A long-life catalyst for glycerol dehydration to acrolein†

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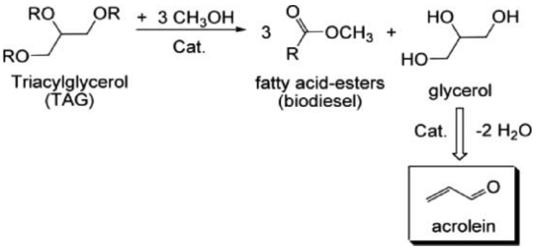
While the initial catalytic performances of silica-supported silicotungstic acid are high in the glycerol dehydration reaction, they rapidly decrease with time on stream and the acrolein yield quickly decreases.

In the biodiesel production process, vegetable oils and fats—most usually from canola, soy or corn—are reacted with a mono-alcohol (usually methanol) to cleave the fatty acids from their glycerol backbone. The resulting fatty acid esters are directly used as biodiesel, whereas glycerol remains as a rather valueless by-product. As a consequence, various reactions have been investigated for valorizing glycerol, such as reforming, oxidation, hydrogenolysis, etherification and dehydration.[1] When considering a commercial target, the dehydration of crude glycerol to yield acrolein (Scheme 1) is one of the most promising options due to the important role of acrolein as a precursor for the synthesis of DL-methionine and acrylic acid.[2]



Scheme 1 The principle of acrolein production using the glycerol by-product of biodiesel synthesis.

The dehydration of glycerol to acrolein requires acid catalysts with active sites of a suitable strength in order to efficiently promote the reaction while limiting coke formation. Solid acid catalysts with a Hammett acidity between −3 and −8, such as zeolites, supported inorganic acids and metal oxides, have previously shown good performances with yields of up to 80%.[3–5] Unfortunately, the rather strong acidic properties of these catalysts are also responsible for the formation of coke, which results in their rapid deactivation.[6–8] For instance, Chai *et al.* reported a decrease in catalytic activity by a factor two after only 10 h on stream for HZSM-5 catalysts or phosphotungstic acid supported on alumina,[4] which is obviously an important drawback when targeting industrial applications.

Among the possible formulations, supported inorganic acids have been extensively studied by several research groups, who have investigated either common inorganic acids like phosphoric acid or more complex acids like Keggin-type heteropolyacids (HPA). Apparently, the use of an HPA as an active phase offers the possibility of easily controlling the acidity, and thereby the catalytic performance, through fine tuning of the HPA composition. HPA-based catalysts have been tested using several supports, such as silica,[7] alumina,[8] zirconia[9] and active carbon.[10] Among them, silica and zirconia seem to be especially interesting:

—Silica offers the advantage of facile control of the pore size distribution, which has been identified as an important parameter for obtaining good catalytic performance. Tsukuda *et al.* have shown that the pore diameter (PD) of the silica should be chosen to be around 10 nm to obtain the best performance.[7] Additionally, silica does not alter the acidic properties of the supported HPAs, contrarily to alumina.[8]

—As claimed by Chai *et al.*, Zirconia offers an increased long-term stability of catalysts. Nevertheless, over pure zirconia supports, the acrolein yield does not exceed 54% after 10 h on stream.[9]

In this paper, we report for the first time the combination of the advantages of these two components by using ZrO_2-grafted silica as a support for an HPA active phase. SBA-15, prepared by the method of Roggenbuck *et al.*[11],† was chosen as the preferred silica host support. It offers the feature of a controlled PD, adjusted here to 8 nm, which is consistent with the optimal pore size postulated by Tsukuda *et al.*[7] A commercial silica (CARiACT®-Q10, Fuji Silysia) was also chosen for checking the influence of its larger PD of 15 nm. An SBA-15 support with a PD of 6 nm† was also used as a comparative sample. The silica host support was grafted using zirconium *n*-propoxide as a ZrO_2 precursor in order to yield a ZrO_2 loading from 10 to 40 wt%.† The obtained supports were then impregnated with 10 to 30 wt% silicotungstic acid (STA). Impregnated catalysts based on non-grafted silica were also prepared as comparative samples.

The actual quantities of deposited ZrO_2 were determined by elemental analysis. The measured contents were only slightly lower than the theoretical ones,† with a maximal relative error for the 10 wt% ZrO_2 sample, which contained 7.2 wt% ZrO_2 (Table S1†). The textural properties of the prepared supports

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and catalysts were determined using nitrogen physisorption (Table S2†). Grafting with ZrO_2 led to a decrease in both the specific surface area (SSA) and the pore volume (PV). A comparison between the theoretical and the experimental SSAs and PVs suggests that plugging of the micropores occurred with low amounts of ZrO_2 (10 wt%). On the other hand, samples containing 20 and 40 wt% ZrO_2 showed higher experimental values than those theoretically predicted. This can be attributed to the porous character of the deposited zirconia, which develops its own surface and PV. Meanwhile, neither the impregnation with 10–30 wt% STA (Fig. S1†) nor the grafting with quantities of ZrO_2 to 20 wt% affected the PD (7.2 ± 0.4 nm; Fig. 1; Table S2†). Only in the case of 40 wt% ZrO_2 was a decrease in the PD observed (5.9 nm), which was attributed to the formation of large zirconia crystal domains, as evidenced by XRD (detection of tetragonal zirconia; Fig. S2†) and HRTEM (Fig. S3-b1†).

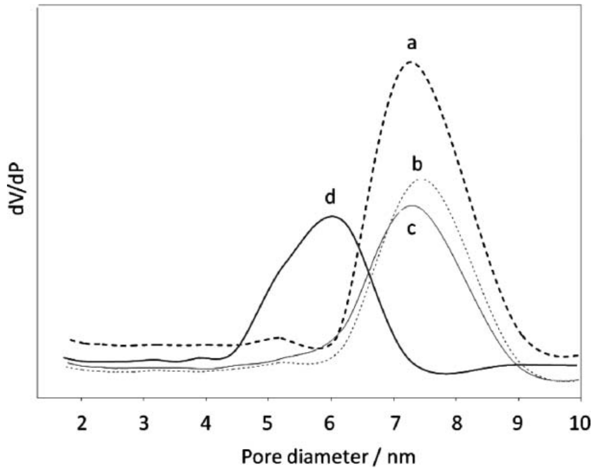


Fig. 1 Pore size distribution of SBA-15 grafted with (a) 0 wt%, (b) 10 wt%, (c) 20 wt% and (d) 40 wt% ZrO_2.

Catalytic performances were determined at 548 K according to the procedure described in the ESI.† First, the influence of the amount of ZrO_2 was investigated at an iso-HPA loading (20 wt%). The catalytic performances during the first 5 h on stream were similar for samples containing up to 20 wt% ZrO_2, with an acrolein yield of *ca.* 70% (Table 1). The yield over the sample grafted with 40 wt% ZrO_2 was lower (59%) due to the low selectivity for acrolein (65%). Note that the selectivity for hydroxyacetone doubled by introducing ZrO_2 (12–13% *vs.* 5%). After 24 h on stream, the beneficial effect of the zirconia grafting was revealed, whereas the conversion of the catalyst without ZrO_2 was divided by a factor of two (41% after 24 h *vs.* 84% during the first 5 h). The catalysts containing ZrO_2 continued to exhibit rather high glycerol conversions of 60% (40 wt% ZrO_2), 62% (10 wt% ZrO_2) and even 78% (20 wt% ZrO_2). However, the selectivity for acrolein of the sample grafted with 40 wt% zirconia remained low (44%).

Table 1 The catalytic performances of the catalysts supported on SBA-15 with a mean pore diameter of 8 nm

ZrO_2 amount (wt%):		0	10	20	40	20	20	20
STA amount (wt%):		20	20	20	20	0	10	30
TOS 0–5 h	C (%)	84	87	96	90	34	87	89
	S_{AC} (%)	83	77	74	65	19	49	75
	S_{HA} (%)	5	12	12	13	10	13	10
	Y (%)	71	67	71	59	6	42	67
	CB (%)	91	89	96	80	75	62	86
TOS 24–25 h	C (%)	41	62	78	60	—	70	66
	S_{AC} (%)	57	69	88	44	—	44	78
	S_{HA} (%)	5	13	12	13	—	14	12
	Y (%)	24	43	69	26	—	31	52
	CB (%)	85	90	100	75	—	63	83

TOS = time on stream, C = glycerol conversion, S_{AC} = selectivity for acrolein, S_{HA} = selectivity for hydroxyacetone, Y = yield of acrolein, CB = carbon balance.

The above results show the beneficial effect of zirconia in preventing catalytic deactivation. The best catalytic performance was obtained over the 20 wt% ZrO_2 catalyst, which showed a quite stable acrolein yield of 69% after 24 h *vs.* 71% during the first 5 h. To understand the effect of the zirconia on the catalytic performance of the supported STA, the acidity of the catalysts containing 20 wt% STA on ZrO_2-grafted SBA-15 and on bare SBA-15 were compared using ammonia temperature programmed desorption (TPD). The initial SBA-15 host support showed almost no acidity (0.004 mmol g^{-1}), whereas the grafting of zirconia led to a significant increase in the number of acid sites (+0.174 mmol g^{-1}; Fig. 2), which are supposedly of Lewis-type due to the nature of the support. After STA impregnation, the total number of acid sites increased (+0.335 mmol g^{-1} over SBA-15 and +0.274 mmol g^{-1} over ZrO_2-grafted SBA-15). While the catalyst prepared from bare SBA-15 had slightly fewer acid sites than its ZrO_2-grafted homologue (0.339 mmol g^{-1} *vs.* 0.442 mmol g^{-1}, respectively), it was rather stronger (ΔT = 25 K; Fig. 2). This effect is attributed to a difference in the electronic interaction between the HPA and the support. Similar to what was proposed for Al_2O_3-supported HPAs by Atia *et al.*,[8] we suggest hereafter that STA has a stronger interaction with ZrO_2 than with SiO_2. In contact with water, the hydroxyl groups at the surface of MO_x supports (M = Al, Si or Zr) are protonated, which yields M–OH_2^+ species (Scheme S1†). These species strongly interact *via* electronic effects with the negatively-charged heteropolyanion, as postulated by Wu *et al.*[13] Depending on the acidic character of the support, this interaction can be either strong (over ZrO_2 and Al_2O_3) or weak (over SiO_2), and its strength has an influence on the Brønsted acidity and thermal stability of the supported

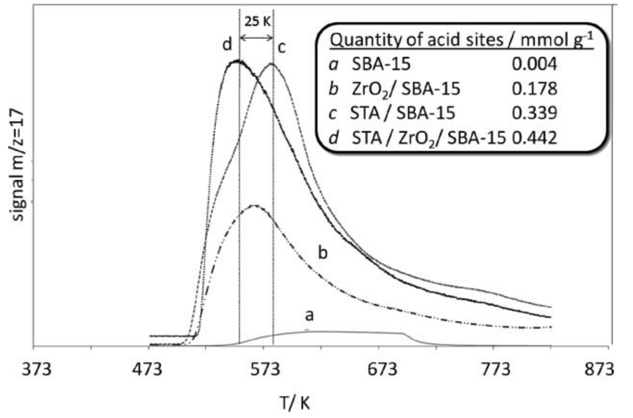


Fig. 2 Temperature programmed NH_3 desorption of the (a) host SBA-15, (b) 20 wt% ZrO_2-grafted SBA-15, (c) STA on SBA-15 catalyst and (d) STA on 20 wt% ZrO_2-grafted SBA-15 catalyst.

HPA.[8] A strong interaction leads to distortion of the Keggin structure, which induces a decrease in the acid strength. This slight diminution of acid strength leads to less formation of coke, with a higher carbon balance (96% *vs.* 91% for 0 and 20 wt% ZrO_2, respectively). As a second effect, the strong interaction between zirconia and STA stabilizes the Keggin structure, which results in a higher thermal stability of the HPA. This was confirmed by thermogravimetric analysis (Fig. S4†).

Furthermore, the low selectivity for acrolein over the catalyst containing 40 wt% ZrO_2 can be explained by the decreased pore diameter (5.9 nm) and the presence of the large zirconia domains, as detected by XRD and HRTEM. Tsukuda *et al.* and Atia *et al.* have demonstrated that the selectivity for acrolein decreases with smaller pores.[7–8] On the other hand, the aforementioned zirconia domains, formed due to Zr overloading, increase the Lewis acid character of the catalyst. The Lewis acid sites are known to favor the formation of acetol (Scheme 2).[12–13] In fact, Brønsted acid sites directly protonate the secondary hydroxyl group of glycerol, which finally leads to the formation of acrolein (Scheme 2a). On the other hand, the Lewis acid sites lead to activation of the terminal OH-group of glycerol, whereby acetol is formed (Scheme 2b). The Lewis acid site is thereby transformed into a pseudo-Brønsted acid site, which can then either catalyse the dehydration of glycerol in the same way as 'normal' Brønsted acid catalysts or regenerate the initial Lewis site by the loss of water. As a consequence, the selectivity for acetol is increased over Lewis-acid catalysts. This effect was observed for all ZrO_2-containing catalysts, which—without exception—showed significantly increased selectivity for acetol compared to the ZrO_2-free examples.

The impact of the amount of deposited STA on the catalytic performance was further investigated for samples containing the optimal ZrO_2 content of 20 wt%. The catalytic performances during the first 5 h on stream were rather similar for the samples containing 20 and 30 wt% STA, with an acrolein yield of 71 and 67%, respectively. In contrast, the acrolein yield over the catalyst containing a low amount of active phase (10 wt%) was only 42% due to a low selectivity for acrolein of 49% (Table 1). After 24 h, the catalyst containing 30 wt% STA showed a significantly lower conversion (66%) than that containing 20 wt% STA (78%), while the performance of the 10 wt% STA catalyst was lower still, again due to its low selectivity for acrolein (44%).

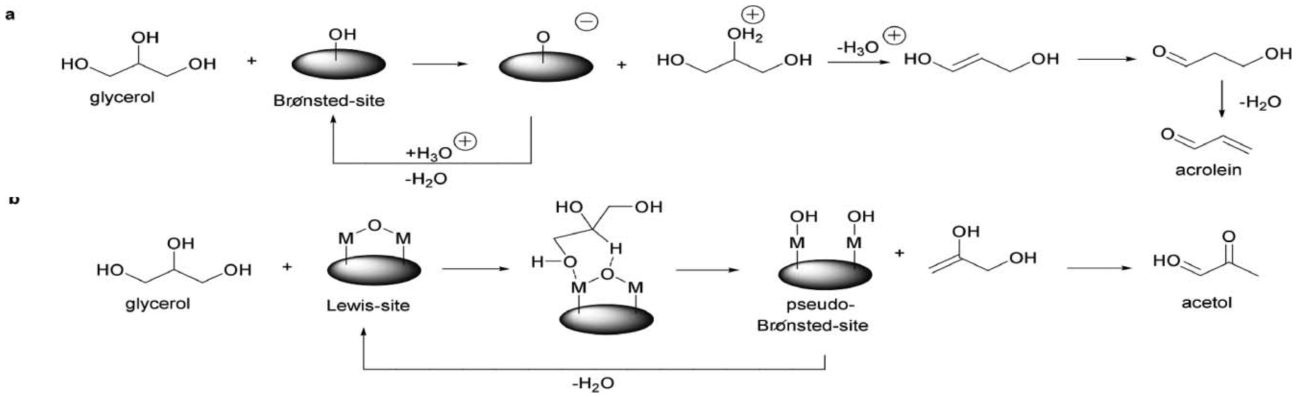
From this last series of experiments, two different factors affecting the catalytic performance were identified: (i) the surface density of acid sites and (ii) the nature of the acid sites. A low amount of STA (*i.e.*, 10 wt%) resulted in partial coverage (Table S3†) of the ZrO_2-grafted support. Accordingly, the Lewis acid character of the uncovered zirconia became dominant, which led to a low selectivity for acrolein (also observed at a high ZrO_2 loading (40 wt%)). On the other hand, a high amount of STA (*i.e.*, 30 wt%) led to the deposition of a larger quantity of active phase over bare silica, thereby the acid strength increased again. As a consequence, coke formation became more dominant (CB of 86% *vs.* 96%), which resulted in accelerated deactivation after 24 h on stream.[6–8]

From the above results, we conclude that the Brønsted acid site strength of the STA is decreased over zirconia, which has a positive impact on long-term catalytic performance due to reduced carbon deposits and therefore a slowed deactivation of the catalyst. On the other hand, the presence of bare zirconia adds Lewis acidic character to the catalyst, which favors side reactions and leads to a decrease in the selectivity for acrolein.[12–13] Therefore, these two effects must be properly balanced.

As the best results were obtained for 20 wt% STA, this loading was chosen for the last study, where the PD of the silica support was varied using an SBA-15 with a PD of 6 nm and a commercial silica with a PD of 15 nm (CARiACT®-Q10). For these supports, ZrO_2 grafting also led to enhanced long-time performances compared to those over catalysts based on bare silica. Nevertheless, the positive impact of zirconia on the long-term performance was less important than in the case of SBA-15 with an 8 nm PD (Table S4†). This is consistent with the results of Tsukuda *et al.*, who suggested an optimal pore size close to 10 nm.[7]

Conclusion

The increased long-time performance in the reaction of glycerol dehydration to acrolein of a catalyst based on silicotungstic acid supported on an SBA-15 modified by zirconia grafting is interpreted in terms of a modified electronic interaction between the support and the HPA, which results in a slightly lower Brønsted acidity.



Scheme 2 The possible reaction mechanism over (a) Brønsted acid and (b) Lewis acid catalysts, as proposed by Alhanash *et al.*[12]

The important parameters for optimizing the performance are: (i) the amount of zirconia, (ii) the amount of active phase and (iii) the pore size of the support. The best catalyst was obtained by using an 8 nm pore size SBA-15 grafted with a 20 wt% zirconia support that was impregnated with 20 wt% silicotungstic acid after an intermediate calcination step at 923 K. The high catalytic performance of this catalyst (71% acrolein yield after 5 h on stream) was stable (69% acrolein yield after 24 h on stream) and is particularly remarkable.

Acknowledgements

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