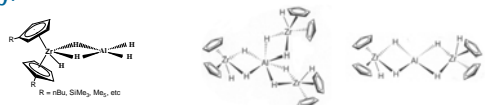


Influence of Supporting Conditions on the Performance of Zirconocene Aluminohydrides

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Introduction

Zirconocene aluminohydrides are metallocene-derivative complexes with bridged and terminal hydride ligands with very high homogeneous polymerization activity.¹



We recently supported them onto two porous SiO₂ (PQ and silica gel) carriers² according to the method reported for classical metallocenes. However, significant catalyst leaching was observed, which affected the polymer particle morphology.

In this work we supported aluminohydride complexes on SiO₂ sylopol-948, and obtained significantly improved results.

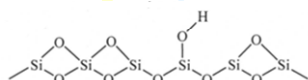
Experimental

SiO₂

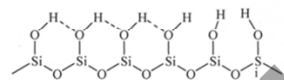
Sylopol-948 A=295 m²/g size avg = 50μ

400°C, 6h, N₂

200°C, 2h, N₂



Dehydrated SiO₂



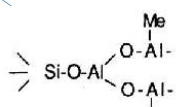
Partially dehydrated SiO₂

MAO
without AlMe₃

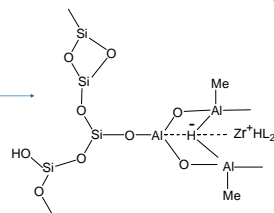
AlMe₃

7% Al

7% Al



nBu-Cp₂ZrH₃AlH₂



References

1) *Organometallics*, **2006**; 25(22); 5366

2) a) PCT/IB2006/002932 b) *Journal of Molecular Catalysis A: Chemical*, **2009**, 307, 98-104.

2.3% Zr (MAO)

2.0% Zr (TMA)

Objectives

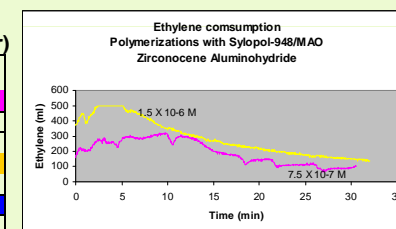
Investigate how supporting zirconocene aluminohydrides on SiO₂ sylopol-948 with different MAO-modification methods affects the catalytic activity of the supported species for ethylene polymerization, polyethylene properties, and particle morphology.

Results Ethylene Polymerizations

nBu-Cp₂ZrH₃AlH₂/Sylopol-948/MAO at low ratios Al/Zr (MAO activator)

Exp	Cat (gr)	MAO (gr)	Co-Cat (Al/Zr)	A KgPE/molZr h	Mn g/mol	Mw g/mol	Mw/Mn
1	0.003	0.1	230	17,450	100,502	287,052	2.8
2	0.005	0.06	80	161	94,117	253,208	2.6
3	0.005	0.1	140	13,700	87,229	267,354	3.0
4	0.006	0.12	140	14,300	90,326	253,840	2.8
5	0.006	0.25	285	7,400	58,064	174,230	3.0
6	0.006	0.5	570	10,650	90,133	243,887	2.7
7	0.015	1.5	680	2,980	61,101	211,851	3.4

T = 70°C, 150 mL hexane, P_{C₂} = 65 psi, 500 rpm, t = 0.5 h, [Cat] = 0.75-3.8 X 10⁻⁶ M



nBu-Cp₂ZrH₃AlH₂/Sylopol-948/MAO and high ratios Al/Zr (MAO activator)

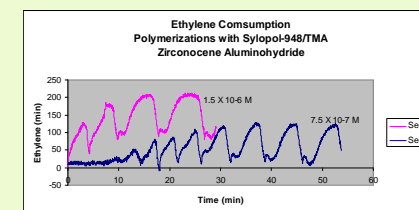
Exp	Cat (gr)	MAO (gr)	Co-Cat (Al/Zr)	A KgPE/molZr h	Mn g/mol	Mw g/mol	Mw/Mn
8*	0.010	1.5	1,000	5,200	124,967	350,362	2.8
9	0.008	1.0	1,300	7,200	114,680	285,954	2.5
10	0.006	1.5	1,700	10,700	71,315	258,119	3.6
11	0.005	1.5	2,000	8,300	84,473	263,915	3.0

T = 70°C, 150 mL hexane, P_{C₂} = 65 psi, 500 rpm, t = 0.5 h *Exp 8 T = 60°C, [Cat] = 0.75-3.8 X 10⁻⁶ M

nBu-Cp₂ZrH₃AlH₂/Sylopol-948/TMA at low ratios Al/Zr (MAO activator)

Exp	Cat (gr)	MAO (gr)	Co-Cat (Al/Zr)	A KgPE/molZr h
1	0.010	0.72	230	4,133
2	0.034	0.1	570	5,108

T = 70°C, 150 mL hexane, P_{C₂} = 65 psi, 500 rpm, t = 0.5 h, [Cat] = 0.75-1.5 X 10⁻⁶ M



Concluding Remarks

Sylopol-948 silica modified with MAO and TMA (in-situ MAO synthesis) had the same Al and Zr content when the zirconocene aluminohydride system (nBuCp₂ZrH₃AlH₂) was supported at the same conditions.

The aluminohydride zirconocene supported on Sylopol-948 had higher activity for ethylene polymerization when the silica was modified directly with MAO, instead of with TMA.

It is likely that the TMA could not be completely hydrolyzed to MAO in the TMA-treated Sylopol-948.