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Additives boosting the performance of tungsten bis(imido)-mediated ethylene dimerization systems for industrial application

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While activation of tungsten bis(imido) complexes [WCl₂(NAr)₂(dme)] with EtAlCl₂ affords active, and moderately selective ethylene dimerization catalysts, addition of Et₃N or Oct₄NCl leads to a doubling in productivity and activity, along with increased selectivity (e.g., > 93% C₄, > 99% 1-C₄). The performance of the resulting tungsten-based catalyst package is competitive with that of Axens’ commercialised Ti-based AlphaButol process and exemplifies the wide potential of similar additives in selective oligomerization.

Linear alpha olefins (LAOs) are essential components in the manufacture of a host of everyday materials including engine lubricants, plastics, detergents, flavours and fragrances. As a result, the annual production of LAOs is approximately 5 million metric tons, with a market worth USD 8.26 billion in 2018. In this arena, 1-butene is one of the most important LAOs. Not only is it used as a co-monomer in the production of linear low density polyethylene, LLDPE (with an average annual market increase of 5.3%), but also as the principle starting material for the manufacture of a range of valuable synthetic intermediates. However, current 1-butene demand that is available through conventional refinery sources necessitating development of alternative supply chains such as catalytic ethylene dimerization. Amongst the homo- and hetero-geneous catalytic ethylene dimerization systems reported, Axens’ AlphaButol process stands out, producing 25% of the total 1-butene consumed worldwide since the mid-1980s. AlphaButol’s success can be attributed mainly to the use of inexpensive titanium alkoxides, reasonable activity of up to 21 × 10³ mol C₂H₄)(mol Ti)⁻¹ h⁻¹, good productivity of ~ 250 g ethylene converted per hour, low polyethylene make, and excellent selectivity of up to 95 wt% 1-butene content. These impressive performance parameters make it challenging to establish different, economically competitive ethylene dimerization catalysts. Currently, although many of the alternatives are reasonably active, they lack the selectivity (giving both polymer and 2-butene) and/or productivity (low ethylene conversions of only a few grams) necessary for industrial application.

In this context, we recently described the dimerization of ethylene mediated by tungsten bis(imido) complexes activated with EtAlCl₂. These systems achieve high activities and productivities, albeit with only moderate selectivities (up to 409 mol C₂H₄)(mol W)⁻¹ h⁻¹ and 1-butene selectivity of up to 82 wt%). In order to enhance the performance of these tungsten-based systems we sought to exploit the use of so-called “modifiers” (e.g., THF, Et₃N, Oct₄NCl, Ph₃P, and Ph₃PO). These have been previously reported to give enhancements in catalytic ethylene oligomerization performance of titanium, nickel, cobalt, and zirconium-based systems, but have surprisingly received very little subsequent attention in the literature. Therefore, we now describe our findings on the effects of the modifiers Oct₄NCl (Oct = octyl) and Et₃N on catalysis initiated by tungsten bis(imido) pro-catalysts. We highlight not only the extremely beneficial effects of the modifiers, but also demonstrate the development of a tungsten-based dimerization system that rivals the performance of the commercialised AlphaButol process.

Pro-catalysts 1-3 (Chart 1) were chosen as a starting point for this investigation of the effect of modifiers since their dimerization behaviour has been explored in detail previously and showed promising performance. Thus, a baseline catalytic performance of complexes 1-3 activated with 15 EtAlCl₂ was first established as summarised in Table 1 (full details are presented in the ESI†). Note, where catalytic tests resulted in filling of the reactor vessel to capacity, the productivities (TONs) reported in Table 1 are underestimated since catalysis had to be stopped. As established previously, a limiting concentration of tungsten ≥ 0.2 mM is required for productive catalysis. Subsequently, we explored the effect of the potential modifiers Et₃N and Oct₄NCl (the latter preferred over Et₄NCl due to its greater solubility) upon the catalytic performance of...
1–3/EtAlCl₂. The use of ammonium chloride salts was considered a promising starting point since it has been demonstrated previously that increasing the chloride content in the activator (e.g., replacing Et₃Al by EtAlCl₂) is beneficial to catalysis with this type of tungsten imido system as well as having been shown to modulate the selectivity of related titanium and tantalum polymerisation catalysts.³⁹,¹³

Solutions of each of the pro-catalysts 1–3 were treated with either Et₃N or Oct₄NCl prior to activation with EtAlCl₂, and the resulting systems tested for their ethylene dimerisation performance. The data summarized in Fig. 1 show that addition of Et₃N and, especially Oct₄NCl, leads to significant improvements in catalytic activity and selectivity compared with those achieved in the absence of modifiers. Addition of 4 eq. of Et₃N before activation of 1 with 15 equivalents EtAlCl₂ leads to doubling in activity (Table 2, entry 2), while use of Oct₄NCl gave rise to a roughly three-fold increase. Furthermore, the addition of Et₃N and Oct₄NCl also leads to improvements in both the selectivity towards the dimer fraction (from 73 to 87% for 6 eq. of modifier added) and in the selectivity to 1-butene within the dimers fraction (98 to 99%). This level of performance brings the selectivity towards butenes for the bis(imido) tungsten pro-catalysts to within 8 wt% of that reported for AlphaButol, while matching performance in terms of selectivity towards 1-butene within the C₄ fraction.⁵⁸

The increase in the percentage of 1-butene within the C₄ fraction is especially significant since 1-butene of low purity is not suitable for polyethylene manufacturing applications (its principle market), requiring costly super-fractionation prior to use.⁷ In addition, for pro-catalyst 1 the selectivity towards butenes was found to increase almost linearly with the amount of modifier used (Fig. 1), reaching values of 95 wt% when 10 eq. of Oct₄NCl are employed. This degree of selectivity is, within experimental error, analogous to that reported for AlphaButol.⁶,¹⁴ However, this enhanced selectivity achieved with 1/Oct₄NCl/EtAlCl₂ came at a cost to this system’s activity and productivity (Table 2, entries 1–8).

Similar to the change in catalytic performance observed with pro-catalyst 1 in combination with 4 Et₃N or 2 Oct₄NCl, pro-catalyst 2 also demonstrated increased activity in the presence of each of the modifiers, reaching a value of over 500 × 10⁶ (mol C₂H₄)(mol W)⁻¹ h⁻¹ whilst maintaining selectivity towards C₄ of ~ 80 wt% (Table 2, entries 9 and 10). In marked contrast, pro-catalyst 3 was poisoned by both Et₃N and Oct₄NCl, resulting in a dramatic decrease in activity from 409 × 10⁶ to

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**Table 1** Catalytic performance of complexes 1–3 at 45 barg ethylene pressure and 70 °C under varying conditions

| Entry | Pro-cat. (μmol) | [W], g | tₑ(min) | TON⁶ | Activity⁷ | Prod. C₄, wt% | C₄/i-C₄ in C₄, % |
|-------|----------------|-------|---------|------|------------|---------------|-----------------|
| 1      | 1(20)          | 270   | 45      | 134  | 179        | 75            | 73(98)          |
| 2      | 1(40)          | 270   | 136     | 443  | 195        | 497           | 69(99)          |
| 3      | 2(20)          | 270   | 29      | 143  | 293        | 80            | 74(98)          |
| 4      | 2(40)          | 270   | 65      | 392  | 362        | 440           | 77(99)          |
| 5      | 3(20)          | 270   | 21      | 142  | 409        | 80            | 82(98)          |
| 6      | 3(40)          | 270   | 105     | 362  | 208        | 406           | 84(98)          |

*Conditions: 15 eq. EtAlCl₂; PhCl (74 mL); 70 °C; ethylene pressure 45 barg; stirrer speed 1000 rpm; nonane standard (1.000 mL); 0.25 L reactor; no polyethylene detected. Unless stated otherwise, catalytic runs were performed until consumption of C₂H₄ dropped below 0.2 g min⁻¹ or until the reactor was filled. Activity (TOF) reported in [mol C₂H₄] [mol W]⁻¹ h⁻¹. Selection to butenes and selectivity of 1-butene in the butenes fraction. Reaction mixture filled reactor so reported activity and selectivity are underestimated. Performed in a 1.2 L reactor with 148 mL PhCl and 2.000 mL nonane standard.

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**Table 2** Effect of Et₃N and Oct₄NCl on the catalytic performance of pro-catalysts 1–3 in combination with EtAlCl₂ at 45 barg ethylene pressure and 70 °C

| Entry | Pro- Modifier | tₑ(min) | TON⁶ | Activity⁷ | Prod. C₄, wt% | C₄/i-C₄ in C₄, % |
|-------|---------------|---------|------|------------|---------------|-----------------|
| 1      | Et₃N(2)       | 32      | 144  | 269        | 81            | 80(99)          |
| 2      | Et₃N(4)       | 23      | 144  | 366        | 81            | 81(99)          |
| 3      | Et₃N(6)       | 24      | 144  | 364        | 81            | 87(99)          |
| 4      | Et₃N(10)      | 55      | 102  | 111        | 57            | 91(99)          |
| 5      | Oct₄NCl(2)    | 18      | 143  | 473        | 81            | 79(99)          |
| 6      | Oct₄NCl(4)    | 18      | 142  | 477        | 80            | 83(99)          |
| 7      | Oct₄NCl(6)    | 18      | 140  | 471        | 79            | 87(99)          |
| 8      | Oct₄NCl(10)   | 19      | 36   | 111        | 11            | 20(93)          |
| 9      | Et₃N(4)       | 15      | 142  | 574        | 80            | 80(99)          |
| 10     | Oct₄NCl(2)    | 15      | 141  | 574        | 79            | 79(99)          |
| 11     | Et₃N(4)       | 46      | 15   | 10        | 20            | 8(93)           |
| 12     | Oct₄NCl(2)    | 34      | 142  | 248        | 79            | 86(98)          |
| 13     | Oct₄NCl(2)    | 38      | 368  | 584        | 413           | 84(99)          |
| 14     | Oct₄NCl(2)    | 62      | 708  | 690        | 397           | 84(99)          |
| 15     | Oct₄NCl(2)    | 89      | 675  | 458        | 379           | 82(99)          |

*Conditions: 20 μmol W; 15 eq. EtAlCl₂; PhCl (74 mL); 70 °C; ethylene pressure 45 barg; stirrer speed 1000 rpm; nonane standard (1.000 mL); no polyethylene was detected. TON (productivity) is reported in (mol C₂H₄)/([mol W])⁻¹ h⁻¹. TOF (activity) is reported in [mol C₂H₄]/([mol W])⁻¹ h⁻¹. Selection to butenes expressed in wt% and %selectivity of 1-butene in the butenes fraction. Performed in a 1.2 L reactor with 148 mL PhCl and 2.000 mL nonane standard. 80 μmol W used.
20 \times 10^3 and 248 \times 10^3 (mol C_2H_4/(mol W)^{-1} h^{-1}, respectively (Table 2, entries 11 and 12). Additionally, the selectivity towards 1-butene in the C_4 fraction using pro-catalyst 3 combined with Et_3N or Oct_4NCl was not as good as that obtained using pro-catalysts 1 and 2 (97% and 98% vs. >99%).

Since catalysis employing complexes 1 and 2 in combination with EtAlCl_2 and Oct_4NCl filled a 0.25 L reactor to capacity, further testing was carried out in a 1.2 L vessel. Catalysis mediated by pro-catalyst 1 (40 \mu mol) in combination with EtAlCl_2 (15 eq.) and 2 eq. of Oct_4NCl led to formation of 413 g of product, filling the 1.2 L reactor to capacity. This corresponds to an activity of 584 \times 10^3 (mol C_2H_4/(mol W)^{-1} h^{-1} (Table 2, entry 12), surpassing the activity of the same system achieved in the 0.25 L reactor (Table 2, entry 5) by 100 \times 10^3 (mol C_2H_4)/(mol W)^{-1} h^{-1}. This increase in activity observed when the experiment from entry 5 of Table 2 was repeated in the 1.2 L reactor suggests that when the latter test was stopped (since the reactor had been filled; see ESI†) the reaction was in the nascent stages of catalysis and that even higher activities and productivities should be possible if catalysis was allowed to reach completion. This behaviour became more evident on comparing the shape of the ethylene conversion profiles (Fig. 2) as a function of time for high-performing reactions, where the reactor was filled (Table 2, entries 5 and 14), and poorly-performing reactions where catalysis stopped as a result of catalyst deactivation (e.g., Table 2, entry 4) resulting in a plateau in the reaction profile (Fig. 2, dotted line). A similar trend was observed for the reaction selectivity: the longer catalysis was run the more selective the system became, something demonstrated by the increase in selectivity towards butenes from 79 to 84 wt% when the reaction described in entry 5 of Table 2 was performed in the larger 1.2 L reactor (Table 2, entry 13). This increased selectivity when the reaction was run at higher productivities is characteristic of the tungsten imido systems and results from the majority of by-products being formed during the activation phase of the catalytic system.

When the test employing 40 \mu mol of pro-catalyst 1 (Table 2, entry 13) was repeated with half the amount of 1 (Table 2, entry 14), an extremely high-performing system was achieved, with a productivity of 708 \times 10^3 (mol C_2H_4)/(mol W)^{-1}, an activity of 690 \times 10^3 (mol C_2H_4/(mol W)^{-1} h^{-1}, selectivity to butenes and to to 1-butene within the C_4 fraction off 84 wt% and 99%, respectively. Here, again, the nature of the imido substituents is intimately linked to controlling catalytic performance; repeating the same test with pro-catalyst 2 (20 \mu mol) rather than 1 gave poorer results (Table 2, entry 14).

Notably, the activity and productivity achieved employing 20 \mu mol of pro-catalyst 1 (Table 2, entry 14) are both at least 30 times higher than those reported for the commercial Alpha-Butol titanium alkoxide-based systems.\(^6,7,9,20\) Additionally, both the selectivity towards 1-butene within the C_4 fraction and the extent of polymer formation is very similar for both the tungsten and titanium systems, although Alpha-butol shows slightly higher selectivity (~8 wt%) to C_4.

Currently, the mode of action by which Et_3N and Oct_4NCl improve the catalytic performance of the tungsten bis(imido) pro-catalysts 1 and 2 activated by EtAlCl_2 remains elusive. Indeed, the activation pathway of transition metal polymerization and oligomerization pro-catalysts continues to be a topic of debate.\(^{16,17}\) Neither complex 1 nor 2 reacts with either Et_3N or Oct_4NCl. However, in contrast, the reaction of complex 1 with 6 eq. of EtAlCl_3 leads to the formation of multiple unassignable products, together with ethane (W : C_2H_6 = 1 : 1). This is consistent with Al-to-W transmetalation to afford a tungsten diethyl species, which undergoes [β-hydride elimination and reductive elimination. While no further reaction takes place on subsequent addition of ethylene at 1 barg, performing this reaction in the presence of ethylene (>10 barg) results in ethylene dimerization.\(^8\)

Previously we have shown that 1 reacts with 6 eq. Me_3Al to yield [WMe_2(N[Dipp]AlMe_2(μ-Cl)](N[Dipp])] \(^4\), which is inert towards ethylene.\(^8\) However, reaction of 4 with THF or NEt_3, displaces the bound Me_3Al forming a labile complex [WMe_2(N[Dipp])_2(L)] (L = THF, NEt_3), which is active for catalytic ethylene dimerization. Consequently, it is proposed tentatively that these modifiers enhance catalytic activity by scavenging the residual aluminium salt from the tungsten during or after alkylation has occurred. For instance, triethylamine can react with R_4AlCl\(^{3–4}\) to form adducts of the type Et_3N·AlCl_4(R_4Cl)\(^{2–3}\).\(^9,19\) While reaction with Oct_4NCl affords aluminates salts such as [Oct_4N][AlCl_5] or [Oct_4N][AlCl_2],\(^20\)

Thus, the presence of either Et_3N or Oct_4NCl gives enhanced catalytic performance as a result of efficient formation of the necessary coordinatively unsaturated tungsten species.\(^19\) Higher concentrations of the modifiers (e.g., 10 eq. relative to tungsten, see Fig. 1) will eventually lead to their coordination at tungsten, thus blocking olefin binding hence reducing the system’s catalytic performance. These conclusions are also consistent with the poor ethylene dimerization performance of complex 3: the electron withdrawing nature of the trifluorophenyl group results in strong coordination of the Lewis basic additive to the tungsten centre stabilizing it to an extent that hampers increased reactivity.

In summary, complexes 1–3 in combination with 15 eq. of EtAlCl_3 are active and moderately selective catalysts for the

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**Fig. 2** Amount of ethylene converted to products over time for pro-catalyst 1 with 2 eq. Oct_4NCl or 10 eq. Et_3N modifier in a 250 mL and 1.2 L reactor. Catalysis with 1 and 2 eq. Oct_4NCl was far from completion at the point the reactor became filled demonstrating the industrial potential of these systems.
dimerization of ethylene. However, the addition of Et₃N or Oct₃NCl as modifiers significantly boosts activity, productivity, and selectivity of both pro-catalysts 1 and 2. The resulting catalytic performance of the pro-catalyst 1,2/modifier package is entirely comparable to that of the principle ethylene dimerization system used commercially for the production of 1-butene, AlphaButol. Importantly, this study indicates that the full potential of the tungsten imido ethylene dimerization system has yet to be fully realized in terms of activity, productivity, and selectivity. Additional advances are expected in the future following an on-going exploration of the mode of action of these modifiers with bis(imido) tungsten pro-catalysts. We have demonstrated here that modifiers act on the aluminium activators rather than the transition metal pro-catalyst component and so, consequently, we propose that this is something that is not specific to just these tungsten bis(imido) systems, but rather should be very widely applicable to the many different types of previously explored selective oligomerization catalysts.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

§ This effect is also observed when the catalytic performance of pro-catalysts 1 and 2 was tested without modifiers, Table 1, entries 3 vs. 4.

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