Highly efficient catalyst for the decarbonylation of lactic acid to acetaldehyde†

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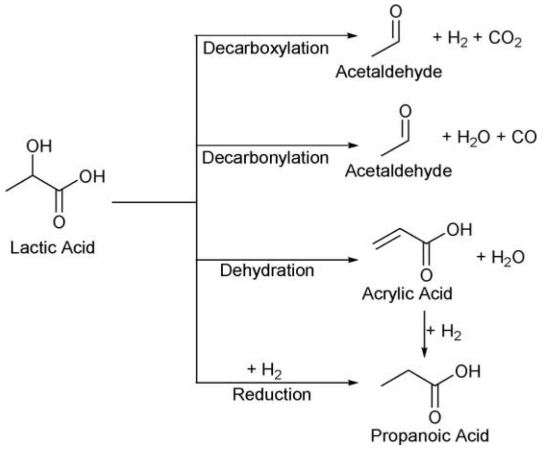
The gas phase decarbonylation of lactic acid was performed over various silica-supported heteropolyacids. The obtained performances were, by far, higher than those previously described in the literature. In particular, the best results were obtained for silicotungstic acid-based catalysts, which showed very high yields of acetaldehyde (81–83%) at high lactic acid conversion (up to 91%).

The use of renewable feedstocks as raw materials for chemical processes has become more and more important due to the progressive depletion in fossil resources like oil, natural gas and coal. For some industrial applications, biomass has already been proven to be a competitive substitute compared to fossil reactants.[1,2]

Unlike petroleum feedstocks, which generally consist of hydrocarbons, the compounds in biomass-derived resources usually contain a large number of reactive oxygenated functional groups, leading to difficulties in realizing their selective transformation. Therefore, one of the challenges in the emerging renewable chemical industry is the development of processes that enable a decrease in the oxygen content of these molecules, thereby directing the conversion selectively to the desired final product.[3]

Lactic acid, which contains a hydroxyl and a carboxy group, is an example of a highly functionalized biomass-derived molecule. It can be obtained from biomass at low cost by bacterial fermentation or chemical reactions.[4] Due to its potential for producing biodegradable polymers (polylactic acid), the production of lactic acid has recently significantly increased. In addition, lactic acid has the potential to become a central feedstock for the chemical industry, *e.g.* for the synthesis of pyruvic acid.[5] Herein, we propose a new strategy for selectively transforming this bioresource to acetaldehyde by a catalytic process of decarbonylation. Usually, the decarbonylation of lactic acid is observed as a side reaction in the dehydration of lactic acid to acrylic acid. Therefore, the previously published yields for acetaldehyde using zeolites, niobium oxide or alumina as catalysts do not exceed 31%.[6–9] However, the current production of acetaldehyde is mainly based on the Wacker process, which uses fossil feedstock-derived ethylene as a starting material. Thus, efficiently realizing the decarbonylation reaction of lactic acid would open up perspectives for the sustainable production of acetaldehyde.[10] This compound is widely used as a precursor in the chemical industry with, for example, applications in condensation, addition and polymerization reactions.†

C–C bond cleavage in lactic acid molecules can follow one of two different pathways: decarboxylation or decarbonylation (Scheme 1), both of which require acid catalysts.[11] Whereas the decarbonylation reaction leads to the formation of carbon monoxide as a co-product together with water, the decarboxylation reaction releases hydrogen and CO_2 as a by-product. In the latter case, the production of hydrogen can also cause problems for keeping a high selectivity to acetaldehyde, as it is known that hydrogen can reduce lactic acid to propanoic acid in the presence of redox catalysts.[8]



Scheme 1 Some valorisation routes for lactic acid.

In regard to these demands for acidic properties, Keggin-type heteropolyacids (HPA) are excellent candidates for catalysing this reaction. HPAs are actually known as very strong Brønsted acids, at least stronger than common inorganic acids such as HCl, HNO_3, H_2SO_4, *etc.* and sometimes even classified as superacids.[12,13] The acid strength of a Keggin-type HPA strongly depends on the nature of its addenda atoms. Hence, HPAs containing tungsten are more acidic than those containing molybdenum, while these latter examples exhibit a more pronounced redox character. The strong acidity of HPAs gives them the ability to efficiently catalyze dehydration, alkylation, esterification or isomerization reactions. HPAs can also be strong redox catalysts.[14,15] This property can be tuned by the composition of the Keggin heteropolyanion. Hence, the redox power of HPAs increases in the series of addenda atoms in the order W, Mo, V, and in the order Si, P for the central

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heteroatom. The highest redox potential is observed for vanado-phosphomolybdic acids.[12]

In this work, we study the selective decarbonylation of lactic acid to acetaldehyde over various silica-supported HPAs. A commercially available silica (CARiACT® Q-15, Fuji Silysia) and an SBA-15—prepared by the method of Roggenbuck *et al.*[16]†—were chosen as silica host supports, of which the good hydrothermal stability was checked and validated prior to use (Table S1, Fig. S1†). These silica host supports were impregnated with 20 wt% of commercially available silicotungstic acid, phosphotungstic acid or phosphomolybdic acid. Additionally, a catalyst based on $H_4PMo_{11}VO_{40}$ was synthesized by following the procedure of Rabia *et al.*[17]†

The performances of the catalysts were determined at 548 K using 300 mg of catalyst packed into a fixed-bed reactor fed with a 20 wt% aqueous solution of lactic acid as a reactant feed. After 1 h of stabilization, the reaction products were condensed over 4 h using ice traps. Analyses of the condensed liquid products were performed by the HPLC technique, and gas phase analysis was performed using a gas chromatograph equipped with a TCD.† The accuracy and reproducibility of the measurements were carefully checked (Table S2†).

The performances of the catalysts based on HPAs supported on CARiACT Q-15 are shown in Fig. 1. The activity and selectivity are strongly dependant on the type of supported active phase. The catalysts prepared from phosphomolybdic acid and vanado-phosphomolybdic acids showed comparatively low conversions of lactic acid (*i.e.*, 70 and 60%, respectively), whereas the catalysts based on silicotungstic and phosphotungstic acids were significantly more active, with conversions exceeding 90%. This is not surprising, as molybdenum-containing HPAs are less acidic than tungsten-based examples. The resulting acetaldehyde yield was in the region of 80% for the tungsten-containing compounds, which was twice as much as observed for the molybdenum-based HPAs, the yields of which were no more than 34% acetaldehyde. Furthermore, in these latter cases, the formation of propanoic acid was observed, with 3% yield over the phosphomolybdic acid and even 8% over the vanado-phosphomolybdic acid, whereas the silicotungstic and phosphotungstic acids exclusively showed the formation of acetaldehyde.

These results can be discussed in regard to the pathways presented in Scheme 1. The analyses of the gaseous products showed that the decarboxylation is more important over the molybdenum-based HPAs, whereas the tungsten-containing HPA show nearly no formation of CO_2.† Phosphomolybdic acid and vanadium-substituted phosphomolybdic acid are furthermore known for their increased redox character. This explains the increased selectivity for propanoic acid in this case, by a redox process over the catalysts, using the hydrogen co-produced with CO_2.

Due to the superior performances of the W-containing HPA-based catalysts, we further focused our study on this kind of active phase. In a second series of experiments, we studied the impact of the HPA surface density on the catalytic performance at an iso-HPA wt% loading (20 wt%), but on silica supports with very different specific surface areas. Taking into account a mean diameter of the Keggin unit of 12 Å, we evaluated the theoretical coverage of the support.[12] Accordingly, the surface coverage was estimated at 36% in the case of the catalyst prepared with 20 wt% HPA on CARiACT. The surface acidic density was decreased by using an SBA-15 with a significantly higher specific surface area (541 *vs.* 272 $m^2\ g^{-1}$), on which the surface coverage was then 14%.

The catalytic results are reported in Fig. 2. On the one hand, a lower density in the active phase, *i.e.*, a lower density of acid sites, resulted in a decrease in activity (namely 91–94% over CARiACT *vs.* 85–86% over SBA-15). On the other hand, we observed an increase in the yield of acetaldehyde for silicotungstic acid supported on SBA-15, with a value as high as 83% (thus corresponding to a selectivity for acetaldehyde of 98%) compared to a yield of 76% over SBA-15-supported phosphotungstic acid. For both HPAs, the formation of very small amounts of propanoic acid was observed over SBA-15 (1%), which was not the case when using CARiACT. Irrespective of the support, silicotungstic acid showed a slightly lower activity, but was more selective to acetaldehyde than phosphotungstic acid, which is not a significant feature when considering the well known interdependence of the conversion/selectivity couple. It is worth mentioning that no decrease in their activity was observed during the time on stream of these catalysts,

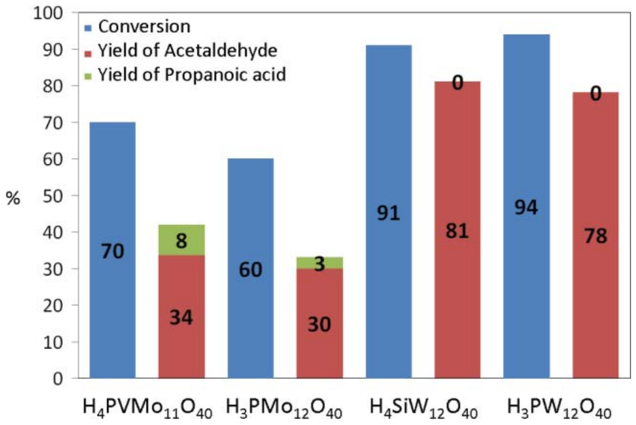

Fig. 1 The catalytic performances of HPAs deposited on CARiACT Q-15.

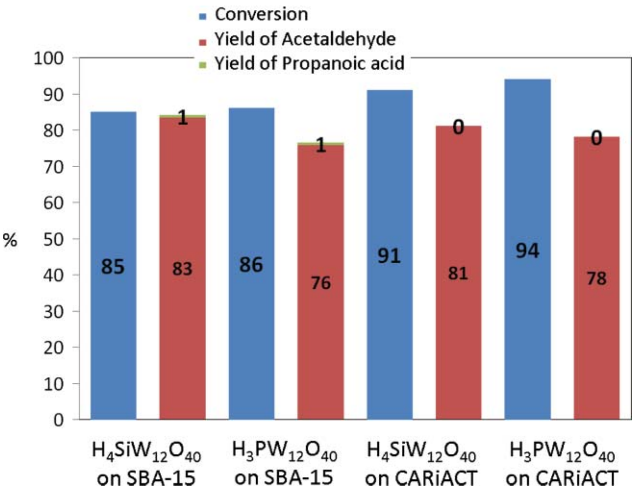

Fig. 2 The catalytic performances of W-containing HPAs supported on CARiACT Q-15 and SBA-15.

the performances of which were thus very stable (Fig. S2†). Furthermore, one can state that the observed performance over HPAs in the catalytic decarbonylation of lactic acid largely outperforms the results previously published for other acid catalysts such as zeolites, niobium oxide and alumina, which do not exhibit a yield in acetaldehyde exceeding 31%.[6–9]

The aforementioned selectivity for propanoic acid that is only observed over SBA-15 and not over CARiACT-supported silicotungstic acid leads to a question about the structural integrity of the active phase on this former support. Indeed, the decomposition of silicotungstic acid yielding tungsten oxide could be an explanation for the presence of the newly formed redox properties. Nevertheless, the IR spectrum of fresh and spent catalyst containing 20 wt% silicotungstic acid over SBA-15 exhibited the characteristic absorption bands of the Keggin unit at 981 and 928 cm^{-1} (Fig. 3).† This suggests the structural integrity of the HPA after impregnation and also, after test, we cannot even exclude the notion that a small undetectable part might be decomposed.

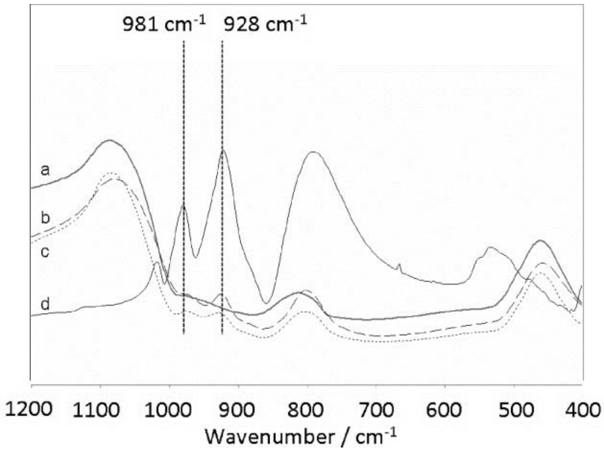

Fig. 3 FT-IR spectra of (a) bare SBA-15 support, catalyst containing 20 wt% silicotungstic acid (b) before and (c) after test, and (d) pure silicotungstic acid.

Furthermore, the dispersion of the active phase in the silica host support was evaluated using nitrogen physisorption experiments.† The results of these textural analyses, which were carried out on catalysts based on 20 wt% silicotungstic acid on SBA-15 and CARiACT, are given in Table 1. A *ca.* 20% decrease in specific surface was observed after impregnation. This decrease is mechanically linked to the weight of the introduced active phase. Due to the non-porous character of HPAs, the HPA layer does not generate a new surface, meaning that the specific surface decreases proportionally to the weight of the introduced active phase. Therefore, one can state that the impregnation leads to the formation of a well-distributed layer over the silica surface. Overloading of the active phase would indeed result in the plugging of pores, which would induce a significant decrease in the specific surface area. As this phenomenon was not observed in the present case, one can consider that pore blocking is locally limited, and that the majority of the porous network of the catalyst should be accessible to the reactants.

Table 1 The textural properties of supports and catalysts based on silicotungstic acid[a]

Silica support:	SBA-15		CARiACT	
$H_4SiW_{12}O_{40}$ amount (wt%):	0	20	0	20
S_{BET}/m^2 g^{-1}	541	431	272	246
V_p/cm^3 g^{-1}	1.20	1.05	1.25	1.06
D_p/nm	9	9	15	15

[a] S_{BET} = specific surface area (BET), V_p = pore volume, D_p = pore diameter.

Linkage of the HPA to the silica surface was experimentally probed using nuclear magnetic resonance spectroscopy with magic angle spinning (MAS-NMR) on the silicon nucleus.† The ^{29}Si MAS-NMR spectra of the initial SBA-15 support and of the catalyst containing 20 wt% silicotungstic acid are shown in Fig. 4. Deconvolution of the spectra (Fig. S3; Table S3)† clearly shows that the relative intensities of the Q^2 [(SiO)$_2$–*Si*–(OH)$_2$; −94 ppm] and Q^3 [(SiO)$_3$–*Si*–OH; −104 ppm] signals decreased after impregnation of the SBA-15 host support with the HPA, whereas the Q^4 [*Si*–(SiO)$_4$; −113 ppm] signal relative proportion remained constant. This means that some of the silanol groups (Si–OH) on the surface were covered with silicotungstic acid.† Therefore, new silica species, namely Q^3-HPA [(SiO)$_3$–*Si*–HPA] and Q^2-HPA [(SiO)$_2$–*Si*–HPA], were formed with an identical chemical shift of −108 ppm, which made discrimination between them impossible by this technique. However, the deconvolution clearly shows that the loss in the Q^2 and Q^3 signal relative contribution is proportionally compensated-for by the appearance of the contribution of the combined Q^3-HPA and Q^2-HPA signals. This contribution is quantified at 14% (Fig. S3; Table S3†). Accordingly, the coverage of the silica species on the surface was subsequently calculated as the ratio of the number of covered surface silica species (combined Q^2-HPA and Q^3-HPA peak area) to the total number of surface silica species in the initial SBA-15 support (Q^2 and Q^3 peak areas). This gives an experimental coverage of 17%, which is consistent with the theoretically obtained value of 14%. This confirms the good distribution of the HPA on the SBA-15 surface, as already suggested by the results of the N_2 physisorption experiments.

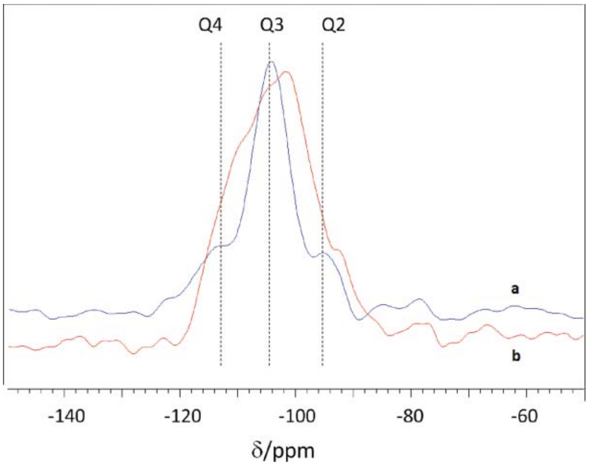

Fig. 4 ^{29}Si MAS-NMR spectra for (a) SBA-15 and (b) the catalyst containing 20 wt% silicotungstic acid on SBA-15.

Conclusion

In this work, a highly selective decarbonylation of lactic acid to acetaldehyde was achieved. When using less acidic heteropolycompounds like phosphomolybdic acid or $H_4PMo_{11}VO_{40}$, the decarboxylation pathway became more important. Due to the increased redox character of these latter compounds, the hydrogen liberated during decarboxylation supposedly easily reduces lactic acid to propanoic acid.

The best results were obtained when using 20 wt% silicotungstic acid supported on SBA-15 or CARiACT. Whereas the CARiACT-supported silicotungstic acid catalyst showed a higher conversion of lactic acid (91% *vs.* 85%), the SBA-15-based catalyst was more selective for acetaldehyde, whereby a slightly higher yield of 83% (*vs.* 81% over CARiACT) was achieved. Both results represent remarkable performances, especially when compared to conventional acid catalysts such as zeolites, alumina and niobium oxide, which are selective to acrylic acid but give no more than a 31% yield of acetaldehyde.[6–9] However, when considering the aim of elaborating an economical industrial process, the use of CARiACT seems to be a more reasonable option regarding the catalysts' preparation costs.

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