HOMOGENEOUS CATALYSIS IN SUPERCRITICAL CARBON DIOXIDE IN A CONTINUOUS FLOW PROCESS

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A modified Wilkinson catalyst is studied for hydrogenation reactions in supercritical carbon dioxide ($scCO_2$). In this work, the hydrogenation of 1-octene is used as a model reaction. Batch experiments are carried out to determine the kinetics for which the catalyst is prepared in situ from the Rh-precursor and fluorous version of the ligand. The catalyst is a Wilkinson-type Rh-complex with triphenylphosphine ligands. It is known that the phosphine ligand to rhodium molar ratio has an influence on the rate of hydrogenation. For the hydrogenation carried out in $scCO_2$ the optimum phosphine ligand to rhodium ratio is considerably higher than 2:1. The kinetic results will be used to determine the optimal conditions for a continuous membrane process.

1   INTRODUCTION

The use of $scCO_2$ as a solvent in a homogeneously catalyzed continuous flow process can offer a number of advantages, as compared to traditional production methods. The catalyst, gaseous and liquid reactants can be solubilised to a one-phase system in $scCO_2$. Furthermore, because of the good miscibility of gases with $scCO_2$ one has a direct way to influence the concentrations of reactant gases like H_2, CO and O_2. These aspects make $scCO_2$ an ideal solvent for continuous operation in combination with homogeneous catalysis. Important issues for successful application of homogeneous catalysis in $scCO_2$ are the solubility and the recycling of the homogeneous catalyst.

The phase behaviour of a solution of gaseous and liquid reactants and a solid catalyst in CO_2 differs from that of pure CO_2. This has been demonstrated for the hydrogenation and hydroformylation of propene in $scCO_2$ [1,2]. Organic liquids tend to have a co-solvent effect improving the overall solubility. Low molecular weight gases decrease the overall density of a supercritical system and, in general, this results in an anti-solvent effect.

This work is a continuation of the work in which 1-butene was hydrogenated to *n*-butane with a fluorous derivative of the Wilkinson catalyst in a continuous flow membrane reactor [3,4]. The catalyst, $RhCl\{P[C_6H_4\text{-}p\text{-}Si(CH_3)_2CH_2CH_2C_8F_{17}]_3\}_3$, which was developed by Richter et al. [5] had a size of 2-4 nm and was therefore retained by the microporous silica membrane which had an average pore diameter of less than 1 nm. The solubility of the catalyst was monitored by UV-vis spectrometry.

During the homogeneous catalytic cycle the ligand will dissociate from and associate with the metal centre. Therefore, it is important that both the metal-complex and ligand stay in the system. Changing the size and the degree of "CO_2-philicity" of the ligand has an effect

on the retention by the membrane and on the activity of the catalyst complex as a whole. Common transition metal complexes generally do not dissolve that well in $scCO_2$. For example, the Wilkinson's catalyst, $Rh(PPh_3)_3Cl$, has a solubility of less than 10^{-5} mol/L at 323 K and 100 bar [6]. However, exchanging the low soluble triphenylphosphine with ligands with perfluoroalkyl groups improves the overall solubility of the metal complex substantially [7]. Considering the ligand, tris(p-trifluoromethylphenyl)phosphine has a 80 times higher solubility than triphenylphosphine at 320 K and 120 bar [8].

Here preliminary results are presented of batch kinetics experiments for the hydrogenation of 1-octene catalyzed by a in-situ prepared fluorous version of the Wilkinson's catalyst, $RhCl\{P[C_6H_3\text{-}3,5\text{-}CF_3]_3\}_3$, using a high-pressure variable volume optical cell. In particular, the effect of the phosphine to rhodium (L:Rh) ratio on the kinetics was studied. The variable volume high-pressure reactor makes convenient sampling possible without a pressure drop in the reactor and without a considerable change in the concentrations of the reactants.

2   EXPERIMENTAL

The gases used, hydrogen, carbon dioxide and argon were all supplied by Hoekloos and had a purity of 99.999%, 99.99% and 99.999% respectively. 1-Octene 98% was obtained from Aldrich and was degassed and kept under argon. CO_2 was further purified using a Messer Oxisorb filter to minimize the oxygen concentration. Chloro(1,5-cyclooctadiene)rhodium(I) dimmer, 98% purity from Aldrich was used as received. The phosphine, $P[C_6H_3\text{-}3,5\text{-}CF_3]_3$, was kindly provided by M.C.A. van Vliet (ATOFINA Vlissingen B.V.), and used as received. Both catalyst precursors were stored under argon.

A typical hydrogenation experiment was started by rinsing the optical cell, from SITEC, with argon. The rhodium and phosphine precursors, corresponding to overall concentrations of 4×10^{-4} and 1.2×10^{-3} mol/L respectively, were weighted in the reactor under an argon flow. In all the experiments the concentration of rhodium was kept constant, while the concentration of phosphine was varied. Assuming complete solubility, the maximum concentration of the catalytic complex is 4.0×10^{-4} mol/L. The reactor was closed and evacuated and rinsed with argon. Subsequently, the cell was filled with hydrogen to achieve a concentration of 0.4 mol/L. The reactor was heated electrically to a temperature of 323 K. CO_2 was pumped into reactor up to a pressure of 150 bar. Then the volume of the cell, which can be varied between 11 and 25 mL, was reduced by applying CO_2 pressure on the piston to establish a pressure of 200 bar. The cell was kept at these conditions for 2 h. The volume was then restored to its maximum and the cell was allowed to cool down to ambient temperature. The catalyst was kept overnight under stirring. Before adding 1-octene the cell was heated till 323 K and pressurized to 200 bar by reducing the volume. After 1 h, 1-octene with a concentration of 0.1 mol/L was fed into the reactor with CO_2 to a total pressure of approximately 230 bar at a volume of 25 mL.

Samples were taken using a VALCO 6-port sampling valve equipped with a 250 μL sample loop. The sample volume was bubbled through a hexane solution, which was subsequently analyzed using a Fisons Instruments gas chromatograph equipped with a FID detector and a Restek Rtx-5 column.

3 RESULTS AND DISCUSSION

Figure 1 depicts a typical concentration profile for 1-octene and its reaction products as function of time. In addition to the hydrogenation of 1-octene to *n*-octane also the isomerisation of 1-octene occurs. The sampling and analyzing method seems to be accurate if one looks at the total concentrations obtained. In general, during the reaction a clear yellow/orange phase is observed, which indicates good solubility of the metal-complex. The total concentration of 1-octene and its products from the samples corresponds nicely with the concentration based on the quantity of 1-octene of volume introduced in the reactor. This is a good indication, together with the visual observation of the colour, that the reaction took place in a one-phase supercritical system. The 1-octene dissolves almost instantly upon introduction in to the cell and the reaction starts almost immediately. The first sample shows a slightly smaller total concentration as compared to the samples taken at later times.
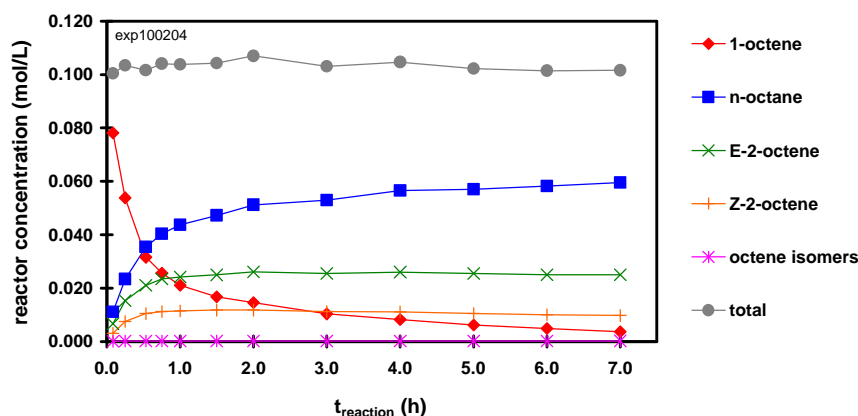

Figure 1: Concentration profile of a typical hydrogenation experiment at 323.2 ± 0.7 K and 230 ± 4.5 bar. Amount of 1-octene used was 0.2817 g; with a hydrogen pressure of 9.6 bar at 295 K; 2.5×10^{-3} g Rh-precursor (MW = 493.1 g/mol) and 20.2×10^{-3} g of phosphine ligand (MW = 670.28 g/mol).
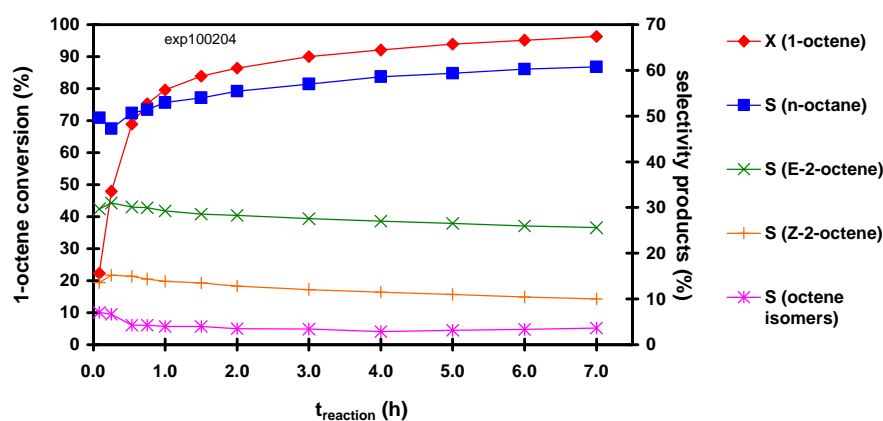

Figure 2: Conversion (X) and selectivity (S) at the same conditions as given in Figure 1.

For the homogeneously catalysed hydrogenation the selectivity, after 7 h of reaction, for *n*-octane, E-2-octene and Z-2-octene are: 60.8%, 25.6% and 10%, respectively (see Figure 2). These results for the selectivity show good agreement with values reported for the

hydrogenation of 1-octene in scCO$_2$ using a Wilkinson-type catalyst with ligands grafted on a fluoroacrylate copolymer [9].

For the hydrogenation of cyclohexene dissolved in benzene with the Wilkinson catalyst with various phosphine ligands there is an optimum in the reaction rate as a function of the L:Rh ratio [10]. In this case, the optimum phosphine to rhodium ratios is about 2:1, which is mainly determined by the re-association equilibrium. An excess of ligand inhibits the reaction, which is also reported by Duckett et al. [11]. For the homogeneously catalysed hydrogenation of 1-octene in scCO$_2$ the optimum L:Rh ratio is clearly larger than 2:1. As compared to the hydrogenation in benzene, besides the equilibrium between the different species also the solubility in the scCO$_2$ might affect the reaction rate.

4   CONCLUSION AND OUTLOOK

Hydrogenation and isomerisation of 1-octene using a fluorous variant of the Wilkinson's catalyst was carried out successfully. The ligand to rhodium ratio (L:Rh) has a significant influence on the rate of the reaction. All reactants and the catalyst were solubilised to one supercritical phase. The investigated conditions are therefore suitable for continuous operation. The retention for the ligand as compared to that of the reactants has to be determined, to establish whether the ligand is suitable for a continuous flow process.

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