

Zeolite-catalysed conversion of C₃ sugars to alkyl lactates

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The direct conversion of C₃ sugars (or trioses) to alkyl lactates was achieved using zeolite catalysts. This reaction represents a key step towards the efficient conversion of bio-glycerol or formaldehyde to added-value chemicals such as lactate derivatives. The highest yields and selectivities towards the desired lactate product were obtained with Ultrastable zeolite Y materials having a low Si/Al ratio and a high content of extra-framework aluminium. Correlating the types and amounts of acid sites present in the different zeolites reveals that two acid functions are required to achieve excellent catalysis. Brønsted acid sites catalyse the conversion of trioses to the reaction intermediate pyruvic aldehyde, while Lewis acid sites further assist in the intramolecular rearrangement of the aldehyde into the desired lactate ester product. The presence of strong zeolitic Brønsted acid sites should be avoided as much as possible, since they convert the intermediate pyruvic aldehyde into alkyl acetals instead of lactate esters. A tentative mechanism for the acid catalysis is proposed based on reference reactions and isotopically labelled experiments. Reusability of the USY catalyst is demonstrated for the title reaction.

1. Introduction

The synthesis of lactic acid or alkyl lactates is a process of great appeal in the areas of renewable biomass conversion and green chemistry: these versatile products find applications in the chemical-, food-, pharmaceutical- and cosmetic industries.¹ In particular, they are increasingly employed as environmentally friendly solvents and as starting materials for the synthesis of polylactic acid (PLA), a biodegradable polymer with a wide range of applications.^{2,3} The most common commercial processes to produce lactic acid are based on carbohydrate fermentation. Drawbacks of such processes include low productivities and the need for expensive and energy-inefficient separation and purification steps. In this context, the development of an alternative, sustainable method for producing lactic acid and lactates from renewable sources would be of great relevance.

Here, we report the catalytic formation of alkyl lactates from triose monosaccharides in alcohol solvents. The two trioses, *i.e.* dihydroxyacetone and glyceraldehyde, can be obtained either biochemically or catalytically from glycerol,^{4–9} which is the main by-product of the transesterification of triglycerides used to produce bio-diesel.^{10–12} Bio-diesel represents a promising alternative to fossil fuels provided that its production does not affect food supply and does not cause damage to the

environment. This could be achieved through the development of sustainable processes, *e.g.* using microorganisms, *viz.* algae, as a source of triglycerides.^{13,14} Considering the expected increase in the worldwide production of glycerol, its efficient conversion to valuable chemicals, such as propylene glycol, acrolein, propylene oxide, 1,3-propanediol, but also to lactates becomes an environmentally and economically attractive reaction, and represents an important step towards a complete, sustainable process for the use of biomass feedstock.^{1,15–29}

In addition to the glycerol-route, dihydroxyacetone synthesis is also feasible from natural gas sources *via* the thiazolium-ylide-catalysed condensation of formaldehyde.³⁰

The first catalysts reported for the conversion of trioses to lactic acid or to alkyl lactates contained transition metals either as homogenous complexes or supported on an ion exchange resin.^{31–34} The highest yields were obtained with Cr-based catalysts, making the process unattractive for health- and environmental reasons. More recently, tin halides were found to catalyse the reaction of trioses with alcohols to produce alkyl lactates with high yield and selectivity.³⁵ However, the intrinsic obstacle represented by the separation of homogeneous catalysts from the products and the corrosive nature of tin halides pose serious limitations to this system. Therefore, the development of an efficient heterogeneous catalyst for a sustainable process to convert trioses to lactic acid or its derivatives free of any heavy metal is of utmost interest. The present work describes the conversion of dihydroxyacetone and glyceraldehyde to alkyl lactate in alcohol solvents, using a range of zeolites as catalysts. Zeolites are renowned stable heterogeneous catalysts, employed as environmentally benign alternatives to hazardous catalysts in many chemical processes,^{36,37} including recent applications in biomass conversion.^{22,38,39}

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2. Experimental

2.1 Materials

Zeolite NH₄-Y 450 [FAU] was obtained by calcination of the NH₄-Y zeolite ZF110 provided by Zeocat at 450 °C. Na-Y [FAU] (CBV 100), Ultrastable zeolites Y [FAU] (CBV 500, CBV 600, CBV 712, CBV 720, CBV 760 and CBV 780) and ZSM-5 [MFI] (NH₄-ZSM-5 CBV 8020) were obtained from PQ Zeolites. Zeolite-Beta [BEA] (H-Beta PB-1) was obtained from Uetikon. Prior to use, all the zeolites were calcined in air at 450 °C (from 25 to 80 °C at 1 °C min⁻¹; 6 h at 80 °C; 80 to 450 °C at 1 °C min⁻¹; 6 h at 450 °C). After calcination, the solids were kept at 100 °C.

2.2 Characterisation

The fraction of Al located in the framework of FAU zeolite was determined by means of solid-state ²⁹Si MAS NMR analysis of the calcined zeolites using the formula of Thomas.⁴⁰ The ²⁹Si MAS NMR spectra were recorded on a Bruker MX300 spectrometer (7.0 T). 3900 scans were accumulated with a recycle delay of 60 s. The samples were packed in 4 mm rotors. The spinning frequency of the rotor was 5000 Hz. Tetramethylsilane (TMS) was used as shift reference. Deconvolution was performed with the Bruker WinFit software. Gaussian curves were used for the simulation of the peaks, with the exception of the Si(OAl) line of USY CBV600, 712 and 720, for which a Lorentzian curve was used. The fraction of framework Al determined for USY CBV 760 and 780 contain a higher level of uncertainty owing to the presence of a broad peak due to amorphous silica, which hindered the accurate simulation of the other peaks.

The fraction of Al located in the framework of H-ZSM-5 and H-Beta zeolite was determined from ²⁷Al MAS NMR spectra assuming negligible amounts of invisible Al. The ²⁷Al MAS NMR were recorded on a Bruker DSX400 spectrometer (9.4 T). The samples were packed in 2.5 mm zirconia rotors. 36000 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(NO₃)₃·9H₂O was used as reference.

2.3 High-throughput experimentation catalytic tests

Catalytic tests were performed by means of High-Throughput Experimentation (HTE)^{41,42} on a FLAMAC platform.⁴³ The HTE platform included a Powdermium solid-handling robot, used to weigh the solids, and a Tecan Cavro liquid-handling workstation with integrated heating and magnetic stirring units, used to dispense the liquids and to perform the catalytic tests. A tailored approach was used for the kinetic studies: a separate sample was used to measure the activity of each zeolite at each reaction time. This approach guarantees an increased reliability of the obtained results as opposed to conventional kinetic experiments. The effect of concentration variations generated by consecutive removal of sample aliquots for GC analysis during the course of the reaction is efficiently avoided.⁴³ A number of HT catalytic tests were performed in duplicate or in triplicate: in those cases, the average product yields are reported.

In a typical catalytic test, 5 ml of an alcohol solution containing dihydroxyacetone (0.4 M, prepared from the 1,3-dihydroxyacetone dimer, which readily converts into the monomer³⁵) and 1,4-dioxane (GC internal standard) was added to 0.2 g of catalyst. The reaction was performed in tightly closed glass vials (363 K) or in stainless-steel autoclaves (383 and 393 K), with stirring. The same reaction conditions and concentrations were used when glyceraldehyde, pyruvic aldehyde (as a 40 wt% solution in H₂O) or phenyl glyoxal were used as substrate. The product yields (*Y*, %) 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) as a consequence of the rapid heating and cooling system of the short column (Ultra-Fast Module). The assignment of the products was confirmed by Gas Chromatography-Mass Spectrometry analysis (GC-MS) on an Agilent 6890 N Gas Chromatograph (WCOT fused silica column, 30 m, 0.25 mm) coupled to an Agilent 5973 MSD Mass Spectrometer. The conversion of dihydroxyacetone (*X*_{DHA}, %) was calculated from the sum of the yields of the two observed products, alkyl lactate and dialkyl acetal of pyruvic aldehyde, because the direct quantification of dihydroxyacetone by GC analysis is somewhat hindered by its low response factor. ¹³C{¹H} NMR spectra were measured at 25 °C on a Bruker Avance 300 spectrometer (7.05 T, 300 MHz).

Two alternative approaches were followed for the recycling of the catalysts. The first one is a washing procedure: initially the reaction solution was removed from each sample; then, 5 ml of ethanol were added to each vial and the samples were stirred for 5 min. The samples were centrifuged for 5 min at 3500 rpm to deposit the solid catalyst. The supernatant ethanol solution was removed. The washing procedure was repeated 3 times. After the last washing step, the supernatant solution was analysed by GC to confirm the absence of residual reaction components. Finally, the samples were dried for 16 h in an oven at 100 °C. A calcination procedure was also evaluated: a washing step with ethanol was carried out as described above, followed by calcination in air at 450 °C (from 25 to 80 °C at 1 °C min⁻¹; 6 h at 80 °C; 80 to 450 °C at 1 °C min⁻¹; 6 h at 450 °C).

3. Results and discussion

3.1 Conversion of trioses over zeolites

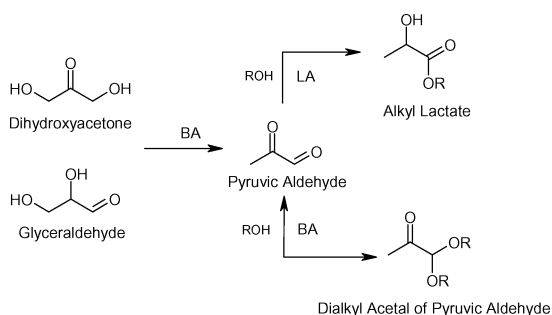
The conversion of trioses in various alcohol solvents was studied with different zeolites as catalysts. The employed zeolites were selected in order to investigate the effect of the type and amount of Brønsted and Lewis acid sites and of different porous structures: zeolite Na-Y and NH₄-Y 450, a series of commercial Ultrastable zeolite Y in the H⁺-form (USY, CBV series) with different level of steaming and acid-leaching treatment, an H-ZSM-5 and an H-Beta zeolite.

In a first screening of the zeolites in EtOH, the same two main products were always observed (Table 1): ethyl lactate and the diethyl acetal of pyruvic aldehyde. The presence of these products suggests that the reaction starts with the formation of a pyruvic aldehyde intermediate, from which it can proceed towards the lactate by rearrangement with incorporation of an

Table 1 Conversion of dihydroxyacetone (DHA) and product yields over different zeolites in ethanol^a

Entry	Zeolite	Bulk Si/Al	Al _{Framework} ^b (%)	Y _{lactate} (%)	Y _{acetal} (%)	S _{lactate} (%)
1	Na-Y	2.6	100	0	1	0
2	NH ₄ -Y 450	2.7	89	18	74	20
3	USY CBV 500	2.6	56	54	41	57
4	USY CBV 600	2.6	27	59	18	77
5	USY CBV 712	5.8	35	56	23	71
6	USY CBV 720	15	68	35	41	46
7	USY CBV 760	27	99	3	34	8
8	USY CBV 780	40	99	9	20	32
9	H-ZSM-5	40	95	4	6	37
10	H-Beta	9.9	76	31	27	54
11	(Blank) ^c	—	—	1	0	n.a.

^a Conditions: 5 ml ethanol solution containing dihydroxyacetone (0.4 M) and 0.2 g of zeolite, 363 K (6 h), batch reactor. Y_{lactate} = mol% yield of ethyl lactate. Y_{acetal} = mol% yield of diethyl acetal of pyruvic aldehyde. S_{lactate} = ethyl lactate selectivity in mol%, calculated on the basis of lactate and acetal yields (S_{lactate} = Y_{lactate} / (Y_{lactate} + Y_{acetal})). ^b % of framework Al as measured by ²⁹Si NMR in the case of FAU⁴⁰ or by ²⁷Al NMR in the case of H-ZSM-5 and H-Beta.⁴⁶ ^c At 383 K (4 h).

**Scheme 1** Conversion of trioses over acidic zeolites. LA = Lewis Acid; BA = Brønsted Acid.

ethanol molecule or towards the acetal by addition of ethanol (Scheme 1).

While all tested zeolites in their H⁺-form are active in the conversion of dihydroxyacetone, the product yields and distributions vary considerably with the catalyst (Table 1). The fraction of dihydroxyacetone converted is inversely proportional to the Si/Al ratio of the zeolite, indicating that aluminium sites are the catalytic active centres.

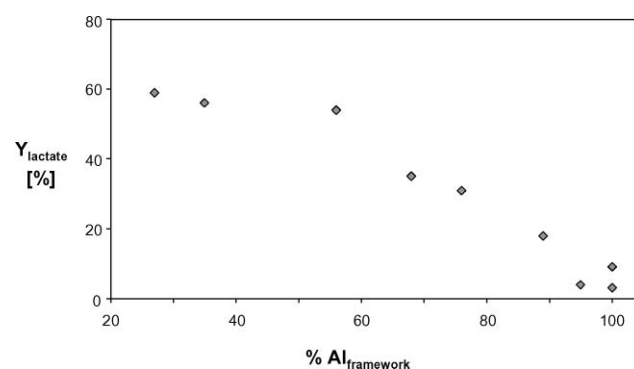
Zeolite NH₄-Y 450 exhibits very high conversion of dihydroxyacetone, though with a very low selectivity towards the desired ethyl lactate (Table 1, entry 2). USY CBV 500 combines a similarly high conversion with high yield of both the ethyl lactate and the acetal (Table 1, entry 3). High conversions are obtained with zeolites USY CBV 600, CBV 712 and CBV 720 (Table 1, entries 4–6), while the conversion with USY CBV 760 and CBV 780 are markedly lower (Table 1, entries 7 and 8). When no zeolite was present, or Na-Y was used, negligible dihydroxyacetone conversion and alkyl lactate formation was observed (Table 1, entries 1 and 11).

The product distribution varies along the series of USY zeolites: high selectivities towards ethyl lactate are observed with zeolites with low values of Si/Al ratio and with a large population of extra-framework Al species (CBV 600, CBV 712),

while the dialkyl acetal becomes the major product with zeolites with high Si/Al. USY CBV 600, with a 59% yield and 77% selectivity towards ethyl lactate at 363 K, exhibits results similar to the best tin halide catalysts,³⁵ with the advantage of being a commercially available, structured heterogeneous catalyst.

These results evidence that the different product distributions obtained when traversing the USY zeolite series is determined by the nature of their aluminium sites. The USY zeolites employed here are prepared from zeolite NH₄-Y by different degrees of dealumination generated by steaming and acid leaching treatments, which influence the type and amount of their aluminium sites.⁴⁴ Despite many characterisation studies, the nature of the different aluminium sites in zeolites USY is still a matter of debate and each of them can play a different catalytic role in different reactions.^{45–49} While framework Al species are unequivocally associated with Brønsted acid sites, Al in extra-framework positions may occur in different forms (Al³⁺, Al(OH)²⁺, Al(OH)₂⁺, Al(OH)₃, AlO(OH) and Al₂O₃) displaying Lewis acid properties. In the series from CBV 600 to CBV 780, by increasing the Si/Al ratio, the number of Brønsted acid sites decreases, while their strength increases (up to Si/Al ~ 5.8) and the amount of extra-framework aluminium is reduced.^{50,51}

In order to correlate the catalytic results in the conversion of trioses with the type of Al species in the zeolite catalysts, the fraction of the extra-framework aluminium was determined using ²⁹Si MAS NMR and ²⁷Al MAS NMR. A clear trend can be observed in the plot of ethyl lactate yield against the fraction of framework Al in the tested zeolites (Fig. 1): the yield of lactate shows a proportionality to the amount of extra-framework Al species. Therefore, we conclude that the formation of the desired ethyl lactate product is catalysed by the presence of Lewis acid sites in the form of extra-framework aluminium species. On the other hand, it is known that the reaction of aldehydes with alcohols generating acetals is catalysed by Brønsted acids.^{52,53} Therefore, we infer that the formation of the diethyl acetal of pyruvic aldehyde is due to Brønsted acid sites located in the framework, the acetal yield being proportional to the number and strength of these acid sites.

**Fig. 1** Ethyl lactate yield over different zeolites as a function of the fraction of aluminium located in the framework of the zeolites employed in this work. The fraction of framework aluminium was determined using ²⁹Si NMR for the FAU zeolites (NH₄-Y 450 and USY) and was based on ²⁷Al NMR data for H-Beta and H-ZSM-5.⁴⁶

Thus, returning to Scheme 1, the formation of pyruvic aldehyde, *i.e.* the first step in the reaction pathway, is catalysed by

Brønsted acids. The formed pyruvic aldehyde then further reacts either to the desired ethyl lactate on the Lewis acid sites (extra-framework Al) or into the ethyl acetal on the strong Brønsted acid sites. In other words, the reaction selectivity is determined by the ratio of Lewis vs. strong Brønsted acids.

The above differentiation in catalytic active sites provides a consistent explanation of the results obtained with the various zeolites. This is clearly exemplified by the comparison of the results obtained with $\text{NH}_4\text{-Y}$ 450, USY CBV 500 and USY CBV 600, which present the same type of framework [FAU] and have analogous bulk Si/Al ratio, but have different distribution of type of aluminium sites (Table 1). USY CBV 500 and USY CBV 600 are both generated by steaming of $\text{NH}_4\text{-Y}$ zeolite, the degree of the treatment and, therefore, the ratio of extra-framework Al species vs. framework Al being higher for USY CBV 600 (Table 1). The increasing selectivity towards ethyl lactate passing from zeolite $\text{NH}_4\text{-Y}$ 450 to USY CBV 500 and USY CBV 600 thus evidences how the removal of aluminium from the framework of zeolite Y upon steaming generates catalytic species that favour the formation of ethyl lactate while decreasing the number of Brønsted acid sites that catalyse the formation of the acetal product (Table 1).

The catalytic behaviour of the H-ZSM-5 and H-Beta follows the description of the role of the different aluminium sites discussed above. Poor conversion and low selectivity towards ethyl lactate were obtained with H-ZSM-5 (Table 1, entry 9), in agreement with its high Si/Al ratio (low conversion) and high fraction of framework Al (low selectivity). H-Beta displays intermediate conversion and selectivity (Table 1, entry 10) in line with the Si/Al ratio and the presence of extra-framework species in this type of zeolite.⁴⁶

The four catalysts that showed the highest yields of ethyl lactate, USY CBV 500, 600, 712 and 720, were studied in detail by following the kinetics of the formation of the two products during the reaction (Fig. 2). Ethyl lactate and the diethyl acetal of pyruvic aldehyde show rather different kinetic profiles: while the yield of lactate is still increasing after 6 h of reaction, the yield of acetal tends to reach a plateau after 3 h. This implies that the ratio between lactate and acetal increases as the reaction proceeds: with all the four catalysts the selectivity towards the lactate displays an increase with increasing degree of conversion of dihydroxyacetone (Fig. 3). This indicates that, if there are sites suitable for catalysing its formation, ethyl lactate is the thermodynamically favoured product of the studied reaction. The argument is supported by the fact that the acetal formation under acid catalysis is reversible.⁵² Therefore, the formed diethyl acetal of pyruvic aldehyde can be reconverted to pyruvic aldehyde and, from there, yield the desired lactate product. In this sense, the acetal can be considered as a reservoir of the reaction intermediate pyruvic aldehyde (Scheme 1). This observation led us to propose that higher lactate yields would be obtained at higher temperature. Indeed, when the reaction is carried at 383 K and 393 K higher lactate yields are observed (Table 2, entries 12–17). At the highest temperature, more than 90% of the starting dihydroxyacetone is converted into the desired ethyl lactate (entry 17). This value is the highest yield achieved for the ethyl lactate yield in this work, and rivals the best soluble-tin chemistry.³⁵ The use of different alcohols as solvent does not influence significantly the degree of conversion of

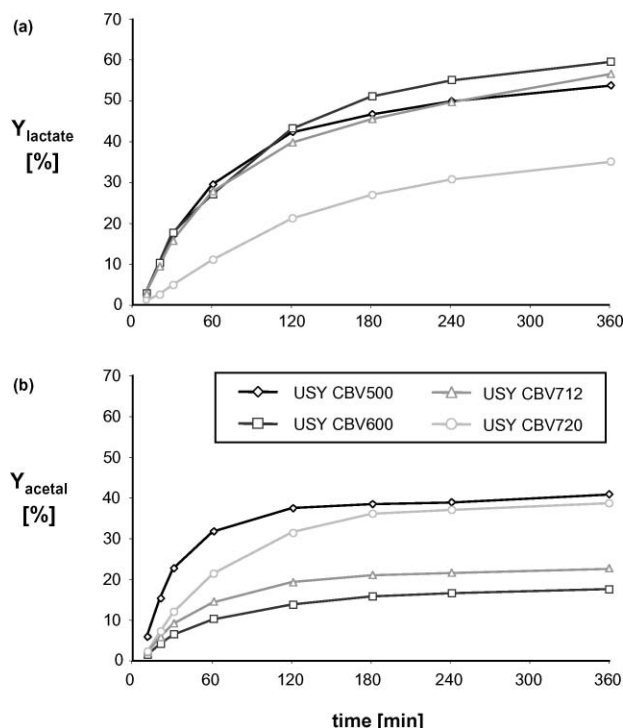


Fig. 2 Conversion of dihydroxyacetone catalysed by different USY zeolites at 363 K in ethanol: yield of ethyl lactate (a) and yield of diethyl acetal of pyruvic aldehyde (b) as a function of reaction time.

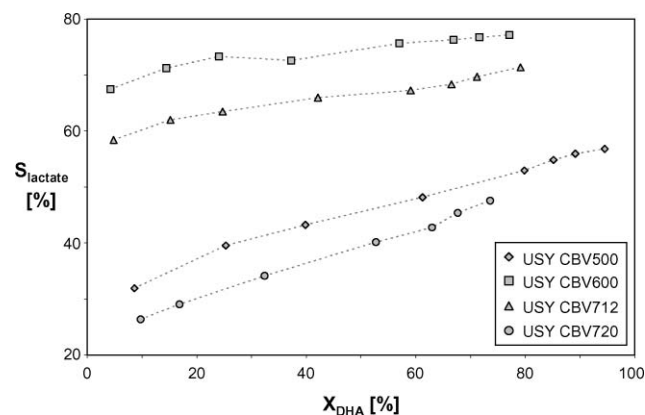


Fig. 3 Selectivity towards ethyl lactate (S_{lactate}) as a function of the conversion of dihydroxyacetone ($X_{\text{DHA}} = Y_{\text{lactate}} + Y_{\text{acetal}}$) over zeolites USY CBV 500, 600, 712 and 720 at 363 K in ethanol.

dihydroxyacetone, while the selectivity towards the alkyl lactate is lower with linear alcohols with longer chains.

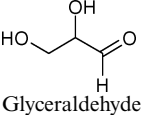
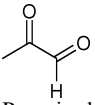
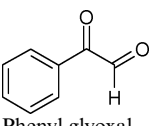
Further tests showed that USY CBV 600 also catalyses the selective conversion of glyceraldehyde to the corresponding alkyl lactate (Table 3, entry 18). This observation is very interesting in view of our challenge to convert glycerol directly to alkyl lactates. As both trioses, *viz.* glyceraldehyde and dihydroxyacetone, can be transformed into the desired lactate product, the difficult regioselective oxidation of either the primary or the secondary alcohol function of glycerol is not further required.

Table 2 Conversion of dihydroxyacetone and product selectivity over zeolite USY CBV 600 in various alcohols^a

Entry	ROH	Y_{lactate} (%)	Y_{acetal} (%)	S_{lactate} (%)
12	MeOH	82	1 (7) ^b	91
13	EtOH	81	18	81
14	<i>n</i> -PrOH	69	29	69
15	<i>i</i> -PrOH	83	16	83
16	<i>n</i> -BuOH	71	28	71
17 ^c	EtOH	91	9	91

^a Conditions: 5 ml of an alcohol solution containing dihydroxyacetone (0.4 M) and 0.2 g of zeolite USY CBV 600, 383 K (4 h). ^b Yield of tetramethyl diacetal of pyruvic aldehyde. ^c At 393 K (3 h).

Table 3 Conversion of glyceraldehyde, pyruvic aldehyde and phenyl glyoxal and product selectivity over zeolite USY CBV 600 in ethanol^a

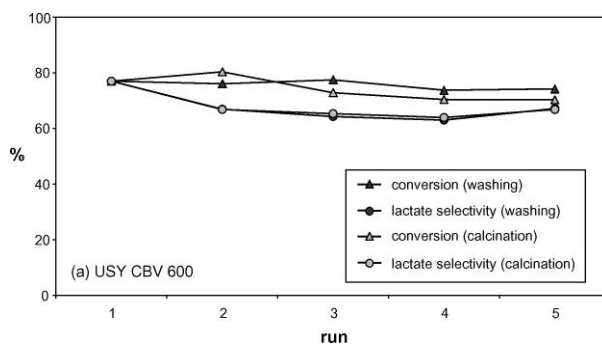
Entry	T (K)	Reaction time (h)	Substrate	Y_{ester} ^c (%)	S_{ester} ^c (%)
18	383	4	 Glyceraldehyde	76	83
19	363	1.5	 Pyruvic aldehyde ^b	33	89
20	363	2.5	 Phenyl glyoxal	95	97

^a Conditions: 5 ml of an ethanol solution containing the chosen substrate (0.4 M) and 0.2 g of zeolite USY CBV 600. ^b As a 40 wt% solution in water. ^c Formation of ethyl lactate from glyceraldehyde and pyruvic aldehyde; formation of ethyl mandelate from phenyl glyoxal.

3.2 Recycling of the catalysts

In view of a possible industrial application, it is important to evaluate the reusability of the catalysts: for this purpose, commercial zeolite USY CBV 600, the best catalyst identified in this work, was tested in several catalytic cycles at 363 K in ethanol (6 h). Before each successive catalytic test, the zeolites were recovered either by washing with ethanol and drying at 373 K or by washing with ethanol followed by calcination in air at 723 K. The calcination step guarantees a complete removal of organics present on the catalyst but might as well induce undesired variations in the zeolite structure.

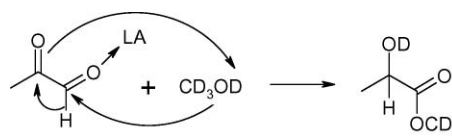
USY CBV 600 can be recycled without significant loss of activity both by washing and by calcination (Fig. 4), proving the stability of this material under the employed reaction and recycling conditions. However, it should be noted that the selectivity towards ethyl lactate slightly decreases from the first to the second run and then remains constant in the successive cycles. Since both recycling procedures prove equally efficient, for energetic reasons the washing procedure might be the most favourable for future applications.

**Fig. 4** Recycling of zeolite USY CBV 600 as catalyst for the conversion of dihydroxyacetone, using either a washing or a calcination procedure.

3.3 Reaction mechanism

The proposed mechanism for the reaction involves the formation of pyruvic aldehyde as a reaction intermediate by dehydration and rearrangement of dihydroxyacetone (Scheme 1). Pyruvic aldehyde further rearranges with incorporation of a solvent alcohol molecule to yield the corresponding alkyl lactate. This last step bears a clear resemblance to the conversion of pyruvic aldehyde to D-lactate catalysed by the glyoxalase system.⁵⁴ Traces of pyruvic aldehyde are indeed detected in the reaction mixture and the mechanism is further supported by the presence of the diethyl acetal product of pyruvic aldehyde, which is formed by addition of the alcohol to the aldehyde functional group. In addition, the reaction of pyruvic aldehyde (40 wt% in H₂O) in ethanol using USY CBV 600 in similar reaction conditions selectively produces ethyl lactate (Table 3, entry 19). Similarly, phenyl glyoxal is converted selectively into the corresponding ethyl mandelate (Table 3, entry 20).

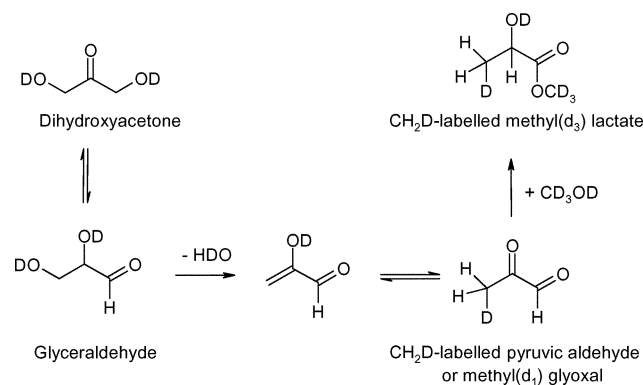
Isotope labelling experiments using CD₃OD showed no incorporation of deuterium into the hydrocarbon backbone of methyl lactate when obtained from pyruvic aldehyde (step 2 top reaction, Scheme 1). This is clear from the spectral data (MS and ¹³C NMR data, summarized in ref. 55) of the formed methyl lactate product: there is no triplet signal observed in ¹³C NMR for the –CH₃ group, while the typical fragment bearing the –CH₃ group is not deuterated. As no deuterium incorporation is observed in the lactate product, the mechanism can be regarded as a formal intramolecular Cannizzaro reaction of the α -keto aldehyde, *viz.* pyruvic aldehyde. The mechanism is very similar to that of the glyoxalase system and their reported Lewis-acid catalysed biomimetic reactions.^{31,32,54,56} (Scheme 2).

**Scheme 2** Conversion of pyruvic aldehyde to methyl lactate in CD₃OD. Spectral data of the product in ref. 55.

Usually, the reaction in Scheme 2 has been reported in presence of a base catalyst,⁵⁷ *viz.* NaOH, but also a Lewis acid is capable of catalysing the reaction by activating the carbonyl function of the aldehyde, allowing the fast attack of a methoxide moiety to the C=O carbonyl function, followed by an intramolecular rearrangement with a shift of the hydride. It is

known that when such an internal Cannizzaro reaction is carried out in deuterated solvents, no deuteration of the α position to the alcohol function occurs. This is indeed observed for the reaction of Scheme 2 in presence of the USY zeolite catalyst.

When the triose dihydroxyacetone or glyceraldehyde instead of pyruvic aldehyde was used as substrate in CD_3OD , it was converted to methyl lactate with one deuterium atom incorporated into the methyl group of the lactate product (the MS and ^{13}C NMR data are collected in ref. 58). Since in the second step of the mechanism deuterium is not substituting hydrogen in the hydrocarbon backbone (see Scheme 2), deuterium incorporation likely occurs after the dehydration step, catalysed by the Brønsted acid sites, *via* tautomerisation of the enol intermediate into CH_2D -labelled methyl(d_3) lactate (Scheme 3).



Scheme 3 Conversion of trioses to methyl lactate in CD_3OD with incorporation of deuterium during the dehydration/tautomerization step. A selection of the spectral data of the lactate product is summarized in ref. 58.

On the basis of the above-mentioned mechanism and of the catalytic results, a complete description of the reactions occurring is achieved. The dehydration of trioses leading to the pyruvic aldehyde intermediate is catalysed by Brønsted acid sites, which are present in all the tested materials with the exception of the inactive Na-Y. Mild Brønsted acidity is sufficient to catalyse this step, as indicated by the formation of pyruvic aldehyde as the sole product when acetic acid is used as a reference weak acid catalyst. From pyruvic aldehyde, the reaction proceeds to the dialkyl acetal in the presence of strong zeolitic Brønsted acidity, while the formation of alkyl lactate from pyruvic aldehyde is catalysed by extra-framework aluminium sites that act as Lewis acid sites, in agreement with previous work from other groups on homogeneous systems.^{31–34,56} This explains why USY CBV 600, presenting a high amount of extra-framework with the lowest fraction of framework aluminium species (Table 1), displays good activity combined with the highest lactate selectivity. It is thus concluded that a material with a suitable combination of Lewis acid and Brønsted acid sites, like in USY CBV 600, is required to efficiently and selectively catalyse the dual-site mechanism for the conversion of trioses to alkyl lactates.

4. Conclusions

Zeolites with different number and type of acid sites were studied as catalysts for the liquid-phase conversion of dihydroxyacetone or glyceraldehyde to alkyl lactate. Zeolite USY

CBV 600 displayed the best catalytic results, achieving similar lactate yields as the best homogeneous catalysts known for this reaction, with the advantage of being a commercially available heterogeneous catalyst that can be reused in various successive cycles without loss of activity. Besides the reusability, the presented heterogeneous catalyst is free of any heavy metals like Sn or Cr, which is key factor on the way to a sustainable process.

A subtle combination of acid sites, *viz.* mild Brønsted acidity and Lewis acidity in the form of extra-framework aluminium species, catalyses the formation of alkyl lactates, while strong Brønsted acidity, as typically present in zeolites with high Si/Al ratio, in sulfonated silica⁵⁹ or carbon,⁶⁰ in acid resins⁵³ and in soluble strong acids, *viz.* H_2SO_4 ,⁵² is detrimental because it catalyses the formation of the diethyl acetal of pyruvic aldehyde side product, thus reducing the selectivity towards the desired lactate product.

The method reported here offers a valid alternative route to the slow and complex fermentation process presently used to produce lactic acid. The next step will involve the extension of the catalytic process to the direct conversion of glycerol to lactic acid and derivatives, with the aim of finding a more suitable process compared with the recently reported hydrothermal reaction requiring stoichiometric amounts of NaOH and high temperatures⁶¹ or with the liquid-phase reaction *via* oxidative dehydrogenation catalysed by noble metals supported on carbon, which has moderate selectivity and also requires relatively high temperatures and high concentrations of a strong base.^{62,63}

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