CATALYTIC UPGRADING OF LEVULINIC ACID TO ETHYL LEVULINATE USING RE-USABLE SILICA-INCLUDED WELLS-DAWSON HETEROPOLYACID AS CATALYST

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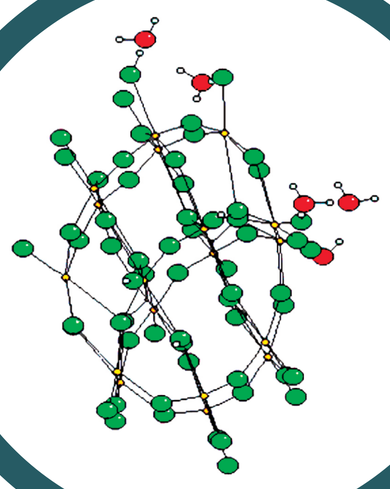
WELLS-DAWSON ACID (WDA) AS HETEROGENOUS CATALYSTS FOR THESE PROCESS NEEDS:

Strong acidity / Insoluble in polar solvents / Re-usable without deactivation / Proper particle size



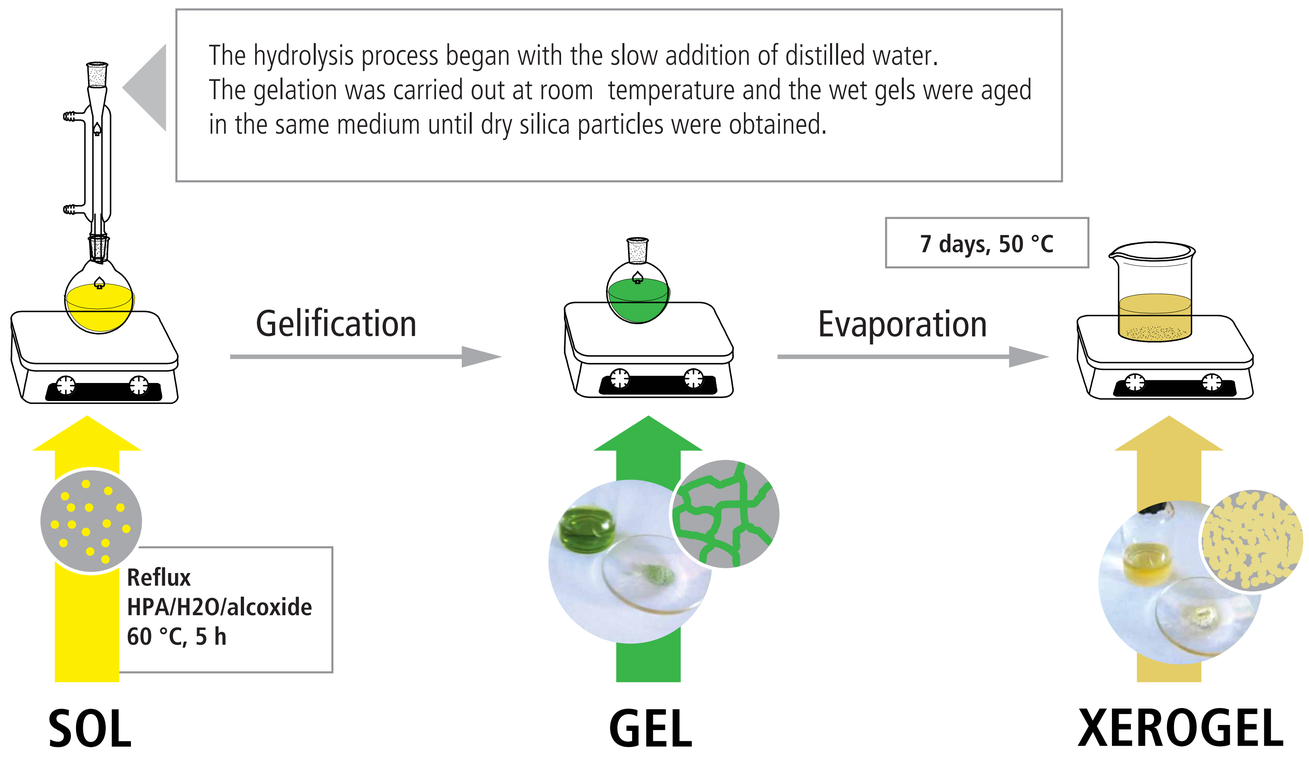
- **Secondary structure of WDA is constituted by: polyanions, protons and H_2O.**
- **Posseses Brönsted acidity, and their protons play a role of catalytic active sites.**
- **Water molecules are associated with H^+ as H_3O^+, $H_5O_2^+$ y $H^+(H_2O)n$ species.**
- **The acidity depends on: hydration state, strenght of acid sites, accesibility of H^+**

SYNTHESIS BY SOL-GEL OF SILICA-INCLUDED WELLS-DAWSON HETEROPOLYACID

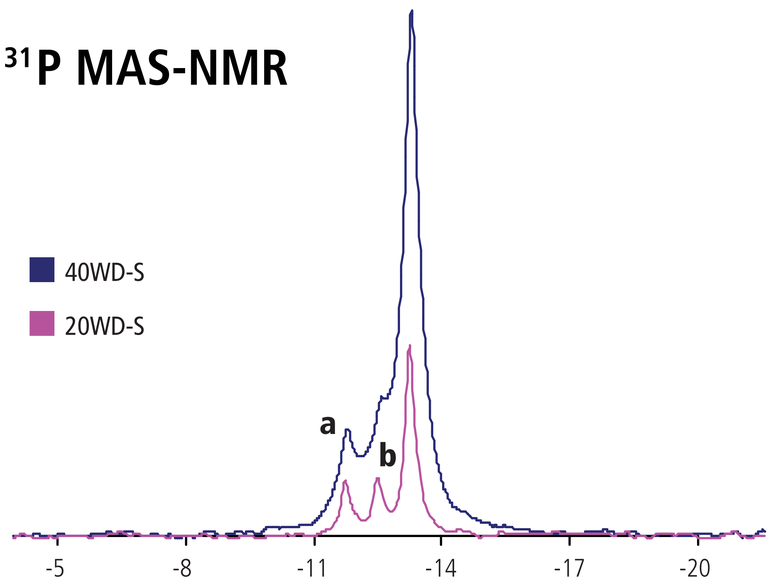
CATALYTIC TESTS

Typical experiments: A stirred batch reactor was loaded with 30 mmol of absolute ethanol, 250 mg of 40WD-S (5 x 10^{-4} mmol de WDA/g SiO_2) and 2 mmol of LA, T= 78ºC, 10 hs. Reaction was followed by TLC. The catalyst was filtered off and washed twice with ethanol. The filtrate and the washing liquids were concentrated in vacuum. The residue was dissolved in CH_2Cl_2, the solution washed with $NaHCO_3$ 5% and water, to separated LA. The organic phase was died with Na_2SO_4, the solvent was evaporated, to afford crude ethyl levulinate (EL). The product was identified via mass spectra analysis.

Stability tests: WDA silica-included catalysts were tested running three consecutive reactions in the same conditions. After each test, the catalyst was separated from the reaction mixture by filtration, washed, dried under vacuum and reused. No traces of W (analysis by ICP) in the filtrate.



^{31}P MAS-NMR OF SILICA-INCLUDED WDA



31P MAS-NMR spectra of silica-included WDA samples, a) 40WD-S and b) 20WD-S

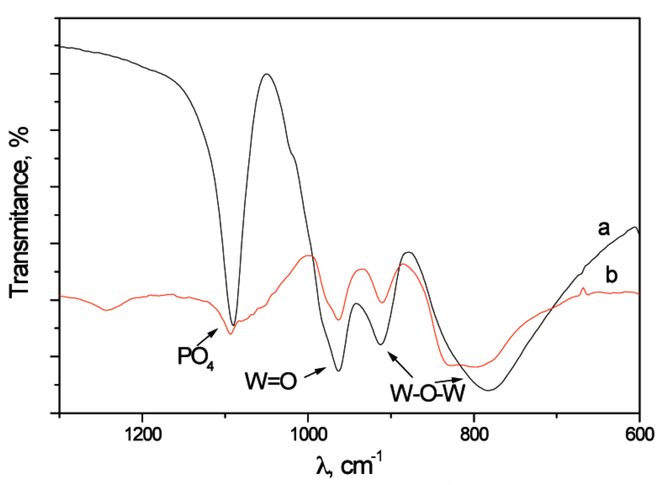
The ^{31}P MAS-NMR technique is the "fingerprint" of HPA compounds.

Pure WDA has two equivalent P atoms, it has only one peak at NMR spectrum in the range of δ =12.8-13 ppm.

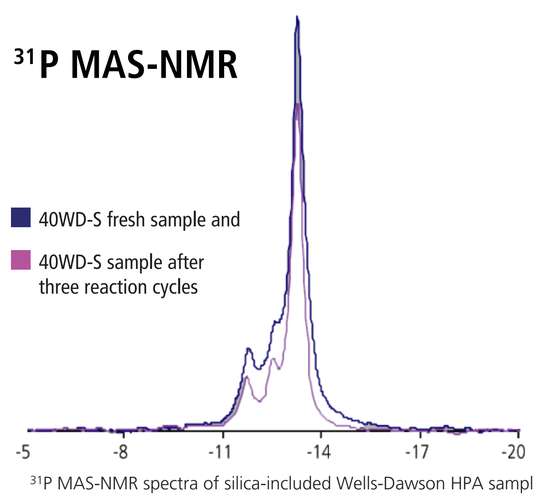
The signals at 12 and -11 ppm could be related to WDA species with strong interaction with Si-OH groups and lacunar species like $P_2W_{21}O_{71}^{-6}$, respectively.

Both 31P MAS-NMR and FTIR measurements show that after the WDA acid keeps its Dawson structure after their immobilization on silica.

FTIR spectra of bulk WDA

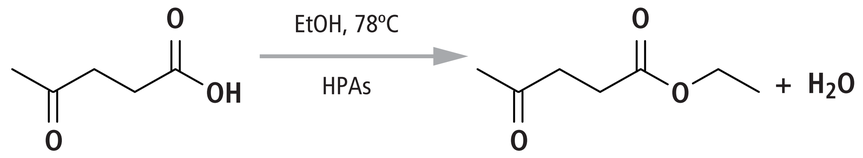


FTIR spectra of bulk WDA (curve a) and b) 40WD-S sample

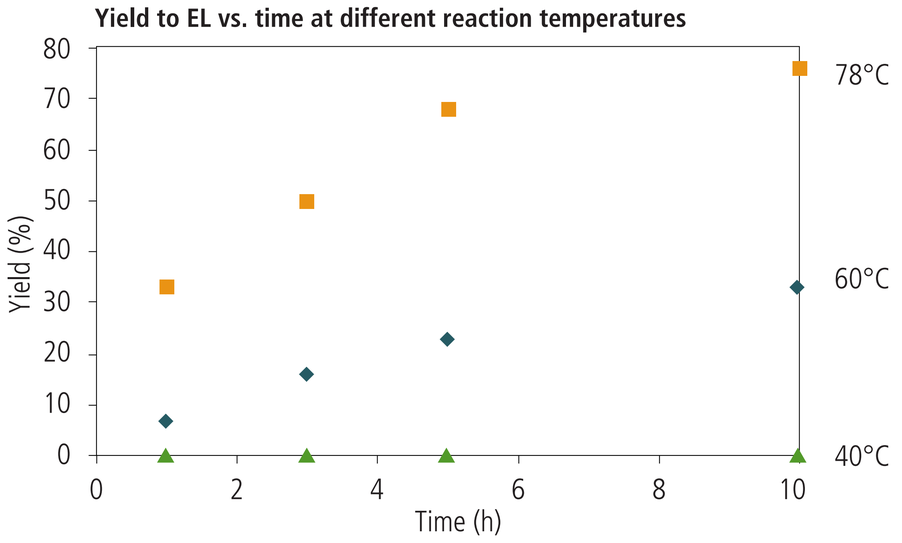


31P MAS-NMR spectra of silica-included Wells-Dawson HPA samples

EVALUATION IN ESTERIFICATION REACTION WITH ETHANOL



Yield to EL vs. time at different reaction temperatures



Stability studies of the 40WD-S catalyst

Entry	Catalytic cycle	Yield to EL (%)
1	First use	76
2	1st re-use	68
3	2nd re-use	68
4	3rd re-use	68

Experimental conditions: 0.01 mmol catalyst, 2 mmols of levulinic acid, 7.5 ml (128 mmoles) of absolute ethanol; 10 h. 78ºC, molar ratio ethanol/LA 64/1

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