







MASTER DE CHIMIE DE PARIS CENTRE - M2S2 Proposition de stage 2018-2019 Internship Proposal 2018-2019

Spécialité(s) / Specialty(ies) :

□ Chimie Analytique, Physique, et Théorique / Analytical, Physical and Theoretical Chemistry : □ Chimie Moléculaire / Molecular Chemistry :

Matériaux / Materials:

Ingénierie Chimique / Chemical Engineering:

Laboratoire d'accueil / Host Institution

Intitulés / *Name* : Laboratoire de Réactivité de Surface Adresse / *Address* : Tour 43-33 3^{ème} étage, Sorbonne Université, 4, place Jussieu, 75005 Paris Directeur / *Director (legal representative) : Hélène Pernot* Tél / *Tel* : 01 44 27 55 33 E-mail : helene.pernot@sorbonne-universite.Fr

Equipe d'accueil / Hosting Team :

Adresse / Address : Laboratoire de Réactivité de Surface Responsable équipe / Team leader : Site Web / Web site : Responsable du stage (encadrant) / Direct Supervisor : Juliette Blanchard Fonction / Position : Chargée de Recherche Tél / Tel : 0144274914 E-mail : juliette.blanchard@upmc.fr

Période de stage / Internship period * : 5-6 mois à partir du 21 janv 2019 Gratification / Salary :ca. $535 \in$

Sujet / Title : zeolite@basic-oxides core-shell nanocomposites as catalysts for tandem acid-base reactions

Projet scientifique (1 page maximum) / Scientific Project (maximum 1 page):

1. Projet / Project

The synthesis of complex organic molecules usually requires several successive catalytic steps and, between them, intermediate isolation and purification steps. Performing all these catalytic steps in a single reactor (so-called one-pot multi-steps catalysis) is highly desirable because it is simpler, more cost-effective and more environmentally-benign (thanks to waste reduction). This usually requires the simultaneous presence of two or more catalysts in the reactor. Immobilisation of these catalysts on a support is often a major requirement, not only because it allows an easier recovery of the catalysts but also because a site isolation of the different catalysts is often necessary to avoid mutual quenching of the active sites.

This is specifically the case for acid-base bifunctional catalysis, that plays a key role in the synthesis of many fine chemicals [1,2]. Indeed, homogeneous acid and base are antagonist catalysts that will immediately neutralize each other when put in the same reactor, whereas anchoring these two catalysts on a solid support can prevent their neutralization by keeping them apart [3]. This can be achieved by two different approaches: either by anchoring each catalyst on a different support or by anchoring both

^{* 5-6} mois à partir du 21 janv 2019 / 5-6 months not earlier than January, 21st 2019.

catalysts on the same support. In both cases the balance between acid and basic sites must be carefully adjusted in order to reach optimal activities and selectivities[1].

Anchoring both catalytic functions on the same support is usually achieved by grafting, on a silica support functionalized silanes (e.g. amine and sulfonic acid precursors). However, such catalysts require tedious preparation and often suffer from deactivation or active site leaching. For the other approach, it is possible to use two inorganic materials, an acidic one (e. g. an acidic clay) and a basic one (e.g. an hydrotalcite) that are introduced simultaneously in the reactor. However, as the two types of sites are located on separated materials, the formation of the final products may be slowed down by the diffusion of intermediates.

The objective of the present project will be to design "all-inorganic" core/shell composites with different intimacies between the acid and basic domains. The core of the catalysts will be made of a zeolite nanoparticle (bearing the acidic function) and the shell of basic oxides (MgO). The two components will be associated through heterocoagulation [4]. This new type of catalyst will associate the good stability of inorganic materials with a high intimacy of the acid & basic



functions thanks to nano-scale intimacy of the two components. These catalysts will be tested as tandem acid-base bifunctional catalysts in order to investigate the effect of the intimacy between the acid and basic component on activity and selectivity.

2. Techniques ou méthodes utilisées / Specific techniques or methods

Synthesis: preparation of inorganic colloidal particles (zeolite and Mg(OH)₂, preparation of mixed oxides)

<u>Characterization</u>: X-ray diffraction, Physisorption, TEM, measurement of particle size (DLS) and of their zeta potential, FTIR of probe molecules (density of acidic and basic sites) Catalvsis (if the project's progress unables it): catalvtic test in batch reactor and liquid phase,

<u>Catalysis</u> (if the project's progress unables it): catalytic test in batch reactor and liquid phase, chromatograpy

3. Références / References

[1] S. Shylesh, W.R. Thiel, Bifunctional Acid–Base Cooperativity in Heterogeneous Catalytic Reactions: Advances in Silica Supported Organic Functional Groups, ChemCatChem. 3 (2011) 278–287. doi:10.1002/cctc.201000353.

[2] D. Jagadeesan, Multifunctional nanocatalysts for tandem reactions: A leap toward sustainability, Appl. Catal. Gen. 511 (2016) 59–77. doi:10.1016/j.apcata.2015.11.033.

[3] T.L. Lohr, T.J. Marks, Orthogonal tandem catalysis, Nat. Chem. 7 (2015) 477–482. doi:10.1038/nchem.2262.
[4] O. Ben Moussa, L. Tinat, X. Jin, W. Baaziz, O. Durupthy, C. Sayag, J. Blanchard, ACS Catalysis 8 (2018) 6071-6078.