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# Effect of surface properties of TiO<sub>2</sub> on the performance of Pt/TiO<sub>2</sub> catalysts for furfural hydrogenation†

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Hydrogenation of biomass-derived furfural is an important process in biofuel production. Herein, different Pt-supported TiO<sub>2</sub> morphologies: nanorod (NR), nanoparticle (NP), and hollow microsphere (HMS) were prepared by the impregnation–chemical reduction method. The furfural conversion increased with an increase of Pt dispersion. However, cyclopentanone selectivity was affected by TiO<sub>2</sub> properties, the strong metal–support interaction (SMSI) effect, and the reaction conditions. The Pt/TiO<sub>2</sub> NR catalyst exhibited the highest cyclopentanone selectivity of 50.4%. Based on the H<sub>2</sub>-temperature programmed desorption (H<sub>2</sub>-TPD) and X-ray photoelectron spectroscopy (XPS) results, the Pt/TiO<sub>2</sub> NR catalyst showed a SMSI effect, which was introduced by the chemical reduction method. We suggest that electron charge transfer from Ti species to Pt in the Pt/TiO<sub>2</sub> NR catalyst affects the cyclopentanone selectivity by controlling the adsorption strength between the reactant and the Pt surface, thus retarding the formation of byproducts.

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## 1. Introduction

TiO<sub>2</sub> is widely used in the chemical industry as a semiconductor, photocatalyst, and catalyst support owing to its unique properties.<sup>1</sup> TiO<sub>2</sub> has various advantages as a catalyst support, including chemical stability, acid–base properties, and strong metal–support interactions (SMSIs). Recently, various types of TiO<sub>2</sub> with zero-dimensional (0D, nanoparticles (NPs)), one-dimensional (1D, nanowires, nanorods (NRs), and nanobelts), two-dimensional (2D, nanosheets), and three-dimensional structures (3D, hollow microspheres (HMSs)) have been applied as catalysts or catalyst supports. Tian *et al.* reported that Pd/TiO<sub>2</sub> nanowires exhibited higher catalytic activity than Pd/TiO<sub>2</sub> (P25) in the selective hydrogenation of phenolics to cyclohexanones,<sup>2</sup> as Lewis acid and basic sites exposed on the TiO<sub>2</sub> surface improved the cyclohexanone selectivity. Song *et al.* reported the selective oxidation of benzyl alcohol to benzaldehyde over a Pt/TiO<sub>2</sub> nanosphere catalyst.<sup>3</sup> In

this system, the hollow TiO<sub>2</sub> structure enhanced the diffusion and infiltration of reactants. Alqurashi *et al.* reported that TiO<sub>2</sub> NPs contributed to the formation of small and uniform Fe<sub>2</sub>O<sub>3</sub> NPs, resulting in high activity for benzyl alcohol oxidation.<sup>4</sup> The performance of a catalyst is strongly affected by the support properties, such as acid–base properties, specific surface area, oxygen vacancies, and porosity.

With the depletion of fossil fuels, alternative energies have received considerable attention. Furfural derived from biomass resources is considered an important starting material for the production of valuable chemical products such as furfuryl alcohol (FA), tetrahydrofurfuryl alcohol (THFAL), tetrahydrofuran (THF), 2-methylfuran (2-MF), and cyclopentanone (CPO) by hydrogenation or rearrangement. These materials are mostly used for manufacturing biofuel, bioplastics, and pharmaceuticals. In particular, the selective rearrangement of furfural to CPO has attracted attention because CPO is widely used in the pharmaceutical, food and chemical industries. Various supported catalysts, such as Pd/TiO<sub>2</sub>, Pd–Cu/C, Pt/C, and Ru/C, have been used in hydrogenation reactions.<sup>5–8</sup> However, few studies have investigated on the effect of TiO<sub>2</sub> properties on the catalytic performance of Pt/TiO<sub>2</sub> catalysts for furfural hydrogenation. Herein, we prepared Pt-supported TiO<sub>2</sub> catalysts (NR, NP, and HMS supports) by impregnation and chemical reduction. The catalytic activities were determined using the aqueous phase hydrogenation of furfural to CPO. Furthermore, the contribution of the strong metal–support interaction (SMSI) effect to the activity and selectivity of the Pt/TiO<sub>2</sub> catalysts for furfural hydrogenation was investigated.

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## 2. Experimental

### 2.1. Synthesis of TiO<sub>2</sub> supports

**2.1.1. TiO<sub>2</sub> NR.** The TiO<sub>2</sub> NR were prepared using a titanium glycolate precursor.<sup>9,10</sup> Typically, 1.75 g of titanium(IV) butoxide (97%, Sigma-Aldrich) was added to 200 mL of ethylene glycol (99%, Alfa Aesar). The solution was stirred at 30 °C for 1 h. The solution was heated to 150 °C and then stirred for 14 h. The suspension was then filtered, washed with ethanol and deionized water for several times, and then dried at 105 °C for 24 h in an oven.

**2.1.2. TiO<sub>2</sub> NP.** The TiO<sub>2</sub> NP were prepared using a titanium glycolate precursor with acetone.<sup>11</sup> Typically, 5.0 g of titanium(IV) butoxide was added to 50 mL of ethylene glycol. The solution was vigorously stirred at 25 °C for 24 h. Then, 340 mL of acetone and 2.7 mL of deionized water were added and vigorously stirred at 25 °C for 1 h 30 min. The suspension was centrifuged and washed with ethanol and deionized water, and then dried at 105 °C overnight in an oven. Subsequently, 1.0 g of the prepared white powder was added to 200 mL of deionized water and then heated to 90 °C for 1 h under stirring. The suspension was filtered, washed with ethanol and deionized water, and dried at 105 °C for 24 h in an oven.

**2.1.3. TiO<sub>2</sub> HMS.** The TiO<sub>2</sub> HMS were prepared by a template-free solvothermal method.<sup>3</sup> Typically, 16 g of oxalic acid (98%, Sigma-Aldrich) was added to 50 mL of ethanol, and then the suspension was vigorously stirred at 25 °C for 10 min. Then, 2.0 g of titanium(IV) butoxide was quickly added and vigorously stirred at 25 °C for 10 min. The mixture was transferred to a 100 mL hydrothermal reactor, which was heated to 140 °C for 12 h in an oven. The suspension was filtered, washed with ethanol and deionized water, and dried at 105 °C for 24 h in an oven. All the TiO<sub>2</sub> supports were calcined at 500 °C (heating rate = 5 °C min<sup>-1</sup>) for 2 h under flowing air.

### 2.2. Preparation of Pt/TiO<sub>2</sub> catalysts

5wt% Pt/TiO<sub>2</sub> catalysts were prepared by the impregnation-chemical reduction method. Briefly, the H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (37.5%, Wako Pure Chemical Cooperation) was added to 50 mL of deionized water. Then, 0.65 g of TiO<sub>2</sub> support was added and stirred at 25 °C for 1 h. The Pt/TiO<sub>2</sub> catalysts were reduced in the liquid phase using 5 mL of NaBH<sub>4</sub> (0.15 M, 99%, Sigma-Aldrich) solution. The suspension was stirred at 25 °C for 12 h and then filtered, washed with deionized water, and dried at 105 °C for 24 h in an oven.

### 2.3. Characterization

Specific surface area, pore diameters and volumes were calculated by Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) analyses of N<sub>2</sub> isotherm curves at 77 K using a Micromeritics ASAP 2020 instrument. The X-ray diffraction (XRD) analysis was carried out on a Bruker D8 Focus instrument using a Cu K $\alpha$  radiation. The temperature-programmed reduction of H<sub>2</sub> (H<sub>2</sub>-TPR) and temperature-programmed desorption of H<sub>2</sub> or NH<sub>3</sub> (H<sub>2</sub>-TPD or NH<sub>3</sub>-TPD) were carried out using a Micromeritics AutoChem 2920 instrument equipped with

a TCD detector. In the H<sub>2</sub>-TPR analysis, 100 mg of catalyst was pre-treated under a continuous He flow at 150 °C for 2 h. The catalyst was heated to 750 °C (heating rate = 10 °C min<sup>-1</sup>) under a H<sub>2</sub> (5% H<sub>2</sub> in He balance) flow. In the H<sub>2</sub>-TPD analysis, 50 mg of catalyst was pre-treated under H<sub>2</sub> (10% H<sub>2</sub>/Ar) flow at 400 °C for 1 h. Then, the catalyst was cooled into ambient temperature and heated to 800 °C (heating rate = rate = 10 °C min<sup>-1</sup>) under a He flow. In the NH<sub>3</sub>-TPD analysis, 100 mg of catalyst was pre-treated under He flow at 150 °C for 2 h. Subsequently, NH<sub>3</sub> (10% NH<sub>3</sub> in He balance) adsorption was carried out at 50 °C for 0.5 h. The catalysts were heated to 600 °C (heating rate = 10 °C min<sup>-1</sup>) under a constant He flow. X-ray photoelectron spectroscopy (XPS) was carried out using a Thermo Fisher Scientific K Alpha+ instrument with Al K $\alpha$  radiation. The surface morphologies of the supports were determined by scanning electron microscopy (SEM) on a Hitachi SU8020 instrument operated at 15 kV. Pt dispersion was estimated by CO pulse chemisorption using a Micromeritics AutoChem 2920 instrument. The average particle size and distribution of Pt in Pt/TiO<sub>2</sub> catalysts were measured by field-emission transmission electron microscopy (FE-TEM) using a JEOL JEM-2100F instrument operating at 200 kV.

### 2.4. Furfural hydrogenation

Furfural hydrogenation was conducted in a 250 mL batch reactor using 0.1 g of Pt/TiO<sub>2</sub> catalyst, and 100 mL of deionized water containing 2.5 g of furfural. After rapidly transferring the mixture into the reactor, the reactor was sealed and introduced with hydrogen three times to remove air. After reaching the desired temperature, reactor was pressurized with hydrogen 20 bar under stirring at 500 rpm. The liquid product was analyzed by gas chromatography (7890A, Agilent, FID) with a DB-Wax column (30 m  $\times$  0.32 mm  $\times$  0.25  $\mu$ m).<sup>7</sup>

## 3. Results and discussion

### 3.1. Characterization of supports and Pt catalysts

Fig. 1 shows the N<sub>2</sub> isotherm curves and pore size distributions of the TiO<sub>2</sub> supports and Pt/TiO<sub>2</sub> catalysts. All the TiO<sub>2</sub> supports had type IV of N<sub>2</sub> adsorption-desorption isotherms. TiO<sub>2</sub> NP exhibited a H1 hysteresis loop, which is indicative of a mesoporous material according to the IUPAC classification. In contrast, TiO<sub>2</sub> NR and TiO<sub>2</sub> HMS showed a hysteresis loop of type H2 (b) type with an ink bottle pore structure. The total pore volumes were calculated by adsorption isotherms at  $P/P_0 \sim 0.995$ . Capillary condensation in the TiO<sub>2</sub> NP and TiO<sub>2</sub> HMS supports was initiated at a relative pressure ( $P/P_0$ ) of  $\sim 0.48$ , whereas that in the TiO<sub>2</sub> NR support occurred at a relative pressure of 0.6, which can be attributed to a larger pore size.<sup>12</sup> After Pt loading, the Pt/TiO<sub>2</sub> catalysts exhibited similar characteristics. The physical properties of the TiO<sub>2</sub> supports and Pt/TiO<sub>2</sub> catalysts are listed in Table 1. The TiO<sub>2</sub> NP support has the largest BET surface area and pore volume (56 m<sup>2</sup> g<sup>-1</sup> and 0.16 cm<sup>3</sup> g<sup>-1</sup>, respectively), whereas the TiO<sub>2</sub> NR support has the lowest specific surface area and pore volume (10 m<sup>2</sup> g<sup>-1</sup> and 0.04 cm<sup>3</sup> g<sup>-1</sup>, respectively). However, the TiO<sub>2</sub> NR support has



the largest pore diameter, which is in agreement with the above-mentioned results.

After Pt loading, the BET surface area and pore volume decreased, which indicates that Pt NPs block the pores for the Pt/TiO<sub>2</sub> NP. Despite of decrease in the BET surface area, the pore volume and pore diameter was slightly increase for the Pt/TiO<sub>2</sub> HMS. It was inferred that the addition of NaOH may filled the pores of TiO<sub>2</sub>, which reduces the pore volume and pore size.<sup>13</sup>

Fig. 2 shows the XRD patterns of the TiO<sub>2</sub> supports and Pt/TiO<sub>2</sub> catalysts. The TiO<sub>2</sub> NR and TiO<sub>2</sub> HMS supports exhibited mixtures of anatase (31% and 79%, respectively) and rutile phases (69% and 21%, respectively). In contrast, the TiO<sub>2</sub> NP

support exhibited only the anatase phase. The amounts of anatase and rutile phases were calculated using eqn (1) and are listed in Table 1.<sup>14</sup>

$$A (\%) = 100 / (1 + 1.265(I_R/I_A)) \quad (1)$$

where  $I_A$  is the intensity of the anatase peak ( $2\theta = 25.3^\circ$ ) and  $I_R$  is the intensity of the rutile peak ( $2\theta = 27.4^\circ$ ). After Pt loading, the XRD patterns of all the Pt/TiO<sub>2</sub> catalysts exhibited a characteristic Pt peak at  $40^\circ$  (Fig. 1), which corresponded to the (111) crystal face of Pt. However, the relative amounts of anatase and rutile phases for each type of support were similar before and after Pt loading.

The acid properties of the TiO<sub>2</sub> supports and Pt/TiO<sub>2</sub> catalysts were estimated by NH<sub>3</sub>-TPD, as shown in Fig. 3 and Table 1. The acidities of the supports and catalysts play an important role in the formation of CPO during furfural hydrogenation. Desorption peaks around 50–200, 200–500, and >500 °C correspond to weak acid sites, medium acid sites, and strong acid sites, respectively. The TiO<sub>2</sub> NP support showed desorption peaks at 120 and 280 °C, whereas the TiO<sub>2</sub> HMS support showed desorption peaks at 80, 310, and 530 °C. Compared with the other supports, the TiO<sub>2</sub> NR support showed desorption peaks at lower temperatures (70, 280, and 530 °C). The total acidity of the TiO<sub>2</sub> supports decreased in the following order: TiO<sub>2</sub> NP

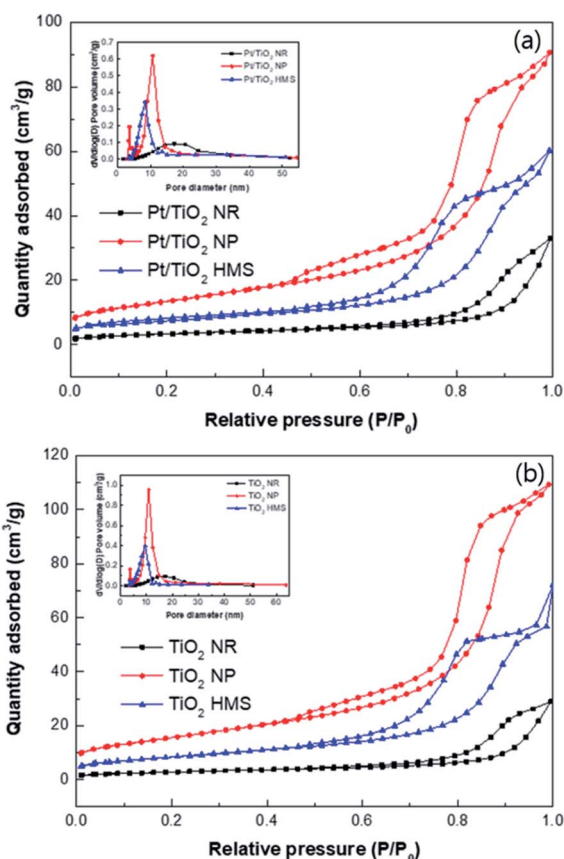


Fig. 1 N<sub>2</sub> isotherm curves and pore size distributions of (a) TiO<sub>2</sub> supports and (b) Pt/TiO<sub>2</sub> catalysts.

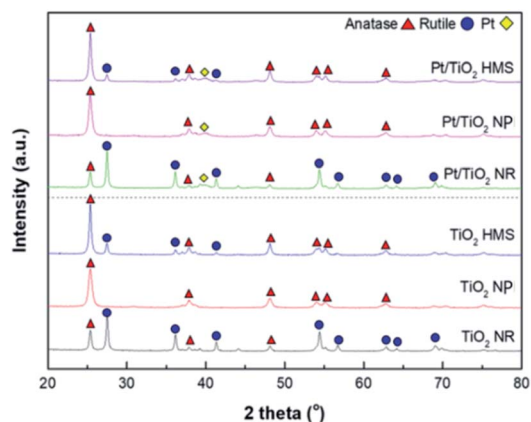


Fig. 2 XRD patterns of TiO<sub>2</sub> supports and Pt/TiO<sub>2</sub> catalysts.

Table 1 Physical and chemical properties of TiO<sub>2</sub> supports and Pt/TiO<sub>2</sub> catalysts

	$S_{\text{BET}}$ (m <sup>2</sup> g <sup>-1</sup> )	$V_{\text{Total}}$ (cm <sup>3</sup> g <sup>-1</sup> )	Pore diameter (nm)	Weight (%)		Acidity (mmol g <sup>-1</sup> )	Binding energy (eV)		Metal dispersion (%)
				Anatase	Rutile		Ti <sup>4+</sup>	Pt <sup>0</sup>	
TiO <sub>2</sub> NR	10	0.04	14.8	31	69	0.10	458.7	—	—
TiO <sub>2</sub> NP	56	0.16	9.70	100	—	0.31	458.9	—	—
TiO <sub>2</sub> HMS	30	0.08	8.50	79	21	0.27	458.6	—	—
Pt/TiO <sub>2</sub> NR	12	0.05	15.7	31	69	0.11	459.1	71.07	9
Pt/TiO <sub>2</sub> NP	48	0.14	9.20	100	—	0.30	459.3	71.20	12
Pt/TiO <sub>2</sub> HMS	27	0.09	9.30	79	21	0.28	459.3	71.20	3



(0.31 mmol g<sup>-1</sup>) > TiO<sub>2</sub> HMS (0.27 mmol g<sup>-1</sup>) > TiO<sub>2</sub> NR (0.1 mmol g<sup>-1</sup>). After Pt loading, similar results were observed.

Fig. 4 shows the H<sub>2</sub>-TPR profiles of the TiO<sub>2</sub> supports and Pt/TiO<sub>2</sub> catalysts. The TiO<sub>2</sub> supports showed two reduction peaks around 400–500 and 750 °C, which are corresponded to the reduction of the TiO<sub>2</sub> support.<sup>15,16</sup> The TiO<sub>2</sub> NR exhibited lower reduction temperature than other support, indicating the TiO<sub>2</sub> NR can be more easily formation Ti<sup>3+</sup> and oxygen vacancies on surface.<sup>17</sup> All the Pt/TiO<sub>2</sub> catalysts showed a reduction peak around 300–500 °C ascribed to the reduction of Pt–TiO<sub>x</sub> interface sites by an interaction between Pt and TiO<sub>2</sub>.<sup>18</sup> The Pt/TiO<sub>2</sub>

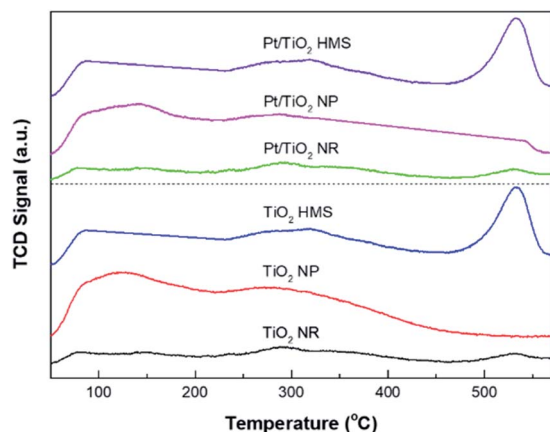


Fig. 3 NH<sub>3</sub>-TPD profiles of TiO<sub>2</sub> supports and Pt/TiO<sub>2</sub> catalysts.

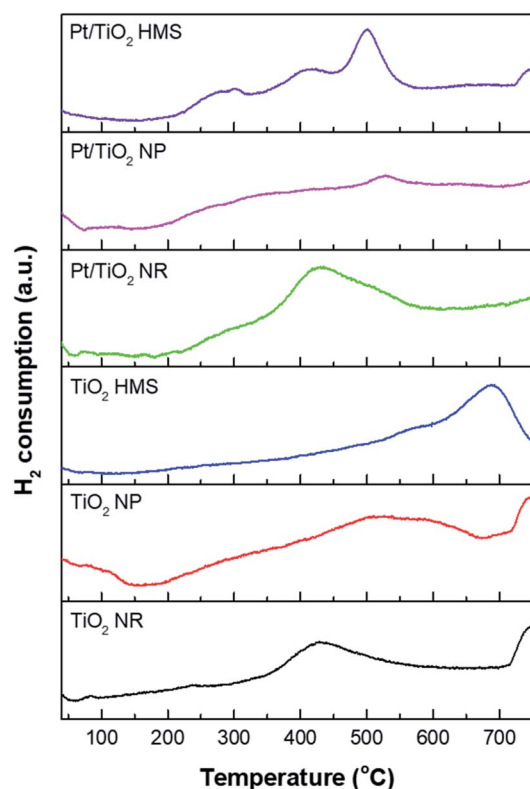


Fig. 4 H<sub>2</sub>-TPR profiles of TiO<sub>2</sub> supports and Pt/TiO<sub>2</sub> catalysts.

HMS catalyst exhibited three reduction peaks around 300, 400, and <500 °C. The first peak is related to the reduction of PtO species weakly interacting with the TiO<sub>2</sub> support,<sup>19</sup> the second peak is related to the reduction of Pt–TiO<sub>x</sub> interface sites, and the third peak correspond to the reduction of the surface-capping oxygen on the TiO<sub>2</sub> support.<sup>17,18</sup>

Fig. 5 exhibits the H<sub>2</sub>-TPD profiles for the Pt/TiO<sub>2</sub> catalysts. The desorption temperature is relevant to the adsorption energy of hydrogen and the nature of hydrogen species. For Pt/TiO<sub>2</sub> HMS and Pt/TiO<sub>2</sub> NP catalysts, the double peaks were revealed under 300 °C, indicating hydrogen adsorption on Pt surface.<sup>20</sup> Compared to the Pt/TiO<sub>2</sub> NP catalyst, the Pt/TiO<sub>2</sub> HMS had a large amount of hydrogen adsorbed on Pt due to its 3D structure. The Pt/TiO<sub>2</sub> NR showed double peaks at 74 °C and 535 °C, resulting from hydrogen on Pt and H spillover species, respectively. This H spillover can induce SMSIS owing to the reduction of TiO<sub>2</sub> supports to TiO<sub>x</sub> (x < 2), leading to improving the catalytic activity and selectivity.<sup>21</sup>

The XPS spectra of the TiO<sub>2</sub> supports and Pt/TiO<sub>2</sub> catalysts in the Ti 2p and Pt 4f regions are shown in Fig. 6 and the results are summarized in Table 1. The TiO<sub>2</sub> supports exhibited two peaks at 458.7 and 464.5 eV corresponding to the Ti 2p<sub>3/2</sub> and Ti 2p<sub>1/2</sub> peaks of Ti<sup>4+</sup>, respectively.<sup>22</sup> After Pt loading, the Ti 2p peaks shifted toward higher binding energies, which is indicative of an interaction between Pt and TiO<sub>2</sub>.<sup>23</sup> The binding energy of the Ti 2p peak for the Pt/TiO<sub>2</sub> NR catalyst was lower than those for the Pt/TiO<sub>2</sub> NP and Pt/TiO<sub>2</sub> HMS catalysts, indicating that Ti<sup>3+</sup> species exist on the Pt/TiO<sub>2</sub> NR catalyst.<sup>24</sup> As shown in Fig. 6c, two Pt peaks are observed at 71.0 and 74.3 eV corresponding to Pt 4f<sub>7/2</sub> and Pt 4f<sub>5/2</sub>, respectively. The Pt 4f<sub>7/2</sub> peak at 71.0 eV corresponds to the metallic state. The binding energies of the Pt 4f<sub>7/2</sub> peaks for the Pt/TiO<sub>2</sub> NR catalyst are slightly lower than those for the Pt/TiO<sub>2</sub> NP and Pt/TiO<sub>2</sub> HMS catalysts. Generally, SMSIS in metal-supported TiO<sub>2</sub> catalysts are introduced during thermal treatment in the range of 150–600 °C under H<sub>2</sub> flow.<sup>25,26</sup> Rui *et al.* reported that an SMSI effect in a Pt/TiO<sub>2</sub> catalyst was produced by chemical reduction using NaBH<sub>4</sub> or HCHO solution.<sup>27</sup> Among the prepared Pt/TiO<sub>2</sub>

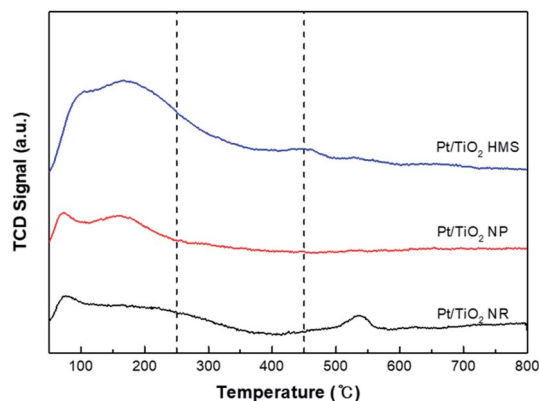


Fig. 5 H<sub>2</sub>-TPD profiles of Pt/TiO<sub>2</sub> catalysts.





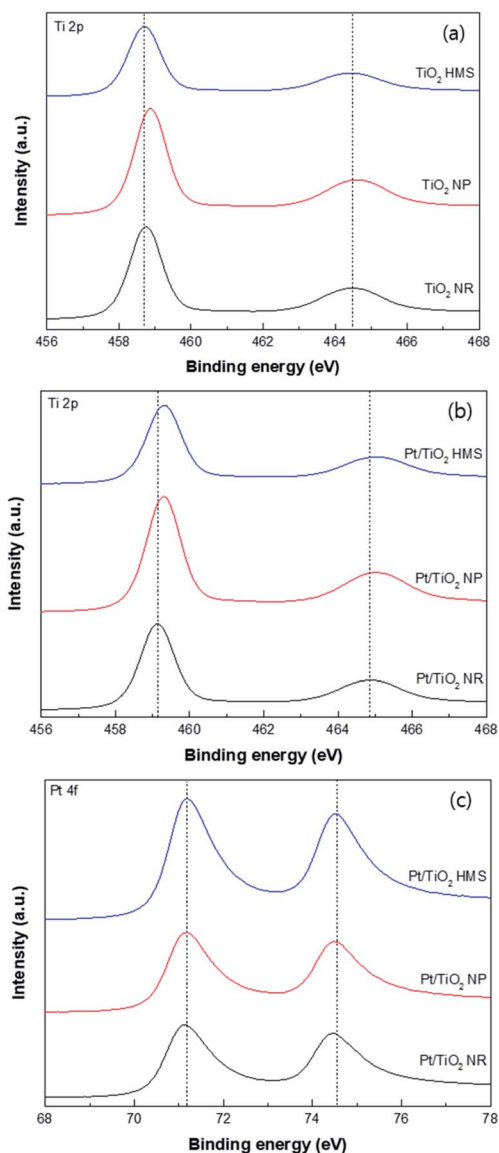


Fig. 6 XPS spectra of  $\text{TiO}_2$  supports and  $\text{Pt/TiO}_2$  catalysts: (a) Ti 2p of  $\text{TiO}_2$ , (b) Ti 2p of  $\text{Pt/TiO}_2$ , and (c) Pt 4f of  $\text{Pt/TiO}_2$ .

catalysts, the  $\text{Pt/TiO}_2$  NR catalyst exhibited a lower binding energy for the peak at 70.18 eV, which was attributed to an SMSI effect.

Fig. 7 shows the FE-SEM images of the  $\text{TiO}_2$  supports. The  $\text{TiO}_2$  NR support shows linear structures with lengths of 500 nm to 1  $\mu\text{m}$ . The  $\text{TiO}_2$  NP support contains NP with sizes of 300–500 nm. The  $\text{TiO}_2$  HMS support shows HMS with sizes of 3–5  $\mu\text{m}$ . Fig. 8 shows representative FE-TEM images and particle size distribution of the  $\text{Pt/TiO}_2$  catalysts. The average particle size was measured using 200 spherical Pt NP. The average particle size in the  $\text{Pt/TiO}_2$  catalysts increased in the order  $\text{Pt/TiO}_2$  NP (4.52 nm) <  $\text{Pt/TiO}_2$  NR (5.25 nm) <  $\text{Pt/TiO}_2$  HMS (6.48 nm). The dispersion of Pt in the  $\text{Pt/TiO}_2$  catalysts was estimated by CO chemisorption (Table 1). The  $\text{Pt/TiO}_2$  NP catalyst exhibited the highest Pt dispersion of 12%, whereas the  $\text{Pt/TiO}_2$  HMS catalyst

exhibited the lowest Pt dispersion of 3%. These results correspond to the FE-TEM results.

### 3.2. Hydrogenation of furfural

The catalytic activities of the prepared  $\text{TiO}_2$  supports and  $\text{Pt/TiO}_2$  catalysts were investigated with respect to the hydrogenation of furfural under 20 bar of  $\text{H}_2$  at 170  $^\circ\text{C}$  for 2 h; the results are summarized in Table 2. Furfural hydrogenation did not proceed to any significant extent over the  $\text{TiO}_2$  supports alone. The conversion of furfural decreased with Pt dispersion in the order  $\text{Pt/TiO}_2$  NP >  $\text{Pt/TiO}_2$  NR >  $\text{Pt/TiO}_2$  HMS. However, the  $\text{Pt/TiO}_2$  NR catalyst exhibited the highest CPO selectivity of 35.2%. The selectivity for CPO can be affected by several factors such as support properties, hydrogen pressure, and solvent effects. Firstly, the catalytic activities were affected by  $\text{TiO}_2$  properties. The  $\text{Pt/TiO}_2$  NP with 0D structure revealed the highest conversion of furfural due to the largest specific surface area. Although the  $\text{Pt/TiO}_2$  HMS had 3D structure to facilitate hydrogen adsorption, the lowest conversion and selectivity were obtained. This is ascribed to a large quantity of strong acid sites, which causes polymerization and lowers the

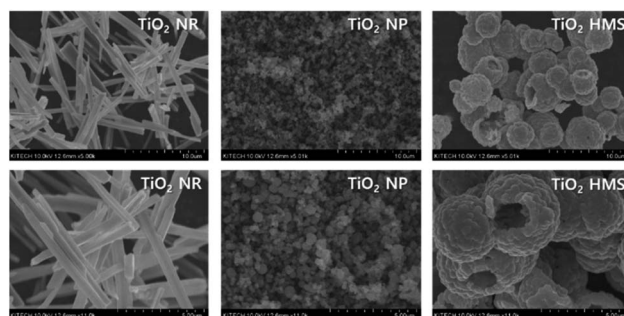


Fig. 7 FE-SEM images of  $\text{TiO}_2$  supports.

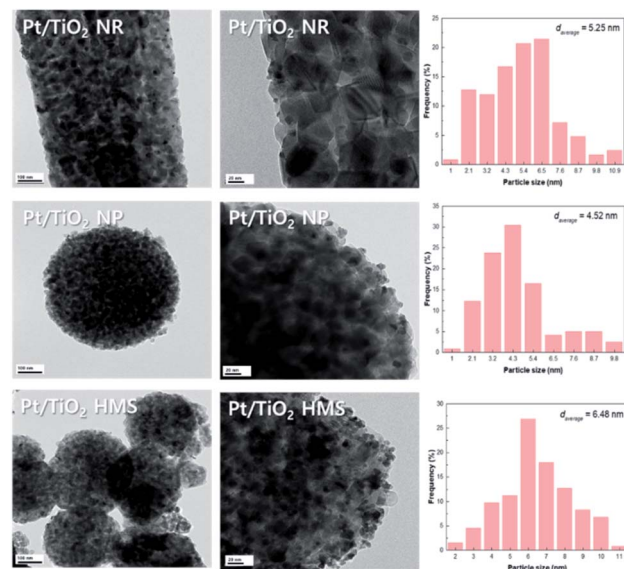


Fig. 8 FE-TEM images of  $\text{Pt/TiO}_2$  catalysts.



Table 2 Hydrogenation of furfural over TiO<sub>2</sub> supports and Pt/TiO<sub>2</sub> catalysts<sup>a</sup>

	Conversion (%)	Selectivity (%)				
		FA	THFAL	CPO	CPL	Others
TiO <sub>2</sub> NR	0.3	—	—	—	—	100
TiO <sub>2</sub> NP	1.2	—	—	—	—	100
TiO <sub>2</sub> HMS	0.3	—	—	—	—	100
Pt/TiO <sub>2</sub> NR	90	2.3	1.5	35.2	—	61
Pt/TiO <sub>2</sub> NP	96	2.0	—	13.6	1.8	82.6
Pt/TiO <sub>2</sub> HMS	78	4.0	—	14.2	—	81.8

<sup>a</sup> Reaction conditions:  $P_{H_2} = 20$  bar, reaction temp. = 170 °C, and reaction time = 2 h.

catalytic activity.<sup>28,29</sup> In contrast, the Pt/TiO<sub>2</sub> NR (1D) showed the highest CPO selectivity regardless of Pt dispersion and specific surface area. We suggested that the large pore size of Pt/TiO<sub>2</sub> NR catalyst can easily access furfural molecules to inside the catalyst pore with minimized steric hindrance.<sup>30</sup> In addition, furfural and FA can be converted into polymers by heat treatment or acid sites.<sup>31,32</sup> Based on the NH<sub>3</sub>-TPD results, the Pt/TiO<sub>2</sub> NR catalyst has the lowest total acidity and thus can produce more CPO by rearrangement. Cyclopentanol (CPL), THFAL, and other non-identified materials were detected as byproducts.

The effect of reaction time on furfural hydrogenation over the Pt/TiO<sub>2</sub> catalysts was investigated under at 170 °C,  $P_{H_2} = 20$  bar, and reaction time in the range of 30 min to 240 min (Fig. 9). As the reaction time increased, the furfural conversion gradually increased. With the Pt/TiO<sub>2</sub> NP catalyst, a furfural conversion of 99.8% was achieved at 170 °C for 3 h. This catalyst exhibited the highest catalytic activity due to its high Pt dispersion. Interestingly, the Pt/TiO<sub>2</sub> NP catalyst showed higher CPO selectivity than the Pt/TiO<sub>2</sub> HMS catalyst despite having a higher total acidity, likely because the Pt/TiO<sub>2</sub> NP catalyst mainly contained weak acid sites, whereas strong acid sites were predominant on the Pt/TiO<sub>2</sub> HMS catalyst. Although the Pt/TiO<sub>2</sub> NP catalyst had higher acidity than the Pt/TiO<sub>2</sub> NR catalyst, the acid site distribution was dominant in weak acid sites compared to Pt/TiO<sub>2</sub> HMS. The Pt/TiO<sub>2</sub> NP catalyst exhibited high CPO selectivity. We suggested that selectivity of product affected by two perspective; SMSI effect and hydrogen adsorption strength. Based on the XPS and H<sub>2</sub>-TPD results, the SMSI effect was occurred over Pt/TiO<sub>2</sub> NR catalyst. The SMSI effect induced by H spillover species during the reduction process with NaBH<sub>4</sub> solution. The H spillover species on Pt surface can diffuse into TiO<sub>2</sub> NR and reduce TiO<sub>2</sub> surface, resulting in the formation of Pt covered from TiO<sub>x</sub> and oxygen vacancy. The covered Pt particles from TiO<sub>x</sub> affect the adsorption strength of H<sub>2</sub>, resulting higher CPO yield with retarding over-hydrogenation or polymerization. The C=O (carbonyl) group in furfural adsorbs selectively on the oxygen vacancies and is hydrogenated with the H spillover species.<sup>33–36</sup>

Based on the XPS results, the Ti 2p and Pt 4f binding energies of the Pt/TiO<sub>2</sub> NR catalyst in Ti 2p and Pt 4f are lower than

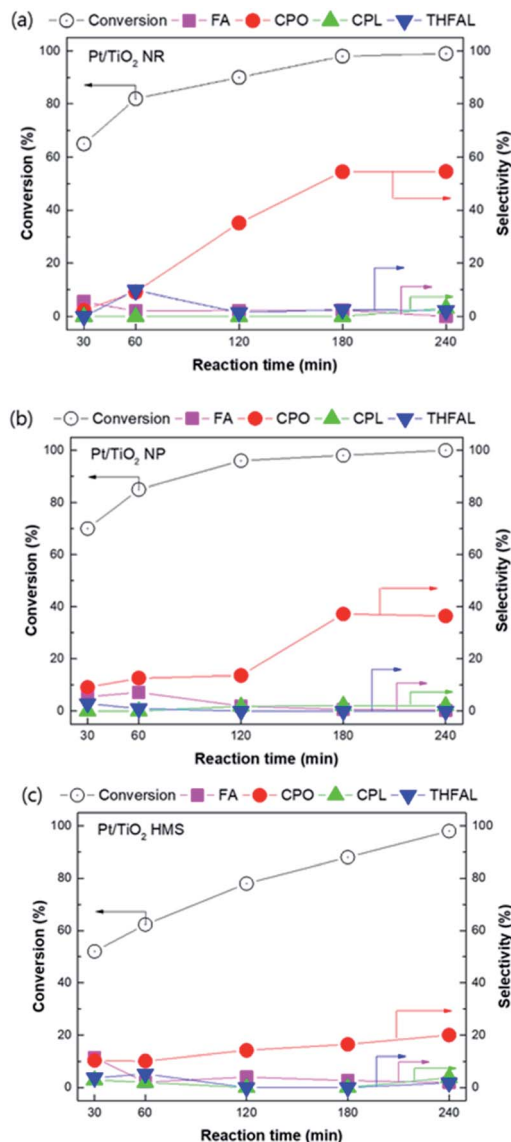


Fig. 9 Furfural hydrogenation over (a) Pt/TiO<sub>2</sub> NR, (b) Pt/TiO<sub>2</sub> NP, and (c) Pt/TiO<sub>2</sub> HMS catalysts.

those of the other catalysts. Riyapan *et al.* reported that electron charge transfer from Ti species to Pd affects the adsorption strength of ethylene on the Pd surface, resulting in high selectivity for ethylene.<sup>37</sup> Lee *et al.* reported that the interaction between TiO<sub>y</sub> species generated at various temperatures and Co NPs provides bifunctional sites for the selective hydrogenation of furfural by controlling the SMSI effect.<sup>38</sup> As the reaction time increased, the CPO selectivity gradually increased over the Pt/TiO<sub>2</sub> NR and Pt/TiO<sub>2</sub> NP catalysts. However, only a slight increase in the CPO selectivity occurred over the Pt/TiO<sub>2</sub> HMS catalyst. Although Pt/TiO<sub>2</sub> NR exhibited SMSI effect, we considered the effect of TiO<sub>2</sub> phase. Aschauer *et al.* reported that oxygen vacancies in reduced anatase phase of TiO<sub>2</sub> has favorable adsorption site for H<sub>2</sub> atoms.<sup>39</sup> Islam *et al.* reported that molecular of H<sub>2</sub> cannot easily interaction with rutile phase of TiO<sub>2</sub> support.<sup>40</sup> From the XRD results, the Pt/TiO<sub>2</sub> NR catalyst



exhibited higher amount of rutile phase than other catalysts. We suggest that the SMSI effect and hydrogen adsorption strength may affect CPO selectivity in furfural hydrogenation. Furfural hydrogenation involves various reaction pathways, including C=C and C=O hydrogenation, hydrogenolysis, and rearrangement to produce various materials such as FA, CPO, CPL, 2-methylfuran, *n*-butanol, and 2-pentanol. The Pt/TiO<sub>2</sub> NR catalyst showed the highest catalytic performance in the selective hydrogenation of furfural to CPO. Thus, electron charge transfer from Ti species to Pt in the Pt/TiO<sub>2</sub> NR catalyst having high content of rutile phase may affect the selectivity for these products by controlling the adsorption strength between the reactant and the Pt surface, which can retard the formation of byproducts (Fig. 10).

The effect of reaction temperature on furfural hydrogenation over the Pt/TiO<sub>2</sub> NR catalyst was investigated under at  $P_{H_2} = 20$  bar for 3 h at reaction temperature in the range of 110–190 °C (Fig. 11). Furfural conversion increased with increasing reaction temperature. In the range of 110–130 °C, FA was predominantly produced and FA selectivity increased from 72.2% to 84.1%. However, at reaction temperatures over 130 °C, FA selectivity dramatically decreased with a concomitant increase in CPO selectivity. At high temperatures, the rearrangement of FA into 4-hydroxy-2-cyclopentanone (HCP) is promoted by H<sup>+</sup> ions in the aqueous phase.<sup>41,42</sup> The produced HCP can be converted into CPO by further hydrogenation. At higher temperatures, more H<sup>+</sup> ions are generated, thereby increasing CPO selectivity. However, as the reaction temperature increased from 170 to 190 °C, CPO selectivity was dramatically decreased to 0% owing to the formation of oligomers at high temperatures.<sup>43,44</sup>

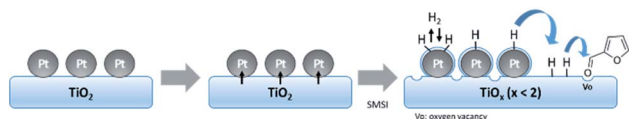


Fig. 10 Illustration of the SMSI effect in the Pt/TiO<sub>2</sub> NR catalyst.

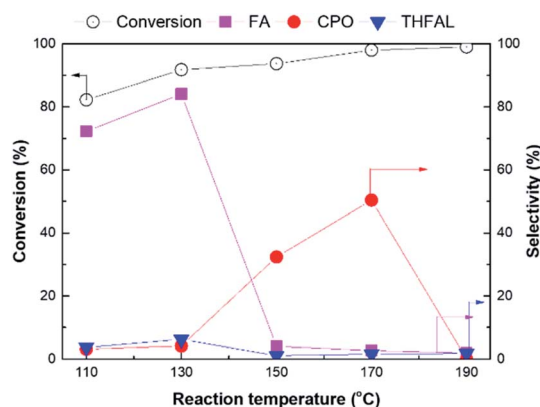


Fig. 11 Effect of reaction temperature of furfural hydrogenation over the Pt/TiO<sub>2</sub> NR catalyst.

## 4. Conclusions

Pt/TiO<sub>2</sub> NR, NP, and HMS catalysts were prepared by the impregnation–chemical reduction method for the selective hydrogenation of furfural to CPO. Although furfural conversion increased with Pt dispersion, CPO selectivity was strongly affected by TiO<sub>2</sub> properties and the SMSI effect. The Pt/TiO<sub>2</sub> HMS catalyst, which had the highest acidity, exhibited the lowest CPO selectivity at reaction times from 30 to 240 min owing to polymerization. The Pt/TiO<sub>2</sub> NP catalyst had predominant weak acid sites and higher total acidity than Pt/TiO<sub>2</sub> NR, resulting in lower CPO selectivity than Pt/TiO<sub>2</sub> NR. We suggested that two perspective on the TiO<sub>2</sub> properties effect and SMSI effect. Among three different supports, the Pt/TiO<sub>2</sub> NR with the largest pore size facilitated the furfural molecules inside the catalyst and minimized the steric hindrance between the reactant and catalyst, enhancing the CPO selectivity. Based on the XPS results, an SMSI effect was observed after Pt loading on the TiO<sub>2</sub> NR support. Electron charge transfer from Ti species to Pt in the Pt/TiO<sub>2</sub> NR catalyst may control the adsorption strength between the reactant and the Pt surface, resulting in higher CPO selectivity over the Pt/TiO<sub>2</sub> NR catalyst than over the Pt/TiO<sub>2</sub> NP catalyst. The Pt/TiO<sub>2</sub> NR catalyst showed highest catalytic activity for 98% furfural conversion and 50.4% CPO selectivity.

## Conflicts of interest

There are no conflicts to declare.

## Author contributions

Mi Yeon Byun: conceptualization, methodology, investigation, writing – original draft. Ye Eun Kim: investigation, data curation, visualization, Jae Ho Baek: visualization, Jungho Jae: supervision, Man Sig Lee: writing – review & editing, supervision.

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## Notes and references

- X. Wang, Z. Li, J. Shi and Y. Yu, One-Dimensional Titanium Dioxide Nanomaterials: Nanowires, Nanorods, and Nanobelt, *Chem. Rev.*, 2014, **114**, 9346–9384.
- C. Tian, H. Fang, H. Chen, W. Chen, S. Zhou, X. Duan, X. Liu and Y. Yuan, Photodeposition of Pd onto TiO<sub>2</sub> nanowires for aqueous-phase selective hydrogenation of phenolics to cyclohexanones, *Nanoscale*, 2020, **12**, 2603–2612.
- H. Song, Z. Liu, Y. Wang, N. Zhang, X. Qu, K. Guo, M. Xiao and H. Gai, Template-free synthesis of hollow TiO<sub>2</sub> nanospheres supported Pt for selective photocatalytic





- oxidation of benzyl alcohol to benzaldehyde, *Green Energy Environ.*, 2019, **4**(3), 278–286.
- 4 G. K. Alqurashi, A. Al-Shehri and K. Narasimharao, Effect of TiO<sub>2</sub> morphology on the benzyl alcohol oxidation activity of Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> nanomaterials, *RSC Adv.*, 2016, **6**, 71076–71091.
  - 5 M. Hronec, K. Fulajtárová, I. Vávra, T. Soták, E. Dobročka and M. Mičušík, Carbon supported Pd-Cu catalysts for highly selective rearrangement of furfural to cyclopentanone, *Appl. Catal., B*, 2016, **181**, 210–219.
  - 6 J. Wu, G. Gao, J. Li, P. Sun, X. Long and F. Li, Efficient and versatile CuNi alloy nanocatalysts for the highly selective hydrogenation of furfural, *Appl. Catal., B*, 2017, **203**, 227–236.
  - 7 M. Y. Byun, D. Park and M. S. Lee, Effect of oxide supports on the activity of Pd based catalysts for furfural hydrogenation, *Catalysts*, 2020, **10**, 837.
  - 8 V. V. Ordonsky, J. c. Schouten, J. Van Der Schaaf and T. A. Nijhuis, Biphasic single-reactor process for dehydration of xylose and hydrogenation of produced furfural, *Appl. Catal., A*, 2013, **451**, 6–13.
  - 9 Y. Wang, X. Jiang and Y. Xia, A solution-phase, precursor route to polycrystalline SnO<sub>2</sub> nanowires that can be used for gas sensing under ambient conditions, *J. Am. Chem. Soc.*, 2003, **125**, 16176–16177.
  - 10 S. Lee, G. Sang, J. Lee, J. Lee and H. Suk, Mesoporous TiO<sub>2</sub> nanowires as bi-functional materials for dye-sensitized solar cells, *Electrochim. Acta*, 2012, **74**, 83–86.
  - 11 G. Cheng, M. S. Akhtar, O. B. Yang and F. J. Stadler, Structure modification of anatase TiO<sub>2</sub> nanomaterials-based photoanodes for efficient dye-sensitized solar cells, *Electrochim. Acta*, 2013, **113**, 527–535.
  - 12 T. Z. Ren, Z. Y. Yuan and B. L. Su, Surfactant-assisted preparation of hollow microspheres of mesoporous TiO<sub>2</sub>, *Chem. Phys. Lett.*, 2003, **374**, 170–175.
  - 13 H. Huang and D. Y. C. Leung, Complete oxidation of formaldehyde at room temperature using TiO<sub>2</sub> supported metallic Pd nanoparticles, *ACS Catal.*, 2011, **1**, 348–354.
  - 14 R. A. Spurr and H. Myers, Quantitative analysis of anatase-rutile mixtures with an X-ray diffractometer, *Anal. Chem.*, 1957, **29**, 760–762.
  - 15 V. Bratan, C. Munteanu, C. Hornoiu, A. Vasile, F. Papa, R. State, S. Preda, D. Culita and N. I. Ionescu, CO oxidation over Pd supported catalysts-In situ study of the electric and catalytic properties, *Appl. Catal., B*, 2017, **207**, 166–173.
  - 16 K. Czupryn, I. Kocemba and J. Rynkowski, Photocatalytic CO oxidation with water over Pt/TiO<sub>2</sub> catalysts, *React. Kinet., Mech. Catal.*, 2018, **124**, 187–201.
  - 17 T. Ekou, L. Ekou, A. Vicente, G. Lafaye, S. Pronier, C. Especel and P. Marécot, Citral hydrogenation over Rh and Pt catalysts supported on TiO<sub>2</sub>: influence of the preparation and activation protocols of the catalysts, *J. Mol. Catal. A: Chem.*, 2011, **337**, 82–88.
  - 18 S. Pisduangdaw, O. Mekasuwandumrong, H. Yoshida, S. I. Fujita, M. Arai and J. Panpranot, Flame-made Pt/TiO<sub>2</sub> catalysts for the liquid-phase selective hydrogenation of 3-nitrostyrene, *Appl. Catal., A*, 2015, **490**, 193–200.
  - 19 S. Bhogeswararao and D. Srinivas, Catalytic conversion of furfural to industrial chemicals over supported Pt and Pd catalysts, *J. Catal.*, 2015, **327**, 65–77.
  - 20 J. T. Miller, B. L. Meyers, F. S. Modica, G. S. Lane, M. Vaarkamp and D. C. Koningsberger, Hydrogen temperature-programmed desorption (H<sub>2</sub> TPD) of supported platinum catalysts, *J. Catal.*, 1993, **143**, 395–408.
  - 21 W. C. Conner and J. L. Falconer, Spillover in heterogeneous catalysis, *Chem. Rev.*, 1995, **95**, 759–768.
  - 22 J. Liqiang, F. Honggang, W. Baiqi, W. Dejun, X. Baifu, L. Shudan and S. Jiazhong, Effects of Sn dopant on the photoinduced charge property and photocatalytic activity of TiO<sub>2</sub> nanoparticles, *Appl. Catal., B*, 2006, **62**, 282–291.
  - 23 L. Yu, Y. Shao and D. Li, Direct combination of hydrogen evolution from water and methane conversion in a photocatalytic system over Pt/TiO<sub>2</sub>, *Appl. Catal., B*, 2017, **204**, 216–223.
  - 24 X. Yao, L. Chen, J. Cao, F. Yang, W. Tan and L. Dong, Morphology and crystal-plane effects of CeO<sub>2</sub> on TiO<sub>2</sub>/CeO<sub>2</sub> catalysts during NH<sub>3</sub>-SCR reaction, *Ind. Eng. Chem. Res.*, 2018, **57**, 12407–12419.
  - 25 R. T. K. Baker, E. B. Prestridge and L. L. Murrell, Electron microscopy of supported metal particles. III. The role of the metal in an SMSI interaction, *J. Catal.*, 1983, **79**, 348–358.
  - 26 H. Huang, D. Y. C. Leung and D. Ye, Effect of reduction treatment on structural properties of TiO<sub>2</sub> supported Pt nanoparticles and their catalytic activity for formaldehyde oxidation, *J. Mater. Chem.*, 2011, **21**, 9647–9652.
  - 27 Z. Rui, L. Chen, H. Chen and H. Ji, Strong metal-support interaction in Pt/TiO<sub>2</sub> induced by mild HCHO and NaBH<sub>4</sub> solution reduction and its effect on catalytic toluene combustion, *Ind. Eng. Chem. Res.*, 2014, **53**, 15879–15888.
  - 28 T. D. Swift, H. Nguyen, Z. Erdman, J. S. Kruger, V. Nikolakis and D. G. Vlachos, Tandem Lewis acid/Brønsted acid-catalyzed conversion of carbohydrates to 5-hydroxymethylfurfural using zeolite beta, *J. Catal.*, 2016, **333**, 149–161.
  - 29 C. Wang, Z. Yu, Y. Yang, Z. Sun, Y. Wang, C. Shi, Y.-Y. Liu, A. Wang, K. Leus and P. V. D. Voort, Hydrogenative ring-rearrangement of furfural to cyclopentanone over Pd/UIO-66-NO<sub>2</sub> with tunable missing-linker defects, *Molecules*, 2021, **26**, 5736.
  - 30 Z. Yu, L. Zhang, Z. Zhang, S. Zhang, S. Hu, J. Xiang, Y. Wang, Q. Liu, Q. Liu and X. Hu, Silica of varied pore sizes as supports of copper catalysts for hydrogenation of furfural and phenolics: impact of steric hindrance, *Int. J. Hydrogen Energy*, 2020, **45**, 2720–2728.
  - 31 M. Hronec and K. Fulajtárová, Selective transformation of furfural to cyclopentanone, *Catal. Commun.*, 2012, **24**, 100–104.
  - 32 T. Kim, R. S. Assary, R. E. Pauls, C. L. Marshall, L. A. Curtiss and P. C. Stair, Thermodynamics and reaction pathways of furfural alcohol oligomer formation, *Catal. Commun.*, 2014, **46**, 66–70.
  - 33 R. Gao, X. Li, L. Guo, Z. Tong, Q. Deng, J. Wang, Z. Zeng, J.-J. Zou and S. Deng, Pyrochlore/Al<sub>2</sub>O<sub>3</sub> composites supported Pd for the selective synthesis of





- cyclopentanones from biobased furfurals, *Appl. Catal., A*, 2021, **612**, 117985.
- 34 Q. Deng, R. Gao, X. Li, J. Wang, Z. Zeng, J.-J. Zou and S. Deng, Hydrogenative ring-rearrangement of biobased furanic aldehydes to cyclopentanone compounds over Pd/pyrochlore by introducing oxygen vacancies, *ACS Catal.*, 2020, **10**, 7355–7366.
- 35 Z. Tong, R. Gao, X. Li, L. Guo, J. Wang, Z. Zeng, Q. Deng and S. Deng, Highly controllable hydrogenative ring rearrangement and complete hydrogenation of biobased furfurals over Pd/La<sub>2</sub>B<sub>2</sub>O<sub>7</sub> (B = Ti, Zr, Ce), *ChemCatChem*, 2021, **13**, 4549–4556.
- 36 T. W. van Deelen, C. H. Mejia and K. P. de Jong, Control of metal-support interactions in heterogeneous catalysts to enhance activity and selectivity, *Nat. Catal.*, 2019, **2**, 955–970.
- 37 S. Riyapan, Y. Boonyongmaneerat, O. Mekasuwandumrong, P. Praserttham and J. Panpranot, Effect of surface Ti<sup>3+</sup> on the sol-gel derived TiO<sub>2</sub> in the selective acetylene hydrogenation on Pd/TiO<sub>2</sub> catalysts, *Catal. Today*, 2015, **245**, 134–138.
- 38 J. Lee, S. P. Burt, C. A. Carrero, A. C. Alba-Rubio, I. Ro, B. J. O'Neill, H. J. Kim, D. H. K. Jackson, T. F. Kuech, I. Hermans, J. A. Dumesic and G. W. Huber, Stabilizing cobalt catalysts for aqueous-phase reactions by strong metal-support interaction, *J. Catal.*, 2015, **330**, 19–27.
- 39 U. Aschauer and A. Selloni, Hydrogen interaction with the anatase TiO<sub>2</sub>(101) surface, *Phys. Chem. Chem. Phys.*, 2012, **14**, 16595–16602.
- 40 M. M. Islam, M. Calatayud and G. Pacchioni, Hydrogen adsorption and diffusion on the anatase TiO<sub>2</sub>(101) surface: a first-principles investigation, *J. Phys. Chem. C*, 2011, **115**, 6809–6814.
- 41 M. Hronec, K. Fulajtárova and T. Soták, Highly selective rearrangement of furfuryl alcohol to cyclopentanone, *Appl. Catal., B*, 2014, **154–155**, 294–300.
- 42 M. Kronec, K. Fulajtarova and T. Sotak, Kinetics of high temperature conversion of furfuryl alcohol in water, *J. Ind. Eng. Chem.*, 2014, **20**, 650–655.
- 43 Y.-F. Ma, H. Wang, G.-Y. Xu, X.-H. Liu, Y. Zhang and Y. Fu, Selective conversion of furfural to cyclopentanol over cobalt catalysts in one step, *Chin. Chem. Lett.*, 2017, **28**, 1153–1158.
- 44 Y. Li, X. Guo, D. Liu, X. Mu, X. Chen and Y. Shi, Selective conversion of furfural to cyclopentanone or cyclopentanol using Co-Ni catalyst in water, *Catalysts*, 2018, **8**, 193.

