Electronic Supporting Information

Preparation of SBA−15 supported Pt/Pd bimetallic nano−catalysts using supercritical fluid reactive deposition and their application in hydrogenation of levulinic acid to γ−valerolactone: How do solvent effects during material synthesis affect catalytic properties?

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Experimental Section

Materials:
Levulinic acid (98%), Pluronic 123, tetraethyl orthosilicate and concentrated HCl were purchased from Sigma Aldrich and used directly. Dimethyl(1,5-cyclooctadiene)platinum [(Me)$_2$Pt(COD)] (97% content) was purchased from Sigma Aldrich and used without further purification.

[CpPd(allyl)] was synthesized according to literature to afford a reddish, needle-shaped solid at room temperature.[1,2] δ_H (300 MHz; C$_6$D$_6$): 2.10 (2H, d), 3.39 (2H, d), 4.56 (H, m), 5.83 (5H, s); δ_C (75 MHz; C$_6$D$_6$): 45.28, 94.08, 94.18; m/z (EI) 212; Toluene, *n*-pentane and THF were dried before usage both for the preparation of CpPd(allyl) and for the impregnation process. Their water contents were less than 10 ppm determined by Karl Fischer Titration. SBA-15 was synthesized according to a literature precedure.[3]

Experimental procedure
Synthesis of SBA-15: 29.35 g of Pluronic 123 was dissolved in 533 mL of water and 16 g of concentrated HCl using a polypropylene bottle (Sigma Aldrich, B8532). Except from addition steps the bottle was kept closed. The mixture was stirred at 38 °C over night, followed by addition of 57.9 g tetraethyl orthosilicate (TEOS) at 38 °C and further stirred at this temperature for 24 h. Afterwards the stirring bar was removed and the closed bottle was placed for 24 h in a drying oven at a temperature level of 90 °C. The solution was separated with the help of a centrifuge and the remaining solid was washed with 100 mL of water two times using also a centrifuge for phase separation. Afterwards, the sample was dried at 90 °C overnight and calcined in 10 g fractions at 550 °C for 5 h (heating rate 2 K / min).

Synthesis of bimetallic 3% Pt$_1$-Pd$_3$/SBA-15 (loading amount of metals is 3 wt%, n (Pt) : n (Pd)=1:3) using SFRD: All depositions from scCO$_2$ were conducted in a 80 mL high-pressure stainless steel autoclave (the actual volume inside was 55.8 mL). SBA-15 support (300 mg), (Me)$_2$Pt(COD) (6.0 mg, 17.6 μmol) and CpPd(allyl) (11.2 mg, 52.8 μmol) were filled in the autoclave inside the glove box. Then the vessel was loaded with CO$_2$ (m = 39.0 g, ρ = 0.7 g/mL; purity > 99.99%, Air Liquid) using a compressor and a balance. Afterwards the autoclave was placed in a circulating constant-temperature bath (50 °C) for 2 h. Hydrogen addition (purity >99.99%, Air Liquid) was achieved with the help of a mass flow controller by which both the hydrogen amount (n (H$_2$) : n (metal) = 10:1) and its addition rate (100 mL$_n$/min) were controlled. The reaction mixture was then further stirred for 30 min in order to assure a complete reduction. Finally, the autoclave was cooled down to room temperature with ice water and depressurized in a controlled manner for about 30 min.

Synthesis of bimetallic 3% Pt$_1$-Pd$_3$/SBA-15 using conventional solvents: SBA-15 support (300 mg), (Me)$_2$Pt(COD) (6.0 mg, 17.6 mmol) and CpPd(allyl) (11.2 mg, 52.8 mmol) were filled in the autoclave under air atmosphere (the complexes are not air sensitive). Then 20 mL solvent (*n*-pentane or toluene or THF) was added and the autoclave was flushed with Ar for several minutes to remove the air. The rest of the procedure was identical with the one described for scCO$_2$ as a reaction media. The solid inside the autoclave was separated by centrifugation and washed with solvent for 3 times (2 mL x 3) and dried in air.

Synthesis of other metal compositions using SFRD: Synthesis of 3% Pd/SBA-15, 3% Pt/SBA-15, 3% Pt$_1$-Pd$_1$/SBA-15 and 3% Pt$_3$-Pd$_1$/SBA-15 were similar to the synthesis of 3% Pt$_1$-Pd$_3$/SBA-15, except for varying amounts of [(Me)$_2$Pt(COD)] and [CpPd(allyl)] precursors.

Hydrogenation of levulinic acid (LA) into γ-valerolactone (GVL): The hydrogenation of LA to GVL was performed in a 28 mL autoclave made of hastelloy (material number: 2.4819) Under continuous stirring (normally 400 rpm with a mechanical stirrer), catalyst (25 mg), LA (5.0 g) and deionized water (5.0 mL) were mixed inside the autoclave. The autoclave was flushed with H$_2$ for three times before it was pressurized with 100 bar H$_2$. The starting point of the reaction time was defined for the moment at which the inner temperature of the autoclave reached 220 °C (this took nearly 30 minutes). After reaction, the autoclave was cooled down to room temperature in a controlled manner using an ice water bath. The product mixture was firstly centrifuged for 10 min, and then filtrated over RC 4 syringe filter. To the clear, colorless aqueous solution 1-hexanol was added as an internal standard and acetone was added for homogenization. Then the mixture was analyzed by GC (AT 6890N, column: 30 m DB Waxetr, FID). GC-MS was used to identify peaks from unknown products (mainly 2-methyl-tetrahydrofurane and pentonic acid with less than 1% selectivity) under otherwise identical conditions.

$$Conv.\,(LA) = \frac{n\,(GVL) + n\,(2MeTHF)}{n_0(LA)}$$

$$n(product) = \frac{A\,(product) \cdot n\,(internal\ standard) \cdot F\,(product)}{A\,(internal\ standard)}$$

with

- internal standard: 1-hexanol
- GC factors: F (GVL) = 1.66; F (2Me-THF) = 1.18

In a preparative scale experiment GVL was isolated from a reaction mixture in which 5.0 g of LA (43.1 mmol) was hydrogenated in 5 mL of water. The GVL yield was determined to be 93.3% by GC. The workup started with an addition of Na$_2$CO$_3$ (460 mg) and treatment in an ultrasonic bath for few minutes. GVL was then extracted from the water solution by DCM (3 x 15 mL). After evaporation 3,67 g was isolated containing 3 wt-% of DCM which was determined by NMR. So overall a GVL yield of 3.56 g (35.5 mmol, 82,4%) could be isolated.

Materials characterization

Obtained composite materials were characterized by elemental analysis, sorption isotherms (N$_2$-BET), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX) and scanning transmission electron microscopy (STEM).

The *elemental analysis* of C and H was performed on an Elementar Vario EL III Elementa instrument. Low angle *XRD* patterns were recorded on a STOE θ-θ powder diffractometer operating in reflection mode using Cu Kα$_1$ radiation in the range between 0.6-3.0° 2θ (0.02° 2θ step). High angle XRD patterns were recorded on STOE STADIP transmission diffractometer with Cu Kα$_{1,2}$ radiation from 25-55° 2θ (0.01° 2θ step). *XPS* measurements were performed with a Kratos spectrometer with a hemispherical analyzer. The monochromatized Al Kα X-ray source (E=1486.6 eV) was operated at 15 kV and 15 mA. For the narrow scans, analyzer pass energy of 40 eV was applied. The hybrid mode was used as lens mode. The base pressure during the experiment in the analysis chamber was 4 x 10^{-7} Pa. To account charging effects, all spectra have been referred to C 1s at 284.5 eV. *TEM* was used to investigate structural features of the supported nanocatalysts with a Hitachi HF–2000 instrument. *STEM* was performed on a Hitachi HD-2700 instrument (200kV, x2000k). Sections are around 30 nm thick, transferred to a 1000mesh copper-grid and coated with carbon (2 nm every side). The corresponding SEM analysis was performed on Hitachi S-5500 (30kV, x801k) and EDX analysis (S-5500) with Thermo Scientific™ NORAN™ System 7, X-ray Microanalysis System and Thermo Scientific™ UltraDry EDS Detector 30mm^2 (SDD) as the detector. *Nitrogen adsorption* data have

been measured on an ASAP 2010 sorption analyzer (Micromeritics) at 77 K. The *EDX* measurements were performed with an S-3500N Hitachi Scanning Electron Microscope. The EDX detector used is designated Si (Li) Pentafet Plus Oxford Instruments GmbH.

Table S1. scCO$_2$ extraction of freshly prepared 3%Pt$_1$-Pd$_3$/SBA-15

element	CSTR setup[1]		PFR setup[1]	
	before extraction	after extraction	before extraction	after extraction
C	1.73	1.05	2.55	1.58
H	1.20	0.97	2.11	1.32

[1] The given abbreviation stand for continuously stirred tank reactor and plug flow reactor
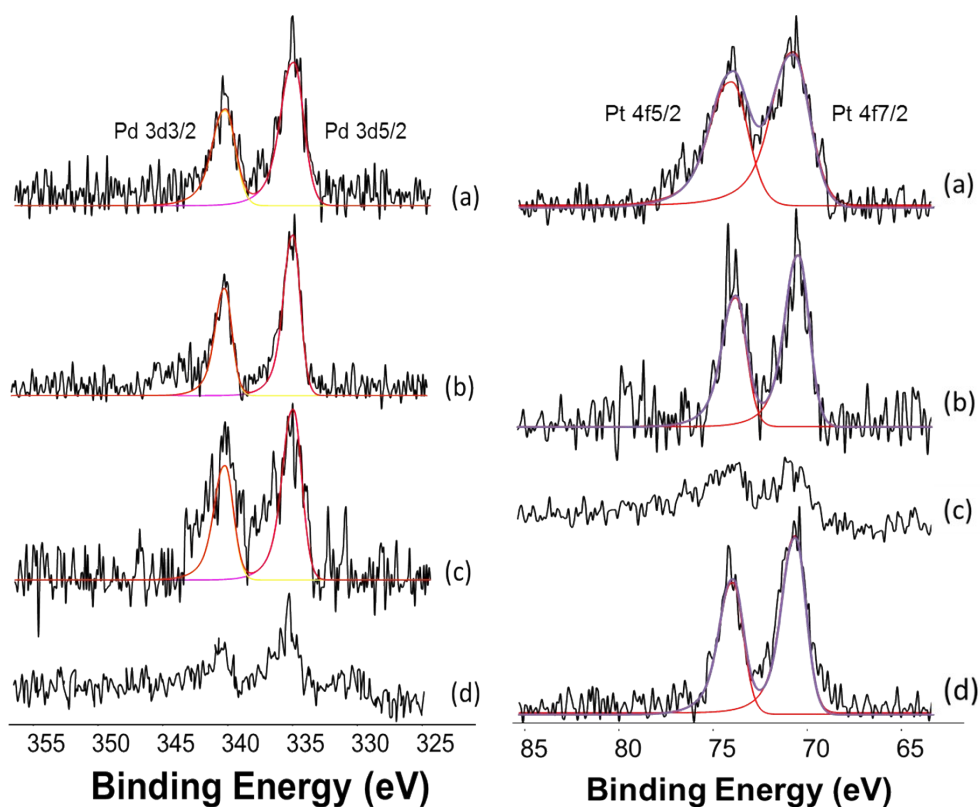
Figure S1. High resolution Pd 3d and Pt 4f XPS spectra of Pd (left) and Pt (right) in the supported 3% Pt$_1$-Pd$_3$/SBA-15 synthesized in (a) scCO$_2$; (b) *n*-pentane; (c) toluene; (d) THF.
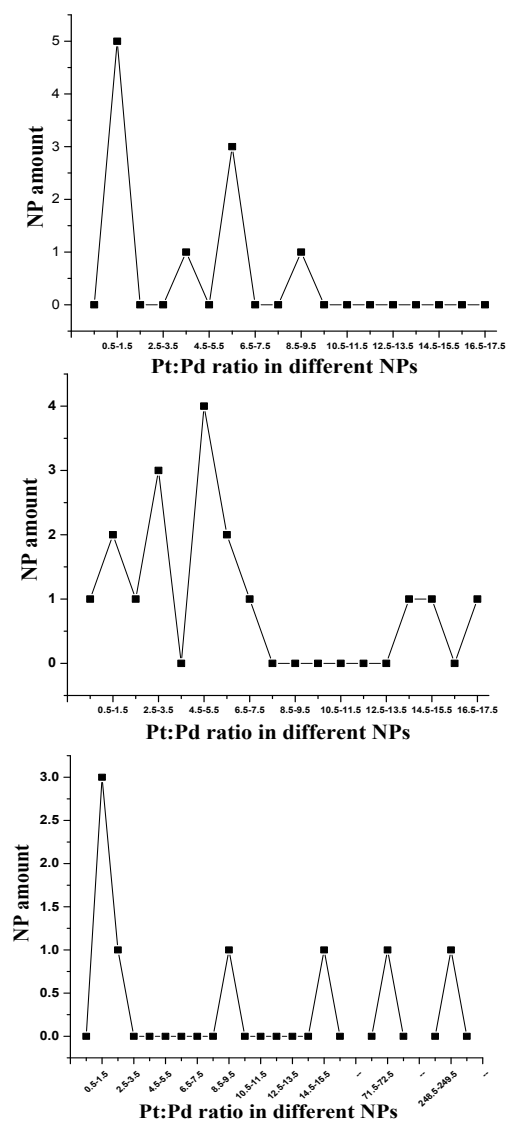
Figure S2. Pd:Pt ratios in different NPs of 3%Pt$_1$–Pd$_3$/SBA–15 synthesized in scCO$_2$ (upper), *n*–pentane (middle) and THF (bottom).
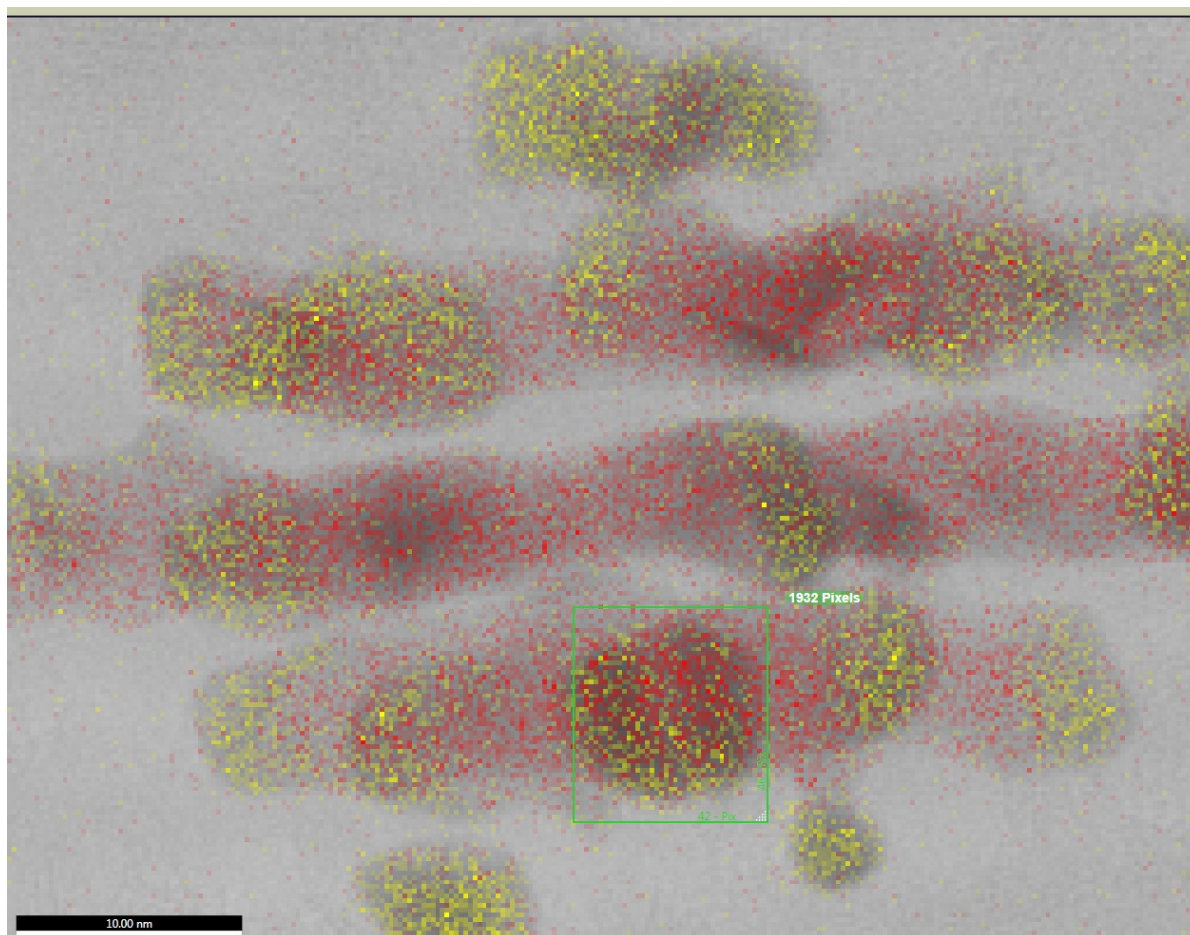
Figure S3. STEM-EDX analysis of 3%Pt_1–Pd_3/SBA–15 synthesized in THF: Pt particles are shown in yellow, Pd in red.

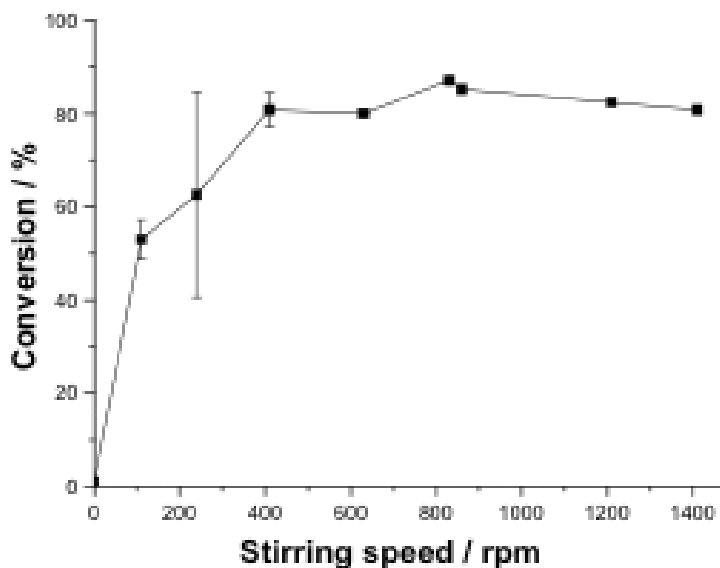**Additional catalytic data**

Figure S4. Stirring speed effect on the conversion of LA. Ranges of experimental results are indicated by error bars.
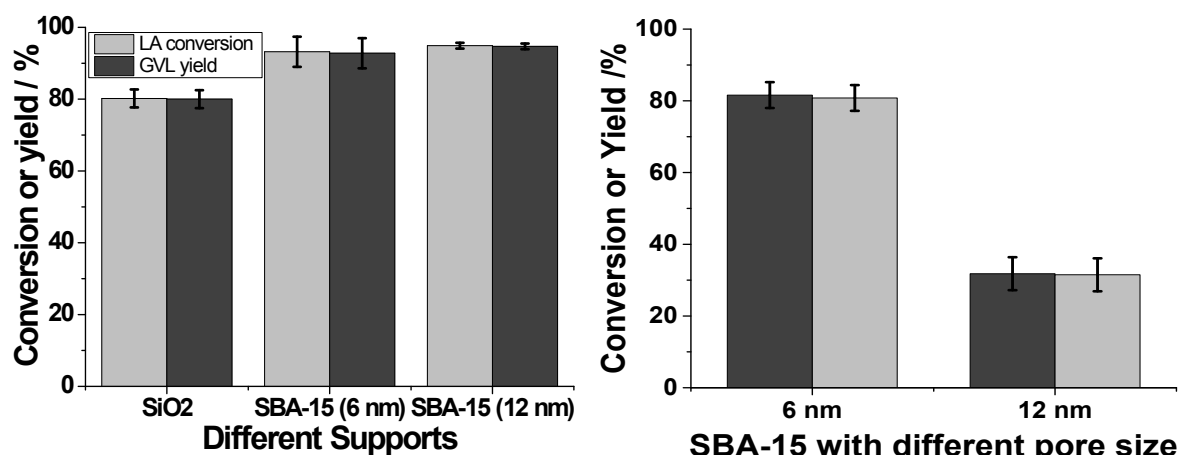

Figure S5. (A: left) Activity tests of LA to GVL using different supports; (B: right) Activity tests of LA to GVL using SBA-15 with different pore sizes.

Reaction conditions: m (LA): 5.0 g; deionized water: 5.0 mL; 100 bar H_2 at r.t.; T = 220 °C; stirring speed: 400 rpm; V (autoclave) = 28 mL. In each case GVL selectivity exceed 99%. All activity tests were reproduced at least two times; ranges are indicated. For A: m (catalyst): 100 mg, t = 4 h; For B: m (catalyst): 25 mg, t = 2 h.

References

1. W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties and B. W. Howk, *J. Am. Chem., Soc.* 1961, **83**, 1601.

2. Y. Tatsuno, T. Yoshida, S. Otsuka, *Inorg. Synth.*, 1990, **28**, 342.

3. *"Transformation of Biogenic Carbohydrates into Levulinic Acid and further Hydrogenation using Supported Nanoparticles Catalysts Synthesized by Chemical Fluid Deposition",* PhD thesis of Kai Yan, 2011, RWTH Aachen.