OXIDATION OF ROSALVA TO COSTENAL ON SILVER CATALYST IN MICROSTRUCTURED REACTORS

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Summary

Oxidation of rosalva (9-decen-1-ol) to costenal (9-decen-1-al) was carried out in silicon-glass microreactors on silver catalysts at the temperature range 420-475°C. Reactors with increased surface area where silver was deposited were employed with a view to enhance reaction performance. The results showed a significant improvement of the reaction with silver deposited on porous silicon surface. Rosalva conversion increased from 8-35% on non-porous silicon to 67-95% on porous silicon under the same reaction conditions (rosalva:O_2:He =1:3:57, residence time=20 ms). Selectivity to costenal higher than 95% was also achieved.

Keywords

Microreactor, porous silicon, silver catalyst, rosalva oxidation

Introduction

The selective oxidation of alcohols is a fundamental process in synthetic chemistry [1]. During recent years, most of research of "green" oxidation of alcohols has focused on metal catalysts using molecular oxygen to replace traditional stoichiometric oxidants [2]. The aim is to oxidize the alcohol to its corresponding aldehyde, not to the corresponding acid, as the aldehyde is widely used to make flavors, agrochemicals, pharmaceuticals and fragrances. The oxidation of alcohols on metal catalysts with molecular oxygen can be performed in the liquid phase or in the gas phase, depending on the thermal stability and volatility of reagents and products. The oxidation of alcohols in the gas phase with air or oxygen represents an attractive route for the industrial production of aldehydes and ketones. The gas phase oxidation for simple alcohols is well established at the industrial scale (e.g. methanol oxidation to formaldehyde). Although the method is not usually employed for the synthesis of fine chemicals due to concerns that reactants and products may degrade at high reaction temperature, examples have been shown that such reactions can be carried in catalytic reactors, provided that very short residence time and fast quenching after reaction can be achieved. In the BASF process for citral synthesis, isoprenol was converted to isoprenal on a supported silver catalyst at 500°C with a residence time of about 0.001s [3]. Gallezot et al. reported the oxidation of rosalva to costenal over Ag/SiC; the best selectivity of 73% was achieved at 70% conversion at 450 °C with 0.03 s contact time [4].

In our previous research, oxidative dehydrogenation of prenol (3-methyl-2-buten-1-ol) to the corresponding aldehyde was performed in microreactors on silver catalyst with high selectivity [5]. The silver catalyst was incorporated into the reaction channel by sputtering. The thin film deposition may not provide enough surface area required for catalytic reactions. Various methods have been reported to generate high surface areas in thin film, including anodic oxidation of silicon [6], sol-gel coating [7] or more recent development on growing nanoparticles and nanosprings on surfaces [8]. In this work, we report the investigation of the effect of the surface area of silver catalyst on oxidative dehydrogenation of rosalva to costenal by producing porous silicon in the microreaction channel.

Experimental

The microreactor was made of silicon wafer (n-type, <100>, 1-10 Ωcm) using lithography and dry etching. Porous silicon was produced using metal (Ag) assisted chemical etching in HF/H_2O_2 for 30 min [9]. Silver catalyst was deposited onto the reaction channels by sputter coating using a shadow mask, producing a catalyst area of 6×12 mm^2. The silver deposited on non-porous silicon surface and on porous silicon surface is denoted as Film-Ag and PSi-Ag respectively. The silicon reactor was anodicaly bonded with a glass wafer. Both reactors contained 0.19 mg silver. The overall size of the microreactors was 17×51 mm. The

dimensions of the reaction channel were 6 mm (width) × 0.12 mm (depth). The inlets/outlet were located at one end of the microreactor which is sealed using O-rings in an aluminium connector (Fig. 1B). The microreactor was heated on both sides using two ceramic heaters with a graphite spacer (Fig. 1A). The assembled microreactor system, is shown in Fig. 1C. At the outlet of the reactor, the gas flow was directed to a condenser/gas-liquid separator which was kept in an ice-water bath. The liquid sample collected was analyzed using a GC with a HP-INNOWax column and FID. The non-condensable gas was directed to a second GC with Carboxen 1006 column and TCD to determine the amount of CO_2 formed.

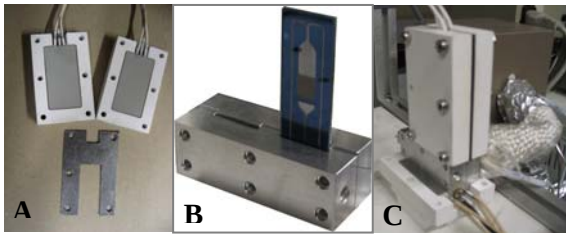

Figure 1. Microreactor system: A) ceramic heaters with graphite spacer; B) silicon-glass microreactor and inlet/outlet connector; C) assembled reactor system

Results and Discussion

Effect of reaction temperature

The effect of temperature on rosalva conversion and selectivity to costenal was studied at temperature of 420, 450 and 475°C with a liquid flow of 0.5 mmol h^{-1}, 1.5 mmol h^{-1} of O_2 and Helium as inert (rosalva:O_2:He=1:3:53). Residence time was 20 ms calculated at 450°C. Fig. 1 shows the effect of temperature on conversion of rosalva. It can be seen that conversion increased with temperature for both catalysts. With the catalyst Film-Ag, conversion increased from 8% at 420°C to 35% at 475°C. Significant improvement of performance was observed on PSi-Ag catalyst, showing an increase in conversion from 67% to 96% in the same temperature range.

Selectivity to costenal was higher than 95% and was not significantly affected by the catalyst surface area (Table 1). At 450°C conversion at the PSi-Ag reactor was 81% and selectivity 97%, which compares favorable with the results of Gallezot et al. [4]. The main side products were CO_2 and other heavier organic compounds with a total selectivity less than 5% which slightly increased with reaction temperature.

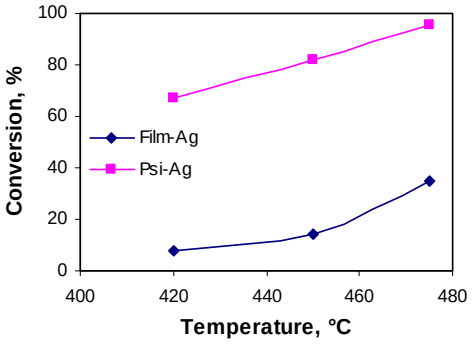

Figure 2. Effect of temperature on conversion of rosalva on two forms of silver catalyst

Table 1. Effect of temperature on selectivity (%) to costenal and CO_2

T, °C	Film-Ag		PSi-Ag	
	Costenal	CO_2	Costenal	CO_2
420	100.0		97.2	1.0
450	98.9	1.1	96.7	1.8
475	95.3	1.7	94.9	3.6

These results show clearly that the performance of the microreactor is significantly enhanced by increasing the surface area of silver catalyst. Optimization of the reactor performance will be carried out by investigating the effect of the structure of porous silicon (pore size and thickness of porous layer), oxygen and rosalva concentrations and residence time on the reaction.

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