A Flat Model Approach to Tethered Bis(imino)pyridyl Iron Ethylene Polymerization Catalysts

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Summary: A surface science model for a silica supported bis(imino)pyridyl iron complexes is applied to reveal the surface chemistry of these heterogeneous polymerization catalysts. The polymerization activity of these models and the molecular weight distribution of the resulting polymer are comparable to similar catalysts supported on amorphous silica. The catalyst deactivates partially during the first hour of ethylene polymerization. Based on photoelectron spectroscopy (XPS) we attribute this deactivation to iron extrusion by the aluminium alkyl activator.

Keywords: bis(imino)pyridyl iron catalyst; catalyst deactivation; model catalyst; photoelectron spectroscopy; polyethylene

Introduction

After decades of domination by the classic Ziegler-Natta and Phillips catalysts in catalytic production of polyolefin, metallocene and other homogeneous catalysts are now presenting new opportunities for the polyolefin industry. However, few people believe that the homogeneous catalysts will replace the established catalyst systems in the near future. The biggest problem for the homogeneous system is that during polymerization, uncontrollable polymer growth takes place, which causes undesired depositions of polymer on the walls and other components of the reactor.

To circumvent this ‘‘fouling’’ problem and let the reactor run continuously for weeks, months or even years without shutdown, one of the solutions is to run the polymerization in a solution medium which can dissolve the resulted polymer or apply the process above the melting point of the polymer. Yet another solution, which is much more universal, is to immobilize the homogeneous catalysts to a carrier and to apply them in the so-called particle-forming technology with gas- or slurry-phase processes.

Gas- or slurry-phase processes have been used for Ziegler-Natta and Phillips catalysts for polyolefin production for more than 50 years and are extremely efficient and well-understood technologies. The success of these processes relies on the forming of the polymer particle of appropriate size and shape, replicating the morphology of catalyst particle. Various materials, such as silica gel, $MgCl_2$ or polymers, have been used as the carrier to immobilize the homogeneous polyolefin catalysts. Among them, silica gel is the one receiving most attention.[1,2] This choice is based on several reasons: firstly, chemists have studied and used silica as catalyst support for Ziegler-Natta and Phillips catalysts for decades; secondly, the preparation of silica particles with desired physical and chemical properties is a well-refined art; last, but not the least, surface hydroxyl groups from silica surface provides various opportunities for chemists to attach catalysts via surface reactions.

There are two major approaches to immobilize homogeneous polyolefin cata-

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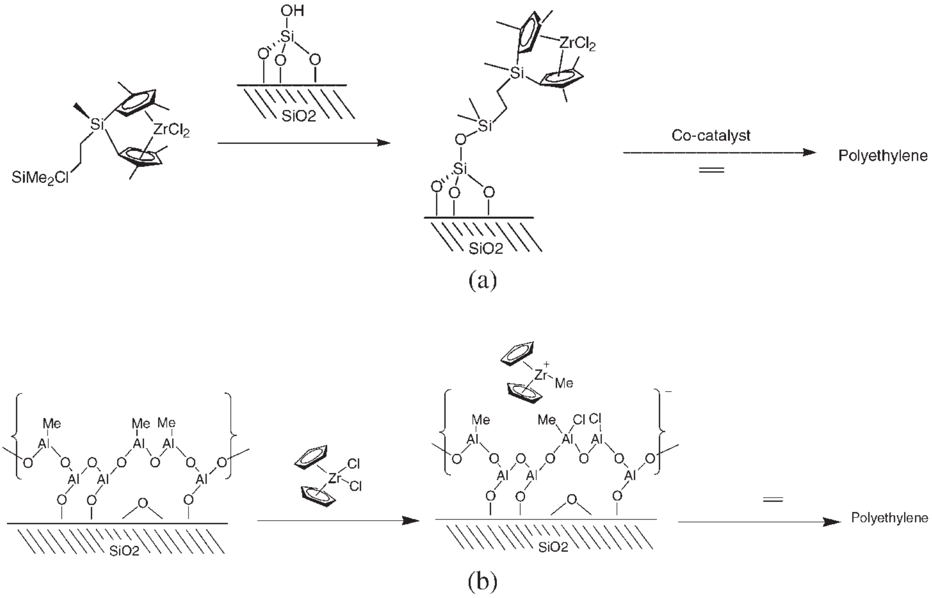
lysts to the silica surface. One is to immobilize the catalyst precursor component to the support, followed by addition of the co-catalyst (an example is shown in Scheme 1(a)); the other is to immobilize the co-catalyst with subsequent addition of a catalyst precursor (an example is shown in Scheme 1(b)).

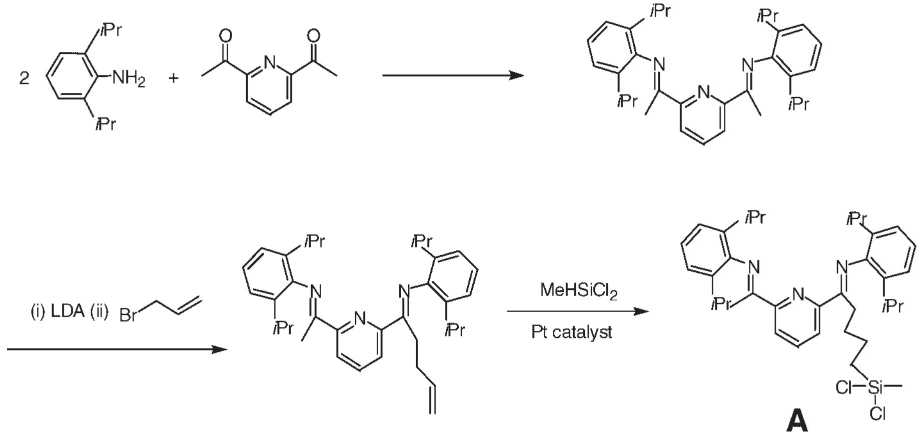
In order to elucidate the surface chemistry of heterogeneous olefin polymerization catalysts we have developed model catalyst, which are supported on flat carrier, usually silicon wafers covered with an ultra flat layer of thermal silicon oxide. Such model catalyst offer several advantages for fundamental studies on (olefin polymerization) catalysts[3]

- All catalytically active material is exposed and not hidden in pores. This makes it easier to achieve a correlation between catalyst activity and surface characterization: the surface that is probed by spectroscopy techniques is identical to the active surface.
- The polymer growth occurs in the direction normal to the catalyst plane to form a film with fractioning of catalyst particle which gives access to the intrinsic kinetics of polymerization of heterogeneous catalyst.
- The silica layer is sufficiently thin to conduct and minimize the effects of charging on applying techniques like X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM).

We have developed to investigate the Phillips catalyst and detailed insight into the surface chemistry of the active phase[4,5] (chromate species anchored to silica), polymerization activity and kinetics[6–10] and into the interplay between the catalysts and the nascent polymer morphology [11] In an attempt to model silica-supported single-site catalysts impregnated Metallocene catalysts with MAO or borate co-catalysts on flat silica for ethylene polymerisation.[12,13] However, in these initial studies of supported homogeneous catalysts, the active sites lacked covalent bonding to the catalyst surface, which resulted in the formation of inhomogeneous polyethylene film with ball shaped particles upon polymerization in gas phase. Nevertheless, in

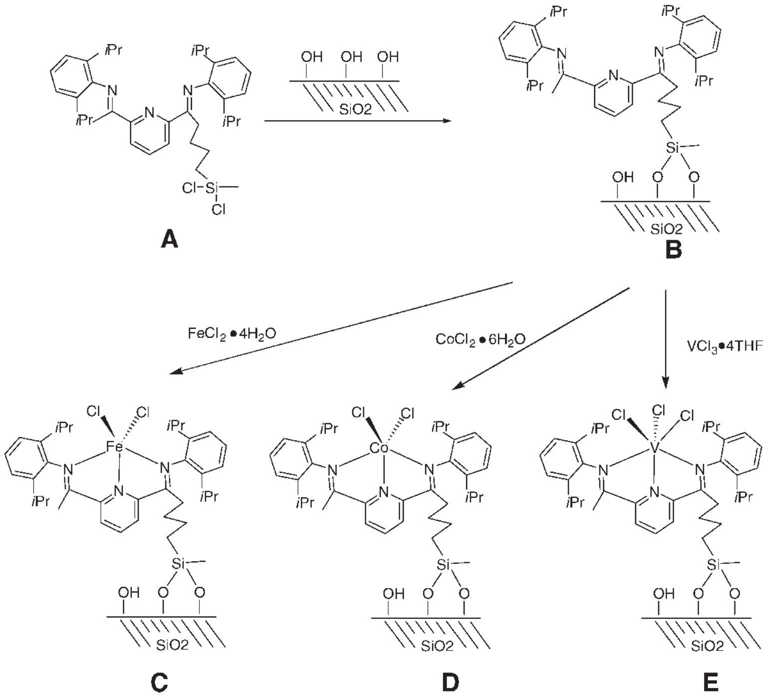


Scheme 1.
Examples of how to immobilize catalysts for ethylene polymerization (adapted from reference[1]).



Scheme 2.
Synthesis of the bis(imino)pyridyl ligand with a ω-chlorosilane function attached to the acetyl position (A).

an ideal supported catalyst system, the catalysts should be anchored to the surface and remain strongly immobilized during polymerization. For that reason we developed immobalized bis(imino)pyridyl metal complexes[14,15] as well-defined model systems for supported homogeneous polyolefin catalysts. In this communication we describe some aspects of the surface chemistry of these model catalysts, their polymerization properties, kinetic profile and catalyst deactivation.



Scheme 3.
preparation of anchored bis(imino)pyridyl metal complexes.

Experimental Part

Details on catalyst preparation and analytical techniques used in this work have been published elsewhere.[16,17] Briefly the bis (imino)pyridyl ligand with a ω-chlorosilane function (complex A) is prepared as described in.[18,19]

This ligand reacts with the surface hydroxyl groups of the silica wafer to form a tethered bis(imino)pyridyl ligand (B). Treating these surface ligands with metal chlorides affords the anchored bis(imino)-pyridyl metal complexes (C-E).

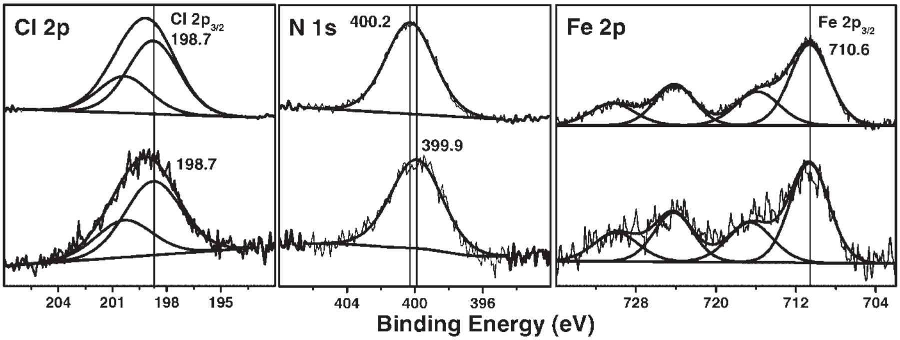
Anchoring of Supported Bis(imino)pyridyl Iron Complexes to the Flat Silica Support

Bis(imino)pyridyl by complex (A) readily reacts with the surface silanol function of the flat silica support. The surface coverage of the anchored complex can be tuned by varying the concentration of the grafting solution, the impregnation time and the dehydroxylation temperature of the silica surface, the maximum loading of the ligand amounts to about 0.5 nm^{-2}, which is slightly less than the 0.7 nm^{-2} reported by Hermann et.al.[18] XPS confirms that grafting of metal chlorides complexes in gives the corresponding metal complexes in quantitative yield.[16]

Ethylene Polymerization Over Supported Bis(imino)pyridyl Iron Complexes

Bis(imino)pyridyl iron complex (C) that is supported onto the flat silica model substrate becomes an extremely active ethylene polymerization catalyst when activated with aluminium alkyls.[16] The polymerization activity (1.8 $kg_{(PE)}$ $(mmol_{cat}\ h\ bar)^{-1}$ for a three hour polymerization runat room temperature) is very reproducible and independent on the ethylene pressure. Even though the molecular weight distribution is broad ($M_w/M_n \approx 10$) the MWD curves remain unaltered when changing the ethylene pressure.

The above observations clearly indicate that both chain propagation and termination and chain termination are first order in ethylene pressure, which is in agreement with observation of similar catalyst supported on amorphous silica reported by Li et.al.[20] while homogeneous catalysts result in a more or less pronounced low molecular weight fraction in the MWD, which is attributed to chain transfer to aluminum being 0th order in ethylene.[21] This chain termination channel is blocked in the presence of a silica surface. If we assume a Cossee-Arlman propagation mechanism as is generally accepted for this type of catalyst[21] the broad molecular weight distribution reflects the presence of more



XPS spectra of purified bis(imino)pyridyl iron complex and the silica supported bis(imino)pyridyl iron complex supported on a flat silica substrate (C)

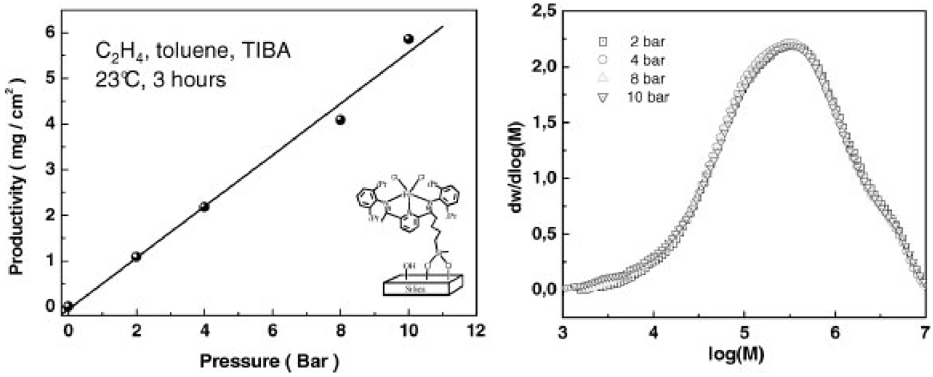


Figure 1.
Effect of ethylene pressure on productivity the molecular weight distribution using SiO_2/Si(100) wafer-supported iron catalyst (C).

than one type active site during polymerization. It is interesting to note that we observe extremely reproducible MWD curves even though the catalytic system involves multiple sites. In addition the catalyst deactivates rapidly especially during the first hour of polymerization while a significant catalyst activity remains even after several hours of polymerization. At the same time the distribution shifts

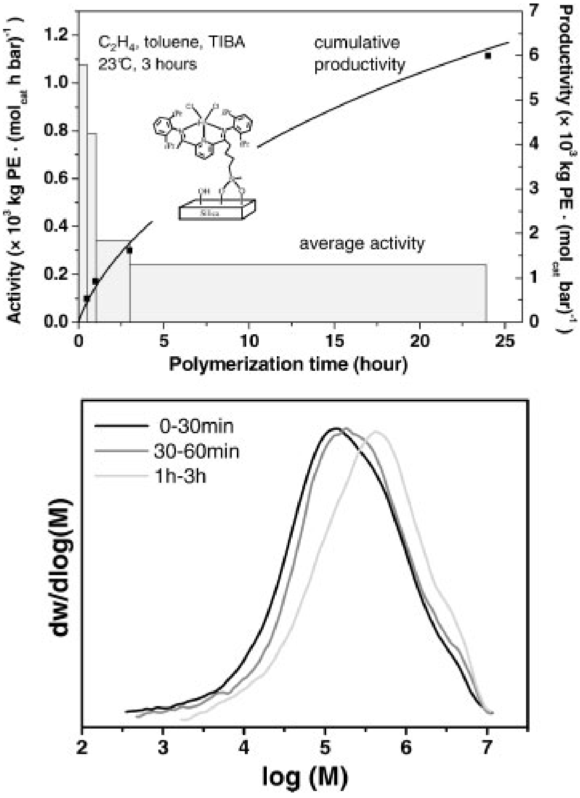


Figure 2.
Effect of polymerization time on polymerization activity and molecular weight distribution (MWD).

significantly towards higher masses indicating that the propagation rate deactivates slower than the termination rate, presumably as low molecular weight sites deactivate faster than high molecular weight sites.

Stability of the Supported Bis(imino)pyridyl Iron Complexes

This degradation is not dependant on the ethylene pressure and is probably related to the degradation of the active bis(imino)-pyridyl iron complexes by reaction with the aluminium alkyl including ligand alkylation or extrusion of the iron. Such chemistry has recently been highlighted for homogeneous catalysts by Budzelaar et al.[22–25]

In an attempt to elucidate similar chemistry on our silica supported (imino)-pyridyl iron complexes we employed XPS on our model catalysts after treatment with aluminium alkyls (Figure 3).

We indeed observe a significant decrease (about 30%) in the iron concentration on the silica surface within the first hour of treatment with aluminium alkyls, while nitrogen (indicative of the bis(imino)pyridyl complex remains virtually constant. On the other hand XPS detects a monotonous increase of alumina amount on the silica surface (spectra not shown). Our results are in nice agreement with the proposed iron extrusion by iron to alumina transmetallation as proposed in ref.[23] The stability of the N1s emission with respect to intensity and peak shape may indicate that the nitrogen environment does not change further during interaction with aluminium alkyls. However, the sensitivity of XPS with respect to more subtle changes in the ligand is rather limited. We propose that the observed iron depletion is at least in part responsible for the deactivation of the supported bis(imino)pyridyl iron catalyst.

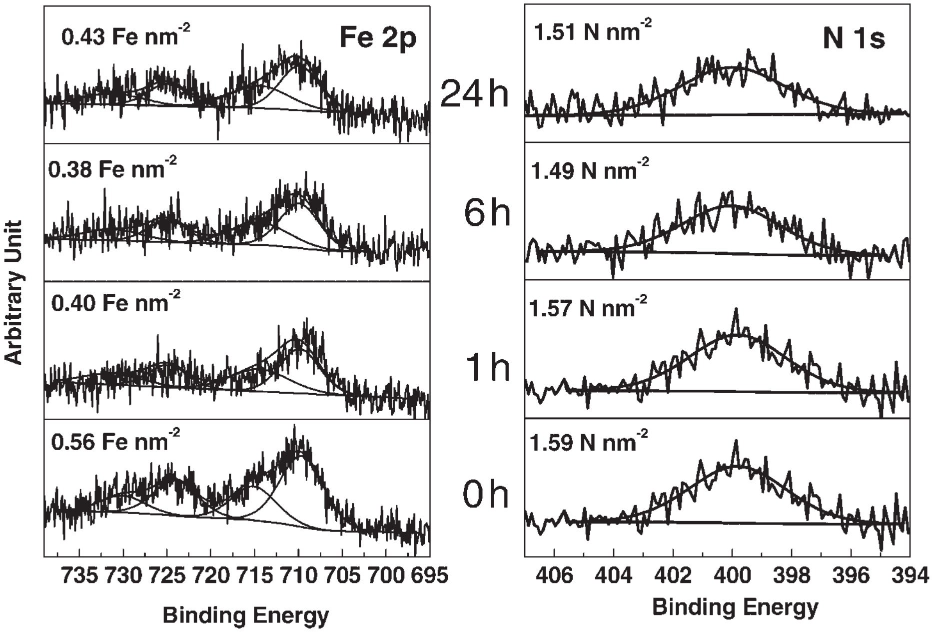


Figure 3.
Evolution of the Fe 2p and N1s photoemission upon treatment of the anchored bis(imino)pyridyl iron complexes with trisobutyl aluminium solution (0.01M in toluene) at room temperature. The iron and nitrogen surface concentration and the treatment times are indicated.

Conclusions

Flat model catalysts for silica supported bis(imino)pyridyl complexes greatly facilitate a detailed surface analysis of the heterogenized polymerization catalyst. In combination with reactivity studies and the analysis of the polymer resin this gives access to certain aspects of surface chemistry of the catalytic system, which are difficult to obtain with other approaches. In this communication we have demonstrated this approach by looking into the deactivation of the silica supported bis(imino)pyridyl iron ethylene polymerization catalyst. We attribute the deactivation to proposed iron extrusion by iron to alumina transmetallation. As this process does not completely remove the iron from the anchored ligand an appreciable polymerization activity remains even after several hours of ethylene polymerization. The stable supported iron sites are the one that produce relatively high molecular weight polyethylene. If all of the remaining iron is still active it would imply that the propagation rate is also relatively low compared to the fast deactivating fraction of the active sites.

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