Solid Catalyst with Ionic Liquid Layer (SCILL) – A Concept to Improve the Selectivity of Selective Hydrogenations

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Abstract

Catalytic hydrogenations are important for refinery processes, petrochemical applications as well as for numerous processes of the fine chemicals industry. In some cases, hydrogenations consist of a sequence of consecutive reactions, and the desired product is the intermediate. An important goal is then a high yield and selectivity to the intermediate, if possible at a high conversion degree. The selectivity to an intermediate primarily depends on the chemical nature of the catalyst, but may also be influenced by diffusion processes.
Ionic liquids (ILs) are low melting salts (< 100 °C) and represent a promising solvent class. This paper focuses on the concept of a *Solid Catalyst with Ionic Liquid Layer* (SCILL), where the solid catalyst is coated with a thin IL layer to improve the selectivity.

Introduction

The following applications of ionic liquids (ILs) for heterogeneous catalysis are particularly attractive:

1. ILs may immobilize metal nanoparticles or metal clusters on porous solids [1 - 7].
2. ILs may act as catalyst itself and is immobilized - e.g. by covalent bonds - on a porous support, as shown for Friedel-Crafts alkylation [8], acetylization [9], cycloaddition of CO_2 [10, 11], and epoxidation of olefines [12].
3. In the concept of *Supported Ionic Liquid Phase* (SILP) a thin IL-film and a homogeneous catalyst dissolved therein is confined on the surface of a porous solid, e.g. by physisorption. This concept has been tested for hydroformylation and hydrogenations [13 - 19].
4. In the foreground of this paper is the concept of a *Solid Catalyst with Ionic Liquid Layer* (SCILL, Fig. 1) as a novel method to improve the selectivity of a heterogeneous catalyst. The SCILL-concept [20 - 22], which was claimed as a patent in cooperation with Süd-Chemie [23], was introduced in 2007 [21] and combines the following strategies:
    - Similar to the SILP-technology, a porous solid is coated with an IL, but the solid is now a heterogeneous catalyst and not an inert support. Thus a homogeneous catalyst is not involved in the SCILL-concept, although a combination with the SILP-technology could be a future option to integrate homogeneous and heterogeneous catalysis.
    - The activity and selectivity of the solid catalyst may be changed by the coating of the internal surface with an IL in two ways: (1) The IL may have a positive influence on the "chemical" properties of the catalyst ("co-catalytic effect"). (2) The IL may change the effective concentrations of educt(s) and intermediate(s) compared to the uncoated case, if the solubility of liquid or gaseous reactants are in an appropiate way different in the IL compared to the organic phase ("physical solvent effect"). For example, the selectivity to the intermediate is favoured, if it is less soluble in the IL than the feed.

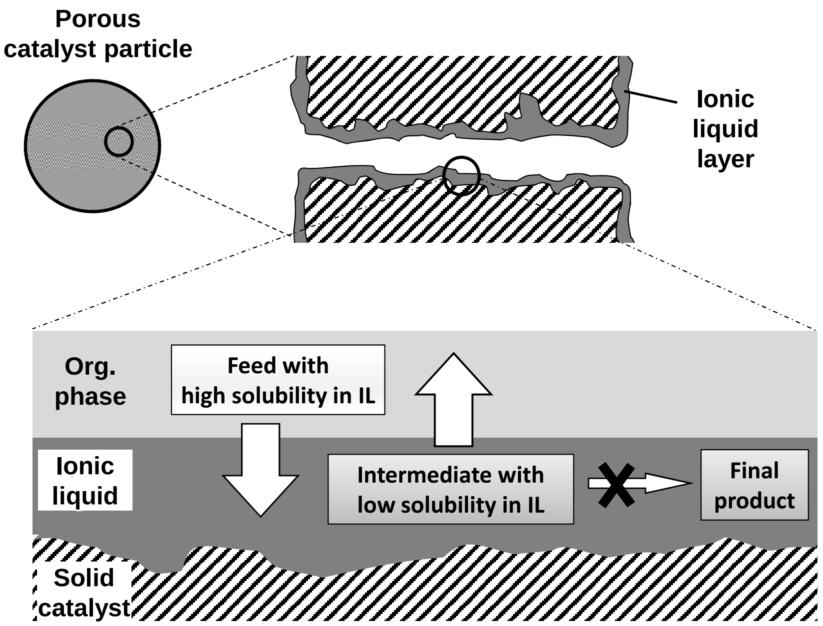

Fig. 1: Ilustration of *SCILL*-concept.

To test the SCILL-concept, four sequential hydrogenation reactions were tested (Fig. 2), the Ni-catalyzed hydrogenation of 1,5-cyclooctadiene, octine and cinnamaldehyde, as well as the Ru-catalyzed hydrogenation of naphthaline utilizing different ILs for the coating (Tab. 1).

Tab. 1: Hydrogenation reactions and SCILL-systems discussed in this work [20 - 22].

Sequential hydrogenation of	Catalyst	ILs used for catalyst coating
Cyclooctadiene → cyclooctene → cyclooctane	NiSAT G-33 RS[1]	[BMIM][$MeSO_4$], [BMIM][$OcSO_4$] [BEBIM][Br], [BMIM][BF_4], [TBA][Br], [TBA][Cl], [TBA][BF_4]
Octine → octene → octane	NiSAT G-33 RS	[BMIM][$OcSO_4$]
Cinnamaldehyde → hydrocinnamaldehyde/cinnamic alcohol → hydrocinnamic alcohol	NiSAT G-33 RS	
Naphthaline → tetralin → decalin	Ru-cat. K-0401[2]	

[1] 37 wt-% Ni on SiO_2; 6 x 6 mm cylinders; ρ_p: 1.4 g/cm^3; A_{BET}: 115 m^2/g; V_{pore}: 0.38 cm^3/g (Süd Chemie).

[2] 5 wt-% Ru on carbon; 25 - 63 µm particle size; ρ_p: 1.5 g/cm^3; A_{BET}: 783 m^2/g; V_{pore}: 0.83 cm^3/g (Heraeus).

Although the results presented here show the potential of the SCILL-concept to “tune” the selectivity of solid catalysts, it must be noted that the concept has two basic limitations: (1) The temperature is limited by the decomposition of the IL, e. g. for [BMIM][n-$C_8H_{17}OSO_3$] to about 120°C [20], and (2) the organic phase and the IL must form a biphasic system without any IL-leaching as otherwise the IL-film would be washed out of the catalyst. (Remark: In case of a gas phase reaction, e. g. the hydrogenation of volatile hydrocarbons, the leaching of the IL can be excluded, and only slow evaporation and/or thermal decomposition may play a role. But up to now, only liquid phase reactions were tested for the SCILL-concept, but gas reactions may be an interesting option for the SCILL-concept also.)

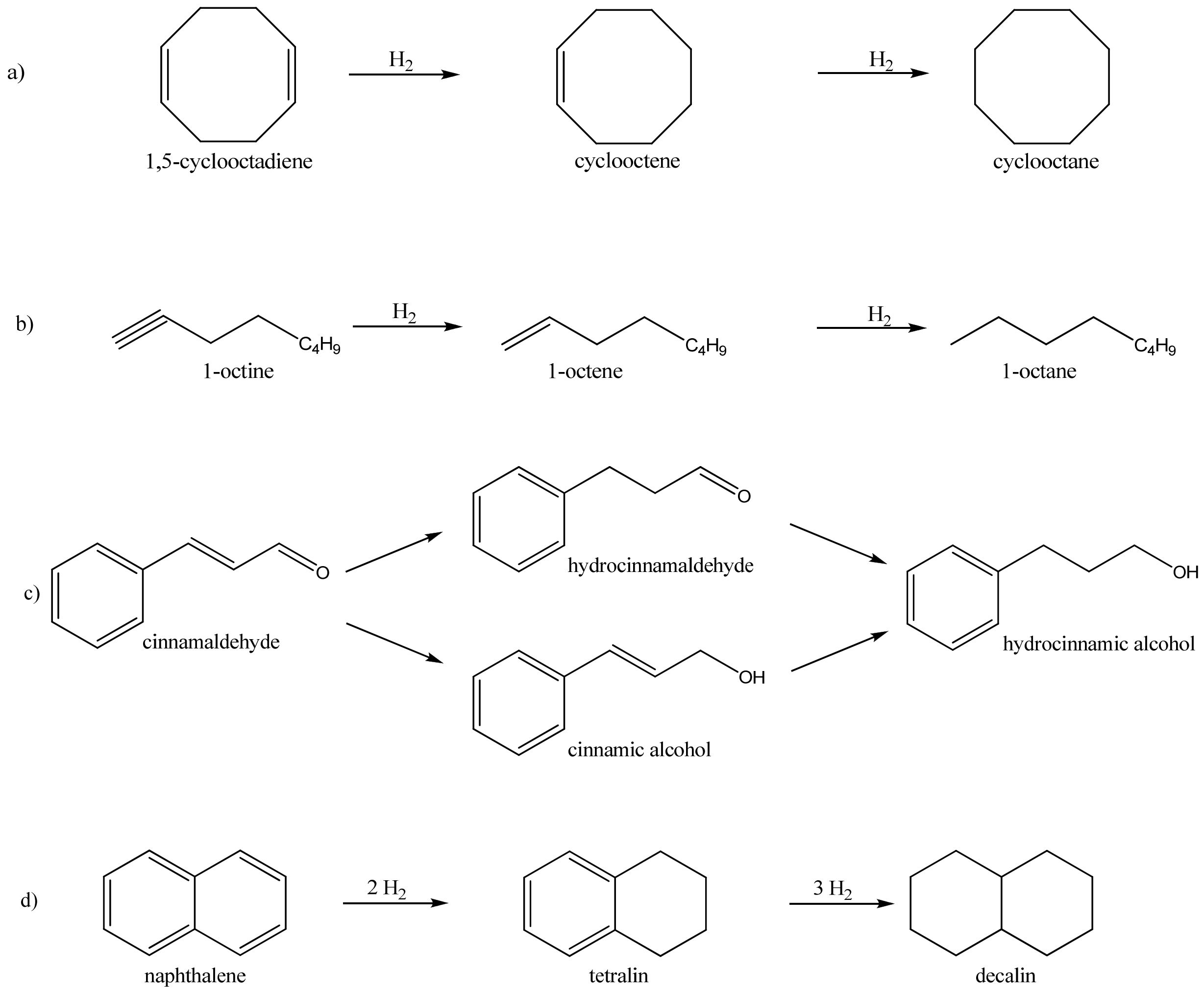

Fig. 2: Reactions tested for the SCILL-concept.

Preparation and characterisation of SCILL-systems

The SCILL-catalysts were prepared by coating a commercial nickel or ruthenium catalyst (see footnotes of Tab. 1) with an IL (e.g. [BMIM][OcSO$_4$]) up to a filling degree of the initial pore volume of 65%. For the preparation of the SCILL-catalyst, typically 1 g of catalyst was crushed (in case of the Ni-cat.), dried at 150°C over night and then reduced by hydrogen at 350°C for three hours. Thereafter, an appropiate amount of IL was diluted in dichloromethane (HPLC grade), usually in a volumetric ratio in an order of magnitude of 1/1000, and the catalyst was added to this solution. Subsequently, the volatile solvent dichloromethane was slowly (2 h) removed from the slurry by evaporation under low vacuum (620 mbar, 30°C), which leads to a complete intrusion of the IL into the pores (details on the preparation of SCILL-catalysts in [20, 21]). The IL-coated catalysts are fluid powders, which show no change of their original appearance. Finally, the catalyst was dried (20°C, 1 h) under high vacuum to ensure a complete removal of the solvent, and was then stored under hydrogen.

The SCILL-concept is limited to biphasic systems, i. e. the IL (e. g. [BMIM][OcSO$_4$]) has to be insoluble in the organic phase. In case of cyclooctadiene (COD) hydrogenation, a mixture of the solvent *n*-dodecane with the organic reactant COD and the products cyclooctene (COE) and cyclooctane (COA) was utilized. With regard to the effective concentrations of the reactants at the surface of the IL-coated catalyst, the concentrations in the IL-layer have to be considered, which are governed by Nernst´s law of partition. The Nernst partition coefficient K_N of a substance i (e. g. of COD, COE or COA), which is distributed between an ionic liquid and a solvent (here for example *n*-dodecane) is defined as

$$K_N = \frac{m_{i,IL} / m_{IL}}{m_{i,dodecane} / m_{dodecane}} \tag{1}$$

with $m_{i,IL}$ and $m_{i,dodecane}$ as the mass of COD, COE or COA dissolved in the IL and in *n*-dodecane, respectively.

In general, the solubility of an intermediate in the IL should be as low as possible (compared to the feed) to remove the intermediate from the IL-phase that is in direct contact with the surface of the catalyst to suppress further hydrogenation. The K_N-values which were measured by the initial and final concentrations of COD, COE or COA in the organic phase in contact with the different ILs (Tab. 2) indicate that the feed COD ($K_{N,50°C}$ = 0.37) has a higher solubility in the IL [BMIM][OcSO$_4$] than the intermediate COE ($K_{N,50°C}$ = 0.31). For the other ionic liquids, the partition coefficients of COD and COE were slightly lower, but the one of COE was still always lower compared to COD (Tab. 2).

The following parameters were used to characterise the structure of the SCILL-catalyst: the surface area A_{BET} (related to the mass m_{cat} of the uncoated catalyst), the pore volume V_{pore}, the pore diameter d_{pore}, and the loading ε and pore filling degree α of the IL-coated catalyst:

$$\varepsilon = \frac{m_{IL}}{m_{cat}} \tag{2}$$

$$\alpha = \frac{V_{IL}}{V_{pore,0}} \tag{3}$$

$V_{pore,0}$ is the specific pore volume of the uncoated catalyst (m^3/kg), and m_{IL} and V_{IL} are the mass and volume of the IL used to prepare the SCILL-systems.

The BET-analysis indicates that both the pore volume and the surface area decrease with increasing filling degree. The values of the total residual pore volume of the SCILL-catalysts (BET-analysis, Hg-porosimetry) agree well with those calculated based on the IL-volume used to prepare the SCILL system and on the initial pore volume [20, 21].

The micro- and mesopores (2 to 100 nm) are partially or completely filled by capillary forces for a pore filling degree of more than about 20%, which explains the strong decrease of the surface area, as the originally dominant contribution of micro- and mesopores to the surface area more and more diminishes [20 - 22]. For example, the surface area is still 55 m^2/g for a filling degree α of 15 % compared to 115 m^2/g of uncoated catalyst, but drastically decreases to 30 and 13 m^2/g for α-values of 20% and 35%, respectively. The surface area and the pore filling degree are average structural parameters of the catalyst particle but do not provide an insight into the thickness of the IL-layer in the pores. More details are found in [20 - 22].

Kinetic studies of the hydrogenation of cyclooctadiene with SCILL-catalysts

The experiments were carried out in a Berghof HR-700 autoclave. Good stirring was ensured by a magnetic rotor (1000 rpm) and three agitator blades. For hydrogenation of octine and cyclooctadiene, *n*-dodecane (400 ml) was used as solvent (conditions see Tab. 2 and 3). For naphthaline and cinnamaldehyde *n*-heptane was used. Typically, an initial COD-concentration of 8 mol/m^3 (0.45 wt-% in dodecane), a constant H_2-pressure of 50 bar, 50°C, and a particle diameter of 30 to 50 μm were used. The conditions of the other hydrogenation reactions (octine, cinnemaldyhyde, naphthaline) were similar. Selected experiments with the uncoated and IL-coated catalyst were also conducted with different particle sizes (< 25 μm up to 1.5 mm). To test the stability of the IL-layer, the N-content of the organic phase was measured (Antek 9000, pyrofluorescence detector, detection limit: 1 ppmw N) as in case of an IL-leaching (nitrogen content of BMIM-ILs is 8 wt-%) this would have been detected.

The isomerisation of 1,5-COD to 1,3- or 1,4-COD can be excluded for the Ni-catalyst [20]. The yield of *trans*-cyclooctene is by a factor of more than 20 lower compared to *cis*-COE, and the rates of the subsequent hydrogenation of *cis*- and *trans*-COE to COA were found to be equal [20]. Therefore, both COE isomers were treated as one pseudo-component COE.

The most interesting aspect when using a SCILL-catalyst is the question whether and to what extent the coating affects the selectivity to the intermediate, here cyclooctene (COE). Surprisingly a very pronounced and positive effect was found (Figs. 3 and 4, Tab. 2, 5th row). The maximum yield for the intermediate COE increases almost twofold for the coated catalyst (α = 10%) to about 70% (Fig. 3) compared to the uncoated catalyst with only about 36% (Fig. 4), if [BMIM][$OcSO_4$] is used. For the other tested ILs, similar enhancements of the intermediate selectivity were found ($Y_{max,COE}$ in a range of 58 to 72%, see Tab. 2). The corresponding plot of the selectivity to COE versus the conversion of COD is shown in Fig. 5.

This strong influence of the IL-layer on the selectivity can not be explained by the influence of the IL on the effective concentrations of COD and COE compared to the uncoated catalyst. For two first order reactions occuring in series in a porous catalyst (here hydrogenation of COD to COE and COA), the maximum yield of the intermediate COE is given by

$$Y_{COE,max} = (R)^{\frac{R}{(1-R)}} \quad \text{for } \eta_{pore} = 1,\ R = k_{COE}/k_{COD}. \qquad (4)$$

For the uncoated catalyst, the k_{COE}-to-k_{COD} ratio (= R) for [BMIM][$OcSO_4$] is 1.1, as calculated by Eq. (4) based on the measured maximum COE-yield of 36% (Fig. 4) (or by the best fit of the measured influence of X_{COD} on S_{COE} , Fig. 5). The $K_{N,COE}$-to-$K_{N,COD}$ ratio is 0.84 (Tab. 2, 50°C) and could therefore only explain a decrease of k_{COE}/k_{COD} for the SCILL-catalyst from 1.1 to 0.9 (= 1.1 x 0.84). This would increase the maximum COE-yield from 36% to 39% and would only lead to a relative small selectivity improvement compared to the measured maximum COE-yield of 72% and the corresponding k_{COE}-to-k_{COD} ratio of 0.15 (Fig. 5).

For the given particle size of about 40 μm, an influence of pore diffusion on the selectivity can be excluded, as proven by additional experiments [20 - 22]. One explanation of the strong selectivity enhancement is that the IL acts as a co-catalyst, e. g. by the hindrance of a (re)adsorption of COE (or hydrogen) on the active Ni-sites.

Beside [BMIM][OcSO$_4$], other ILs were also tested for the SCILL-concept and the model reaction of COD-hydrogenation (Tab. 2). Three of them are liquid at the reaction temperature of 50°C ([BMIM][MeSO$_4$], [BMIM][BF$_4$], and [TBA][Cl]), and three are solid ([BEBIM][Br], [TBA][Br], and [TBA][BF$_4$]). Tab. 2 shows that the maximum COE-yield at the applied filling degree of 15% is in a range of 58% to 72% compared to 36% for the uncoated catalyst.

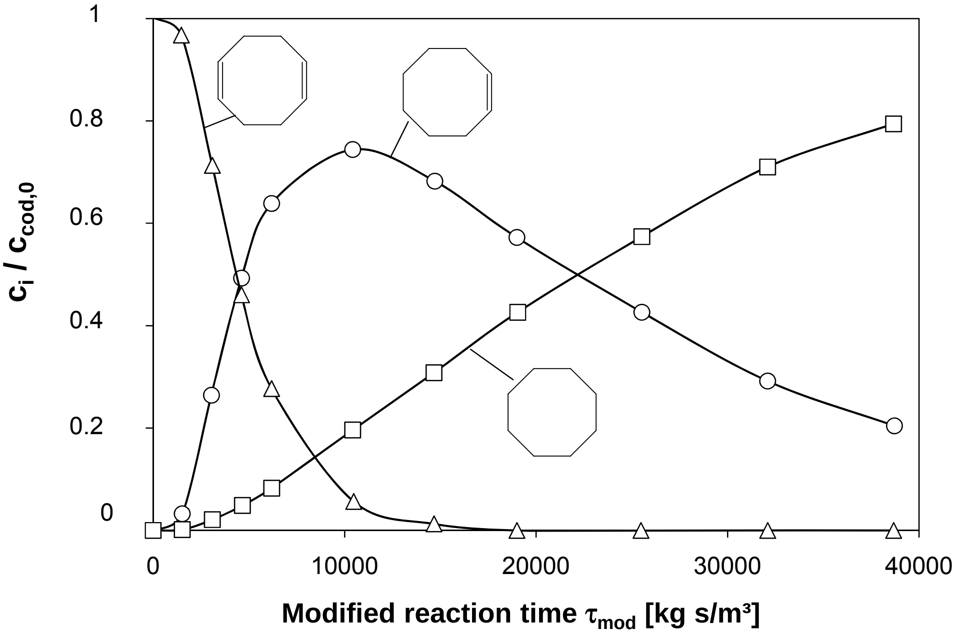

Fig. 3: Hydrogenation of cyclooctadiene: Residual COD-content and yields of COE and COA on the coated Ni-cat. (c_{cat} = 1.7 kg/m^3, 50°C, d_p = 30 - 50 μm, $c_{COD,0}$ = 8 mol/m^3 (0.1 wt-% in dodecane), $p(H_2)$ = 50 bar, pore filling degree with [BMIM][OcSO$_4$] = 15% [20 - 22].

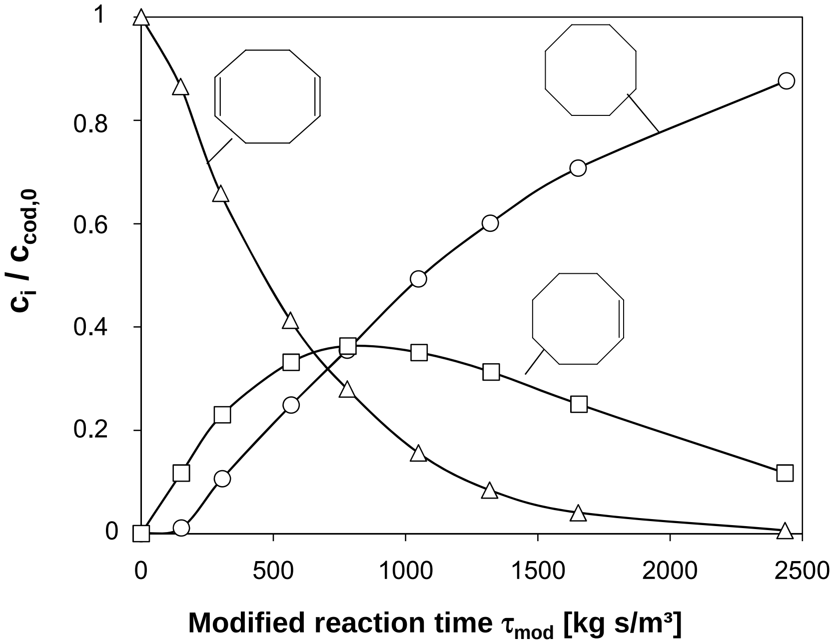

Fig. 4: Hydrogenation of cyclooctadiene: Residual COD-content and yields of COE and COA on the uncoated Ni-cat. (conditions see Fig. 3) [20 - 22].

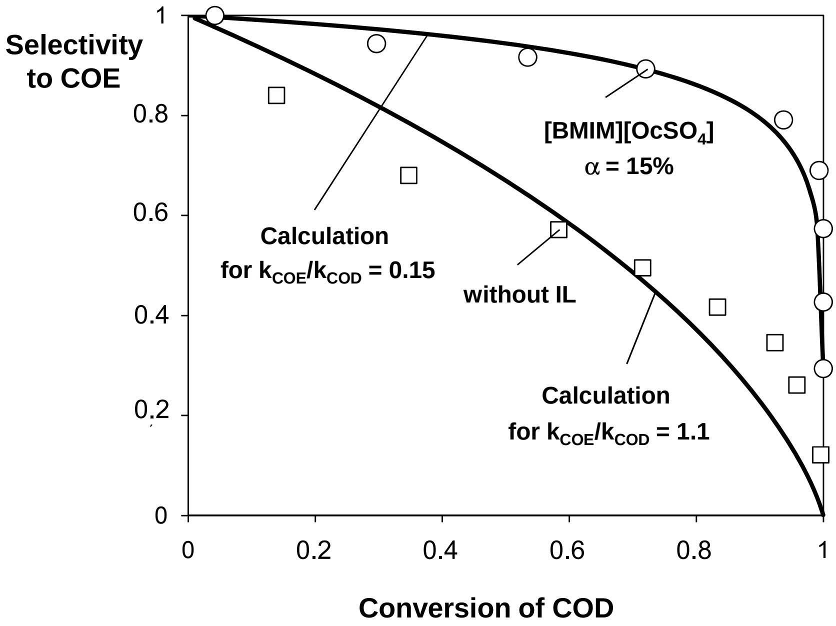

Fig. 5: Hydrogenation of COD: Selectivity to intermediate COE versus conversion of COD for the coated and uncoated Ni-catalyst (conditions see Fig. 3) (data from [20 - 22]).

The influence of the pore filling degree (α) on the maximum yield of the intermediate COE was investigated with two different ILs, [BMIM][$OcSO_4$], which is liquid at the reaction temperature of 50°C, and for [TBA][Br], which is then a solid. Up α = 10% the maximum COE-yield steadily increases in both cases, which indicates that the surface is still only partly covered with the IL. For α > 10%, a constant maximum COE-yield of 70% is reached. The surface is now completely covered with the IL. So only a filling degree of 10% - almost only one monolayer - is needed to reach the full SCILL-effect. This effect does not depend on the fact, whether the IL is a solid or liquid under the applied reaction conditions (Tab. 2).

Tab. 2: Hydrogenation of COD on a Ni-catalyst coated with different ILs: partition coefficients (in *n*-dodecane), max. yield of intermediate COE, and rate of COD-conversion for X_{COD} = 50% (p_{H2} = 50 bar, 50 °C, ε = 0.06, α = 0.15, d_p = 35 µm) [20, 22]

IL used	$K_{N,COD}$	$K_{N,COE}$	$K_{N,COE}/K_{N,COD}$	$Y_{COE,max}$	r_{COD} in 10^{-3} mol kg^{-1} s^{-1}
without IL	-	-	-	*36%*	*11*
[TBA][BF_4][1]	-	-	-	58%	3.2
[BMIM][BF_4]	0.15	0.13	0.87	72%	2.0
[BMIM][$MeSO_4$]	0.10	0.07	0.70	68%	1.9
[BMIM][$OcSO_4$]	0.37	0.31	0.84	72%	1.1
[TBA][Cl]	0.23	0.18	0.78	66%	0.9
[TBA][Br][1]	-	-	-	68%	0.8
[BEBIM][Br][1]	-	-	-	67%	0.05

[1] These ILs are solid at the reaction temperature of COD-hydrogenation of 50°C. The melting points are 160°C for [TBA][BF_4], 100°C for [TBA][Br], and 75°C for [BEBIM][Br].

Tab. 2 (column 6) shows that the reaction rate of COD-hydrogenation decreases for all ILs by the coating of the Ni-catalyst compared to the uncoated case. The influence of the "solid" ILs is not stronger compared to the ILs, which are liquid at the reaction temperature (50°C), at least for the given low filling degree of 15%. The layer thickness is then only in the order of magnitude of a monolayer, and thus the terms "*solid*" or "*liquid*" probably make no sense anymore. In order to clarify this point in more detail, the influence of the filling degree on the reaction rate was also investigated for higher α-values than 15%, i. e. for the case that multilayers and a bulk phase of the ionic liquid is established in the pores. Then, the reactions rate strongly decreases for "solid" ILs [20 - 22]

Kinetics of the hydrogenation of octine, cinnamaldehyde and naphthaline

To test the SCILL-concept further, three other sequential hydrogenation reactions were tested in own works until today, the Ni-catalyzed hydrogenation of octine and cinnamaldehyde, and the Ru-catalyzed hydrogenation of naphthaline, thereby utilizing [BMIM][OcSO$_4$] for the coating with a constant filling degree of 15%, which is according to the COD experiments the IL-loading sufficient to utilize the maximum SCILL-effect. The results are listed in Tab. 3 and Tab. 4. For comparison, main results of COD-hydrogenation are also given.

Tab. 3: Reaction rate of the hydrogenation of cyclooctadiene, octane, cinnamaldehyde, and naphthaline with and without ionic liquid coating ([BMIM][OcSO$_4$], d_p = 35 µm) [20, 22].

Hydrogenation of	$K_{N,feed}$[1]	**Rate** at 50% conversion (*theoretical value*[2]) in 10^{-3} mol kg^{-1} s^{-1}		**Remaining surface area** (relative to initial) for α = 0.15	**Catalyst** (see Tab. 1) **and reaction conditions**
		without IL	[BMIM][OcSO$_4$], α = 0.15		
Cyclooctadiene	0.37	*11*	1 (*2*)	0.48	Ni-cat., 50 bar, 50°C
Octine	0.58	*18*	7 (*5*)		
Cinnamaldehyde	10.2	*15*	45 (*73*)		Ni-cat., 50 bar, 60°C
Naphthaline	0.78	*9*	2 (*3*)	0.49	Ru-cat., 50 bar, 60°C

[1] Nernst partition coefficient of the system IL/*n*-dodecane (for cyclooctadiene and octane) and of IL/*n*-heptane (for cinnamaldehyde and naphthaline).

[2] The theoretical value given in brackets is estimated based on the Nernst partition coefficient of the feed and the measured decrease of the internal surface area. It is thereby assumed that the rate is zero order with regard to hydrogen, which was only verified for the hydrogenation of cyclooctadiene [22].

All three additional test reactions confirm the statements already derived about the SCILL-concept based on the experiments of COD-hydrogenation:

- For intermediates with a lower solubility in the IL than the feed (octene compared to octine, hydrocinnamaldehyde to cinnamaldehyde, and tetralin compared to naphthaline) the maximum yield of the intermediate increases compared to the uncoated case

(Tab. 4). For cinnamyl alcohol, this is reverse, and the yield decreases on the SCILL-catalyst.

- In all four investigated systems, the measured increase of the yield of the intermediate is stronger compared to what is expected purely by the physical solvent effect (Tab. 4 “calculation” versus “experiment”), indicating an additional co-catalytic effect of the IL.
- For those systems, where the educt has a lower solubility in the IL compared to the organic phase, the reaction rate is lowered (COD, octane, naphthaline). For a higher solubility, this is reverse (cinnamaldehyde), see Tab. 3.

Tab. 4: Maximum yield of intermediate(s) during hydrogenation of COD, octine, cinnamaldehyde, and naphthaline with/without coating with [BMIM][$OcSO_4$] (cond. see Tab. 3) [20, 22].

Hydrogenation of	**Intermediate(s)**	**Ratio of Nernst coefficients** $K_{N,intermediate}/K_{N,feed}$	$Y_{max,\ intermediate}$ *in %*		
			without IL	[BMIM][$OcSO_4$], $\alpha = 0.15$	
				Experiment	Calculation[1]
Cyclooctadiene	Cyclooctene	0.84	*36*	72	4
Octine	Octene	0.72	*23*	38	28
Cinnamaldehyde	Cinnamyl alcohol	8.9	*2*	1	-
	Hydrocinnamaldehyde	0.44	*70*	75	81
Naphthaline	Tetralin	0.55	*50*	65	61

[1] Calculation considering only the solubility effect and the decreased surface area are considered.

Meanwhile, the SCILL-concept was also tested by *Claus* and co-workers, thereby using citral hydrogenation as model reaction and Pd-catalysts coated with [$N(CN)_2$]-, [NTf_2]- and [PF_6]-based ILs [24 - 27]. The best results were achieved with [BMPL][$N(CN)_2$], where selectivities to the intermediate citronellal of 99% (at 80% conversion) were reached compared to 45 without IL coating.

Conclusions and outlook

The results of the sequential hydrogenation of cyclooctadiene, octane, cinnamaldyde, naphthaline on Ni- and Ru-catalysts coated with different ionic liquids demonstrate the promising concept of a *Solid Catalyst with Ionic Liquid Layer* (SCILL).

For an almost complete coating of the internal surface area with the IL (monolayer), a pore filling degree of only about 10% is needed, which typically leads to a decrease of the surface area by 50%. This may lead to an (unfavourable) decrease of the activity. In case that the educt is better soluble in the IL than in the liquid organic phase, this may be more than compensated, i.e. the activity of a SCILL-catalyst may be even higher than of the uncoated catalyst, as shown by the experiments on the hydrogenation of cinnamaldehyde.

More important than the potential negative influence of the IL on the reaction rate is the surprisingly positive effect of the coating on the selectivity of intermediates, e.g. of cyclooctene for cyclooctadiene hydrogenation. The maximum yield without IL is only 40% and increases by the coating to more than 70%. The coating is robust without detectable IL-leaching.

Research on the SCILL-concept is still at the very beginning, and more studies are needed for a better understanding, and for the practical use of the concept. The directions of future research are the investigation of other (parallel and consecutive) reactions including not only hydrogenations, but also oxidations. Long-term tests on the thermal stability and the mass loss by evaporation of the IL-layer (in case of gas phase reactions) are also needed, and finally the catalyst-IL-interactions and the influence of the IL-loading on the internal surface, pore diameter and layer thickness should be analyzed in further detail.

Acknowledgements

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Symbols and abbreviations

Symbols

A_{BET}	$[\mathrm{m^2\ kg_{cat}^{-1}}]$	BET-surface area
α	[-]	pore filling degree α (= fraction of pore volume occupied by the IL)
c_i	$[\mathrm{mol\ m^{-3}}]$	concentration of component i
c_{cat}	$[\mathrm{kg\ m^{-3}}]$	concentration of catalyst in the liquid
d_p	[m]	diameter of particle
ε	$[\mathrm{kg_{IL}\ kg_{cat}}]$	loading of the catalyst with IL
k_{COD}	$[\mathrm{m^3\ kg^{-1}\ s^{-1}}]$	rate constant of COD-conversion
k_{COE}	$[\mathrm{m^3\ kg^{-1}\ s^{-1}}]$	rate constant of COE-conversion
K_N	[-]	partition coefficient according to Nernst
m	[kg]	mass
r_{COD}	$[\mathrm{mol\ kg^{-1}\ s^{-1}}]$	reaction rate of COD-conversion
r_{COE}	$[\mathrm{mol\ kg^{-1}\ s^{-1}}]$	reaction rate of COE-conversion
R	[-]	ratio of the intrinsic rate constants, k_{COE}/k_{COD}
ρ_p	$[\mathrm{kg\ m^{-3}}]$	(apparent) density of particle
V_{IL}	$[\mathrm{m^3\ kg_{cat}^{-1}}]$	volume of pores occupied by IL
$V_{pore,o}$	$[\mathrm{m^3\ kg_{cat}^{-1}}]$	initial pore volume of uncoated catalyst
X	[-]	conversion
Y	[-]	yield

Abbreviations and subscripts

0	initial
[BDMIM]	1-butyl-2,3-dimethylimidazolium
[BEBIM]	1-butyl-3-ethylbenzimidazolium
[BF_4]	tetrafluoroborate
[BMIM]	1-Butyl-3-methylimidazolium
[BMPL]	N-butyl-N-methylpyrrolidinium
cat	catalyst
COD	cyclooctadiene
COE	cyclooctene
COA	cyclooctane
IL	ionic liquid
[$MeSO_4$]	methylsulfate
[$N(CN)_2$]	dicyanamide
[NTf_2]	bis(trifluoromethanesulfonly)amide
[$OcSO_4$]	octylsulfate
[PF_6]	hexafluorophosphate
[TBA]	tetra-n-butylammonium

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