SHORT TERM SCIENTIFIC MISSION (STSM) – SCIENTIFIC REPORT

The STSM applicant submits this report for approval to the STSM coordinator

Action number: 40343
STSM title: Modelling study of butanoic and pentanoic acids oxidation and pyrolysis
STSM start and end date: 16/04/2018 to 30/04/2018
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PURPOSE OF THE STSM

The aim of this Short Term Scientific Mission (STSM) is to extend the collaboration between the *Dipartimento di Chimica, Materiali e Ingegneria Chimica* at *Politecnico di Milano* and *Laboratoire Réactions et Génie des Procédés (Nancy, France)* within the SMARTCATS COST Action (CM1404).

I have performed an experimental investigation of the pyrolysis and the oxidation of some acids over the supervision of Dr. Frédérique Battin- Leclerc and Dr. Olivier Herbinet. Dr. Frédérique Battin- Leclerc is also, together with Dr. Olivier Herbinet, group leader of the first work group (WG1: Smart Energy Carriers gas phase chemistry: from experiments to kinetic models) of the SMARTCATS program. This work is linked to the IMPROOF project. A part of this project is to carry out laboratory studies on alternative fuels, especially those derived from biomass. My PHD subject is focused on this part and especially bio-oil, in which carboxylic acids are present in a large amount. The acids studied were the butanoic acid (C4H8O2) and the pentanoic acid (C5H10O2). Pyrolysis was only performed on pentanoic acid, but oxidation was studied for both molecules.

The main purpose of the collaboration is to use the experience and the knowledge of Prof. Faravelli team in modeling to help the applicant to develop a model for the combustion of acids using the previously acquired data. This mechanism will be then added to the one of Polimi in order to succeed in the modeling of bio-oil combustion. This model will be used in the scope of the IMPROOF project to model new furnaces using alternative fuels like bio-oil. The final aim is with these tools to develop the next generation of steam-cracking furnaces.

DESCRIPTION OF WORK CARRIED OUT DURING THE STSM

During the STSM, I have used the resources of the team of Prof. Faravelli to develop a mechanism for the pyrolysis of pentanoic acid.

The aim was to reproduce the experimental results obtained in Nancy with the latest version of the POLIMI model upgraded with the new set of reactions specific to the decomposition of pentanoic acid. The final goal is to obtain rate rules for the decomposition of acids in general.

All the modelling activity was performed with the software developed in Milano by Prof. Faravelli team, OpenSmoke++.

Their previous work on acetic acid was used as a base for the understanding and the production of the mechanism. We used their calculations on acetic acid and corrected them to correspond to pentanoic acid. So molecular decompositions pathways were identified and added in the mechanism. H-atom abstractions on the acid specific function by H, OH and CH3 radicals were also estimated from this study.

A theoretical analysis was also performed using Thergas, a software developed in Nancy, to determine the bond dissociation energy for pentanoic acid. This study was used to determine the kinetics value for the first step of the mechanism: unimolecular decompositions. However, some ab initio calculations are still needed to have more accurate values.

An assumption was made to describe an acid molecule as two parts: one acid and the rest alkane-like (R-CH2-COOH). So many estimations for kinetics value were also made using kinetics parameters from alkanes mechanism.

DESCRIPTION OF THE MAIN RESULTS OBTAINED

Here are the main results of this work:

- Sensitivity analysis on the bond dissociation energy has shown that they have a huge impact on the decomposition of the molecule, and specially on the C-C bond. That is why ab initio calculations must be performed.
- Decompositions pathways have been identified and have shown that some radicals are critical in the system. For example: CH2COOH and HOCO are the most important provider of CO2 and CO. CH2COOH is also suspected to be a radical able to abstract H-atom from the fuel. These decompositions pathways have also shown the importance of H-abstractions at low-temperature.
- It also seems that the assumption describing acids in two moieties (one characteristics of acids and the other corresponding to alkanes one) is valid. Using kinetics parameters from alkanes decomposition leads to a good agreement between our experimental data and the modelling values.
- At the end of this STSM we succeed to have a model giving values in a relative good agreement with the experimental data, but it can still be improved with a better description of the molecule bond energy. Some pathways leading to some minor products have also to be identified and better assessed.

FUTURE COLLABORATIONS (if applicable)

The further development of the model of pentanoic acid pyrolysis will still be in collaboration with the team of Prof. Faravelli. They will perform some ab initio calculations on the molecule bonds and on relevant reaction pathways and I will implement the results in the model. Missing pathways have also to be identified to reproduce even the minor products formation.

The next step is to determine rate rules for acid decomposition and to extend them to their oxidation. The final model should be able to reproduce the oxidation of butanoic and pentanoic acids.