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GREEN HYDROGENATION OF AN ALKYNE

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INTRODUCTION

The use of supercritical carbon dioxide (scCO₂) is of interest in the fields of industrial applications, food industry, pharmacy, development of materials and environment. ScCO₂ is particularly attractive for synthesis reaction, because it is an environmentally acceptable replacement to the harmful conventional organic solvents due to its non-toxicity, its non-flammability, its moderate critical parameter and a potentially easy separation. In addition, scCO₂ affords some potential advantages: a complete miscibility with hydrogen, high diffusivity, and good mass and thermal transport properties. A number of heterogeneously catalysed hydrogenations have been successfully carried out in scCO₂, often with higher reaction rates and different product distributions, in comparison with hydrogenations in organic solvents.

The present study is focused on the hydrogenation of an alkyne: 2-butyne-1,4-diol (Fig. 1) which is an important product in fine chemicals as well as its hydrogenated derivatives. This reaction is generally carried out in a triphasic, gas + liquid + solid catalyst system [1-8]. Under these conditions, the gas phase is quite exclusively composed of hydrogen whereas the solvent (aqueous solution or organic solution), reactants and products constitute the liquid phase. The use of catalysts containing noble metals as palladium or platinum makes it possible to work with more flexible operating conditions [2]. Moreover, different side products (n-butyraldehyde, n-butanol) are obtained when the reaction is performed [4]. The present objective is to carry out hydrogenation reaction in a homogeneous (supercritical) medium with carbon dioxide as solvent and palladium as catalyst.

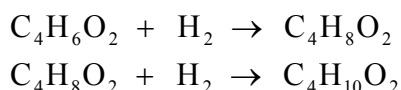


Figure 1: Reactions of interest for the hydrogenation of 2-butyne-1,4-diol.

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MATERIALS AND METHODS

Chemicals. Hydrogen and carbon dioxide were supplied by Air Liquide, with a stated purity of 99.998 mol%. 2-butyne-1,4-diol (purity: $\geq 99\%$), cis-2-butene-1,4-diol (purity: 95%), butane-1,4-diol (purity: $\geq 99\%$), ethanol (purity $\geq 99.5\%$) were supplied by MERCK. Glycerol (purity $\geq 98\%$) was supplied by Prolabo.

Catalyst. 5 % wt. Pd/C catalyst, particle size between 50 and 100 μm .

The hydrogenation experiment of 2-butyne-1,4-diol is performed with an apparatus consisting of a one-litre stainless steel reactor in which it possible to implement reaction until 30 MPa and 473K (Fig.2). The reaction temperature is maintained constant by a circulation of oil in an external jacket connected to a thermostat. A stirrer agitates the mixture (600 rpm). Safety arrangements like rupture disc and high temperature cut-off are also provided.

The hydrogenation of 2-butyne-1,4-diol is carried out at 323.15 K, in the presence of 0.07 g of catalyst. First, the reactor is loaded with the catalyst and the reactive mixture. Then, liquid carbon dioxide is pumped into the reactor up to 18 MPa while the desired reaction temperature is set. A mass flow controller measures the quantity of hydrogen introduced into the autoclave. It is important to stir the mixture while hydrogen is introduced because hydrogen is greatly soluble in carbon dioxide. If the mixture is not agitated during this step, a time evolution of the total pressure only due to the slow mixing of carbon dioxide and hydrogen is observed. Samples are collected in a vial, and bubbled through a measured amount of ethanol.



Figure 2: Photograph of the pilot.

The analysis of the samples is conducted by gas chromatography method. The gas chromatograph is equipped with a 30 m x 0.32 mm internal diameter TR-wax column, and a flame ionization detector. The oven temperature program is: 373.15 K for 1 minute, a ramp to 523.15 K at a rate of 15 K.min⁻¹, and 523.15 K for 3 minutes. The injector and detector temperatures are set to 593.15 and 623.15 K, respectively. Glycerol is used as internal standard for quantitative GC analysis.

RESULTS AND DISCUSSION

Since the autoclave is not equipped with a sapphire window, it is not possible to detect visually the physical state of the reactive mixture. To answer this problem, samples have concurrently been taken from different levels of the reactor (from the top, the middle and the bottom of the reactor). The analyses of the samples allowed us to determine the physical state of the reactive mixture: homogeneous or heterogeneous (vapour and liquid phases).

This work focuses on the investigation of hydrogen concentration influence on the distribution of products obtained from the 2-butyne-1,4-diol hydrogenation under supercritical conditions.

First of all, no side products have been detected during hydrogenation of 2-butyne-1,4-diol in supercritical medium. In all experiments, the distribution profiles of the components are similar (Fig. 3). The 2-butyne-1,4-diol content rapidly decreases. The concentration profile of the 2-butene-1,4-diol admits an extremum. Then, the amount of the intermediate product first increases, passes through a maximum value, and decreases down to zero. The butane-1,4-diol is produced as soon as the reaction begins and its content increases with time. After two hours, 2-butyne-1,4-diol and 2-butene-1,4-diol have quantitatively reacted and the conversion rate into butane-1,4-diol is 100%.

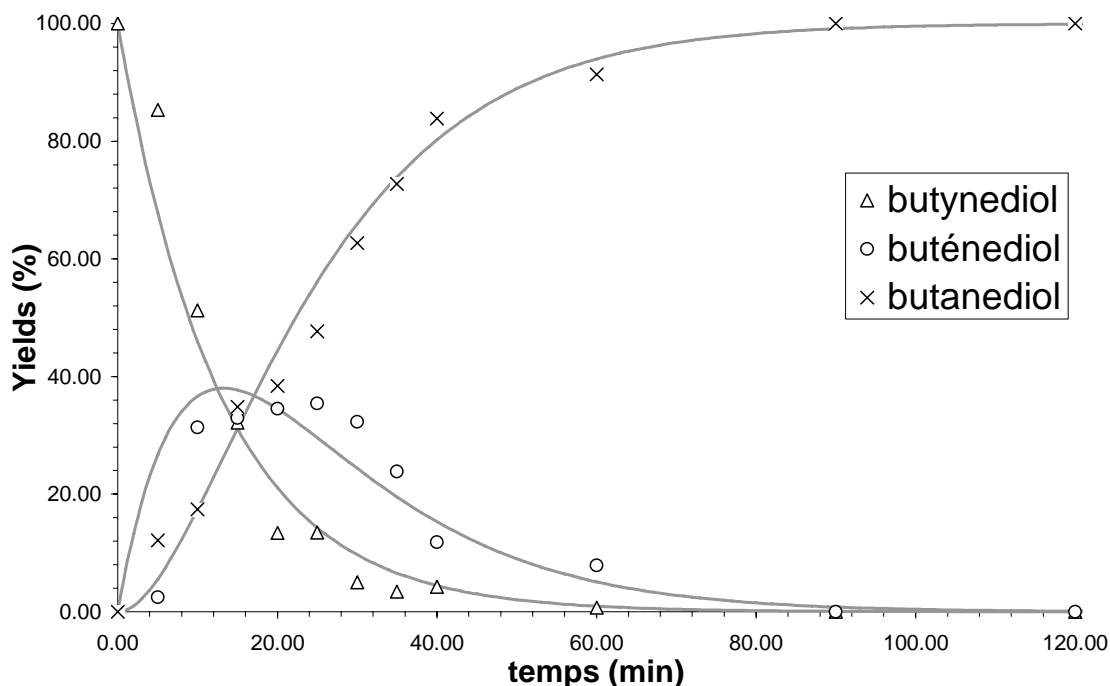


Figure 3: Evolution with time of (\square) butynediol, (\bullet) butenediol and ($+$) butanediol) at 323.15 K and 18 MPa of CO_2 pressure. The initial H_2 content is $2,75 \text{ E-}2$ mol.

The effect of hydrogen concentration on the conversion profiles of 2-butyne-1,4-diol, 2-butene-1,4-diol and butane-1,4-diol was studied over a range from 0.2 to 0.8 MPa and at 323.15 K. In all experiments, the complete conversion into butane-1,4-diol is obtained in less than 2 hours: the higher the hydrogen concentration is, the faster the 2-butyne-1,4-diol reacts. In 20 minutes, only 40% of the 2-butyne-1,4-diol has reacted at the lowest hydrogen pressure, against more than 80% at the highest one. The higher the amount of hydrogen, the faster the butane-1,4-diol formation is. Nevertheless, this effect seems weaker at high concentrations of hydrogen. Experimental butane-1,4-diol concentration profiles are very close when working with a hydrogen concentration greater than 0.056 kmol/m^3 . The effect of hydrogen pressure on 2-butene-1,4-diol concentration profile is similar to the effect on butane-1,4-diol. The coordinate of the extremum is a characteristic point of the profile. Experimentally, when the hydrogen content increases, this point appears sooner, but its value is smaller (see table 1). So, the maximum for the intermediate product content is observed with the minimum hydrogen concentration.

Table 1: coordinate of the extremum in the 2-butene-1,4-diol profile

| Initial Hydrogen pressure (MPa) | Time | Yield (%) |
|---------------------------------|------|-----------|
| 0.2 | 20 | 48 |
| 0.3 | 15 | 39 |
| 0.4 | 12 | 32 |

CONCLUSIONS

The hydrogenation of 2-butyne-1,4-diol has been carried out in an homogenous medium catalysed by carbon-supported palladium. The solvent of the reaction was high pressurised carbon dioxide. The experimental results obtained in this work show that no side products are detected and the conversion to butane-1,4-diol is complete in a maximum of two hours. Moreover, the influence of the hydrogen concentration on the reaction was investigated. The higher the hydrogen concentration, the shorter the reaction time for the overall conversion to the final product is. In addition, the time of total conversion is shorter when the hydrogen concentration increases. However, the maximum of the intermediate product, 2-butene-1,4-diol, is observed for the minimum hydrogen concentration. Even if it is difficult to compare our results with those obtained in biphasic mixture, because the conditions (pressure and temperature levels, catalysts...) are different, it seems that the reaction velocity is higher in supercritical media.

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