

BIPHASIC HYDROGENATION AND ISOMERISATION OF TERPENES IN SUPERCRITICAL CARBON DIOXIDE

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Terpene + supercritical carbon dioxide (scCO₂) systems are interesting model systems to determine the factors that control heterogeneous catalysis in biphasic vs. monophasic conditions. Based on this idea, hydrogenation and isomerisation of different terpenes with carbon-supported catalysts was performed in the presence of high-pressure carbon dioxide. Experiments were performed at different carbon dioxide pressures, so that the reaction mixture would be either two-phase (liquid + gas) or one (supercritical) phase.

INTRODUCTION

For reactions involving gaseous reactants, supercritical solvents present specific advantages, due to a high mutual miscibility, over common liquid solvents. However, CO₂ is a poor solvent of most liquids, thus, reactions must be performed under biphasic (liquid-gas) conditions. In general, scCO₂ is highly soluble in most terpenes: at pressures close to the critical pressure, the liquid phase in a biphasic mixture may contain 80 mol% or more of CO₂. Moreover the critical pressures of these mixtures are reasonably low, often lower than 10 MPa. There is also a large body of published research on phase behaviour and mechanisms are well known.

Herein we report studies of the catalytic hydrogenation of α -pinene and isomerisation of R-limonene in scCO₂, using a carbon-supported platinum catalyst and a carbon-supported molybdenum catalyst respectively. CO₂ pressures corresponding to biphasic and monophasic conditions were chosen. The technique involves the use of a high-pressure view cell, which allows direct visual observation of the number of phases in the reactor.

I - MATERIALS AND METHODS

The catalyst used for hydrogenation was based on Pt (1%) supported on carbon (Nobel method). It was prepared by wet impregnation [1], followed by reduction with H₂ at 720K. The catalyst used for isomerisation was based on Mo (5%) also supported on carbon and prepared by wet impregnation, followed by oxidation with N₂O at 773K.

Hydrogen, oxygen and carbon dioxide were supplied by Air Liquide, with a stated purity of 99.998 mol%. α -Pinene (purity: 99%), cis-pinane (purity > 99%), R(+)-limonene (purity: 98%) were supplied by Fluka.

Hydrogenation

Experiments were carried out at 50°C, in a newly built apparatus. This apparatus consists essentially of two cells connected by a pump. The first cell is a sapphire-windowed reactor (New Ways of Analytics), with an internal volume of approximately 50 cm³. This reactor is provided with a magnetically driven stirrer and anchor for efficient mixing of the components (max. speed: 2500 rpm), as well as a large sapphire window (diameter: 36 mm, thickness: 16mm). The temperature control is achieved by means of a PID controller (*Eurotherm 2216e*) connected to a Pt-100 probe located in the reactor and two 100 W-resistance inserted in the reactor walls. The pressure inside the reactor is measured with a pressure transducer (*Setra C204*). The second cell is the actual chemical reactor. It is a short tube, which encloses a catalyst bed. Electrical heating wire is wrapped around the tube, also connected to a controller and a Pt 100 temperature sensor. The reactants are continuously withdrawn from the bottom of the view cell by a high-pressure piston pump, circulated through the catalyst bed, and sent back to the upper entrance of the first cell. A liquid chromatography valve at the outlet of the reactor may be used to sample from the re-circulation loop, right after the reactants pass through the catalyst.

Reaction experiments were performed at 50°C (set at the beginning), using 2ml α -pinene and about 0.4 g of catalyst. Hydrogen at pressures between 10 MPa and 11 MPa was circulated through the catalyst cell about 15 h before each reaction run. Samples are taken at regular intervals through the valve into a sampling loop. The carbon dioxide in the loop is then carefully vented to the atmosphere and the remaining solutes washed with hexane. The product/reagent ratio was measured by gas chromatography. The concentrations of α -pinene and of pinane in the collected samples are determined using dodecane as the internal standard.

Isomerisation

Reaction experiments were carried out in the apparatus described above at 50°C, using 1 ml of R-(+) limonene and about 0.4g of catalyst. Samples were also taken at regular intervals into the sampling loop following the same procedure as for the hydrogenation reactions. The product/reagent ratio was measured by gas chromatography using dodecane as internal standard.

II - RESULTS

Hydrogenation

The hydrogenation of α -pinene to pinane, catalysed by palladium and platinum supported on carbon was previously studied within the group. Both Chouchi *et al.*[2] and Milewska *et al.* [3] obtained faster hydrogenation of α -pinene at lower pressures of carbon dioxide, when a biphasic

(vapour + liquid) system and solid catalyst were present (Figure 1). The difference in reaction rates was, however, much larger in the case of the palladium catalyst.

New results obtained in this work with platinum-based catalysts have shown that the reaction rates are highly dependent on the distribution of platinum on the carbon surface. Therefore, when the catalyst was badly dispersed and the Pt was mainly on the surface of the carbon, high reaction rates were obtained for the hydrogenation of α -pinene. On the contrary, when the Pt was largely in the pores of the carbon (good dispersion), very low conversions were observed. This might be an indication that the kinetics is controlled by the adsorption of α -pinene to the catalyst active sites. On the contrary, there are no mass transfer limitations for hydrogen, even in biphasic conditions.

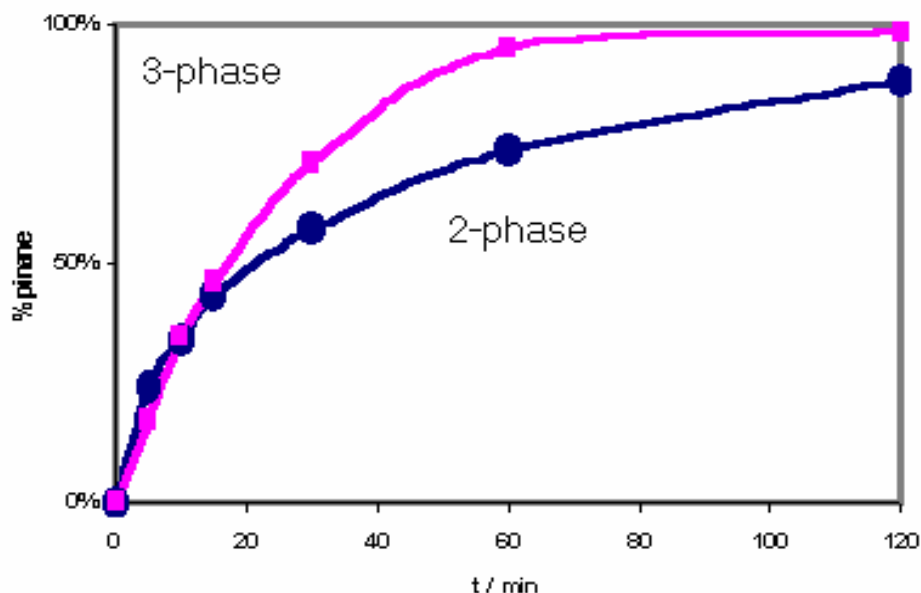


Figure 1: Hydrogenation of α -pinene, using 4 MPa of H_2 and at two different pressures of CO_2 :
| 8.5 MPa, corresponding to biphasic conditions; ? 14 MPa, corresponding to one phase.

Isomerisation

The isomerisation of limonene to α -terpinolene, catalysed by a molybdenum carbon-supported catalyst, was studied at 50°C. The reaction was carried out under different conditions, in order to analyse the influence of some reaction parameters like: CO_2 pressure and substrate concentration.

First of all the CO₂ pressure effect was studied. Completely opposite results to the hydrogenation of α -pinene were observed, meaning that the reaction was found to be faster in one supercritical phase than in biphasic conditions. The reaction occurred very fast and the difference in rates is quite remarkable during the first hour of reaction.

The amount of substrate added into the view cell is a factor to take into consideration. A lower concentration of limonene gave better yields to the main product. This could be explained by the fact that probably the catalyst is deactivating along the reaction by metal leaching.

Furthermore, this reaction was initially tested for the oxidation of limonene with molecular oxygen and to our surprise, the molybdenum oxide catalyst was found to be a very good catalyst for the isomerisation of limonene but not for its oxidation.

As for the product selectivity, in this particular case, the reaction is highly selective (>95%, quantified by gas chromatography) to the main reaction product, α -terpinolene.

CONCLUSION

For the hydrogenation of α -pinene it was observed that the reaction was faster in 3-phase (solid catalyst + liquid + gas) than in 2-phase (solid catalyst + supercritical mixture) conditions. The explanation given was based on the possibility that the limiting step for the catalysis might be the access of α -pinene, and not hydrogen, to the catalyst.

The latter is also confirmed with the results obtained for the hydrogenation of α -pinene showing that the reaction rates were high only when the platinum was badly dispersed on the carbon. Hence, α -pinene could easily access the metal (Pt) and catalysis could occur.

In the case of isomerisation of limonene, the results showed that the reaction is faster in one supercritical phase than in biphasic conditions and that is fast and selective to one major product (α -terpinolene).

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