Macromolecules **2002,** *35,* 1499−1503

A Chemically Functionalized Carboxylate−Alumoxane Nanoparticle Support for Olefin Polymerization Catalysts

Stephen J. Obrey[1a] **and Andrew R. Barron***[,1a,b]

Department of Chemistry, Rice University, Houston, Texas 77005, and Department of Mechanical Engineering and Materials Science, Rice University, Houston, Texas 77005

Received February 22, 2001; Revised Manuscript Received November 12, 2001

ABSTRACT: A metallocene/MAO-based solid olefin polymerization catalyst has been developed using chemically functionalized nanoparticles (carboxylate−alumoxanes) as a well-defined substrate. Reaction of *p*-hydroxybenzoate−alumoxane (*p*-HB-A) nanoparticles, formed from the acid with boehmite, with methylalumoxane (MAO) results in a solid nanoparticle-based MAO (n-MAO), which in combination with zirconocenes [including Cp_2ZrCl_2, Cp_2ZrMe_2, and $(^nBuCp)_2ZrCl_2$] produces an active solid catalyst for olefin polymerization. The catalytic activity of the n-MAO-based catalyst is comparable to the homogeneous analogue and a traditional silica-supported catalyst under identical reaction conditions and with the same $Al_{(MAO)}$:Zr ratio. The n-MAO approach offers the potential of the MAO being easily chemically modified.

Introduction

Although it was known since the 1950s that compounds of aluminum react with water to give species containing aluminum−oxygen bonds, commonly termed alumoxanes,[2] it was not until the work of Manyik et al.[3] that their application to olefin catalysis was first appreciated. Subsequently, it was shown that the addition of water to the soluble metallocene/alkylaluminum catalyst systems resulted in a large increase in catalyst activity.[4] The high catalytic activity of a metallocene in combination with preformed methylalumoxane (MAO) was shown by the pioneering work of Kaminsky and Sinn.[5] Subsequently, much of the research in the field has been to make these catalysts industrially feasible, engineering the specific polymer properties, understanding the roles of the catalyst and cocatalyst play in the polymerization process, and developing alternative cocatalysts to MAO.[6]

Industrially, a supported catalyst is desirable to allow for drop-in replacement of the metallocene catalysts in slurry or gas-phase plants.[7] Supported metallocene/MAO catalyst systems were first suggested by Kaminsky and co-workers,[8,9] and a wide range of supports, both inorganic (e.g., silica, alumina, magnesium chloride, and zeolites) and organic (e.g., polystyrene, polysiloxanes, methyl acrylate), have been investigated. Supported metallocene/MAO catalysts fall into three general classes: (a) supporting the MAO (or other activator) followed by reaction with the metallocene; (b) supporting the metallocene and then reacting with the MAO; (c) reacting the metallocene/MAO mixture with the support.[10] Most examples of supporting the metallocene component involve attaching the metallocene through a specific functional group or "tether". The activity of the metallocene/MAO catalyst has been shown to be dependent on the identity of this tether.[11] In contrast, direct support of MAO has been limited to the reaction of MAO with the surface hydroxides of partially hydrate silica.[12] There has been little effort to tether the MAO through a well-defined linkage group.

A further issue with the supports tried to date is that, while it is clear that MAO is more active per Al when reacted with a surface, it is unclear why this occurs. *Is the increased activity solely a function of minimizing bimetallic activation of the metallocene, does the MAO undergo a structural rearrangement to a more active form, or are the inactive components of MAO removed?* It is desirable to be able to tailor the surface to enhance the cocatalyst activity of MAO, since the activity of MAO is related to the identity of the surface. One last caveat to any new support is that it should ideally form a uniform dispersion on the nanometer range in the final polymer so as not to have a detrimental effect on the transparency of blown films. Thus, a nanoparticle support with a surface that can be chemically modified with a variety of reactive moieties should be ideal. As a result, we have focused our attention on a class of chemically modified alumina nanoparticles, carboxylate−alumoxanes.[13]

Carboxylate−alumoxanes are inexpensive aluminum oxide nanoparticles prepared by the reaction of the mineral boehmite with carboxylic acids,[14,15] whose size (10 to >100 nm) may be controlled by changing the nature of the carboxylic acid and reaction conditions used in the synthesis.[16] Most importantly, these materials may be prepared with an almost limitless variety of functional groups, allowing alteration of the chemical characteristics of the surface as well as the ability to covalently bond to MAO.[17]

Results and Discussion

Synthesis, Characterization, and Reactivity of n-MAO. For our initial studies we have concentrated on a single functional group that readily simulates a hydroxylated surface of an inorganic oxide: *p*-hydroxybenzoate−alumoxane (*p*-HB-A). We have previously reported that *p*-HB-A may be prepared from the reaction of *p*-hydroxybenzoic acid and boehmite.[18] Furthermore, contact angle measurements of *p*-hydroxybenzoate-modified alumina surface show that the *p*-phenol group has a higher acidity than the native oxide.[19]

Reaction of *p*-HB-A with MAO solution yields MAO-substituted alumina nanoparticles, n-MAO (Scheme 1). It is interesting that there is no apparent reaction at

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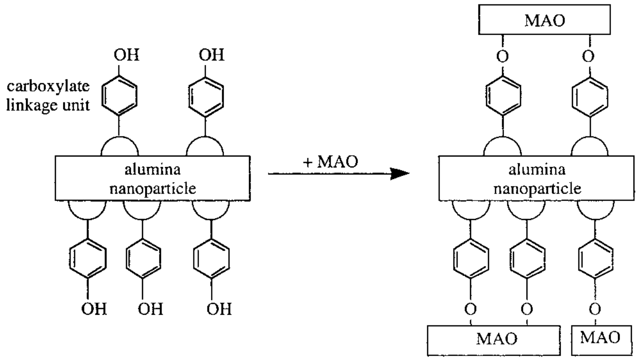
* To whom correspondence should be addressed: e-mail: arb@rice.edu; URL www.rice.edu/barron.

10.1021/ma010314m CCC: $22.00 © 2002 American Chemical Society
Published on Web 01/29/2002

Scheme 1. Schematic Representation of the Reaction of Carboxylate-Substituted Alumina Nanoparticle (Carboxylate−Alumoxane) with MAO To Form n-MAO



room temperature, and refluxing is required for the formation of the surface bound MAO. The resulting slurry is filtered and then washed with excess toluene to ensure that all the MAO (and any $AlMe_3$ present[20]) is chemically bound to the carboxylate−alumoxane. Reaction of *p*-HB-A with $AlMe_3$ did not result in the formation of an active catalyst.

Evidence for chemically bonding between the carboxylate−alumoxane and MAO is confirmed by loss of the 3498 cm^{-1} stretch in the IR spectrum associated with the phenolic hydroxide. The presence of peaks at 1603 and 1552 cm^{-1} associated with the bridging carboxylate[21,22] also confirms that the carboxylate groups are still bound to the surface of the alumina nanoparticle. Analysis of n-MAO by solid-state $^{1}H-^{13}C$ CP-MAS NMR spectroscopy shows the presence of four peaks in the aromatic region, all of which are slightly shifted compared to the parent *p*-HB-A (see Experimental Section). A single peak is seen at 171 ppm, corresponding to the α-carbon of a carboxylate bound to the surface of the alumina particle.[23] The $Al-CH_3$ groups of the MAO appear as two broad resonances at −2.1 and −13.7 ppm. Similar shift ranges have been observed for solid and supported MAO.[24] The thermogravimetric/differential thermal analysis (TG/DTA) of n-MAO shows a decrease of ca. 170 °C in the temperature at which thermal decomposition occurs as compared to the *p*-HB-A support. On the basis of the analysis of both n-MAO and *p*-HB-A, the Al:Me ratio in MAO (i.e., excluding the *p*-HB-A support) is estimated to be ca. 1:1, and the "MAO" aluminum content is approximately 50 wt %.

Reaction of the n-MAO with zirconium metallocenes in toluene suspension produces active polymerization catalysts (vide infra). Although Cp_2ZrMe_2 and $(^{n}BuCp)_2ZrCl_2$ have been employed, the majority of catalysis experiments, described below, used Cp_2ZrCl_2. The catalyst material was scrupulously washed with toluene to ensure that the metallocene/n-MAO catalyst was chemically bound and not physically adhered. Although the solid-state $^{1}H-^{13}C$ CP-MAS NMR spectrum shows the presence of the carboxylate and MAO, we were unable to unambiguously assign peaks due to the cyclopentadienyl groups. The presence of Zr was confirmed by use of energy-dispersive X-ray (EDX) analysis and was determined to be between 1.5 and 2.5 atom % depending on the region of the sample analyzed with an $Al_{(MAO)}$:Zr ratio of ca. 10:1. The low $Al_{(MAO)}$:Zr ratio is a function of the high zirconocene content required for EDX analysis, the surface bias of the technique, and the strong correction required for Zr analysis. However, the highly uniform distribution of Zr and Al is readily seen from the two-dimensional X-ray elemental maps (see Figure 1).

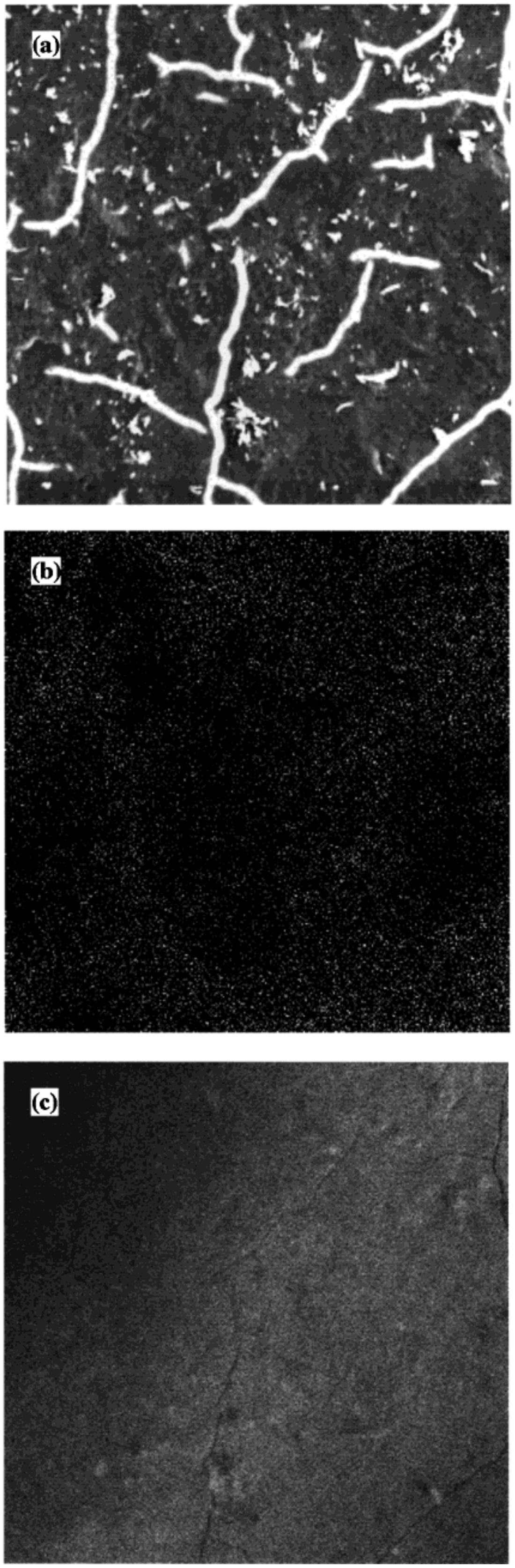


Figure 1. SEM image (a) and associated Zr (b) and Al (c) elemental maps of a pressed pellet of n-MAO reacted with Cp_2ZrCl_2 showing uniformity of the zirconocene throughout the matrix. The white features in the SEM image are charging areas associated with cracks in the surface of the pressed pellet.

Table 1. Polymerization of Ethylene with Zirconocenes Activated by Alumoxane Cocatalysts[a]

zirconocene	alumoxane	Al:Zr	mp (°C)	Δmp (°C)	activity (kg of PE mol of Zr^{-1})[a,b]
	n-MAO		n/a	n/a	n/a
Cp_2ZrCl_2	n-MAO	300	132	15	≤1942
Cp_2ZrCl_2	MAO	300	130	16	≤1663
Cp_2ZrCl_2	MAO/SiO_2	300	131	15	≤1306
$(^nBuCp)_2ZrCl_2$	n-MAO	300	133	14	≤2003

[a] All runs performed over 10 min. [b] Maximum yield observed for multiple catalytic runs; see text.

FESEM images of n-MAO and its reaction products with zirconocenes show fluffy particles approximately 1−10 μm in diameter. Upon closer inspection it can be seen that these are agglomerates of individual particles about 100 nm in diameter. Some unreacted particles of boehmite are observed in the FESEM images, depending on sample preparation. Separate experiments show that boehmite itself does not react with MAO and does not form an active catalyst.

It is important to note that the n-MAO/zirconocene catalyst system may also be synthesized by a one-pot synthesis. Reaction of *p*-HB-A with a preformed reaction mixture of Cp_2ZrCl_2 and MAO was found to give a homogeneous dispersion of zirconium. This preparation does not appear to have a different catalytic activity as compared to the stepwise reaction.

Olefin Polymerization Using n-MAO. Polymerization of ethylene with the n-MAO/zirconocene catalyst was performed at atmospheric pressure and room temperature as slurries in either hexane or toluene.[25] Test reactions were performed using an $Al_{(MAO)}$:Zr ratio of ca. 300:1. The reaction mixtures were quenched with methanol to stop production of polyethylene (PE). Multiple catalyst runs were performed under each reaction condition investigated. A certain degree of variability in polymerization activity was observed (especially for the homogeneous reference system). This variability is a common feature of metallocene polymerization catalysts due to the high degree of dependence on the Al:Zr ratio, as well as susceptibility toward impurities such as water and oxygen. With this in mind we have reported the optimum activity for each catalyst system. A summary of the polymerization activities is given in Table 1. The activity of n-MAO with Cp_2ZrMe_2 was found to be essentially identical to that with Cp_2ZrCl_2, while a comparable activity was observed for $(^nBuCp)_2ZrCl_2$. No effect on the polymerization activity was observed on the identity of the solvent, i.e., hexane vs toluene.

As may be seen from Figure 2, the n-MAO/Cp_2ZrCl_2 catalyst has a high initial activity (ca. 3000 kg of PE mol of Zr^{-1} h^{-1}) that decreases as the amount of PE produced increases. The PE production reaches a maximum after approximately 1 h. As is shown in Table 2, the polymer yield increases with increased zirconocene concentration (with constant n-MAO content), reaching a maximum at an $Al_{(MAO)}$:Zr ratio of ca. 350. However, as has been observed for other supported systems,[11] the catalyst initial activity increased with increasing $Al_{(MAO)}$:Zr ratio (see Figure 3).

In all the polymerization using n-MAO, the resulting polymer was confirmed to be high-density PE by its melting point (see Table 1)[26] and ^{13}C CPMAS NMR spectroscopy (δ 32.7).[27] As expected, the PE is readily extruded and shaped.[28] The polymer morphology (e.g., Figure 4) was found to generally mimic the shape and texture of the n-MAO. The average particle size of 8 μm is significantly (ca. 80 times) larger than that of the n-MAO. EDX microprobe analysis of a 5 min polymerization run confirms, along with the expected carbon content, a highly uniform distribution of aluminum and zirconium at very low concentration (<1% and 0.1%, respectively).

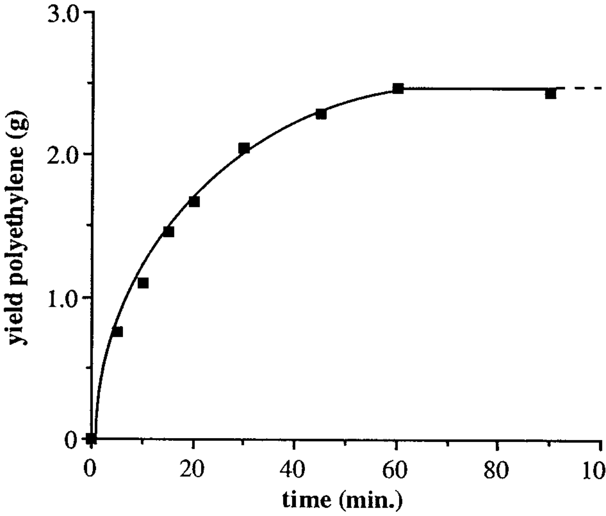


Figure 2. Plot of PE yield as a function of time for a n-MAO/Cp_2ZrCl_2 catalyst. Reactions were performed at 25 °C, under 1 atm, in hexane (20 mL), with n-MAO (100 mg) and Cp_2ZrCl_2 (1.0 mg).

Table 2. Polymerization of Ethylene with Cp_2ZrCl_2 Activated by n-MAO Cocatalysts as a Function of Cp_2ZrCl_2 Concentration[a]

Cp_2ZrCl_2 (mg)	n-MAO (mg)	yield (mg)	activity (kg of PE mol of Zr^{-1})[a]
0	100		
0.05	100	181	1058
0.1	100	298	871
0.5	100	589	344
1	100	753	220
2	100	829	121
5	100	767	44
10	100	360	10

[a] All runs performed over 5 min.

If a solid sample of n-MAO-Zr is exposed to ethylene, then the initial growth of PE may be followed by solid-state NMR spectroscopy. Figure 5 shows the ^{13}C CP MAS NMR spectrum of a sample of n-MAO/Cp_2ZrCl_2 exposed briefly to ethylene. The n-MAO carboxylate groups are unchanged, indicating that the MAO is not detached from the nanoparticle during polymerization. The covalent linkage is maintained throughout the polymerization reaction as well as after the quench with methanol.

Since an unknown amount of boehmite appeared to be present in some samples of n-MAO, it is important to know the affect, if any, of the unreacted boehmite on the polymerization. In this regard, a heterogeneous catalyst based on the mineral boehmite was prepared. A slurry of boehmite was refluxed in a solution of 30%

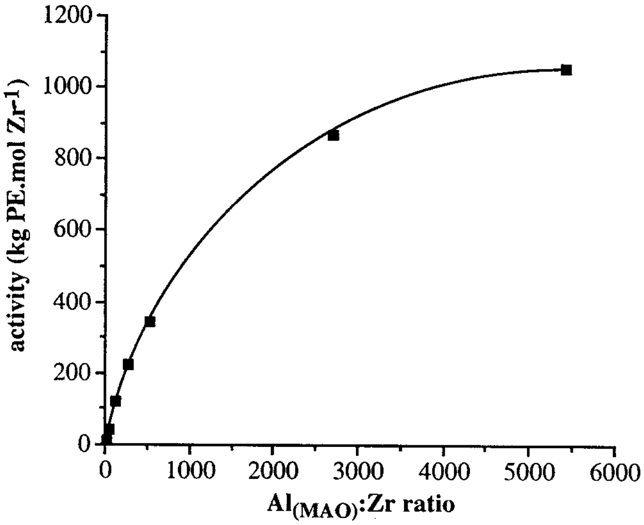


Figure 3. Plot of polymerization activity (kg of PE mol of Zr^{-1}) as a function of Al$_{(MAO)}$:Zr ratio for a n-MAO/Cp$_2$ZrCl$_2$ catalyst. Reactions were performed for 5 min at 25 °C, under 1 atm, in hexane (20 mL), with n-MAO (100 mg).

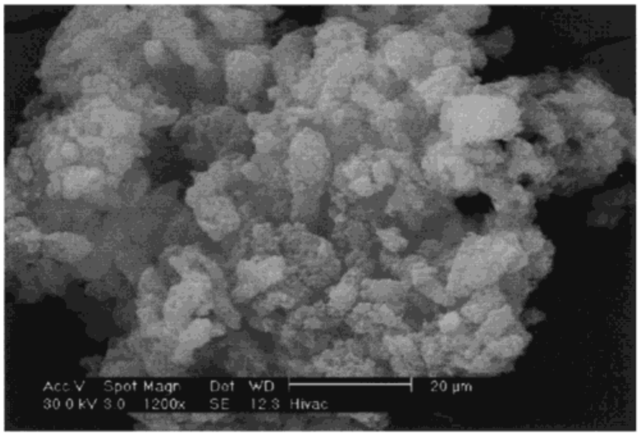


Figure 4. SEM image of a representative sample of PE prepared with n-MAO/Cp$_2$ZrCl$_2$.

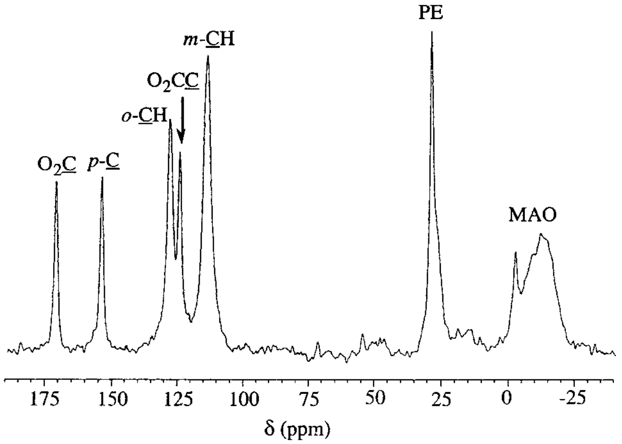


Figure 5. ^{13}C CP MAS NMR spectrum of a sample of n-MAO/Cp$_2$ZrCl$_2$ exposed briefly to ethylene.

MAO and Cp$_2$ZrCl$_2$, filtered, and washed with toluene in a manner similar to the preparation of n-MAO. Upon exposure to ethylene, this boehmite material showed no catalytic activity. However, the presence of boehmite catalyst in a slurry with a known silica catalyst showed no deleterious effects on yield or activity. Therefore, it assumed that the presence of any unreacted boehmite in the n-MAO/zirconocene catalyst would not be an active participant in the production of PE, not hinder its production, and may be thought of as only dead weight (filler).

Comparison of the highest activities obtained for the n-MAO and silica-based heterogeneous catalysts under the same conditions (Table 1) shows a higher activity for n-MAO at the same Al$_{(MAO)}$:Zr ratio. Further optimization will be required before we are able to make any detailed comparison.

Conclusions

A new heterogeneous polyolefin catalyst has been synthesized on the basis of carboxylate−alumoxane nanoparticles. This supramolecular alkyl alumoxane, n-MAO, has been shown to have similar activities to other known heterogeneous catalysts using an equivalent Al$_{(MAO)}$:Zr ratio. This study has been concerned with the activity of the n-MAO cocatalyst and not the physical properties of PE produced per se; however, the PE has similar physical characteristics to that formed with other heterogeneous systems such as those using silica supports.

Future studies will be aimed at reducing the content of any benign unreacted boehmite in the *p*-HB-A and controlling the morphology of the n-MAO-Zr catalyst agglomerates to allow for processing in Unipol-style fluidized bed reactors. Most importantly, we will investigate the effect of the number and identity of the linkage units (cf. Scheme 1) to ascertain the possibility of controlling the activity of the surface bound MAO.

Experimental Section

All solvents were distilled and degassed before use. Ethylene (Matheson polymer grade) was used as received. MAO (30 wt % in toluene) was generously provided by Albemarle Corp. Homogeneous and silica-supported MAO catalysts were prepared according to literature procedures.[5,29] Multiple runs were performed for each catalyst system. Unless otherwise noted, all procedures were preformed under purified nitrogen.

Microprobe analysis was conducted on a Cameca SX50 EDAX system. To facilitate Zr analysis, samples were prepared with 3 mg of zirconocene per 100 mg of n-MAO. FESEM studies were preformed on a Philips Electroscan XL30 FESEM. Solid-state ^{1}H−^{13}C CP-MAS NMR spectra were obtained at 50.5 MHz ^{13}C on a Bruker Avance 200 spectrometer equipped with a VTN probe designed for use with a 7 mm o.d. rotor. Carboxylate−alumoxanes were studied via the standard software's cptppm pulse program with a 5.0 kHz MAS, a 3.5 μs 90° ^{1}H pulse, 1 ms contact time[30] at the same power, TPPM decoupling[31] with 3 dB less power during the 33 ms FID, and a 5 s relaxation delay. The FID was processed with only 5 Hz of exponential line broadening. Thermogravimetric and differential thermal analyses were measured on a Seiko 200 TG/DTA instrument.

Synthesis of *p*-Hydroxybenzoate−Alumoxane (*p*-HB-A). A mixture of boehmite (10.0 g, 0.167 mol) and *p*-hydroxybenzoic acid (23.0 g, 0.167 mol) was refluxed overnight in 200 mL of water. The thick, white solid was removed by centrifugation and then washed with water, ethanol, and ether before being air-dried. Yield: 26 g. Ceramic yield (TGA): 23%. Particle size (average) = 394 nm. Surface area = 71.98 m^2 g^{-1}. IR (cm^{-1}): 3610 (m), 3240 (b), 2980 (m), 1690 (s), 1613 (s), 1562 (s), 1434 (s), 1260 (s), 1178 (s), 1070 (s), 794 (s). ^{13}C CP-MAS NMR: δ 173.2 (O$_2$*C*), 156.9 (*p*-*C*O), 128.6 (*o*-*C*H), 122.1 (O$_2$C*C*), 114.6 (*m*-*C*H).

Synthesis of Methylalumoxane−Hydroxybenzoate−Alumoxane (n-MAO). A solution of MAO in toluene (30%, 73.1 g) was added to a slurry of 4-hydroxybenzenatoalumoxane (10 g) in toluene (300 mL). The reaction mixture was stirred for 3 h at room temperature and then refluxed for 12 h. The reaction mixture was cooled to room temperature and filtered. The resulting white solid was washed with toluene (1 × 150 mL). The white solid was dried to yield 20.2 g. IR (cm^{-1}): 1608 (ν_{CO}, m), 1552 (ν_{CO}, m), 1261 (m), 1068 (m), 1012 (m), 799 (s). ^{13}C CPMAS NMR: δ 171.7 (O_2C), 154.7 (*p*-*C*O), 128.6 (*o*-*C*H), 124.9 (O_2CC), 114.2 (*m*-*C*H), −2.1 (Al-CH_3), −13.7 (Al-CH_3).

Polymerization of Ethylene Using n-MAO. The metallocene catalyst, Cp_2ZrCl_2 (3.0 mg) or (^{n}BuCp)$_2$ZrCl$_2$ (4.0 mg), was added to a slurry of n-MAO in hexane or toluene (20−30 mL). The slurry was stirred for 1 h, after which ethylene was bubbled through the slurry at atmospheric pressure. After the required reaction time the reaction mixture was quenched with methanol and filtered. The resulting white solid was dried and weighed. No variation in activity was observed if the n-MAO/metallocene mixture was washed with solvent before exposure to ethylene. Multiple catalyst runs were performed under each reaction condition to limit experimental variability. No variation in catalytic activity is observed if the solid metallocene/n-MAO is isolated dry, washed with toluene, and resuspended in solvent before addition of ethylene.

Synthesis of Boehmite Catalyst. A solution of MAO in toluene (30%, 7.3 g) was added to a slurry of boehmite (1.0 g) in toluene (300 mL). The reaction mixture was stirred for 3 h at room temperature and then refluxed for 12 h. The reaction mixture was cooled to room temperature and filtered. The resulting white solid was washed with toluene (1 × 30 mL). The white solid was dried to yield 0.9 g.

Acknowledgment. Financial support for this work is provided by the Robert A. Welch Foundation. The Bruker Avance 200 NMR spectrometer was purchased with funds from ONR Grant N00014-96-1-1146. MAO solutions were generously provided by Albemarle Corp.

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MA010314M