

Electronic Supporting Information

Cr-catalysed ethylene dimerization in an ionic liquid-organic solvent biphasic system with perfect 1-butene selectivity

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Experimental Section

Chemicals

Chromium(III) acetylacetonate ($\text{Cr}(\text{acac})_3$, 99.99%), tris(tetrahydrofuran) chromium trichloride ($\text{CrCl}_3(\text{THF})_3$, 97%), modified methylaluminoxane (MMAO-12, 7 wt.% aluminum in toluene), diethylaluminum chloride solution (AlEt_2Cl , 25 wt.% in toluene), 1-decyl-3-methylimidazolium tetrafluoroborate ($\text{C}_{10}\text{Im-BF}_4$, 96.5%), chlorodiphenylphosphine (Ph_2PCl , 96%), isopropylamine (99.5%), 1-bromooctane (99%), and 1-bromodecane (99%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). 1-Methylimidazole (99%), bis(trifluoromethane)sulfonimide lithium salt (LiTf_2N ; >98%), and potassium hexafluorophosphate (KPF_6 ; >95%) were supplied by Tokyo Chemical Industry (Tokyo, Japan). Toluene (99.8%) was purchased from Alfa Aesar (Haverhill, MA, USA). Acetonitrile (MeCN ; 99.9%), dichloromethane (CH_2Cl_2 , 99.9%), diethyl ether (99%), ethanol (99.5%), and methanol (99.8%) were purchased from Samchun Chemicals (Seoul, South Korea).

Ionic liquid synthesis

1-Methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide ($\text{C}_1\text{C}_8\text{Im-Tf}_2\text{N}$): A solution of 1-methylimidazole (5.97 g, 72.7 mmol) and 1-bromooctane (21.05 g, 109 mmol) in MeCN (40 mL) was refluxed for 24 h. After cooling to room temperature, the reaction mixture was concentrated by using a rotary evaporator. The residue was dissolved in MeOH (5 mL) and diethyl ether was added under vigorous stirring. The precipitated liquid was washed thrice with diethyl ether. Drying in a vacuum oven yielded a yellow liquid ($\text{C}_1\text{C}_8\text{Im-Br}$, 15.8 g, 79%). Ion exchange of Br^- with Tf_2N^- was conducted as follows: a mixture of the liquid bromide salt $\text{C}_1\text{C}_8\text{Im-Br}$ (5.0 g, 18.2 mmol) and LiTf_2N (6.78 g, 23.6 mmol) in deionized water (15 mL) was stirred at room temperature for 4 h. After decanting the upper layer, the precipitated liquid was washed thrice with deionized water. Drying in a vacuum oven at 353 K yielded a pale-yellow liquid (7.52 g, 87%). The residual halide and moisture contents in the as-synthesized IL were examined by AgNO_3 precipitation and Karl Fischer titration analyses, respectively. No halides were found in the AgNO_3 test. The water content was determined to be 33 ppm. Proton nuclear magnetic resonance (^1H NMR) was performed using a Varian VNMRs 500 MHz spectrometer. ^1H NMR (500 MHz, CDCl_3) δ 8.68

(s, 1H), 7.27 (s, 1H), 7.23 (s, 1H), 4.09 (t, $J = 7$, 2H), 3.85 (s, 3H), 1.82 (m, 2H), 1.20–1.25 (m, 10H), 0.80 (t, $J = 7$, 3H), which is identical to a previous report [1].

Methyl-3-octylimidazolium hexafluorophosphate ($C_1C_8Im-PF_6$): Ion exchange reaction using C_1C_8Im-Br (7.00 g, 25.4 mmol) and KPF_6 (7.83 g, 33.1 mmol) yielded a pale-yellow liquid (7.17 g, 83%). No halides were detected during the $AgNO_3$ test. H_2O content = 65 ppm. 1H NMR (500 MHz, $CDCl_3$) δ 8.40 (s, H, 1H), 7.25 (s, 1H), 7.22 (s, 1H), 4.06 (t, $J = 7$, 2H), 3.84 (s, 3H), 1.79 (m, 2H), 1.20-1.24 (m, 10H), 0.80 (t, $J = 7$, 3H), which is identical to a previous report [1].

1-Decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($C_1C_{10}Im-Tf_2N$): Same procedures as that used for the synthesis of $C_1C_8Im-Tf_2N$, except for using 1-bromodecane (24.10 g, 109 mmol). A yellow liquid ($C_1C_{10}Im-Br$, 19.3 g, 88%) was obtained. The ion exchange reaction using $C_1C_{10}Im-Br$ (9.00 g, 29.7 mmol) and $LiTf_2N$ (11.07 g, 38.6 mmol) afforded a pale-yellow liquid (13.8 g, 93%). No halides were detected during the $AgNO_3$ test. H_2O content = 78 ppm. 1H NMR (500 MHz, $CDCl_3$) δ 8.64 (s, 1H), 7.27 (s, 1H), 7.24 (s, 1H), 4.08 (t, $J = 7$, 2H), 3.86 (s, 3H), 1.78 (m, 2H), 1.18-1.24 (m, 14H), 0.80 (t, $J = 7$, 3H), which is identical to a previous report [1].

1-Decyl-3-methylimidazolium hexafluorophosphate ($C_1C_{10}Im-PF_6$): The ion exchange reaction of $C_1C_{10}Im-Br$ (9.00 g, 29.7 mmol) and KPF_6 (7.09 g, 38.6 mmol) afforded a pale-yellow liquid (9.29 g, 85%). No halides were detected during the $AgNO_3$ test. H_2O content = 47 ppm. 1H NMR (500 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.24 (s, 1H), 7.21 (s, 1H), 4.05 (t, $J = 7$, 2H), 3.82 (s, 3H), 1.78 (m, 2H), 1.17-1.24 (m, 14H), 0.80 (t, $J = 7$, 3H), which is identical to a previous report [1].

PNP ligand synthesis

A bis(diphenylphosphino)(isopropyl)amine (PNP) ligand was synthesized by modifying a previously reported procedure [2]. Isopropylamine (5.0 mL, 58.4 mmol) was added to a mixture of chlorodiphenylphosphine (24.0 mL, 129.7 mmol) and triethylamine (24.3 mL, 174.6 mmol) in CH_2Cl_2 (58 mL) at 238 K. The mixture was stirred at room temperature for 24 h and then concentrated using a rotary evaporator. The resulting off-white solid was dissolved in degassed CH_2Cl_2 and filtered through a short Al_2O_3 column to remove triethylammonium chloride salt. After the removal of the solvent, the PNP ligand was obtained as a white solid (21.18 g, 85% yield). 1H NMR (500 MHz, $CDCl_3$) δ 7.27-7.36 (m, 20 H), 3.69-3.79 (m, 1H), 1.13 (d, $J = 6.5$ Hz, 6 H).

Ethylene dimerization

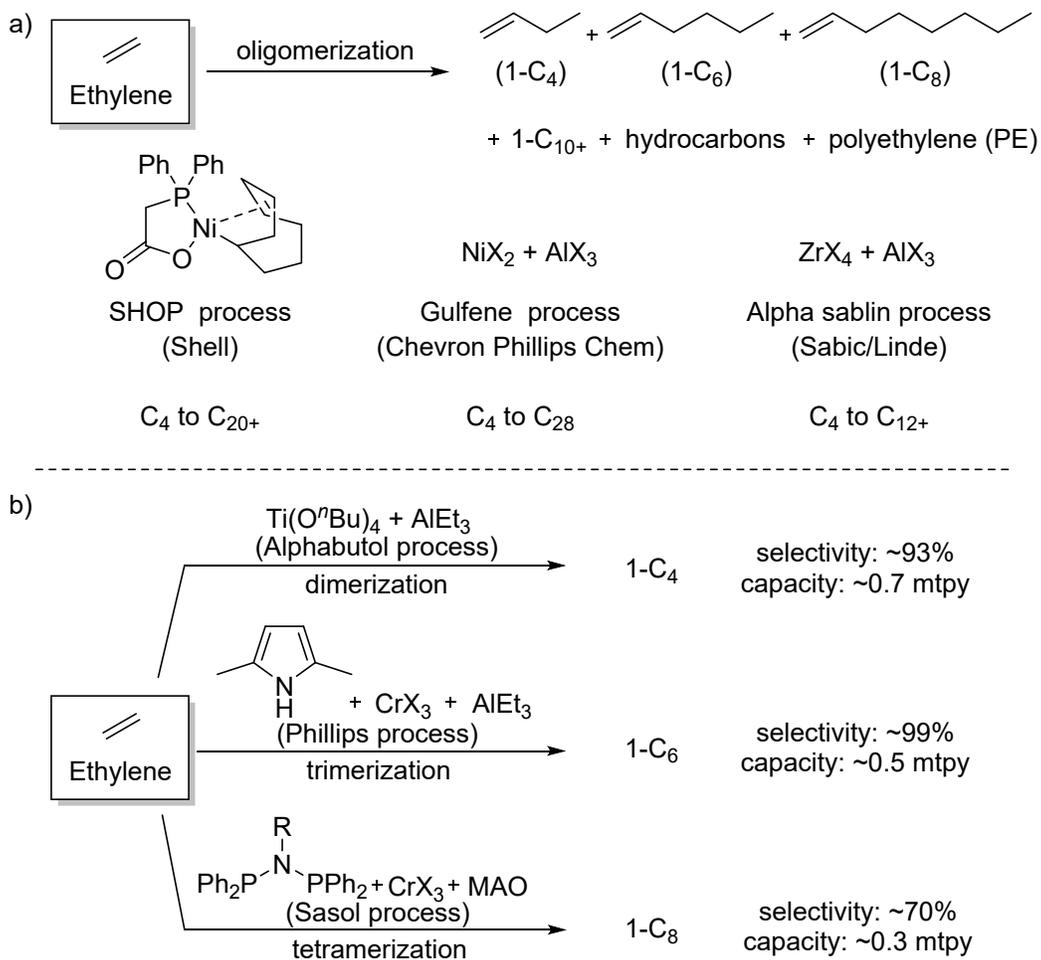
Ethylene dimerization was performed in a high-pressure autoclave reactor (internal volume: 100 mL, 4560 series, Parr Instrument, Moline, IL, USA) connected to a high-pressure gas burette (internal volume: 1000 mL, Parr Instrument). Typically, a Cr catalyst (0.02 mmol), MMAO or AlEt₂Cl as the co-catalyst (standard Al/Cr molar ratio = 300:1), IL (1 mL), and toluene was mixed in the high-pressure autoclave reactor under an inert atmosphere. After purging with Ar thrice, the reactor was heated and pressurized with ethylene. After the reactor was stabilized at 283 K by using a water jacket connected to a refrigerated/heating circulator (Julabo F25-HE) and 20 bar with a back pressure regulator (Tescom), the reaction was initiated by stirring the magnetically-driven impeller and maintained for 1 h. During the reaction, the ethylene pressure drop in the gas burette was monitored to calculate the amount of ethylene used. At the end of the reaction, the reactor was rapidly cooled down in an ice bath and disconnected from the gas burette. Upon quenching via the addition of 10% HCl in methanol, the organic layer of two phase-solution was separated and filtered through a 0.2- μ m PTFE syringe filter. The separated solution (1 mL), including undecane (0.1 mL, external standard), was analyzed by using a gas chromatography (GC, 7890B, Agilent Technologies, Santa Clara, CA, USA) equipped with a flame ionization detector (FID) and a Petrocol DH column (Sigma-Aldrich, 100 m \times 0.25-mm I.D. \times 0.5 μ m film). The reaction performance of the catalyst, such as activity and selectivity towards C₄–C₁₈ products, was calculated as follows. It is noted that the mass of active site Cr (g) means the mass of Cr atom without ligand.

$$\text{Activity (g/g}_{\text{Cr}} \cdot \text{h)} = \frac{\text{Mass of the consumed ethylene (g)}}{\text{Mass of active site Cr (g)} \times \text{Time (h)}}$$

$$\text{Selectivity, } S_i \text{ (wt. \%)} = \frac{\text{Mass of compound } i}{\sum \text{Mass of all compounds}} \times 100 \quad (\text{where } i = \text{C}_4; 1\text{-C}_4; \dots; \text{C}_{18}, 1\text{-C}_{18})$$

Catalyst recycling was performed to evaluate the reusability of the catalyst. For example, after completion of the first ethylene dimerization in the presence of a fresh catalyst, the reactor was cooled down, disconnected from the gas burette, depressurized, and purged with Ar. After a

small amount of the reaction solution was extracted for GC analysis, MMAO was replenished and a recycling test run was conducted. The recycling run was performed thrice in the same manner.



Scheme S1. a) Commercial ethylene oligomerization processes affording broad molecular weight olefin products; b) Commercial on-purpose ethylene dimerization, trimerization, and tetramerization processes for the selective production of 1-butene, 1-hexene, and 1-octene, respectively.

Table S1. Reaction performances of various catalysts for ethylene dimerization

Entry	Catalyst	Activator	TOF (h ⁻¹)	Selectivity (wt%)		Ref.
				1-C4	C4	
1	Ni-ZIF-8	MMAO	1,116,000	85	97	[3]
2	Ni-UMOFN	AlEt ₂ Cl	2,393	92.8	n.d.	[4]
3	Ni-CFA-1	MMAO	37,100	87.1	95.5	[5]
4	Ni-MFU-4	AlEt ₂ Cl	41500	92	97.4	[6]
5	Ni(II)/[BMI][Cl]/AlCl ₃	AlEt ₂ Cl	1731	83	100	[7]

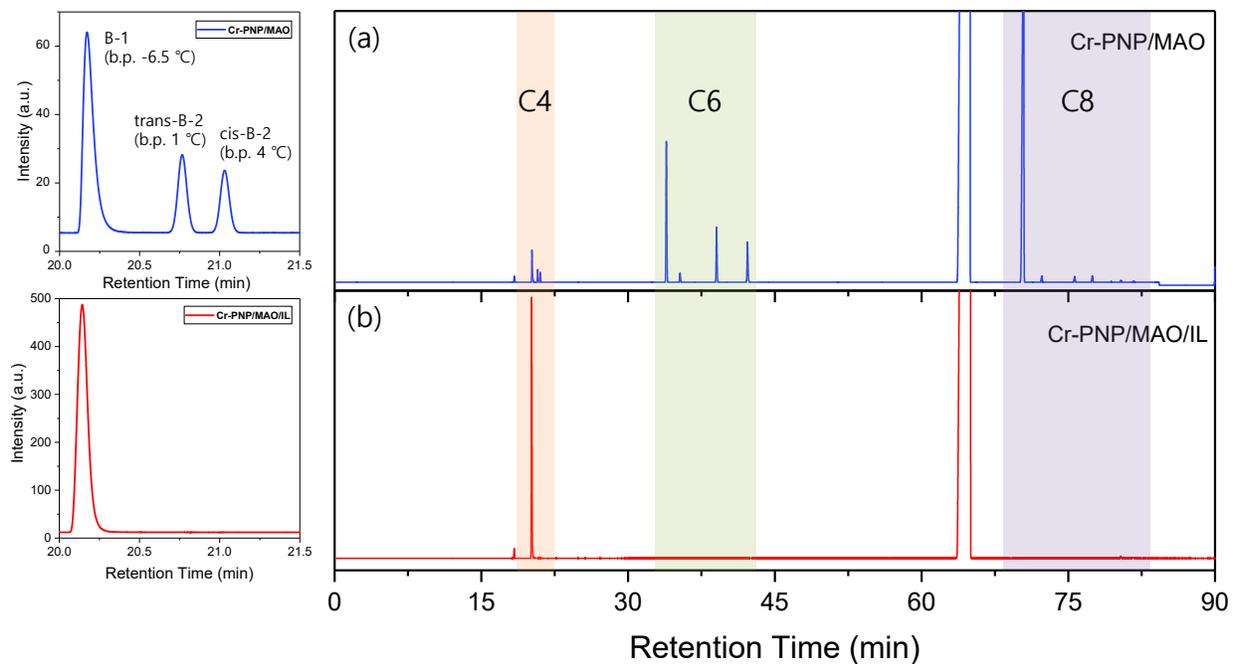


Fig. S1. GC chromatograms of reaction products obtained from: (a) homogeneous ethylene oligomerization by using a Cr-PNP catalyst and (b) biphasic ethylene dimerization in the presence Cr-PNP / C₁C₁₀Im-PF₆.

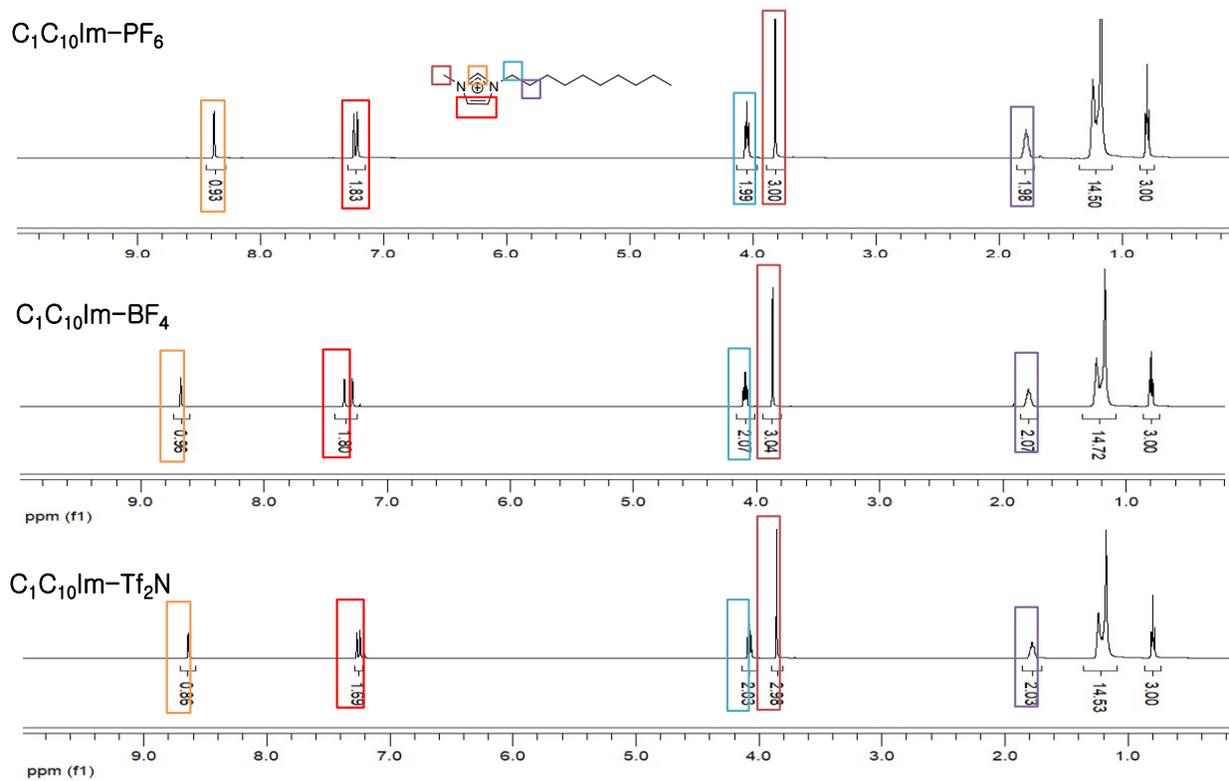


Fig. S2. ¹H-NMR spectra of three imidazolium salts in CDCl₃: a) C₁C₁₀Im-PF₆, b) C₁C₁₀Im-BF₄, and c) C₁C₁₀Im-Tf₂N (296 K, 500 MHz).

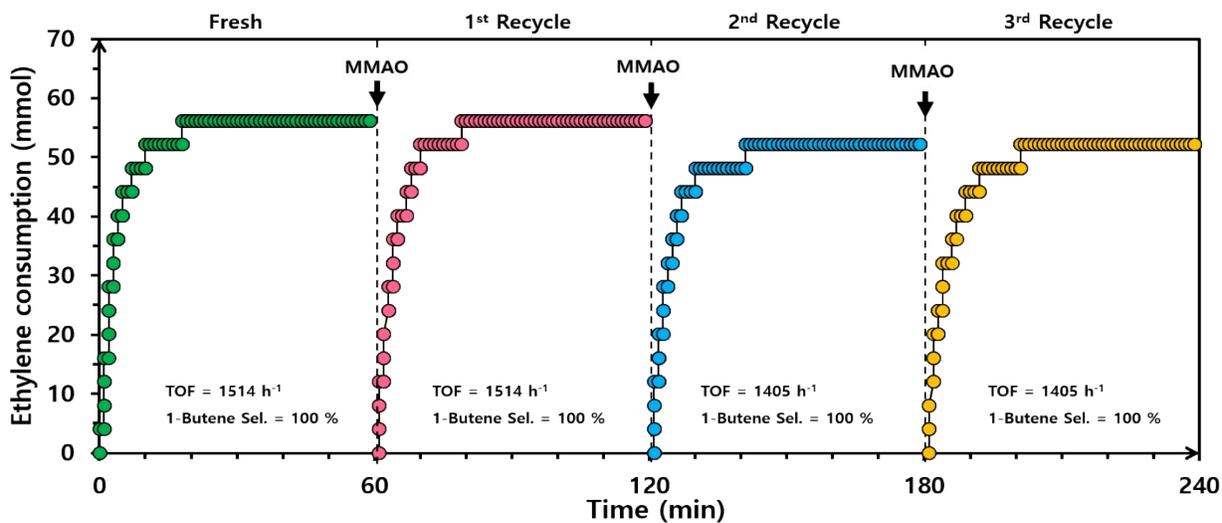


Fig. S3. Changes in the ethylene consumption during catalyst recycle of an ionic liquid-organic solvent biphasic system. Reaction conditions: $\text{Cr}(\text{acac})_3$ (0.02 mmol), MMAO (6 mmol), $\text{C}_1\text{C}_{10}\text{Im-PF}_6$ (1 mL), toluene (30 ml), ethylene pressure (20 bar), temperature (283 K), reaction time (1 h).

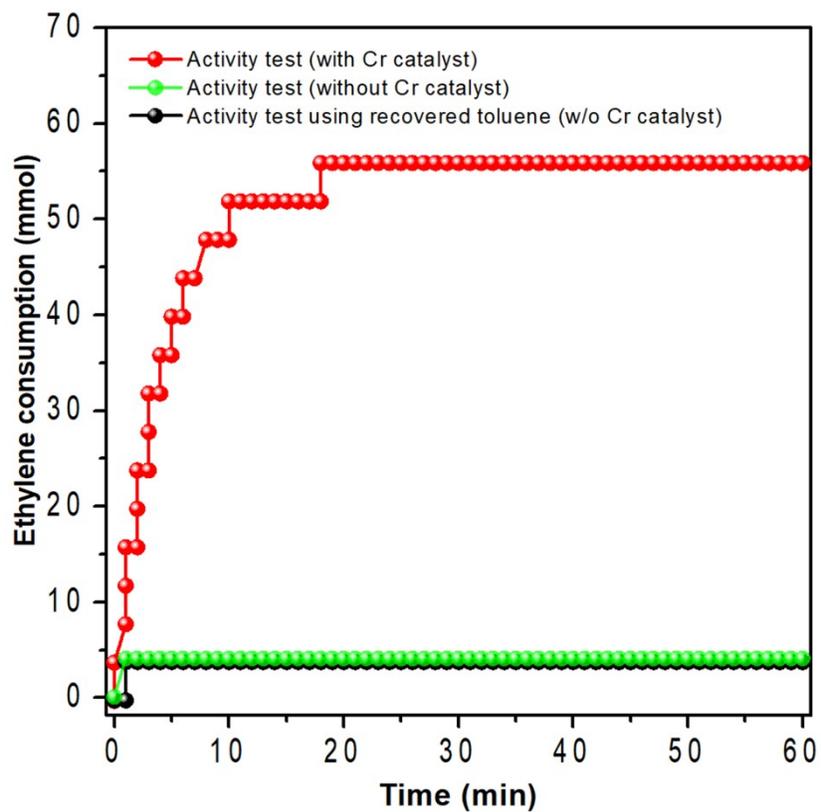


Fig. S4. Ethylene consumption during ethylene dimerization with recovered organic phase (toluene). Not mentioned reaction conditions were as same as those of Fig. 3.

Reference

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