# **Electronic Supporting Information (ESI)**

# Pentanoic Acid from γ-Valerolactone and Formic Acid using Bifunctional Catalysis

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## **Experimental section**

#### Materials

Formic acid (98-100%) was purchased from *Merck Millipore*. Zeolites *i.e.*, ZSM-5 (CBV2314, CBV8014, CBV5524G and CBV28014), Beta (CP814E) and USY (CBV 760 and CBV 780) were supplied by *Zeolyst*. Each from abovementioned zeolite have been given a code according to its Si/Al ratio as the following: ZSM-5(11, 24, 42 and 146), Beta (12) and USY (6 and 30).  $\gamma$ -Valerolactone ( $\geq$ 99%), 2, 3, and 4-pentanoic acid ( $\geq$ 99%), tetraammineplatinum(II) nitrate (Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>) (99.99%), hydrofluoric acid (48%), hydrochloric acid (37%), nitric acid (70%), Platinum on Carbon and boric acid (99.5%) were obtained from *Sigma-Aldrich*. All chemicals were used as received without further purification.

## Catalysts preparation and characterization

The supported 2.0 wt.-% Pt on the above mentioned ZSM-5, Beta and USY zeolite were prepared via incipient wetness impregnation (IWI). In this regard, appropriate amount of  $Pt(NH_3)_4(NO_3)_2$  was dissolved in a certain volume of deionized water equal to the pore volume of the parent ZSM-5, Beta and USY. Afterwards, the metal precursor solution was added dropwise to the support material with continuous stirring until a slurry was formed, followed by drying at 333 K in static air. Prior the calcination and activation steps, 0.8 g of catalyst powders

were pelletized using hydraulics press, crushed, and sieved in range of 500–250  $\mu$ m pellets in order to ensure a homogeneous gas flow through the sample during calcination and reduction steps. Later, 0.8 g of catalysts powders were calcined at 573 K with heating ramp of 1 K min<sup>-1</sup> for 3 h in flow of 0.02 L min<sup>-1</sup> of O<sub>2</sub>. Before the reaction, the catalysts were activated via reduction step at 573 K with heating ramp of 1 K min<sup>-1</sup> for 3 h in flow of 0.02 L min<sup>-1</sup> of N<sub>2</sub> (95%) and H<sub>2</sub> (5%).

The abovementioned prepared catalysts were characterized N<sub>2</sub>-sorption, XRD, elemental analysis via ICP-OES, NH<sub>3</sub>-TPD, TEM and H<sub>2</sub>-chemisorption.

 $N_2$ -physisorption isotherms were determined by using a Micromeritics Tristar II instrument at 77 K. Samples were degassed prior the analysis under  $N_2$  flow at 573 K for 6 h. The specific surface areas ( $S_{BET}$ ) were determined using Brunauer–Emmett–Teller (BET) model. The t-plot method was used to discriminate between micro- and mesoporosity. The total pore volume ( $V_p$ ) was estimated from the  $N_2$  uptake at a relative pressure (p  $p_0^{-1}$ ) of 0.99. The pore width distribution ( $d_p$ ) was calculated from the desorption branch using the Barrett-Joyner-Halenda (BJH) method.

NH<sub>3</sub>-TPD was performed using a U-type quartz glass microreactor. The evolved gases were analyzed with a quadrupole mass spectrometer (Pfeiffer GSD 301). Prior to the analysis, the catalysts were pretreated in He (0.03 L min<sup>-1</sup>) at 523 K for 1 h. After cooling to 368 K, the catalyst samples were loaded with six consecutive pulses of NH<sub>3</sub> (0.001 L for each pulse) were employed to reach complete saturation adsorption on the surface of the catalyst. Physisorbed NH<sub>3</sub> was removed by flowing He (0.03 L min<sup>-1</sup>) until no NH<sub>3</sub> could be detected in the effluent. Afterwards, the samples were heated up to 823 K (heating rate: 10 K min<sup>-1</sup>) in the same He flow while analyzing the amount of desorbed NH<sub>3</sub> by MS (m/z = 16). The total number of acid sites (µmol NH<sub>3</sub> g<sup>-1</sup> of parent zeolite or 2 wt.-% Pt supported on the above mentioned zeolite) was determined from the total amount of desorbed NH<sub>3</sub> by correlating the integrated peak area of the desorbed NH<sub>3</sub> from the catalyst samples to a the integrated peak area of reference test, *i.e.*, pulsing 0.001 L of NH<sub>3</sub> over 50.0 mg of inert quartz.

The metal content was determined by optical emission spectroscopy with inductively coupled plasma (ICP-OES) using a Vario EL-Heraeus microanalyzer. Sample preparation was done as the following: (0,005 g) of the Pt/zeolite was mixed with nitro-hydrochloric acid (each acid volume was 0.003 L) and HF (0,002 L) in a polytetrafluorethene bottles. This mixture was kept at room temperature for 1 h. Subsequently, the mixture was transferred to a polytetrafluorethene flask, and bi-distilled water (0.01 L) and boric acid (2.8 g) were added. When the boric acid was dissolved completely, the solution was diluted with water and homogenized.

The morphology of selected samples were characterized using a transmission electron microscopy (TEM, JEOL-2100F, Japan) at 200 kV accelerating voltage, and the elemental mappings of the catalysts were carried out by energy dispersive spectroscopy (EDS) attached to TEM.

 $H_2$ -Chemisorption analysis was conducted in an AutoChem II 2920, USA with U-shape tube quartz reactor with a thermal conductivity detector (TCD).  $H_2$  was firstly pulsed into the tube until it reached saturated adsorption. Finally, desorption procedure was conducted with the temperature increased (10 K min<sup>-1</sup>).

Thermogravimetric analysis (TGA) was performed with a STA409 instrument from Netzsch in order to evaluate the mass loss in used 2.0Pt/H-ZSM-5(11). For the measurement, 50.0 mg of the sample was heated to 850 K with a heating ramp of 10 K min<sup>-1</sup> in a dynamic stream of air (75 cm<sup>3</sup> min<sup>-1</sup>).

Catalytic hydrogenation of γ-valerolactone to pentanoic acid and the one-pot aqueous-phase conversion of levulinic acid to pentanoic acid using formic acid as a reducing agent

All reactions were carried out in a 0.1 L stainless steel batch reactor with head stirrer (Model # 4560), as well as an external temperature, and stirring speed controller (Model # 4848) from *Parr Instruments Company*. Typically, the catalytic experiments were conducted by suspension of 0.8 g of the reduced catalyst in 5.0 g of each GVL (1.2 mol L<sup>-1</sup>), FA (2.7 mol L<sup>-1</sup>) in 0.04 L of

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distilled water at 543 K with stirring speed of 400 rpm under autogenous pressure. Prior to each catalytic experiment, the air was purged out of the reactor by flowing 0.6 MPa of N<sub>2</sub> for 3 times. Sample from the suspension were withdrawn periodically, *i.e.*, at 0 (when the desired temperature was reached) and after 3, 6, 12 and 24 h. Reaction products were analyzed by <sup>1</sup>H-NMR using a Bruker Avance 400 spectrometer with autosampler. The samples for <sup>1</sup>H-NMR analysis were prepared by addition of 0.0007 L of dimethyl sulfoxide-d6 (DMSO-d6) and 0.1 g of tetramethylsilane (TMS) as an internal standard to  $2 \times 10^{-5}$  dm<sup>3</sup> of the withdrawn sample in an NMR tube. In order to calculate the conversion of GVL (eqs. 1 and 2), as well as yield of PA (eqs. 3). The conversion of GVL and FA was calculated by correlating the integral of the TMS (internal standard) peak to the GVL and FA peak. For this purpose, the peak area was integrated of the compounds as a function of reaction time (0, 3, 6, 12 and 24 h), *i.e.*, –CH<sub>3</sub> in GVL (doublet at chemical shift: 1.25 ppm and 1.27 ppm), single proton (-H) at FA (singlet at chemical shift: 8.10 ppm), respectively. Similarly, PA yield was calculated by correlating the integral of the TMS (internal standard) peak to PA peak as a function of reaction time (0, 3, 6, 12 and 24 h), *i.e.*, –CH<sub>3</sub> in PA (triplet at chemical shift: 0.74 ppm, 0.76 ppm and 0.78 ppm).

**Caution:** It is worth to mention here that activity observed in the absence of catalysts may be due to presence of minor amounts of leached Pt that remain deposited on the wall of the reactor and hard-to-reach cavities in the reactor set-up, and therefore not completely removed, not even after several washing steps prior to the start of a new experiment. Additionally, the reaction conditions (pH = 1.9) at elevated temperature (543 K) may also lead to metals leaching from wall material of the stainless steel reactor (stainless steel type 316), *i.e.*, Fe, Ni, Cr and Mo, which are within the composition of the reactor material. However, the amount of these metals was not quantified in this work.

The one-pot aqueous-phase upgrading of levulinic acid were conducted by suspension of 0.8 g of the reduced catalyst in 5 g of each LA (1.0 mol  $L^{-1}$ ), FA (2.7 mol  $L^{-1}$ ) in 0.04 L of distilled water

at 543 K with stirring speed of 400 min<sup>-1</sup> under autogenous pressure. The quantification of the reaction mixture were done simillar to the above mentioned procedure.

Conversion of 
$$GVL = \frac{M_{0,GVL} - M_{t,GVL}}{M_{0,GVL}} \times 100$$
 (1)

Conversion of 
$$LA = \frac{M_{0,LA} - M_{t,LA}}{M_{0,LA}} \times 100$$
 (2)

Conversion of FA = 
$$\frac{M_{0,FA} - M_{t,FA}}{M_{0,FA}} \times 100$$
 (3)

Yield of 
$$PA = \frac{M_{t, PA}}{M_{theoretical, PA}} \times 100$$
 (4)

 $M_{0,GVL and FA}$ : initial GVL and FA mass fraction,  $M_{t PA}$ : PA mass fraction at specific reaction time and  $M_{theoretical, PA}$ : mass fraction calculated based on reaction stoichiometry.

For the reusability experiment, The catalyst were filtered and washed or 5 times using distilled  $H_2O$ . Finally, the washed catalyst was dried at 373 K and used again in the aqueous-phase hydrogenation of GVL to PA in the presence of FA as a reducing agent using the abovementioned procedure.

#### **Catalyst Characterization**



**Figure S1.** N<sub>2</sub> sorption isotherms for Pt catalysts supported on USY(30), USY(6), Beta(12) and ZSM-5(11). For clarity, isotherms were vertically displaced by 100 cm<sup>3</sup> g<sup>-1</sup>, respectively.



**Figure S2.** N<sub>2</sub> sorption isotherms for Pt catalysts supported on ZSM-5(146), ZSM-5(42), ZSM-5(24) and ZSM-5(11). For clarity, isotherms were vertically displaced by 80 cm<sup>3</sup> g<sup>-1</sup>, respectively.



Figure S3. TEM images for the catalysts (A) 0.5Pt/ZSM-5(11), (B)2.0Pt/ZSM-5(11) and (C) 4.7Pt/ZSM-5(11).



**Figure S4.** XRD patterns for fresh Pt catalysts supported on USY(30), USY(6), Beta(12) and ZSM-5(11).



**Figure S5.** XRD patterns for Pt catalysts supported on USY(30), USY(6), Beta(12) and ZSM-5(11) after it have been used in the aqueous-phase hydrogenation of GVL to PA in the presence of FA as a reducing agent; reaction conditions:  $C_{\text{GVL}} = 1.2 \text{ mol } \text{L}^{-1}$ ,  $C_{\text{FA}} = 2.7 \text{ mol } \text{L}^{-1}$ ,  $V_{\text{reactant}} = 0.05 \text{ L}$ , T = 543 K,  $m_{\text{catalyst}} = 0.8 \text{ g}$ , N = 400 rpm,  $t_{\text{reaction}} = 24 \text{ h}$ .



Figure S6. NH<sub>3</sub>-TPD profiles for fresh and spent 2.0Pt/ZSM-5(11).





**Figure S7**. GVL and FA conversion (top and middle) and PA yield (bottom) as a function of reaction time with no catalyst, ZSM-5(11), 0.5Pt/ZSM-5(11), 2.0Pt/ZSM-5(11) and 4.7Pt/ZSM-5(11) in the aqueous-phase hydrogenation of GVL to PA in the presence of FA as a reducing agent; reaction conditions:  $c_{GVL} = 1.2 \text{ mol } L^{-1}$ ,  $c_{FA} = 2.7 \text{ mol } L^{-1}$ ,  $V_{reactant} = 0.05 \text{ L}$ , T = 543 K,  $m_{catalyst} = 0.8 \text{ g}$  and N = 400 rpm and  $t_{reaction} = 24 \text{ h}$ .



**Figure S8**. GVL conversion (top) and PA yield (bottom) as function of reaction time over 2.0Pt/ZSM-5(11) in the aqueous-phase hydrogenation of GVL to PA in the presence of FA as a reducing agent; reaction conditions:  $c_{GVL}$  = 1.2 mol L<sup>-1</sup>,  $c_{FA}$  = 2.7 mol L<sup>-1</sup>,  $V_{reactent}$  = 0.05 L, T = 543 K,  $m_{catalyst}$  = 0.8 g, N = 200, 400, 600 and 800 rpm and  $t_{reaction}$  = 24 h.



**Figure S9**. GVL conversion (top) and PA yield (bottom) as a function of reaction time over 2 wt.-% Pt catalysts supported on four different ZSM-5(11, 24, 42 and 146) in the aqueous-phase hydrogenation of GVL to PA in the presence of FA as a reducing agent; reaction conditions:  $C_{GVL}$ = 1.2 mol L<sup>-1</sup>,  $C_{FA}$  = 2.7 mol L<sup>-1</sup>,  $V_{reactant}$  = 0.05 L, T = 543 K,  $m_{catalyst}$  = 0.8 g, N = 400 rpm and  $t_{reaction}$  = 24 h.



**Figure S10**. GVL conversion (top) and PA yield (bottom) as function of reaction time over 2.0Pt/ZSM-5(11) and 2.8Pt/Carbon (commercial) in the aqueous-phase hydrogenation of GVL to PA in the presence of FA as a reducing agent; reaction conditions:  $c_{GVL}$  = 1.2 mol L<sup>-1</sup>,  $c_{FA}$  = 2.7 mol L<sup>-1</sup>,  $V_{reactent}$  = 0.05 L, T = 543 K,  $m_{catalyst}$  = 0.8 g, N = 400 rpm and  $t_{reaction}$  = 24 h.





**Figure S11**. GVL and FA conversion (top and middle) and PA and LA yield (bottom) as a function of reaction time at different GVL/FA molar ratio using 2Pt/ZSM-5(11) in the aqueous-phase hydrogenation of GVL to PA in the presence of FA as a reducing agent; reaction conditions:  $C_{\text{GVL}} = 1.2 \text{ mol L}^{-1}$ ,  $C_{\text{FA}} = 0.5$ , 1.3, 2.7 and 3.8 mol L<sup>-1</sup>,  $V_{reactant} = 0.05 \text{ L}$ , T = 543 K,  $m_{\text{catalyst}} = 0.8 \text{ g}$ , N = 400 rpm and  $t_{\text{reaction}} = 24 \text{ h}$ .





**Figure S12**. GVL and FA conversion (top and middle) and PA yield (bottom) as a function of reaction time at different reaction temperature using 2Pt/ZSM-5(11) in the aqueous-phase hydrogenation of GVL to PA in the presence of FA as a reducing agent; reaction conditions:  $C_{\text{GVL}} = 1.2 \text{ mol } \text{L}^{-1}$ ,  $C_{\text{FA}} = 2.7 \text{ mol } \text{L}^{-1}$ ,  $V_{\text{reactant}} = 0.05 \text{ L}$ , T = 503 K, 523 K and 543 K,  $m_{\text{catalyst}} = 0.8 \text{ g}$ , N = 400 rpm and  $t_{\text{reaction}} = 24 \text{ h}$ .



**Figure S13.** TGA for the used Pt catalyst supported ZSM-5(11) in the aqueous-phase hydrogenation of GVL to PA in the presence of FA as a reducing agent; reaction conditions:  $C_{GVL}$  = 1.2 mol L<sup>-1</sup>,  $C_{FA}$  = 2.7 mol L<sup>-1</sup>,  $V_{reactant}$ = 0.05 L, T = 543 K,  $m_{catalyst}$  = 0.8 g, N = 400 rpm and  $t_{reaction}$  = 24 h.



**Figure S14.** XRD patterns for the fresh Pt catalysts supported ZSM-5(11), after 1<sup>st</sup> use and 2<sup>nd</sup> use in the aqueous-phase hydrogenation of GVL to PA in the presence of FA as a reducing agent; reaction conditions:  $C_{GVL}$  = 1.2 mol L<sup>-1</sup>,  $C_{FA}$  = 2.7 mol L<sup>-1</sup>,  $V_{reactant}$ = 0.05 L, T = 543 K,  $m_{catalyst}$  = 0.8 g, N = 400 rpm and  $t_{reaction}$  = 24 h.