

Highly Active, Thermally Robust V-based New Olefin Polymerization Catalyst System

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A new ethylene polymerization catalyst system containing a phenoxy-imine ligated V complex and a MgCl_2 -based compound has been discovered. Unlike ordinary V-based catalysts, the system exhibits higher activities at elevated temperatures, and the activity reached a very high value of 65100 kg-PE/mol-cat/h at 75 °C, representing the first example of a highly active, thermally robust V-based ethylene polymerization catalyst system.

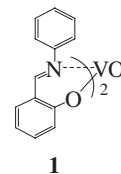


Figure 1. Structure of phenoxy-imine ligated vanadium complex **1**.

V-based catalysts, such as VOCl_3 and $\text{V}(\text{acac})_3$ combined with alkylaluminum compounds, play a significant role in coordination polymerization of ethylene and α -olefins.¹ In fact, they have been put to widespread commercial use [e.g., ethylene/propylene copolymers, and ethylene/propylene/diene elastomers (EPDM)]. While V-based catalysts possess many desirable properties as single-site catalysts, they have a serious drawback: V-based catalysts display low productivity especially at high process temperatures mainly due to the thermal instability of the active species. Catalyst deactivation processes often include reduction of V metal [typically to V(II)] and ligand migration.

Therefore, the development of V-based catalyst systems capable of exhibiting high productivity at elevated temperatures has been actively investigated for many years. A number of notable V-based catalysts exhibiting useful properties have been developed.² There is, however, no report of a highly active, long-lived V-based catalyst at high process temperatures.

During our efforts to develop high-performance new catalyst systems for olefin polymerization, we have explored well-defined transition metal complexes containing non-symmetric chelate ligands.³ Additionally, we have currently investigated new cocatalysts, other than methylalumoxane (MAO) and fluoroaryl-based compounds, capable of bringing out the best catalytic properties of the transition metal complexes. During the course of our studies on new cocatalysts,⁴ we discovered a MgCl_2 -based compound that works as an excellent cocatalyst as methylalumoxane (MAO) for phenoxy-imine ligated Ti complexes.^{4a} Further research on MgCl_2 -based compounds has led to the discovery of unique V-based catalyst systems. We describe herein a highly active, thermally robust V-based new catalyst system containing a phenoxy-imine ligated V complex and a MgCl_2 -based compound.

The MgCl_2 -based compound employed in this study, $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$, was prepared by the de-alcoholysis of a $\text{MgCl}_2/2$ -ethyl-1-hexanol adduct with Et_3Al using a procedure similar to one described previously.^{4a}

The ethylene polymerization behavior of complex **1**⁵ (Figure 1) with and without $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$ was investigated in toluene in the presence of Et_2AlCl and ethyl trichloroacetate (ETA)⁶ under ethylene at atmospheric pressure.⁷ The relevant results are tabulated in Table 1.⁸ For comparison, the polymerization results with VOCl_3 are also included. The data

obtained at 25 °C demonstrated that, although the complex **1** catalyst system displayed somewhat higher activities both with and without $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$, the polymerization behavior of the two catalyst systems is similar to each other (Entries 1, 4, 7, and 10). These results suggest that the phenoxy-imine ligand and $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$ have no significant effects on catalytic performance under the given conditions. The polyethylene (PE) formed with complex **1**/ $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$ (Entry 4) displays good morphology whereas that obtained without $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$ (Entry 1) exhibits ill-defined polymer morphology. These results indicate that complex **1** is heterogenized on the surface of a solid $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$, in other words, $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$ functions as a support.

The effects of varying the polymerization temperatures (50 and 75 °C) were studied using complex **1** and VOCl_3 . A comparison of the data indicated that thermal behavior was considerably different from each other depending on the complex and the presence or absence of $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$. VOCl_3 had considerably reduced activity at higher temperatures independent of the presence or absence of $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$ (Entries 8, 9, 11, and 12). While phenoxy-imine ligated complex **1** without $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$ behaved as a poor catalyst similar in behavior to the VOCl_3 catalyst system (Entries 2 and 3), that with $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$ turned out to be a remarkable catalyst. For complex **1**/ $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$, increasing the temperature afforded a corresponding increase in activity (Entries 5 and 6), and displayed a very high activity of 65100 kg-polymer/mol-cat/h at 75 °C (Entry 6).⁹ The results are of great significance because higher activity at elevated temperatures is desired for process and economic considerations for V-based catalysts. These results as well as the single-site behavior of the catalyst system⁸ suggest that the combination of the phenoxy-imine ligand and MgCl_2 -based compound results in the unique V-based catalyst, in which the phenoxy-imine ligand remains attached to the V during the course of the polymerization.

The productivity of complex **1** with $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$ catalyst system was examined over 5–60 min polymerization time at 75 °C. Significantly, the polymer yield increased linearly with the polymerization time [Figure 2, (a)], suggesting that the catalyst deactivation is negligible even at 75 °C and atmospheric pressure for 60 min. In contrast, VOCl_3 with and without $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$ decayed rapidly and became practically in-

Table 1. Ethylene Polymerization Results with Complex **1** and VOCl_3^a

Entry	Complex	Mg /mmol	Et_3Al /mmol	Temp. /°C	Yield /g	Activity ^b
1	1	0	0	25	5.00	20000
2	1	0	0	50	3.32	13300
3	1	0	0	75	1.23	4900
4	1	0.80	2.40	25	4.68	18700
5	1	0.80	2.40	50	11.53	46100
6	1	0.80	2.40	75	16.28	65100
7	VOCl_3	0	0	25	3.15	12600
8	VOCl_3	0	0	50	2.03	8100
9	VOCl_3	0	0	75	1.39	5600
10	VOCl_3	0.80	2.40	25	2.07	8300
11	VOCl_3	0.80	2.40	50	1.67	6700
12	VOCl_3	0.80	2.40	75	1.34	5400

^aConditions: 0.1 MPa ethylene pressure; solvent, toluene 400 mL; polymerization time, 15 min; complex **1** or VOCl_3 1.0 μmol , Et_2AlCl 0.4 mmol, ETA 0.4 mmol. ^bActivity: kg of polymer/mol-cat/h.

active after about 15 min under identical conditions. These facts show that the combination of the phenoxy-imine ligand and $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$ confers unusual stability to an otherwise unstable active V center at elevated temperatures. Complex **1**/ $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$ represents the first example of a highly active, long-lived V-based catalyst at technical process temperatures.

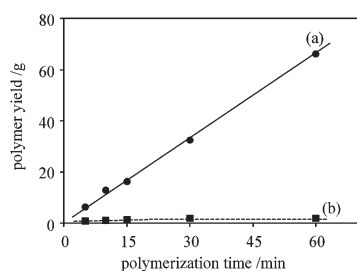


Figure 2. Relationship between the polymerization time and the polymer yield obtained with complex **1**/ $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$ and VOCl_3 . Conditions: 75 °C, 0.1 MPa ethylene pressure; solvent, toluene 400-1600 mL; (a) complex **1** 1.0 μmol , $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$ 0.8 mmol (Mg), Et_2AlCl 0.4 mmol, ETA 0.4 mmol; (b) VOCl_3 1.0 μmol , Et_2AlCl 0.4 mmol, ETA 0.4 mmol.

Considering that V(IV) is readily reduced to V(II) state, which is one of the common deactivation pathways for V catalysts, the phenoxy-imine ligand may stabilize the higher oxidation state of the V center. In addition, $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$ which works as a support probably suppresses ligand migration from the V center as well as bimolecular deactivation of the V catalyst.^{2g} Thus, the combination of the phenoxy-imine ligand and $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$ gave rise to the unprecedented V-based olefin polymerization catalyst system.

In summary, a V-based new catalyst system containing a phenoxy-imine ligated V complex and MgCl_2 -based compound has been introduced, which represents the first example of a highly active, thermally robust catalyst for olefin polymerization. Future work will focus on the mechanistic studies and

the scope and limitation of the V-based new catalyst systems.

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- General polymerization procedure: Ethylene gas (100 L/h) was blown into toluene (400 mL) at a prescribed temperature. To this solution, a 0.10 M $\text{MgCl}_2/2$ -ethyl-1-hexanol adduct solution (8.00 mL, 0.80 mmol as Mg) and a 1.00 M Et_3Al solution in toluene (2.40 mL, 2.40 mmol) were added and stirred for 5 min to give $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$. A 1.00 M Et_2AlCl solution in toluene (0.40 mL, 0.40 mmol) and then a 0.50 M ETA solution in toluene (0.80 mL, 0.40 mmol) were added to the resultant mixture and stirred for 5 min. Subsequently, a 0.001 M toluene solution of complex **1** or VOCl_3 (1.00 mL, 1.0 μmol) was added to the reactor with vigorous stirring (1200 rpm) to initiate polymerization. After a prescribed time, the polymerization was quenched by an injection of *i*-butyl alcohol (10 mL).
- Complex **1** with a MgCl_2 -based compound catalyst system had very high molecular weight PEs ($[\eta] > 30$) of which we were unable to determine molecular weight (M_w) and molecular weight distribution (M_w/M_n) using GPC analysis. PEs produced with the catalyst system using H_2 (ethylene/ H_2 , 100/25 L/h) as a chain transfer agent possessed narrow molecular weight distributions (M_w/M_n 2.50), probably suggesting single-site behavior.
- $\text{V}(\text{acac})_3$ with $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$ displayed much reduced activity at elevated temperatures (e.g., 25 °C: 59000 kg-PE/mol-cat/h, 75 °C: 8600 kg-PE/mol-cat/h), indicating that the phenoxy-imine ligand plays a role of vital importance in realizing the thermally robust V-based catalyst system.