supported on solvothermal-derived TiO₂ with average crystallite sizes of 9 and 15 nm are denoted as Pd/TiO₂_9 and Pd/TiO₂_15, respectively. The bimetallic (ca. 0.5 wt% of Pd and 1.0 wt% of Au) catalysts were prepared by the combination of impregnation of Pd and deposition-precipitation of Au according to Ref. [23]. Firstly, HAuCl₄.3H₂O, which was used as gold precursor, was dissolved in 100 cm³ of deionized water. The pH was adjusted to 7 by using 0.1 M of NaOH. The Pd/TiO₂ catalyst was dispersed in the solution and the pH was adjusted

again to 7 with 0.1 M NaOH. The suspension was vigorously stirred for 2 h at 80°C. After that the suspension was cooled and centrifuged five times with deionized water in order to remove chloride and then dried at 110° C. The bimetallic catalysts supported on the solvothermal-derived TiO₂ with average crystallite sizes of 9 and 15 nm were denoted as Au/Pd/TiO₂_9 and Au/Pd/TiO₂_15, respectively.

2.2 Catalyst characterization

The physisorption of nitrogen was performed using a Micromeritics ASAP 2020 automated system to evaluate the BET specific surface area, pore volume, and average pore diameter. The XRD patterns of the catalysts were measured from 10 to $80^{\circ} 2\theta$ using a SIEMENS D5000 X-ray diffractometer and Cu K_a radiation with a Ni filter. TEM was carried out using a JEOL JEM 2010 transmission electron microscope that employed a LaB_6 electron gun in the voltage range of 80–200 kV with an optical point to point resolution of 0.23 nm. The XPS measurement was carried out using an AMICUS photoelectron spectrometer equipped with an Mg K_{α} X-ray as a primary excitation and KRATOS VISION2 software. XPS elemental spectra were acquired with 0.1 eV energy step at a pass energy of 75 eV. All the binding energies were referenced to the C 1s peak at 285.0 eV of the surface adventitious carbon. The CO species adsorbed on the Pd/TiO₂ 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°C. The temperature was kept constant for 30 min and then cooled to the room temperature with He gas. After that, carbon monoxide was passed to the system for 15 min. The IR spectrum of CO adsorbed onto the catalyst

was recorded in the $600-4000 \text{ cm}^{-1}$ range after the gaseous CO was removed from the cell by He flow.

2.3 Reaction study in the liquid-phase hydrogenation of 1-heptyne

The liquid-phase hydrogenation of 1-heptyne (98%, Aldrich) was carried out in a magnetically stirred 50-cm³ Teflon-lined stainless steel autoclave reactor. Prior to the reaction testing, the catalyst sample was reduced by hydrogen gas at a flow rate of 50cm³/min at 40°C for 2 h. Then, 0.01 g of the sample was dispersed in 10 cm³ of toluene (99.9%, Merck) containing 2 vol. % 1-heptyne. The effect of mass transfer on the reaction rate was negligible by using a high stirring rate (1000 rpm). The reaction was carried out under flowing hydrogen at 1 bar and 30°C for 10-120 min. The liquid reactants and products were analyzed by a gas chromatograph equipped with an FID detector (Shimadzu GC-14A and TC-WAX column).

3. Results and discussion

3.1 Catalyst characterization

The XRD patterns of the TiO₂ supports and TiO₂ supported Au–Pd catalysts are shown in **Figure 1**. All the samples showed the characteristic peaks of pure anatase phase titania at 2 θ degrees = 25° (major), 37°, 48°, 55°, 56°, 62°, 71°, and 75° without contamination of the other phases such as rutile and brookite [24]. The average crystallite sizes of TiO₂ were calculated from the full width at half maximum of the XRD peak at 2 θ = 25° using the Scherrer equation. As shown in **Table 1**, the solvothermal-derived TiO₂ had average crystallite sizes of 9 and 15 nm with specific surface area 145 and 79 m²/g, respectively. The XRD characteristic peaks

corresponding to palladium and gold species were not detected for all the catalysts probably due to the low amount of metals present.

Typical TEM images the monometallic Pd and the bimetallic Au–Pd catalysts are shown in **Figure 2**. The TiO₂_9 and TiO₂_15 supports obtained from the solvothermal method showed uniform particle size of average size of 9 and 15 nm, respectively. The metal dispersion on the catalysts can be observed from the TEM images. The average Pd particles size on the monometallic Pd/TiO₂_9 catalyst was in the range of sub-nano particles (< 1 nm) whereas that of Pd/TiO₂_15 catalyst was larger (~ 2 nm). Similarly, for the bimetallic Au–Pd catalysts much smaller Au–Pd particles were seen on the Au/Pd/TiO₂_9 than on the Au/Pd/TiO₂_15. The metal particles on the Au/Pd/TiO₂_9 and Au/Pd/TiO₂_15 had a uniform particle size distribution in the range of sub-nano particles (< 1 nm) and 2-3 nm, respectively. It is suggested that the size of Au–Pd particles depend on the original size of the Pd particles, which is itself a function of the TiO₂ crystallite size.

The surface properties and the chemical states of Pd and Au on the different catalysts were investigated by XPS. The binding energies and atomic concentrations of Pd and Au determined by XPS are given in **Table 2**. The Pd 3d spectra of the monometallic and bimetallic catalysts are shown in **Figure 3(a)** and **3(b)**, respectively. For the Pd/TiO₂_9 and Pd/TiO₂_15 catalysts, the binding energies (B.E.) of Pd 3d_{5/2} were detected at 336.5-337.1 eV which could be attributed to the presence of palladium in the form of PdO. On the other hand, the Pd 3d spectra of the Au/Pd/TiO₂_9 and Au/Pd/TiO₂_15 catalysts were fitted by two peaks at higher and lower binding energies of 336.0-336.2 eV and 334.8-335.2 eV, which were attributed to Pd–Au alloy and metallic Pd⁰, respectively [25, 26]. It has been reported that Pd particles in the bimetallic catalysts were highly resistant to oxidation, compared to those of the

monometallic catalysts [27]. The atomic percent of the species at 336.0-336.2 eV (Au– Pd alloy) for Au/Pd/TiO₂_9 and Au/Pd/TiO₂_15 catalysts were determined by peak fitting to be 19% and 18%, respectively. The percentages of Au–Pd alloy formation were not significantly different on the different bimetallic Au–Pd catalysts. The Au 4f spectra of the bimetallic catalysts are shown in **Figure 3(c)**. The Au 4f peaks were detected at the binding energy of 83.0-83.2 eV, which were shifted from the typical metallic gold (B.E. 84.0 \pm 0.1). A small shift of binding energies could be attributed to charge transfer from Pd to Au on the grounds of the bulk electronegativity differences and could also be indicative of alloy formation [27].

The infrared spectra obtained after CO adsorption at 30°C on the Pd monometallic and Au–Pd bimetallic catalysts are shown in **Figure 4**. The spectral envelopes were deconvoluted into individual vibrational bands in order to identify the specific adsorbed species. The CO adsorption on Pd-based catalysts generally reveals two main regions: a first one between 2100 and 2030 cm⁻¹ and a larger second one in 2000–1800 cm⁻¹ range. The IR spectra for Pd monometallic and Au–Pd bimetallic catalysts represent four adsorption modes of CO, linear (2100-2030 cm⁻¹), compressed bridged (1995-1975 cm⁻¹), isolated bridged (1960-1925 cm⁻¹), and tricoordinated (1890-1870 cm⁻¹) bonds, as described in Ref. [28]. Compared to the monometallic Pd catalysts, the peaks corresponding to linear CO adsorbed species were shifted to lower wavenumbers after Au addition for all the Au–Pd bimetallic catalysts, suggesting the Pd–Au alloy formation [28, 29].

3.2 Hydrogenation of 1-heptyne

The catalytic behavior of the mono and bimetallic catalysts was evaluated in the liquid-phase semihydrogenation of 1-heptyne to 1-heptene under mild conditions. The conversion of 1-heptyne and the selectivity to 1-heptene as a function of reaction time are shown in Figure 5(a) and 5(b), respectively. The hydrogenation rates of the bimetallic Au-Pd catalysts were higher than those of the monometallic Pd ones and were found to be in the order: $Au/Pd/TiO_2_{15} > Au/Pd/TiO_2_{9} > Pd/TiO_2_{15} >$ Pd/TiO₂_9. The conversion of 1-heptyne was completed in 30 min for all the catalysts, except the Pd/TiO₂_9 in which complete conversion was achieved after 40 min reaction time under the conditions used. The dependence of hydrogenation activity of supported Pd catalysts on Pd particle size has been investigated extensively. Typically, specific activity of Pd in the liquid-phase selective hydrogenation decreases as Pd particle size decreases especially when the average Pd size is very small ($\leq 3-5$ nm) [30]. Diminishing activity of small metal particles was probably due to the different band structure characteristics of nano-sized metal compared to bulk metals, through which the nano-sized metal particles are electron deficient [31]. The results were consistent to the previous study on the comparison of Pd catalysts supported on micron- and solvothermal-derived nanocrystalline TiO₂ in the liquid-phase selective hydrogenation of phenylacetylene. The activity for hydrogenation of phenylacetylene of Pd supported TiO₂ with large crystallite size was higher than that of supported TiO₂ with small crystallite size, due to the smaller Pd particle size deposited on the smaller TiO_2 crystallite size. However, the selectivity of catalyst supported on the small TiO₂ crystallites was still higher than that of catalyst supported on the larger ones. Moreover, the nanocrystalline TiO₂ exhibited strong metal-support interaction (SMSI) when reduced at 500 °C [20, 21].

All the present catalysts exhibited high selectivity to 1-heptene (> 97%) up to nearly full conversion of 1-heptyne. During 120 min, the selectivity of 1-heptene decreased further after complete conversion of 1-heptyne due to the hydrogenation of 1-heptene to heptane. Nonetheless, the selectivities to 1-heptene of the monometallic catalysts were higher than those of the bimetallic catalysts. The selectivity to 1-heptene for the bimetallic catalysts at 120 min was in the order: Au/Pd/TiO₂_9 (54 %) > Au/Pd/TiO₂_15 (41 %) whereas the selectivity was not much different among the monometallic catalysts (70%).

Unlike the alkyne hydrogenation activity, the selectivity to alkene formation was irrespective of Pd particle diameter for most reactants in the selective alkyne hydrogenation [32-34]. It is rather affected by electronic modification of Pd metal (i.e., alloy formation and presence of the strong metal-support interaction effect). In our recent papers [12], the rate of 1-heptene hydrogenation in the second step was greatly enhanced as the Pd species became electron-rich in the Au-Pd alloy particles. In other words, the Au species acted as an electronic promoter for Pd and greatly promoted the second step of hydrogenation of 1-heptene to heptane. In our previous studies, the formation of Au-Pd alloy was found to be dependent on the loading sequence [12] and the preparation method used [35]. The results in the present work emphasized that the formation of Au-Pd alloy was responsible for the increased hydrogenation activity of 1-heptene to heptane in the selective hydrogenation of 1-heptyne and this suggests the dependence of alkene hydrogenation rate on the Au-Pd particle size. The exertion of electronic modification of Pd by Au-Pd alloy formation was more pronounced for Au/Pd on the larger TiO_2 (15 nm) than on the smaller one (9 nm), resulting in higher hydrogenation activity and lower selectivity to 1-heptene on the former catalyst.

The catalyst performance plots in terms of 1-heptene selectivity versus conversion of 1-heptyne are shown in Figure 5(c). Both high conversion of 1-heptyne (~95%) and high selectivity for 1-heptene (97%) can be obtained from the bimetallic Au/Pd/TiO₂-15 nm catalysts under the reaction conditions used at 20 min, giving the highest yield of 1-heptene among all the catalysts used in this study (92.15%). The highest yield of 1-heptene over monometallic Pd/TiO₂ was ca. 80% at 40 min reaction time. Such results suggest the advantages of the bimetallic AuPd catalysts over the monometallic Pd in the selective alkyne hydrogenation.

4. Conclusions

Smaller Pd metal and/or Pd-Au alloy (< 1 nm) were obtained on the TiO₂_9 than on TiO₂_15 (2-3 nm). In the bimetallic Au-Pd alloy, the Au species acted as an electronic promoter for Pd and greatly promoted the second step of hydrogenation of 1-heptene to heptane. The catalytic behavior of Au/Pd/TiO₂ strongly depended on the crystallite size of TiO₂ and Au-Pd alloy particle size. The smaller particles size of Pd and/or Pd-Au alloy provided a higher selectivity to 1-heptene in the selective hydrogenation of 1-heptyne under mild reaction conditions.

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Table 1 Properties of TiO_2 support

T'O manual	Phase	Crystallite size	BET surface area	Pore volume	Average pore diameter			
11O ₂ support		(nm)	(m ² /g)	(cm^3/g)	(nm)			
TiO ₂ _9	Anatase	9	145	0.42	8.1			
TiO ₂ _15	Anatase	15	79	0.40	14.9			
		A CY						

					2	
Sample	Pd	3d _{5/2}	Au 4f _{7/2}		Atomic concentration	
Sample	B.E. (eV)	FWHM (eV)	B.E. (eV)	FWHM (eV)	Pd (%)	Au (%)
Pd/TiO ₂ _9	336.7	0.924	n/a	n/a	0.12	n/a
Au/Pd/TiO. 0	(1) 334.9	1.336	83.2	1.173	(1) 0.69	0.50
Au/1 u/ 1102_9	(2) 336.0	1.372	05.2		(2) 0.16	
Pd/TiO ₂ _15	337.1	0.775	n/a	n/a	0.07	n/a
$\Delta u/Pd/TiO_{1}$ 15	(1) 334.8	1.365	83.0	1.226	(1) 0.46	0.43
Au/10/1102_13	(2) 336.2	1.452	65.0		(2) 0.10	

Table 2 XPS results of TiO_2 supported Pd and Au/Pd catalysts

Figure Captions

Figure 1	XRD patterns of TiO ₂ _9, Pd/TiO ₂ _9, Au/Pd/TiO ₂ _9, TiO ₂ _15,					
	Pd/TiO ₂ _15 and Au/Pd/TiO ₂ _15.					
Figure 2	TEM images of Pd/TiO ₂ _9, Au/Pd/TiO ₂ _9, Pd/TiO ₂ _15 and					
	Au/Pd/TiO ₂ _15.					
Figure 3(a)	XPS Pd 3d core level spectra of Pd/TiO ₂ _9 and Pd/TiO ₂ _15.					
Figure 3(b)	XPS Pd 3d core level spectra of Au/Pd/TiO ₂ 9 and Au/Pd/TiO ₂ 15.					
Figure 3(c)	XPS Au 4f core level spectra of Au/Pd/TiO ₂ 9 and Au/Pd/TiO ₂ 15.					
Figure 4	FTIR spectra of adsorbed CO at room temperature on Pd/TiO ₂ _9,					
	Au/Pd/TiO ₂ _9, Pd/TiO ₂ _15 and Au/Pd/TiO ₂ _15.					
Figure 5	Hydrogenation of 1-heptyne on Pd/TiO ₂ _9, Au/Pd/TiO ₂ _9, Pd/TiO ₂ _15					
	and Au/Pd/TiO2_15 carried out under flowing hydrogen at 1 bar and					
	30°C for 10-120 min: % 1-heptyne conversion (a) and %1-heptene					
	selectivity (b).					
	\mathbf{O}					
X						



Fig1



Figure 2



Fig3







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Effects of TiO₂ crystallite size on the solvothermal-derived nanocrystalline TiO₂ supported Au-Pd catalysts in the liquid-phase hydrogenation of 1-heptyne

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- Au-Pd catalysts were prepared on TiO₂ with average crystallite sizes 9 and 15 nm.
- The size of Au-Pd alloy depended on the TiO₂ crystallite size.

- Electronic effect by Au-Pd alloy formation was more pronounced on the larger TiO₂.
- Au acted as an electronic promoter for Pd, which promoted 1-heptene hydrogenation.