Continous fixed-bed gas-phase hydroformulation of butene using supported ionic liquid-phase (SILP)

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Abstract

Continous flow gas-phase hydroformylation of butene was performed using supperted ionic liquid-phase (SILP) catalysts with immobilized Rh complexes with biphosphine ligand (sulfoxantphos) in the halogen-free ionic liquid 1-*n*-butyl-3-mythelimidazolium *n*-octylsulfate on silica support. It has been innvestigated wether the catalyst loses activity or its selectivity is influenced due washing with cyclohexane. Furthermore the partial reaction order of hydrogen was determined and the impact of various partial pressures has been analysed. This report extends the knowledge on SILP based hydroformylations which have been reported already.

Key words: Supported Ionic liquid phase (SILP) catalysis, Hydroformylation, Butene, Rhodium, Sulfoxantphos, BMIM

1 Introduction

Ionic Lqiuids (ILs) are mostly referred to be room-temperature "molten salts", which classifies them as ionic compounds in liquid state. They have a long and useful history, but got into focus of research and technical application during the last decade. Before that, they were only used a very specialized material in military application and sometimes in very specific processes without thinking about their potential. Although the military research in the 1960s and 70s initiated a broad scientific interest [1], which lead to many publications in all fields of interest. In the last decade room-temperature ionic liquids (ILs) have received increasing interest due to their potential as fluid for processes, catalysis and as functional fluids [2]. ILs are sometimes referred as "green solvents", although is their impact on environment and their toxicology still mostly unknown [3].

A lot of development focused on two-phase liquid aqueous-organic catalytic systems with substitution of water with IL as the immobilizating phase for organometallic catalysts. Especially hydroformylation was investigated by several groups gaining excellent results.** In hydroformylation ILs were used providing an effective medium for catalyst recycling and separation, but although a good catalyst immobiliza-tion by the use of charged ligands was ensured, good selectivities were rare.

Due to high prices of IL and better handling of "heterogenized" catalysts the well known concept of generally supporting a liquid or aqueous phase by a solid was introduced [4]. Depending on the role of the ionic liquid, a distinction between Supported Ionic Liquid Catalyst (SILC) [5], where the IL is actually the catalyst and Supported Ionic Lqiuid Phase (SILP), where the IL dissolves the catalyst, was established [6].

In recent development especially the hydroformylation catalysts using the sulfonated xantphos ligand (Fig. 1) showed excellent *n/iso* ratios.
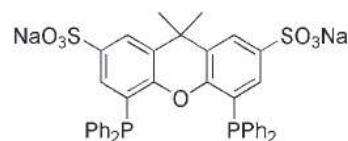

Fig. 1. Sulfonated xantphos ligand "sulfoxantphos"

In this work a Rh based sulfoxantphos catalyst is used, which is immobilized in a halogen free 1-*n*-butyl-3-mythelimidazolium *n*-octylsulfate ([BMIM][$n - C_8H_{17}OSO_3$], Fig. 2) IL which is used for hydroformylation of butene.
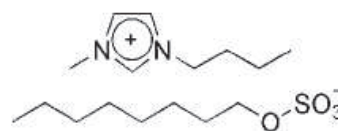

Fig. 2. 1-*n*-butyl-3-mythelimidazolium *n*-octylsulfate

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Table 1
Reaction conditions and results

	washed catalyst	H$_2$ partial pressure variation		
		run 1	run 2	run 3
total pressure / *bar*	10.0	10.0	10.0	10.0
temperature / °C	100	100	100	100
H$_2$/CO-ratio	1 : 1	0.1	0.24	0.4
hydrogen molar flow / $mol \cdot min^{-1}$	0.002	0.0002	0.0005	0.0008
CO molar flow / $mol \cdot min^{-1}$	0.002	0.002	0.002	0.002
butene molar flow / $mol \cdot min^{-1}$	0,001	0.002	0.002	0.002
residence time / s	–	0.296	0.296	0.296
average activity / $mol\ aldehyde\,(mol\ Rh)^{-1}\,h^{-1}$	80.4	116.3	147.6	189.3
average selectivity / n/iso aldehyde ratio	43.0	–	–	–
conversion rate	–	3.3 %	4.2 %	5.4 %

2 Setup

The rig (Fig. 3) consists mainly of gas storage, (loop) reactor and gas chromatograph. Liquid butene is taken out of a gas bottle by means of a HPLC pump, evaporated and mixed with synthesis gas (H$_2$ + CO) and inert gas (He). A pressure control unit dosing inert gas keeps the pressure constant.
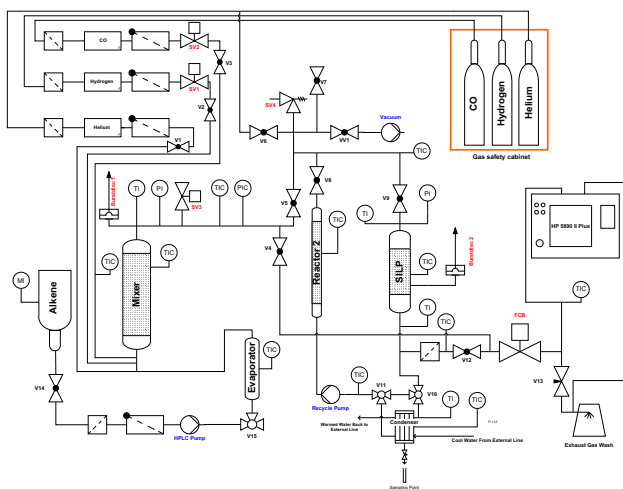

Fig. 3. Experimental setup

The reaction mixture enters the heated reactor containing the fixed bed of SILP catalyst and leaves the rig to GC analysis. After analysis the exhaust gas is washed by an ionic liquid to adsorb the toxic CO. A water cooled condenser to discharge the reaction products is optionally available. In an optional second downstream reactor isomerization of butene takes place at an acid zeolithe catalyst before the gas stream enters the main reactor again. For evacuating the system prior to use and invstigation on catalyst reactivation a vacuum pump is installed. Online analysis is performed by an Hewlett-Packard gas chromatograph, which takes samples every 20 minutes. A flame ionisation detector (FID-GC) is used to evaluate. The aquired data lead directly to the activity (TOF) and selectivity (n/iso) of the catalyst. For calibration of the retention times and peak values, mixtures of *n*-Pentanal, *iso*-Pentanal and 1-Pentanol with cyclohexane are used.

The catalyst material consists of a silica support material containing the IL [BMIM][*n*-C$_8$H$_1$7OSO$_3$]. Ionic liquid loading α is 0.1 which equals 10 *w*%. Rhodium acting as catalytic active compound equals 0.2 *w*% and is immobilized by the ligand sulfoxanthphos. The catalyst to ligand ratio is 1:10 as recent investigations have shown that ligand has to be present in large excess to compensate detrimental surface reactions.[7]

3 Experimental

3.1 Washing of catalyst particles

First of all deactivated catalyst particles from an earlier run are to be be regenerated. Therefore they are washed with cyclohexane to extract pore clogging side products. An amount of 1.9893 *g* yellow colored catalyst powder is washed three times with 30, 25 and 25 *ml* cyclohexane stirring 30 minutes each. The washing suspension is separated by filtration and prepared for analysis via offline gas chromatography, NMR-spctroscopy and ICP (inductevely coupled plasma).

It is noteworthy that the first eluate is slightly yellow, the second one is nearly colorless and the third one is completely colorless. The bright yellow colored catalyst is then dried alternately under vacuum (6 *mbar*) and argon atmosphere for another 30 minutes. The catalyst after washing has a weight of 1.8173 *g* most likely due to residues in washing and drying equipment.

3.2 Check for activity and selectivity

The washed catalyst is filled into the tubular reactor closed by a porous frit and covered with glass wool to

prevent catalyst entrainment. To check for activity and selectivity the reactor is operated under reproducable conditions (see table 1) for 15 h. Reaction conditions are the same as used before.[7]

3.3 Variation of H_2 partial pressure

For determination of reaction order of hydrogen the partial pressure of H_2 is varied over three runs. The conditions are shown in table 1.

4 Results

4.1 Change in activity and selectivity due to washing

To evaluate the catalyst's activity and selectivity three subsequent hydroformylation runs are compared. Respectively, with fresh catalyst, used catalyst and catalyst after washing as explained in chapter 3.1.

The plot of activity vs. time (Fig. 4) shows that activity of used catalyst is significantly lower than the fresh catalyst (-62.3%). This is probably due to high boiling side products such as 1-pentanol ($T_{boil} = 174\,°C$), 2-ethyl-octanal and 2-ethyl-octanol clogging the pores of silica and lowering diffusion. The aim of washing is to extract this detrimental species. Considering the run after washing there is no noteworthy observable change in activity (-1.0%).

Concerning n/iso selectivity there is only a small decrease of 0.1 % from first (98.0 % n-pentanal) to second (97.9 %) and 0.2 % from second to third run (97.7 %) observable. Hence it must be assumed that catalyst performance is reduced by and by.
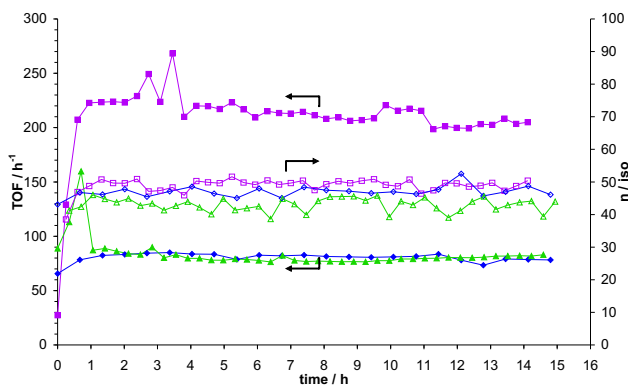

Fig. 4. Hydroformylation of butene using fresh catalyst (■, □), used catalyst (◆, ◇) and washed catalyst (▲, △). Plots of activity (filled symbols) and selectivity (open symbols) as a function of reaction time.

This observation arises the question, which components are removed from the IL film due to washing. The washing solutions were analysed with GC and NMR in order to detect those (polar) high-boiling condensation products, which are possibly enriching in the IL film and are candidates for possible catalyst deactivation. ^{13}C NMR spectrums of the washing solutions

show only peaks of the solutant cyclohexane, but no significant peaks above background noise for possible condensation products. Because the time of measurement in NMR apparatus was possibly to short and ^{13}C is rare (about 1 %, [8]), not all possible peaks might have been detected.

In order to find out, wether phosphorous ligands might have been washed out, a [34]P NMR spectrum was detected, which showed no peaks. This leads to the conclusion that the sulfoxantphos ligand is immobilzed properly in IL.

GC data of the washing solutions show peaks for 1-pentanol, iso-pentanal, n-pentanal and some unidentified high boiling alcohols and aldehydes (Fig. 5). Although there are peaks for the these high-boilers, the percentage of those is low (0.65 %), compared to the solutant cyclohexane (98.8 %).
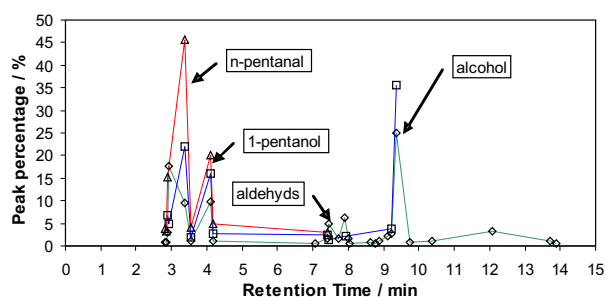

Fig. 5. GC analysis of the washing solutions. Plot shows 1st wash (◇), 2nd wash (△) and Third wash (□). Percentages of the components excluding solutant (cyclohexan).

4.2 Catalyst loss due to washing

Although the activity and selectivity is only slightly influenced, the question arises wether the Rh-catalyst is to be found in the washing solution. In case, that all Rhodium was washed out, the 25 ml solution would only hold about 1.55 ppm. ICP was calibrated by an 10 ppm Rh solution, which showed significant peaks. All three wash solution showed no significant absorption. Because the catalyst is still active and working, this leads to the conclusion, that the Rh is still immobilzed.

4.3 Determination of H_2 partial reaction order

According to power law the reaction rate for butene hydroformylation is determined as follows.

$$r = k \cdot c_{butene}^{n_{butene}} \cdot c_{H_2}^{n_{H_2}} \cdot c_{CO}^{n_{CO}} \tag{1}$$

As described in section 3.3 the hydrogen partial reaction order is determined by variation of H_2 partial pressure. The GC analysis tool delivers area counts that are comparable among each other by means of calibration factors. Thus the butene-normalized area counts can directly be used for calculation of conversion

$$X = \frac{\text{total aldehyde+side products}}{\text{total aldehyde+side products+butene}} \tag{2}$$

yielding together with butene concentration and residence time τ the effective reaction rate

$$r_{eff} = \frac{c_{butene} \cdot X}{\tau} \qquad (3)$$

The average H_2 concentration present in the reactor is determined as follows.

$$c_{H_2} = c_{H_2,inlet}\left(1 - \frac{X}{2}\right) \qquad (4)$$

These results are plotted according to differential method as $\ln r_{eff}$ vs. $\ln c_{H_2}$ (Fig. 6). The slope equals the H_2 partial reaction order and can be determined as $n_{H_2} = 0.3447$.
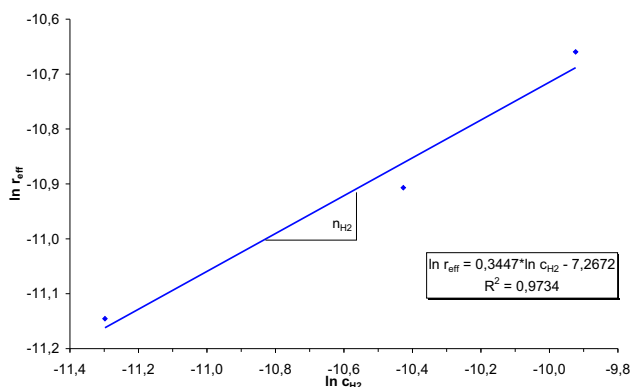

Fig. 6. Plot of $\ln r_{eff}$ vs. $\ln c_{H_2}$ according to differential method for determination of H_2 partial reaction order.

5 Summary and outlook

Our investigation shows that catalyst cannot be reactivated by means of washing with cyclohexane. Possibly the unpolar cyclohexane is not able to remove those polar high-boilers out of the polar IL film. Hence the challenge for further investigation is to find another way to extract detrimental deposits.

For example the way to extract high boilers with high vacuum isn't fully explored yet. Indeed we used vacuum (about $6\,mbar$) during drying a combination of high temperature and high vacuum could be more promising.

Another chance could be the variation of washing fluid, like using a slightly more polar one. Due to high polartity of the IL strong polar organic side products as we have to assume are tightly adsorbed to the IL layer. Against this backgound a extraction with supercritical CO_2 could be an imaginable alternative [9,10]. Although possible condensation products are not completely removed, the insight that the catalyst remains in the IL film during wash opens the field for further investigations concerning continous recovery of supported IL phase catalysts.

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