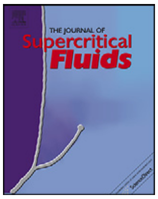
J. of Supercritical Fluids 46 (2008) 47–56

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu



Evaluation of pressure and correlation to reaction rates during homogeneously catalyzed hydroformylation in supercritical carbon dioxide

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ARTICLE INFO

Article history:
Received 21 August 2007
Received in revised form 21 February 2008
Accepted 27 February 2008

Keywords:
Supercritical carbon dioxide
Hydroformylation
Homogeneous catalysis
1-Octene
Phosphine ligand
Rhodium catalyst

ABSTRACT

For the hydroformylation of 1-octene in supercritical carbon dioxide the relationship between the change in pressure and the change in reaction mixture composition as a function of time has been investigated. The activity and selectivity has been studied for the catalyst based on tris(3,5-bis(trifluoromethyl)phenyl)phosphine and rhodium(I) dicarbonyl acetylacetonate. The influence of the ligand to rhodium ratio on the hydroformylation has been used to demonstrate how the pressure can be correlated to the conversion and yield. The initial rate of reaction is in good agreement with the initial pressure change in the batch reactor. Up to an aldehyde yield of 80%, the pressure drop appears to be independent of the reaction rate and selectivity. The highest average reaction rate, 7170 $\text{mol}_{\text{1-octene}}\ \text{mol}_{\text{Rh}}^{-1}\ \text{h}^{-1}$, has been obtained for a ligand to rhodium ratio of 50 and an initial concentration of 1-octene of 0.5 $\text{mol}\ \text{L}^{-1}$. Both the reaction rate and the selectivity increase when the ligand to rhodium ratio is increased. The Peng–Robinson equation of state has been used to describe the pressure as a function of the concentration of the reactants and products. The calculated pressure corresponds reasonably well with the observed reactor pressure. Following the progress of the reaction by monitoring the pressure is a good alternative to reaction mixture sampling, especially for fast reactions.

1. Introduction

Hydroformylation of alkenes using homogeneous catalysts has been successfully operated commercially for decades. The catalysts are organometallic complexes of rhodium or cobalt, commonly with phosphines or phosphites as modifying ligands, which are used to convert an alkene, hydrogen, and carbon monoxide into an aldehyde product. Rhodium is generally more active and selective in hydroformylation than cobalt and allows a lower working pressure and temperature [1].

The use of supercritical fluids in homogeneously metal catalyzed reactions can offer advantages over commonly applied organic solvents including, a high solubility of reactant gases like hydrogen, carbon monoxide and oxygen, the possibility to create a one phase system resulting in the absence of phase boundaries, and "tunability" of solvent characteristics. Carbon dioxide is most commonly used as a "supercritical solvent" and is regarded as an environmentally benign alternative to organic solvents due to its low toxicity and nonflammability. Furthermore, the use of supercritical fluids provides different possibilities to integrate (or to reduce the number of) reaction and separation steps [2,3]. However, to follow the progress of reactions in supercritical fluids by sampling requires, in general, careful and time-consuming procedures. Therefore, sampling as a function of reaction time is usually omitted, and the catalyst performance in terms of activity and selectivity is obtained from the product composition after cooling down and depressurizing at the end of the experiment.

For hydroformylation in supercritical carbon dioxide ($scCO_2$) the pressure will change under isothermal, isochoric conditions as a result of the conversion of the reactants [4]. Thus, similar to other in situ methods, like UV–vis or infrared spectroscopy [2], monitoring the pressure can provide on-line information about the reaction.

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doi:10.1016/j.supflu.2008.02.012

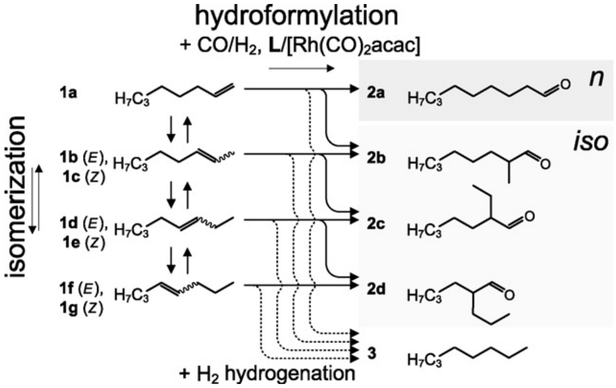

Fig. 1. Reaction scheme for the hydroformylation of 1-octene (**1a**), with the two main products *n*-nonanal (**2a**) and 2-methyloctanal (**2b**). The side products are (*E*, *Z*)-2-octene (**1b**, **1c**), (*E*, *Z*)-3-octene (**1d**, **1e**), (*E*, *Z*)-4-octene (**1f**, **1g**), 2-ethylheptanal (**2c**), 2-propylhexanal (**2d**), and *n*-octane (**3**).

One of the first examples of hydroformylation performed in carbon dioxide rich supercritical mixtures has been monitored using NMR [5]. For polymerization reactions performed in the presence of CO_2 the conversion has been determined by measuring the pressure in combination with detailed knowledge of the thermodynamic behavior of the different reactants, products and solvent involved [6–8].

Hydroformylation performed in carbon dioxide rich supercritical media has been studied extensively during the past decade [2d] with the hydroformylation of propene among the earliest examples [5a,9]. However, in literature little attention has been given to what extent the development of the pressure during the reaction can give information about the course of the reaction. In this work, the relation between the reaction progress obtained by sampling the reaction mixture and the online measured pressure is investigated for the hydroformylation of 1-octene in $scCO_2$ using an in situ prepared catalyst based on rhodium(I) dicarbonyl acetylacetonate and tris(3,5-bis(trifluoromethyl)phenyl)phosphine. The reaction scheme is depicted in Fig. 1.

The pressure as a function of time will be correlated to the composition of the mixture in two ways. First, the initial reaction rate will be correlated to the (initial) change in pressure by comparing the slope of the yield profile with the slope of the pressure profile. Second, the pressure for a given composition will be calculated using the Peng–Robinson equation of state (P–R EOS) [10] and the calculated pressure will be compared to the experimentally determined pressure. Previously the P–R EOS has been used to predict the regioselectivity for the hydroformylation of propene in $scCO_2$ [11]. For the hydroformylation of propene and the allylic epoxidation of *trans*-2-hexen-1-ol, both with CO_2 as the solvent, the P–R EOS has been used to predict the phase behavior [12,13].

2. Experimental

2.1. Materials

Carbon dioxide, carbon monoxide, and hydrogen, grade 5.0, 4.7 and 5.0, respectively, were obtained from Hoekloos (The Netherlands). Prior to use CO_2 was passed over a Messer Oxisorb filter to remove oxygen and moisture. 1-Octene, **1a**, obtained from Aldrich, was passed over activated alumina, dried with pre-treated molsieves 3A (Aldrich, 4–8 mesh), and stored under argon.

The rhodium precursor, rhodium(I) dicarbonyl acetylacetonate, ($[Rh(CO)_2acac]$), was obtained in the form of dark green crystals from Fluka. Tris(3,5-bis(trifluoromethyl)phenyl)phosphine, Ligand **I**, is a white to light yellow solid and was supplied by Arkema (Vlissingen, The Netherlands). All catalyst precursors were stored under argon and manipulated using Schlenk techniques.

The solvent toluene (Merck, analytical grade), the internal standard *n*-decane (Aldrich, >99% purity) and the substances involved in the reaction, *n*-octane (Aldrich, >99%), 2-octene (ABCR, mixture of *E* and *Z*, 98%) and nonanal (Fluka, >95%) used for the GC-analysis were used as received.

2.2. High pressure setup

The stainless steel (AISI 316/316L) reactor (custom built Janssen Engineering), depicted in Fig. 2, was designed to withstand a maximum working pressure of 60 MPa at a maximum working temperature of 150 °C. Stirring was achieved with a magnetic stirrer head (Premex Minipower) equipped with a Rushton type turbine impeller (Janssen Engineering). Carbon monoxide and hydrogen were dosed through two mass flow controllers (Bronkhorst EL-Flow) independently or together up to a pressure of 9 MPa. CO_2 was fed to the reactor by a syringe pump (Thar Technologies SP300-2, FP1); the substrate 1-octene was added with a manual operated syringe pump (Sitec, FP2). The pressures of the reactor and the manual syringe pump for reactant feed were monitored with calibrated pressure transducers (Kulite HKM-375, accuracy ±0.07 MPa). The total reactor volume was composed of the reactor volume (102.7 mL), the tubing connecting the sample volume and the sample pump (1.2 mL), and the variable volume of the sample pump (1.6–5.6 mL, Sitec, SP).

The risks involving the use of flammable hydrogen, toxic and flammable carbon monoxide and flammable organic liquids in combination with high pressure were extensively assessed and the appropriate safety measures were taken.

2.3. Hydroformylation in $scCO_2$

The general procedure for a hydroformylation experiment was started by charging the desired amounts of $[Rh(CO)_2acac]$ and the phosphine ligand into the empty reactor and closing the reactor. The reactor volume was then carefully flushed with argon and subsequently evacuated for three times. Next, the stirring was turned on with a revolution speed of 700 rpm and the desired amount of carbon monoxide and hydrogen gas was fed to the reactor at room temperature. The reactor content was then heated electrically to a temperature of 50 °C and consecutively CO_2 was charged into the reactor at a constant flow up to a pressure of about 26 MPa. These conditions were maintained for at least 0.5 h before heating further to the desired reaction temperature. In total a period of about 1 h was considered sufficient to allow the active catalyst complexes to be formed in situ from $[Rh(CO)_2acac]$ and **I**. The reaction was started by the addition of the alkene, which was done by opening the valve between the pump and the reactor. A fast pressure equalization occurred and consecutively the desired volume of **1a** was pumped into the reactor, which as a rule did not take more than 30 s. During reaction the temperature was maintained at 70 ± 0.5 °C.

Three different L:Rh ratios were applied: 4:1, 10:1 and 50:1. These experiments were done in duplicate. One experiment was carried out in which no phosphine ligand was applied. In one of the experiments using L:Rh = 4:1 only one sample was taken after 3 h of reaction.

2.4. Sampling during batch reaction in supercritical carbon dioxide

First the contents of the tubing connecting the sample volume (SV) and reactor (R) was rinsed with a small volume high-pressure