Macromolecules

Volume 36, Number 18 September 9, 2003

Communications to the Editor

Preparation of Silica-Supported Bis(imino)pyridyl Iron(II) and Cobalt(II) Catalysts for Ethylene Polymerization

Il Kim,* Byeong Heui Han, Chang-Sik Ha, Jae-Kon Kim, and Hongsuk Suh

Department of Polymer Science and Engineering, Department of Chemistry and Chemistry Institute for Functional Materials, Pusan National University, Jangjeon-dong, Geumjeong-gu, Busan 609-735, Korea

Received May 27, 2003

Revised Manuscript Received July 23, 2003

Recently, it was shown that a series of pyridyl bis(imide) complexes of cobalt(II) and iron(II) exhibit very high activities for ethylene polymerization.[1−4] The protective bulk of the ortho substituents above and below the metal center is critical to the molecular of the resulting polyethylenes.[2−5] In contrast to the nickel and palladium systems, there is no chain walking and the polyethylene is strictly linear with very high density.[5] Regardless of the virtues these homogeneous new catalysts possess, it is required to support these catalysts on inorganic support materials if they can be adapted to run in commercial polymerization processes. Heterogenization is required to operate the continuous process smoothly by avoiding fouling of the reactor, overheating of the particle, and melting of the polymer, which could result in the particles adhering to form sheets on the reactor walls and agitator.

Homogeneous metallocene catalysts have been successfully supported using numerous methods on many different types of carriers.[6,7] Also, they have been studied toward the immobilization of late transition metal catalysts. Covalently attaching Ni(II) diimine complexes to the support was demonstrated to be an effective method.[8,9] Recently, covalently attached bis(imino)pyridyl Fe(II) catalysts to silica gel were used successfully for ethylene polymerization.[10] The bis(imino)pyridyl Fe(II) complexes were also activated and heterogenized with a cocatalyst consisting of partially hydrolyzed trimethylaluminum on silica gel and were used for ethylene polymerization.[11]

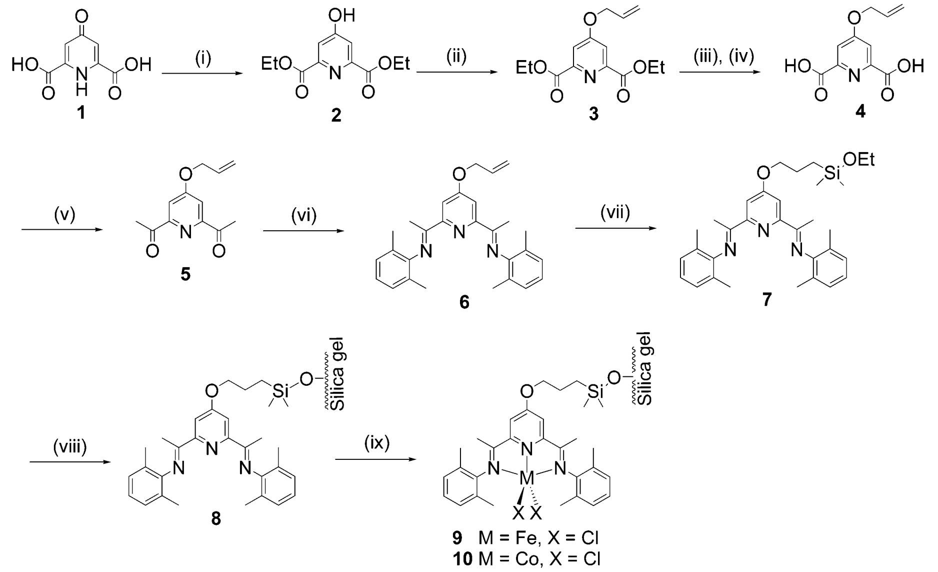
Herein we report a versatile heterogenization technique to covalently immobilize bis(imino)pyridyl Co(II) and Fe(II) complexes onto silica gel, which exhibit high activity in ethylene polymerization after activation with methylaluminoxane (MAO).

The synthetic route of a new supported 2,6-bis(imino)pyridyl ligand is shown in Scheme 1. Cheldamic acid **1** was esterified in ethanol in the presence of sulfuric acid as catalyst to give the diethyl ester **2** in 71% yield and then alkylated with allyl bromide in the presence of K_2CO_3 in acetone to obtain **3** (81%). Ester compound **3** was hydrolyzed with aqueous 5 N NaOH in tetrahydrofuran (THF) to give the desired carboxylic acid **4**. Carboxylic acid **4** was treated with $SOCl_2$, which was converted to the diacetylpyridine **5** using CuI(I) and methyllithium in 47% yield. The pyridyl diimine **6** was prepared by the Schiff-base condensation with 2,6-dimethylaniline and 4-(allyloxy)-2,6-diacetylpyridine (**5**) in 51% yield. Utilizing the known methodology of chiral stationary phase formation,[12] pyridyl diimine **6** was reacted with chlorodimethylsilane in the presence of $H_2PtCl_6{\cdot}6H_2O$ as a catalyst in methylene chloride and then treated with the mixed solvent of ethanol−triethylamine (1:1, v/v) to afford hydrosilylated compound **7** in 48% yield. The resulting hydrosilyl compound **7** was refluxed for 72 h with toluene and 5 μm silica gel in a flask equipped with Dean-stark trap and then was filtered and washed with toluene, ethyl acetate, methanol, acetone, diethyl ether, and hexane to afford **8**. Elemental analysis of **8** (C, 6.95%; H, 0.79%) showed a loading of 0.199 mmol (based on C) of **7** per gram of **8**. Exact standard procedures are described in the Supporting Information. The supported iron(II) and cobalt(II) catalyst precursors **9** and **10** were synthesized by treating silica gel supported bis(imino)pyridyl compound **8** with $FeCl_2{\cdot}4H_2O$ (or $CoCl_2{\cdot}4H_2O$) in THF.

The supported catalysts were tested in slurry polymerization runs at an atmospheric pressure of ethylene in toluene at temperature between 10 and 50 °C. A poly-

10.1021/ma0347060 CCC: $25.00 © 2003 American Chemical Society

Scheme 1. Synthetic Route of New Supported 2,6-Bis(imino)pyridyl Fe(II) and Co(II) Complexes[a]



[a] (i) EtOH, concentrated H_2SO_4, 90 °C; (ii) K_2CO_3, allyl bromide, acetone, reflux; (iii) 5 N NaOH, THF, 50 °C; (iv) $SOCl_2$, DMF, 90 °C; (v) CuI(I), MeLi, Et_2O, THF, −78 °C; (vi) **6**, 2,6-dimethylaniline EtOH, AcOH, reflux; (vii) $(CH_3)_2SiHCl$, $H_2PtCl_6{\cdot}6H_2O$ (catalyst), CH_2Cl_2, EtOH:Et_3N = 1:1; reflux; (viii) 5 μm silica gel, toluene, 120 °C; $FeCl_2$ or $CoCl_2$, THF.

Table 1. Experimental Results for Polymerization with Homo- and Heterogeneous Catalysts in Combination with MAO[a]

run no.	cat.	loading (μmol)	temp (C)	$\bar{R}_p{}^b \times 10^{-7}$ (g of PE/ (mol of Mt h bar))	$\bar{R}_p{}^b \times 10^{-3}$ (g of PE/ (g of cat. h bar))	$\bar{M}_v{}^c \times 10^{-3}$	$T_m{}^d$ (C)	$\Delta H_f{}^d$ (J/g)	$X_c{}^e$ (%)
1	**9**	19.99	10	1.71	3.42	202.3	131.8	156.4	57.9
2			30[f]	4.92	9.84	152.3			
3			30	3.08	6.18	165.9	131.9	171.5	63.5
4			30[g]	2.52	5.04	164.2			
5			50	4.87	9.75	114.4	131.7	178.6	66.2
6	**10**	19.99	10	2.10	4.20	68.3	129.9	166.2	62
7			30	2.59	5.19	50.3	129.1	177.0	66
8			50	1.60	3.19	40.6	128.3	158.9	62
9	**11**	6.04	10	163.74	3296.5	36.7	127.6	191.63	71
10			30	203.88	4104.7	18.4	126.4	197.3	73
11			50	251.01	5054.7	17.9	127.3	197.3	73
12	**12**	6.04	10	158.87	3198.6	4.5	118.5	221.3	82
13			30	156.59	3152.6	2.4	114.8	229.4	85
14			50	54.99	1099.0	2.2	107.6	240.2	89

[a] 250 mL reactor, 80 mL of toluene, 30 min runs, atmospheric pressure, [MAO]/[M] = 700 equiv. [b] Average rate of polymerization for the period of polymerization. [c] Viscosity-average molecular weights calculated from the equation[13] $[\eta] = 6.2 \times 10^{-4}\bar{M}_v{}^{0.7}$. [d] Melting temperature (T_m) and heat of fusion (ΔH_f) of the polymer determined by DSC. [e] Crystallinity calculated by $(\Delta H_f/\Delta H_f) \times 100$ ($\Delta H_f = 269.9$ J/g for folded-chain polyethylene[14]). [f] Polymerization run time of 3 min. [g] Polymerization run time of 60 min.

merization run time was 30 min. Polymerizations of ethylene were also carried out using nonsupported bis(imino)pyridyl complexes $[(2,6\text{-}C_6H_3Me_2N{=}C(Me))_2C_5H_3N]MCl_2$ [M = Fe (**11**); Co (**12**)] at the same conditions for the comparison. The results are summarized in Table 1. The iron(II) and cobalt(II) complexes covalently attached to silica gel through silicon ethoxide functionalized ligands show high activities in ethylene polymerization when activated with MAO. Supported iron precatalyst **9** shows polymerization activity of 4.87 × 10^7 g of PE/(mol of Fe h bar) at 50 °C and cobalt precatalyst **10** 1.60 × 10^7 g of PE/(mol of Co h bar) at the same polymerization temperature. These supported catalysts showed about 100-fold lower activity than analogue homogeneous catalysts. This is widely ascribed to diffusion limitation of monomer into the interior pores of the supported catalyst, but may also be the result of reduced active sites present in the heterogeneous variant. Catalyst sites could be deactivated when supported or may not be generated in the metal−cocatalyst interaction. A similar supported catalyst prepared by immobilization of alkenyl functionalized $[(2,6\text{-}C_6H_3(i\text{Pr})_2N{=}C(Me))_2C_5H_3N]FeCl_2$ on modified silica via hydrosylation showed a polymerization activity of 4.53 × 10^6 g of PE/(mol of Fe h bar) for 45 min of polymerization time.[10] Peter and Brookhart reported supported catalysts prepared by using aryl α-diimine Ni(II) complexes substituted with amino functionality and silica pretreated with trimethylaluminum showing similar activities.[9]

The molecular weight (as $\bar{M}_v$) of the polyethylene produced by supported catalysts was higher than that of polyethylene by analogue homogeneous catalysts. In addition, the molecular weight was observed not to be run time dependent. The polymer obtained from a 3 min run had an $\bar{M}_v$ of 1.52 × 10^5 while the polymers from 30 and 60 min runs had $\bar{M}_v$ of 1.66 × 10^5 and 1.64 × 10^5. The higher molecular weight notwithstanding lower activity of supported catalysts suggests that the lower activity of the catalyst is due to a reduced number of active sites; were the propagation rate lower for a supported catalyst, the rate of termination would have to be reduced proportionately or more for these molecular weight observations to hold. The decrease of catalytic activity and the increase of molecular weight by heterogenization were also observed in metallocene catalysts.[1,6] Tait and co-workers determined that 91% of zirconocenes sites were activated by MAO in solution, but when the metallocene was supported on silica, the concentration of active sites generated by MAO was only 9% of the total zirconium supported.[15] Table 1 shows that the molecular weight of the polymer decreases as the increase of polymerization temperature for both supported and unsupported catalysts. In transition-metal-catalyzed polymerizations, the chain termination reaction has normal activation energy and therefore can be controlled by temperature. Since the activation energy for the termination is somewhat higher than that for propagation, the molecular weight can be controlled by temperature.

All of the catalysts reported converts ethylene to highly linear polyethylene as determined by differential scanning calorimetry (show only one T_m peak). The T_m values of polymer increased by about 4 °C for iron catalyst and over 10 °C for cobalt catalyst by heterogenization. The increase of melting temperature is evidently ascribed to the increase of molecular weight. Mathot and Pijpers studied with DSC the melting and crystallilization behavior of polyethylene fractions of widely varying molecular weight, concluding the melting temperature increases with molecular weight of 20 000 up to an almost asymptotic value.[16] The higher crystallinities of lower molecular weight polymers obtained by homogeneous catalysts (**11** and **12** in Table 1) demonstrate that at higher molecular weight the chains are so large that parts of them can independently crystallize due to a delaying effect of entanglement.

In summary, we report a new heterogeneous silica-supported Fe(II) and Co(II) catalysts with a bis(imino)-pyridyl group containing silicon ethoxide functionality on the pyridine ring. By reaction of this functionality with activated silica, the catalysts were covalently bound to the support. These silica-supported catalysts showed high activity (up to 4.87×10^7 g of PE/(mol of Fe h bar)) and gave high molecular weight polymer (up to $\bar{M}_v = 2.02 \times 10^5$). These new silica-supported late transition metal catalysts are a new family of promising catalysts for the polymerization of ethylene. The supported catalysts with different aryl ligands and detailed kinetic studies using the said catalysts are under investigation.

Acknowledgment. This research was supported by the Korea Research Foundation (NONDIRECTED FUND, 2001). I.K. is grateful to the center for Ultramicrochemical Process Systems and to the Brain Korea 21 Project in 2003. C.-S. Ha is also grateful to the National Research Laboratory Program.

Supporting Information Available: Synthesis of compounds **9** and **10**, supporting procedures, and polymerization details. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169 and references therein.
(2) Small, B. L.; Brookhart, M.; Bennet, A. M. A. *J. Am. Chem. Soc.* **1998**, *120*, 4049.
(3) Britovsek, G. J. P.; Gibson, V. C.; Kimberly, B. S.; Maddox, P. J.; McTavish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 849.
(4) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428.
(5) Britovsek, G. J. P.; Bruce, M.; Gibson, V. C.; Kimberly, B. S.; Maddox, P. J.; Mastroianni, S.; McTavish, S. J.; Redshaw, C.; Solan, G. A.; Stromberg, S.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1999**, *121*, 8728.
(6) Hlatky, G. G. *Chem. Rev.* **2000**, *100*, 1347 and references therein.
(7) Fink, G.; Steinmetz, B.; Zechlin, J.; Przybyla, C.; Tesche, B. *Chem. Rev.* **2000**, *100*, 1377.
(8) Boussie, T. R.; Murphy, V.; Hall, K. A.; Coutard, C.; Dales, C.; Petro, M.; Carlson, E.; Turner, H. W.; Powers, T. S. *Tetrahedron* **1999**, *55*, 11699.
(9) Peter, P.-P.; Brookhart, M. *Macromolecules* **2002**, *35*, 6074.
(10) Kaul, F. A. R.; Puchta, G. T.; Schneider, H.; Bielert, F.; Mahalios, D.; Herrmann, W. A. *Organometallics* **2002**, *21*, 74.
(11) Schmidt, R.; Welch, M. B.; Palackal, S. J.; Alt, H. G. *J. Mol. Catal.* **2002**, *179*, 155.
(12) Hyun, M. H.; Na, M. S.; Jin, J. S. *J. Chromatogr., A* **1996**, *77*, 752.
(13) Chiang, R. *J. Polym. Sci.* **1957**, *28*, 235.
(14) Soga, K. *Makromol. Chem.* **1989**, *190*, 995.
(15) Tait, P. J. T.; Monterio, M. G. K.; Yang, M.; Richardson, J. L. *Proceedings of MetCon 1996*, Houston, TX, 12−13 June 1996.
(16) Mathot, V. B. F.; Pijpers, M. J. F. *Polym. Bull. (Berlin)* **1984**, *11*, 297.

MA0347060