Studies on alkane formation in vanadium-based ethylene polymerizations

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Summary

Alkanes from vanadium-based ethylene polymerizations were found to originate from ethylene insertion into the Al-R bond in the cocatalyst and from the polymerization catalyst. The alkanes from the catalyst mostly came from vanadium sites that are related to the silica support and the quantity of alkanes can be reduced by chemical treatment of the silica. The polymerization conditions also affected the quantity of alkanes with low hydrogen concentration, addition of comonomer, and the use of TMA (trimethylaluminum) as a cocatalyst reducing the concentration of alkanes in the polymer.

Introduction

A number of supported vanadium catalysts based on VCl_4, VCl_3, or $VOCl_3$ used for the polymerization of ethylene have been described in the literature (1). The vanadium is deposited on, or chemically anchored to supports, such as silica, and these catalysts generally provide polyethylene with a relatively broad molecular weight distribution (MWD). Broad molecular weight distribution polyethylene is used extensively for producing blow-molded parts and films, and is typically produced by chromium oxide supported on silica. Vanadium-based catalysts are much more hydrogen sensitive than chromium-based catalysts. Therefore, with a vanadium-based catalyst, it is possible to produce relatively low molecular weight polyethylene which in turn has a relatively low melt viscosity. A low melt viscosity allows the polymer to be extruded at lower temperatures and at higher rates which results in less energy consumption.

However, vanadium-based ethylene polymerization catalysts tend to produce low molecular weight ethylene oligomers, or alkanes (2-6). The quantity of alkanes in the polymer range from around 2,000 to 5,000 ppm. The alkanes have relatively low boiling points and at polymer processing temperatures of about 220°C, the alkanes in the resin vaporize and, upon exposure to ambient air, condense into airborne droplets, creating smoke (2). The smoke is objectionable to processors and has limited the acceptability of vanadium-based polyethylenes. In this article we discuss our studies as to the cause of alkanes in vanadium-based polyethylenes and methods to limit alkane formation.

Experimental

The polymerization procedure, catalyst precursor synthesis and materials were described previously (7). Polymerizations were conducted at 93°C and 3.79×10^6 N/M^2 (550 psi)

in 1500 mL isobutane for 1 h in a 3.785 L reactor. Hydrogen was added as a pressure differential on a 1000 mL vessel (delta psi H_2). Propylene copolymerizations were conducted by adding 30 ml of propylene to the polymerization reactor to give a concentration of 0.24 M/l. Melt index (MI) results were measured using ASTM method D1238-86 and are reported in grams per 10 min.

The quantification of polymer alkanes (smoke) in polyethylene was accomplished by gas chromatography, which measured the even numbered straight chain alkanes. Approximately four grams of polymer particles from the polymerization reactor were extracted with cyclohexane for three and one-half hours at 55°C. A portion of the filtrate was introduced into a calibrated gas chromatograph for separation and quantitation of the even numbered (C_8-C_{26}) straight chain alkanes. Reproducibility of the results were good and were not influenced by polymer particle size. In this study we report the C_8-C_{18} portion of the alkanes which better represents the potentially volatile alkanes in the polymer.

The catalyst precursors had the following formulations on a millimoles per gram of silica basis (TEA = triethylaluminum, DEAC = diethylaluminum chloride, HMDS = 1,1,1,3,3,3-hexamethyldisilazane) A= 953 silica 0.05 $VOCl_3$/ 1.4 TEA/ 0.1 VCl_4/ 0.1 2-methoxyethanol. Catalyst precursor A was used in Tables 3, 4, and 5. B= 953 silica/ 1.4 TEA/ 0.1 VCl_4/ 0.1 2-methoxyethanol. C= 953 silica/ 2.4 TEA/ wash/ 0.1 VCl_4/ 0.1 2-methoxyethanol. D= 953 silica/ 2.4 DEAC/ wash/ 0.1 VCl_4/ 0.1 2-methoxyethanol. E= HMDS 948/ 0.05 $SiCl_4$/ 0.7 TEA/ 0.1 VCl_4/ 0.1 2-propanol. F= HMDS 948/ 1.5 $SiCl_4$/ 0.7 TEA/ 0.1 VCl_4/ 0.1 2-propanol. G= HMDS 948/ 1.5 $SiCl_4$/ 0.7 TEA/ 0.1 VCl_4/ 0.1 2-propanol.

Results and Discussion
Background Alkanes
Background alkanes are produced in the polymerization reactor without the polymerization catalyst present. These alkanes are probably caused by the insertion of ethylene into the aluminum alkyl bonds of the cocatalyst (8), followed by a reaction with H_2 to eliminate the alkane (9). Thermal decomposition of the Al-R bond yields Al-H and an alpha-olefin (8). However, G.C. experiments showed very little alpha-olefin was formed and alkanes were the primary products. This result suggests that, at our conditions with hydrogen present in the reactor, termination of the growing Al-R chain takes place by a reaction with hydrogen.

Two methods for quantifying background alkanes produced were used. The first method involved charging 1000 ml of heptane into the reactor and then adding typical amounts of cocatalyst, H_2, ethylene, and $CHCl_3$ promoter at standard conditions (no polymerization catalyst added). At the end of one hour the heptane was analyzed by G.C., and the alkanes were quantified. The second method involved subjecting a known quantity of polymer with a known quantity of alkanes to polymerization conditions and then retesting the polymer for alkanes after the experiment. The increase in alkanes was attributed to background alkanes.

Table 1 shows the quantity of alkanes produced without catalyst in the reactor. With heptane more alkanes were produced when both TEA and $CHCl_3$ were added to the reactor compared to when only TEA was added. The results indicate that alkanes are produced in the reactor without catalyst present and the addition of $CHCl_3$ increases the

quantity of alkanes produced. Using the second method with a seed polymer powder, with no added TEA or $CHCl_3$, there was no increase in the quantity of alkanes suggesting that the isobutane used in the study was free of alkanes and that TEA and/or $CHCl_3$ is important in the production of background alkanes. With added TEA and $CHCl_3$ the quantity of alkanes increased. In one experiment the quantity of polymer added to the reactor was increased from 10 to 400g. It was expected that the quantity of alkanes in ppm would drop, but the quantity in grams would remain unchanged. However, the quantity of alkanes in ppm was unchanged and the quantity in grams increased. This result suggests that there is an upper limit to the amount of alkanes the polymer used in this study can adsorb. An upper absorption limit (of around 800 ppm) would explain why no increase in alkanes was seen when both TEA and $CHCl_3$ were added to the reactor compared to the TEA only experiments.

For both the heptane and polymer analysis the results clearly show the presence of background alkanes. Because the quantity of background alkanes is small compared to the sum of background and catalyst alkanes from most vanadium catalysts, we turned our attention towards studying the effect of catalyst and process variables on polymer alkanes.

Catalyst Alkanes - Two Sites
Examination of the alkane extraction test results indicates that the alkane distribution is distinctly separated from the polymer MWD and that no significant "tail" from the polymer MWD extends into the alkane distribution. Contributions to the quantity of alkanes from the polymer MWD should result in an upturn in the quantity of alkanes at the longer alkane chain lengths. Typical alkane extraction test results show the quantity of alkanes peak at C_{18} and then start to decrease as the chain length increases. These results are consistent with the proposition that different sites are responsible for the production of alkanes and for polymerization.

GPC results show that the polymer MWD is clearly separated and distinct from the alkane distribution which is consistent with different sites being responsible for alkane formation and polymerization. Examination of GPC results from polyethylene produced with these catalysts shows that the lowest molecular weight portion of the polyethylene distribution is above a molecular weight of 1000. A molecular weight of 1000 is equal to about 70 carbon atoms in the lowest molecular weight portion of the polymer distribution which represents a significantly greater degree of polymerization than found in the alkane portion of the distribution.

Table 1 - Background Smoke Studies

	Heptane Analysis	
	TEA only	TEA and $CHCl_3$
C_8-C_{18}	0.072 g	0.15 g

	Polymer Treatment in Isobutane	
Comments	Increase in C_8-C_{18} in ppm	Increase in C_8-C_{18} in grams
No TEA or $CHCl_3$,10g PE	0	0
TEA only, 10g PE	609	0.0061
TEA only, 10g PE	631	0.0063
TEA and $CHCl_3$, 10g PE	657	0.0066
TEA and $CHCl_3$, 400g PE	607	0.24

Malpass shows examples of vanadium-based ethylene polymerizations where the melt index ratio, which is an indication of MWD, does not correlate with the amount of alkanes that are found in the polymer (2). We also have several proprietary examples where the MWD of the polymer does not correlate with the quantity of alkanes.

The alkane extraction test, GPC, and comparison of MWD vs alkanes results suggest that the alkane-producing sites on the catalyst are not the same sites that produce the polymer. The alkanes can be thought of as very short polyethylene chains and it has incorrectly been presumed that the polymerization sites are responsible for the formation of alkanes (2,3,5,6). We believe that there are two distinctly different categories of catalytically active sites, one for polymerization and one for alkane formation.

Chemical Treatment of Silica

We developed several polymerization catalysts that gave low quantities of alkanes by chemically treating the silica prior to addition of the vanadium compound. The results from two methods of chemical treatment are shown in Table 2. The first method involved adding an excess of TEA or DEAC to the silica, allowing it to react, then washing away the excess unreacted aluminum alkyl. The second method involved adding $SiCl_4$ to the silica which did not require a wash step in the catalyst preparation. The $SiCl_4$, once reacted with the silica, is still capable of reacting with TEA. The "silica-$SiCl_4$-$AlEt_3$" complex is then capable of reacting with VCl_4 preventing soluble vanadium species from polymerizing and fouling the reactor. Several different loadings of $SiCl_4$ were studied and all the catalysts gave similarly low quantities of alkanes. We also prepared catalysts which contained $SiCl_4$ or TEA added at later steps in the catalyst preparation. However, the catalysts with $SiCl_4$ or TEA added later in the preparation gave polyethylene with higher quantities of alkanes. The catalysts in Table 2 produce polyethylene which has low quantities of alkanes for the polymerization conditions used. Almost all of the alkanes in these polymers are thought to be due to background alkanes from the reaction of TEA with ethylene. Our results show that the reaction of TEA, DEAC, or $SiCl_4$ with silica reduces the alkane production from vanadium-based catalysts. In addition, there are examples in the literature where the vanadium was allowed to react directly with the silica support in the catalyst preparation (10). These catalysts were noted for producing significant amounts of alkanes in the polymerization (4).

We speculate that the alkanes from the catalyst precursors are formed at a vanadium site, resulting from the reaction of VCl_4 and a surface hydroxyl group or a reactive siloxane group. By adding excess TEA or $SiCl_4$ to the silica, the number of hydroxyl and reactive siloxane groups are reduced (11). Therefore, the number of hydroxyl and reactive siloxane groups available for reaction with VCl_4 are reduced.

Process Conditions

Effect of H_2

Decreasing the hydrogen in a polymerization decreases the quantity of alkanes. Table 3 shows that as the hydrogen added to the reactor is decreased, the quantity of alkanes decreases. This result is consistent with the reported observation of a correlation between polymer melt index (MI) and alkane production (3). Hydrogen is added to the reactor to control the molecular weight of the polyethylene produced. However, it has been shown that the concentrations of cocatalyst and promoter can have a large effect on the polymer molecular weight (12). To obtain a low quantity of alkanes, the H_2 concentration should

be kept at a minimum and target MI's obtained by changing cocatalyst and promoter concentrations. The alkanes are probably not due to an aluminum hydride species because Ti/AlR$_3$ catalyst systems require more H$_2$ than their vanadium counterparts and generally give a lower quantity of alkanes and the same quantity of alkanes were produced when di-isobutylaluminum hydride (1824 ppm) was tested in comparison to tri-isobutylaluminum (1629 ppm).

Effect of Comonomer
Addition of propylene as a comonomer decreases the quantity of alkanes (Table 4). In addition to decreasing the quantity of alkanes the comonomer increases polymer MI and increases catalyst reactivity. The increase in polymer MI allowed for a reduction in the hydrogen concentration needed for a target MI. The decrease in hydrogen concentration further lowered the quantity of alkanes. It is thought that the propylene functions by increasing the rate of polymerization (as indicated by higher catalyst activity) but not increasing the rate of alkane formation. The net result is that the same amount of alkanes are diluted into a larger mass of polymer, thereby decreasing the alkanes concentration in the polymer.

TMA vs. TEA
Replacing the TEA (triethylaluminum) cocatalyst with TMA (trimethylaluminum) reduces the quantity of alkanes (Table 5). A possible explanation is that TMA is less likely to oligomerize ethylene than TEA and therefore produce fewer background alkanes. There are reports in the literature that TMA oligomerizes ethylene much more slowly than TEA (13). It is not expected that the reaction chemistry of TMA with vanadium should be much different than TEA.

Table 2 - Silica Treatment

Catalyst Precursor		C$_8$-C$_{18}$ in ppm
C	excess TEA-wash	1008
D	excess DEAC-wash	1200
E	0.05 mMole SiCl$_4$	1201
F	0.15 mMole SiCl$_4$	1301
G	0.70 mMole SiCl$_4$	1006

Table 3 - Effect of H$_2$ on Polymer Alkanes

Delta psi H$_2$	C$_8$-C$_{18}$ in ppm	MI
70	4286	11.0
115	7504	84.2
150	10,352	211.2

Table 4 - Effect of Propylene Comonomer

C$_8$-C$_{18}$ in ppm	MI	Delta psi H$_2$	Reactivity	Comments
1421	0.19	30	282 g/g	no comonomer
940	3.18	30	470 g/g	0.24 M/l propylene
565	0.21	15	595 g/g	0.24 M/l propylene
301	0.07	10	751 g/g	0.24 M/l propylene

Table 5 - TMA vs TEA

C_8-C_{18} in ppm	Cocatalyst
2127	TEA
1095	TMA

Conclusions

Chemical treatment of the silica support significantly reduces alkane formation from vanadium-based ethylene polymerization catalysts. However, alkanes are still found in the polymer due to ethylene insertion into Al-R bonds of the aluminum alkyl cocatalyst. Future studies should focus on reducing the formation of background alkanes in vanadium-based polymerizations.

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