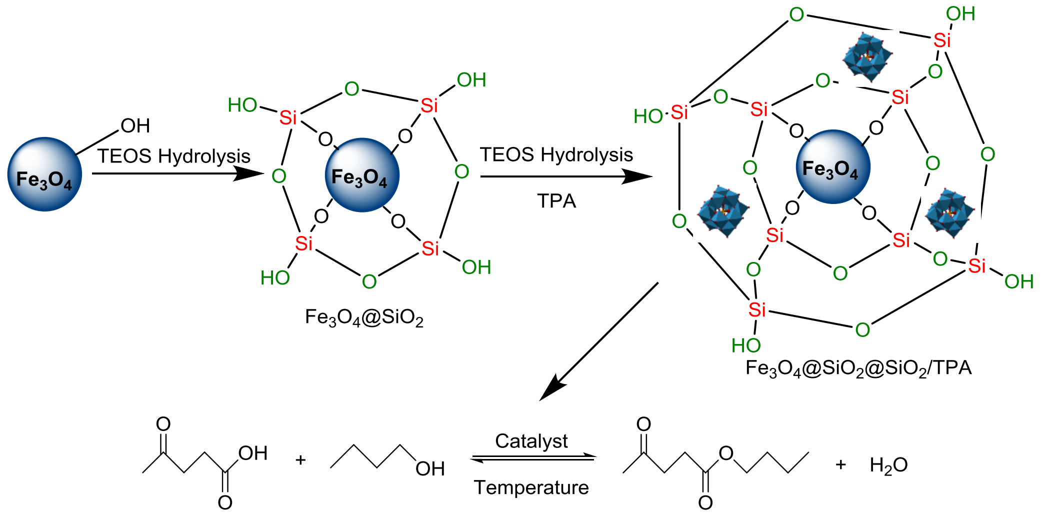
SUPPLEMENTARY MATERIAL



Graphical abstract

Effective diffusion coefficient of levulinic acid (LEA) in n-butanol (BOH).

The diffusion coefficient for LEA into BOH was estimated using the Wilke-Chang equation[1]

$$D_{AB} = \frac{7.4\mathrm{X}10^{-8} \text{ x T x} (\phi_B M_B)^{1/2}}{V_{bA}^{0.6} \text{x} \mu}$$

Where all symbols with indicator A are for solute (LEA) and B are for BOH:

D_{AB}= diffusivity of LEA in BOH, cm^2/s

M_B= molecular weight of BOH, 74.12 g/mol

T= temperature, K

μ*= viscosity of BOH at temperature T, cP

V_{bA}**= LEA molar volume at its normal boiling point, 129.4 cm3/mol

ϕ_B= association factor of BOH (1.5)

*To calculate the viscosity of the BOH at different temperatures was used the following formula[2]:

$$log = A + B/T + CT + DT^2$$

Where A, B, C and D are regressions coefficients for BOH and correspond to:

A= -5.3970

B= 1325.6

C= $6{,}2223\text{x}10^{-3}$

D=$-5.5062\text{x}10^{-5}$

T= temperature, K

** LEA molar volume at its normal boiling point was calculate used the following formula[3]:

$$V_{bA} = 0{,}285\ x\ V_C{}^{1{,}048}$$

Where

V_c= Critical volume for LEA[4], 343 cm^3/mol

The effective diffusion coefficient (D_{eff})

Was calculate used the following formula[5]:

$$D_{eff} = \frac{D_{AB}\varepsilon_p\sigma}{\tau}$$

D_{AB} = Molecular diffusion coefficient of LEA in the mixture, m^2/s

τ = Catalyst tortuosity

ε_p = Catalyst porosity

σ = Constriction factor (accounting for the variation in the cross-sectional area that is normal to diffusion)

Internal mass transfer resistance: *Weisz-Prater criterion*

$$N_{WP} = \frac{\Re x r_p{}^2}{C_s x D_{eff}} \leq 0.3$$

Here:

$\Re$= reaction rate, $mol/m^3_{cat}\cdot s$

r_p = radius of catalyst particle, m

C_s= concentration of the component at the catalyst surface, mol/m^3

D_{eff}= effective diffusion coefficient of the component, m^2/s

Radius of the catalyst particles.

All catalysts/supports were provided in the millimeters range and were crushed and sieved to particle diameters between 600-620 nm. As such, an average particle radius of 3,10x10^{-7} m was taken for the particle radius.

Concentration of LEA at the catalyst surface.

When assuming that external mass-transfer limitations can be neglected, the concentration of substances at catalyst surface are taken equal to the bulk concentration of substances (C_A = C_B). The bulk concentration of LEA at the start of the reaction (highest value, worst case scenario) is known for all experiments.

Experimental reaction rates.

The reaction rates were calculated by the initial velocity method by varying the concentration of LEA.

Table S1. Calculation of the effective diffusion coefficient of LEA in BOH

T (K)	μ (cP)*	D_{AB} (cm^2/s)	D_{eff} (cm2/s)	N_{W-P}
323	1,39	9,81 x10^{-06}	8,18x10^{-07}	2,23x10^{-09}
333	1,11	1,27x10^{-05}	1,05x10^{-06}	5,10x10^{-09}
343	0,90	1,60x10^{-05}	1,33x10^{-06}	1,22x10^{-08}
353	0,74	2,02x10^{-05}	1,68x10^{-06}	3,72x10^{-09}

Acidity measurements

The acid strength was determined by potentiometric titration with n-butylamine. In a typical procedure, the solid (0.05 g) was suspended in acetonitrile and stirred for 3 h. Then, the suspension was titrated with n-butylamine in acetonitrile 0.05 N using Metrohm 794 Basic Titrino apparatus with a double junction electrode.

FT-IR TPA analysis

The structure of the Keggin ions of the $PW_{12}O_{40}$ is well known and consists of a tetrahedron PO_4 surrounded by four W_3O_{13} groups formed by edge-sharing octahedra. These groups are connected to each other by corner-sharing oxygens. This structure gives rise to four types of oxygen, being responsible for the four bands known as the Keggin ion fingerprint. These bands are at 1080 cm^{-1} corresponding to the $P\text{-}O_a$ bond, 964 cm^{-1} of the $W = O_d$ bond, and 891 and 814 cm^{-1} of $W\text{-}O_c\text{-}W$ bonds [6, 7].

Quantification by Normalization Method:

Normalization method is applicable for the determination of single component content in multi-component samples. There is a prerequisite to using the method, that all the components in the sample flow out the chromatographic column and have measurable chromatographic peaks. Given that in the present work the only product was n-butyl levulinate (BLE), the conversion percentage was calculated, and the quantization parameters used were the chromatographic areas of levulinic acid (LEA) and product (BLE). Quantitative equation is given as follows:

$$\mathrm{BLE}(\%) = \frac{f_{BLE}.A_{BLE}}{f_{LEA}.A_{LEA} + f.A_{BLE}} \times 100\ \%$$

Where *BLE (%)* is the conversion percentage of n-butyl levulinate in the reaction sample taken for each time interval; f is the quantitative correction factors of each component, and A_{BLE} and A_{LEA} are the peak area of levulinic acid and product BLE in GC-FID, respectively. Due to the response factor gave a value of 1, consequently, the previous equation becomes in:

$$\mathrm{BLE}(\%) = \frac{A_{BLE}}{A_{LEA} + A_{BLE}} \times 100\ \%$$

The limit of detection and quantification was determined by the method based on the signal/noise.

Detection limit: 0.12 ppm

Quantification limit: 0.27 ppm

Statistical analysis was performed using the Origin Pro 8.0 (OriginLab Inc., USA)

Biography

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