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Influence of Crystallite Size of TiO₂ Supports on the Activity of Dispersed Pt Catalysts in Liquid-phase Selective Hydrogenation of 3-Nitrostyrene, Nitrobenzene, and Styrene

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Abstract Supported Pt catalysts were prepared using several kinds of TiO₂ supports different in the crystallite size in the range of 10 – 500 nm and their catalytic activity was tested for the liquid-phase hydrogenation of 3-nitrostyrene, nitrobenzene, and styrene. With Pt on smaller TiO₂ crystallites (nanocrystals), the selectivity to vinylaniline was improved in the hydrogenation of 3-nitrostyrene (regioselective hydrogenation) and the selectivity to aniline was promoted in the hydrogenation of a mixture of nitrobenzene and styrene (chemoselective hydrogenation). The effects of TiO₂ crystallite size were discussed on the basis of the results of turnover frequency and FTIR of CO adsorbed on dispersed Pt particles. Low coordinated and/or electron-rich Pt sites should be formed on the surface of nanocrystal TiO₂ supports. Nanocrystal TiO₂ support is an important factor for controlling and improving the catalytic performance of dispersed Pt particles.

Keywords Titania • Crystallite size • Nanocrystal • Platinum • Hydrogenation

1 Introduction

TiO₂ is one of useful common materials that can serve as a catalyst and a catalyst support for heterogeneous catalytic reactions [1]. Recently nano-sized TiO₂ materials have been attracting a growing interest in their unique catalytic actions, in particular, in photocatalytic reactions [2]. The nano-sized TiO₂ materials are prepared by several methods such as solvothermal [3-5], precipitation [6], sol-gel [7-9], and thermal decomposition [10] methods. It is also interesting and significant to examine the nano size effects of TiO₂ as a support for dispersed metal catalysts in organic synthetic reactions. Panpranot and co-workers used micron- and nano-sized TiO₂ materials prepared by solvothermal method for Pd catalysts for the liquid-phase selective hydrogenation of phenylacetylene [11, 12]. They demonstrate that a higher catalytic performance can be achieved with Pd catalyst supported on nano-sized TiO₂ and reduced at a high temperature of 500 °C. This is ascribed to easier occurrence of strong metal – support interactions for Pd on nano-sized TiO₂ than on micron-sized one. Those results indicate that the size of TiO₂ supports is a useful parameter to control the catalytic performance of TiO₂-supported metal catalysts. In the present work, several TiO₂ materials different in the crystallite size between 10 nm and 500 nm have been selected and used to prepare supported Pt catalysts. The performance of these TiO₂-supported Pt catalysts has been tested in the liquid phase hydrogenation of 3-nitrostyrene, nitrobenzene, and styrene and the influence of TiO₂ crystallite size on the total conversion and the product selectivity has been examined. The surface of Pt particles has been examined by FTIR using a probe molecule of CO and the relationship between the TiO₂ crystallite size and the nature of exposed Pt sites has been found. Smaller TiO₂ crystallites has been shown to expose rougher Pt crystal planes, which are beneficial for the hydrogenation of nitro group than vinyl group, on the surface of supported Pt particles, resulting in the regio- and chemo-selective hydrogenation.

2 Experimental

2.1 Support Materials and Catalyst Preparation

Two kinds of nanocrystal TiO₂ materials were prepared by solvothermal method [13]. In brief, 20 cm³ titanium *tert*-butoxide (Wako) and 60 cm³ 1,4-butanediol (Wako) were mixed well in a glass tube in a 100 cm³ stainless steel autoclave. The reactor was purged with N₂ for three times and heated up to 300 °C with a heating rate of 2.5 °C/min, and the temperature was held at 300 °C for 5 min and 30 min in order to obtain different sized TiO₂ crystallites. After cooling to a room temperature, the resultant solid material was washed by methanol and

separated by centrifugation for five times. The material so obtained was dried in an oven at 110 °C overnight and then calcined in air at 450 °C for 1 h. Commercially available TiO₂ samples were also used as supports without any treatment. Using H₂PtCl₆ (Wako) as a precursor, Pt was loaded onto these TiO₂ supports in 0.5 wt.-% by impregnation method. The Pt-loaded TiO₂ sample was dried at 110 °C for 5 h and reduced by 4 % H₂ in N₂ at 200 °C for 3 h.

2.2. Catalyst Characterization

The average crystallite size of TiO₂ was determined by X-ray diffraction (XRD) line broadening using JEOL JDX-8020 with Ni-filtered CuK α radiation using the Scherrer's equation, $D = K\lambda/((B - b) \cos\theta)$, where K is shape factor (assuming 0.90 in this work), λ the X-ray wavelength (0.15418 nm), θ the Bragg angle, B the line broadening at half the maximum intensity (FWHM) of the Ti(111) diffraction for a sample, and b the line broadening at FWHM of the Si(220) diffraction for a reference Si crystal. The surface area of TiO₂ was measured by nitrogen adsorption/desorption (Quantachrome NOVA 1000) using the Brunauer, Emmet and Teller's (BET) equation. The degree of Pt dispersion was measured by CO pulse chemisorption (BEL Japan BEL-METAL) at 50 °C using a pulse of 1% CO in He [14]. Prior to the chemisorption, the samples were treated in a stream of 100% H₂ at 100 °C for 30 min. Diffuse reflectance FTIR (DRIFT) spectra of CO adsorbed on the Pt/TiO₂ catalysts were collected with FTIR spectrometer (JASCO FTIR-620) and MCT detector. The catalyst sample was set in an IR cell, reduced at 80 °C by flowing H₂ for 30 min, and cooled to ambient temperature in a He stream. Then, a spectrum of the catalyst was taken as the background and then a 1% CO in He was passed over the catalyst for 10 min. After the CO gas in the cell was removed by flowing He, a spectrum of CO adsorbed on the catalyst was collected.

2.3. Activity Measurement

The hydrogenation reaction runs were carried out in a 50 cm³ stainless steel autoclave [15]. In a typical run, 3.4 mmol substrate (3-nitrostyrene, nitrobenzene, styrene) and 20 mg Pt/TiO₂ catalyst were charged into the reactor. It was flushed with H₂ for three times to remove the air and heated in a water bath. When the reactor temperature reached to 50 °C, H₂ (4 MPa) was introduced into it. The reaction was conducted while stirring the reaction mixture with a magnetic stirrer. After the reaction, the reactor was cooled with an ice-water bath and then depressurized carefully. The composition of reaction mixture was analyzed by a gas chromatograph (GL Science GC-390B) using a capillary column (GL science TC-1701) and a flame ionization detector. In several runs, the conversion of substrate was controlled by

changing the catalyst amount and the reaction time used. The total conversion of the substrate was determined from the final amount of the substrate unreacted divided by the initial amount of the substrate loaded. The selectivity to a product was determined from the amount of the product formed divided by the total amount of products formed.

3. Results and Discussion

In the present work, seven different TiO₂ materials were used as supports for dispersed Pt catalysts, which were different in anatase/rutile ratio, crystallite size, and surface area as shown in Table 1. These supports were loaded with 0.5 wt.-% Pt by impregnation and reduced in H₂ at 200 °C for 3 h. The catalysts so prepared were used for the hydrogenation of 3-nitrostyrene (NS) at 50 °C. Under the conditions used, 3-vinylaniline (VA), 3-ethylnitrobenzene (ENB), and 3-ethylaniline (EA) were observed to form as products (Scheme 1). Figure 1 gives typical selectivity – conversion results obtained with a few selected catalysts, indicating a common trend that the selectivity to VA did not change so much with conversion but the selectivity to ENB decreased while that to EA increased. That is, the fully hydrogenated product of EA was mainly produced through the hydrogenation of ENB but not from VA. The selectivity to VA was determined by the relative rates of hydrogenation of nitro and vinyl groups of the NS substrate. The selectivity to the main product of VA was different depending on the catalysts used. Table 2 summarizes the results of NS hydrogenation collected at similar conversion levels. It was observed that the selectivity to VA was different in the range of 42 – 73% and TOF in the range of 9 – 31 s⁻¹ depending on the catalysts used.

Table 1, Scheme 1, Figure 1, Table 2

Influence of the crystallite size of TiO₂ supports on the reaction results of dispersed Pt catalysts was then examined. Figure 2 presents the plot of either TOF or VA selectivity against the diameter of TiO₂ crystallites used as supports. The TOF and VA selectivity values tend to decrease with the TiO₂ diameter. According to Corma et al. [16, 17], the hydrogenation of NS on Pt/TiO₂ is a structure-sensitive reaction and exposed low coordinated Pt sites are more active for the hydrogenation of nitro group than vinyl group. Figure 2 indicates that the surface of Pt particles dispersed over smaller TiO₂ crystallites should become more beneficial to the hydrogenation of nitro group of NS rather than that of its vinyl group. There was no relationship between the Pt dispersion and the TiO₂ crystallite size.

Figure 2

The characteristics of the surface of dispersed Pt particles was examined by FTIR of a probe molecule of CO adsorbed on the catalysts (Fig. 3). There existed CO absorption bands in the range of frequency of 2000 – 2100 cm^{-1} and the absorption occurred in different frequency regions depending on the catalysts examined. The absorption band at around 2050 cm^{-1} may be due to a linear type of CO adsorption; the absorption band at 2070 – 2100 cm^{-1} should be the absorption of CO adsorbed on highly coordinated Pt surfaces like Pt(111) and Pt(100) while that at 2000 – 2066 cm^{-1} on low coordinated Pt sites like kink, edge, and corner ones [18-23]. An attempt was made to separate the absorption band measured into two (or three) independent bands to estimate the relative quantities of saturated (highly coordinated) and unsaturated (low coordinated) Pt sites on the catalysts. The results of the deconvolution are given in Fig. 3 and Table 3. Figure 4 shows that low coordinated Pt sites are more active for the hydrogenation of nitro group of NS into VA and the relative quantity of these sites is reduced with an increase in the crystallite size of TiO_2 support.

Figure 3, Table 3, Figure 4

The activity of Pt catalysts on different TiO_2 supports was further examined by the hydrogenation of a mixture of monofunctional substrates of nitrobenzene (NB) and styrene (ST). Table 4 summarizes the results obtained at not so high conversion levels and Fig. 5 shows the plot of the ratio of TOF of NB hydrogenation against total TOF of NB and ST hydrogenation. The low coordinated Pt sites are more active for the hydrogenation of NB than for that of ST.

Table 4, Figure 5

The present results demonstrate that smaller TiO_2 crystallite size is effective for the formation of a larger fraction of low coordinated Pt sites on the surface of dispersed Pt particles. The FTIR results of adsorbed CO indicate the absence of cationic Pt sites on the surface of Pt/ TiO_2 catalysts reduced at 200 $^\circ\text{C}$, which is detected by a CO absorption at a higher frequency $> 2125 \text{ cm}^{-1}$ [19, 23]. The degree of Pt dispersion is not so different among the Pt/ TiO_2 catalysts as compared to large differences in the crystallite size and in the surface area among the TiO_2 supports (Tables 1, 2). The reduction of Pt precursors occurs similarly but the formation of Pt particles should depend on the TiO_2 supports used. The surface geometry of support materials is likely to influence that of small metal particles formed over them. The Pt particles in the present Pt/ TiO_2 catalysts are in the range of metal dispersion of 8 – 23% determined by CO chemisorption (Table 2), corresponding to the diameter of 11 – 4 nm. It is assumed that smaller TiO_2 crystallites tend to expose rougher planes on their surfaces,

producing small Pt particles also exposing less coordinated Pt sites. In addition, a larger fraction of less coordinated Ti sites should exist on the surface of smaller TiO₂ crystallites, which promotes the electron donation from the Ti to Pt particles. This may be supported by the FTIR results of CO adsorption (Fig. 3) that the absorption band of the CO adsorbed on Pt is red-shifted to more extent on smaller TiO₂ support. The Pt particles on smaller TiO₂ crystallites are likely to facilitate the adsorption of the nitro group but not the vinyl group. As a results of these geometrical and/or electrical effects, the Pt catalyst on smaller crystallite TiO₂ support is more effective for the hydrogenation of nitro group (NS, NB) rather than vinyl group (NS, ST). Thus, the catalyst of Pt dispersed on nano-sized TiO₂ can promote the regio- and chemo-selective hydrogenation of NS and a mixture of NB and ST, respectively.

4. Conclusion

The crystallite size of TiO₂ supports is an important factor for controlling and improving the catalytic properties of Pt particles dispersed on them. Nanocrystal TiO₂ support facilitates the formation of Pt particles that are effective for the hydrogenation of nitro group (3-nitrostyrene, nitrobenzene) rather than that of vinyl group (3-nitrostyrene, styrene). Over the Pt on nanocrystal TiO₂ support, the selectivity to vinylaniline is improved in the hydrogenation of 3-nitrostyrene, promoting its regioselective hydrogenation. For a mixture of nitrobenzene and styrene, the conversion of the former occurs at a larger rate than that of the latter and so the Pt/nanocrystal TiO₂ catalyst can improve the chemoselectivity. These results should result from the changes in the geometrical and/or electrical properties of dispersed Pt particles with the size of TiO₂ crystallites.

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Table 1 Properties of TiO₂ supports used in the present work

Entry	Support ^a	A:R ratio ^b	TiO ₂ diameter ^c	Surface area
		(-)	(nm)	(m ² g ⁻¹)
1	TiO ₂ (1)	10:0	9	125
2	TiO ₂ (2)	0:10	14	90
3	TiO ₂ (3)	8:2	15	53
4	TiO ₂ (4)	10:0	18	98
5	TiO ₂ (5)	7:3	21	53
6	TiO ₂ (6)	10:0	217	11
7	TiO ₂ (7)	0:10	517	3

a. Source: 1: laboratory-made by solvothermal method; 2 and 5: Catalysis Society of Japan JRC-TiO-6 and -4(2); 3 and 4: Nanjin High Technology Nano Material Co.; 6 and 7: Aldrich.

b. Determined by XRD through the equation of % rutile = $100 / ((A/R) \times 0.884 + 1)$ where A and R are the peak areas for the major anatase ($2\theta = 25^\circ$) and rutile ($2\theta = 28^\circ$), respectively. [Refs. a, b]

[a] K. Y. Jung, S. B. Park, J. Photochem. Photobiol. A 127 (1999) 117-122

[b] J. Panpranot, K. Kontapakdee, P. Prasertdam, J. Phys. Chem. B 110 (2006) 8019-8024.

c. Determined by XRD line broadening through the Scherrer's equation

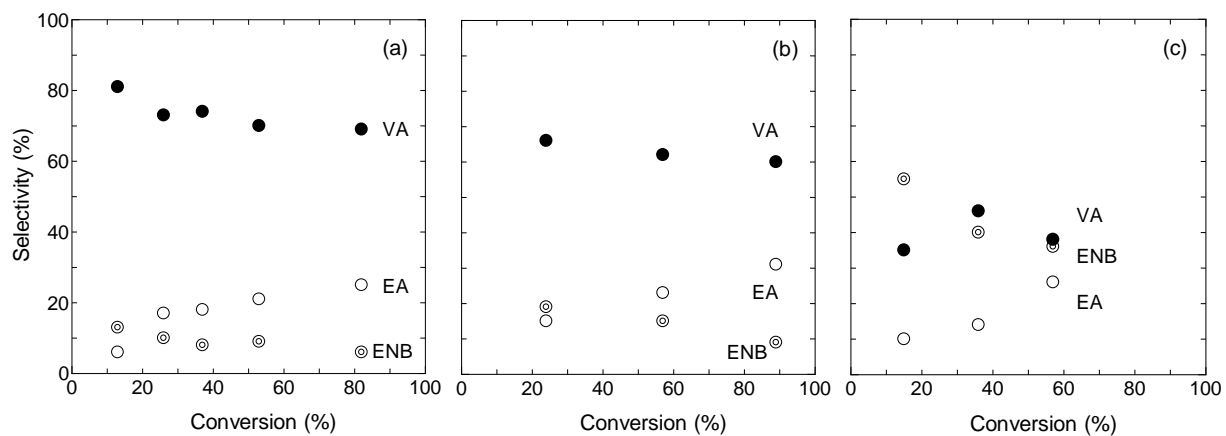
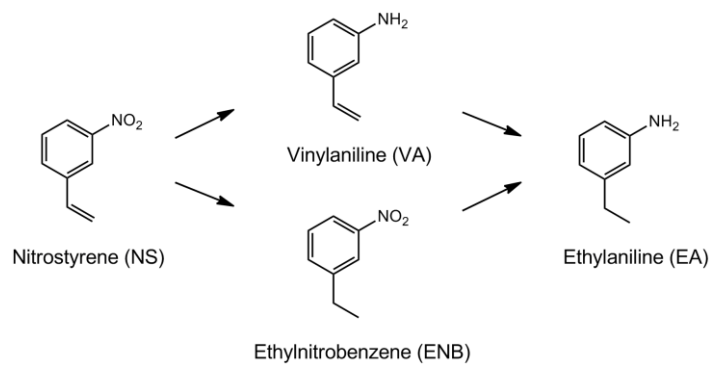


Fig. 1 Selectivity – conversion relationship in hydrogenation of 3-nitrostyrene over Pt catalysts using TiO₂(1) (a), TiO₂(5) (b), and TiO₂(6) (c) (see Table 1)



Scheme 1 Reaction pathways in hydrogenation of 3-nitrostyrene

Table 2 Properties of Pt catalysts on different TiO₂ supports and their catalytic performance in hydrogenation of nitrostyrene

Entry	Catalyst	D _{Pt} ^a	W _{cat} ^b	X _{total} ^c	S _{VA} ^d	TOF ^e
		(%)	(mg)	(%)	(s ⁻¹)	(s ⁻¹)
1	Pt/TiO ₂ (1)	8 (11)	20	26	73	23
2	Pt/TiO ₂ (2)	20 (4.5)	20	22	69	12
3	Pt/TiO ₂ (3)	23 (3.9)	10	33	50	31
4	Pt/TiO ₂ (4)	18 (5.0)	10	21	63	9
5	Pt/TiO ₂ (5)	10 (9.0)	10	24	66	26
6	Pt/TiO ₂ (6)	8 (11)	20	36	46	9
7	Pt/TiO ₂ (7)	23 (3.9)	10	37	42	9

Reaction conditions: 3-nitrostyrene 3.4 mmol, temperature 50 °C.

a. Degree of Pt dispersion measured by CO chemisorption assuming a stoichiometry of CO/Pt =1/1. Figures in parentheses are Pt diameters in nm estimated from Pt dispersion through average diameter of metal particles (nm) = 0.9 / the degree of metal dispersion (M. Boudart, G. Djéga-Mariadassou, Kinetics of Heterogeneous Catalytic Reactions, Princeton Univ., Princeton, 1984, p. 26).

b. Amount of Pt/TiO₂ catalyst used for the reaction

c. Total conversion of nitrostyrene

d. Selectivity to vinyllaniline

e. Turnover frequency of hydrogenation of 3-nitrostyrene

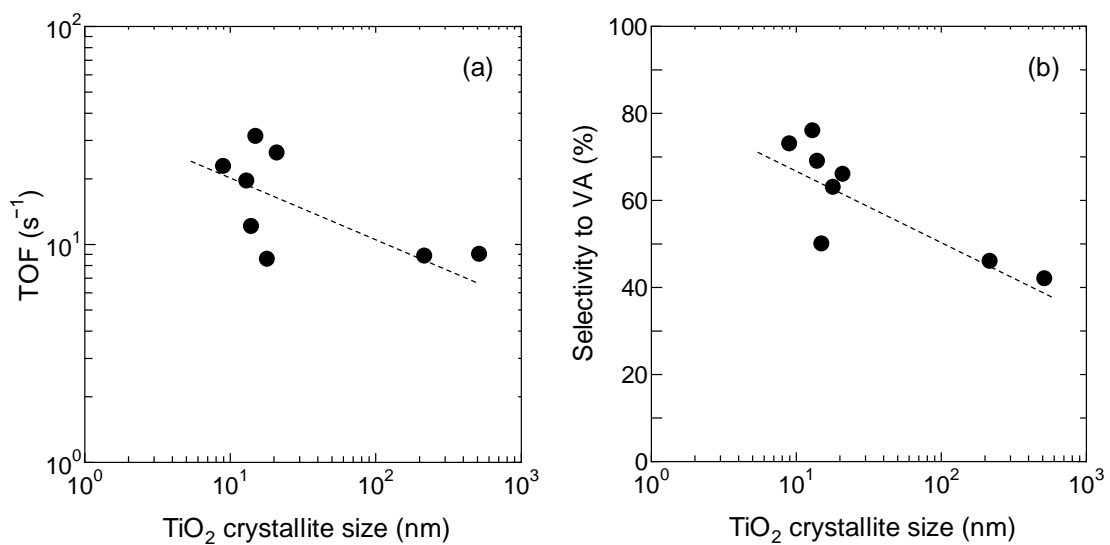


Fig. 2 Influence of TiO_2 crystallite size on TOF (a) and VA selectivity (b) for Pt/ TiO_2 catalysts in hydrogenation of 3-nitrostyrene

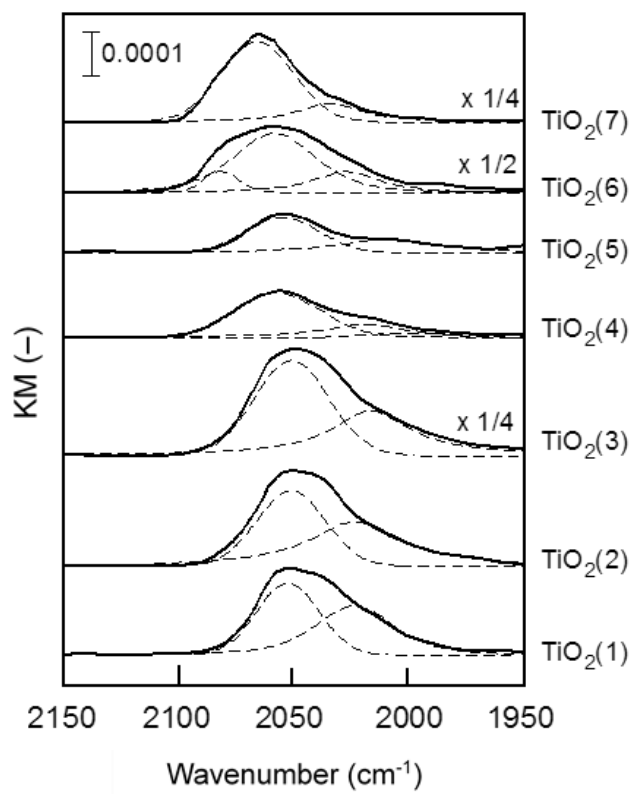


Fig. 3 FTIR spectra of a probe molecule of CO adsorbed on Pt catalysts dispersed on different TiO₂ supports. Broken lines are the results of deconvolution.

Table 3 Results of FTIR measurements ^a of a probe molecule of CO adsorbed on Pt catalysts dispersed different TiO₂ supports

Catalyst	Peak position (cm ⁻¹)			Relative peak area (-)	
	Low	Middle	High	Low	Middle & High
Pt/TiO ₂ (1)	2040	2053		0.52	0.48
Pt/TiO ₂ (2)	2023	2051		0.55	0.45
Pt/TiO ₂ (3)	2015	2050		0.43	0.57
Pt/TiO ₂ (4)	2020	2058		0.33	0.67
Pt/TiO ₂ (5)	2010	2055		0.44	0.56
Pt/TiO ₂ (6)	2027	2058	2081	0.24	0.76
Pt/TiO ₂ (7)	2034	2066		0.23	0.77

a. The deconvolution of FTIR spectra was made assuming Gaussian and/or Lorentzian types of absorption bands.

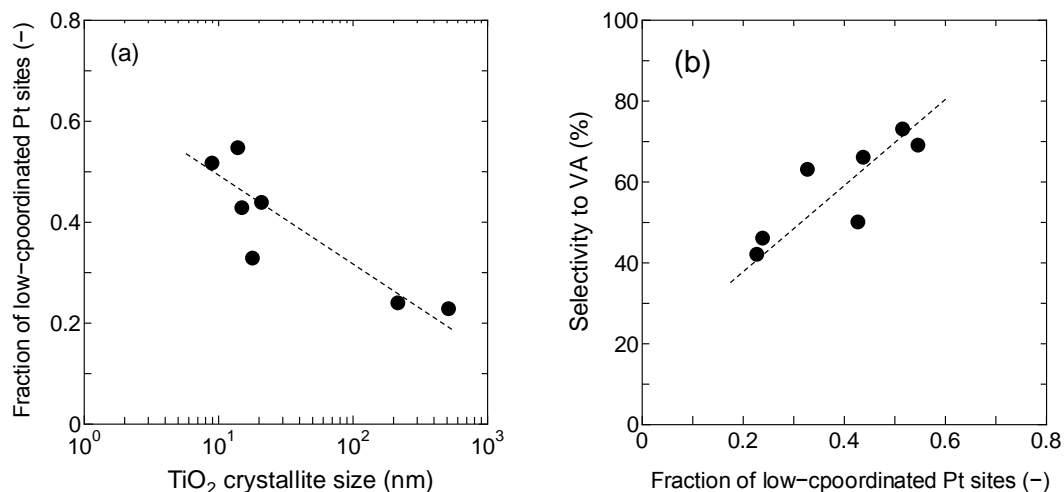


Fig. 4 Relationships between TiO₂ crystallite size and fraction of low-coordinated Pt sites of Pt/TiO₂ catalysts (a) and between the fraction of low-coordinated Pt sites and VA selectivity (b) in hydrogenation of 3-nitrostyrene

Table 4 Results of hydrogenation of a mixture of nitrobenzene (NB) and styrene (ST) over different Pt/TiO₂ catalysts

Entry	Catalyst	Conversion (%)		$x_{NB}/(x_{NB} + x_{ST})$ (-)
		x_{NB}	x_{ST}	
1	Pt/TiO ₂ (1)	37	18	0.67
2	Pt/TiO ₂ (2)	35	17	0.67
3	Pt/TiO ₂ (3)	39	29	0.57
4	Pt/TiO ₂ (4)	30	15	0.67
5	Pt/TiO ₂ (5)	30	20	0.60
6	Pt/TiO ₂ (6)	7	32	0.18
7	Pt/TiO ₂ (7)	25	41	0.38

Reaction conditions: NB 2.25 mmol, ST 2.45 mmol, catalyst 10 mg, temperature 50 °C, time 10 min.

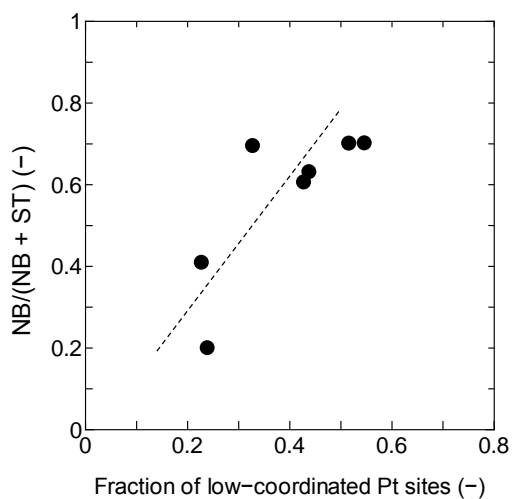
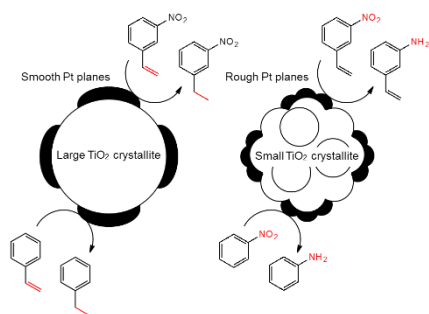


Fig. 5 Ratio of hydrogenation rates of NB and NB + ST in hydrogenation of a mixture of NB and ST against the fraction of low-coordinated Pt sites of Pt/TiO₂ catalysts. NB: nitrobenzene, ST: styrene.

Graphical Abstract

Influence of crystallite size of TiO₂ supports on the activity of dispersed Pt catalysts in liquid-phase selective hydrogenation of nitrostyrene, nitrobenzene, and styrene

H. Yoshida, N. Igarashi, S. Fujita, J. Panpranot, M. Arai



Smaller TiO₂ crystallites give rougher Pt crystal planes on the surface of Pt particles, beneficial for the hydrogenation of nitro group than vinyl group.