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Preparation and EXAFS analysis of isospecific metallocene olefin polymerization catalysts covalently tethered on solid supports

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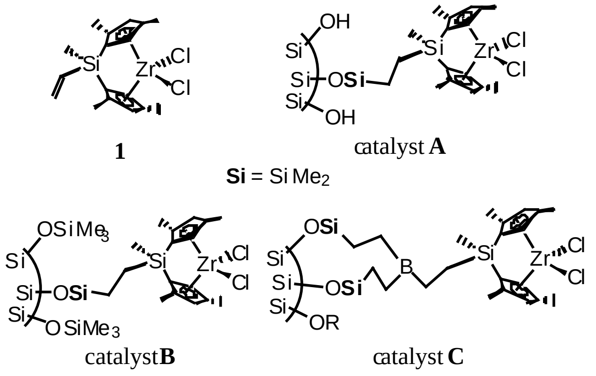
Introduction

The group 4 metallocene catalysts for olefin polymerization have been extensively investigated in a last few decades. Heterogenization of the metallocene catalysts is of importance recently, since it is desired for industrial application. Adsorption of the metallocene catalysts on the methylaluminoxane(MAO)-treated surface of solid supports is a commonly adopted method. On the other hand, some examples for immobilization of metallocene complexes with covalent bonds on supports have been reported. However, examples of *isospecific* metallocene complexes chemically anchored on solid supports are very rare[1-3]. We recently reported preparation of isospecific *ansa*-zirconocene complexes that are tethered on silica surfaces [1,2].

Results and discussion



1   catalyst **A**

Si = SiMe2

catalyst**B**   catalyst **C**

Figure 1 Covalently immobilized isospecific metallocene catalysts

We previously reported that purely racemic complex **1** can be obtained easily. Three kinds of supported catalysts **A**, **B** and **C** were prepared from **1** (Figure 1).

Propylene was polymerized with these catalysts to afford isotactic polymers using MAO as cocatalysts (Table 1). The present catalysts, in particular **C**, showed satisfactory catalytic activity and isospecificity. However, the catalytic performance highly depended on the preparative methods. We reasoned that the difference among the catalysts would be due to the chemical structures around zirconium atoms in the catalysts.

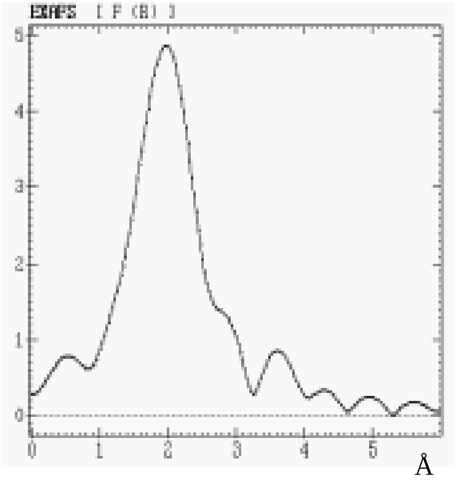


Figure 2. EXAFS of $(C_5H_5)_2Zr(CH_3)_2$

In order to get information on the structure around zirconium in the catalysts, Zr(IV)-K edge EXAFS spectra were measured for the prepared catalysts at BL-10B of the Photon Factory. The spectra were measured by transmission mode and Si(311) channel cut monochrometer was used. The EXAFS spectra were analyzed with a curve-fitting methods. The spectrum for dimethylbis(cyclopentadienyl)zirconium is shown in Figure 2. Carbon atoms are observed at ca. 2 Å from Zr. The analysis on the catalysts is now on progress to see if Zr has mainly Zr-Cl or Zr-O bonds.

References

[1] N. Suzuki et al., Chem. Lett. 341 (1999).
[2] N. Suzuki et al., Appl. Catal., A; General. submitted.
[3] DE 195 27 652 A1.

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Table. Polymerization of propylene: comparison of catalysts **A**, **B** and **C**[a]

run	catalyst	Zr/wt%	cat./mg	Al/Zr	PP yield/g	activity[b]	M_w	M_w/M_n	[*mmmm*]	mp
1	**A**	0.78	30	2300	0.64	83	74500	2.87	86.9	146.1
2	**B**	0.47	15	3900	2.03	879	98600	2.60	86.8	152.5
3	**C**	0.36	10	5100	4.18	3570	80900	1.46	94.7	154.5
4	Ref.	0.76	30	2400	0.14	18	106000	2.06	93.2	159.0
5	homo[c]	Zr = 0.1 µmol		5000	2.35	7840	76500	1.99	95.7	157.1

[a] Reaction conditions: toluene = 30 mL, propylene = 3 atm, 30 °C, 1 h. [b] kg-PP/mol-Zr·h·atm[c] homogeneous reaction