

An Organic/Inorganic Hybrid Cocatalyst/Support Capable of Activating Metallocenes for the Polymerization of α -Olefins

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Introduction

In typical olefin polymerization protocols using supported single-site catalysts, methylaluminoxane (MAO) is contacted with a silica surface and the combination is used as the supported cocatalyst. To this support/activator, a wide array of single-site precatalysts can be added to give myriad different polymer products. However, quite often, severe reactor fouling and metal leaching are noticed when this approach is used in slurry reactions. As a method to prevent reactor fouling and precatalyst leaching, silica tethered olefin polymerization precatalysts have been synthesized in recent years.[1-2] Unfortunately, these materials are limited by their design – a support with a fixed precatalyst and external cocatalyst requires many different supported precatalysts be designed to obtain a versatile array of polymer products. This has motivated the design of new support/cocatalyst combinations. For instance, Marks and coworkers reported the use of sulfated metal oxides (SMOs) as a novel activator/support for olefin polymerizations.[3-4] However, the shelf-life of the SMOs is substantially limited, resulting in an inconvenient replacement for MAO/silica cocatalysts.

We present here a method using a stable organic/inorganic hybrid sulfonic acid cocatalyst capable of activating various metal precatalysts for the polymerization of ethylene or propylene when small amounts of trimethylaluminum (TMA) are added.

Materials and Methods

The synthesis of the supported sulfonic acid is similar to a previous report (SBA-FSO₃H) as shown in Figure 1A.[6] For the polymerizations, the supported fluorinated sulfonic acid was mixed with toluene (dried with sodium/benzophenone), trimethylaluminum (TMA) and the metallocene precatalyst (Cp₂ZrMe₂, Cp*₂ZrMe₂, or *rac*-Et(Ind)₂ZrCl₂) in a N₂ drybox. The reactor was removed from the drybox and ethylene or propylene was added to the reactor at 60 psig. The cocatalyst/support was characterized by the methods listed. The XRD patterns were collected on a PAN analytical X'Pert Pro powder X-ray diffractometer using Cu K α radiation and a PW3011 proportional detector with a parallel plate collimator. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a Netzsch STA409. Nitrogen physisorption measurements were conducted on a Micromeritics ASAP 2010 at 77 K. A Phi model SCA 1600 X-ray photoelectron spectrometer was used to determine surface composition of the silica substrate before and after addition of the acid precursor.

Results and Discussion

The polymerizations of ethylene (Figure 1B) or propylene with various metal precatalysts are successful when the supported sulfonic acid is mixed with small amounts of

TMA. Solution ¹³C NMR data show evidence that the perfluoro-sulfonic acid interacts with the transition metal precatalyst strongly enough to prevent the insertion of the monomer in the absence of TMA. However, the addition of TMA allows for *in situ* capping of the surface silanols (Si-OH groups), while directing the interactions of the tethered sulfonic acid groups with the aluminum metal, rather than the transition metal precatalyst. The tethered sulfonic acid is proposed to react with the TMA, creating a strongly Lewis acidic cocatalyst that can extract a methyl group from the precatalyst to form an active catalyst. Experimental data support this hypothesis, as the order of addition of components is important. There is no activity associated using TMA supported on a bare silica surface as a cocatalyst under these conditions. When performing these experiments, the TMA can react violently with the sulfonic acid groups, producing an exothermic reaction. The order that the components should be added is as follows: SBA-FSO₃H, solvent, TMA, precatalyst. Filtration tests were performed to determine if the activated catalyst leaches from the surface and performs the polymerization in solution. However, the tests indicate that the active sites are coordinated to the surface, creating an active heterogeneous catalyst, which prevents reactor fouling.

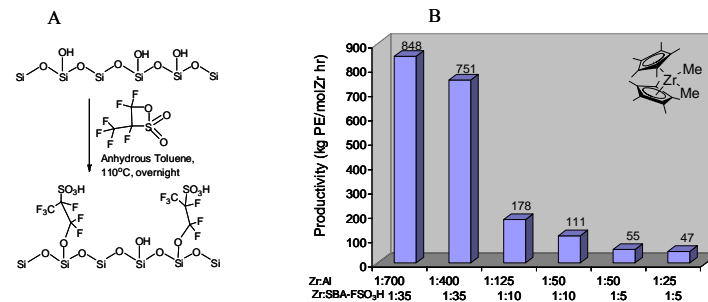


Figure 1. (A) Method of producing the supported organic/inorganic cocatalyst. (B) Ethylene polymerization data with Cp*₂ZrMe₂ using various amounts of SBA-FSO₃H and TMA.

Significance

This is the first report in the open literature involving an organic/inorganic hybrid material as a cocatalyst for olefin polymerizations. Experimental data suggests that the active catalytic sites are coordinated to the surface, which prevents reactor fouling and metal leaching. This heterogeneous cocatalyst was used with multiple precatalysts and olefins, showing the versatility of the material.

References

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