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#### Applied Organometallic Chemistry

### Influence of ionic liquid counterions on activity and selectivity of ethylene trimerization using chromium-based catalysts in biphasic media

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Funding information Iran National Science Foundation, Grant/ Award Number: 96001818 In recent years ionic liquids (ILs) have attracted much interest because of their widespread use in various fields. Several trimerization and oligomerization catalysts have been evaluated in ILs with different organic-inorganic hybrid structures. High catalytic activity and selectivity, easy product separation, and recycling of the catalyst are the advantages of a biphasic catalyst system compared to the homogeneous catalysts. In this study, the influence of IL counteranions on activity and selectivity of the ethylene trimerization catalysts based on Cr-SNS-R was investigated. All synthesized materials were characterized using Fourier-transform infrared spectroscopy, <sup>1</sup>H NMR, <sup>13</sup>C NMR, UV-Vis. spectroscopy, thin-layer chromatography, and elemental analysis (CHNS). In ethylene trimerization reaction, the dodecyl substituent in the SNS ligand exhibited better activity and selectivity than the butyl substituent. The results revealed that the presence of  $BF_4^-$  as a counter-anion in the IL led to an increase in activity and selectivity compared to Br<sup>-</sup> and I<sup>-</sup> counter-anions. It was found that the BF<sub>4</sub><sup>-</sup> counter-anion plays a conclusive role in the development of 1-hexene activity and selectivity to a maximum amount of 71,132  $g_{1-C6}/(g_{CT} \times h)$  and more than 99%, respectively. Finally, the catalyst was reused thrice without losing its 1-hexene selectivity.

#### KEYWORDS

1-hexene, biphasic catalysis, Chromium, ethylene trimerization, ionic liquids

### **1** | INTRODUCTION

Linear alpha olefins (LAOs) are primarily prepared through the industrial process of ethylene oligomerization. These linear alpha olefins are widely used to produce plasticizers, detergents, and lubricants and are used as a comonomer in the production of polyethylene. Comonomers such as 1-hexene and 1-octene are especially used in the production of the linear low-density polyethylene.<sup>[1-3]</sup>

Therefore, the selective production of LAOs, particularly by ethylene trimerization, in the laboratory and

large scales, has been carried out by many researchers and companies.<sup>[4]</sup> Chromium-based complexes are the appropriate choices for both selective and nonselective catalytic oligomerization of ethylene among all coordination complexes.<sup>[5–7]</sup>

Metal pincer complexes containing SNS ligands have been rarely used in catalytic systems compared to other tridentate ligands such as tridentate phosphine (PNP) ligands. However, it was found that the Cr-SNS catalysts are valuable complexes for ethylene trimerization, research on the SNS ligands has made great progress.<sup>[8–13]</sup> The synthesis of the mentioned ligands (SNS) is simple and does not require rigorous conditions, whereas PNP ligands are sensitive to oxygen and need special reagents. On the contrary, the tridentate SNS ligands tend to be hemilabile because of the donor atoms in their structure (hard N and soft S) that can coordinate with a broad range of metals and are useful in many catalytic applications.<sup>[14]</sup>

Because of its structure, the homogeneous catalyst has many advantages such as excellent selectivity and activity in organic reactions, easy mixing at low temperatures, mild reaction conditions, and no diffusion problem. In most cases, the variation in the ligands and central metal atoms can control the electronic and steric properties of the active species.<sup>[15]</sup> According to the literature, ethylene trimerization using homogeneous Cr-SNS-R catalysts (SNS = RSCH<sub>2</sub>CH<sub>2</sub>N(H)CH<sub>2</sub>CH<sub>2</sub>SR) with different R substituents such as methyl,<sup>[8–10]</sup> ethyl,<sup>[8–10,16]</sup> *n*-butyl,<sup>[3,8,9]</sup> *t*butyl,<sup>[10]</sup> pentyl,<sup>[16]</sup> cyclopentyl,<sup>[3]</sup> cyclohexyl,<sup>[12,13,16]</sup> benzyl,<sup>[16]</sup> *n*-decyl,<sup>[8–10]</sup> and dodecyl<sup>[16–19]</sup> has exhibited high activity and more than 98% selectivity for 1-hexene. But many homogeneous catalytic systems cannot be commercialized because of difficulties related to separation/recycling.

On the contrary, the liquid-liquid biphasic catalysis system is a noteworthy alternating technology to overcome the difficulty in catalyst separation and decrease the formation of by-products. The catalyst is immobilized in a polar liquid phase like ionic liquids (ILs), which is slightly miscible in organic products. After phase separation, the catalyst in the IL phase can be separated from the organic products. This unique process both has the advantages of homogeneous catalysts and enables the catalyst to be easily recycled. High catalytic activity and selectivity,<sup>[20,21]</sup> easy product separation,<sup>22,23</sup> and recycling of the catalysts are the advantages of the biphasic catalysis systems compared with homogeneous catalysts.<sup>[24,25]</sup> The liquid–liquid biphasic catalysis system has received much attention, and the possibility of using this technology in industrial processes is being investigated by many researchers.<sup>[15,26]</sup>

In recent decades the ILs have attracted much attention because of their extensive applications in organic synthesis,<sup>[27–33]</sup> catalytic oligomerization of ethylene,<sup>[4,17,25]</sup> chemical separation,<sup>[34–36]</sup> material, and energy science.<sup>[37,38]</sup> For example, the chloroaluminate IL has been used as solvents in ethylene oligomerization reactions in the presence of nickel complexes to overcome the deactivation of the catalyst.<sup>[39–43]</sup> Among them, ILs, based on imidazolium cation because of their high stability, are also widely used in organic reactions in laboratories or industries.<sup>[44,45]</sup>

Various oligomerization reactions have been explored in the IL media containing different inorganic anions and organic cations.<sup>[46,47]</sup> The first industrial process for the application of biphasic liquid–liquid technology was performed in the Shell higher olefin process.<sup>[48]</sup> ILs containing imidazolium cations are usually liquid at room temperature compared to ILs containing ammonium or pyridine cations. Meanwhile, imidazolium-based ILs exhibit a low tendency to absorb water compared to ILs with other cations. For these reasons, this family of ILs has been highly regarded among chemists.

Here, the application of the imidazolium-based ILs containing various counter-anions in the trimerization of ethylene using the Cr-SNS-R catalytic systems (R is the alkyl substituent in the SNS ligands such as butyl and dodecyl) in the biphasic media was investigated. The effect of the reaction temperature, IL/Cr molar ratio, and ethylene pressure as well as the role of IL counter-anions  $(BF_4^-, Br^-, and I^-)$  on the catalytic system performance have been considered.

### 2 | EXPERIMENTAL

### 2.1 | Materials

All synthesis methods were performed under standard Schlenk line conditions using the 99.999% argon (grade 5) atmosphere in the glovebox. Toluene, diethyl ether (Et<sub>2</sub>O), and tetrahydrofuran (THF) were refluxed in benzophenone-sodium to remove water under an inert gas previously used. The polymer-grade ethylene and inert gases were passed through the cylinders containing dry desiccants such as silica gel and molecular sieves (3 Å). The modified methyl aluminoxane (MMAO) (7 wt.% in toluene) as a cocatalyst, complex of chromium(III) chloride tetrahydrofuran (1:3) CrCl<sub>3</sub>(THF)<sub>3</sub>, triethylaluminium, and molecular sieve (3 Å) were purchased from Sigma-Aldrich (Munich, Germany). Bis(2-chloroethyl)amine hydrochloride, n-dodecyl mercaptan, butanethiol, 1-bromohexane, 1-iodohexane, 1-methylimidazole, sodium tetrafluoroborate (NaBF<sub>4</sub>), sodium hydroxide (NaOH), sodium hydrogen carbonate (NaHCO<sub>3</sub>), anhydrous Na<sub>2</sub>SO<sub>4</sub>, dichloromethane (DCM), hydrochloric acid (HCl), methanol, and ethanol were purchased from Merck (Darmstadt, Germany).

### 2.2 | Synthesis of SNS tridentate ligands

SNS ligands containing butyl<sup>[8]</sup> and *n*-dodecyl<sup>[16]</sup> substituents were synthesized according to the literature methods (Scheme 1). A solution of NaOH (150 mmol, 6 g) and thiol (1-dodecanethiol [150 mmol, 35.93 ml] or butanethiol [150 mmol, 16.16 ml]) in EtOH (150 ml) was added to bis(2-chloroethyl)amine hydrochloride (50 mmol, 8.92 g) solution in EtOH (100 ml) at 0 °C. The



final mixture was stirred for 3 h at 0 °C and 20 h at ambient temperature, and filtered. Then the filtrate was evaporated, and the precipitate was, respectively, washed using Et<sub>2</sub>O and *n*-hexane. After re-filtration, the solvent was evaporated to produce the SNS ligands.

### 2.2.1 | Bis(2-butylsulfanyl ethyl) amine (SNS-B) ligand

SNS-B was obtained as a colorless oil (70% yield). Fourier-transform infrared (FT-IR) (KBr) ( $v_{\text{max}}$  cm<sup>-1</sup>): 3305 (NH), 2960 (CH<sub>3</sub>, asymmetric stretching), 2852 (CH<sub>2</sub>, symmetric stretching), 1464 (C-N), 1378 (CH<sub>3</sub>, symmetric bending), 1278, 1126, 728 (C-S). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>), δ: 0.76 (6H, t, CH<sub>3</sub>), 1.98 (1H, NH), 1.25 (4H, q, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.41 (4H, q, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.38 (4H, t, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.56 (4H, t, NHCH<sub>2</sub>CH<sub>2</sub>), 2.72 (4H, q, NHCH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C NMR (60 MHz, CDCl<sub>3</sub>), δ: 13.41 (CH<sub>3</sub>), 21.73 (CH<sub>2</sub>CH<sub>3</sub>), 29.48  $(SCH_2CH_2CH_2CH_3),$ 30.54 (SCH<sub>2</sub>C<sub>2</sub>H<sub>4</sub>CH<sub>3</sub>), 31.44 (SCH<sub>2</sub>CH<sub>2</sub>NH), 46.08 (SCH<sub>2</sub>CH<sub>2</sub>NH). Elemental analysis: calculated for  $C_{12}H_{27}NS_2$  (found): H 10.91 (11.45), N 5.61 (5.52), C 57.77 (57.26), and S 25.71 (25.77).

### 2.2.2 | Bis(2-dodecylsulfanyl ethyl) amine (SNS-D) ligand

SNS-D was isolated as a colorless oil (84% yield). FT-IR (KBr) (v<sub>max</sub> cm<sup>-1</sup>): 3438 (NH), 2922 (CH<sub>3</sub>, asymmetric stretching), 2852 (CH<sub>2</sub>, symmetric stretching), 1463 (C-N), 1377 (CH<sub>3</sub>, symmetric bending), 1278, 1125, 993, 721 (C-S). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>), δ: 0.79 (6H, t, CH<sub>3</sub>), 1.10-1.18 (36H, m, SC<sub>2</sub>H<sub>4</sub>C<sub>9</sub>H<sub>18</sub>CH<sub>3</sub>), 2.08 (1H, NH), 1.49 (4H, q, SC<sub>2</sub>H<sub>4</sub>CH<sub>2</sub>C<sub>8</sub>H<sub>16</sub>CH<sub>3</sub>), 1.68 (4H, q, SCH<sub>2</sub>CH<sub>2</sub>C<sub>9</sub>H<sub>18</sub>CH<sub>3</sub>), 2.42 (4H, t, SCH<sub>2</sub>C<sub>10</sub>H<sub>20</sub>CH<sub>3</sub>), 2.59 (4H, t, NHCH<sub>2</sub>CH<sub>2</sub>), 2.72 (4H, q, NHCH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C NMR (60 MHz, CDCl<sub>3</sub>),  $\delta$ : 13.96 (CH<sub>3</sub>), 22.59  $(\mathbf{C}\mathrm{H}_{2}\mathrm{C}\mathrm{H}_{3}),$ 29.17-29.57  $(SC_4H_8C_7H_{14}CH_3),$ 28.44  $(SC_{2}H_{4}CH_{2}C_{8}H_{16}CH_{3}),$  $(SCH_2CH_2C_9H_{18}CH_3),$ 28.80 31.85 (SCH<sub>2</sub>C<sub>10</sub>H<sub>20</sub>CH<sub>3</sub>), 39.05 (SCH<sub>2</sub>CH<sub>2</sub>NH), 47.88 (SCH<sub>2</sub>CH<sub>2</sub>NH). Elemental analysis: calculated for C<sub>28</sub>H<sub>59</sub>NS<sub>2</sub> (found): H 12.58 (13.21), N 2.95 (3.30), C 70.97 (70.48), and S 13.50 (13.01).

### 2.3 | Synthesis of Cr-SNS-R catalysts

The Cr-SNS-R catalysts were synthesized using previous methods (Scheme 2).<sup>[16-19]</sup> The solution of ligands (0.293 mmol, 0.138 g) in THF (5 ml) was added dropwise to a solution of CrCl<sub>3</sub>(THF)<sub>3</sub> (0.268 mmol, 0.1 g) in THF (5 ml) by stirring at ambient temperature for 15 min. After the solvent was evaporated, Et<sub>2</sub>O (15 ml) was added, and the resulting mixture was cooled overnight in the refrigerator. Finally, the mixture was centrifuged, washed thrice with 15 ml of Et<sub>2</sub>O, and dried under vacuum.

### 2.3.1 | Cr-SNS-B catalyst

The blue-green solid was obtained as the Cr-SNS-B catalyst (60% yield). IR (KBr) (v<sub>max</sub> cm<sup>-1</sup>): 3439 (N-H), 2942 (CH<sub>3</sub>, asymmetric stretching), 2858 (CH<sub>2</sub>, symmetric stretching), 1617 (Cr-Cl), 1456 (C-N), 1379 (CH<sub>3</sub>, symmetric bending), 1225, 1038, 991, 600 (C-S), 521 (Cr-N). Elemental analysis: calculated for C<sub>12</sub>H<sub>27</sub>Cl<sub>3</sub>CrNS<sub>2</sub> (found): H 6.67 (6.23), N 3.43 (3.70), C 35.34 (35.44), and S 15.72 (15.94).

### 2.3.2 | Cr-SNS-D catalyst

The blue-green solid was achieved as the Cr-SNS-D catalyst (82% yield). IR (KBr) (v<sub>max</sub> cm<sup>-1</sup>): 3410 (N–H), 2929 (CH<sub>3</sub>, asymmetric stretching), 2854 (CH<sub>2</sub>, symmetric stretching), 1611 (Cr-Cl), 1462 (C-N), 1378 (CH<sub>3</sub>, symmetric bending), 1078, 1040, 997, 612 (C-S), 516 (Cr-N). Elemental analysis: calculated for C<sub>28</sub>H<sub>59</sub>Cl<sub>3</sub>CrNS<sub>2</sub> (found): H 9.41 (9.63), N 2.22 (1.97), C 53.19 (53.53), and S 10.14 (10.56).

### 2.4 | General procedure for the synthesis of ILs ([HMIM][Br] and [HMIM][I])

1-Bromohexane (12 mmol, 1.68 ml) or 1-iodohexane (12 mmol, 1.82 ml) was added to a solution of 1-methylimidazole (10 mmol, 0.80 ml) in dry toluene (100 ml) with vigorous stirring in an argon atmosphere kept under reflux for 40-50 h (Scheme 3). During this process, the reaction mixture becomes two-phasic, and





the brown viscous phase containing IL was separated from the upper phase, including the solvent and unreacted substances. For further purification, the resulting phase having the IL was refluxed with dry toluene (50 ml) for 3 h for the dissolution of the unreacted materials in toluene.<sup>[49]</sup> These steps were repeated at least thrice. Then the obtained material was washed with saturated NaHCO<sub>3</sub> (2 × 5 ml) to remove the HX (X: Br or I) produced during the IL synthesis. During the synthesis, 1-methylimidazole removes the HX from alkyl halide.<sup>[50]</sup>

After the addition of methanol, the water was evacuated from the mixture at an azeotropic point (80  $^{\circ}$ C) under vacuum. Then, DCM was added, extracted using the liquid–liquid method, and dried with anhydrous sodium sulfate. After the DCM solvent evaporated, the pure IL was obtained and dried in the oven to remove water. Finally, the IL was stored in an inert gas container.

# 2.4.1 | 1-Hexyl-3-methylimidazolium bromide

The yellow viscous liquid obtained was 1-hexyl-3-methylimidazolium bromide ([HMIM][Br]) (90% yield). IR (KBr) ( $v_{\text{max}}$  cm<sup>-1</sup>): 3461 (OH stretching, moisture), 3143, 3079 (C-H, aromatic stretching), 2929 (CH<sub>3</sub>, asymmetric stretching), 2856  $(CH_2,$ symmetric stretching), 1627, 1571 (C=C, aromatic bending), 1465 (CH<sub>2</sub>, scissoring), 1379 (CH<sub>3</sub>, symmetric bending), 1338, 1168 (C-N, aromatic stretching), 865-623 (C-H, aromatic bending). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>),  $\delta$ : 0.38 (3H, t, NC<sub>5</sub>H<sub>10</sub>CH<sub>3</sub>), 0.83 (6H, m, NCH<sub>2</sub>CH<sub>2</sub>C<sub>3</sub>H<sub>6</sub>CH<sub>3</sub>), 1.46 (2H, m, NCH<sub>2</sub>CH<sub>2</sub>C<sub>3</sub>H<sub>6</sub>CH<sub>3</sub>), 3.67 (3H, s, CH<sub>3</sub>NCHN), 3.89 (2H, t, NCH<sub>2</sub>C<sub>4</sub>H<sub>8</sub>CH<sub>3</sub>), 7.24 (2H, d, CH<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>N), 7.38 (2H, d, CH<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>N), 9.72 (1H, s, CH<sub>3</sub>NCHN). <sup>13</sup>C NMR (60 MHz, CDCl<sub>3</sub>), δ: 13.53 (NC<sub>5</sub>H<sub>10</sub>CH<sub>3</sub>), 21.90 (NC<sub>3</sub>H<sub>6</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 25.36 (NC<sub>3</sub>H<sub>6</sub><u>C</u>H<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 29.82 (NC<sub>2</sub>H<sub>4</sub><u>C</u>H<sub>2</sub>C<sub>2</sub>H<sub>4</sub>CH<sub>3</sub>), 30.59 (NCH<sub>2</sub><u>C</u>H<sub>2</sub>C<sub>3</sub>H<sub>6</sub>CH<sub>3</sub>), 36.27 (<u>C</u>H<sub>3</sub>NCHN), 49.55 (N<u>C</u>H<sub>2</sub>C<sub>4</sub>H<sub>8</sub>CH<sub>3</sub>), 122.00 (CH<sub>3</sub>NCH<sub>2</sub><u>C</u>H<sub>2</sub>N), 123.56 (CH<sub>3</sub>N<u>C</u>H<sub>2</sub>CH<sub>2</sub>N), 136.40 (CH<sub>3</sub>N<u>C</u>HN). TLC (thin-layer chromatography):  $R_{\rm f}$  0.64 (1:10, methanol:chloroform).  $\lambda_{\rm max}$ : 192 nm.

# 2.4.2 | 1-Hexyl-3-methylimidazolium iodide

The dark-brown viscous liquid obtained was 1-hexyl-3-methylimidazolium iodide ([HMIM][I]) (86% yield). IR (KBr) ( $v_{\text{max}}$  cm<sup>-1</sup>): 3459 (OH stretching, moisture), 3141, 3074 (C-H, aromatic stretching), 2930 (CH<sub>3</sub>, asymmetric stretching), 2857 (CH<sub>2</sub>, symmetric stretching), 1629, 1569 (C=C, aromatic stretching), 1463 (CH<sub>2</sub>, scissoring) 1380 (CH<sub>3</sub>, symmetric bending), 1340, 1166 (C-N, aromatic stretching), 831-619 (C-H, aromaticbending). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>),  $\delta$ : 0.33 (3H, t,  $NC_{5}H_{10}CH_{3}$ ), 0.80 (6H, m,  $NCH_2CH_2C_3H_6CH_3$ ), 1.42 (2H, m, NCH<sub>2</sub>CH<sub>2</sub>C<sub>3</sub>H<sub>6</sub>CH<sub>3</sub>), 3.62 (3H, s, CH<sub>3</sub>NCHN), 3.82 (2H, t, NCH<sub>2</sub>C<sub>4</sub>H<sub>8</sub>CH<sub>3</sub>), 7.20 (2H, d, CH<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>N), 7.25 (2H, d, CH<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>N), 9.22 (1H, s, CH<sub>3</sub>NCHN). <sup>13</sup>C NMR (60 MHz, CDCl<sub>3</sub>), δ: 13.60 (NC<sub>5</sub>H<sub>10</sub>CH<sub>3</sub>), 21.88 (NC<sub>3</sub>H<sub>6</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 25.29 (NC<sub>3</sub>H<sub>6</sub> $CH_2CH_2CH_3$ ), 29.74 (NC<sub>2</sub>H<sub>4</sub> $CH_2C_2H_4CH_3$ ),  $(NCH_2CH_2C_3H_6CH_3),$ 30.55 36.82 (CH<sub>3</sub>NCHN), 49.65 (NCH<sub>2</sub>C<sub>4</sub>H<sub>8</sub>CH<sub>3</sub>), 122.19 (CH<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>N), 123.54 (CH<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>N), 135.75 (CH<sub>3</sub>NCHN). TLC: R<sub>f</sub> 0.47 (1:10, methanol:chloroform).  $\lambda_{max}$ : 223 nm.

# 2.5 | General procedure for anion exchange in IL

According to the literature,<sup>[49]</sup> to exchange the Br<sup>-</sup> anion, 1-methyl-3-hexylimidazoleimbromide (4 mmol, 1 g) was



**SCHEME 3** General procedure for the synthesis of imidazolium-based ionic liquids

dissolved in dry acetone (30 ml). Then, NaBF<sub>4</sub> (6 mmol, 0.654 g) was added to the mixture with stirring at ambient temperature for 48 h. Next, the mixture was filtered, and NaBr was separated. The solution was washed with saturated NaHCO<sub>3</sub> (2 × 5 ml), and the obtained IL was dried according to the procedure in the previous section (Scheme 4).

# 2.5.1 | 1-Hexyl-3-methylimidazolium tetrafluoroborate

The yellow viscous liquid obtained was 1-hexyl-3-methylimidazolium tetrafluoroborate ( $[HMIM][BF_4]$ ) with 75% yield. IR (KBr)  $cm^{-1}$ ):  $(v_{\rm max})$ 3382 (OH stretching, moisture), 3138, 3080 (C-H, aromatic stretching), 2930 (CH<sub>3</sub>, asymmetric stretching), 2858 (CH<sub>2</sub>, symmetric stretching), 1639, 1564 (C=C, aromatic bending), 1466 (CH<sub>2</sub>, scissoring), 1379 (CH<sub>3</sub>, symmetric deformation), 1338, 1180 (C-N, aromatic stretching), 863-623 (C-H, aromatic bending). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta = 0.66$  (3H, t, NC<sub>5</sub>H<sub>10</sub>CH<sub>3</sub>), 1.11 (6H, m, NCH<sub>2</sub>CH<sub>2</sub>C<sub>3</sub>H<sub>6</sub>CH<sub>3</sub>), 1.66 (2H, m, NCH<sub>2</sub>CH<sub>2</sub>C<sub>3</sub>H<sub>6</sub>CH<sub>3</sub>), 3.78 (3H, s, CH<sub>3</sub>NCHN), 4.02 (2H, t, NCH<sub>2</sub>C<sub>4</sub>H<sub>8</sub>CH<sub>3</sub>), d, CH<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>N), 7.31 (2H, d, 7.28 (2H, CH<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>N), 8.78 (1H, s, CH<sub>3</sub>NCHN). <sup>13</sup>C NMR (60 MHz, CDCl<sub>3</sub>):  $\delta = 13.71$  (NC<sub>5</sub>H<sub>10</sub>CH<sub>3</sub>), 22.14 (NC<sub>3</sub>H<sub>6</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 25.56 (NC<sub>3</sub>H<sub>6</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 29.82 (NC<sub>2</sub>H<sub>4</sub>CH<sub>2</sub>C<sub>2</sub>H<sub>4</sub>CH<sub>3</sub>), 30.81 (NCH<sub>2</sub>CH<sub>2</sub>C<sub>3</sub>H<sub>6</sub>CH<sub>3</sub>), 36.02 (CH<sub>3</sub>NCHN), 49.77  $(NCH_2C_4H_8CH_3),$ 122.19  $(CH_3NCH_2CH_2N),$ 123.67  $(CH_3NCH_2CH_2N),$ 135.95 (CH<sub>3</sub>NCHN). TLC: R<sub>f</sub> 0.73 (1:10, methanol:chloroform).  $\lambda_{\rm max}$ : 211 nm.

### 2.6 | Ethylene trimerization

A 200-ml stainless steel 304 high-pressure reactor outfitted with a Lauda circulator (RP 845); mechanical stirrer; and controller of temperature, pressure, and stirrer speed was used for the ethylene trimerization reaction. First, the argon was purged at 100  $^{\circ}$ C for 2 h to remove the oxygen and moisture from the reactor. Then the temperature was decreased, and the reactor was charged with toluene/cyclohexane (40 ml, 80/20) as solvent and MMAO as cocatalyst. After 10 min, a mixture of the

IL/catalyst/reaction solvent was charged into the reactor. The ethylene was charged to the reactor kept under constant pressure for 30 min. After 30 min, the reaction was quenched with HCl/MeOH (10% v/v). After the reactor was cooled to -5 °C, the final solution was collected and examined using gas chromatography (GC). The swelled by-product was isolated, washed with methanol, and dried.

### 2.7 | Instruments

FT-IR measurements were performed using a Bruker IFS 48 spectrophotometer to approve the successful synthesis of the prepared ligands, catalysts, and ILs. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of the synthesized materials such as ligands and ILs were assigned using a Brucker Advance DPX-250 MHZ apparatus at ambient temperature in CDCl<sub>3</sub> solvent. Elemental composition analysis was performed using a Vario EL III CHNS elemental analyzer. After trimerization, the resulting mixture was evaluated using GC CP 9000 with flame ionization detection fitted with a 60 m × 0.25 mm i.d. packed with 1  $\mu$ m of 95% methyl polysiloxane and 5% of phenyl (HP-5ms). UV–Vis. absorbance spectra of the samples were recorded over a range of 200–800 nm using a Shimadzu UV-1650PC UV–Vis. spectrophotometer.

### **3** | **RESULTS AND DISCUSSION**

# 3.1 | Characterization of the ligands and catalysts

The characterization of the ligands and Cr-SNS-R (R = butyl [B] and dodecyl [D]) catalysts using <sup>13</sup>C NMR, <sup>1</sup>H NMR, FT-IR, elemental analysis (CHNS), and UV–Vis. spectroscopy confirms the successful synthesis and purity of the products.

The FT-IR spectrum of the SNS-R ligands was compared with their corresponding Cr-SNS-R catalysts (Figure 1). Some control peaks were observed in the spectrum of the catalysts and ligands, which will be useful for identification.

After the coordination of the ligands with chromium, significant shifts in vibration frequencies were observed.



For example, the v(C–N) and v(C–S) stretching vibrations that appeared in the SNS-D ligand at 1463 and 721 cm<sup>-1</sup> (1464 and 728 cm<sup>-1</sup> in SNS-B), respectively, shifted to 1462 and 612 cm<sup>-1</sup> in the Cr-SNS-D catalyst (1456 and 600 cm<sup>-1</sup> in Cr-SNS-B), consistent with the results of previous studies.<sup>[8,15]</sup> These results indicate the successful complexation of S- and N-donor located on ligands with the chromium center. The C–H asymmetric and symmetric stretching vibrations were observed at 2922 and 2852 cm<sup>-1</sup> for SNS-D ligand and at 2960 and 2852 cm<sup>-1</sup> for SNS-B ligand, respectively. After the complexation of the ligands with the chromium center, the C–H asymmetric and symmetric stretching vibrations were shifted to 2929 and 2854 for Cr-SNS-D and to 2942 and 2858 cm<sup>-1</sup> for Cr-SNS-B catalysts, respectively.

### 3.2 | Characterization of ILs

The full identification of the ILs using FT-IR, UV–Vis., TLC, and <sup>13</sup>C NMR and <sup>1</sup>H NMR spectroscopy confirms the purity of the synthesized products. A comparison between the vibration frequencies of the ILs is shown in Table 1. ILs can easily absorb water because of their hygroscopic nature. The broad band around 3400–3500 cm<sup>-1</sup> is related to the presence of –OH groups on the surface.<sup>[51]</sup>

As shown in Figure 2, the actual numbers of hydrogen atoms contributing to the peak are directly related to the integrated area under each set of peaks. The switch of counter-anions in imidazolium ILs has caused changes in chemical shifts of the protons belonging to the imidazole ring of the cations and also the alkyl chains (e.g., decreasing the chemical shifts by changing the anion from Br<sup>-</sup> to BF<sub>4</sub><sup>-</sup>). A comparison of <sup>1</sup>H NMR spectra of different ILs, such as [HMIM][BF<sub>4</sub>], [HMIM][BF],



and [HMIM][I], showed that the protons belonging to the imidazole ring are assigned at 7.20–7.37 and 8.78–9.72 ppm. Protons that appeared at 3.78–78.62 and 4.02–3.22 ppm are attributed to CH<sub>3</sub>NCHN and NCH<sub>2</sub>C<sub>5</sub>H<sub>11</sub>, respectively. Protons that appeared at 0.33–1.66 ppm are also attributed to the hexyl chains (Figure 2).

Moreover, the  $\lambda_{max}$  of the ILs containing different counter-anions obtained using UV–Vis. spectroscopy is consistent with the result achieved by Lateef et al., which is given as follows:<sup>51</sup>

$$[\text{HMIM}][\text{I}] (\lambda_{\text{max}} = 223) > [\text{HMIM}][\text{BF}_4] (\lambda_{\text{max}} = 211) > [\text{HMIM}][\text{Br}] (\lambda_{\text{max}} = 192)$$

### 3.3 | Ethylene trimerization using IL/Cr-SNS-R

ILs, despite the common salts such as NaCl, have asymmetric bulky organic cations and inorganic/organic anions.<sup>[52]</sup> ILs have unique chemical and biological features such as good solubility in polar organic molecules, inorganic salts, and gases; low volatility; low melting temperature (usually <100 °C); ability to stabilize the transition metal complexes; negligible vapor pressure; no flammability; and easy handling properties.<sup>[53]</sup> Because of these unique properties, we used ILs in ethylene trimerization reactions. ILs tend to be immiscible in nonpolar toluene solvent and LAO products. Therefore, the reaction mixture can also lead to creating the biphasic mixture. In this new mixture, the IL phase containing the transition metal catalysts can be separated from the final reaction mixture without difficulty.

**FIGURE 1** The Fourier-transform infrared spectrum of the ligands and catalysts

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Bond	Vibration	[HMIM][BF <sub>4</sub> ]	[HMIM][Br]	[HMIM][I]
C=C aromatic	Bending	1639, 1564	1627, 1571	1629, 1569
C–H aromatic	Stretch	3138, 3080	3143, 3079	3141, 3074
C-H aromatic	Bending	623-863	623-865	619-831
C–N aromatic	Stretch	1338	1338	1340
CH <sub>2</sub>	Symmetric, stretch	2858	2856	2857
CH <sub>2</sub>	Scissor, bending	1466	1465	1463
CH <sub>3</sub>	Asymmetric, stretch	2930	2929	2930
CH <sub>3</sub>	Symmetric, bending	1379	1379	1380

TABLE 1 Comparison between the important vibration frequencies of the synthesized ionic liquids

Ethylene trimerization tests were performed using a Buchi reactor provided with a mechanically agitated stirrer and a temperature sensor. Then the reactor was purged several times with argon gas (grade 5), and toluene-cyclohexane solvent mixture (40 ml, 80:20 mixing ratio) was injected with mechanical stirring at ambient pressure. At the desired temperature, IL, MMAO cocatalyst, Cr-SNS-R catalyst, and ethylene gas were injected into the reactor.

# 3.4 | Effect of [HMIM][BF<sub>4</sub>]/Cr-SNS-D molar ratio

According to our previous studies, the ILs containing  $BF_4^-$  counter-anion exhibited higher activity and

selectivity in ethylene trimerization than those containing Cl<sup>-</sup> counter-anion.<sup>[18]</sup> Therefore, [HMIM][BF<sub>4</sub>] IL was selected to optimize ethylene trimerization in biphasic media. Initially, the Cr-SNS-R catalysts, including butyl and dodecyl substituents, were compared in ethylene trimerization. The results revealed that the activity of Cr-SNS-D catalyst in ethylene trimerization was greater than that of Cr-SNS-B catalyst because of the greater solubility of the ligand-bearing dodecyl substituent in the reaction solvent mixture (Table 2, entries 1 and 2). Therefore, Cr-SNS-D catalyst was designated for further optimization.

The other exclusive property of ILs is their ability for dissolution of different metal complexes, transition metals, and gases.<sup>[54–56]</sup> In this regard, the influence of the IL to catalyst ([HMIM][BF<sub>4</sub>]/Cr-SNS-D) molar ratio



**FIGURE 2** <sup>1</sup>HNMR spectra of the synthesized 1-hexyl-3-methylimidazolium bromide ionic liquid in CDCl<sub>3</sub> solvent

on activity and selectivity of Cr-SNS-D catalyst was investigated, as presented in Table 2. Increasing the [HMIM] [BF<sub>4</sub>]/Cr-SNS-D molar ratio from 0:1 to 5:1 led to an enhanced catalyst activity of 68,312  $g_{1-C6}/(g_{Cr} \times h)$ , which can be attributed to increased solubility of the catalyst in the IL phase of the biphasic mixture. This finding is consistent with the result achieved by Gao et al. (Table 2, entries 2–6).<sup>[25]</sup>

According to Table 2, the greater increase in [HMIM]  $[BF_4]/Cr$ -SNS-D molar ratio from 5:1 to 50:1 causes a reduction in catalyst activity (entries 6–8). Increasing the imidazolium cations as well as the number of carbon groups in their aliphatic chains thickens the diffusion layer created by the ILs. Consequently, the ethylene gas solubility and diffusion to the catalytically active centers in the IL phase will be difficult. Moreover, increasing the IL content shifts the reaction mixture from oligomers to polyethylene.<sup>[57]</sup>

At the end of the reaction, the resulting LAO products could be simply separated from the IL phase. Therefore, in the present study, the application of imidazolium-based ILs containing six carbon atoms in the alkyl chain caused 1-hexene production with selectivity more than 99%.

### 3.5 | Effect of the reaction conditions

The results of ethylene trimerization for Cr-SNS-D catalyst (2.3  $\mu$ mol of Cr-SNS-D catalyst, 11.5  $\mu$ mol of [HMIM] [BF<sub>4</sub>] IL, 40 ml of toluene/cyclohexane) are presented in Table 3. All trimerization reactions were performed at 30 min because McGuinness et al. in 2003<sup>[8]</sup> reported that the highest turnover frequency (TOF) for the SNS catalysts in the ethylene to 1-hexene conversion was observed

at 30 min (selectivity = 99.3 wt.% and TOF = 95,470 h<sup>-1</sup>). To evaluate the performance of the recycled catalyst under similar conditions, the reaction time in the ethylene trimerization using the recycled catalyst was kept at 30 min. The activity of ethylene trimerization increases with temperature and eventually reaches its highest value at 70 °C (Table 3, entries 1–4) because of the formation of the suitable active sites. Above this temperature, the activity of the catalyst decreases because of the decomposition of the catalyst structure (Table 3, entry 4). Therefore, further investigations were performed at 70 °C (Table 3, entries 5–8).

The solubility of ethylene in the solvent decreases with an increase in temperature,<sup>58</sup> but because of the decrease in the viscosity of ILs at high temperatures, ethylene gas diffuses into the catalytically active sites located in IL phase more easily. Therefore, at a high temperature (above 80 °C) despite the high catalytic activity, a significant amount of polyethylene was formed, and selectivity decreased probably because of the formation of rings larger than metallocyloheptane and the formation of oligomers higher than 1-hexene, including polyethylene. In the following experiments, based on the literature and various patents, as well as several preliminary analyses and previous studies,<sup>[16–19]</sup> the effect of the cocatalyst molar ratio and pressure of monomer on the catalyst activity was investigated.

The activity of the catalyst depends on nature of the cocatalyst and the molar ratio of Al/Cr. Increasing the Al/Cr molar ratio up to 900 increased the catalyst activity, which is due to ease of chromium reduction.<sup>[59]</sup> In this study, Al/Cr ratios of 500, 700, and 900 were tested. There is no noticeable difference between the activity of the catalyst at 700 and 900 Al/Cr ratios. Therefore, the Al/Cr molar ratio of 700 was preferred as the optimum

TABLE 2	Effect of	[HMIM][BF	]/Cr-SNS-D	molar ratio on	1-hexene activit	v and selectivity
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Entry	IL/Cr@SNS-D molar ratio	1-C <sub>6</sub> (ml)	Selectivity of 1-C <sub>6</sub> (wt.%)	$\begin{array}{l} Activity \times 10^{-4} \ (g_{1\text{-}C6} / \\ (g_{Cr} \times h)) \end{array}$	Polyethylene (g)
1	0:1	5.40	99.9	6.07	0.05
$2^{\mathrm{a}}$	0:1	4.74	99.9	5.33	0.04
3	1:1	3.95	99.7	4.44	0.04
4	2:1	4.70	99.8	5.29	0.06
5	3:1	5.68	99.9	6.50	0.08
6	5:1	6.07	99.9	6.83	0.08
7	10:1	3.46	98.3	3.89	0.11
8	50:1	1.15	97.2	1.29	0.30

*Note.* Reaction conditions: catalyst (Cr-SNS-D = 1.45 mg, 2.3  $\mu$ mol Cr), 80 °C, C<sub>2</sub>H<sub>2</sub> 25 bar, Al/Cr (700:1), cyclohexane/toluene (40 ml, 20/80 v/v), reaction time 30 min; IL, ionic liquid; [HMIM][BF4], 1-hexyl-3-methylimidazolium tetrafluoroborate. The bold data are the optimum conditions to obtain the 1-hexene with maximum productivity among different IL/Cr-SNS-D molar ratios. <sup>a</sup>Catalyst: Cr-SNS-B.

TABLE 3 Effect of ethylene trimerization reaction conditions such as pressure and temperature on 1-hexene activity and selectivity

Entry	Т (°С)	P (bar)	Al/Cr	1-C <sub>6</sub> (ml)	Selectivity of 1-C <sub>6</sub> (wt.%)	$\begin{array}{l} Activity \times 10^{-4} \ (g_{1\text{-}C6} / \\ (g_{Cr} \times h)) \end{array}$	Polyethylene (g)
1	50	25	700	2.24	97.1	2.52	0.05
2	60	25	700	4.19	98.5	4.71	0.07
3	70	25	700	6.32	99.9	7.11	0.08
4	80	25	700	6.07	99.9	6.83	0.08
5	70	10	700	1.35	99.2	1.51	0.31
6	70	15	700	2.85	99.5	3.20	0.11
7	70	25	500	5.11	98.9	5.75	0.09
8	70	25	910	6.39	99.8	7.19	0.10

*Note.* Reaction conditions: catalyst (Cr-SNS-D = 1.45 mg, 2.3  $\mu$ mol Cr); 1-hexyl-3-methylimidazolium tetrafluoroborate = 11.5  $\mu$ mol, 2.92 mg; ionic liquid/Cr = 5:1; cyclohexane/toluene (40 ml, 20/80 v/v); and reaction time 30 min. The bold data are the final optimum conditions to obtain the 1-hexene with maximum productivity and selectivity.

value with higher activity and lower polyethylene content as a by-product. With higher alkyl aluminum concentrations, MMAO plays the role of a poison in the reaction because of the cocatalyst sorption on the catalyst centers instead of the ethylene monomers (Table 3, entries 3, 7, and 8).

With increasing the ethylene pressure from 10 to 25 bar, the catalyst activity increases probably because of its higher solubility in the solvent as well as the IL (Table 3, entries 3, 5, and 6).<sup>[60]</sup> Therefore, the activity of the catalyst is reduced in ethylene trimerization.<sup>[61]</sup>

### 3.6 | Effect of the IL counter-anions

After the reaction conditions were optimized, the influences of different IL counter-anions such as  $BF_4^-$ ,  $Br^-$ , and I<sup>-</sup> were studied. As shown in Table 4 (entries 1–3 in comparison with entries 4–6) in the biphasic media including ILs and a mixture of cyclohexane/toluene solvents, Cr-SNS-R catalysts containing dodecyl substituent exhibited higher activity than Cr-SNS-B under the same reaction conditions. In the Cr-SNS-D catalysts, the activity decreased from 7.11  $g_{1-C6}/(g_{Cr} \times h)$  for BF<sub>4</sub><sup>-</sup> counteranion to 5.43 and 2.66 g  $_{1-C6}/(g_{Cr} \times h)$ , respectively, for I<sup>-</sup> and Br<sup>-</sup> counter-anions. In the Cr-SNS-B catalyst, the activity also decreased from 5.58 and 3.99 to 2.39  $g_{1-C6}/(g_{Cr} \times h)$ . These data are consistent with the results reported in the previous literature for the SNS catalysts, including dodecyl and butyl substituents.<sup>[3,16]</sup> Increasing the activity can be attributed to the alkyl chains in SNS ligands as well as the type of counter-anions in IL.

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ILs have an inherent tendency to absorb moisture, and there is a relationship between the absorbed moisture content and the nature of the counter-anions. ILs having  $Br^-$  and  $I^-$  anions ([HMIM][Br] and [HMIM] [I]) are more hygroscopic than those having [HMIM] [BF<sub>4</sub>].<sup>[62]</sup> The absorbed moisture content is directly related to the size and electronegativity of the halide anions. The  $Br^-$  anion moiety with a smaller atomic radius and higher electronegativity has the greatest moisture content among all three anions. The order of

TABLE 4 Effect of different ionic liquid (IL)/catalyst systems on 1-hexene activity and selectivity

Entry	IL:catalyst	1-C <sub>6</sub> (ml)	Selectivity of 1-C <sub>6</sub> (wt.%)	Activity $\times 10^{-4} \left(g_{1\text{-}C6}/(g_{Cr} \times h)\right)$	Polyethylene (g)
1	[HMIM][BF4]/Cr-SNS-D	6.32	99.9	7.11	0.08
2	[HMIM][Br]/Cr-SNS-D	2.67	99.2	2.66	0.09
3	[HMIM][I]/Cr-SNS-D	4.83	99.6	5.43	0.12
4	[HMIM][BF4]/Cr-SNS-B	4.96	99.8	5.58	0.07
5	[HMIM][Br]/Cr-SNS-B	2.13	98.9	2.39	0.07
6	[HMIM][I]/Cr-SNS-B	3.55	99.5	3.99	0.08

*Note.* Reaction conditions: catalyst (Cr-SNS-D = 1.45 mg, 2.3  $\mu$ mol Cr), [HMIM][X] = 11.5  $\mu$ mol, IL/Cr = 5:1, 70 °C, C<sub>2</sub>H<sub>2</sub> 25 bar, Al/Cr (700:1), cyclohexane/toluene (40 ml, 20/80 v/v), reaction time 30 min; [HMIM][Br], 1-hexyl-3-methylimidazolium bromide; [HMIM][BF4], 1-hexyl-3-methylimidazolium tetrafluoroborate; [HMIM][I], 1-hexyl-3-methylimidazolium iodide.

electronegativity for the investigated anions is  $BF_4^- < I^- < Br^{-}$ .<sup>[63]</sup> Therefore, the presence of higher moisture content as a possible catalyst poison reduces the catalyst activity (Table 4, entries 2 and 5).

Also, the lower activity with ILs containing Br<sup>-</sup> counter-anions (dodecyl = 2.66 and butyl = 2.39  $g_{1-C6}/(g_{Cr} \times h)$ ) can be related to the coordination of bromine with metal active centers in competition with the ethylene. This finding is consistent with the observations of Sanchora et al., who predicted the electronegativity of halide anions in ILs.<sup>[63]</sup>

Also, there is another reason for lower catalyst activity in ethylene trimerization in the presence of  $Br^$ counter-anions. The viscosity value of the IL containing  $Br^-$  counter-anions is higher than that of the IL having  $BF_4^-$  counter-anion, and also the heat capacity and heat conductivity of [HMIM][BF<sub>4</sub>] is higher than those of [HMIM][Br].<sup>[63]</sup> Therefore, ethylene gas dissolved well in the [HMIM][BF<sub>4</sub>] ILs containing catalysts compared to [HMIM][Br] ILs, and the catalyst activity increased (Table 4, entries 1 and 2 and 4 and 5).

Previous investigation and analyses in the field of metal catalysts with BF<sub>4</sub> anions have clarified the role of this anion in enhancing activity (dodecyl = 7.11 and butyl = 5.58 g<sub>1-C6</sub>/(g<sub>Cr</sub> × h)) and selectivity (>99.8 wt.%). According to the literature, BF<sub>4</sub> anions weakly coordinate with the active sites of the catalyst and result in the creation of active cationic chromium catalyst species required for the trimerization of ethylene.<sup>[64,65]</sup>

The postulated mechanism for trimerization of ethylene catalysts with ILs is illustrated in Scheme 5.<sup>[10]</sup> The active cationic chromium species tends to rapidly coordinate with two ethylene molecules and form metallocyclopentane. Because 1-butene is not formed, the reaction is thought to move toward the insertion of the third ethylene molecule and form a seven-membered metallocycloheptane ring. It seems that further dissolution of ethylene in the ILs facilitates this step and also ethylene insertion into the metallocyclopentane. Subsequently, opening of the metallocycloheptane ring leads to releases of 1-hexene. However, the replacement of the new ethylene molecule may form larger rings, which results in the release of 1-octene or even higher olefins such as 1-decene. However, 1-decene was not observed experimentally.<sup>[16]</sup> The role of the metal oxidation state in the SNS-Cr catalyst for ethylene trimerization was investigated by Jabri et al.<sup>[13]</sup> Their observations strongly suggest the effect of the Cr oxidation state on the selectivity of these catalytic systems by identifying the products of the reaction of the Cr(II) and Cr(III) complexes bearing SNS ligands with various organoaluminum reagents. In Scheme 5, exact amounts of oxidation numbers for chromium are mentioned.



**SCHEME 5** Proposed mechanism for trimerization of ethylene using chromium-based catalysts in biphasic media

## 3.7 | Recycling of [HMIM][BF<sub>4</sub>]/Cr-SNS-D catalyst

[HMIM][BF<sub>4</sub>]/Cr-SNS-D catalyst was selected to investigate the reusability and ethylene trimerization tests that were performed in the biphasic media under constant optimized reaction conditions. At the end of the trimerization reaction and after cooling the reaction mixture, the gas was slowly evacuated, and about 2 ml of the liquid phase inside the reactor was collected for GC analysis under argon atmosphere. The residual catalyst in the reactor was used for subsequent trimerization reactions. Therefore, the temperature was then increased, 2 ml of fresh solvent mixture was used, the MMAO cocatalyst was injected, and the ethylene pressure was increased to initiate the ethylene trimerization reaction. The recycling procedures were repeated four times, and the activity of the catalysts was measured after each recycling run, as shown in Figure 3.

The catalytic activity decreased sharply in the third run, and the catalyst was fully deactivated in the fifth run. The by-products such as polymers or oligomers on the surface of the catalyst probably reduced the catalyst activity. On the contrary, polymer swelling and growth of the polymer layers on the catalytically active centers probably lead to the mechanical destruction of the catalyst and its deactivation. Although the activity of the trimerization reaction decreased after each run, considering the recycling of the catalyst is valuable in the chemical industry.<sup>[25]</sup> Table 5 presents a comparison of our catalyst with other catalytic systems consisting of ILs. Our synthesized catalyst exhibited a better catalyst activity in the designed conditions.



**FIGURE 3** Recycling of 1-hexyl-3-methylimidazolium tetrafluoroborate/Cr-SNS-D catalyst

TABLE 5	Comparison of our catalyst with other catalytic
systems consisti	ng ionic liquids (ILs)

Conditions	Gao et al. <sup>25</sup> PNP-Cr/IL catalyst	Our study SNS-D-Cr/IL catalyst
Al/Cr	300:1	700:1
IL/Cr	3:1	5:1
IL	[BMIM][AlCl <sub>4</sub> ]	[HMIM][BF <sub>4</sub> ]
Pressure (bar)	8	25
Temperature (°C)	50	70
Time (min)	30	30
Activity $(g_{1-C6}/(g_{Cr} \times h))$	21,400	71,132
Selectivity	96.15	99.9
Recycling	3	4

Note. [HMIM][BF<sub>4</sub>], 1-hexyl-3-methylimidazolium tetrafluoroborate.

### 4 | CONCLUSION

In this study, the influence of IL counter-anions on the activity and selectivity of the Cr-SNS-R catalysts in ethylene trimerization was investigated. The results demonstrated that the presence of ILs containing  $BF_4^-$  counter-anion compared to the  $Br^-$  and  $I^-$  counter-anions leads to increased activity and selectivity. The highest activity and selectivity were obtained at the IL/Cr-SNS-D molar ratio of 5 with  $BF_4^-$  counter-anion, because the  $BF_4^-$  anions weakly coordinate with the active sites of the catalyst and result in the creation of active cationic chromium catalyst species required for the

trimerization of ethylene. The catalyst recovery was tested 5 times, and the results showed that the catalytic activity decreased sharply in the third run and the catalyst was fully deactivated in the fifth run.

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