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Comparison of Silyl Chromate and Chromium Oxide Based Olefin Polymerization Catalysts

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Summary: A comparison of the ethylene polymerization performance conducted with an oxo and a triphenylsilyl chromate catalyst on silica was performed. The oxo catalyst has higher activity and better comonomer response. The silylchromate catalyst has a much longer induction time and made a much broader molecular weight distribution polymer compared to the oxo analogue. Performance similar to silylchromate on silica was observed when triphenylsilanol (TPS) was added to the oxo chromium catalyst. The oxo catalyst was converted to the silyl chromate catalyst by ligand substitution. Analysis of the catalyst components when TPS was added to the oxo chrome analogue showed that bis triphenylsilyl chromate can form and be removed from the support.

Keywords: catalysts; chromium; polyethylene; polymerization; silyl chromate

Introduction

Polymerization of ethylene with supported chromium based catalysts has been known for over forty years. Most of the chromium based catalyst work has focused on oxo chromium systems, commonly referred to as the Phillips-type catalyst (Cr/SiO_2)[1,2]. However, there has also been a significant amount of work based on the organochromium systems chromocene[3] and organosilyl chromate. Of the organochrome-based systems, silyl chromate [4,5,6] derived catalysts are used extensively for commercial PE production. Organochrome-based systems may have a different ligand environment than that found with air activated oxo catalysts. A study has been conducted to better understand the relative structure and performance of the Cr^{+6} catalysts based on chromium oxide and silyl chromate.

Results and Discussion

The oxo chromium catalyst is well known and prepared by thermal oxidation of silica impregnated with a variety of chromium compounds. Activation is done in air between 600-

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850 °C. The silyl chromate catalyst is formed by chemisorption of bis(triphenylsilyl) chromate on dehydrated silica in a hydrocarbon slurry producing triphenyl silanol (TPS) as a byproduct after the interaction (Figure 1).

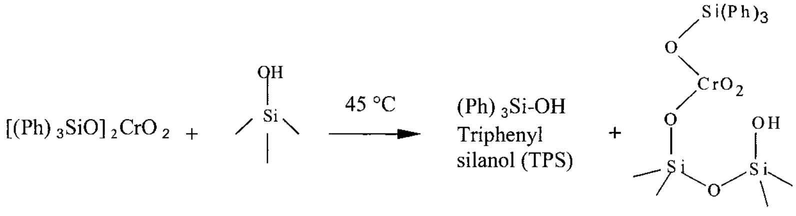
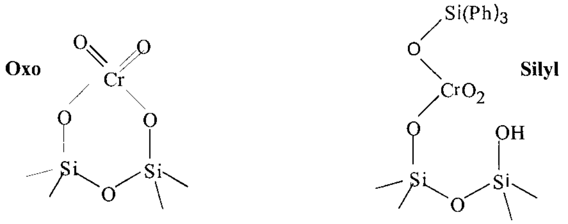


Figure 1. Chemisorption of silyl chromate on silica

Using the most simplistic models for Cr^{+6} catalysts based on the oxo [7] and organosilanol [6] (triphenylsilanol) derivatives, it can be seen that the structural features of these catalyst precursors are quite similar (Figure 2).



Cr^{+6} Oxide on 955-SiO_2 Silyl chromate on 955-SiO_2

Figure 2. Possible structures of Oxo and Silyl chromate catalysts on silica

The oxo-derived system is anchored through surface inorganic siloxides. The silyl chromate is anchored by one surface siloxide with triphenyl siloxide as the other organosiloxide ligand. Although similar in structure the polymerization performances of these catalyst precursors are very different.

Ethylene polymerization comparisons (Table 1): Employing the same silica support for each system (Davison 955 silica, 1.6 cc/g, $300 m^2/g$) it was observed that the oxo catalyst has much higher productivity. The silyl chromate catalyst is not only less active but has a prolonged

Table 1. Ethylene Polymerization Performance of Oxo and Silylchromate Catalysts

Response / Catalyst	*Induction Time*	*Productivity*[a)]	*FI(I_{21})*	*Density*	*Bulk Density*
	min	*gPE/g Cat*	*gPE/10 min*	*g/cc*	*g/cc*
Oxo	72	1630	13.7	0.9428	0.41
Silyl	158	302	9.8	0.9549	0.51

[a)] Polymerization Conditions: 600 cc isobutane, T = 95°C, 500 cc H_2, pC_2 = 200 psi, 10 cc 1-hexene comonomer

induction period. The comonomer incorporation rate for the oxo catalyst is also much higher based on observed lower polymer density. Higher polymer bulk density and molecular weight is found with the silyl chromate catalyst compared to the oxo catalyst under these reaction conditions.

The polymer molecular weight distribution (MWD) is very different for the two systems (Figure 3). Both catalysts produce broad MWD distribution polymers, but the silyl chromate catalyst produces broader polymer distributions (broader on both the high and low molecular weight ends) with a pronounced high molecular weight tail, almost indicative of a second type of active site. It appears that one of the TPS groups remains at the site after the active site is formed.

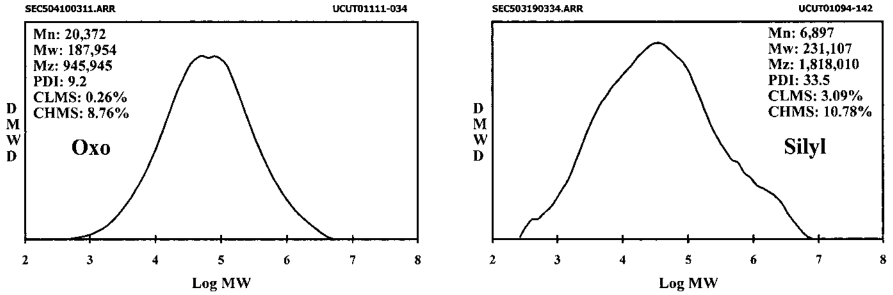


Figure 3. MWD of polymer made with oxo and silyl chromate catalysts

Conversion of Oxo to triphenylsilyl chromate catalyst: Since the catalyst structures are similar in nature it appears that it might be possible to form the silyl chromate derived structure shown in Figure 2 by ligand displacement on the oxo chromate compound. This was explored by adding triphenylsilanol (TPS) in hexane to the activated oxo chrome catalyst followed by drying under vacuum (eq. 1).

$$\mathrm{Cr(O)x/silica} + \text{TPS in Hexane} \xrightarrow{\text{Vacuum}} \text{slurry TPS/Cr(O)x/silica dry catalyst} \qquad (1)$$

The effect of the TPS on polymerization performance can be seen immediately (Figure 4). One equivalent of TPS results in a small decrease in activity and an increase in the initiation period. Addition of two equivalents of TPS results in a significant lowering of the catalyst activity with a large induction period. The kinetic profile produced with the oxo catalyst and two equivalents of TPS is typical of that observed with the silyl chromate catalyst. Table 2 shows the polymerization results. The catalyst productivity is lower with the TPS present due to a combination of lower inherent activity and increased induction times. The comonomer incorporation rate was also observed to decrease. This was determined by measuring the amount of 1-hexene incorporated into the polymer by ^{13}C NMR.

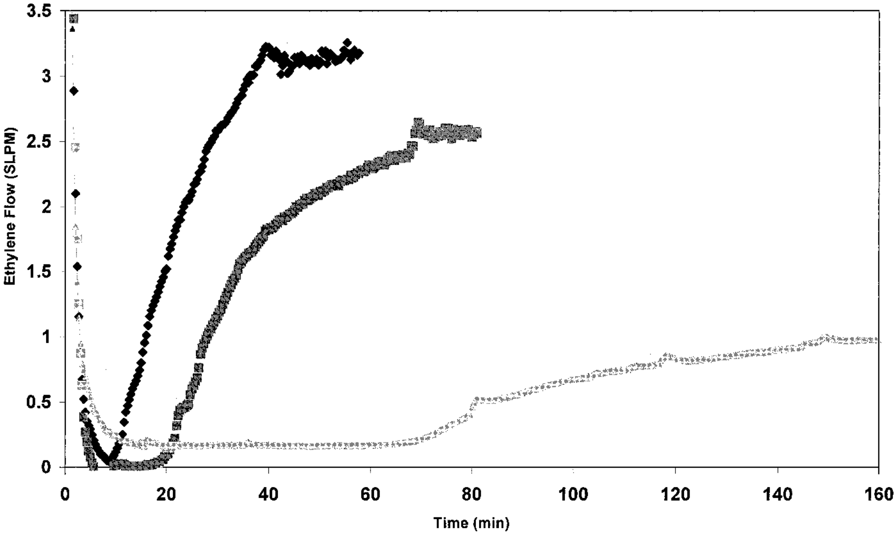


Figure 4. Effect of TPS on Oxo chromium ethylene polymerization kinetic profile; $T = 85°\mathrm{C}$, $P = 10$ bar, 500 ml hexane slurry, 10 ml 1-hexene,
♦ = Oxo, ▨ = Oxo + 1 TPS, ▲ = Oxo + 2 TPS

It is interesting that the presence of TPS inhibits the rate of active site formation (longer induction time) and lowers the rate of comonomer incorporation.

Table 2. Ethylene Polymerization Performance of Oxo Catalyst After TPS Addition

Catalyst Type	*Yield* *g*	*Productivity* *g PE/g cat/h*	*FI(I_{21})* *dg/10 min*	*BBF*[a)]	*Density* *g/cc*
Oxo	153	1,429	2.6	3.7	0.9392
Oxo + 1 eq TPS	161	607	2.1	2.9	0.9533
Oxo + 2 eq TPS	101	102	2.6	1.9	0.9517

[a)] Butyl Branching frequency /1000 C as determined by ^{13}C NMR

The presence of the TPS may lower the oxidative capacity (less electro-positive) of the Cr^{+6} precursor which slows the initial reduction-oxidation reaction with monomer during site formation. The effect of TPS is still present after site formation as seen in poorer comonomer incorporation. Most likely the TPS is present as a ligand even in the reduced catalyst.

Measurement of the polymer produced in the experiments in Table 2 by size exclusion chromatography (SEC) shows that the TPS broadens the MWD of the polymer (Figure 5). One equivalent results in an increase of the dispersity index from near 10 to 13 with slight development of a high molecular shoulder.

It can be seen that the Mz component is rising faster than the Mw. The second addition of TPS results in formation of a polymer that matches very well the polymer produced by the silyl chromate catalyst.

The distribution is very broad and the high molecular shoulder is fully developed. Based on

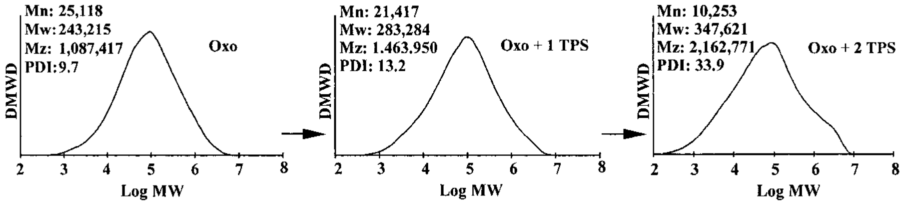


Figure 5. Effect of TPS on Oxo Chromium Polymer MWD

these results it looks like the silyl chromate catalyst can be formed through an oxo chrome intermediate.

Analysis of TPS addition to oxo chromium catalysts: Several reactions were conducted in which TPS was added to oxo chromium catalysts slurried in hexane under nitrogen. Thirty minutes after the TPS was added an aliquot of the liquid was taken. The remaining liquid was decanted away and the catalyst was washed three times more with hexane then dried under high vacuum. The reaction of TPS with oxo chromium catalyst was monitored by following the initial and final chromium loading on the support as well as the amount of chrome that dissolved in the hexane.

The first experiment shown in Table 3 was conducted on a chromium oxide catalyst activated at 825 °C with 0.4 wt % chrome present determined by ICP (Inductively-Coupled Plasma) elemental analysis. Measurement of the amount of Cr^{+6} present was determined by a standard starch iodine titration[6]. Addition of one equivalent of TPS to catalyst slurried in hexane resulted in a slight amount of chromium dissolving in the hexane.

Table 3. Effect of TPS on Oxo Chrome (Cr on Davison-955) Activated at Different Temperatures

Cr[a] on support	*Activation temperature*	*Cr^{+6}[b] on support*	*TPS/Cr*	*Cr[a] on support after wash*	*Fraction of Cr on support after wash*	*Fraction of Cr lost from support*	*Fraction of Cr[b] dissolved in hexane*
wt %	*°C*	*wt %*		*wt %*	*%*	*%*	*%*
0.39	825	0.40	1	0.36	92	8	<4
0.39	825	0.40	2	0.28	72	28	22
0.27	600	0.27	1	0.26	>96	<4	<2
0.27	600	0.27	2	0.26	>96	<4	<3
0.48	600	0.49	1	0.45	94	6	<3
0.48	600	0.49	2	0.44	92	8	13

[a] Determined by elemental analysis
[b] Determined by starch iodine titration[6]

After extensive washing 92% of the chrome was found to be remaining on the support. This shows that the chromium mostly remained on the support. However, the results for the polymerization reactions with a catalyst with the same ratio of TPS/Cr show that the TPS is affecting polymerization kinetics and polymer properties. The second experiment employs the same oxo catalyst starting material but two equivalents of TPS were used. In this experiment the hexane turned yellow. Analysis of the hexane revealed that the solution contained in the form of Cr^{+6} up to 22 % of the chrome that was on the initial oxo catalyst. The dissolved chromium appears to be bis(triphenyl silyl) chromate, which is soluble in hexane. After extensive washing only 72% of the chrome was found to be present on the solid catalyst. This result shows that it is possible to make the silyl chromate catalyst by direct conversion of the chromium oxide catalyst with TPS. The reason chromium dissolved after formation of the silyl chromate derivative, even though as shown in Figure 1 silyl chromate reacts with the surface silanols, is because the surface becomes supersaturated at this chrome loading. It has been reported elsewhere[8] that 955 silica dehydrated at 825 °C becomes saturated with silyl chromate at a loading of only 0.16 wt % Cr.

The next two experiments in Table 3 were conducted with the same TPS /Cr ratios but the initial chrome loading and dehydration temperature were lower. Here, in both experiments the chromium was not observed to come off the support. The known silyl chromate saturation level on 955 silica activated at 600 °C is 0.25 wt % Cr[8]. Therefore even if all the chromium oxide was converted to silyl chromate, the silyl chromate could completely be consumed by reaction with the surface silanols. The last two experiments in this table employ 600 °C dehydrated silica with higher chromium loading. If silyl chromate formed it would exceed the surface reaction saturation level. One equivalent of TPS results in loss of chromium, but with two equivalents the chromium can be seen to begin to dissolve (based on color and the presence of Cr^{+6} in solution) and chrome loss is observed in the final washed product.

These experiments show that it is possible to make silyl chromate catalyst directly from the oxo analogue. It also shows that it is not possible to maintain the higher chrome loadings that are achievable with the oxo catalyst when the TPS is added.

As shown in Figure 2 only one equivalent of TPS should be needed to form the chemisorbed silyl chromate analogue. However, the polymerization data showed that two equivalents were required to get complete conversion. It is possible that the TPS may not selectively react with the oxo chromate and the second equivalent of TPS is needed to complete the reaction. It is also interesting that supersaturation of the silyl chromate formed by addition of TPS to the already chemisorbed chromium oxide was observed. If the oxo chromium species were already anchored to the surface, would the bis(triphenylsilyl) chromate be able to form and migrate off the surface upon TPS addition? If the saturation level of the large bis(triphenylsilyl) chromate molecule on silica is dictated by a steric constraint, then it seems difficult to see how the second TPS molecule could approach the mono-triphenylsilylchromate anchored on the support. It should not be able to form a molecule in a pore in which the final product cannot fit.

Conclusion

Although similar in structure the oxo and triphenylsilyl chromate catalyst perform very differently in polymerization reactions. The presence of the TPS ligand is what leads to these differences. This can be seen by the clear conversion of polymerization performance observed with oxo chromium based catalysts to that observed with silyl chromate type catalysts by the addition of TPS into the former.

Acknowledgements

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