

BIPHASIC HYDROGENATION AND OXIDATION OF TERPENES IN SUPERCRITICAL CARBON DIOXIDE

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Hydrogenation and oxidation with dioxygen of different terpenes with carbon-supported catalysts was carried out 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. The technique involves the use of a high-pressure view cell, which allows visual observation of the number of phases in the reactor.

INTRODUCTION

Supercritical fluids are especially attractive solvents for reactions involving gaseous reactants, due to a high mutual miscibility. In many cases, however, other reactants are poorly soluble in the fluid, and the reactions must be carried out in biphasic conditions.

Terpenes + supercritical carbon dioxide (scCO₂) systems are interesting model systems to determine the factors that control heterogeneous catalysis in biphasic vs. monophasic conditions: well-known reaction mechanisms, scCO₂ highly soluble in most terpenes, critical conditions readily accessible (critical pressures often < 10 MPa), and a large body of published research on phase behaviour.

Herein we report studies of the catalytic hydrogenation of α -pinene and oxidation of limonene in supercritical CO₂, 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 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, followed by reduction with H₂ at 720K. The catalyst used for oxidation 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%) and (\pm)-linalool (purity: 97%) 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 323K, using 2ml α -pinene and about 0.4 g of catalyst. Hydrogen at pressures between 100 bar and 110 bar was circulated through the catalyst cell about 15h 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 an internal standard (response factor for α -pinene: 0.90; response factor for pinane: 0.81).

Oxidation

Reaction experiments were carried out in the apparatus described above at 323K, using 1 ml of R-(+) limonene and about 0.4g of catalyst. Samples were taken also 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 (response factor for R-(+) limonene: 0.83; response factor for linalool: 0.81).

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.[1] and Milewska et al. [2] obtained faster hydrogenation of α -pinene at lower pressures of carbon dioxide, when a biphasic (vapour + liquid) system and solid catalyst were present. 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 inside the catalyst pellets. 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.

Oxidation - Reaction Kinetics

The oxidation of limonene with dioxygen, 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: CO₂ pressure, O₂ pressure and substrate concentration.

Two different CO₂ pressures were used, 180 bar and 90 bar corresponding to one-phase and two-phase respectively. These conditions were verified by visual inspection of the reaction mixture in the view cell, and were kept in the presence of oxygen and during reaction time. Completely opposite results to the hydrogenation of α -pinene were observed, meaning that the reaction is faster in one supercritical phase than in biphasic conditions. In this case we may well have some mass transfer problems when the reaction is taking place in two phases due to oxygen being heavier compared to hydrogen.

The effect of O₂ pressure was also examined (Figure 1). The reaction is fast with very low pressure of oxygen (1.5 bar). At higher pressure of O₂ (11.5 bar) the reaction becomes clearly slower.

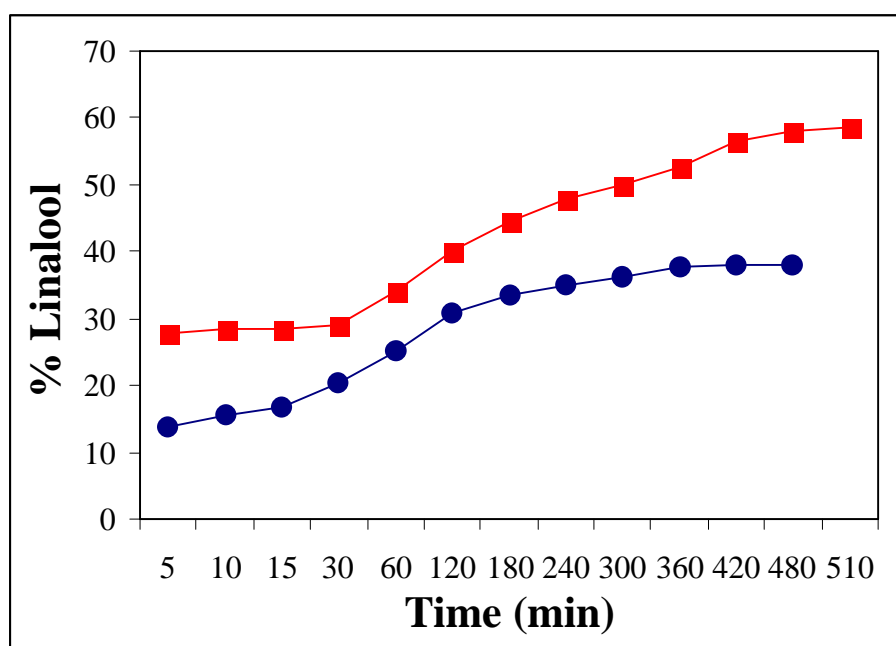


Figure 1: Results for the oxidation of limonene, using 180 bar of CO₂ and two different pressures of oxygen: ■ 1.5 bar, ● 11.5 bar.

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

Oxidation - Product Selectivity

Linalool is the key material for production of a wide variety of fragrance compounds such as geraniol, nerol, cytral and its derivatives, as well as for Vitamins A and E synthesis [3]. In this particular case the reaction is highly selective (>95%, quantified by gas chromatography), to the main reaction product, linalool.

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 by the authors 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.

In the case of oxidation of limonene, the results show that the reaction is faster in one supercritical phase than in biphasic conditions and that the oxygen pressure is a very important factor to take into account.

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