Electronic Supplementary Information

Highly efficient catalyst for decarbonylation of lactic acid to acetaldehyde

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Remarks on economical aspects

The authors are aware of the fact that, under the current economic conditions, the decarbonylation of lactic acid to yield acetaldehyde is not yet competitive. Whereas the actual price of lactic acid is evaluated around 0.70 US$/lbs, acetaldehyde costs no more than 0.50 US$/lbs.[1] Nevertheless, lactic acid is becoming a central intermediate for biomass-derived polymers, whereby a significant decrease in its price is forecasted by 2015, according to reduced production costs from scaling effects.[2]

Preparation of the catalysts

Preparation of SBA-15

The SBA-15 support with pore size of 8 nm was 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 at 403 K. After filtration, the

[1] http://www.icis.com
[2] http://www.lactic.com

silica was washed with distilled water and dried at 353 K. Calcination was performed in static air at 823 K for 3 h (heating ramp 1 $K \cdot min^{-1}$).

Preparation of $H_4PMo_{11}VO_{40}$

We added 17.8 g of sodium phosphate dihydrate ($Na_2HPO_4 \cdot 2H_2O$; purum; Fluka) to a freshly prepared hot solution consisting of 12.2 g of sodium metavanadate ($NaVO_3$; purum; Aldrich) dissolved in 500 mL of boiling water. After cooling to room temperature, 10 mL of concentrated hydrochloric acid (37 wt.%; Fluka) were added. The addition of an aqueous solution of 266 g of sodium molybdate dihydrate ($Na_2MoO_4 \cdot 2H_2O$, p.a.; Fluka) in 500 mL of water resulted in a change in color from yellow to brown. Subsequently, the reaction mixture was acidified with 400 mL of hydrochloric acid, which resulted in obtaining an orange solution. The mixture was then kept at ambient temperature overnight.

The protonated heteropolyanion was extracted with diethylether. The heavy phase of HPA etherate appeared next to the aqueous phase. Extraction was stopped when a lighter third phase of pure diethylether became visible; 75 mL of water were added to the collected etherate. The biphasic system was kept at ambient temperature until all diethylether evaporated. The remaining solution was cooled at 277 K to finalize the crystallization process.

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 or $H_3PW_{12}O_{40}$; Sigma or $H_3PMo_{12}O_{40} \cdot 12H_2O$; Sigma or $H_4PMo_{11}VO_{40} \cdot 12H_2O$) 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 for 24 h at 343 K before use.

Analytical instruments

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 type 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 the spectra.

The analyses of the condensed reaction products were performed using an HPLC (THERMO – SpectraSystem) with a THERMO HyperRez XP (250 mm length, 8 µm particle size) column as a stationary phase and sulfuric acid (5 mmol/L; 0.5 $mL \cdot min^{-1}$; isocratic) as an eluting agent. The system was equipped with a refractometer (THERMO Surveyor Plus RI) used as a detector. Injection of the samples was performed using a calibrated automatic sampling system ('auto-sampler'), which enabled high accuracy and reproducibility. As an example, we report the results obtained using a same sample analysed 10 times in Table S2

(page 5 of this document). The maximum relative deviation from the mean value was 3.77 % for acetaldehyde and 2.12 % for lactic acid, which can be considered as satisfactory.

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).

Test of the hydrothermal stability of silica supports and catalyst

It is known that under steam-rich atmosphere, the silica supports can be hydrolyzed. Indeed, hydrothermal reaction conditions can result in a partial collapse of the structure of the silica. The reaction conditions used for the catalytic tests in the present work are close to these limits, as a 20 wt.% aqueous solution of lactic acid results in a partial pressure of steam of 47.2 % at 548 K. Therefore, the resistance of the bare silica supports and also of an impregnated sample were tested in steam atmosphere before considering their use in the present work. The reaction conditions for the hydrothermal tests were chosen with regard to the conditions of the actual catalytic test. About 1 g of the sample was loaded in the reactor and flushed with helium. Then, the reactor was heated at 548 K before a mixture of steam (54 Vol.%) in helium was passed through the reactor for 16 h. Afterwards, the sample was isolated and its structural properties were analyzed by N_2-desorption measurements. The observed changes in the textural properties of the samples were minor, and largely remained within the magnitude of error of the physisorption technique (Table S1). Thereby, one can conclude that the silica supports used in the present work are not subjected to hydrolysis upon contact with vapor at 548 K, and were thus considered as sufficiently stable under the reaction conditions.

Table S1 Comparison between textural properties of CARiACT, SBA-15 and catalyst containing 20 wt.% STA on SBA-15 before and after hydrothermal treatment.

Sample	S_{BET} [m²/g]	V_P [cm³/g]	D_P [Å]
CARiACT	272	1.26	149
- After steam	272	1.25	146
SBA-15	523	1.12	80
- After steam	507	1.25	78
20 wt.% STA on SBA-15	431	1.05	90
- After steam	412	0.98	90

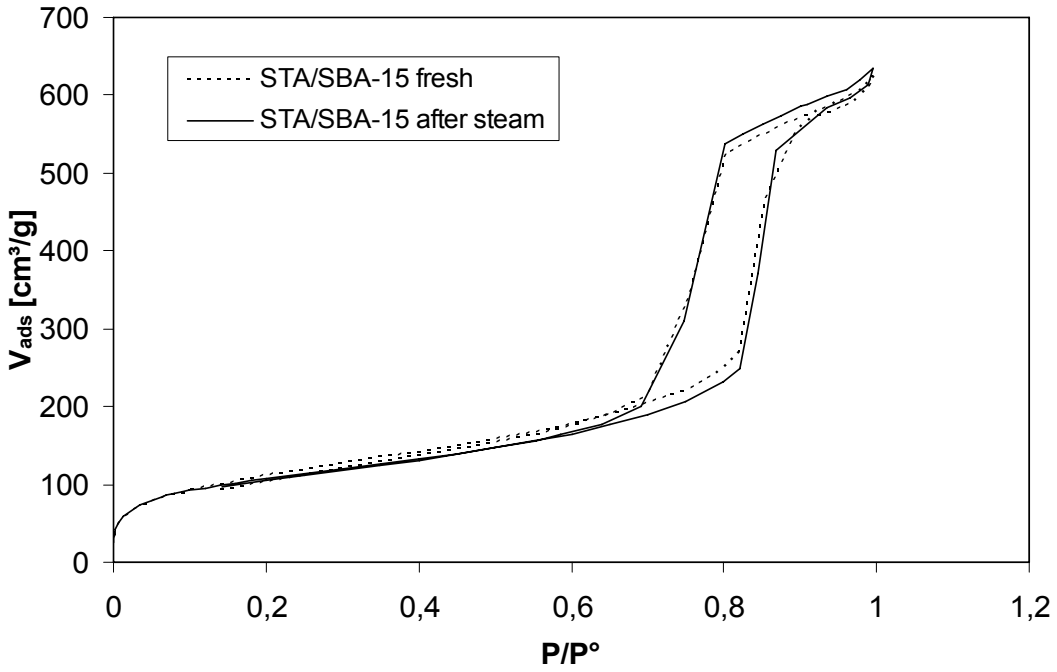

Fig. S1 Nitrogen physisorption isotherms of catalyst containing 20 wt.% STA/SBA-15 before and after steam exposure.

Table S2 Lactic acid and acetaldehyde peaks areas obtained using the HPLC technique, for 10 successive analyses of the same sample.

	Lactic acid		Acetaldehyde	
Injection number	**peak Peak area**	**Rel. deviation from mean value (%)**	**Ppeak area**	**Rel. deviation from mean value (%)**
1	15847532	0.61	11965108	0.15
2	15868408	0.48	12002139	0.16
3	15952546	0.05	12100739	0.98
4	15950460	0.04	12372083	3.25
5	15999383	0.34	11953302	0.25
6	15621542	2.03	11531833	3.77
7	16038927	0.59	12097301	0.95
8	16131653	1.17	12025496	0.35
9	16282143	2.12	12101206	0.98
10	15755271	1.19	11682654	2.51

Calculation of conversion and selectivity

$$\text{Lactic acid conversion (\%)} = \frac{\text{Moles of Lactic acid in the feed} - \text{Moles of Lactic acid in outlet}}{\text{Moles of Lactic acid in the feed}} \times 100$$

$$\text{Product selectivity (\%)} = \frac{\text{Moles of product in outlet}}{\text{Moles of Lactic acid in the feed} - \text{Moles of Lactic acid in outlet}} \times 100$$

$$\text{Product yield (\%)} = \text{Conversion (\%)} * \text{Selectivity (\%)} / 100$$

Evolution of catalytic performances with time on stream

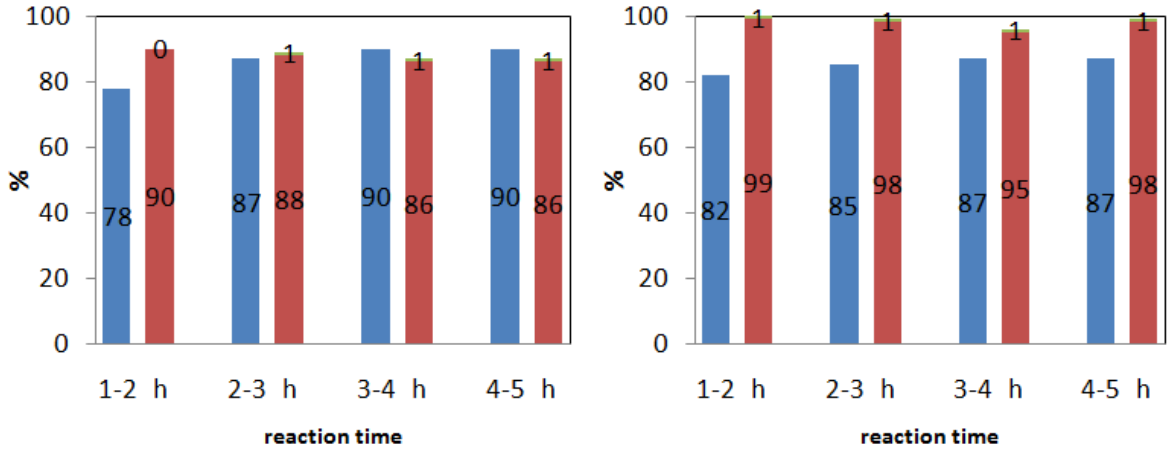

Fig. S2 Evolution of the catalytic performances with time on stream for SBA-15 based catalysts loaded with phosphotungstic acid (left) and silicotungstic acid (right) as active phases.

From the results presented in Fig. S2, one can see that the catalysts were not subjected to deactivation during the whole sampling time, with catalytic performances remarkably stable. Nevertheless, the authors do not definitely exclude possible deactivation issues for longer reaction times.

Remarks on the carbon balance

Due to the different sampling techniques used for the quantification of the gaseous (online) and the condensed products (offline), the carbon balance must be indirectly evaluated. The online gas analysis enables the calculation of the instant selectivity to CO/CO_2, whereas the offline analysis using ice-traps gives a cumulated selectivity for acetaldehyde and propanoic acid during the time of the sampling (4 h). Nevertheless, for the tungsten-containing acids, we could evaluate the molar ratio of acetaldehyde to carbon monoxide in the magnitude of one for one, which is fully coherent with the mechanism postulated for decarbonylation. Furthermore, the presence of carbon dioxide was only detected for the molybdenum-containing heteropolyacids, which are much less of interest concerning the observed performances, and were thus no more investigated as catalysts for the present reaction.

Results from the deconvolution of the ^{29}Si-NMR MAS-spectra

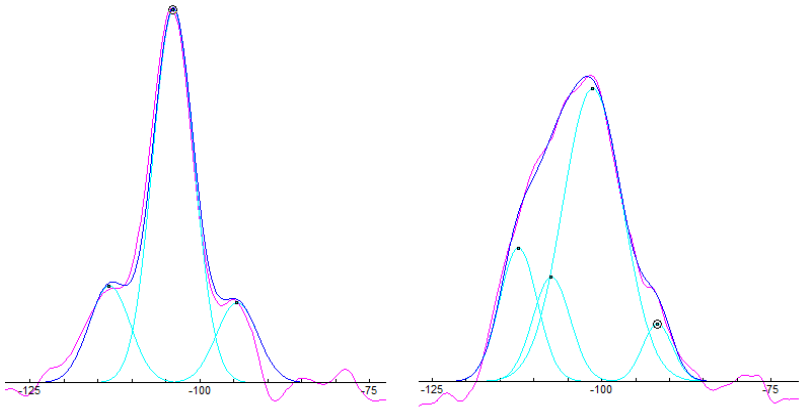

Fig. S3 Deconvolution of the spectra obtained for SBA-15 (left) and for the catalyst containing 20 wt.% of $H_4SiW_{12}O_{40}$ on SBA-15 (right).

Table S3 Quantitative results deduced from the deconvoluted ^{29}Si-NMR-MAS spectra presented in Fig S3.

δ/ ppm		SBA-15	20 wt.% $H_4SiW_{12}O_{40}$ on SBA-15
-94	(Q2)	15 %	6 %
-102	(Q3)	67 %	62 %
-108	(Q2-HPA) or (Q3-HPA)	-	14 %
-112	(Q4)	18 %	18 %