POLYETHYLENE SURFACE TREATED IN A CO$_2$ PLASMA AS A NEW SUPPORT OF METALLOCEN CATALYST

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Abstract

CO$_2$ plasma treatment is chosen to create new type of supported metallocen catalyst on high density polyethylene (HDPE) support without any surface degradation.

The study is focused on the CO$_2$ plasma chemistry with the purpose of increasing the acidic surface groups. Different plasmas composed of mixtures of CO$_2$ and H$_2$O vapor have been tested. However it appears that, whatever the water proportion in the plasma phase is, whatever the discharge power is, the carboxylic groups density is decreasing. Optical emission and mass spectroscopies reveal that the acidic groups are formed onto the surface through the bombardment of CO$_2$ and/or CO$_2^+$. But, H$_2$O adduct in the CO$_2$ plasma phase leads to a more important dissociation of these CO$_2$ and/or CO$_2^+$ reactive species into CO, O et O$_2$ through an excitation transfer mechanism. In addition, hydrogen atoms originated from H$_2$O plasma are shown to react with CO molecules and form formaldehyde whose density can reach the value of 6 to 8 % depending on plasma conditions.

The attachment of the metallocene catalyst corresponds to a multi-steps synthesis from the polyethylene surface treated in such CO$_2$ plasma conditions. The unique superficial catalytic structure is demonstrated. The activities of the system tested with the polymerization of styrene are in good agreement with usual activities observed for similar heterogeneous metallocenes.

1. Introduction

Supported catalysis reactions of the metallocene type are nowadays used for production of polyolefins$^{1,2}$ due to the fact that these reactions are extremely fast and occur at low temperature. However, part of the catalyst is released from the surface due to the absence of pure covalent bond between the support and the catalyst$^3$. In order to create covalent bonds between the catalyst and the support, carboxylic acid fixation onto the polyethylene surface through the CO$_2$ or CO$_2$ + H$_2$O plasma treatment has been tested. In the first part of this study, some attempts are described to optimize the concentration of carboxylic functions incorporated onto the polyethylene surface through the plasma treatment. One of them is dealing with gases mixtures plasmas.
2. Experimental Part

High-density polyethylene (HDPE, Tm = 115°C, 75 - 77 % crystalline fraction) with a 10 μm thickness was supplied by Goodfellow. The plasma equipment used here is a microwave plasma apparatus. The carboxylic groups titration\textsuperscript{4,5}, metalocene catalyst post-fixation\textsuperscript{6} and polymerization\textsuperscript{6} procedures are described.

3. Results and discussion

Study of the plasma and the interactions plasma / HDPE

Study\textsuperscript{7} on the HDPE modification in CO\textsubscript{2} plasma has demonstrated the major role of CO\textsubscript{2} plasma species in different energy states and, the COOH surface reaches a value around 3 sites / nm\textsuperscript{2} is obtained. By comparing the nature of the function to be fixed (COOH) and the nature of the species formed into CO\textsubscript{2} plasma (mainly CO and CO\textsubscript{2})\textsuperscript{8}, the presence of H or OH species in the plasma would increase the proportion of carboxylic acids onto the polyethylene surface. Therefore, the water vapor (H\textsubscript{2}O) is chosen as second gas.

However, results (Fig.1) show that the water addition in the CO\textsubscript{2} plasma does not increase the proportion of surface carboxylic groups but on the contrary, decreases it. Thus, no reactions of recombination between the various plasma species leading to the formation of COOH plasma species and, consequently to the increase of surface carboxylic groups are taken place.

![Fig. 1: Dependence of the carboxylic functionalization of HDPE treated in CO\textsubscript{2} / H\textsubscript{2}O plasma versus gas composition and discharge power.](image)

The mass spectroscopy studies with gases mixture plasma reveals the appearance of unexpected peaks corresponding to the species at 28, 29 and 30 a.m.u (Fig.2). The formation of the CO\textsuperscript{+} species at 28 a.m.u. is probably related to a fragmentation of the carbon dioxide combined with that of water molecule during electronic bombardment in the ionization chamber. Ihara and coll.\textsuperscript{9} showed also in CO\textsubscript{2} / H\textsubscript{2}O plasma the formation of methanol (32 a.m.u.), in a less proportion the formation of formaldehyde (30 a.m.u.) and the presence of hydrogen peroxide (34 a.m.u.) and of oxalic acid (90 a.m.u.) was characterized by chromatographic analysis of the gas products. Here, only the formaldehyde (29 and 30 a.m.u.) is identified.
Fig. 2: Mass spectrum of neutral species in CO\textsubscript{2}/H\textsubscript{2}O plasma.

The formation of such a product is indicated below:

$$\text{C} = \text{O}_\text{f} + \text{H}^+ \rightarrow \text{C} = \text{O}_\text{f} + \text{H} \quad (m/z = 28)$$

$$\text{H} \quad (m/z = 29)$$

$$\text{C} = \text{O}_\text{f} + \text{H}^+ \rightarrow \text{C} = \text{O}_\text{f} + \text{H} \quad (m/z = 30)$$

No peak appears at 45 a.m.u. (COOH), this implies that no recombination reaction occurs between CO\textsubscript{2} and H\textsubscript{2}O plasma species leading to the formation of carboxylic functions precursor species. Mass spectrometry shows also that the dissociation of H\textsubscript{2}O molecule involves the fragmentation of CO\textsubscript{2} molecule as a mechanism of excitation transfer\textsuperscript{10} (Fig. 3) and thus explains the decrease of the concentration of surface carboxylic acids characterized previously.

Fig. 3: Dependence of the ratio of the mass peak intensity of CO\textsubscript{2}\textsuperscript{+} / Σ all intensities of the plasma versus water composition.
Catalyst fixation

The catalyst synthesis is described in the following Fig. 4.

Fig. 4: Surface fixation of the indenyl ligands and metal tetrachloride reaction on the polymer support.

After the CO₂-plasma treatment, the HDPE surface support contains carboxylic functions able to create pure covalent bonds between the catalyst and the support. The structure of the supported catalyst is confirmed by several surface analyses (FTIR-RAS, XPS, ICP...) (Fig.5).
Polymerization results

Polymerization of styrene was conducted at temperature between 25 and 60°C for 48 h with the supported catalyst using MAO as cocatalyst. Compared to the literature values of polymerization with homogeneous metalloene\(^{11-13}\) (Table 1), its catalytic activity seems to be much lower due to the steric effect of the support surface. Nevertheless, results (Table 2) seem to be in agreement with other heterogeneous systems. Furthermore, the presence of a bridge between the two-indenyl ligands seems to markedly increase the catalytic activity because of a higher space for the monomer coordination.

<table>
<thead>
<tr>
<th>Catalytic System</th>
<th>Monomer</th>
<th>[Al]/[M]</th>
<th>Polym. Temp.</th>
<th>Activity (kg pol./(mol M.h))</th>
<th>(M_n) (lp) (g.mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Cp}_2\text{ZrCl}_2/\text{MAO})</td>
<td>Ethylene</td>
<td>11 1000</td>
<td>60°C</td>
<td>20 000</td>
<td>384 000(-)</td>
</tr>
<tr>
<td>(\text{Ind}_2\text{Zr(CH}_3\text{)}_2/\text{MAO})</td>
<td>Ethylene</td>
<td>22 3200</td>
<td>50°C</td>
<td>198 500</td>
<td>395 000 (2.20)</td>
</tr>
<tr>
<td>(\text{Me}_2(\text{Ind}_2\text{ZrCl}_2)/\text{MAO})</td>
<td>Propylene</td>
<td>15 0000</td>
<td>70°C</td>
<td>190 000</td>
<td>36 000(2.21)</td>
</tr>
<tr>
<td>(\text{PPh}_3/\text{Ind}_2\text{TiCl}_4/\text{MAO})</td>
<td>Styrene</td>
<td>517 000</td>
<td>60°C</td>
<td>92 8</td>
<td>9072 (2.21)</td>
</tr>
</tbody>
</table>

Table 1: Comparison of our results (*) with results of homogeneous catalysts.

<table>
<thead>
<tr>
<th>Catalytic System</th>
<th>Monomer</th>
<th>[Al]/[M]</th>
<th>Polym. Temp.</th>
<th>Activity (kg pol./(mol M,h))</th>
<th>(M_n) (lp) (g.mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{SiO}_2/\text{CpIndZrCl}_2/\text{MAO})</td>
<td>Ethylene</td>
<td>500 000</td>
<td>40°C</td>
<td>32</td>
<td>91700 (4.7)</td>
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<tr>
<td></td>
<td></td>
<td>1000</td>
<td></td>
<td>68</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2000</td>
<td></td>
<td>79</td>
<td>130</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5000</td>
<td></td>
<td>130</td>
<td></td>
</tr>
<tr>
<td>(\text{SiO}_2/\text{CpTiCl}_3/\text{MAO})</td>
<td>Styrene</td>
<td>225 000</td>
<td>50°C</td>
<td>1.36</td>
<td>79300 (4.6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>480 000</td>
<td></td>
<td>5.27</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1000</td>
<td></td>
<td>12.25</td>
<td></td>
</tr>
<tr>
<td>(\text{PE/Ind}_2\text{ZrCl}_2/\text{MAO})</td>
<td>Styrene</td>
<td>266 000</td>
<td>50°C</td>
<td>57.3</td>
<td>56122 (2.32)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>532 000</td>
<td></td>
<td>100.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>882 000</td>
<td></td>
<td>135.2</td>
<td></td>
</tr>
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</table>

Table 2: Comparison of our results (*) with results of heterogeneous catalysts.
Whatever the polymerization conditions, only one mass distribution is observed showing that there is only one catalytic species fixed on the polyethylene support. But the atactic nature of the polystyrene\textsuperscript{14} was confirmed. Increasing the temperature leads to a large increase of the catalytic activity and a slight decrease of the molecular weight ($\overline{M_n}$). The titanium-based support shows a more important evolution of the catalytic activity than the zirconium one. The catalytic activity and the molecular weight ($\overline{M_n}$) show both a maximum for a [Al]/[M] ratio of about 900 whatever the temperature as observed before\textsuperscript{15}. While the catalytic activity tends to stabilize for a monomer concentration up to 0.8 mol.L\textsuperscript{-1}, the molecular weight shows a progressive decrease.

Finally, the efficiency of the supported catalyst is checked. After the first use, a slight decrease of the activity is observed suggesting that a little part of the catalytic center be deactivated irreversibly. After three uses, the catalytic activity stabilizes and represents about 90% of the initial activity. The molecular weight stays constant whatever the number of uses.

Some molecular modelizations are also run for a better understanding of the conformation of the catalyst onto the HDPE surface and its activity towards the styrene polymerization.

4. Conclusion

In this study, an illustration of cold plasma post treatment is given. The incorporation of convenient fixation groups on a polymer surface allows the covalent attachment of a unique form of metalloocene catalyst and the catalytic activity is comparable to similar heterogeneous system. The synthesized polystyrenes show low molecular weight due probably to MAO and monomer chain transfer reactions. The MMD study conclude to a meso conformation, which explains the atactic nature of the polystyrene.

References