'Physique et Chimie des Matériaux' – ED 397 – année 2020

PhD project for funding (max 1p), to send to

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Research unit (full name + acronym) : Laboratoire de Réactivité de Surface (LRS)
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Keyword 1 : Catalysis Keyword 2 : Co-precipitation
Keyword 3 : Acid-base properties Keyword 4 : Metallic silicate
Select co-funding programme if applicable : select

Project title : Study of the structural and chemical properties governing the catalytic activity of metallic silicates for transesterification reaction

In the field of bio-sourced molecules valorisation, heterogeneous catalysis faces new challenges to find efficient catalysts in the conversion of platform oxygenated molecules (alcohols, esters, etc.), requiring surface properties (basicity for example) little studied in the context of petroleum chemistry. Among them, transesterification reactions have attracted wide interest. Indeed, the main industrial application, in liquid phase, is the production of biodiesel from bio-sourced triglycerides and methanol, but other works in the literature show the interest of the transesterification in the production of lubricants, polyethylene terephthalate or glycerol carbonate [1]. However, very few studies aiming to identify the inter-relationship between structural parameters and catalytic performances have been reported. In this aim, preliminary studies, conducted at Laboratoire de Réactivité de Surface (LRS) in a transesterification model reaction, demonstrated the interest of magnesium silicates as catalysts in a liquid phase process but also the importance of their surface properties determined by synthesis route [2-4]. In particular, co-precipitation in aqueous solution and at room temperature was shown to give efficient catalysts due to the surface formation of a Magnesium Silicate Hydrate (MSH) phase. Furthermore, an optimization of magnesium silicate synthesis process is currently performed to control and tune the critical structural characteristics (specific surface area, morphology, local composition homogeneity, etc.) of (co-)precipitated (hydr)oxides allowing a better control of the catalytic properties. Now, it's time to study, at a molecular level, the influence of the structural properties of the magnesium silicates on the acido-basic surface properties and their relation with the catalytic one.

In line with these preliminary results, the objectives of this thesis proposal are to:

- Synthetize, in a controllable manner, Mg silicate as well as Ca and Zn silicates material by co-precipitation methods. Indeed, it's seems to be easier to prepare metallic silicate with tuneable acido-basic properties by varying the nature of the metal rather than the Metal/Si ratio.
- Deeply characterize the surface acido-basic properties of well-selected series of samples.
- Evaluate the catalytic performances in transcarbonation (often seen as a transesterification reaction) between dimethyl carbonate and glycerol to obtain glycerol carbonate of the previously selected metallic silicates.
- Establish structure-properties-activity inter-relationship.

The choice of the co-precipitation processes (double-jet batch processes or continuous processes with a micromixer) will guarantee the local homogeneity of the product and the reproducibility of the synthesis. Structural and textural informations on silicates will be obtain by XRD, electronic microscopy and N2 adsorption. Global and local compositions will be characterised by EDX, 29Si NMR, XPS and vibrational spectroscopy.

Moreover, the acid-base properties of these materials will be investigated by studying their reactivity in a model reaction, the conversion of 2-methyl-3-butyn-2-ol, and by adsorption of probe molecules (pyridine, propyne) followed by IR and calorimetry to evaluate the nature, the number and the strength of the acid or basic sites.

Finally, the catalytic performances of these silicates will be evaluated in transcarbonation reaction between dimethyl carbonate (a green solvent) and glycerol (by product of biomass valorisation) to obtain glycerol carbonate (bio-sourced solvent, etc.). As the reaction proceed in liquid phase, the occurrence of possible leaching phenomena and the stability of the materials will also be examined.

[1] M. O. Sonnati et al., Green Chem., 2013, 15, 283-306.
[2] D. Cornu et al., Catal. Sci. Technol., 2017, 7, 1701-1712.
[3] L. Lin et al., ChemCatChem, 2017, 9, 2399-2407.
[4] L. Lin et al., Catal. Sci. Technol., 2019, 9, 6072-6084.