



Reaction integrated separation of homogenous catalysts in the hydroformylation of higher olefins by means of organophilic nanofiltration

Markus Priske^{a,*}, Klaus-Dieter Wiese^b, Anja Drews^c, Matthias Kraume^c, Goetz Baumgarten^a

^a EVONIK Degussa GmbH, Paul Baumann-Straße 1, 45764 Marl, Germany

^b EVONIK Oxeno GmbH, Paul Baumann-Straße 1, 45764 Marl, Germany

^c Technische Universität Berlin, Fachgebiet Verfahrenstechnik, Straße des 17. Juni 136, 10623 Berlin, Germany

ARTICLE INFO

Article history:

Received 30 June 2009

Received in revised form 21 April 2010

Accepted 1 May 2010

Available online 8 May 2010

Keywords:

Organophilic solvent-resistant nanofiltration
Hydroformylation
Catalyst recycling

ABSTRACT

Discovered in 1938, hydroformylation is one of the most important reactions using homogeneous precious metal catalysts. In the process, olefins react to aldehydes using hydrogen and carbon monoxide (synthesis gas). The main problem for the sensitive and expensive catalyst system, however, is the downstream processing of the reaction products, typically done by thermal separation, by which the catalyst system deactivates and is lost by clustering. In contrast, organophilic nanofiltration allows the catalyst to be separated under stabilizing conditions in a gentle and also energy saving way. As a first step to an integrated membrane reactor concept for homogeneous catalysis, two different membranes and the influence of CO on the separation were investigated for the Rh catalysed hydroformylation of octene and dodecene as examples. Catalyst rejections in excess of 99% in a single stage membrane separation combined with a high CO partial pressure that prevents the catalyst from deactivation and losses through the formation of clusters during the separation shows that organophilic nanofiltration can be a benchmark setting separation technology in homogeneous catalysis.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Hydroformylation, discovered by Roelen in 1938 [1], is the reaction of an alkene with synthesis gas in the presence of a homogenous transition-metal catalyst to produce an aldehyde (Fig. 1).

The reaction takes place at the double bond of the alkene. Linear or branched aldehydes will arise, depending on the carbon atom of the double bond at which the reaction takes place.

The catalysts used have a metal centre, usually consisting of rhodium or cobalt, with rhodium having the highest activity. If other ligands besides H₂ and CO are coordinated around the metal centre, the catalyst is called a ligand-modified catalyst. Phosphine and phosphite ligands are used in technical applications [2].

The worldwide production capacity of hydroformylation products is 8 million tons per year [3]. Aldehydes are intermediate products for manufacturing carboxylic acids, especially amines and alcohols. Applications are extensive, ranging from surfactants for the detergent industry and plasticizers for the plastics industry to the manufacture of polyesters, synthetic resins and lubricants [4]. Moreover, branched aldehydes produced through asymmetrical hydroformylation play a key role in the syn-

thesis of chiral building blocks for pharmaceuticals, flavouring agents, and aromatic principles. One of the ways Evonik uses hydroformylation with rhodium catalysts is in a patented process for converting dodecene to isotridecanal, a high-boiling aldehyde essential for the manufacture of special surfactants [5].

In rhodium catalysed hydroformylation processes, it is essential that the rhodium catalyst be recovered because of the very high price of rhodium. Currently the 12-month average is about €160/g [6]. Two-phase processes utilizing mixer-settler or stripper with high rhodium retention, like the low-pressure oxo process (LPO) or the Ruhrchemie/Rhône Poulenc process, can be used only for short-chain alkenes. For macromolecular alkenes, the use of a thermal separation stage has so far been state of the art [7].

The biggest problem for the sensitive catalyst system, however, is the irreversible destruction of the catalyst during thermal separation of the reaction products [8]. Fig. 2 shows how metal carbonyls cluster under thermal separation conditions. Particularly in the high-molecular system discussed here, almost no CO remains after high-vacuum distillation, and at the same time, high temperatures are required for the separation.

The conditions in the thermal separation stage are harmful to the catalyst system, so that the catalyst irreversibly precipitates onto the apparatus walls as metallic rhodium [8]. The clustering model shown in Fig. 2 describes this process.

* Corresponding author. Tel.: +49 2365 49 4972; fax: +49 2365 49 804972.

E-mail addresses: markus.priske@evonik.com, priske@gmx.net (M. Priske).

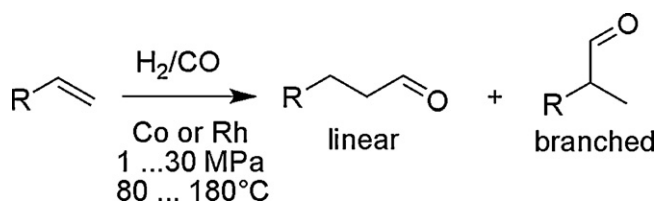


Fig. 1. Basic hydroformylation reaction.

In the reaction mixture, the dirhodium(octacarbonyl) complex formed under synthesis gas from the catalyst precursor, a stable preform of the catalyst. The actual active monomolecular hydride complex forms under high CO pressure and at low temperature. In contrast, low CO pressure and a high temperature results in the formation of larger clusters up to the precipitation of metallic rhodium. Thermal separation at high CO pressure and low temperature is not possible. Things are different in organophilic nanofiltration. In this case, the separation can take place under conditions optimized for the catalyst system.

Nanofiltration (NF) is an established membrane process in water treatment for the removal of multivalent ions – for example, water softening or desalination of dyes in water-based process industry applications [9]. These successes inspired researchers in 1970s to expand membrane use to non-aqueous applications. On the basis of typically hydrophilic membrane materials, the limits of NF and RO soon became clear [10]. In 1990s, Koch Membrane Systems introduced to the market solvent-stable membranes based on polydimethyl siloxane (PDMS), which were stable in most organic solvents [11]. GKSS (Germany) was able to use radiation modification to significantly improve chemical stability and rejection of PDMS based membranes [12]. These products are commercially available from GMT (Germany). Additional membranes that are commercially available are e.g. the polyimide-based (PI) membranes of Grace Davison, which are sold by MET (Great Britain), and the polyamide-imide (PAI) membranes of Solsep (The Netherlands). Further details can be found in [13].

Only a few large-scale processes using organophilic nanofiltration exist. Even ten years after commissioning, Mobil's Max-Dewax™ process is the world's largest organophilic nanofiltration process with a feed rate of 8500 m³/day. The Max-Dewax™ process is used for solvent recovery in lube dewaxing and allowed 20% energy savings and 3–5% increased yield [14,15]. Several other promising processes in solvent-resistant nanofiltration recently described by Vandezande et al. [13] have not yet been brought to industrial scale.

The separation of homogeneous catalysts by use of organophilic nanofiltration has been a topic in several publications. Nair et al. [16] examined the activity of the palladium Heck catalyst during a batch wise recycling using solvent-resistant nanofiltration membranes. The membranes used were the polyimide-based membrane Starmem 122 by Grace Davison and the MPF60 by Koch, a silicone-based membrane. For the description of the catalyst activity they used the turn over number. During six recycles the activity dropped

to 20% of the initial activity. Rejections up to 96% were observed during the nanofiltration steps.

Datta [17] also used the Heck reaction as an example for the recycling of homogeneous catalysts. A focus of their research was the development of polymer-enlarged catalysts. In the experiments, PDMS membranes on a polyacrylonitril support by GKSS were tested. The rejection was above 99.5% and the catalyst activity dropped by 10% after recycling.

The aim of this study is to investigate the interaction of a typical ligand-modified rhodium hydroformylation reaction and the recycling of its catalyst systems via organophilic nanofiltration (oNF) under the influence of the synthesis gas pressure during the oNF. Therefore the catalyst activity will be studied during several recycles. From the membrane separation point of view the development of permeability and retention during successive oNF runs for two different solvent-resistant membranes are investigated.

2. Experimental

2.1. Setup and procedure

The experimental setup consists of three parts, the reactor for the hydroformylation reaction, the nanofiltration circuit and the filling apparatus. Filling, reaction and nanofiltration were used successively. The function of the filling apparatus is not only the first filling including the catalyst and the refilling of the reactor with new reactants. It also has the function of flushing back the catalyst concentrate from the permeate loop after each nanofiltration step. Therefore the pressurized filling apparatus is directly connected to the nanofiltration circuit to allow the catalyst concentrate being flushed back into the reactor. The experimental setup is shown in Fig. 3.

The hydroformylation is carried out in a 5 L autoclave to provide enough feed for the nanofiltration in order to enable mass concentration factors of up to 20. Synthesis gas is added via a pressure controlled valve and the reactor is kept at constant temperature by a thermostat. The reactor pressure can be checked by a manometer. Samples from the reactor are taken via a capillary tube.

The reactions are stopped after 4 h. The reactor then serves as a surge tank for the nanofiltration. A high-pressure pump generates the needed transmembrane pressure of 25 bar. A recirculation pump is used to adjust the cross-flow velocity (1.7 m/s) over the flat sheet membrane (80 cm²). The cross-flow velocity is monitored by a coriolis flow meter. To keep a temperature of 60 °C in the nanofiltration circuit a heat exchanger is placed in the circuit. The permeate flow was measured gravimetrically and the transmembrane pressure is calculated from manometer readings in feed and permeate. A concentration factor of approximately 5–12 is achieved during the filtration.

After filtration has been completed, the olefin for the next reaction is used to rinse the concentrate through the filtration circuit into the reactor in order to carry out another reaction with the recycled catalyst. This is necessary to assess the effect of the nanofiltration on the catalyst system. Altogether, three filtrations and four

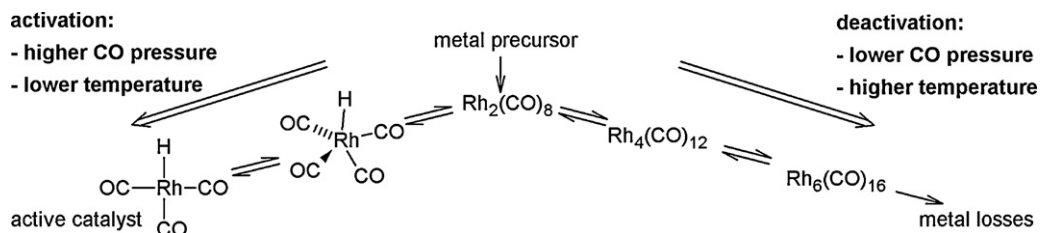


Fig. 2. Formation and deactivation of active catalyst species [8].

Download English Version:

<https://daneshyari.com/en/article/635885>

Download Persian Version:

<https://daneshyari.com/article/635885>

[Daneshyari.com](https://daneshyari.com)