Supporting Information

A smart use of biomass derivatives to template ad hoc hierarchical SAPO-5 acid catalyst

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Experimental

Monosaccharides (MsB) production starting from waste biomass

The biomass used for monosaccharides production was post-harvest tomato plant (PHTP), which was previously dried and blade milled. PHTP (3 g) was suspended in 30 mL HCl (1 N) in a 45 mL glass vial; the suspension was then heated in a MW reactor (SynthWave, MLS GmbH, Milestone Srl, Bergamo, Italy) at 423 K for 2 min., under stirring with a nitrogen pressure equals to 40 bar. The reactor was then cooled to room temperature and the suspension was filtered on paper filter under vacuum; washing the filtered with water (20 mL); the solution was neutralized with 30 mL weak base ion exchange resin Amberlite IRA96 (25% mol excess) in a beaker under stirring (500 rpm) overnight. The neutralized solution was then recovered after filtration on sintered glass filter and freeze-dried.

GC-MS spectra of the mixture were recorded after proper derivatization: 10 mg of dry monosaccharides were derivatized in 1 mL pyridine using 150 μL N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) + Trimethylchlorosilane (TMCS) 99:1 in oil bath at 338 K, in 45 min. under stirring. An Agilent Technologies 6850 Network GC System with a 5973 Network Mass Selective Detector and 7683B Automatic Sampler, using a capillary column (HP-5MS; length, 30 m; i.d., 0.25 mm; film thickness, 0.25 μm) (Agilent Technologies, Santa Clara,
CA) was employed for MsB characterization. Injection conditions: split 1:20, injector temperature 523 K, detector temperature 553 K. Gas carrier: helium (1.2 mL/min).

A typical GC-MS chromatogram is reported:

![GC-MS chromatogram]

Different compounds were identified using NIST05 library, as follows:

| RT       | MONOSACCHARIDE            |
|----------|---------------------------|
| 19.956   | arabinofuranose           |
| 20.007   | arabinopyranose           |
| 20.118   | D-(-)-ribofuranose        |
| 20.151   | mannose                   |
| 20.256   | arabinofuranose           |
| 20.375   | arabinose                 |
| 20.690   | arabinose                 |
| 20.930   | mannose                   |
| 21.083   | xylopyranose              |
| 21.668   | xylose                    |
| 22.050   | glucofuranose             |
| 22.324   | b-(D)-galactofuranose     |
| 22.578   | ribofuranose              |
| 22.748   | talose                    |
| 23.088   | b-(D)-glucopyranose       |
| 23.197   | lyxose                    |
| 23.939   | glucopyranose             |

**Hierarchical SAPO-5 synthesis**

Aluminium isopropoxide (7.00 g, Sigma Aldrich) was dissolved in deionized water (5 ml), along with 2.76 ml of triethylamine (TEA) (Sigma Aldrich) and the mixture was stirred for 1 h. Silica fumed (1.20 g, Sigma Aldrich) and 19.29 ml of deionized water were slowly added and the mixture was further stirred for 2 h. SDA$_{meso}$ was dissolved in deionized water (3 ml) and the resulting solution was added to the synthetic gel. After stirring the mixture (30 min), phosphoric acid (2.19 ml, 85 % in H$_2$O, Sigma Aldrich) was added and the mixture was further stirred for 30 min. The gel was transferred to a Teflon-lined stainless-steel autoclave and crystallized at 473 K for 60 h under
autogenous pressure. The solid product was then recovered by filtration and washed with water. The as-prepared product was dried in air at 373 K and calcined in a tube furnace under air flow at 873 K for 16 h to produce a white crystalline solid.

**Microporous SAPO-5 synthesis**

Aluminium isopropoxide (7.00g, Sigma Aldrich) was added slowly to tetraethylammonium hydroxide (TEAOH) (14.00 ml, 35wt% in H₂O, Sigma Aldrich) under stirring. Deionized water (21 ml) was added and the mixture was stirred for 1 h. Tetraethylorthosilicate (TEOS) (1.14 ml, Sigma Aldrich) was added dropwise under stirring and the mixture was further stirred for 2 h. Phosphoric acid (2.33 ml, 85wt% in H₂O, Sigma Aldrich) was added dropwise under stirring. The gel was vigorously stirred for 30 min to produce a white gel with the following composition:

1.0 Al: 1.0 P: 0.15 Si: 1 TEA: 50 H₂O

The gel was transferred to a Teflon-lined stainless-steel autoclave and crystallized at 473K for 60 h under autogenous pressure. The solid product from autoclave was then recovered by filtration and washed with water. The as-prepared product was dried in air at 373K and calcined in a tube furnace under air flow at 873K for 16h to produce a white crystalline solid.

**Characterization methodologies**

Before undertaking structural, volumetric and spectroscopic analysis, calcined samples were outgassed at 573K to remove adsorbed water.

X-ray powder diffraction (XRD) patterns were obtained using an ARL XTRA48 diffractometer with Cu Kα radiation (λ = 1.54062 Å).

N₂ physisorption measurements were carried out at 77 K in the relative pressure range from 1x10⁻⁶ to 1 P/P₀ by using a Quantachrome Autosorb1MP/TCD instrument. Prior to the analysis, the samples were outgassed at 573 K for 3 h (residual pressure lower than 10⁻⁶ Torr). Specific surface areas were determined using the BET equation, in the relative pressure range from 0.01 to 0.1 P/P₀. The desorption branch of the N₂ physisorption isotherm was analyzed by means of the NLDFT (non-local density functional theory) method, to obtain the pore size distribution of the materials.

Thermogravimetric analyses (TGA/DTG) of materials were performed under argon flow (100 mL min⁻¹) with a SETSYS Evolution TGA-DTA/DSC thermobalance, heating from 40 to 1000 °C at 5 °C min⁻¹.

Solid-state (SS) NMR spectra were acquired on a Bruker Avance III 500 spectrometer and a wide bore 11.7 Tesla magnet with operational frequencies for ¹H, ²⁹Si, ³¹P and ²⁷Al of 500.13, 99.35, 202.45 and 130.33MHz, respectively. A 4mm triple resonance probe with magic angle spinning
(MAS) was employed in all the experiments and the samples were packed on a Zirconia rotor and spun at a MAS rate of 15 kHz. The magnitude of radio frequency fields, \( \mu_{\text{rf}} \), were 100, 83 and 42 kHz for \(^1\text{H}, ^{31}\text{P} \) and \(^{29}\text{Si} \), respectively. The \(^{27}\text{Al} \) MAS spectra were acquired on large sweep width with small pulse angle \((\pi/12)\) to ensure quantitative interpretation. In the case of \(^{29}\text{Si}, ^{31}\text{P} \) and \(^{27}\text{Al} \) MAS NMR, high-power proton decoupling was applied. The relaxation delay, \( d_1 \), between accumulations was 5, 1, 20, and 60 s for \(^1\text{H}, ^{27}\text{Al}, ^{31}\text{P} \) and \(^{29}\text{Si} \) MAS NMR spectroscopy, respectively. All chemical shifts were reported by using \( \delta \) scale and are externally referenced to TMS for \(^1\text{H} \) and \(^{29}\text{Si} \) NMR, \( \text{Al(H}_2\text{O)}_6^{3+} \) ion in 1.0 m \( \text{AlCl}_3 \) solution for \(^{27}\text{Al} \) NMR and \( \text{H}_3\text{PO}_4 \) (85\%) for \(^{31}\text{P} \) NMR. The chemical shifts reported for \(^{27}\text{Al} \) are not corrected for second-order quadrupole effects.

\(^1\text{H} \) MAS NMR spectra were fitted with DMFIT functions for quantitative deconvolution of overlapping peaks. The samples were packed on a NMR rotor and dehydrated at 573K under vacuum (1x 10\(^{-4}\) mbar) for 2 h prior to the loading into the magnet and recording of the NMR spectrum.

FTIR spectra of self-supporting pellets were collected under vacuum conditions (residual pressure <10\(^{-5}\) mbar) using a Bruker Equinox 55 spectrometer equipped with a pyroelectric detector (DTGS type) with a resolution of 4 cm\(^{-1}\). \( \text{NH}_3, \) pyridine, 2,4,6-trimethylpyridine (2,4,6-TMP, collidine) were adsorbed at room temperature using specially designed cells permanently connected to a vacuum line to perform adsorption–desorption \textit{in situ} measurements. FTIR spectra were normalized with respect the pellet weight and, whenever specified, are reported in difference-mode by subtracting the spectrum of the sample in vacuum from the spectrum of the adsorbed molecules.

The total number of accessible Brønsted acid sites (N) was estimated using the Lambert–Beer law in the form \( A = \varepsilon N \rho \), where \( A \) is the integrated area of the bands of the protonated species, \( \varepsilon \) is the molar extinction coefficient (cm\(^2\) \( \mu\)mol\(^{-1}\)), \( N \) is the concentration of the vibrating species (mmol g\(^{-1}\)), and \( \rho \) is the density of the disk (mass/area ratio of the pellet, mg cm\(^{-2}\)). The accessibility factor (AF) is defined as the number of Brønsted sites detected detected by pyridine or 2,4,6-TMP adsorption, divided by the total number of Brønsted acid sites detected by ammonia adsorption.
X-ray powder diffraction (XRD) patterns

Figure S1 - The XRD pattern of MicroSAPO-5 (curve a) and HierSAPO-5 (curve b).
**Thermogravimetric measurements**

Fig. S2 - TGA and DTG analysis of the HierSAPO-5 (red curve) and MicroSAPO-5 (black curve)
Solid-state (SS) NMR spectra

**Figure S3** - $^{27}$Al MAS NMR spectra of microporous (black curve) and hierarchical (red curve) SAPO-5.
Figure S4 - $^{31}$P MAS NMR spectra of microporous (black curve) and hierarchical (red curve) SAPO-5.
Figure S5 - $^{29}$Si NMR of microporous (black curve) and hierarchical (red curve) SAPO-5.
FTIR spectra

Figure S6 - FTIR spectra, in the O-H stretching region, of microporous (black curve) and hierarchical (red curve) SAPO-5.

MW-assisted conversion of glucose
Hierarchical SAPO-5 Zeolite was kept in oven overnight (393 K) before the reaction. 100 mg of glucose and 200 mg of zeolite were suspended in 1mL γ-valerolactone and heated in the MW reactor (SynthWave, MLS GmbH, Milestone Srl, Bergamo, Italy) to 443 K for 20 minutes (plus 5 minutes ramp) under stirring and N₂ pressure (40 bar). Mixtures without the addition of zeolites were also prepared as the control. The crude suspension was then centrifuged in 2mL Eppendorf at 260000 rpm for 5 minutes in a Beckman Coulter Allegra 64R Centrifuge. 75µL of the clarified solution were dissolved in 1mL pyridine and GC-MS chromatograms were recorded after proper derivatization using 150µL N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) + Trimethylchlorosilane (TMCS) 99:1 in an oil bath (338 K), for 45 minutes under
stirring. An Agilent Technologies 6850 Network GC System with a 5973 Network Mass Selective Detector and 7683B Automatic Sampler, using a capillary column (HP-5MS; length, 30 m; i.d., 0.25 mm; film thickness, 0.25 μm) (Agilent Technologies, Santa Clara, CA) was employed for Ms characterization. Injection conditions: split 1:20, injector temperature 523 K, detector temperature 553 K. Gas carrier: helium (1.2 mL/min).

The amount of products in the solution was estimated through a calibration curve using 5-HMF (Sigma Aldrich) and lactic acid (Sigma Aldrich) as external standards.

**X-ray powder diffraction (XRD) patterns before and after reaction**

![Graph showing XRD patterns](image)

**Figure S7** – Comparison among the XRD patterns of HierSAPO-5 before (green) and after reaction (dark green) and of MicroSAPO-5 before (blue) and after reaction (light blue).

XRD measurements on both MicroSAPO-5 and HierSAPO-5 samples before and after reaction in GVL were carried out. The comparison of the XRD spectra indicates firstly that the structure of the
HierSAPO-5 catalyst is maintained after reaction under MW irradiation. In addition, small variations of the relative intensity of the peaks were detected after reaction. This can be due to preferential orientation in some crystallographic directions corresponding to the (200), (210), (002), (211), (311), and (312) planes under reaction conditions (note that the measurements were performed using a rotating spinner to avoid preferential orientations due to the preparation of the samples). Interestingly, this behaviour was also observed for MicroSAPO-5, however in this case it was accompanied by an evident shift of the peaks toward lower 2 Theta angles, that was more pronounced at higher angles, which means a variation of crystallographic lattice plane distances $d$ and an increase of the cell parameters, due to the strain induced by the presence of reaction products and by-products in the microporous framework. Therefore, basing on these findings, the important advantage of introducing mesopores results in an improved stability of the HierSAPO-5 catalyst under reaction conditions with respect to MicroSAPO-5. This feature opens the door to the design of robust heterogeneous catalysts for biomass conversion.