



Nickel catalyzed dimerization of propene in chloroaluminate ionic liquids: Detailed kinetic studies in a batch reactor

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ARTICLE INFO

Article history:

Received 24 June 2009

Received in revised form 14 August 2009

Accepted 14 August 2009

Available online 22 August 2009

Keywords:

Dimerization

Propene

Nickel

Ionic liquid

Kinetics

ABSTRACT

The dimerization of propene in the presence of homogeneous nickel catalysts in acidic chloroaluminate ionic liquids has been investigated. The solubility of both substrate and products has been carefully determined in order to interpret kinetic findings. Detailed kinetic studies have indicated strong mass transport limitation of the overall reaction rate. The diffusion coefficient of propene in the ionic liquid has been determined from gas solubility measurements. This established method allowed the calculation of the Hatta number to be 4.9, indicating the severe mass transport limitation. For such fast biphasic reactions a loop reactor design is suggested.

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1. Introduction

The immobilization of transition metal complexes is an attractive goal in order to combine the advantages of homogeneous and heterogeneous catalysis [1]. Implementation of highly active and selective homogeneous catalysts in industrial processes is sometimes only hampered by the loss of catalyst during product isolation. Separation of the catalyst phase from the product phase via miscibility gap is a simple and elegant way to overcome this drawback [2]. In this context ionic liquids (ILs) have proven to be suitable reaction media that allow a facile product and catalyst separation [3]. In many cases organic solvents could be substituted and energy intensive downstream processing like distillation would become obsolete. In the recent literature there are many examples for successful applications of ionic liquids in chemical reactions [4]. Due to the great variety of anion and cation combinations, ionic liquids can be tailored for many purposes. Especially the solubility properties of ionic liquids can be adjusted to offer a high solubility for substrates, while the products have a lower solubility. In this scenario the products are extracted from the ionic liquid catalyst phase *in situ* and consecutive reactions can be suppressed [5]. An important example of such a reaction system is the dimerization of

short alkenes in slightly acidic ionic liquids that can be catalyzed by several nickel complexes as depicted in Scheme 1.

Chauvin and co-workers at the *Institut Français du Pétrole* (IFP) reported the dimerization of propene in chloroaluminate ionic liquids (e.g. 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) with added AlCl₃ or AlEtCl₂) as early as 1990 [6].

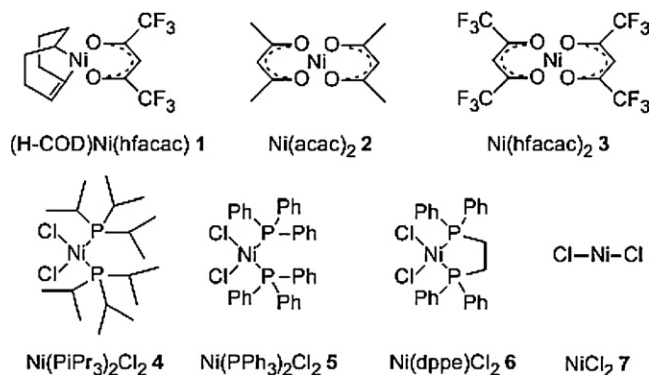
The selectivity toward linear or branched dimers is strongly influenced in this reaction by the presence and nature of the phosphine ligand attached to the nickel. Electron poor phosphines give mainly linear dimers whereas more basic phosphines give branched dimers predominantly [7]. However, in a chloroaluminate ionic liquid system the phosphine ligand reacts with the [Al₂Cl₇]⁻ anion, by which the ligand is removed from the nickel according to Scheme 2 [8].

Since highly branched propene dimers are desired for industrial applications as, e.g. fuel additives, the concentration of [Al₂Cl₇]⁻ anions has to be reduced in chloroaluminate ionic liquid systems to protect the ligand from being abstracted from the metal.

Addition of aromatic bases like tetramethylbenzene (TMB) or N-methylpyrrole (N-MP) could minimize the ligand degradation via scavenging of the [Al₂Cl₇]⁻ anion [8]. Since the [Al₂Cl₇]⁻ anion does not only deteriorate phosphine ligands, but can also initiate cationic oligomerization reactions, it is of vital importance to keep its concentration low. Replacing AlCl₃ by AlEtCl₂ was found to suppress the cation oligomerization reaction [6,9]. However, an excess of AlEtCl₂ is known to reduce the nickel(II) catalyst to elemental nickel at temperatures above 0 °C. The system compris-

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Scheme 1. Chemical structures of nickel dimerization catalysts employed in the dimerization of 1-alkenes.

ing [BMIM]Cl/AlCl₃/AlEtCl₂ in a 0.435/0.522/0.042 ratio exhibited high activity and low cationic oligomerization tendency. Recently, IFP established this biphasic alkene dimerization in ionic liquids named Difasol as part of their licensing portfolio [10]. Compared to the homogeneous Dimersol process, the ionic liquid process gives higher dimer selectivity and required less nickel by a factor of 10 [11].

In organic solvents, the catalyst complex **1** is reported to yield linear dimers with 75% selectivity in propene dimerization and 80% in 1-butene dimerization with turnover frequencies (TOFs) of 770 h⁻¹ (propene) and 330 h⁻¹ (1-butene) at 75 °C [12]. This high linearity especially of the butene dimers will make this catalyst highly attractive for industrial applications if it can be effectively recycled. We previously reported the dimerization of 1-butene using **1** immobilized in acidic ionic liquids composed of 1-butyl-4-methylpyridinium chloride ([4-MBP]Cl)/AlCl₃ either buffered with LiCl or AlEtCl₂ [13]. At 25 °C a TOF of 7500 h⁻¹ was observed, with a selectivity toward octenes of 75% and a linearity within the octene fraction of 30%.

This contribution summarizes parts of a detailed study of the biphasic dimerization of propene and 1-butene in buffered chloroaluminate ionic liquids catalyzed by different homogeneous Nickel ligand catalyst systems previously published in German [13(a)]. The study takes into account both kinetic and phase equilibria aspects of the liquid–liquid systems. The present publication extends the original findings by measured data for the alkene diffusion coefficients in ionic liquids which allows a more accurate calculation of the mass transfer influence.

2. Experimental

2.1. Chemicals and general techniques

All chemical manipulations were carried out using standard Schlenk techniques under an Argon 4.6 atmosphere. Ionic liquids, AlCl₃ (puriss., Fluka) and catalyst complexes **1–4** were stored in a glove box (Braun MB 150 B-G) prior to use. Complex **1** was stored in a freezer at –35 °C inside the glove box. N₂ (99.999%) and Argon (99.996%) were purchased from Westfalen AG. Propene (99.8%) and

1-butene (99.6%) were purchased from Gerling, Holz & Co., Hamburg and were dried over 4 Å mole sieve. Liquid 1-alkenes were purchased from Sigma–Aldrich and Fluka and were used without further purification. AlEtCl₂ (1 M in hexane, Fluka) and Al(OEt)Et₂ (1 M in toluene, Sigma–Aldrich) were used as received. The ionic liquids 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl)/AlCl₃ (0.45/0.55 molar ratio) and [BMIM]Cl/AlCl₃ (0.45/0.55 molar ratio) were synthesized according to literature procedures and their purity was assigned using NMR analysis [14]. The catalyst complex **2** was purchased from Dyanamit Nobel and was dried *in vacuo* over P₂O₅. In all kinetic experiments 3.7 wt% of the buffering base *N*-methylpyrrole (Fluka) was added to the ionic liquid catalyst solution.

2.2. Gas solubility studies

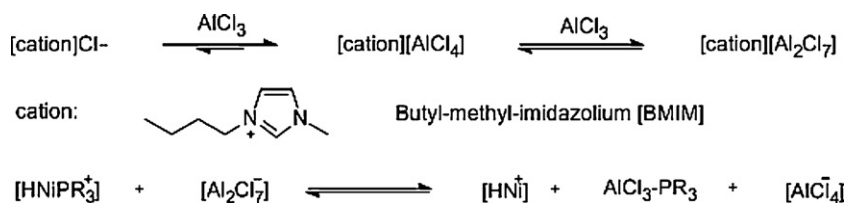
The gas solubility of the propene substrate was determined in buffered chloroaluminate melts. A defined amount of ionic liquid was placed in a 75 ml autoclave with internal magnetic stirrer and the vessel was flushed with propene under atmospheric pressure until the vessel volume had been replaced three times. The vessel was closed and the weight of the vessel was measured. The first propene partial pressure was adjusted via a regulatory valve and the weight of the vessel was measured immediately afterwards, so that no significant amount of propene could dissolve in the ionic liquid. Thus, the mass gain of the gaseous propene inside the reactor was determined. The magnetic stirrer was then switched on for 30 min while dissolved propene was constantly made up via a needle valve. After 30 min, the stirring was stopped, the needle valve was closed and the weight of the reactor was measured. By this procedure the amount of dissolved propene in the ionic liquid $m_{propene,IL}$ could be determined. This procedure was repeated for several partial pressures. With the known mass of ionic liquid the mass ratio of propene in the ionic liquid could be calculated according to Eq. (1):

$$w_{propene,IL} = \frac{m_{propene,IL}}{m_{IL} + m_{propene,IL}} \quad (1)$$

The mass ratio was converted into the molar ratio via the molar masses of ionic liquid and propene.

2.3. Liquid alkene solubility studies

The distribution coefficient for the liquid 1-hexene was determined via an extraction method. A defined amount of heptane was mixed with a defined amount of 1-hexene. The ionic liquid was added to this mixture and the two phases were mixed vigorously. After 30 min mixing the two phases were allowed to separate. A sample of the upper organic phase was analyzed in the gas chromatograph and allowed the mass ratio $w_{1-hexene,org}$ to be calculated. A second sample was taken from the saturated ionic liquid phase and the 1-hexene was extracted three times with fresh cyclohexane. The amount of 1-hexene in the re-extraction agent was determined via GC and thus the mass ratio $w_{1-hexene,IL}$ was determined. The mass related distribution coefficient $K_{w,1-hexene}$ could



Scheme 2. Equilibria of chloroaluminate ionic liquids (top) and degradation of phosphine ligands in the presence of [Al₂Cl₇]⁻ anions.

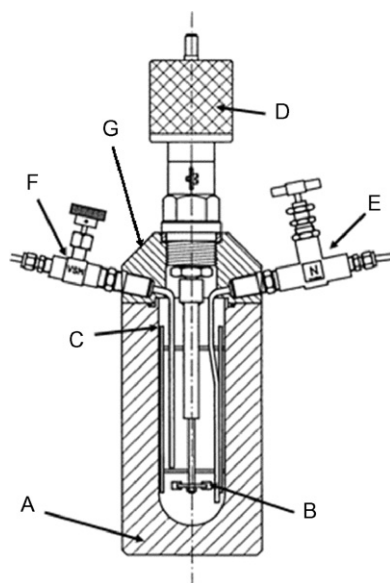


Fig. 1. 200 ml autoclave used in the dimerization experiments. A, stainless steel (1.4571) vessel; B, six-blade stirrer; C, baffles; D, magnetic coupling; E, needle valve for ionic liquid phase sampling; F, needle valve for organic phase sampling; G, reactor lid with release valve (not visible).

then be calculated according to Eq. (2):

$$K_{w,hexene} = \frac{w_{hexene,org}}{w_{hexene,IL}} = K_{c,hexene} \frac{\rho_{IL}}{\rho_{org}} \quad (2)$$

With the known densities of the ionic liquid and the organic phase the concentration related distribution coefficient $K_{c,1-hexene}$ was calculated as shown in Eq. (2).

2.4. Kinetic studies in a batch reactor

The dimerization experiments were carried out in a 200 ml stainless steel autoclave as depicted in Fig. 1. The autoclave was equipped with a six-blade stirrer B and baffles C. A pressure gauge (Wika) and an electronic pressure transducer (Brandt) allowed monitoring the reaction progress. The temperature inside the reactor was monitored via a thermocouple and regulated via a PID regulator (Eurotherm 818 series).

The autoclave was dismantled and placed into an oven prior to reaction in order to remove traces of washing solvents and moisture. The weight of the assembled reactor plus argon purging gas was measured. The assembled reactor was flushed three times with argon to remove traces of oxygen. The heptane solvent and the ionic liquid catalyst solution were filled in the reactor under argon counter flow via a valve on top of the reactor lid G. Propene was condensed into a 300 ml stainless steel vessel equipped with needle valves at both sides. The weight of the vessel was measured and the lower needle valve was connected to the top valve of the reactor. The upper needle valve was connected to either valve E or F in order to equilibrate the pressure when opening the storage vessel to the autoclave. The connecting lines were flushed with propene in order to remove air. After opening the bottom valve of the bomb, the reaction time was started. Samples were taken at regular intervals by switching off the stirrer, allowing phase separation for 20 s and opening valve F for sampling the organic phase. Immediately after sampling, the stirrer was started again. Samples of the ionic liquid phase could be taken via valve E using a similar procedure. The composition of the gas phase was determined by taking samples via the top valve of the reactor and flushing them through a glass tube, equipped with shut off valves at both ends and a septum. From this gas trap they were injected into the GC.

2.5. Gas chromatography

All samples were analyzed by GC using a Siemens Sichromat GC with FID detection. Three different columns and temperature programs were used to analyze the liquid samples, the octene fraction and the gaseous samples. Liquid samples were analyzed on a 50 m Pona HP 25 column, temperature program 30 °C (20 min isothermal) to 230 °C (20 °C min⁻¹), injector temperature 250 °C, carrier gas H₂, on column pressure 1.5 bar. Octenes were analyzed on a 200 m Benzochinoline column, temperature program 10 °C isothermal, injector temperature 225 °C, carrier gas H₂, on column pressure 0.5 bar. Gaseous samples were analyzed on a 50 m Plot-FS-Al 203/KCl column, temperature program 70 °C (4 min isothermal) to 180 °C (10 °C min⁻¹), injector temperature 250 °C, carrier gas N₂, on column pressure 1.0 bar.

3. Results

For detailed kinetic studies of the liquid–liquid dimerization reaction reliable solubility data for propene and the different product alkenes in both, the ionic liquid catalyst phase and the organic extraction phase are a prerequisite. These data have been determined and calculated under equilibrium conditions and the results are described in the following paragraph. It is noteworthy in this context that during the catalytic reaction the biphasic system is unlikely to be always equilibrated. However, the equilibrium concentration determines the driving force and marks the end point of each mass transport process across the liquid–liquid phase boundary. Thus, the knowledge of the equilibrium distribution coefficients is critical information for the interpretation of our kinetic results.

3.1. Solubility studies of 1-alkenes in ionic liquids

3.1.1. Propene

For propene, experiments were initially conducted using the chloroaluminate melt composed of 45 mol% [EMIM]Cl, 55 mol% AlCl₃ and buffered with *N*-methylpyrrole. This ionic liquid was of the same type which was used for the 1-butene dimerization [13(a)]. Traces of nickel in the AlCl₃ initiated a slow dimerization. To avoid this undesired reaction in solubility studies, AlCl₃ was purified by sublimation and a neutral melt consisting of 50.2 mol% [EMIM]Cl and 49.8 mol% AlCl₃ was prepared. In this neutral melt no dimerization was observed. Fig. 2 shows the mass ratio of propene as a function of propene partial pressure at different temperatures.

The graphs indicate that the solubility of propene became minimal at 40 °C and increased with higher and lower temperatures. Since the trend lines in Fig. 1 did not show a linear behavior, the Henry law could only be applied in the range between 2 and 8 bar propene pressure.

In a next step the mass ratio of propene in the organic heptane phase $m_{propene,org}$ had to be determined. In the case of ideal behavior of both phases, the molar ratio was calculated by Raoult's law in Eq. (4):

$$x_{alkene} p_{alkene}^s = y_{alkene} P \quad (4)$$

The saturation pressure of propene was calculated from a reduced form of the Clausius–Clapeyron equation.

$$\log_{10}(p_{alkene}^s) = -\frac{A}{T} + B \quad (5)$$

Values for A and B (in Torr) were taken from the Landolt–Börnstein data base and are compiled in Table 1 [15–17].

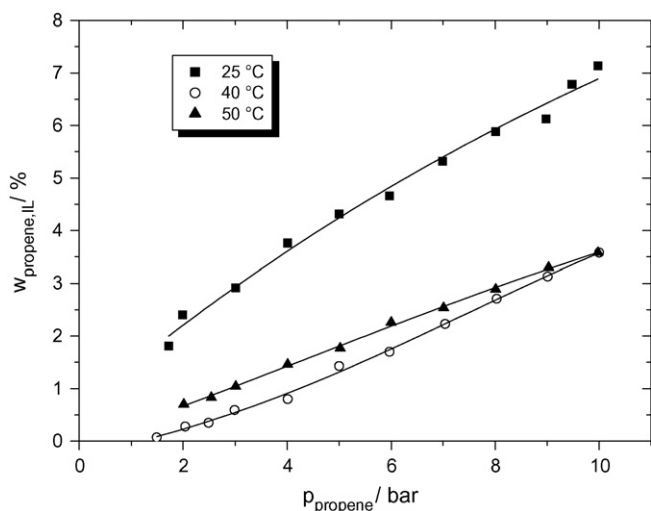


Fig. 2. Mass ratio of propene dissolved in the ionic liquid [EMIM]Cl/AlCl₃ (molar ratio = 0.502/0.498) as a function of propene partial pressure at different temperatures. (■) 25 °C, (○) 40 °C, (▲) 50 °C.

Table 1

Constants required for calculation of the vapor pressure line.

Entry	Substrate	A (Torr)	B (Torr)	Refs.
1	Propene	975.1	7.205	[15]
2	1-Hexene	1587.0	7.625	[16]
3	n-Heptane	1812.0	7.757	[17]

The vapor line of a propene/heptane mixture was calculated with these data according to Eq. (6):

$$x_{propene,org} = \frac{p - p_{heptane}^s}{p_{propene}^s - p_{heptane}^s} \quad (6)$$

The calculated vapor line at 25 °C was compared to experimental values based on the gravimetric analysis of dissolved propene according to Eq. (1). As can be seen from Fig. 3, the measured data matched the calculated ones in good agreement.

Transfer of the molar ratio of propene in the heptane phase into a mass ratio allowed determination of both the mass related and concentration related distribution coefficients according to Eq. (2). Fig. 4 shows the correlation between $w_{propene,IL}$ and $w_{propene,org}$

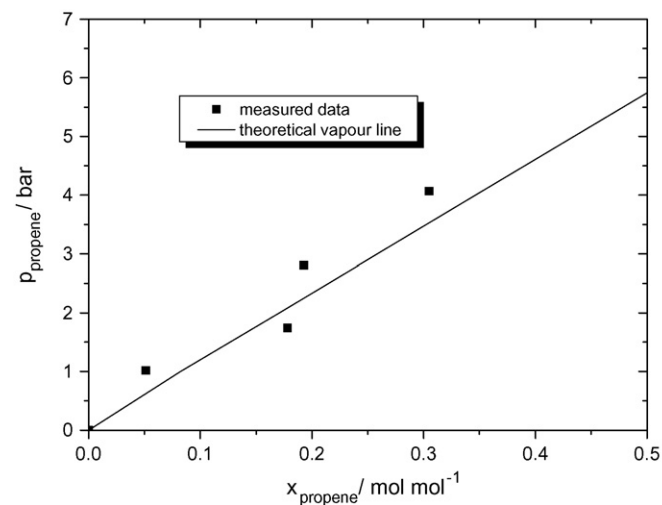


Fig. 3. Theoretical vapor and dew lines for the propene/heptane system at 25 °C. Measured values for the vapor line are shown as ■.

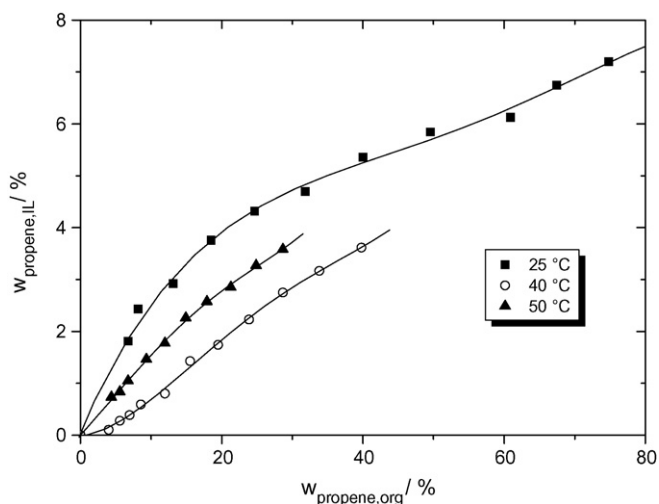


Fig. 4. Mass ratio of propene dissolved in the ionic liquid [EMIM]Cl/AlCl₃ (molar ratio = 0.502/0.498) as a function of propene mass ratio in the organic phase. (■) 25 °C, (○) 40 °C, (▲) 50 °C.

and in Table 2 the calculated K_w and K_c values are compiled and compared to 1-hexene.

In Fig. 4 the solubility of propene in the ionic liquid shows a non-linear trend at 25 °C whereas at 40 and 50 °C the solubility follows a linear trend. The reason for the nonlinearity at 25 °C is not clear yet and is currently being investigated in our laboratory.

3.2. 1-Hexene

During the dimerization of propene only minor amounts of 1-hexene are formed compared to the branched hexenes. Nevertheless, 1-hexene is a suitable model compound for the C6 fraction. Therefore its distribution coefficient has been determined. In Fig. 5 the mass ratio of 1-hexene in the ionic liquid phase is plotted against the mass ratio of 1-hexene in the organic phase. Using the buffered acidic ionic liquid [EMIM]Cl/AlCl₃ (molar ratio = 0.45/0.55), a linear increase of dissolved 1-hexene with increasing amount of 1-hexene in the organic phase was observed.

The solubility of 1-hexene was increased slightly with increasing temperature. Assuming constant densities of organic and ionic liquid phase, the concentration related distribution coefficient $K_{c,1-hexene}$ for 1-hexene was calculated in the same procedure as the one for propene from the mass related coefficient $K_{w,1-hexene}$. Table 2 compiles the data for propene and 1-hexene solubility. With increasing temperature the solubility in the ionic liquid increased for 1-hexene while for propene a minimum solubility was observed at 40 °C. As the solubility of propene in IL is temperature dependent and the solubility of propene in heptane is temperature dependent, we assume that the unusual solubility minimum at 40 °C is a result of the interplay of both trends.

At 25 °C the longer chain 1-hexene was less soluble in the ionic liquid phase by a factor of ca. 22. At 40 and 50 °C still a factor of 6–7 was observed. This lower solubility is an important prerequisite for high selectivity toward dimers instead of trimers, which are obtained by consecutive reactions in the ionic liquid phase of the hexenes with propene [10]. Based on these thermodynamic considerations the dimerization of propene to yield predominantly hexenes should be feasible.

3.3. Kinetic studies in a batch reactor

3.3.1. Propene dimerization

The kinetics of propene dimerization were determined using the nickel catalyst [(H-COD)Ni(hfacac)] **1**. By performing stirring

Table 2

Calculated distribution coefficients for propene and 1-hexene (a) in [EMIM]Cl/AlCl₃ (molar ratio = 0.502/0.498) at $c_{propene,org} = 2.0 \text{ mol l}^{-1}$ and (b) in buffered [EMIM]Cl/AlCl₃ (molar ratio = 0.45/0.55) at $c_{1-hexene,org} = 2.0 \text{ mol l}^{-1}$ at different temperature.

Entry	Temperature (°C)	$K_{w,propene} (\text{kg}_{alkene} \text{ kg}_{org}^{-1} / \text{kg}_{alkene} \text{ kg}_{IL}^{-1})$	$K_{w,1-hexene} (\text{kg}_{alkene} \text{ kg}_{org}^{-1} / \text{kg}_{alkene} \text{ kg}_{IL}^{-1})$	$K_{c,propene} (n_{alkene} n_{org}^{-1} / n_{alkene} n_{IL}^{-1})$	$K_{c,1-hexene}$
4	25	4.0	88.9	2.2	48.1
5	40	10.2	62.8	5.6	33.9
6	50	6.4	42.6	3.5	23.0

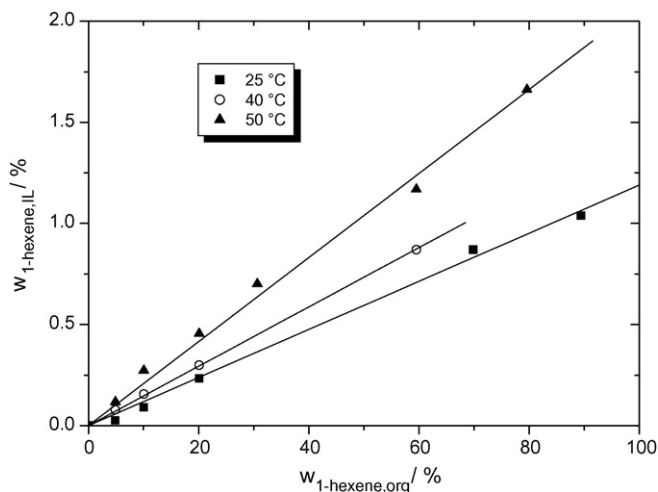


Fig. 5. Mass ratio of 1-hexene dissolved in the buffered ionic liquid [EMIM]Cl/AlCl₃ (molar ratio = 0.45/0.55) as a function of 1-hexene mass ratio in the organic phase. (■) 25 °C, (○) 40 °C, (▲) 50 °C.

tests with a glass autoclave, it was found that a stirrer speed of 2000 min⁻¹ was necessary to allow a complete dispersion of the dense ionic liquid ($\rho_{IL} = 1.25 \text{ g ml}^{-1}$) in the light organic phase ($\rho_{org} = 0.67 \text{ g ml}^{-1}$). In an additional study, the stirrer speed was varied and the changes in effective rate were monitored.

The calculated values for the volumetric mass transport coefficient $k_{propene,org,total}$ and the measured values for the effective rate constant $k_{propene,eff}$ were in good agreement as depicted in Fig. 6. The calculation for $k_{propene,org,total}$ can be found in the supporting information. The reaction rate increased with increasing stirrer speed and with increasing interfacial area respectively. Thus the reaction seemed to be strongly influenced by mass transport.

In Fig. 7 a typical run in the biphasic system heptane/[EMIM]Cl/AlCl₃ (molar ratio = 0.45/0.55) is depicted. The propene concentration decreased in an exponential fashion over time.

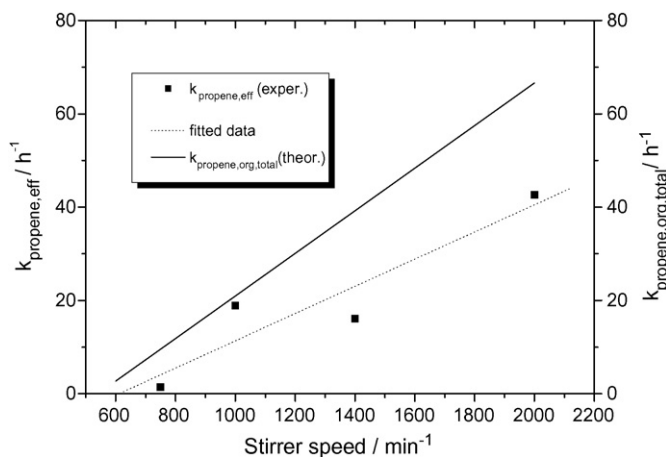


Fig. 6. Influence of stirring speed on propene dimerization with catalyst **1** in buffered [EMIM]Cl/AlCl₃. $T = 10^\circ\text{C}$, $c_{Ni,IL} = 0.83 \text{ mmol l}^{-1}$, 25 g [EMIM]Cl/AlCl₃ (molar ratio = 0.45/0.55) (3.7 wt% N-MP), 110 g heptane, 12 g propene.

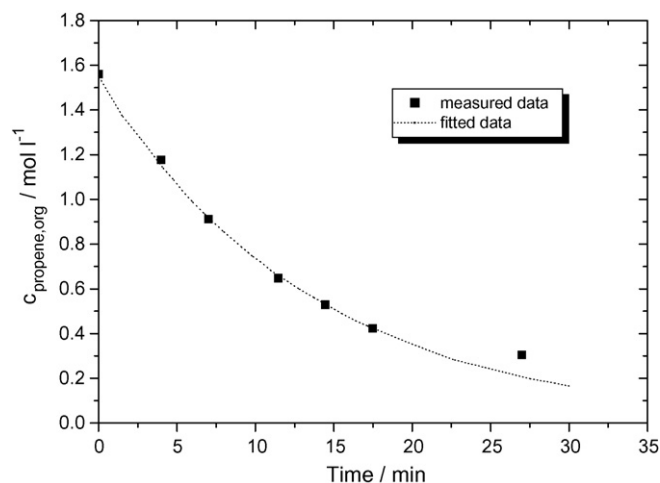


Fig. 7. Propene dimerization with catalyst **1** in buffered [EMIM]Cl/AlCl₃. $T = 10^\circ\text{C}$, stirrer speed $n = 2000 \text{ min}^{-1}$, $c_{Ni,IL} = 0.83 \text{ mmol l}^{-1}$, 25 g [EMIM]Cl/AlCl₃ (molar ratio = 0.45/0.55) (3.7 wt% N-MP), 110 g heptane, 12 g propene.

Assuming a first order in propene concentration, the experimental values could be fitted according to Eq. (7):

$$\frac{c_{propene,org}}{c_{propene,org,0}} = \exp\left(-k_{r,eff} \frac{V_{IL}}{V_{org}} t\right) \quad (7)$$

As can be seen from the dotted line in Fig. 7, the first order assumption allowed good representation of the experimental values. From stoichiometric considerations a second order with respect to $c_{propene}$ would have been expected. Either the rate determining step (RDS) in the catalytic cycle involves insertion of one molecule of propene, or the overall mass transport is the RDS, having a first order in $c_{propene}$. The effective rate constant $k_{r,eff}$ determined from the experiments was in the range of 25–50 h⁻¹ depending on the reaction conditions (temperature, IL volume, stirrer speed, catalyst concentration).

The catalyst concentration in the ionic liquid [EMIM]Cl/AlCl₃ (molar ratio = 0.45/0.55) was varied between 0.5 and 1.8 mmol l⁻¹ and the effective rate constant was determined in a similar fashion from the experimental data. In Table 3 the dependency of rate constant on catalyst concentration is presented.

Table 3

Effective reaction rate constant $k_{propene,eff}$ as a function of catalyst concentration and temperature. Catalyst **1**, c_{Ni} = variable, $c_{propene,org} = 1.6 \text{ mol l}^{-1}$, stirrer speed $n = 2000 \text{ min}^{-1}$, 25 g [EMIM]Cl/AlCl₃ (molar ratio = 0.45/0.55) (3.7 wt% N-MP), 110 g heptane, 12 g propene.

Entry	Temperature (°C)	$c_{Ni,IL} (\text{mmol l}^{-1})$	$k_{propene,eff} (\text{h}^{-1})$
7	10	0.5	38.1
8	10	0.8	42.6
9	10	1.2	39.5
10	10	1.7	44.3
11	6	0.8	41.6
12	15	0.8	32.5
13	19	0.8	31.1
14	32	0.8	34.8

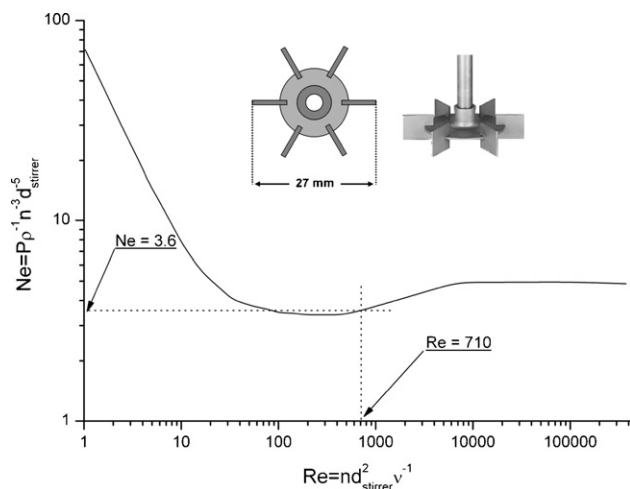


Fig. 8. Power input (Ne) of a six-blade stirrer with baffles as a function of stirring speed (Re). The graph has been reproduced from [23]. Characteristic dimension and picture of the stirrer are shown in the insert.

Remarkably, the effective rate constant was not strongly depending on the catalyst concentration in the ionic liquid phase (Entry 7–10). One reasonable explanation for this finding is that the reaction is not controlled by the reaction kinetics but by the mass transport of alkene into the ionic liquid phase. This corresponds to the results from the stirrer speed variation in Fig. 8. In order to further investigate the influencing factors for the effective rate, the temperature dependency on the rate constant was studied between 6 and 32 °C.

Interestingly, the effective rate constant was found to decrease slightly with increasing temperature (Entry 11–14). In contrast to this, an exponential increase of the reaction rate with increasing temperature according to Arrhenius would be expected if the reaction would be controlled by kinetics. However, assuming a diffusion influenced reaction rate, the lower solubility of propene in the ionic liquid at higher temperatures would result in an increase in $K_{c,propene}$, thus slowing down the mass transport. This lower propene solubility at higher temperatures has indeed been confirmed in our solubility measurements (see Fig. 2).

3.4. Estimation of the Hatta number

In case of a strongly mass transport influenced reaction, the Hatta number is expected to be larger than 3. For the reaction of two propene molecules the Hatta number, derived from an assumed steady state of the mass balance in the two-film theory, can be written according to Eq. (8) [18]:

$$Ha = \frac{\sqrt{k_r D_{propene,IL} C_{propene,org}}}{k_{propene,IL}} \quad (8)$$

A second order reaction in propene concentration can be assumed according to the mechanism and several publications, studying the kinetics in homogeneous systems [19,20]. The binary diffusion coefficient of propene in the acidic ionic liquid was estimated from gas solubility measurements following an established literature procedure to be $D_{propene,IL} = 3.78 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ [21]. Details can be found in the supporting information. The reaction rate constant was taken from literature results in which a similar catalyst system in a molecular solvent system was used [20]. The rate constant $k_r = 29.65 l^2 \text{ mol}^{-2} \text{ s}^{-1}$ indicated second order behavior with respect to propene concentration. The transport coefficient $k_{propene,IL}$ was calculated from the Charpentier Eq. (9)

Table 4

Product composition of the hexene fraction as a function of reaction time. Catalyst **1**, $C_{Ni,IL} = 0.83 \text{ mmol l}^{-1}$, $T = 10^\circ \text{C}$, stirrer speed $n = 2000 \text{ min}^{-1}$, 25 g [EMIM]Cl/AlCl₃ (molar ratio = 0.45/0.55) (3.7 wt% N-MP), 110 g heptane, 12 g propene.

Entry	Time (min)	Conversion (%)	$S_{hexenes}$ (%)	S_{LH} (%)	S_{MP} (%)	S_{DMB} (%)
15	4	24.6	97.3	22.6	73.5	4.8
16	7	41.5	97.0	22.2	72.6	4.8
17	12	58.5	96.9	22.6	72.6	5.2
18	15	66.1	96.6	22.2	73.0	5.2
19	18	72.9	96.8	22.6	72.2	5.2
20	27	80.5	96.4	22.2	72.6	4.8

[22]:

$$k_{propene,IL} a_{IL} = 0.0173 \sqrt{\frac{P}{V}} \sqrt{\frac{D_{propene,IL}}{2.4 \times 10^{-9}}} \quad (9)$$

The energy input P of the six-blade stirrer (gs) in the reaction volume V was calculated from a graphical correlation between the Reynolds number ($Re = n d_{stirrer}^2 / \nu = 710$) and the Newton number Ne [23]. From the graph in Fig. 8 a Newton number of 3.6 was calculated, which corresponded to an energy input of 1.46 W.

From the energy input the Sauter diameter d_{32} of the ionic liquid droplets in the organic phase was calculated to be 0.13 mm, resulting in an exchange surface a_{IL} of 46154 m^{-1} . From Eq. (9) a transport coefficient of $k_{propene,IL} = 1.34 \times 10^{-5} \text{ ms}^{-1}$ was calculated. Using a different approach, the transport coefficient for propene in the ionic liquid phase was estimated from the Newman correlation (10), assuming no circulation inside the ionic liquid droplets and only molecular diffusion as transport process [24].

$$k_{propene,IL} = 6.58 \frac{D_{propene,IL}}{d_{32}} \quad (10)$$

From Eq. (10) a transport coefficient of $k_{propene,IL} = 1.91 \times 10^{-5} \text{ ms}^{-1}$ was calculated. Inserting the larger value of $k_{propene,IL}$ into Eq. (8) resulted in a Hatta number of 4.9. This indicates that the dimerization of propene in ionic liquids is a very fast reaction and mass transport from the organic into the ionic liquid phase can be expected to be the rate determining step in the process [21]. Additionally, since an order of two can be expected from mechanistic considerations, the first order determined in the biphasic system reflects the influence of mass transport on the overall kinetics.

3.5. Selectivity and activity

The product distribution, analyzed over time during the experiment, is summarized in Table 4. Methylpentenes (MP) were the largest fraction inside the hexene products with more than 70%. Linear alkenes (LA) were produced around 22% and only a small fraction of dimethylbutenes (DMB) were found. This composition did not change over time, indicating the absence of isomerization between the products.

The overall selectivity to hexenes was exceptional and decreased only slightly from 97.3% (Entry 15) to 96.4% (Entry 20). For comparison the catalyst complex **1** was also studied in homogeneous dimerization using toluene as solvent. In the [EMIM]Cl/AlCl₃ (molar ratio = 0.45/0.55) system the TOF exceeded $70,000 \text{ h}^{-1}$ (Entry 21) whereas in toluene only 770 h^{-1} were observed (Entry 23) as shown in Table 5. This was attributed to an activation of the nickel complex by the slight Lewis acid character of the ionic liquid catalyst support thus forming a much more active catalyst. Taking into account that the reaction in the [EMIM]Cl/AlCl₃ (molar ratio = 0.45/0.55) system was mass transport limited, the intrinsic activity difference of the nickel catalyst in IL vs. the catalyst in toluene might be even higher.

Table 5

Propene dimerization with different catalyst precursors in toluene and ionic liquid. Stirrer speed $n=2000\text{ min}^{-1}$, $c_{\text{Ni,IL}}=0.83\text{ mmol l}^{-1}$, 25 g [EMIM]Cl/AlCl₃ (molar ratio = 0.45/0.55) (3.7 wt% N-MP), 110 g heptane, 12 g propene.

Entry	Cat.	System	T (°C)	Conversion (%)	TOF (h ⁻¹)	S _{hexenes} (%)	S _{LA} (%)	S _{MP} (%)	S _{DMH} (%)
21	1	Ionic Liquid	10	25	70,000	97	22	73	5
22	1	Ionic Liquid	10	73	44,000	97	22	73	5
23	1	Toluene	75	73	770	60	75	24	1
24	2	Ionic Liquid ^a	30	50	530,000	97	23	71	6
25	3	Ionic Liquid ^a	15	46	480,000	94	24	71	5

^a $c_{\text{Ni,IL}}=0.31\text{ mmol l}^{-1}$, 35 g [EMIM]Cl/AlCl₃ (molar ratio = 0.45/0.55) (3.7 wt% N-MP), 100 g heptane, 35 g propene.

Noteworthy, the higher activity is obtained at 10 °C in ionic liquids, whereas in toluene the catalyst required temperatures above 70 °C. The selectivity toward the dimeric products was increased from 60% (toluene) to 97% ([EMIM]Cl/AlCl₃ = 0.45/0.55) at the same conversion. This increased dimer selectivity can be understood by taking into account the much lower solubility of C6 products in the ionic liquid compared to the propene feedstock. Consecutive reactions of hexenes with propene can therefore be suppressed. However, inside the hexene fraction the amount of linear hexenes was much higher in toluene (75% compared to 22% in ionic liquids).

When using the catalyst system **1** in combination with the ionic liquid [EMIM]Cl/AlCl₃ = 0.45/0.55, the buffering base was N-MP. In Entry 24 the catalyst **1** was replaced by the complex Ni(acac)₂ **2**, whereas in Entry 25 the electron poor nickel complex Ni(hfacac)₂ **3** was used. In both experiments AlEtCl₂ was used as activator. The different conversions in entries 21/22 and 24/25 stem from different catalyst concentrations and temperatures. Within 10 min reaction time 50% conversion were obtained for catalyst **2**, resulting in an average TOF of 530,000 h⁻¹. This high value was attributed to the lower catalyst concentration. The product composition did not deviate from the one obtained with catalyst **1**, indicating that the active species in the ionic liquid phase was not influenced by ligands under these reaction conditions.

4. Conclusion

In the present work we reported the results on nickel catalyzed dimerization of propene in acidic chloroaluminate ionic liquids [13]. We investigated the solubility behavior of both the substrate and the products by determining the equilibrium constants K_w and K_c . By using 1-hexene as a suitable model compound for the hexene fraction, we found out that the solubility of 1-hexene was up to 22 times lower than the solubility of the propene substrate. This large difference in solubility is a prerequisite for a selective dimerization process in ionic liquids, since the consecutive reaction of formed hexenes with propene to C9 alkenes is minimized. In good agreement with this observation, we obtained with around 97% a high selectivity towards hexene dimers in the kinetic batch experiments. This selectivity was significantly higher than the one obtained in toluene. Within the hexene fraction predominantly branched hexenes were formed, although ligand modified nickel catalysts were used that were known to give high linearity in toluene. This low linearity is a strong indication of ligand degradation in the presence of [Al₂Cl₇]⁻ anions present in the ionic liquid over time. The reaction was first order with respect to propene partial pressure, although the stoichiometry would account for a second order reaction. In case of mass transport being the rate determining step, a first order reaction would be observed. The fact that the reaction rate did neither increase with increasing nickel concentration nor temperature can be regarded as proof for mass transport limitations. This has been further exemplified by the high Hatta number of 4.9 estimated from our data, indicative of a fast chemical reaction and mass transport limitation. In order to reduce the mass transport

limitation an intense mixing between the two phases is mandatory. Such mixing can be achieved in a loop reactor with internal baffles operating at high flow rates.

Acknowledgements

M.E. and W.K. would like to thank BP Chemical for funding. The other authors gratefully acknowledge the funding of the German Research Council (DFG), which, within the framework of its 'Excellence Initiative' supports the Cluster of Excellence 'Engineering of Advanced Materials' (www.eam.uni-erlangen.de) at the University of Erlangen-Nuremberg.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2009.08.015.

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