Dalton Transactions

PAPER

Cite this: Dalton Trans., 2013, 42, 9089

Received 4th January 2013, Accepted 13th February 2013 DOI: 10.1039/c3dt00040k

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Introduction

The search for new "non-metallocene" olefin polymerization catalysts based on transition metal complexes is a field of major interest involving many academic and industrial research groups.1 The relatively ill-defined nature of these paramagnetic olefin polymerization catalysts with respect to coordination environment and oxidation state, however, have prompted considerable efforts to synthesize well-defined homogeneous single-site Cr-based catalysts.^{1b,2} Anionic non-Cp ligands have produced effective polymerization catalysts, with the ligand structure displaying significant effect on catalyst activity and polymer properties. Chromium(III) complexes with β -diimine ligands were reported as efficient catalysts both for ethylene homopolymerization and copolymerization with α -olefins.³ Chromium(III) complexes based on monoanionic phenoxyamide ligands were reported as efficient catalysts for ethylene polymerization.⁴ The iminopyrrolide chromium complexes showed moderate ethylene polymerization activity in the presence of diethylaluminum chloride.5 Recent research suggested that chromium catalysts based on phosphorous-

^aState Key Laboratory of Molecular Engineering of Polymers, Department of Chemistry, Fudan University, Shanghai 200433, P. R. China.

E-mail: gxjin@fudan.edu.cn; Fax: (+86)-21-65643776

Ethylene polymerization by new chromium catalysts based on carborane [SSO] ligands[†]

Ping Hu,^a Ya-Lin Qiao,^a Zhen-Hua Li,^a Jian-Qiang Wang^b and Guo-Xin Jin*^a

Tridentate carborane [S, S, O] ligands **2a–2b** [(HOC₆H₂R₂-4,6)(CH₂)SC(B₁₀H₁₀)C(Ph)₂P \Longrightarrow S, R = ^tBu (**2a**), R = Me (**2b**)] were synthesized and characterized. Reaction of CrCl₃(THF)₃ with the sodium salts of ligands **2a** and **2b** afford six-coordinated chromium complexes **3a** and **3b**. EXAFS spectroscopy performed on complex **3a** to describe the coordination chemistry of ligand **2a** around chromium center. DFT calculations were also performed on complexes **3a** to analyze the structure. The preliminary screening results revealed that six-coordinated chromium complexes **3a–3b** displayed good catalytic activities towards ethylene polymerization in the presence of modified methylaluminoxane. The effect of polymerization parameters such as cocatalyst, reaction temperature, ethylene pressure, and reaction time on polymerization behavior were investigated in detail. The polymer obtained from this homogeneous catalytic reaction has a fibroid morphology.

incorporated ligands exhibited high activities in ethylene polymerization or ethylene copolymerization with other α -olefins.^{6–8} Li's group developed new chromium catalysts based on aminopyrrolide ligands which were efficient catalysts for ethylene polymerization.⁹ Furthermore, they found that the CrCl₃(thf)₃–ligand system containing soft donor (sulfur or phosphorous atoms) ligands displayed higher activity than the hard donor ones (oxygen or nitrogen atoms), in line with the results of the titanium-based catalyst system reported by Gibson and co-workers.¹⁰

A three-dimensional aromatic, soluble and high thermally stable bulky carborane cage, has been used as a ligand to construct various metal complexes since the first report on a metalladicarbollide complex by Hawthorne and coworkers.^{11,12} We are interested in using carborane ligands to synthesize effective olefin polymerization catalysts.¹³ These carborane ligands contain a highly electron-deficient carborane moiety, which should enhance the Lewis acidity of the central metal ion and, thus, increase the activity of the resulting transition metal complexes. On the other hand, the good solubility of transition metal complexes with carborane ligands is of benefit for high catalytic activity. As an extension of our investigation of transition metal complexes with carborane ligands, tridentate [S, S, O] carborane ligands 2a-2b were prepared and characterized. The soft pendant donors in this ligand are sulfur atoms, while the hard donor is an oxygen atom. In this work, we report the chromium complexes based on this type of [S, S, O] carborane ligands, which show high activities for ethylene polymerization to produce high molecular weight PE when activated with MMAO.

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^bShanghai Synchrotron Radiation Facility, Chinese Academy of Sciences, Shanghai 201204, P. R. China

 $[\]uparrow \rm CCDC$ 916907 (2a). For crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt00040k

Results and discussion

Synthesis and characterization

The synthesis of ligands **2a–2b** are outlined in Scheme 1. Compound **1** [1-(2'-(S)PPh₂)-o-carborane] was prepared by the monophosphino *o*-carborane reacted with elemental sulfur in the presence of Et₃N.^{13d} The lithium salt of compound **1** was treated with elemental sulfur then reacted with 2,4-di-*tert*-butyl-6-chloromethylphenol or 2,4-dimethyl-6-chloromethylphenol affording tridentate carborane [S, S, O] ligands **2a** [(HOC₆H₂^tBu₂-4,6)(CH₂)SC(B₁₀H₁₀)C(Ph)₂P=S] and **2b** [(HOC₆H₂Me₂-4,6)(CH₂)SC(B₁₀H₁₀)C(Ph)₂P=S] in good yields. These ligands are stable in air and moisture, and were resolvable in common organic solvents such as THF, CH₂Cl₂, toluene, and ethyl ether.

NMR spectroscopic data of ligands **2a–2b** are consistent with the described structures. The crystal of compound **2a**, which was grown by the slow evaporation from toluene solution, was determined by X-ray diffraction (Fig. 1).

Chromium complexes **3a–3b** were obtained by easy synthetic routes in good yields (Scheme 2). After deprotonation by



Scheme 1 Synthetic route to ligands 2a–2b.



Fig. 1 Molecular structure of ligand 2a with thermal ellipsoids drawn at the 30% level.



Scheme 2 Synthesis of chromium complexes 3a-3b

sodium hydride at 0 °C in THF, ligands **2a** and **2b** could react with $CrCl_3(THF)_3$ to give the six-coordinated complexes **3a** and **3b**. The severe line broadening in the ¹H NMR spectra for complexes **3a** and **3b** in $CDCl_3$ indicates that these chromium complexes are paramagnetic species. However, their IR spectra and elemental analysis are consistent with the described structure (see Experimental section). The FTIR spectra of **2a** and **3a** were studied and the results indicated the disappearance of a broad peak representing stretching frequencies of OH at about 3000 cm⁻¹. Instead, stretching frequencies of tetrahydrofuran at about 3405, 3060, and 2970 cm⁻¹ were observed. In addition, the peak representing stretching frequencies of P=S bond at around 680 cm⁻¹ has no obvious shift. Like the comparison of **2a** and **3a**, a similar difference in FTIR spectra was observed for **2b** and **3b**.

However, the structures of complexes **3a–3b** are not the expected structures. The chromium atom in complex **3a** is coordinated with oxygen atoms of solvent (THF) instead of the terminal P—S type sulfur atom of the ligand.

The local atomic environment and charge state of metal center in complex 3a were further confirmed by X-ray absorption spectroscopy, including extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) (Fig. 2). The EXAFS spectra allows us to get information on the environment around the metal center, which has already been used to characterize transition metal complexes for olefin polymerization.¹⁴ The Cr K-edge absorption spectrum, plotted in Fig. 2, shows a typical line peak at 6013 eV for Cr compounds. The fitting of the EXAFS spectra (Table 1) of 3a was performed with a three-shells model, in which the first coordination shell at 1.98 Å consists of the three oxygen atoms from the functional carborane ligand and THF solvent. The second shell is the chlorine backscatterer at about 2.31 Å. The third shell at 2.93 Å consists of the sulfur atom from the functional carborane ligand.

The efforts to separate the two kinds of coordinating oxygen failed due to the close bond lengths of Cr–O(ligand)



Fig. 2 Cr K-edge XANES spectra of sample for **3a**; Fourier transform of experimental data and fit for **3a** (inset).

Table 1 Fit parameters of Cr EXAFS spectra for complexes 3a

	Shell	N^{a}	R^b	$\sigma^{2\ c} \left(10^{-3} \text{ \AA}^2\right)$	$\Delta E_0^{\ d} (\mathrm{eV})$
3a	Cr–O Cr–Cl Cr–S	3.3 ± 0.6 1.8 ± 0.4 0.8 ± 0.2	$\begin{array}{c} 1.98 \pm 0.01 \\ 2.31 \pm 0.01 \\ 2.93 \pm 0.02 \end{array}$	5.3 ± 0.6 4.8 ± 0.8 2.2 ± 1.6	-1.0 ± 0.9 -0.3 ± 0.2 19.4 ± 1.1

 a Coordination number. b Distance between absorber and backscatterer atoms. c Debye–Waller factor. d Inner potential correction.

and Cr–O(THF). With the help of EXAFS analysis, the solidstate structure of **3a** was confirmed to be the six coordinated model as [O, O, O, Cl, Cl, S].

DFT calculations were performed on complex **3a** to analyze the structure.¹⁵ Possible structures were considered and optimized. The geometries of six possible structures are shown in Fig. 3. Relative energies (in kcal mol⁻¹) of these structures are also shown in Fig. 3.

The results indicate that structure **S1**, in which the chromium atom is bonded to only one sulfur atom and two tetrahydrofuran, is the lowest energy structure. The thioether-type sulfur has a better bonding ability to chromium than the terminal P—S type sulfur (Fig. 3, **S1**, **S2** *vs*. **S3**, **S4**). Complexes with more or less than two tetrahydrofuran ligands are less stable (Fig. 3, **S1**, **S2** *vs*. **S3**, **S4**, **S5**, **S6**). Moreover, the structures with two chloride atoms in the *trans*-position have lower relative energies (Fig. 3, **S1** *vs*. **S2**, **S3** *vs*. **S4**). These DFT calculation results had proved that the structure **S1** which was described as complex **3a** in Scheme 2 was reasonable.



Fig. 3 Geometries of the six optimized structures and their relative energies (in kcal mol⁻¹). Green, yellow, red, blue, orange, pink, and gray balls are chlorine, sulfur, oxygen, chromium, phosphorus, boron and carbon atoms, respectively. The hydrogen atoms are omitted for clarity.

Ethylene polymerization. Upon activation with modified methylaluminoxane (MMAO), chromium complexes **3a–3b** were found to be active for ethylene polymerization. The polymerization results are summarized in Table 2.

The polymerization was performed in a 100 mL Schlenk flask. The flask was repeatedly evacuated and refilled with argon, and finally filled with ethylene gas. MMAO or other cocatalysts were added *via* a syringe. The catalyst, dissolved in toluene under dry argon, was transferred into the Schlenk flask to initiate the polymerization. The polymerization was initiated by the addition of a heptane solution of MMAO and a toluene solution of the chromium catalyst.

The reaction conditions in ethylene polymerization have been optimized for precatalyst 3a. We began our studies by searching for the optimal cocatalyst to chromium catalyst system (entries 1-4, Table 2). Good catalytic performances are observed in the presence of MAO or MMAO as the cocatalyst, of which MMAO gives better results than MAO. For example, for the molar ratio of Al/Cr = 2000, under 1 atm ethylene pressure, the catalytic activity is 170 kg PE mol⁻¹(Cr) h⁻¹ using MAO, while the system with MMAO gives 225 kg PE $mol^{-1}(Cr)$ h^{-1} . In addition to MAO and MMAO, triethylaluminum (TEA) and triisobutylaluminum (TIBA) were also used as cocatalysts. However, only a trace amount of polymer was obtained in those cases, as shown in Table 2 (entries 3-4). Therefore detailed investigations have been carried out employing MMAO through varying the ratio of Al/Cr, reaction temperature, and time, and the results are tabulated in Table 2.

The amount of cocatalyst MMAO was found to have a dramatic effect on catalyst activity and molecular weights of the polymer. According to the data at different Al/Cr ratios ranging from 1000 to 3000 (entries 4–7), the maximum activity is shown at an Al/Cr molar ratio of 2000 (entry 4). The reaction temperature also considerably affects the catalytic activities and molecular weights. As can be seen from Table 2 (entries 4, 8–10), with increasing temperature from 0 to 80 °C, the catalytic activities of complex **3a** first increase and reach a maximum at room temperature and then decrease. The molecular weights of polyethylene decrease with elevating temperature due to a faster chain transfer and termination at higher temperature.

To determine the effect of reaction time on the activity and molecular weight (M_v) of the resulting polymers, ethylene polymerization using the complex 3a/MAO catalytic system was conducted over different time periods, namely, 10, 30, 60 and 90 min (entries 4, 11–13 in Table 2), the highest activity (310 kg of PE (mol of Cr)⁻¹ h⁻¹) was obtained in a period of 10 min.

With the ethylene pressure increased, the catalytic activity generally notably improved. Increasing the ethylene pressure from 1 to 10 atm, the polymerization activity further increased to 630 kg PE mol⁻¹(Cr) h⁻¹ in current catalytic system (entry 14, Table 2). Moreover, no significant enhancement in molecular weight was seen even at 10 atm ethylene pressure (entries 4 and 14, Table 2), which was similar to the literature results.⁹ The apparent nondependence of the molecular weight on

Table 2 Ethylene polymerization results with chromium complexes 3a-3b^a

Entry	Cat.	Cocatalyst	Al/Cr ratio	Temp (°C)	Time (min)	Activity ^b	$M_{ m v}^{\ c}$
1	3a	TEA	2000	25	30	Trace	d
2	3a	TIBA	2000	25	30	Trace	d
3	3a	MAO	2000	25	30	170	64
4	3a	MMAO	2000	25	30	225	63
5	3a	MMAO	3000	25	30	90	57
6	3a	MMAO	1500	25	30	180	66
7	3a	MMAO	1000	25	30	97	68
8	3a	MMAO	2000	0	30	102	69
9	3a	MMAO	2000	50	30	120	59
10	3a	MMAO	2000	80	30	32	42
11	3a	MMAO	2000	25	10	310	50
12	3a	MMAO	2000	25	60	110	71
13	3a	MMAO	2000	25	90	54	83
14^e	3a	MMAO	2000	25	30	630	64
15	3b	MMAO	2000	25	30	110	69

^{*a*} Conditions: [Cr] 2 µmol, toluene (total volume 50 mL), 1 atm of ethylene. ^{*b*} Activity in kg PE mol⁻¹(Cr) h⁻¹. ^{*c*} M_v measured by the Ubbelohde calibrated viscosimeter technique in decahydronaphthalene at 135 °C, units of 10⁴ g mol⁻¹. ^{*d*} Undetermined. ^{*e*} 10 atm of ethylene.



Fig. 4 SEM image of polyethylene obtained with complex 3a/MMAO.

ethylene pressure is a strong indication for chain transfer by β-hydride transfer to the monomer rather than to the metal. The R group on the ligand has a significant effect on catalytic activity. Complex **3a** with a ^{*t*}Bu group on the *ortho*-position, show higher activities than complex **3b**, indicating that proper steric hindrance on the ligand may avoid active species deactivating to some extent.

The fibroid morphology of polyethylene obtained from the reaction catalyzed by the homogeneous catalyst **3a/MMAO** (see Fig. 4) is different from the sponge-like morphology catalyzed when other homogeneous catalysts are used.¹⁶

Conclusion

In conclusion, novel chromium complexes based on carborane [SSO] ligands were synthesized and employed as catalysts for ethylene polymerization to produce high molecular weight PE with good activities under mild conditions in the presence of MMAO as a cocatalyst. The reaction parameters such as cocatalyst concentration, polymerization temperature, ethylene pressure, and reaction time significantly affect the catalytic activity. Further investigations exploring higher activity chromium catalysts based on other carborane ligands and possibilities for copolymerization of ethylene with other olefins using these types of catalysts are underway.

Experimental

General considerations

All manipulations of air and/or water-sensitive compounds were carried out under dry argon using standard Schlenk techniques. Tetrahydrofuran (THF), hexane, and toluene were distilled from sodium benzophenone. Commercial reagents, namely, NaH, CrCl₃(THF)₃, *n*-BuLi (1.6 M in hexane) were purchased from Aldrich. Methylaluminoxane (MAO, 1.46 M in toluene), modified methylaluminoxane (MAO, 1.88 M in heptane solution), triethylaluminum (TEA) and triisobutylaluminum (TIBA) were purchased from Akzo Nobel Chemical Inc. Commercial ethylene was directly used for polymerization without further purification. The other reagents and solvents were commercially available.

¹H NMR and ¹³C NMR measurements were obtained on a Bruker AC 400 spectrometer in CDCl₃ solution. ³¹P NMR (162 MHz) spectra were measured with a VAVCE DMX-400 spectrometer. IR spectra were measured on a Nicolet Avatar-360 spectrophotometer. Elemental analyses for C and H were carried out on an Elementar III Vario EI analyzer.

The investigation of the structure of polyethylene was performed by scanning electron microscopy (SEM) using a Philips XL30 FEG FE-SEM instrument at 10 kV.

Preparation of ligands 2a and 2b. Compound 1 was synthesized according to our previously reported methods.^{13d} To a solution of compound 1 (180 mg, 0.5 mmol) in dry Et₂O (10 mL) at -78 °C was dropwise added 1.6 M of *n*-BuLi in hexane (0.32 mL, 0.5 mmol) and the reaction mixture stirred for 1 h at -78 °C. Sulfur (16 mg, 0.5 mmol) was added after the reaction mixture was warmed to room temperature. Stirring was maintained for 1 h. After a solution of 2,4-di-*tert*-butyl-6-chloromethylphenol (127 mg, 0.5 mmol) or 2,4-di-

methyl-6-chloromethylphenol (85 mg, 0.5 mmol) in Et_2O (10 mL) was added, a white precipitate was generated. Stirring was maintained for 2 h at room temperature. The mixture was filtered and the solvent of the filtrate was removed under vacuum. Recrystallization of the product from hexane afforded ligands 2a and 2b as white needles in yields of 70%(2a) and 68%(2b).

2a: IR (KBr, cm⁻¹), 2995 m(OH), 2575 s(B-H), 1650 w, 1550 m, 1450 s(Ph), 1188 m(P-Ph), 680 m(P=S). ¹H NMR (CDCl₃, 400 MHz): δ 8.37–8.32 (m, 5H, Ph-H), 7.59–7.53 (m, 5H, Ph-H), 6.97 (s, 1H, Ph-H), 6.49 (s, 1H, Ph-H), 4.38 (S, 2H, CH₂), 3.39–1.80 (br, 10H, B-H), 1.45 (s, 9H, ^tBu), 1.26 (s, 9H, ^tBu). ¹³C NMR (CDCl₃, 100 MHz): δ 159.13 (Ph-C), 151.72 (Ph-C), 143.07 (Ph-C), 138.22 (Ph-C), 125.23 (Ph-C), 128 (PPh₂), 121.01 (Ph-C), 89.78 (carborane-C), 85.36 (carborane-C), 39.49 (SCH₂), 35.40 (^tBu), 33.94 (^tBu), 31.51 (^tBu), 28.44 (^tBu) ppm. ³¹P NMR (162 MHz, CDCl₃, H₃PO₄, 25 °C): δ 41.49 (s, -P(S) Ph₂) ppm. Anal. Calcd for C₂₉H₄₃B₁₀OPS₂: C, 57.02; H, 7.10. Found: C, 57.11; H, 7.16.

2b: IR (KBr, cm⁻¹), 2990 m(OH), 2575 s(B-H), 1656 w, 1562 m, 1450 s(Ph), 1184 m(P-Ph), 676 m(P=S). ¹H NMR (CDCl₃, 400 MHz): δ 8.36–8.31 (m, 5H, Ph-H), 7.61–7.53 (m, 5H, Ph-H), 6.95 (s, 1H, Ph-H), 6.47 (s, 1H, Ph-H), 4.38 (S, 2H, CH₂), 3.37–1.76 (br, 10H, B-H), 1.32 (s, 3H, Me), 1.21 (s, 3H, Me). ¹³C NMR (CDCl₃, 100 MHz): δ 158.88, (Ph-C), 154.66 (Ph-C), 147.02 (Ph-C), 140.13 (Ph-C), 127.03 (Ph-C), 125.34 (PPh₂), 121.28 (Ph-C), 89.55 (carborane-C), 85.37 (carborane-C), 39.45 (SCH₂), 31.40 (Me), 29.94 (Me) ppm. ³¹P NMR (162 MHz, CDCl₃, H₃PO₄, 25 °C): δ 41.52 (s, -P(S)Ph₂) ppm. Anal. Calcd for C₂₃H₃₁B₁₀OPS₂: C, 52.45; H, 5.93. Found: C, 57.42; H, 5.95.

Preparation of complexes 3a–3b. To a stirred suspension of NaH (48 mg, 2.0 mmol) in 10 mL of THF was added ligand **2a** (76.2 mg, 0.125 mmol) or **2b** (65.8 mg, 0.125 mmol) dropwise at 0 °C. Stirring was maintained for 2 h at room temperature. The mixture was filtered. Then the filtrate was added dropwise to $CrCl_3(THF)_3$ (46.3 mg, 0.125 mmol) in dried THF (20 mL) over a 30 min period at -78 °C. The mixture was allowed to warm to room temperature and stirred overnight. A green solution was obtained, and the solvent was removed under vacuum. After the residual solid was dissolved in CH_2Cl_2 and filtered to remove inorganic salts, the filtrate was concentrated to about 2 mL and mixed with hexane (20 mL). Cooling to -30 °C gave green needles in yields of 65% (**3a**) and 69% (**3b**).

3a: IR (KBr, cm⁻¹), 3405, 3060, 2970 (furan), 2962 m(Bu), 2571 s(B-H), 1637 w, 1555 m, 1478 s(Ph), 1188 m(P-Ph), 687 m(P=S). Anal. Calcd for $C_{37}H_{58}B_{10}Cl_2CrO_3PS_2$: C, 50.67; H, 6.67. Found: C, 50.64, H, 6.69.

3b: IR (KBr, cm⁻¹), 3410, 3057, 2969 (furan), 2960, 2870 m (Me), 2575 s(B-H), 3411, 3058, 2965 (CH, furan), 1620 w, 1560 m, 1455 s(Ph), 1181 m(P-Ph), 685 m(P=S). Anal. Calcd for $C_{31}H_{46}B_{10}Cl_2CrO_3PS_2$: C, 46.96; H, 5.85. Found: C, 46.93; H, 5.89.

Single-crystal X-ray structure determination of ligand 2a

For compound 2a, no samples showed signals of decomposition during X-ray data collection, which was carried out at Paper

Table 3 Summary of crystallographic data for 2a

	2a			
Formula	$C_{29}H_{43}B_{10}OPS_2$			
fw	610.82			
T (K)	296(2)			
Cryst syst	Monoclinic			
Space group	P2(1)/n			
a (Å)	12.437(3)			
b (Å)	15.925(4)			
<i>c</i> (Å)	17.870(4)			
α (°)	90			
β (°)	101.657(4)			
γ (°)	90			
Volume (Å ³)	3466.6(13)			
Z	4			
$D_{\text{calc}} (\text{Mg m}^{-3})$	1.170			
Absorp coeff (mm^{-1})	0.223			
F(000)	1288			
Cryst size (mm)	$0.22 \times 0.09 \times 0.07$			
2θ range (°)	1.83-27.63			
No. of refins collected/unique	$25 \ 401/7994 \ [R(int) = 0.0829]$			
No. of data/restraints/params	7994/1/408			
Goodness of fit on F^2	0.980			
Final <i>R</i> indices $[I > 2\sigma(I)]^a$	$R_1 = 0.0541, wR_2 = 0.1305$			
Lgst diff peak and hole (e $Å^{-3}$)	0.338 and -0.297			
^{<i>a</i>} $R_1 = F_0 - F_c / \sum F_0 ; wR_2 = [\sum w(F_0^2 - F_c^2)^2 / \sum w F_0^2 ^2]^{1/2}.$				

room temperature. The intensity data of the single crystal were collected on a CCD-Bruker Smart APEX system. All determinations of the unit cell and intensity data were performed with graphite-monochromated MoK α radiation (λ 0.71073 Å). All data were collected at room temperature using the ω -scan technique. These structures were solved by direct methods, using Fourier techniques, and refined on F^2 by a full-matrix least-squares method. All the calculations were carried out with the SHELXTL program.¹⁷ All the non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were included but not refined. Crystallographic data are summarized in Table 3.

XAFS data collection

The X-ray absorption data at the Cr K-edge of the sample were measured in the fluorescent mode with a Lytle fluorescence detector on beam line BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF), China. The station was operated with a double crystal monochromator, Si(111), detuned to 40% intensity to minimize the presence of higher harmonics. All measurements were done in transmission or fluorescent mode using ion chambers filled with a mixture of He and N₂ to have an X-ray absorbance of 20% in the first and 80% in the second chamber. Data processing and analysis data processing was performed using the program ATHENA.¹⁸ All fits to the EXAFS data were performed using the program ARTEMIS.¹⁸

DFT calculations

All total energy density functional theory (DFT) calculations were carried out using the SIESTA package with numerical atomic orbital basis sets and Troullier–Martins norm-conserving pseudopotentials.^{19,20} The DFT functional utilized is the PBE functional,²¹ a generalized gradient approximation DFT

method. A double-ζ plus polarization (DZP) basis set was employed. The orbital-confining cutoff radii were determined from an energy shift of 0.01 eV. The energy cutoff for the real space grid used to represent the density was set as 150 Ry. The "External" function of the Gaussian 03 program²² was used to call SIESTA to return the energy and Cartesian forces on the atoms to the geometry optimizer of the Gaussian 03 program. The default geometry convergence criteria of the Gaussian 03 program was used where the forces and displacements of the relaxed coordinates were all less than 0.00045 Hartree Bohr⁻¹ and 0.0018 Å, respectively. The molecule was placed in the center of a cubic supercell with a length of 50 Å for each edge. Only Γ-point was used to sample the Brillouin zone in our calculations due to the large lattice parameter of the supercell.

Procedures for ethylene polymerization under 1 atm of ethylene

A 100 mL flask was equipped with an ethylene inlet, a magnetic stirrer, and a vacuum line. The flask was filled with 30 mL of freshly distilled toluene, MMAO (1.88 M in heptane) was added, and the flask was placed in a bath at the desired polymerization temperature for 30 min. The polymerization reaction was started by adding a toluene solution of the catalyst precursor (0.002 mmol) with a syringe. Then the solvent toluene was added to make the total volume of the solution 50 mL. The polymerization was carried out for the desired time and then quenched with 3% HCl in ethanol (250 mL). The precipitated polymer was filtered and then dried overnight in a vacuum oven at 80 °C.

General procedure for ethylene polymerization at high pressure

A 100 mL autoclave was charged with 50 mL of toluene under argon. MMAO (1.88 M in heptane) was added. A solution of the precatalyst in toluene was added. After three times of ethylene gas exchange, the ethylene pressure was raised to 10 atm and maintained for a certain time. The polymerization was terminated by addition of ethanol and dilute HCl (3%). The solid polyethylene was filtered, washed with ethanol, and dried at 80 °C under vacuum.

Acknowledgements

We are grateful to the National Science Foundation of China (91122017), the Program for Changjiang Scholars and Innovative Research Team in University (IRT1117), the National Basic Research Program of China (2011CB808505) and the Shanghai Science and Technology Committee (12DZ2275100).

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