Supplementary Information

Hydrothermal water enabling one-pot transformation of amines to alcohols via supported Pd catalysts

Lanxin Wu,[a] Yang Yang,*[a] Jiong Cheng,[a] Xiaoguang Wang,[a] Qing Huang,[b] and Fangming Jin*[a,b,c,d]

[a] School of Environmental Science and Engineering, State Key Lab of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai 200240, China

[b] College of Ecology and Environment, Hainan University, Haikou, 570228, China

[c] Center of Hydrogen Science, Shanghai Jiao Tong University, Shanghai, 200240, P.R. China

[d] Shanghai Institute of Pollution Control and Ecological Security, Shanghai 200092, P.R. China

Corresponding Authors:

* Yang Yang: +86-21-54745410, yangyang0120@sjtu.edu.cn

* Fangming Jin: +86-21-54745410, fmjin@sjtu.edu.cn

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Materials and Methods

Materials

L-Glutamic acid (99%) was supplied from Saan Chemical Technology (Shanghai) Co., Ltd.. γ-Aminobutyric acid (99%), hexylamine (99%), pentanol (99.5%), and K_2PdCl_4 (Pd≥32.6%) were obtained from Shanghai Macklin Biochemical Technology Co., Ltd.. Butyrolactone (98%) and hexanol (>99%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd., and 2-pyrrolidone (99%) was obtained from Afaisha (China) Chemical Co., Ltd.. Zinc powder (99.99%), phosphoric acid (≥99%) and propionic acid (≥99.5%) were procured from Sinopharm Chemical Reagents Co. Ltd., and sodium hydroxide (96%) was obtained from Beijing Yinuokai Technology Co., Ltd.. γ-Al_2O_3 (99.99%), ZrO_2 (99.99%), CeO_2 (99.95%), γ-Fe_2O_3 (99.99%), ZnO (99.99%), and SiO_2 (99.99%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd., and active carbon (>98%) was bought from Shanghai Macklin Biochemical Technology Co., Ltd.. Ar (99.9995%, 50 L) and N_2 (99.99%, 50 L) were procured from Air Liquide (Shanghai) Compressed Gas Co., Ltd.. All chemical reagents were used as received without further treatment and aqueous solutions were prepared using deionized water with a resistivity of 18.25 $M\Omega \cdot cm^{-1}$.

Experimental procedures

The transformation of amines to alcohols were performed in a series of SUS 316 tubular reactor, which are stainless-steel reactors with a cap at each end (the inner column is 5.7 mL). The schematic diagram and details of the reactor can be found in our previous reports [s1]. In a typical procedure, hexylamine, γ-aminobutyric acid or glutamic acid (0.1 $mol \cdot L^{-1}$) was added into the reactor. For the reaction with hexylamine, Zn (0.1 g) and Pd/C (0.1 g) were also added, and for the reaction with glutamic acid, Pd based catalyst (0.1 g) was added. Subsequently, H_2O (2.85 mL) was introduced to the reactor. The reactor was sealed and then immersed in a preheated salt bath at desired temperature for preset time. When the reaction was over, the reactor was rapidly cooled in room-temperature water, and samples were collected for further analysis. All the experiments were repeated for 3 times.

Analysis of reaction samples

Liquid samples were analyzed by an Agilent 7890A gas chromatography-mass spectrometry (GC-MS), which was equipped with an HP-INNOWAX column (30 m × 0.25 mm × 0.25 μm) and tested by a 5975C inert MSD with Triple-Axis detector. During the test, temperatures of inlet and detector were kept at 220 °C and 240 °C, respectively, and the temperature program of the oven was from 40 °C (maintaining for 1 min) to 230 °C at a ramp of 7 °C/min. Meanwhile, liquid samples were quantified by gas chromatography-flame ionization detector (GC-FID), using the external standard method based on the average values of at least three parallel experiments. A Hewlett-Packard model 5890 Series II GC system equipped with a flame ionization detector (FID) was used. The samples separation was achieved with an Agilent 19091N-233HP-INNOWax Polyethylene Glyco column (30 m x 250 μm x 0.5 μm), and He at a flow rate of 1 mL/min was used as the carrier gas. The program procedures for oven operation were the same to GC-MS analysis.

Synthesis of Pd-based catalyst

Pd/support (support = SiO_2/ ZrO_2/ CeO_2/ γ-Al_2O_3/ ZnO/ active carbon) catalysts were synthesized through the following procedure. Typically, a certain amount of support was added into the water (50 ml) under continuous stirring with a rate of 500 r/min at room temperature for 1 h. Then K_2PdCl_4 was added into the mixture and stirred at the same rate for 6 h to form the precursor. Next, 0.5 $mol \cdot L^{-1}$ KOH solution was added to the suspension drop by drop until the pH became 10.0 and then $NaBH_4$ solution was slowly added to reduce the Pd ions for 2 h. Finally, the suspension was washed by suction filter with 50 mL deionized water for several times to become neutral, and then the acquired solids were dried in a lyophilizer overnight. All the catalysts were synthesized with 5 wt.% metal loading.

Analysis of Pd-based catalysts

The metal phases of the catalysts were determined by XRD using a Rigaku D/max2550V with Cu-Kα radiation at room temperature. The X-ray tube was operated at 40 kV and 30 mA, and the X-ray diagram was scanned in the 2θ range from 10° to 80°. XPS was performed using a Thermo ESCALAB 250Xi with monochromatic Al-Kα radiation by the Thermo Fisher Scientific to investigate the structure and valence states of the metals. The nanostructure and distribution of the catalysts were investigated using transmission electron microscopy (TEM; JEM-2100F) with an accelerating voltage of 200 kV, and scanning electron microscopy (SEM, Sirion 200).

Supplementary Figures

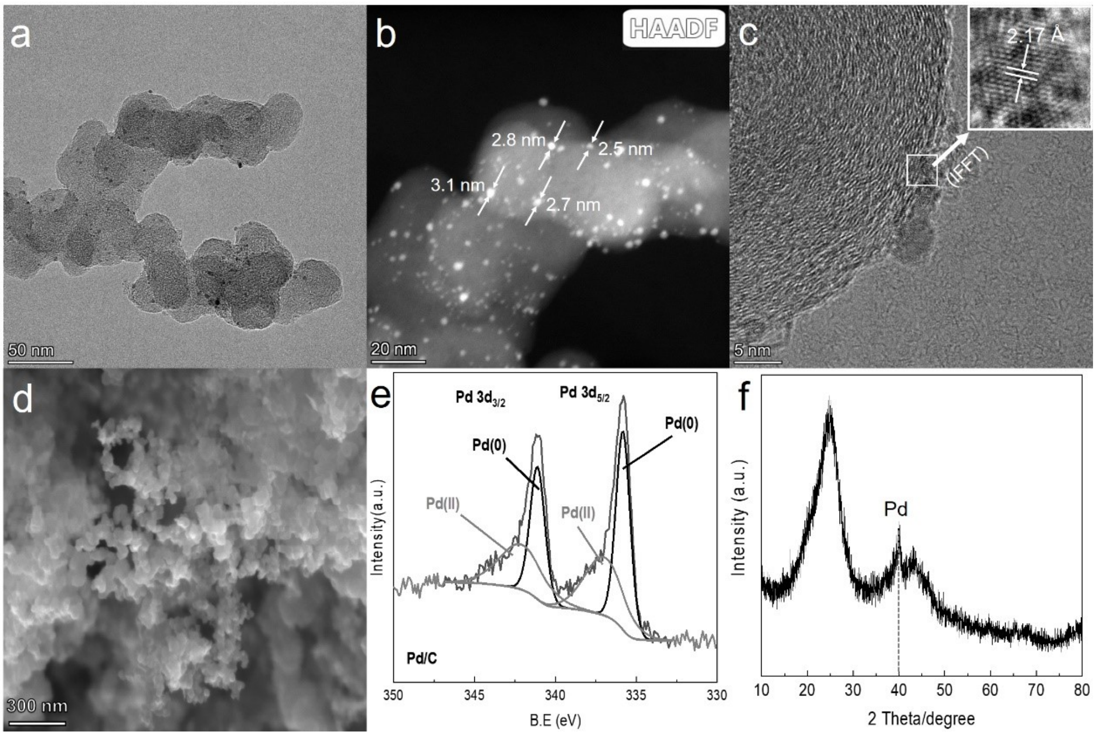

Fig. S1 TEM (a), HADDF-STEM (b), HRTEM image (c), SEM (d), XPS (e) and XRD (f) of the as-synthesized Pd/C catalyst.

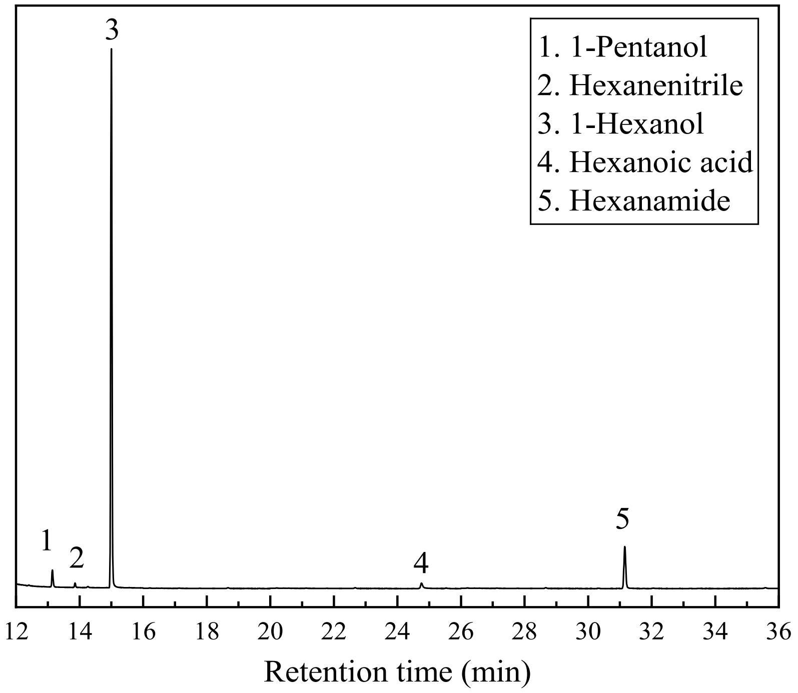

Fig. S2 GC-MS spectrum of hydrothermal conversion of hexylamine (Reaction conditions: 0.1 mol·L^{-1} hexylamine, 0.1 g 5% Pd/C, 0.1 g Zn, 50% water filling, 2 h, 300 °C).

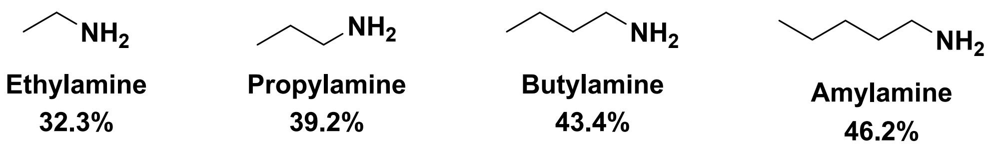

Fig. S3 The yields of corresponding alcohols from aliphatic amines (Reaction conditions: 0.1 mol·L^{-1} aliphatic amine, 0.1 g 5% Pd/C, 0.1 g Zn, 50% water filling, 300 °C, 2 h).

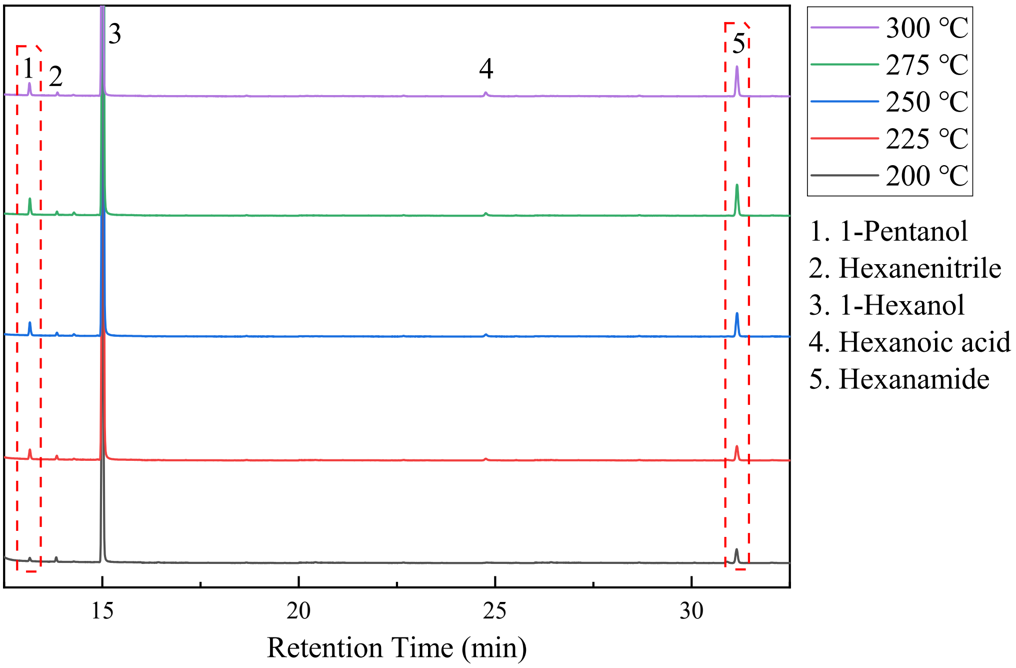

Fig. S4 GC-MS spectra of hydrothermal conversion of hexylamine as the function of reaction temperature (Reaction conditions: 0.1 mol·L^{-1} hexylamine, 0.1 g 5% Pd/C, 0.1 g Zn, 50% water filling, 2 h).

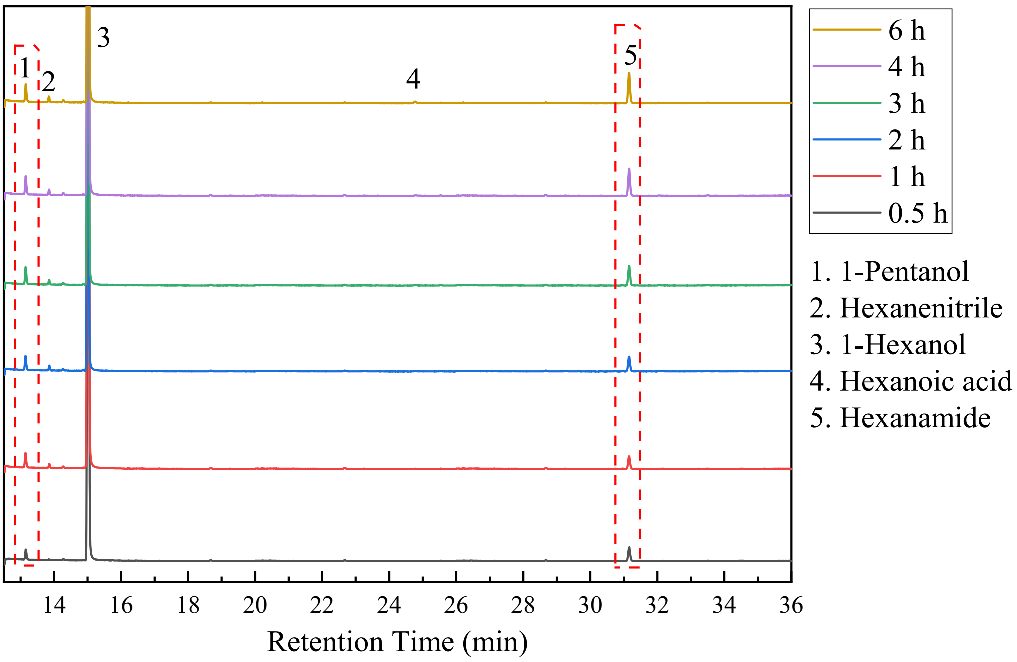

Fig. S5 GC-MS spectra of hydrothermal conversion of hexylamine as the function of reaction time (Reaction conditions: 0.1 mol·L^{-1} hexylamine, 0.1 g 5% Pd/C, 0.1 g Zn, 50% water filling, 225 °C).

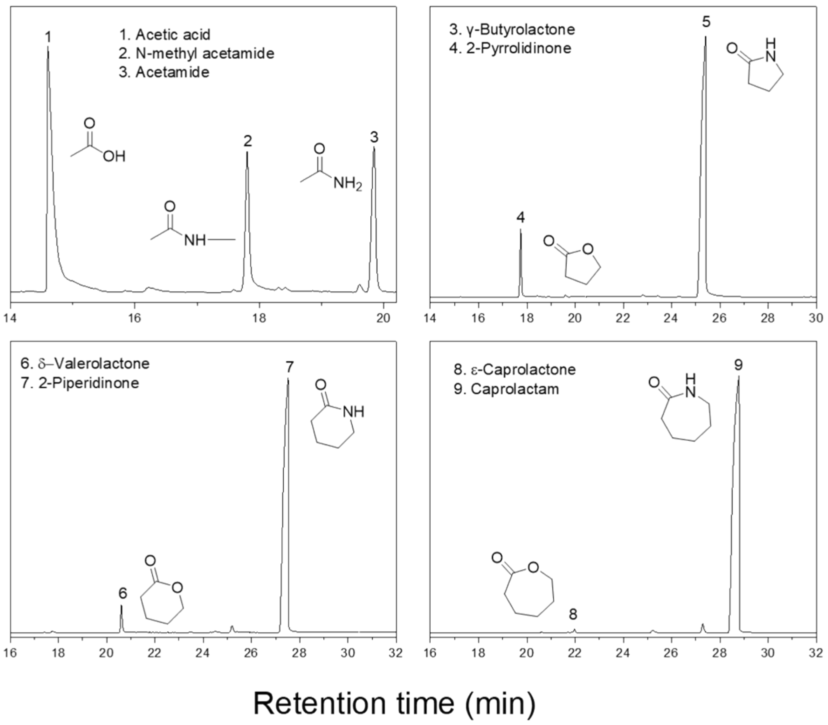

Fig. S6 GC-MS spectrum of hydrothermal conversion of β-aminopropanoic acid, γ-aminobutyric acid, 5-aminopentanoic acid and 6-aminohexanoic acid (Reaction conditions: 0.1 mol·L^{-1} reactant, 50% water filling, 1 h, 300 °C).

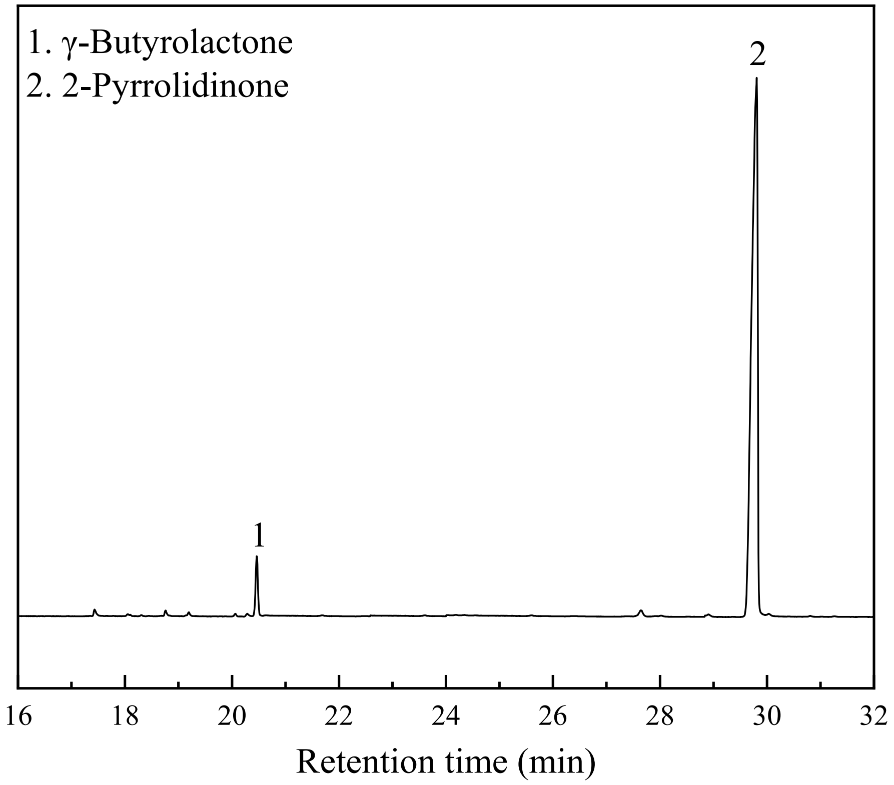

Fig. S7 GC-MS spectrum of hydrothermal conversion of glutamic acid (Reaction conditions: 0.1 mol·L^{-1} glutamic acid, 50% water filling, 3 h, 300 °C).

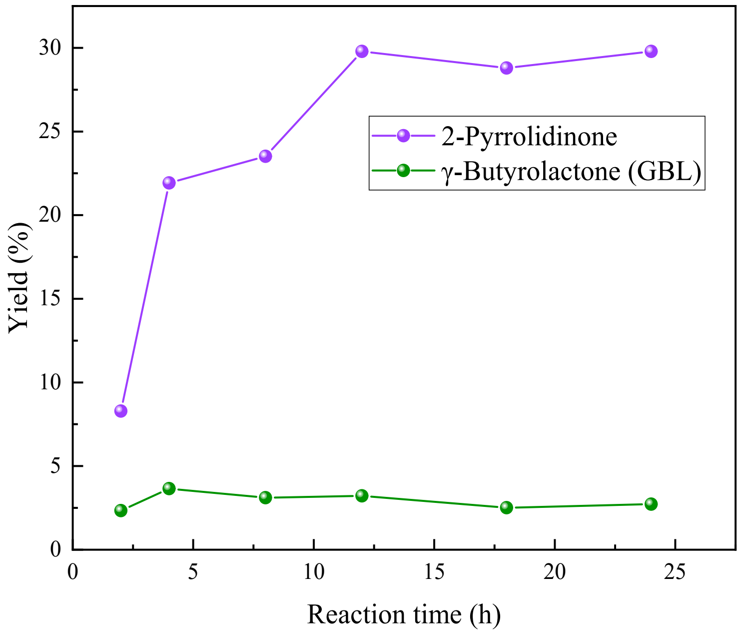

Fig. S8 The variation of γ-butyrolactone (GBL) and 2-pyrrolidinone yields with reaction time in the hydrothermal conversion of glutamic acid (Reaction conditions: 0.1 mol·L^{-1} glutamic acid, 50% water filling, 300 °C).

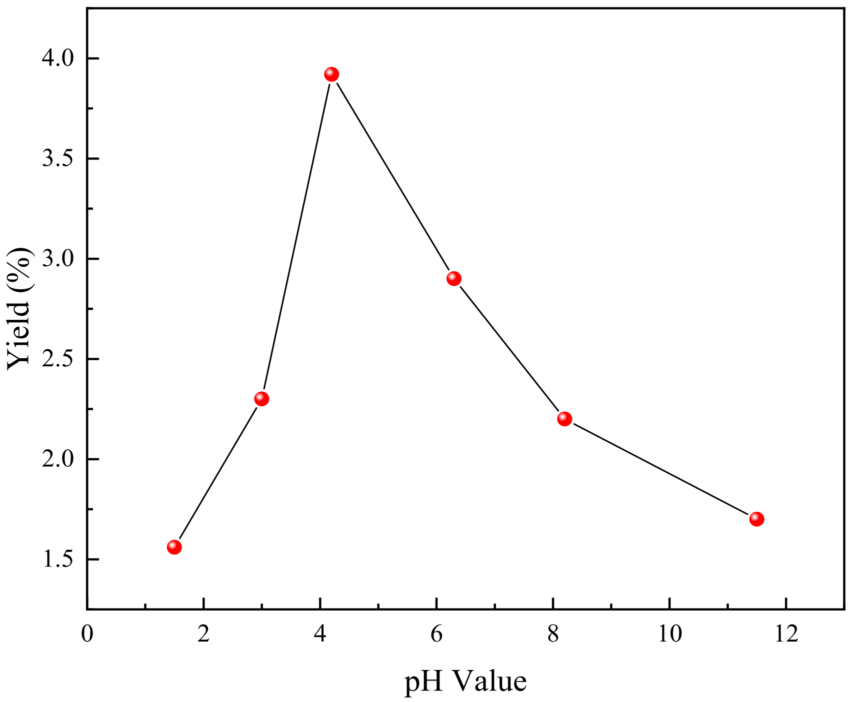

Fig. S9 The variation of γ-butyrolactone (GBL) yield with pH in the hydrothermal conversion of glutamic acid (Reaction conditions: 0.1 mol·L^{-1} glutamic acid, 50% water filling, 300 °C, 3 h).

Supplementary Tables

Table S1. The molar enthalpy of hexylamine conversion to hexanol

$C_6H_{15}N + H_2O = C_6H_{14}O + NH_3$

T **°C**	**deltaH** **kJ**	**deltaS** **J/K**	**deltaG** **kJ**
150.000	91.245	208.381	3.068
175.000	89.246	203.790	-2.082
200.000	87.460	199.910	-7.127
225.000	85.867	196.627	-12.083
250.000	84.435	193.822	-16.963
275.000	83.122	191.369	-21.777
300.000	81.882	189.157	-26.533

Table S2. Acid-base properties of different supports[a]

Entry	Support	pH
1	C	6.23
2	SiO_2	4.36
3	Al_2O_3	3.43
4	ZnO	7.90
5	ZrO_2	3.70
6	CeO_2	8.93

[a] To obtain the acid-base properties of the different supports, materials were suspended in 3 mL H_2O and stirred constantly for 12 h. After that pH of solutions was detected by pH meter.

Reference:

S1. X. Wang, Y. Yang, H. Zhong, T. Wang, J. Cheng and F. Jin, *Green Chemistry*, 2021, **23**, 430-439.