

## *Supplementary Information*

# Effect of Heterogeneous Acid-Base Catalysis on Conversion of 5-Hydroxymethylfurfural into A Cyclopentanone Derivative

J. Ohyama,<sup>a,b\*</sup> R. Kanao,<sup>a</sup> Y. Ohira,<sup>a</sup> and A. Satsuma<sup>a,b\*</sup>

<sup>a</sup> Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan

<sup>b</sup> Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, Katsura, Kyoto 615-8520, Japan.

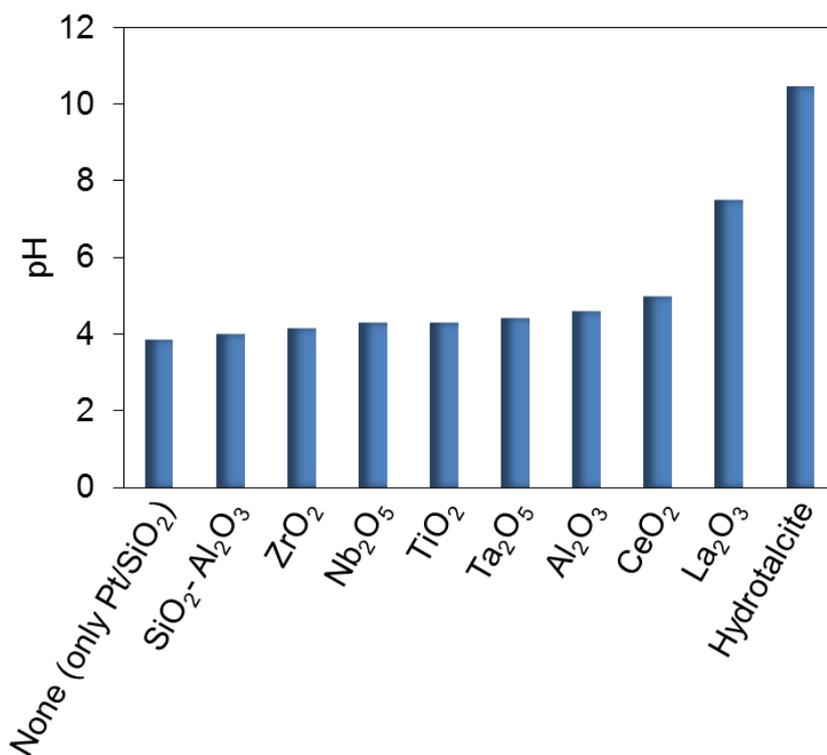
## Experimental

**Material.** Ta<sub>2</sub>O<sub>5</sub>, Nb<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O, CeO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub> and hydrotalcite were obtained from Kojundo Chemical Laboratory Co. Ltd., CBMM, Rhodia, Kishida Chemical Co., Ltd., and Kyowa Chemical Industry Co. Ltd., respectively. SiO<sub>2</sub> (JRC-SIO-5), ZrO<sub>2</sub> (JRC-ZRO-5), TiO<sub>2</sub> (JRC-TIO-8), Al<sub>2</sub>O<sub>3</sub> (JRC-ALO-8), SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (JRC-SAH-1), were supplied from Catalysis Society of Japan. All of the above metal oxides were calcined at 500°C before use. Pt(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>·4H<sub>2</sub>O and 2,5-Hydroxymethylfurfural (HMF) were purchased from Mitsuwa Chemical Co. Ltd. and Tokyo Chemical Industry Co., Ltd., respectively. The other chemicals were purchased from Kishida Chemical Co., Ltd.

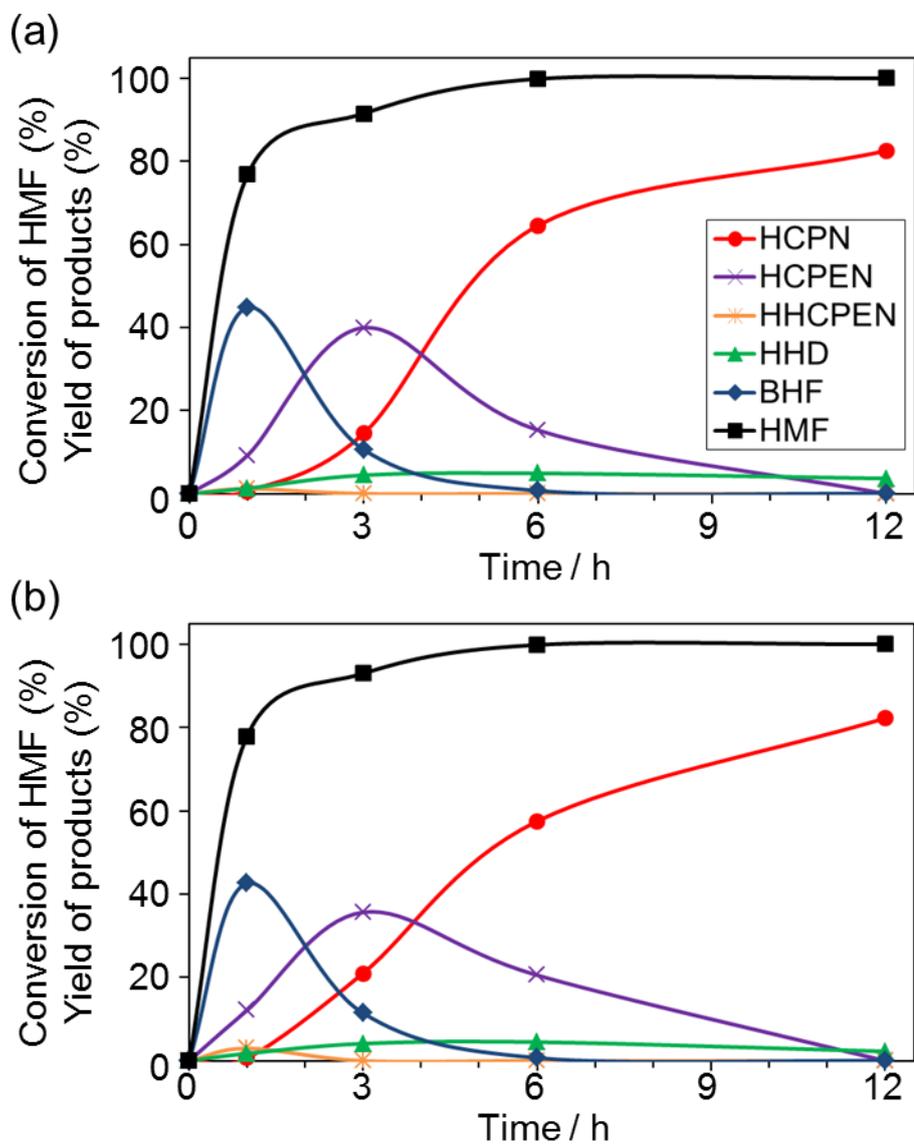
**Catalyst preparation.** Pt/SiO<sub>2</sub> (1 wt% of Pt loading) was prepared by an impregnation method. A suspension composed of Pt(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>·4H<sub>2</sub>O (0.0090 g), SiO<sub>2</sub> (0.495 g), and water (50 mL) was stirred for 1 h at room temperature, and then the water was evaporated at 60°C. The remaining solid was dried at 80°C overnight, and calcined at 300°C under air for 3 h to obtain Pt/SiO<sub>2</sub>. For comparison, Au/Nb<sub>2</sub>O<sub>5</sub> was prepared by a deposition precipitation method as reported previously.<sup>1</sup>

**Catalytic test.** Prior to catalytic tests, Pt/SiO<sub>2</sub> was pretreated under H<sub>2</sub> at 200°C. Subsequently, Pt/SiO<sub>2</sub> was treated under O<sub>2</sub> at 200°C, since our previous study suggested that the O<sub>2</sub> treatment of supported Pt catalysts is effective for selective hydrogenation of HMF to BHF.<sup>1</sup> The treated Pt/SiO<sub>2</sub> (10 mg), a metal oxide (10 mg), and an aqueous solution of HMF (0.067 M, 3 mL) were added to an autoclave with a gas in- and outlet (30mL, Taiatsu Techno Co., TVS-1 type). The reactor was pressurized with 3 MPa of H<sub>2</sub> after 5 times of replacement of air in an autoclave by ca. 1 MPa of H<sub>2</sub>. The reaction was carried out at 140°C for 12 h. The reaction solution was analyzed using a gas chromatograph (SHIMADZU GC-8A) equipped with FID with Ultra ALLOY+-5 capillary column (Frontier Laboratories Ltd.) and GC-MS (SHIMADZU-QP5000) with Rtx-5 capillary column.

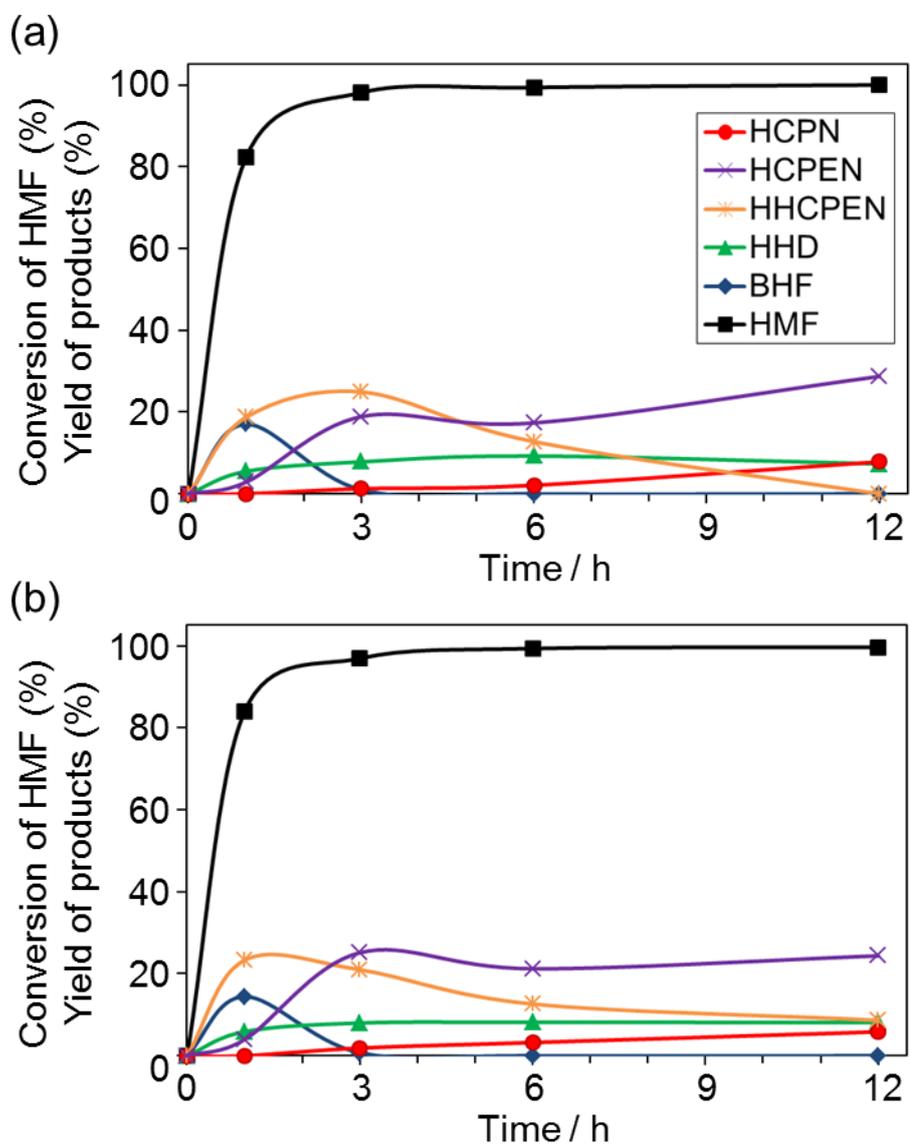
**FT-IR spectroscopy.** FT-IR spectra of the metal oxides were taken on a JASCO FT/IR-6100 (JASCO Co.) equipped with DLATGS and MCT detectors with a spectral resolution of 4 cm<sup>-1</sup>. A metal oxide (30-200 mg) was pressed into a wafer with 20 mm diameter. In the case of Ta<sub>2</sub>O<sub>5</sub>, Nb<sub>2</sub>O<sub>5</sub>, ZrO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, and CeO<sub>2</sub>, the wafer was pretreated under 10%O<sub>2</sub>/Ar flow (100 mL min<sup>-1</sup>) at 200°C for 10 min, and a FT-IR spectrum was recorded as background. Then, the wafer was exposed to pyridine vapor (12.4 μmol) under Ar flow (90 mL min<sup>-1</sup>) at 150°C. After 15 min, a FT-IR spectrum of adsorbed pyridine was recorded. In the case of La<sub>2</sub>O<sub>3</sub> and hydrotalcite, the wafer was pretreated under 10%H<sub>2</sub>/Ar flow (100 mL min<sup>-1</sup>) at 670°C (to remove carbonate species on surface). The wafer was exposed to pyridine vapor (24.8 μmol) under Ar flow (90 mL min<sup>-1</sup>) at r.t. for 10 min and a FT-IR spectrum was recorded.



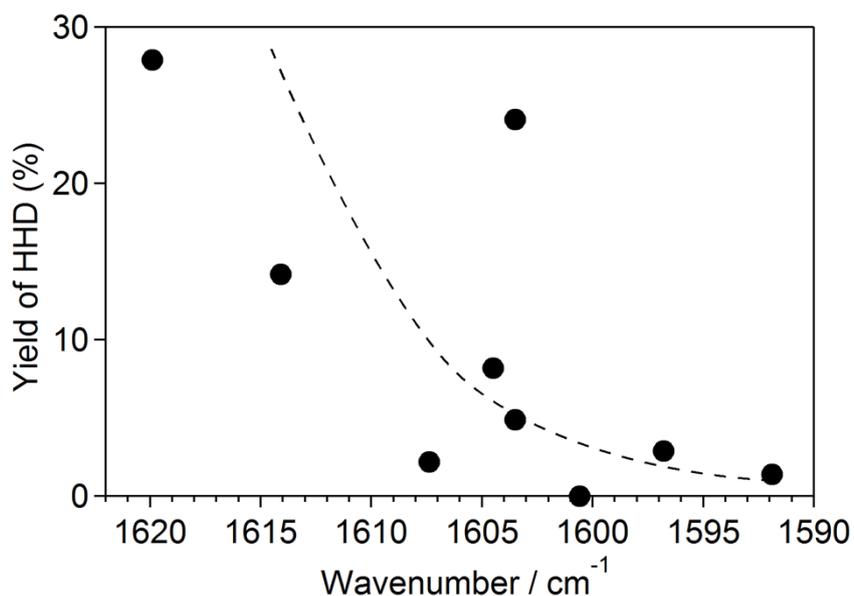
**Fig. S1.** The pH of the reaction solution with various catalysts. The pH of the solution in the presence of Ta<sub>2</sub>O<sub>5</sub>, Nb<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, and CeO<sub>2</sub> with Pt/SiO<sub>2</sub> (the pH = 4 - 5) did not significantly change from the pH in the presence of only Pt/SiO<sub>2</sub> (the pH = ca. 4). On the other hand, when adding La<sub>2</sub>O<sub>3</sub> and hydrotalcite, the pH increased from that of the reaction solution with Pt/SiO<sub>2</sub>. Although the pH did not significantly change by addition of Ta<sub>2</sub>O<sub>5</sub>, Nb<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, the yield of HCPN largely increased. Furthermore, the addition of La<sub>2</sub>O<sub>3</sub> caused an increase of the yield of HCPN (and also the total of product of the cyclization (HCPN+HCPEN)) in spite of the increase of the pH. It is suggested that another factor than the pH (ca. 4 - 8), that is, the Lewis acid on metal oxide surface, is important for production of HCPN. On the other hand, the pH in the presence of hydrotalcite was much larger (pH = ca. 11) than that in the presence of Pt/SiO<sub>2</sub>, and the yield of HCPN (and the total of product of the cyclization (HCPN+HCPEN)) was smaller than that in the presence of Pt/SiO<sub>2</sub>. In addition, the reaction using hydrotalcite gave 1,2,6-hexanetriol, which can be produced through total hydrogenation of BHF and following hydrogenolysis.<sup>2</sup> The result suggests that the high pH of the solution (ca. 11) or the surface strong base sites of hydrotalcite lead the different reaction path of BHF.



**Fig. S2.** Duplicate catalytic tests using  $\text{Pt/SiO}_2$  and  $\text{Ta}_2\text{O}_5$ . The differences in the conversions and yields between (a) and (b) are indicated in Fig. 2(a) by error bars.



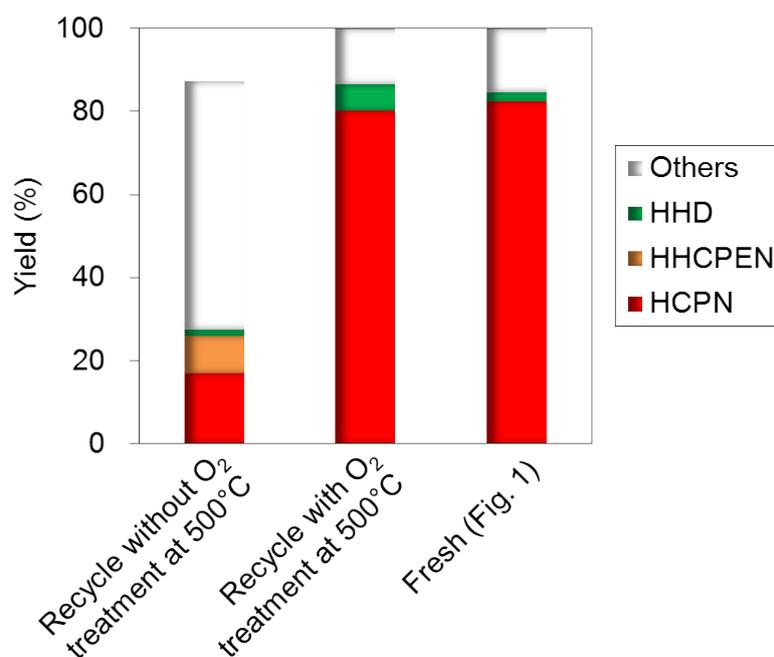
**Fig. S3.** Duplicate catalytic tests using only Pt/SiO<sub>2</sub>. The differences in the conversions and yields between (a) and (b) are indicated in Fig. 2(a) by error bars.



**Fig. S4.** Plot of the HHD yields (Fig. 1) against the peak wavenumbers of adsorbed pyridine ( $\nu_{8a}$ ) at around 1610  $\text{cm}^{-1}$  (Fig. 3). There is a tendency to increase the yield of HHD as the peak wavenumber increases. The result indicates that the yield of HHD increases with the acid strength. Based on Scheme 1, the high yield of HHD can be explained by decrease of the reaction rate of HHED to HHCPEN, because it will relatively increases the hydrogenation rate of HHED to HHD on Pt/SiO<sub>2</sub>. The decrease of the reaction rate of HHED to HHCPEN might be due to the poisoning of the strong acid sites by humins.<sup>3</sup> The poisoning can also explain the remaining intermediate (HCPEN) on Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (Fig. 1), because the poisoning of acid sites decreases the rate of the ring-rearrangement reaction.

### Recycle test

After the reaction using Pt/SiO<sub>2</sub> and Ta<sub>2</sub>O<sub>5</sub>, the suspension was filtered off, and the residue was washed with 50 mL of water for three times. After dryness at 80°C, the resulting catalyst was used for the reaction after the treatment at 200°C under H<sub>2</sub> for 10 min and O<sub>2</sub> for 10min as is the case with the fresh catalyst. On the other hand, the used and washed catalyst was treated at 500°C under O<sub>2</sub>.for 60 min. Then, the catalyst was used for the reaction after the treatment at 200°C under H<sub>2</sub> for 10 min and O<sub>2</sub> for 10min. The results of the recycle tests are shown in Fig. S5. The recycled catalyst without treatment at 500°C showed 17% of HCPN yield, which is ca. 1/5 of the HCPN yield on the fresh catalyst (Fig. 1). But, the recycled catalyst with treatment at 500°C showed higher yield of HCPN (80%) compared to that without the treatment, and the HCPN yield was almost the same as the fresh catalyst (82%). Therefore, the O<sub>2</sub> treatment at 500°C regenerates the catalyst. Based on the results, it is possible that poisoning of the catalyst by humins generated under the reaction decreases the catalytic activity, and the humins can be removed by the O<sub>2</sub> treatment at 500°C to regenerate the catalytic activity.



**Fig. S5.** Results of the reaction on the used catalyst (Pt/SiO<sub>2</sub> + Ta<sub>2</sub>O<sub>5</sub>), together with that on the fresh catalyst shown in Fig. 1 for comparison.

### References

1. J. Ohyama, R. Kanao, A. Esaki and A. Satsuma, *Chem. Commun.*, 2014, **50**, 5633.
2. Yao, S.; Wang, X.; Jiang, Y.; Wu, F.; Chen, X.; Mu, X. *ACS Sustain. Chem. Eng.*, 2014, **2**, 173.
3. A. Takagaki, S. Nishimura, K. Ebitani, *Catal. Surv. Asia*, 2012, **16**, 164.