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ABSTRACT

Catalyst stability
Ketonic decarboxylation
Ketone hydrodeoxygenation
Pt/alumina
Zirconium oxide

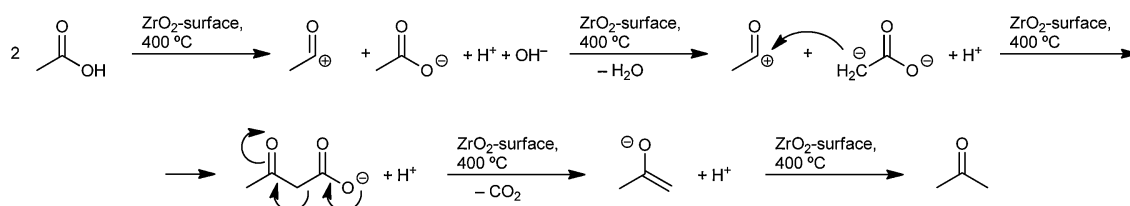
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$$\begin{array}{ccc} \text{HOH}_2\text{C} & & \\ & \diagdown & \diagup \text{O} \\ \text{HO} & & \text{OH} \\ & \diagup & \diagdown \\ \text{HO} & & \text{OH} \end{array} \xrightarrow[-3 \text{H}_2\text{O}]{[\text{H}^+]} \text{HOH}_2\text{C} \begin{array}{c} \diagup \text{O} \\ \diagdown \end{array} \text{CHO}$$

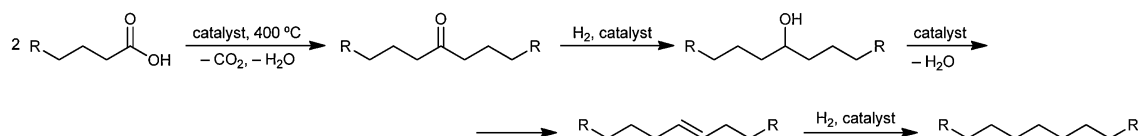
$$\xrightarrow[+ 2 \text{H}_2\text{O}]{[\text{H}^+]} \text{CH}_3\text{C}(=\text{O})\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{OH} + \text{HCOOH}$$

For both, fuels and chemicals, the reduction of the oxygen content is an important issue. Hereby, the reduction of levulinic acid into valeric (pentanoic) acid is straightforward via γ -valerolactone (GVL) [8,9]. In a certain version of the reaction exploiting the raw material to a maximum, formic acid co-produced in the rehydration of HMF has been used as hydride donor in the first step [10,11]. For further reducing the oxygen content when treating carboxylic acids, and increasing the molecular weight at the same time which is also highly desired in biomass transformations, the ketonic decarboxylation is a very suitable and environmentally

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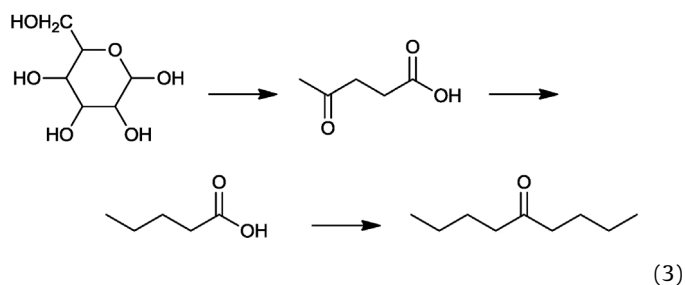
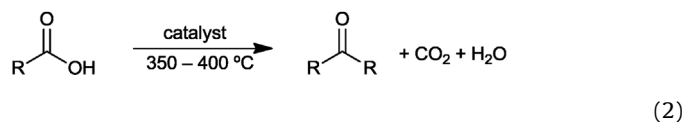


Scheme 1. Kinetically favored mechanism on zirconium oxide as established by theoretical DFT calculations (see [18]). Two molecules of carboxylic acid are adsorbed in a different way onto the zirconium oxide surface, one by double deprotonation and the second by dehydroxylation. Then a carbon–carbon bond is formed between both molecules resulting in a β -keto acid. The latter is decarboxylated easily and protonation and desorption provides the ketone.



Scheme 2. Reaction sequence involving ketonic decarboxylation, hydrogenation of the resulting ketone to an alcohol, dehydration of this compound, and hydrogenation of the intermediary olefin. For $R = n$ -octyl see [21]; $R = \text{Me}$, this work.

benign reaction [12]. This reaction is carried out at elevated temperatures (350–400 °C) in the presence of a catalyst and two molecules of carboxylic acid are fused to a ketone, expelling one molecule of carbon dioxide and one of water (Eq. (2)). Further reagents are not required. Hence, from this sequence, i.e., dehydration, rehydration, hydrogenation, and ketonic decarboxylation, compounds such as 5-nonanone are available from hexoses (Eq. (3)).



Probably the ketonic decarboxylation also plays a decisive role in the stabilization of the above mentioned bio-oils. When using them as a co-feed in fluid catalytic cracking units (FCCs) they need a significant up-grade due to their high oxygen content [13]. Catalysts (e.g., alkali and alkaline earth metal oxides supported on amorphous silica alumina) and reaction conditions (450 °C) [14] resemble those of the ketonic decarboxylation for which a catalytic action of these oxides has been established in other cases [15,16]. Furthermore, increased decarboxylation and dehydration has been observed for the pyrolysis in presence of these catalysts together with the reduction of the carboxylic acid amount.

Hence, these examples show the increasing interest in the ketonic decarboxylation for the production of ketones since first performed more than a century ago [12]. Then, the reaction mechanism [17] has been studied in detail by means of theoretical DFT calculations [18,19]. Thereby, it has been found that a reaction mechanism via a β -keto acid requiring hydrogen atoms in α -position is kinetically favored (Scheme 1). In a first step, two molecules of carboxylic acid are adsorbed onto the surface and

“stabilized” for the reaction in a different way. One molecule is deprotonated twice to yield an enediolate and the other molecule is dehydroxylated. Then, the methylene group attacks nucleophilically the carbonyl group of the dehydroxylated acid forming a β -keto acid. The latter is decarboxylated to an enolate. Protonation and desorption of all reaction products allow to close the catalytic cycle.

This theoretical study has been carried out with zirconium dioxide as catalyst which has been shown to be the most active material among zirconium–cerium mixed oxide, cerium oxide, alumina or silica [18]. The catalytic advantages of zirconium oxide have been confirmed in a further study [20]. Therefore, this is a material to be tested in multi-step transformations such as presented for the conversion of fatty acids into diesel and lubricants [21]. In a cascade reaction the fatty acids have been converted into fatty ketones over magnesium oxide, the ketones hydrogenated to alcohols and hydrocarbons have been obtained by subsequent dehydration and olefin hydrogenation (Scheme 2). The maximum selectivity towards the corresponding hydrocarbon, i.e., tricosane from lauric acid, was 58%. However, except for one case and using approximately the same amount of feed as the weight of catalyst, deoxygenation was lower than 80% since, generally, the corresponding ketone was observed with more than 20% selectivity. The activity of the ketonic decarboxylation catalyst decreased with time on stream.

In the present manuscript, we show the possibility of obtaining good yields of kerosene from levulinic acid in a two-bed one fixed-bed continuous reactor by combining ZrO_2 and $\text{Pt/Al}_2\text{O}_3$ in the presence of hydrogen. The catalyst is stable under reaction conditions.

2. Experimental part

Valeric acid (98%) and decanoic acid (99%) were purchased from Sigma–Aldrich and 5-nonanone from Acros. All reagents were used without any further purification. ZrO_2 , Al_2O_3 , and SiO_2 were received from ChemPur and activated carbon from Norit. $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (99%, Aldrich) and $\text{Pd}(\text{OAc})_2$ (Aldrich, 99%) were employed as noble metal precursors.

The metal catalysts were prepared by the incipient wetness impregnation method. Solutions with the corresponding concentrations of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and of $\text{Pd}(\text{OAc})_2$ were prepared in water and toluene, respectively. The metal oxide supports were impregnated as pellets (0.4–0.8 mm) and dried in vacuum. In the case of $\text{Pd}(\text{OAc})_2$ several impregnation steps were required to

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