Ionic liquids and magnesium-aluminum-alkyls as activator for Ziegler–Natta catalysts

Dario Pindric[a], Julia Schwarz[a], Christian Paulik[a,*]

[a] Institute for Chemical Technology of Organic Materials, Johannes Kepler University Linz/Austria, *christian.paulik@jku.at

Institute for Chemical Technology of Organic Materials

Conclusion

An ionic liquid and a magnesium-aluminum-alkyl were tested as co-catalysts in Ziegler–Natta catalyst systems in comparison with triethylaluminum (TEA). Therefore, the catalyst activity (R_P) and the dispersity ($Đ$) of the resulting polymer were analyzed.

Using ionic liquids as activator leads to polyethylene with a smaller $Đ$ compared with TEA, but the overall R_P at different Al:Ti ratios is lower than when using TEA.

The Mg-Al-alkyl performs similar to TEA in terms of R_P, but only at a Al:Ti ratio of 75. The resulting polymer has an almost constant $Đ$ at different Al:Ti ratios, which is also lower in comparison to TEA.

Introduction

Ionic liquids have a variety of usages like Friedel–Crafts or isobutane alkylation. [1,2] Recent studies show, that ionic liquids can be used as co-catalysts for the coordinative polymerization of ethylene using Ziegler–Natta catalyst systems. [3] In other investigations, Mg-Al-alkyls are used for the activation of the Ziegler–Natta catalysts instead of TEA. [4]

The aim of this work is to evaluate the effects of the ionic liquids and Mg-Al-alkyls in comparison with TEA on the coordinative polymerization of ethylene. This is done by varying the Al:Ti ratio of the catalyst/co-catalyst system.

Experimental

For the preparation of the ionic liquid, 3 mmol of methyltrioctylammonium chloride are stirred with TEA in a ratio of 1:5 for 24 hours at room temperature. The Mg-Al-alkyl is synthesized by adding TEA to a solution of 3 mmol butyl-octyl-magnesium (BOMAG, 20 % in *n*-heptane) in a ratio of 1:2.

The polymerization is conducted using a 0.5 L reactor system (Figure 1). The catalyst/co-catalyst system is injected into the reactor after a precontacting time of 5 minutes. The polymerization is performed for 45 minutes at 70 °C. The obtained product is then analyzed with High Temperature - Size Exclusion Chromatography.

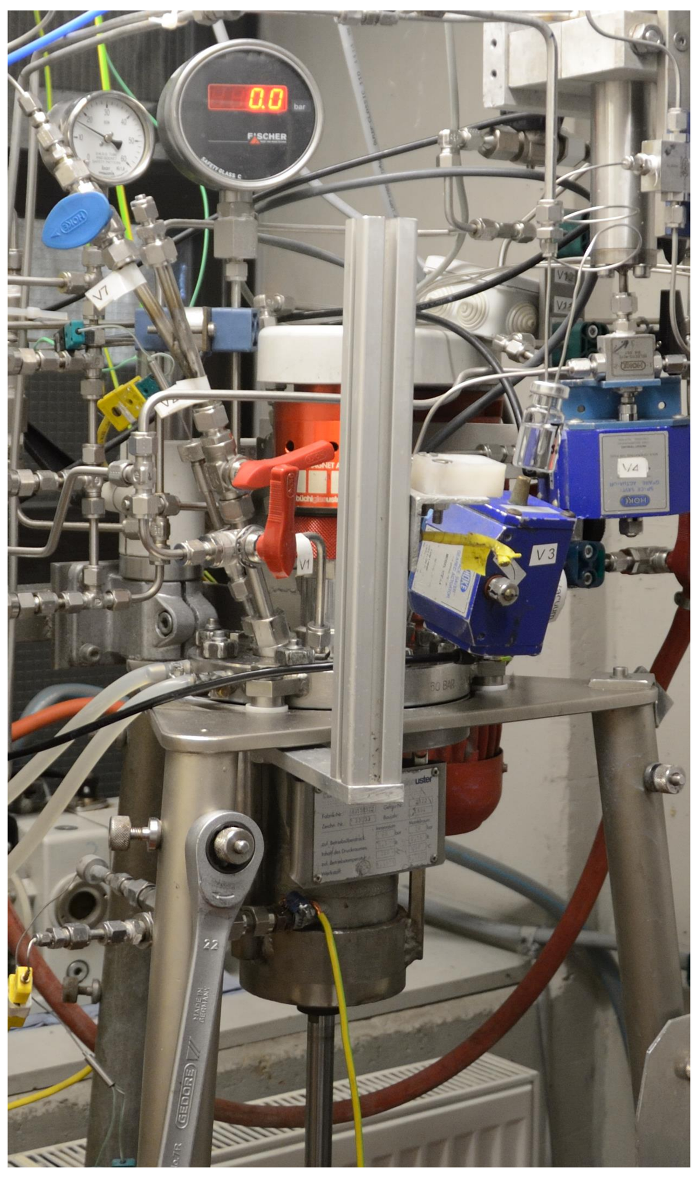

Figure 1: 0.5 L reactor with internal heating coil and equipped stirrer.

Results and Discussion

The results in Figure 2 show the effect of the co-catalyst on the catalyst activity at different Al:Ti ratios. The ionic liquid performs worse in comparison to TEA, as a higher Al:Ti ratio is necessary for catalyst activation.

The Mg-Al-alkyl has a different pattern according to the catalyst activity, with an optimum at an Al:Ti ratio of 75, whereas TEA has a wide range of Al:Ti ratios, where it can perform at a similar level.

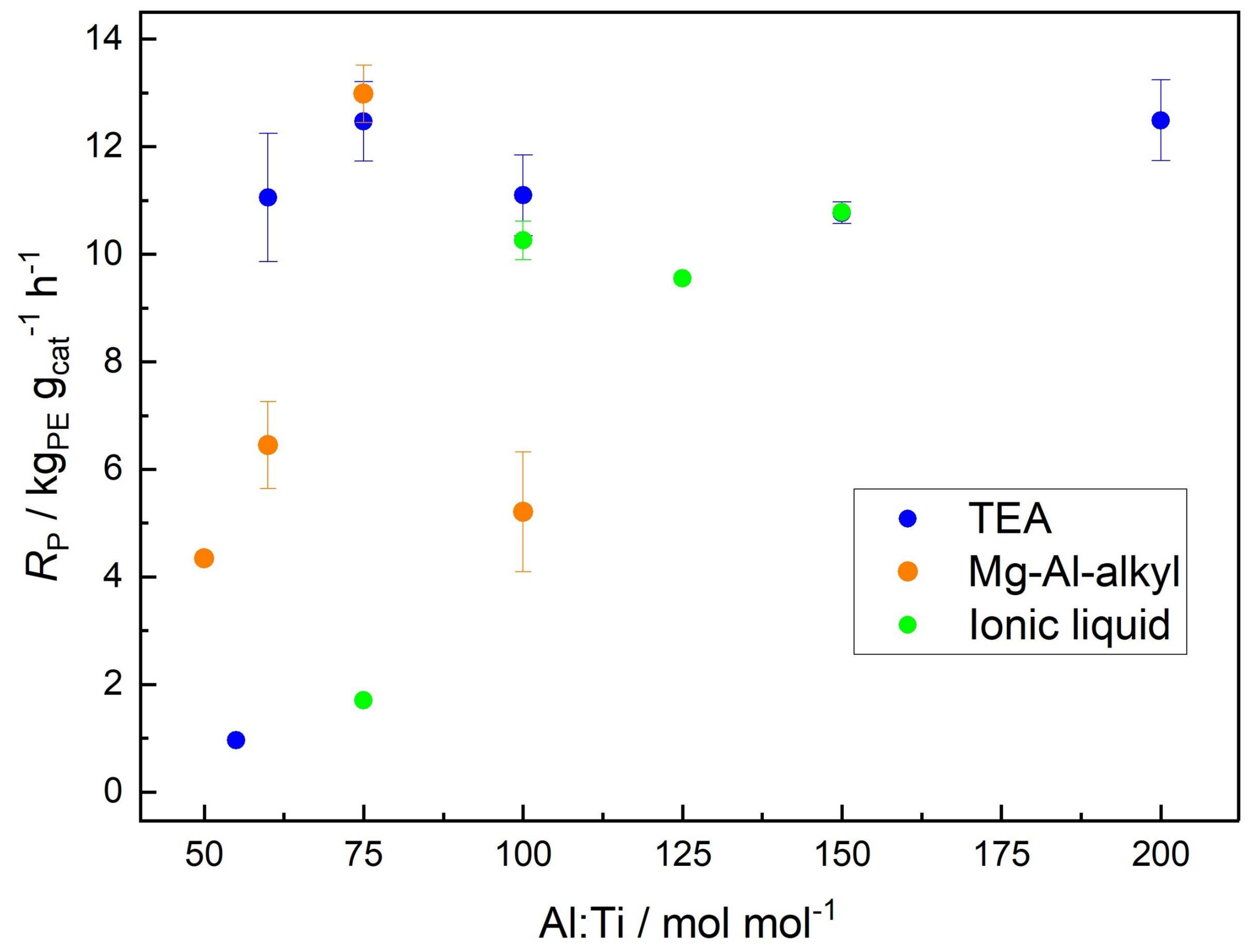

Figure 2: Catalyst activities for each co-catalyst at different Al:Ti ratios.

When comparing the dispersity of the resulting polymers at different Al:Ti ratios, as shown in Figure 3, it can be seen, that both the ionic liquid and the Mg-Al-alkyl produce polyethylene with a smaller $Đ$ than TEA. The ionic liquid shows a similar pattern, when comparing the Al:Ti ratios to TEA, with decreasing $Đ$ at higher Al:Ti ratios. The dispersity of the Mg-Al-alkyl is almost constant throughout the different ratios.

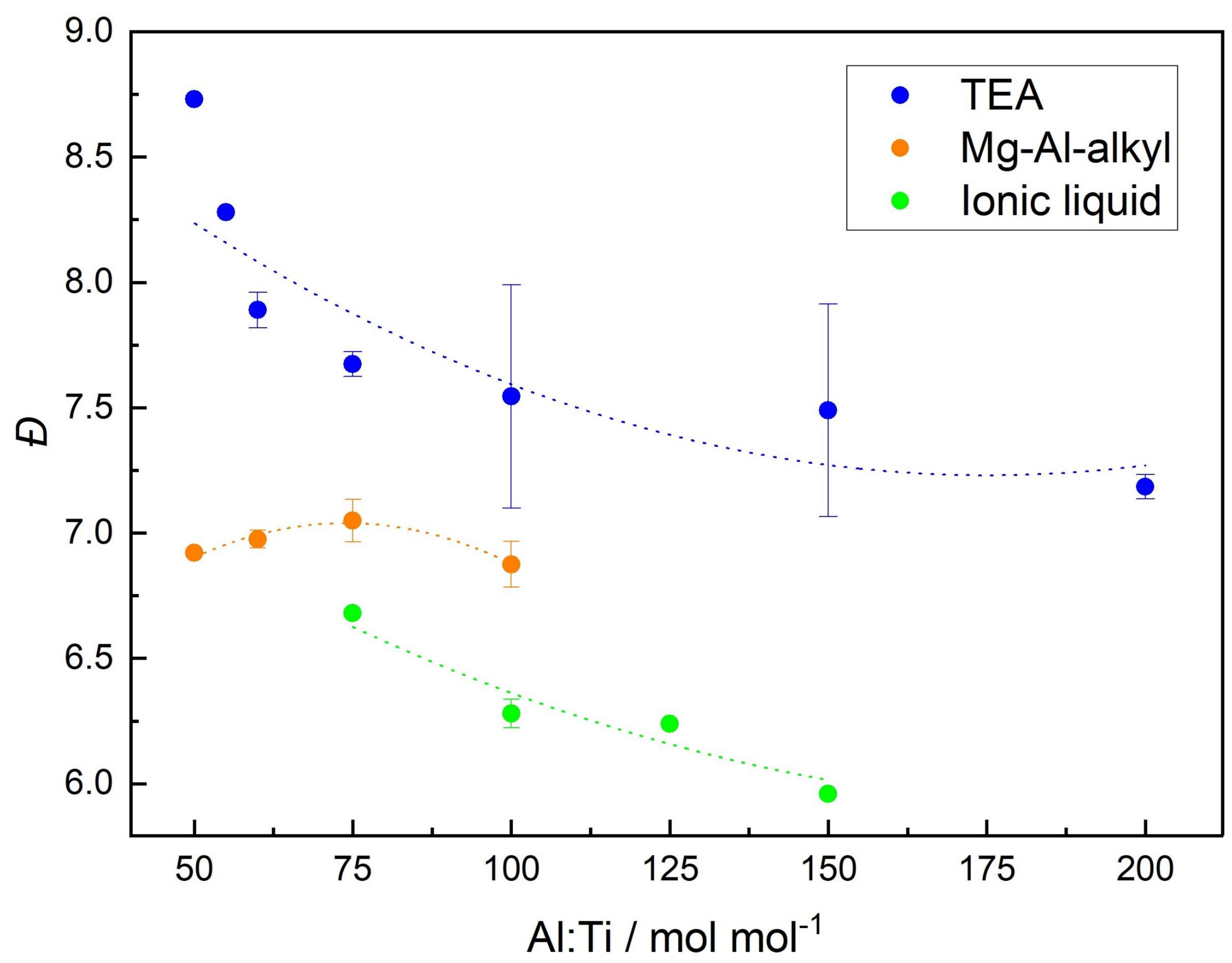

Figure 3: Dispersity for each co-catalyst at different Al:Ti ratios.

About the author

Dario Pindric is currently working on his master thesis in the field of coordinative polymerization of ethylene using Ziegler–Natta catalysts. The focus lies on evaluating the effects of different catalyst/co-catalyst systems.

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