

**Investigations on Alkylation of Isobutane with
2-Butene Using Highly Acidic Ionic Liquids as
Catalysts**

by

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Overview

1. Introduction to the alkylation process and ionic liquids
 - 1.1 The alkylation process
 - 1.2 (Acidic) Ionic Liquids
2. Results of the alkylation
 - 2.1 Experimental setup
 - 2.2 Preselection of Acidic Ionic Liquids
 - 2.3 Catalytic performance of the (selected) ILs [OMIM]Br/ AlCl_3 and [Et₃NH]Cl/ AlCl_3
 - 2.4 Catalytic performance of doped [OMIM]Br/ AlCl_3 and [Et₃NH]Cl/ AlCl_3 ILs:
 - using H₂O as additive
 - using Acidic resins or ILs containing SO₃H-group as additives
 - using transition metal halogenides as additives
 - 2.5 Reusability
3. Summary

1.1 Introduction- Worldwide oil demand

(in million barrels per day)

Country	1995	2000	2010	2020
OECD*	42.2	44.6	47.5	49.1
OPEC	5.3	6.2	7.4	8.6
Other developing countries	13.2	16.6	21.8	26.4
Former Soviet Union	4.5	4.4	5.2	5.8
China	3.2	4.4	6.5	8.7
Other European countries	1.4	1.6	1.8	2.0
Total world	69.9	77.8	90.2	100.7

Gasoline: 44%

Other fuel (diesel, home heating, industry, electric power generation...): 38 %

Others : 18%

*Organisation for Economic Cooperation and Development

1.1 Introduction – Gasoline properties

Gasoline properties	Desired effects on the engine performance	Undesired impact on the engine performance	Impact on the environment
Octane number (ON)	High ON avoids engine knocking, increases compression ratio, engine power and efficiency		ON boosting compounds are environmentally harmful (e.g. lead additives, benzene or other aromatics, olefins).
Volatility (Reid vapor pressure-RVP)	Suitable RVP enables engine cold start due to adequate vaporisation of fuel	Chamber deposits if gasoline contains heavy components (RVP too high)	Too many light components: hydrocarbon loss and atmospheric pollution Too many heavy components: release of unburned hydrocarbon into the atmosphere (smog, ozon in lower atmosphere)
Content of organic sulfur	Lubricant for the engine (diesel oil pump)	Decrease of engine efficiency	Corrosive, foul smelling Increase SO2 emission (acid rain)
Content of olefins	Enhancement of the ON	Deposits and gum formation	Raise of emission of toxic compounds
Content of aromatics	Enhancement of the ON	Increase engine deposits	CO and carcinogenic substances (e.g. benzene) in the exhaust
Content of alkylate	High ON, moderate RVP	None	None

1.1 Introduction- Reformulated gasoline

Development of reformulated gasoline (RFG) specifications in the European Union.

	1999	2000	2010
Sulfur, max. ppm wt.	500	150	10
Aromatics, max. vol.%	No spec.	42	35
Benzene, max. vol.%	5	1	1
Alkenes, max. vol%	No spec.	18	18
Octane, MON/RON (min)	95/98	95/98	95/98
RVP, max. kPa	80	60	60

1.1 Introduction- Blending components for gasoline

Blending components	Typical % of gasoline	Sulfur, ppm	Octane number
FCC Gasoline	30-50	800	86
LSR* Gasoline	3	150	73
MTBE	5	20	110
Alkylate	10-15	16	92-96
Butanes	5	10	92
Isomerate	5	3	87
Reformate	20-40	0	88

World productivity of alkylate approx. 102 million tons/year

Demand for alkylate as gasoline blend is currently increasing!

1.1 Introduction - Alkylate

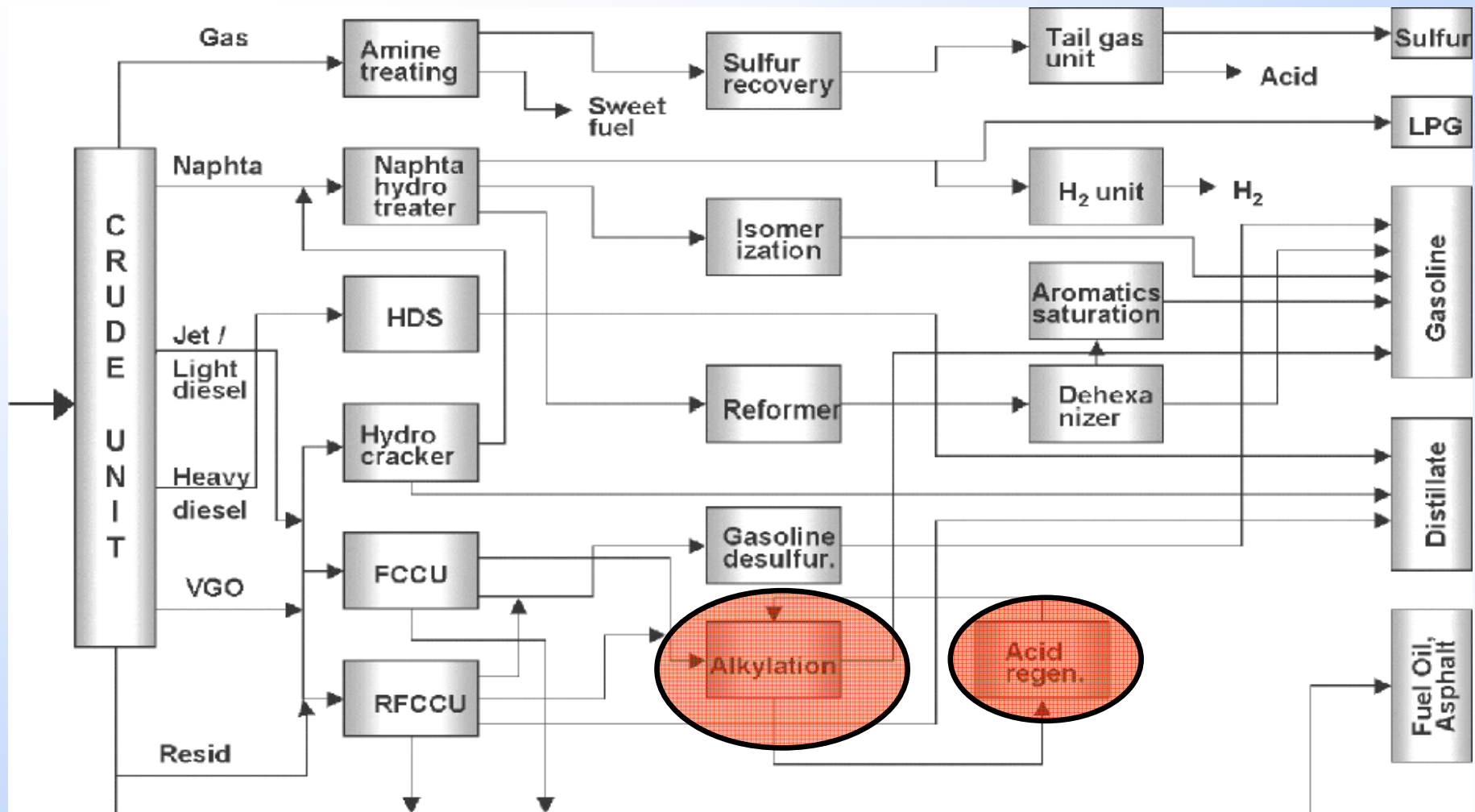
Why is alkylate a good component for gasoline?

Advantages of alkylate

- High octane number (92-96)
- Low Reid vapor pressure (RVP)
- No content of aromatics
- Very low content of sulfur, nitrogen, alkenes
- Low octane sensitivity (research octane number-motor octane number)

Aim: Production of highly branched alkanes (alkylate) which is an excellent blending component for environmentally friendly and high octane number gasoline

1.1 Introduction- Process units in a modern refinery



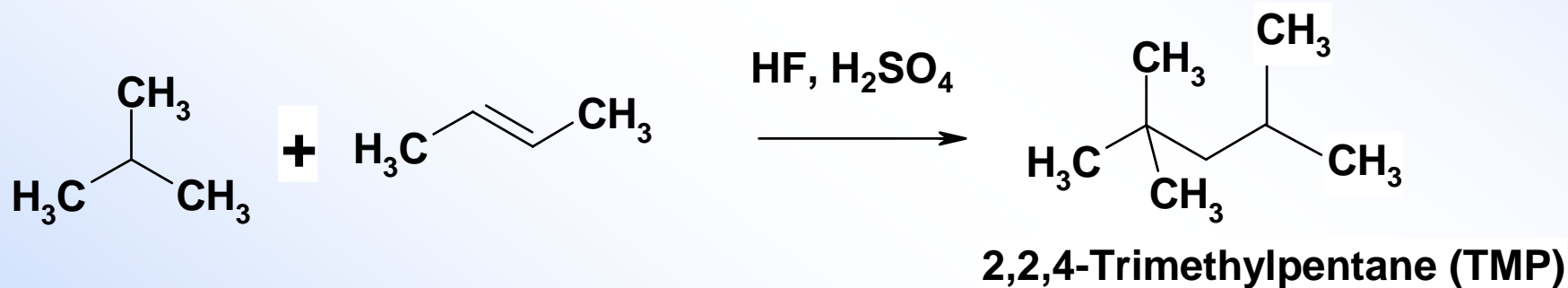
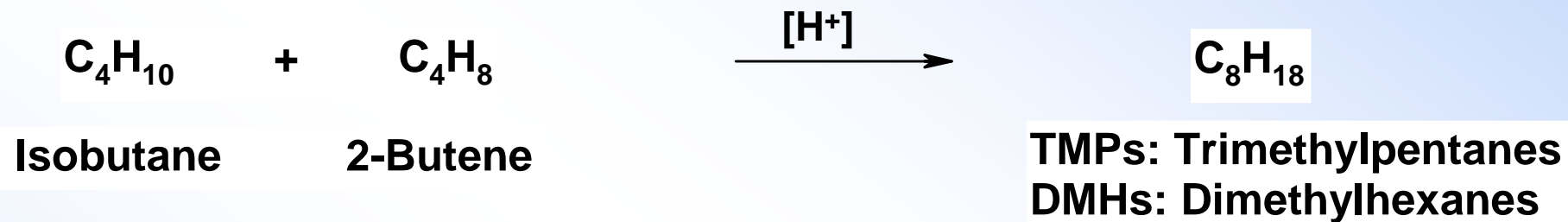
1.1 Introduction- Industrial processes

Industrial processes

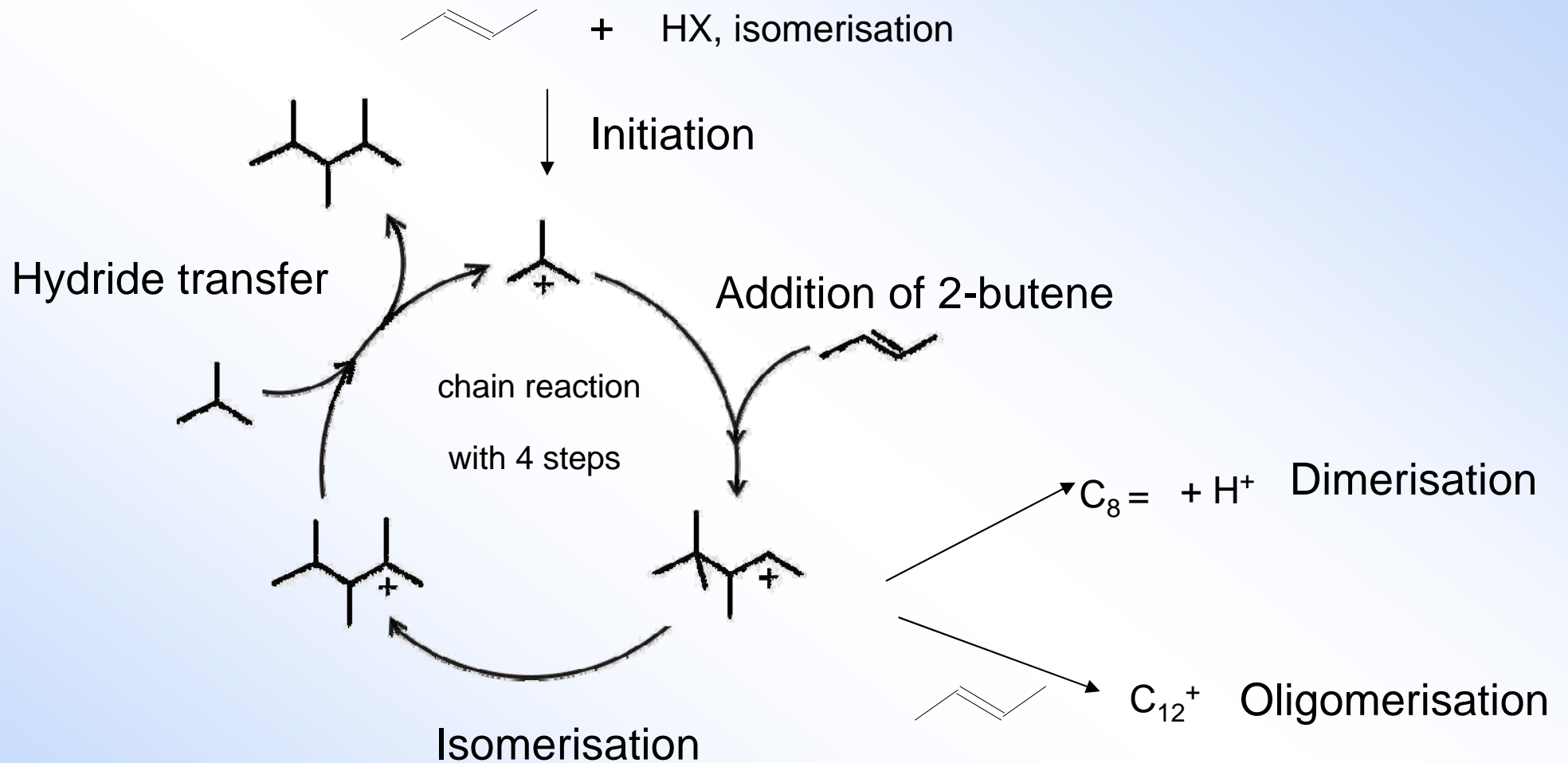
Catalyst	H ₂ SO ₄	HF
Pros	<ul style="list-style-type: none">- High conversion, rather high alkylate quality- Very low volatility, easy handling	<ul style="list-style-type: none">- Higher conversion and alkylate quality: high RON, high TMPs content- The feed (alkenes) is more flexible
Cons	<ul style="list-style-type: none">- High acid consumption, 70-100 kg acid/ton alkylate. Spent acid contains water and heavy HCs(ASO)- H₂SO₄ can oxidize HCs forming water and SO₂	<ul style="list-style-type: none">- Volatile and highly toxic when released into the atmosphere- Plants are expensive due to safety devices to avoid HF leakage.

→ **Researches focussed on alternative catalysts are desired**

1.1 Introduction – Reaction scheme of the alkylation



1.1 Introduction – Scheme of the reaction mechanism



1.1 Introduction - Studying substitution catalysts

Two main types of solid catalysts have been studied

1. Active materials (e.g. BF_3 , SbF_5 ... or 12-tungstophosphoric acid) were adsorbed on inert supports such as alumina or silica.
2. Solid acids as catalysts : zeolite (e.g. USYH), superacid based on sulfate-promoted metal oxides (sulfated zirconia).

They are active catalysts but have also some disadvantages

- Fast deactivation
- Blockage of small pores
- Leaching (1)
- Activity could not be completely recovered
- High cost of active components (1) and regeneration (2)

1.2 Introduction – Acidic Ionic liquids as alternative catalyst concepts

Why Acidic ionic liquids (ILs)?

Acidic ILs have valuable characteristics (for the alkylation reaction)

Important characteristics:

- tunable acidity (formation of superacidic systems required for the reaction)
- tunable solubility (for hydrocarbons) leading to an easy product separation

- Negligible vapor pressure
- Reusing and recycling of the ionic liquid catalysts

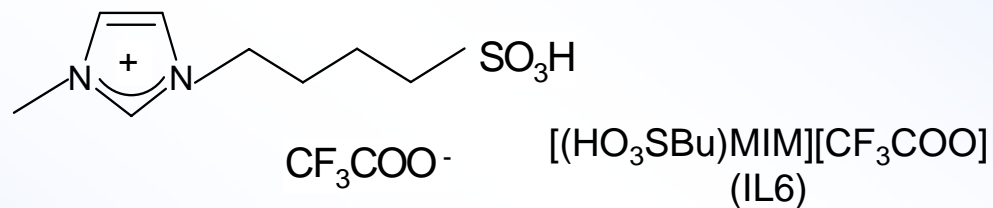
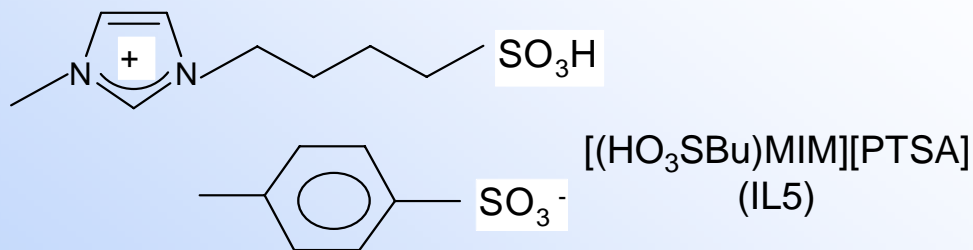
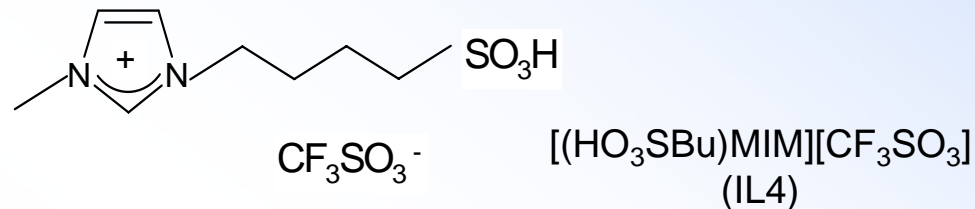
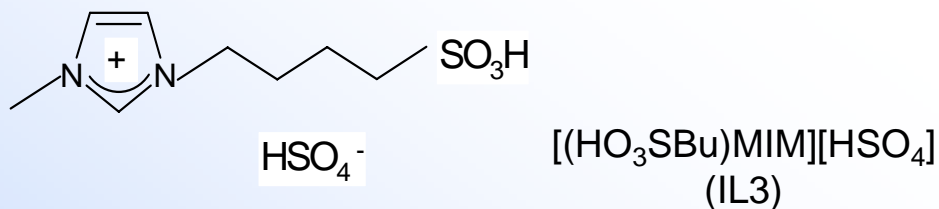
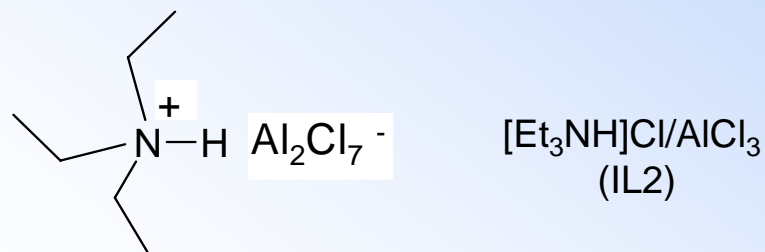
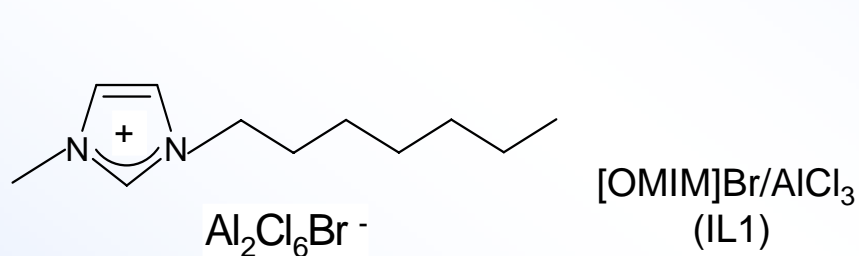


Highly acidic ILs as alternative catalysts

1.2 Introduction – What are Ionic Liquids?

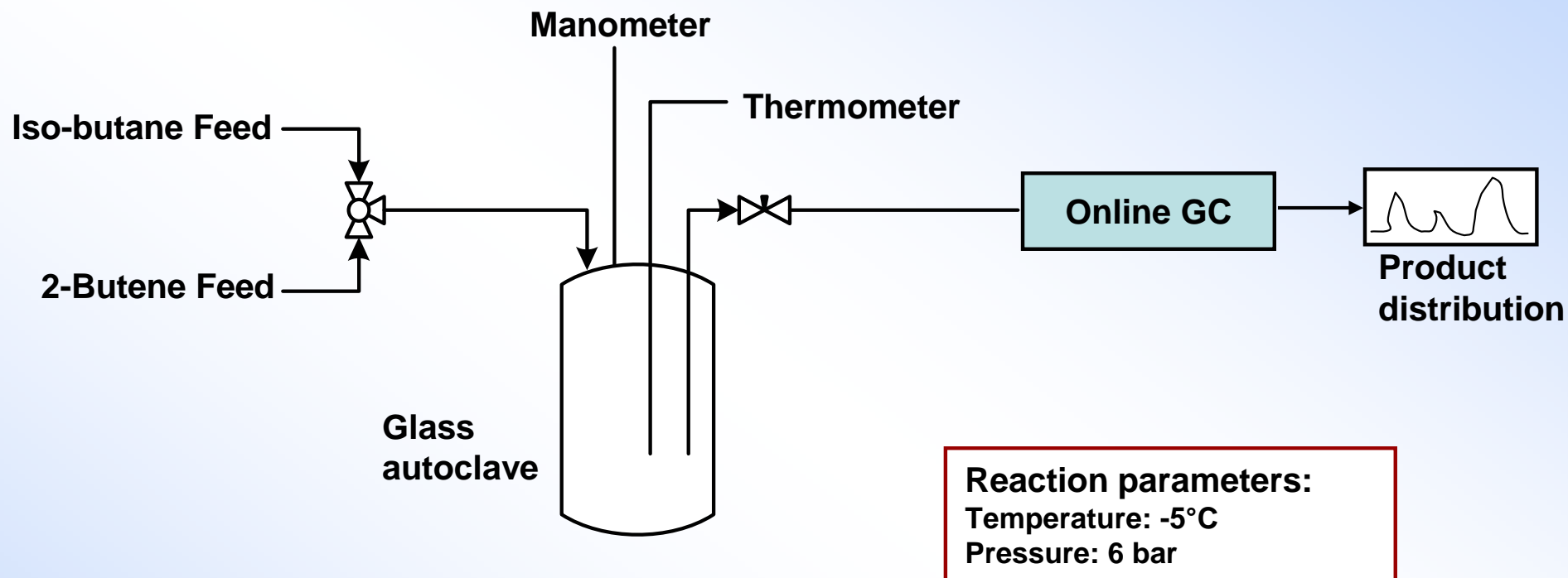
Definition: Ionic Liquids are salts melting below 100° C

Examples of (Brønsted and Lewis acidic) ILs (used in this work)



2. Results

2.1 Results – Experimental setup



Investigations on the acidity of the catalytic systems were performed by FT-IR spectroscopy and ^{13}C -NMR spectroscopy (Hammett acidity function)

2.2 Results – Preselection of acidic ILs systems studied in this work

List of preselected IL systems studied to find suitable catalysts for the alkylation and main results.

N°	Ionic liquid	TMPs content in product (wt-%)	Conversion of 2-butene (%)
1	[BMIM]Cl/ AlCl_3	30.9 44.6 [1] ; 60 to 70 [2]	96 98; 98
2	[HMIM]Cl/ AlCl_3	37.9 50.4 [1]	95 98
3	[OMIM]Cl/ AlCl_3	39.4	96
4	[BMIM]Br/ AlCl_3	38.3	98
5	[OMIM]Br/AlCl_3	41.4	98
6	[HMIM]Br/ AlCl_3	40.1	98
7	[(HO_3SBu)MIM][HSO_4]	0	0
8	[(HO_3SBu)HIM][HSO_4]	0	0
9	$\text{Et}_3\text{NHCl}/\text{AlCl}_3$	54.8 46.5 [1]; 56.2 [3]	98 98; 97
10	[HIM] $^+$ [HSO_4] $^-$	0	0

1. C.Huang, Z. Liu, Q. Shi et al; Journal of the University of petroleum, China 27 (2003), p. 120-122.

2. Y. Chauvin, A. Hirschauer, H. Olivier; J. Mol. Catal. 92 (1994), P. 155-165

3. C.P. Huang, Z.C. Liu, C. M. Xu, B. H. Chen, and Y. F. Liu; Applied catalysis A: General 277 (2004), p. 41-43

2.2 Results – Preselection of acidic ILs systems studied in this work

List of doped ionic liquid mixtures tested in this work and main results

N ^o	IL as catalyst	IL as additive	TMPs content in product (wt-%)	Conversion of 2-butene (%)
11	[OMIM]Br/AlCl ₃	-	21.3	98
12	[OMIM]Br/AlCl ₃	[(HO ₃ SBu)MIM][HSO ₄]	52.7	100
13	[OMIM]Br/AlCl ₃	[(HO ₃ SBu)HIM][HSO ₄]	53.3	100
14	[OMIM]Br/AlCl ₃	[(HO ₃ SBu)MIM][CF ₃ SO ₃]	These mixture are too viscous. Therefore, the magnetic stirrer did not work and the alkylation could not be carried out.	
15	[OMIM]Br/AlCl ₃	[(HO ₃ SBu)MIM][CH ₃ SO ₃]		
16	[OMIM]Br/AlCl ₃	[(HO ₃ SBu)MIM][PTSA*]		

1. C.Huang, Z. Liu, Q. Shi et al; Journal of the University of petroleum, China 27 (2003), p. 120-122.
2. Y. Chauvin, A. Hirschauer, H. olivier; J. Mol. Catal. 92 (1994), P. 155-165
3. C.P. Huang, Z.C. Liu, C. M. Xu, B. H. Chen, and Y. F. Liu; Applied catalysis A: General 277 (2004), p. 41-43

2.3 Results – Selected Acidic Ionic Liquid systems

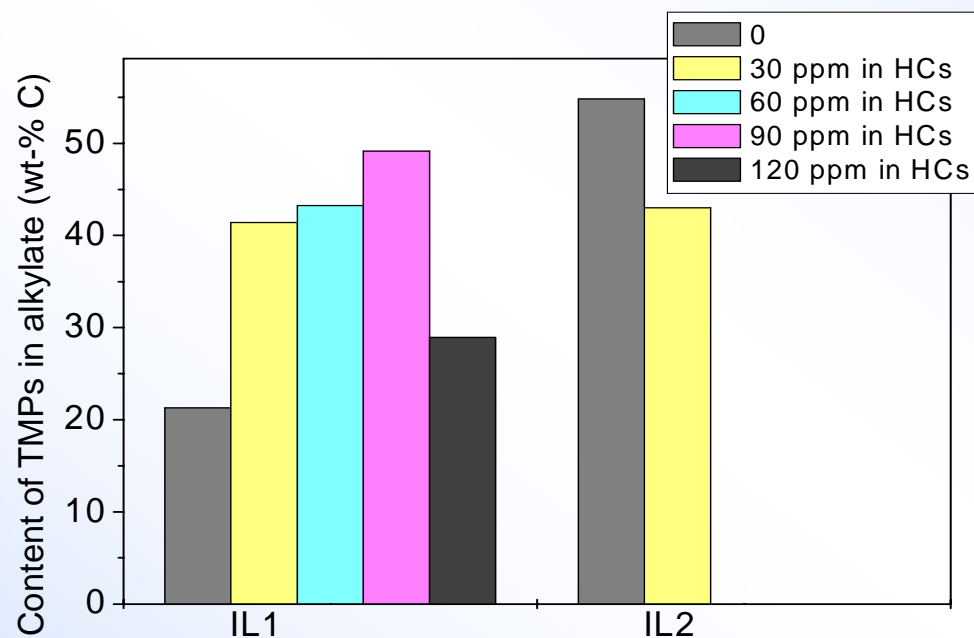
Best catalytic performance: IL systems [OMIM]Br/AlCl₃ and [Et₃NH]Cl/AlCl₃

Optimal reaction conditions

	IL/olefin (molar ratio) (0.2-0.6)	Molar fraction of AlCl ₃ (0.56-0.67)	Temperature [° C] (-15 to -5° C)	Stirring time [min] (1 – 60 min)	TMP [wt-% C]	RON
[OMIM]Br/AlCl ₃ (IL1)	0.4	0.6	-15 to - 5	15	21.3	90.5
[Et ₃ NH]Cl/AlCl ₃ (IL2)	0.4	0.6	- 5	20	54.8	94.5

- Neat IL2 produces higher content of TMPs and RON than neat IL1
- Neat IL1: Content of heavy products is higher and is more affected by reaction conditions
- Neat IL2: Content of light products is higher and is more affected by reaction conditions

2.4 Results – ILs/H₂O (Influence on the performance)



IL1: [OMIM]Br/AlCl₃

IL2: [Et₃NH]Cl/AlCl₃

Reaction parameters:

Temperature: -5°C

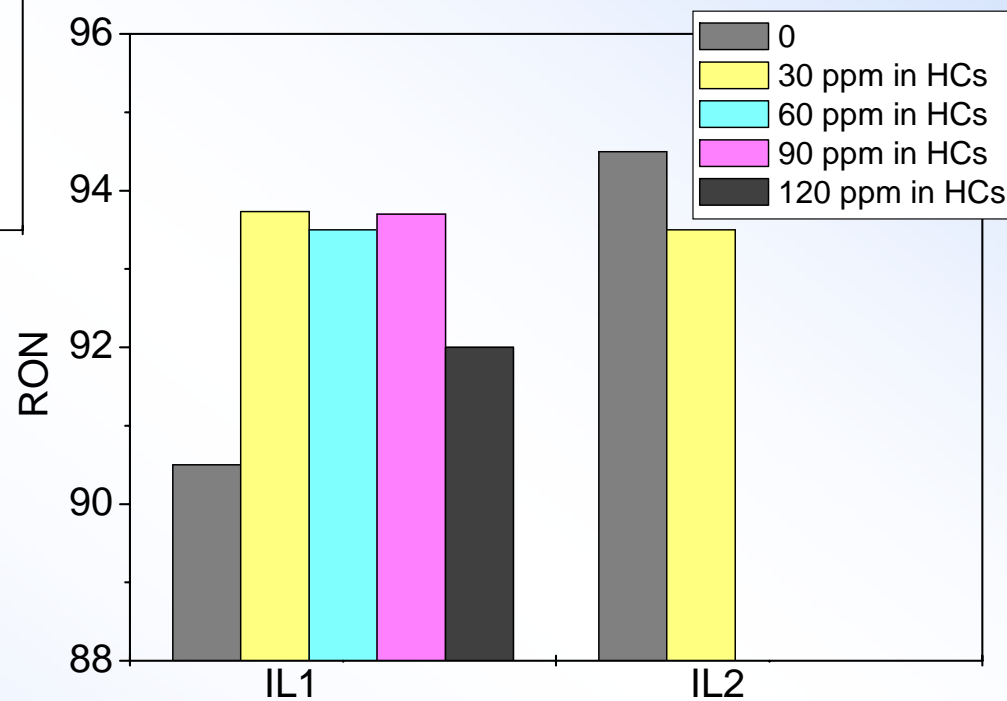
Pressure: 6 bar

P/O ratio (mol): 13

Stirring time: 1h

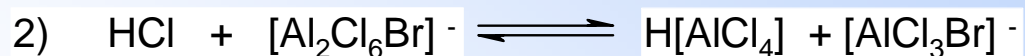
Molar fraction of AlCl₃ = 0.6

Molar ratio of IL/olefin: 0.4



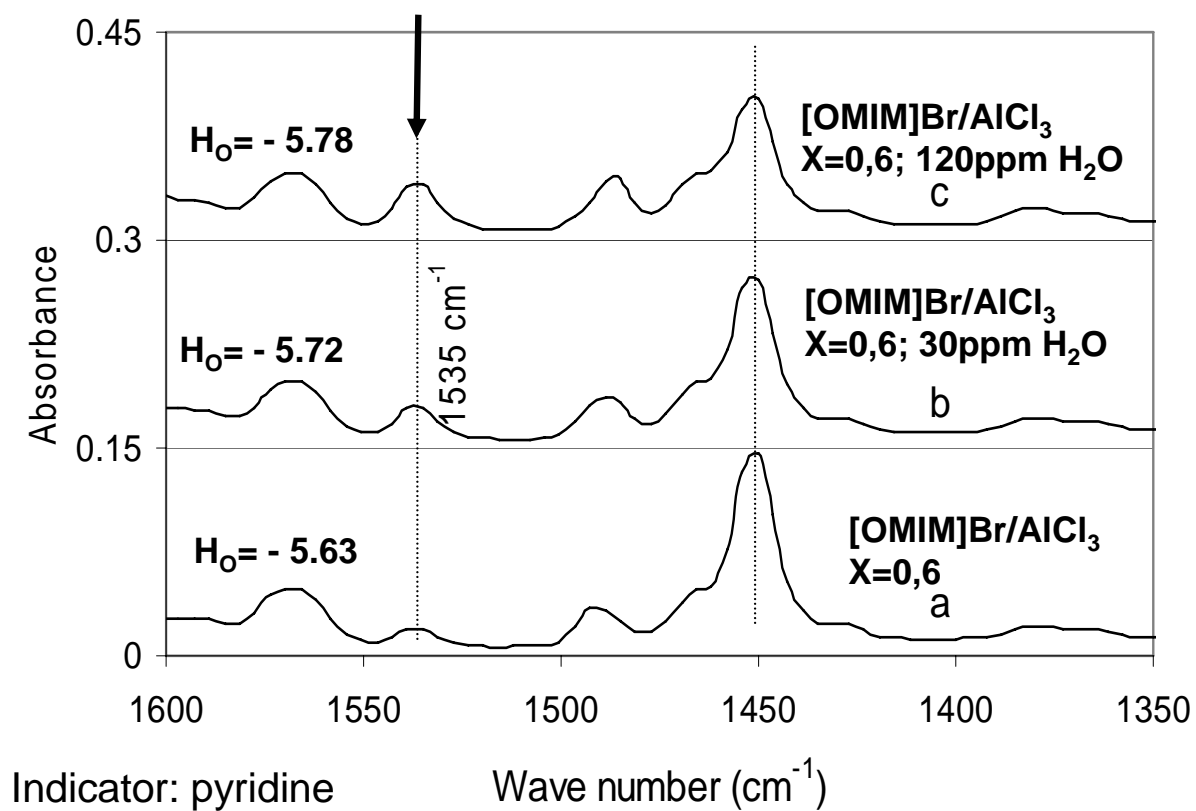
2.4 Results – [OMIM]Br/AlCl₃/H₂O (Influence on the catalyst)

Formation of Brønsted superacidic species:

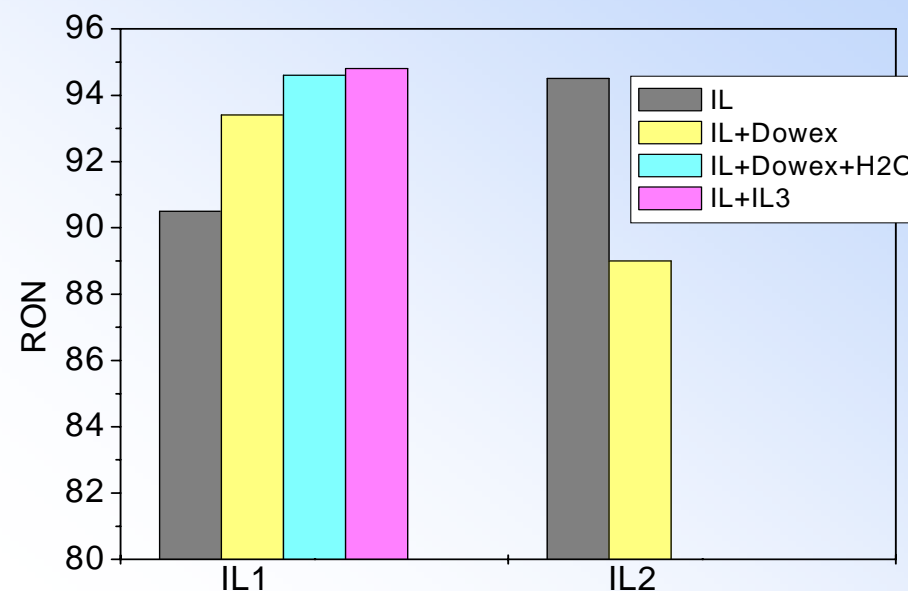
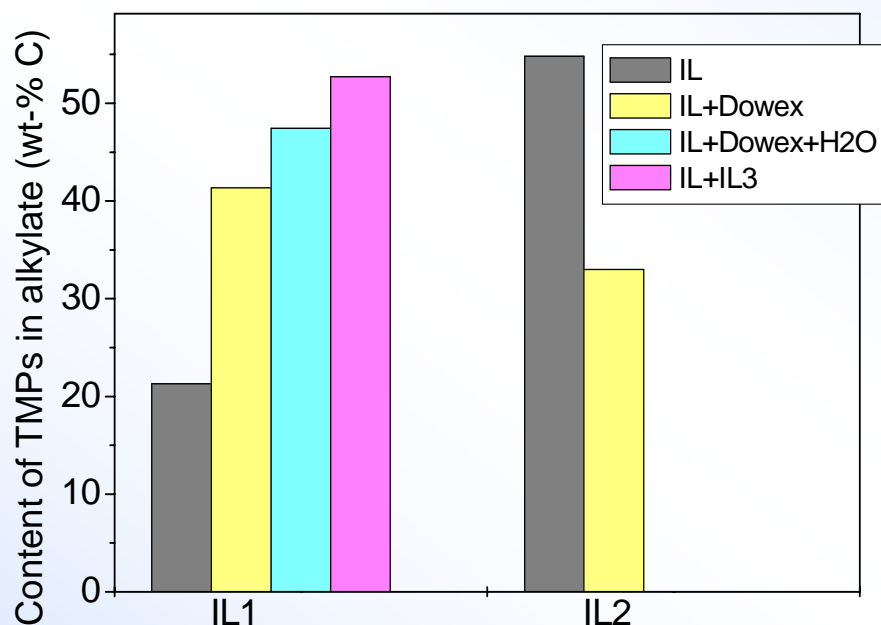


FT-IR spectra

Brønsted acidity change ($\nu = 1535 \text{ cm}^{-1}$): More active centers



2.4 Results – ILs/SO₃H-group containing additives (Influence on the performance)



Dowex: cationic acidic exchange resin

IL1: [OMIM]Br/AlCl₃

IL2: [Et₃NH]Cl/AlCl₃

IL3: [(HO₃SBu)MIM][HSO₄]

IL4: [(HO₃SBu)MIM][CF₃SO₃]

IL5: [(HO₃SBu)MIM]PTSA

IL6: [(HO₃SBu)MIM][CF₃COO]

Reaction parameters:

Temperature: -5°C

Pressure: 6 bar

P/O ratio (mol): 13

Stirring time: 1h

Molar fraction of AlCl₃ = 0.6

Molar ratio of IL/olefin: 0.4

Molar ratio of additive/IL = 0.5

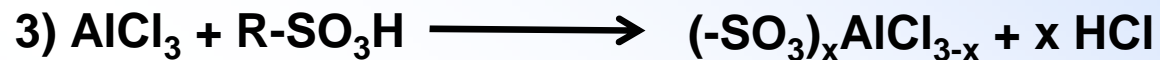
Content of water = 30 ppm in HCs

2.4 Results – [OMIM]Br/AlCl₃/Dowex and water (Influence of some factors)

Product quality	Effect of H ₂ O content in resin [wt-%]				Effect of resin content [mol of resin/mol of IL]				Effect of surface area of resin [m ² /g]	
	0	1.5	3	6	0	0.25	0.50	1.00	30 (Dowex)	45 (Amberlyst)
TMPs	41.4	50.4	57.8	46.8	21.3	30.3	57.8	23.8	57.8	63.9
RON	93.4	94.9	95.2	94.7	90.5	92.4	95.2	91.2	95.2	96.2

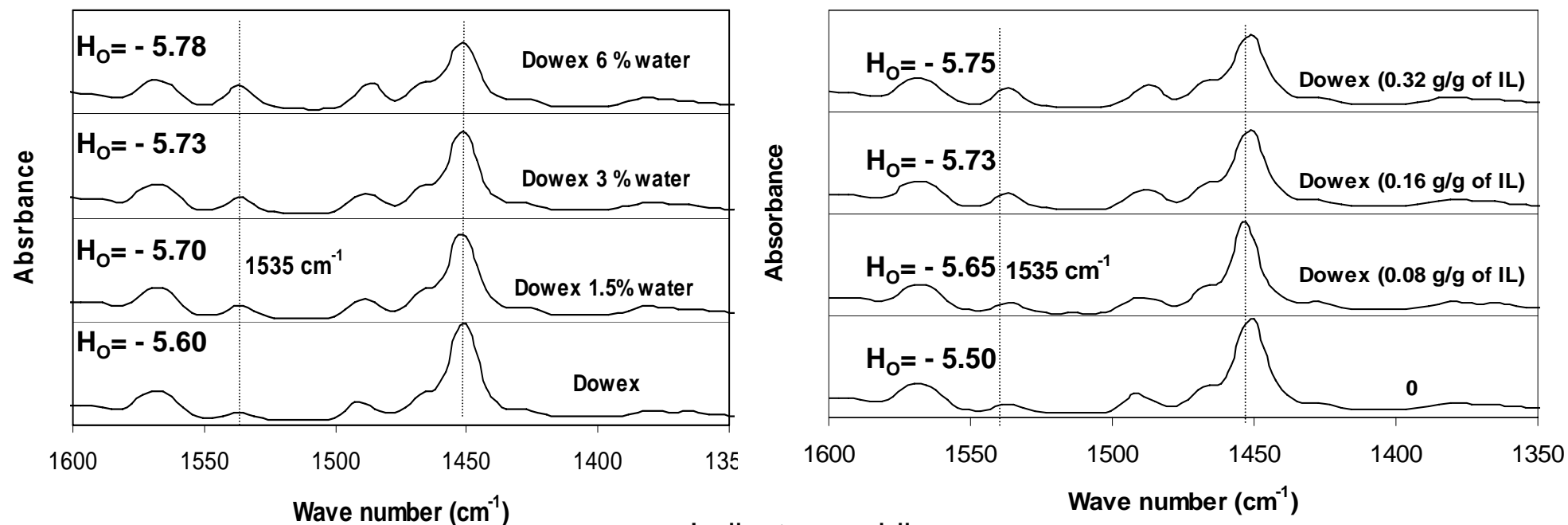
2.4 Results – [OMIM]Br/AlCl₃/resins-SO₃H (Influence on the catalyst)

Formation of superacids



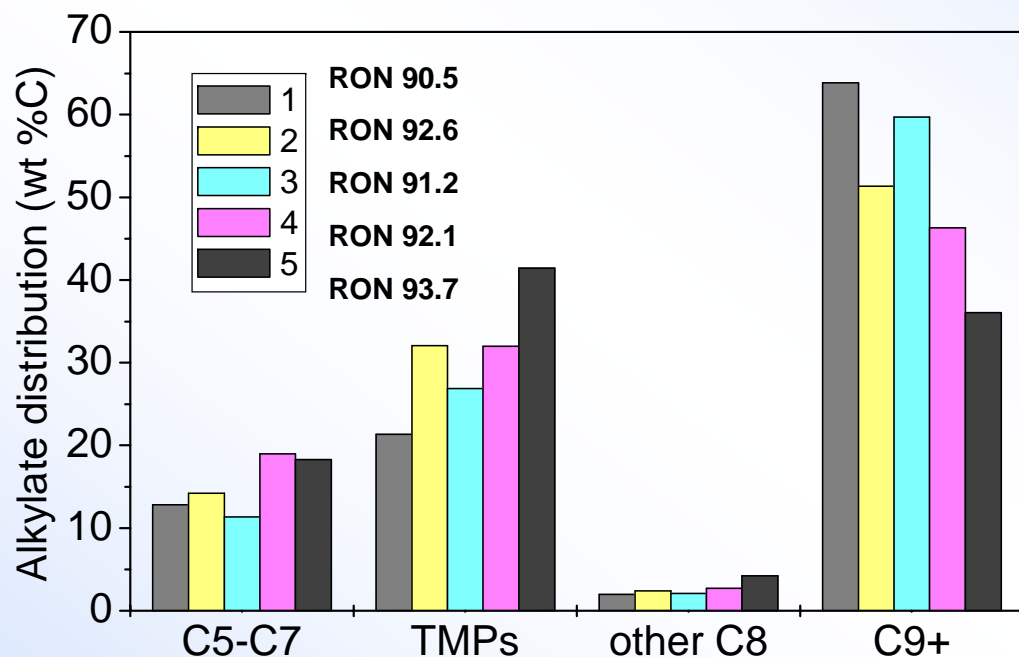
Lewis superacids

FT-IR spectra



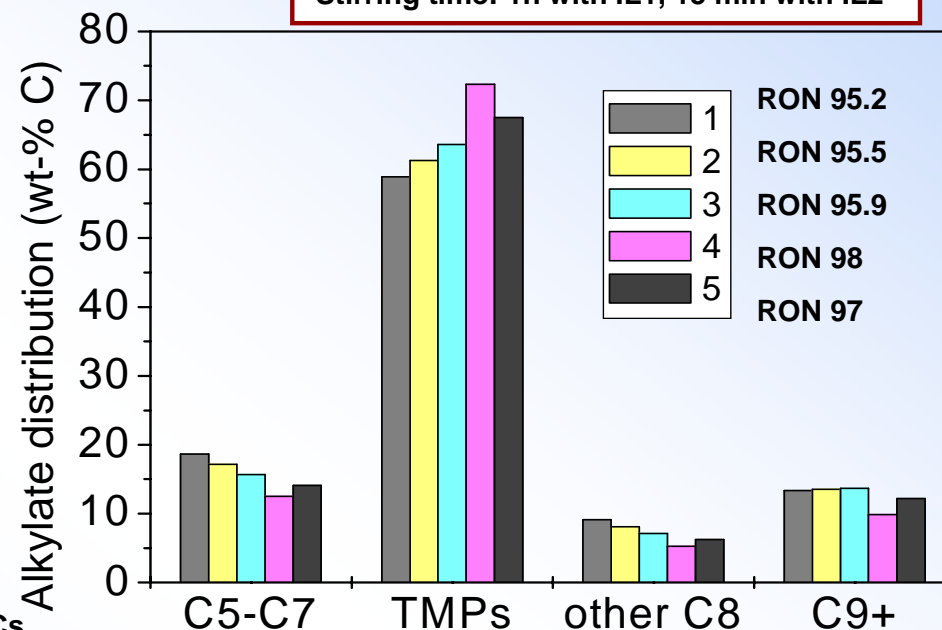
Indicator: pyridine

2.4 Results – ILs/metal salts (Influence on the performance)



- 1: [OMIM]Br/AlCl₃ (IL1)
- 2: [OMIM]Br/AlCl₃ + CuCl (1.7% mol to used AlCl₃)
- 3: [OMIM]Br/AlCl₃ + CuCl₂ (1.7% mol to used AlCl₃)
- 4: [OMIM]Br/AlCl₃ + CuCl (1.7% mol to used AlCl₃) + 30 ppm H₂O in HCs
- 5: [OMIM]Br/AlCl₃ + 30 ppm H₂O in HCs

Reaction parameters:
 Temperature: -5°C
 Pressure: 6 bar
 P/O ratio (mol): 13
 Molar fraction of AlCl₃ = 0.6
 Molar ratio of IL/olefin: 0.4
 Stirring time: 1h with IL1, 15 min with IL2

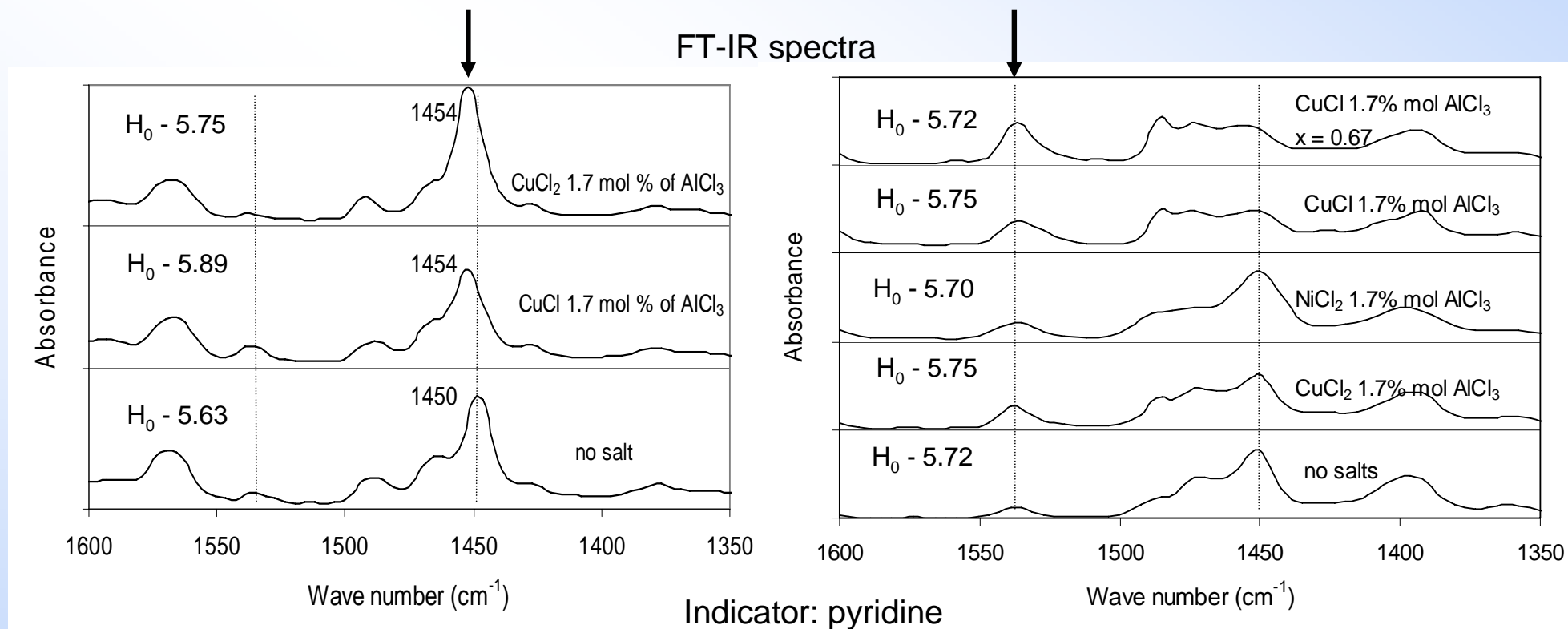


- 1: [Et₃NH]Cl/AlCl₃ (x = 0.6) (IL2)
- 2: [Et₃NH]Cl/AlCl₃ (x = 0.6) + CuCl₂ (1.7% mol to used AlCl₃)
- 3: [Et₃NH]Cl/AlCl₃ (x = 0.6) + NiCl₂ (1.7% mol to used AlCl₃)
- 4: [Et₃NH]Cl/AlCl₃ (x = 0.6) + CuCl (1.7% mol to used AlCl₃)
- 5: [Et₃NH]Cl/AlCl₃ (x = 0.67) + CuCl (1.7% mol to used AlCl₃)

2.4 Results – ILs/metal salts (Influence on the catalyst)

Lewis acidity change ($\nu = 1450 \text{ cm}^{-1}$)

Brønsted acidity change ($\nu = 1535 \text{ cm}^{-1}$)



[OMIM]Br/AlCl₃ (X=0.6) (IL1)

[Et₃NH]Cl/AlCl₃ (X=0.6) (IL2)

2.5 Results – Reusability of the selected catalytic IL-systems

Reaction parameters:

Temperature: -5°C

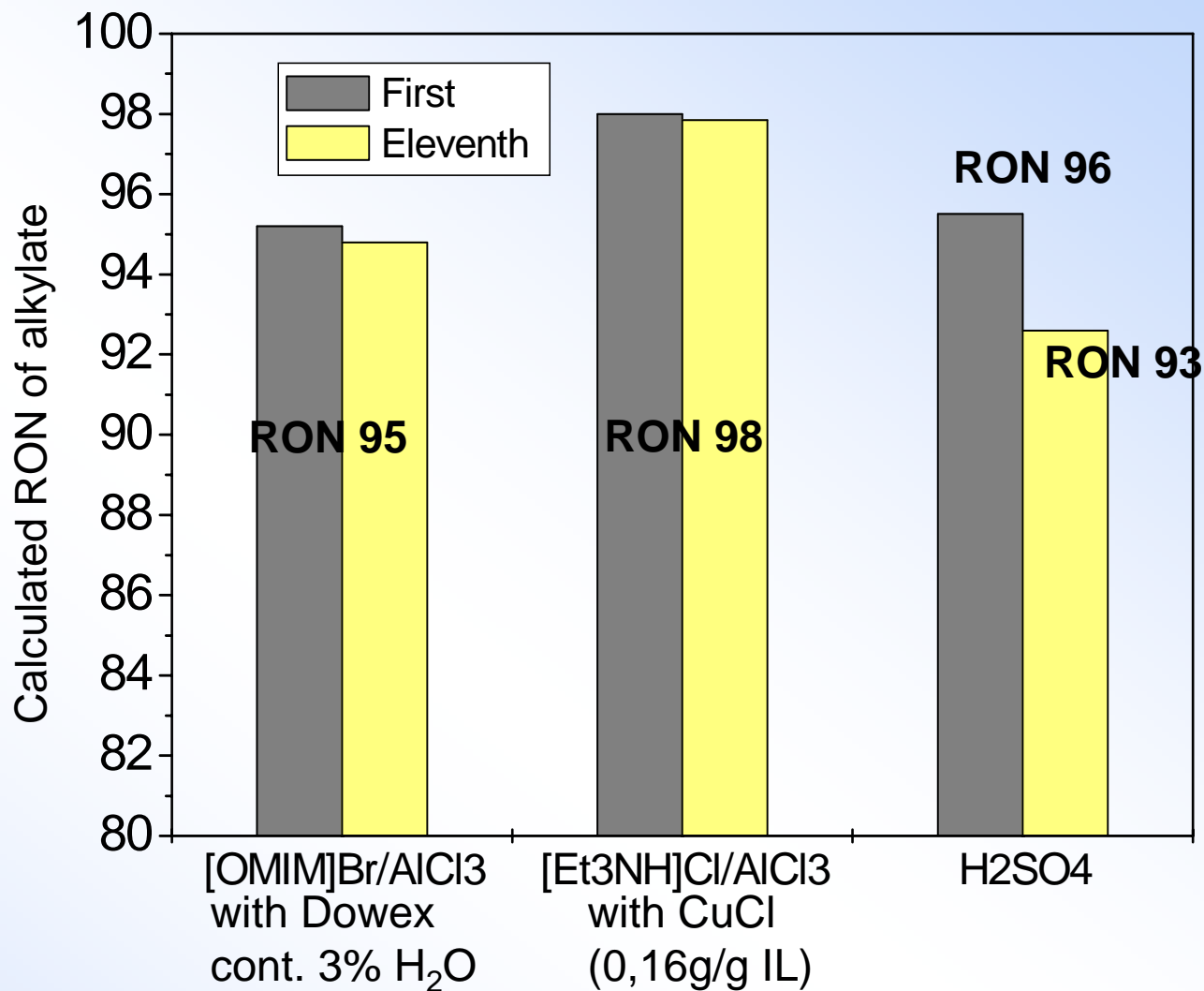
Pressure: 6 bar

P/O ratio (mol): 13

Stirring time: 15 min

Molar fraction of $\text{AlCl}_3 = 0.6$

Molar ratio of IL/olefin: 0.4



3. Summary

- Highly acidic ionic liquids are suitable as alternative catalysts for the alkylation process (as shown for acidic [OMIM]Br/ AlCl_3 and $[\text{Et}_3\text{NH}]\text{Cl}/\text{AlCl}_3$)
- IL acidity and the IL concentration show a great influence on the catalytic performance (alkylate quality, selectivity)
- The performance of the chosen Acidic ILs can be improved by additives like
 - water
 - compounds containing a $-\text{SO}_3\text{H}$ group (acidic exchange resins, $[(\text{HO}_3\text{SBu})\text{MIM}]\text{HSO}_4$)
 - transition metal salts (e.g. CuCl)(Keyword: Change of the acidity)
- The selectivity of the investigated catalyst systems is comparable or even higher than that of sulfuric acid
- The catalysts can be reused showing only a minor loss of catalytic activity (or a small decrease in alkylate quality)

*Thank you for your
kindly attention*