Si-Al NANOSPHERES FOR THE VALORIZATION OF GALACTOSE AND AGAROSE INTO 5-HYDROXYMETHYLFURFURAL

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Introduction

5-hydroxymethylfurfural (HMF) is a compound that has gained attention to potentially substitute fossil resources in areas such as the polymer industry or the production of energy vectors. HMF is produced from the acid treatment of hexoses, such as glucose or galactose. In this sense, algae biomass has gained interest as it can be grown in both, sweet and salt water and their growth rate and CO_2 fixation are several times higher than those of terrestrial plants. Red algae, which are rich in agarose, a galactose and 1,6-dehydrogalactose heteropolymer, can potentially be used as feedstock to produce HMF [1].

Hence, in this work, alumina supported nanospheres have been synthetised and employed as acid catalysts due to their high acidity and porosity that allows the selective conversion of these biomass derived compounds into valuable HMF.

Catalyst Synthesis

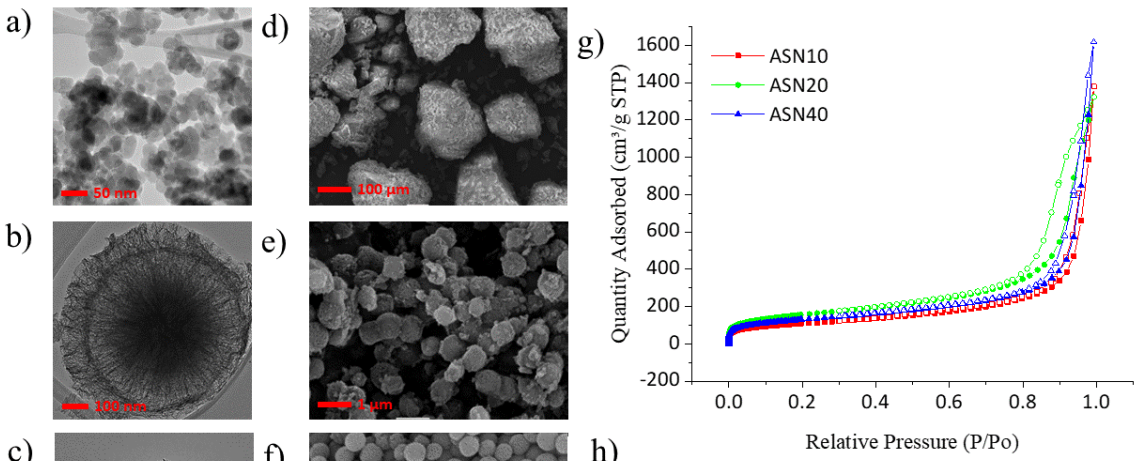
To produce the nanospheres, the synthesis reported by Choi et al. was followed. [2] Cetylpyridinium chloride (1 g) and urea (0.6 g) were dissolved in water. Another solution was prepared dissolving 2.5 g TEOS and 1.5 mL 1-pentanol in cyclohexane. The solution of cyclohexane was added to the aqueous solution and stirred for 30 minutes before transferring to an autoclave that was heated for 2.5 h at 120ºC. Once the solution as cooled down at room temperature, HCl 2 M was used to adjust the pH to 5. Then, Aluminium was incorporated on the surface of the produced silica nanospheres with the addition of the desired amount of $Al_2(SO_4)_3$. The resultant mixture was heated in autoclave for 4 h at 120ºC, mixed with acetone in 1:1 volume ratio and filtrated after it has cooled to room temperature. The solid was dried overnight at 70ºC before calcination at 550ºC. Three different alumina-covered nanospheres were produced, with a total Si:Al ratio of 10, 20 and 40, denoted as ASN10, ASN20 and ASN40 respectively.

Catalyst Characterization

Using Transmission electron microscopy (TEM) (**Figure 1a**, **b**, **c**) and Scanning Electron Microscopy (SEM) (**Figure 1d**, **e**, **f**) the spherical morphology of the particles is confirmed. It can be seen that with increasing amount of aluminium, the spherical morphology loses stability. While ASN40 are perfectly spherical, in ASN10 the aluminium content has caused the decomposition of the nanospheres in favour of agglomerates of small and amorphous particles. On the other hand, The Si:Al ratio present in ASN20 favours outgrowths present in the surface of the ASN20 particles caused a substantial increase in the mesopore area of the material compared to the other catalysts, easily noticeable in the N_2 adsorption-desorption isotherms at -196ºC of the catalysts (**Figure 1g, h**), which is beneficial for the diffusion of reactants and products. The hysteresis loop indicates easily accessible, and not sinuous, porosity present on the surface. The solids were characterised by X-ray Photoelectron Spectroscopy (XPS) (**Figure 1h**) to study the chemical composition of the surface of the material. Due to the synthesis method, the aluminium is deposited over the silicon core and the Si:Al relation obtained by this method is much lower than the total Si:Al ratio.

Catalytic Process

The materials were employed in both, the dehydration of galactose and the transformation of agarose into HMF, using a water:methyl isobuthyl ketone biphasic system (1.5 mL and 3.5 mL, respectively) at 170ºC. Galactose dehydration was successfully carried out by the nanospheres (Figure 2a), with HMF yields reaching 38% after 7 h of reaction and high conversion values. Small quantities of tagatose were identified, acting as intermediate between galactose and HMF. Higher aluminium contents were observed to be more active. However, when agarose polymer was employed as feedstock, diffusion was the limiting factor. In this case, ASN20, with its enhanced porosity resulted the most active and selective in the production of HMF. Also, HMF yields were much higher than those obtained from pure galactose thanks to the 1,6-dehydrogalactose monomers present in the polymer, that undergo dehydration more easily than galactose itself. A final 78% HMF yield could be obtained with ASN20 after 7 h of reaction at 170ºC.



	XPS Si:Al ratio	*BET Surface Area (m^2/g)*	*t-plot External Surface (m^2/g)*
ASN10	10	516	424
ASN20	12	591	576
ASN40	15	435	415

Figure 1. TEM images obtained from: a) ASN10, b) ASN20, c) ASN40. SEM images of d) ASN10, e) ASN20, f) ASN40. G) N_2 adsorption-desorption isotherm of the studied materials

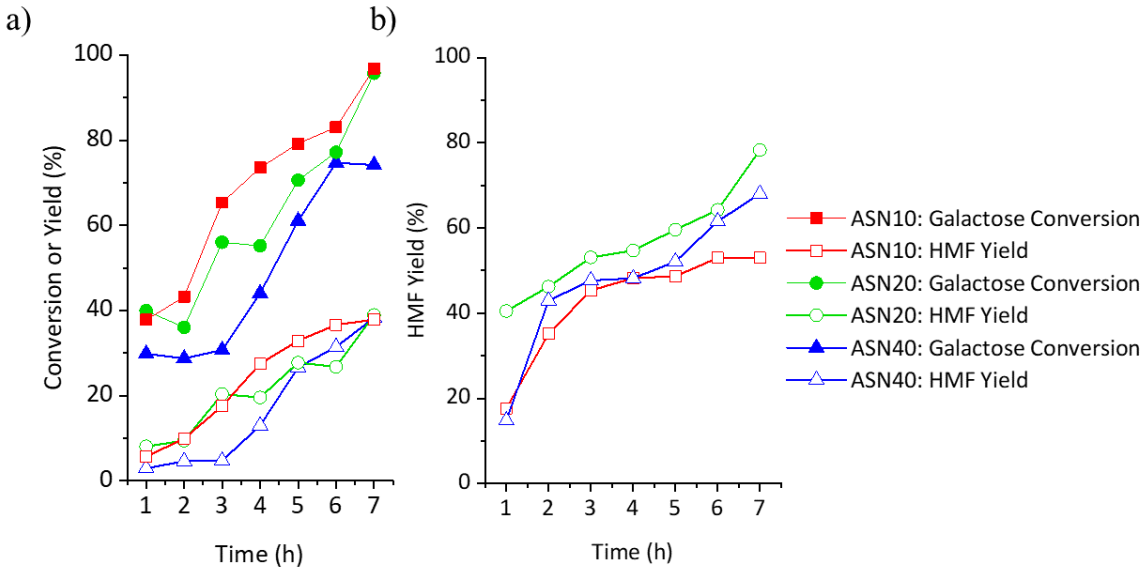


Figure 2. a) Galactose conversion and HMF yield observed during galactose transformation. b) HMF yield obtained from agarose conversion.

References

1) Aswathi Mohan, A., et al., Algal biopolymers as sustainable resources for a net-zero carbon bioeconomy. Bioresource Technology, 2022. 344: p. 126397.
2) Choi, Y., et al., A facile approach for the preparation of tunable acid nano-catalysts with a hierarchically mesoporous structure. Chemical Communications, 2014. 50(57): p. 7652-7655.