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Carbocationic polymerization of isobutylene by using supported Lewis acid catalyst on polypropylene

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Summary

This paper describes a new class of supported Lewis acid catalysts which are based on partially crystalline polypropylene. The Lewis acid, such as $EtAlCl_2$, is chemically bonded to the side chain of polypropylene and serves as catalyst for the cationic polymerization of isobutylene. This type supported catalyst can be easily recovered and reused for many reaction cycles without significant loss of its reactivity. The unique features of the structure of polypropylene offers the catalyst with high surface area and good mobility which account for the high catalytic activity. In addition, polypropylene is chemically and physically stable during the processes.

Introduction

An enormous effort has been devoted on supported catalysts as a means to increase the catalyst efficiency, particularly in heterogeneous catalysts which are usually supported on inorganic oxides[1-3], such as alumina, silica, zeolites, and activated carbon. In fine powder form these highly dispersed particles allow high utilization of the metal in chemical reactions. Most supported catalysts are prepared by dispersing metal salts on the substrate, followed by calcination/reduction[4] at a high temperature to generate the active species. In many cases, control and understanding of the active sites are very difficult. After reaction the supported catalysts are usually hydrolyzed and become part of the waste stream.

Reuse of the catalyst for many reaction cycles presents several important advantages, such as reducing wastes, minimizing catalyst cost and simplifying product purification. All of them also save energy and environment. These considerations become even more important when the reactions require a large quantity of catalyst, such as in the oligmerization of olefins. There are some examples[5-7] of using polymers as the solid support for both heterogeneous and homogeneous catalysts. The most common one is crosslinked polystyrene[8,9]. After a reaction cycle, the supported catalyst can be recovered from the reaction mixture by filtration. However, most of the supported catalysts lose their activity[6] either partially or fully after a few reaction cycles. Part of the reason must be related to the chemical and physical stability of the polymer substrate. For example, Gates and coworkers[10] have reported using $AlCl_3$ for generating superacids on crosslinked polystyrene surfaces. This polymer cannot withstand Lewis acid catalysis conditions and the catalyst becomes deactivated very fast by unknown pathways.

Results and Discussion

In this paper, a new type of polymer substrate, functionalized polyolefin, is discussed. The idea to use polyolefin as the substrate was based on several considerations, mainly (1) the stability of polyolefin which allows the application of the supported catalyst under more severe reaction conditions. (2) the crystallinity of polyolefin which not only offers good mechanical strength and processibilty of the immobile phase but also results in a high surface area for the

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*To whom offprint requests should be sent catalyst. The crystallization of polyolefin may force the active species to the surface of the crystalline phases. To demonstrate the idea, $EtAlCl_2$, was covalently bonded to semicrystalline hydroxylated polypropylene. This supported catalyst was evaluated in the carbocationic polymerization of isobutylene. Many attempts[11,12] have failed to prepare supported Lewis acid catalysts for this polymerization.

The hydroxylated polypropylene[13] was prepared by Ziegler-Natta polymerization with borane containing monomer and propylene. Borane groups in copolymers were subsequently oxidizeded to hydroxy groups by $NaOH/H_2O_2$. These hydroxylated polymers not only have the functional groups but also preserve crystallinity and thermostability. As shown in Figure 1, the combination of "brush-like" microstructure[14] and crystallinity of polypropylene segment results in a unique arrangement, in which the functional groups are mostly located on the surface of crystalline phases.

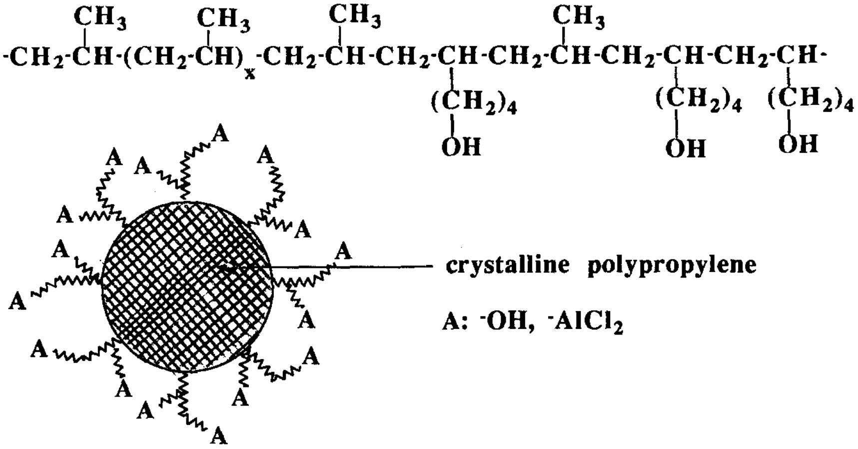
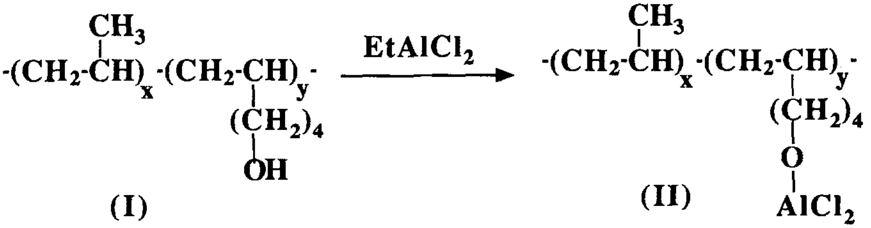


Figure 1:
Schematic arrangement of chains in "brush-like" hydroxylated polypropylene.

The hydroxylated polypropylene (I) swells slightly in toluene. The hydroxyl groups react with $EtAlCl_2$, so that the aluminum compound gets attached to the polymer (II), as shown in Equation 1.



$$-(CH_2\text{-}\underset{}{\overset{CH_3}{CH}})_x\text{-}(CH_2\text{-}\underset{\underset{OH}{(CH_2)_4}}{CH})_y\text{-} \xrightarrow{EtAlCl_2} -(CH_2\text{-}\overset{CH_3}{CH})_x\text{-}(CH_2\text{-}\underset{\underset{\underset{AlCl_2}{O}}{(CH_2)_4}}{CH})_y\text{-}$$

(I) (II)

Equation 1

This reaction is very effective under mild conditions. In most cases, the suspended fine powder of polymer (I) reacts with excess of $EtAlCl_2$ in solution at room temperature. Elemental analysis indicates that the conversion from hydroxyl group to $-OAlCl_2$ is quite complete. Most of the hydroxyl groups in polymer (I) are available for the reaction. This result also implies the picture shown in Figure 1.

The solid state ^{27}Al NMR spectrum of the polyolefin-supported catalyst (II) is shown in Figure 2 (a). It shows only a single peak at 89 ppm, corresponding to -OAlCl$_2$ with four coordination[15], and the absence of a resonance at 170 ppm, corresponding to EtAlCl$_2$.

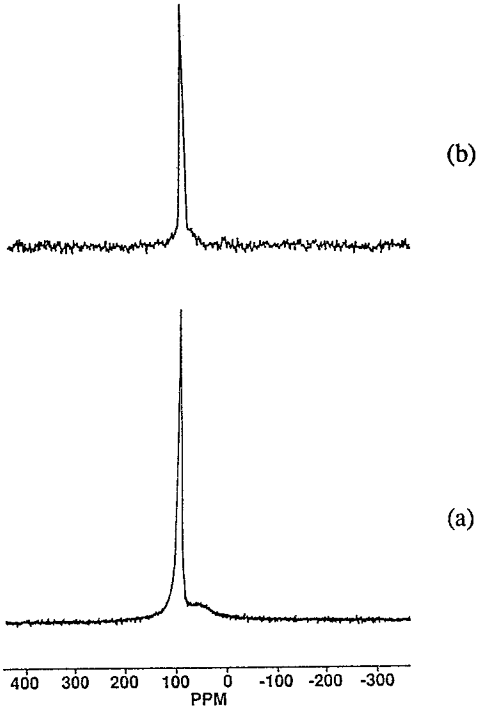


Figure 2:
^{27}Al NMR spectra of the supported catalyst, PP-OAlCl$_2$ (a) and C_5-OAlCl$_2$ (b).

It is quite unexpected that the alkyl-aluminum bond is much more reactive than the aluminum-halide bond in reaction with alcohol. In fact, the same reaction was also observed in a control reaction by using 1-pentanol, instead of the hydroxylated polypropylene, and a stoichmetric amount of EtAlCl$_2$ under the same conditions. The solution ^{27}Al NMR spectrum in Figure 2(b) of the resulting adduct (C_5-OAlCl$_2$) shows the same single chemical shift, corresponding to -OAlCl$_2$. In the elemental analysis of C_5-OAlCl$_2$, the theoretical and experimental mole ratios between the elements are almost identical, which strongly reconfirms the reaction shown in Equation 1.

Polymer II was used as catalyst for the polymerization of isobutylene. After polymerization, the supported catalyst was recovered by filtration and was reused. This procedure was repeated many times as shown in Table 1 without significant reduction in activity. Both elemental analysis and ^{27}Al NMR results showed no significant change in the aluminum species after more than 5 polymerization cycles. Overall, the catalyst activity is quite high despite its heterogeneous nature. Most polymerizations of isobutylene were completed in 15 minutes. The high surface and good mobility of the catalyst remained. The molecular weight of polyisobutylene was determined by GPC. In general, the molecular weight of polyisobutylenes prepared by the supported aluminum catalysts is slightly higher than those prepared by soluble ones[17], such as AlCl$_3$, EtAlCl$_2$, Et$_2$AlCl, BF$_3$, etc.. The molecular weight of polyisobutylene produced was about 4,000 g/mol at 0° C as shown in Table 1. The relatively higher molecular weight may be due to the slower chain tranfer (βproton elimination) because of the alkoxide ligand donates π-electron density to aluminum active site and stabilizes the propogating center. It is interesting to note that Mw=120,000 and Mn= 49,100 g/mol of polyisobutylene can be obtained at -45 ^{0}C in comparison with those prepared by soluble Lewis acid catalysts.

Table 1 : A Summary of Polyisobutylene* Prepared by Supported Catalyst**.

Run #	Time (min.)	Temp. (^{0}C)	Yield (%)	M_w	PDI
1	30	0	100	4900	2.4
2	15	0	100	5500	3.0
3	10	0	80	5450	2.6
4	5	0	65	4670	2.4
5	15	0	100	6800	2.4
6	15	0	100	4250	2.1
7	15	25	100	1340	2.4
8	10	25	85	1235	2.3

* Using 4 ml of isobutylene in hexane solution

** Polypropylene (fine powder) containing 5 mole % of -OAlCl$_2$ groups.

Figure 3 shows the ^{1}H NMR spectrum of resulting polyisobutylene. Overall, the spectrum is very similar to that of a polyisobutylene prepared by a conventional catalysts such as AlCl$_3$, EtAlCl$_2$, Et$_2$AlCl.

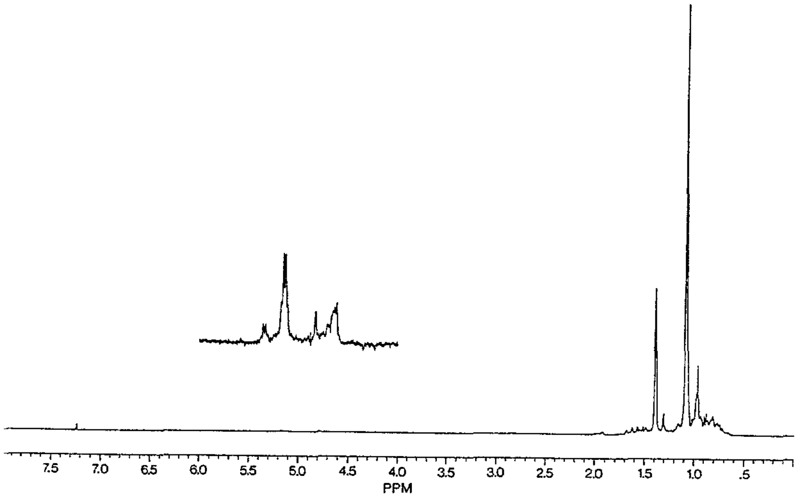


Figure 3:
^{1}H NMR spectrum of polyisobutylene prepared by PP-OAlCl$_2$ catalyst.

The peaks in the region from 4.5 to 6.0 ppm correspond to olefinic hydrogens. The double bond is evidence of proton transfer (β-proton elimination) during the polymerization. There are two quartets at 5.4 and 5.2 ppm and two singlets at 4.9 and 4.6 ppm. The singlets at 4.9 and 4.6 ppm are indicative of two types of nonequivalent vinylidene hydrogens[18] which are located at the end of the polymer chain. The quartets at 5.4 and 5.2 ppm are the trisubstituted olefinic hydrogens, corresponding to the internal double bonds. A significant amount of internal double bonds are present, which indicates "in situ" isomerization[18] during the reaction. The integrative intensity of olefinic region, in conjunction with the molecular weight information implies one double bond per polymer chain.

Experimental

Materials and Measurements

Isobutylene (Matheson) and $AlEtCl_2$ were used as received. HPLC grade toluene and hexane were distilled from sodium anthracide. All the manipulations were carried out in an innert atmosphere glove box or on a Sclenck line. The molecular weight of polyisobutylene was determined using a Waters GPC. The columns used were of Phenomenex Phenogel of 10^4, 10^3, 500 and 100 A. The flow rate was 0.7 ml/min and the mobile phase was THF. Narrow molecular weight polystyrene samples were used as standards. All the solution NMR were done on Bruker AM 300 instrument. In ^{27}Al NMR studies, toluene was used as solvent with deuterated toluene as lock solvent. For ^{1}H NMR studies, deuterated chloroform was used as solvent. MAS ^{27}Al NMR were done at CSU NMR Center on Bruker AM 600 NMR spectrometer (^{27}Al resonance frequency of 156.4 MHz and 14.5 KHz MAS speed).

Immobilization of $EtAlCl_2$

The hydroxylated polypropylene containing 5 mole % hydroxyl groups was slightly swellable in toluene. The reactions with the reagent were carried out at room temperature under the inert atmosphere. In a typical example, the hydroxylated polyolefin (150 mg) polymer, suspended in toluene (15 ml), was mixed with excess $EtAlCl_2$ (~10 mmole). After 3 hrs, the polyolefin was filtered and washed with hexane repeatedly to remove the remaining aluminum compound. Based on the elemental analysis and ^{27}Al NMR studies, most of hydroxyl groups were reacted without any unreacted aluminium compound in the polymer. In the control reaction, pentanol (0.5 ml, 4.6 mmole) dissolved in 5 ml toluene was reacted with 0.48 ml (4.6 mmole) $EtAlCl_2$ which was diluted with 5 ml toluene. The solution of $EtAlCl_2$ was cooled to -78°C and to this cooled solution pentanol solution was added dropwise. It was stirred at -78°C for 15 minutes and then warmed up to room temperature. Toluene was removed under vacuum.

Polymerization of Isobutylene

Polymerization were carried out in a high vacuum apparatus which consists of two 100 mL flasks (A and B), and one stopcock (a) was used to separate the flasks. The other stopcock (b) was used to control the vacuum and nitrogen flow. In the dry box, the supported Lewis acid catalyst, such as 100 mg of catalyst (A), was charged to the flask A, the valve (b) was then closed. The whole apparatus was moved to a vacuum line and was pumped to high vacuum before closing the valve (b). Isobutylene (4ml, 50 mmole) was condensed in flask B and dissolved in about 20 mL hexane which was vacuum-distilled into flask B. Isobutylene solution was warmed up to required temperature and transferred to the catalyst in flask A. After stirring the reaction mixture for the required time, polyisobutylene solution was separated from the supported catalyst by filtration in the dry box. Polyisobutylene was obtained by evaporating the solvent under vacuum. The supported catalyst was then recharged to flask A and the entire process was repeated.

Conclusions

A new class of immobilized Lewis acid catalysts based on functionalized polypropylene are found to be useful in the cationic polymerization of isobutylene. The catalyst can be recovered and reused for many reaction cycles. The advantages of using polypropylene as the substrate are many fold, mainly (1) the chemical and physical stability of the substrate. (2) the crystallinity of the polyolefin to form supported catalysts with high surface area. (3) the flexible side chain between catalyst and polyolefin offering good catalyst mobility. (4) the convenient catalyst implantation.

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