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Ordered Materials, Organometallics & Catalysis

Amino Acid functionalized Periodic Mesoporous Organosilicas as Bifunctional Catalysts

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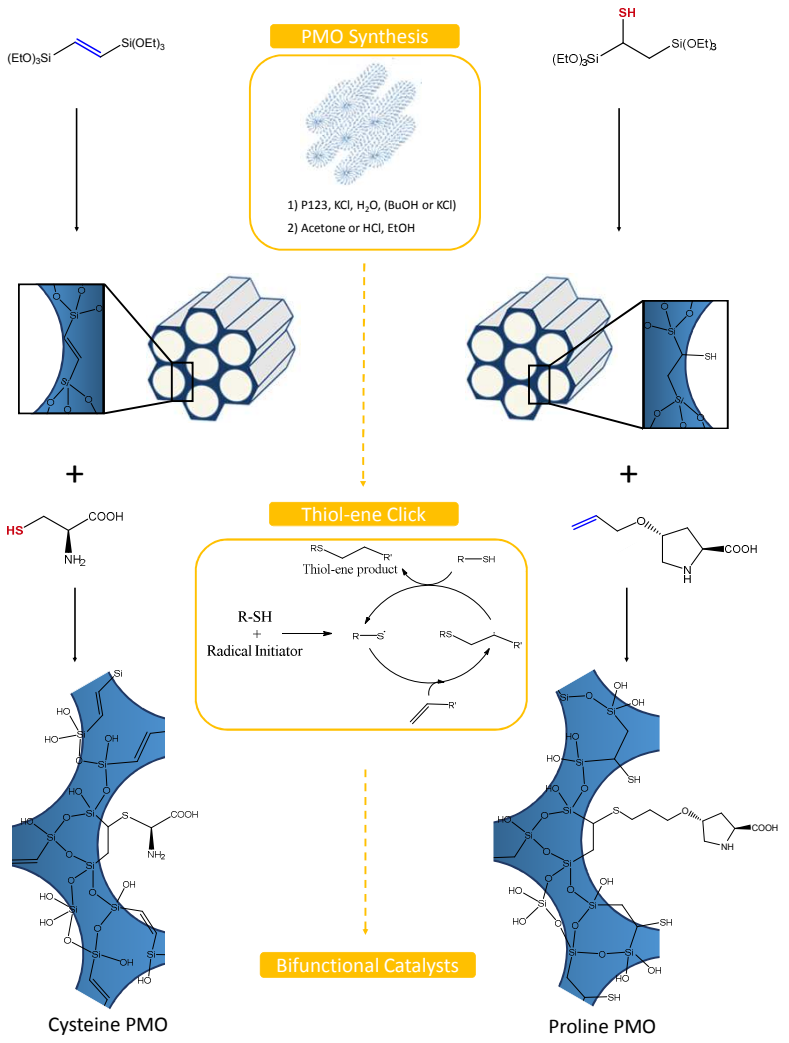
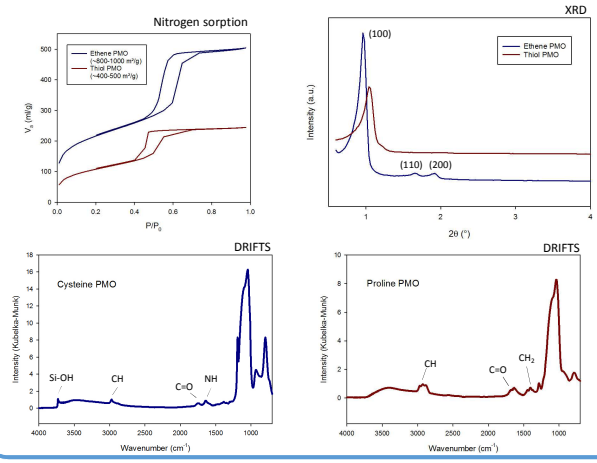
Introduction

Periodic Mesoporous Organosilicas, commonly known as PMOs, are a class of hybrid mesoporous materials. The materials are formed by the hydrolysis and condensation of an organobissilane precursor of the form $(R'O)_3Si\text{-}R\text{-}Si(OR')_3$ around a structure directing agent. In this study, two PMOs which were developed in COMOC, namely an E-ethene-PMO [1] and a thiol-PMO [2], are functionalized with amino acids via a thiol-ene click reaction. The bifunctional acid-base catalysts obtained this way are tested in an aldol condensation reaction.

Synthesis

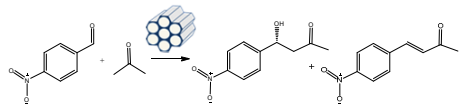


Characterization

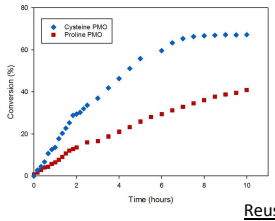


Catalysis

Aldol reaction of p-nitrobenzaldehyde and acetone



Comparison of cysteine and proline

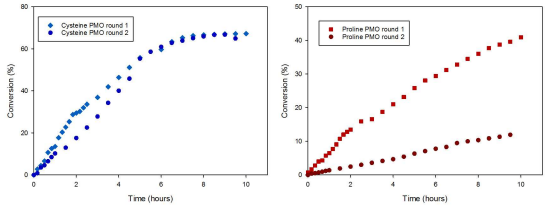


Elemental Analysis

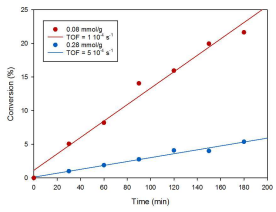
Cysteine PMO: 0.53 mmol/g

Proline PMO: 1.15 mmol/g

Reusability



Comparison of different loadings



When cysteine PMOs with differnt loadings are compared, we see that the lower loading gives the highest conversion. At high loadings, we think that H-bonding occurs, which deactivates the catalyst.

Conclusions

Both bifunctional catalysts were found to be active in the aldol reaction of acetone and nitrobenzaldehyde. The first catalytic tests showed that the cysteine functionalized PMO was more active than the proline functionalized PMO and also showed good reusability. Later studies revealed that the loading of the amino acid has a big influence and possibly the proline PMO was less active due to a higher loading.

In the future, the enantioselective properties of the catalysts will also be investigated.

[1] C. Vercaemst, M. Ide, B. Allaert, N. Ledoux, F. Verpoort, P. Van Der Voort, *Chem Commun* **2007**, 2261-2263.
[2] D. Esquivel, O. van den Berg, F.J. Romero-Salguero, F. Du Prez, P. Van Der Voort, *Chem Commun* **2013**, *49*, 2344-2346.

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