Early Stages of Ethylene Polymerization Using the Phillips CrO*x*/Silica Catalyst

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The reaction of ethylene with CO prereduced CrO*x*/silica polymerization catalyst has been monitored by quadrupole mass spectrometry. Evolution of 1-hexene is observed shortly after ethylene adsorption. This corresponds to the formation of a chromacyclopentane intermediate species which can also participate in ethylene polymerization.

1. Introduction

Polymerization of ethylene by CrO*x*/silica catalysts has been widely studied, and a variety of different mechanisms have been put forward. The overall reaction pathway may be broken down into three separate stages: initiation, propagation, and chain termination.[1,2] Initiation encompasses the attachment of the very first monomer unit to the catalytic site. Subsequent ethylene molecules add on during the propagation step to form alkyl chains fixed to the chromium center. Termination involves the separation of the polymer chain away from the catalyst surface. The propagation and termination steps are well understood and are therefore described first.

Two types of mechanisms are generally accepted for the propagation of transition-metal-catalyzed olefin polymerization systems: these are known as the Cossee[3] and Green-Rooney[4] mechanisms named after the researchers who first proposed them. The Cossee mechanism[3] requires a vacant coordination site on the metal center in the position adjacent to the growing alkyl chain. A monomer molecule then π-bonds to the metal via this site, followed by a migratory insertion reaction that extends the growing alkyl chain by one monomer unit (thereby regenerating the vacant coordination site on the metal center). The Green-Rooney mechanism[4] requires two vacant coordination sites at the metal center. The growing polymer chain first eliminates an α-hydrogen to produce a metal−carbene species. An ethylene molecule then coordinates at the remaining vacant site. This is followed by addition across the metal−carbene double bond in a metathesis-type reaction to form a metallacycle species. Reductive elimination causes the ring to open, thus producing an alkyl chain that has been extended by one monomer unit in conjunction with the reappearance of the original two vacant coordination sites at the metal center.

Termination is understood to occur via β-H elimination.[1,5] This mechanism not only fits the known chemistry of metal alkyls but also produces polymer containing vinyl groups at the terminating end. Infrared and NMR analyses have shown that polymer chains usually contain one vinyl and one methyl end group.[1] Quick-kill experiments have identified the presence of methyl groups during the early stages of reaction but the absence of any vinyl centers;[1] this has been taken as being indicative of methyl group formation during initiation and vinyl group production upon termination.

The initiation step for the Phillips CrO*x*/silica ethylene polymerization catalyst is poorly understood and in the past has mainly been studied by infrared spectroscopy.[6−13] Hogan[5] suggested that polymer chains were initiated by monomer insertion into a M−H bond; the resulting metal−alkyl species then propagates via a Cossee mechanism.[3] A prerequisite for this scheme is that there must be a M−H bond present prior to the onset of polymerization. Some groups have suggested that surface silanol groups provide a source of additional hydrogen atoms.[6,14] Hydride transfer may occur between a silanol group and a supported Cr^{2+} ion to yield an O^{2-} species and a $Cr^{3+}-H$ bond (into which the first ethylene can insert).[14] Alternatively, it has been proposed that ethylene adsorption directly onto a surface silanol group is followed by its coordination to an adjacent chromium ion along with the migration of a proton from the silanol group onto the metal center.[6] Mechanisms such as these, which involve silanol species, are considered to be unlikely,[1] since excellent catalysts can be obtained using completely dehydroxylated precursor materials. Metallacyclic and/or carbene reaction intermediates circumvent the prerequisite for a source of additional hydrogen atoms.[15,16] For example, the interaction of two ethylene molecules coordinated to the same chromium center can lead to the formation of a metalla-cyclopentane species, which can then β-eliminate to generate an allyl species.[1] Chain growth can then proceed either at the monohapto chromium−allyl bond or at the Cr−H bond. Alternatively, the metallacyclopentane species can undergo α-hydrogen elimination onto an oxygen atom bridging the chromium center to the support; this will produce a metallacy-clocarbene structure.[7] Such an intermediate can then undergo propagation via a Green-Rooney[4] type mechanism. Another possibility is where carbene species are generated via the dissociative adsorption of ethylene onto two adjacent chromium sites.[9] A second ethylene molecule then forms an alkyl chain bridge between the two chromium sites; this can subsequently propagate via either the Cossee[3] or the Green-Rooney[4] mechanism. More recently, it has been suggested that adsorption of ethylene onto a chromium site to form a linear carbene species via π-complexation and rearrangement may occur.[8] Propagation is then predicted to occur via a modified Green-Rooney mechanism, where ethylene adds across the carbene double bond to form a metallacycle, which then undergoes α-hydrogen elimination. Reductive elimination of this hydrogen opens up the ring to regenerate a linear carbene species that has been extended by one monomer unit.[8]

Such studies have primarily concentrated on identifying adsorbed moieties and have therefore tended to overlook the

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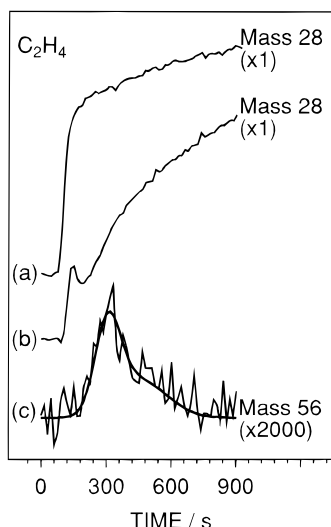
Figure 1. Mass signal intensities: (a) m/z 28 response during ethylene exposure in the presence of calcined silica; (b) m/z 28 response during ethylene exposure in the presence of calcined and prereduced CrO$_x$/SiO$_2$ catalyst; and (c) m/z 56 evolution for (b).

Figure 2. Mass profiles during exposure of calcined and prereduced CrO$_x$/SiO$_2$ catalyst to deuterated ethylene (C$_2$D$_4$): (a) m/z 45 and (b) m/z 46.

Figure 3. Mass profiles during exposure of calcined and prereduced CrO$_x$/SiO$_2$ catalyst to deuterated ethylene (C$_2$D$_4$): (a) m/z 63 and (b) m/z 64.
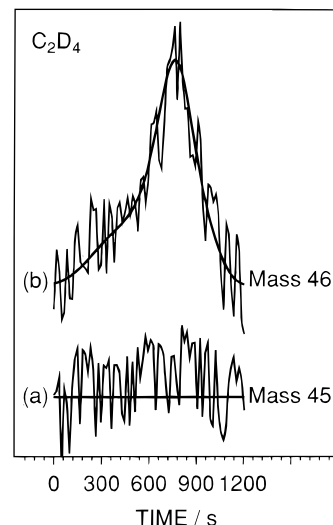
formation and desorption of short-lived intermediate species. This is addressed in the present investigation, where quadrupole mass spectrometry has been employed to identify the gaseous species evolved during ethylene polymerization over CrO$_x$/silica catalysts.
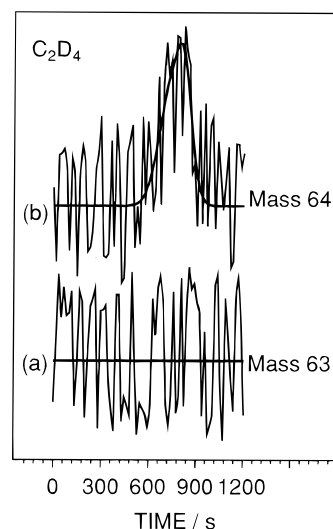
2. Experimental Section

The CrO$_x$/silica catalyst precursor (Crosfield Chemicals) was prepared by impregnating silica with an aqueous solution of basic chromium(III) acetate and then drying. The supported catalyst contained 1 wt % chromium loading. Oxygen, argon, and carbon monoxide (BOC; 99.5%, 99.998%, and 99.9% purity, respectively) were dried through a concentrated H$_2$SO$_4$ bubbler, followed by a P$_2$O$_5$ drying column, and then a 3A molecular sieve (Aldrich), at a flow rate of 1.5 dm^3 h^{-1}. Ethylene (Scott Specialty Gases; 99.8% purity) was dried through a P$_2$O$_5$ drying column, followed by a 3A molecular sieve at a flow rate of 1.5 dm^3 h^{-1}. Deuterated ethylene (C$_2$D$_4$, MSD Isotopes; 99% minimum isotopic purity) was used at a flow rate of 1.5 dm^3 h^{-1} without further purification. All experiments were carried out at atmospheric pressure.

One gram of catalyst precursor material was loaded into a quartz microreactor tube and heated under a flow of O$_2$ carrier gas at 1 K min^{-1} up to 1053 K using a Eurotherm temperature controller.[17] The furnace was maintained at this high temperature under flowing O$_2$ for 5 h; the feed gas was then switched over to argon and the catalyst cooled at 5 K min^{-1} down to 623 K. This was followed by reduction with CO for 15 min. The advantage of using a CO reduction pretreatment is that it eliminates any potential interference from the induction period normally associated with direct ethylene exposure of the calcined CrO$_x$/silica catalyst.[1] Next, the temperature of the activated catalyst was lowered to 383 K under argon; at this point either ethylene or deuterated ethylene was introduced to make up a 50:50 mixture with argon. In the case of C$_2$H$_4$, a 15 min exposure was used, while C$_2$D$_4$ was passed over the prereduced catalyst CrO$_x$/silica for 20 min. Upon completion of each experiment, the reactor was allowed to cool to room temperature under a flow of argon.

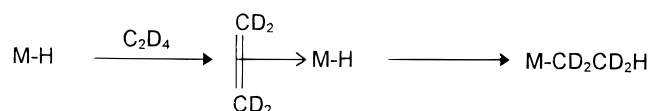A Vacuum Generators SX200 quadrupole mass spectrometer connected via a heated fine capillary tube to the microreactor outlet was used for simultaneous acquisition of up to 50 mass profiles. For each set of experiments, the whole background mass spectrum (m/z 0−200) was recorded during ethylene exposure as a function of time, hence facilitating the identification of all the desorbing species during polymerization. Each experiment was then repeated using freshly activated catalyst, but on this occasion, the intensities of the previously identified mass peaks were tracked versus time, to obtain a corresponding set of reaction profiles.

The white powdered material collected at the end of each experiment was mixed with potassium bromide and pressed into disks for infrared analysis using a FTIR Mattson Polaris instrument. Typically 100 scans were acquired at a resolution of 4 cm^{-1}.

3. Results

CO reduction of the calcined CrO$_x$/silica catalyst caused a change in its appearance from bright orange to pale blue/green. Subsequent exposure of ethylene to this activated catalyst at 383 K was found to be accompanied by a delay in the m/z 28 (C$_2$H$_4$) signal intensity, followed by a small dip, prior to gradually increasing toward a saturation value. (This behavior

Early Stages of Ethylene Polymerization

J. Phys. Chem. B, Vol. 102, No. 16, 1998 **2993**

SCHEME 1

$$M\text{-}H \xrightarrow{C_2D_4} \overset{CD_2}{\underset{CD_2}{\parallel}} \longrightarrow M\text{-}H \longrightarrow M\text{-}CD_2CD_2H$$

was not observed in the absence of activated CrO_x/silica catalyst or in the presence of calcined silica, Figure 1.) The rise after the dip coincides with a small pulse of masses at m/z 41, 42, 43, and 56 (maximum intensity ∼1/3000 of the saturation value for ethylene). These mass fragments are characteristic of many different types of hydrocarbon species.[18] The presence of m/z 43 suggested that the desorbing hydrocarbon molecules must contain more than three sp^3 hybridized carbon atoms (otherwise no propyl cation could be formed); i.e., this rules out butene and propene. On comparing mass fragmentation patterns,[18] 1-hexene and 1-octene were found to be the only possible contenders. A more specific assignment was carried out by comparing the measured m/z 56:43 ratio (=1.4) with values obtained using reference hydrocarbon compounds (1-hexene, 1.4; 1-octene, 0.65). These observations suggest that 1-hexene is produced during the initiation step of ethylene polymerization over a CO prereduced CrO_x/silica catalyst.

Further experiments using deuterated ethylene were carried out in order to verify the formation of 1-hexene during the initial stages of polymerization over the prereduced CrO_x/silica catalyst and also to find out whether hydrogen species from the support participate in this reaction. The major fragment for fully deuterated 1-hexene should be m/z 46, or 45 if there is a hydrogen atom present (these mass fragments correspond to m/z 41 in the case of nondeuterated 1-hexene), while the second largest fragment is expected be m/z 64 if fully deuterated, or m/z 63 if a hydrogen atom is present (these mass fragments correspond to m/z 56 in the case of nondeuterated 1-hexene). Exposure of the CO prereduced CrO_x/silica catalyst to C_2D_4
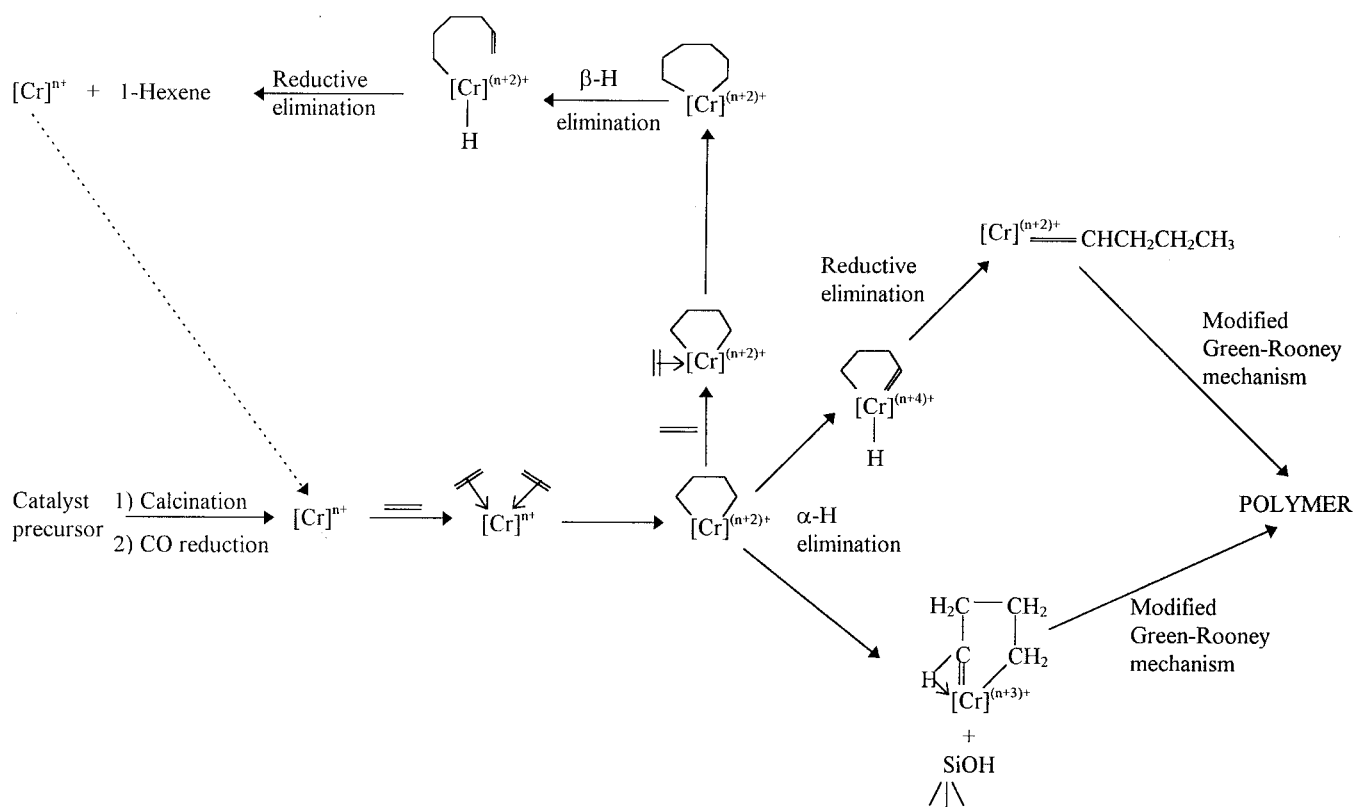
resulted in the evolution of only fully deuterated 1-hexene mass fragments, i.e., m/z 46 and 64 (Figures 2 and 3); this proves that no additional hydrogen atoms are involved during the initiation step. The possibility of 1-hexene being produced via dimerization of trace amounts of propene impurity was also eliminated, since the deuterated ethylene was not found to contain any propene impurity.

For both monomers, polymerization resulted in the production of white granules, which were confirmed by FTIR to be polyethylene. In the case of C_2H_4, absorbances were identified at 2920 and 2850 cm^{-1} (C−H stretches), 1469 cm^{-1} (methylene bending mode), and 719 cm^{-1} (methylene rocking mode).[19] All remaining absorbances could be assigned to the silica support material.[20] Polymer produced using C_2D_4 gave rise to the expected ∼$1/\sqrt{2}$ shift in C−D stretching frequency (i.e., 2193 and 2083 cm^{-1}) compared to the C−H absorbances observed for C_2H_4 polymerization.[21]

4. Discussion

In the present study, the observed dip in ethylene signal prior to its rise toward maximum intensity during exposure to the prereduced CrO_x/silica catalyst occurs before there is any evolution of oligomeric mass fragments; this is consistent with ethylene adsorption onto the catalyst surface taking place first, which is then followed by reaction. The deuterated ethylene experiments produced fully deuterated 1-hexene fragments, thereby proving that no additional hydrogen atoms are required for the initiation step (e.g., from surface silanols[6,14]). Hence, a conventional linear mechanism[3] is not responsible for 1-hexene formation, since it would require a M−H bond for ethylene to insert into (Scheme 1); furthermore, this type of mechanism would not explain why the oligomer chains terminate upon reaching 6-carbon atoms. The possibility of 1-hexene being formed at surface sites that are not sufficiently active to catalyze

SCHEME 2

the growth of longer chains would be expected to lead to the continuous evolution of 1-hexene as well as the formation of a distribution of oligomers. Clearly this is not the case, since 1-hexene is only formed upon initial exposure of ethylene and no other oligomers were detected during this period.

Selective trimerization of ethylene to form 1-hexene has previously been reported for homogeneous chromium center catalysts and proposed to proceed via metallacyclic intermediates;[22-24] this involves coordination of two ethylene molecules to each chromium center followed by rearrangement to form a chromacyclopentane species. Another ethylene molecule then inserts into the ring to produce a highly reactive chromacycloheptane[22-24] which can undergo decomposition to form 1-hexene.[25] This is consistent with small rings (<7-membered) being unable to β-eliminate easily[22,26] and is analogous to ethylene insertion into a metallacyclobutane ring.[27] Metallacycloheptane is conformationally flexible enough to achieve the M−C−C−H planarity required for β-H elimination;[26] this is followed by reductive elimination to yield 1-hexene along with the original chromium species (Scheme 2).

If 1-hexene is produced, as suggested, via a chromacyclopentane species, then it is possible that the initiation of polymerization may also proceed via this intermediate. Although β-H elimination from chromacyclopentane is inhibited, α-H elimination to either the chromium atom or a surface oxygen[7,28] atom could lead to the formation of a reactive cyclic carbene species (Scheme 2). In the case of the transferal of a hydrogen atom onto the chromium center, subsequent reductive elimination of hydrogen will produce a linear carbene species, which may then propagate via a modified Green-Rooney type mechanism.[8] (This involves the addition of ethylene across the carbene double bond to form a metallacyclobutane species.) Alternatively, the cyclic carbene species created by hydrogen transfer to a surface oxygen atom may propagate via a modified Green-Rooney mechanism.[7,28]

5. Conclusions

Initiation of ethene polymerization over prereduced CrO$_x$/silica catalysts leads to the transient evolution of 1-hexene. This can be taken as being evidence for the formation of a chromacyclopentane intermediate species which is also capable of proceeding onto the propagation step of ethylene polymerization.

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