



Insights in the mechanism of selective olefin oligomerisation catalysis using stopped-flow freeze-quench techniques: A Mo K-edge QEXAFS study

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ABSTRACT

The activation of $[\text{MoX}_3(\text{L})]$ (with $\text{X} = \text{Cl}, \text{Br}$; $\text{L} =$ tridentate ligands with S_3 and SNS donor sets) by AlMe_3 , analogous to the industrially important $[\text{CrCl}_3(\text{L})]$ catalysts for selective oligomerisation of alkenes, has been investigated by Mo K-edge X-ray absorption (XAS) and UV–visible spectroscopies. Time-resolved stopped-flow XAS, in combination with a newly developed anaerobic freeze-quench approach, have established the complete alkylation of the Mo centres and a slower, stepwise sequence for $[\text{MoBr}_3(\text{L})]$. No evidence for directly bonded or bridged Mo–Mo dimers was observed at the high Mo: AlMe_3 ratios used in this study. Decomposition of the complexes is in competition with the activation and resulted in precipitation of particulate Mo over time and explains the deactivation as observed in catalytic tests. The novel freeze-quench approach, which can trap reaction solutions within 1 s of mixing, opens up a large field of homogeneous catalysis and liquid chemistry to be studied, being able to quench this rapidly, whilst characterisation techniques with long data acquisition can be performed.

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1. Introduction

The efficient catalytic conversion of small molecules into more complex species in commercial demand continues to be a very important feature of the global chemical industry, and the ability to increase the specificity and selectivity of these processes is essential for clean, energy efficient processes. Oligomerisation of alkenes usually occurs via transition metal or aluminium catalysed processes to produce mixtures of alkenes in the C_4 – C_{26} range [1,2]. However, the selective trimerisation and tetramerisation of ethene to produce the linear α -olefins (LAOs) 1-hexene and 1-octene, respectively, are of major significance due to the importance of these co-monomers in the production of linear low-density polyethylene (LLDPE) [2–4]. LLDPE accounts for around 50% of the LAO co-monomers produced industrially. A variety of transition metal catalysts facilitate the selective trimerisation of ethene, most of which are based on early transition metals such as titanium, tantalum or, most importantly, chromium [2–4]. These form the basis of several key industrial catalysts, including the Phillips pyrrolide system, the Sasol mixed heteroatom systems and the BP diphosphine systems [5–7].

The extremely high selectivity for 1-hexene is thought to occur via a mechanism based upon a metallocyclic intermediate formed through the reaction of Cr(III) pre-catalysts with ethene in the presence of methylaluminoxane (MAO) co-catalyst [2,6,8]. The auxiliary ligand on Cr(III) is generally a tridentate ligand incorporating Group 15 or 16 donor atoms, e.g. $[\text{CrCl}_3(\text{SNS})]$ ($\text{SNS} = \text{RS}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{SR}$) and $[\text{CrCl}_3\{\text{R}_2\text{P}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{PR}_2\}]$ ($\text{R} =$ long-chain alkyl group). Chromium complexes containing the ligand $\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2$ (PNP) are highly selective catalyst precursors for the tetramerisation of ethylene to 1-octene when activated with MAO, and improved activities are achieved when aluminate or BARF activators are introduced [9–11]. The pursuit of catalysts with ever higher specificities and selectivities for these oligomerisations and polymerisations demands a detailed understanding of the individual stages of the catalytic cycle, the dependence upon metal, promoter and/or co-catalyst. However, developing such catalyst systems is hindered by characterisation difficulties due to the paramagnetism of the majority of the Cr complexes (precluding NMR analysis), and since MAO is not a single chemical entity, therefore its precise role is difficult to establish. The role of the ligand donor types (hard versus soft) and architectures are undoubtedly very important in defining the mechanisms in these processes, promoting different reaction pathways. Further, whilst Cr complexes with softer P/S donor atoms tend to lead to trimer/tetramer, the use of harder donor ligands only (e.g. amines) favours a Shultz–Flory distribution of oligomers [2].

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Work on the industrially important $[\text{CrCl}_3(\text{SNS})]$ with various alkylating agents by Gambarotta and co-workers suggests that at low Cr:Al ratios Cl-bridged dimers are formed, including $[\{(\text{SNS})\text{CrMe}\}_2(\mu\text{-Cl})_2]^{2+}$ [12]. Braunstein et al. have also recently shown that for the $[\text{CrCl}_3(\text{NPN})]$ (NPN = bis(2-picolyl)phenylphosphine) chloro-bridged dimers, as well as mononuclear clusters with a mixture of alkyl and halide ligands can be formed, depending on the alkylating agent and reaction conditions [13]. It is however important to note that the ratio of Cr:MMAO in the operating catalyst system is significantly higher than used in these studies.

Previously, we have examined a range of Cr(III) complexes with various neutral tridentate N-, S- and O-donor ligands comprised of three distinct architectures: facultative ($\text{S}(\text{CH}_2\text{CH}_2\text{SC}_{10}\text{H}_{21})_2$ (SSS-Decyl) and $\text{O}(\text{CH}_2\text{CH}_2\text{SC}_{10}\text{H}_{21})_2$ (SOS-Decyl), tripodal ($\text{MeC}(\text{CH}_2\text{SC}_4\text{H}_9)_3$, $\text{MeC}(\text{CH}_2\text{SC}_{10}\text{H}_{21})_3$) and macrocyclic ($\text{C}_{10}\text{H}_{21}_3[9]\text{aneN}_3$ ($[9]\text{aneN}_3 = 1,4,7\text{-triazacyclononane}$) as catalysts for olefin oligomerisation and polymerisation and probed the identity of the species before and after addition of the molecular alkylating agent, AlMe_3 , using IR, UV/visible and EPR spectroscopy along with X-ray Absorption Fine Structure (XAFS) studies [14]. Treatment of these complexes with excess (300 mol. equivs.) modified MAO (MMAO) leads to catalytically active species and shows significant dependence upon the ligand donor set. UV/visible and EPR measurements suggest that a change in the oxidation state of the chromium metal centre occurs in all these examples upon addition of excess AlMe_3 , lending support to the proposal that the catalysis involves a Cr(II)/Cr(IV) redox cycle. The partial structures of the AlMe_3 -activated species were probed via XAFS spectroscopy. It appears that when the Cr(III) complexes are treated with AlMe_3 , the Cl ligands are substituted by methyl groups and some ligands substantially dissociate from the metal centre; with the resulting species catalysing the oligomerisation and polymerisation of ethylene.

Whilst these are the first XAFS studies probing the activation of the Cr-based oligomerisation/polymerisation pre-catalysts, the timescale for the measurements (usually 2–4 h to acquire sufficient data from ~ 5 mM solutions – corresponding to the approximate Cr concentration in the operating catalyst – for partial structure analysis) mean that, by definition, these are ‘end-state’ investigations. The information that can be obtained from such measurements provides limited insight into the active species given that under the operating conditions the catalyst lifetime is typically < 1 h.

XAS (in energy dispersive mode (EDE)) was for the first time successfully synchronised with a stopped-flow experiment in 1990, in which the oxidation of Fe^{III} aq by hydroquinone was investigated [15]. More recently, stopped-flow systems have been developed for homogeneous catalysis studies, to probe homogeneous catalytic intermediates *in situ* and time-resolved (milliseconds) [16–18]. In the stopped-flow system, the evolution of the reaction mixture can be monitored in time with EDE or Quick-XAS (QEXAFS), allowing full Extended X-ray Absorption Fine Structure (EXAFS) spectra to be obtained in the millisecond to second timescale [19]. The problem with this set-up is that XAFS data acquisition in fluorescence mode is not possible (only transmission), and therefore, a relatively high concentration of the species under investigation is required. At the same time, the complete reaction mixture, i.e. including solvents and reagents, should not be too absorbing at the X-ray energies required for the experiment. The stopped-flow EDE method has been proven for homogeneous Pd¹⁶ and Re [20] systems with a high energy Pd K- and Re L-edge, enabling the *in situ* transmission experiments. However, although the method has been proven for homogeneous Ni (8.333 keV)¹⁶ and Cu (8.979 keV)¹⁸ systems, the Cr K-edge is at an even lower energy of 5.989 keV. Not only the solvent and reactant molecules, but even a few cm of air, are highly absorbing at these energies, severely hampering the transmission experiment.

We have pursued two methods to allow easier characterisation of these catalytic systems: (i) substituting the Cr(III) for the heavier 4d Mo(III) organometallic systems to model the early stages of the activation and (ii) modification of the stopped-flow system in order to maintain the advantages of the time resolution of the instrument, but also trapping the intermediates to allow long data acquisition via XAS to be conducted.

1.1. Mo(III) complexes

We have prepared the analogous Mo(III) trichloro complexes, $[\text{MoCl}_3(\text{L})]$ (L = SNS and SSS) and investigated their utility as stoichiometric model systems for the Cr catalysts by determining their reactivities with AlMe_3 . $[\text{MoCl}_3(\text{SNS-R})]$ complexes for a variety of R groups have been reported previously, although they show negligible catalytic activity towards ethene oligomerisation [21]. However, it is reasonable that the Mo systems might undergo similar chemistry in the early stages of activation, the slower kinetics at Mo will aid identification of individual species in the reaction. Furthermore, the Mo systems are also chosen as model systems because of the higher Mo K-edge energy at which the X-ray experiment can be undertaken and thus the increased time resolution of the XAS experiment to be obtained. Mo will allow time-resolved transmission studies in which real reaction intermediates are likely to be probed instead of the final (often decomposed) end-states of the Cr systems. With the Mo K-edge being present in the similar high energy range of Pd (i.e. ~ 20 keV)¹⁶ the potential of the stopped-flow EDE approach for these systems is high. In a further modification, the $[\text{MoBr}_3(\text{L})]$ analogues were also synthesised in order to aid distinction between the S of the ligand and the halide in the EXAFS analyses, which is not possible for S and Cl since they are corresponding neighbours in the periodic table with similar backscattering amplitudes.

1.2. Stopped-flow freeze-quench XAS development

In order to overcome the inherent obstacles associated with stopped-flow XAS studies, as mentioned, and to allow accurate characterisation of reaction intermediates, a XAFS cell that allows ‘trapping’ (stabilisation) of the intermediate species present at various stages of activation and catalysis reaction, by rapid quenching of the catalyst system is required. With the catalytic intermediate ‘trapped’, XAFS experimentation can subsequently be performed in fluorescence mode with long data acquisition times as required for low energy systems like Cr. The development of such a XAFS quench cell to allow highly reactive transients to be trapped on a sub-second timescale and analysed structurally and electronically will be complementary to the established stopped-flow EDE procedure, allowing in principle the in-depth study of any homogeneous process. This approach will provide detailed structural and electronic insights in homogeneous (catalytic) reaction mechanisms. Although freeze-quench (also in combination with stopped-flow methodologies) is used frequently for biological and bio-inorganic systems [22], this is a new approach in homogeneous catalysis and requires considerable modifications of the apparatus (*vide infra*).

Here, we report on the Mo(III) organometallic complexes and their activation with AlMe_3 , as well as a special quench-freeze XAFS cell designed to allow detailed XAFS and XANES studies to be performed to probe the early stages of activation and catalysis and thus provide a more detailed understanding of the activation stages of the polymerisation and oligomerisation catalyst systems rather than end-state studies. The results are shown for Mo systems, and their analogy to the Cr is made.

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