Spectroscopic investigation of the activation of a chromium pyrrolyl ethene trimerization catalyst

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Introduction. Selective ethene oligomerization is an industrially applied process which is used to produce either 1-hexene or 1-octene. Various catalytic systems have already been commercialized and typically consist of a chromium precursor, a ligand and alkylaluminium activators. Despite commercial success of these systems, questions remain regarding the operation mechanism of these catalysts. It is known that the mechanism involves metallacyclic intermediates and that the metal operates via a Cr\textsuperscript{n}/Cr\textsuperscript{n+2} redox couple. It however remains subject to debate whether this is a Cr\textsuperscript{I}/Cr\textsuperscript{III} or a Cr\textsuperscript{II}/Cr\textsuperscript{IV} redox couple\textsuperscript{1}.

In this study we have applied, amongst others, Cr K edge XAS spectroscopy to study the first commercialized ethene trimerisation catalyst system (Chevron Phillips Chemical), i.e. chromium 2-ethylhexanoate, triethylaluminium (AlEt\textsubscript{3}), diethylaluminium chloride (AlEt\textsubscript{2}Cl) and 2,5-dimethylpyrrole (DMP)\textsuperscript{2}.

Experimental methods. The system under investigation consists of chromium 2-ethylhexanoate, DMP, AlEt\textsubscript{3} and AlEt\textsubscript{2}Cl, mixed in a ratio of 1:3:11:8 respectively. The system was investigated using EPR, stopped-flow UV-Vis and freeze-quench XAS. The composition of the reaction mixture was probed at various points in time to gain information about its composition. The XAS information obtained is combined with different complementary spectroscopic methods as well as catalysis to obtain a complete picture of the activation of the catalyst.

Results and discussion. Reaction of the Cr\textsuperscript{III} precursor with a mixture of AlEt\textsubscript{3}, AlEt\textsubscript{2}Cl and DMP leads to reduction of the Cr\textsuperscript{III} precursor to a novel Cr\textsuperscript{II} carboxylate. This complex shows no incorporation of the pyrrolyl ring yet. Over time, this Cr\textsuperscript{II} carboxylate is partially converted to a novel chloro-bridged dinuclear Cr\textsuperscript{II} pyrrolyl complex. Characteristic of this Cr\textsuperscript{II} species is that it shows \pi-coordination of the pyrrolyl ring to the metal center.

In addition to the formation of Cr\textsuperscript{II} complexes, Cr\textsuperscript{I} complexes are being formed. In cyclohexane, a small quantity of an unknown Cr\textsuperscript{I} complex (<1%) is being formed; this complex is unobservable via XAS, but can be probed with EPR. In toluene, a much larger quantity of Cr\textsuperscript{I} complexes is being formed; this is due to the facile formation of bis(arene)Cr\textsuperscript{I} complexes in aromatic solvents in the presence of alkylaluminium complexes. It is proposed that the formation of these bis(arene)Cr\textsuperscript{I} complexes leads to deactivation of the catalyst in aromatic solvents.

Conclusion. Spectroscopic characterization shows facile reduction of the Cr\textsuperscript{III} precursor to multiple Cr\textsuperscript{II} complexes. Solvent was found to have a significant effect on activation: in the presence of aromatic solvents, deeper reduction to Cr\textsuperscript{I} becomes more facile. Formation of Cr\textsuperscript{I} complexes in toluene could explain the reduced performance of the catalyst in aromatic solvents.

References.

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