

# A High-Throughput Experimentation Study of the Synthesis of Lactates with Solid Acid Catalysts

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**Abstract** The conversion of dihydroxyacetone to ethyl lactate catalysed by different solid acids was investigated by means of High-Throughput Experimentation. A mesoporous amorphous aluminosilicate catalyst displaying very high selectivity and a good yield towards the lactate was identified. The correlation between the type of acid sites and the catalytic behaviour is discussed.

**Keywords** Lactates · Biomass-derived trioses · Solid acid catalysts · High-Throughput Experimentation

## 1 Introduction

Lactic acid and alkyl lactates are relevant compounds finding a broad range of applications in the chemical, food, pharmaceutical and cosmetic industries [1]. Particularly interesting is the use as starting material for the synthesis of polylactic acid (PLA), a polymer that is receiving growing attention for its use as biodegradable plastic [2, 3]. Commercial methods for producing lactic acid are generally based on carbohydrates fermentation. However, these processes are characterised by low productivities and require costly and polluting separation and purification steps. Therefore, the development of an alternative,

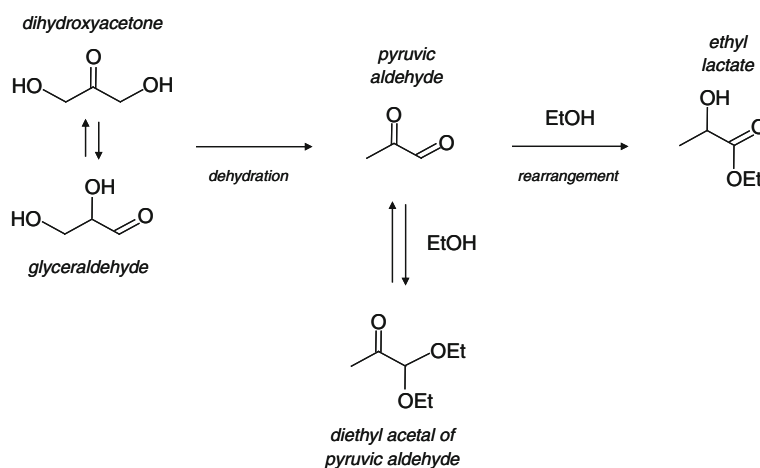
sustainable method for producing lactic acid and lactates is of utmost interest. An attractive reaction path would consist in the conversion of glycerol to lactates. Glycerol is the main by-product of the transesterification of triglycerides used to produce biodiesel [4–7], which represents a promising alternative to fossil fuels provided that competition with food production is avoided and a low impact on the environment is granted in the production of the feedstocks. With the expected development of a sustainable process to produce biodiesel, e.g. using algae as a source of triglycerides, a surplus in the worldwide production of glycerol is envisaged and its conversion to lactates would become both an environmentally and economically appealing reaction.

The direct conversion of glycerol to lactate via oxidative dehydrogenation has been reported in a liquid-phase process catalysed by noble metals supported on carbon [8, 9]. The first step of the process is the partial oxidation of glycerol to glyceraldehyde catalysed by noble metals. Then, glyceraldehyde is converted to lactate in a base-catalysed reaction. This process requires relatively high temperature and high concentration of strong base in solution, the selectivity is moderate and the stability of the expensive catalysts might be an issue. Alternatively, the conversion of glycerol to lactates can be achieved with two separate synthesis steps. First, glycerol is partially oxidised to one of the two monosaccharides known as trioses, i.e. dihydroxyacetone and glyceraldehyde [10–13]. Then, the trioses are converted to the desired lactate product by dehydration with the formation of a pyruvic aldehyde intermediate and by a consecutive rearrangement with incorporation of a solvent alcohol molecule (Scheme 1). Tin halides have been reported as active homogeneous catalysts for this reaction [14]. Aiming at an industrial application, the difficult separation of homogenous

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**Scheme 1** Conversion of trioses to ethyl lactate



catalysts from the products and the corrosive nature of tin halides represent serious drawbacks of this system. Recently, we discovered that Ultrastable zeolites Y (USY) with low Si/Al ratio catalyse the conversion of trioses to alkyl lactates with comparable results to those of the best tin halide catalysts, with the advantage of being commercially available heterogeneous catalysts that could be reused in various successive cycles without loss of activity [15]. This result was obtained by investigating the performance of different zeolites by means of High-Throughput Experimentation (HTE) [16–18]. The study highlighted the importance of the type and strength of the zeolite acid sites in determining the yield and the selectivity of the reaction. A combination of mild Brønsted acidity and of Lewis acidity, in the form of extra-framework aluminium species, was proposed to be the most suitable for catalysing the formation of alkyl lactates. On the other hand, strong Brønsted acidity proved to be detrimental because it catalyses the formation of the diethyl acetal of pyruvic aldehyde (Scheme 1), thus reducing the selectivity towards the desired lactate.

Since the nature of the acid species appeared to have a crucial influence on the catalytic results, the investigation of other heterogeneous catalysts with different number and type of acids sites may lead to the discovery of materials with improved activity and selectivity in the conversion of trioses to alkyl lactates. Here, we report the study of a library of solid acid catalysts in the conversion of dihydroxyacetone to ethyl lactate. The library consists of a variety of materials in which various types of metal centres provide a population of different amounts and sorts of Brønsted and Lewis acid sites:

- Al-pillared clays.
- Mesoporous aluminosilicates.
- Zeolites (both ion-exchanged and not).
- Si-substituted crystalline aluminophosphates (SAPO's).

The use of High-Throughput Experimentation techniques made possible the rapid and efficient testing of this large collection of heterogeneous catalysts.

## 2 Experimental

### 2.1 Materials

The library of solid acid catalysts consists of both freshly prepared materials and of catalysts from the vast archive available at the Centre for Surface Chemistry and Catalysis of the K.U. Leuven. All the catalysts except the ion-exchanged zeolites were calcined in air at 450 °C for 5 h (from 25 to 450 °C at 2 °C/min). The ion-exchanged zeolites were calcined in air at 450 °C for 1.5 h (from 25 to 450 °C at 5 °C/min) unless otherwise stated. After calcination, the solids were kept at 100 °C until reaction start.

Al-pillared beidellite clays were prepared by adding a hydroxy-aluminium pillaring solution to an aqueous suspension of the clay (2 wt%), according to a previously reported method [19]. A volume of hydroxy-aluminium solution containing 30 meq of Al was used per gram of clay. The hydroxy-aluminium solutions were prepared by dropwise addition of a 0.5 M aqueous solution of NaOH to a 0.2 M aqueous solution of aluminium nitrate. Two different solutions with an OH/Al molar ratio of 1.2 and 1.4 were employed.

Two amorphous mesoporous aluminosilicates (AMSiAl) with Si/Al ratio of 10 and 50 (in the synthesis mixture) were prepared following a similar procedure to that employed for the synthesis of zeolite ZSM-5, but without hydrothermal treatment [20]. SiO<sub>2</sub> and Al(OH)<sub>3</sub> precursors were dissolved in an aqueous solution of tetrapropylammonium hydroxide, and aqueous HCl 1.0 M was added to adjust the pH to 9. The obtained gels were aged at room temperature

for 24 h, washed with deionised H<sub>2</sub>O and dried at 60 °C for 48 h and subsequently at 110 °C for 48 h. This synthesis procedure leads to the formation of mesoporous structures with an average pore diameter around 4 nm [20, 21]. Powder X-ray diffraction (XRD) analysis of the two materials confirmed their amorphous nature.

Two zeolites Y with different degree of dealumination, SiCl<sub>4</sub>-dealuminated LiNa-Y (250 °C) and SiCl<sub>4</sub>-dealuminated LiNa-Y (400 °C), were prepared from zeolite Na-Y [FAU] by reaction with SiCl<sub>4</sub> [22, 23]. To prepare SiCl<sub>4</sub>-dealuminated LiNa-Y (250 °C), zeolite Na-Y was exchanged for 68% with Li<sup>+</sup>, dehydrated for 2 h at 350 °C under N<sub>2</sub> flow, reacted with SiCl<sub>4</sub> for 35 min at 250 °C, heated to 440 °C under N<sub>2</sub> flow, washed with deionised water until the material was free of chloride and finally dried at 125 °C. To prepare SiCl<sub>4</sub>-dealuminated LiNa-Y (400 °C), zeolite Na-Y was exchanged for 40% with Li<sup>+</sup>, dehydrated for 2 h at 350 °C under N<sub>2</sub> flow, reacted with SiCl<sub>4</sub> for 35 min at 400 °C (with an initial temperature of 250 °C and a heating rate of 10 °C/min), heated to 520 °C under N<sub>2</sub> flow, washed with deionised water, ion-exchanged with ammonium chloride and finally dried at 125 °C.

The ion-exchanged zeolites were prepared following an in-house developed High-Throughput protocol [24] on a FLAMAC platform consisting of a Powdermill solid-handling workstation, used to weigh the solids, and a Tecan Cavro liquid-handling workstation with integrated heating and magnetic stirring units, used to dispense the ion-exchange solutions, to mix the samples and finally to wash them. Copper acetate and the chlorides of the other di- and trivalent cations were used to prepare the aqueous solutions for ion-exchange. The parent zeolites, Na-Y [FAU] with a Si/Al = 2.7 (CBV 100) and Na-X [FAU] with a Si/Al = 1.2, were obtained from PQ Zeolites and Uetikon, respectively.

The La-exchanged Na-X and the La-exchanged Na-Y calcined at 800 °C were prepared by three successive exchange steps followed by intermediate washing, drying and calcination. The final calcination was performed for 4 h at 550 °C for the zeolite X sample and at 800 °C for the zeolite Y sample.

Zeolite H-ZSM-23 [MTT] was synthesised according to a literature procedure [25]. A set of microporous crystalline Si-substituted aluminophosphates (SAPO) were prepared according to literature methods: SAPO-5 with different levels of Si content (0.10, 0.40 and 0.90 mol of SiO<sub>2</sub> per mol of Al<sub>2</sub>O<sub>3</sub> in the composition of the synthesis mixture) [26]; SAPO-11 (0.46) [27]; SAPO-34 (0.06) [26]; SAPO-37 (0.86) [28]; SAPO-44 (1.1) [29].

## 2.2 Catalytic Tests

Straightforward and rapid testing of the selected library of catalysts was performed by means of High-Throughput

Experimentation on the FLAMAC platform described in Sect. 2.1. The reliability and reproducibility of the results obtained using this High-Throughput platform was carefully evaluated and demonstrated in previous work [24]: the standard deviation for a set of 24 parallel tests using the same catalyst was found to be lower than 2%. For the catalytic test, 5 mL of an ethanol solution containing dihydroxyacetone (0.4 M) and 1,4-dioxane as GC internal standard was added to 0.2 g of each catalyst of the library. The solution was prepared using the 1,3-dihydroxyacetone dimer, which readily converts into the monomer [14]. The reaction was performed in tightly closed glass vials under stirring at 90 °C for 6 h. The yields of the products (ethyl lactate and diethyl acetal of pyruvic aldehyde) were determined by Gas Chromatography (GC) on a Finnigan Trace GC Ultra (RTX-5 column, 5 m, 0.1 mm), allowing very fast analysis of each sample (2 min) thanks to the rapid heating and cooling system of the short column (Ultra Fast Module). The temperature profile during the analysis was: 30 s at 70 °C, 70–270 °C at 200 °C/min, 30 s at 270 °C. The conversion of dihydroxyacetone was calculated as the sum of the yields of the two observed products, ethyl lactate and diethyl acetal of pyruvic aldehyde, because the direct quantification of dihydroxyacetone by GC analysis is hindered by its low response factor and by the breadth of its GC peaks.

## 2.3 Characterisation

The <sup>27</sup>Al MAS NMR spectra of zeolites Na-Y, SiCl<sub>4</sub>-dealuminated LiNa-Y (250 °C) and La-exchanged Na-Y calcined at 800 °C were recorded on a Bruker DSX400 spectrometer (9.4 T). The samples were packed in 2.5 mm Zirconia rotors. 36,000 scans were accumulated with a recycle delay of 100 ms. The spinning frequency of the rotor was 20 kHz. A 0.1 M aqueous solution of Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O was used as shift reference.

Powder X-ray diffraction (XRD) patterns of AMSiAl(10) and AMSiAl(50) were measured in transmission mode on a STOE Stadi P instrument using CuKα<sub>1</sub> radiation (λ = 0.154 nm).

## 3 Results and Discussion

In previous work by our group, a mechanism for the conversion of dihydroxyacetone or glyceraldehyde to lactate was proposed on the basis of the results obtained with different zeolites in their H-form and with zeolite Na-Y (Scheme 1) [15]. The initial dehydration of the trioses leading to the pyruvic aldehyde intermediate is catalysed by Brønsted acid sites. From pyruvic aldehyde, the reaction proceeds to the dialkyl acetal in the presence of strong

Brønsted acidity. On the other hand, it was proposed that the formation of alkyl lactate from pyruvic aldehyde is catalysed by extra-framework aluminium species that act as Lewis acid sites. The library of solid acid catalysts presented in this work exhibits a variety of number and types of Brønsted and Lewis acid sites. The members of this library were chosen with the aim of discovering new and promising catalysts and to gain further insight into the catalytic role of the different types of acid sites. The results obtained by the High-Throughput screening of this library of catalysts in the conversion of dihydroxyacetone to ethyl lactate are reported in Table 1.

The two Al-pillared beidellite clays used in this study display moderate conversion of dihydroxyacetone and intermediate selectivity towards ethyl lactate (Fig. 1; Table 1, entries 1–2). These materials consist of layers of

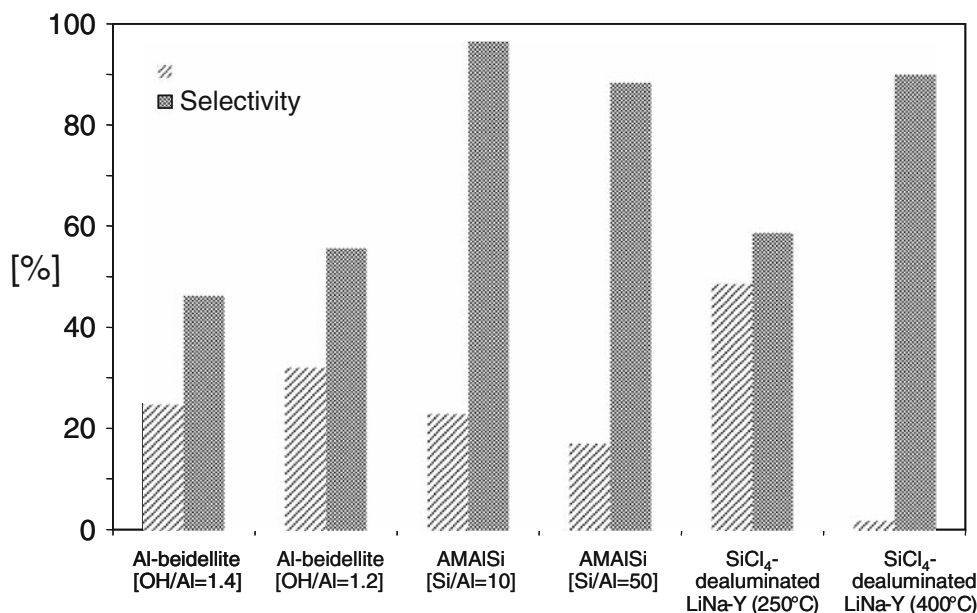
beidellite, a clay mineral of the smectite family, intercalated with  $\text{Al}^{3+}$  ions [19]. Pillaring of clays with aluminium generates Lewis and Brønsted acidity. In the past, Al-pillared clays found application as catalysts for different reactions. It was observed that their activity is influenced by the nature of the clay mineral: compared to other Al-pillared clays, those prepared from beidellite display much stronger Brønsted acid sites, imparting catalytic properties similar to those of USY zeolites [19]. The presence of rather strong Brønsted acidity combined to that of Lewis acidity explains the catalytic results obtained in the conversion of dihydroxyacetone. Similarly to what observed for USY zeolites presenting both framework (Brønsted acids) and extra-framework (Lewis acids) aluminium sites, both the desired lactate product and the diethyl acetal of pyruvic aldehyde by-product are obtained

**Table 1** Conversion of dihydroxyacetone in ethanol: product yields and selectivity towards ethyl lactate with different solid acid catalysts after 6 h at 90 °C

Entry	Catalyst	$Y_{\text{EL}}$ (%)	$Y_{\text{DA}}$ (%) <sub>X</sub>	$S_{\text{EL}}$ (%)
1	Al-beidellite [OH/Al = 1.4]	11	13	46
2	Al-beidellite [OH/Al = 1.2]	18	14	56
3	AMAlSi [Si/Al = 10]	22	1	96
4	AMAlSi [Si/Al = 50]	15	2	88
5	$\text{SiCl}_4$ -dealuminated LiNa-Y (250 °C)	28	20	59
6	$\text{SiCl}_4$ -dealuminated LiNa-Y (400 °C)	2	0.2	90
7	20% Mg-exchanged Na-Y	0	1	0
8	50% Mg-exchanged Na-Y	0	2	0
9	20% Ca-exchanged Na-Y	0	0	0
10	50% Ca-exchanged Na-Y	0	0	0
11	20% Mn-exchanged Na-Y	0	0	0
12	50% Mn-exchanged Na-Y	0	3	0
13	20% Co-exchanged Na-Y	0	0	0
14	50% Co-exchanged Na-Y	0	0	0
15	20% Cu-exchanged Na-Y	1	33	3
16	50% Cu-exchanged Na-Y	1	83	1
17	30% Ce-exchanged Na-Y	1	8	11
18	50% Ce-exchanged Na-Y	9	50	15
19	90% Ce-exchanged Na-Y	11	77	13
20	30% La-exchanged Na-Y	1	17	6
21	50% La-exchanged Na-Y	2	47	4
22	90% La-exchanged Na-Y	6	84	7
23	La-exchanged Na-Y calcined at 800 °C	49	43	53
24	La-exchanged Na-X	35	48	42
25	H-ZSM-23	5	14	27
26	SAPO-5 (0.10)	1	4	18
27	SAPO-5 (0.40)	1	4	26
28	SAPO-5 (0.90)	0.5	0	100
29	SAPO-11	1	14	7
30	SAPO-34	3	4	37
31	SAPO-37	9	65	13
32	SAPO-44	13	8	62

$Y_{\text{EL}}$  = yield of ethyl lactate,  
 $Y_{\text{DA}}$  = yield of diethyl acetal of  
 pyruvic aldehyde,  $S_{\text{EL}}$  = ethyl  
 lactate selectivity, calculated on  
 the basis of lactate and acetal  
 yields

**Fig. 1** Conversion of dihydroxyacetone and selectivity towards ethyl lactate with Al-pillared clays, amorphous mesoporous aluminosilicates and  $\text{SiCl}_4$ -dealuminated zeolites



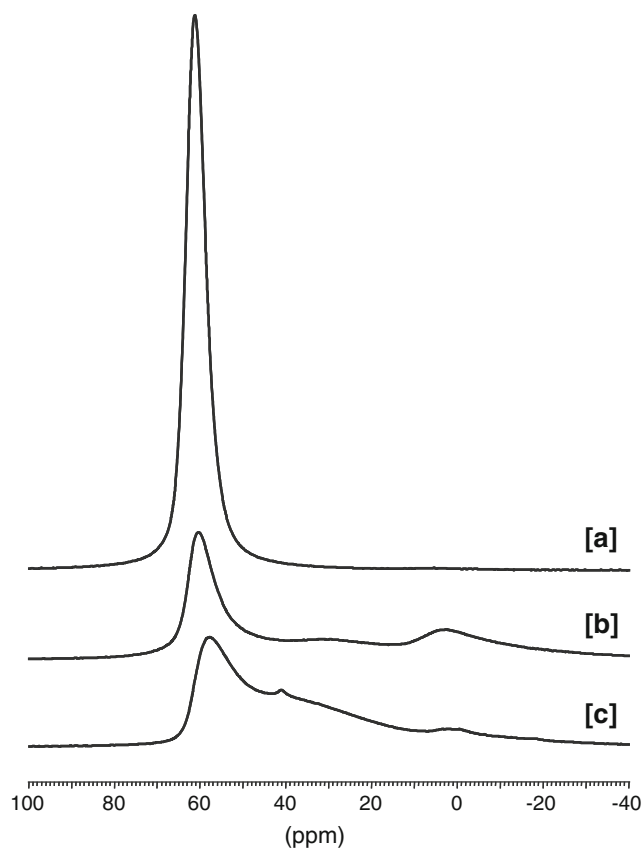
[15]. However, neither the yields nor the selectivity towards the lactate found with the two Al-pillared beidellite clays reach the levels of the best of the USY zeolites catalysts.

The two mesoporous amorphous aluminosilicates with Si/Al ratio of 10 and 50, denoted as AMSiAl(10) and AMSiAl(50), give moderate conversion of dihydroxyacetone with very high selectivity towards the desired lactate product (Fig. 1; Table 1, entries 3–4). The material with the highest aluminium content exhibits the highest activity, in agreement with what found with H-zeolites [15]. AMSiAl(10) displays the highest selectivity towards ethyl lactate (96%) among all the solid acid catalysts explored in this study or previously reported [15]. This is a very promising result, although the obtained yield (22%) is markedly lower than that obtained with the best zeolite catalyst under the same reaction conditions (59% lactate yield and 77% lactate selectivity with USY CBV 600 with Si/Al = 2.6) [15]. The catalytic behaviour of AMSiAl(10) and AMSiAl(50) can be explained in terms of their population of acid sites. These two mesoporous amorphous aluminosilicates were prepared using similar synthesis conditions to those employed to prepare zeolite ZSM-5, with the difference that the gels were not subjected to a hydrothermal treatment [20]. This prevented the crystallisation of the aluminosilicates. Since the strength of the Brønsted acid sites in zeolites is related to the strained geometry of the tetrahedral units in the crystalline structure, the lack of crystallinity of these materials implies that their Brønsted acidity is milder compared to that of zeolites with the same Si/Al ratio, similarly to what observed in ordered mesoporous aluminosilicates [30, 31]. Therefore,

the very high selectivity found with AMSiAl(10) and AMSiAl(50) is ascribed to the fact that these materials present mild Brønsted acid sites, active in catalysing the initial dehydration step, but are devoid of the strong Brønsted acidity typical of H-zeolites, which would catalyse the formation of the diethyl acetal by-product. In analogy with the mechanism proposed for the reaction catalysed by zeolites (vide supra), it is inferred that the formation of ethyl lactate from pyruvic aldehyde is catalysed by octahedrally coordinated aluminium species, which are abundant in these materials in line with their amorphous character [20].

$\text{SiCl}_4$ -dealuminated LiNa-Y (250 °C), a zeolite Na-Y ion-exchanged for 68% with  $\text{Li}^+$  and mildly dealuminated by reaction with  $\text{SiCl}_4$ , shows good activity and moderate lactate selectivity (Fig. 1; Table 1, entry 5). In contrast, very low conversion of dihydroxyacetone with high selectivity towards ethyl lactate was observed with  $\text{SiCl}_4$ -dealuminated LiNa-Y (400 °C), which underwent a more extensive dealumination treatment (Fig. 1; Table 1, entry 6). Both samples were reacted with  $\text{SiCl}_4$  with the aim of removing aluminium from the zeolite framework [22, 23]. This dealumination process generates extra-framework aluminium species that catalyse the formation of ethyl lactate. The formation of extra-framework aluminium can be monitored by comparing the  $^{27}\text{Al}$  MAS NMR spectrum of the parent Na-Y with that of  $\text{SiCl}_4$ -dealuminated LiNa-Y (250 °C) (Fig. 2). The reaction with  $\text{SiCl}_4$  and the following thermal treatment were performed at lower temperatures with  $\text{SiCl}_4$ -dealuminated LiNa-Y (250 °C) compared to  $\text{SiCl}_4$ -dealuminated LiNa-Y (400 °C). As a consequence, the aluminium content and the degree of



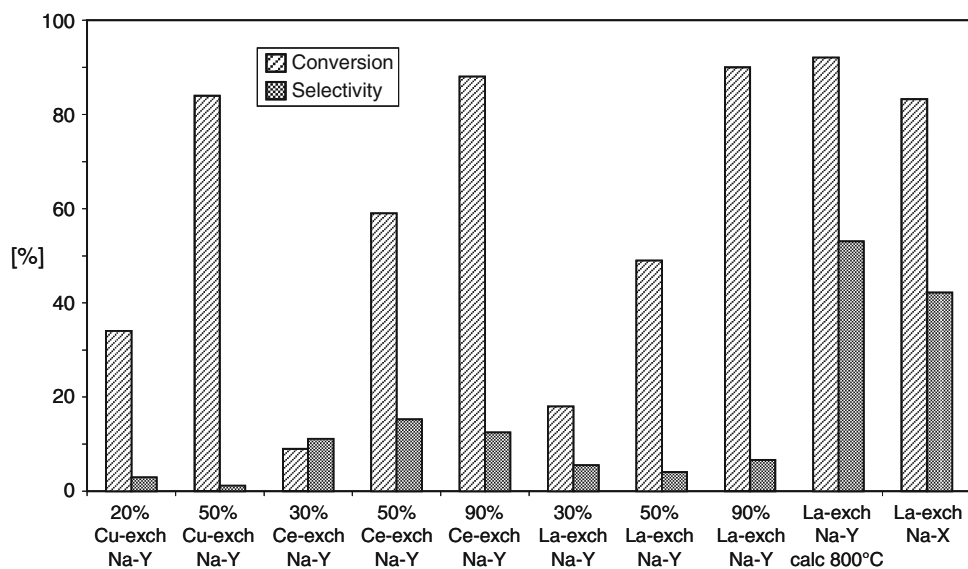


**Fig. 2**  $^{27}\text{Al}$  MAS NMR spectra of zeolites Na-Y [a],  $\text{SiCl}_4$ -dealuminated LiNa-Y (250 °C) [b] and La-exchanged Na-Y calcined at 800 °C [c]. The peak around 60 ppm is due to tetrahedral framework aluminium. The peak around 0 ppm belongs to octahedral extra-framework aluminium species. The broad peaks between 30 and 40 ppm are assigned to penta-coordinated and to distorted tetrahedral species [39]

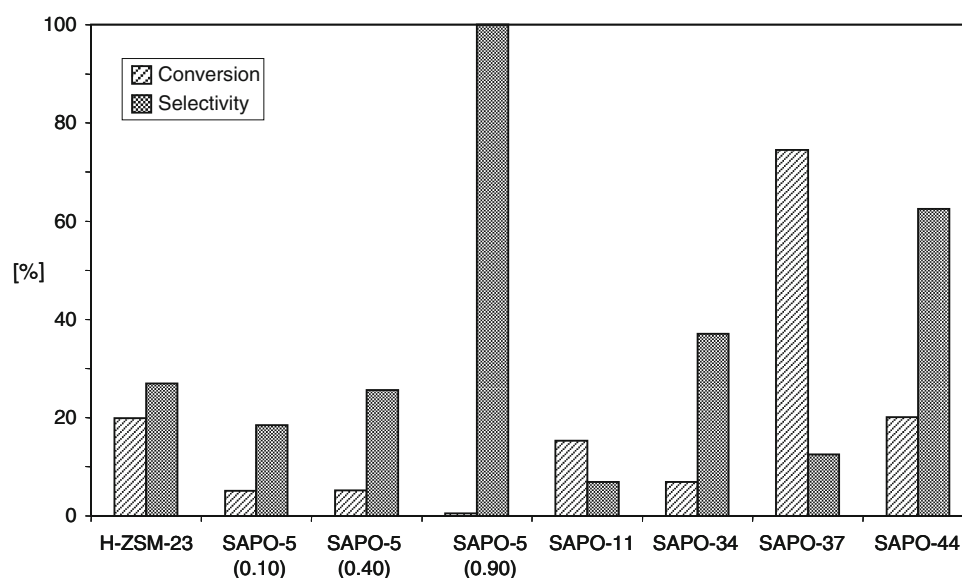
crystallinity are higher in the former sample [22].  $\text{SiCl}_4$ -dealuminated LiNa-Y (250 °C) contains strong Brønsted acidity, stemming from framework aluminium sites ion-exchanged with protons formed during the washing after reaction with  $\text{SiCl}_4$ , and Lewis acid sites in the form of extra-framework aluminium species generated by dealumination and of  $\text{Li}^+$  and  $\text{Na}^+$  ions. This combination accounts for the observed formation of both the lactate and the acetal products.  $\text{SiCl}_4$ -dealuminated LiNa-Y (400 °C) has a low number of catalytic active sites due to its low aluminium content, and a lack of the strong Brønsted acid sites normally present in zeolite frameworks as a result of its low level of crystallinity. This combination accounts for the very low activity and high selectivity of this catalyst in the conversion of dihydroxyacetone to ethyl lactate.

The results of the conversion of dihydroxyacetone with Na-Y and Na-X zeolites ion-exchanged with a variety of di- and trivalent cations at different levels of the theoretically possible cation-exchange capacity (CEC) are reported in Table 1 and Fig. 3. Although some of the ion-exchanged zeolites are active in the conversion of dihydroxyacetone to ethyl lactate, none of these catalysts displayed higher lactate yield and selectivity compared to the most promising zeolite identified in the previous series of catalytic tests (USY CBV 600 with  $\text{Si}/\text{Al} = 2.6$ ) [15]. The Na-Y zeolites ion-exchanged with the divalent ions  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mn}^{2+}$  or  $\text{Co}^{2+}$  at 20 and 50% of the CEC display negligible or very poor conversions of dihydroxyacetone and no formation of lactate (Table 1, entries 7–14), similarly to what observed with untreated Na-Y [15]. These results are ascribed to the lack of Brønsted acidity of these catalysts as a consequence of the selective exchange of sodium with these divalent

**Fig. 3** Conversion of dihydroxyacetone and selectivity towards ethyl lactate with copper-, cerium- and lanthanum-exchanged zeolites



**Fig. 4** Conversion of dihydroxyacetone and selectivity towards ethyl lactate with H-ZSM-23 and with SAPO structures



ions leading to their full coordination to the zeolite framework, expectedly at SI and SI' positions [32]. On the other hand, zeolite Na-Y ion-exchanged with  $\text{Cu}^{2+}$  (20 and 50% of CEC) is active in the conversion of dihydroxyacetone with an almost complete selectivity towards the diethyl acetal product, the activity being proportional to the degree of ion-exchange (Fig. 3; Table 1, entries 15–16). Similarly, zeolites Na-Y ion-exchanged with different amounts of the trivalent ions  $\text{Ce}^{3+}$  and  $\text{La}^{3+}$  (30, 50 and 90% of CEC) are active in the conversion of dihydroxyacetone and yield diethyl acetal as the main product (Fig. 3; Table 1, entries 17–22). Very high conversion of dihydroxyacetone is achieved with the zeolites 90%-exchanged with  $\text{Ce}^{3+}$  and  $\text{La}^{3+}$ ; however, the selectivity towards the desired lactate product is very low in both cases. This behaviour is explained by the formation of strong Brønsted acid species during the ion-exchange process, typical of multivalent cations. For example, in La-exchanged zeolite Y the lanthanum ion is initially exchanged in its hydrated form to sites located in the supercage of the Faujasite structure [33]. Upon thermal treatment the lanthanum species dehydrate and migrate to the sites located at the six-ring openings of the sodalite cage (SI and SI') [34]. During this process, the  $\text{La}^{3+}$  ions (Lewis acids) tend to react with water leading to the formation of LaOH groups and of strong Brønsted acid sites [35, 36]. These strong Brønsted acid sites are responsible both for the high conversion of dihydroxyacetone and for the high yield of diethyl acetal, in agreement with the mechanism proposed for this reaction (vide supra). This conclusion is supported by the observation that the activity of the Cu-, Ce- and La-exchanged zeolites is proportional to the degree of ion-exchange.

To investigate whether a higher calcination temperature would lead to dehydroxylation of the LaOH groups with formation of active Lewis acid sites as  $\text{La}^{3+}$  ions located at the six-ring openings of the sodalite cage, a sample of fully La-exchanged zeolite Y was subjected to calcination at 800 °C (instead of 450 °C). The obtained catalyst gives similar conversion but much higher lactate yield (49%) and selectivity (53%) compared to the 90% La-exchanged zeolite Y (Fig. 3; Table 1, entry 23). This result shows that this thermal treatment reduces the amount of strong Brønsted acids and creates Lewis acid sites able to catalyse the formation of ethyl lactate.  $^{27}\text{Al}$  MAS NMR analysis indicates that after calcination at 800 °C a large fraction of aluminium species have been removed from their tetrahedral framework position (Fig. 2). This suggests that the active Lewis acid species are provided by these aluminium species in alternative to or together with  $\text{La}^{3+}$  ions confined in the not very accessible SI and SI' sites of zeolite Y. In a similar way, the relatively good yield of ethyl lactate given by La-exchanged Na-X (Fig. 3; Table 1, entry 24) can be attributed to the high tendency of this aluminium-rich type of zeolite framework to undergo dealumination during the ion-exchange process and the successive thermal treatment [36], and in the second instance to the presence of  $\text{La}^{3+}$  Lewis acid sites favoured by the higher number of aluminium sites suitably located for the full coordination of the trivalent lanthanum ions in zeolite X compared to zeolite Y.

Zeolite H-ZSM-23 gives moderate conversion of dihydroxyacetone with low selectivity towards ethyl lactate (Fig. 4; Table 1, entry 25). This result is comparable with those obtained with other zeolites in their H-form and with a high Si/Al ratio [15].

All the tested microporous crystalline silicoaluminophosphates (SAPO) show low or very low yields of lactate (Table 1, entries 26–32). This suggests that this group of catalysts presents small amounts of suitable sites for catalysing the reaction of the pyruvic aldehyde intermediate to ethyl lactate, in agreement with the Brønsted nature of their acid sites. The silicon atoms present in the SAPO materials are not uniformly distributed through the solid and each SAPO structure has a different tendency to form aluminosilicate and silicoaluminophosphate domains of various size and composition and in different proportions [37, 38]. These differences can explain the catalytic behaviour of the screened SAPO structures. Aluminium in aluminosilicate domains and silicon in silicoaluminophosphate domains generate Brønsted acid sites. However, the strength of these acid sites is lower compared to that observed in aluminosilicate zeolites. Only the acid sites located at the border between the two types of domains are expected to be strong [38]. Among the studied materials, SAPO-37 presents acid sites in the aluminosilicate domains, in the silicoaluminophosphate domains and at the boundaries between the two. It has been reported that this combination of sites imparts a Brønsted acid behaviour similar to that of the isostructural zeolite H-Y [37]. This is in line with the high conversion of dihydroxyacetone and low selectivity towards ethyl lactate that are observed both with SAPO-37 (Fig. 4) and with zeolite H-Y [15]. The Brønsted acid sites of SAPO-5, located in the silicoaluminophosphate domains [37], are too weak to efficiently catalyse the formation of the diethyl acetal of pyruvic aldehyde. The low conversion observed with SAPO-34 can be explained with similar arguments. SAPO-11 displays slightly higher activity due to the location of its Brønsted acid sites in the aluminosilicate domain and at the interface between the aluminosilicate and the silicoaluminophosphate domains [37]. SAPO-44 is the only material of the SAPO family that catalysed the formation of ethyl lactate in moderate yield and with good selectivity. This result is ascribed to the amorphous alumina and penta-coordinated aluminium species that were reported to be present in this kind of material [29] and that can act as Lewis acid sites for catalysing the formation of the lactate.

#### 4 Conclusions

A library of solid acid catalysts was tested in the conversion of dihydroxyacetone to ethyl lactate by means of High-Throughput Experimentation. The product yields and selectivities were determined by the type and amount of acid sites present in the various catalysts. Strong Brønsted acidity was detrimental for the selectivity towards the desired lactate product. The most promising catalyst

identified in this study was an amorphous mesoporous aluminosilicate that displayed very high selectivity towards ethyl lactate (96%). These results indicate that further research on this topic should be directed towards the identification of a catalyst with an optimum balance between mild Brønsted acid and Lewis acid sites.

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