**Supporting information**

# Hybrid organic-inorganic nanoparticles with associated functionality for catalytic transformation of biomass substrates

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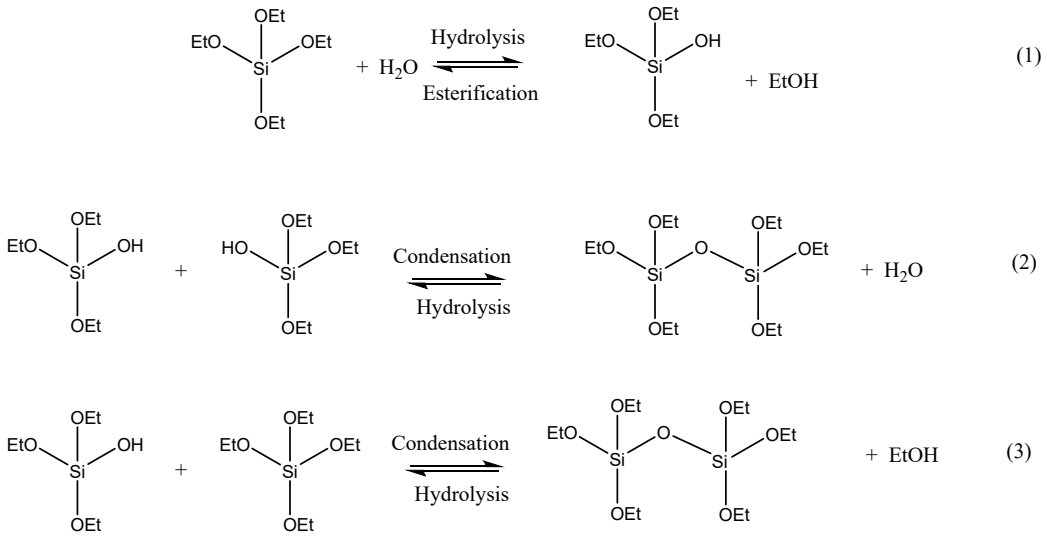
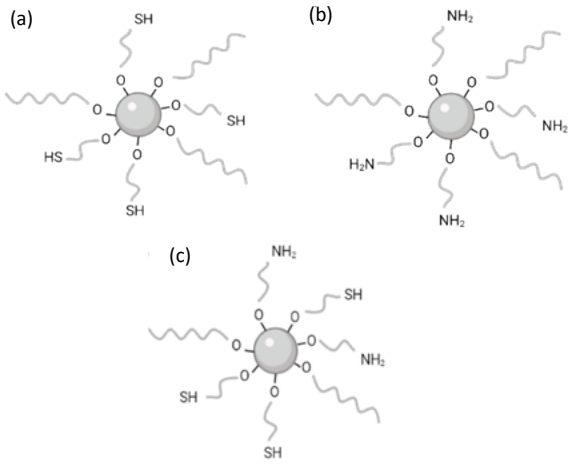



**Scheme S1**. Hydrolysis and condensation reactions during the synthesis process of silica nanoparticles.




**Scheme S2**. Representation of multi-functional silica nanoparticles: a) NPs-$SiO_2$ -$C_{18}$-SH, b) NPs-$SiO_2$ -$C_{18}$- $NH_2$. c) Tri-functional material: NPs-$SiO_2$-$C_{18}$-$SO_3H$-$NH_2$.

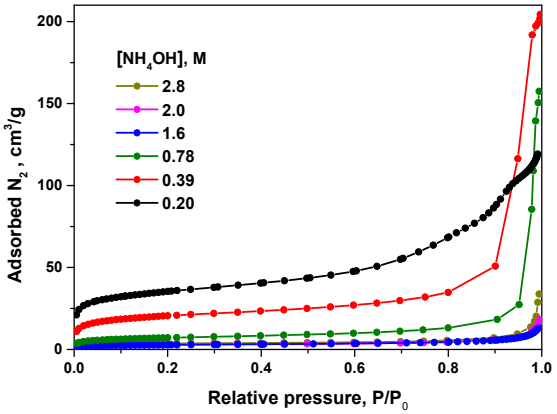
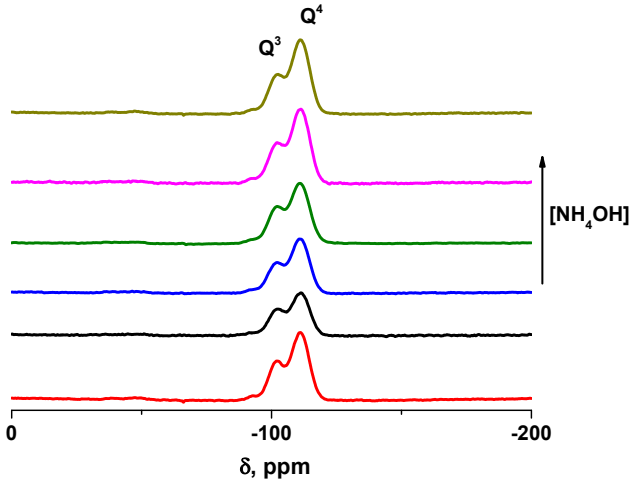



**Figure S1**. $N_2$ adsorption isotherms of NPs-$SiO_2$ obtained with different $NH_4OH$ concentrations.




| [$NH_4OH$], M | % $Q^4$ | % $Q^3$ |
|---|---|---|
| 2.8 | 75 | 25 |
| 2.0 | 72 | 28 |
| 1.6 | 71 | 29 |
| 0.78 | 70 | 30 |
| 0.39 | 75 | 25 |
| 0.20 | 73 | 27 |

**Figure S2**. $^{29}Si$ BD MAS NMR spectra of NPs-$SiO_2$ when varying $NH_4OH$ concentration. Inserted table: percentage of $Q^3$-type and $Q^4$-type silicon atoms obtained in the different materials obtained with different $NH_4OH$ concentration.

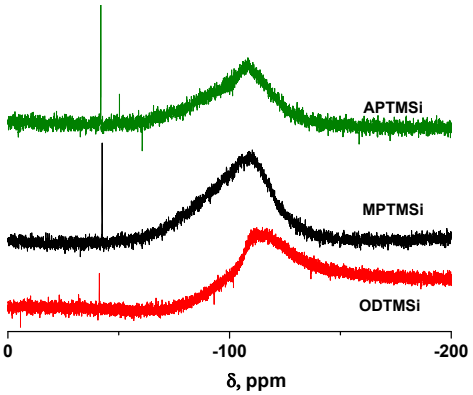



**Figure S3**. Liquid $^{29}$Si NMR spectra of monomeric organosilane precursors.

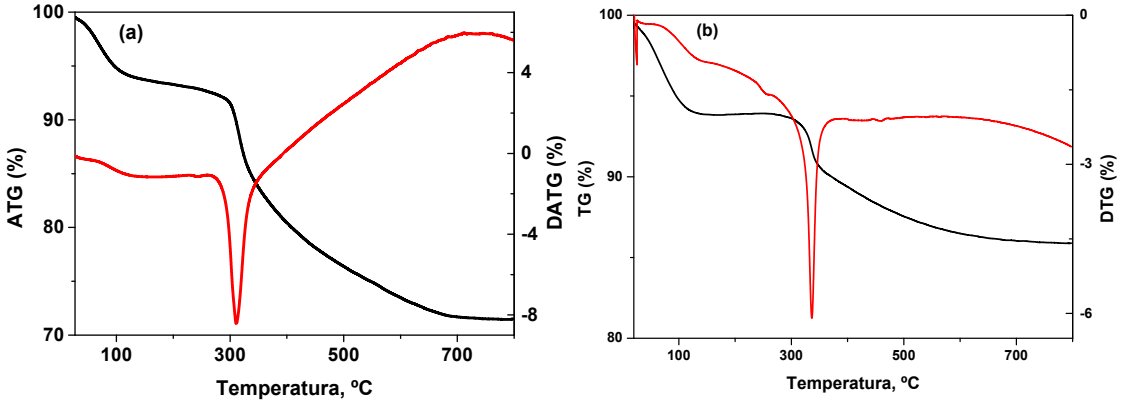



**Figure S4.** Thermogravimetrical analysis of a) NPs-$SiO_2$-$C_{18}$-$NH_2$, b) NPs-$SiO_2$-$C_{18}$-$SO_3H$ materials.

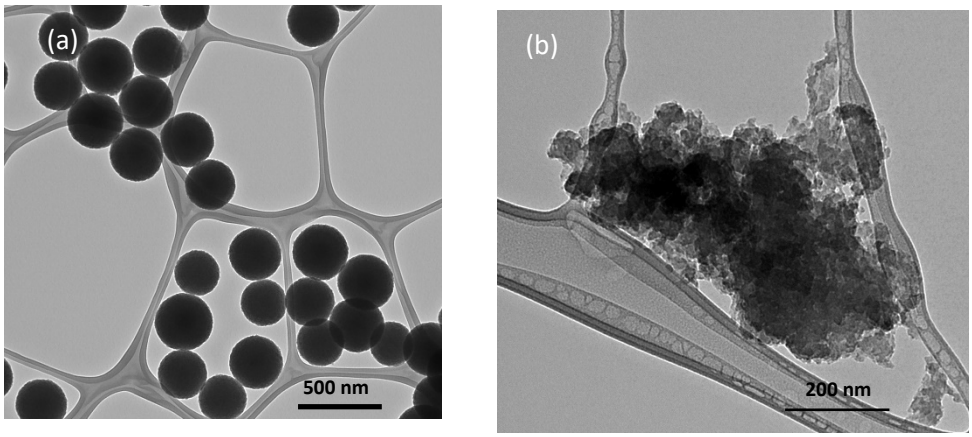



**Figure S5**. TEM images of NPs-$SiO_2$-$C_{18}$-$SO_3H$. a) [$NH_4OH$] = 1.6 M, b) [$NH_4OH$] = 0.20 M.

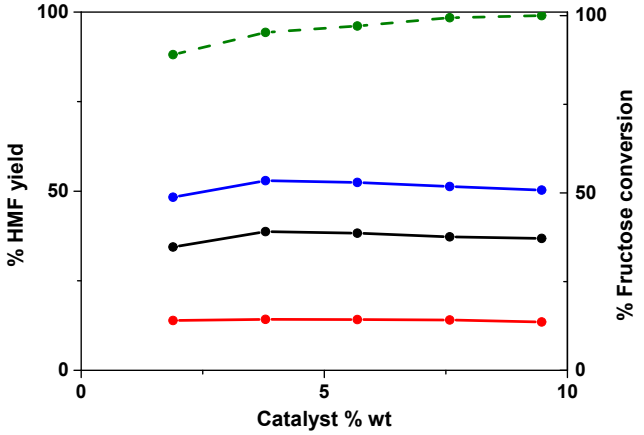
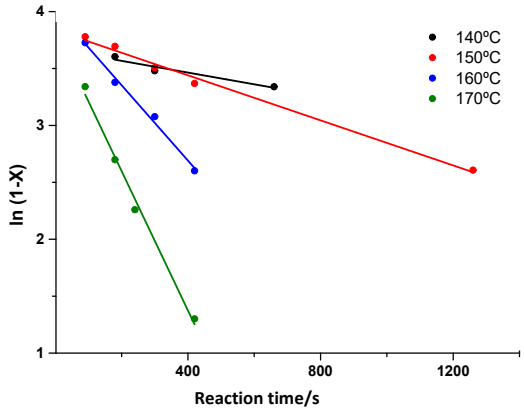



**Figure S6**. Catalytic activity as a function of catalyst amount at 180 ºC and 3 min. Yield to HMF (•), fructose conversion (•), $HMF_{aqueous\ phase}$ (•) and $HMF_{organic\ phase}$ (•). Reaction conditions: 300 mg fructose solution (44 wt%), 900 mg MIBK:BuOH 70:30 and 3.8 %wt catalyst NPs-$SiO_2$-$C_{18}$-$SO_3H$ (1:4), particle size of ~30 nm.




| Temperature | K, $s^{-1}$ | $R^2$ |
|---|---|---|
| 140ºC | $5.1 \cdot 10^{-4}$ | 0.885 |
| 150ºC | $9.9 \cdot 10^{-4}$ | 0.990 |
| 160ºC | $3.3 \cdot 10^{-3}$ | 0.988 |
| 170ºC | $6.1 \cdot 10^{-3}$ | 0.988 |

**Figure S7**. Kinetic constants at different temperatures. Reaction conditions: 300 mg fructose solution, 900 mg MIBK:BuOH 70:30 and 3.8 %wt catalyst NPs-$SiO_2$-$C_{18}$-$SO_3H$ 1:4 $C_{18}$/SH molar ratio, particle size of ~30 nm.

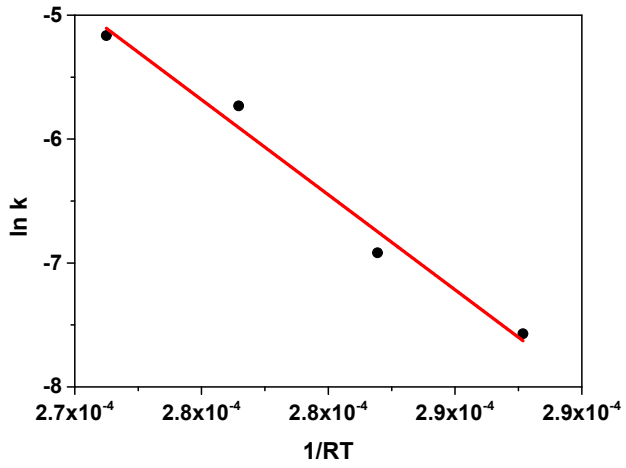



**Figure S8**. Determination Ea: linear fitting according to the Arrhenius equation.

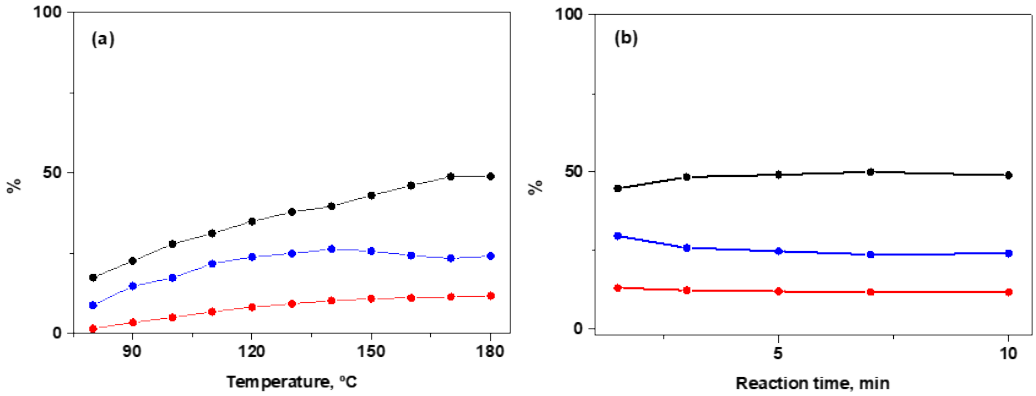



**Figure S9**. Catalytic activity of NPs-$SiO_2$-$NH_2$, particle size of ~30 nm, for glucose isomerization when varying: a) reaction temperature and b) time. Glucose conversion (•), fructose selectivity (•) and glucose yield (•).

**Table S1**. Textural properties obtained from the nitrogen adsorption isotherms of the NPs-$SiO_2$.

| [$NH_4OH$], M | Diameter, nm[a] | $S_{BET}$, $m^2/g$ | $S_{Ext}$, mg/g [b] | $S_{Micro}$, $cm^3/g$ |
|---|---|---|---|---|
| 2.8 | 415 ± 14 | 12 | 9.1 | 3.2 |
| 2.0 | 407 ± 16 | 10 | 9.0 | 1.4 |
| 1.6 | 421 ± 17 | 9.5 | 7.8 | 1.7 |
| 0.78 | 148 ± 9 | 25 | 23 | 2.1 |
| 0.39 | 66 ± 6 | 71 | 61 | 10 |
| 0.20 | 27 ± 3 | 120 | 99 | 21 |

[a] Average size of the different silica nanospheres estimated after the measurement of 100 – 130 individual particles from different TEM images. Error was calculated as standard deviation. [b] $S_{EXT}= S_{BET} – S_{micro}$ from *t*-plot.

**Table S*2***. Textural properties obtained from nitrogen adsorption isotherms of mono, bi and tri-functionalized NPs-$SiO_2$.

| **Entry** | **Catalyst** | **[$NH_4OH$]** | **$S_{BET}$, $m^2/g$** | **$S_{Ext}$, $m^2/g$** | **$S_{Micro}$, $cm^3/g$** |
|---|---|---|---|---|---|
| 1 | NPs-$SiO_2$-$SO_3H$ | 1.6 | 34.6 | 31.9 | 2.7 |
| 2 | NPs-$SiO_2$-$C_{18}$ | 1.6 | 9.46 | 9.46 | - |
| 3 | NPs-$SiO_2$-$NH_2$ | 1.6 | 13.0 | 12.4 | 0.6 |
| 4 | NPs-$SiO_2$-$NH_2$ | 0.20 | 228 | 228 | - |
| 5 | NPs-$SiO_2$-$C_{18}$-$SO_3H$ | 1.6 | 49.7 | 49.1 | 0.6 |
| 6 | NPSi-$SiO_2$-$C_{18}$-$SO_3H$ | 0.20 | 281 | 281 | - |
| 7 | NPs-$SiO_2$-$C_{18}$-$NH_2$ | 1.6 | 16.3 | 16.3 | - |
| 8 | NPs-$SiO_2$-$C_{18}$-$NH_2$ | 0.20 | 94.8 | 94.8 | - |
| 9 | NPs-$SiO_2$-$C_{18}$-$SO_3H$-$NH_2$ | 0.20 | 91.5 | 91.5 | - |

**Table S3.** Recycling tests for fructose dehydration. Reaction conditions: 180ºC, 3 min, 3.8 wt% catalyst. Reaction composition: 300 mg fructose solution, 900 mg MIBK:BuOH 70:30 and catalyst NPs-$SiO_2$-$C_{18}$-$SO_3H$ (1:4), particle size of ~30 nm.

| **Cycle** | **% Yield $HMF_{Organic\ phase}$** | **% Yield $HMF_{Aqueous\ phase}$** | **% Yield $HMF_{Total}$** | **% Fructose conversion** |
|---|---|---|---|---|
| 1 | 45 | 15 | 60 | 98 |
| 2 | 29 | 13 | 42 | 81 |

**Table S4**. Elemental analysis (EA) of fresh and re-used catalyst.

| Cycle | %N | %C | %H | %S |
|---|---|---|---|---|
| 1 | 0 | 13.2 | 3.3 | 3.9 |
| 2 | 0 | 14.0 | 3.1 | 2.7 |

**Table S5**. Fructose dehydration into 5-hydroximethylfurfural.

| Catalyst | Reaction conditions | Solvent | % HMF yield | % Fructose conversion | Ref |
|---|---|---|---|---|---|
| Amberlyst-70 | 180°C, 20min | $H_2O$ | 47 | 80 | 45 |
| $Nb_2O_5$ | 165°C, 3h | $H_2O$ | 57 | 76 | 46 |
| $TiO_2$-$SO_3H$ | 165°C, 3h | $H_2O$/secBuOH/MIBK | 65 | 98 | 47 |
| $SO_4^{2-}/TiO_2$ | 150°C, 6h | $H_2O$/DMSO | 75 | 100 | 48 |
| $PrSO_3H$/GF | 120°C, 1h | DMSO | 87 | - | 49 |
| LDMCC | 180°C, 2h | DMSO | 96 | 99 | 50 |
| PSSA–$AlCl_3$ | 150°C, 4h | $H_2O$ /MIBK/BuOH | 55 | - | 51 |
| PMO-1a | 160°C, 45 min | $H_2O$ /MIBK/BuOH | 58 | 95 | 20 |
| $SiO_2$-$C_{18}$-$SO_3H$ | 180°C, 3 min | $H_2O$ /MIBK/BuOH | 60 | 98 | This work[a] |

[a] Reaction conditions: 300 mg fructose solution, 900 mg MIBK:BuOH 70:30 and 3.8 wt% catalyst, into a 2 mL microwave vial reactor. The reaction was carried out in a Biotage® Initiator + microwave apparatus.

**Table S6**. Glucose isomerization to fructose.

| Catalyst | Reaction conditions | % Fructose yield | % Glucose conversion | Ref |
|---|---|---|---|---|
| Triethylamine | 100°C, 20 min | 32 | 51 | 21 |
| CM-Molten | 60°C, 1 h | 12 | 20 | 52 |
| SnMFI-NS | 90°C, 12h | 27 | 31 | 53 |
| Bentonite | 110°C, 1 h | 39 | 45 | 54 |
| MIL-101(Al)–$NH_2$ | 120°C, 2h | 26 | 44 | 55 |
| $SiO_2$-$NH_2$ | 180°C, 3 min | 12 | 52 | This work[a] |

[a] Reaction conditions: 5 g of water, 0.5 g of glucose and solid catalyst with 5 mol% N respect to glucose were added into a 5 mL microwave vial reactor. The reaction was carried out in a Biotage® Initiator + microwave apparatus with 2 min pre-stirring.