Linear dimerisation of but-1-ene in biphasic mode using buffered chloroaluminate ionic liquid solvents

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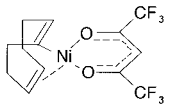
The use of a buffered ionic liquid as a solvent for catalysts known to produce linear dimers from but-1-ene has been explored; this resulted in a significant enhancement of the activity of known catalysts, combined with the retention of both dimer selectivity and product linearity; in addition, the biphasic mode of operation allows easy catalyst recovery and recycle.

The dimerisation and oligomerisation of olefins in the presence of homogeneous Group VIII transition metal catalysts has been studied extensively. With higher olefins, the products typically consist of mixtures of branched isomers. Few catalysts are known which catalyse the linear dimerisation and oligomerisation of C_4-olefins. Linear C_8-olefin dimers are highly-desirable intermediates for the production of C_9-plasticizers, exhibiting better thermal properties than those produced from highly-branched C_8-olefin dimer feedstock (IFP Dimersol, Hüls).

To our knowledge, the best system for producing linear dimers from higher olefins originated from our group in 1979,[1] namely a catalyst based on square planar Ni-*O,O′* chelating systems, with an easily replacable group such as cod, methallyl, allyl, *etc., e.g.* (cod)Ni(hfacac) **1**.



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The above catalyst is active in organic solvents at >50 °C, but reaches its maximum activity at 90 °C, with a turnover frequency of 500 h^{-1} with but-1-ene as feedstock. With an overall dimer selectivity of 85%, the selectivity to the linear dimer product is typically as high as 75%. Although the product quality produced by catalyst **1** is of industrial interest, the combination of high ligand costs, low catalyst activity and difficult catalyst recovery from the homogenous reaction mixture, has so far prevented industrial development.

Recently, a new approach has been adopted for catalyst separation and recycling in oligomerisation reactions, involving the use of a solvent known as an ionic liquid, which is simply a salt mixture of melting point below ambient. A well studied example involves salt mixtures of aluminium halides in combination with suitable substituted organic cations such as 1-butyl-3-methylimidazolium or 1-butylpyridinium cations.[2–4]

The oligomerisation of propene and butenes using ionic liquids as catalyst/solvent has been described by Chauvin *et al.*[5–8] These authors used a slightly acidic ionic liquid of the type [cation]X/AlX_3/$AlEtCl_2$ as a solvent for a Ni(II)-catalyst precursor known to produce highly-branched dimer products. Use of the ionic liquid solvent imparted significantly higher activity to highly branched dimer products with high activity. Moreover, the high solubility of the Ni-complex but poor solubility of the olefins produced in the ionic liquid facilitated a simple decantation step allowing complete catalyst separation.

In the case of butene oligomerisation[7] using $[Ni(MeCN)_6][BF_4]_2$ as catalyst, the distribution of butene dimers, typically 39 ± 1% dimethylhexenes, 56 ± 2% monomethylheptenes and 6 ± 1% *n*-octenes, was reported to be independent of the addition of phosphine ligands. Moreover, the product mix was independent of feedstock, with both but-1-ene and but-2-ene yielding the same dimer distribution, with only 6% of the high-value linear dimer.

In the present article, we report the use of slightly acidic 1-butyl-4-methylpyridinium chloroaluminates, buffered with weak organic bases, as solvents for the linear dimerisation of but-1-ene in biphasic mode catalysed by the Ni-complex **1**.

The ionic liquids were initially prepared by mixing 1-butyl-4-methylpyridiniumchloride (4-MBP Cl) with $AlCl_3$. The Ni-catalyst **1** was dissolved in this binary mixture. Additional alkali metal chloride or organic bases were added afterwards to adjust the desired melt composition. The oligomerisation reactions were carried out in a glass autoclave. After the reaction the remaining organic layer was hydrogenated for determination of the linearity of the dimer products (determination of products by GC–MS and comparison with authentic samples).

It was found that **1** is deactivated by basic chloroaluminate ionic liquids ($X_{AlCl_3} < 0.5$) owing to excess free Cl^- anions, which probably block the free coordination sites of the catalyst (Table 1, entry 1). In acidic chloroaluminate ionic liquids ($X_{AlCl_3} > 0.5$) a large number of branched higher oligomers was formed, with only 8% dimer products formed. Clearly, the dimerisation activity of **1** is swamped by the fast cationic oligomerisation reaction initiated by the intrinsic acidicity of the ionic liquid solvent (Table 1, entry 2). Both results fit well to previous observations with other Ni-catalyst in the oligomerisation of monoolefins and are already described elsewhere in some detail.[5]

It is known that cationic side reactions catalysed by the ionic liquid itself can be avoided if a chloroethylaluminate melt is used as catalyst solvent.[5] However, with **1** the use of this melt as solvent leads to an immediate catalyst decomposition (Table 1, entry 3). At −10 °C, rapid decomposition could be avoided but the linearity of the dimer products was still low (Table 1, entry 4). Probably, even at this low temperature, $AlEtCl_2$ transfers ethyl-groups to the Ni and destroys the Ni-*X,Y* chelating system, which is known to be responsible for the desired high linearity.[1] Moreover, $AlEtCl_2$ is known to exhibit isomerisation activity[9] for converting but-1-ene rapidly into the thermodynamic distribution of butenes (*ca.* 4% but-1-ene at room temperature). While dimer selectivity was enhanced using a mixed system of the form 4-MBP/$AlCl_3$/$AlEtCl_2$ as used by Chauvin *et al.* in previous oligomerisation, dimer linearity was still unsatisfying low at 37% (Table 1, entry 5).

As an alternative way to avoid cationic side reactions, we tested **1** in buffered ionic liquids. The Lewis acidity of ionic liquids is routinely buffered by the addition of alkali metal chloride.[10] Since excess alkali metal chloride does not dissolve in the neutralised resulting ionic liquid, buffering in this manner is very efficient. Our dimerisation experiments were carried out in buffered ionic liquids with and without excess of solid alkali metal chloride. In the first case (Table 1, entry 6), almost no Ni-catalysed dimerisation was observed. Obviously, the slightly Lewis-acidic Ni-catalyst center is ‘buffered’ by the excess of

Table 1 Catalytic results with Ni-complex **1** in different ionic liquid systems.

Entry	Ionic liquid system (mol% composition)	T/°C	TOF^a/h^{-1}	S(C_8)^b (%)	L(C_8)^c
1	4-MBPCl/$AlCl_3$ (0.65/0.35)	25	0	—	—
2	4-MBPCl/$AlCl_3$ (0.45/0.55)	25	^{d}	8	41
3	4-MBPCl/$AlEtCl_2$ (0.36/0.64)	25	0^e		
4	4-MBPCl/$AlEtCl_2$ (0.36/0.64)	−10	61	96^f	12
5	4-MBPCl/$AlCl_3$/$AlEtCl_2$ (0.43/0.53/0.04)	25	415	73	37
6	4-MBPCl/$AlCl_3$ (0.45/0.55) buffered with excess LiCl^g	25	^{h}	—	—
7	4-MBPCl/$AlCl_3$ (0.33/0.66) buffered with excess LiCl^i	25	^{d}	16	28
8	4-MBPCl/$AlCl_3$ (0.45/0.55) buffered with excess LiCl^i	25	7500	75	30
9	4-MBPCl/$AlCl_3$/pyrrole (0.43/0.53/0.04)	25	1350	86	56
10	4-MBPCl/$AlCl_3$/*N*-methylpyrrole (0.43/0.53/0.04)	25	2100	98^f	51
11	4-MBPCl/$AlCl_3$/chinoline (0.43/0.53/0.04)	25	1240	98^f	64
12	4-MBPCl/$AlCl_3$/pyridine (0.43/0.53/0.04)	25	550	78	33
13	4-MBPCl/$AlCl_3$/2,6-dimethylpyridine (0.43/ 0.53/0.04)	25	2480	55	68
14	4-MBPCl/$AlCl_3$/2,6 di-*tert*-butylpyridine (0.43/0.53/0.04)	25	2100	49	32

General conditions: 4 g ionic liquid, 0.04 g **1**, 12 g but-1-ene, reaction time was varied to reach comparable conversions of 15–20%. [a] Turnover frequency (TOF) in mol of butene converted per mol of Ni per h. [b] Selectivity to dimer product in %. [c] Selectivity to linear dimer in the dimer fraction of the product in %. [d] The product is mainly formed by a cationic oligomerisation mechanism of the acidic ionic liquid. The calculation of a turnover frequency related to the amount of nickel catalyst would be meaningless in this case. [e] Catalyst decomposes and forms a black solid of elemental Ni. [f] No products resulting from a parallel cationic side reaction are detected. [g] Ionic liquid was buffered with excess of dry LiCl (dried for 14 days over P_2O_5 at 150 °C). The ionic liquid used for reaction contained solid excess LiCl. [h] Traces of cationic oligomers. [i] Ionic liquid was buffered with excess of dry LiCl (dried 14 days over P_2O_5 at 150 °C). Solid excess LiCl was filtered off. The ionic liquid used for reaction was a clear liquid and contained no solid excess LiCl.

solid alkali metal chloride to a non-reactive Ni-species. Without excess of solid alkali metal chloride, the extent of cationic side reaction is dominated by the chemical behaviour termed 'latent acidity'.[11,12] Even very weak bases (B:) form an $AlCl_3$ adduct in neutral buffered melts. The additional driving force for this reaction apparently results from the precipitation of the solid alkali metal chloride: $AlCl_4^- + Li^+ + B: \rightleftharpoons B:AlCl_3 + LiCl\ (s)$. In our experiments, the but-1-ene feedstock seems to react as such a weak base. We found that the extent of cationic side reaction correlates well with the $Al_2Cl_7^-$ content of the melt from which the buffered ionic liquid was prepared (Table 1, entries 7, 8). However, a comparison of entries 2 and 8 clearly demonstrates the efficiency of an alkali metal chloride buffer in suppressing the formation of cationic oligomers.

Alternatively, we looked for new methods to buffer acidic ionic liquids so as to avoid the precipitation of an alkali metal chloride. We found that a slightly acidic melt buffered with small amounts of weak organic bases provides a solvent which allows a selective, ligand-controlled, biphasic reaction with the Ni-catalyst **1**. The function of the base is to trap any free acidic species in the melt which may initiate cationic side reaction (Table 2).

The base has to be system-adapted to provide high solubilty in the ionic liquid in question, while at the same time being non-coordinating with respect to the catalytic active Ni-center. Possible bases are any cyclic, heterocyclic or aliphatic, aromatic or non-aromatic bases which have these properties. Specially favorable are pyrrole, *N*-methylpyrrole and chinoline (Table 1, entries 9–11).

Experiments with different pyridine derivatives as buffer are interesting in two different respects (Table 1, entries 12–14): While the pyridine-buffered but-1-ene oligomerisation shows a significantly lower activity, this is not the case for the 2-substituted pyridines. This is probably due to a stronger coordination of the unsubstituted pyridine to the active center during reaction, in contrast to the sterically more demanding pyridine derivatives. Moreover, the S(C_8) selectivity clearly decreases with the steric demand of the *o*-substitutent on the pyridine. Assuming that the S(C_8) can be regarded as an indicator of the efficiency of the buffering process, this is a clear sign for a considerable contribution of a sterically demanding step in the buffering process. If only superacidic protons were responsible for the observed cationic side reaction in acidic ionic liquids, these should be perfectly buffered by a strong base like 2,6-di-*tert*-butylpyridine, which is not the case. It is assumed therefore that the reaction $Al_2Cl_7^-$ + base $\rightleftharpoons$ $AlCl_3$–base + $AlCl_4^-$ plays a major role in the buffering process.

Table 2 Function of the added organic base B

$$Al_2Cl_7^- + B \rightleftharpoons B\text{-}AlCl_3 + AlCl_4^-$$

$$B\text{-}AlCl_3 + HCl \rightleftharpoons HB^+ + AlCl_4^-$$

$$Al_2Cl_7^- + HCl + B \rightleftharpoons HB^+ + 2\,AlCl_4^-$$

Overall, the buffering procedures reported here facilitate use of an ionic liquid solvent for catalyst **1**, permitting reaction to take place in biphasic reaction mode with facile catalyst separation and catalyst recycling. The high intrinsic dimer linearity of catalyst **1** is maintained, but with significant enhancement of catalyst activity over that observed in toluene solvent.

In addition, our new concept of producing a latent-acidic chloroaluminate ionic liquid, by buffering a slightly acidic melt with weak organic bases, could prove to be useful in other transition metal catalysed reactions. In contrast to the known systems,[4–7] it avoids any addition of alkylaluminium and thereby allows the use of reduction-sensitive metal complexes at higher temperatures.

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