



Selective hydrogenation of cinnamaldehyde to cinnamyl alcohol on a Pt nanoparticle based catalyst using the H-Cube® Flow Reactor

INTRODUCTION

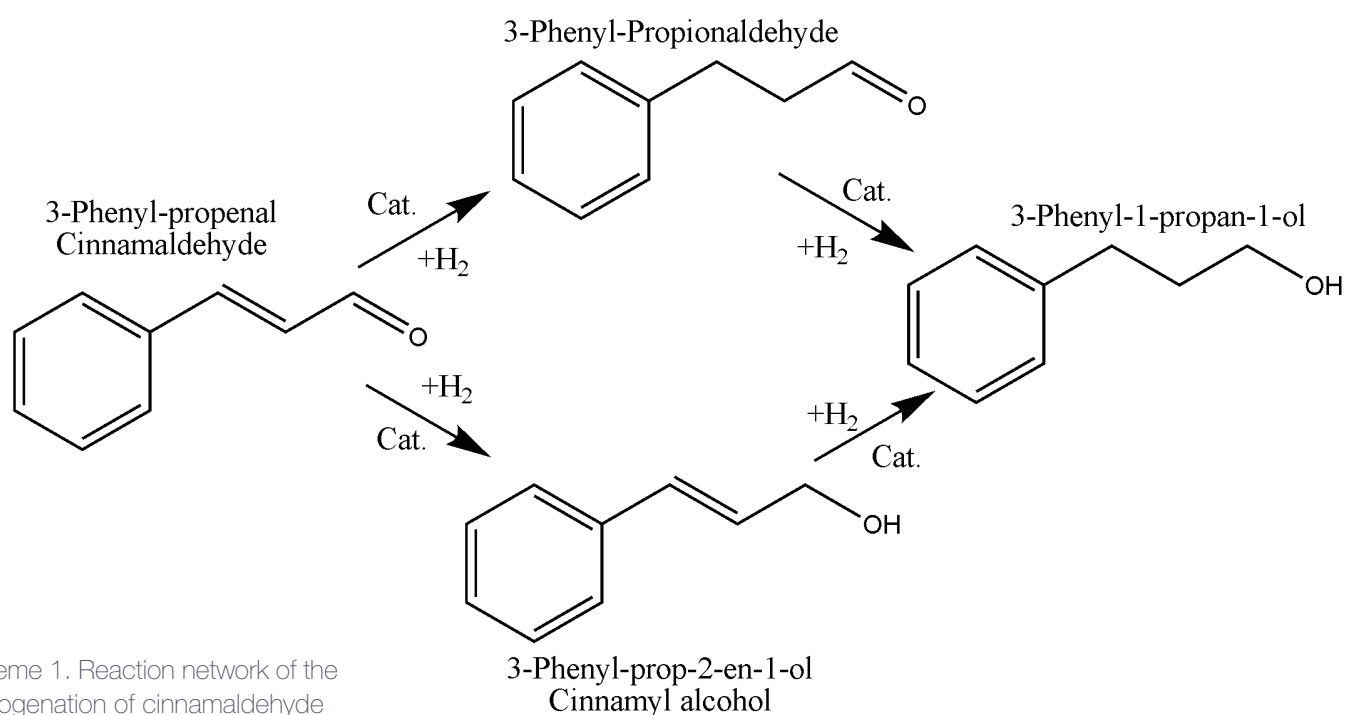
Selective catalytic hydrogenation of α - β -unsaturated aldehydes is an important step in the industrial preparation of fine chemicals and attracts much interest for fundamental research in catalysis¹. Cinnamyl alcohol plays an important role in the perfume and flavouring industries. The process can, however, lead to three different products: saturated aldehyde, saturated alcohol and the desired unsaturated alcohol (see Scheme 1.).

The hydrogenation of the C=C bond in α - β -unsaturated aldehydes is both kinetically and thermodynamically more favorable than that of the C=O group².



The most significant factors determining the selectivity are: the type and the structure of the active metal, the type of the substrate, and the conditions of the reaction, namely, the hydrogen pressure and the reaction temperature.

The influence of the latter factors can be easily investigated by using the H-Cube®, which is a standalone hydrogenation reactor combining continuous-flow microchemistry with on-demand hydrogen generation and a disposable catalyst cartridge (CatCart®) system³.



Scheme 1. Reaction network of the hydrogenation of cinnamaldehyde

CATALYST

Well-defined platinum nanoparticles with an average size of 2-3 nm were prepared by a continuous flow alcohol reduction process according to a recently described method⁴. The active metal building blocks were then anchored onto a high specific surface area silica support, and the catalyst was activated by temperature pre-treatment prior to use. The catalyst shows superior activity and selectivity in the hydrogenation of cinnamaldehyde to conventional Pt/SiO₂.

STANDARD EXPERIMENTAL PROTOCOL

After switching on the H-Cube® and filling the water reservoir with de-ionized water, the desired CatCart® is fixed into its holder. After selecting the required flow rate, the reaction solvent is initially allowed to flow through the CatCart® for 1 minute to remove the air from the system. The temperature and pressure of the system were set, the hydrogen production activated, and the mixture of solvent and hydrogen allowed to flow through the CatCart®. A sample of the substrate was pumped through the H-Cube® and the total amount of reaction mixture was collected in a sample vial. The column was then washed with the eluent to remove any material still absorbed on the CatCart®. The product mixture was analyzed by GC-MS.

EXPERIMENTAL PROCEDURE

Using 1% Pt/Silica as catalyst, 200 mL Cinnamaldehyde (0.02 mol, 2.64 g) in ethanol was pumped through the H-Cube® at a 1 mL/min flow rate. In order to avoid production of the undesired chelate between cinnamaldehyde and ethanol, freshly prepared reaction mixture has to be used! To find the optimal parameters of this selective hydrogenation, the effect of pressure and temperature on the the yield of the desired product, cinnamyl alcohol, were investigated. The applied pressures were 30, 60 and 90 bar, the applied temperatures were 20, 40, 60, 80 and 100°C, respectively.

After the CatCart® was washed with ethanol for 10 minutes, the reaction mixture was allowed to flow through the reactor. Product samples for GC-MS analysis were taken after 15 min. reaction time in each case. The CatCart® was then washed with pure ethanol for 15 min.

RESULTS

The results of the experiments investigating the effect of temperature and pressure on the formation of cinnamyl alcohol are given in Figure 1. below.

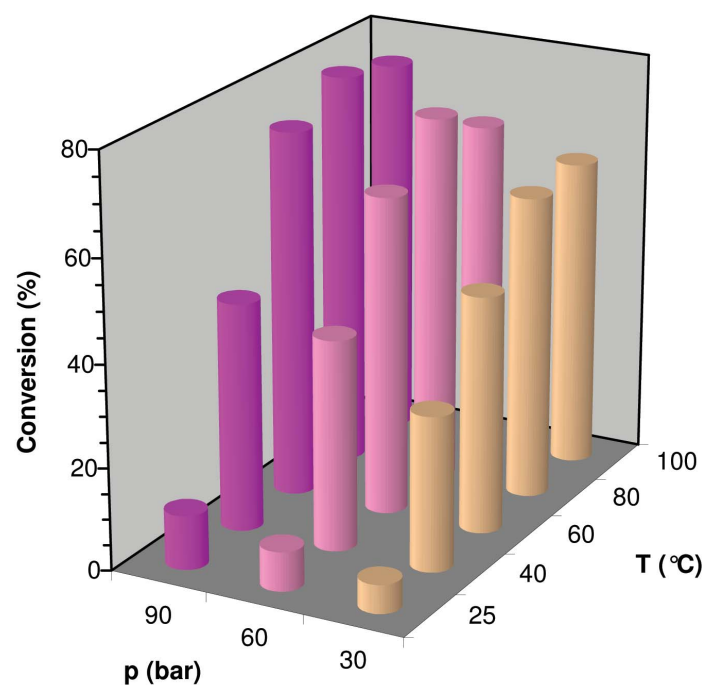


Figure 1.
Conversions as a function of reaction temperature and pressure

It is clearly seen that increasing pressure and reaction temperature shifts the cinnamaldehyde transformation reaction to higher conversions. At high temperature and pressure conversions above 70% were detected. The selectivity of the desired cinnamyl alcohol as a function of the pressure and reaction temperature is shown in Figure 2.

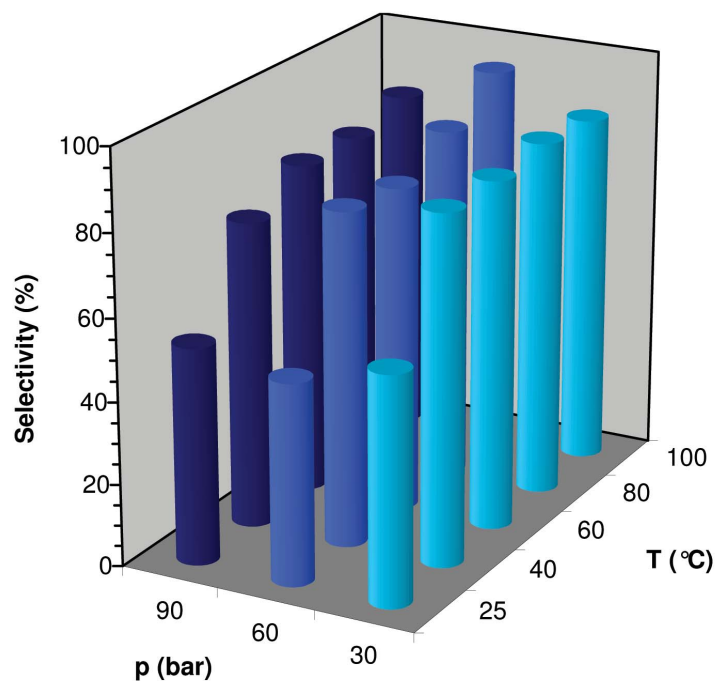


Figure 2.

Selectivity of produced cinnamyl alcohol as a function of temperature and pressure

The figure shows that the effect of pressure on the selectivity of cinnamyl alcohol is hardly observed. On the other hand, increasing reaction temperature favours the formation of the desired unsaturated alcohol product. In reactions at high temperatures, selectivities between 80 and 100% were observed. The formation of by-products, benzene propanol and benzene propanal were also detected.

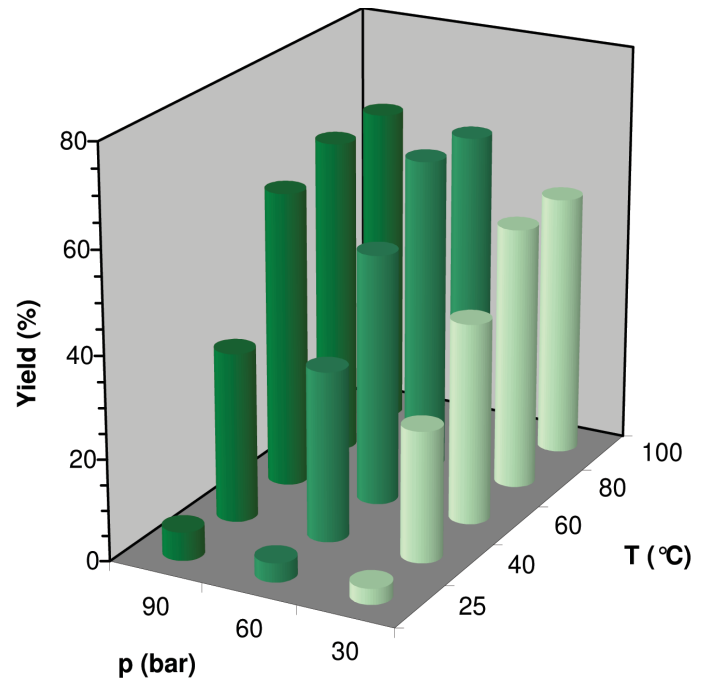


Figure 3.

Yield of cinnamyl alcohol as a function of temperature and pressure

The dependence of product yield on the pressure and reaction temperature is shown in Figure 3. It is clearly seen that the increasing pressure gives higher yield values. The same effect can be obtained when reaction temperature is increased. At high pressures and temperatures yield values above 70% were determined.

OPTIMAL REACTION CONDITIONS

In order to increase the yield, flow rate was reduced stepwise by 0.1 mL/min at the optimal conditions of $T=80^{\circ}\text{C}$ and $p=60$ bar. The highest cinnamyl alcohol yield was observed at $v=0.25$ mL/min. Analysis of the reaction mixtures using GC-MS under these optimal conditions is shown in Figure 4. The conversion was 86.3%, the selectivity towards cinnamyl alcohol was 93% and the determined yield was 60.2%.

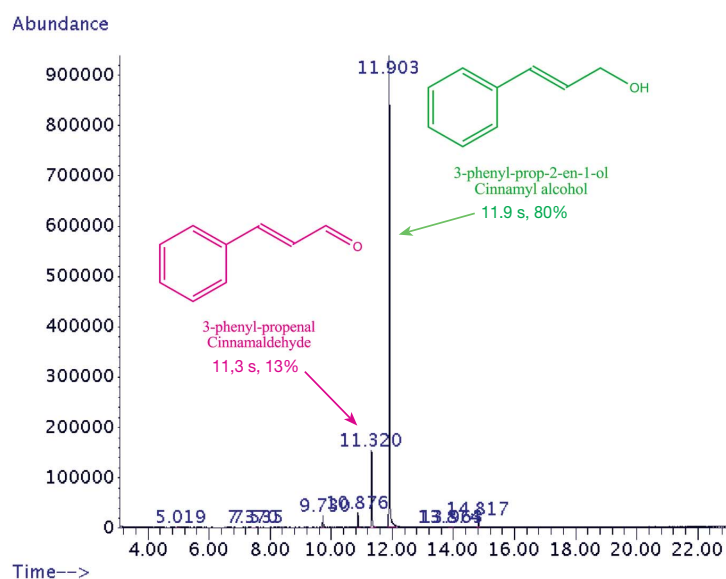


Figure 4. GC-MS spectrum of cinnamaldehyde transformation in an H-Cube® at $T=80^{\circ}\text{C}$, $p=60$ bar, $v=0.25$ mL/min



LITERATURE COMPARISON

The reduction of cinnamaldehyde on the H-Cube[®] was compared with literature batch reactions. In the literature, 40-100% conversions and 50% selectivity of the cinnamyl alcohol were observed^{5,6}.

It is widely accepted in the literature that high pressure is required for the selective hydrogenation of the C=O bond in α - β -unsaturated alcohols^{1,7}. In autoclave reference experiments^{5,6} however, a maximum of 50 bar pressure was applied. Therefore, the applied high pressure, and well-controlled liquid-gas ratio, ensured by H-Cube[®], is responsible for the high selectivity observed.

However, the well-controlled, narrow particle size distribution of Pt on the catalyst surface can be the other reason for the high performance.

CONCLUSION

The results show that the selectivity of the H-Cube[®] flow reactor in the reduction of cinnamaldehyde is substantially higher when compared with the same reaction carried out in batch. The optimal reaction parameters were 80°C and 60 bar giving a conversion of 86.3%, a selectivity of 93% and a yield of 60.2%. The high performance of the catalyst under flow conditions is determined by the well-defined nature of the nanoparticles developed.

The catalyst is a product of ComErgen. CatCarts[®] are available from ThalesNano.

Please check at www.thalesnano.com.

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