Selective Hydrogenation of 1,3-Butadiene from Crude C_4 Cracker Stream with a Solid Catalyst with Ionic Liquid Layer (SCILL) – DSC and Solubility Study

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Abstract

In petroleum as well as in fine chemical industry, selective catalytic hydrogenation is an important reaction. The selective hydrogenation of 1,3-butadiene (BD) to butene (trans-,1- and cis-butene) from the crude C4 steam cracker fraction represents one example, but under today's technical conditions undesired butane forms inevitably in relevant amounts. To increase the butene yield, the concept of Solid Catalyst with Ionic Liquid Layer (SCILL) [1] was employed. The SCILL catalyst, in contrast to the uncoated catalyst, yielded a remarkably high selectivity to butenes ($S_{butenes} > 99$ %) even at high residence times or at high hydrogen partial pressure. Nearly no butane ($S_{butane} \approx 0$ %) was analytically detected. We expected that due to different solubility, the poorer soluble compounds discharged from the ionic liquid and, thus, caused the shift in selectivity to a great extent. Temperature dependent solubility measurements in the used ionic liquid ([DMIM][DMP]) revealed that the order of increasing solubility is 1,3-butadiene > butenes > butane which matches the assumption. However, since differences in solubility cannot explain this SCILL effect satisfyingly, ionic liquids are expected to affect the surface of the catalyst (side-specific ligand-type effect). Investigations using spectroscopic methods (e.g. FTIR) confirmed this suggestion [2].

Introduction

In the steam cracking process naphtha is converted to yield ethylene and propylene as essential starting compounds in chemical industry. Thereby, the crude C4 fraction is also produced and part to the product stream containing paraffins (iso-butane, butane), olefins (iso-butene, 1-butene, 2-butenes), and diolefins (e.g. 1,3-butadiene).

Apart from the C2 and C3 olefins, especially 1,3-butadiene (BD) contributes to the economic benefit of the steam cracking process. Nevertheless, due to azeotrope formation with butane, BD has to be extracted. Hence, if the situation occurs that the quantity of the C4 fraction is small and butadiene extraction is not economically feasible, the selective hydrogenation to monoolefins is preferred (Figure 1) since the butenes, especially 1-butene, are used for various applications, e.g. as co-monomer in polyethylene (LLDPE/HDPE) in the chemical industry.

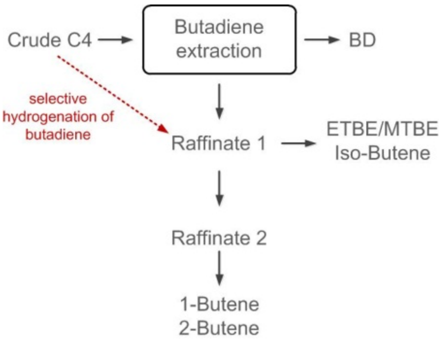

Figure 1: Possibility to bypass butadiene extraction

However, butane is formed inevitably in relevant amounts. Hence, improvement of the selectivity to the valuable butenes is desired with only minor changes in the catalyst's shape. To achieve this goal, the concept of Solid Catalyst with Ionic Liquid Layer (SCILL) was applied for this reaction. In the SCILL concept, a thin layer of an ionic liquid (IL) coats the surface of a heterogeneous catalyst, where the ionic liquid layer can act as diffusion barrier due to different solubility of the substrates in the IL and shifts the selectivity in the desired direction (In this case: to butene). However, ligand effects of the ionic liquid on the catalyst's surface are also likely to influence the outcome of the reaction [2].
In the present case, the SCILL catalyst consists of a commercial hydrogenation eggshell catalyst (0.3 wt.-% Pd on Al_2O_3) coated with a thin film (α = 0.16) of the ionic liquid 1,3-dimethylimidazolium dimethyl phosphate ([DMIM][DMP]) (see Figure 2).

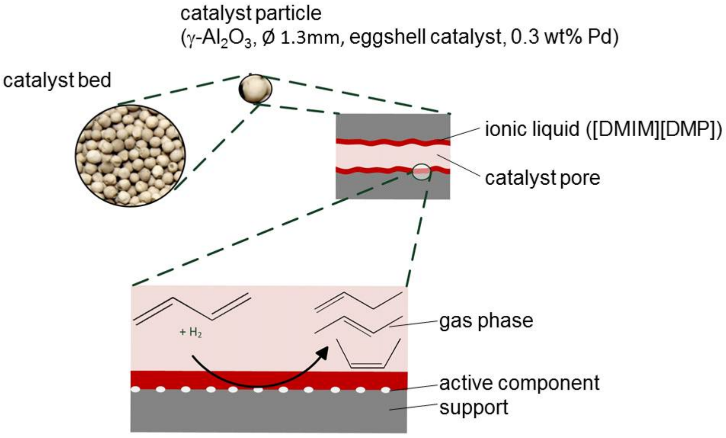

Figure 2: Principle of a Solid Catalyst with Ionic Liquid Layer

The study shows that the SCILL catalyst enhances the selectivity to butenes significantly which can partly be ascribed to solubility differences of the C4 hydrocarbons in the ionic liquid. The solid-liquid phase behavior of the ionic liquid [DMIM][DMP] in confined spaces is also presented.

Solubility of C4 compounds in Dimethylimidazolium Dimethyl Phosphate

We assume that the improved butene selectivity of the SCILL system is connected with the different solubility of the C4 species in the IL layer (Dimethylimidazolium dimethyl phosphate). Hence, the dissolved amount of butane, butene and 1,3-butadiene were quantitatively determined in a magnetic suspension balance allowing precise measurement of small weight differences under controlled reaction conditions (pressure, temperature, etc).
Figure 3 shows the data (fitted values) and reveals that the order is 1,3-butadiene > butenes > butane. The results give evidence that solubility in the ionic liquid drives the selectivity shift, at least to a certain degree, since the solubility of BD is by a factor of 2.6 higher than butene and a factor of 16 higher than butane. Hence, BD is hydrogenated to butene and diffuses into the gas phase. Therefore, the butenes do not dissolve in the IL and the formation of butane is suppressed.

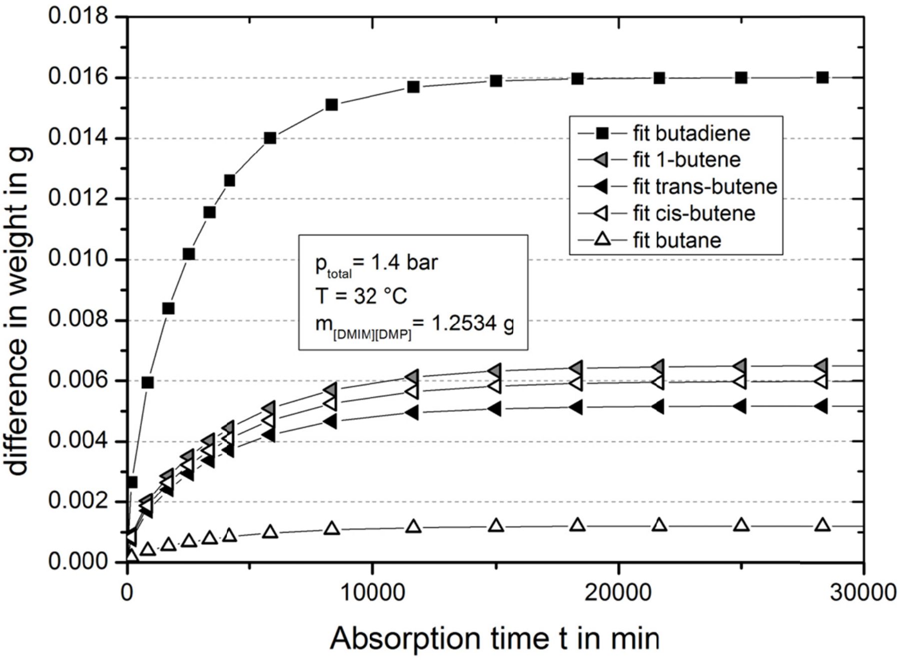

Figure 3: fitted values for difference in weight for all C4-compounds at p_{total} = 1.4 bar and T = 32 °C

Furthermore, the temperature dependence of the solubility with regard to the C4 components was studied. To calculate the concentration of C4 inside the ionic liquid at different reaction temperatures, the Henry coefficient ($k_{H,pc}(T)$) was determined (in this case $k_{H,pc}(T)$ of butadiene).

$$k_{H,pc}(T) = \frac{p}{c_{Butadiene\ in\ IL}} \qquad (1)$$

The temperature dependence of the Henry coefficient is defined by an alternative form of the van't Hoff equation.

$$k_{H,pc}(T) = k_{H,pc}(T^{\theta}) * e^{-C*(\frac{1}{T}-\frac{1}{T^{\theta}})} \qquad (2)$$

$$\ln k_{H,pc}(T) = \ln k_{H,pc}(T^{\theta}) - C * (\frac{1}{T} - \frac{1}{T^{\theta}}) \qquad (3)$$

Here, the Henry coefficient $K_{H,pc}(T^{\theta})$ at standard temperature (T = 298 K) and constant C is obtained by interception with the y-axis and slope of the linearization.

$K_{H,pc}(T^{\theta})$ = 3.48 L bar mol^{-1}
C = 1927.4 K

With higher temperatures, the solubility of C4 components decreases, this implies a higher $K_{H,pc}(T)$. For all components (butadiene, butenes, butane), the slope (constant C) is approximately the same. This implies that different reaction temperatures do not influence the composition of C4 compounds in the ionic liquid.

The difference in solubility has a significant effect on butene selectivity and the catalyst activity. However, these differences cannot explain the SCILL effect entirely.

With the obtained Henry- and diffusion-coefficients, the concentration of C4 components in the IL can be calculated. Based on these data a presumable conversion of butene (as only C4 component in hydrogen) can be estimated. The output variables are the solubility and the diffusion coefficient. The solubility of butadiene in [DMIM][DMP] is 2.6 times higher than the solubility of e.g. 1-butene. The diffusion coefficient of butadiene in IL is about 1/3 higher than the one of 1-butene in IL. This is discussed in the following paragraph.

Comparison of coated and uncoated Catalyst

To study the effect of the SCILL concept, both, an uncoated and coated commercial heterogeneous Pd catalyst (0.3 wt.-% Pd on Al_2O_3; 0.3 wt.-% Pd on Al_2O_3, [DMIM][DMP]) were used for the hydrogenation of 1,3-butadiene by varying the residence time. The reactions were conducted in a tubular reactor (see Fig. 4 and 5 for reaction conditions).

Fig. 4 pictures that with increasing residence time or in other words at higher conversion the butene selectivity (trans-, cis- and 1-butene) drops for the uncoated catalyst (Figure 4). The hydrogenation to butane proceeds inevitably and, at high conversion, the main product of the hydrogenation reaction is the paraffin. Furthermore, the selectivity to 2-butene depends on residence time and is governed by the thermodynamic equilibrium (Figure 6).

In comparison to the uncoated hydrogenation catalyst, the coated SCILL catalyst (Figure 5) offers a much higher butene selectivity. Even at full conversion of BD (modified residence times of τ higher than 200 kg s m^{-3}), the selectivity to butene remains constant at the same high level and virtually no butane forms during the reaction (see Figure 5). The selectivity to butene isomers (~60 % 1-butene, ~40 % trans-butene) remains also constant over the whole range of conversion (see Figure 7). The SCILL catalyst causes no isomerization; the thermodynamic equilibrium is not reached.

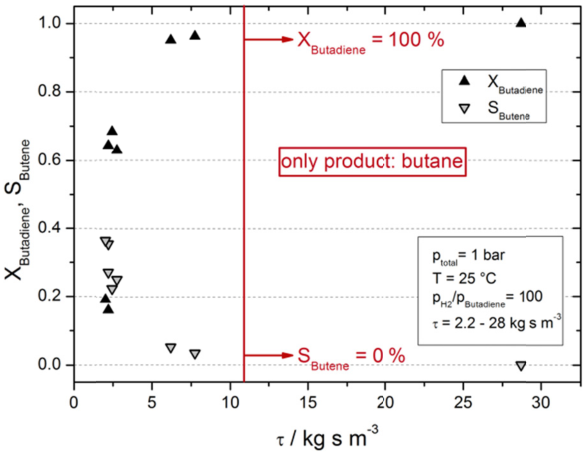

Figure 4: Uncoated catalyst: Selectivity to butene over the whole range of conversion

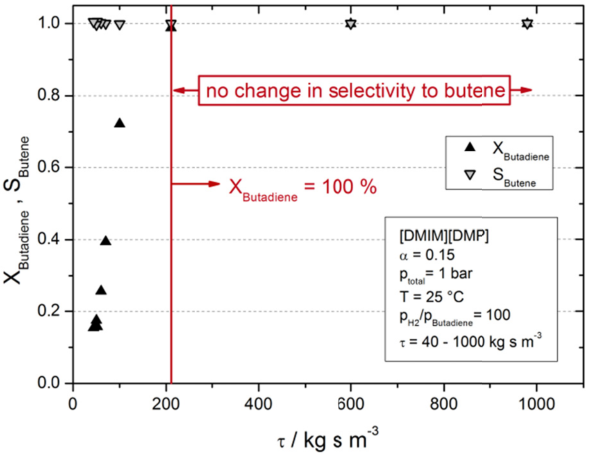

Figure 5: SCILL catalyst: Selectivity to butene over the whole range of conversion

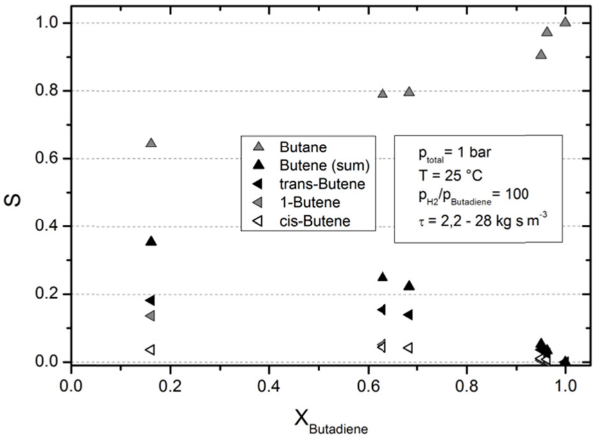

Figure 6: Uncoated catalyst: Product distribution

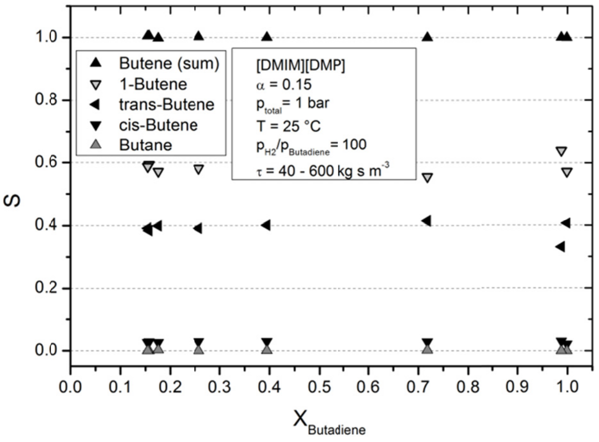

Figure 7: SCILL catalyst: Product distribution

The results clearly show that the amount of valuable product rises significantly when the SCILL system is used, whereas the ionic liquid governs the outcome of selectivity as shown in selective hydrogenation of citral and acetylene [3][4].

As shown in Figure 5, butadiene conversion reaches 100%, when the modified residence time exceeds 220 kg s / m³. To estimate the butene conversion, when only butene is used as substrate, the diffusion coefficient of butene needs to be factored into the residence time by 1/3. This means, at a residence time τ of 290 kg s / m³, butene conversion is expected to be 2.6 times lower than butadiene conversion at 220 kg s/ m³. This sums up to an estimated butene conversion of about 39%.
However, applying the same reaction conditions as in BD hydrogenation at a sustained residence time of 1000 kg s m^{-3}, the 1-butene conversion yields only about 2%. This shows that the different solubility of both 1,3-butadiene and 1-butene does not entirely account for the selectivity shift. Hence, other effects need to be taken into account.

The data of hydrogenation of BD and butene indicate that competing surface adsorption of ionic liquid and both substrates is likely to be responsible for the SCILL effect. Here, the differences in adsorption enthalpies of the ionic liquid, butadiene and butene are crucial. We assume that BD shows a higher adsorption enthalpy than the ionic liquid and interacts more closely with the active component and, thereby, replaces, at least partially, the IL from the active component (Pd). In Pd-catalysis, the adsorption enthalpy of butadiene is known to be about twice as high as the adsorption enthalpy of butene [5]. Since butene was not hydrogenated it is suggested that butene owns a lower adsorption enthalpy than the IL and cannot replace the ionic liquid. Consequently, solubility and adsorption enthalpy control the selective butadiene hydrogenation. A competing adsorption between IL and substrates occurs, as already shown in [2,6] for ([BMIM][NTF_2]) and CO on Pd. Besides, the hydrogenation using the SCILL catalyst is relatively fast. Hence, hydrogen is, despite its low solubility in ionic liquids, available on the catalyst's surface. We suggest that the high adsorption enthalpy of H_2 on Pd accounts for sufficient hydrogen on the catalytically active metal by replacement of the IL as proposed in [7].

Differential Scanning Calorimetry (DSC)

The ionic liquid layer affects the active sites of the catalyst and, hence, improves the butene selectivity. Therefore, the focus is primarily set on the solid-liquid phase behavior of ILs in porous supports. Trapped in confined spaces, ILs can show a melting point shift that is either a depression or elevation; both effects are already shown in literature [8, 9, 10].
Solidification at elevated temperature may form crystals or crystalline-like IL blocking active sites responsible for butane formation.
To compare the melting point of supported ionic liquid [DMIM][DMP] in confined spaces with the bulk phase, DSC measurements were conducted.

Table 1 shows the results of DSC measurements. The experiments were performed for both bulk and supported IL, applying a pore filling degree of α = 1 (complete filling of the pore volume). With this α-value, clear signals are ensured.

Table 1: Results of DSC measurements

material	heating rate [K/min]	Ø onset temperature [°C]	Ø peak temperature [°C]
pure IL [DMIM][DMP]	10	- 65.5	- 58.1
SCILL $\alpha = 1$	10	- 75.5	- 67.6
pure IL [DMIM][DMP]	5	- 65.2	- 60.5
SCILL $\alpha = 1$	5	- 86.3	- 81.2

DSC-measurements were conducted with two different heating rates, namely 10 K/min and 5 K/min. For the supported [DMIM][DMP], heating rates resulted in a melting point depression of about 10 K (10 K/min) and 20 K (5 K/min), respectively. This clearly shows that crystallization of the ionic liquid also changes when it is confined in pores [8, 9, 10].

The melting point depression illustrates that [DMIM][DMP] is liquid at the reaction temperatures which makes blocking of active palladium sites due to crystallization unlikely.

Conclusion

The hydrogenation of 1,3-butadiene over a SCILL catalyst leads to a significantly high selectivity to the butenes (ca. S = 100%) even at high residence times. This result is connected with the different solubility of butadiene and butene. As expected, the solubility of crude C4 components in [DMIM][DMP] decreases as follows: butadiene > butene > butane. Thus, hydrogenation of the diolefin is favored and butene removes from the reaction system, which prevents the consecutive hydrogenation to butane.

Nevertheless, the SCILL effect cannot be entirely attributed to differences in solubility, as nearly no hydrogenation of butene takes place even at long residence times and high hydrogen partial pressure. Due to the experimental data of butene hydrogenation, competing surface adsorption of ionic liquid and substrate on the catalytically active metal is assumed to explain to the SCILL effect. Here, the differences in adsorption enthalpy of the ionic liquid, butadiene and butene (all in the liquid phase) are crucial and decide the outcome of the reaction.

DSC-measurements showed that the ionic liquid [DMIM][DMP] is liquid at the reaction temperature of the hydrogenation reaction. Thus, we assume that blocking of active palladium sites due to crystallization of the ionic liquid is unlikely.

Although the H_2 solubility in ionic liquids is generally low, the hydrogenation is relatively fast. We suggest that the high adsorption enthalpy of H_2 on Pd accounts for sufficient hydrogen on the catalytically active metal by replacement of the IL.

Experiments regarding adsorption behavior of ionic liquids, C4 substrates and H_2 in a SCILL catalyst are currently the focus of research to evaluate our assumption.

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