Catalytic construction

Dr Susannah Scott describes her group's fascination with the Phillips catalyst and how they hope their research will increase the efficiency in catalysts associated with commercial polymerisation processes

Could you begin by providing an overview of your project and its key objectives?

The coordination polymerisation of α-olefins to form polyolefins is a major class of commercially important catalytic reactions. The most widely used is polyethylene; it is durable, lightweight, strong, chemically resistant, non-toxic and readily recycled, and whilst usually made from petrochemical ethylene, polyethylene is now also being manufactured from renewable feedstocks, via dehydration of carbohydrate-derived ethanol. Long-chain macromolecules are generated through enchainment of the ethylene monomer subunits, giving rise to the polymer; the Phillips catalyst mediates each step in the process.

The active site of the catalyst is a cation of a transition metal, chromium (Cr), that captures the monomer, guiding its insertion into a growing polymer chain coordinated to the same metal site. Early chain termination leads to oligomers of varying sizes that can be reincorporated into a growing polymer chain to provide branches. Both short and long chain branches are generated spontaneously during polymerisation by the Phillips catalyst, ultimately determining the properties of the polymer, such as its flexibility and impact strength.

From the broad distribution of molecular weights in the polymer, we know that there are multiple types of active sites, but their precise nature is not known; it is likely that certain sites generate oligomers, while others are responsible for making polymers. This lack of understanding limits our ability to control the polymerisation process; we aim to construct knowledge about the number and types of sites participating in the reaction, as well as those that do not, in order to create well-defined catalysts.

One of your major goals is to develop a unified framework for understanding and controlling the ability of supported metal oxide catalysts used in olefin transformations. Could you explain more about this framework and its importance?

We are fascinated by the Phillips catalyst's unique ability to initiate ethylene polymerisation spontaneously, without a co-catalyst to supply the first metal-carbon single bond. The Phillips catalyst also shows increasing activity with time on-stream in the reactor, suggesting that new active sites are continuously being formed, or that deactivated sites are being reactivated.

There are related types of supported metal oxide catalysts that initiate olefin metathesis spontaneously, without preexisting metal-carbon double bonds; interestingly, these catalysts contain metals closely related to Cr (Mo, W and Re).

We believe these catalysts contain the key to making catalysts 'resilient', or capable of generating their own active sites on demand and regenerating them when deactivated. They have considerable appeal because of the potential to extend active site longevity, making catalysts more productive and requiring less metal, which we recognise as valuable, and sometimes strongly limited, natural resources. We aim to extend this concept to other types of catalysts where the use of rare or exotic metals makes increased productivity highly desirable.

What aspects of your project are the most challenging?

Since we cannot conduct real catalytic reactions in a high vacuum chamber, it is very challenging to handle small amounts of extremely air-sensitive materials. The organochromium sites in the active catalyst are highly dispersed and very dilute. Fortunately, we know when they have been compromised (usually by exposure to traces of oxygen) because they are no longer able to initiate polymerisation. It is also hard to synthesise active sites on a surface because purification – that is, separation of the desired product from all the byproducts to obtain a uniform material – is generally not possible. We have to design highly selective reactions that produce only volatile byproducts, so that we can remove them by evacuation.

What have your results revealed so far and how do they impact on your research going forward?

We have learned that silica-supported organochromium (IV) sites, are simply not active enough to be considered competent sites in the Phillips catalyst. We have identified the immediate environment of the organochromium sites, including chromasiloxane ring size and additional Cr-siloxane interactions involving the silica support, as contributing to the heterogeneity of the active sites. It appears that the polymerisation active sites are neutral organochromium (III) moieties bound to a non-displaceable siloxane ligand, while the oligomerisation active sites are neutral organochromium (IV) species for which additional siloxane coordination is absent.

What are the wider implications of your research?

Until now, catalyst discovery has always been largely dominated by serendipity. Understanding the essential features of the active sites will allow us to design new catalysts, or modify existing ones, in a rational way for the first time and thereby fine-tune catalytic reactions to be more efficient and selective.

Driving innovation in catalyst synthesis

Researchers at the University of California are applying their expertise in chemistry and chemical engineering with both experimental and computational modelling to study catalysts used in polyethylene production

WITH A HUGE range of consumer and industrial applications, polyethylene is the world's most common plastic. Like many influential developments in the history of science, the discovery and subsequent rediscovery of polyethylene synthesis was accomplished largely by accident. However, since the first reproducible methods were developed at ICI in 1935, this ubiquitous material has become a familiar feature of modern life across the globe.

The most widely used type of polyethylene is the crystalline, high density form (HDPE): more than 30 million tonnes are produced worldwide every year in durable, sterile, biocompatible and weather-resistant products ranging from toys (the Hula Hoop was the first successful application, in 1954), to detergent bottles and rubbish bins. Easily assembled modular pressure pipe systems are another common application of this tough, inert plastic. Ultrahigh molecular weight polyethylene is used to make bullet-proof clothing, and in artificial joint (hip, knee, spine) replacements.

Polyethylene is formed from ethylene, upon contact with a catalyst, in a highly exothermic polymerisation process. A thermoplastic consisting of long hydrocarbon chains, its varying mechanical properties depend on the degree of crystallinity in the polymer and the amount of branching in its chains. With a low degree of branching, HDPE exhibits stronger intermolecular forces and tensile strength. More branches can be introduced by copolymerising ethylene with longer olefins, allowing some degree of control over the final polymer properties.

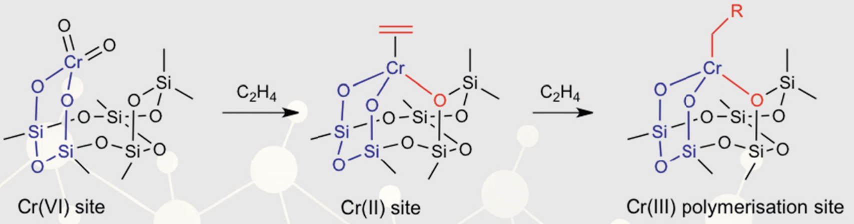
CATALYSTS FOR ACTION

Catalysts promote the rates of chemical reactions by providing alternate pathways with lower energy barriers relative to the corresponding uncatalysed reactions. For highly active polymerisation catalysts, monomer insertions can occur many thousands or even millions of times per second. The large amount of heat generated by the reaction must be quickly dissipated to avoid decomposition of the catalyst. To control the polymerisation rate, active sites can be dispersed on a finely divided solid support, such as amorphous silica, using the resulting catalyst particles to create a fluidised bed in the polymerisation reactor. Catalysts are used to induce polymerisation at milder temperatures and pressures, and to affect the molecular structure of the polymer; the environment of the active catalyst site controls the orientation of the monomer during enchainment, as well as frequency of chain termination and branching.

The Phillips catalyst, which is prepared by depositing chromium (VI) oxide on silica, is one of the most widely-used supported catalysts for polyethylene, along with the Ziegler-Natta catalysts (named after the scientists who received the 1963 Nobel Prize for developing them). Both methods are commonly used in industrial application, but the Phillips catalyst is less expensive and more versatile in terms of the range of polyethylene types it can make. It was discovered in 1951 at Phillips Petroleum, when researchers attempting to make synthetic gasoline from natural gas over a nickel catalyst added a chromium promoter. The small amount of white powder produced turned out to be a new material, crystalline polypropylene, and the discovery gave rise to a whole new industrial process. A team of researchers, led by Dr Susannah Scott and co-principal investigator Dr Baron Peters of the University of California, is looking into unraveling the nature of the active sites in the Phillips catalyst.

Many previous studies have failed to make much headway because the fraction of chromium sites that polymerise ethylene is very small, typically on the order of 1 per cent. Spectra of the solid catalyst are often dominated by signals from inactive sites, or from the bulk polymer. Attempts to make well-defined, small molecular models have also failed in reproducing the self-activating behaviour of the Phillips catalyst.

The team at the University of California opted to embark on a synthetic strategy involving the



rational construction of well-defined active sites that involve silica itself as a supporting ligand. This requires making choices about the metal, its oxidation state and its nearest neighbours.

The surface of amorphous silica is terminated with hydroxyl groups, which provide a convenient point of attachment for active sites; both inorganic and organochromium complexes in various oxidation states were allowed to react with these surface hydroxyl groups to create highly uniform, grafted active site candidates. By evaluating their reactivity individually, relationships between structure and activity were uncovered, adding to our knowledge of how the real Phillips catalyst functions.

A MULTIDISCIPLINARY COLLABORATION

Computational modelling was a key part of the project; reaction mechanisms were modelled *in silico* to identify key transition states. This analysis aided in the assignment of experimental spectra by predicting spectroscopic signatures associated with specific structures. For structural analysis by X-ray absorption spectroscopy, it provided models to use for comparison between computed and fitted interatomic distances, and proved an excellent way to test mechanistic hypotheses, since it enabled the calculation of activation barriers that ruled out energetically prohibitive reactions.

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The challenge with computational modelling for this type of catalyst is that precisely how the active sites interact with the support is still a mystery, since the silica itself is an amorphous material. It has been shown that the support is critical to the reactivity of the sites, and probably contributes to the active site heterogeneity, but it is not yet possible to represent this heterogeneity computationally, other than to compute a number of possible structures. Whether the best guesses of the team included the actual structures is still unknown.

The project involved collaboration between experts in chemical engineering and chemistry, a crossing of disciplines which brings many benefits. The science of chemical synthesis – that is, designing new materials with a pre-determined, desired structure and making them with atomic-level precision – is well understood by chemists, yet heterogeneous catalysts are not made in this way. Instead, chemical engineers design processes using them based on their practicality. The team at the University of California brought the power of synthesis to bear on the study of this important class of materials for the first time, with successes in numerous areas. Using techniques from synthetic organometallic chemistry the team synthesised a family of molecular complexes to mirror the reactivity of organochromium (IV) intermediates, measuring their structural parameters using X-ray absorption spectroscopy. They also studied the variability inherent in the ability of amorphous silica to act as a ligand, and synthesised highly-uniform Cr (II) active site precursors, by reducing grafted chromium sites, to study the mechanism by which the organochromium sites are formed.

This study represents a major step in the direction of improved polymerisation catalysts. Thanks to this groundbreaking work, the future will undoubtedly allow them to answer more questions about these complex systems. For example, incorporating Ti is known to accelerate the onset of polymerisation; deconstructing the origin of this effect may shed light on how the first active sites are formed, and supports other than silica, such as isoelectronic $AlPO_4$, may also now be investigated for their potential to make ethylene oligomers selectively.

INTELLIGENCE

A SYNTHETIC APPROACH TO ACTIVE SITE DECONVOLUTION IN SUPPORTED Cr CATALYSTS FOR OLEFIN POLYMERISATION

OBJECTIVES

The goal of the project is to develop a unified framework for understanding and controlling the ability of supported metal oxide catalysts used in olefin transformations, specifically olefin metathesis and polymerisation, to self-activate in the presence of the substrate. The activity profiles and product distributions for well-defined model catalysts will be correlated with sites of well-defined geometrical and electronic structure.

KEY COLLABORATORS

Professor Jeroen van Bokhoven of ETH-Zurich, deploys X-ray absorption spectroscopy to analyse the structure of supported catalysts • **Professor Al Stiegman** of Florida State University, synthesises model systems • **Professor Boping Liu** of East China University of Science and Technology, Shanghai, studies the behaviour of supported polymerisation catalysts • **Dr Takashi Mono**i of Japan Polyethylene Corporation, is investigating the commercial potential of new types of Phillips catalysts.

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