

Letter

Oxidative dehydrogenation of rosalsa to costenal on supported silver catalysts

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Abstract

The synthesis of costenal (dec-9-enal) was achieved by oxidative dehydrogenation of rosalsa (dec-9-en-1-ol) on silicon carbide supported silver catalysts (4.5% Ag/SiC) at 450°C in a flow reactor. The substrate was vapourized in a stream of oxygen diluted with 25 volumes of nitrogen (flow rate 140–650 l h⁻¹). The optimum oxygen to substrate ratio was ca. 1.5. The highest costenal yield (51%) was obtained at 70% conversion as the contact time of the gas flow with the catalyst was the shortest (0.028 s). The activity was stable for a period of 96 h on stream. © 1998 Elsevier Science B.V.

Keywords: Oxidative dehydrogenation; Silver catalyst; Costenal synthesis

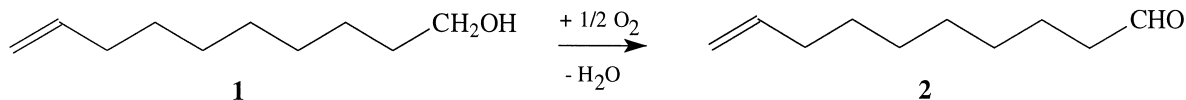
1. Introduction

The reactions of oxidative dehydrogenation of alcohols in vapour phase on metal catalysts are used for the preparation of bulk chemicals (e.g., formaldehyde from methanol), or specialties chemicals (e.g., glyoxal from ethylene glycol). These reactions are rarely employed for the synthesis of fine chemicals because it is feared that reactants and products may not sustain high temperatures without degradation. Nevertheless, oxidative dehydrogenation of thermally fragile molecules can be carried out provided they are converted with a very short residence time in catalytic reactors. Thus, in the BASF process of citral synthesis, one important step is the preparation of isoprenal by oxidative dehydrogenation of isoprenol at 500°C on silver catalysts. Indeed, vapour phase oxidative dehydrogenation of alcohols could be useful for the preparation of aldehyde molecules since liquid phase oxidation of alcohols may give poor yields in aldehydes because of their subsequent oxidation into the corresponding acids.

In the present work, vapour phase oxidative dehydrogenation on metals was applied to the synthesis of aldehydes of interest in the flavour and fragrance industry. More specifically, dec-9-en-1-ol

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(rosalva **1**) was converted into dec-9-enal (costenal **2**) which is employed, with other C₈–C₁₁ aldehydes, to enhance the «top note» of various perfumes. This reaction can potentially be catalysed by copper–chromite, but these catalysts may induce the formation of various isomers by migration of the C=C bond. Furthermore, they should be avoided in the long run because of more stringent environmental regulations on the disposal of toxic metals. The oxidative dehydrogenation of rosalva was carried out on silicon carbide-supported, silver catalysts, similar to those employed in an earlier study on the preparation of glyoxal from ethylene glycol [1,2].



2. Materials and methods

Silicon carbide under the form of irregular bits of 3 ± 1 mm was impregnated with an aqueous solution of silver nitrate. A quantity of 75 g of SiC was introduced in a rotating flask with 6.22 g of silver nitrate dissolved in 365 ml of water. The solvent was evaporated for 180 min at 80°C then for 150 min at 60°C under reduced pressure. The impregnated catalyst was dried in air at 85°C and reduced in a quartz cell by heating from 25 to 500°C with a ramp of 2°C min⁻¹ under flowing hydrogen (8 l h⁻¹), and kept at this temperature for 20 h. Analysis by ICP–AES of the solution obtained after acidic attack of the catalyst, indicated that the silver content was 5 wt.%. The oxidative dehydrogenation was carried out in a setup involving a vapourizer, a reactor and a condenser. The vapourizer consisted of an ultrasonic nebulizer (US1 Lechler) transforming the liquid, pumped from a reservoir with a peristaltic pump, into an aerosol of fine (10–20 μm) droplets. The aerosol was vapourized in a stream of nitrogen and oxygen heated at 450°C. The gaseous mixture was then flown at atmospheric pressure through a 75 cm³ cylindrical reactor in pyrex glass. The fixed bed of Ag/SiC catalyst was supported on quartz wool at the bottom of the reactor. The temperature was controlled with a thermocouple placed in the catalyst bed. At the outlet of the reactor, the gas flow was either directed to vent or to a condenser consisting of two consecutive traps filled with ethanol cooled at 0°C. A better condensation of the reaction products was achieved by flowing the gas through glass frits immersed inside the traps. The ethanol solution in both traps was analysed after various time on stream to determine the amounts of reactant converted and products formed. Analysis was made by GC (Shimadzu GC-14A) with a quadrex FFAP column. The amount of carbon dioxide formed was determined by measuring the weight uptake of a limewater trap placed after the two ethanol traps.

3. Results and discussion

The reaction was carried out at 450°C with 10 g of catalyst, 6 ml h⁻¹ of rosalva, 50 l h⁻¹ of nitrogen, 12 l h⁻¹ of air (rosalva:O₂:N₂ = 1:3:74; residence time: 0.12 s). Under these conditions 90%

Table 1
Effect of the molar ratio of reactants

Molar ratio (O ₂ /1)	Conversion (%)	Costenal yield (%)	Selectivity (%)
0	10	1	
1	61	27	44
1.7	80	36	45
3.0	86	32	37

Reaction conditions: 10 g of 5 wt.% Ag/SiC catalyst.

of the rosalsa was converted giving 40% of costenal (45% selectivity with respect to converted rosalsa). The activity was 60 mmol h⁻¹ g_{Ag}⁻¹. The reaction did not yield costenal isomers nor dec-9-enoic acid. The only other product detected was carbon dioxide, however, light molecules which would not be trapped and small amounts of cracking products may be formed. A blank experiment was run without catalyst under similar conditions. A 40% conversion of rosalsa was measured with small amount of costenal formed (5%) and carbon dioxide as main product. This indicates that total oxidation is taking place in the gas phase or on the walls of the vapourizer and reactor heated at 450°C.

The activity and selectivity of the catalyst were stable over a period of 96 h on stream, which indicates that the catalyst surface was not appreciably modified, for instance by sintering or formation of carbonaceous deposits.

The reaction was conducted at various oxygen/rosalsa molar ratios. Table 1 shows that an optimum yield was obtained for a ratio close to 1.5. It was also shown that increasing the temperature above 450°C had an adverse effect on the selectivity because total oxidation was favoured. The effect of lowering the reaction temperature under 450°C was not investigated, therefore the optimum temperature of the reaction has yet to be determined.

The reaction kinetics was followed as a function of the residence time on the catalyst. Table 2 gives the reaction data as a function of residence times on the catalyst obtained by changing either the gas flow rate (140–650 l h⁻¹) or the catalyst mass (10–30 g). The highest costenal yield (51%) was obtained at 70% conversion as the contact time of the gas flow with the catalyst was the shortest (0.028 s). The selectivity decreased rather slowly with residence time since at 95% conversion the selectivity was still 41%.

Table 2
Effect of the residence time

Residence time (ms)	Rosalva conversion (%)	Costenal yield (%)	Selectivity ^a (%)
28	70	51	73
34	63	45	71
59	69	42	61
116	80	37	46
229	94	40	43
343	95	39	41

^aWith respect to transformed rosalsa.

Reaction conditions: 450°C, 4.5 wt.% Ag/SiC catalyst.

4. Conclusion

In conclusion, this preliminary work demonstrates the feasibility of the oxidative dehydrogenation of rosalva to costenal on silver catalysts. Future work on this, or any similar reaction, would have to optimize the selectivity by minimizing the total oxidation. This can be achieved by reducing the rate of oxidation in the homogeneous phase by decreasing the temperature, particularly that of the vapourizer. The most interesting result is that costenal could be obtained without isomerization of the double bond which means that oxidative dehydrogenation allows a clean, one pot, synthesis of a highly priced product.

References

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