

## Glycerol Dehydration to Acrolein, from Catalyst Development to Process

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Due to the increasing amount of glycerol by-produced with biodiesel, its upgrading by dehydration to acrolein is driving much attention. This reaction can be catalyzed by various solid acid catalysts, which have all in common that they deactivate by coking. We studied the possibility of *in situ* regeneration of spent catalysts based on Keggin-type silicotungstic acid (STA -  $H_4SiW_{12}O_{40}$ ). Two samples were prepared with 20 wt.% STA, the first one supported on bare SBA-15, and the second one supported on SBA-15 in which 20 wt.% of  $ZrO_2$  nanoparticles were dispersed. The acidity of the catalysts was determined by  $NH_3$ -TPD and the thermal stability of the active phase was studied by TGA. The catalytic performances were determined at 275 °C in a fixed bed down flow reactor. The STA/ $ZrO_2$ /SBA-15 catalyst showed significantly increased long-term performance (69 % vs. 24 % yield in acrolein after 24 h of reaction). Grafting with zirconia led to a decrease in the acid strength of the STA, which was assigned to a modified electronic interaction between the active phase and the support, with further an increased thermal stability of the active phase. Thanks to this latter property, STA decomposition during one-shot regeneration of the catalyst by coke burning under air was suppressed, and the initial catalytic performance could be essentially recovered. In contrast, over the  $ZrO_2$ -free catalyst, the regeneration step led to a significant loss in acrolein yield (30 %) due to thermal destruction of STA. As this decomposition proceeds via the loss of constitutional water from the Keggin-structure, addition of water in the regeneration feed enabled recovering a slightly higher yield in acrolein (42 %), due to equilibrium displacement. Finally, cyclic regeneration of the catalyst was performed using iso-chronical cycles of 10 min for reaction and coke burning. The STA/ $ZrO_2$ /SBA-15 catalyst exhibited then poor performances (35 % yield in acrolein), which was explained by the longer activation period needed by this catalyst. On the other hand, the non-grafted catalyst exhibited rather stable performances (74 % yield in acrolein), without STA destruction. This was attributed to the shortness of the cycles, with thus only small amounts cokes to be burnt, then preventing the formation of harmful hotspots during regeneration. At last, we developed an integrated process for simultaneous reaction and regeneration, based on a Two-Zone Fluidized Bed Reactor (TZFBR) technology we patented.

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Franck Dumeignil is Professor at the University of Lille North of France, and the Deputy Director of UCCS. After his PhD at the University of Lille (1998), he spent 6.5 years in Japan. After a 2 years post-doctoral stay at NIMC in Tsukuba, he was subsequently employed at the Tokyo University of Agriculture and Technology (TUAT), first with a 2 years post-doctoral position, and then as an associate professor, within the frame of a Centre of Excellence (Scientific Cluster). In January 2010, he was nominated vice-director of UCCS, UMR CNRS 8181, France, which comprises more than 200 persons. Franck Dumeignil has further been nominated as a Junior Member of the prestigious IUF academy from the 1st of October 2010. He is co-author of more than 50 scientific articles, 6 patents, and more than 200 communications (oral and poster) in national and international congress.