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Catalysis Today 117 (2006) 265–270

CATALYSIS TODAY

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Clean process for propanal oxidation to lactic acid

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Abstract

There is growing interest to use lactic acid in the production of biodegradable plastics and solvents. A clean process has been developed for oxidation of propanal to lactic acid using heterogeneous catalysts. The process involves five steps. The first step is the acetalization of propanal with alcohol over zeolite, followed in step two by the conversion of the acetal to vinyl ether. In step three, the vinyl ether is oxidized to the hydroxyl acetal using hydrogen peroxide or organic peroxide over Ti-molecular sieves. Hydrolysis of the hydroxyl acetals over zeolite (step four) resulted in two products: hydroxypropanal as a major product and hydroxyacetone. In step five the hydroxypropanal is oxidized to lactic acid with air using Pt/C. The overall yield is above 80% to lactic acid. Only hydroxyacetone was formed as a by-product, which is a high value chemical.

Keywords: Propanal; Lactic acid; Hydroxypropanal; Oxidation; Ti-molecular sieves; Zeolite

1. Introduction

Lactic acid has become an important compound in the growing field of biodegradable plastic, solvents, metal pickling and food additives [1]. Currently, most lactic acid is made by fermentation. A minor quantity is produced synthetically, involving acetaldehyde and hydrogen cyanide (Reactions 1 and 2). Both processes are not without drawbacks. The synthetic route employs highly toxic and expensive feeds stock, acetaldehyde and hydrogen cyanide [2]. The fermentation route is a complex and sensitive process, especially the recovery steps. It has a limited production capacity and involves regional supply of biomass. It takes 2–8 days to complete the reaction. The pH and temperature must be carefully monitored. The yields to lactic acid are 85–95% based on fermentable sugars [3].

Many routes for producing lactic acid were investigated but never commercialized [4]. The most promising route is the Monsanto process [5]. Monsanto developed a process for preparing lactic acid by the hydrocarboxylation of vinyl acetate catalyzed by a phosphine-stabilized palladium complex (Reaction 3). The yield to the α-acetoxypropionic acid is around 70%. This was achieved at 30 bars and at 150 °C.

An alternative and completely new synthesis route is therefore desirable. This publication describes a generic route to produce α-hydroxy acids and uses lactic acid as an example. The process involves heterogeneous catalysis in each step, and produces minor quantities of useful side-products, which are two important aspects of the chemistry.

2. Results

2.1. Direct oxidation of propanal to lactic acid

Direct oxidation of propanal to lactic acid is extremely difficult. Aldehydes undergo facile autoxidation to acid, even at ambient temperatures. α H–C–C=O activation via autoxidation results in C–C bond cleavage and generally, the products are CO_2 and water. There are two systems which are known for inserting oxygen to α H–C–C=O position. Molybdenum peroxide MoO_5PyHMA reacts with a variety of ketones and esters at temperatures of −70 to −40 °C [6]. Selenium dioxide is a reagent for the oxidation of ketones and aldehydes to 1,2-dicarbonyl compounds [7]. These reactions involve the use of stoichiometric amounts of reagent. In the case of selenium, colloidal selenium may be used and organoselenium compounds are formed as by-products. Indeed, our data

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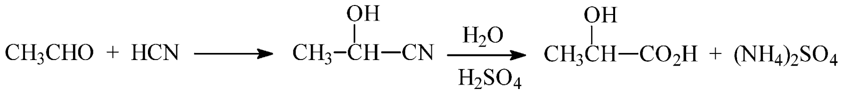
doi:10.1016/j.cattod.2006.05.060



$$CH_3CHO + HCN \longrightarrow CH_3-\overset{OH}{\overset{|}{C}}H-CN \xrightarrow[H_2SO_4]{H_2O} CH_3\overset{OH}{\overset{|}{C}}H-CO_2H + (NH_4)_2SO_4$$

Plate 1. Synthetic route for lactic acid production.

$$\textbf{Glucose} \longrightarrow \textbf{2 Lactic acid + 2ATP}$$

Plate 2. Fermentation route for lactic acid production.

on propanal oxidation using SeO_2 show that α-hydroxyl propanal and lactic acid were formed. However, the selectivity was very poor. To achieve the objective of propanal oxidation to lactic acid, an indirect route comprising five steps was studied.

2.2. *Acetal formation in the presence of molecular sieves*

The reaction of propionaldehyde and methanol leads to the acetal via the hemiacetal intermediate (Reaction 4) [8]. The hemiacetal formation is catalyzed by both bases and acids. In contrast to hemiacetal formation, acetal formation is catalyzed *only* by acids. The addition of the first methanol to the propanal is the rate determining step.

Possible side reactions are the aldol and Tischenko condensation [9]. Dehydration of methanol to dimethyl ether can also occur in gas phase. A continuous gas phase and batch liquid phase were used for investigating the following parameters: temperature, space velocity, different alcohols, different molar ratio alcohol/propanal. Zeolite beta was identified as the best catalyst in batch screening runs. High conversion (>95%) and selectivity (100%) were achieved at the following conditions: temperature 80 °C, methanol:propanal molar ratio 16. By substituting the methanol with ethylene glycol, similar conversion and selectivity were achieved at much lower Ethylene glycol:propanal ratio 1:2 (Fig. 1). The high conversion is presumably caused by the two functional groups and the formation of two layers.

2.3. *1-Methoxypropene (VE) formation*

The vinyl ether (VE) can be formed either by thermal decomposition of the acetal (Reaction 5) or by addition of acid catalyst (Reaction 6). Hoelderich and Goets [10] studied this reaction over zeolites such as ZSM-5, mordenite and SAPO-5 and found that mildly acidic or basic zeolites are more selective than strongly acidic zeolites. In addition SZE-Ming Yang and Wang [11] reported that high activities and low catalyst deactivation are observed over weakly acidic, medium and small pore aluminophosphate molecular sieves. Strong acid sites and large pore sizes facilitate coke formation and accelerate the deactivation of the catalyst. High conversion (97%) and high selectivity (98%) for the vinyl ether were obtained at 300 °C.

For our case vinyl ether was made by thermal decomposition. At 300 °C, 60% conversion and 100% selectivity were achieved. Higher conversion (90%) at the same selectivity was achieved at higher temperature (400 °C).

2.4. *1-Methoxypropene epoxidation*

Many reports describe the epoxidation of olefins using peracids or a combination of various oxidants (e.g. hydrogen peroxide or hydroperoxide) and metal catalysts [12–14]. Four commercial epoxidation technologies are available:

- The Arco process using *tert*-butyl hydroperoxide (TBHP) and Mo catalyst.
- The Shell process using ethyl benzene hydroperoxide (EBHP) and TiO_2/SiO_2.
- The Sumitomo process using cumene hydroperoxide (CHP) and Ti–zeolite.
- The BASF process using hydrogen peroxide and TS-1.

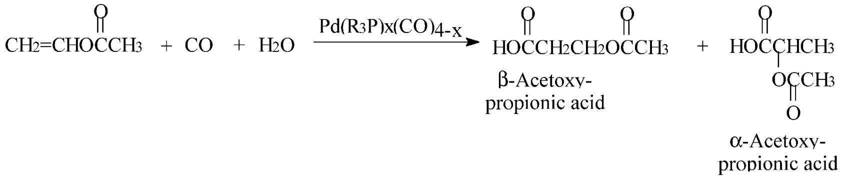


Plate 3. Hydrocarboxylation of vinyl acetate catalyzed by a phosphine-stabilized palladium complex.

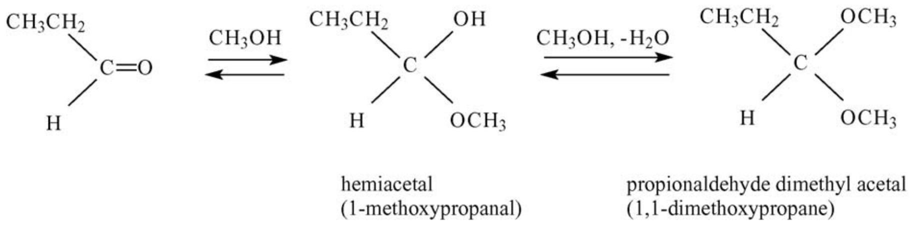


Plate 4. Propanal acetalization with methanol.

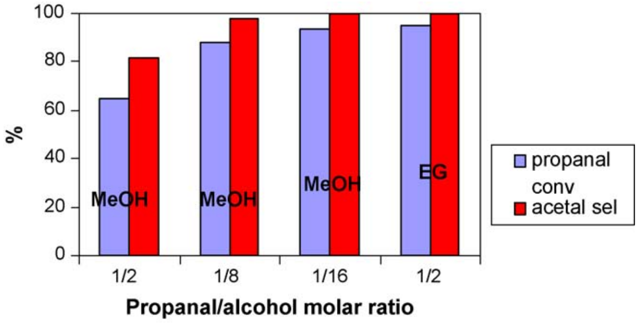
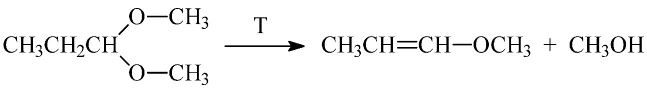
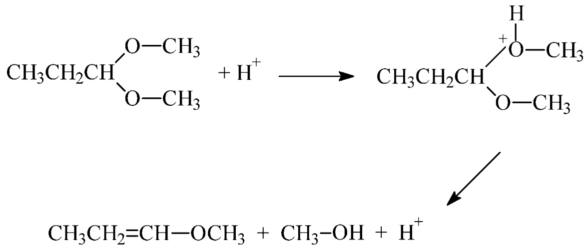


Fig. 1. Acetalization of propanal with alcohols over zeolite beta.



$$\mathrm{CH_3CH_2CH}\begin{matrix}\mathrm{O{-}CH_3}\\ \mathrm{O{-}CH_3}\end{matrix} \xrightarrow{T} \mathrm{CH_3CH{=}CH{-}OCH_3} + \mathrm{CH_3OH}$$

Plate 5. Acetal thermal decomposition to vinyl ether.



$$\mathrm{CH_3CH_2CH}\begin{matrix}\mathrm{O{-}CH_3}\\ \mathrm{O{-}CH_3}\end{matrix} + \mathrm{H^+} \longrightarrow \mathrm{CH_3CH_2CH}\begin{matrix}\overset{\mathrm{H}}{\overset{|}{\mathrm{O}^{+}}}\mathrm{{-}CH_3}\\ \mathrm{O{-}CH_3}\end{matrix} \longrightarrow \mathrm{CH_3CH_2{=}CH{-}OCH_3} + \mathrm{CH_3{-}OH} + \mathrm{H^+}$$

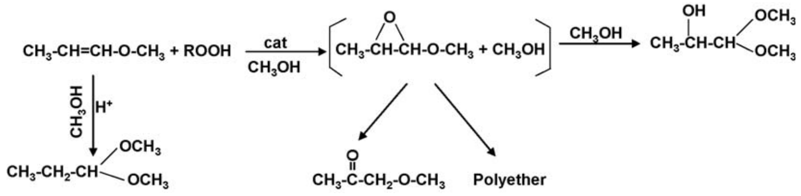
Plate 6. Catalytic decomposition of acetal to vinyl ether.

No use of these systems has yet been reported in the epoxidation of vinyl ether.

Frimer [15] describes the epoxidation of enol ether in alcoholic solvent. The oxidizing agents used are *m*-chloroperbenzoic acid or MoO_5HMPA. There remains a need, however for a vinyl ether epoxidation method in which the oxidizing agent is more readily available or in which its conversion rate is high. We have now found that these catalytic systems (homogeneous or heterogeneous) in combination with hydroperoxide (hydrogen peroxide or alkyl hydroperoxide) exhibit remarkable reactivity and selectivity toward vinyl ether oxidation to α-hydroxyacetal. Epoxyether is presumed to be the intermediate, but it could not be isolated at the reaction conditions.

Epoxyether is reactive to alcohols, water and acids. It is very labile to acid catalyzed rearrangement to α-methoxyacetone; polymerizes to polyether; and hydrolyses in the presence of stoichiometric amounts of water to α-hydroxypropanal. The corresponding cleavage product is formed in the presence of hydrophobic solvent (Scheme 1). All of the undesired reactions can be circumvented by converting the epoxyether to α-hydroxyacetal. Several titanium molecular sieves (TS-1, Ti-β and TiMCM-41) were prepared in different forms (H^+, Li^+) and tested in oxidation of vinyl ether with hydrogen peroxide or *t*-butyl hydroperoxide. The catalytic activity of $Mo(CO)_6$ was also evaluated under the same conditions.

By using methanol as a solvent, in addition to the hydroxyacetal, the corresponding acetal was formed at 50–95% selectivity. Since the formation of the acetal is catalyzed by acid sites, an obvious way to circumvent this is to neutralize these sites by alkali metal exchange. In the case of Ti-β, high selectivity to acetal is obtained, caused by protonation of the vinyl ether at the acidic aluminum sites. Pre-treatment of the titanium molecular sieve catalysts with aqueous solution of lithium acetate [16] prior to their use results in a dramatic increase in the hydroxyacetal selectivity, whilst maintaining the activity. So far, the highest selectivity (88%) to hydroxyacetal was observed when the acid site of TS-1 was neutralised by Li or by using stoichiometric amounts of methanol. High selectivity (82%) can be also obtained by using homogeneous Mo catalyst



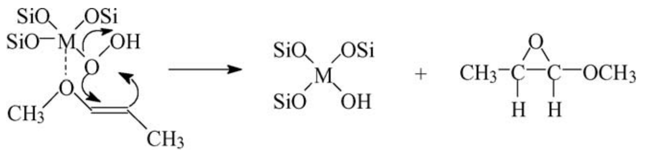
Scheme 1.

Table 1
Epoxidation of vinyl ether in the presence of different hydroperoxide over Ti-molecular sieves

Catalyst	Oxidant (mmol)	Temperature (°C)	Oxidant conversion (mol%)	Oxidant efficiency (mol%)	Sub. conversion (mol%)	HO-acetal selectivity (mol%)	Acetal selectivity (mol%)
TS-1	H_2O_2 (5)	40	98	100	46	54	46
LiTS-1	H_2O_2 (5)	40	100	100	28.2	88	12
H-Ti-β	H_2O_2 (5)	40	15	98	100	4	96
Li-Ti-β	H_2O_2 (5)	40	100	100	75	34	66
Ti-MCM-41*	TBHP (14)	100	99	56	99	56	38
Li-Ti-MCM-41	H_2O_2 (5)	40	100	100	83	30	70

Reaction conditions: 20 mmol substrate, 5 mmol oxidant, 5 g methanol, 0.25 g catalyst, time 2 h.

* TBA was used as a solvent.



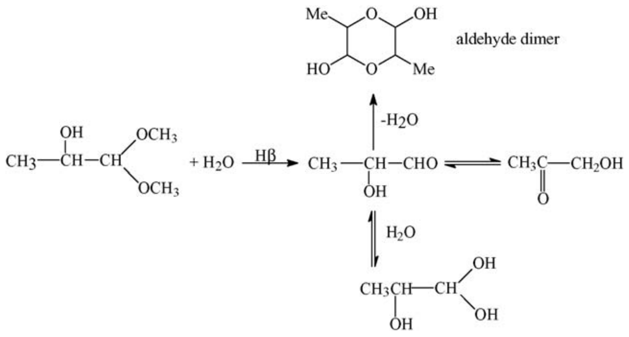
Scheme 2. Mechanism for the interaction of vinyl ether with the catalytic sites during the epoxidation reaction.

and TBHP as oxidant. Table 1 shows the results of 1-methoxypropene oxidation with hydroperoxide.

Clerici et al. [17] reported that the epoxidation rate of olefins is much dependent on the nature of the olefins i.e. steric configuration. His kinetic study showed that cis olefins are epoxidized 16 orders of magnitude faster than trans ones. However, our results show that *trans*-vinyl ether is much more reactive than *cis*-isomer in both epoxidation and addition reactions. This different behavior leads to a significant finding with respect to the mechanism of epoxidation of vinyl ether. Clearly, the presence of the methoxy group at the site of the double bond is strongly rate enhancing. The epoxidation of vinyl ether involves an interaction of the catalytic site with the methoxy function prior to a rate determining delivery of the peroxy oxygen to the olefins site as shown in Scheme 2.

2.5. Hydrolysis of α-hydroxyacetal to α-hydroxypropanal over molecular sieves

The selective hydrolysis of α-hydroxyacetal is a tough challenge for a number of reasons. The α-hydroxypropanal is converted to several isomers as shown in Scheme 3. In aqueous solution, three reactions can occur with the free aldehyde.



Scheme 3.

(1) Free aldehyde is in equilibrium with the monomeric hydrated aldehyde.
(2) An equilibrium exist between α-hydroxyaldehyde and hydroxy acetone under acidic or basic conditions via the ene-diol intermediate. Therefore, α-hydroxyacetal can serve as precursor for the preparation of α-hydroxyketone. Thus, this work represents a convenient synthesis of α-hydroxy acetone from the corresponding propanal.
(3) In a non-aqueous environment α-hydroxypropanal exists predominantly as the cyclic hemiacetal. Our results show that the equilibrium mixture contains about 5% free aldehyde and the remainder is the dimer.

The reaction rate and the selectivity were found to be strongly influenced by several parameters. The major factors we investigated are

- Water/substrate molar ratio: 5/1, 10/1, 20/1 and 50/1.
- Temperature: 20, 50, 70 and 90 °C.
- Catalyst concentration: 1, 5, 10 and 20 wt.%.
- Comparison of H-ZSM-5 and H-beta activity and selectivity.

H-beta was the best catalyst in terms of both activity and selectivity for the hydrolysis of hydroxyacetal. The reaction profile of the hydroxyacetal hydrolysis catalyzed by H-beta or H-ZSM-5 at 5 wt.%, 90 °C, and water:substrate ratio 20:1 is shown in Fig. 2. High selectivity to hydroxypropanal can be

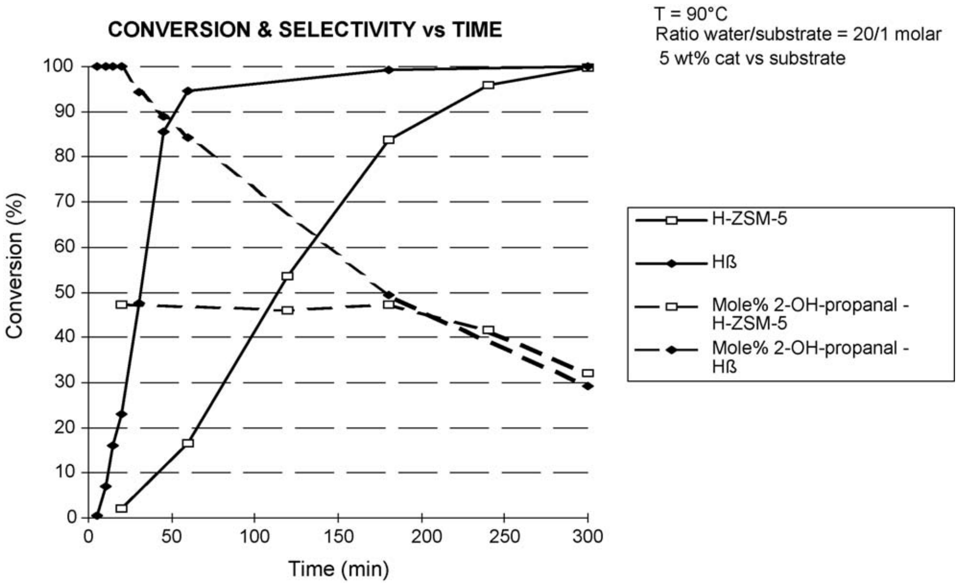


Fig. 2. Hydroxyacetal hydrolysis over zeolite beta and ZSM-5.

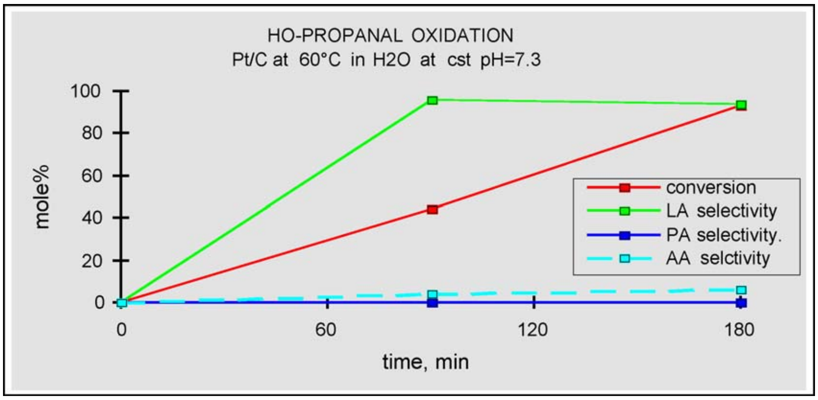


Fig. 3. Hydroxy propanal oxidation with air. Reaction conditions: 1.2 g H.P., 0.56 g H_2O, 0.1 g Pt/C (5%).

achieved at 95% conversion. We observed that at longer reaction time the selectivity is dramatically decreased to 30%, because of the rearrangement of 2-hydroxy propanal to hydroxyacetone.

2.6. *Oxidation of α-hydroxypropanal to lactic acid with air over Pt on carbon*

Oxidation of alcohols or hydrated aldehydes over noble metal catalysts can be described as an oxidative dehydrogenation reaction mechanism. Important work on the oxidation of sugars and other substrates over noble metal catalyst is reviewed in Ref. [18]. Pd catalyst shows a lower selectivity versus Pt catalysts, for the oxidation of substrates containing aldehyde and alcohol functions. This can be understood by the higher oxygen tolerance of Pt. The reactions are usually performed in a neutral or slightly alkaline medium under atmospheric pressure and at temperatures below 60 °C in order to minimize the various and consecutive reactions. Modification of Pt and Pd catalyst with Bi, Pb and several other metals has been suggested in order to suppress catalyst deactivation and improve selectivity [19]. The primary reason for catalyst deactivation is related to the strongly bonded carboxylic acid on metal surfaces in the form of carboxylates. It is clear that desorption of acids from the metal surface must be promoted. The simplest way to solve catalyst deactivation by the desorption of the acids from the surface is by carrying out the oxidation reactions at higher pH values so that the adsorption species tend to leave the surface to form acid salts in the liquid phase. Our preliminary study on oxidation of hydroxypropanal shows that, depending upon the reaction conditions and upon the nature of the catalyst, it is possible to orientate the selectivity of hydroxypropanal to lactic acid. Oxidation of hydroxypropanal under acidic conditions without neutralization of the formed acid shows high selectivity to lactic acid (93%). However, the conversion is low (45%). An alternative approach to increasing the oxidation rate is the use of alkaline solution. By adding a catalytic amount of KOH (1 mol%) better conversion (72%) could be achieved at the same selectivity (92%). At high pH 9, the selectivity to lactic acid was decreased dramatically due to the rearrangement to hydroxyacetone and further oxidation of the latter to pyruvic acid.

As shown in Fig. 3, high conversion and selectivity to lactic acid were achieved by controlling the pH at 7.3. An alternative approach to increasing the oxidation rate without the use of neutralizing agent is to oxidize the lactaldehyde dimer to lactic acid dimer. Proof-of-principle for demonstrating the oxidation of lactaldehyde dimer to lactic acid dimer, under anhydrous conditions, shows that indeed this can be done without the need for addition of base.

3. Conclusion

This preliminary study shows that, by controlling the reaction conditions and the nature of the catalyst, it is possible to direct the selectivity of propanal oxidation towards lactic acid. We have shown that all steps are feasible at high conversion and selectivity using heterogeneous catalysts. By modifying the synthesis conditions it is possible to obtain other main products. The intermediate α-hydroxypropanal can be isomerized to hydroxyacetone. Alternatively, it is possible to convert the α-hydroxyacetal to methoxyacetone. Both the hydroxyacetone and methoxyacetone contain useful functional groups, which may render them advantageous for specific applications, or as building blocks for other chemicals. Clearly, a true clean process is presented in which a less toxic chemical (lactic acid) is produced in an environmentally friendly way without emission of harmful by-products.

Acknowledgements

The authors would like to acknowledge Dr. Georges Mathys for the fruitful discussions and many helpful suggestions and are grateful to ExxonMobil for permission to publish this work.

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