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Ethylene polymerization with silica-supported bis(imino)pyridyl iron(II) catalysts

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Abstract

Two strategies have been developed to prepare silica-supported bis(imino)pyridyl Fe(II) catalysts for ethylene polymerization. The bis(imino)pyridyl ligands were modified by the introduction of reactive ethoxysilane or Si–Cl end groups, allowing the immobilization of them via the direct reaction of the ethoxysilane or Si–Cl groups with the silanols on the silica surface. The resultant silica-supported bis(imino)pyridyl ligands were characterized by analytical and spectroscopic (NMR, Raman, FTIR, and XPS) techniques. The complexation reactions of the supported ligands with $FeCl_2 \cdot 4H_2O$ give rise to silica-supported Fe(II) precatalysts, which exhibit high catalytic activities for ethylene polymerization in the presence of modified methylaluminoxane (MMAO). The molecular weights of the polyethylenes obtained with the supported precatalysts are much higher than those produced with corresponding homogeneous Fe(II) precatalyst under the same conditions.

Keywords: Silica support; Iron catalyst; Heterogeneous catalysis; Ethylene polymerization

1. Introduction

Recently, the late transition metal catalysts for olefin polymerization have gained much attention because of their potential to yield polymers with different microstructures and their greater tolerance of functionalized monomers [1–4]. In 1998, the groups of Brookhart and Gibson independently discovered that pyridinebisimine iron(II) complexes can be activated with methylaluminoxane (MAO) to afford highly active catalysts for ethylene polymerization [5–10]. However, the homogeneous catalysts easily lead to an extremely exothermic polymerization process and result in serious fouling of the reactor in the slurry process of olefin polymerization [11–13]. Thus the application of these catalysts in a continuous process has been difficult. In general, the way to solve these problems is to immobilize the catalysts on suitable carriers.

Most often, homogeneous catalysts have been supported on inorganic materials such as silica or $MgCl_2$ [14–26] and on organic materials such as polystyrene and polypropylene [27–35]. For late transition-metal catalysts, covalently attaching bis(imino)pyridyl Fe(II) catalysts to silica was demonstrated to be an effective method for ethylene polymerization, and the work reported by the groups of Kim and Herrmann is an example of success with this method [21,22]. However, the routes by which they chose to support the catalysts seem somewhat tedious to use, and loadings were relatively low.

Here we report two new strategies for immobilizing bis(imino)pyridyl Fe(II) catalyst. The Fe(II) catalyst can easily be supported on silica through a covalent bonding with much higher Fe loading than that observed with the methods of Kim and Herrmann. Especially when the Fe(II) catalyst bearing two allyl arms was supported, the loadings even reached 50 mg_{Fe}/g_{cat}, which is almost four times than those reported by Kim and Herrmann [21,22]. High loading is important for reducing the amount of inorganic impurities in

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the polymers produced. After activation with MMAO, the heterogeneous Fe(II) catalysts showed high activity.

2. Experimental

2.1. General procedures and materials

All work involving air- and/or moisture-sensitive compounds was carried out with standard Schlenk techniques. NMR data were obtained on a Bruker 300 MHz spectrometer at ambient temperature, with $CDCl_3$ as solvent and TMS as internal standard. Infrared spectra were recorded on a Bio-Rad FTS135 spectrometer. Raman spectra were recorded on a FT-Raman 960 (THER TONIC) spectrometer. XPS spectra were recorded on a VGEscalab MK II spectrometer with the use of Al-K_α exciting radiation from an X-ray source operated at 10.0 kV and 10 mA. The elemental analysis of Fe was conducted with a PE AA800 Atomic Absorption spectrometer, and the elemental analyses of C, H, and N were performed with a Flash EA 1112 spectrometer. DSC measurements were performed with a Perkin-Elmer Pyris 1 differential scanning calorimeter at a rate of 10 °C/min. GPC measurements of the polyethylene were conducted at 150 °C with a PL-GPC 220-type high-temperature chromatograph equipped with three PLgel 10-μm Mixed-B LS-type columns. 1,2,4-Trichlorobenzene (TCB) was used as the solvent at a flow rate of 1.0 ml/min. The calibration was made with polystyrene standard EasiCal PS-1 (PL Ltd). The intrinsic viscosity of the polymer sample was measured in decalin at 135 °C with an Ubbleohed viscometer, and the average of molecular weight was calculated with the following equation [36]:

$$[\eta] = 6.2 \times 10^{-4} M_v^{0.7}.$$

Modified methylaluminoxane (MMAO, 7% aluminum in heptane solution) was purchased from Akzo Nobel Chemical Inc. Silica was purchased from Aldrich Chemicals (200 mesh; surface area, 480 m^2/g) and pretreated by heating under vacuum at 150 °C for 12 h to remove the water absorbed before use. Tetrahydrofuran, hexane, and toluene were dried over sodium with dibenzophenone as an indicator, and the other chemicals were commercially available and used without further purification. The ligands **1** [4-Allyl-2,6-$i\mathrm{Pr}_2\mathrm{PhN{=}CMe(C_5H_3N)MeC{=}NPh}i\mathrm{Pr}_2$-2,6] and **3** [(4-Allyl-2,6-$i\mathrm{Pr}_2\mathrm{PhN{=}CMe)_2(C_5H_3N)}$] were prepared according to a published procedure by Jin and colleagues [35].

2.2. Synthesis of compound **2** [4-allyl-2,6-$i\mathrm{Pr}_2\mathrm{PhN{=}CMe(C_5H_3N)MeC{=}NPhMe_2}$-2,6]

To a 100-ml flask was added 2,6-diacetylpyridine (0.65 g, 4 mmol), 2,6-dimethylaniline (0.77 g, 8 mmol), and 2 ml of formic acid in 30 ml of dry methanol, and then the solution was stirred at room temperature for 20 h. A yellow solid product was isolated by filtration, washed with cold methanol, and identified as the desired 2-acetyl-6-monoiminepyridine by ^{1}H NMR. The 2-acetyl-6-monoiminepyridine was dissolved in 30 ml isopropyl alcohol, followed by the addition of 10 ml methylene chloride, 2 ml formic acid, and excess 4-allyl-2,6-diisopropylaniline. The solution was refluxed at 60 °C for 20 h, and the desired yellow solid was isolated by filtration. After being dried at 60 °C for 24 h in a vacuum oven, compound **2** was yielded as a yellow powder (1.39 g, 75%). (^{1}H NMR ($CDCl_3$): δ 8.54–8.65 (m, 2H, Py-Hm), 7.89 (m, 1H, Py-H_p), 7.11–7.19 (m, 4H, Ph-Hm), 6.85–7.07 (m, 1H, Ph-H_p), 6.03 (m, 1H, –CH=C), 5.08 (t, 2H, $C{=}CH_2$), 3.42 (d, 2H, CH_2–C=C), 2.72 (br, 2H, $C\mathit{H}(Me)_2$, 2.27 (s, 6H, CH_3), 2.20 (s, 6H, $PhCH_3$), 1.09–1.19 (br, 12H, $C(CH_3)_2$). ^{13}C NMR ($CDCl_3$): δ 12.83, 16.17, 23.62, 28.72, 40.26, 115.35, 122.14, 122.99, 123.17, 123.56, 131.28, 134.78, 135.71, 135.77, 136.83, 138.24, 144.59, 146.54, 155.24, 167.42. Anal. calc. for $C_{32}H_{39}N_3$: C, 82.53; H, 8.44; N, 9.02. Found: C, 82.73; H, 8.40; N, 8.87.)

2.3. Synthesis of ethoxysilane-modified bis(imino)pyridyl ligand **4**

To a 100-ml flask was added bis(imino)pyridyl compound **1** (2.04 g, 4 mmol), chlorodimethylsilane (1.9 g, 20 mmol) in 40 ml of THF, and H_2PtCl_6 (1 mg) as a catalyst. The solution was stirred and refluxed at 70 °C for 8 h, and then the solvent was removed under reduced pressure. The remaining residue was dissolved in 10 ml of methylene chloride, and 10 ml of a solution of triethylamine and absolute ethanol (1:1 mixture, V) was added. The resultant solution was stirred at room temperature for 5 h and filtered to remove the precipitated triethylamine hydrochloride, and the filtered solution was concentrated under reduced pressure. The residue was purified by flash column chromatography, after being dried at 60 °C for 24 h in a vacuum oven, giving ligand **4** (1.25 g, 50%) as a yellow powder. (^{1}H NMR ($CDCl_3$): δ 8.5–8.64 (br, 2H, Py-Hm), 7.89 (t, 1H, Py-Hp), 7.23 (d, 2H, Ph-Hm), 7.11 (t, 1H, Ph-Hp), 6.95 (s, 2H, Ph-Hm), 3.64 (q, 2H, OCH_2Me), 3.37 (m, 2H, $\mathrm{Ph}\mathit{CH_2}\mathrm{CH_2CH_2Si}$), 2.73 (br, 4H, $CHMe_2$), 2.25 (s, 6H, CH_3), 1.97 (m, 2H, $\mathrm{PhCH_2}\mathit{CH_2}\mathrm{CH_2Si}$), 1.17 (m, 27H, CMe_2 and $SiOCCH_3$), 0.81 (m, 2H, $\mathrm{PhCH_2CH_2}\mathit{CH_2}\mathrm{Si}$), 0.094 (s, 6H, $SiMe_2$). ^{13}C NMR ($CDCl_3$): δ −1.63, 16.17, 17.55, 18.95, 23.27, 23.63, 23.72, 28.72, 40.07, 58.72, 122.96, 123.43, 124.15, 124.94, 136.11, 136.31, 137.32, 137.31, 137.71, 146.57, 152.93, 155.39, 155.90, 166.88, 167.62. Anal. calc. for $C_{40}H_{59}N_3OSi$: C, 76.75; H, 9.50; N, 6.71. Found: C, 76.58; H, 9.44; N, 6.65.)

2.4. Synthesis of ethoxysilane-modified bis(imino)pyridyl ligand **5**

The preparation procedure is similar to that used for ligand **4**. (Yield: 56%. ^{1}H NMR ($CDCl_3$): δ 8.68 (m, 2H, Py-Hm), 7.92 (m, 1H, Py-H_p), 7.11–7.19 (m, 4H, Ph-Hm), 6.88 (m, 1H, Ph-H$_p$), 3.69 (q, 2H, OCH$_2$CH$_3$), 3.36 (m, 2H, Ph*CH$_2$*CH$_2$CH$_2$Si), 2.78 (br, 2H, CH(Me)$_2$, 2.27 (s, 6H, CH$_3$), 2.20 (s, 6H, Ph-CH$_3$), 1.95 (1m, 2H, PhCH$_2$*CH$_2$*CH$_2$Si), 1.07–1.19 (m, 15H, CMe$_2$ and SiOCCH$_3$), 0.86 (m, 2H, PhCH$_2$CH$_2$*CH$_2$*Si), 0.074 (s, 6H, SiMe$_2$). ^{13}C NMR (CDCl$_3$): δ −1.66, 13.42, 16.24, 17.55, 23.27, 23.63, 23.72, 40.04, 58.61, 122.98, 123.42, 124.15, 124.96, 131.42, 135.88, 136.45, 141.37, 146.36, 152.93, 156.73, 165.74. Anal. calc. for $C_{36}H_{51}N_3OSi$: C, 75.87; H, 9.02; N, 7.37. Found: C, 75.53; H, 8.96; N, 7.45.)

*2.5. Synthesis of ethoxysilane-modified bis(imino)pyridyl ligand **6***

The preparation procedure is similar to that used for ligand **4**. (Yield: 48% H NMR (CDCl$_3$): δ 8.35 (d, 2H, Py-H*m*), 7.96 (t, 1H, Py-H$_p$), 7.06 (s, 4H, Ph-H$_m$), 3.62 (q, 4H, OCH$_2$CH$_3$), 3.42 (m, 4H, Ph*CH$_2$*CH$_2$CH$_2$Si), 2.74 (br, 4H, CHMe$_2$), 1.82 (m, 4H, PhCH$_2$*CH$_2$*CH$_2$Si), 1.15–1.22 (m, 24H, CMe$_2$), 1.06 (m, 6H, SiOCCH$_3$), 0.87 (m, 4H, PhCH$_2$CH$_2$*CH$_2$*Si), 0.026 (s, 6H, SiMe). ^{13}C NMR (CDCl$_3$): δ −1.63, 16.19, 17.32, 23.64, 23.72, 40.08, 58.44, 124.14, 124.85, 136.09, 136.35, 141.46, 146.28, 146.84, 152.89, 166.49. Anal. calc. for $C_{47}H_{75}N_3O_2Si_2$: C, 73.28; H, 9.81; N, 5.46. Found: C, 73.53; H, 9.73; N, 5.40.)

*2.6. Synthesis of Si-Cl-modified bis(imino)pyridyl ligand **7***

To a 100-ml flask was added bis(imino)pyridyl compound **1** (2.04 g, 4 mmol), dichloromethylsilane (2.31 g, 20 mmol) in 40 ml THF, and H_2PtCl_6 (1 mg) as a catalyst. The solution mixture was refluxed at 70 °C for 5 h. Excess dichloromethylsilane and THF were removed under reduced pressure, after being dried at 60 °C for 24 h in a vacuum oven, giving ligand **7** (1.74 g, 75%) as a yellow powder. (^{1}H NMR (CDCl$_3$): δ 8.39 (br, 2H, Py-H*m*), 8.03 (t, 1H, Py-H*p*), 7.35 (d, 2H, Ph-H*m*), 7.21 (t, 1H, Ph-H*p*), 6.95 (s, 2H, Ph-H*m*), 3.76 (m, 4H, Ph*CH$_2$*CH$_2$CH$_2$Si), 2.84 (br, 4H, CHMe$_2$), 2.28 (s, 6H, CH$_3$), 1.85 (m, 2H, PhCH$_2$*CH$_2$*CH$_2$Si), 1.17 (m, 24H, CMe$_2$), 0.86 (m, 2H, PhCH$_2$CH$_2$*CH$_2$*Si), 0.035 (s, 3H, SiMe). ^{13}C NMR (CDCl$_3$): δ 1.25, 16.35, 16.82, 23.23, 24.54, 25.89, 25.99, 28.81, 40.15, 123.06, 124.79, 125.11, 125.89, 137.54, 138.32, 143.2, 144.04, 147.42, 152.87, 155.35, 155.84, 167.32, 167.63. Anal. calc. for $C_{33}H_{43}Cl_2N_3Si$: C, 68.25; H, 7.24; N, 6.60. Found: C, 68.49; H, 7.17; N, 7.30.)

*2.7. Synthesis of Si–Cl-modified bis(imino)pyridyl ligand **8***

The preparation procedure is similar to that used for ligand **7**. (Yield: 82%. ^{1}H NMR (CDCl$_3$): δ 8.38 (m, 2H, Py-Hm), 7.96 (m, 1H, Py-H$_p$), 7.16 (m, 4H, Ph-Hm), 6.88 (m, 1H, Ph-H$_p$), 3.68 (m, 4H, Ph*CH$_2$*CH$_2$CH$_2$Si), 2.78 (br, 2H, CH(Me)$_2$, 2.27 (s, 6H, CH$_3$), 2.22 (s, 6H, Ph-CH$_3$), 1.84 (m, 2H, PhCH$_2$*CH$_2$*CH$_2$Si), 1.16 (m, 12H, CMe$_2$), 0.86 (m, 2H, PhCH$_2$CH$_2$*CH$_2$*Si), 0.034 (s, 3H, SiMe). ^{13}C NMR (CDCl$_3$): δ 1.28, 13.82, 16.44, 17.69, 23.44, 23.62, 40.18, 58.34, 122.96, 123.46, 124.64, 124.87, 131.38, 135.92, 136.56, 141.45, 146.39, 153.21, 166.48. Anal. calc. for $C_{37}H_{51}Cl_2N_3Si$: C, 69.78; H, 8.07; N, 6.60. Found: C, 69.49; H, 8.00; N, 6.53.)

*2.8. Synthesis of Si–Cl-modified bis(imino)pyridyl **9***

The preparation procedure is similar to that used for ligand **7**. (Yield: 73%. ^{1}H NMR (CDCl$_3$): δ 8.30 (d, 2H, Py-H*m*), 7.94 (t, 1H, Py-H$_p$), 7.06 (s, 4H, Ph-H$_m$), 3.70 (m, 4H, Ph*CH$_2$*CH$_2$CH$_2$Si), 2.74 (br, 4H, CHMe$_2$), 2.28 (s, 6H, CH$_3$), 1.80 (m, 4H, PhCH$_2$*CH$_2$*CH$_2$Si), 1.15–1.24 (m, 24H, CMe$_2$), 0.87 (m, 4H, PhCH$_2$CH$_2$*CH$_2$*Si), 0.024 (s, 6H, SiMe). ^{13}C NMR (CDCl$_3$): δ 1.34, 16.33, 17.54, 23.82, 23.94, 40.16, 58.67, 124.18, 124.88, 136.14, 136.47, 141.54, 146.32, 146.54, 152.84, 166.83. Anal. calc. for $C_{41}H_{59}Cl_4N_3Si_2$: C, 62.18; H, 7.51; N, 5.31. Found: C, 62.43; H, 7.42; N, 5.40.)

*2.9. Synthesis of silica-supported bis(imino)pyridyl ligands **10–12***

To a 100-ml flask was added ethoxysilane-modified bis(imino)pyridyl ligand **4** (0.8 g), silica (1.5 g), and toluene 40 (ml). The mixture was refluxed for 48 h and then cooled to room temperature. The solid was filtered and washed copiously with diethyl ether, hexane, and THF and then dried under reduced pressure to afford silica-supported bis(imino)pyridyl ligand **10** (1.64 g) as a yellow powder. (FTIR (cm^{-1}) 1037, 1100, 1172, 1365, 1385, 1398, 1445, 1475, 1590, 1645, 2881, 2938, 2977. Raman: ν(C=N), 1645 cm^{-1}.)

Silica-supported bis(imino)pyridyl ligands **11** and **12** were prepared via the method similar to that used for supported ligand **10**.

*2.10. Synthesis of silica-supported bis(imino)pyridyl ligands **13–15***

To a 100-ml flask was added Si–Cl-modified bis(imino)-pyridyl ligand **7** (0.8 g), silica (1.5 g), triethylamine (5 ml), and toluene (40 ml). The mixture was refluxed for 48 h and then cooled to room temperature. The solid was isolated by filtration and washed copiously with diethyl ether, hexane, and THF, then heated at reduced pressure to afford silica-supported bis(imino)pyridyl ligand **13**. (FTIR (cm^{-1}) 1038, 1101, 1172, 1365, 1383, 1398, 1444, 1476, 1646, 2942, 2977. Raman: ν(C=N), 1646 cm^{-1}.)

Silica-supported bis(imino)pyridyl ligands **14** and **15** were prepared with a method similar to that used for supported ligand **13**.

2.11. Synthesis of silica-supported Fe(II) precatalysts

To a 100-ml flask was added silica-supported bis(imino)-pyridyl ligand **10** (1.2 g) in 30 ml THF and $FeCl_2 \cdot 4H_2O$

(0.159 g, 0.8 mmol), which was stirred at room temperature for 4 h. The solution was concentrated, and then hexane was added to afford the precipitate as a blue powder. The crude product was washed twice with diethyl ether, filtered, and dried at vacuum to afford **C1** (1.2 g, 95%). (Calc.: Fe, 8.80 mg/g. Found: Fe, 8.80 mg/g_{cat}.)

Precatalysts **C2–6** were prepared with a method similar to that used for **C1**.

2.12. Procedure for ethylene polymerization

Ethylene polymerization was carried out under atmospheric pressure in toluene in a 150-ml glass reactor equipped with a mechanical stirrer. Toluene (40 ml) was introduced into the nitrogen-purged reactor and stirred vigorously (600 rpm). The toluene was kept at a prescribed polymerization temperature, and then an ethylene gas feed (100 l/h) was started. After 30 min, polymerization was initiated by the addition of a toluene solution of MMAO and then a toluene solution of silica-supported Fe precatalyst to the reactor with vigorous stirring (600 rpm). After a prescribed time, isobutyl alcohol (10 ml) was added to terminate the polymerization reaction, and the ethylene gas feed was stopped. The resulting mixture was added to the acidic methanol (1 ml concentrated HCl in 500 ml methanol). The solid polyethylene was recovered by filtration, washed with methanol, and dried at 60 °C for 24 h in a vacuum oven.

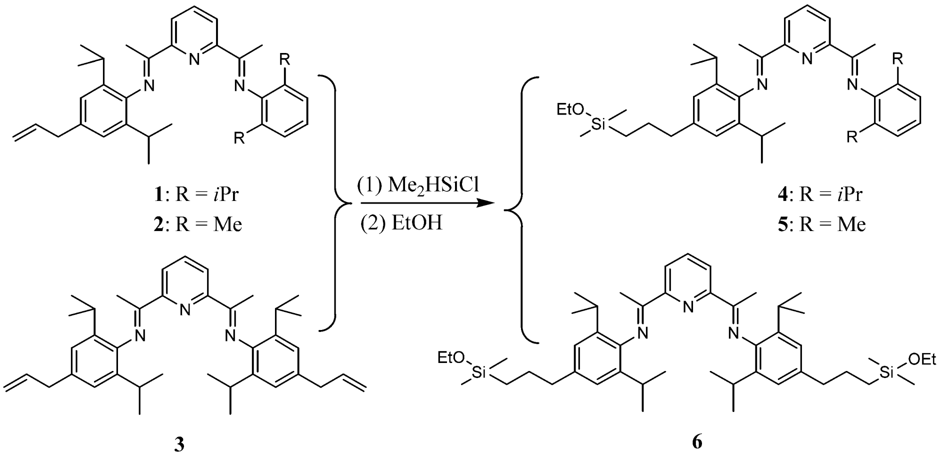
High-pressure polymerization was carried out in a 200-ml stainless-steel reactor equipped with a mechanical stirrer and internal cooling water coils. The reactor was baked under nitrogen flow for 24 h at 150 °C, subsequently cooled to the desired reaction temperature, and then purged with ethylene three times. Reagents and toluene were transferred to the reactor via a gas-tight syringe. Ethylene was introduced into the reactor, and pressure was maintained at 10 atm throughout the polymerization run with a continuous feed of ethylene gas. After allowing the polymerization to proceed for 30 min, we stopped it by turning the ethylene off and relieving the pressure. The reaction mixture was poured into a solution of HCl/ethanol (10 vol%). The polymer was isolated by filtration, washed with ethanol, and dried under vacuum.

3. Results and discussion

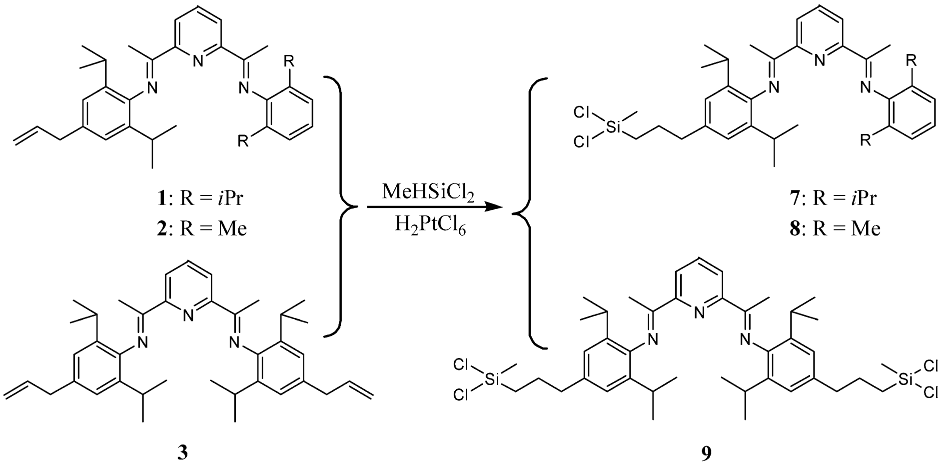
As shown in Scheme 1, ethoxysilane-modified bis(imino)pyridyl ligands **4–6** were prepared in good yields via the Pt-catalyzed hydrosilylation reactions of bis(imino)pyridyl containing allyl **1–3** with chlorodimethylsilane according to the method reported by Roovers and Setferth [37,38], and the succedent reactions of the resulting silane chloride with EtOH, with triethylamine as HCl capturer. Si–Cl-modified bis(imino)pyridyl ligands **7–9** were prepared by the hydrosilylation reaction of bis(imino)pyridyl containing allyl **1–3** with dichloromethylsilane, with H_2PtCl_6 as a catalyst (Scheme 2).

Two different methods were explored for the immobilization of bis(imino)pyridyl ligands on the surface of silica. One method is based on a direct reaction of the ethoxysilyl group of ethoxysilane-modified bis(imino)pyridyl ligands **4–6** with surface silanols of silica to form Si–O–Si bonds with concomitant release of ethanol (Scheme 3). The other method is based on a direct reaction of the Si–Cl group of Si–Cl-modified bis(imino)pyridyl ligands **7–9** with surface silanols in the presence of triethylamine as a capturer of HCl, forming Si–O–Si bonds (Scheme 4).

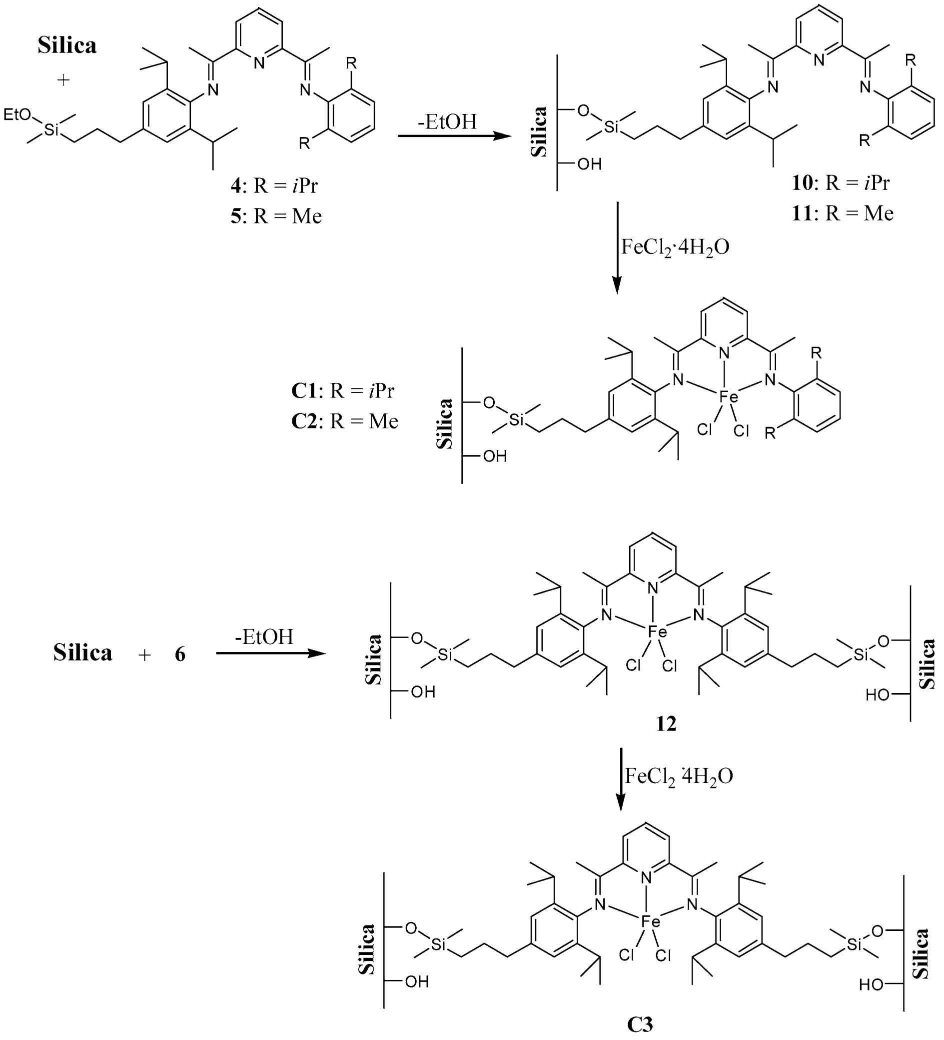
The immobilization of bis(imino)pyridyl ligands was characterized via FTIR, Raman, XPS spectroscopy, and ^{29}Si MAS NMR spectroscopy. From the FTIR spectra presented in Fig. 1, some characteristic features can be distinguished: for instance, the band at 1101 cm^{-1} indicates the presence of Si–C bonds in the Si–O–Si stretching region [39], the occurrence of a sharp peak at 1475 shows the presence of CH_2, the peak at 1385 cm^{-1} shows the presence of a $-CH_3$ group, and the bands at 2942 and 2977 cm^{-1} are attributed to ν_{C-H} ($-CH_3$ and $-CH_2-$). The Raman spectra shown in Fig. 2 also confirmed the immobilization of bis(imino)pyridyl lig-



Scheme 1. Preparation of the ethoxysilyl modified bis(imino)pyridyl ligands.

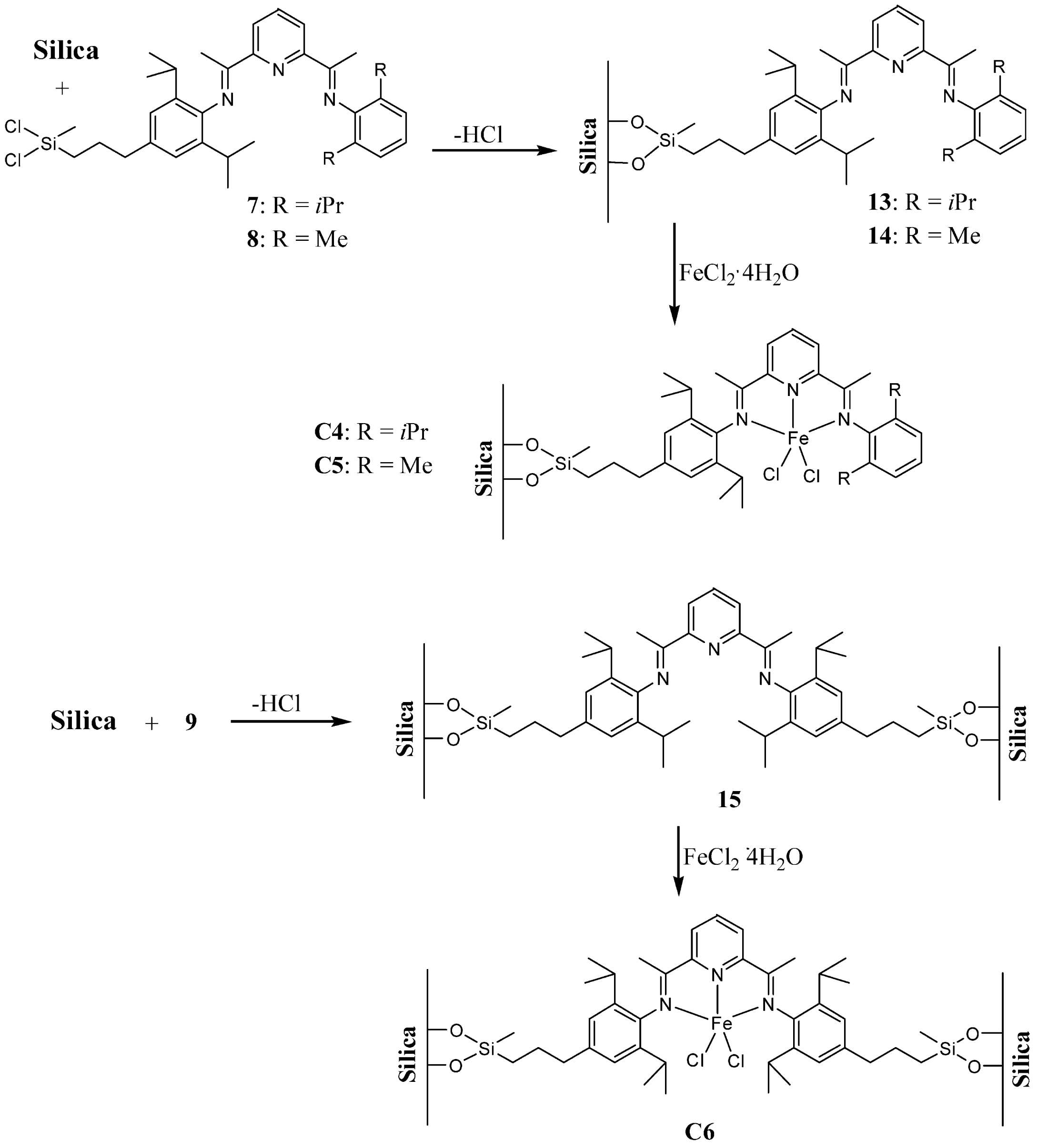


Scheme 2. Preparation of the Si–Cl modified bis(imino)pyridyl ligands.



Scheme 3. Method 1 to immobilize the bis(imino)pyridyl Fe(II) on silica surface.

ands, the sharp band at 1645 cm^{-1} indicates the presence of C=N (which is extremely weak at FTIR; Fig. 1), and the two sharp bands at 1579 and 1606 cm^{-1} come from pyridyl. The ^{29}Si MAS NMR spectrum of representative samples was shown in Fig. 3. The large ^{29}Si peaks at −103 and −111 ppm are from the silica framework (d); the peaks at −58 and −67 ppm correspond to the Si of silica linking the $-CH_2CH_2CH_2SiO-$ groups bearing a OH (b) or not (c), re-



Scheme 4. Method 2 to immobilize the bis(imino)pyridyl Fe(II) on silica surface.

spectively; and the peaks at −15 and −23 derive from the $CH_2CH_2CH_2Si$ (a) group [39,40].

Silica-supported precatalysts **C1–6** were obtained as blue powders via the complexation reactions of $FeCl_2 \cdot 4H_2O$ with the corresponding silica-supported bis(imino)pyridyl ligands. XPS spectra were used to investigate the binding energy of reactive atoms in the formation of the silica-supported bis(imino)pyridyl Fe(II) precatalysts, and the following changes in the XPS spectra were observed (Table 2): the binding energies of N 1*s* of ligand **15** are 398.8 and 401.2 eV (from Ph-N and pyridine-N, respectively), after complexation they change to 399.5 eV (**C6**), there is a drop of 0.3 eV in the binding energy of Fe $2p_{3/2}$ of silica-supported Fe(II) precatalyst **C1** over that of $FeCl_2 \cdot 4H_2O$, and there is a drop of 0.7 eV in the binding energy of Cl 2*p* of silica-supported Fe(II) precatalyst **C1** over that of $FeCl_2 \cdot 4H_2O$. These imply strong interactions between ligand **15** and $FeCl_2$ immobilized on the surface of silica. It can be seen from Table 2 that the binding energy value of Fe $2p_{3/2}$ in the homogeneous catalyst **C** is lower than that of the silica-supported catalyst **C6**. The increase in the binding energy from the homogeneous catalyst to the heterogeneous catalyst is indicative of the presence of some weak secondary interactions between Si–OH and Fe–Cl.

The data listed in Table 1 indicate that when Method 2 was used, the loadings were relatively high because of the easy reaction between Si–Cl and Si–OH. For example, the Fe loading of immobilized precatalyst **C6** is up to 45.9 mg_{Fe}/g_{cat}, about 4 times higher than obtained with the method reported by Kim and Herrmann [21,22]. From the

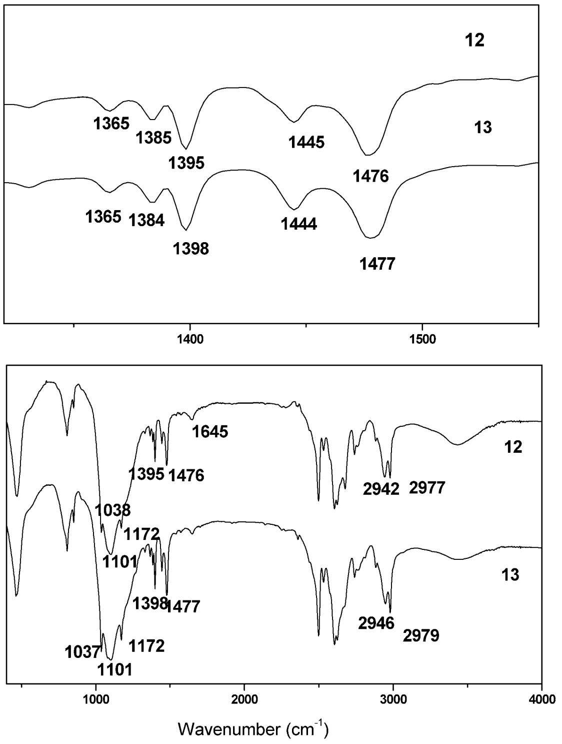


Fig. 1. FTIR spectra of silica supported bis(imino)pyridyl ligands **12** and **13**.

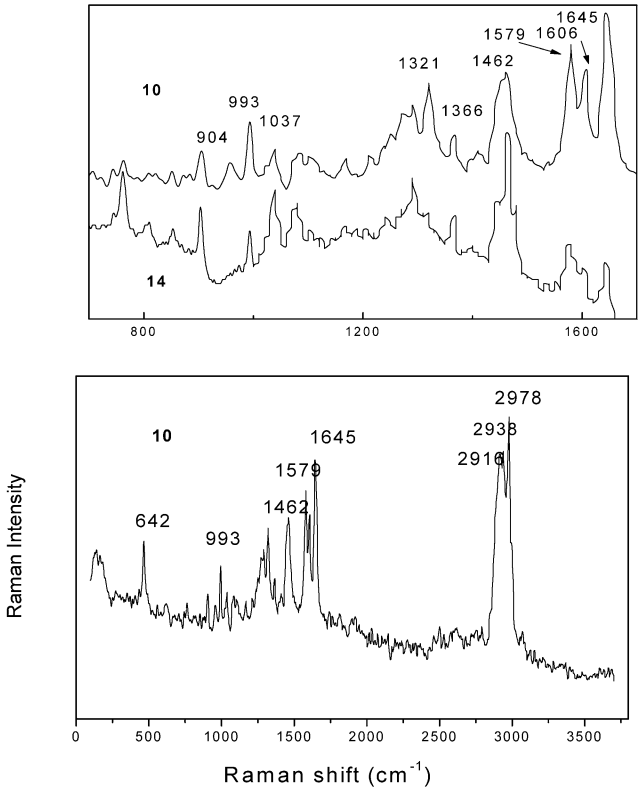


Fig. 2. Raman spectra of silica supported bis(imino)pyridyl ligands **10** and **14**.

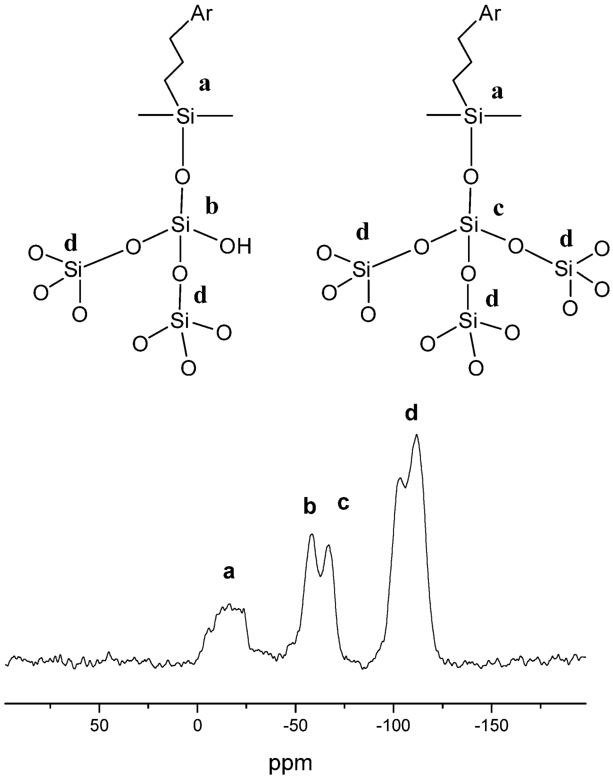


Fig. 3. ^{29}Si MAS NMR spectra of silica supported bis(imino)pyridyl ligand **10**.

Table 1
Results of supporting bis(imino)pyridyl Fe(II)

Precatalyst	N (%)	C (%)	H (%)	Loading (mmol/g)	Loading (mg_{Fe}/g)
C1	0.66	8.02	1.31	0.157	8.80
C2	0.76	7.44	1.19	0.18	10.1
C3	0.88	10.8	1.42	0.21	11.8
C4	2.03	21.3	2.56	0.48	26.9
C5	2.77	26.2	2.92	0.66	37.0
C6	3.34	40.3	4.94	0.82	45.9

Table 2
XPS binding energy values of silica supported bis(imino)pyridyl Fe(II) precatalyst C6, homogenous Fe(II) catalyst **C**, silica supported bis(imino)pyridyl ligand 15, and $FeCl_2 \cdot 4H_2O$

Compound	Binding energy (eV)		
	Fe $2p_{3/2}$	N 1*s*	Cl 2*p*
C6	712.2	399.5	198.6
C	710.8	399.8	198.9
15		398.8, 401.2	
$FeCl_2 \cdot 4H_2O$	711.9		199.3

FTIR spectra presented in Fig. 1, we can see clearly that some hydroxyls on the silica surface left after the supporting reaction, which indicates that the hydroxyls could not react with the ligands completely. In other words, the loadings were not fully determined by the number of hydroxyl groups on the surface of the silica. The two-arm ligands possess more Si–Cl groups than the corresponding single-arm ones, so the two-arm ligands have more chance to react with the hydroxyls on the silica surface, thus lead to the higher

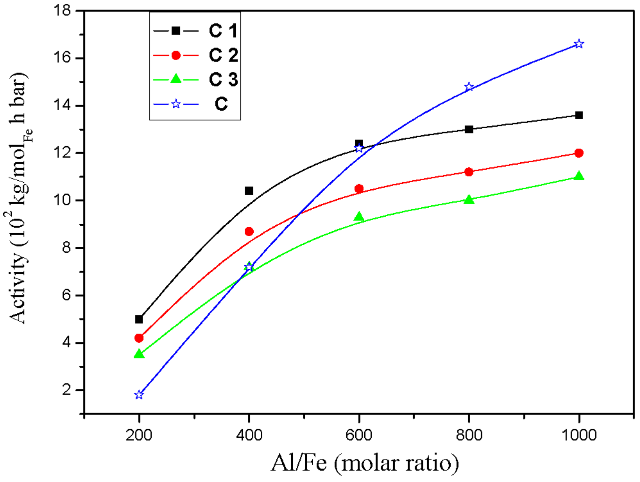


Fig. 4. Plot of catalytic activity of supported and non-supported Fe(II) catalysts versus Al/Fe molar ratio. 2.0 µmol Fe, $V_{total} = 50$ ml, Ethylene pressure = 1 atm, polymerization at 25 °C for 15 min.

loading of the two-arm precatalysts (**C3** and **C6**) compared with the single-arm ones (**C1** and **C4**).

The polymerizations of ethylene were conducted at atmospheric or 10 atm pressure of ethylene in toluene, with the immobilized precatalysts and the homogeneous precatalyst $[2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N{=}CMe(C}_5\text{H}_3\text{N)MeC{=}NC}_6\text{H}_3i\text{Pr}_2\text{-}2,6]\text{FeCl}_2$ (**C**) activated with modified methylaluminoxane (MMAO). At atmospheric pressure, we investigated the relationships among Al/Fe molar ratio, the activities of precatalysts **C1**–**3**, and the properties of the polyethylenes obtained. As shown in Fig. 4, the effect of Al/Fe molar ratio on the activity of the heterogeneous catalysts is similar to that of the corresponding homogeneous **C**. However, the catalytic activities of the supported precatalysts increase more slowly with the increase in Al/Fe molar ratio than does that of the corresponding homogeneous **C**. It is noteworthy that the supported precatalysts exhibit much higher activities than homogeneous precatalyst **C** at a low Al/Fe molar ratio, although precatalyst **C** displays higher activity at high Al/Fe molar ratio. In other words, favorable performances can be obtained for all of the heterogeneous catalysts at a lower Al/Fe ratio. For example, when the Al/Fe molar ratio equals 400, the activity of supported precatalysts **C1** is up to 1.04×10^3 kg$_{PE}$/(mol$_{Fe}$ h bar), higher than that of **C** (0.62×10^3 kg$_{PE}$/(mol$_{Fe}$ h bar)). The reason for this is that the crowded environment due to silica restrains the iron active center from deactivation to some extent. In order to further explore this, we prolonged the polymerization time to 1 h; the kinetic profiles of ethylene polymerization obtained with precatalysts **C1** and **C3** are shown in Fig. 5. The activities of silica-supported precatalysts show slow attenuation, which obviously differs from that of homogeneous precatalyst. (The activities of the homogeneous Fe(II) precatalyst decrease rapidly with time because of deactivation [41].) This also indicates that the surrounding silica can restrain the iron catalytic active center from deactivation.

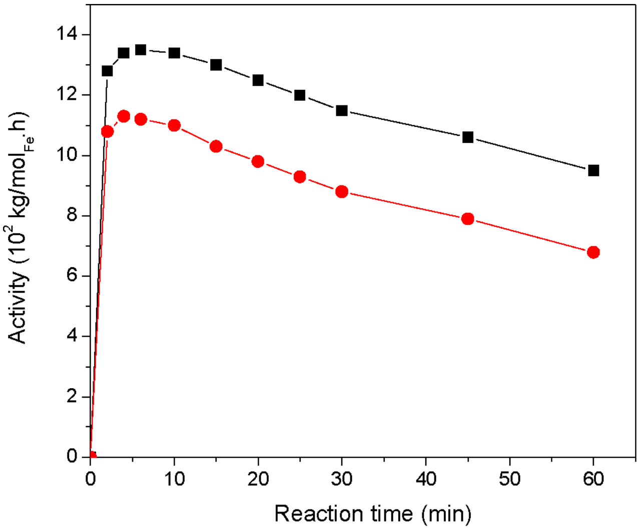


Fig. 5. Plot of catalytic activity of supported Fe(II) catalysts versus polymerization time (■, **C1**; ●, **C3**). 2.0 µmol Fe, Al/Fe = 600, $V_{total} = 50$ ml, polymerization reaction under atmospheric pressure and at 25 °C.

Table 3
The results of ethylene polymerization with the heterogeneous iron precatalysts[a]

Entry	Precatalyst	Al/Fe (molar ratio)	Activity (10^2 kg$_{PE}$/(mol$_{Fe}$ h bar))	T_m[b] (°C)	M_v[c] (10^4 g/mol)
1	**C1**	200	5.0	139.3	62.3
2		400	10.4	136.7	34.7
3		600	12.4	134.8	25.7
4	**C2**	200	4.2	138.4	56.2
5		400	8.7	137.2	37.3
6		600	10.5	134.6	24.6
7	**C3**	200	3.5	140.2	66.3
8		400	7.2	138.6	45.3
9		600	9.3	135.3	31.2
10	**C4**	200	4.2	139.3	61.2
11		400	6.9	136.7	35.7
12		600	11.2	134.2	22.7
13	**C5**	200	3.8	138.4	58.2
14		400	6.3	135.2	36.3
15		600	10.1	133.6	27.6
16	**C6**	200	3.3	140.2	66.3
17		400	6.8	137.6	39.3
18		600	9.3	135.3	31.2
19	**C**	200	1.8	128.2	8.3
20		400	7.2	127.8	6.5
21		600	12.2	125.8	5.4

[a] Polymerization conditions: 2.0 µmol Fe, $V_{total} = 50$ ml, 1 atm pressure of ethylene, polymerization at 25 °C for 15 min.

[b] Melting temperature determined by DSC with a heating rate of 10 °C/min in nitrogen.

[c] Viscosity-average molecular weights calculated from the equation $[\eta] = 6.2 \times 10^4 M_v^{0.7}$ [36].

Typical results for ethylene polymerization at atmospheric pressure with silica-supported catalysts **C1**–**6** and the homogeneous catalyst **C** activated with MMAO are summarized in Table 3. The data listed in Entries 1–18 indicate that the catalytic performances of two kinds of the immo-

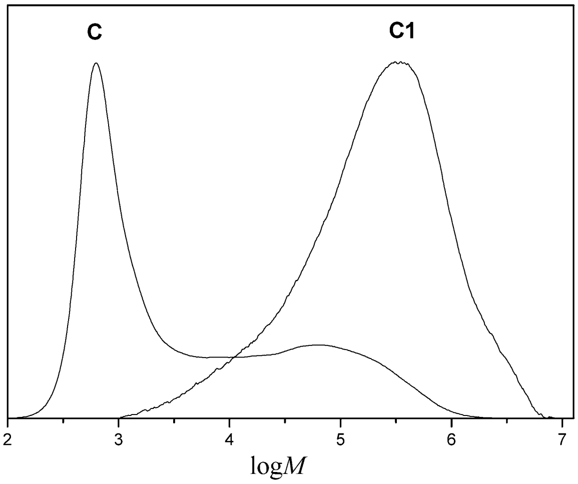


Fig. 6. GPC curves of the polyethylene prepared with silica supported Fe(II) catalyst **C1** and homogenous Fe(II) catalyst **C**. 2.0 µmol Fe, $V_{\text{total}} = 50$ ml, Ethylene pressure = 1 atm, polymerization at 25 °C for 15 min.

Table 4
The results of ethylene polymerization with the heterogeneous iron precatalysts[a]

Entry	Precatalyst	Al/Fe (molar ratio)	Activity (10^2 $\text{kg}_{\text{PE}}/(\text{mol}_{\text{Fe}}$ h))	T_m[b] (°C)	M_v[c] (10^4 g/mol)
1	**C1**	300	8.8	136.3	36.8
2		400	10.4	135.4	28.7
3	**C2**	300	7.6	136.8	38.2
4		400	9.4	134.2	27.4
5	**C3**	300	7.5	137.8	46.3
6		400	8.9	135.9	35.3
7	**C4**	300	6.7	137.6	39.2
8		400	8.4	135.2	28.4
9	**C5**	300	7.8	137.4	38.9
10		400	9.7	135.2	31.3
11	**C6**	300	6.6	138.2	52.3
12		400	9.2	135.6	34.7

[a] Polymerization conditions: 2.0 µmol Fe, $V_{\text{total}} = 50$ ml, 10 atm pressure of ethylene, polymerization at 70 °C for 30 min.

[b] Melting temperature determined by DSC with a heating rate of 10 °C/min in nitrogen.

[c] Viscosity-average molecular weights calculated from the equation $[\eta] = 6.2 \times 10^{-4} M_v^{0.7}$ [36].

bilized precatalysts prepared (**C1**–**3** vs. **C4**–**6**) by different methods are comparable. In the case of a low Al/Fe molar ratio, the heterogeneous catalysts **C1**–**6** all show high activities and convert ethylene to high-molecular-weight linear polyethylene as determined by DSC (show only one T_m peak). The melting temperature (T_m) values of the polymers produced with the heterogeneous precatalysts increase by ca. 10 °C compared with that with homogeneous catalyst **C**, which is evidently ascribed to the increase in molecular weight (e.g., Entry 1, **C1**, $T_m = 139.3\,°\text{C}$, $M_v = 62.3 \times 10^4$ g/mol; Entry 13, **C5**, $T_m = 138.4\,°\text{C}$, $M_v = 58.2 \times 10^4$ g/mol; Entry 19, **C**, $T_m = 128.2\,°\text{C}$, $M_v = 8.3 \times 10^4$ g/mol). In addition to the variation in molecular weights, a difference in the molecular weight distributions (MWD) of the resultant polymers could be observed in Fig. 6, which shows two GPC traces for polymerization tests of homogenous precatalyst **C** and heterogeneous **C1** under the same conditions. When precatalyst **C**/MMAO is used, the MWD of PE displays clearly bimodal distribution, and the low-molecular-weight fraction is dominant. In contrast, using precatalyst **C1**/MMAO, we obtained high-molecular-weight and unimodal distribution polymer (weight-averaged molecular weight $\overline{M}_w = 50.1 \times 10^4$ g/mol, polydispersity index PDI = 9.7). In comparison with precatalyst C, the silica-supported precatalysts produce much higher molecular weight polymers with unimodal MWD. This may be ascribed to the steric surrounding due to silica, which hinders β-H transfer reaction and chain transfer toward organic aluminum to some extent.

A series of high-pressure polymerization experiments were carried out to further evaluate the performance of the silica-supported Fe(II) precatalyst. Under 10 atm of ethylene pressure, we conducted the polymerization at a high temperature of 70 °C, with all of the heterogeneous catalysts **C1**–**6**. Representative results are listed in Table 4. At high temperature, homogeneous bis(imino)pyridyl Fe(II) displayed no or very low catalytic activity toward ethylene polymerization and produced oligomers, due to deactivation and chain transfer, even though under high-pressure conditions. However, the data listed in Table 4 indicate that the heterogeneous Fe(II) precatalysts display moderate catalytic activity and produce high-molecular-weight polyethylenes under the same conditions. For instance, precatalysts **C1** and **C4** display catalytic activities of up to 880 and 670 $\text{kg}_{\text{PE}}/(\text{mol}_{\text{Fe}}\ \text{h})$, respectively, and produce high-molecular-weight polymers (Entry 1, **C1**, $M_v = 36.8 \times 10^4$ g/mol, $T_m = 136.3\,°\text{C}$. Entry 7, **C4**, $M_v = 39.2 \times 10^4$ g/mol, $T_m = 137.6\,°\text{C}$) at 70 °C, at a low Al/Fe molar ratio. However, compared with lower temperature, the activity decreased greatly under high temperature because of deactivation; this result is similar to that reported by Herrmann [21].

The data listed in Tables 2 and 3 indicate that precatalysts **C1**–**2** and **C4**–**5** display higher activities than precatalysts **C3** and **C6** bearing two arms supported by silica in the aryl, respectively. In contrast, precatalysts **C3** and **C6** produce higher molecular weight polyethylenes compared with precatalysts **C1**–**2** and **C4**–**5** bearing only one arm supported by silica in the aryl. This result implies that the insertion of ethylene monomer into the active center of the Fe(II) catalysts supported by two arms from silica becomes a little more difficult, and meanwhile the steric crowding also restrains the chain transfer reaction.

In conclusion, we reported two methods to immobilize bis(imino)pyridyl Fe(II) precatalysts on silica by one or two arms. The loadings are much higher than that used before. Though initial activities of the silica-supported Fe(II) precatalysts are much lower than that of the corresponding homogeneous one, these heterogeneous precatalysts possess a long lifetime, still display relatively high catalytic activities toward ethylene polymerization half an hour later, and produce much higher molecular weight polymers. What cheers us is that the heterogeneous precatalysts can maintain relatively high activities, even in the case of a low Al/Fe molar ratio and at high reaction temperature.

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References

[1] S.D. Ittel, L.K. Johnson, M. Brookhart, Chem. Rev. 100 (2000) 1169.
[2] L.S. Boffa, B.M. Novak, Chem. Rev. 100 (2000) 1479.
[3] S. Mecking, Angew. Chem. Intern. Ed. 40 (2001) 534.
[4] B. Rieger, L.S. Baugh, S. Kacker, S. Striegler, Late Transition Metal Polymerization Catalysis, Wiley–VCH, Weinheim, 2003.
[5] B.L. Small, M. Brookhart, A.M.A. Bennnett, J. Am. Chem. Soc. 120 (1998) 4049.
[6] B.L. Small, M. Brookhart, J. Am. Chem. Soc. 120 (1998) 7143.
[7] B.L. Small, M. Brookhart, Macromolecules 32 (1999) 212.
[8] G.J.P. Britovsek, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S.J. McTavish, G.A. Solan, A.J.P. White, D.J. Williams, Chem. Commun. (1998) 849.
[9] G.J.P. Britovsek, M. Bruce, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S. Mastroianni, S.J. McTavish, C. Redsha, G.A. Solan, S. Stroemberg, J.P. White, D.J. Williams, J. Am. Chem. Soc. 121 (1999) 8728.
[10] G.J.P. Britovsek, V.C. Gibson, B.S. Kimberley, S. Mastroianni, C. Redshaw, G.A. Solan, A.J.P. White, D.J. Williams, J. Chem. Soc., Dalton Trans. (2001) 1639.
[11] G.G. Hlatky, Chem. Rev. 100 (2000) 1347.
[12] R. Duchateau, Chem. Rev. 102 (2002) 3525.
[13] G.S.B. Fink, J. Zechlin, C. Przybyla, B. Tesche, Chem. Rev. 100 (2000) 1377.
[14] T. Uozumi, T. Toneri, K. Soga, T. Shiono, Macromol. Rapid Commun. 18 (1997) 9.
[15] C.J. Miller, D.ó. Hare, Chem. Commun. (2004) 1710.
[16] S. Collins, W.M. Kelly, D.A. Holden, Macromolecules 25 (1992) 1780.
[17] E.I. Iishola, S. Timonen, T.T. Pakkanen, O. Harkki, P. Lehmus, J.V. Seppala, Macromolecules 30 (1997) 2853.
[18] P.C. Thune, J. Loos, U. Weingarten, F. Muller, W. Kretschmer, W. Kaminsky, P.J. Lemstra, H. Niemantsyerdriet, Macromolecules 36 (2003) 1440.
[19] J.R. Severn, J.C. Chadwick, V. Van Axel Castelli, Macromolecules 37 (2004) 6258.
[20] B.Y. Lee, J.S. Oh, Macromolecules 33 (2000) 3194.
[21] F.A.R. Kaul, G.T. Puchta, H. Schneider, F. Bielert, D. Mihalios, W.G.A. Herrmann, Organometallics 21 (2002) 74.
[22] Il Kim, B.H. Han, C.S. Ha, J.K. Kim, S.H. Suh, Macromolecules 36 (2003) 6689.
[23] L. Britcher, H. Rahiala, K. Hakala, P. Mikkola, J.B. Rosenholm, Chem. Mater. 16 (2004) 5713.
[24] R.B. Huang, D.B. Liu, S.B. Wang, B.Q. Mao, Macromol. Chem. Phys. 205 (2004) 966.
[25] C.B. Liu, T. Tang, B.T. Huang, J. Catal. 221 (2004) 162.
[26] M.W. McKittrick, C.W. Jones, J. Catal. 227 (2004) 186.
[27] S.B. Roscoe, J.M. Frechet, J.F. Walzer, A.J. Dias, Science 280 (1998) 270.
[28] H. Nishida, T. Uozumi, K. Soga, Macromol. Rapid Commun. 16 (1995) 821.
[29] M. Stork, M. Koch, M. Klapper, K. Mullen, H. Gregorius, U. Rief, Macromol. Rapid Commun. 20 (1999) 210.
[30] M. Koch, M. Stork, M. Klapper, K. Mullen, H. Gregorius, Macromolecules 33 (2000) 7713.
[31] S.J. Obrey, A. Barron, Macromolecules 35 (2002) 1499.
[32] G.X. Jin, D. Zhang, J. Polym. Sci. Part A 42 (2004) 1018.
[33] M. Schlogl, S. Riethmueller, C. Troll, M. Moller, B. Rieger, Macromolecules 37 (2004) 4004.
[34] S.C. Hong, T. Teranishi, K. Soga, Polymer 39 (1998) 7153.
[35] C.K. Liu, G.X. Jin, New J. Chem. 26 (2002) 1485.
[36] R. Chiang, J. Polym. Sci. 28 (1957) 235.
[37] L.L. Zhou, J. Roovers, Macromolecules 26 (1993) 963.
[38] D. Setferth, D.Y. Son, Organometallics 13 (1994) 2682.
[39] J. Evans, A.B. Zaki, M.Y. EI-Sheikh, S.A. EI-Safty, J. Phys. Chem. B 104 (2000) 10271.
[40] H. Juvaste, E.I. Iiskola, T.T. Pakkanen, J. Mol. Catal. A Chem. 150 (1999) 1.
[41] J.Y. Liu, Y.S. Li, J.Y. Liu, Z.S. Li, Macromolecules 38 (2005) 2559.