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Catalytic transformation of 2,5-furandicarboxylic acid to adipic acid over niobic acid-supported Pt nanoparticles

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Experimental details

1. Materials and catalyst preparation

Al_2O_3, SiO_2, CeO_2, MgO, ZrO_2, $NbCl_5$, $NH_3 \cdot H_2O$, $H_2PtCl_6 \cdot 6H_2O$, $RuCl_3 \cdot 3H_2O$, $RhCl_3 \cdot 3H_2O$, $IrCl_3 \cdot 3H_2O$, $NaBH_4$, dimethyl sulfoxide (DMSO), ethanol and ethylene glycol were purchased from Sinopharm Chemical Reagent Co., Ltd. TiO_2 was obtained from Degussa, and HZSM-5 was purchased from Nankai University Catalyst Co. 2,5-furandicarboxylic acid (FDCA) was purchased from Aladdin. Tetrahydrofuran-2,5-dicarboxylic acid (THFDCA) was purchased from Jiangsu Aikang Biomedical Research and Development Co., Ltd. 2-hydroxyadipic acid (HAA) was purchased from Shanghai Shaoyuan Co. Ltd. Adipic acid (AA) was purchased from Alfa Aesar (China) Chemicals Co., Ltd. $Nb_2O_5 \cdot xH_2O$ was synthesized by a simple hydrothermal method.[1] Typically, 1.0 g $NbCl_5$ was dissolved in 10 mL ethanol under continuous stirring to obtain a settled solution. Then, a 4 wt% $NH_3 \cdot H_2O$ aqueous solution (50 mL) was added to the above solution with stirring for 2 h. After filtration and washing, the solid was dispersed in 50 mL ultrapure water and the pH of mixture was adjusted to 6 by $NH_3 \cdot H_2O$ aqueous solution. $Nb_2O_5 \cdot xH_2O$ was finally obtained after hydrothermal reaction at 513 K for 24 h, followed by filtration, washing and drying at 333 K under vacuum for 12 h.

Supported Pt or other noble metal catalysts were prepared by a chemical reduction method using $NaBH_4$ as a reductant. As an example, the preparation of $Pt/Nb_2O_5 \cdot xH_2O$ was described as follows. 0.30 g $Nb_2O_5 \cdot xH_2O$ was dispersed into 30 mL ultra-pure water. After stirring for 30 min, an aqueous solution of H_2PtCl_6 (1.2 mL) with a concentration of 12.55 mg mL^{-1} was added into the above suspension under stirring. The mixture was further stirred for another 30 min. Then, a fresh $NaBH_4$ (0.150 mol L^{-1}) aqueous solution (5 mL) was added into the above mixture at 298 K. After stirring for 4 h, the solid catalyst was recovered by filtration, followed by washing and drying. The $Pt/Nb_2O_5 \cdot xH_2O$ catalyst thus obtained has a mean Pt particle size of 4.2 nm.

The series of $Pt/Nb_2O_5 \cdot xH_2O$ catalysts with different mean sizes of Pt NPs (denoted as Pt-$d/Nb_2O_5 \cdot xH_2O$, where d was the mean Pt particle size in nm) were prepared by choosing different reductants and different reduction conditions (temperatures and reduction times). For the preparation of catalysts with mean Pt sizes of 4.2, 7.2 and 9.3 nm, the Pt precursor (H_2PtCl_6 aqueous solution) was mixed with $Nb_2O_5 \cdot xH_2O$ and then underwent reduction by $NaBH_4$ at temperatures of 298 , 323 and 348 K for 4 h, respectively. For the preparation of catalyst with a mean Pt size of 5.2 nm, the reduction temperature was 273 K and reduction time 8 h. The catalyst with a mean Pt size of 3.8 nm was obtained by reduction of $H_2PtCl_6·6H_2O$ at 433 K for 4 h using ethylene glycol as a reductant. The catalyst with a mean Pt size of 1.8 nm was prepared by calcination of $Nb_2O_5·xH_2O$-impregnated Pt precursor (H_2PtCl_6) at 773 K for 4 h in air, followed by reduction at 673 K for 4 h under 5% H_2/N_2 gas flow(flow rate, 60 mL min^{-1}).

2. Catalyst characterization

The transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) measurements were performed using a Tecnai F20 electron microscope operated at an acceleration voltage of 200 kV. The N_2 physisorption was performed on a Micromeritics Tristar 3020 surface area to measure the specific surface area, pore volume and pore size of the catalysts. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250Xi using Al-Kα radiation. The binding energy was calibrated using the C 1s photoelectron peak at 284.6 eV as a reference. Inductively coupled plasma (ICP) optical emission spectrometry was performed by using an Agilent 700 ICP-OES instrument to measure the actual loading amounts of Pt. The diffuse reflectance Fourier-transform infrared (FT-IR) spectroscopy was carried out with a Nicolet 6700 spectrometer. For the CO-adsorbed FT-IR, the catalyst sample was loaded into an IR cell and calcined at 473 K for 1 h with Ar flow. After cooling to 303 K in Ar, a spectrum was collected as the background. Subsequently, CO was introduced into the IR cell and the adsorption of CO was conducted at 303 K for 30 min, and then another spectrum was recorded after fluxing the IR cell with Ar flow. The spectrum of CO adsorbed on the surface of catalysts was obtained by subtracting these spectra.

3. Catalytic reaction

The catalytic transformation of FDCA to AA was performed in a batch-type Teflon-lined stainless-steel autoclave (30 mL). The temperature of the reactor was controlled by an oil bath with a magnetic stirring. Typically, the catalyst (0.020 g) and 0.10 mmol FDCA (0.0156 g) were added into the reactor that was precharged with ultrapure water (5 mL). Then the reactor was sealed and purged ten times with H_2 at a fixed pressure (typically 3 MPa). The reaction was started by vigorous stirring when the temperature reached 433 K. After a fixed reaction time, the reactor was quickly cooled by ice water to room temperature to terminate the reaction. For the recycling uses, the catalyst was recovered by centrifugation, washing with deionized water and drying at 333 K for 12 h. Then, the recovered catalyst was used for the next reaction. After reaction, gaseous products were collected in a gas bag. The gaseous products were analysed by a gas chromatograph (GC 2060) equipped with an RT-Plot-Q capillary column, and a thermal conductivity detector (TCD) and a flame ionization detector (FID) to detect CO_2 and alkanes. Possible furan chemicals in the gas phase were also identified by the GC-MS (GC-2010 SHIMADZU, GCMS-QP2010 Plus) equipped with total ions chromatograph (TIC). Liquid products were analysed by electrospray ionization mass spectrometry (ESI-MS) (AmaZon SL, Bruker Daltonics Inc.) and quantified by a high-performance liquid chromatography (HPLC) with an instrument (Shimazu LC-20A) equipped with a refractive index (RI) detector and a Shodex SUGARSH-1011 column (8 mm × 300 mm) using a dilute H_2SO_4 aqueous solution as a mobile phase. FDCA was analysed by the nuclear magnetic resonance (NMR) (Ascend III 500), in which 0.6 mL solution was mixed with 0.1 mL D_2O and 0.1 mL DMSO (diluted to 100 ppm by ultrapure water) as an internal standard. The one-dimensional ^1H spectrum was measured by the water suppression method.[2]

The conversion of FDCA was calculated by the following equation.[3]

Conversion (%) = $(C_{i,0} - C_{\mathrm{i},\mathrm{final}}) / C_{i,0} \times 100\%$

The yield, selectivity and carbon balance (denoted as C balance) were calculated on a molar carbon basis by the following equations:

Yield (%) = (Number of carbon atom in product $j \times C_{j,\mathrm{final}}$) /(Number of carbon atom in $i \times C_{i,0}$) × 100%

Selectivity (%) = (Number of carbon atom in product $j \times C_{j,\mathrm{final}}$) /(Number of carbon atom in $i \times (C_{i,0} - C_{i,\mathrm{final}})$) × 100%

C balance (%) = $\sum$ (Number of carbon atom in product $j \times C_{j,\mathrm{final}}$) /(Number of carbon atom in $i \times (C_{i,0} - C_{i,\mathrm{final}})$) × 100%

$C_{i,0}$ was the initial concentration of the substrate (FDCA, 20 mmol/L). $C_{i,\mathrm{final}}$ was the final concentration of the substrate (FDCA). $C_{j,\mathrm{final}}$ was the final concentration of liquid product (e.g., THFDCA, HAA and AA).

The site time yield for the formation of AA was calculated by the following equation:

Site time yield = Molar amount of AA formed/(Molar amount of Pt in the catalyst × Pt dispersion × reaction time)

The Pt dispersion was calculated by the following equation:[4]

Pt dispersion = 1.13/d (diameter, unit: nm)

In the above equation, d was the mean diameter of Pt NPs.

Supplementary Tables and Figures

Table S1 Conversion of FDCA over Pt/HZSM-5 and Pt/CeO_2 catalysts.

Catalyst	Conversion (%)	Selectivity (%)			AA yield (%)	C balance (%)
		AA	THFDCA	HAA		
Pt/HZSM-5	96	8	7	76	7.4	91
Pt/HZSM-5[a]	98	10	8	26	10	44
Pt/CeO_2	71	12	58	14	8.5	84
Pt/CeO_2[a]	98	2	42	8	1.6	52

Reaction conditions: FDCA 0.10 mmol, catalyst (Pt loadings 5 wt%) 0.020 g, H_2O 5 mL, H_2 3 MPa, 473 K, 4 h. [a] 10 h. FDCA, AA, THFDCA and HAA denote 2,5-furandicarboxylic acid, adipic acid, tetrahydrofuran-2,5-dicarboxylic acid and 2-hydroxyadipic acid, respectively.

Table S2 Conversion of FDCA over $Pt\text{-}MoO_x/TiO_2$ catalyst.

Reaction cycle	Conversion (%)	Selectivity (%)			AA yield (%)	C balance (%)
		AA	THFDCA	HAA		
1st use	>99	22	1	9	22	32
2nd use	>99	18	1	7	18	26

Reaction conditions: FDCA 0.10 mmol, catalyst 0.020 g, H_2O 5 mL, H_2 3 MPa, 473 K, 8 h. FDCA, AA, THFDCA and HAA denote 2,5-furandicarboxylic acid, adipic acid, tetrahydrofuran-2,5-dicarboxylic acid and 2-hydroxyadipic acid, respectively.

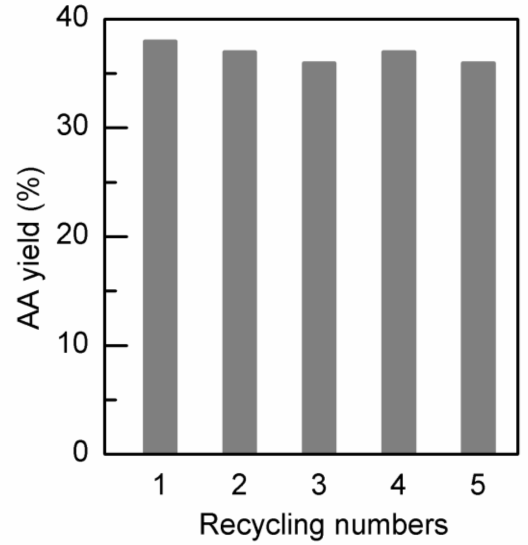

Fig. S1 Recycling uses of Pt/$Nb_2O_5 \cdot xH_2O$ catalyst. Reaction conditions: FDCA 0.10 mmol, catalyst (Pt loadings 5 wt%) 0.020 g, H_2O 5 mL, H_2 3 MPa, 473 K, 8 h.

Table S3 Conversion of FDCA over $Nb_2O_5 \cdot xH_2O$-supported noble metal catalysts.

Catalyst	Conversion (%)	Selectivity (%)			AA Yield (%)	C balance (%)
		AA	THFDCA	HAA		
Pt/$Nb_2O_5 \cdot xH_2O$	>99	38	7	1	38	46
Pd/$Nb_2O_5 \cdot xH_2O$	>99	2	77	3	2.2	82
Ru/$Nb_2O_5 \cdot xH_2O$	>99	5	0.3	0.4	5.2	5.7
Rh/$Nb_2O_5 \cdot xH_2O$	>99	4	0.4	1	3.6	5.4
Ir/$Nb_2O_5 \cdot xH_2O$	>99	4	3	0.5	4.2	7.5

Reaction conditions: FDCA 0.10 mmol, catalyst (metal loadings 5 wt%) 0.020 g, H_2O 5 mL, H_2 3 MPa, 473 K, 8 h. FDCA, AA, THFDCA and HAA denote 2,5-furandicarboxylic acid, adipic acid, tetrahydrofuran-2,5-dicarboxylic acid and 2-hydroxyadipic acid, respectively.

Table S4 Effect of Pt loading amounts on catalytic behaviours of Pt/$Nb_2O_5 \cdot xH_2O$ catalyst for the conversion of FDCA.

Pt loadings (wt%)	Conversion (%)	Selectivity (%)			AA yield (%)	C balance (%)
		AA	THFDCA	HAA		
0	1.0	0	0	0	0	0
1	34	17	17	37	5.7	71
2.5	76	23	22	50	18	95
5	>99	30	21	32	30	83

Reaction conditions: FDCA 0.10 mmol, Pt/$Nb_2O_5 \cdot xH_2O$ 0.030 g, H_2O 5 mL, H_2 3 MPa, 433 K, 8 h. FDCA, AA, THFDCA and HAA denote 2,5-furandicarboxylic acid, adipic acid, tetrahydrofuran-2,5-dicarboxylic acid and 2-hydroxyadipic acid, respectively.

Table S5 Conversion of HAA over the Pt/$Nb_2O_5 \cdot xH_2O$ and Pt/SiO_2.

Catalyst	Temperature (K)	HAA conversion (%)	AA selectivity (%)	AA yield (%)
Pt/$Nb_2O_5 \cdot xH_2O$	433	57	61	35
	453	79	43	34
	473	>99	24	24
Pt/SiO_2	433	16	22	3.4

Reaction conditions: HAA 0.10 mmol, catalyst (Pt loading 5 wt%) 0.030 g, H_2O 5 mL, 8 h. HAA and AA denote 2-hydroxyadipic acid andadipic acid, respectively.

Table S6 Synthetic conditions for the Pt-*d*/$Nb_2O_5 \cdot xH_2O$ catalysts with different mean sizes of Pt particles.

Catalyst	Reductant	Reduction temperature (K)	Reduction time (h)
Pt-1.8/$Nb_2O_5 \cdot xH_2O$	H_2	673	4
Pt-3.8/$Nb_2O_5 \cdot xH_2O$	Ethylene glycol	433	4
Pt-4.2/$Nb_2O_5 \cdot xH_2O$	$NaBH_4$	298	4
Pt-5.2/$Nb_2O_5 \cdot xH_2O$	$NaBH_4$	273	8
Pt-7.2/$Nb_2O_5 \cdot xH_2O$	$NaBH_4$	323	4
Pt-9.3/$Nb_2O_5 \cdot xH_2O$	$NaBH_4$	348	4

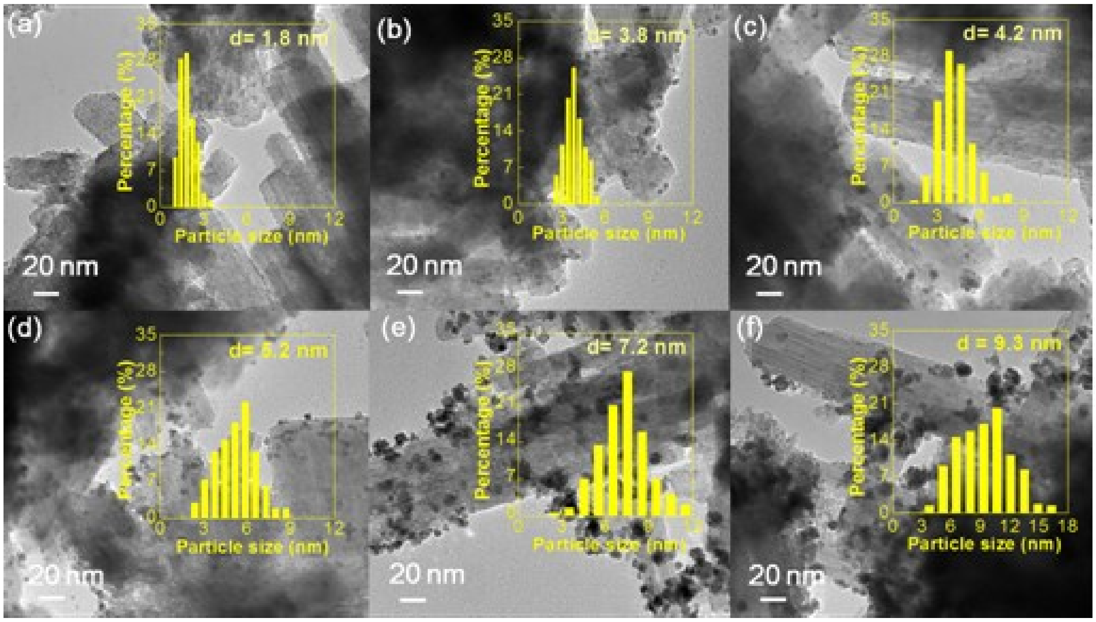

Fig. S2 TEM images and the corresponding Pt particle size distributions for Pt-*d*/$Nb_2O_5 \cdot xH_2O$. Mean size of Pt particles: (a) 1.8 nm, (b) 3.8 nm, (c) 4.2 nm, (d) 5.2 nm, (e) 7.2 nm and (f) 9.3 nm.

Table S7 Physical properties for Pt-*d*/$Nb_2O_5 \cdot xH_2O$ catalysts with different mean sizes of Pt particles.

Catalyst	Pt loadings (wt%)[a]	Surface area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)[b]	Pore size (nm)[b]	Pt dispersion (%)[c]
Pt-1.8/$Nb_2O_5 \cdot xH_2O$	4.9	60	0.12	10	63
Pt-3.8/$Nb_2O_5 \cdot xH_2O$	4.6	62	0.12	9.3	30
Pt-4.2/$Nb_2O_5 \cdot xH_2O$	4.6	61	0.12	11	27
Pt-5.2/$Nb_2O_5 \cdot xH_2O$	4.6	58	0.13	11	22
Pt-7.2/$Nb_2O_5 \cdot xH_2O$	4.7	54	0.13	10	16
Pt-9.3/$Nb_2O_5 \cdot xH_2O$	4.8	53	0.11	11	12

[a] Measured by ICP measurement. [b] Measured by N_2 physical adsorption; [c] Calculated by using the equation: Pt dispersion = 1.13/*d*, where *d* is the mean size of Pt nanoparticles.[4]

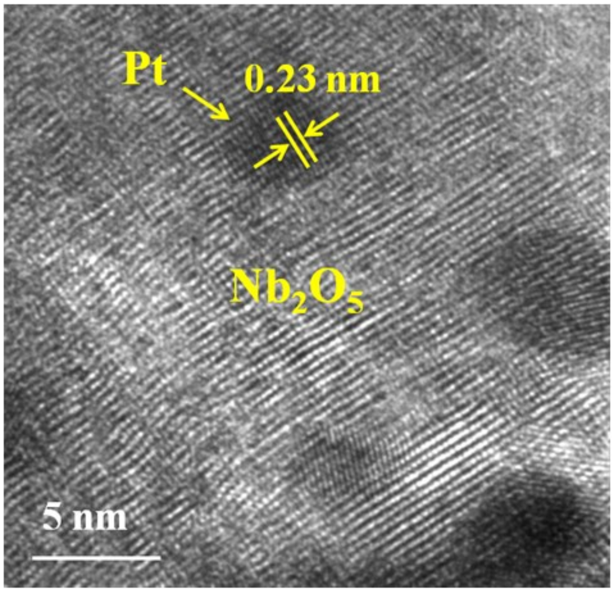

Fig. S3 High-resolution TEM image for the Pt-3.8/$Nb_2O_5 \cdot xH_2O$ catalyst.

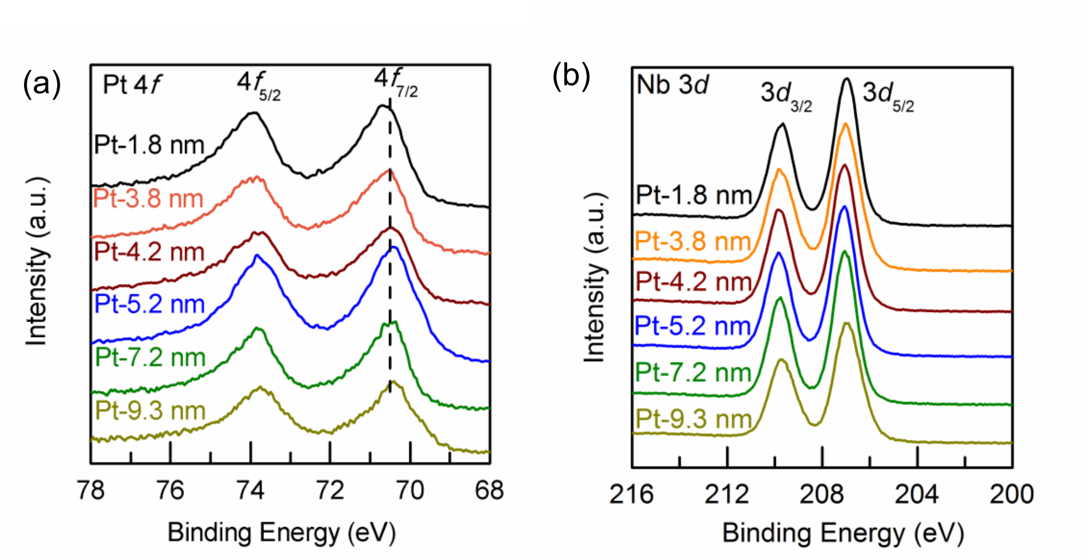

Fig. S4 XPS spectra for Pt-*d*/$Nb_2O_5 \cdot xH_2O$ catalysts with different mean sizes of Pt particles. (a) Pt 4f. (b) Nb 3d.

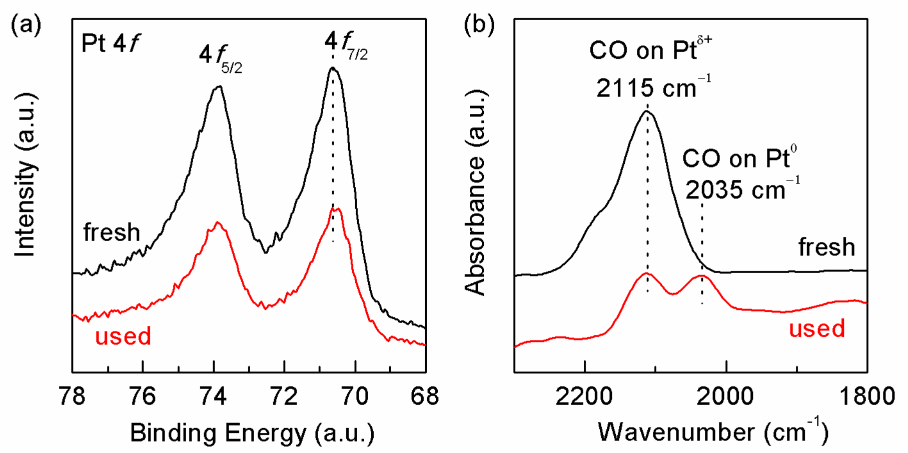

Fig. S5 (a) XPS spectra and (b) CO-adsorption IR spectra for Pt-1.8/$Nb_2O_5 \cdot xH_2O$ catalysts.

Table S8 Conversion of FDCA with the liquid and solid phases separated from the thermal treatment media for Pt-3.8/$Nb_2O_5 \cdot xH_2O$ via hot filtration.[a]

Catalytic phase	Conversion (%)	Selectivity (%)			AA yield (%)	C balance (%)
		AA	THFDCA	HAA		
Liquid	28	0	2.0	0	0	2.0
Solid[b]	>99	37	6	1	37	44

[a] Reaction conditions: FDCA 0.10 mmol, H_2 3 MPa, 473 K, 8 h. FDCA, AA, THFDCA and HAA denote 2,5-furandicarboxylic acid, adipic acid, tetrahydrofuran-2,5-dicarboxylic acid and 2-hydroxyadipic acid, respectively. Pt-3.8/$Nb_2O_5 \cdot xH_2O$ was treated under the standard reaction conditions (H_2O 5 mL, H_2 3 MPa, 473 K, 8 h) and then the mix was separated into liquid and solid phases via hot filtration. [b] H_2O 5 mL.

Table S9 Conversion of FDCA over the Pt-3.8/$Nb_2O_5 \cdot xH_2O$ catalyst under different H_2 pressures.

H_2 pressure (MPa)	Conversion (%)	Selectivity (%)			AA yield (%)	C balance (%)
		AA	THFDCA	HAA		
0.5	99	21	13	28	21	62
1	>99	27	12	20	27	59
2	>99	31	10	8	31	49
3	>99	38	7	1	38	46

Reaction conditions: FDCA 0.10 mmol, Pt/$Nb_2O_5 \cdot xH_2O$ (Pt loading 5 wt%) 0.020 g, H_2O 5 mL, 473 K, 8 h. FDCA, AA, THFDCA and HAA denote 2,5-furandicarboxylic acid, adipic acid, tetrahydrofuran-2,5-dicarboxylic acid and 2-hydroxyadipic acid, respectively.

Table S10 By-products during the conversion of FDCA over Pt-3.8/$Nb_2O_5 \cdot xH_2O$ catalyst at different reaction temperatures.

Temperature (K)	Conversion (%)	By-products Selectivity (%)				
		CO_2	C_1-C_6 alkanes	HCA	DHHA	1,6-hexanediol
433	99	3.5	1.1	0.5	0	0
453	>99	6.5	0.6	2.5	0.2	0.14
473	>99	12	1.1	3.7	4	0.23

Reaction conditions: FDCA 0.10 mmol,Pt-3.8/$Nb_2O_5 \cdot xH_2O$ (Pt loading 5 wt%) 0.020 g, H_2O 5 mL, 8 h. FDCA, HCA and DHHA denote 2,5-furandicarboxylic acid, hydroxycaproic acid, and 5,6-dihydroxyhexanoic acid, respectively.

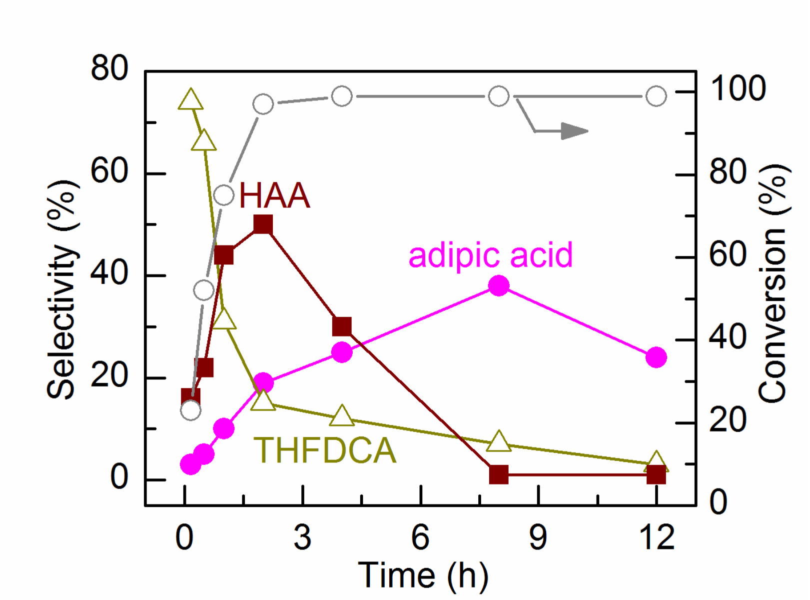

Fig. S6 Time-course result for Pt-3.8/$Nb_2O_5 \cdot xH_2O$-catalyzed conversion of FDCA. Reaction conditions: FDCA 0.10 mmol, catalyst 0.020 g, H_2O 5 mL, H_2 3 MPa, 473 K. THFDCA and HAA denote tetrahydrofuran-2,5-dicarboxylic acid and 2-hydroxyadipic acid, respectively.

Table S11 Conversion of AA over Pt-3.8/$Nb_2O_5 \cdot xH_2O$ catalyst.

Temperature (K)	AA conv. (%)	Yield (%)			
		CO_2	C_1-C_6 alkanes	HCA	1,2-hexanediol
433	6.9	2.4	1.4	2.9	0
473	35	2.7	10	17.5	4.2

Reaction conditions: AA 0.10 mmol,Pt-3.8/$Nb_2O_5 \cdot xH_2O$ (Pt loading 5 wt%) 0.020 g, H_2O 5 mL, 8 h. AA and HCA denote adipic acid and hydroxycaproic acid, respectively.

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