Halloysite based nanocatalysts for the catalytic conversion of biomass

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ABSTRACT

The selective conversion of fructose to 2,5-furandicarboxylic acid (FDCA) represents one of the most important reactions involving the use of biomass and its derivatives. FDCA is indeed an extremely requested chemical compound, being a valid alternative to terephthalic acid for the production of bioplastics.[1]
In this work, we report some preliminary investigation about the possibility to use halloysite-based nanomaterials as bifunctional catalysts for the reaction above. To this aim, halloysite nanotubes were modified on the outer surface with an organic compound, AEAPTMS, to induce the attachment of gold nanoparticles to the amino group of the siloxane chain. They were then investigated as heterogeneous catalysts for the oxidation of HMF to FDCA, being HMF the intermediate compound in the biomass conversion.

REACTION

The first step of a computational analysis was to study the conversion of **HMF** to **HDFF** using both AEAPTMS and APTES as surface modifiers, bearing the latter an organic chain with a single amino group.
The energetical barrier found for the transition state is 85.7 kJ/mol, whilst the overall energy of the reaction is -25.7 kJ/mol.
H_2O_2 is tentatively used as the oxidizing agent since the ΔG of the overall reaction

$$HMF + 3\ H_2O \rightarrow FDCA + 4\ H_2O$$

was calculated to be ca. -1000 kJ/mol.

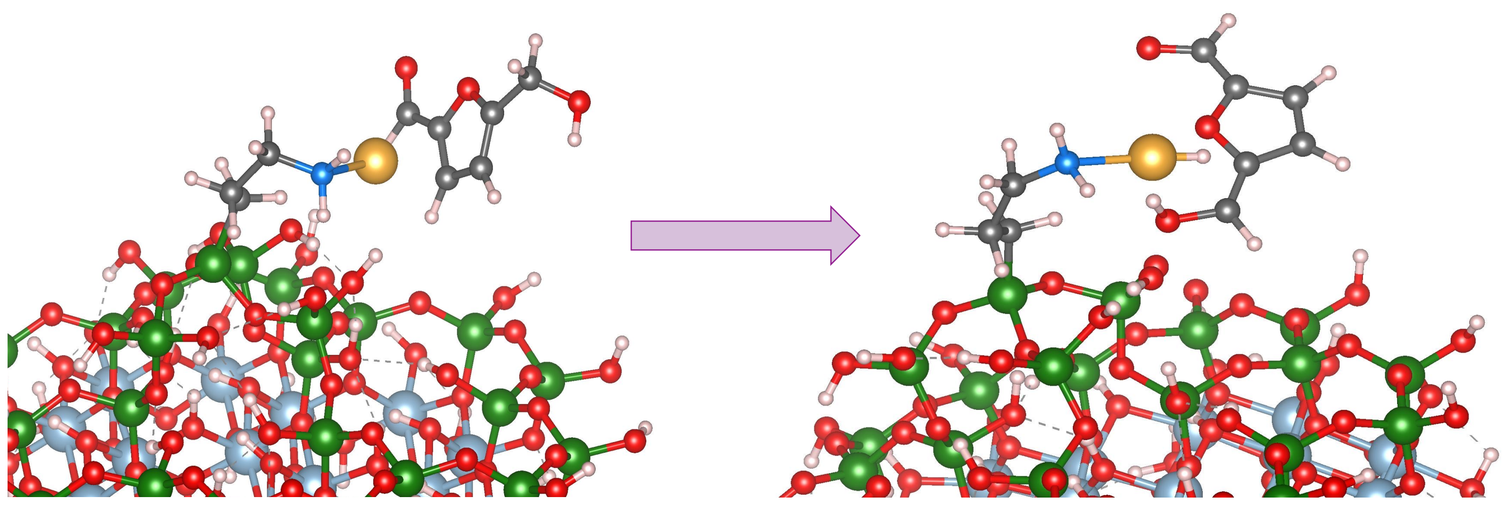

Fig. 1 Conversion of HMF to HDFF (red, green, cyan, grey, blue and yellow spheres represent oxygen, sylicon, aluminum, carbon, nitrogen and gold atoms).

EXPERIMENTAL PROCEDURE

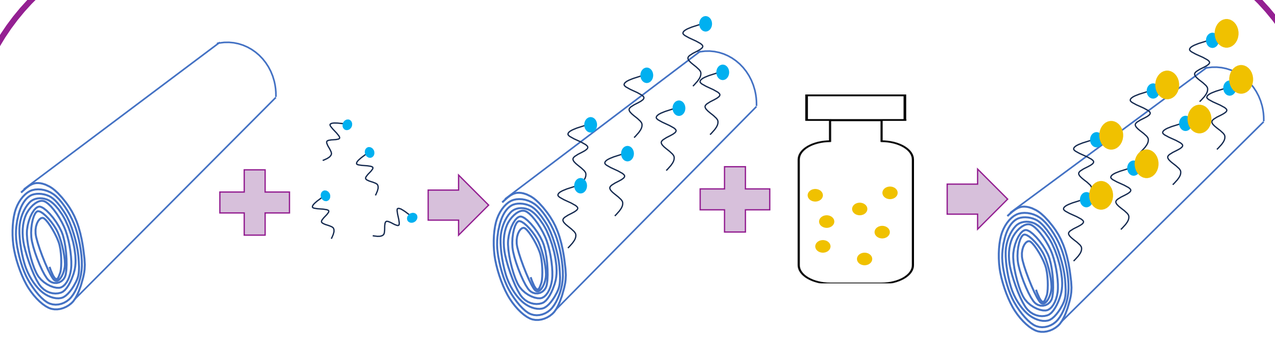

Fig. 2 Experimental procedure for the loading of AuNPs: the pristine halloysite is functionalized with AEAPTMS; then the AuNPs are loaded on the modified HNTs.

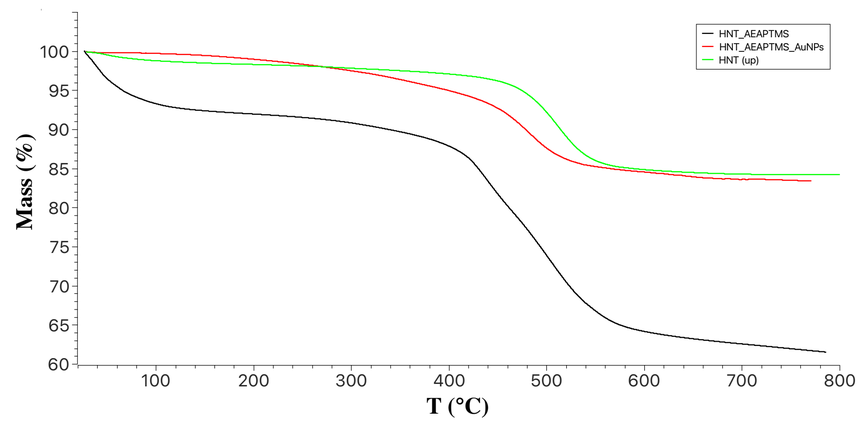

Fig. 3 Thermogravimetric analysis (TGA) of pristine halloysite, AEAPTMS and AuNPs loaded.

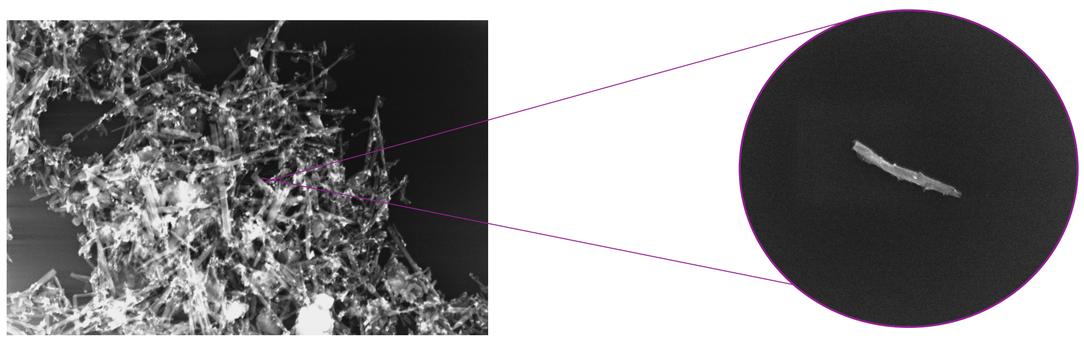

Fig. 4 SEM analysis of the loaded halloysite nanotubes.

COMPUTATIONAL DETAILS

Calculation were performed by using the Gaussian 16 software. The overall reaction was studied with the ONIOM procedure (DFT/UFF) using the M06 exchange-correlation functional joined with the cc-pVDZ as basis set as high level method.

FINAL REMARKS

The next computational steps will include the study of the other species involved in the overall reaction with H_2O_2 and how they will interact with the whole halloysite system.
The experimental procedure will aim to obtain an homogeneously decorated nanotube with smaller gold nanoparticles.

Acknowledgements

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[1] Xu, S.; Zhou, P.; Zhang, Z.; Yang, C.; Zhang, B.; Deng, K.; Bottle, S.; Zhu, H. Selective Oxidation of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid Using O2 and a Photocatalyst of Co-Thioporphyrazine Bonded to g-C3N4. *J. Am. Chem. Soc.* **2017**, *139* (41), 14775–14782. https://doi.org/10.1021/jacs.7b08861.