

Insights into gold-catalyzed synthesis of azelaic acid†

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A novel green route for the synthesis of azelaic and pelargonic acid *via* aerobic gold-catalyzed cleavage of 9,10-dihydroxystearic acid (DSA) was investigated recently. In this study, the examination of the reaction mechanism is described. The results of the application of ^{18}O -labeled molecular oxygen and sodium hydroxide as well as of diastereomeric pure erythro- and threo-DSA were discussed. Assumed reaction intermediates were synthesized and subjected to the same reaction conditions as with DSA. As a conclusion from the obtained data, an oxidative dehydrogenation mechanism was postulated. Additionally, the aging of the gold catalyst used under different storage conditions was explored.

Introduction

Partially biobased polymers obtained from azelaic acid (AA) as one of the monomeric building blocks are niche products with very special properties for particular applications. For example, polyamides 69 and 6/69 were reported to be used as flexible extruded films for food packaging, as coating for wires and further applications in the electronics and automobile industry.^{1,2} The usage of AA leads to an improved flexibility, elasticity and hydrophobicity of the formed polymers.³ Its admixture to co-polyamide hotmelt adhesives enables very low processing temperatures. Flexible polyester resins containing AA are suitable for impact resistant floor coverings.⁴ Furthermore, azelaic acid-based plasticizers are used to enhance low temperature flexibility in resilient PVC products.⁵

The present industrial production of AA occurs by the ozonolysis of oleic acid. However, an improvement of this process towards a more ecologically benign one is highly desired due to the toxicity of ozone, serious safety risks and the high energy demand of the ozonolysis. Therefore, a range of alternative syntheses were developed in the last few decades.⁶

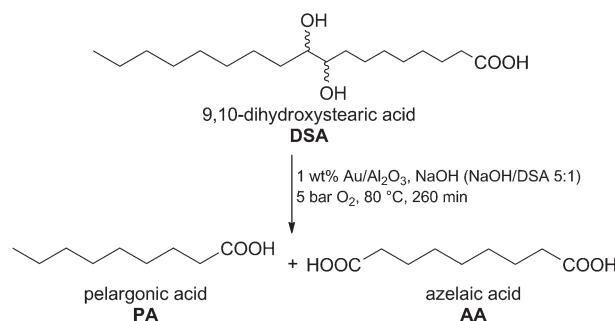
Recently, some of the authors reported on a reaction that may contribute to a more sustainable process, *i.e.* the aerobic gold-catalyzed^{7,8} cleavage of 9,10-dihydroxystearic acid (DSA) to AA and pelargonic acid (PA) applying different supported gold catalysts in an aqueous solution.⁹ Some phenomena observed during these investigations such as an unsteady catalyst activity, depending on the storage conditions and storage

time, and the question of the reaction mechanism deserved further research. The results of these investigations are presented in this study.

Results and discussion

Mechanistic investigations

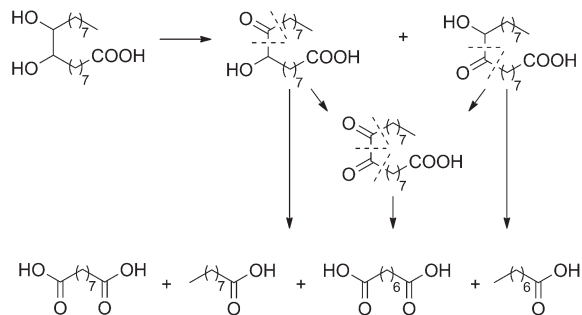
Background. The cleavage of DSA applying $\text{Au}/\text{Al}_2\text{O}_3$, molecular oxygen and an aqueous-alkaline medium produced up to 86% yield of AA and 99% yield of PA (1 mmol DSA, 0.2 mol% $\text{Au}/\text{Al}_2\text{O}_3$, 5 mmol NaOH, 20 mL H_2O , 80 °C, 260 min, 5 bar O_2).⁹ Besides these target products, only the by-products suberic acid (SA) and caprylic acid (CA), shorter by one carbon atom compared to AA and PA, were exclusively formed in a yield of about 3–5% during the reaction (Scheme 1). A tracking of the conversion of DSA *versus* time showed a parallel formation of AA, PA as well as SA and CA. Further shorter-chained by-products should be found if the reaction pathway includes an over-oxidation or oxidative degradation, following a radical reaction pathway. The formation of only products with 9 or 8 carbon atoms in the chain might be



Scheme 1 Cleavage of 1,19-dihydroxystearic acid (DSA).

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Scheme 2 Assumed formation and degradation of intermediates.

explained with keto group-containing intermediates such as 9(10)-hydroxy-10(9)-oxostearic acid (hydroxyketone, HK) and 9,10-dioxostearic acid (diketone, DK) (Scheme 2). Such a mixture of products with n and $n - 1$ carbon atoms was also observed in the cleavage of ω -acyl-substituted fatty esters.¹⁰ To support this hypothesis, the presumed intermediates were synthesized and subjected to the same reaction conditions as DSA.

Preparation and investigation of potential intermediates. HK and DK were prepared according to improved literature procedures^{18,19} (see ESI†). A complete isolation and characterization of these pure compounds by NMR spectroscopy and mass spectrometry was carried out (see ESI†). The isolated HK and DK were used as starting materials in the gold-catalyzed cleavage reaction (0.1 mmol substrate, 1 wt% Au/Al₂O₃, 2 mL H₂O, substrate–NaOH 1:5 (mol mol^{−1}), 80 °C, 5 bar O₂, 260 min). The main products derived from these experiments were AA (26–28%) and PA (18–26%). The C8 by-products CA (1–3%) and SA (4–9%) were found to a lesser extent. Unfortunately, a recovery rate of only 29% could be calculated by using GC data. The MS/ESI spectrograms of the crude products showed besides the signals of AA, PA, CA and SA also a few peaks of higher molecular compounds, *e.g.* the signal [M – H][−] 605 denoted a dimer of DK (structure in ESI†). This oligomerization may be explained by a higher concentration of the reactive DK as a starting material compared to the situation of an intermediary formation of DK in the cleavage of DSA. Additional experiments using AA and PA as starting materials under the general cleavage conditions did not show any conversion at all. This result supports the assumption that AA and PA are stable under the reaction conditions and not intermediate products in a further degradation to SA and CA.

Different reactivity of threo and erythro diastereomers. A different reactivity of the two diastereomers of DSA, threo and erythro, in the gold-catalyzed synthesis of AA might be supposed. Therefore, the diastereomerically pure forms of DSA were synthesized according to the literature procedures^{11,12} (see ESI†). Fig. 1 shows the area of peaks related to erythro- and threo-DSA in gas chromatograms of product mixtures after the exposure of the pure diastereomers to different reaction conditions. Only marginal isomerization took place even in the presence of the gold catalyst if oxygen was excluded. To demonstrate the necessity of oxygen, a NaOH solution

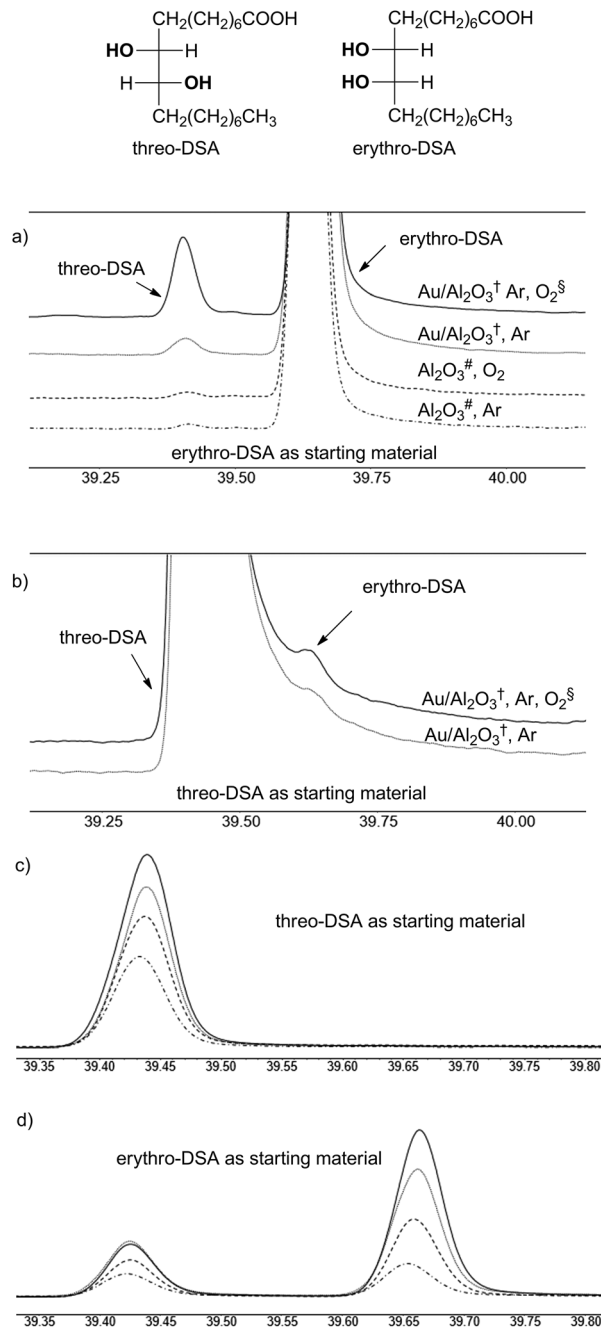


Fig. 1 Gas chromatograms of reaction mixtures (detail of signals denoted to DSA) in the conversion of diastereomeric pure threo- and erythro-DSA subjected to different conditions. (a) Reaction conditions: 0.1 mmol DSA, 0.5 mmol NaOH, 2 mL H₂O, 260 min, 5 bar Ar, [†]0.2 mol% Au/Al₂O₃, [‡]6.5 mg Al₂O₃, [§]small amount of O₂ dissolved in the NaOH solution. (b) Reaction conditions: 0.1 mmol DSA, 0.2 mol% Au/Al₂O₃, 0.5 mmol NaOH, 2 mL H₂O, 260 min, 5 bar Ar, [§]small amount of O₂ dissolved in the NaOH solution. (c) Temporal tracking of the cleavage of pure threo-DSA. (d) Temporal tracking of the cleavage of pure erythro-DSA.

containing small amounts of dissolved oxygen was used. Erythro-DSA (Fig. 1a) isomerized to the threo form at a considerably increased rate when Au/Al₂O₃ and O₂ were both present. Threo-DSA did also isomerize in the presence of

Au/Al₂O₃ and O₂ (Fig. 1b). In Fig. 1c and 1d, GC peaks of erythro- and threo-DSA obtained from product samples taken every 15 min are plotted. Thus, the temporal tracking of isomerization/cleavage can be visualized. Obviously, threo-DSA isomerized more slowly or at least as fast as the cleavage of the formed erythro-DSA happened. Therefore, a peak assigned to erythro-DSA cannot be observed in Fig. 1c. In contrast, both peaks of threo-DSA and erythro-DSA are found in the GC using pure erythro-DSA as the starting material (Fig. 1d). Probably, threo-DSA cannot be cleaved directly or, if at all, it reacts very slowly.

However, the cleavage might start exclusively from the erythro form. A further confirmation of this supposition, *e.g.* by FTIR spectroscopy, was not possible due to the alkaline aqueous medium and the low concentration of the catalyst and reactants.

Investigations using ¹⁸O₂ and Na¹⁸OH

To clarify the origin of the oxygen needed for the formation of AA and PA from DSA, experiments using both ¹⁸O isotope labeled molecular oxygen and aqueous sodium hydroxide were carried out. The isotope pattern of the obtained reaction products was determined by MS-ESI. In addition, temporal tracking experiments using ¹⁸O₂ as an oxidant were performed.

When using ¹⁸O₂, the MS-ESI signals show an increasing intensity of the peak caused by a single ¹⁸O-labeled AA ([M – H][–] 189) depending on the conversion (Fig. 2) (since the isotope peaks of AA were larger and more efficient for analysis than those of PA, further discussion is focused on AA). The ratio of signals assigned to the masses [M – H][–] 189/[M – H][–] 187 increased linearly within the range of conversion between 15% and 99% (Fig. 3). The large fraction of labeled AA may be explained by the reaction of H₂¹⁸O not desorbing from the catalyst surface, formed from adsorbed ¹⁸O₂ (see Scheme 3). Therefore, its local concentration on the catalyst surface might

be much higher than in the aqueous medium, thus being included preferentially in the catalytic cycle.

The role of Na¹⁸OH (used as an H₂¹⁸O solution) may be ambivalent. First it neutralized the formed acids. Furthermore, an OH group exchange in the carboxylic groups of the substrate and the products may occur during the entire reaction time.

However, the insertion of ¹⁸O atoms forming the acid groups of the cleavage products cannot only be explained by an OH-group exchange. In Fig. 4a, the isotope pattern (MS/ESI spectrogram) can be obtained by stirring 2 mL of 0.25 M Na¹⁸OH solution (in H₂¹⁸O) with 0.1 mmol AA under argon at 80 °C for 260 min.

A slight enrichment of ¹⁸O singly doped AA is found besides the main quantity of undoped AA. Fig. 4b shows the received isotope pattern of AA from the cleavage of DSA under comparable reaction conditions, except that 1 wt% Au/Al₂O₃ was added and the reaction was carried out at 5 bar ¹⁶O₂ in

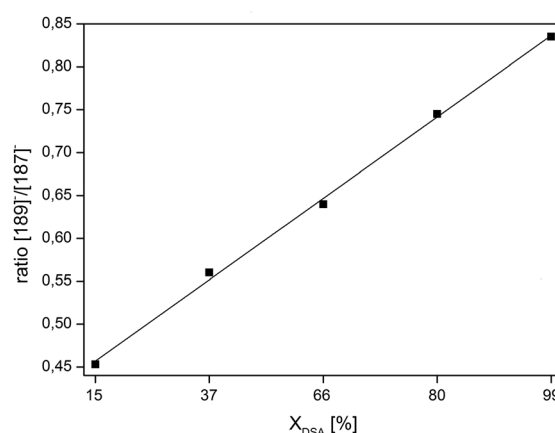


Fig. 3 Dependence of [M – H][–] 189/[M – H][–] 187 ratio from conversion.

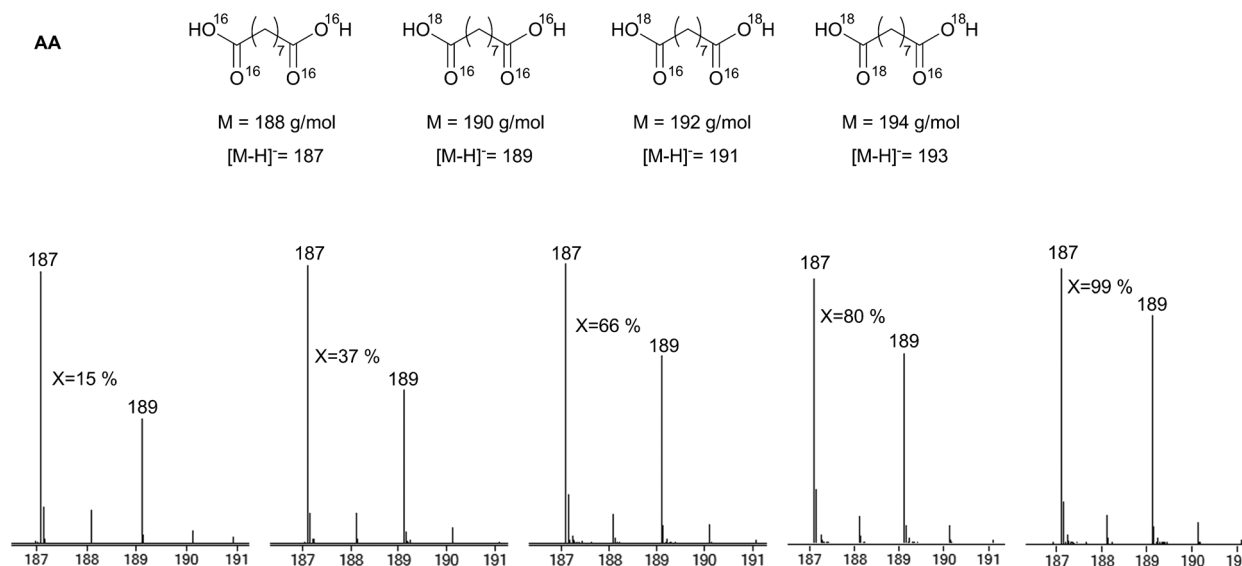
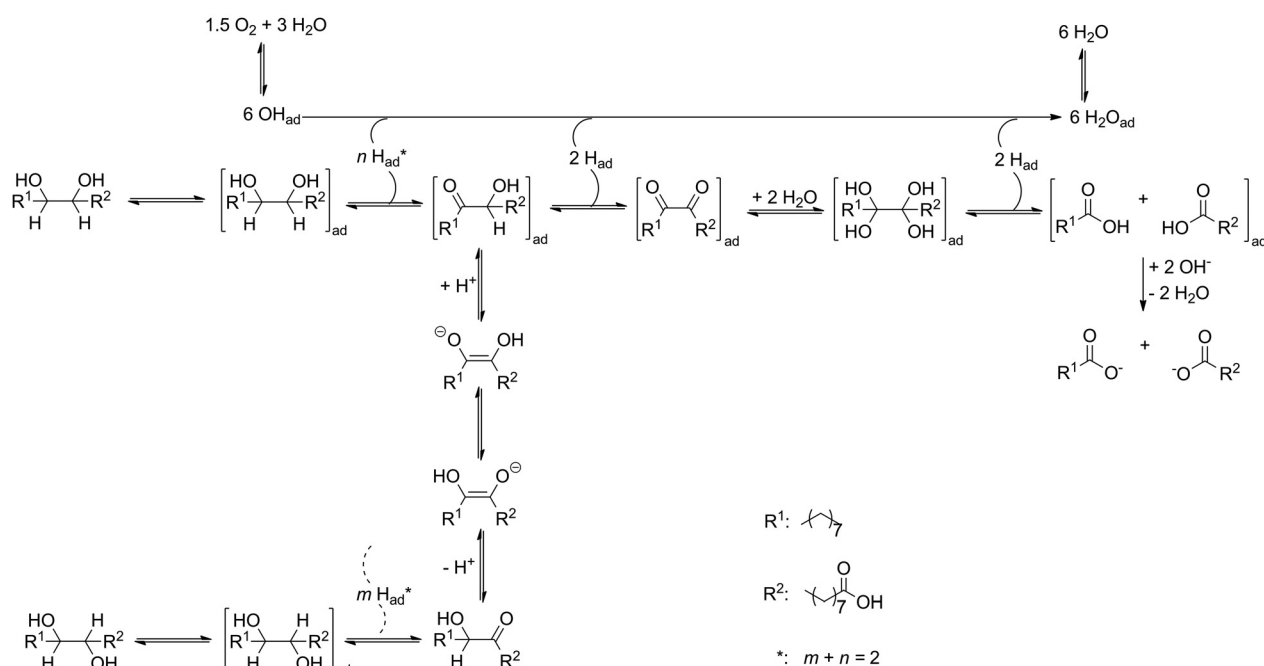


Fig. 2 MS/ESI spectrograms showing isotope pattern of AA in product mixtures obtained by cleavage of DSA in the presence of ¹⁸O₂.



Scheme 3 Proposed reaction mechanism of the oxidative dehydrogenation of DSA.

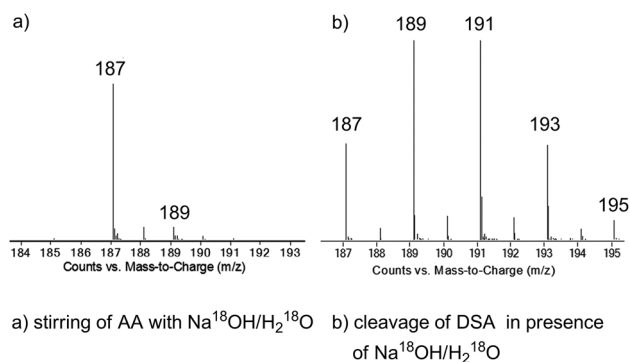


Fig. 4 MS/ESI spectrograms of experiments with $\text{Na}^{18}\text{OH}/\text{H}_2^{18}\text{O}$.

place of argon (0.1 mmol DSA, 0.2 mol% Au, 2 mL of 0.25 M Na¹⁸OH solution, 80 °C, 260 min). As can be seen, the isotope patterns obtained differ significantly. Beside a smaller signal for only ¹⁶O atoms containing AA and two main peaks at [M – H][–] 189 and [M – H][–] 191 denoting a single and double insertion of ¹⁸O atoms, even peaks for a three- and four-fold incorporation of ¹⁸O atoms at [M – H][–] 193 and [M – H][–] 195 are found in the pattern of AA obtained from the gold-catalyzed cleavage in the presence of oxygen. The intensity of the signals and their ratio to each other as a function of time and conversion only change marginally. This finding gives rise to the assumption that NaOH might also be involved in the mechanism.

In conclusion of all the facts presented above, a mechanism of an oxidative dehydrogenation¹³ is in line with these results and seems to be the most plausible (Scheme 3). According to this mechanism, O₂ dissociates and forms together with H₂O–

OH species adsorbed at the catalyst surface. These OH species are converted to H_2O by stepwise hydrogen abstraction and finally the water desorbs from the gold surface. Through this abstraction, HK and DK are formed gradually, and the tetrahydroxy species resulting finally by water addition is not stable and decomposes into AA and PA. Now these acids desorb and are converted into their salts in the alkaline reaction medium. In the case of using $^{18}\text{O}_2$, the concentration of $^{18}\text{OH}^-$ and H_2^{18}O rises with the proceeding reaction that causes the linear increase observed in Fig. 3. If $\text{Na}^{18}\text{OH}/\text{H}_2^{18}\text{O}$ is applied *ab initio*, an approximately 1000-fold molar excess of labeled species exists directly compared to DSA. Therefore, it is likely that a rapid exchange of the equilibria formulated in Scheme 3 and a fast multiple insertion of ^{18}O species may occur. The threo/erythro isomerization might proceed *via* the hydroxyketone and an endiolate as known from comparable epimerizations of sugars.¹⁴

Catalyst aging

During the course of the studies described in ref. 9, it became obvious that the activity of the gold catalysts used changed over time. Therefore, a study using a freshly prepared 1 wt% Au/Al₂O₃ was carried out, which was divided into several portions. These aliquots were stored each under different external conditions (Table 1) for one year.

In addition, further aliquots were also stored under various conditions in a membrane pump vacuum (Table 2) for three months.

The results of the influence of storage conditions on the aging behavior and morphology of the gold catalyst are presented. The conversion of DSA and the yield of the target

Table 1 Storage conditions of catalysts stored for one year

Entry	Storage conditions
1	Freshly prepared catalyst
2	Air, room temperature, daylight
3	Argon, room temperature, daylight
4	Argon, room temperature, darkness
5	Argon, ~5 °C, darkness
6	Air, ~5 °C, darkness

Table 2 Storage conditions of catalysts stored for three months under vacuum and their influence on the conversion of DSA and the yield of AA

Entry	Storage conditions ^a	X _{DSA} [%]	Y _{AA} [%]
1	Freshly prepared catalyst	96	71
2	Vacuum, calcined, darkness, ~-15 °C	93	57
3	Vacuum, unreduced, darkness, ~-15 °C	98	54
4	Vacuum, calcined, darkness, RT	84	44
5	Vacuum, unreduced, darkness, RT	75	38
6	Vacuum, calcined, daylight, RT	50	28
7	Vacuum, unreduced, daylight, RT	43	24

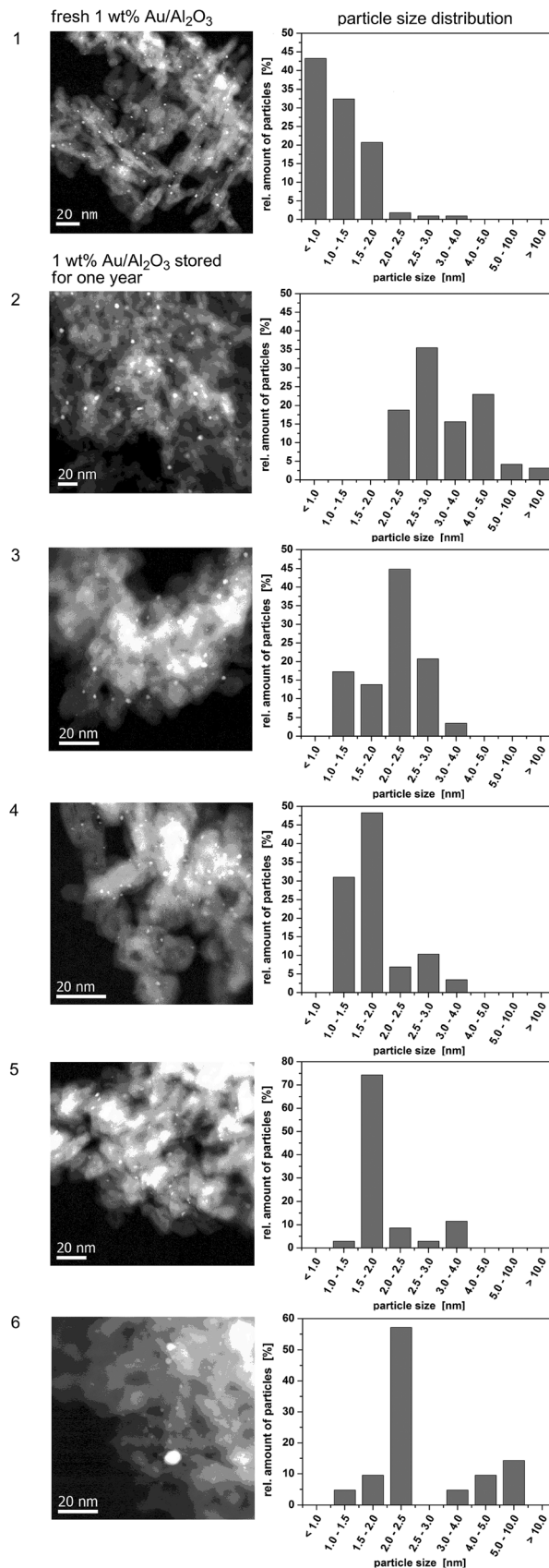
^a Vacuum 8–16 mbar, calcination at 250 °C for 3 h.

product AA in the catalytic cleavage of DSA were chosen to compare the catalyst activity and to describe aging effects.

It is known from the literature that gold particle size and in consequence the activity of the catalyst depend on different parameters. Akita *et al.* and Daté *et al.* reported on the effect of the calcination temperature of Au/TiO₂.^{15,16} Zanella and Louis showed a significant influence of the conditions of thermal pretreatment, such as the gas flow rate, the sample weight, the calcination temperature and the usage of air, H₂ or Ar. Moreover, they discovered the problem of gold particle growth during the catalyst storage of calcined and unreduced samples of Au/TiO₂.¹⁷

This gold particle growth may play a more significant role in the case of structurally sensitive reactions.

The oxidative cleavage of DSA using fresh and stored catalysts was implemented every three months over a period of one year. In addition, TEM observations were done in the same time intervals (Fig. 5). The average particle size distribution was determined to evaluate the extent of the aging process. About 100 Au particles were considered for its calculation. While the fresh catalyst exhibited at an average very small gold particles (<1 nm–2 nm, Fig. 5, entry 1), a significant particle growth was observed after a storage time of one year. The largest growth was shown by the catalysts exposed to air. In this case, Au particles with diameters up to about 10 nm or even larger in part were found. The least particle growth was observed when the catalyst was stored under argon and in the dark (Fig. 5, entries 4 and 5). They featured mainly particles 1–2 nm in size. Obviously, an inert atmosphere and storage in the dark are necessary conditions for the utmost preservation of the original catalyst morphology. The temperature does not have such a significant influence. However, all stored catalysts

**Fig. 5** TEM images and particle size distribution of catalysts stored for one year (numbers relate to the entries/conditions in Table 1).

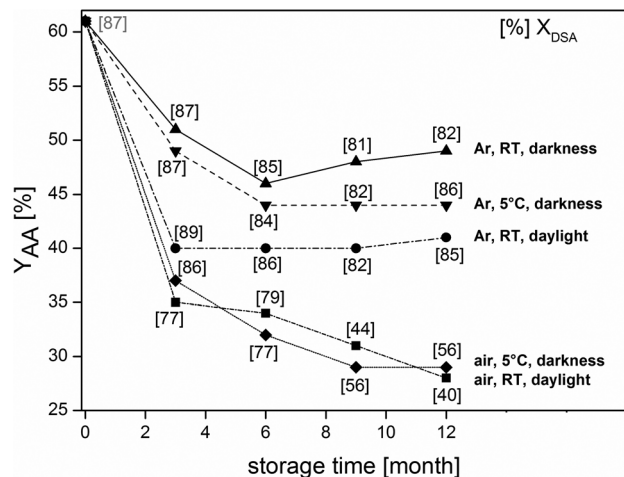


Fig. 6 Influence of storage conditions and time on the yield of AA.

had in common that particles smaller than <1 nm disappeared. Their percentage in the fresh catalyst was about 46%.

The aging of the catalysts was also visualized by their color. The fresh catalyst possessed a light beige color whereas larger gold particles induced a darker purple hue.

The activity of supported gold catalysts in the cleavage of DSA depends significantly on the size of the gold nanoparticles. Fresh 1 wt% Au/Al₂O₃ catalyst with very small particles (size between <1 nm and 2 nm) showed the highest activity. All stored catalysts lost activity in the cleavage of DSA (Fig. 6). A decrease of product yields was observed already after a storage time of only three months.

The decline in the yield of AA correlated with the average particle sizes determined by TEM. The least decrease in yield of AA was observed using catalysts stored under argon in the dark, which possessed the smallest gold particles of all stored catalysts after one year (see Fig. 5, entries 4 and 5).

Investigations concerning the catalyst storage of calcined and unreduced samples in a vacuum at different temperatures as well as in the presence and in the absence of light (see Table 2) were only done in a period of three months. Therefore the evaluation of TEM images obtained from these catalysts was not executed, the effect of the particle growth may not be large enough.

Calcination provokes a stabilization of gold particles (even if an agglomeration due to the increased temperature applied cannot be excluded). Thus, the change in particle size caused by storage may be a little lower, and slightly higher yields of AA were observed in the cleavage of DSA using catalysts directly calcined after preparation. Storage in the dark had a favourable influence on the yield of AA, but a slightly positive effect of storage at about −15 °C in the freezer was also observed. However, a decrease in activity cannot be prevented either by storage in a vacuum or by preliminary calcination. Attempts to regenerate the aged catalysts by their exposition to different atmospheres and temperatures failed (Fig. 7). The yield of AA could not be improved significantly using the regenerated catalysts in the cleavage of DSA.

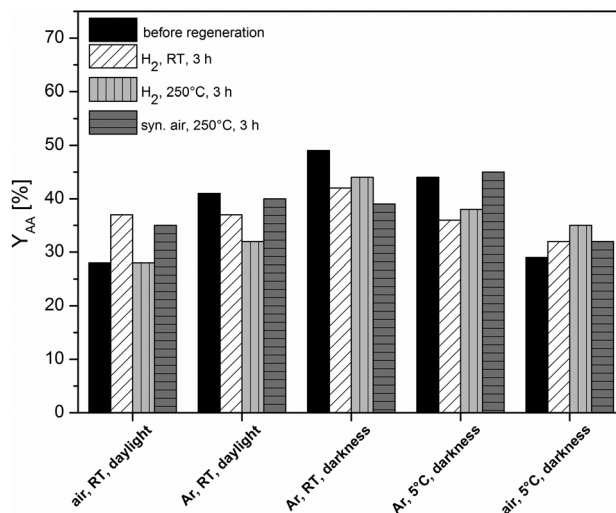
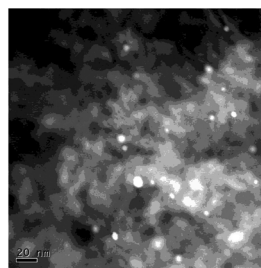


Fig. 7 Results of attempts to regenerate aged catalysts.

used 0.76 wt% Au/Al₂O₃



particle size distribution

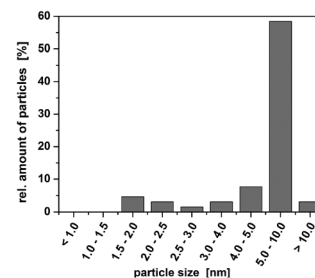


Fig. 8 TEM image and particle size distribution of a 0.76 wt% Au/Al₂O₃ catalyst used five times in the cleavage of DSA.

For comparison of aging effects, the particle size distribution of a used 0.76 wt% Au/Al₂O₃ catalyst (another batch of the catalyst employed in the tests described here) was also determined (Fig. 8). For this experiment, the freshly prepared catalyst was used repeatedly five times in the catalytic cleavage of DSA (for catalytic results and reaction conditions see ref. 9). The gold particle size distribution shows that the largest fraction has a size of 5–10 nm after five cycles. This result also suggests that the observed catalyst deactivation (decrease of AA yield from 62% after the first run to 33% after the fifth run⁹) may be caused by particle growth.

Conclusions

A mechanism of oxidative dehydrogenation as the main reaction pathway in the gold-catalyzed cleavage of DSA was made likely by selective investigations. Respective hydroxyketone and diketone intermediates were synthesized and cleaved to AA and PA. AA with different ¹⁶O/¹⁸O isotope distribution in the carboxyl groups was obtained using labeled ¹⁸O₂ or Na¹⁸OH/H₂¹⁸O in the reaction. Its formation was discussed in accordance with the mechanism postulated. Threo- and erythro-DSA

show different reactivity. Probably the cleavage of erythro-DSA in a mixture of both diastereomers goes along with a preliminary isomerization of threo to erythro diastereomer. The problem of aging of the gold catalysts used was also studied. Storage conditions (such as the atmosphere and the presence or absence of light) have a strong influence on the gold particle growth and in consequence on the catalyst activity. The cleavage of DSA to AA and PA with the aged catalysts applied as a test reaction was repeated every three months within one year. All catalysts lost activity; the highest yield of AA after a catalyst storage time of 1 year was received with a catalyst which was stored under argon in the dark. The reason for the loss was the disappearance of very small gold particles of ≤ 1 nm size due to agglomeration. Comparing all catalysts used in the oxidative cleavage of DSA, the best results after a storage time of 3 months were obtained using the catalyst stored in vacuum at -15 °C in the dark. A conclusion from this behavior for further investigations may be that the catalysts have to be prepared freshly before use. Probably, also a higher activity of gold catalysts on other oxidic supports as described in ref. 9 might be observed using freshly synthesized catalysts. Methods of stabilization of gold particles, possibly by the formation of bimetallic catalysts, should be explored.

Experimental

1 wt% Au/Al₂O₃ catalyst,⁹ 9(10)-hydroxy-10(9)-oxostearic acid¹⁸ and 9,10-dioxostearic acid¹⁹ were prepared according to the improved literature procedures (see ESI†).

A typical reaction procedure for the oxidative cleavage of DSA to AA and PA is as follows: in typical experiments, 1 mmol DSA, a 0.2 mol% gold catalyst (1 wt% Au/Al₂O₃), 5 mmol NaOH and 20 mL H₂O were placed in a 100 mL Parr autoclave. The autoclave was flushed three times with argon and the suspension was heated to a reaction temperature of 80 °C. The autoclave was pressurized with 5 bar O₂ for the reaction time of 260 min. After the reaction was finished, the catalyst was separated from the liquid phase by filtration. The conversion of DSA and the yields of products were determined by GC-MS after derivatization. Experiments using isotope labelled sodium hydroxide and oxygen were measured by MS-ESI.

Reaction of DSA using ¹⁸O₂: in order to ensure that no ¹⁶O₂ is contained in the reaction mixture all arrangements of the experiments were carried out in the glovebox under an Ar atmosphere. In this experiment 2 mmol DSA, 0.2 mol% gold (1 wt% Au/Al₂O₃), and 40 mL of 0.25 M NaOH (refluxed under Ar for removal of ¹⁶O₂) solution were placed in a 100 mL Parr autoclave. The suspension was heated to a reaction temperature of 80 °C. The autoclave was pressurized with 0.5 bar ¹⁸O₂. For temporal tracking experiments samples of 1 mL were taken after 1 h (Y_{AA} = 4%), 2 h (Y_{AA} = 8%), 4 h (Y_{AA} = 22%), 6 h (Y_{AA} = 35%), and 24 h (Y_{AA} = 63%). After the reaction was complete, the samples were treated as described above.

Reaction of DSA using Na¹⁸OH/H₂¹⁸O: in this study, 0.1 mmol DSA, 0.4 mol% gold (1 wt% Au/Al₂O₃), and 2 mL of

0.25 M Na¹⁸OH solution were placed in a 5 mL glass vial (equipped with a screw cap, cannula and stirrer), which was put into the Parr autoclave. The autoclave was flushed three times with argon and the suspension was heated to a reaction temperature of 80 °C using a heating bath. The autoclave was pressurized with 5 bar O₂ for a reaction time of 260 min (Y_{AA} = 58%). After the reaction was complete, the samples were treated as described above.

Cleavage of HK and DK: both these experiments were carried out in 5 mL glass vials using 0.1 mmol substrate (HK or DK) 0.2 mol% gold (1 wt% Au/Al₂O₃) and 2 mL of 0.25 M NaOH solution. The continuing implementation was performed as already described in the preceding paragraph. The yields of AA were 26% (cleavage of HK) and 28% (cleavage of DK).

Acknowledgements

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