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Glycerol conversion

One of the most promising valorization ways for glycerol consists on its dehydration to acrolein.^{1,2,3} Acrolein is used as an intermediate for the synthesis of DL-methionine as well as for polyacrylate-based polymers. Glycerol dehydration to acrolein can proceed over various solid acid catalysts, such as zeolites, supported inorganic acids or mixed metal oxides (i.e., WO₃). The main drawback of acid catalysis is the deactivation by coking. This issue can be tackled from two strategic angles, either by optimizing the catalysts or from the process side. Concerning the optimization of the catalysts, the crucial parameters are pore diffusion and acid strength. It is well agreed in the literature that medium acid sites and rather large pores are favorable for increased long-term stability. Hence, we focused on silica-supported silicotungstic acid (STA) and optimized the catalytic long-term stability by i) choosing SBA-15 as a support with a tailor-made pore-size of 8 nm and ii) introducing zirconia nanoparticles in SBA-15 in order to moderate the acid-strength of the subsequently supported STA by modulated electronic interactions.⁴ These tailor-made properties resulted in outstanding long-term performances with an acrolein yield of 69 % after 24 h with only slight deactivation (initial yield of 74 %) vs. only 24 % for the ZrO₂-free catalyst.

Furthermore, the regeneration of the SBA-15-supported catalytic systems was studied, by burning the carbonaceous species in oxidative atmosphere.⁵ Over STA/SBA-15, the regeneration under air led to a significant loss in acrolein yield (30 %) due to the thermal destruction of STA. On the other hand, the catalyst based on zirconia-grafted silica fully recovered its performances due to an increased thermal stability of the active phase, which was ascribed to the strong electronic interaction between STA and zirconia. This specific interaction was also responsible for the slight decrease in the acid strength of the supported STA, just sufficient to avoid coking while still enabling the realization of the glycerol double dehydration reaction. Finally, the cyclic regeneration of the catalysts was performed using periodical switching between a glycerol feed and an air feed with 10

minutes for each cycle. Surprisingly, the catalyst based on zirconia-grafted silica exhibited poor performances (35 % acrolein yield) whereas the catalyst based on bare silica exhibited high and stable performances (74 % yield in acrolein). These results can be understood considering the initial performance of these two catalysts. In fact, while the zirconia-grafted catalyst exhibited outstanding long-term performance, it requires an activation period of about 1 h. In the beginning (0-1 h), the zirconia-grafted catalyst exhibits a poor selectivity to acrolein of no more than 38 %, against 79 % for the catalyst based on bare silica. This type of activation period is well reported for Lewis acid catalysts in the dehydration of glycerol.⁶ In fact, Lewis acid sites present on the fraction of zirconia that is not covered by STA first catalyze the selective formation of acetol. Thereby, pseudo-Brønsted sites are formed by hydroxylation, which can then catalyze the selective dehydration to acrolein. As a conclusion, whereas the zirconia-grafted catalyst was adapted to long runs due to a slowed down deactivation and a high thermal stability, the catalyst based on bare silica was adapted to short run/regeneration.

With respect to the possibility of using the catalyst based on bare silica in short reaction / regeneration cycles, we then focused on the process. As aforementioned, the problem of catalyst deactivation can also be tackled from the process side, meaning, i.e., the use of a moving bed reactor or a fluidized bed reactor. Hereby, we focused on a fluidized bed enabling – at the same time – the reaction and the regeneration in the same reaction vessel. The corresponding concept is referred as the two zones fluidized bed reactor (TZFBR).⁷ The catalyst is fluidized by means of a pre-heated fluidizing gas (nitrogen or air). Inside the fluidized bed, glycerol can be introduced via a distributor located at the end of a plunging cane. Since glycerol is dragged with the fluidizing gas, the catalytic bed contains two zones. The zone over the glycerol injector is referred as the reaction zone, where the glycerol is catalytically converted to acrolein, and the zone lower than the glycerol distributor is used as a regeneration zone. In this latter part, the deposited carbonaceous species are oxidized with the oxygen co-injected with the carrier gas. With respect to the high cross-mixing of the catalyst in the fluidized bed, the as-regenerated catalyst is constantly exchanged with the catalyst from the reaction zone, allowing thus continuous and efficient regeneration.

The drastic increase in catalyst lifetime motivated us studying the use of “green” acrolein from glycerol dehydration in cascade reactions, and, especially in the ammoxidation of acrolein to acrylonitrile. The synthesis of acrylonitrile from glycerol can proceed either via a direct or an indirect pathway, whereby in the latter case, two independent coupled reactors (tandem reactor concept) must be employed. Although the direct ammoxidation of glycerol appears as advantageous since it requires only one reactor and one catalyst, the subject is discussed controversially in the literature.⁸ Thus, we focused on the indirect ammoxidation of glycerol using tungsten oxide on titania as a catalyst for the dehydration of glycerol to acrolein and antimony-iron mixed oxide as a catalyst for the ammoxidation of acrolein to acrylonitrile.⁹ After optimization of the

reaction conditions, a high and stable yield of 40 % was achieved.¹⁰ Surprisingly, this yield in acrylonitrile using the tandem reactor setup was even higher than that theoretically predicted from the performances of the two reactions taken independently (40 % vs. 28 %), suggesting that byproducts from the glycerol dehydration step were also ammoxidized to acrylonitrile. An enlarged study indeed revealed that notably allyl alcohol can give a yield in acrylonitrile as high as 84 % over the antimony-iron oxide catalyst.¹¹ These results are very promising when considering allyl alcohol as a new platform molecule, which can be actually derived from glycerol in high yields using DODH reaction over a Re-based catalyst with 2-hexanol as H-donor.¹²

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