Calorimetry and FTIR co-adsorption studies for reactional mechanism and surface interaction energy determination in one-step acrolein production from bio-alcohols.

Etude de co-adsorptions par calorimétrie et IRTF pour déterminer le mécanisme réactionnel et les énergies d'interaction réactifs-surface catalytique dans la production d'acroléine en une seule étape à partir d'alcools biosourcés.

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Context

Acrolein, the simplest unsaturated aldehyde, is produced industrially from propylene and mainly used as a building block to other chemical compounds. Growing shortage of fossil resources has increased the interest in acrolein synthesis from renewable raw materials. The current project proposes the production of acrolein from bio-alcohols, a two step process, as shown in the following figure:

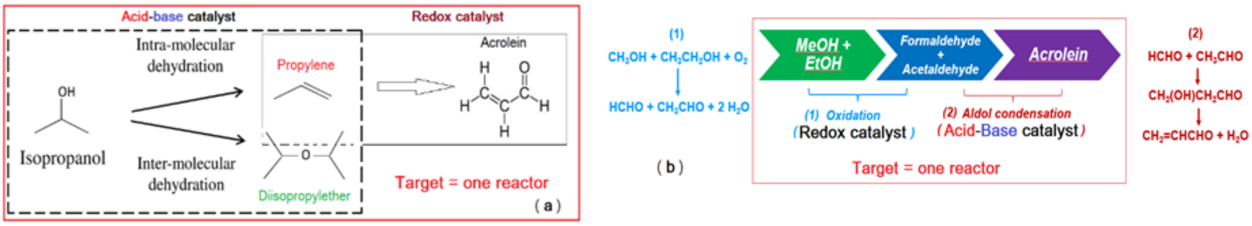

Figure: Two examples of acrolein production from bio-alcohols: (a) the oxy-dehydration of isopropanol and (b) the oxidative coupling of methanol and ethanol.

Both given examples require one redox catalyst and one catalyst with tuned acid-base properties.The aim here is to synthesize acrolein in one-step process in a single reactor with:

(i) a double-catalyst bed or
(ii) a bifunctional catalyst.

In the former case, while a traditional oxidation catalyst will be used, an environmentally friendly acid-base catalyst needs to be designed, able to perform under oxidative atmosphere required for acrolein generation (a) or alcohols oxidation (b). The advantage of developping a bifunctional catalysts (second case), combining suitably controlled acid-base properties with properly tuned oxidizing features, contained in a single catalytic bed, would be the better long-term performance. In both cases, the development and further optimization of catalysts requires a deep understanding of the nature of active sites, the mechanisms involved, and the key parameters to tune activity/selectivity.

A combined approach coupling adsorption microcalorimetry, FTIR analysis and catalytic testing will be used in this project to establish relationships between surface acid–base properties and the catalytic reactivity of selected catalysts. Determination of the strength and nature of the active sites exposed on the solid surface as well as their distribution is a necessary requirement to understand the catalytic properties of solids. Among the methods that allow the identification of the surface active sites, infrared spectroscopy

(FTIR) and adsorption calorimetry have a particular role. Heat flow microcalorimetry is one of the best methods known for measuring accurately the differential heats of adsorption and so of characterizing a catalyst by the energy distribution of its surface sites. FTIR is a powerful technique to evidence the nature of the sites allowing a qualitative picture of the surface active sites of the catalyst.

Description of the research project

During his/her thesis, the PhD student will dedicate his work on various aspects of heterogeneous catalysis, namely the preparation of catalysts and their modifications, the study of their reactivity and their physico-chemical characterization, in order to establish structure - activity relationships.

The following main steps will be considered:

-determination of the acid/base properties of a series of oxide catalysts followed by a tuning of the surface acidity if necessary.
-determination of the adsorption properties of the catalysts towards reactants and products (co-adsorption studies in order to determine the predominant reactant).
-determination of the catalytic performances in acrolein synthesis from bio-acohols.
-finding correlations between surface and catalytic properties in order to enhance the yield and selectivity.
Dedicated assessments will be performed on the stability of the developed catalytic systems and on the influence of the addition of water on their catalytic properties.

Required profile: Master degree or similar, with good knowledge in catalysis/physicochemistry. Basic knowledge in synthesis will be appreciated.

References

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ChemSusChem 10 (2017) 3459 (DOI : 10.1002/cssc.201701040)
ACS Catal., 5 (2015) 4423 (DOI: 10.1021/acscatal.5b00723)
ChemSusChem 5 (2012) 1162 (DOI : 10.1002/cssc.201100447)

Application

Please provide the following documents:

- CV
- Motivation letter
- 1 or 2 recommendation letters with referees contact details
- Grades of Master 1 & 2 or Engineer degree.