Catalytic dehydration of glycerol to acrolein: catalysts and processes

Seminar given by Prof. Sébastien Paul (18/05/2016)
UCCS (Unité de Catalyse et Chimie du Solide – UMR CNRS 8181) / Ecole Centrale de Lille
Villeneuve d'Ascq, France
E-mail: sebastien.paul@ec-lille.fr

The valorization of glycerol has been widely studied notably due to the oversupply of the latter from biodiesel production. Among the different upgrading reactions, dehydration to acrolein is of high interest due to the importance of acrolein as an intermediate for polymer industry (via acrylic acid) and for feed additive (synthon for DL-methionine). It is known that acrolein can be obtained by glycerol catalytic dehydration over acid catalysts. Zeolites and heteropolyacid catalysts are initially highly active, but deactivate rapidly with time on stream by coking, whilst mixed metal oxides are more stable catalytic systems but less selective and in addition they require an activation period.

In this talk, the strategy we followed is described. It consisted in a parallel approach in which we developed supported heteropolyacid-based catalysts with increased stability and acrolein selectivity by using a ZrO_2-grafted SBA-15 playing the role of the support for silico-tungstic acid active phase, as well as a new concept based on a two zones fluidized bed reactor (TZFBR) to tackle the unavoidable deactivation issue of the HPA catalysts. This type of reactor comprises – in one single capacity – reaction and regeneration zones.

It was shown that depending on the type of reactors used (classical plug flow fixed-bed reactor or TZFBR) the optimal HPA-based catalyst is different. In the first case the catalyst based on ZrO_2-grafted SBA-15 allows a slow deactivation but still need periodic regeneration by coke burning with oxygen. In the case of TZFBR a fast deactivating catalyst is better because of the short cycle encountered in the fluidized-bed. This time the HPA catalyst supported on CARIACT is preferable.

In conclusion, the issue of the formation of carbonaceous species during the catalytic dehydration of glycerol over acid catalyst can be tackled by using catalysts with optimized acidity or using a process enabling the continuous regeneration of the catalysts. By employing a TZFBR, the catalytic performance can be preserved for a long time under stream.

In the second part of the lecture the REALCAT platform was introduced. REALCAT (French acronym standing for 'Advanced High-Throughput Technologies Platform for Biorefineries Catalysts Design') is an highly integrated platform devoted to the acceleration of innovation in all the fields of industrial catalysis with an emphasis on emergent biorefinery catalytic processes. In this extremely competitive field, REALCAT consists in a versatile High-Throughput Technologies (HTT) platform devoted to innovation in heterogeneous, homogeneous or biocatalysts AND their combinations under the ultra-efficient very novel concept of hybrid catalysis. The REALCAT platform, representing a 8.7 M€ funding from the French Government, is a complete, unique, and top-level HTT workflow including (i) robots for the automated synthesis of catalysts and novel biocatalysts, (ii) rapid characterization tools and (iii) a series of versatile parallel continuous and batch reactors - for gas phase, liquid phase or three phases reactions - combined with ultra-fast analytical tools at the top of the state-of-the-art for the analysis of the products in the reactors effluents. Finally, results obtained for glycerol dehydration to acrolein in the frame of the collaboration between UCCS and Malaga Universities were presented. Using the tools of REALCAT permitted to accelerate by at least a factor of 10 the optimization of the operating conditions of glycerol dehydration to acrolein over an heteropolyacid-based supported catalyst.

Acknowledgments

The REALCAT platform is benefiting from a governmental subvention administrated by the French National Research Agency (ANR) within the frame of the 'Future Investments' program (PIA), with the contractual reference 'ANR-11-EQPX-0037'. The Nord-Pas-de-Calais Region and the FEDER as well as the Centrale Initiatives Foundation are thanked for their financial contribution to the acquisition of the equipment of the platform.