

N,N,N-Tridentate iron(II) and vanadium(III) complexes Part II: Catalytic behavior for the oligomerization and polymerization of ethene and characterization of the resulting products

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Abstract

A series of *N,N,N*-tridentate vanadium(III) complexes were tested after activation with methyl aluminoxane (MAO) for ethene oligomerization and polymerization. Variations in the catalyst structure as well as the influence of physical parameters were investigated and the properties of the obtained oligomeric products were determined. Methods of altering the Schulz–Flory distribution of the oligomeric products were investigated. The product properties of the polymers and oligomers obtained with the vanadium(III) complexes and the structurally identical iron(II) complexes were compared. Depending on their substitution pattern, the *N,N,N*-tridentate vanadium(III) catalysts exhibit high productivities and selectivities towards α -olefin oligomerization products under mild conditions when activated with MAO whereas the corresponding iron complexes produce higher molecular weight materials. The synthesis of these new vanadium(III)- and iron(II)-diiminepyridyl complexes was reported earlier.

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1. Introduction

The world-wide demand for valuable products that can be produced in high yields and purities grows strongly year after year. The driving force is a strong economic incentive to find better and more cost effective catalyst systems that can produce these value added products. New catalysts can provide the potential to shift the production of expensive niche products to value added commodity products.

Beginning in the 1950s with the work of Hogan and Banks [1,2] and the experiments of Ziegler et al. [3–6] and Natta et al. [7,8], the interest in olefin oligomerization and polymerization catalysts has grown dramatically over the years

[9–21]. Even today, new highly active catalysts and cocatalysts [22–31] that produce new and better products are being synthesized.

In addition to the development of metallocene technology [9,32–37], other catalytic systems have also been developed [19]. In 1995, Brookhart et al.'s [38–48] nickel diimine complexes were synthesized and tested successfully as olefin polymerization and oligomerization catalysts after activation with a cocatalyst such as methylaluminoxane (MAO) [49–52]. Then in 1998, Bennet, Brookhardt and Gibson presented diiminopyridyl complexes of iron and cobalt [53–59] as oligomerization and polymerization catalysts after activation with MAO.

Prior to this work, iron complexes were regarded as “inactive” with respect to olefin oligomerization or polymerization reactions. This led to the search for even newer catalytic sys-

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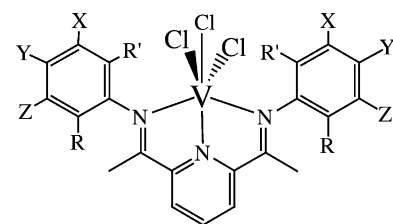
tems that are able to promote the oligomerization or polymerization of olefins and polar monomers. In 1999, Reardon et al. [54] reported that *N,N,N*-tridentate vanadium diiminopyridyl complexes, when activated with MAO, are active catalysts for olefin polymerization reactions, and Schmidt [53] reported that *N,N,N*-tridentate vanadium diiminopyridyl complexes, when activated with MAO, are catalysts for both polymerization and oligomerization reactions. To further explore the significance of the oligomerization discovery, a series of differently substituted vanadium diiminopyridyl complexes were synthesized [53,55].

In this publication, we report the catalytic behavior of various vanadium(III) diiminopyridyl-activated complexes for the oligomerization and polymerization of ethene and the characterization of the resulting products. In addition, we compare these results to those obtained for structurally similar iron complexes [53,55,66].

2. Results and discussion

2.1. Oligomerization and polymerization results of the MAO-activated V(III) complexes

The objective of our investigations was to find highly active catalysts that selectively convert olefins to α -olefin oligomers that are highly valued in various industrial applications. For this purpose, the previously described vanadium(III)- and corresponding iron(II)-diiminopyridyl complexes [55], were tested for their ability to oligomerize ethene after activation with MAO. In this publication, we focus on the influence of catalyst structure, the addition of hydrogen and 1-hexene, as well as the effect of experimental variables on catalyst performance (Fig. 1).



R, R' = H, alkyl
X, Y, Z = H, alkyl, Cl, Br

Fig. 1. Basic structure of the *N,N,N*-tridentate vanadium(III) complexes.

The properties of the obtained products (oligomers and polymers) using the vanadium(III) complexes are compared with the products obtained from the corresponding isostructural iron(II) complexes (data obtained for these tridentate iron complexes were reported earlier [16,17,53,66]). The most active catalysts were then investigated intensively and underwent various screening tests.

2.1.1. Productivities after activation with MAO

All complexes were first screened for catalytic activity following activation with MAO. In Table 1, the productivities based on ethene-uptake are listed. For accuracy, the shown productivities exclude the solvent-saturation with ethene under the chosen run conditions. In these preliminary catalyst screening tests, the run duration was 30 min, the Al/V molar ratio was set at 500/1, the run temperature was 60 °C, the ethene pressure was set at 250 psig, and the solvent was purified cyclohexane.

The addition of small amounts of hydrogen to a run generally lowered catalyst productivity and/or yield of oligomeric product. Hydrogen addition studies were, therefore, not pursued further.

Table 1
Catalyst productivities, yield of oligomeric products and purity of the C₆ fraction

Catalyst number	Catalyst	Productivity (total) kg (product)/g (V)/h	% Purity of 1-hexene fraction/wt.% liquids
1	R = R' = X = Y = Z = H	196	80.2/25.3
2	R = methyl; R' = X = Y = Z = H	580	94.7/98.3
3	R = ethyl; R' = X = Y = Z = H	356	96.4/89.1
4	R = <i>iso</i> -propyl; R' = X = Y = Z = H	63	94.8/45.3
5	R = <i>iso</i> -propyl; R' = X = Z = H; Y = methyl	76	95.2/51.3
6	R = <i>tert</i> -butyl; R' = X = Y = Z = H	61	86.7/71.0
7	R = methyl; X = chloro; R' = Y = Z = H	1,140	94.4/98.1
8	R = methyl; Y = chloro; R' = X = Z = H	463	88.1/94.1
9	R = methyl; Z = chloro; R' = X = Y = H	596	97.5/98.1
10	R = X = methyl; R' = Y = Z = H	654	94.9/98.4
11	R = Y = methyl; R' = X = Z = H	68	92.8/79.0
12	R = Z = methyl; R' = X = Y = H	349	95.9/94.4
13	R = methyl; Y = bromo; R' = X = Z = H	88	92.0/79.7
14	R = R' = methyl; X = Y = Z = H	523	NA/9.8
15	R = R' = ethyl; X = Y = Z = H	284	NA/(low <i>M_w</i> polymer obtained)
16	R = <i>iso</i> -propyl; R' = methyl; X = Y = Z = H	161	NA/(low <i>M_w</i> polymer obtained)
17	R = R' = <i>iso</i> -propyl; X = Y = Z = H	84	86.7/14.3
18	R = R' = Y = methyl; X = Z = H	263	NA/(low <i>M_w</i> polymer obtained)
19	R = R' = Y = methyl, X = H; Z = bromo	326	88.8/10.4

NA = not available.

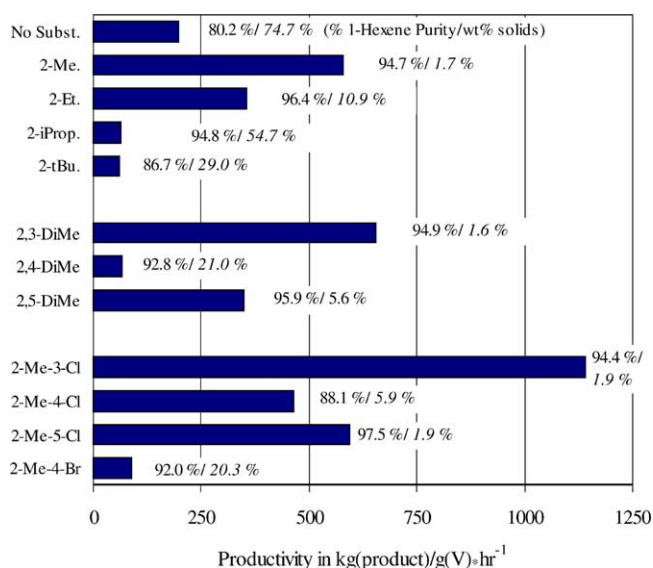


Fig. 2. Comparison of steric and electronic effects on productivities, hexene purity and fraction of solids in the product.

The reported productivities are based on the sum of the oligomeric and polymeric products. The hexene fraction was selected to monitor α -olefin purity. The reported purity of 1-hexene represents the 1-hexene in the C₆ fraction without further purification.

2.2. Steric and electronic effects on catalyst activity

The influence of steric and electronic effects on the catalyst productivity is illustrated in Fig. 2. Variations in the substitution pattern on the aniline precursor significantly impact the catalyst productivity. As the bulk of the alkyl-substituent in the 2-position of the phenyl ring increases, the productivity decreases. Simultaneously, the formation of solids increases from a very low level <2 wt.% to 55 wt.% of the product. The 1-hexene content in the hexene fraction varies between 87 and 96%. The lowest 1-hexene amounts occur with the bulkiest catalyst substitution patterns.

The 'unsubstituted' complex **1** is an exception to these trends. While it exhibits a higher activity than the more sterically hindered complexes **4** and **6**, it exhibits a lower activity than complexes **2** and **3**. The fact that this complex shows activity at all is quite surprising as the corresponding iron(II) complex is inactive [57,59–61]. It has been argued [55] that the lack of activity of the iron complex can be attributed to the formation of a salt of the following formula [Fe(ligand)₂][FeCl₄] [62–64] or the formation of a dimeric species. The dimer explanation seems unlikely as the corresponding CoCl₂ complex is monomeric [65].

Surprisingly, addition of a second like substituent at the 6-position of the phenyl moiety had very little effect on productivity (complexes **2–4** compared to **14**, **15**, and **17** in Table 1). However, the products were greatly affected. Like substitution in both the 2- and 6-positions of the phenyl ring

shifts the product distribution from mainly oligomers, >45% oligomers, to mostly low molecular weight solids, >85 wt.% solids. When the oligomer fraction was at levels below 10%, it was often not possible to accurately determine the purity of the 1-hexene fraction and thus this data was not reported.

The influence of substituents in other aromatic ring positions in addition to a methyl group in the 2-position was investigated. Placing a substituent in the 3-position seemed to be especially beneficial for yielding high productivities, high α -olefin purities and low amounts of polymer. A chloro substituent in position 5 provides similar benefits but at slightly reduced productivities. A methyl substituent in position 5 increases polymer production significantly. The highest productivity by almost a factor of two was achieved with chloro functionality in the 3-position, complex **7**. It also produced high purity 1-hexene and low amounts of polymer.

Substitution in both the 2- and 4-positions proved to be disadvantageous. In all cases, productivities and 1-olefin purities were lower, and polymer formation increased significantly (Fig. 2).

When there was substitution in both the 2- and 6-positions, productivities varied from 80 to 520 kg (product)/g (vanadium)/30 min. However, the products consisted mainly of polymer.

2.3. Influence of temperature, pressure and other parameters on the vanadium(III)/MAO catalytic system

The screening tests revealed a tremendous impact of the catalyst structure on the catalyst performance with regard to activity and yield of oligomers. The same impact was observed by changes in the run conditions. In order to study these influences further, additional experiments were conducted with the best performing catalyst, complex **2**, under slightly different run conditions. The selected run conditions were an Al/V molar ratio of 500/1, a reaction temperature of 60 °C, an ethene pressure of 300 psig, an isobutane solvent and a residence time of 1 h. The data in the remaining tables and figures were run at these conditions.

2.3.1. Influence of the Al/V molar ratio

Earlier work has shown that the corresponding iron(II) complexes, under heterogeneous conditions, show a strong response towards the aluminum to iron molar ratio chosen. Surprisingly, it was found that the tridentate iron(II) complexes had a maximum activity at low Al/Fe molar ratios of about 220/1 [66] in contrast to MAO-activated metallocene complexes [29,53]. In fact, metallocene catalysts frequently show increases in activity as the aluminum to transition metal ratio is increased above 1000/1. When run under homogeneous conditions without silica support, the iron(II) complexes were highly active for ethene polymerization but the experiments resulted in heavy reactor fouling [53].

Attempts to prepare analogous heterogeneous vanadium systems for comparison were successful, but none of the prepared catalysts showed appreciable activity.

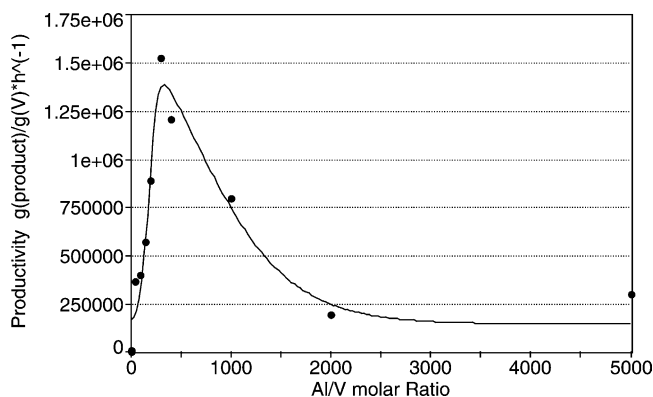


Fig. 3. Productivity vs. Al/V molar ratio for complex 2/MAO.

Instead, the effects of the Al/V molar ratio on the homogeneous vanadium(III) complexes were studied. The model compound, complex **2**, was tested in an Al/V molar ratio range of 0–5000. The results in Fig. 3 show that the homogeneous vanadium system is equally sensitive to the Al/V molar ratio. The maximum productivity was observed at a molar ratio of about 300/1. Both the heterogeneous iron and homogeneous vanadium catalysts exhibit a dramatic increase in activity as the level of MAO is reduced to the Al/metal molar ratios mentioned earlier [66].

Decreasing the Al/metal molar ratio further (<200/1) reduces the productivity of both the heterogeneous iron(II) as well as the homogeneous vanadium(III) catalysts. But even then, their catalytic activity still exceeds most other oligomerization and polymerization processes [19,65–77].

2.3.2. Influence of run temperature

The productivity of all tested vanadium(III)/MAO catalysts showed a strong response to the reaction temperature. In general, it was found that the productivity was inversely proportional to the reactor temperature at constant ethene concentration. High temperatures lead to a significant loss in productivity. This loss appeared to be permanent as lowering the temperature during the run did not result in increased activity. This behavior can be attributed to decomposition of the active species. Fig. 4 shows

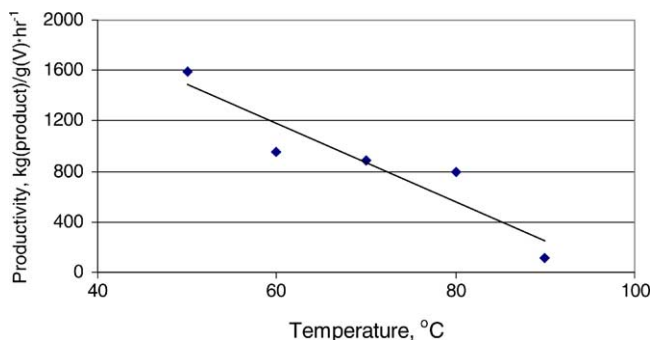


Fig. 4. Complex **2**/MAO run at various reaction temperatures (average of two experiments per temperature) and at a constant ethene concentration of 19.2 mol% in isobutane.

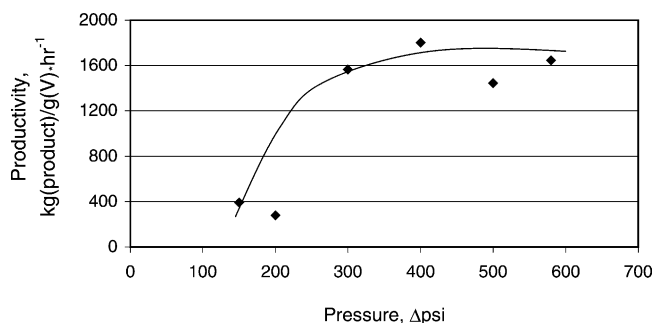


Fig. 5. Ethene concentration vs. productivity: complex **2**/MAO.

the strong correlation between reaction temperature and productivity.

2.3.3. Influence of ethene pressure

The effect of the ethene pressure on the catalyst is shown in Fig. 5. As expected, productivities increased directly with ethene pressure initially. At low ethene pressures the catalyst is ‘starved’ for monomer. Surprisingly though at ethene pressures above 400 psig, the productivity of the catalyst ceased to increase. Structurally similar catalysts showed the same behavior. As diffusion limitations often theorized for heterogeneous systems do not apply in this case, it is difficult to explain the observed behavior.

2.3.4. Influence of hydrogen and comonomers

The influence of hydrogen and comonomer on catalyst productivity and product properties was also studied. It was found that hydrogen had very little effect on the productivity or products of the vanadium(III) complex/MAO systems. The addition of hydrogen during the reaction resulted in a slight decrease in activity and had little effect on the product distribution or α -olefin purity. This is in contrast to the heterogeneous iron(II) systems where hydrogen addition dramatically increases productivities [66].

Addition of large amounts of α -olefin comonomer to the ethene/vanadium reaction medium resulted in virtually no change in the amounts of branched oligomers formed. This fact and the low levels of branching observed during the oligomerization suggest that ethene oligomerization is apparently much faster than the incorporation of higher α -olefins.

However, tests with olefins in the absence of ethene have resulted in the slow formation of unusual dimers and trimers [21].

2.4. Oligomeric products

In our work, we focused on the oligomerization behavior of these new vanadium(III) complexes due to the increasing demand in the chemical industry for high purity α -olefins. The wide variety of applications [67,68] for pure, unbranched α -olefins renders them attractive and valuable.

Table 2
Comparison with commercial catalytic oligomerization processes for the production of α -olefins

Catalyst	Aluminum growth process	Nickel SHOP process	Vanadium
Pressure [psig]	>3,000	1,500	200–600 ^a
Temperature [°C]	150–290	90	40–80
Product distribution	Schulz–Flory	Schulz–Flory	Schulz–Flory
α -Olefin purity ($1 - C_6^-$) [%]	97–99 ^b	99 ^b	98
Productivity [g (product)/g (metal)/h]	1,000–8,000	1,500	5,000–2,500,000

^a Higher pressures possible.

^b High purities result only after distillation.

Various catalytic processes for their production have been developed [69–77] but their yields and/or the reaction conditions can be made more favorable (see Table 2).

The *N,N,N*-tridentate vanadium(III) complexes, to our knowledge, show by far the highest activities among all known commercial catalytic oligomerization processes for the production of high purity α -olefins with the additional benefit of low solids formation.

2.4.1. Influence of Al/V molar ratio on α -olefin purity

The influence of the Al/V molar ratio on α -olefin purity for the C₆–C₁₀ range olefins is shown in Fig. 6. In general, the purity of the obtained 1-olefins is very high and for 1-hexene can exceed 97% with selected complexes.

At low Al/V molar ratios, the purity is lower and reaches a maximum at about the same Al/V molar ratio where the highest productivities are found. Further increases in the Al/V molar ratio show no additional benefits in increasing α -olefin purity. In fact, in some cases we see a slight decrease in α -olefin purity at the higher Al/V molar ratios. The decrease of olefin purity with increasing molecular weight of the oligomers illustrate that branched olefins are more likely to be formed but the extent of the purity drop in the C₈ fraction was unexpected.

2.4.2. Effects on product distribution

All but one commercial processes [78–86] produce a variety of 1-olefins that follows a Schulz–Flory type distribution. Side-products include branched alkenes, internal olefins and small amounts of polymeric products.

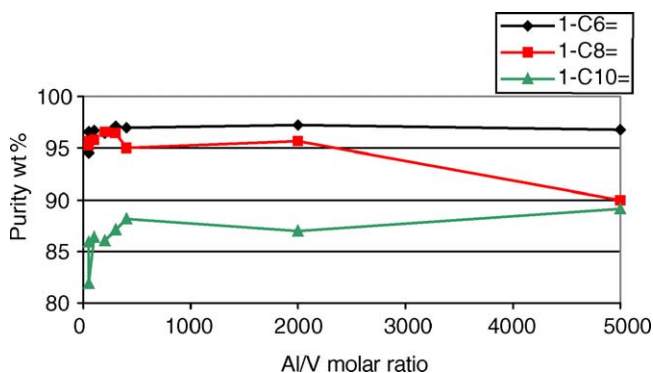


Fig. 6. Purities of the obtained 1-olefins in the C₆–C₁₀ range vs. the Al/V molar ratio for complex 2/MAO.

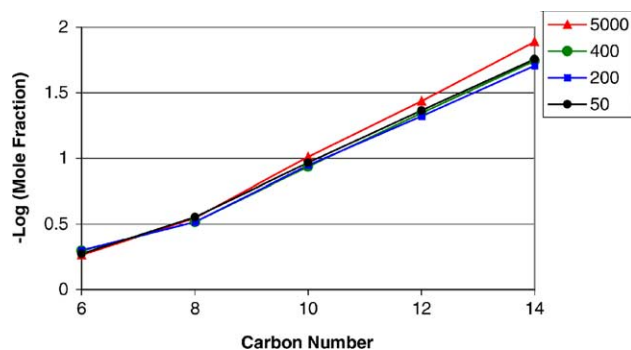


Fig. 7. The produced 1-olefins follow a Schulz–Flory distribution independent of the Al/V molar ratio for complex 2/MAO. Note: not all obtained data shown for reasons of clarity.

The α -olefin products produced with the 2/MAO catalyst follow a Schulz–Flory (Fig. 7) distribution as expected [87–90]. The Schulz–Flory constant value α was determined by the average molar ratio of the C₁₀, C₈ and C₁₂, C₁₀ fractions. The obtained α -values range between 0.36 and 0.40 for the catalytic oligomerization runs shown. This behavior is almost independent of the Al/V molar ratio. The α numbers found in our experiments are lower than those described for ethene oligomerization experiments catalyzed by monoalkyl-substituted iron complexes which reach values of 0.70–0.85 [16,20].

The non-linear behavior for 1-hexene (Figs. 7 and 8) results from losses in our standard work-up procedure. Similarly, large amounts of 1-butene were lost during sample handling and, therefore, the data is not reported.

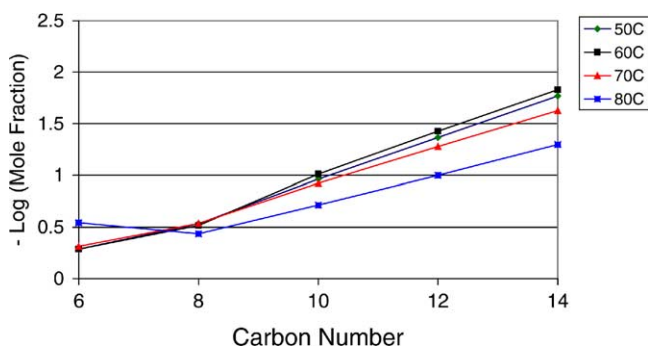


Fig. 8. Dependence of the olefin-product distribution on the run temperature for complex 2/MAO (Schulz–Flory distribution): Al/V molar ratio = 500/1; pressure = 300 psig.

2.4.3. Effect of temperature on α -olefin purity and distribution

Without optimizing the process and without further purification, linear 1-hexene purity often exceeded 97% depending on the vanadium compound employed. The reason for such high purities is the lack of significant double bond isomerization activity, and the preference of the catalyst for ethene versus product olefins. As the temperature of the oligomerization increased, the purity of the various olefin fractions decreased marginally. As expected, the purity of the 1-olefin products was found to be in the order: 1-hexene >96%; 1-octene >93%; 1-decene \sim 84%. Some of the scatter in this data for a specific run may be due to the fact that initially the complex/MAO mixing time was not held constant. After discovering that the mixing time was an important variable, attempts were made to minimize this variable [56].

The distribution of the various oligomers formed, followed Schulz–Flory rules at the various temperatures studied (Fig. 8). As the run temperature increased, the slope of the Schulz–Flory plot decreased indicating that heavier olefins are favored at higher temperatures. This is in agreement with the data obtained on the amount of polymer formed (Fig. 12). Deviations observed at higher temperatures may be due to catalyst deactivation and/or decomposition.

2.4.4. Influence of pressure on α -olefin purity

Purity of the α -olefins produced increased marginally as pressure increased to 500 psig and then appeared to decline slightly with further increases in ethene concentration. It was not possible to verify this trend at higher pressures due to technical limitations (Fig. 9).

The effect of increasing pressure on the distribution of the 1-olefins was almost undetectable. Only at the highest pressures tested was a minor change in the distribution observed. At all the pressures studied, a Schulz–Flory distribution was observed (Fig. 10).

2.5. Solid formation

A critical parameter in α -olefin synthesis on a commercial scale is the formation of solids as their removal adds cost

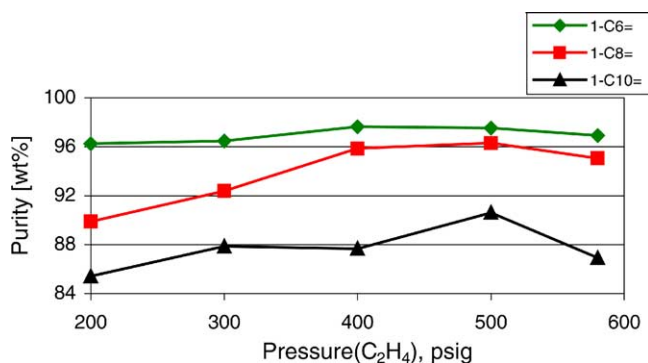


Fig. 9. Effect of pressure on α -olefin purity during oligomerization reaction with complex **2**/MAO (Al/V molar ratio = 500/1; $T = 60^\circ\text{C}$).

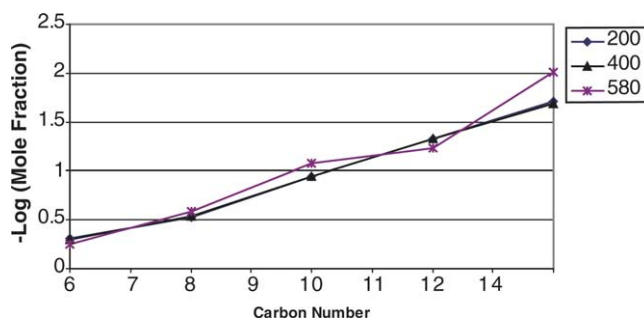


Fig. 10. Effect of pressure on distribution during oligomerization reaction with complex **2**/MAO (Al/V molar ratio = 500/1; $T = 60^\circ\text{C}$). Note: not all obtained data shown for reasons of clarity.

to the process. All commercial oligomerization processes in use today produce some low molecular weight waxes and polymers. The ability to control polymer formation via ligand synthesis has already been discussed. Here, we will discuss polymer formation control utilizing process variables.

2.5.1. Effect of Al/V Ratio on Polymer Formation

Model complex **2**, activated with various molar ratios of MAO, produced only very low levels of solids (1–4 wt.%) at low Al/V molar ratios. Even at Al/V = 2000/1, no increase in polymer formation was noted. Increasing the Al/V molar ratio further strongly increased the amount of solid formed to values above 20 wt.% (Fig. 11).

2.5.2. Temperature influence on polymer formation

The percentage of the product as polymer was found to increase rapidly as reaction temperature was increased (Fig. 12). At this time, it is not known whether the yield of polymer increases or if the number of oligomerization sites decreases while the number of polymerization sites remains constant. At the highest temperature studied the product obtained with complex **2** was almost exclusively polymer.

2.5.3. Pressure influence on polymer formation

The fraction of the product that was solid polymer remained essentially constant at about 1.5 wt.% of the product over the range of ethene partial pressures studied (Fig. 13). There was no change in the Schulz–Flory plots with ethene concentrations in the range investigated.

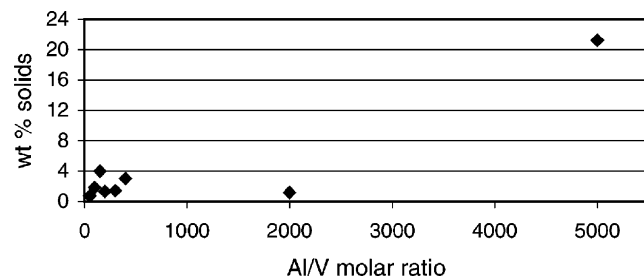


Fig. 11. Influence of Al/V molar ratio on solid formation using complex **2**; ($T = 60^\circ\text{C}$; pressure = 300 psig).

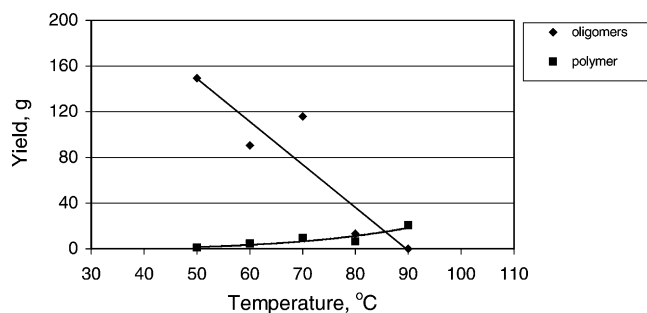


Fig. 12. Effect of run temperature on the amount of polymer formed with complex 2/MAO (Al/V molar ratio = 500/1; pressure = 300 psig).

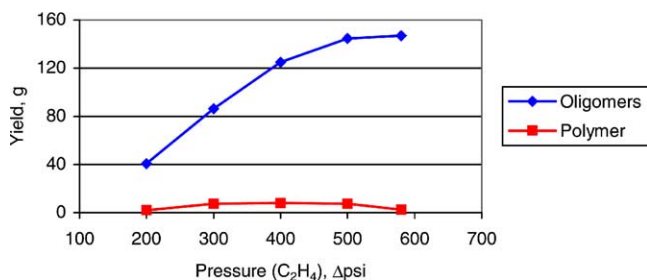


Fig. 13. Solid formation at various ethene concentrations with complex 2/MAO (Al/V molar ratio = 500/1; $T = 60^\circ\text{C}$).

2.6. Comparison of *N,N,N*-tridentate vanadium(III) and iron(II) complexes

Despite the difference in oxidation state, the diiminopyridyl vanadium(III) and iron(II) halide complexes, when activated by MAO, form highly active catalysts for ethene oligomerization and polymerization reactions (Table 3). The iron complexes can be easily heterogenized. In fact, in our experiments, they performed better as heterogeneous catalysts [53,66]. Experiments to heterogenize the vanadium complexes were found to be more difficult. After a heterogenization procedure similar to the corresponding iron complexes [30,53,66], the vanadium complexes showed little to no activity.

Under homogeneous and heterogeneous conditions, both types of catalysts are poor incorporators of higher α -olefins. While low concentrations of hydrogen significantly increased the activity of iron(II) catalysts, the same concentrations of

hydrogen had little effect on the activity or properties of vanadium(III) catalysts or their products. The major difference between both types of catalysts is the shift of the molecular weight of the products.

In our experiments under standardized (see Section 4) homogeneous run conditions, the MAO-activated iron(II) catalysts formed mainly polymers while the isostructural vanadium(III) catalysts formed predominately oligomers.

Recent reports on structurally similar iron(II) complexes indicate that they are good oligomerization and/or polymerization catalysts after MAO activation [91–94]. Some substitution patterns on the aniline moiety permit the formation of low molecular weight polymer while fluorine substituents allow the formation of α -olefins [95]. Although a direct comparison with these reported data is difficult due to differences in experimental conditions, the reported yields seem to outperform commercial processes but do not attain the performance of vanadium(III) complexes under the experimental comparisons utilized here.

According to Reardon et al. [54], the vanadium(III) complexes undergo structural changes after the addition of either MAO or methyl lithium which may help to explain the differences in activity as well as the catalyst performance overall. Due to these findings, we studied several vanadium(III) and iron(II) complexes by time-dependent UV-spectroscopy. The results will be presented [56].

2.7. Comparison of *N,N,N*-tridentate vanadium(III) and commercial oligomerization catalysts

To assess the commercial viability of the new vanadium(III)/MAO catalytic system for oligomerizing ethene, a comparison was made with Shell's oligomerization process (SHOP [69–71,73–76,96,97]) and the aluminum growth process [77] (Table 2). In all cases, broad product distributions are obtained with minor amounts of waxes and polymeric products. A significant advantage of the new vanadium catalysts is that they require much lower ethene pressures to achieve good productivities. For the commercial processes, reaction pressures of 1500 to >3000 psig are required while for the new vanadium catalysts pressures can remain under 500 psig. Even though pressures are significantly lower, the productivity of the vanadium catalysts are up to 2500 times greater.

Although a direct comparison of the 1-hexene purity as it exits the oligomerization reactor was not possible due to sample availability, it is apparent that the purity of the 1-hexene from the vanadium catalyzed reaction, as it exits the reactor, is close to that of the commercial processes.

One significant hindrance to commercialization of the vanadium catalysts is, of course, their costs. Synthesis of the ligands and the use of MAO are both contributors to the higher cost structure of these catalysts but the high productivities reduce this cost impact.

Table 3
Comparison of iron(II) and vanadium(III) catalysts (based on our experimental results)

Characteristic	Fe(II)	V(III)
Productivity	High	High
M_w (Products)	Mainly polymers	Mainly oligomers
Comonomer incorporation	Not observed	Not observed
Oligomeric products	α -Olefins	α -Olefins
Oligomer distribution	Schulz–Flory	Schulz–Flory
Oligomer purity	High	High

3. Summary

A series of *N,N,N*-tridentate vanadium(III) complexes were synthesized and tested for ethene oligomerization after their activation with MAO. The productivities as well as the product properties are reported. It was shown that the tested vanadium catalysts were highly active oligomerization catalysts under very mild conditions. The maximum activities were attained at low Al/V molar ratios. The obtained oligomers were predominantly α -olefins, which were produced with high selectivities. When ethene was used as feedstock, no significant comonomer incorporation was observed. Depending on the vanadium compound selected and the reaction conditions chosen, the polymer content of the product can be minimized. Increasing the reaction temperature decreases productivities and promotes polymer formation. The produced α -olefins follow a Schulz–Flory distribution.

The results of this work suggest that vanadium catalysts have the potential to be good candidates for future commercial ethene oligomerization processes.

4. Experimental

All procedures were performed under an inert gas atmosphere using standard Schlenk techniques or a glove box in order to eliminate traces of air or moisture. Purified and dried nitrogen (BTS catalyst, molecular sieve) was used as the inert gas. All solvents were purchased as technical grade purity and purified by distillation over Na/K alloy under nitrogen atmosphere. Polymerization grade ethene was used for all experiments. The ligand and complex syntheses are described elsewhere [53,55,66,98].

4.1. Oligomerization reactions

The initial catalyst screening tests were carried out in a 1 L batch reactor. The temperature was controlled at the desired point by an internal steam/water-cooling coil. Reactor pressure was 500 psig during the oligomerization run with ethene being fed on demand. A typical run was carried out using the following procedure.

The reactor was purged with nitrogen at 100 °C for at least 15 min. The catalyst was added via syringe to a charge tube and then flushed into the reactor with 450 mL cyclohexane. The reactor was then allowed to come back to operating temperature (typically 60 °C, if not stated otherwise). Hydrogen, if used, was added next. The reactor was then pressurized with ethene to operating pressure (typically 500 psig) and ethene was fed on demand. A sample of the reactor product was collected after 30 min using a sample cylinder. The product was analyzed by GC (HP 5890 series II). The ethene consumption was measured using a flow meter. The reactor was then cooled, vented and the liquids analyzed by GC. Any solid polymer was collected, dried and weighed.

After the catalyst screening, the most active catalysts were extensively tested according to the above-described procedure but in a 4 L autoclave. The standard solvent used in these experiments was purified isobutane. The run length was extended to 60 min.

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