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New route for the production of Acrolein from a mixture of light alcohols: an In Situ X-ray Photoelectron Spectroscopy study

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PURPOSE OF THE ABSTRACT

Nowadays because of decreasing amount of fuel, alternative ways of several compounds production are actively researched. Therefore, products obtained from biomass became more popular and their valorization is now examined. Bioethanol is one of the most largely produced biosourced compound which finds many industrial applications thanks to its easy conversion to high value products. Its mixture with methanol can lead to the formation of acrolein using the ad-hoc catalyst. In this study, we will present the results obtained using the so-called FeMo based catalyst industrially used for formaldehyde production. A Design of Experiments (Figure 1) has been used and the different step of FeMo synthesis and of acrolein formation reaction have been characterized using ex-situ and in-situ techniques. In order to understand the mechanism taking place during the catalytic reaction, information about the surface are needed.

The grail in catalytic research is to determine the structure of the surface and describe the catalyst active site involved in the chemical operations. Catalysts for selective oxidative reaction are often bulk transition metal oxides making In-Situ/Operando spectroscopic studies difficult because one usually monitors the global signal of the solid while modifications arising from its contact with the reactants occur only on the surface. In order to address this problem, we applied Near Ambient Pressure X-Ray Photoelectron Spectroscopy (NAP-XPS) which offers direct access to the oxidation state of the catalyst surface at elevated pressures [1]. The catalyst has been studied under a mixture of methanol and ethanol at millibar pressures under reaction conditions at the SOLEIL TEMPO B beamline.

The whole redox processes occurring on Fe and Mo surface centers and the identification of surface intermediate species have been monitored by recording Mo 3d, Fe 2p, C 1s, and O 1s spectra. The gas-phase reactants and products have been analyzed simultaneously by mass spectrometry (MS) while C1s and O1s spectra of the adjacent gas-phase have also been recorded. Thanks to the high flux of the SR radiation, the evolution of Mo and Fe oxidation state was followed during either reduction and oxidation reaction as a function of time and temperature. Thanks to this technique we evidence clearly that the reduction of the catalyst during the reaction occurs through the molybdenum atoms (Figure 2). This in situ study demonstrated the great potential of the NAP-XPS to determine and understand the behavior of a real catalyst under working conditions.

Thanks to the understanding of the mechanism taking place at the catalyst surface we modified the raw materials adding basic elements. Its modification leads up to 50% of acrolein yield which is, from our knowledge, the best one obtained starting from light alcohols, reported in the literature.

Acknowledgment
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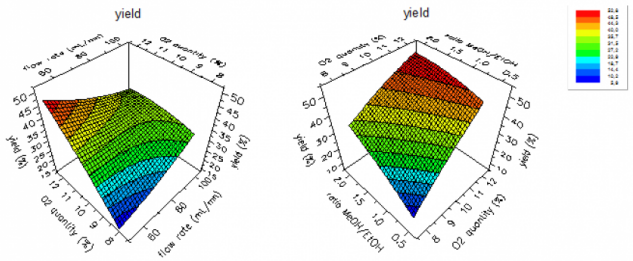
References
[1] H.Bluhm et al, J. Phys. Chem. B 108 (2004) 14340.
[2] PCT Patent WO2014068213, assigned to Arkema France, Priority date Oct 17, 2013.
[3] Liu L. et al. ChemSusChem 5 (2012) 1162-1180.

FIGURES



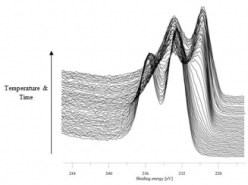


FIGURE 1

Figure 1:

mathematical model obtained after the DoE to optimize the acrolein Yield.

FIGURE 2

Figure 2:

The Mo spectra evolution as a function of time and temperature (250 ? 320 °C) during reaction under methanol and ethanol flow.

KEYWORDS

alcohols valorization | acrolein production | NAP XPS

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[1] H.Bluhm et al, J. Phys. Chem. B 108 (2004) 14340.

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