

Understanding the Mechanism of Chromium-Catalyzed Ethylene Trimerization

Researchers at Sasol Technology (Pty) Ltd. and Accelrys have used DMol³ to propose and investigate a mechanism for ethylene trimerization, catalyzed by Cr-pyrrolyl complexes.

The results not only characterize this reaction mechanism in detail, but also provide insight into the general requirements for the ligands needed to create effective catalysts.

The calculations show that the proposed metallacycle mechanism is energetically favorable, with metallacycle growth identified as the rate-determining step. In addition, it is demonstrated that different bonding modes of pyrrole are preferred at different stages in the proposed mechanism.

The results will lead to the design of better catalysts for α -olefins that are used in plasticizers, detergent alcohols, and synthetic lubricants.

The transition metal catalyzed oligomerization of ethylene is traditionally used to synthesize α -olefins, which are important for applications in the production of linear low-density polyethylene plasticizers, detergent alcohols, and synthetic lubricants.¹ Selective trimerization of ethylene to produce 1-hexene is highly desirable because it would avoid the production of unwanted olefins that conventional transition metal oligomerization processes produce. Chromium-based catalysts are found to be especially well suited for this process.^{2,3}

In this work,⁴ scientists from Sasol Technology (Pty) Ltd. and Accelrys propose and investigate an ethylene trimerization mechanism based on Cr-pyrrolyl complexes, which represents one of the most successful ethylene trimerization systems known.^{2,3}

Mechanism of Ethylene Trimerization

The proposed mechanism⁵⁻⁷ for ethylene trimerization with a pyrrole-based system is illustrated in Fig. 1.

Industry Sectors

Petrochemicals
Chemicals

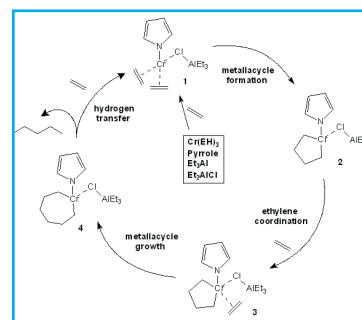
Organization

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Key Product

MS Modeling's DMol³



▲ Fig. 1 Mechanism of ethylene trimerization via the Cr-pyrrolyl complex

Catalyst initiation is assumed to yield the neutral Cr(II) species **1** as the first active intermediate in the catalytic cycle. The anion fragment of **1** in this study consists of a ClAlEt_3^- unit. Metallacycle formation involves oxidative addition of the two ethylene fragments to yield a five-membered Cr(IV) metallacycle **2**. This is followed by the coordination of a third ethylene molecule to yield **3**. Subsequent metallacycle growth results from insertion of the third ethylene molecule into the five-membered metallacyclic ring, yielding the seven-membered metallacycle species **4**. 1-Hexene liberation is afforded by β -hydrogen migration, and regeneration of the active catalytic Cr(II) species **1** occurs upon coordination of two ethylene molecules.

In this theoretical work, Accelrys' premium density functional theory (DFT) code DMol³ was used to assess the validity of the proposed mechanism. Throughout this study pyrrole was used as a model ligand for 2,5-dimethylpyrrole, which is commonly used in experimental studies and is depicted in Fig. 1.

Results

For the ethylene trimerization mechanistic cycle, two bonding modes of the pyrrole ligand were explicitly considered for all optimized geometries, viz., a η^5 - and σ -bonded pyrrole. Two model anions were used when modeling both bonding modes: a stripped-down model consisting of only Cl^- and a full model consisting of ClAlMe_3^- as anion. In addition, a detailed analysis to determine the preferred ground spin state for the active Cr(II) and Cr(IV) species was conducted.

These calculations predicted triplet spin ground states for both Cr(II) and Cr(IV) at the GGA/PW91 level of theory. Additional possible spin states for both species were found to be significantly less favorable; local minima as well as the transition states connecting them were 10-25 kcal/mol higher in energy than the corresponding structures with triplet spin states. The main conclusion from these results was that spin state crossing during the proposed mechanism is unlikely to occur.

The calculated Gibbs free energy profiles at 298.15 K using the Cl^- model for the full reaction cycle in Fig. 1 were found to be favorable on thermodynamic grounds, with a ΔG of -20.9 kcal/mol for a η^5 -bonded pyrrole and -17.1 kcal/mol for a σ -bonded pyrrole.

The rate-determining step in the mechanism for either bonding mode of pyrrole was the metallacycle growth from the metallacyclopentane reagent **3** to the metallacycloheptane product **4** with a free energy of activation of 38.2 and 33.1 kcal/mol for η^5 -bonded and σ -bonded pyrrole, respectively.

It was found that the change of pyrrole bonding mode is an important consideration in the proposed mechanism. A η^5 -bonding mode of pyrrole is calculated to be favored for metallacycle formation, whereas a σ -bonding mode is favored for metallacycle growth.

No preference was found for η^5 - or σ -pyrrole in the final liberation of 1-hexene. Transition state geometries were calculated for pyrrole ring slippage from η^5 to σ and back, which showed that the activation barrier for bonding mode change is small. These results suggest that facile change of pyrrole bonding mode enhances the catalytic efficiency of the Cr-pyrrolyl ethylene trimerization.

Calculations using the more realistic ClAlMe_3^- anion models showed remarkable similarities to the potential energy surfaces obtained with the stripped-down Cl^- models. One important difference for calculated activation energy for metallacycle growth was, however, found for the σ -coordinated pyrrole models. A significant lowering of activation energy of the rate-determining step by 11.3 kcal/mol is found for the ClAlMe_3^- model compared to the smaller Cl^- model. This result suggests that the full aluminate anion may have an important role in controlling the reactivity of the Cr-pyrrolyl catalyst system.

Dr P. J. Steynberg, Research and Development, Sasol Technology (Pty) Ltd., said "The use of density functional theory modeling was vital in this work because it allowed for an efficient theoretical investigation and understanding of the chromium catalyzed ethylene trimerization mechanism which was hitherto unavailable. Chromium oxidation states with unpaired electrons are notoriously difficult in quantum calculations and the latest version of MS Modeling's DMol³ proved to be very efficient in handling these systems."

References

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