Effective *n*-octane isomerization under exceptionally mild conditions using a novel class of superacidic ionic liquids

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Superacidic chloroaluminate ionic liquids of the general formula [cation]Cl/AlCl₃[X(AlCl₃) > 0.5] + H_2SO_4 effectively isomerize *n*-octane to form branched liquid hydrocarbon isomers. Due to the highly acidic character of the ionic liquid the reaction proceeds under extremely mild conditions in a liquid–liquid biphasic reaction mode leading to a minimum of undesired cracking side-reactions.

In recent years, the application of a number of Research Octane Number (RON) booster compounds in automotive fuels has been stopped (in the case of Pb-alkyles) or severely restricted (in the case of MTBE or even aromatics) for environmental reasons. This development has considerably increased the interest in the large-scale refinery production of highly branched alkanes as the latter combine high RON with benign toxicology and ecotoxicology properties.¹ Alkane isomerization to highly branched hydrocarbons of the same carbon number by acidic catalysis is a highly attractive way to achieve this goal due to low feedstock cost. Technologies using solid acids such as zeolites,² modified alumina³ and sulfated zirconia⁴ in combination with metallic sites to provide an additional hydrogenation/dehydrogenation functionality in the catalytic material have been reported in the literature.⁵ These reactions are typically performed in the temperature range of 403 K up to 553 K with cracking and coking being typical problems for the catalyst selectivity and lifetime. According to recent references, hydroisomerization of *n*-octane and higher alkanes using zeolithes is industrially not applicable yet due to the high consumption of hydrogen as a consequence of the significant hydrocracking activity.⁶

In contrast to hydroisomerization using solid catalysts, homogeneous catalyzed alkane isomerization with superacidic systems has been shown to proceed at temperatures as low as 298 K. Typical catalysts consist of a mixture of strong Lewis acids (such as *e.g.* SbF₅, TaF₅, NbF₅) and a Brønsted acid (CF₃COOH, CF₃SO₃H).⁷ However, a clear disadvantage of these homogeneous superacids is their highly toxic and corrosive nature that is strongly linked to the presence of free HF in these systems.

Since the first pioneering studies by Wilkes and coworkers in the late 70s, the use of highly acidic ionic liquids has been studied for a large number of organic transformations including Friedel–Crafts alkylation and acylation, cracking and isomerization.⁸ The key feature of these ionic liquid systems that were usually based on chloroaluminate ions is their ability to form liquid–liquid biphasic systems with typical unpolar organic product mixtures thus enabling recycling of the acidic ionic reaction phase by simple phase separation. Moreover, the acidity of such low-melting chloroaluminate melts is tuneable according to the adjusted [cation]Cl/AlCl₃ ratio. The higher the molar ratio of AlCl₃, the more acidic is the ionic liquid. Note that the upper limit for pure chloroaluminate systems is $X(AlCl_3) = 0.66$ due to melting point and solubility restrictions.⁹

Acidic chloroaluminate melts are known to form superacids when contacted with HCl. This is due to the reaction of the chloride with the acidic anions $[Al_2Cl_7]^-$ and $[Al_3Cl_{10}]^$ forming a "naked" superacid proton.¹⁰ The Hammett acidity of these protons has been determined by different groups using both spectroscopic methods¹¹ and test reactions¹² and values down to $H_0 = -18$ have been reported.

For the skeleton isomerization of *n*-alkanes superacidity is required as concentrated sulfuric acid (H_0 of 100% sulfuric acid = -11.9) is known to be not acidic enough to catalyze this reaction.¹³ Thus, superacidic ionic liquids of the general type [cation]Cl/AlCl₃/HCl have been tested by a few groups in alkane isomerization. Berenblyum *et al.* studied C7-mixtures (including branched C7) using [(CH₃)₃NH]Cl/AlCl₃/HCl.¹⁴ Zhang and coworkers investigated the isomerization of *n*-pentane in the system [Et₃NH]Cl/AlCl₃ (here some superacidity originated obviously from traces of water in the system).¹⁵ A similar system using different acidic chloroaluminate ionic liquids with a N-containing cation and no added Brønsted acid was also claimed earlier in a patent for alkane isomerization under very mild conditions.¹⁶

In the patent literature, systems of the general type [cation]Cl/AlCl₃/H₂SO₄ have been also disclosed.¹⁷ The systems have been claimed to isomerize a distillation cut of paraffinic hydrocarbons (including branched starting material) at temperatures as mild as 298 K. Unfortunately, the patent gives no information on the role of the added sulfuric acid, on kinetics and on the obtained product distribution. With respect to the latter point the ratio of feedstock isomerization *vs.* feedstock cracking is of utmost importance for the practical relevance of the catalyst system and its evaluation against state-of-the-art heterogeneous isomerization catalysts.

In this paper we report for the first time a systematic study on the isomerization of pure *n*-octane, a model compound of the light naphtha refinery cut, using superacidic ionic liquids of the general type [cation]Cl/AlCl₃/H₂SO₄ under extremely mild conditions (T = 283 K up to T = 323 K). Our work focusses on the goal to maximize the yield of liquid organic product (LOP), *i.e.* to favor isomerization and to disfavor cracking. For this purpose liquid–liquid biphasic experiments have been carried out in autoclaves studying in detail both the

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Table 1Liquid organic product (LOP) distribution in *n*-octaneisomerization using the superacidic ionic liquid system $[C_4C_1Im]Cl/AlCl_3/H_2SO_4$ at 303 K with $[C_4C_1Im]Cl/AlCl_3 = 1/2$

Yields _{k (LOP)} (%)	Molar ratio H ₂ SO ₄ /AlCl ₃					
	0.0	0.03	0.14	0.18	0.21	0.75
iso-C4	1.5	4.6	7.3	8.4	7.3	1.5
<i>n</i> -Butane	0.0	0.0	0.0	0.0	0.0	0.1
iso-C5	2.7	7.4	11.3	13.4	11.5	1.9
<i>n</i> -Pentane	0.0	0.0	1.1	1.4	1.1	0.2
iso-C6	2.5	6.4	10.2	13.1	11.1	1.5
<i>n</i> -Hexane	0.0	0.0	0.7	0.9	0.8	0.1
iso-C7	2.0	5.6	7.8	8.5	7.5	0.7
<i>n</i> -Heptane	0.0	0.0	0.0	0.0	0.0	0.0
Iso-Ĉ8	2.4	6.0	10.1	10.8	10.0	1.5
<i>n</i> -Octane	69.4	34.8	28.1	22.8	26.9	75.5
C > 8	1.3	2.4	4.6	7.5	4.6	0.2
$X(n-C8)^{a}$ (%)	30.6	53.6	71.9	77.2	73.1	24.5
$S(iso-C8)^{\hat{b}}$ (%)	7.8	11.2	14.0	14.0	13.7	6.1
Conditions: m(IL)	= 30 g	g; <i>m</i> (n-o	ctane) =	= 30 g;	$t_{\text{react.}} =$	= 4 h.
^a Conversion of <i>n</i>	-octane. ¹	^b Selectiv	ity for	branched	l C8 pro	oducts;
the rest to obtain	100% ref	lects gas	eous C5	and C4	compone	ents of
the product mixtu	re: X_{n-C8}	$= (n_{n_{-}})^{-1}$	$n_{80} - n_n$	$-c_8)/n_{n-c_8}$	ы: Ŷка	OP) =
$n_{\rm r}$ $a_{\rm em} u_{\rm r}$ $a_{\rm r} / n_{\rm r}$	1/1 / 0.00	Sugar	x = Y	$\frac{1}{2} \cos \left X \right $,,,, - r (L	

influence of the system's sulfuric acid concentration and the effect of different reaction temperatures.

Table 1 displays results of a first series of experiments in which the H_2SO_4 to $AlCl_3$ ratio was varied from 0 (pure chloroaluminate melt) to 0.75. All experiments were carried out using a 1-butyl-3-methylimidazolium chloride ([C₄C₁Im]Cl) to AlCl₃ ratio of 0.5.

From Table 1 it is evident that the addition of the Brønsted acid H₂SO₄ to the Lewis-acidic chloroaluminate system increases *n*-octane conversion up to the $H_2SO_4/AlCl_3$ ratio of 0.18, while at even higher sulfuric acid concentration the catalytic activity decreases again. This indicates a maximum of the acidity in this specific composition correlating to a maximum *n*-octane conversion of 77.2% and a yield of branched C4–C8 alkanes of 54.2% (LOP_{C4-C8} selectivity = 70.2%). The yield to branched C6-C8 alkanes is 32.4%. These findings can be understood in the light of the known mechanism of alkane isomerization. The latter is considered to proceed as a chain reaction including an initiation step that requires a superacidic proton to form the first carbocation via direct hydride abstraction.¹⁸ The highest catalytic activity found for the molar ratio range $0.14 < H_2SO_4/AlCl_3 < 0.21$ can be rationalized by the reactions and equilibria present in the ionic liquid system to form superacid, "naked" protons (1 and 2).

$$2[\mathrm{Al}_2\mathrm{Cl}_7]^- + 3\mathrm{H}_2\mathrm{SO}_4 \rightarrow \mathrm{Al}_2(\mathrm{SO}_4)_3(\downarrow) + 6\mathrm{HCl} + 2[\mathrm{Al}\mathrm{Cl}_4]^-$$
(1)

$$6[Al_2Cl_7]^- + 6HCl \rightleftharpoons 12[AlCl_4]^- + 6"H^+"$$
(2)

It is obvious that the highest acidity is obtained if each HCl formed by the complexation of Al with the sulfate ion is reacting with one of the Lewis-acidic ions $[Al_2Cl_7]^-$ (or $[Al_3Cl_{10}]^-$) to form the "naked" protons. In this case the highest concentration of "naked" protons is generated in the least coordinating environment. From the stoichiometry of eqn (1) and (2) it can be assumed that the H₂SO₄/[Al₂Cl₇]⁻ ratio resulting in the highest ionic liquid acidity should thus be

in the ratio of 3/8. Given the fact that the formation of each $[Al_2Cl_7]^-$ ion requires two molar equivalents of AlCl₃ (of which the first is only neutralizing the chloride salt to the neutral [AlCl₄]⁻) one would expect a H₂SO₄/AlCl₃ ratio of 3/16 or 0.1875 in the ionic liquid synthesis to provide the highest acidity. This predicted ideal composition corresponds remarkably well to the sulfuric acid ratio found to be optimum in our catalytic experiments. Exceeding this optimum molar ratio, more [Al₂Cl₇]⁻ and [Al₃Cl₁₀]⁻ anions are consumed by reacting to $Al_2(SO_4)_3$. In this case the molar amount of formed HCl exceeds the molar amount of remaining acidic anions and therefore HCl gas leaves the system and the amount of "naked" protons formed drops. Therefore the overall system acidity drops again at higher sulfuric acid contents. It is notable that in all these experiments the formation of solid $Al_2(SO_4)_3$ in the reaction system is indeed observed and has been confirmed by isolation and analysis of the precipitate using BaCl₂. However, isolation and removal of Al₂(SO₄)₃ was not necessary to apply the superacidic ionic liquid system in catalysis. The precipitation of $Al_2(SO_4)_3$ is a very important aspect to generate the superacidity in this system as the most basic component of the system, the sulfate ion, is removed from the system in this way.

Note that the here described catalytic system [cation]Cl/ AlCl₃/H₂SO₄ is much easier and safer to work with compared to the earlier reported [cation]Cl/AlCl₃/HCl systems (see ref. 10–12 and 14). The handling of toxic and highly corrosive HCl gas is avoided and accurate dosing of the Brønsted-acidic component to the system is not influenced by a gas–liquid mass transport step or solubility issues. The superacidic ionic liquid system is furthermore truly catalytic (TOF = 11.7 h⁻¹ and TON = 47 for the result in Table 1 with a H₂SO₄/AlCl₃ ratio of 0.18) and has been shown to be recyclable (80% of the original TOF demonstrated in a repetitive batch experiment using a recycling procedure with short air contact).

Encouraged by the remarkable catalytic performance of our optimized [cation]Cl/AlCl₃/H₂SO₄ system at a temperature as low as 303 K and these important practical advantages we tested in a next series of experiments whether the isomerization rate and selectivity could be further improved by temperature variation. As can be seen from Fig. 1 it was found that low temperatures are favourable to maximize the LOP and branched LOP yields (16.7% at 283 K vs. 7.4% at 323 K), while temperature increase leads to higher overall n-octane conversion (53.5% at 283 K vs. 91.1% at 323 K). Compared to classical heterogeneous isomerization catalysts operating at temperatures higher than 400 K these results are very remarkable as it is known that isomerization of higher-molecular weight alkanes at higher temperatures leads to a huge amount of cracking products.¹⁹ Another advantage of performing alkane isomerization at very mild temperatures is in the fact that skeleton isomerization is an equilibrium limited reaction in which the formation of the thermodynamically more stable branched isomers is favored by low temperatures if the reaction is conducted till the equilibrium state.

It is furthermore very remarkable that no coke formation was observed in any experiments using our optimized [cation]Cl/AlCl₃/H₂SO₄ system compared to heterogeneously catalyzed alkane isomerizations. Applying, for example, zeolithes



Fig. 1 Yield of LOP, conversion of *n*-octane, selectivity of iso-octanes at various reaction temperatures. $[C_4C_1Im]Cl/AlCl_3 = 1/2;$ H₂SO₄/AlCl₃ = 0.18; *m*(IL) = 30 g; *m*(*n*-octane) = 30 g; *t*_{react.} = 4 h.

for the *n*-octane hydroisomerization at high temperatures (T > 493 K) as reported in the literature²⁰ leads to significant coke formation and the related catalyst deactivation even so hydrogen is used in this case to avoid this undesired side reaction.

In conclusion, we have demonstrated that the system $[cation]Cl/AlCl_3/H_2SO_4$ is a very versatile superacidic liquid catalyst, in particular if the optimum H_2SO_4 to AlCl_3 ratio of 0.1875 is applied in highly acidic chloroaluminate melts. In contrast to the well-established superacidic ionic liquids of the general type [cation]Cl/AlCl_3/HCl, the here presented system avoids the use of toxic and corrosive HCl gas and makes use of *in situ* HCl-production and Al_2(SO_4)_3 precipitation. Applying the optimized [cation]Cl/AlCl_3/H_2SO_4 *n*-octane conversion to high yields of liquid organic products and even a significant amount of iso-octanes could be achieved without the use of additional hydrogen or added precious metals. Coke formation was not observed due to the very mild conditions of our experiments.

With the described attractive performance features we assume these optimized [cation]Cl/AlCl₃/H₂SO₄ systems to be indeed highly attractive liquid catalysts for refinery isomerization processes of higher alkanes in a liquid–liquid biphasic reaction mode.

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