ALTERNATIVE CO-CATALYSTS FOR THE HOMOPOLYMERIZATION OF ETHYLENE USING ZIEGLER-NATTA CATALYSTS

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Introduction

The coordinative polymerization of ethylene is mostly performed using Ziegler-Natta (ZN) catalysts. For the activation of these catalysts an aluminum alkyl (e.g. triethylaluminum (TEA)) is needed. The usage of these alkyls requires special precautions, as they are highly pyrophoric (figure 1) [1]. In this work, alternative activators like ionic liquids (IL) are used instead, while being less pyrophoric (table 1) [2]. Other results show, that magnesium-aluminum (Mg-Al) alkyls can also be utilized as a replacement for TEA for the activation of ZN-catalysts [3].

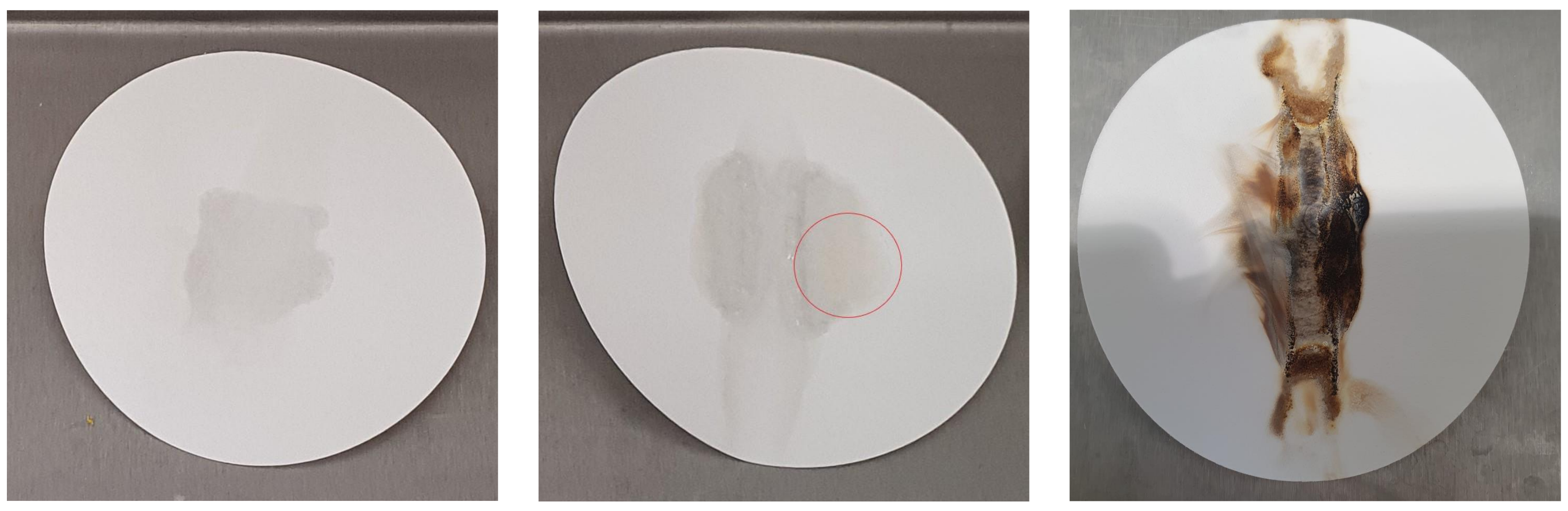

Figure 1: left: Pyrophoricity test with a solution of a 30 wt.% of the ionic liquid in *n*-heptane.
middle: Pyrophoricity test with a solution of a 40 wt.% of the ionic liquid in *n*-heptane.
right: Pyrophoricity test with the pure ionic liquid.

Table 1: Pyrophoric limit of the co-catalyst in *n*-heptane.

TEA	Ionic liquid	Magnesium-aluminum alkyl
12 wt.% [1]	30 – 40 wt.%	14.5 – 29 wt.%

Experimental

- Co-Catalyst: stirring of the mixture for 24 h under inert conditions
  - IL: 3 mmol of methyltrioctyl ammonium chloride ($NMeOct_3Cl$) and 15 mmol of TEA (figure 2 top left)
  - Mg-Al alkyl: 3 mmol of a 20.4 wt.% solution of butyl-octyl magnesium in *n*-heptane and 6 mmol of TEA (figure 2 top right)
- Catalyst: synthesized according [4], amount of titanium 7.4 wt.% (figure 2 bottom left)
- Polymerization
  - Introduction of 165 g propane, 0.05 g hydrogen, and 8 g ethylene into the reactor at 30 °C (figure 2 bottom right)
  - Injection of catalyst/co-catalyst mixture after 5 min precontacting time at the reaction temperature of 70 °C
  - Constant ethylene inlet pressure of 32 bar during the polymerization time of 45 min

Figure 2: top left: IL with $NMeOct_3Cl$ at the ratio 5.
top right: Mg-Al-alkyl with the ratio 2.
bottom left: ZN catalyst with 7.4 wt.% Ti.
bottom right: 0.5 L polymerization reactor.

Results

- TEA: highest catalyst activity for both Al:Ti ratios
- Ionic liquid: performs slightly worse than TEA, performance gap is decreasing with increasing Al:Ti ratio
- Magnesium-aluminum alkyl: lower catalyst activity, performance gap is higher with increasing Al:Ti ratio
- The activation of the catalyst is relatively similar for TEA and the IL. The Mg-Al alkyl takes longer to activate the catalyst.
- The molecular weight distribution of TEA and the IL are relatively similar, for the Mg-Al alkyl a broader distribution is observed.

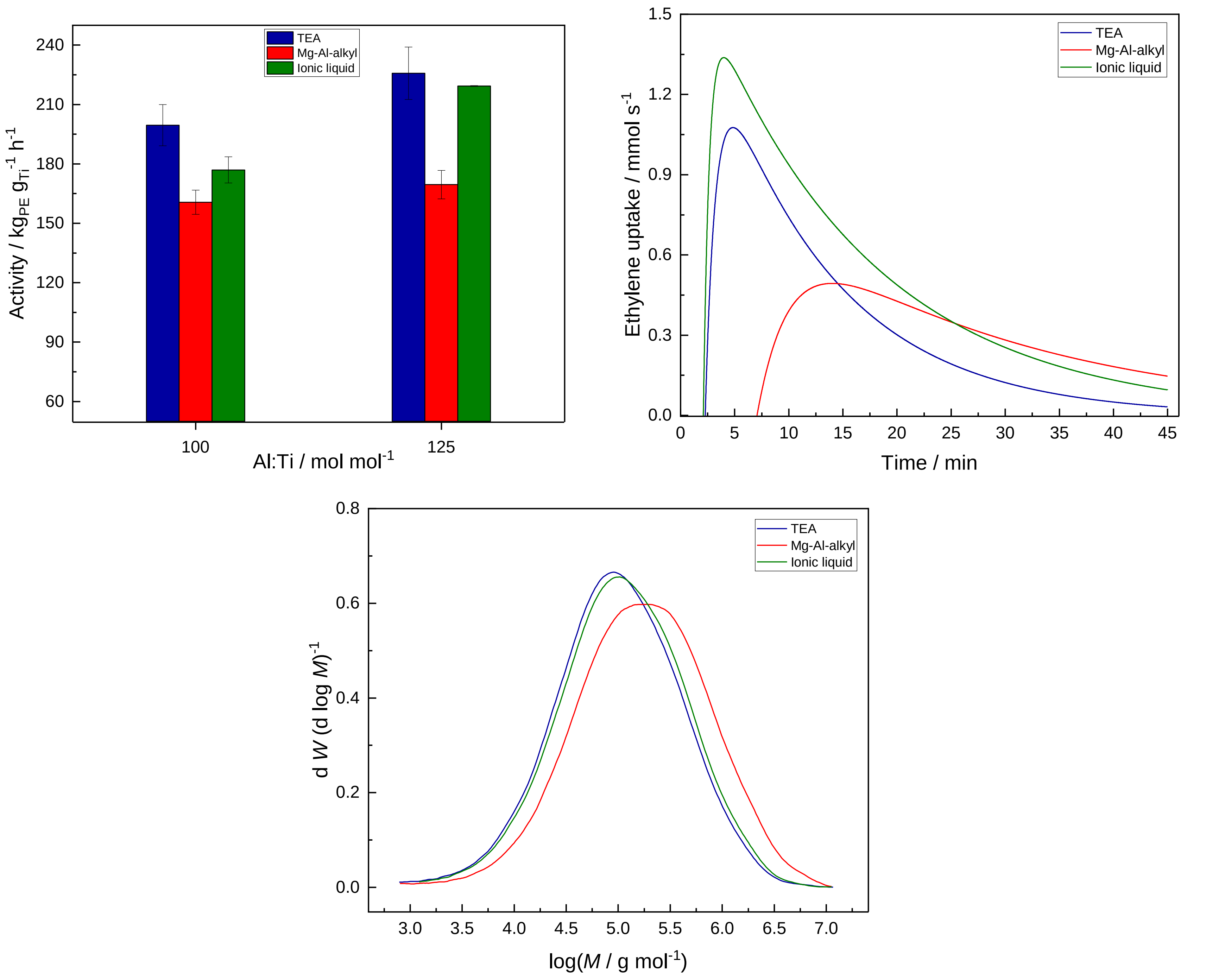

Figure 3: top left: Catalyst activities at the Al:Ti ratios of 100 and 125 for the three co-catalysts TEA, Mg-Al-alkyl and ionic liquid.
top right: Ethylene uptake throughout the polymerization for the three co-catalysts at the Al:TI ratio 100.
bottom middle: Molecular weight distribution for the three co-catalysts TEA, Mg-Al-alkyl and ionic liquid at the Al:Ti ratio 100.

Conclusion

- The performance of the ionic liquid is comparable to TEA in terms of catalyst activity and the molecular weight distribution of the resulting polymer.
- The magnesium-aluminum alkyl performs worse than the other to activators and the resulting polymer shows a broader MWD.
- The IL can be used as a replacement for TEA with the benefit of being less pyrophoric, the Mg-Al alkyl is lesser suitable for this purpose.

About the author

Dario Pindric is currently making his PhD thesis about solvent-based recycling of polyolefins at the Competence Center CHASE GmbH.

References

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