Communication

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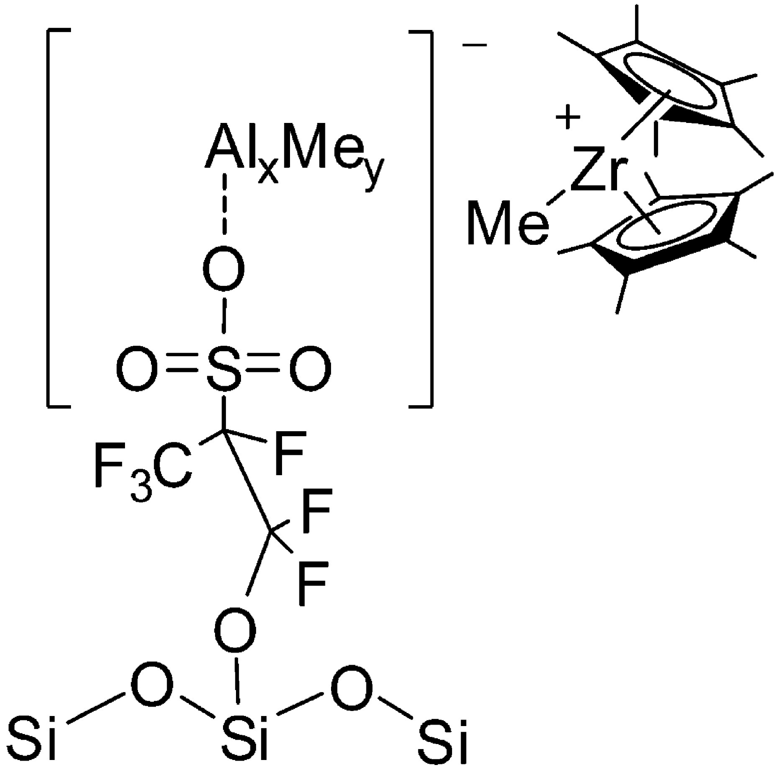

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Sulfonic Acid Functionalized SBA-15 Silica as a Methylaluminoxane-Free Cocatalyst/Support for Ethylene Polymerization

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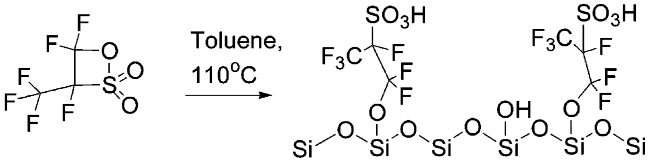
In typical olefin polymerization reactions using supported single-site catalysts, methylaluminoxane (MAO) is adsorbed on a silica support and the combination is used as the supported cocatalyst. To this supported activator, homogeneous single-site precatalysts can be added to produce different polymer products, as influenced by the symmetry of the catalyst, the monomer supplied, etc. As a method to prevent reactor fouling and metal-leaching problems, silica-tethered olefin polymerization precatalysts have been synthesized in recent years.[1] Unfortunately, these materials are impractical and limited by their design—a support with a fixed precatalyst and external cocatalyst requires many different supported precatalysts to obtain a versatile array of polymer products.

To date, only inorganic solids have been utilized as MAO-free solid activator/supports.[2,3] Marks and co-workers reported the use of sulfated metal oxides (SMOs) as support/activators for olefin polymerizations owing to their very high Brønsted acidity.[4] Organic/inorganic hybrids based on organic sulfonic acid functionalized silicas have been utilized for more than a decade in nonpolymerization applications requiring a Brønsted acid.[5] However, there are no reports of organic/inorganic hybrid cocatalyst/supports for olefin polymerization, where the organic functionality plays a critical role in the catalysis. We present here the first use of an organic/inorganic hybrid material as an effective combination cocatalyst/support for activation of various zirconocenes for production of poly(ethylene) in the presence of small amounts of alkylaluminum.

A fluorinated sultone precursor previously reported by Alvaro et al. was tethered to SBA-15 by heating the mixture in toluene at 110 °C overnight (Scheme 1).[6] The SBA-15 material was synthesized with an average Bopp−Jancso−Heinzinger (BJH) pore diameter of 65 Å and Brunauer−Emmett−Teller (BET) surface area of 960 m^2/g.[7] After reaction with the sultone precursor, the pore diameter and surface area decreased to 62 Å and 370 m^2/g, respectively. The sultone ring opened to form a sulfonic acid via reaction with the surface silanols on SBA-15.[6] This supported sulfonic acid is the Brønsted acidic support used here.

The polymerization of ethylene was studied using bis(cyclopentadienyl)dimethylzirconium (Cp_2ZrMe_2) or bis(pentamethylcyclopentadienyl)dimethylzirconium ($Cp^*_2ZrMe_2$) as the metallocene precatalyst. It is necessary to add trimethylaluminum (TMA) for the polymerization to proceed.[2] When the zirconocene and SBA-FSO_3H were mixed without addition of TMA, polymerization was not observed. As shown in Table 1, the productivities of Cp_2ZrMe_2 are higher with a Zr/Al ratio of 1:400 than 1:700. However, ratios of as little as 1:35 and 1:20 of Zr/SBA-FSO_3H are sufficient to activate the metallocene, yielding productivities up to 385 kg PE/mol Zr•h. As a control, the supported sulfonic acid with TMA was tested in the absence of the metallocene, and it was inactive. Using $Cp^*_2ZrMe_2$ as the precatalyst, the productivities were much higher compared to the Cp_2ZrMe_2 analogue. In fact, productivities approaching 1000 kg PE/mol Zr•h were observed (Table 1). In addition, in all cases, reactor fouling was not observed with the SBA-FSO_3H/TMA cocatalyst, whereas it was observed in the control experiments that utilized supported or unsupported MAO (see Supporting Information). To elucidate if the activation was a consequence of the regular mesoporous support, SBA-15, an additional material was synthesized using an amorphous commercial silica material (MS-3030 from PQ Corp.). With this support/activator, the polymerization of ethylene was studied with $Cp^*_2ZrMe_2$ at room temperature [1:20 Zr/FSO_3H, 1:400 Zr/Al]. A catalytic productivity of 413 kg PE/mol Zr•h was observed. When compared to MS-3030/MAO (Zr/Al of 1:400), a productivity of 1510 kg PE/mol Zr•h was achieved, showing that the new organic/inorganic hybrid activator/supports can give activities [best case ∼850 kg PE/mol Zr•h] on the order of MAO/silica.

Scheme 1. Synthesis of Tethered Brønsted Acid Sites



Three mechanisms of activation by the supported sulfonic acid were considered. In all cases, one role of the TMA is the in situ capping of the surface silanols to prevent Zr−O−Si metal deactivation on the silica surface. The three mechanisms are (i) in situ production of MAO from traces of water on the silica support, (ii) direct metallocene activation by the sulfonic acid, or (iii) activation by a combined adduct of the Brønsted acid and TMA. Each of these possible mechanisms was investigated experimentally. As reported by Scott and co-workers, the addition of TMA caps surface silanol groups by forming a bisaluminum bridge on the Si−OH surface groups, evolving methane.[8] Loss of silanols in our work is supported by our FTIR experiments using SBA-FSO_3H/TMA, as the residual OH stretching band from the surface silanols was absent after addition of the sulfonic acid precursor and TMA to the support (see Supporting Information). TMA addition to silica could produce MAO in situ if there was sufficient water present on the support. However, our materials were rigorously dried. In addition, simply capping silanols on bare SBA-15 with TMA in the absence of sulfonic acids did not produce a solid that would activate the metallocene. To further investigate the possibility of in situ MAO formation, a hydrated mercaptopropyl-functionalized SBA-15 control material (SBA-MPTMS) was mixed with TMA and $Cp^*_2ZrMe_2$. This weakly acidic cocatalyst did not produce any poly(ethylene) either. Thus, in situ MAO formation was ruled out as an activation mechanism. Mechanism (ii) for metallocene activation, direct activation of the metallocene by protonation by the Brønsted acid, was deemed unlikely, as well. First, no polymerization was observed under any conditions in the absence of alkyl aluminum. In addition, order of reagent addition is found to be important, with active

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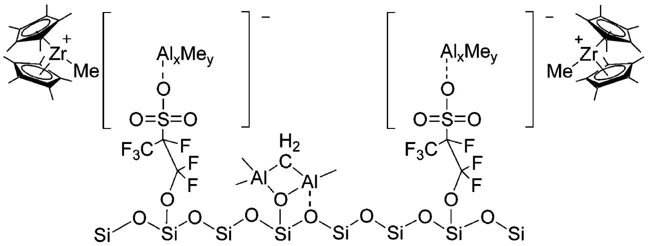
Table 1. Polymerization of Ethylene in Toluene at Room Temperature

entry	catalyst	cocatalyst	Al source	Zr/Al	Zr/SBA-FSO$_3$H	T_m (°C)	productivity (kg PE/mol Zr•h)
1	Cp_2ZrMe_2	SBA-FSO$_3$H	TMA	1:700	1:35	138.1	300
2	Cp_2ZrMe_2	SBA-FSO$_3$H	TMA	1:400	1:35	138.5	385
3	Cp_2ZrMe_2	SBA-FSO$_3$H	TMA	1:700	1:20	138.0	135
4	Cp_2ZrMe_2	SBA-FSO$_3$H	TMA	1:400	1:20	139.5	200
5	Cp_2ZrMe_2	SBA-FSO$_3$H	TIBA	1:700	1:35		
6	Cp_2ZrMe_2	SBA-FSO$_3$H	TIBA	1:400	1:20		
7	$Cp^*_2ZrMe_2$	SBA-FSO$_3$H	TMA	1:700	1:35	141.6	850
8	$Cp^*_2ZrMe_2$	SBA-FSO$_3$H	TMA	1:400	1:35	143.8	750
9	$Cp^*_2ZrMe_2$	SBA-FSO$_3$H	TMA	1:125	1:10	140.6	180
10	$Cp^*_2ZrMe_2$	SBA-FSO$_3$H	TMA	1:50	1:10	140.7	110
11	$Cp^*_2ZrMe_2$	SBA-FSO$_3$H	TMA	1:50	1:5	140.3	55
12	$Cp^*_2ZrMe_2$	SBA-FSO$_3$H	TMA	1:25	1:5	139.2	50
13	$Cp^*_2ZrMe_2$	MAO	MAO	1:125		133.9	1600
14	$Cp^*_2ZrMe_2$	SBA-MAO	MAO	1:125		136.5	1730
15	$Cp^*_2ZrMe_2$	SBA-FSO$_3$H/MAO	MAO	1:125		134.1	1900

Scheme 2. Hypothetical Activated Catalyst[9]



catalysts formed only when the alkyl aluminum is added to the acidic support *before* addition of the metallocene. Additional solution phase studies that suggest the sulfonic acid alone is not the cocatalyst are described in Supporting Information. Thus, our initial evidence suggests activation occurs via metallocene interaction with a combined Brønsted acid−trimethylaluminum adduct (mechanism iii). Scheme 2 depicts a hypothetical activated cation−anion pair.[9]

To elucidate the location of the active catalyst, simple filtration studies were performed. For instance, a mixture of SBA-FSO$_3$H, TMA, toluene, and Cp_2ZrMe_2 or $Cp^*_2ZrMe_2$ was stirred for 30 min and subsequently filtered in a drybox. The filtrate was tested for polymerization activity and found to be inactive. Thus, the active catalyst likely remains coordinated to the support material.[10] Thus, it is proposed that the reaction of TMA and the SBA-FSO$_3$H surface creates a surface-tethered species that can activate the metallocene, creating a weakly coordinating anion and an active metallocenium cation.

We thus report a method to produce active supported zirconocenes on a perfluoroalkanesulfonic acid functionalized silica support. It is necessary, however, to add trimethylaluminum to cap the surface silanols and react with the surface Brønsted acid groups to form a site capable of activating the precatalyst. The results indicate the active catalyst is coordinated to the surface rather than in solution. The productivities are on the order of those observed with MAO-modified silica, but the materials have the advantage of preventing reactor fouling by limiting leaching of active species.

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Supporting Information Available: Materials, experimental methods, XRD, XPS, reactor fouling. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Reaction of TMA with the supported acid evolves methane. A structure for the sulfonic acid/TMA adduct that is suggested to form the non-coordinating anion might be derived from suggested TMA-silica structures described in ref 8 or in the following: Li, J. H.; DiVerdi, J. A.; Maciel, G. E. *J. Am. Chem. Soc.* **2006**, *128*, 17093.

(10) The supported fluorinated acid does leach in the presence of water or alcohols. The leaching experiment described here does not rule out leaching of some inactive species, or leaching of active species that deactivate during filtration.

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