# Mechanistic implications of the unprecedented transformations of ethene into propene and butene over Phillips $CrO_x/SiO_2$ catalyst during induction period

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## Abstract

In this work, an industrial calcined Phillips $CrO_x/SiO_2$ catalyst engaged in the induction period through interaction with ethene at ambient conditions was characterized by temperature-programmed desorption (TPD) equipped with a quadrupole mass spectrometer (MS). It was unprecedented to find that the first hydrocarbon species had already been formed and was observed to be propene instead of the expected butene. In fact, butene is the second hydrocarbon species formed after propene during the induction period. This evidence strongly implied that the initiation in terms of Cr–carbon bond formation on the Phillips catalyst occurs through an ethene metathesis mechanism during the induction period. Three most possible routes regarding the ethene metathesis initiation and formation of the first hydrocarbon species propene during the induction period on the Phillips catalyst were proposed.

## 1. Introduction

As an important catalyst for olefin polymerization, Phillips $CrO_x/SiO_2$ catalyst has achieved spectacular success in the industrial field since early 1950s. However, its main academic aspects concerning the active sites and polymerization mechanism still remain mysterious in spite of half century of great effort [1–5]. In particular, the initiation mechanism of the first chain propagation is poorly understood [3,5]. Within the past five decades, various initiation mechanisms have been proposed based on either pure speculation or controversial evidence (as shown in Scheme 1) [2,3,6–17]. The key to achieving a solution to this critical problem is to obtain specific information about the first hydrocarbon chain formed in the initial stage of ethene polymerization [3,5].

Phillips $CrO_x/SiO_2$ catalyst can be used either in pre-reduced form (defined as $Cr(II)O_x/SiO_2$) [6–19] or in calcined form (non-pre-reduced, defined as $Cr(VI)O_x/SiO_2$) [3]. When a $Cr(II)O_x/SiO_2$ catalyst with surface-stabilized Cr(II) (surface structure is **1**

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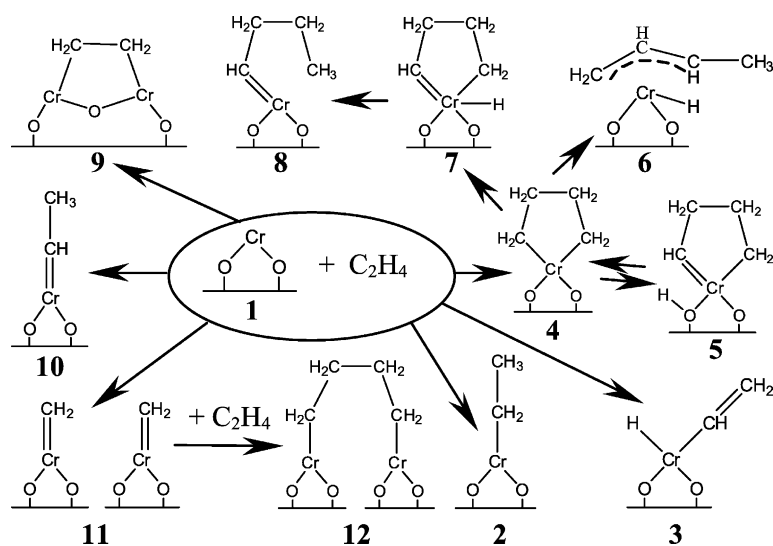
Scheme 1. Various initiation mechanisms of ethene polymerization over the pre-reduced Phillips Cr(II)O$_x$/SiO$_2$ catalyst proposed in the literature.

in Scheme 1) as the initial active precursor is used, polymerization begins immediately after the introduction of ethene monomer [1,3,20]. However, when a Cr(VI)O$_x$/SiO$_2$ catalyst with surface-stabilized Cr(VI) (including monochromate, dichromate and/or polychromate) as the initial active precursor is used, an induction period (also called "dormant period" without measurable activity through a mass flow meter) is usually observed after the introduction of ethene monomer at usual operating temperature (lower than 150 °C) [3]. The most critical problem is that the conventional spectroscopic investigations of the early stage of ethene polymerization (mostly by IR method) were performed exclusively on Cr(II)O$_x$/SiO$_2$ catalysts, mostly CO-pre-reduced [6–17]. Measurements based on this catalyst system were somewhat limited by the short lifetime of the initial species, rapid encapsulation of the catalytic species by polymer layer and low temporal resolution of traditional IR instruments. This leads to various discrepancies in those traditionally proposed initiation mechanisms shown in Scheme 1 [2,3,6–17]. For example, arguments concerning the existence or absence of a Cr-alkylidene species (also called Cr-carbene) [16,21] and contradictory IR band assignments of the C–H bond vibration in a possible Cr-alkylidene species [9,22] are still in dispute. Therefore, the active site

models concerned with Cr-alkylidene species (**5**, **7**, **8**, **10**, **11** shown in Scheme 1) [9–11,13,16,17] under a supposed modified Ivin–Rooney–Green chain propagation [13,21,23] are still waiting for conclusive evidence. The low IR detectability of any possible methyl end groups in the initial growing polymer chains [17,24–26] attached on the active sites also shed great doubts on those proposed active site models relating to metallacyclic species (**4**, **9**, **12** shown in Scheme 1) [10,13–15,17]. Therefore, those active site models (**2**, **3**, **6** shown in Scheme 1) [2,6,11] involving a proposed Cossee–Arlman chain propagation [27], with either Cr–C or Cr–H as active sites similar to conventional Ziegler–Natta catalysts, still hold the most popularity [3,5], although the problem related to the origin of the first hydride scrambling is sometimes still confronted (e.g. for active site model **2**) [3]. These models are mainly speculated from the chain configuration of Phillips polyethene featured with one vinyl and one methyl group on each chain end. The vinyl chain end is supposed to be derived from chain transfer through β-hydride elimination during a Cossee–Arlman chain propagation. More recently, approaches have also been performed on homogeneous models of the Phillips catalyst [28–31], planar CrO$_x$/SiO$_2$/Si(1 0 0) model system [32,33] and molecular simulation [34,35], without much success

regarding the initiation mechanism of ethene polymerization up to now.

The unique feature in this study is to adopt a non-pre-reduced Phillips catalyst and to probe its induction period prior to ethene polymerization. Any possible reactions during the induction period should proceed in a more controllable manner and have never been dealt with before. In our recent work [36,37], an industrial calcined Phillips catalyst engaged in the induction period through interaction with ethene at room temperature (RT) was found to be already partially reduced by ethene accompanied with the formation of formaldehyde as well as possible formation of short olefin chains. Proceeded with this preliminary study, an effort in this work was try to directly capture the first hydrocarbon chain, i.e. the most important fingerprint of the active sites of Phillips catalyst initially formed during the induction period. We successfully got the direct evidence that the first and second hydrocarbon species formed from ethene over the Phillips catalyst during the induction period prior to polymerization were propene and butene, respectively. This evidence strongly implicates an ethene metathesis initiation during the induction period on the Phillips catalyst for ethene polymerization.

## 2. Experimental

### 2.1. Raw materials

Nitrogen of B-grade (total impurity $<5$ ppm, in which $O_2$ $<0.5$ ppm, CO $<1$ ppm, $CO_2$ $<1$ ppm, $CH_4$ $<1$ ppm, dew point of $H_2O$ less than $-70\,°C$), nitrogen of A-grade (total impurity $<2$ ppm, in which $O_2$ $<0.3$ ppm, CO $<0.3$ ppm, $CO_2$ $<0.3$ ppm, $CH_4$ $<0.1$ ppm, $NO_x$ $<0.1$ ppm, $SO_2$ $<0.1$ ppm, dew point of $H_2O$ less than $-80\,°C$) and high purity helium gas (total impurity $<1$ ppm, in which $O_2$ $<0.05$ ppm, $N_2$ $<0.1$ ppm, CO $<0.02$ ppm, $CO_2$ $<0.02$ ppm, $CH_4$ $<0.01$ ppm, dew point of $H_2O$ less than $-80\,°C$) were purchased from Uno Sanso Co. Ethene of research grade ($C_2H_4$ $>99.9\%$, air $<0.03\%$, methane $<0.01\%$, ethane $<0.05\%$, propane $<0.01\%$, analyzed by gas chromatography method) was donated by Mitsubishi Chemical Co. Molecular sieves 4 Å and molecular sieves 13×, which were purchased from

Wako Pure Chemical Industries Ltd., were used as moisture scavenger for gas purification. Q-5 reactant catalyst (13 wt.% of copper(II) oxide on alumina), which was purchased from Aldrich, was used as oxygen scavenger for gas purification. An industrial calcined Phillips catalyst, which was used in our previous report [36–40], was prepared from impregnation of Davison 952 silica gel (BET surface area ca. $280\,m^2/g$) with aqueous solution of $CrO_3$ followed by calcination in dry air up to $800\,°C$ for 20 h. The catalyst sample was distributed and stored in small glass ampoule bottles sealed under nitrogen atmosphere. The chromium content on the catalysts was ca. 1 wt.% (i.e. $0.4\,Cr/nm^2$).

### 2.2. Treatment of the catalyst

The time-scale of the induction period for the calcined Phillips catalyst for ethene polymerization is usually depending on the operating conditions especially temperature [3]. The lower the polymerization temperature and/or the lower monomer pressure, the longer the induction period. When the polymerization temperature goes below ca. $50–60\,°C$, the induction period will become infinitely long [20]. In order to make the reaction process more controllable during the induction period, RT and atmospheric pressure of ethene gas were chosen as the reaction conditions for the interaction between the catalyst and ethene under this preliminary stage of our series studies on the induction period.

The treatment to the catalyst with ethene gas at ambient conditions for 2 h and the subsequent setting of the ethene-treated sample into a quartz micro-reactor for the TPD measurement were carried out in a glove box under the following procedure (see Fig. 1). After putting all the clean and dry experimental parts including the quartz reactor, an ampoule bottle of the catalyst sample, a glass sample bottle, etc. into the glove box, the glove box was purged under nitrogen (B-grade) flow overnight. Then the B-grade nitrogen was switched to A-grade nitrogen for six times of purging and vacuum cycle. The latter was passed through two glass columns filled with Q-5 reactant catalyst and molecular sieves 13×, respectively, for further refinement before entering the glove box. After breaking the ampoule bottle of the catalyst sample (with ca. 200 mg of catalyst), the catalyst sample was
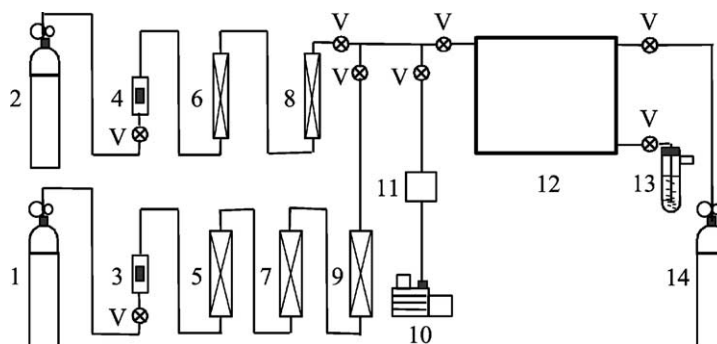
Fig. 1. Schematic diagram of the experimental system for ethene-treatment of Phillips $CrO_x/SiO_2$ catalyst: 1, ethene gas cylinder; 2, $N_2$ gas cylinder (A-grade); 3 and 4, gas flow meter; 5, 4 Å molecular sieves column; 6 and 7, Q-5 catalyst column; 8 and 9, 13× molecular sieves column; 10, vacuum pump; 11, liquid $N_2$ trap; 12, glove box; 13, paraffin liquid seal; 14, $N_2$ gas cylinder (B-grade); V, valve.

introduced into the glass sample bottle. Then, ethene gas was introduced into the glove box with three times of purging and vacuum cycle. The ethene gas was passed through three stainless steel columns filled with molecular sieves 4 Å, Q-5 reactant catalyst and molecular sieves 13×, respectively, for further purification before entering the glove box. In order to prevent possible destruction of active surface chromium species and possible loss of newly-formed surface hydrocarbon species during a milling-promoted mixing as implemented in our previous work [36], carefully and continuously shaking of the glass sample bottle with the catalyst sample was applied to promote the mixing and interaction between the catalyst and ethene gas during the treatment. After 2 h treatment, the ethene gas was pumped out and nitrogen of A-grade was introduced into the glove box again with six times of purging and vacuum cycle. Finally, about 100 mg of ethene-treated catalyst sample was set into the TPD quartz micro-reactor with two closed vacuum valves. The sample was dispersed homogeneously in-between two pieces of fine quartz wool at the bottom part of the micro-reactor.

### 2.3. TPD-MS characterization

The temperature-programmed desorption (TPD)-mass spectrometer (MS) characterization of the ethene-treated catalyst sample was carried out on a multi-task TPD instrument produced by Bel Japan, Inc. equipped with a quadrupole MS. The experimental arrangements is described as following: open type of atmosphere under dynamic vacuum, fixed bed type of reactor with helium gas flowing through the sample and partial pressure monitoring of the whole desorption process by mass spectrometry. In a typical measuring procedure, at first the TPD vacuum system was setup with a stable vacuum at ca. 20–30 Torr for ca. 30 min to remove the residual air and moisture after connecting the quartz micro-reactor with the TPD system. Then helium gas was introduced into the quartz micro-reactor through the sample for 1 h at RT to remove the physically adsorbed species on the catalyst surface. Subsequently, the helium gas flows through the thermal conductivity detector (TCD), MS sampling systems (vacuum ca. $2.5 \times 10^{-8}$ Torr) and finally vent to the TPD glass vacuum line. Simultaneously, the computer system multi-complexed to the MS and furnace temperature controller-programmer was setup for initializing all the controlling parameters including helium gas flow rate (50 ml/min), temperature controlling program, MS sampling time interval (15 s), bridge current (2 mA), number of mass spectroscopy channels in use and corresponding mass to charge ratio numbers (restricted below 100 for this mass spectroscopic instrument), etc. In this work, the temperature was ramped at a linear rate of 2 °C/min from RT to 500 °C. The gaseous components of ethene ($m/e = 28$), formaldehyde ($m/e = 30$), propene ($m/e = 42$), butene ($m/e = 56$), pentene ($m/e = 70$), hexene ($m/e = 84$) and heptene ($m/e = 98$) were continuously monitored using the MS. The original catalyst sample was also characterized as a background.

## 3. Results and discussions

According to the TPD-MS characterization of the calcined Phillips catalyst before and after the treatment within ethene atmosphere for 2 h under ambient conditions, the evolution of three new species, i.e. propene ($m/e = 42$), butene ($m/e = 56$) and formaldehyde ($m/e = 30$) besides ethene ($m/e = 28$) was confirmed without detection of any other higher olefins. The TPD-MS desorption spectrum of monomer ethene from the ethene-treated catalyst is shown in Fig. 1 reflecting a very broad distribution states of surface chromium species during the induction period. Similar phenomenon also can be seen from the TPD-MS desorption spectra of those newly formed species namely propene, butene and formaldehyde from the ethene-treated catalyst as shown in Fig. 2. The relative ratios of the integration area of the four evolution curves shown in Figs. 2 and 3 for ethene ($m/e = 28$), propene ($m/e = 42$), butene ($m/e = 56$) and formaldehyde ($m/e = 30$) were calculated to be 66, 25, 3 and 6%, respectively. In order to get more precise relative ratios of all the desorbed species from the ethene-treated catalyst sample, the fragmentation phenomenon of olefins during a typical quadrupole mass spectroscopic measurement should be taken into consideration [41]. The mass spectra of fragments of ethene, propene and butene during a typical quadrupole mass spectroscopic measurement were shown in Table 1 [41]. The formation of propene fragment ($m/e = 42$) from butene can be completely ruled out. Whereas, a very
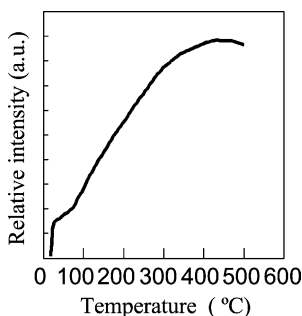


Fig. 2. TPD-MS evolution curve of ethene ($m/e = 28$) from the Phillips catalyst treated in ethene at ambient conditions for 2 h. TPD conditions: temperature elevation rate 2 °C/min, RT ∼500 °C, helium gas flow rate 50 ml/min.
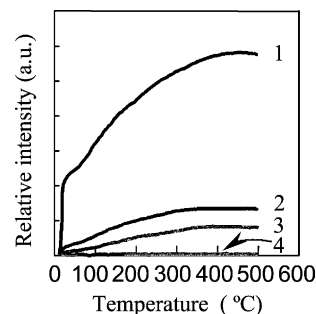


Fig. 3. TPD-MS evolution curves of three new species including formaldehyde and two new short olefins from the Phillips catalyst treated in ethene at ambient conditions for 2 h. Curve 1: propene ($m/e = 42$); curve 2: formaldehyde ($m/e = 30$); curve 3: butene ($m/e = 56$); curve 4: pentene ($m/e = 70$). TPD conditions: temperature elevation rate 2 °C/min, RT ∼500 °C, helium gas flow rate 50 ml/min.

small amount of ethene fragment ($m/e = 28$) generated from butene should be reduced from the whole evolved ethene species. Therefore, the relative ratios of the four evolved species namely ethene, propene, butene and formaldehyde from the ethene-treated catalyst sample were calculated to be 56, 32, 7 and 5%, respectively, supposing that the mass spectrum of the fragment with the strongest relative intensity for each olefin is proportional to its whole concentration desorbed from the surface of the ethene-treated catalyst sample. Moreover, the possible loss of newly formed species including propene, butene and formaldehyde from the catalyst surface during the ethene-treatment

Table 1
The mass spectra of fragments of ethene, propene and butene during a typical quadrupole mass spectroscopic measurement

| Olefin | Typical mass spectra of fragments | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Ethene** | | | | | | | | | | |
| $m/e$[a] | 28 | 27 | 26 | 25 | 14 | 1 | 24 | 13 | 29 | 12 |
| R.I.[b] | 1000 | 648 | 623 | 117 | 63 | 41 | 37 | 35 | 22 | 21 |
| **Propene** | | | | | | | | | | |
| $m/e$[a] | 41 | 39 | 42 | 27 | 40 | 38 | 37 | 26 | 15 | 1 |
| R.I.[b] | 1000 | 711 | 677 | 383 | 289 | 193 | 136 | 105 | 54 | 37 |
| **Butene** | | | | | | | | | | |
| $m/e$[a] | 41 | 56 | 39 | 27 | 28 | 55 | 29 | 26 | 40 | 53 |
| R.I.[b] | 1000 | 370 | 345 | 300 | 295 | 176 | 131 | 101 | 64 | 52 |

[a] $m/e$ indicates the mass to charge ratio of each fragment.
[b] R.I. indicates the relative intensity of the mass spectrum of each fragment.

can be approximately eliminated due to the mild conditions implemented in this experiment. According to the literature [42,43] and our previous report [36,37], ethene firstly reduces the hexavalent chromate species into divalent chromium species accompanied with the formation of a by-product formaldehyde. Subsequently, the divalent chromium species coordinatively-adsorbed with formaldehyde molecules, which cannot be desorbed under the mild conditions, might act as the active precursor to produce the two new short olefins. Judging from the relative ratios of ethene (56%), propene (32%) and butene (7%) in the desorbed gases from the ethene-treated catalyst sample, it can be concluded that the first hydrocarbon species formed on the Phillips catalyst during the induction period is propene instead of the expected dimer of ethene:butene. Butene is in fact the second hydrocarbon species formed after propene. This new experimental evidence obtained from the induction period of ethene polymerization cannot be rationalized by the Cossee–Arlman mechanism, which is still the most generally accepted mechanisms for Phillips catalyst up to now. According to McDaniel [3] and Weckhuysen and Schoonheydt [5], the first hydrocarbon species is the most important fingerprint of the Phillips catalyst and can be utilized as a crucial criterion for an indispensable reconsideration of those traditional initiation mechanisms proposed in the literature shown in Scheme 1.

The conversion of ethene into higher olefins with both odd and even numbers of carbon atoms is a well-established phenomenon which is believed to proceed by ethene metathesis [44–48]. This indicates that coordination of formaldehyde on surface-stabilized divalent chromium species most probably results in the formation of a new kind of active precursor for olefin metathesis, rather than polymerization active precursor. The active sites in heterogeneous transition metal catalyzed olefin metathesis are generally thought to be a transition metal alkylidene species like their well-defined homogeneous analogues [49–52]. The specific formation mechanism of the transition metal alkylidene sites on the heterogeneous counterparts is still open to discussion [49–52]. Nevertheless, this new evidence can be used for a novel mechanistic speculation on the initiation process taking into account of various traditional mechanisms both for ethene

polymerization on Phillips catalysts [2,3,6–17] and for ethene metathesis over various transition metal catalysts [44–52]. Based on the experimental evidence that propene is the first hydrocarbon species formed during the induction period, an ethene metathesis initiation mechanism on the $Cr(VI)O_x/SiO_2$ catalyst is proposed in Scheme 2, including three most plausible mechanistic routes ((I), (II) and (III)) of the formation of Cr-alkylidene species and the first hydrocarbon species propene. As a common initial reaction stage for routes (I), (II) and (III), surface chromate species **13** is reduced by ethene resulting in the formation of **14**, which is surface-stabilized divalent chromium species **1** coordinatively-adsorbed with formaldehyde molecule due to the high coordination unsaturation of **1** as well as the mild conditions [36,37,42,43]. The surface-stabilized divalent chromium species **1** is believed to be the final active precursor of Phillips catalyst for ethene polymerization by most researchers [3,5,6–17]. This indicates that coordination of formaldehyde on the surface-stabilized Cr(II) species **1** may result in **14**, which demonstrates as an ethene metathesis precursor rather than polymerization active precursor. In route (I) as shown in Scheme 2, the first coordination of ethene on **14** with a subsequent 1,2-hydrogen shift leads to a Cr(IV)-ethylidene **15** [11,16]. Further reaction of the Cr(IV)-ethylidene **15** with ethene gives rise to a Cr(IV)-methylidene **19** and the first hydrocarbon species propene through a metallacyclobutane intermediate **17** [53–55]. Route (II) shows the formation of the Cr(IV)-methylidene **19** through direct splitting of the double bond of ethene over two neighboring **14** [17], and propene is made through the reductive decomposition of a metallacyclobutane intermediate **21** [47]. The simultaneous formation of Cr(IV)-methylidene **19** and Cr(IV)-ethylidene **15** is depicted in route (III) showing that the π-allyl Cr(II)-hydride species **25**, formed through the metallacyclopentane intermediate **24**, is converted into metallacyclobutane species **17** [11]. The metallacyclobutane species **17** is subsequently subject to metathesis generating either Cr(IV)-methylidene **19** and the first hydrocarbon species propene or Cr(IV)-ethylidene **15** and a new ethene monomer [52]. The subsequent metathesis of the first hydrocarbon species propene on Cr(IV)-ethylidene **15** and/or Cr(IV)-methylidene **19** in either route will lead to the formation of the

Scheme 2. Three most plausible mechanistic routes (I), (II) and (III) of the ethene metathesis initiation and formation of the first hydrocarbon species propene during the induction period over the calcined Phillips Cr(VI)O$_x$/SiO$_2$ catalyst through interaction with ethene at ambient conditions.

second hydrocarbon species butene through mechanisms similar to Scheme 2 during the induction period [44,47,53–55]. So far, it can be speculated that the initiation mechanisms through **4**, **6**, **10** and **11** in Scheme 1 are most plausible ones, whereas those mechanisms through **2**, **3**, **5**, **7–9** and **12**, which cannot rationalize well the formation of propene as the first hydrocarbon species, own much less possibility.

Another important implication from the new evidence obtained in this work is that a transformation of ethene metathesis active sites into ethene polymerization active sites should proceed when the formaldehyde is desorbed from the Cr-alkylidene species at higher temperature. This speculation is supported by the reports of Schrock and coworkers [56,57] and Scott and coworkers [58–62]. The former reported that a homogeneous Ta-alkylidene catalyst could be active for ethene polymerization [56,57]. While the latter recently have shown a SiO$_2$-supported Cr-alkylidene catalyst to be highly active for ethene polymerization producing high density polyethene (HDPE) with chain configuration and properties similar to the HDPE produced by Phillips catalyst [58–62]. Another support for our mechanistic consideration comes from previous reports of the inter-conversion between olefin metathesis and olefin polymerization using various

transition metal catalysts [49–52,63,64], which still remains a mystery worth further exploring. Further investigation of the induction period of Phillips catalyst under various reaction conditions is still in progress in order to completely elucidate which route within routes (I), (II) and (III) in Scheme 2 is really in function during the induction period. More recently, specific evidence regarding the dynamic inter-conversion between those Cr-metallacyclic and Cr-alkylidene intermediates during the induction period had been obtained, and the transformation of ethene metathesis into ethene polymerization from the induction period to normal polymerization period at elevated temperature on the calcined Phillips catalyst had also been successfully observed. These new results will be reported in a forthcoming publication soon.

## 4. Conclusions

In this work, we adopted an industrial calcined Phillips catalyst and probed its induction period prior to ethene polymerization by TPD method. The evidence demonstrated that the first hydrocarbon species had already been formed during the induction period and was found to be propene instead of the expected

dimer of ethene:butene. Butene is actually the second hydrocarbon species formed after propene during the induction period. The simultaneous formation of propene and butene from ethene indicates that the initiation with respect to Cr–carbon bond formation occurs presumably through an ethene metathesis mechanism during the induction period. Three most plausible mechanistic routes regarding the ethene metathesis initiation and the subsequent formation of the first hydrocarbon species propene during the induction period on the Phillips catalyst were proposed. The active sites involved in the induction period are supposed to be formaldehyde-coordinated Cr(IV)-alkylidene species. A conversion of ethene metathesis into ethene polymerization from the induction period to normal polymerization period can be expected after the desorption of the formaldehyde, a by-product of the redox reaction between the hexavalent chromate species and ethene, from the Phillips catalyst at higher temperature.

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