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Author(s)	Kuhaudomlap, Sasithorn; Mekasuwandumrong, Okorn; Praserthdam, Piyasan; Fujita, Shin-Ichiro; Arai, Masahiko; Panpranot, Joongjai
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The H_2-Treated TiO_2 Supported Pt Catalysts Prepared by Strong Electrostatic Adsorption for Liquid-Phase Selective Hydrogenation

Sasithorn Kuhaudomlap [1], Okorn Mekasuwandumrong [2], Piyasan Praserthdam [1], Shin-Ichiro Fujita [3], Masahiko Arai [3] and Joongjai Panpranot [1,*]

1 Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand; sasithorn9349@gmail.com (S.K.); piyasan.p@chula.ac.th (P.P.)
2 Department of Chemical Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakorn Pathom 73000, Thailand; okornmeka@gmail.com
3 Division of Applied Chemistry, Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan; sfuji@eng.hokudai.ac.jp (S.-I.F.); marai@eng.hokudai.ac.jp (M.A.)
* Correspondence: joongjai.p@chula.ac.th; Tel.: +66-2218-6869; Fax: +66-2218-6877

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Abstract: The H_2-treated TiO_2 supported Pt catalysts were prepared by strong electrostatic adsorption method and tested in the liquid-phase selective hydrogenation of various organic compounds such as 3-nitrostyrene to vinylaniline (VA) and furfural to furfuryl alcohol (FA). A combination of high Pt dispersion, strong interaction of Pt-TiO_x, and the presence of low coordination Pt sites was necessary for high hydrogenation activity. However, while the selectivity of VA in 3-nitrostyrene hydrogenation did not depend much on the catalyst preparation method used, the selectivity of FA in furfural hydrogenation was much higher when the catalysts were prepared by SEA, comparing to those obtained by impregnation in which the solvent product was formed, due probably to the non-acidic conditions used during Pt loading by SEA method.

Keywords: Pt/TiO_2; nitrostyrene hydrogenation; sol-gel TiO_2; strong electrostatic adsorption

1. Introduction

Many intermediates for the production of herbicides, pesticides, cosmetics, pharmaceuticals, vitamins, food flavors, and many commercially important organic fine chemicals are synthesized via selective hydrogenation under liquid-phase conditions. The heterogeneous catalysts is valuable for organic transformations in highly selective reaction improvement based on green sustainable chemistry. The selective hydrogenation of nitrostyrene (NS) to vinylaniline (VA) is challenging because NS includes two reducible functional groups which could be hydrogenated simultaneously [1–3]. Pt-based catalysts are an interesting choice and widely used in the NS hydrogenation due to their high catalytic activity. However, the catalysts can hydrogenate both functional groups, leading to undesired products [2–4]. The catalytic performance of Pt-based catalysts in the selective hydrogenation of NS has been improved by changing conditions of pretreatment [5,6], reaction mediums [2,5], catalyst supports [2], and the addition of modifiers [7]. Recent studies from our group showed that Pt/TiO_2 [1] and $Pt\text{-}Co/TiO_2$ [3] catalysts prepared by the single-step flame spray pyrolysis method exhibited superior performance in the NS hydrogenation with high VA selectivity.

Sol-gel method is an easy route that is widely used for the preparation of nanocrystalline TiO_2 at low temperature. The advantages of this method are good homogeneity and efficient control of crystal phases and particle sizes of the TiO_2 [8–11]. The calcination atmosphere of the obtained powder from

the sol-gel method affected to the properties of sol-gel derived TiO_2 and metal catalysts supported on TiO_2. The use of H_2- and N_2-treated sol–gel derived TiO_2 led to the increasing dispersion of Pd metal and improved catalytic performance, compared to the TiO_2 calcined in air and O_2 in the selective hydrogenation of acetylene [12,13]. Strong electrostatic adsorption (SEA) is one of the wet impregnation, especially slurry can be adjusted to the optimum pH providing the greatest electrostatic interaction between the metal precursor and the support. For the same metal loadings, advantages of the SEA method are the higher metal dispersion than those prepared by other methods [14–16].

In this work, the SEA method was employed for preparation of Pt/TiO_2 catalysts on the H_2 and air-treated sol–gel derived TiO_2. The combined SEA and H_2-treated TiO_2 provided high Pt dispersion and strong $Pt\text{-}TiO_2$ interaction which could be beneficial for the selective hydrogenation reactions. The catalysts were tested in the liquid-phase selective hydrogenation of various organic compounds including the hydrogenation of 3-NS to VA and the hydrogenation of furfural to furfuryl alcohol (FA).

2. Results and Discussion

2.1. Characteristics of the Pt/TiO_2 Catalysts

The Pt catalysts were prepared by SEA and impregnation on the air- and H_2-treated sol–gel TiO_2. There were no differences in the structural properties of the air- and H_2-treated TiO_2. Both had similar average crystallite size of anatase TiO_2 ca. 7–8 nm with average pore diameter 4.7–4.9 nm, pore volume 0.30–0.32 cm^3/g, and BET surface area 139–159 m^2/g. The gas treatment only affected the formation of oxygen vacancy in TiO_2, leading to the creation of unpaired electrons or Ti^{3+} centers [17–19]. A non-oxidizing atmosphere, such as N_2 or H_2 ,can result in Ti ions of lower valences, likely Ti^{3+} [18]. Such results were confirmed by the ESR of the TiO_2 supports and the XPS of the Ti 2p results (shown in Figure 1). A shift of Ti^{4+} peaks to lower binding energies and higher ESR signals corresponding to surface Ti^{3+} on the TiO_2 surface were observed on the TiO_2-H_2.

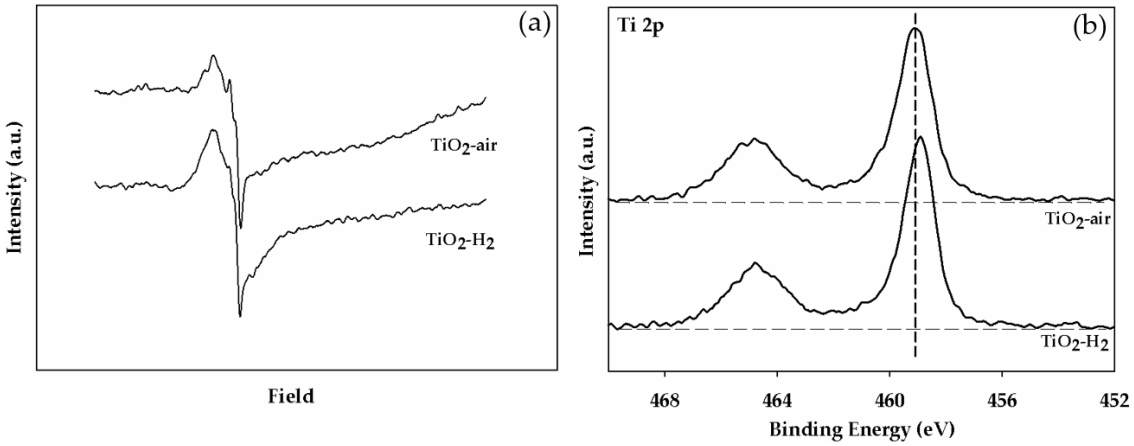


Figure 1. (**a**) The ESR results of TiO_2 calcined under H_2 and air atmosphere at 350 °C and (**b**) XPS spectra of Ti 2p of TiO_2 supports.

There were also no changes in the textural properties of TiO_2 after Pt loading by impregnation and SEA. No sharp peaks for Pt or PtO_x phases were detected in all the XRD results (Figure S1), due possibly to the low metal loading (0.5 wt %) and/or high Pt dispersion as nanoparticles on the TiO_2 supports. The TEM micrographs of 0.5 wt % Pt/TiO_2 catalysts (Figure 2) show spherical shape TiO_2 particles with average particle size ca. 8 nm, which were consistent to the average crystallite size of TiO_2 calculated from the XRD results. However, the metal particles were not distinguishable from the TiO_2 supports. The Pt/PtO_x and $Pt\text{-}TiO_x$ species were observed by the H_2-TPR measurements as shown in Figure 3. The first reduction peak in the TPR profiles at around 100 °C was attributed to the reduction of PtO_x crystallites to metallic Pt [20,21], while the second peak appearing as a larger

peak from 250 °C to 500 °C was associated with the Pt species reduction which interacts with the TiO_2 support or the Pt-TiO_x interface site. The last reduction peak over 500 °C was related to the reduction of surface capping oxygen of TiO_2 [1,21]. The Pt/PtO_x species were not clearly apparent for the catalysts prepared by SEA due probably to smaller Pt particles being formed by SEA method. The peaks corresponding to Pt-TiO_x species were also slightly shifted to higher temperature for the SEA catalysts, compared to the impregnation-made ones, suggesting a stronger metal–support interaction.

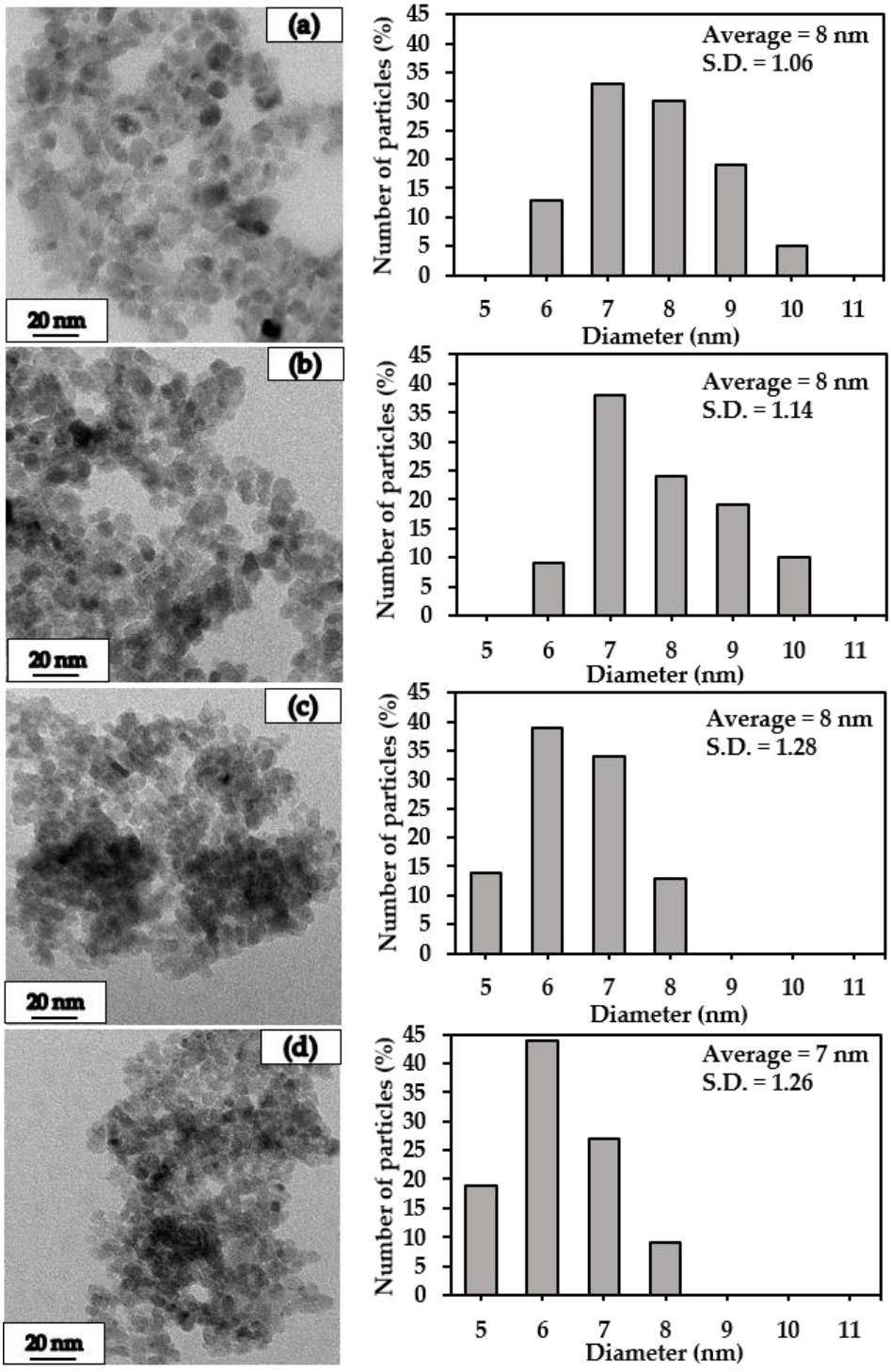


Figure 2. TEM images and size distribution of the Pt/TiO_2 catalysts: (**a**) Pt/TiO_2-H_2-I; (**b**) Pt/TiO_2-air-I; (**c**) Pt/TiO_2-H_2-SEA; and (**d**) Pt/TiO_2-air-SEA.

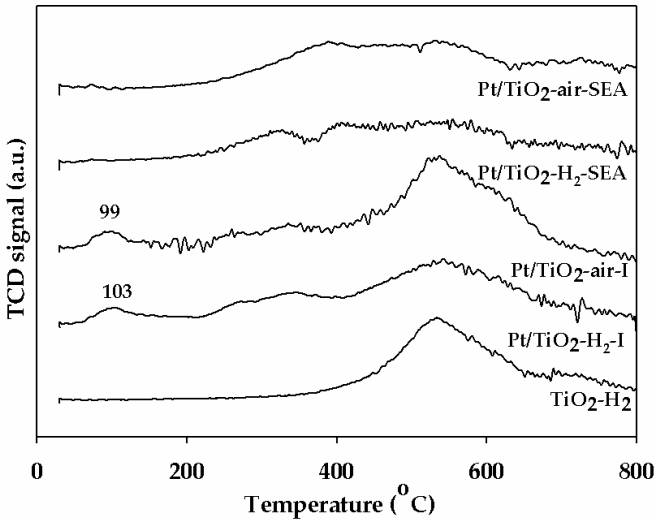


Figure 3. The H_2-TPR profiles of the Pt/TiO_2 catalysts.

From the chemisorption results (Table 1), the number of exposed Pt atoms on the catalyst samples and percentages of Pt dispersion were computed by assumed that one CO molecule adsorbed on one Pt site [1]. Pt loading by the SEA method led to much higher Pt dispersion on the air-treated TiO_2, compared to the conventional impregnation. The use of H_2-treated TiO_2, however, can drastically increase Pt dispersion to 54–57%, regardless of the Pt deposition method used. The presence of higher amount of surface Ti^{3+} on the H_2-treated TiO_2 was important for obtaining high Pt dispersion when the catalysts were prepared by conventional impregnation. Such an effect became less pronounced when using SEA method for Pt deposition. The characteristics of the precursor (anion or cation, size, etc.) and the oxide surface chemistry have great effects on electrostatic interactions between the metal precursor and the support.

Table 1. CO chemisorption results of the 0.5 wt % Pt/TiO_2 catalysts.

Catalyst	Pt/TiO_2-H_2	Pt/TiO_2-Air	Pt/TiO_2-H_2	Pt/TiO_2-Air
Method	Impregnation	Impregnation	SEA	SEA
CO chemisorption (molecule CO × 10^{18}/g Cat.)	8.8	4.5	8.4	7.7
Pt dispersion (%)	57	29	54	50

The characteristics of the Pt nanoparticles deposited on the air- and H_2-treated TiO_2 by SEA and impregnation were further investigated by the IR of adsorbed CO and the results are shown in Figure 4. The adsorption band at around 2000–2100 cm^{-1} was assigned to a linear type of CO adsorption, while IR bands in the 1825 cm^{-1} to bridged-type adsorbed CO [3]. CO generally adsorbed as a bridge-type on larger Pt particles and as the linear-type on small ones [1]. The adsorption band at 2070–2100 cm^{-1} was attributed to the adsorption of CO adsorbed on Pt (111) terraces and Pt (100) whereas the lower frequencies of the 2000–2066 cm^{-1} bands suggest the low coordinated Pt sites as corner, kink, and edge [22]. According to IR results, the whole catalysts shows only low coordinated Pt sites without Pt terraces, Pt (111) and Pt (100) species. Moreover, the CO adsorption of Pt on edge sites as asymmetry band at 2060 cm^{-1} which tends to lower values suggesting the CO adsorption on corner and/or kink sites located at 2035 cm^{-1} [5].

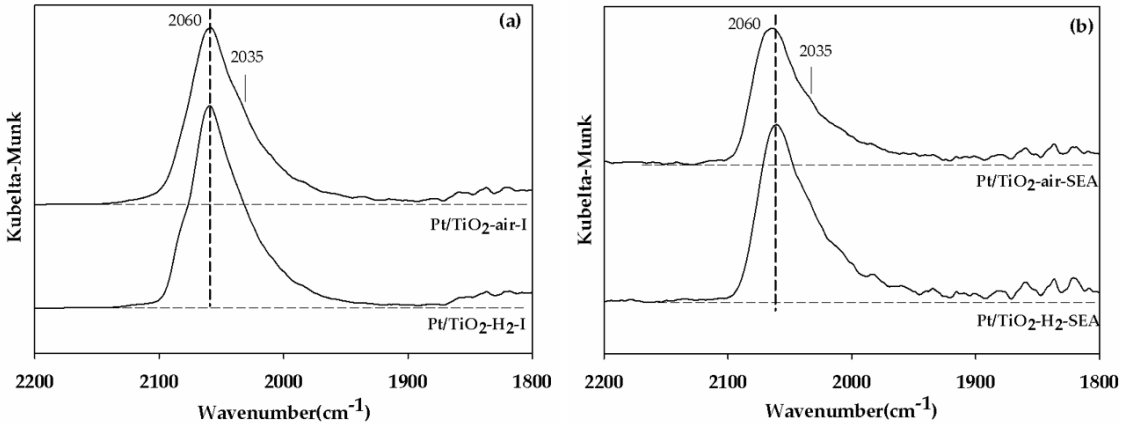
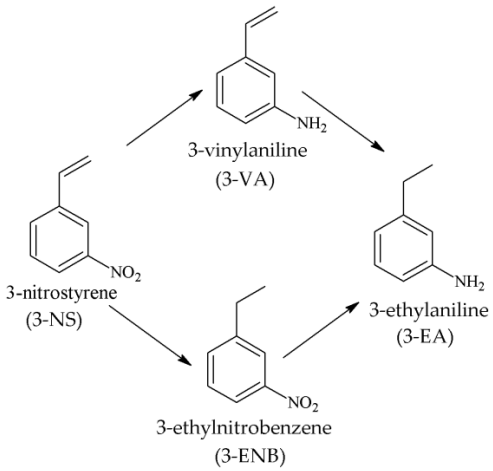


Figure 4. The IR spectra of adsorbed CO on 0.5 wt % Pt/TiO_2 catalysts prepared by: (**a**) impregnation method and (**b**) SEA method.

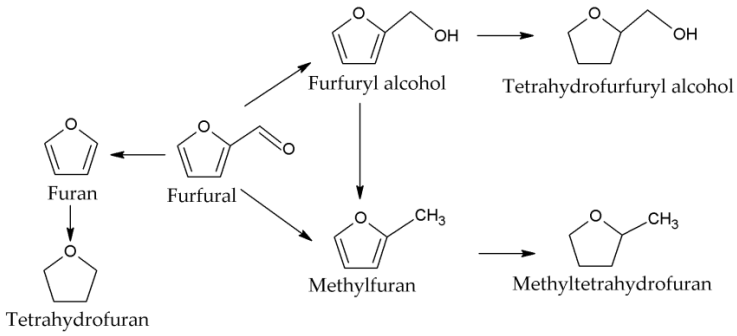
2.2. Reaction Results

As shown in Scheme 1, NS consists of two reduction groups which can transform to 3-VA from hydrogenation of nitro group and to 3-ethylnitrobenzene (3-ENB) in case of C=C double bond hydrogenation [3]. Furthermore, 3-VA and 3-ENB can promptly converted to 3-ethylaniline (3-EA) or both of two reduction groups are hydrogenated [4]. The NS selective hydrogenation results of the Pt catalysts prepared by SEA and impregnation on the air- and H_2-treated TiO_2 are shown in Table 2. The blank reactions were also carried out using the bare H_2-treated TiO_2 support. About 4% of 3-nitrostyrene conversion was obtained with poor selectivity of the desired product (VA ~ 23%). It is confirmed that the catalyst performances in the selective hydrogenation reaction mainly arose from the Pt species on the TiO_2 support. Under the reaction conditions used, VA and ENB were the main products of hydrogenation with the absence of any intermediates. The hydrogenation activities were found in the order: Pt/TiO_2-H_2-I > Pt/TiO_2-H_2-SEA > Pt/TiO_2-air-SEA > Pt/TiO_2-air-I, which were correlated well to the obtainable surface of Pt atoms. VA selectivity was reported to depend largely on the quantity of Pt-TiO_x interface sites [1,6]. For the catalysts prepared by impregnation, the number of Pt-TiO_x increased using the H_2-treated TiO_2 as the support and as a consequence, higher VA selectivities were obtained. Nevertheless, for all the SEA catalysts, the VA selectivities were relatively high (86–89%) and did not depend much on the TiO_2 support. Such results suggest that the stronger metal–support interaction produced by SEA method is benefit for improving VA selectivity of the Pt/TiO_2 catalysts in the selective hydrogenation of NS under mild conditions. Comparison of the performances of the Pt/TiO_2-H_2 in this study and the other reported Pt-based catalysts in the selective NS hydrogenation is shown in Table 3. The state-of-the art for the monometallic Pt catalysts the highest yield of VA at 97–100% can be obtained but surface modification of Pt using α-lipoic acid [7] or the presence of ionic liquid and 2,2′-bipyridine co-stabilizer were required [2] as well as the use of higher reaction temperature (75–80 °C). Bimetallic Pt-Zn catalysts on the hypercross-linked polystyrene also exhibited high VA yield (97%) at 75 °C [23]. Compared to the other Pt-based catalysts with similar Pt loading reported in the literature [5,22], the present Pt/TiO_2-H_2 catalysts prepared by either impregnation or SEA showed relatively high VA yield (>80%) under milder reaction conditions (lower reaction temperature, lower H_2 pressure, or shorter reaction time). After prolonged reaction time (10 h), small amount of Pt leaching from the 0.5 wt % Pt loading occurred and was determined to be around 12.8%. Nevertheless, the catalysts can achieve a high yield of VA in a very short reaction time (20 min) and the leaching problem was negligible.



Scheme 1. Simplified reaction pathways in the hydrogenation of 3-NS.

The reaction pathways for furfural hydrogenation are simplified in Scheme 2. A variety of derivatives can be produced including FA, tetrahydrofurfuryl alcohol, methylfuran, methyltetrahydrofuran, furan, and tetrahydrofuran. FA is an intermediate for the manufacturing of vitamin C, fibers, plasticizers, thermostatic resins, lubricants, and dispersing agents, which can be produced by the selective hydrogenation of biomass-derived furfural [24–27]. Furfural comprises two types of reactive groups, carbonyl group (C=O) and double bonds group (C=C) [28]. Under the reaction conditions used (50 °C, 2 MPa of H_2), all the prepared catalysts gave similar hydrogenation activities with 86–90% furfural conversion after 2 h reaction time. It is suggested that the hydrogenation of C=O double bond group is easier than the hydrogenation of a nitro group of NS. However, the catalysts prepared by SEA method resulted in much higher FA selectivity (80–85%) than the impregnation-made catalysts (FA selectivity ~14–18%). Nevertheless, the only byproduct obtained over the impregnated catalysts was 2-furaldehyde dimethyl acetal which was produced by the solvent reaction via acetalization mechanism in the presence of acid catalysts [29–31]. However, solvent side reaction can be suppressed by using lower reaction temperature and employing more basic catalysts [30]. Pt loading by SEA under basic conditions, therefore, was beneficial not only for improving hydrogenation activities by enhancing Pt dispersion but also for lowering the remaining acidity after Pt loading to maintain high selectivities of FA in furfural hydrogenation. Comparison of the performances of the Pt/TiO_2-H_2 in this study and the other reported Pt-based catalysts in the selective furfural hydrogenation is shown in Table 4. From the tables, the catalysts prepared in this study were found to give relatively high/comparable activities and selectivities of the desired product, compared to those reported in the literature in shorter reaction time under mild conditions.



Scheme 2. Simplified reaction pathways in the hydrogenation of FFR.

Table 2. Reaction results of the 0.5 wt % Pt/TiO_2 catalysts.

Catalyst	Pt/TiO_2-H_2		Pt/TiO_2-Air		Pt/TiO_2-H_2		Pt/TiO_2-Air	
Method	**Impregnation**		**Impregnation**		**SEA**		**SEA**	
Time (min)	20	40	20	40	20	40	20	40
NS conversion (%)	76	89	29	31	69	90	64	80
VA selectivity (%)	92.1	91.9	77.9	77.4	87.9	88.6	88.2	85.6
EA selectivity (%)	4.9	5.9	5.0	5.0	5.1	8.5	5.7	8.4
ENB selectivity (%)	3.0	2.2	17.1	17.6	7.0	2.9	6.1	6.0
FFR conversion (%) [a]	89		86		89		90	
FA selectivity (%) [a]	17.7		14.1		79.8		84.9	
Others [a,b]	82.3		85.9		20.2		15.1	

Reaction conditions: 3.6 mmol NS in 10 mL ethanol at 40 °C with a 20 mg catalyst under 20 bar H_2; 0.6 mmol FFR in 10 mL methanol at 50 °C with a 50 mg catalyst under 20 bar H_2; * Reaction time: [a] = 120 min; [b] = solvent product.

Table 3. Review on the selective hydrogenation of NS to VA on various supported Pt-based catalysts.

Metal Loading (wt %)	Supports	Preparation Method	Reduction Temperature (°C)	Reaction Conditions (Temp., P_{H2})	Solvent	Reaction Time (min)	Reaction Results		Reference No.
							3-NS Conversion (%)	VA Selectivity (%)	
0.5	TiO_2	Impregnation	200	40 °C, 2 MPa	Ethanol	40	89	91.9	This work
		SEA					90	88.6	
0.5	TiO_2	Impregnation	200	50 °C, 4 MPa	Supercritical CO_2 10 MPa	60	64	75	[5]
0.5	TiO_2	Impregnation	200	50 °C, 4 MPa	Ethanol	n/a	26	73	[22]
0.5	TiO_2	Flame spray pyrolysis	600	50 °C, 4 MPa	Ethanol	25	95.8	67.1	[1]
0.2	TiO_2	Impregnation	500	40 °C, 0.3 MPa	Toluene	390	95.1	93.1	[6]
0.4	Carbon nanotubes	Reduction of $H_2Pt(OH)_6$ in formic acid with ionic liquid and co-stabilizer 2,2′-bipyridine	n/a	25 °C, 0.1 MPa	n/a	180	100	86	[2]
1	TiO_2	Impregnation and surface modification using α-lipoic acid	250	80 °C, 1 MPa	Toluene	68	100 [a]	100	[7]
2	ZnO	Ion-exchange	300	75 °C, 1 MPa	Ethanol	n/a	100	97	[4]

n/a = not available, [a] = 4-NS.

Table 4. Review on the selective hydrogenation of furfural to FA on various supported Pt-based catalyst.

Metal Loading (wt %)	Supports	Preparation Method	Reduction Temperature (°C)	Reaction Conditions (Temp., P_{H2})	Solvent	Reaction Time (h)	Reaction Results		Reference No.
							Furfural Conversion (%)	FA Selectivity (%)	
0.5	TiO_2	SEA	200	50 °C, 2 MPa	Methanol	2	89	79.8	This work
0.5	SiO_2	Impregnation	400	250 °C, 0.69 MPa	2-propanol	1.5	12.5	55.8	[32]
2.0	γ-Al_2O_3	-	200	50 °C, Ambient	Methanol	7	80	99	[30]
1.9	MgO	-	200	50 °C, Ambient	Methanol	7	79	97	[30]
2.3	CeO_2	-	200	50 °C, Ambient	Methanol	7	77	98	[30]
1.9	SiO_2	-	200	50 °C, Ambient	Methanol	7	35	90	[30]
1.4	ZnO	-	200	50 °C, Ambient	Methanol	7	7	60	[30]
5.0	Al_2O_3	Wet impregnation	350	25 °C, 2 MPa	Iso-propanol	8	30	99.1	[33]
5.0	Al_2O_3	Wet impregnation	350	240 °C, 2 MPa	Iso-propanol	5	100	30.7	[33]
5.0	SiO_2	Wet impregnation	350	25 °C, 2 MPa	Iso-propanol	8	6	100	[33]
5.0	SiO_2	Wet impregnation	350	240 °C, 2 MPa	Iso-propanol	5	100	51.9	[33]

3. Materials and Methods

3.1. Preparation of TiO_2 by Sol–Gel Method

The TiO_2 support was prepared by sol–gel method using titanium isopropoxide as a precursor. At first 7.33 cm^3 of 70 vol % nitric acid was added to 1000 cm^3 of de-ionized (DI) water under continuous stirring. The titanium isopropoxide 83.5 cm^3 was then added slowly and continuously mixed until clear sol was obtained under room temperature. After that, the dialysis tubing with clear sol inside was submerged in DI water. The water was repeatedly altered until the pH of the water reached 3.5. The dialyzed sol was dried at 110 °C overnight and then was calcined in different gas flows (H_2 and Air) at 350 °C for 2 h. The TiO_2 supports so prepared are referred to as TiO_2-H_2 and TiO_2-Air for those calcined in H_2 and air, respectively.

3.2. Preparation of Pt/TiO_2 by SEA and Impregnation Methods

For the SEA method, the point of zero charge (PZC) is the pH at the net electrical charge density on the support surface equal to zero and is important to determine. Aqueous solution was conducted at many initial pHs values in the range of 1–13. The TiO_2 support was added to the solution and shaken for 1 h. Then, final pH was measured again and the PZC of the solid supports were obtained by plot between the final pH and the initial pH. Tetraammineplatinum (II) chloride hydrate was used as metal precursor. Adsorption experiments were conducted with 10 cm^3 of 200 ppm metal solution so that determine the optimum pH for metal loading at 0.5 wt %. HCl or NaOH were used to adjust the pH of this solution, according to the PZC value of the supports used and then the slurry was shaken for 1 h after TiO_2 adding. For the metal uptake, ICP technique was used to measure the difference in the metal concentrations before and after contact with TiO_2 supports.

For comparison, 0.5 wt % Pt/TiO_2 catalysts were also prepared by impregnation method. The TiO_2 supports were impregnated with an aqueous solution of H_2PtCl_6. The Pt/TiO_2 catalysts were dried at 110 °C overnight and calcined in air at 400 °C for 4 h.

3.3. Catalyst Characterization

The surface and textural properties of TiO_2 and Pt/TiO_2 samples prepared were examined by various techniques. The XRD patterns of TiO_2 supports and Pt/TiO_2 catalysts were measured by using a Bruker D8 advance with CuK_α radiation (Bruker, Karlsruhe, Germany). The Scherrer's equation was used to calculate the average crystallite size (d_{XRD}) of TiO_2. Specific surface area, pore size diameter and pore volume were evaluated by N_2 physisorption with a BEL-SORP automated system. The defects on surface of TiO_2 support were measured by electron spin resonance spectroscopy (ESR) using a Elxys500 at X-band (Bruker Biospin GmbH, Rheinstetten, Germany). The XPS analysis was used to investigate the binding energy and the composition on the catalyst surface with using an AMICUS photoelectron spectrum spectrometer equipped with an MgK_α X-ray as primary excitation and KRATOS VISION2 software (KRATOS analytical LTD., Manchester, UK). The morphology and crystallite sizes of TiO_2 supports were measured by using a JEOL-JEM 2010 transmission electron microscope using energy-dispersive X-ray detector operated at 80–200 kV). The reducibility and reduction temperature of supported Pt catalysts were measured by H_2-TPR technique. The catalyst samples were conducted in a quartz u-tube and were pretreated with 30 cm^3/min of N_2 flow at 200 °C for 1 h. After that, the sample was heated from 30 °C to 800 °C with a carrier gas (10% H_2/Ar) at 30 cm^3/min. Finally, TPR profiles were obtained as a function of temperatures. CO-pulse chemisorption analysis was characterized to determine the amounts of CO-chemisorbed and the metal dispersion on the Pt/TiO_2 catalysts by using ChemiSorb 2750 (Micromeritics, Norcross, GA, USA). Approximately 0.05 g of the catalyst was filled into a glass U-tube and the sample cell was purged with He gas in order to remove the remaining air. Prior to the measurement, the catalyst was reduced with H_2 for 2 h and then cooled to room temperature in He flow. Then, 20 μL of CO was injected over reduced catalyst at this temperature and performed until the desorption peak became

constant. FTIR spectrometers (JASCO FTIR-620, JASCO Inc., Easton, MD, USA) were used to measure the CO adsorbed species on the Pt/TiO_2 catalysts. The catalysts were reduced with H_2 flow for 2 h and cooled to room temperature in He flow. Then, the catalyst samples were passed with a 1% CO in He for 10 min and CO gas was purged from the sample cell with He flow. After that, the IR spectrum of CO adsorbed was recorded.

3.4. Selective Hydrogenation Reactions

Prior to the catalytic tests, the catalyst samples were reduced under H_2 flow (30 cm^3/min) at 200 °C for 2 h. For the NS hydrogenation, approximately 20 mg of catalyst and 0.5 cm^3 of NS (3.6 mmol) was filled into the reactor. The reaction was carried out in a 50 cm^3 autoclave at 40 °C, 2 MPa of H_2 introduced with a high-pressure liquid pump. It was heated to reaction temperature and purged with H_2 to remove the remaining air. The reaction was performed by stirring with magnetic stirrer. Then, the reactor was cooled down to room temperature with ice-water after the reaction.

For the selective hydrogenation of furfural, 50 mg of catalyst was charged into the reactor with 0.6 mmol of furfural and 10 cm^3 of methanol and the experiments were performed at 50 °C and 2 MPa of H_2. The reaction mixtures were analyzed by a gas chromatograph Shimadzu GC-2014 equipped with a flame ionization detector (FID) (SHIMADZU CORP., Singapore science park I, Singapore). The Rtx-5 capillary column with 30 M length and 0.32 mm inside diameter were used. Twenty microliters of the mixture was injected into the column and helium was used as a carrier gas. In the NS hydrogenation, decane was used as an internal standard.

4. Conclusions

The catalytic properties of Pt/TiO_2 catalysts in the selective hydrogenation of 3-NS to VA and the selective hydrogenation furfural to FA were improved by the combined SEA method and the H_2-treated TiO_2 for Pt deposition. The catalysts exhibited high Pt dispersion, strong interaction of Pt-TiO_x, and low coordination Pt sites (kink, edge, and corner), which promoted the hydrogenation activities especially the hydrogenation of the $–NO_2$ group, which was more difficult to be hydrogenated than the C=O and the C=C. The selectivity of VA appeared to depend solely on the presence of low coordination Pt sites and not on the preparation method used. Trace acidity remaining on the catalyst from the impregnation method led to side reaction producing the solvent product. The SEA method thus ensured the high selectivity of FA in the selective furfural hydrogenation.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/8/2/87/s1, Table S1. Pt loading from ICP-OES of the 0.5 wt % Pt/TiO_2 catalysts, Figure S1. The XRD patterns of Pt/TiO_2 catalysts.

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