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Characteristics and Catalytic Behavior of Pd Catalysts Supported on Nanostructure Titanate in Liquid-Phase Hydrogenation

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Titanate nanowire (TNW) and nanotube (TNT) structures were synthesized by the hydrothermal reaction using spherical shape anatase TiO_2 nanoparticles (TNP) as the starting material and employed as Pd catalyst supports for the liquid-phase selective hydrogenation of 1-heptyne to 1-heptene. Pd dispersion was significantly improved as the specific surface area of the supports increased in the order: Pd/TNT > Pd/TNW \gg Pd/TNP. While the hydrogenation rate increased with increasing number of active Pd⁰ surface, the selectivity to 1-heptene depended largely on the degree of interaction between Pd and the supports. The catalysts prepared by impregnation method led to a stronger metal-support interaction than those prepared by colloidal route. The selectivity of 1-heptene at complete conversion of 1-heptyne was obtained in the order: I-Pd/TNT > I-Pd/TNP > Pd/TNT \approx Pd/TNT \approx Pd/TNP.

Keywords: Titanate Nanotube, Nanowire, Selective Hydrogenation, Pd Catalysts.

1. INTRODUCTION

Mesoporous materials especially those with metal-organic frameworks have high potential applications in the fields of gas storage, separations, and catalysis.¹⁻⁴ Nanostructure titanate has recently received considerable attention as both photocatalyst and catalyst support due to its elongated morphology and high surface area.⁵ Typically, there are three main methods for preparation of the titanate nanotubes: template method, anodic oxidation, and hydrothermal method. Among these methods, hydrothermal treatment of TiO₂ in base is probably the simplest and the lowest cost method to generate nanotubular structure. Crystalline phase and morphology of the resulting materials are strongly dependent on the synthesis conditions such as aging time, temperature, and base concentration.⁶ Titanate nanotubes synthesized by this route have been employed as catalyst supports for various metals (i.e., Au, Cu, Pt, Ru, Pd) in many catalytic reactions such as low temperature CO oxidation, ammonia decomposition, selective reduction of NO by NH₃, cinnamaldehyde hydrogenation, double bond migration reaction, phenol hydrogenation, and selective hydrogenation of o-chloronitrobenzene.^{7–11} The use of nanotubular titanate has often shown to result in better metal dispersion and improved catalytic performances. In particular cases, the metal-support interaction was altered and charge transfer from the titanate nanotubes to metal particles were observed.^{10, 11}

The selective alkyne hydrogenation is an important reaction for the manufacturing of fine chemicals and biologically activity compounds.¹² Pd-based catalysts have been widely used in both laboratory and industry because they exhibit high selectivity with respect to the semihydrogenation of alkyne to alkene. A number of previous studies have shown that a strong metal-support interaction (SMSI) effect that occurred on Pd/TiO₂ catalysts is beneficial for improving the catalytic performance in the liquid-phase selective hydrogenation reactions.^{13–14} A remarkable high catalytic hydrogenation activity has also been reported for Pd nanoparticles encapsulated in titania matrix.^{15–17}

In the present work, the characteristics and catalytic properties of Pd nanoparticles supported on TiO_2 nanoparticles (Pd/TNP), titanate nanotubes (Pd/TNT), and titanate nanowires (Pd/TNW) were investigated and

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compared in the liquid-phase selective hydrogenation of 1-heptyne under mild reaction conditions. The catalysts were characterized by X-ray diffraction (XRD), N_2 physisorption, transmission electron microscopy (TEM), CO pulse chemisorption, and X-ray photoelectron spectroscopy (XPS).

2. EXPERIMENTAL DETAILS

2.1. Preparation of Titanate Supports

Preparation of the nanostructured titanates was carried out by the hydrothermal method using anatase TiO_2 (Sigma-Aldrich) as the starting material. First, 1.5 g of TiO_2 powder was suspended with 40 ml of 10 M NaOH and then the mixture was sonicated for 10 min. Thereafter the mixture was transferred to a Teflon-lined stanless steel autoclave, and heated at various reaction temperatures ranging from 110 to 200 °C for 24 h in an oven. After hydrothermal reaction, the autoclave was cooled to room temperature by natural cooled down. Then the sample was washed with 0.1 M HCl for several time and followed by deionized water until pH value approached deionized water. Finally, the sample was dried at 110 °C for 24 h.

2.2. Preparation of Titania and Titanate Supported Pd Catalysts elivered by Ingenta to: Chir

The Pd nanoparticles supported on TNP, TNT, and TNW were prepared using wet impregnation of colloidal Pd nanoparticles which were synthesized by the reduction by solvent method according to that described in our previous study.¹⁸ An appropriate volume of Pd nanoparticles/methanol dispersion was mixed with the support to obtain a final loading of ca. 1 wt% Pd. The mixture was gently stirred at room temperature for 3 days and heated at 60 °C in order to remove the methanol solution. The collected solid was washed with ethanol and water (50/50% V/V) for several times and dried overnight. For comparison purposes, TNT supported Pd catalyst was also prepared by the conventional impregnation using PdCl₂ precursor. After impregnation, the catalyst was dried at 110 °C overnight followed by calcination in air at 450 °C for 3 h and was denoted as I-Pd/TNT.

2.3. Catalyst Characterization

XRD patterns were determined using a Siemens D5000 using nickel filtered CuK_{α} radiation. The morphology and particle size were obtained using a Hitachi s-3400N scanning electron microscope and JEOL-JEM 2010 transmission electron microscope. Specific surface area of sample was measured by nitrogen gas adsorption at liquid nitrogen temperature (-196 °C) using a Micromeritics ChemiSorb 2750 system. The amount of active sites of catalysts were determined by carbon monoxide chemisorption technique

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using Micromeritics ChemiSorb 2750 and ASAP 2101C V.3.00 software. XPS analysis was performed originally using an AMICUS spectrometer equipped with a MgK_{α} X-ray radiation. For a typical analysis, the source was operated at the voltage of 15 kV and current of 12 mA. The pressure in the analysis chamber was less than 10⁻⁶ Pa. The AMICUS system is computer controlled using the AMICUS "VISION 2" software.

2.4. Catalytic Reaction

The selective hydrogenation of 1-heptyne (Aldrich) was carried out in a magnetically stirred 50 cm³ stainless steel autoclave reactor (JASCO, Tokyo, Japan). Prior to the reaction testing, the catalyst sample was reduced by hydrogen gas at a flow rate of 50 cm³/min at 40 °C for 2 h. The reactant containing 0.2 ml of 1-heptyne and 9.8 ml of toluene were mixed in the volumetric flask. Next, the mixture and 20 mg of catalyst were introduced into the autoclave reactor. The reaction was carried out under hydrogen atmosphere at 1 atm and 30 °C. After the reaction, the vent valve was slowly opened to prevent the loss of product. Then the product was analyzed by gas chromatography with flame ionization detector (FID).

3. RESULTS AND DISCUSSION

3.1. Characterization of the Supports

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Figure 1 shows the XRD patterns of the starting anatase TiO₂ nanoparticles and the samples obtained by hydrothermal treatment at different reaction temperatures. The XRD pattern of the products obtained from hydrothermal synthesis at 110 °C remained anatase phase TiO₂. When the reaction temperature increased to 150 °C and 200 °C, the XRD characteristic peaks of titanate were observed at 2θ degrees 24.5° and 48.5° which corresponded to the reflection (100) and (200) plane of H-titanate.¹⁹ The TEM micrographs of various samples are shown in Figure 2. The morphology of TiO₂ commercial is spherical with diameter larger than 100 nm. After hydrothermal treatment at 110 °C, some tubes like structure and sheet were observed. All the sheets transformed into tubular structure titanate at 150 °C. The tubular materials were several hundreds of nanometers which outer and inner diameter of nanotubes were approximately 10-12 nm and 4-6 nm, respectively. Increasing temperature to 200 °C led to a transformation of nanotubes to nanowire with non-hollow morphology with a length of several micrometers and width variations between 60-100 nm.

Specific surface areas of the samples were determined from the N₂ physisorption data using Brunauer– Emmett–Teller (BET) technique. The BET surface area of TiO₂ commercial as starting material was 5 m²/g. After hydrothermal treatment at 110 °C resulted in an increased BET surface area to 158 m²/g. Further increasing



Fig. 1. XRD patterns of the starting TNP and the samples obtained by hydrothermal treatment at different reaction temperatures.

hydrothermal temperature to 150 °C, the BET surface area increased to 192 m²/g. Increasing of BET surface areas was due to the transformation of morphology from nanosheet to nanotubes with hollow structure that possessed higher surface area. The sample synthesized at 200 °C resulted in a low BET surface area (23.2 m²/g) due to non-hollow structure of the TNW.

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3.2. Characterization of Supported Pd Catalysts

The XRD patterns of Pd/TNP, Pd/TNT, Pd/TNW, and I-Pd/TNT catalysts were collected at 2θ degrees 10–80° (results not shown), however, the diffraction peak of Pd⁰ or PdO were not observed for all the catalysts. It is suggested



Fig. 2. TEM micrographs of the starting TNP and the samples obtained by hydrothermal treatment at different reaction temperatures.

that palladium was highly dispersed on the supports or it was due to the low amount of Pd loaded.²⁰ The XRD patterns of titania and titanate supported Pd nanoparticles catalysts prepared by solvent reduction method were not significantly different from the as-synthesized support. On the other hand, impregnation of Pd chloride on TNT support resulted in the disappearance of titanate peaks and exhibited the characteristic peaks of rutile phase of TiO₂ at $2\theta = 27.6$ (major), 36.3, 41.5, 44.3, 55.5, 56.9, 63.3, 64.6, and 69.4°.21 The phase transformation of titanate to rutile TiO2 was due to the presence of acid precursor of palladium chloride and calcination at high temperature. According to Murakami et al.²² TNT could transform into rutile TiO₂ in the presence of Cl⁻ during hydrothermal treatment. Zhu et al.¹⁷ also reported the transformation of TNT to rutile TiO₂ in acidic environment at 60 °C (2.65 M of HNO₃). Normally phase transformation of TNT to rutile TiO₂ occurs after annealing at above 900 °C.²³⁻²⁴

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The dispersion of Pd on the different titania and titanate supports was observed by TEM and the results are displayed in Figure 3. It appears that the particle size and shape of the catalysts prepared via reduction by solvent method were not affected by loading of palladium (no changes in the particle size and shape). The smaller dark spots in catalyst represented the Pd particles. Catalysts prepared by the colloidal method showed average particle sizes of Pd about 4-5 nm. Larger Pd particle sizes were observed on the catalysts prepared by impregnation method. In addition, morphologies of the catalysts were markedly changed after impregnation and calcination. The presence of acid precursor of palladium chloride and calcination at high temperature resulted in the collapse of nanotubes structure and as a consequence the large rods and non-hollow structures were obtained.

Table I summarizes the physicochemical properties of supported Pd catalysts. The BET surface area of solvent



Fig. 3. TEM images of the various supported Pd catalysts.

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Table I

Characteristics and Catalytic Behavior of Pd Catalysts Supported on Nanostructure Titanate

Table 1. Thysicoelectrical properties of the TNT, TNT, and TNW supported to catalysis.					
Catalysts	BET surface area (m ² /g)	Binding energy Pd $3d_{5/2}$ (eV) ^{<i>a</i>}	CO chemisorption $(\times 10^{-18} \text{ molecule CO/gcat.})$	Pd dispersion ^b (%)	$d_P \operatorname{Pd}^0(\operatorname{nm})^c$
Pd/TNP	$4.4 (4.8)^d$	n.d.	n.d.	n.d.	n.d.
Pd/TNT	190.7 (192)	335.1	11.2	35.7	3.1
Pd/TNW	19.8 (23.2)	n.d.	7.1	26.1	4.3
I-Pd/TNT	22.1 (192)	337.4	10.4	14.4	7.8

Notes: ^{*a*}Based on XPS results; ^{*b*}Based on total amount of palladium loading; ^{*c*}Based on d = 1.12/D (nm), where D = fractional metal dispersion.

Physica charminal properties of the TNP TNT and TNW supported Pd actalyst

reduction-made catalysts slightly decreased after deposition process. This was suggested that Pd were deposited in the pores of supports. The impregnation catalysts possessed low BET surface area due to the transformation of titanate nanotubes to rutile TiO_2 during calcination step. The rutile TiO_2 exhibited a rod-like shape that can be clearly observed from TEM images. The actual amount of Pd loading was determined by ICP-OES. For the catalysts prepared with Pd colloid nanoparticles, the Pd loading target 1 wt% was not achieved and the palladium contents were in the range of 0.48–0.57 wt%, indicating some metal loss during the synthesis, probably during the washing step. However, Pd loading 1 wt% was achieved by the impregnation method as expected.

The relative amounts of surface Pd atoms on the catalyst samples were calculated from the CO chemisorption experiments at room temperature. The calculation based on the assumption that one carbon monoxide molecule adsorbs on one palladium site.25 The amounts of CO chemisorption on the catalysts, the percentages of Pd dispersion, and the average Pd metal particle sizes calculated based on the CO chemisorption results are also given in Table I. The active sites of catalysts varied from 7.1 to 11.21×10^{18} site/g-catalyst in the order: Pd/TNT > I-Pd/ TNT > Pd/TNW. The amount of CO chemisorption could not be determined on the Pd/TNP due probably to the amount of Pd active site was lower than the detectability limit of the instrument. The highest Pd active site and dispersion was found on the Pd/TNT. The high surface area of titanate nanotubes promoted dispersion of Pd metal.²⁶⁻²⁷ The Pd dispersion of catalysts prepared via reduction by solvent was also higher than that obtained by impregnation method.

XPS was performed to determine the oxidation state of Pd on the catalysts and the binding energies of Pd $3d_{5/2}$ are reported in Table I. For the Pd/TNT, the binding energies of Pd $3d_{5/2}$ were observed at 335.1 eV, which corresponded to metallic Pd^{0.6-8} The distinctive peaks for Pd $3d_{5/2}$ of impregnation-made catalyst appeared at 337.4 eV, corresponding to the formation of PdO by calcination.

3.3. Catalyst Evaluation

The catalytic performance of catalysts was investigated in the liquid-phase selective hydrogenation of 1-heptyne to 1-heptene under mild reaction conditions. The plots

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of 1-heptyne conversion and 1-heptene selectivity as a function of reaction time are shown in Figures 4 and 5, respectively. The hydrogenation rates were in the order: Pd/TNT > Pd/TNW > Pd/TNP \approx I-Pd/TNT \approx I-Pd/ TNP. The conversion of 1-heptyne was completed in 30 min for Pd/TNT and Pd/TNW and 40 min for Pd/TNP, I-Pd/TNT, and I-Pd/TNP under the conditions used. Alkyne hydrogenation has often been regarded as structure insensitive reaction, in which hydrogenation rate increases with increasing number of exposed Pd surface. The results follow the trend in the literature that high surface area



Fig. 4. The conversion of 1-heptyne as a function of reaction time



Fig. 5. The selectivity of 1-heptene as a function of reaction time

and porosity of nanotubular catalysts were advantageous for enhancing catalytic activity in various hydrogenation reactions.¹⁰ However, it is interesting to note that the I-Pd/TNT exhibited relatively high Pd dispersion (compared to Pd/TNP) but it exhibited poor hydrogenation activity in 1-heptyne hydrogenation. From the XPS results, Pd was in the form of PdO in the I-Pd/TNT sample after calcination at high temperature. Although, all the catalysts were reduced in H₂ at 40 °C for 2 h prior to the reaction test, it is possible that the PdO was not completely reduced or some of the metallic Pd⁰ was transformed back into PdO due to the easy oxidation of Pd upon contact with air at room temperature.²⁸ In addition, the metal-support interaction is usually stronger when pore size of the support was very small.²⁹ This could also be the case for the I-Pd/TNT in this study.

The selectivity of 1-heptene after complete conversion of 1-heptyne was in the order: I-Pd/TNT > I-Pd/TNP > Pd/TNT \approx Pd/TNW > Pd/TNP. The Pd/TNT and Pd/TNW contained metallic Pd⁰ but differed in the degree of Pd dispersion. However, they exhibited similar selectivity of 1-heptene. In other words, the changes in Pd dispersion (Pd particle size) do not affect the selectivity to 1-heptene in the partial hydrogenation of 1-heptyne. This conclusion was in good agreement with previous studies the selectivity to alkene formation was irrespective of the Pd particle diameter for most reactants in the selective alkyne hydrogenation.³⁰⁻³¹ The selectivity of 1-heptene after complete conversion of 1-heptyne was significantly improved on the I-Pd/TNT and I-Pd/TNP catalyst. From our previous studies about 1-heptyne hydrogenation over the Pd/TiO₂ prepared by flame spray pyrolysis method,¹⁵ an intimate contact between the very fine Pd particles and the TiO₂ support could exert some electronic modification of Pd and hence the selectivity of 1-heptene was improved. The presence of stronger interaction between Pd and TiO₂ has been proven to produce beneficial effect in the selective hydrogenation reaction in a variety of catalyst systems.^{13–17} The flame-made Pd/TiO₂ catalysts were also found to exhibit better catalytic performance than the impregnation-made ones. The results in this study indicated that impregnation method led to a stronger metal-support interaction between Pd and the support, and modified catalytic properties. However, among the different TiO₂ and titanate nanostructure in this study, the use of TNT support was proven to be beneficial for the liquid-phase hydrogenation of alkyne to alkene, regardless of the preparation method used.

4. CONCLUSIONS

Hydrolysis of low surface area anatase TNP gave the nanostructure titanate, which possessed much higher surface area. TNT and TNW were formed at 150 and 200 °C. The obtained nanostructure titanate powders were used as the Pd catalyst supports and tested in the selective hydrogenation of 1-heptyne to 1-heptene. Loading of Pd by the colloidal route resulted in well dispersion of metallic Pd⁰ and the degree of dispersion increased in the order: Pd/TNT > Pd/TNW \gg Pd/TNP. In contrast, conventional impregnation of PdCl₂ solution on TNT resulted in the formation of PdO and changes of the TNT structure upon calcination at high temperature in acidic environment. The improved 1-heptene selectivity over the I-Pd/TNT and I-Pd/TNP was attributed to the stronger metal-support interaction exerted by impregnation of PdCl₂ inside the pores of the supports. There were no changes in the electronic properties of the various supported Pd catalysts when Pd was deposited on the supports by colloidal route.

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