Dendritic silica functionalized with SO_3H and Ru as catalysts for the conversion of furfural from lignocellulosic biomass

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Introduction and Objectives

- Fossil fuels comprise ~80% of the world energetic demand [1].
- Climatic changes created a demand for alternatives energy sources [1].
- Lignocellulosic biomass provides a great abundance of renewable compounds which can be converted into alternative fuels [2].
- In this work domino and condensation reactions, involving furfural, and reactions involving levulinic acid and furfuryl alcohol were conducted using dendritic silica functionalized with SO_3H and Ru as active sites.

Experimental

Catalysts synthesis:

- Dendritic silica (DMSi) was synthesized through a biphasic system of oil-water stratification [3].
- DMSi-Ru and DMSi-SO_3H were synthesized by reducing a Ru precursor using sodium borohydride and sulfonation with chlorosulfonic acid [4].

Catalytic evaluation:

- The reactions were performed at 130 ºC using a catalyst mass of 25 mg [3].

Results

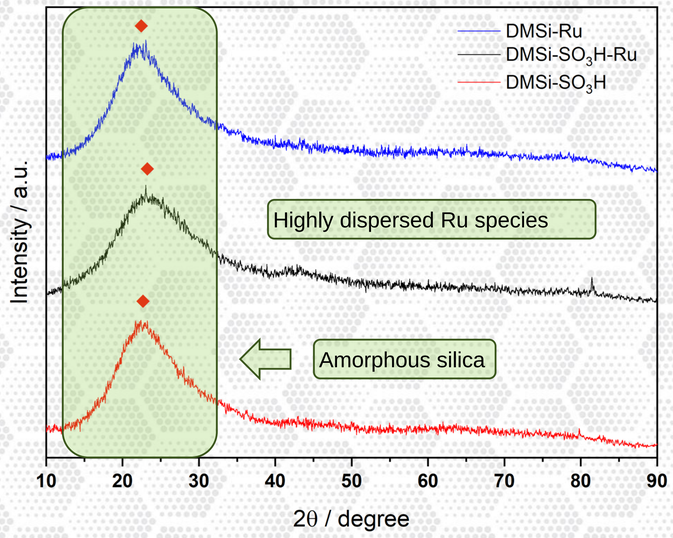

Fig. 1: XRD diffraction patterns of the DMSi-Ru, DMSi-SO_3H and DMSi-SO_3H-Ru catalysts.

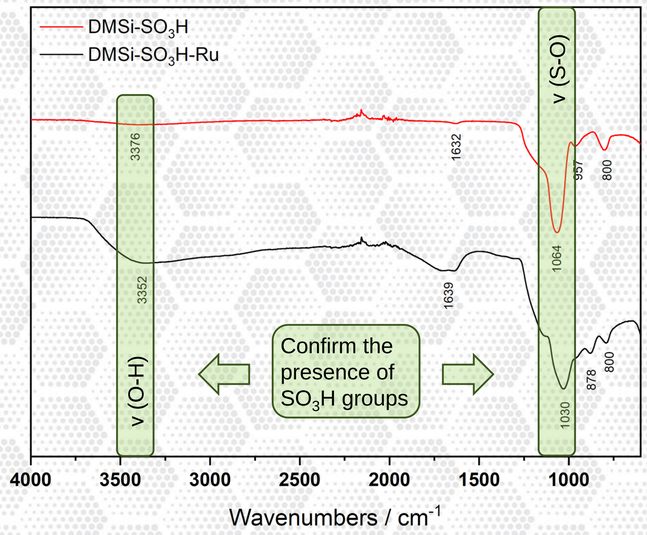

Fig. 2: FTIR spectra of the DMSi-SO_3H and DMSi-SO_3H-Ru catalysts.

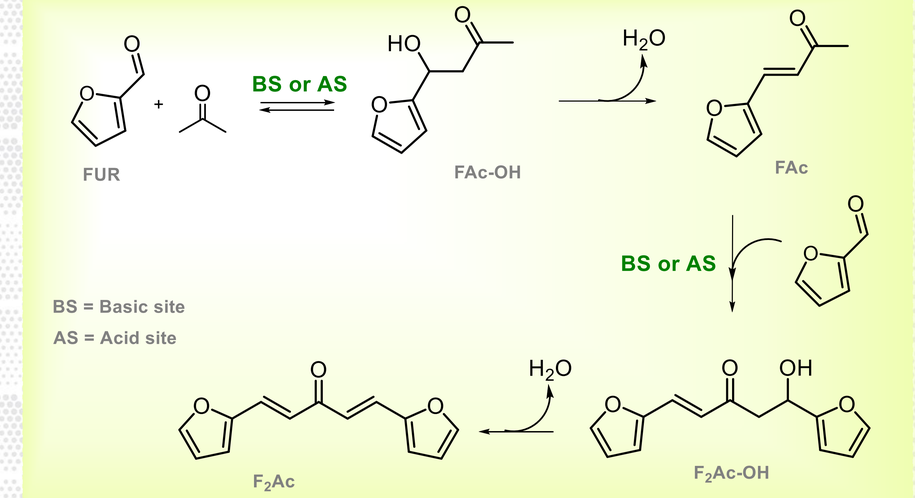

Fig. 5: Aldol condensation reaction pathway of FUR with acetone.

Condensation reaction			
Catalyst	**χ FUR (%)**	**S_{PMF} (%)**	**S_{FAc} (%)**
DMSi-SO_3H	**74.4**	**49.2**	**50.8**
DMSi-SO_3H-Ru	**91.1**	**91.3**	**8.7**

A condensation reaction needs Brønsted acid sites. The functionalization with Ru led to competition between Brønsted and Lewis acid sites, decreasing the selectivity of **FAc**, a condensation product, and increasing **PMF**, a domino reaction product [5].

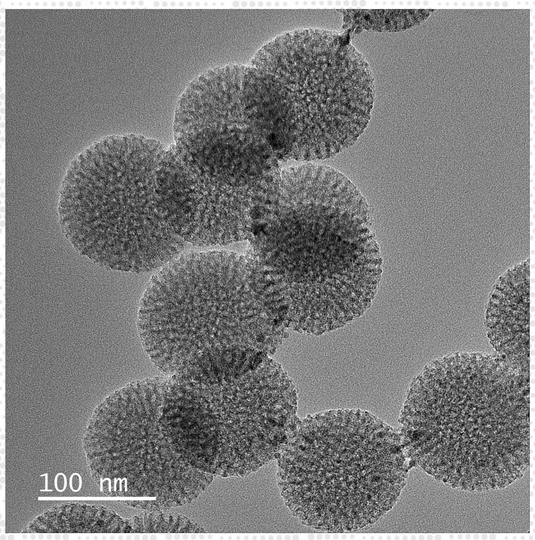

Fig. 3: TEM images of DMSi pure silica.

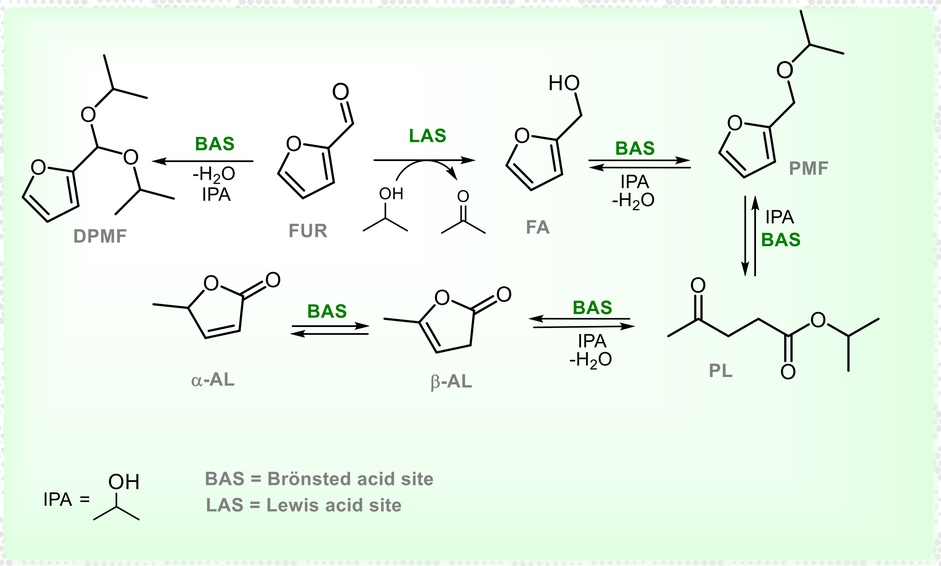

Fig. 4: Domino reaction pathway for FUR and FA conversion to value-added molecules.

Domino reaction using FA as starting material				
Catalyst	**χ FA (%)**	**S_{PL} (%)**	**S_{AL} (%)**	**S_{FUR} (%)**
DMSi-SO_3H	**100.0**	**98.5**	**1.5**	**-**
DMSi-Ru	**2.8**	**-**	**-**	**100.0**
DMSi-SO_3H-Ru	**100.0**	**100.0**	**-**	**-**

Catalysts functionalized with Brønsted acid sites, SO_3H groups, led to the production of domino molecules **PL** and **AL**.
DMSi-Ru catalyzed the oxidation reaction to produce **FUR** [5].

Domino reaction using FUR as starting material			
Catalyst	**χ FUR (%)**	**S_{PL} (%)**	**S_{DPMF} (%)**
DMSi-SO_3H	**47.6**	**-**	**100.0**
DMSi-Ru	**2.4**	**-**	**100.0**
DMSi-SO_3H-Ru	**82.0**	**39.1**	**60.9**

A domino reaction with furfural needs both Brønsted and Lewis acid sites; therefore, only DMSi-SO3H-Ru was capable of producing a domino product, **PL** [4].

Domino reaction using Levulinic Acid as starting material		
Catalyst	**χ LA (%)**	**S_{PL} (%)**
DMSi-Ru	**100.0**	**100.0**

Ru species furnished the necessary acidity to catalyze the esterification reaction of **LA** to **PL**.

Conclusion

It was demonstrated that the functionalization of dendritic silica with SO_3H groups and Ru led to a catalytic activity towards the lignocellulosic biomass valorization reactions. The evaluation of catalysts with Brønsted and Lewis acid sites both separately and jointly led to an obtention of different products and an increase or decrease in selectivity for already obtained products. More characterizations for the catalysts are being conducted to make the work more complete, along with new catalytic tests, product elucidation, and studies related to the catalyst acidity.

References

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