Ionic Liquid Thin Films in Catalysis
Fundamental Aspects and Applications

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To start with: Many thanks!!

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Prof. Jörg Libuda  – Physical Chemistry, FAU

Prof. Hans-Peter Steinrück  – Physical Chemistry, FAU

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1. Ionic liquids - Introduction

Ionic liquids are a class of materials that consist of molecules containing at least one positively charged ion (cation) and one negatively charged ion (anion), with the ions held together by weak forces rather than by covalent bonds. They are often called “ionic liquids” or “ILs.”

Ionic liquids are characterized by their high conductivity and low volatility, which allows them to be used as solvents in various applications. They are also known for their unique physical and chemical properties, such as high density, high viscosity, high surface tension, and high heat capacity.


Properties of ionic liquids include:

- Density
- Viscosity
- Surface tension
- Heat capacity
- Therm. stability
- Electrochem. stability
- Disposal options
- Ionicity
- Volatility
- Price
- Acidity
- Coordination
- Toxicity
**Ionic liquids**

- extremely low vapor pressure
  \( \rightarrow \) compatible to UHV techniques
- some degree of order
  (depending on structure)
- relatively slow diffusion processes

**supercritical CO\(_2\)**

- fluid character
- synthetic strategies
- solvation power
- macroscopically homogeneous nature

<table>
<thead>
<tr>
<th>solid</th>
<th>molecular liquid</th>
<th>gas</th>
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</table>

**Ionic liquid solid-like properties...**

...and molecular liquid-like properties
The ionic liquid „Hype Cycle“

2004
„ILs are unique“, commercial IL production, Green Chemistry

2008
Stability, price, toxicology issues, USP ?, delays in techn. applications

2012
Better physico-chemical understanding, drop-in and thin film applications
Criteria for successful/promising technical applications of Ionic liquids

- **Technical Performance – Unique selling point**

- **Added value**

- **Amount of ionic liquid necessary to reach the desired effect**

- **Ionic liquid stability under process conditions**

- **Ionic liquid cost / kg**
Many of the existing IL applications are Ionic Liquid Thin Film Technologies!

Electrochemistry
- e.g. batteries, electroplating, dye sensitized solar cells

Analytics & sensors
- e.g. new GC-columns, phases for HPLC, matrices for MS, humidity sensors

Reaction
- synthesis, catalysis
- SILP, SCILL biocatalysis

„Engineering fluids“
- e.g. extraction, extractive distillation, lubrication, process machinery, media for particle preparation, supported liquid membranes
General features of IL Thin Film Technologies (I)

With respect to surface reactivity:

- Solid surface is chemically modified by a molecular-defined but extremely low volatile liquid
- Solid surface is protected against detrimental reaction with components from the gas phase (surface inertization)
- Concentration of reactants at the surface is modified by differential IL solubility properties
With respect to IL reactivity:

- Utilization of ionic liquid is much better especially in cases of fast reaction in a viscous IL
- Great specific fluid/IL exchange area without any energy input
- Co-catalytic support effects (support acidity, support basicity)

In IL Thin Film Technologies, the IL-film has the dimension of the IL-side diffusion layer

→ much higher degree of IL utilization

**Scenario:** Reactive gas cleaning

- **Fluid 1** (e.g. gas phase)
- **Catalytic IL phase** (fast reaction, slow diffusion; \( \text{Ha} > 3 \))

\[
P_{1,g} \quad \delta_L
\]

**Bulk IL phase**

*No reaction as \( c_1 = 0 \)!

**IL-side diffusion layer**

mass transprot + reaction
The scientific challenge of IL Thin Film Technologies

Create a better understanding of the nature of IL / wall contact and the nature of IL / fluid contact!!

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Collaborations:
Kirchner, Fröba, Krischok, Licence, Libuda, Welton and Perkin, Baldelli, Jux
Ionic Liquid Surface Science by X-ray photoelectron spectroscopy (XPS)

The method:

\[ E_B = h\nu - E_{\text{Kin}} \]

- VG-ESCALAB 200
- Sample transfer system
- Al Kα radiation \( h\nu = 1486 \text{ eV} (\Delta E = 0.9 \text{ eV}) \)
- Base pressure with IL: \( 5\cdot10^{-10} \text{ mbar} \)

XPS is element specific, oxidation state specific, surface sensitive and quantitative!
Key message
- $0^\circ \Rightarrow 70^\circ / 80^\circ$ Intensity of one element increases $\Rightarrow$ enhancement of that element in near-surface region (full analysis $\Rightarrow$ surface composition)

**AR-XPS of ionic liquids**

<table>
<thead>
<tr>
<th>0° emission</th>
<th>80° emission</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-rays</td>
<td>e$^{-}$</td>
</tr>
<tr>
<td>Information depth 7-9 nm</td>
<td>“bulk sensitive”</td>
</tr>
<tr>
<td>Information depth 1-1.5 nm</td>
<td>“surface sensitive”</td>
</tr>
</tbody>
</table>
Results from pure IL studies

- no surface enrichment!
- hypothesis:

Kolbeck, Killian, Maier, Paape, PW
AR-XPS of [Rh(acac)(CO)$_2$] and Na$_3$TPPTS in [EMIM][EtOSO$_3$] (5.1 mol-%)

Phenyl rings of TPPTS$^{3-}$ are enriched at surface

Rh is rel. enriched in near-surface region (spectra not shown)

Kolbeck, Paape, Cremer, Schulz, Maier, Steinrück, PW, Chemistry- A European Journal 2010, 16(40), 12083-12087
Applications of IL Thin Film Technologies in Catalysis

**Supported Ionic Liquid Phase (SILP) Catalysis**

- the technical sulfuric acid catalyst – catalytic molten salt on support (1914)

**Solid Catalyst with Ionic Liquid Layer (SCILL)**

- Jess et al., Chemical Engineering & Technology **2007**, 30(8), 985)
- Libuda et al. PCCP **2010**, 12(35), 10610)
SILP Catalysis (I) – Ultra-low temp. Water-Gas Shift catalysis

\[ \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO}_2 \]

**Application area:**
- decentralized hydrogen production
- hydrogen from biogas
- on-board hydrogen production

> **50 catalysts screened**; Time of experiment: 10..750 h/cat.
> total: > 15,000 hours TOS catalyst screening experiments
> Optimization of IL, support and additives

Werner, Szesni, Fischer, Haumann, PW, PCCP 2009, 11(46), 10817-10819.
SILP Catalysis (I) – Ultra-low temp. Water-Gas Shift catalysis

...optimized SILP composition vs. Cu/ZnO catalyst (state-of-the-art)

General test conditions: 200 mg catalyst (powder); T = 140°C; p = 3 bar; syn-gas: H\textsubscript{2} 75%, CO 8%, CO\textsubscript{2} 13%, N\textsubscript{2} 4%; steam to gas 1:3

Catalyst composition: support alumina B; ionic liquid (10w%); catalyst precursor Ru(CO)\textsubscript{3}Cl\textsubscript{2} (2w% Ru)

Unique features of SILP ULT-WGS catalysts:

- Highest ever reported catalytic activity @ 120°C, 1 bar \( p_{\text{H}_2\text{O}} \) with realistic syngas.
- Excellent start and re-start behavior of the catalyst → suitable for dynamic use.
- High potential for S- and N- stable WGS catalysts → biogas applications.
SILP Catalysis (II) – Hydroformylation of mixed industrial feeds

\[
R\text{-alkene} + H_2 + CO \xrightarrow{[\text{cat}]} R\text{-CHO} + R'\text{CHO}
\]

- Side reactions:
  - Isomerization
  - Hydrogenation

Applied ligand and industrial feed:

- Applied rig:

Gaseous substrates

Gaseous products + unreacted substrates
SILP Catalysis (II) – Hydroformylation of mixed industrial feeds

Rh-L-SILP catalyst stability.

$T = 100 \, ^\circ C, \, p = 10 \, \text{bar}, \, \tau = 30 \, \text{s},$

$H_2:CO = 1, \, m_{\text{SILP}} = 3 \, \text{g},$

$m_{\text{Rh}} = 0.4 \, \text{wt.-\%}, \, L/Rh = 10,$

$\alpha_{\text{IL}} = 10 \, \text{vol.-\% (IL = [EMIM][NTf_2])}.$

$> \, 35 \, \text{days time-on-stream without loss in performance}$

$> \, 300.000 \, \text{cumulated TON; } 3500 \, \text{h}^{-1} \, \text{TOF ;}$

$> \, 800 \, \text{kg } 1\text{-pentanal per m}^3 \, \text{SILP catalyst and hour !}$

$> \, 100\% \, \text{(within analytic error) Rh recovery after experiment}$

SILP Catalysis (II) – hydroformylation – advantage over traditional system

- High reaction rates in small volumes
- Tunable solubility for higher alkenes (>C3)
- No catalyst recycling required
  - No phase separator
  - No catalyst make-up
- No solvent and no solvent handling
- Very efficient utilization of complex and expensive ligand systems
- Ionic liquid as collector solvent
  - very remarkable performance of the SILP system with diluted feeds

RCH/RP oxo-plant, Oberhausen, Germany
STY = 200 kg m⁻³ h⁻¹ (120 °C, 50 bar)

SILP Catalysis (III) — Hydroaminomethylation

Rh-Xantphos in [MMIM][NTf_2] on PBSAC support

conversion ethylene, □ yield aldol adduct ○ yield aldol condensation product ● yield propionaldehyde ■ yield DEPA).

Reaction conditions: 120°C, 10 bar, L=Xantphos, L/Rh 5/1, 0.2 wt% Rh, PBSAC, α_IL = 0.1, 2.5 g SILP catalyst, 200 NmL/min H_2, 100 NmL/min CO, 10 NmL/min ethylene, 0-17 h: 1 g/h diethylamine, 17-40 h: 2 g/h diethylamine, residence time = 8.4 s.
Clariant (ex Süd-Chemie) SILC-MAX®

SILC: Süd-Chemie Ionic Liquid Catalyst
Salt layer on the surface of the pores
- Active Sites (●) remain part of the solid surface
- Chemical effect of the IL layer as co-catalyst
- Physical solvent effect of the IL modifying concentrations at the catalyst


S,X-plot for various Pd/SiO₂ catalysts in citral hydrogenation

conditions: \( c_0, \text{citral} = 1.1 \, \text{mol/L} \),
\( T = 323 \, K \), \( p(\text{hydrogen})=2.0 \, \text{MPa} \),
\( n = 1200 \, \text{rpm} \), \( t_R = 6 \, h \).
In this case we have to investigate the IL-solid interaction:
→ Preparation of solid samples with ultrathin IL-layer
Model catalyst preparation – „coating“ with [BMIM][Tf₂N]
Evidence for partial poisoning of the catalytic surfaces by [BMIM][Tf₂N] – different effects for Pt/Al₂O₃ and Pd/Al₂O₃

Ionic Liquids vs. Molten salts

Ionic liquids…
→ consist entirely out of ions
→ are liquid below 100°C
→ have an extremely low vapor pressure below the temperature of their thermal decomposition

NaCl

[MIM][NTf₂]

Molten salt (mp > 100°C)

Ionic liquid (mp < 100°C)
But is the world so simple?

Li[NO$_3$] – Na[NO$_2$] - K[NO$_3$] - K[NO$_2$] of mass composition
19.4 - 28.46 - 36.39 - 15.75

mp = 85 °C
η (90 °C, 400 s$^{-1}$)= 400 mPas , η (100 °C, 400 s$^{-1}$)= 100 mPas
thermal stability (long-term) @ 450 °C

H. Gladen, PW, M. Medved, WO 2008071205A1, (filed 13/12/2006)

Li[NO$_3$] – Na[NO$_3$] - Ca[NO$_3$]$_2$ - Cs[NO$_3$] in various mass compositions

mp = down to 65 °C
thermal stability (long-term) @ 485 °C

Are these typical molten salts?

Tetrabutylammonium tetrafluoroborate

\[ \text{mp} = 155 \, ^\circ \text{C} \]

Cs[NTf₂]

\[ \text{mp} = 122 \, ^\circ \text{C} \, [1], \ 134 \, ^\circ \text{C} \, [2] \]
\[ \rho (200 \, ^\circ \text{C}) = 2.06 \, \text{g cm}^{-3} \]
\[ \eta @ 200 \, ^\circ \text{C} = 15 \, \text{mPas} \]

Li/K/Cs [OAc]
(molar composition: 0.2/0.275/0.525)

\[ \text{mp} = 73 \, ^\circ \text{C} \, [3] \, (\text{monohydrate}) \]
\[ \text{mp} = 119 \, ^\circ \text{C} \, (\text{water-free}) \]
\[ \rho (200 \, ^\circ \text{C}) = 2.21 \, \text{g cm}^{-3} \]
\[ \eta @ 200 \, ^\circ \text{C} = 42 \, \text{mPa s} \]
\[ \rho(298 \, \text{K}) \sim 10^{-15\pm2} \, \text{Pa} \]
\[ \Delta_{\text{vap}} H_{298} = 172 \pm 12 \, \text{kJ mol}^{-1} \]

For comparison:
Individual mp's:

\[ \text{Li}[\text{OAc}] = 280 \, ^\circ \text{C} \]
\[ \text{K}[\text{OAc}] = 302 \, ^\circ \text{C} \]
\[ \text{Cs}[\text{OAc}] = 197 \, ^\circ \text{C} \]

Molten Salt - SCILL
a new catalyst technology for MeOH steam reforming
Methanol Steam Reforming

- **Methanol steam reforming**: $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightleftharpoons 3 \text{H}_2 + \text{CO}_2$
- **Methanol decomposition**: $\text{CH}_3\text{OH} \rightleftharpoons 2 \text{H}_2 + \text{CO}$
- **Water gas shift reaction**: $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO}_2$

- Production of hydrogen in high yields
- Reaction conditions:
  - $T = 200$ to $400$ °C; $p = 1$ to $10$ bar
- Heterogeneous catalysts:
  - $\text{Cu/ZnO}$ or transition metal: $\text{Pd/ZnO}$ or $\text{Pt/M}_x\text{O}_y$
- Mechanism: depending on metal and support

S.Sá, Applied Catalysis B: Environmental 99 (2010), 43-47.
Diagramms based on data from Y. Lwin et al.,
Why SCILL?

Ionic liquids are not stable at elevated temperatures in presence of water \((T > 200 \, ^\circ C)\) → hydrolytic cation decomposition

Decomposition liberates coordinating amines

Why molten salts?

- Ionic liquids are not stable at elevated temperatures in presence of water \((T > 200 \, ^\circ C)\) → hydrolytic cation decomposition
- Decomposition liberates coordinating amines
Catalyst Preparation

Heterogeneous Pt on alumina catalyst impregnated with various molten salts

**Catalyst:**

4.86 wt% Pt on γ-alumina (Alfa Aesar)

$A_{\text{BET}} = 130 \text{ m}^2 \text{ g}^{-1}$

$V_{\text{pore,BJH}} = 0.8 \text{ cm}^3 \text{ g}^{-1}$, $d_p \approx 3 \text{ nm}$

Salt loading: $w = \frac{m_{\text{salt}}}{m_{\text{catalyst}}}$

**Molten Salts:**

Li/K/Cs acetate 0.2/0.275/0.525

$T_m = 120 \, ^\circ\text{C}$ [1]

Alkali acetates $T_m = 200-300 \, ^\circ\text{C}$

Alkali carbonates $T_m > 600 \, ^\circ\text{C}$

Alkali hydroxides $T_m > 300 \, ^\circ\text{C}$

Experimental conditions:

Absolute pressure: $p_{abs} = 5$ bar

Partial pressure: $p_{MeOH} = p_{H_2O} = 0.5$ bar

Temperature: $T = 200 – 230 \, ^\circ C$

Selectivity $S_{CO_2} = 100\%$ means maximum $H_2$ production and minimum CO in the product gas!

TOFs are calculated with respect to all metal atoms.
Catalytic Baseline Test: neat heterogeneous Pt alumina catalyst

Stable MeOH steam reforming with Pt on alumina

By-product formation: mainly CO, traces of CH₄ detected

TOF₂₃₀ °C = 23 h⁻¹
S_{CO₂, 230°C} = 62 %
X_{max} = 9 %
E_A = 64 kJ mol⁻¹

Continuous steam reforming of methanol using the uncoated Pt/alumina catalyst (black symbols: TOF; red symbols: selectivity). Experimental conditions: T = 230 – 190 °C (see vertical lines); p_{tot} = 5 bar; P_{MeOH} = P_{H₂O} = 0.5 bar; m_{cat} = 401.4 mg; t = 10 s.
Continuous steam reforming of methanol using the Li/K/Cs[OAc] coated Pt/alumina catalyst $w = 30$ wt% (black symbols: TOF; red symbols: selectivity). Experimental conditions: $T = 230 – 200$ °C; $p_{\text{tot}} = 5$ bar; $p_{\text{MeOH}} = p_{\text{H}_2\text{O}} = 0.5$ bar; $m_{\text{cat}} = 521.8$ mg; $t = 10$ s.
Activity and selectivity depend on amount of salt
Best performance @ 30 wt% Li/K/Cs [OAc] on Pt/alumina
CO-adsorption measurements of acetate coated catalysts with DRIFTS
(Diffuse Reflectance Infrared Fourier Transform Spectroscopy)

These measurements were carried out by our colleagues in Physical Chemistry:
Prof. Jörg Libuda
Dr. Matthias Laurin
**DRIFT – Diffuse Reflectance Infrared FT Spectroscopy**

**CO-Adsorption at salt coated Pt alumina catalysts at T = 35 °C**

Variation in Li/K/Cs[OAc] loading

Uncoated Platinum:

- 2084 cm\(^{-1}\): CO atop on particle terraces
- 2030 cm\(^{-1}\): CO atop on particle edges
- 1840 cm\(^{-1}\): CO bridged on particle terraces

- Alkali [OAc] coated catalyst: loss of intensity at 2084 cm\(^{-1}\) – shift to the two other features
- Alkali metal displaces CO from atop to bridged adsorption sites
Pt on alumina coated with 30 wt% K[OAc]

Same activity and selectivity compared to Li/K/Cs[OAc] coated system

Reaction temperature is below melting point of salt – **influence of water vapor**

**Continuous steam reforming of methanol using the K[OAc] coated Pt/alumina catalyst**

\( w = 30 \text{ wt}\% \) (black symbols: TOF; red symbols: selectivity). Experimental conditions: \( T = 230 – 200 \degree \mathrm{C} \); \( p_{\text{tot}} = 5 \text{ bar} \); \( p_{\text{MeOH}} = p_{\text{H}_2\text{O}} = 0.5 \text{ bar} \); \( m_{\text{cat}} = 521.8 \text{ mg} \); \( \tau = 10 \text{ s} \).

\( T_m = 302 \degree \mathrm{C} \)

\( \text{TOF}_{230 \degree \mathrm{C}} = 36.5 \text{ h}^{-1} \)

\( S_{\text{CO}_2, 230\degree \mathrm{C}} = 99.5 \% \)

\( X_{\text{max}} = 15 \% \)

\( E_A = 53 \text{ kJ mol}^{-1} \)
**Stability measurements: Thermogravimetry**

TG in N$_2$ - rate 2 K min$^{-1}$ – drying for 4 h at T = 120 °C - K[OAc] on Pt alumina

- Decomposition of K[OAc] on Pt alumina
- TG curves depending on loading w
- TG-MS indicates formation of [HCO$_3$]$^-$, [CO$_3$]$^{2-}$, [OH]$^-$,
Comparison: Pt alumina coated with various alkali salts

Values at $T = 230^\circ C$
comparable conditions

- Coating with hydrophilic $K^+$ salts lead to increase in activity and $S_{CO_2} > 99\%$
- $[NTf_2]$ salt coating shows low activity and selectivity even for the $K^+$-salt

Salt - substrate interaction very important!
MeOH Reforming with SCILL type Molten Salt Catalysts

- Salt coating on Pt/alumina has positive effects on activity and selectivity
- Low melting salts not required ($T_m > T_R$) due to role of water vapor: Water condensation $\rightarrow$ water/salt film

- DRIFT and TPD experiments indicate strongly bound CO due to salt coating
- Criteria for salt selection:
  - Potassium doping
  - Salt hygroscopicity
  - Salt basicity

Thank you for your attention!