Cyclodextrin-encapsulated Iron Catalysts for the Polymerization of Ethylene

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Catalytic polymerization of olefins has recently been rejuvenated by Brookhart \cite{1} and Gibson’s seminal works \cite{2} on the use of late transition metal complexes in olefin polymerization. Nitrogen tridentate complexes of iron and cobalt based on the 2,6-bis(iminoaryl)pyridine coordinating fragment are amongst the most studied because of their ability to promote very efficiently the polymerization of ethylene.

The purpose of the present work was the synthesis and use in ethylene polymerization of complexes based on iron fragments encapsulated in conical cavities. The complexes were prepared from methylated \(\alpha\)- and \(\beta\)-cyclodextrin (CDs) derivatives rigidly capped by a 2,6-bis(imino)-pyridyl fragment.\cite{3} In the resulting complexes an \textit{endo}-oriented FeCl\(_2\) moiety sits at the entrance of the cavity.

\begin{center}
\includegraphics[width=0.5\textwidth]{catalyst.png}
\end{center}

After activation with a large excess of MAO, polymerization of ethylene was observed for the \(\beta\)-cyclodextrin complexes. Clearly, the \(\beta\)-CD cavity provides adequate steric protection of the active site for the polymer chain to reach an appreciable length. In contrast the \(\alpha\)-CD derivatives remain inactive, probably because the primary methoxy groups coordinate the metal centre and hence hinder coordination of the incoming ethylene.

Overall this study shows that encapsulation of the metal center in sufficiently large cavities constitutes a viable alternative to the active site steric protection provided by \textit{substituted} imino-pyridyl fragments. The activity and the potential of the metalallocavitands reported in this study may be further improved by using cavities with larger portals.

\textbf{References}

\begin{enumerate}
\item B. L. Small, M. Brookhart, A. M. A. Bennet, J. Am. Chem. Soc. 120, 4049-4050 (1998)
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