Supplementary Material (ESI) for Green Chemistry

Electronic Supplementary Information

Long-Life Catalyst for Glycerol Dehydration to Acrolein

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Preparation of the catalysts

Preparation of SBA-15

The SBA-15 supports with pore size of 6 or 8 nm were synthesized as follows: 3.25 g of triblock-copolymer P123 ($EO_{20}PO_{70}EO_{20}$ Pluronic P123; Aldrich) were dissolved under stirring in a mixture of 101 g of distilled water and 8.7 mL of hydrochloric acid (37 wt.%; Fluka) at 313 K. When the solution became clear, 6.5 g of tetraethyl-orthosilicate (TEOS; purity ≥ 99 %; Aldrich) were added. The resulting molar ratio was 1.0 TEOS : 0.018 P123 : 3.3 HCl : 191 H_2O. The reaction mixture was then kept under slow stirring at 313 K during 24 h and subsequently transferred to a teflon-coated autoclave. The silica-gel was heated for hydrothermal treatment during 24 h either at 403 K (to obtain a SBA-15 with a pore size of 8 nm) or at 373 K (to obtain a SBA-15 with a pore size of 6 nm). After filtration, the silica was washed with distilled water and dried in air at 353 K. Calcination was performed in static air at 823 K for 3 h (heating ramp of 1 K/min).

Zirconia grafting

The preparation of the zirconia-grafted samples was performed as follows: 1.0 g of freshly calcined SBA-15 support was slurried in 10 mL of dry ethanol (anhydrous; Riedel) to obtain a gel-like appearance. After addition of the desired amount of zirconium (IV) propoxide [$Zr(PrO)_4$ 70 wt.% solution in *n*-Propanol; Aldrich], the slurry was left under stirring for 8 h. After filtration, the solid was washed with ethanol and dried in air at 353 K. Calcination was performed in static air at 923 K for 3 h (heating ramp of 1 K/min), in order to remove the organic part.

Impregnation with active phase

The impregnation with heteropolyacid was performed as follows: A solution of 0.2 g of heteropolyacid ($H_4SiW_{12}O_{40}$; Sigma) dissolved in 2 mL of distilled water was added to a slurry of 0.8 g of support placed in 20 mL of water. The reaction mixture was subsequently stirred for another 2 h before the solvent was evaporated under vacuum. The obtained catalyst was dried in air for 24 h at 343 K before use.

Catalytic test

The catalytic test reaction was performed at 523 K using 300 mg of catalyst packed in a fixed-bed down-flow reactor made of stainless steel (15 mm of inner diameter, length of 120 mm). The reaction feed consisted of a 10 wt.% aqueous solution of glycerol distributed by a HPLC pump at 1.5 mL/h. The solution was evaporated at 483 K, diluted in helium (30 mL/min) before being fed to the reactor. The reaction products were condensed in ice-traps during the first 5 h on stream and once again after 24 h, whereby the sampling time length was 1 h. The condensed products were analyzed by the HPLC technique.

Analytical instruments and methods

Nitrogen adsorption/desorption isotherms were recorded at 77 K using a Micromeritics ASAP 2010 analyzer. The specific surface area (S_{BET}) was obtained using the BET method and the pore distribution was calculated according to the Barret-Joyner-Halenda (BJH) formula. The total pore volume (V_p) was determined on the isotherms at a relative pressure (P/P_0) of 0.995.

Distribution of the types of silica species was determined using nuclear magnetic resonance with cross polarization and magic angle spinning (^{29}Si CP-MAS NMR) on a Bruker spectrometer at an operating frequency of 75.4 MHz. Peak chemical shift was referenced to tetramethyl silane (TMS).

The IR spectra were recorded with a spectral resolution of 4 cm^{-1} and 256 scans (acquisition time 52 s) using a Thermo Nicolet 460 Protégé FTIR spectrometer equipped with a MCT detector. A KBr spectrum was used as background for the post-processing of spectra.

The analyses of the condensed reaction products were performed using an HPLC (THERMO – SpectraSystem) with a THERMO HyperRez XP column (250 mm length, 8 μm particle size) as a stationary phase and sulfuric acid (5 mmol/L; 0.5 mL.min^{-1}; isocratic) as an eluting agent. The system was equipped with a refractometer (THERMO Surveyor Plus RI) used as detector.

The analyses of the gaseous reaction products were performed using a gas-chromatograph with a TCD detector (PERICHROM 2100) equipped with a semi-capillary HP Plot-Q column (30 m, 1.2 μm film, 0.53 mm diameter) and a semi-capillary HP Molesieve column (30 m, 1.2 μm film, 0.53 mm diameter).

X-ray diffraction was measured on a Bruker D8 Advance diffractometer, using the CuKα radiation (λ= 1.5506 Å) as an X-ray source, in the range of $10° \leq 2\theta \leq 80°$ by steps of 0.02°/s (integration time 1 s). Phase identification was performed by indexation using the JCPDS database. The size of the zirconia crystallites was estimated using the Sherrer equation.

The acidity of the samples was determined by temperature programmed desorption of ammonia using a Micromeritics AutoChem II 2920 connected to a mass spectrometer (VARIAN). The same apparatus was used to determine the thermal stability of the supported silicotungstic acid by TGA under air atmosphere.

The zirconium content was determined by inductively coupled plasma-mass spectroscopy (ICP-MS) using a Thermo-Fisher X7 ICP-MS apparatus.

Table S1 Theoretical and measured ZrO_2 content in the supports.

Silica support	SBA-15 (8 nm)			
Calculated ZrO_2 amount (wt.%)	0	10	20	40
Measured ZrO_2 amount (wt.%)	0	7.2	18.1	36.6

Table S2 Textural characteristics of the supports.

Silica support	SBA-15 8 nm				SBA-15 6 nm		CARiACT®	
ZrO_2 amount (wt.%)	0	10	20	40	0	20	0	20
S_{BET} [m^2/g]	593	510 (534)	518 (475)	446 (356)	703	572 (562)	272	259 (218)
V_p [cm^3/g]	1.31	1.11 (1.18)	1.06 (1.05)	0.80 (0.79)	0.95	0.74 (1.05)	1.25	0.99 (1.00)
D_p [nm]	7.6	7.4	6.8	5.9	5.6	4.8	14.6	12.5

S_{BET} = Specific surface area (BET); V_p = pore volume; D_p = average pore diameter.
values in brackets are calculated theoretically according to the methodology described hereafter

Theoretical calculated specific surface and pore volume

The support of the catalyst has a known BET surface and pore volume (for example 100 m²/g and 1.00 cm³/g). The impregnation with zirconia (for example 10 wt.%) ideally leads to the formation of a homogenous layer. If this layer does not generate new surface or pore volume, the BET surface and pore volume decrease proportionally to the amount of introduced active phase (in our example, they must respectively decrease to 91 m²/g and 0.91 cm³/g). A negative deviation between experimental and calculated values (*i.e.*, a measured value even lower than the corrected calculated value) can be ascribed to the plugging of pores. On the other hand, a positive deviation (*i.e.*, a measured value larger than the corrected calculated value) is explained with the creation of new surface due to the deposition of a porous structure,[1] here zirconia.

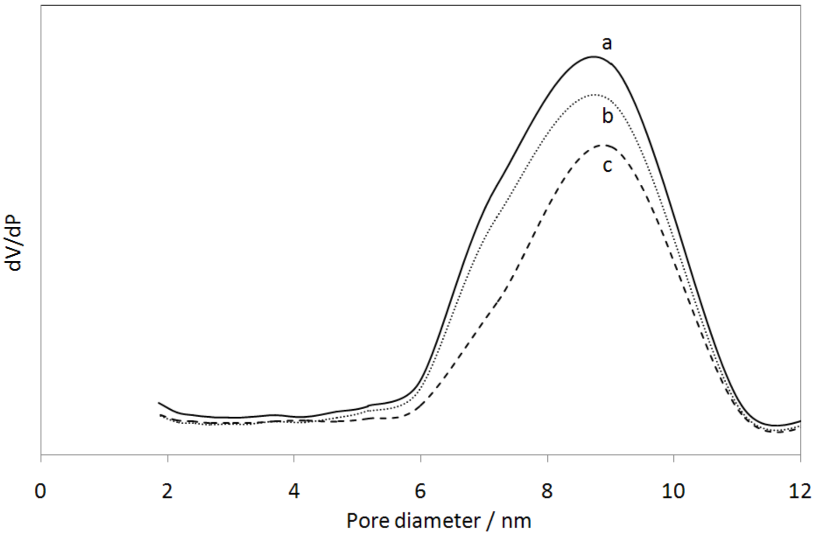


Fig. S1 BJH pore diameter for catalysts containing *(a)* 10 wt.%, *(b)* 20 wt.% and *(c)* 30 wt.% silicotungstic acid on SBA-15, showing that the pore diameter is not affected by the impregnation with active phase.

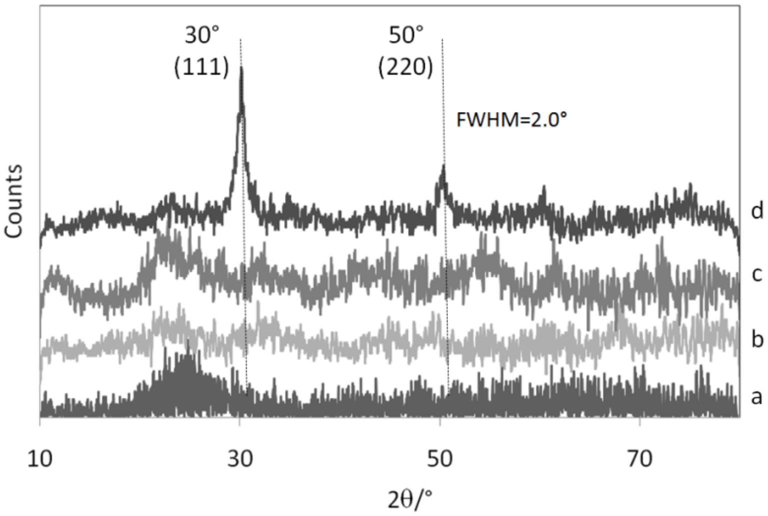


Fig. S2 XRD patterns for *(a)* SBA-15, and SBA-15 grafted with *(b)* 10 wt.% ZrO_2, *(c)* 20 wt.% ZrO_2 and *(d)* 40 wt.% ZrO_2. Tetrahedral zirconia main expected peaks are indicated (JCPDS card 17-0923).

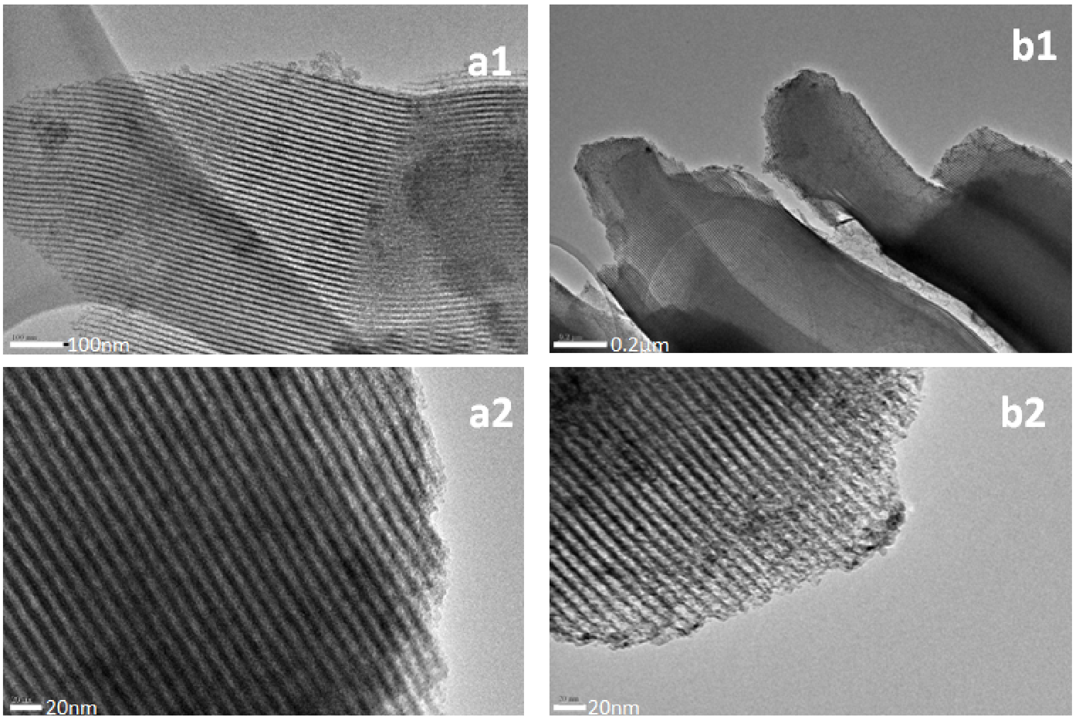
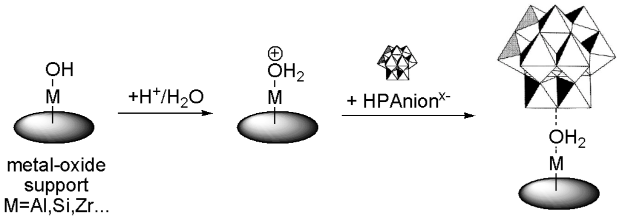


Fig. S3 HRTEM images for SBA-15 grafted with 20 wt.% ZrO_2 (a1 and a2) and 40 wt.% ZrO_2 (b1 and b2). While ZrO_2 particles are well distributed within the SBA-15 loaded with 20 wt.% of ZrO_2, large crystal domains corresponding to tetragonal zirconia (as suggested by XRD, Fig. S2) are observed on the sample loaded with 40 wt.% of ZrO_2.



Scheme S1 Interaction between the HPA and the metal oxide support.

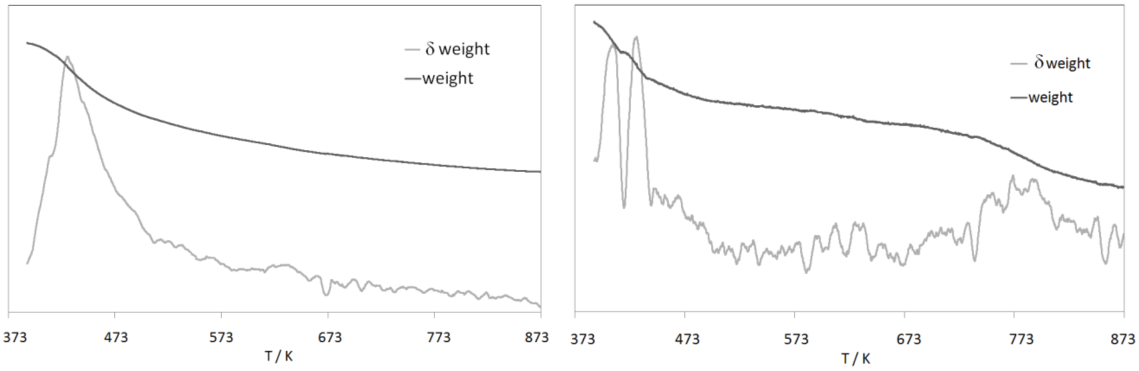


Fig. S4 TGA for silicotungstic acid supported on SBA-15 (right) and zirconia grafted SBA-15 (left).
Both samples exhibit a weight loss between *ca.* 423 and 473 K, which is characteristic for the loss of crystal water. Whereas the sample based on non-grafted SBA-15 (right) shows a second loss of weight starting from 723 K, such a loss is not observed for the zirconia-grafted SBA-15 (left). This second loss is ascribed to the loss of water of constitution, due to the decomposition of silicotungstic acid according to the following reaction: $H_4SiW_{12}O_{40} \rightarrow SiO_2 + 12\ WO_3 + 2\ H_2O$. This experiment illustrates the larger stability of the active phase when supported on zirconia-grafted SBA-15 rather than on bare SBA-15.

Coverage with silicotungstic acid

Taking into account a mean diameter of the Keggin unit of 12 Å, we evaluated the theoretical coverage rate of the support.[2] The calculated surface coverage of the 20 wt.% ZrO_2/SBA-15 support (specific surface area of 518 m²/g) for various STA amounts is shown in Table S3.

Table S3 Coverage of the support with silicotungstic acid.

Catalyst support	20 wt.% of ZrO_2 on SBA-15 (8 nm)		
STA amount (wt.%)	10	20	30
Relative coverage (%)	5.7	12.9	22.1

Table S4 Catalytic performances of all the solids, including SBA-15- as well as CARiACT®-supported STA catalysts.

Silica support		SBA-15 8 nm							SBA-15 6 nm		CARiACT® 15 nm	
ZrO_2 amount (wt.%)		0	10	20	40	20	20	20	0	20	0	20
STA amount (wt.%)		20	20	20	20	0	10	30	20	20	20	20
TOS 0-5 h	*C* (%)	84	87	96	90	34	87	89	9	95	97	92
	S_{AC} (%)	83	77	74	65	19	49	75	77	76	83	83
	S_{HA} (%)	5	12	12	13	10	13	10	5	13	5	14
	Y (%)	71	67	71	59	6	42	67	71	72	80	77
	CB (%)	91	89	96	80	75	62	86	84	92	88	98
TOS 24-25 h	*C* (%)	41	62	78	60	-	70	66	61	72	58	60
	S_{AC} (%)	57	69	88	44	-	44	78	71	75	66	73
	S_{HA} (%)	5	13	12	13	-	14	12	7	15	6	18
	Y (%)	24	43	69	26	-	31	52	43	55	38	44
	CB (%)	85	90	100	75	-	63	83	86	95	84	94

TOS = time on stream; *C* = glycerol conversion; S_{AC} = selectivity to acrolein; S_{HA} = selectivity to hydroxyacetone; *Y* = yield in acrolein; *CB* = carbon balance.

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[1] M. Bonne, S. Pronier, F. Can, X. Courtois, S. Valange, J-M. Tatibouet, S. Royer, P. Marécot, D. Duprez, *Solid State Science*, 2010, *12*, 1002-1012.

[2] M. Misono, T. Okuhara, N. Mizuno, *Catalysis by heteropoly compounds, Successful design of catalysis*, Amsterdam, Elsevier Science Publishers, **1988**, 267.