Effect of different aluminum alkyls on ethylene polymerization

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Polyolefines, which are commonly produced with Ziegler-Natta (ZN) catalysts, are the most common plastics today. ZN catalysts usually consist of $TiCl_4$ supported on $MgCl_2$. Essential for the activation are alkylating agents, generally aluminum alkyls [1]. In the presented work, the influence of different aluminum alkyls on polymerization was investigated.

Experimental

Following alkyls were tested in ethylene homopolymerizations with a commercial catalyst:

- Triethylaluminum (TEA)
- Triisobutylaluminum (TIBA)
- Tridodecylaluminum (TDDA)

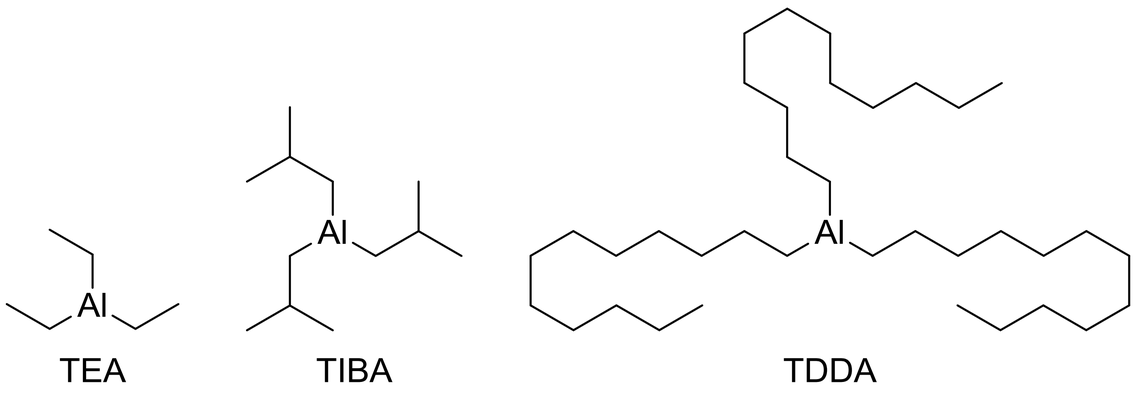

Figure 1: The alkyls used in the experiments.

The concentration was varied between 1.5 and 6 mmol L^{-1} based on the solvent volume used in the polymerization.

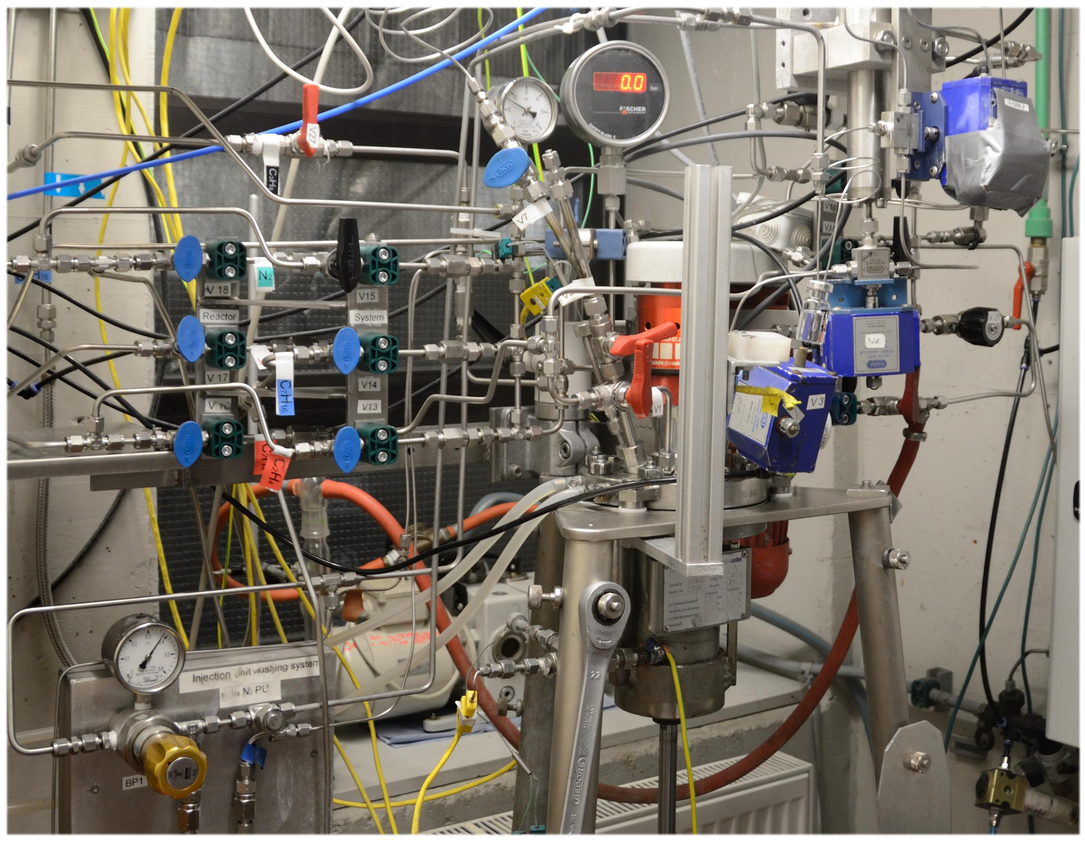

Figure 2: The polymerization experiments were carried out in a 0.5 L reactor system.

Furthermore, the effect of the alkyls on the oxidation state of titanium was examined.

Observations during the experiments indicated that the alkyls dissolve titanium to a different extent.

Results

The type and concentration of the alkyl influenced the polymerization activity. For TEA, activity peaked at 3 mmol L^{-1} and decreased with higher concentrations. Compared to the other alkyls, TEA exists to a considerable extent in a dimeric form, that becomes more dominant with rising concentration [2]. Dimers are unavailable for activation and block active sites.

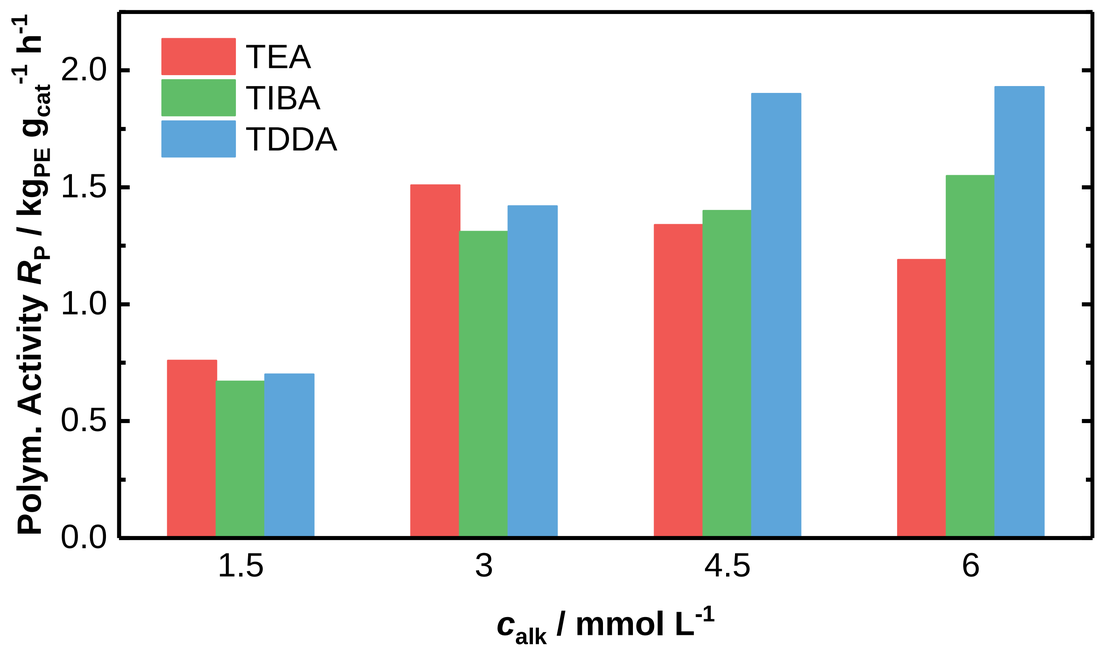

Figure 3: Polymerization activity for different alkyls and their respective concentration.

With TDDA the highest polymerization activity was achieved. Explanation can be found in the distribution of oxidation states. The main active species Ti^{3+} has the highest proportion for TDDA. With lower molecular mass of the alkyls the oxidation state is shifted toward Ti^{2+}, especially for TEA explaining the lower activity.

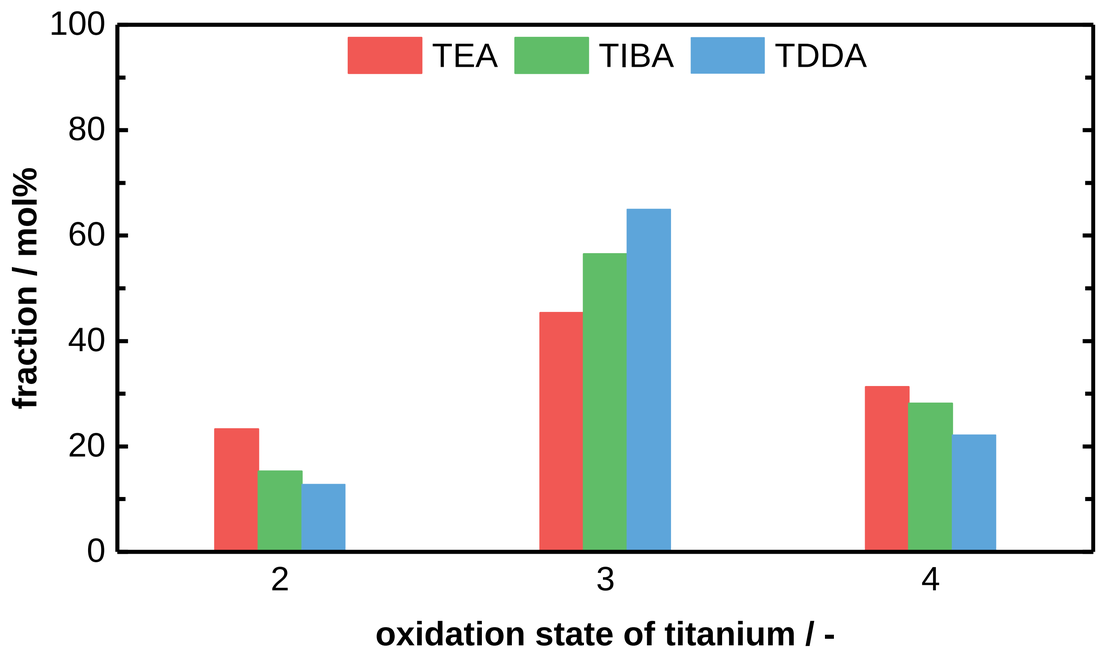

Figure 4: Comparison of the titanium oxidation states for different alkyls.

When TIBA was used as cocatalyst, it dissolved 20 times more titanium compared to TDDA further reducing activity.

Conclusion

In the experiments, the highest polymerization activity was reached with TDDA as it has a low tendency for titanium reduction and dissolution.

References

[1] Malpass D. B., *Introduction to Industrial Polyethylene*, John Wiley & Sons, 2010.
[2] Smith M. B., *J. Phys. Chem.*, *71*(2), 364–370, 1967.