Ionic Liquids

Tomohiro Yamamoto

2012/11/5

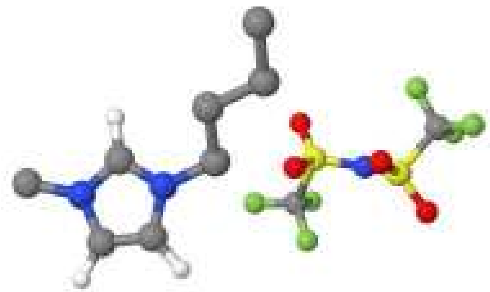
Solvents - classification

H_2O

Hydrogen bond

Organic solvents

Van der Waals interaction



Ionic Liquids

Coulomb interaction

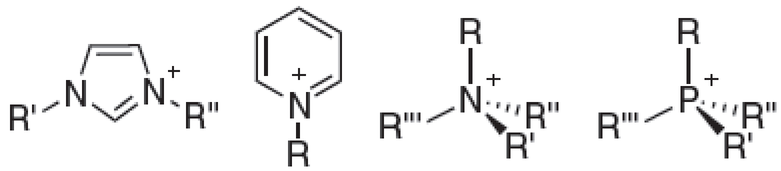
Contents

1. Basic

Definition

- Ionic Liquids are ionic compounds(salts) which are liquid below 100 ℃. More commonly, Ionic Liquids have melting points below room temperature.

cation



anion

$^{-}NTf_2$ BF_4^{-} CH_3COO^{-} CF_3COO^{-}

PF_6^{-} ^{-}OTf NO_3^{-} Br^{-} Cl^{-}

Free Customization!

1. Basic

History

1914 – $[EtNH_3][NO_3]$ (m.p. 12^{o}C) was first described.

1970s~1980s – imidazolium and pyridinium cation, halide anion

1992 – $[BF_4]^-$, $[PF_6]^-$

2000s – $[NTf_2]^-$

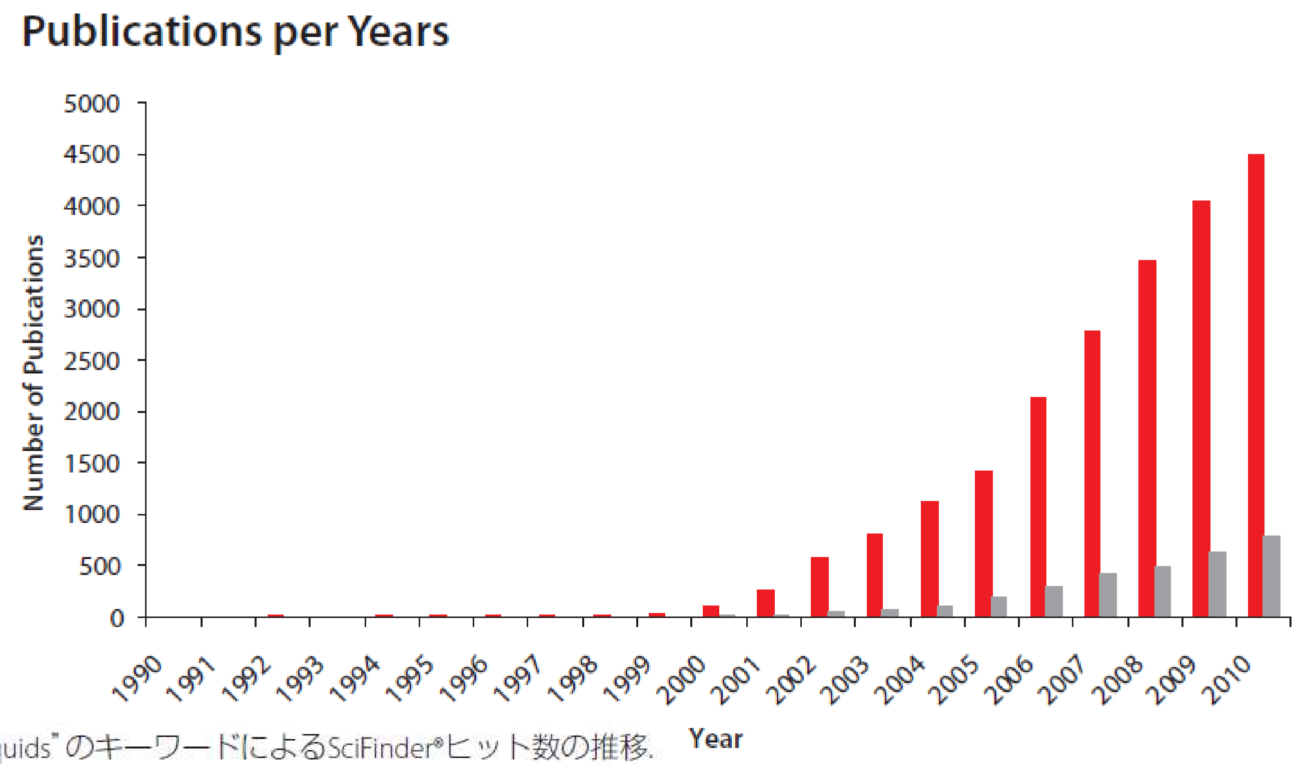
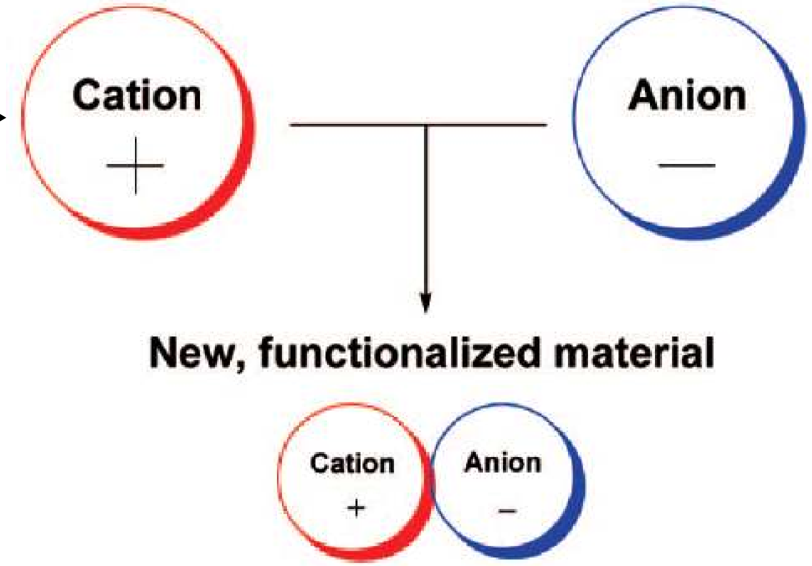


Figure 3. "Ionic Liquids"のキーワードによるSciFinder®ヒット数の推移.
赤は論文、灰色は特許数を示す.

1. Basic

Designers solvent – ionic liquids ①

1. **Viscosity**
2. **Surface tension**
3. **Melting point**



1. **Oxygen balance**
2. **Density**
3. **High energy content ion**

Stability

Functionality

about 1000 ILs are described in the literature,
300 are commercially available.

Designers solvent – ionic liquids ②

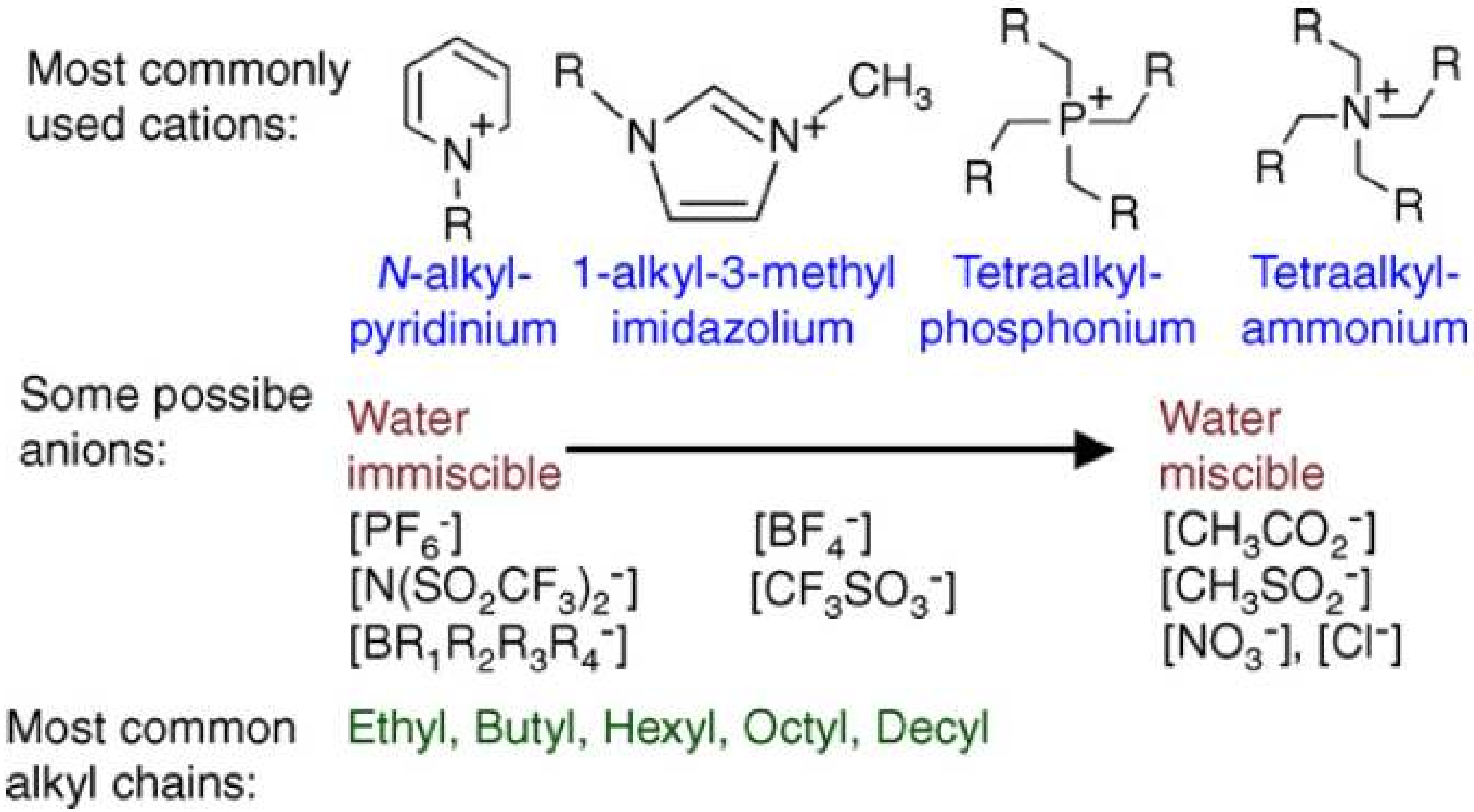


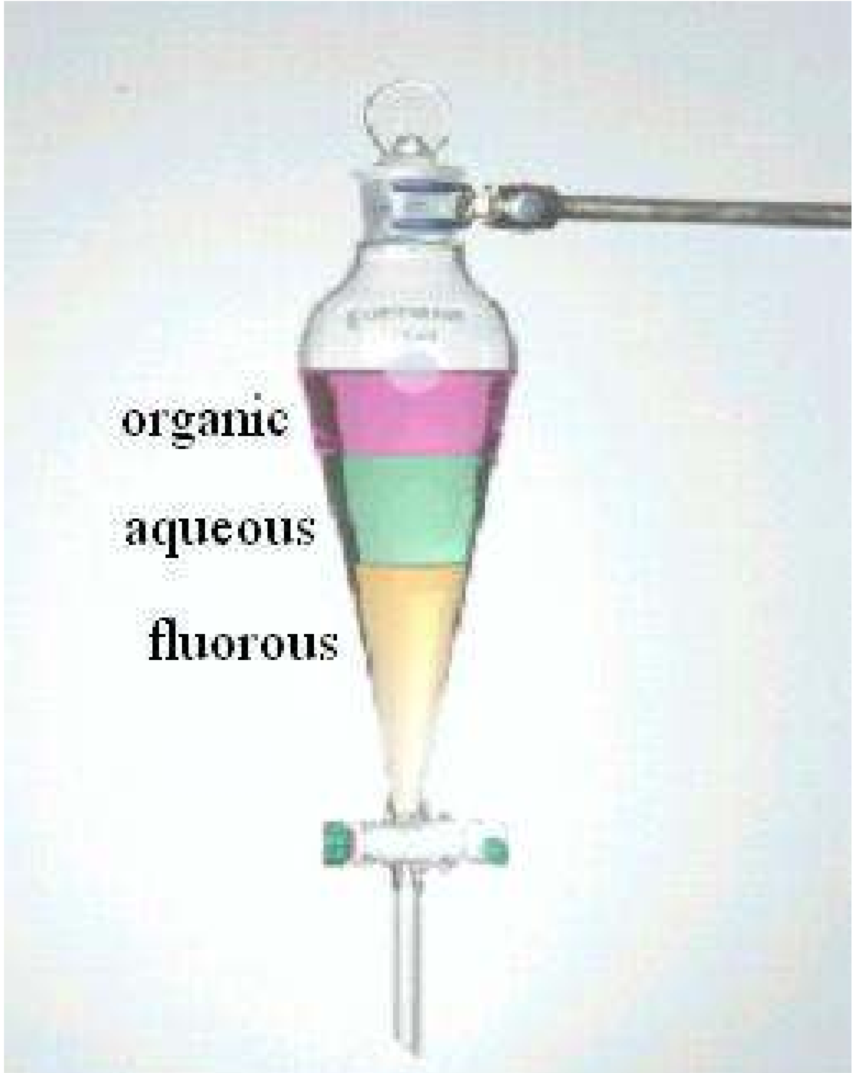
Fig. 3. Most commonly used cation structures and possible anion types [50]

1. Basic

Characteristics ①

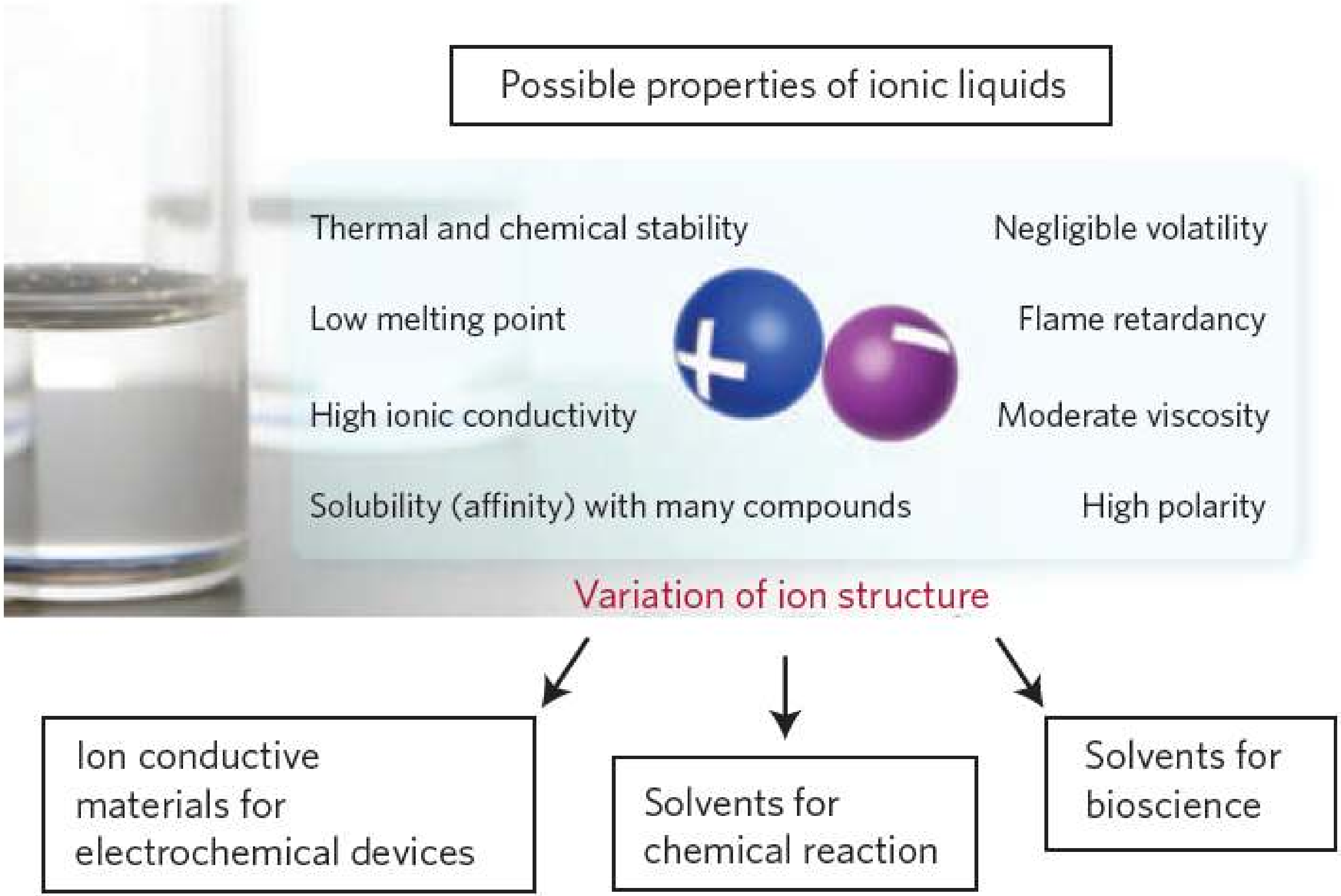
$[BF_4]^-$ $[PF_6]^-$ $[NTf_2]^-$

Fluorous ILs are immiscible
with both organic and aqueous solvents.



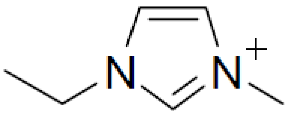
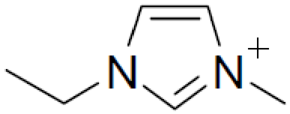
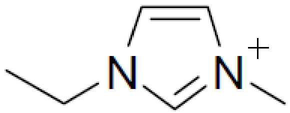
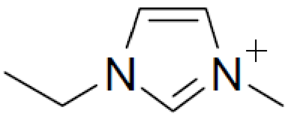
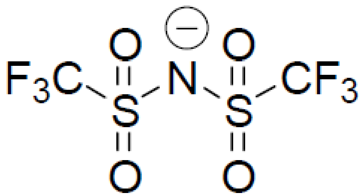
Characteristics ②

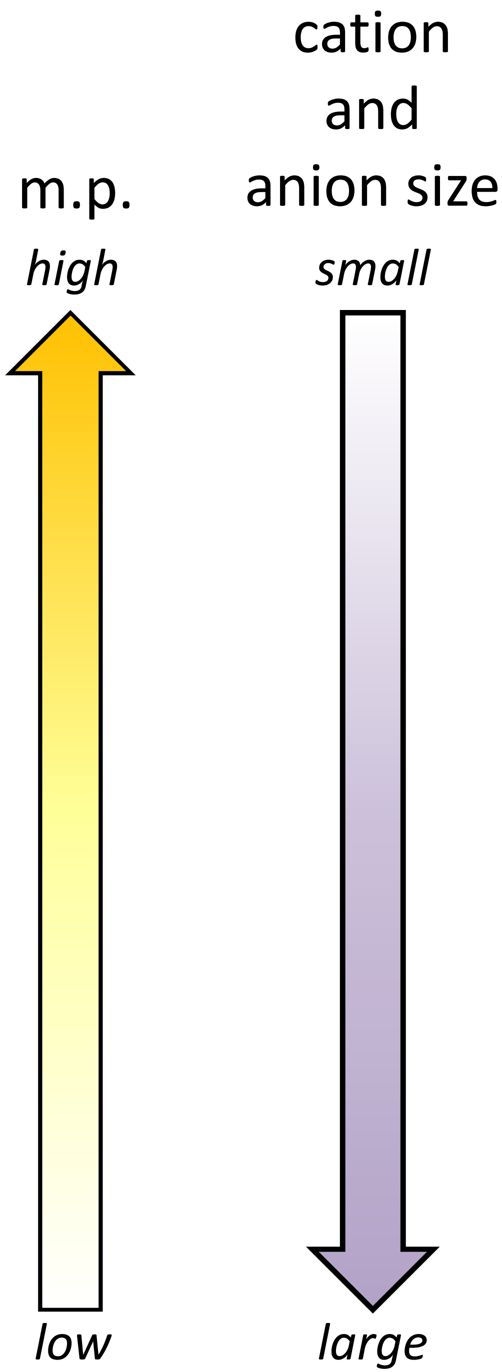
Ionic liquids



1. Basic

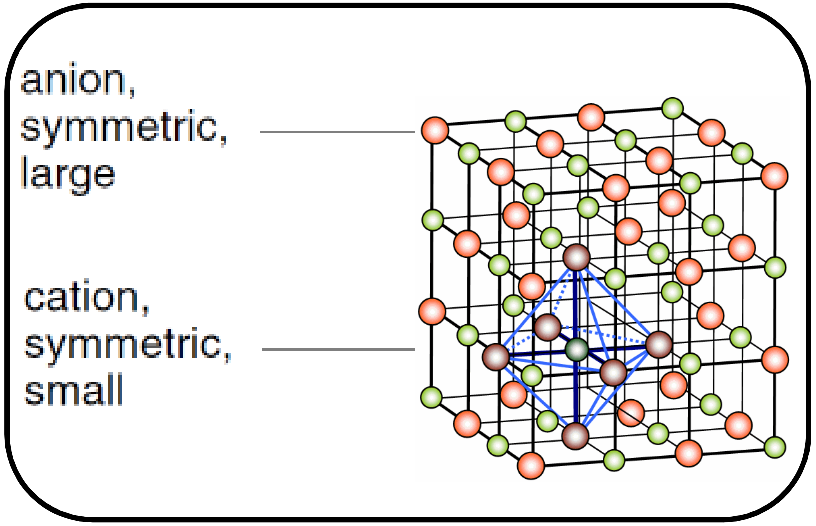
Melting point ①

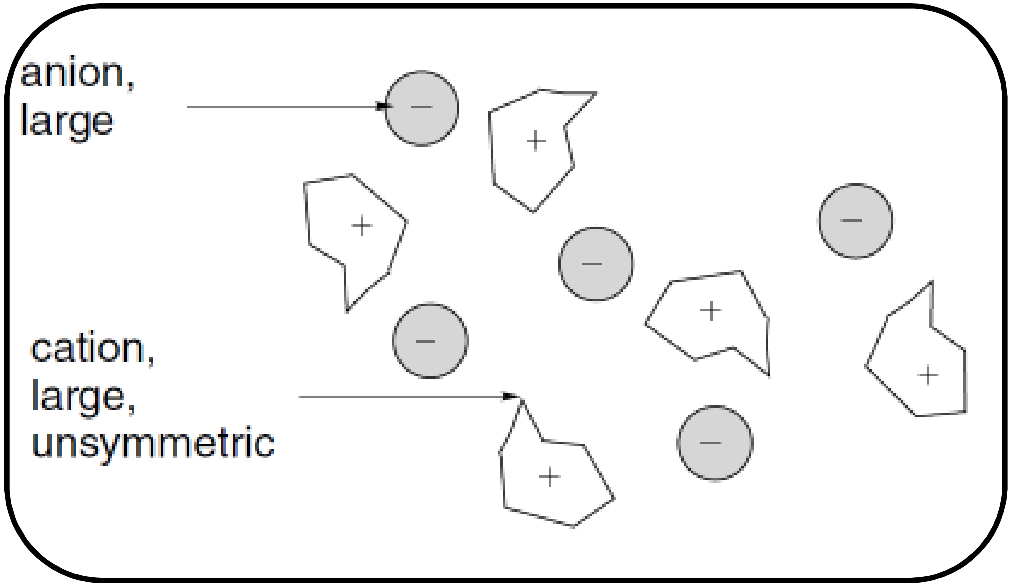
Cation	Anion	T_m / °C
Na^+	Cl^-	801
Cs^+	Cl^-	645
$(Pr)_4N^+$	Cl^-	241
	Cl^-	87
	NO_3^-	38
	BF_4^-	15
		–3



1. Basic

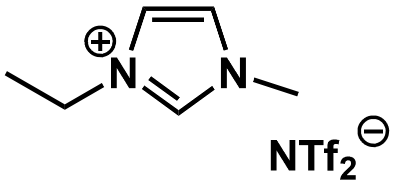
Melting point ②





NaCl

m.p. 801 °C



m.p. -3 °C

1. Basic

DSC (Differential Scanning Calorimetry) ①

DSC is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature.

Using this technique it is possible to observe fusion and crystallization events as well as glass transition temperatures T_g

Fig.1 DSC

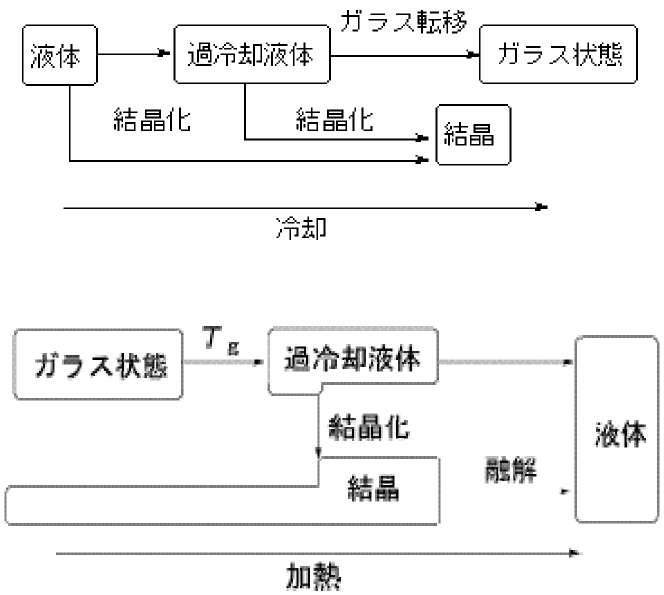


Fig.2

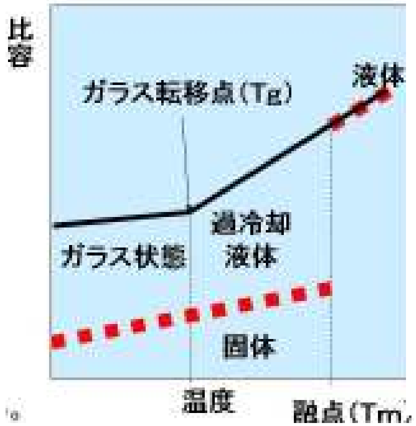


Fig.3

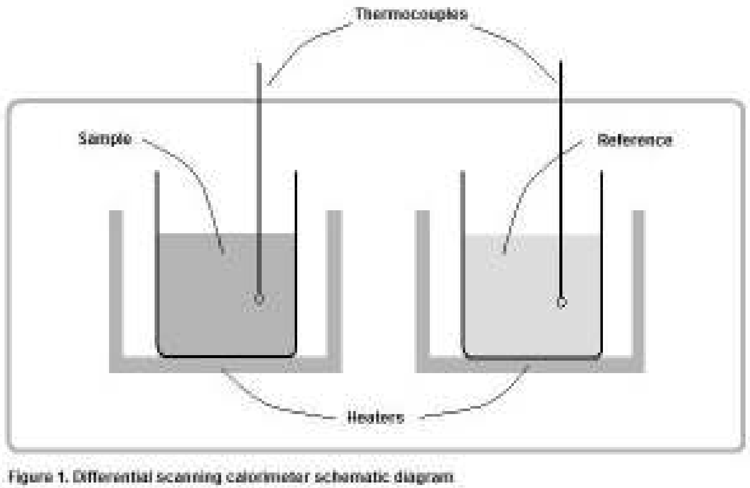
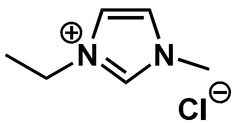


Fig.4

DSC (Differential Scanning Calorimetry) ②



[emim]Cl
m.p. : 87 °C

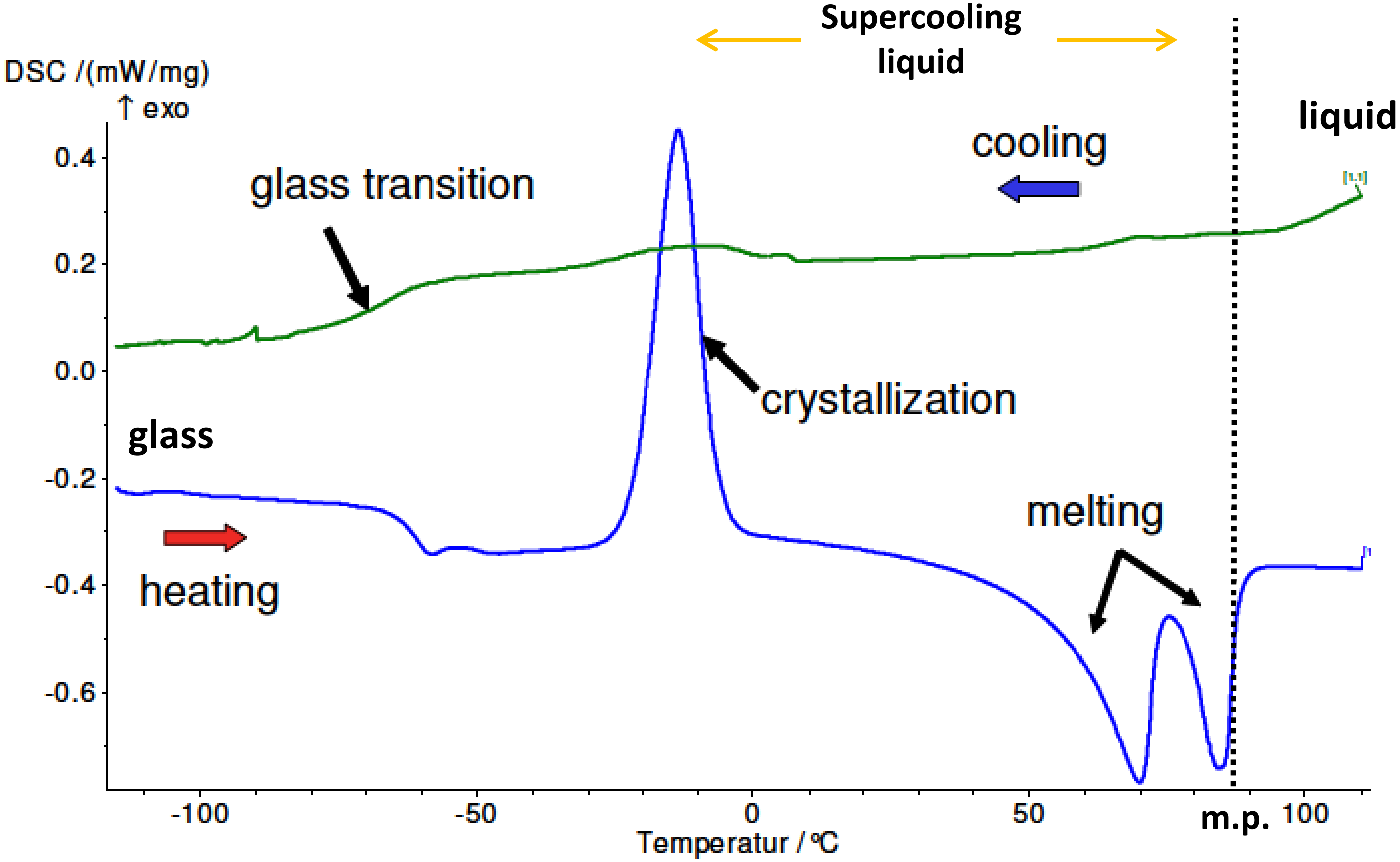
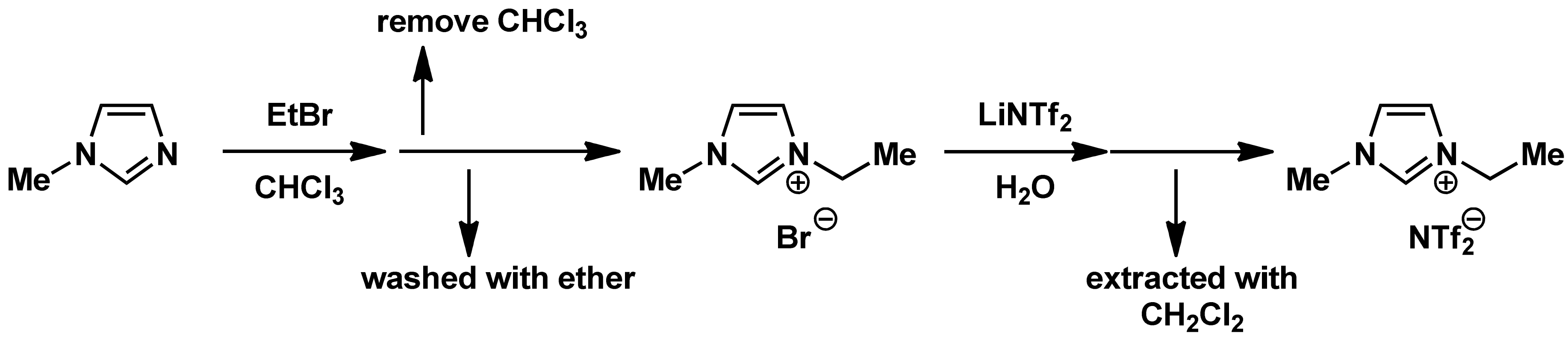


Figure 1: DSC melting and crystallization experiment of EMIM-Chloride , dT/dt = 10K/min

Phase transition is hard to happen. ⟶ **Flexibility of the constituent ions** + **Conformational diversity**

Preparation and Purification



<Purification>

Negligible volatility ⟶ ~~**distillation**~~

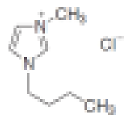
Low melting point ⟶ **recrystallization at low temperature**

1. Basic

Catalog (Aldrich)

1-Butyl-3-methylimidazolium chloride

BMIMCl
[79917-90-1] $C_8H_{15}ClN_2$ FW: 174.67
mp ~70 °C



▶ **≧99.0% (HPLC)**
water: ≦0.2%

04129-5G-F	5 g	¥13,900
04129-25G-F	25 g	¥47,800

1-Butyl-3-methylimidazolium hexafluorophosphate

$BMIMPF_6$
[174501-64-5] $C_8H_{15}F_6N_2P$ FW: 284.18
d 1.38 g/mL (20 °C) n_D^{20} 1.41

▶ **for catalysis, ≧98.5% (T)**
water: ≦0.02%
bromide (Br^-) : ≦10 mg/kg
chloride (Cl^-) : ≦10 mg/kg
nitrate (NO_3^-) : ≦10 mg/kg
phosphate (PO_4^{3-}) : ≦30 mg/kg
sulfate (SO_4^{2-}) : ≦10 mg/kg

18122-5G-F	5 g	¥11,900
18122-50G-F	50 g	¥72,000

1-Ethyl-3-methylimidazolium bromide

[65039-08-9] $C_6H_{11}BrN_2$ FW: 191.07

▶ **dry, ≧98.5% (HPLC/T)**
water: ≦200 ppm

03938-5G	5 g	¥24,600
03938-25G	25 g	¥93,900

Butyltrimethylammonium bis(trifluoromethylsulfonyl)imide

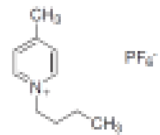
[258273-75-5] $C_9H_{18}F_6N_2O_4S_2$ FW: 396.37

▶ **99%**
water: ≦0.2%
bromide (Br^-) : ≦25 mg/kg
chloride (Cl^-) : ≦25 mg/kg
fluoride (F^-) : ≦10 mg/kg
nitrate (NO_3^-) : ≦25 mg/kg
phosphate (PO_4^{3-}) : ≦10 mg/kg
sulfate (SO_4^{2-}) : ≦25 mg/kg

713007-5G	5 g	¥8,300
713007-50G	50 g	¥40,000

1-Butyl-4-methylpyridinium hexafluorophosphate

$4MBPPF_6$
[401788-99-6] $C_{10}H_{16}F_6NP$ FW: 295.20
mp ~45 °C

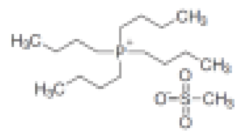


▶ **≧97.0%**
Ionic liquid: reaction kinetics of redox reactions[1]
Lit.cited: 1. D. Behar et al. *J. Phys. Chem. A* **106**, 3139, (2002)

88458-5G	5 g	¥17,000
88458-50G	50 g	¥52,000

Tetrabutylphosphonium methanesulfonate

[98342-59-7] $C_{17}H_{39}O_3PS$ FW: 354.53
mp 59-62 °C



▶ **≧98.0% (NT)**
Lit.cited: 1. M. Badri et al. *Tetrahedron Lett.* **33**, 4435, (1992)
2. R.M. Pomaville et al *J. Chromatogr.* **438**, 1, (1988)

86929-5G	5 g	¥12,900
86929-25G	25 g	¥51,700

Database ①

http://ilthermo.boulder.nist.gov/ILThermo/pureils.uix.do?event=NewSearch

Ionic Liquids Database- (ILThermo)

Property Data of Pure Ionic Liquids
Search by Ionic Liquids

Formula

Molec.Weight

Ionic Liquid Name 1-butyl-3-methylimidazolium chlc

Search

Enter Criteria for Ionic Liquids

Hints: Search is CASE-INSENSITIVE. Enter a Molecular Formula or Name or Just a fragment of these fields

Examples for Name: pyridinium, Imidazolium, CHLORIDE,...

Examples for Formula: C8H15BrN2, c8h15, ClN2,...

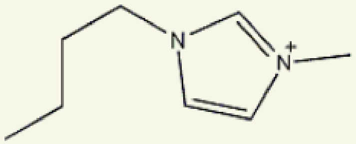
Examples for Molecular Weight: >200, 216.12, ...

Database ②

http://ilthermo.boulder.nist.gov/ILThermo/pureils.uix.do?event=NewSearch

Ionic pair constituting this ionic liquid - 1-butyl-3-methylimidazolium chloride

前へ 1-2 / 2 次へ

Formula	Ionic Charge	Ionic Name	Ionic Structure
C8H15N2	1	1-butyl-3-methylimidazolium	
Cl	-1	chloride	Cl^-

Available properties for this ionic liquid - 1-butyl-3-methylimidazolium chloride

前へ 1-6 / 6 次へ

選択	Property Category	Description	References	Data Points
◉	Heat Capacity and Derived Properties	Heat Capacity at Constant Pressure, J/K/mol	2	14
○	Phase Transition Properties	Glass Transition Temperature, K	1	1
○	Phase Transition Properties	Normal Melting Temperature, K	7	7
○	Refraction, Surface Tension, and Speed of Sound	Surface Tension, N/m	1	20
○	Transport Properties	Viscosity, Pa s	1	9
○	Volumetric Properties	Specific Density, kg/m**3	1	1

References and Data Sets

前へ 1-2 / 2 次へ

選択	Reference Title	Sample No	Data Set	Year Pub.	Authors
◉	Heat Capacities of Ionic Liquids and Their Applications as Thermal	1	1	2003	Holbrey, J. D.; Reichert, W. M.; Reddy, R. G.; Rogers, R. D.

2. Application

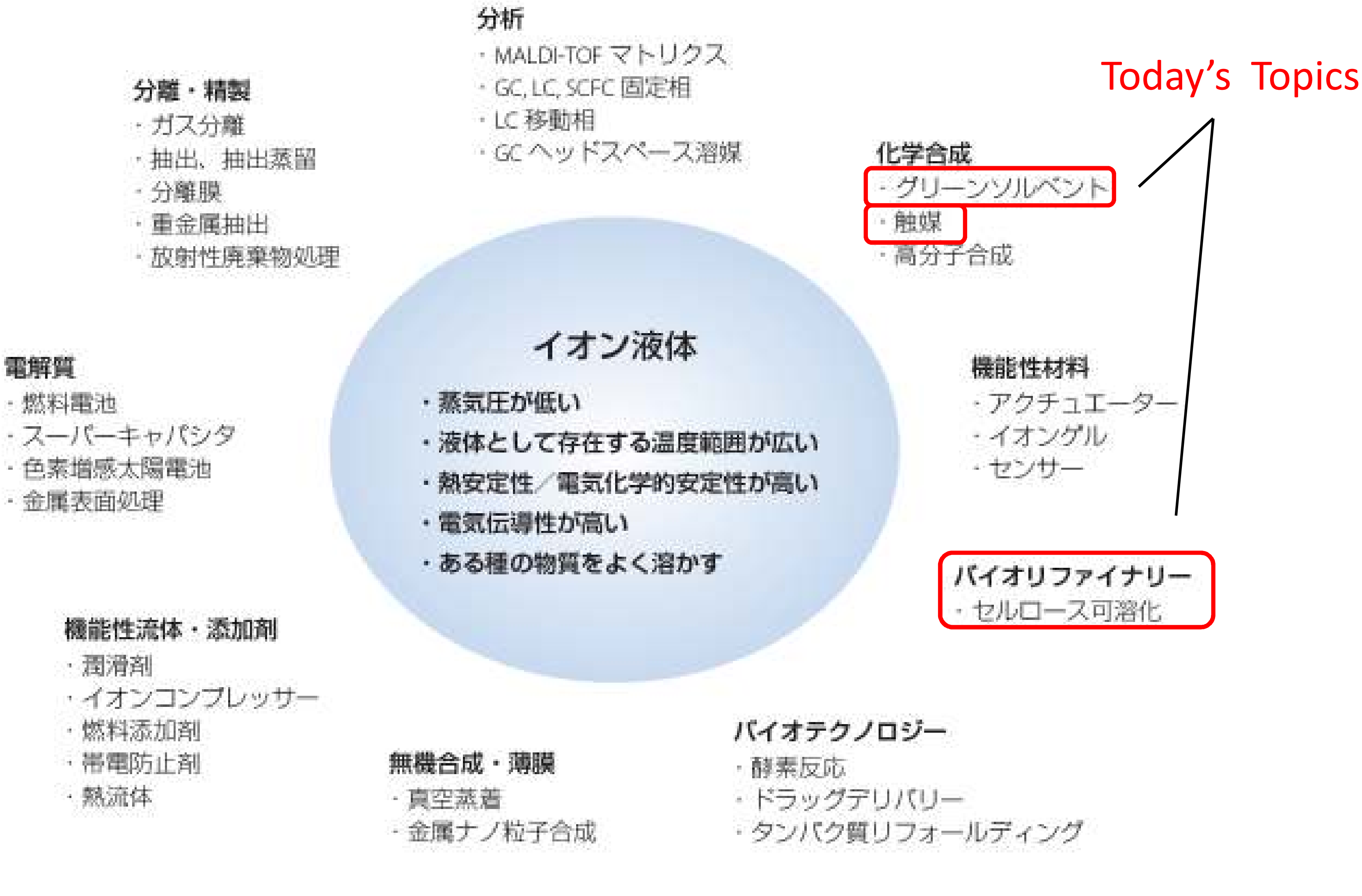
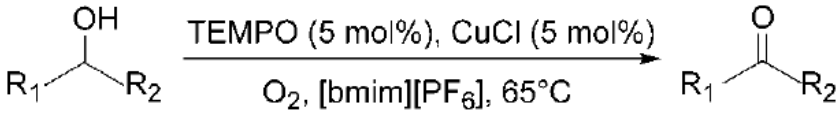


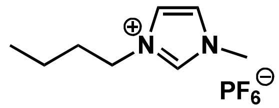
Figure 1. イオン液体の特徴とアプリケーション

2-1.

Organic Reaction (TEMPO oxidation) ①

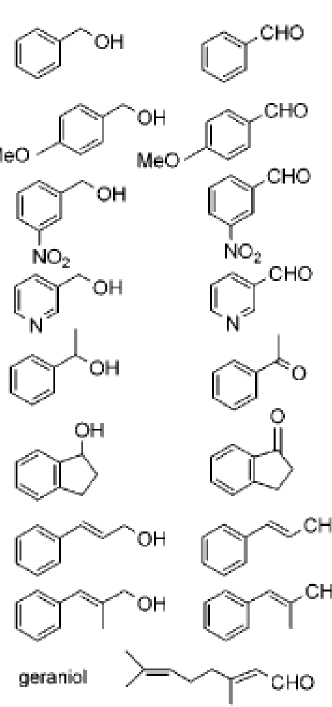


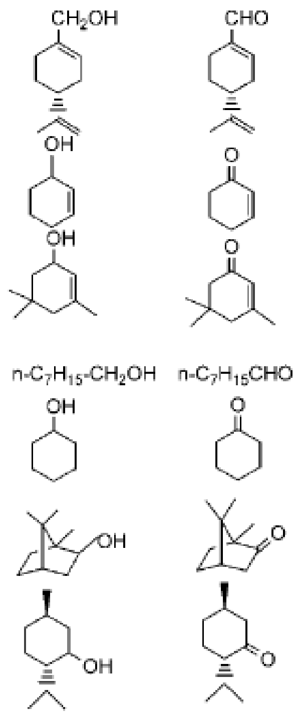
R_1= aryls, alkyls ; R_2= H, alkyls



[bmim][PF_6]

Table 1. Conversion of Alcohols to Aldehydes and Ketones





entry	alcohol	product	time/h	conversion[a]	yield[b]
1			15	98	72
2			9[c]	98	73
3			16	97	90
4			15	97	96
5			36	96	75
6			83	98	73
7			42[d]	98	72
8			30	96	91
9			20	98	75
10			29	97	78
11	geraniol		18	98	85
12			16	98	90
13			24	98	75
14			28	90	60
15	n-C_7H_{15}-CH_2OH	n-$C_7H_{15}CHO$	30	70	
16			60	90	
17			36[d]	98	50
18			48	30	
19			48	no reaction	

[a] GC conversion. [b] Isolated yield. [c] Reaction was carried out at 50 °C with 10% catalyst. [d] 10% catalyst was used.

2-1.

Organic Reaction (TEMPO oxidation) ②

Scheme 2

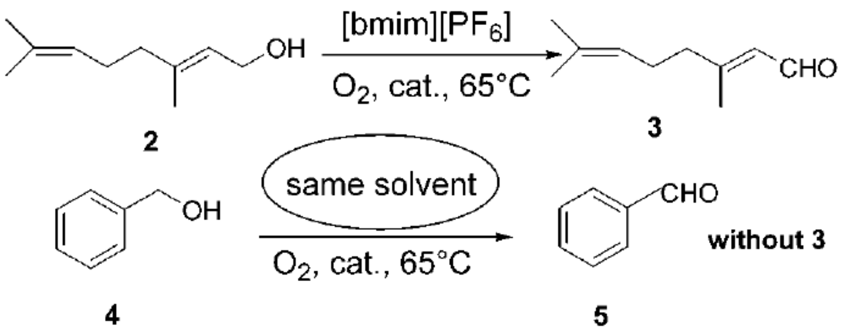


Table 2. Reuse of the Solvent for the Oxidation of Benzyl Alcohol to Benzaldehyde

	run							
	1	2	3	4	5	6	7	8
yield (%)	72	70	68	70	65	64	62	60

R. Gree, *et al. Org. Lett.* **2002**, *4,* 9.

2-1.

Organic Reaction (TEMPO oxidation) ③

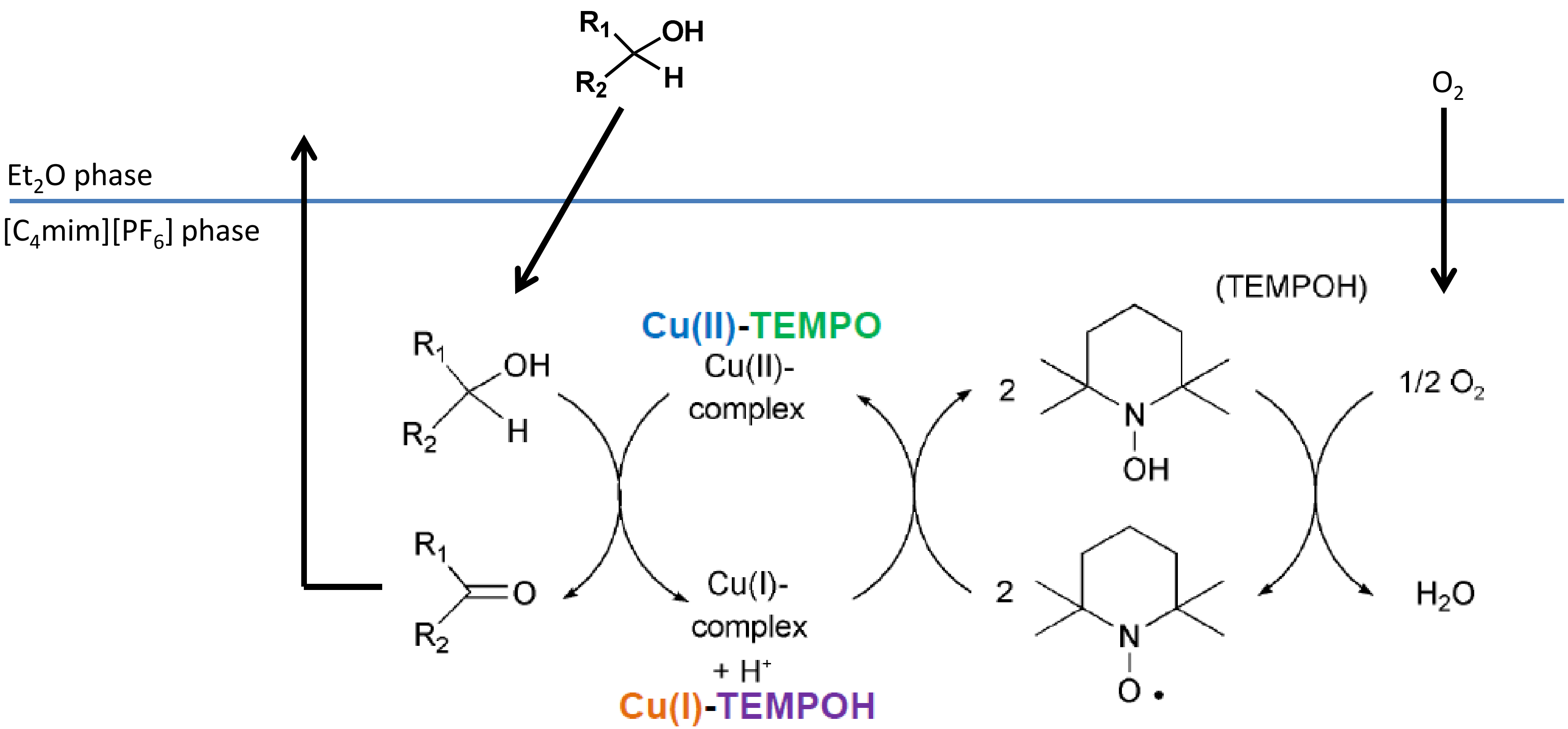


Fig. 3 Copper-centred mechanism for the Cu–TEMPO catalysed aerobic oxidation of alcohols.

2-1.

Organic Reaction (other reactions)

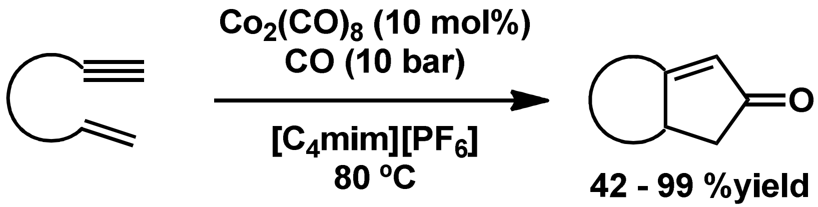


Figure 1. Pauson-Khand reaction

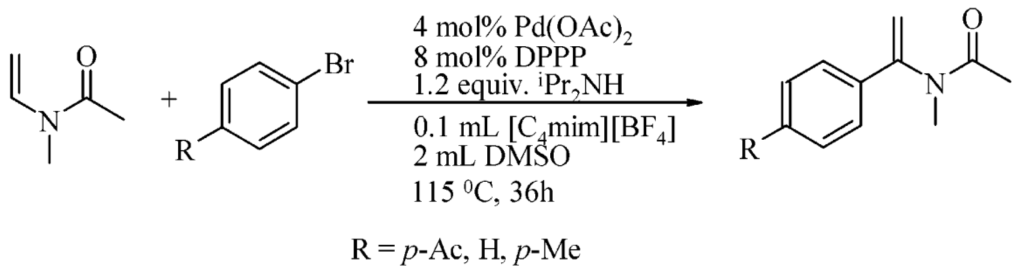


Figure 2. Heck Arylation

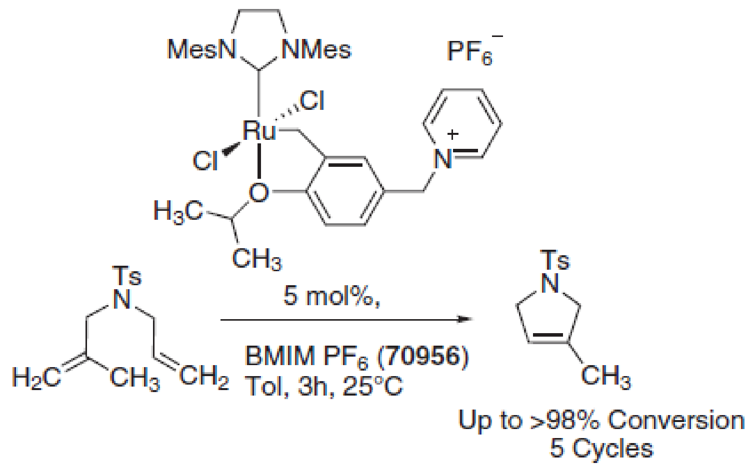


Figure 4. Olefin Metathesis

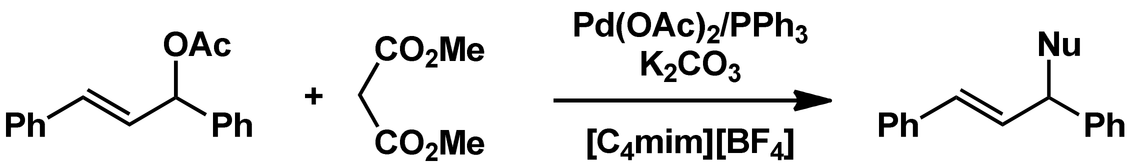


Figure 3. Tsuji-Trost reaction

and so on.

2-2.

Bioscience (Biorefinery) ①

Biomass

Energy

1st step : Extraction and dissolution of polysaccharides from biomass

↓

2nd step : Hydrolysis of polysaccharides into mono-, di-, or oligo-saccharide

↓

3rd step : Conversion of chemical energy, involving the resulting sugars, into electric energy

2-2.

Bioscience (Biorefinery) ②

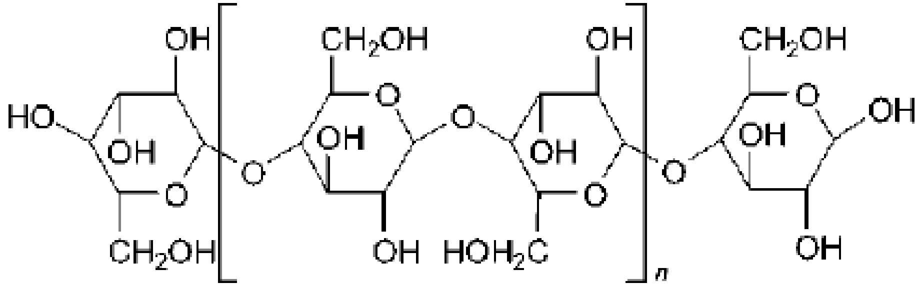


Figure 1. A cellulose polymer chain, *n* is typically 400−1000.

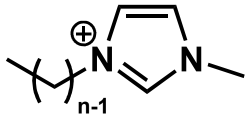
Problem : Cellulose is insoluble in water and common organic reagents.

2-2.

Bioscience (Biorefinery) ③

Table 1. Solubility of Dissolving Pulp Cellulose in Ionic Liquids

ionic liquid	method	solubility (wt %)
$[C_4mim]Cl$	heat (100 °C)	10%
	(70 °C)	3%
$[C_4mim]Cl$	heat (80 °C) + sonication	5%
$[C_4mim]Cl$	microwave heating 3−5-s pulses	25%, clear viscous solution
$[C_4mim]Br$	microwave	5−7%
$[C_4mim]SCN$	microwave	5−7%
$[C_4mim][BF_4]$	microwave	insoluble
$[C_4mim][PF_6]$	microwave	insoluble
$[C_6mim]Cl$	heat (100 °C)	5%
$[C_8mim]Cl$	heat (100 °C)	slightly soluble



$[C_nmim]^+$
(C_n-methylimidazolium)

The melting point of $[C_4mim]Cl$ is 70°C.

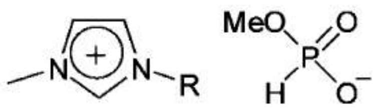
↓

<u>Extra energy is needed to operate with IL based on $[C_4mim]Cl$</u>

R. D. Rogers, *et al. J. Am. Chem. Soc.* **2002**, *124,* 4974.

2-2.

Bioscience (Biorefinery) ④



R = ethyl: 1, allyl: 2, *n*-propyl:3, *n*-butyl: 4

Chart 1 Chemical structure of dialkylimidazolium methylphosphonate.

Chloride anion : 70 °C

↓

Phosphonate anion : r.t.

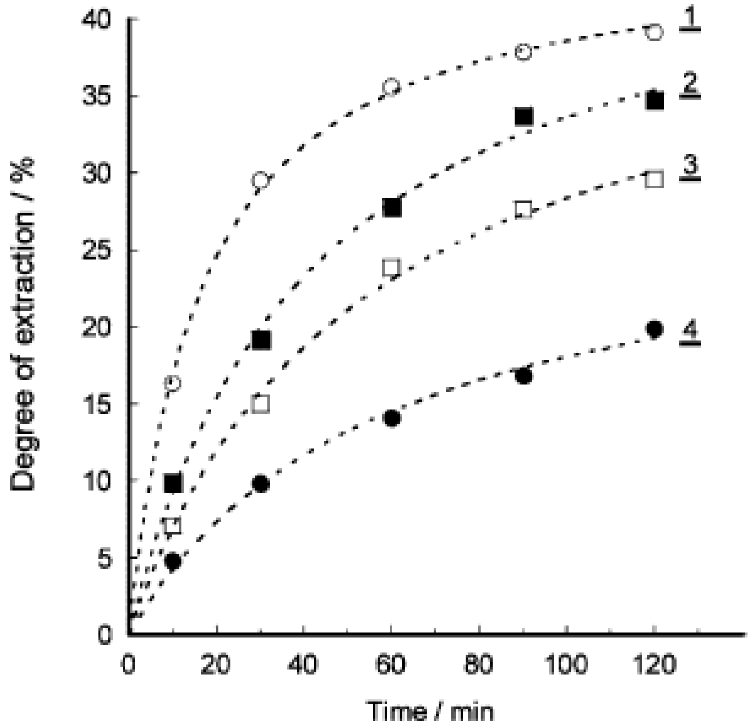


Fig. 3 Degree of extraction for bran with a series of ILs.

@50 °C

H. Ohno, *et al. Green Chem.* **2010**, *12,* 1274.

2-2.

Bioscience (Biorefinery) ⑤

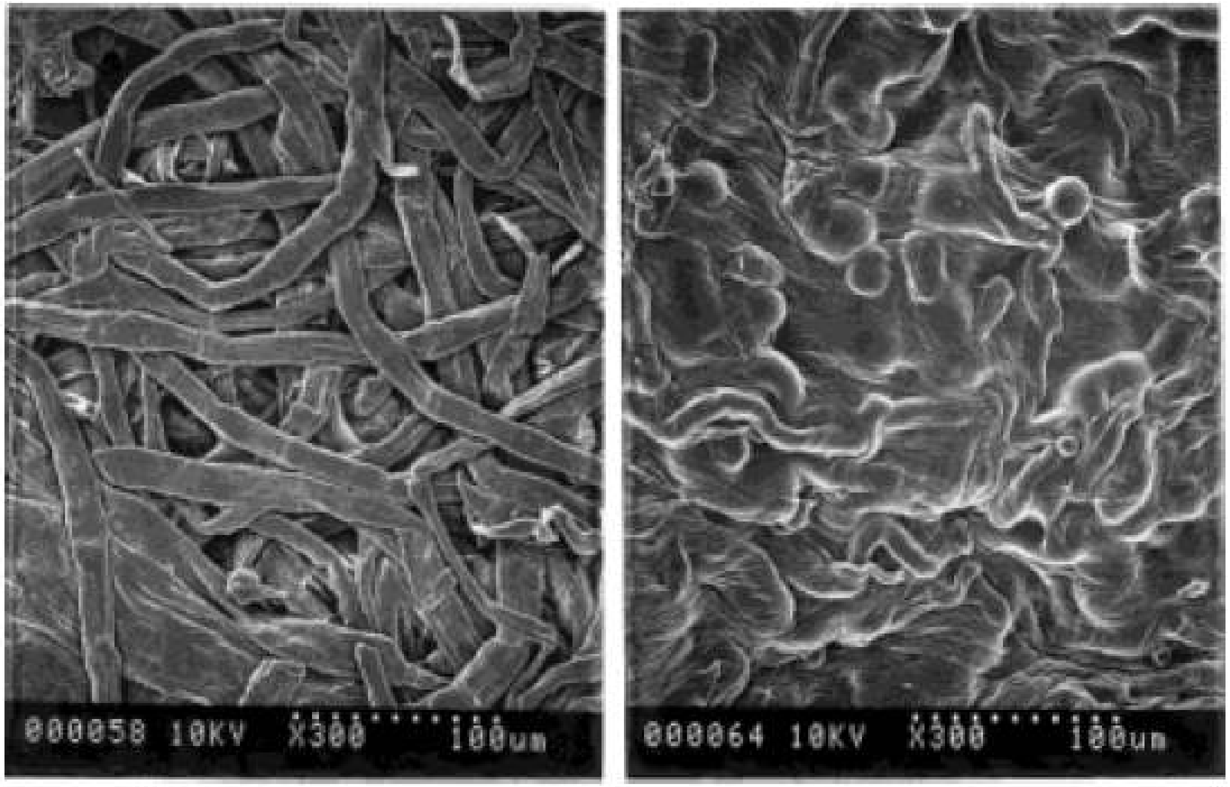
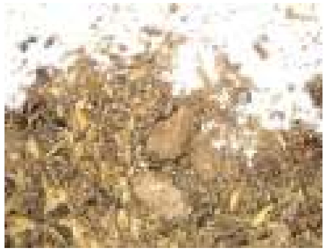


Figure 2. SEM micrographs of the initial dissolving pulp (left) and after dissolution in $[C_4mim]Cl$ and regeneration into water (right).

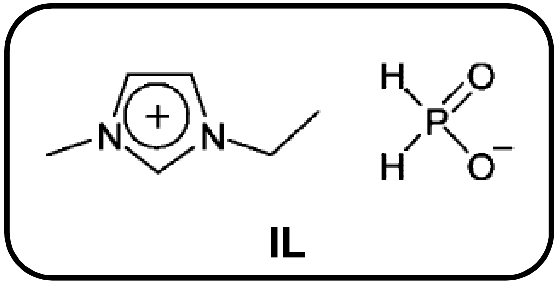
R. D. Rogers, *et al. J. Am. Chem. Soc.* **2002**, *124,* 4974.

2-2.

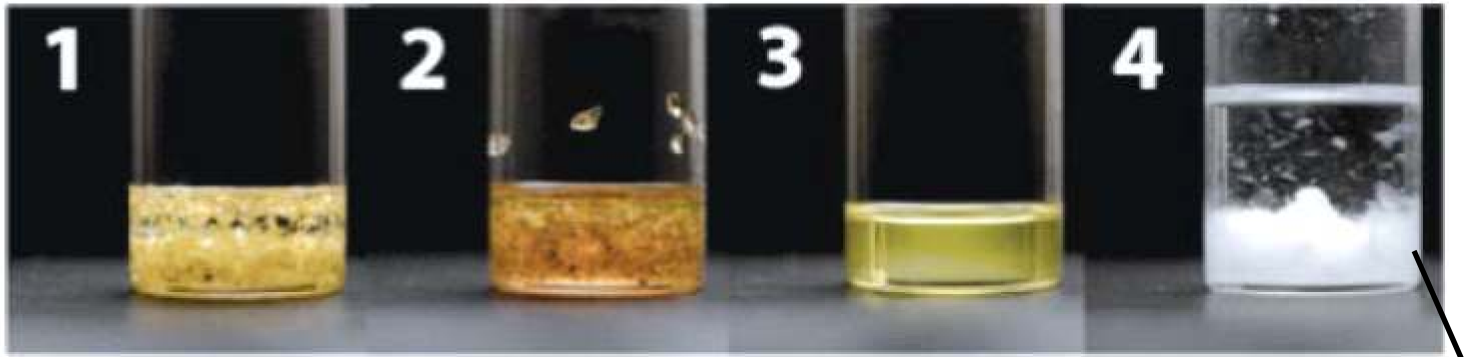
Bioscience (Biorefinery) ⑥



Biomass(bran)



IL



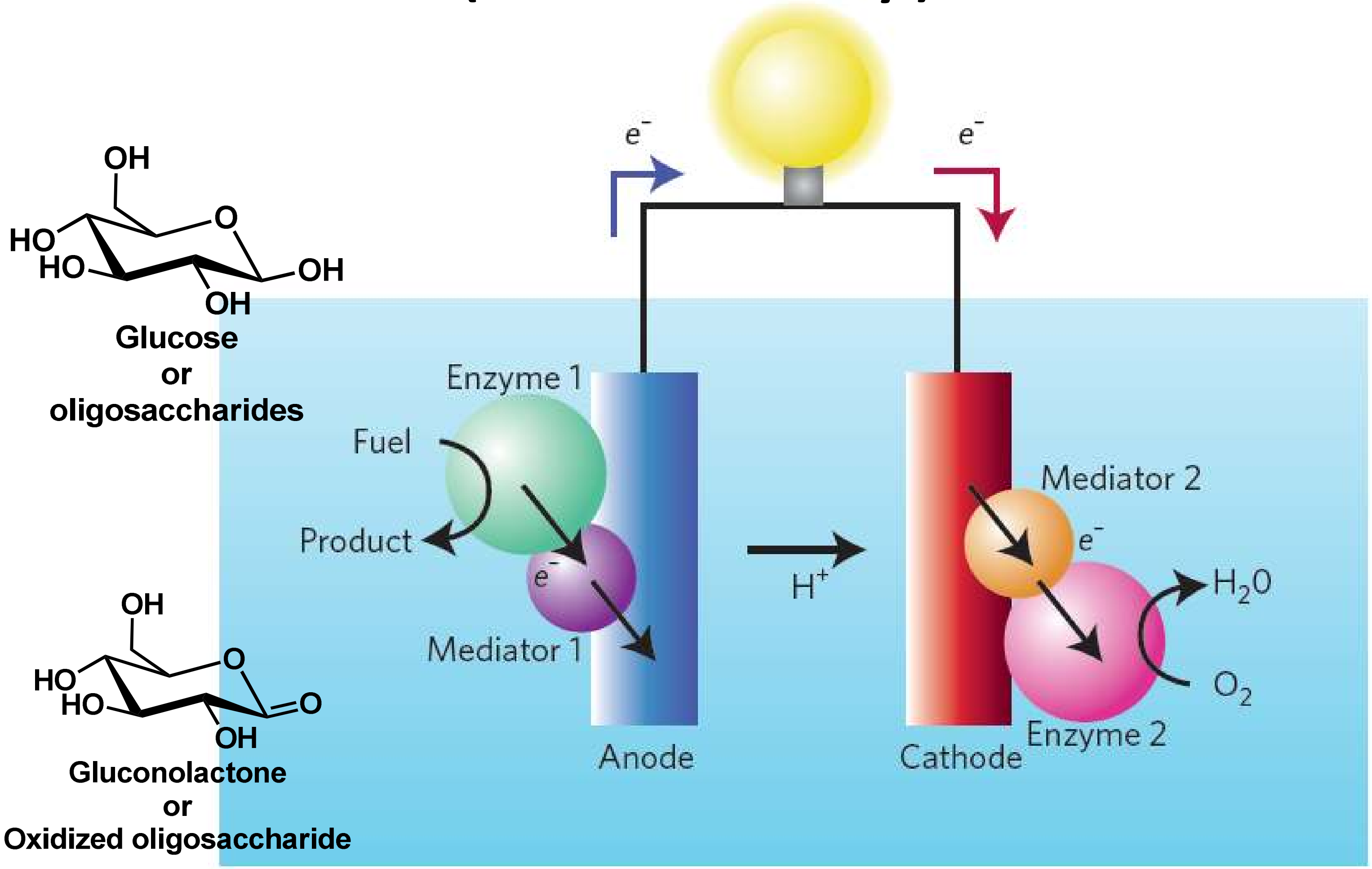
cellulose

Fig. 2 Extraction of polysaccharides from bran. 1: Before heating, 2: after heating for 10 min, 3: filtrate, 4: after addition of ethanol to the filtrate.

H. Ohno, *et al. Green Chem*. **2010**, *12,* 1274.

2-2.

Bioscience (Biorefinery) ⑦



Now ------------> **Future**

H_2O ------------> **Ionic Liquids**

Denaturation of Enzymes

B. Scrosati, *et al. Nature. Mater*. **2009**, *7,* 621.

2-3.

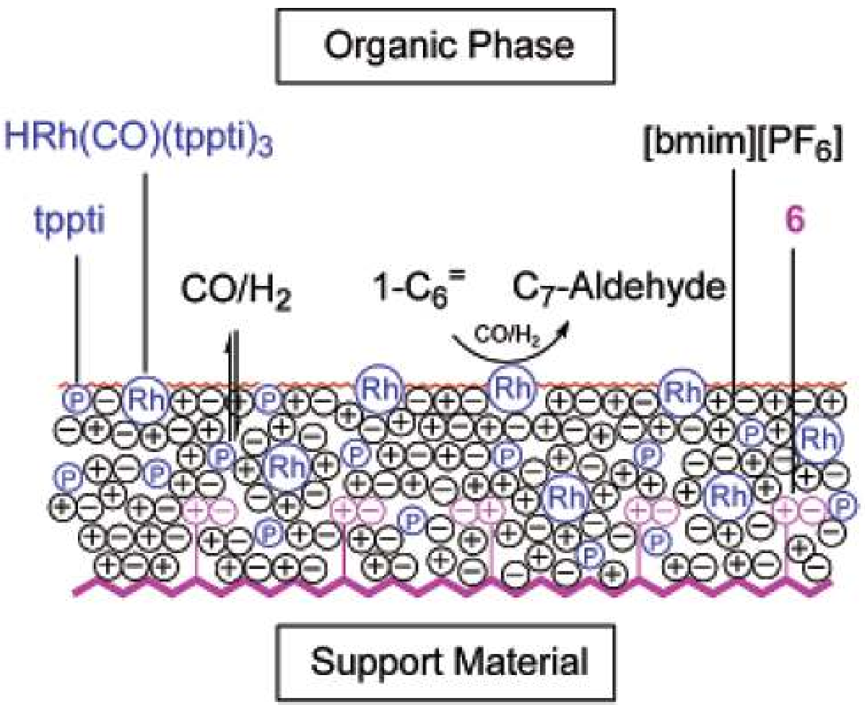
Supported Ionic Liquid Phase (SILP) ①

Homogeneous Catalyst v.s. Heterogeneous Catalyst

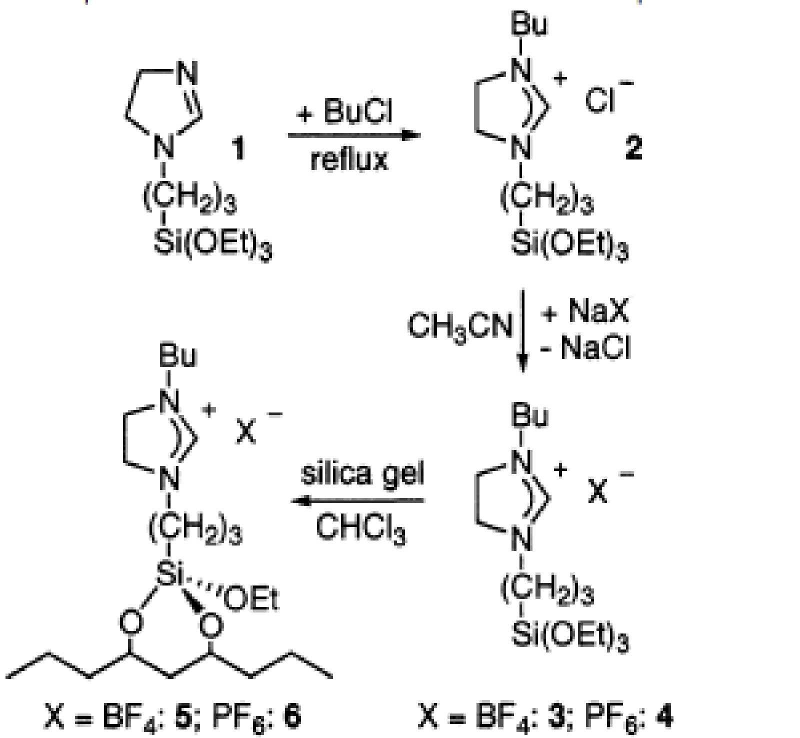
Homogeneous Catalyst		Heterogeneous Catalyst
difficult / expensive	Recovery	easy / cheap
poor	Thermal Stability	good
excellent	Selectivity	poor

Supported Ionic Liquid Phase (SILP) ②

- SILP catalysis is a concept which combines the advantages of ionic liquids with those of heterogeneous support materials.



Scheme 1. Preparation of Surface Anchored Ionic Liquid Phases



C. P. Mehnert, *et al. J. Am. Chem. Soc.* **2002**, *124,* 12932.

2-3.

Supported Ionic Liquid Phase (SILP) ③

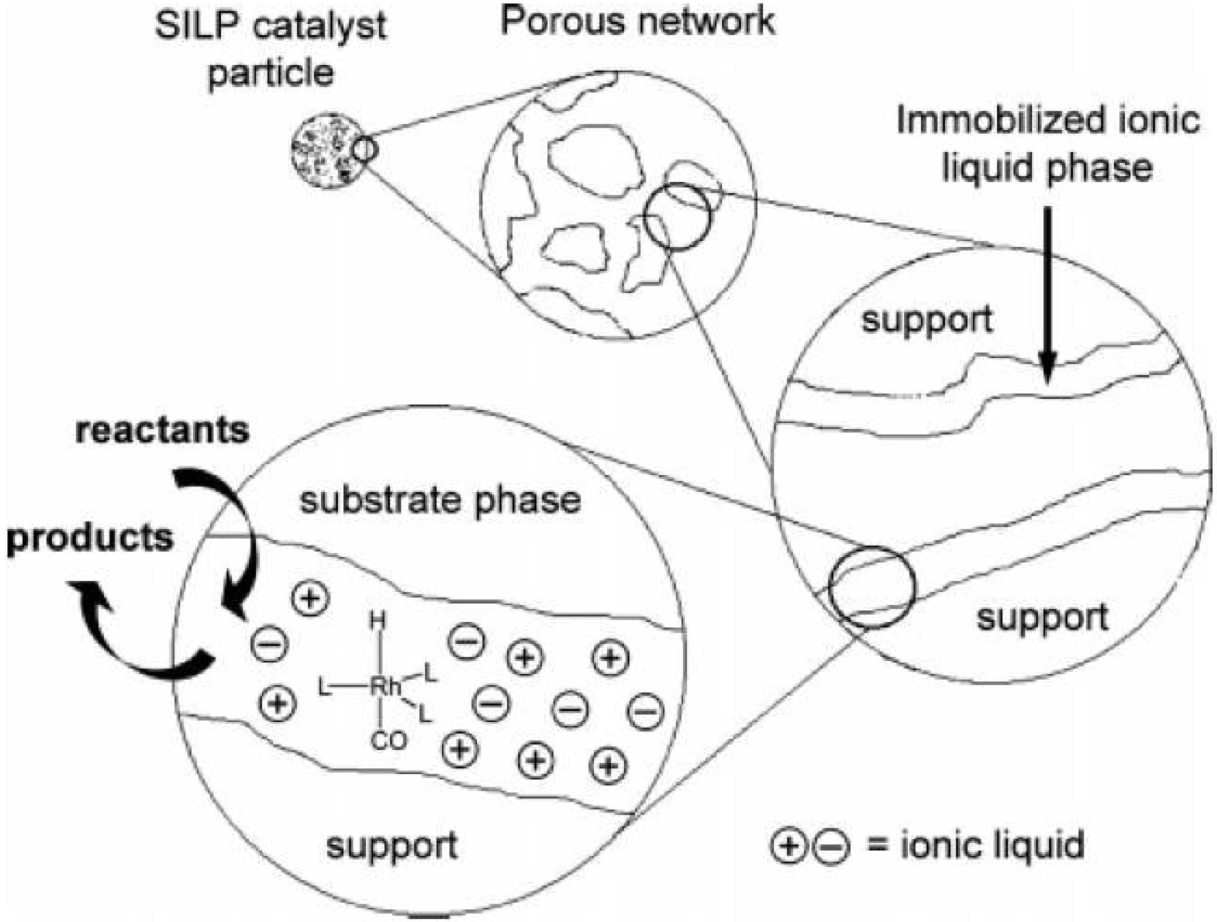


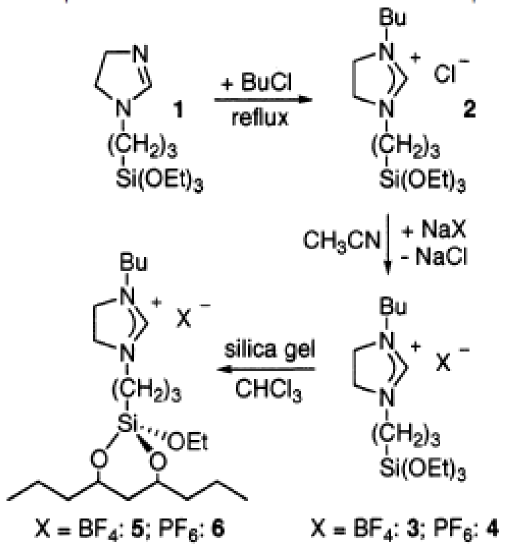
Figure 12. Schematic drawing of a supported ionic liquid-phase (SILP) catalyst.

M. Haumann, A. Riisager, *Chem. Rev*. **2008**, *108,* 1474.

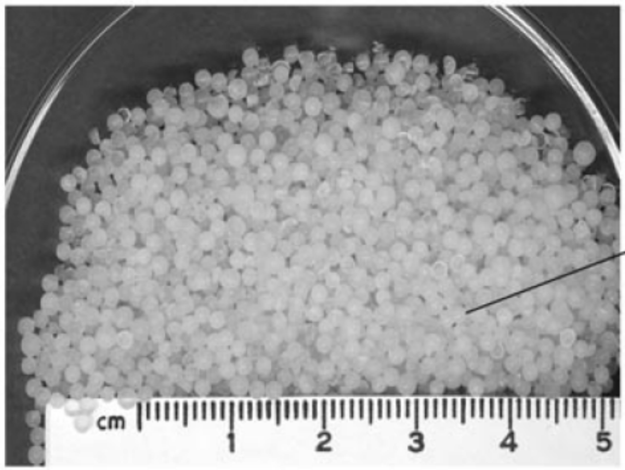
2-3.

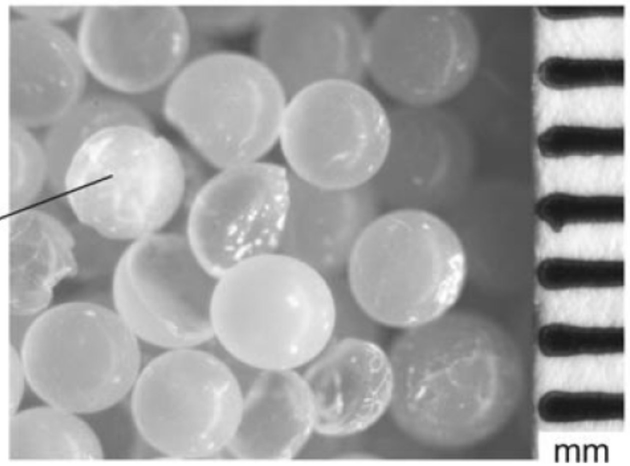
Supported Ionic Liquid Phase (SILP) ④

Scheme 1. Preparation of Surface Anchored Ionic Liquid Phases



- ✓ SILP materials are prepared by dispersing a solution of the catalyst complex in an ionic liquid as a thin film on porous solid materials.
- ✓ This layer serves as the reaction phase in which the homogeneous catalist is dissolved.





C. P. Mehnert, *et al. Chem. Eur. J.* **2005**, *11,* 50.

2-3.

Supported Ionic Liquid Phase (SILP) ⑤

～ For Hydroformylation ～

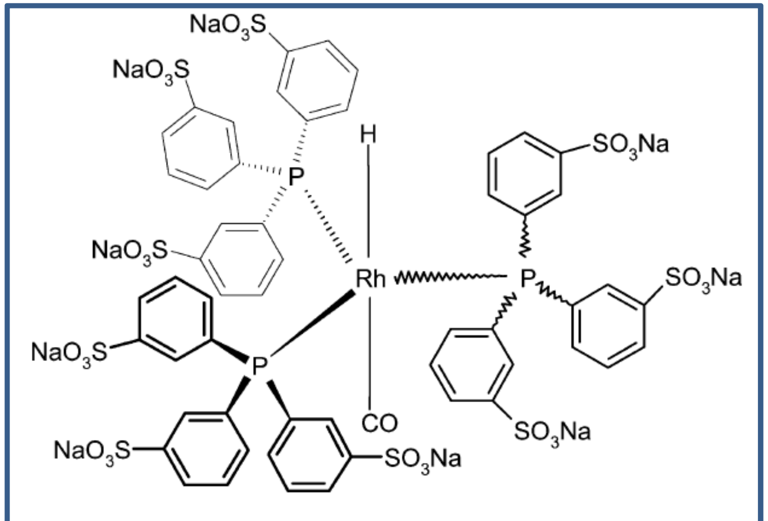
[Industrial process] Ruhrchemie-Rhone-Poulenc process

- Aqueous-organic biphasic catalist

$$CH_3-CH_2=CH_2+CO+H_2 \xrightarrow{cat} CH_3-CH_2-CH_2-CHO+CH_3-CH(CH_3)-CHO$$

$n-butyraldehyde$ $iso-butyraldehyde$

	Unit	Typical value
n-Butyraldehyde	(%)	94.5
iso-Butyraldehyde	(%)	4.5
n-Butyralcohol	(%)	0.5
iso-Butyralcohol	(%)	<0.1
Butyl formates	(%)	Traces
Heavy ends	(%)	0.4
n/*iso* ratio	–	21
Temperature	(°C)	120
Total pressure	(MPa)	50
CO/H_2 ratio	–	1.01
Aqueous/organic phase ratio	–	6
Conversion	(%)	95
Propylene quality	(% propene)	95



cat.

Problem : Phosphite ligands decompose by hydrolysis in water.

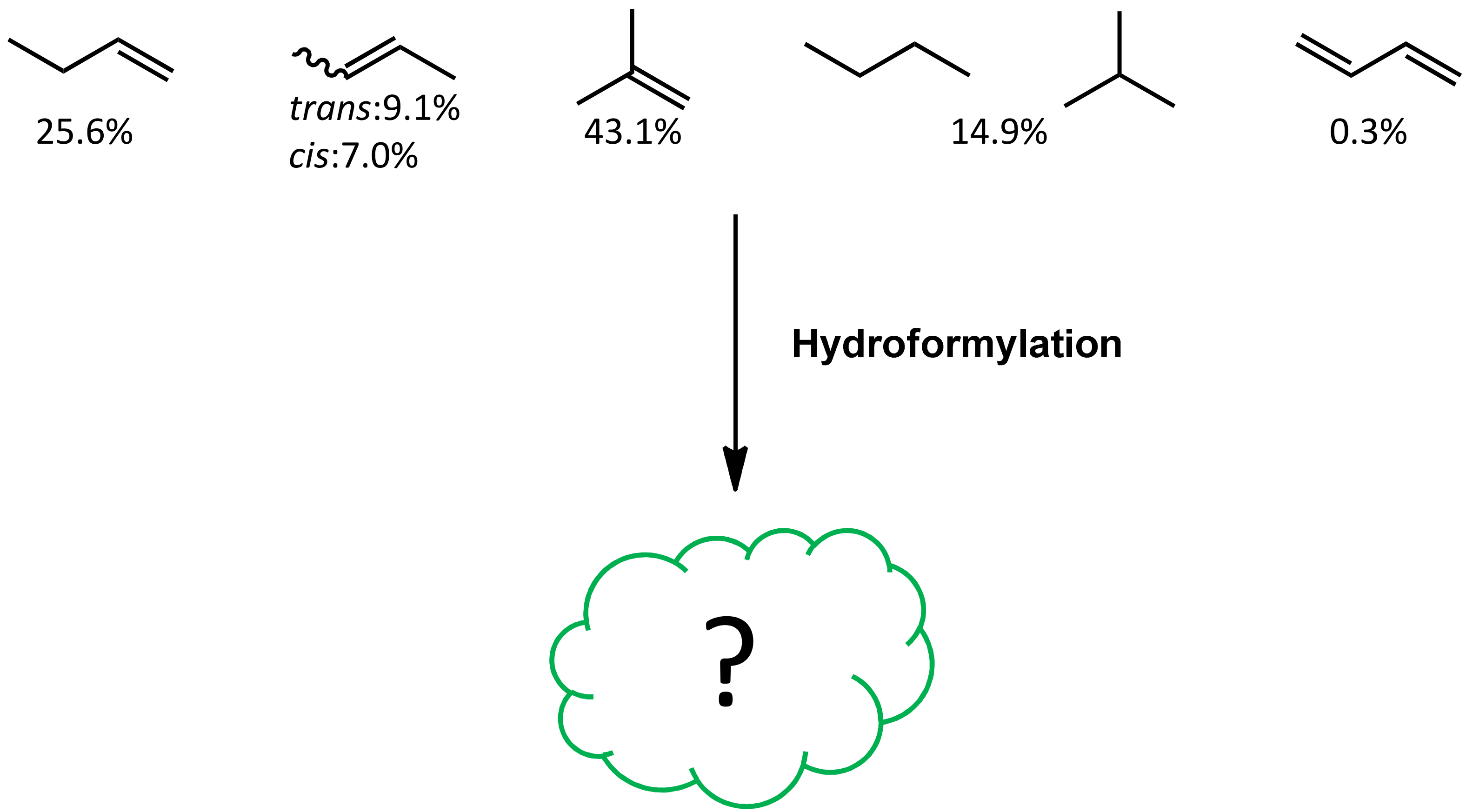
C. W. Kohlpaintner, *et al. Appl. Catal. A.* **2001**, *221,* 219.

2-3.

Supported Ionic Liquid Phase (SILP) ⑥

<Selectivity>

Mixed C_4 Feedstocks



M. Haumann, P. Wassersheid, *et al. Angew. Chem. Int. Ed.* **2011**, *50,* 4492.

Supported Ionic Liquid Phase (SILP) ⑦

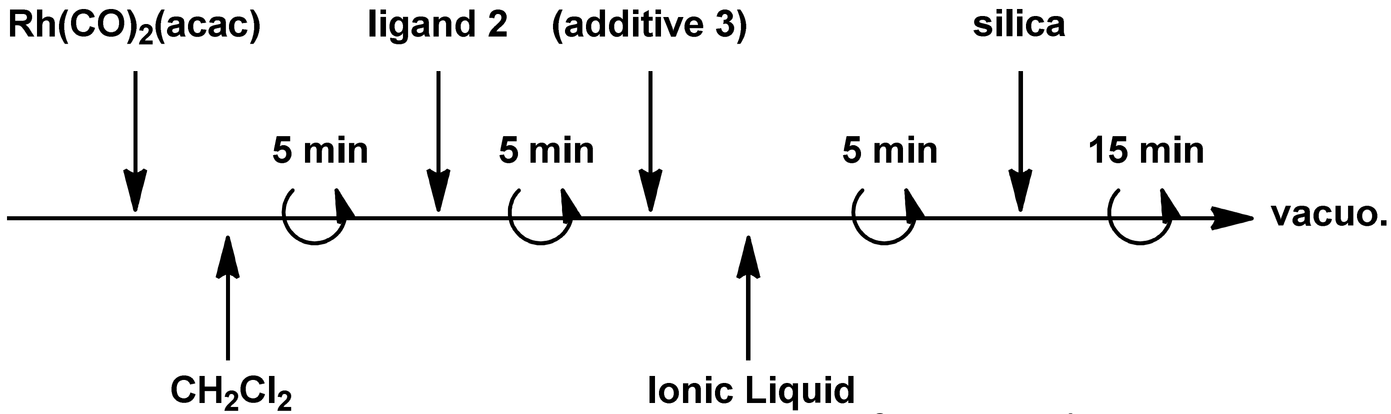
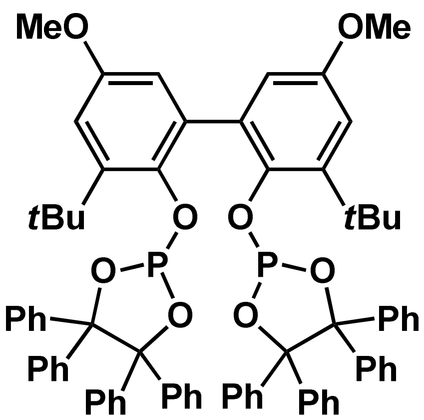
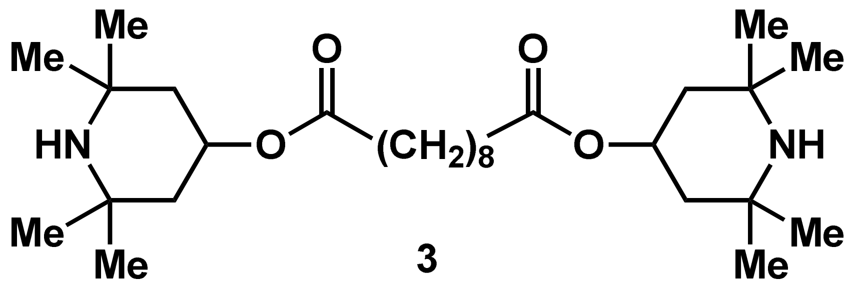


Fig. Preparation of SILP catalyst



2

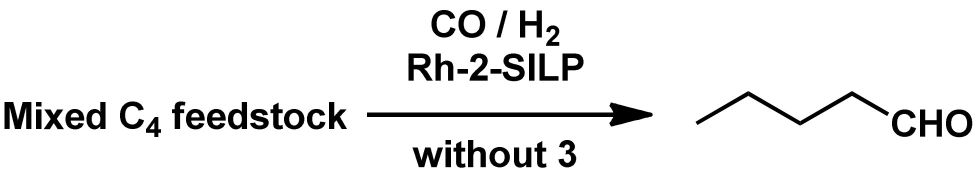


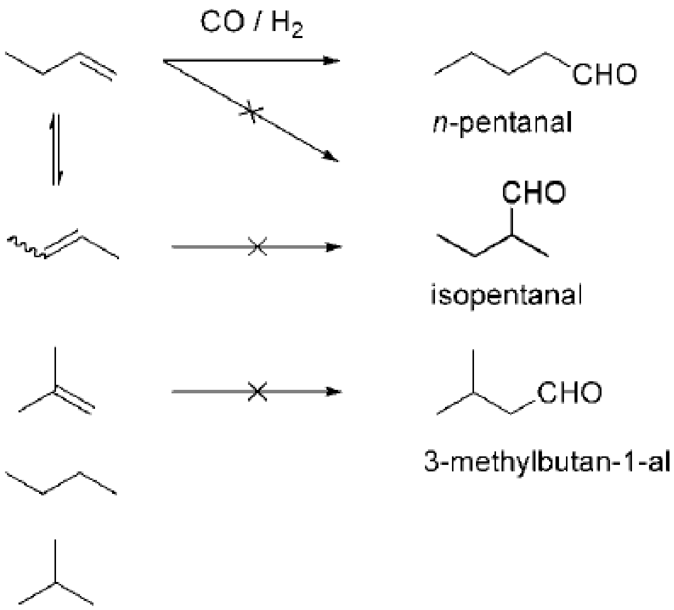
3
(Tinuvin-770)

M. Haumann, P. Wassersheid, *et al. Angew. Chem. Int. Ed.* **2011**, *50,* 4492.

2-3.

Supported Ionic Liquid Phase (SILP) ⑧





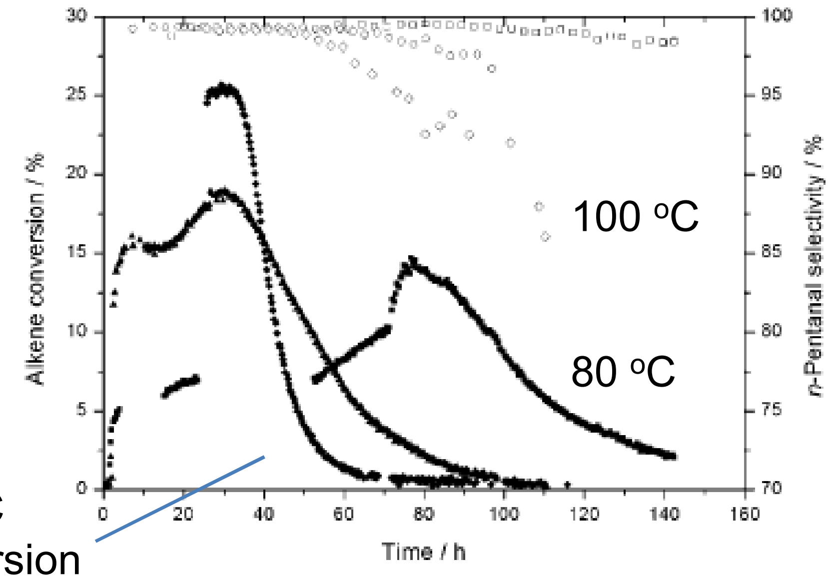


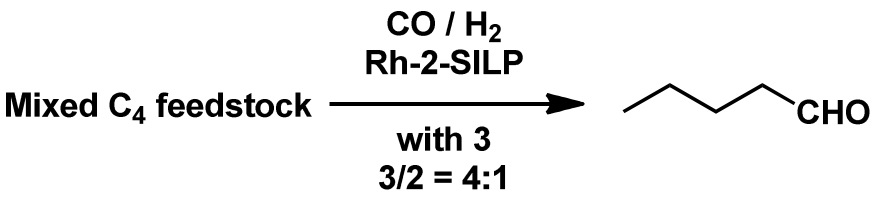
Figure 1. Hydroformylation of an industrial C_4 mixture (raffinate 1, 500 ppm H_2O) in the presence of Rh-**2**-SILP catalyst. $p_{total}=10$ bar, $p_{raffinate\ 1}=2$ bar, $p_{H_2}=p_{CO}=4$ bar. Total volume flow = 13.8 mL min^{-1}, residence time = 29 s, $m_{SILP}=3$ g, $w_{Rh}=0.2$ wt%, **2**/Rh = 10:1, ionic liquid loading = 10 vol% [EMIM][NTf$_2$] relative to total pore volume. Conversion (■, ▲, ◆) and selectivity (□, ○, ◇) plotted over time at 80 (■, □), 90 (▲, ○), and 100 °C (◆, ◇). EMIM = 1-ethyl-3-methylimidazolium, NTf$_2$ = bis(trifluoromethanesulfonyl)imide

Diphosphite ligand 2 decomposition leads to the formation of phosphoric acid.

M. Haumann, P. Wassersheid, *et al. Angew. Chem. Int. Ed.* **2011**, *50,* 4492.

2-3.

Supported Ionic Liquid Phase (SILP) ⑨



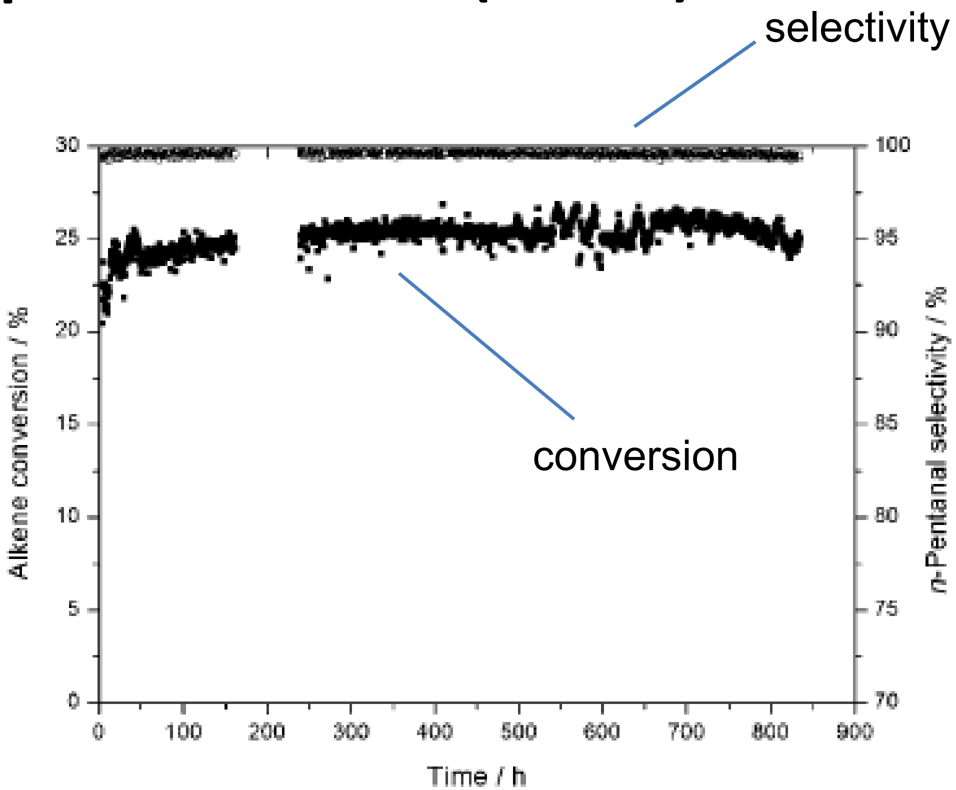


Figure 2. Hydroformylation of an industrial C_4 mixture (raffinate 1, less than 16 ppm H_2O) in the presence of Rh-**2**-SILP catalyst. $T = 100\,°C$, $p_{total} = 10$ bar, $p_{raffinate\,1} = 2$ bar, $p_{H_2} = p_{CO} = 4$ bar. Total volume flow = 29.2 mL min^{-1}, residence time = 15 s, $m_{SILP} = 3$ g, $w_{Rh} = 0.2$ wt%, **2**/Rh = 10:1, **3**/**2** = 4:1, ionic liquid loading = 10 vol% [EMIM][NTf$_2$] relative to total pore volume. Conversion (■) and selectivity (□) plotted over time.

Additive 3 works as acid scavenger that does not interact or react with the active catalytic species.

TON : 350000 !!

M. Haumann, P. Wassersheid, *et al. Angew. Chem. Int. Ed.* **2011**, *50,* 4492.

3. Summary

- Ionic liquids are not simple fruids.
  - the tunability of the cation and anion independently offers almost unlimited access to targeted combinations of physical and chemical properties.
- The scientific and technological importance of ionic liquids today spans a wide range of applications.

References

T. Welton, *Chem. Rev*. **1999**, *99,* 2071.
V. I. Parvulescu, C. Hardacre, *Chem. Rev*. **2007**, *107,* 2615.
M. Haumann, A. Riisager, *Chem. Rev*. **2008**, *108,* 1474.
J. P. Hallett, T. Welton, *Chem. Rev*. **2011**, *111,* 3508.
現代化学**. 2007**, *3.*
現代化学. **2010**, *10*
Sigma-Aldrich, *Aldrich ChemFiles.* **2005**, Vol.5, No.6.
B. Scrosati, *et al. Nature. Mater*. **2009**, *7,* 621.