

PYROLYSIS OF PROPYLENE OVER CARBON ACTIVE SITES II. PYROLYSIS PRODUCTS

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(Received 7 July 1987; accepted 20 December 1987)

Abstract—The pyrolysis of propylene over Graphon, a graphitized carbon black, was studied in the temperature range 873 to 1073 K at a starting pressure of 1.6 Pa. Using this substrate, the effect of the carbon active surface area (ASA) on the type, distribution, and mode of formation of the reaction products was investigated. On a "clean" surface, propylene instantly chemisorbed on some active sites at the beginning of each pyrolysis run and ultimately formed a more unsaturated hydrocarbon complex on the surface. Regardless of the cleanliness of the surface, a carbon deposit was formed on the surface. In the range 873 to 973 K, the major gas phase products consisted of methane, ethylene, and H₂. At pyrolysis temperatures above 973 K, some trace gas phase products appeared. All the major pyrolysis products originate from reactions occurring on the ASA measured by propylene chemisorption at 573 K or on ASA very closely related to it. Neither the amount of hydrocarbon complex nor its H/C ratio was closely related to the ASA. The presence of ASA favors surface carbon over production of gas phase carbon products. A model is proposed to explain the origin of all the pyrolysis products.

Key Words—Pyrolysis, propylene, active sites, graphon.

1. INTRODUCTION

The pyrolysis of hydrocarbons has been studied since Dalton and Henry[1-2], subjected methane and ethylene to a continuous electric spark decomposing them to their elements almost two centuries ago. The first pyrolysis of propylene was by Berthelot[3]. It was not until 1930, however, that a systematic study of propylene pyrolysis was begun by Hurd and Meiner[4]. Most pertinent work from 1930 until the present[5-17] is summarized elsewhere[18].

In the pyrolysis of hydrocarbons, the products vary in kind and amount depending on the temperature, contact time, pressure, reactor geometry, type of reactor wall, and initial concentration. Studies of the pyrolysis of propylene in the temperature range 773 to 1073 K[5-8,19] have established that it is a complex reaction with an overall order close to 1.0 and an activation energy of about 57 kcal/mole. Beyond these simple facts, there is little agreement, in particular, over the identity, distribution, and mode of formation of the reaction products. Each investigator has his or her own pyrolysis mechanism to account for individual experimental results.

The thrust of this study was not to elucidate the mechanism of homogeneous propylene pyrolysis but to investigate the effect that the active surface area (ASA) on a carbon substrate has on each aspect of the pyrolysis reaction. The ASA is composed of active sites that exist on the carbon surface where the valency is not satisfied. On a "clean" carbon surface, these sites would be located on the edges of the basal

planes as well as at points of imperfections in the structure including vacancies, dislocations, and steps on the outer basal plane.

A previous publication in this series[19] dealt with the effect that the carbon active sites have on the kinetics of propylene pyrolysis and carbon deposition. This article describes the effect that the carbon active sites have on the amount and type of elemental carbon formed as well as on the identity, distribution, and mode of formation of the other reaction products. The following article in this series[20] will elucidate the location and reactivity of the elemental carbon formed.

It was of particular interest in this study to ascertain the effect that carbon active sites have on carbon deposition on a substrate during a pyrolysis reaction. This is in contrast to most of the propylene pyrolysis work previously cited where elemental carbon was found but not studied. Depending on experimental conditions that include temperature, pressure, contact time, substrate, and the geometry of the reactor, this carbon can either be formed in the gas phase, on the surface of the reactor, or on the substrate present. The structure and properties of a carbon deposit are related to the pyrolysis conditions because these conditions control the mechanism of carbon formation.

At the conditions used in this study, 873 to 1073 K and a starting pressure of 1.6 Pa, the rate of gas phase (homogeneous) cracking of propylene is very slow. Essentially, all the carbon was formed by heterogeneous reactions at the surface. Some deposited on the carbon ASA and replicated it[20], while other carbon was found to deposit on metallic impurities on the surface until they were rendered less

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active by carbon deposition[19,21]. In addition to carbon deposition, the pyrolysis products included a surface hydrocarbon complex and gas phase products (predominately H₂, methane, and ethylene). In addition to these products, propylene was chemisorbed on active sites at the beginning of the pyrolysis if the surface was "clean."

2. EXPERIMENTAL

2.1 Materials

The carbon substrate used in this study was Graphon, a granular graphitized carbon black, obtained from the Cabot Corporation. Total impurity content was estimated by emission spectroscopy to be 80 ppm, with the major impurities being iron and calcium. Graphon was chosen as a substrate because it is possible, with oxidation, to greatly increase its ASA without an appreciable increase in the total surface area (TSA) of the sample[22]. Thus, the effect of the ASA on the pyrolysis reaction can be studied. Graphon samples were preoxidized from 1 to 24% weight loss in air at 723 K. The BET (N₂) surface area of the prepared samples ranged between 80 and 124 m²/g, while the oxygen ASA, as determined by Laine *et al.*[22], ranged between 0.8 and 5.0 m²/g.

After preoxidation, the sample was treated in 0.1 MPa Cl₂ at 1173 K to remove surface metallic impurities exposed during the oxidation. Upon cooling, the sample was placed in the volumetric adsorption system and heated to 1223 K in vacuo to desorb any chemisorbed chlorine. When a residual pressure of 10⁻⁶ Pa was reached, the temperature was lowered to 1073 K and 6.7 Pa H₂ was introduced to remove any chlorine that remained. The sample was kept in this H₂ atmosphere for 1 h. After this time, gaseous H₂ was pumped out and the temperature was again raised to 1223 K to desorb any chemisorbed hydrogen. When the residual pressure reached 10⁻⁶ Pa (usually overnight), the sample preparation was complete. Surfaces of samples that underwent this preparation were considered "clean," implying an insignificant amount of surface impurities and chemisorbed species.

The gases used in this study were obtained from Air Products and Chemical Inc. The O₂ and H₂ were of research grade with a minimum purity of 99.996%. All the hydrocarbons used had a minimum purity of 99.8%

2.2 Apparatus and procedure

Pyrolysis and adsorption were studied in a volumetric apparatus with a total volume of 17.9 L. The Pyrex high vacuum system was interfaced to a mass spectrometer and to a fused quartz reactor that held the sample. The reactor was of double-wall design with the annular volume evacuated to prevent diffusion of atmosphere gases into the reactor tube at high temperature. The sample was heated by a Linberg resistance furnace, with the temperature being controlled with a West controller and chromel-alu-

mel thermocouple. A CEC model 21-614 residual gas analyzer was used to determine the purity of each gas and to monitor the concentration of gases during adsorption, desorption, and pyrolysis.

Vacuum to 10⁻⁴ Pa was obtained using a liquid N₂-trapped silicon oil diffusion pump in conjunction with a rotary floor pump. Higher vacuum (to 10⁻⁶ Pa) was obtained using a Varian Vacion pump. Adsorption, desorption, and pyrolysis were followed using a MKS Baratron differential capacitance manometer with a sensitivity of 10⁻³ Pa. Pressures less than 10⁻³ Pa were estimated from the discharge current of the Vacion pump.

Before a Graphon sample was used for pyrolysis, the O₂ ASA was determined by the method of oxygen chemisorption first used by Laine *et al.*[22]. Using this technique, a pretreated Graphon sample that had been cleaned in vacuo (10⁻⁶ Pa) at 1223 K was exposed to O₂ at 573 K for 24 h at a starting pressure of 67 Pa. At the end of this time, the sample was evacuated to a pressure of 10⁻⁶ Pa with the temperature held at 573 K. Pumping was then terminated and the sample was raised to 1223 K at 20 K/min and held at that temperature for 15 min. The concentration of CO and CO₂ that desorbed was measured with the mass spectrometer. Knowing the number of moles of each gas desorbed, assuming that one oxygen atom occupies one carbon site, and taking the area of an edge carbon site that chemisorbed an oxygen atom as 0.083 nm², the surface area occupied by oxygen ASA could be determined[22].

To start a pyrolysis run, propylene was introduced to the previously evacuated system at a pressure of about 1.6 Pa. The reactor and mass spectrometer had also been evacuated but were shut off from the rest of the system at that time. With the gas introduced into the system, the mass spectrometer valve was opened and the purity of the gas was ascertained. With the mass spectrometer still open to the system, the gas was allowed to expand into the reactor to start the pyrolysis. The reactor held a 0.25-g Graphon sample previously cleaned in vacuo (10⁻⁶ Pa) at 1223 K and kept between 873 and 1073 K. After equilibrium was established (2 min), a mass spectrometric scan of m/e from 2 to 50 Amu was performed. The valve to the mass spectrometer was then closed and opened periodically throughout the experiment to sample the gas phase species. The pressure of the system was recorded, as was the time before each sampling. The total system pressure drop during sampling was also recorded. The material balance, calculated from the mass spectrometric scan after correcting for pumping loss, gave the amount of carbon and hydrogen on the surface as a function of time.

3. RESULTS AND DISCUSSION

3.1 Pyrolysis products

Carbon deposition on a carbon substrate appears to be very similar to the oxidation of the substrate

although the end result is the opposite. When propylene is introduced into a system containing a carbon substrate at 873 to 1973 K, it chemisorbs on some sites and cracks on other sites in addition to forming a stable hydrocarbon complex on the surface[19]. The pyrolysis products of propylene over a 5.8% burnoff (B.O.) Graphon sample at 923 K and a starting pressure of 1.6 Pa are shown in Fig. 1 as a function of pyrolysis time. The gas phase products consisted of methane, ethylene, and H_2 . At pyrolysis temperatures above 973 K, allene and acetylene were also observed in the gas phase in small quantities. When propylene was pyrolyzed at temperatures above 1073 K, very small quantities of propane and ethane were also observed, but only after 500 min. The origin of these products will be discussed in detail following a discussion of the surface products.

The products formed on the carbon surface consisted of deposited carbon, chemisorbed propylene, and other hydrocarbon species. The study of these surface products is not as straightforward as for those products observed in the gas phase. The quantity of carbon and hydrogen associated with these surface products is shown as unaccounted-for carbon (u-carbon) and unaccounted-for hydrogen (u-hydrogen) in Fig. 1 because these products appeared as unaccounted-for carbon and hydrogen in the gas phase material balance and were determined by difference.

As can be seen from the large initial instantaneous increase in u-carbon and u-hydrogen in Fig. 1, propylene was chemisorbed at the beginning of the pyrolysis. However, note that this occurred only on a clean sample (i.e., a sample that was outgassed at

1223 K under high vacuum). This chemisorbed propylene was not stable at reaction temperature and ultimately cracked to methane and ethylene or became part of the unsaturated hydrocarbon complex.

The instantaneous propylene chemisorption occurs very rapidly without appreciable hydrogen concurrently appearing in the gas phase[23,24]. Thus, if a carbon-hydrogen bond is broken, most of the hydrogen must also chemisorb—at least for a time. However, at reaction temperature (873–1073 K) H_2 soon appears in the gas phase as carbon is deposited and as some of the chemisorbed propylene cracks or becomes more unsaturated. The time for H_2 to appear in the gas phase decreases with increasing reaction temperature as one would expect. The amount of propylene that is instantaneously chemisorbed correlates well with the 573 K propylene ASA as well as with the rate of propylene cracking and carbon deposition[19]. This chemisorbed propylene, along with the hydrocarbon complex described below, are similar to the “stable” oxygen surface complex proposed by Laine *et al.*[22] when they oxidized Graphon. That is, there was a finite amount of a “stable” oxygen complex that formed on some active sites that did not appear to take part in the reaction. However, as Vastola *et al.*[25] later found, in time a portion of this “stable” oxygen complex decomposed producing CO and CO_2 . Similarly, in this study, a portion of the chemisorbed propylene and possibly surface complex cracks to produce methane and ethylene as discussed below.

The sites responsible for the carbon deposit perhaps are similar to the sites on which Laine *et al.*[22] postulated a fleeting reactive intermediate. The reaction on these sites is rapid and dynamic. Propylene comes to these sites, chemisorbs, and cracks in a short time to produce carbon, which itself is another active site. The rate of this reaction is first order with respect to propylene partial pressure.

This deposition of carbon on Graphon appears to produce exactly the opposite effect as during its oxidation. Graphon is a graphitized carbon black which has a very homogeneous surface because it is predominantly basal plane. During oxidation, oxygen is thought to react at the intersections of the basal planes producing what are assumed to be wedge-shaped volumes and greatly increasing the ASA[18]. Using oxygen and propylene chemisorption (Table 1), one can see that there is some sort of size restriction on an unoxidized sample by the fact that the propylene ASA increases with only 0.6% B.O. by a greater percentage than the oxygen ASA. This is because of the smaller size of the oxygen molecule that allows it to enter and chemisorb on sites from which the propylene is excluded. With deposition on the active surface of the burned-out volumes, the process is reversed but the effect on the chemisorption is similar. With deposition, the propylene ASA decrease is greater than for the oxygen ASA.

The third species on the surface is a hydrocarbon complex[19] most of which appears tightly bound to the surface. In contrast to the initial propylene che-

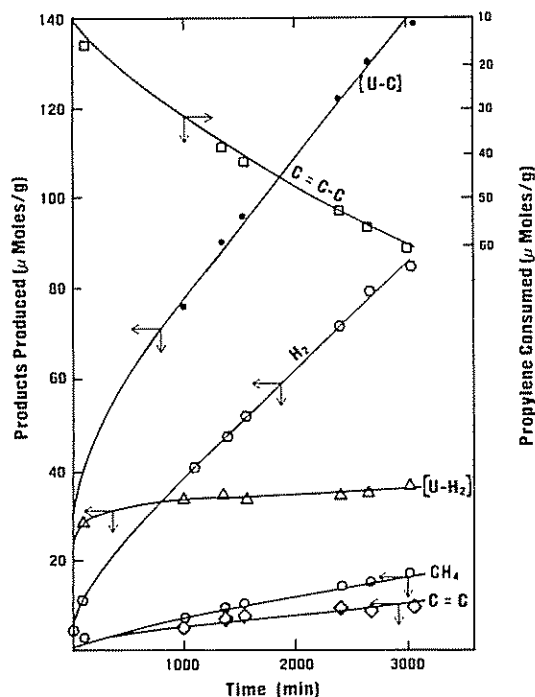


Fig. 1. Pyrolysis of propylene over a 5.8% burnoff Graphon sample at 923 K.

Table 1. Surface areas occupied by various gases at 573 K on Graphon samples of varying burnoff

Sample	Total surface burnoff, %	Nitrogen ^a TSA, m ² /g	Oxygen ^b ASA, m ² /g	Propylene ^c ASA, m ² /g
1	0	76	0.26	0.056
2	0.6 ^d	82	0.94	0.440
3	5.8 ^d	92	2.25	1.060
4	24.5 ^d	124	5.00	1.890
5	1.1 ^e	80	0.75	0.350

^aFrom physical adsorption of N₂ at 77 K.

^bStarting oxygen pressure was 67 Pa; assumed 0.083 nm² occupied by chemisorbed oxygen atom.

^cStarting propylene pressure was 1.6 Pa; assumed 0.23 nm² occupied by chemisorbed propylene molecule.

^dIncludes burnoff during preoxidation and prechlorination[23].

^eDue only to preoxidation.

misorption, the buildup of surface complex proceeds much more slowly and is not very reproducible. This nonreproducibility is one of the striking differences between the hydrocarbon complex and all the other products as will be discussed in the text that follows. From Figs. 1 and 2, one can qualitatively view the buildup of the surface complex by looking at the increase in the u-hydrogen curve (note differences in scale). However, it is impossible to accurately determine the amount of hydrocarbon complex from the u-hydrogen curve without knowing the H/C ratio in the complex. Thus, to determine the amount of surface hydrocarbon complex, one must use the amount of u-carbon associated with the complex. This quantity can be estimated from the propylene consumption in region II of the propylene consumption rate curve[19] or from the semilog plot of

the u-carbon curve. Both methods give similar values. Those from the u-carbon curve were considered more reliable because there was less spread in these values for identical samples. The values obtained from the u-carbon semilog plot were usually slightly higher than those obtained from the propylene consumption rate curve. The u-carbon curve from Fig. 1 is replotted in semilog form in Fig. 3. In this figure, the second linear region, which corresponds to region IV of the propylene consumption rate curve that was just mentioned, is due only to carbon deposition whereas the first linear region also includes complex buildup (i.e., the buildup of both carbon and hydrogen on the surface). By extrapolating the two straight lines to the ordinate, the u-carbon curve can be assigned to chemisorbed propylene, hydrocarbon complex, and deposited carbon. In Fig. 3, the chemisorbed propylene is about 37 μ moles/g and the hydrocarbon complex is about 26 μ moles/g.

To determine if the hydrocarbon complex might be on a portion of the propylene ASA, the area occupied by the chemisorbed propylene and hydrocarbon complex was compared to the 573 K propylene ASA and the TSA. In Table 2 the ratios of the total area occupied by the hydrocarbon complex and chemisorbed propylene to both the propylene

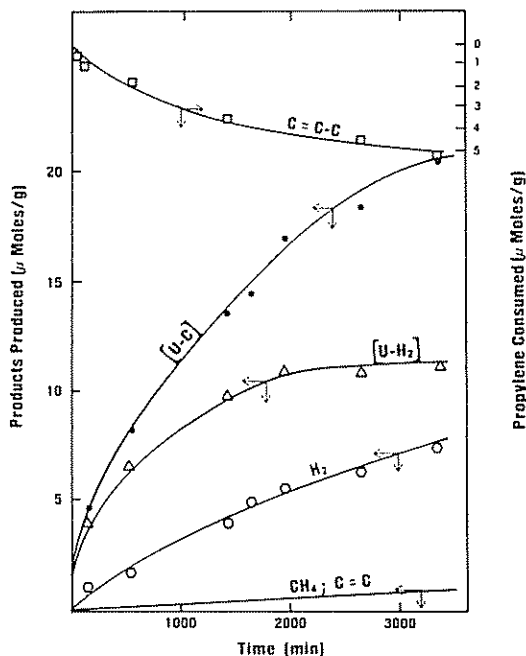


Fig. 2. Pyrolysis of propylene over a 0% burnoff Graphon sample at 923 K.

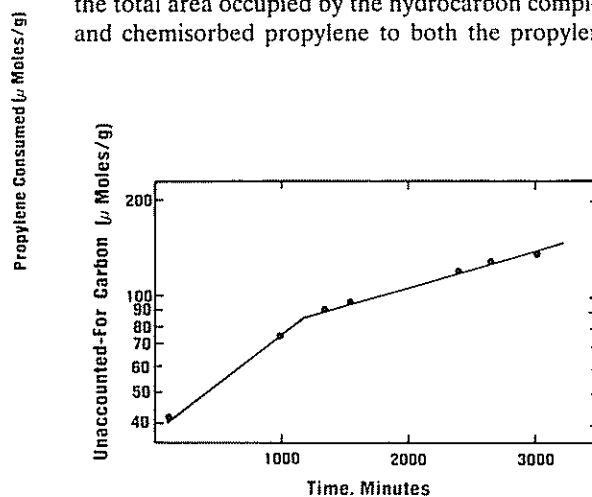


Fig. 3. Buildup of unaccounted-for carbon on a 5.8% burnoff Graphon sample at 923 K.

Table 2. Ratio of area occupied by hydrocarbon complex and chemisorbed propylene to active and total surface area at various temperatures on sample of different burnoff

Sample B.O. (%)	Occupied area ^a (m ² /g)				Occupied area ^b (m ² /g)		
	573 propylene ASA (m ² /g)				Total BET area (m ² /g)		
	923 K	1023 K	1023 K	1073 K	923 K	1023 K	1073 K
0	11.61	33.92	24.51 ^c	126.00	0.003	0.008	0.029
0.6	3.55	12.57	7.45 ^c	16.55	0.006	0.021	0.028
5.8	3.30	9.99	6.44 ^c	—	0.011	0.025	—
24.5	2.73	10.75	9.31 ^c	—	0.007	0.051	—

^aUsed amount of carbon chemisorbed and in complex, assumed monolayer coverage, and took the area of one carbon atom as 0.083 nm².

^bUsed amount of carbon chemisorbed and in complex, assumed monolayer coverage, and took the area of one carbon atom as 0.026 nm².

^cCalculated using break in propylene semilog plot[19] rather than break in carbon deposition plot (Fig. 3).

ASA and the TSA are shown as a function of temperature and B.O. The area occupied by both of these species was calculated by knowing the number of moles of carbon associated with them (63 μ moles/g in Fig. 3) and assuming an area occupied by the carbon atom. For comparison with the 573 K propylene ASA an area of 0.083 nm² was assumed because this is the area occupied by a carbon active site. For comparison with the TSA an area of 0.026 nm² was used because this is the area occupied by a carbon atom in the basal plane. The hydrocarbon complex and chemisorbed propylene are grouped together because once the propylene goes to the surface it is impossible to determine exactly where it is on the surface and how much still closely resembles propylene. In addition, they are grouped together to clearly show that there is too much carbon on the surface associated with the chemisorbed propylene and hydrocarbon complex to all be closely associated with the 573 K propylene ASA if monolayer coverage is assumed.

As can be seen from the surface hydrogen curve in Figure 1, the instantaneous propylene chemisorption proceeds much more rapidly than the buildup of the hydrocarbon complex which takes more than 500 min. A comparison of the buildup in Fig. 1 for the oxidized sample (5.8% B.O.) with that on an unoxidized sample (Fig. 2) shows that the buildup is even slower on the unoxidized sample at the same temperature. The dependence of the rate of buildup of the hydrocarbon complex on the ASA is thought to be due to the propylene, that forms the complex initially, chemisorbing on an active site before it spills over to the basal plane. It is thought that a spillover occurs for several reasons. (1) In Table 2 the amount of complex is not closely related to the ASA and usually greatly exceeds it. (2) It takes longer for the complex to build up on a sample with less ASA (cf. Fig. 1 with Fig. 2). Hence, the complex-forming species are funneled through the active sites to the basal plane. If the complex stayed on the ASA it would take the same or less time to buildup a complex on a sample with less ASA and one could normalize the amount of complex with the ASA, which is not the

case. (3) The amount of complex formed, unlike the other products, is not reproducible. This is probably due to the complex ultimately ending up on imperfections in the basal plane. A surface migration of this type is not unreasonable to assume since Yang and Wong[26] observed that oxygen would adsorb on the basal plane (possibly on imperfections) and then migrate to the active sites located on the edges of the basal planes where it reacted.

From Table 2, it is apparent that the amount of carbon associated with the surface complex and chemisorbed propylene increased with pyrolysis temperature. However, because the rates of carbon deposition and formation of gas phase products also

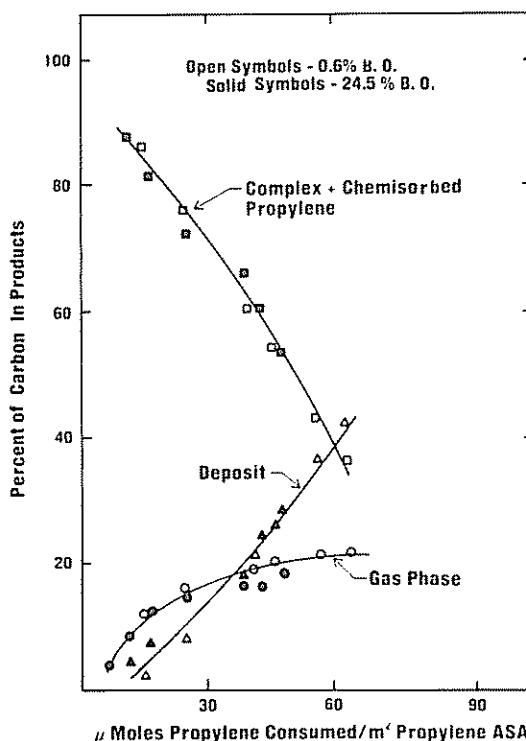


Fig. 4. Distribution of carbon in the products from propylene pyrolysis at 923 K over Graphon samples of different burnoff.

increase with temperature, but by different amounts, the distribution of cracked propylene among the various products will change with temperature. In Figs. 4 and 5, one can see how the propylene that has cracked distributes itself among the products as a function of the amount of propylene consumed at two different temperatures. For all burned-off samples, the percentage of propylene going to gas phase products increases with propylene consumption and levels off at about 20% in the temperature range studied. In each case, because of the instantaneous propylene chemisorption, the percentage of pyrolyzed propylene on the surface as chemisorbed propylene and complex is initially high. At 923 K, the initial percentage is almost 100%. This initial percentage drops to about 75% at 1023 K. The percentage of carbon on the surface as complex and chemisorbed propylene decreases as propylene is cracked and the deposit is built up. This decrease in the complex plus chemisorbed propylene curve with propylene consumption occurs more rapidly at 923 K than at 1023 K.

The H/C atomic ratio for the surface hydrocarbon species, which includes both the initially chemisorbed propylene as well as the surface complex, is not closely related to either the TSA or the ASA (Table 3). The value for the *H* in this ratio comes directly from the *u*-hydrogen curve such as in Figs. 1 and 2. The value for the *C* in this ratio is determined from the semilog plot of the *u*-carbon (Fig.

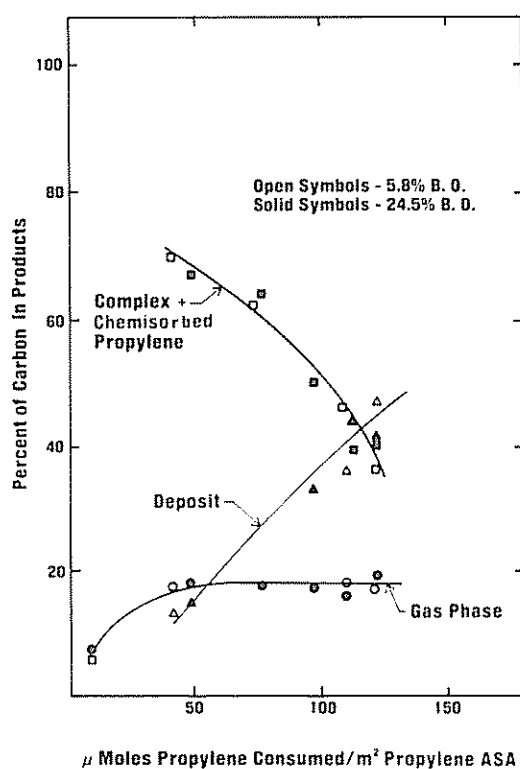


Fig. 5. Distribution of carbon in the products during propylene pyrolysis at 1023 K over Graphon samples of different burnoff.

3). Obviously, the H/C ratio changes as the complex is built up and becomes more unsaturated. However, after the complex is built up, the value is relatively invariant since the *u*-hydrogen curve is usually relatively flat and the *u*-carbon associated with the complex and chemisorbed propylene is assumed constant after the intersection of the curves in Fig. 3. Although there is no surface dependence, the ratio does exhibit a temperature dependence. For all the samples studied, the equilibrium value for H/C at 873 K was approximately 1.62 whereas at 1023 K the ratio had decreased to ≈ 0.65 .

Having discussed the surface products in some detail, let us now turn our attention to the gas phase products. Only the three major gas phase products along with the gas phase carbon will be discussed. The H_2 in the gas phase can come from many sources including carbon deposition directly from propylene, dehydrogenation of the surface complex, and cracking of the hydrocarbon products. No effort was taken to determine what percentage of H_2 came from each source. In addition, note that a portion of the gas phase H_2 is lost as propylene cracks to form methane and ethylene and as ethane and propane are formed at higher temperature.

The origin of methane and ethylene is of more interest than the origin of the H_2 . Looking at Fig. 1, there is an initial more rapid production rate of both methane and ethylene which decreases after about 950 min to a constant value. The shape of these curves would seem to indicate that there are at least two sources of methane and ethylene production.

The imperfections in the basal plane, mentioned above in connection with the spillover of the hydrocarbon complex, may be the sites responsible for the enhanced cracking of propylene to methane and ethylene in the early part of the run. That is, these sites are able to crack propylene to methane and ethylene before they are covered with hydrocarbon complex. This would explain the initial buildup of methane before the linear region. There is some evidence that substantiates this hypothesis. (1) The rate of production of methane and ethylene is continually decreasing and the transition to the constant rate region occurs about at the same time as the intersection of the two curves in Fig. 3 (i.e., at the completion of the coverage by the hydrocarbon complex.) (2) There is no initial more rapid production when the surface has been previously covered with complex or on a 0% sample where imperfections have not been enlarged by oxidation and are therefore not available to propylene. (3) This enhanced production cannot be normalized by the ASA.

The constant rate of methane and ethylene production after the initial buildup implies that the process is zero order in propylene. Thus, methane and ethylene may originate from chemisorbed species on the active sites. That is, propylene chemisorbs, cracks to methane and ethylene which desorb, and then the site chemisorbs another propylene species. This ex-

Table 3. H/C ratio for the hydrocarbon complex and chemisorbed propylene

Sample no.	Temperature (K)	% Burnoff	573 K Propylene ASA (m ² /g)	H/C ratio
18	873	24.5	1.89	1.62
3	923	0.6	0.44	1.42
8	923	5.8	1.06	1.36
12	923	24.5	1.89	1.40
21	923	0.0	0.06	1.74
5	973	0.6	0.44	1.18
9	973	5.8	1.06	1.23
14	973	24.5	1.89	1.10
19	973	0.0	0.06	1.50
6	1023	0.6	0.44	0.62
10	1023	5.8	1.06	0.69
15	1023	24.5	1.89	0.69
20	1023	0.0	0.06	0.62
13	1023	24.5	1.89	0.75
7	1073	0.6	0.44	0.28
22	1073	0.0	0.06	0.58

planation is considered valid because C¹³ studies[20] show that the propylene species that produce methane and ethylene are relatively stable, but do not stay on the surface long enough for isotopic exchange to occur. In addition, the amount of methane and ethylene generated in the linear region not only exceeds that which could be produced from the amount of propylene initially chemisorbed but can be normalized with the 573 K propylene ASA as shown below. Thus, the rate is linear and zero order in propylene because the rate-determining step for the production of methane and ethylene is not adsorption but cracking of the chemisorbed species, surface rearrangement, or desorption.

There was no evidence for the formation of gas phase carbon during the pyrolysis within the experimental conditions used in this study. The amount of u-carbon produced during propylene pyrolysis over a Graphon substrate was surface area dependent and could be normalized with the 573 K propylene ASA after complex buildup was complete. In addition, blank runs below 973 K showed no u-carbon. Above 973 K, the rate of u-carbon production during the blank runs (normalized to the quartz reactor surface area) was about 1% that over a Graphon sample normalized to the propylene ASA. This percentage did not vary with temperature up to 1073 K. Since it is known that a silica surface is active for carbon deposition, it is reasonable to assume that the majority—is not all—of the u-carbon in the blank runs cracked directly on the quartz reactor wall. At any rate, if there was gas phase formation of carbon during propylene pyrolysis over a Graphon sample, it amounted to much less than 1% of the total u-carbon. Thus, the pyrolytic carbon that deposited on the carbon black substrate was formed through direct decomposition of hydrocarbons on the surface after they chemisorbed[9,20]. According to Tes-

ner[27], deposition by direct condensation is energetically favored and is the dominant process during pyrolysis, provided that enough surface area is available to prevent the supersaturation in the gas phase from reaching a level necessary to homogeneously nucleate a gas-born particle. By keeping the initial propylene pressure below 2 Pa, it was possible to prevent carbon formation in the gas phase as well as secondary reactions of the product gases apart from some cracking at higher temperatures.

3.2 Origin of the pyrolysis products

One of the goals of this study was to ascertain the origin of the products resulting from pyrolysis of propylene over carbon active sites. With this in mind, the production of four major pyrolysis products (methane, ethylene, H₂, and u-carbon) as a function of time was normalized to various surface areas. Each of the Figs. 6–11 shows the formation for the individual product at 923 K on four samples of varying burnoff. The information pertaining to the burnoff of the samples and their surface areas is given in Table 1.

A large spread in the curves for the various surfaces resulted (Fig. 6) when the production on each surface was normalized to the total (BET) surface area. (Since the phenomena for the other products is almost identical, only the figure for methane is presented.) This spread was reduced by normalizing the production on each surface to the initial oxygen ASA (Fig. 7). When the production from each surface was normalized to the initial propylene ASA (Figs. 8–11), all the burned-off samples fell on one curve indicating that in each case the product originated from the propylene ASA or an active surface area closely related to it. It must be reiterated here that it is the initial propylene ASA rather than the instantaneous ASA value (which is changing with

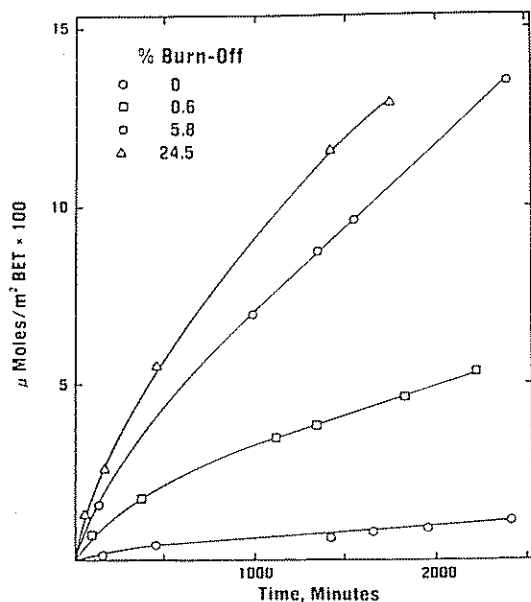


Fig. 6. Methane production from propylene pyrolysis at 923 K normalized to the BET surface area of Graphon.

deposition) that determines the rate of propylene consumption[19] and the rate of production of pyrolysis products. The 0% burnoff curve was always observed to initially be close to the other curve, but to then rise above it. Therefore initially the products originate only from the ASA measured before pyrolysis but later there probably are additional sources.

Since it is possible to normalize the propylene consumption over all Graphon surfaces studied (0–25% burnoff) with the 573 K propylene ASA[19], the question arises as to why it is not possible to normalize the products from the 0% sample to the same

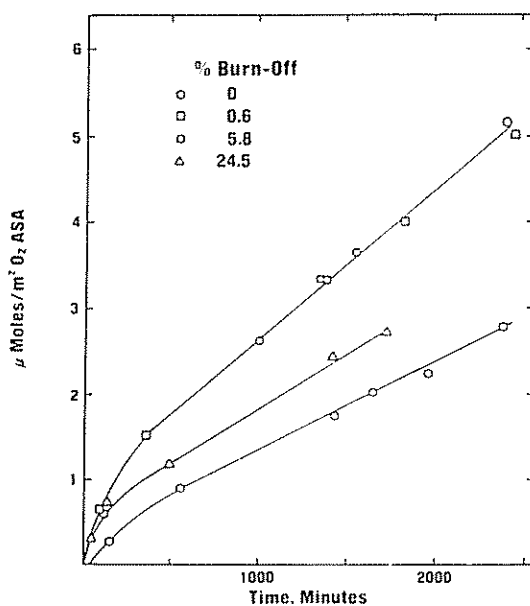


Fig. 7. Methane production from propylene pyrolysis at 923 K normalized to the oxygen ASA of Graphon.

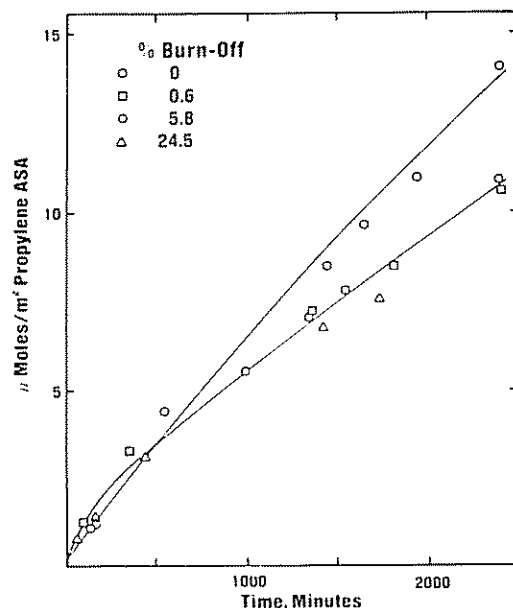


Fig. 8. Methane production from propylene pyrolysis at 923 K normalized to the propylene ASA of Graphon.

curve as the burned-off samples using the corresponding propylene ASA. One might assume that there is a problem with the material balance. This is thought not to be the case. The explanation for this apparent discrepancy is composed of three interrelated aspects. (1) Figures 8–11 apply to regions I to IV of the rate curve for propylene consumption[19] whereas the rate of propylene consumption can only be normalized in region IV. (2) The ASA

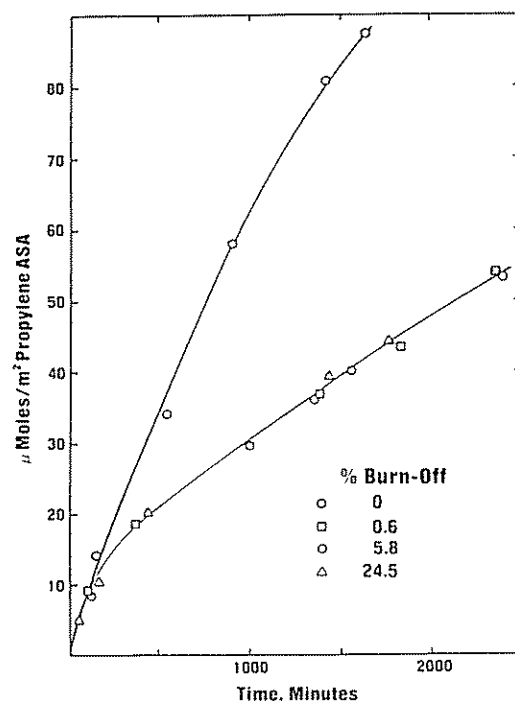


Fig. 9. Hydrogen production from propylene pyrolysis at 923 K normalized to the propylene ASA.

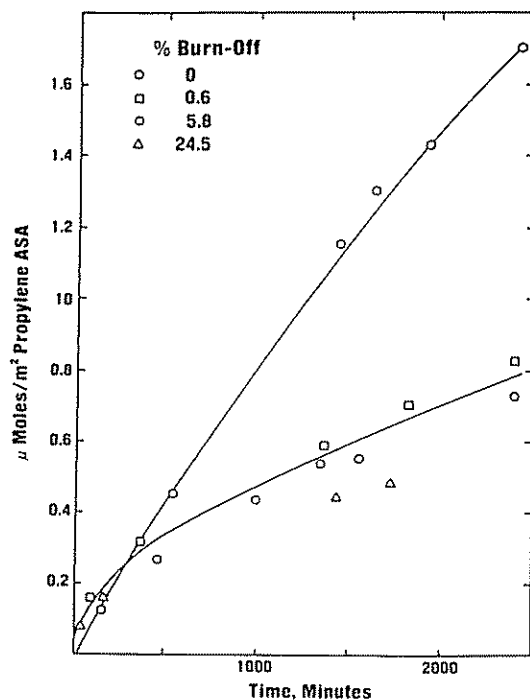


Fig. 10. Ethylene production from propylene pyrolysis at 923 K normalized to the propylene ASA.

of the unoxidized sample is very small and, as a result, contributions to the pyrolysis products from other sources become significant. (3) The surface of the 0% sample is very different from the surface of the burned-off samples. These three aspects will be discussed separately.

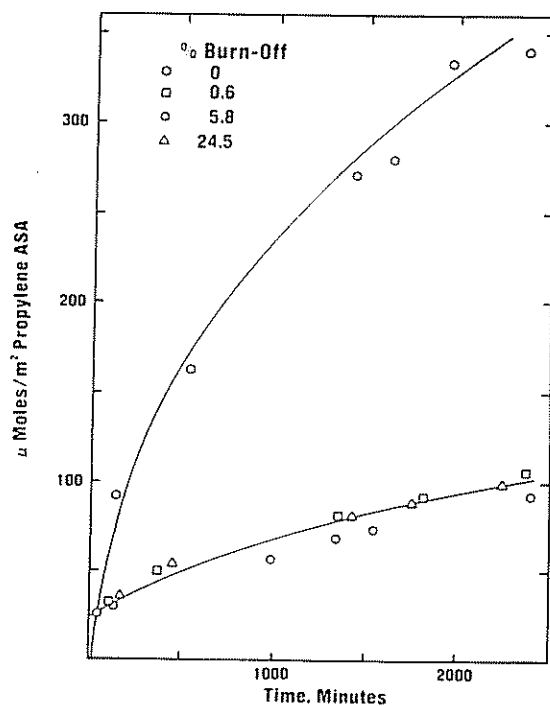


Fig. 11. U-carbon production from propylene pyrolysis at 923 K normalized to the propylene ASA.

1. Propylene consumption over 0 to 25% burnoff Graphon samples can be normalized by the propylene ASA measured at 573 K[19]. However, this correlation applies only to region IV of the rate curve for propylene consumption after complex buildup and cracking over impurities has ceased. This correlation does not apply during the entire pyrolysis because only the cracking over the carbon ASA can be normalized by the propylene ASA. It is not possible, for example, to normalize the amount of propylene that goes to the surface complex with the propylene ASA.

2. The propylene ASA of the burned-off samples used in this study ranged from 8 to 34 times the amount of ASA on the 0% sample. Because of this contributions to the pyrolysis products from other sources might be significant with respect to the products arising from the ASA of the unoxidized sample, but would be insignificant with respect to the pyrolysis products arising from the ASA of the burned-off samples. Because the ASA on the 0% sample is so small, products arising from cracking on the quartz reactor wall and the carbon basal plane, for example, become significant. However, these phenomena would account for at the most 5% of the deviation in Figs. 8 to 11.

3. The surface of the unoxidized sample is very different from the surfaces of the burned-off samples. This was seen previously[19] in two ways. First, the Arrhenius curve for the unoxidized sample can not be normalized with the oxygen ASA to the curve of the burned-off samples. Second, the ASA of the unoxidized sample increased with carbon deposition while the ASA of the burned-off samples decreased with carbon deposition. The increase in ASA with carbon deposition is not completely understood but the effect has been observed by others[28]. It is possible that the effect is due to the geometric configuration of the active sites on the original Graphon surface.

The difference between the unoxidized sample and the burned-off samples can be seen in several other ways. For example, by comparing Fig. 4 with Fig. 12 one can see that there is a difference in the product distribution at 923 K. For instance, on the unoxidized sample (Fig. 12) the percent of carbon from the pyrolyzed propylene going into chemisorbed propylene and complex formation is appreciably higher than for the burned-off samples (Fig. 4). (These data are also tabulated in Table 2 for several samples). This can be seen even more dramatically perhaps in Fig. 13, where the portion of the hydrogen from the pyrolyzed propylene that is associated with the chemisorbed propylene and surface complex is much greater for the 0% sample than for the three burned-off samples. In addition to a difference in the product distribution, one can see from Figs. 1 and 2 that there is a difference in the rate of complex formation. The time for saturation coverage by the u-hydrogen is much longer on the unoxidized sam-

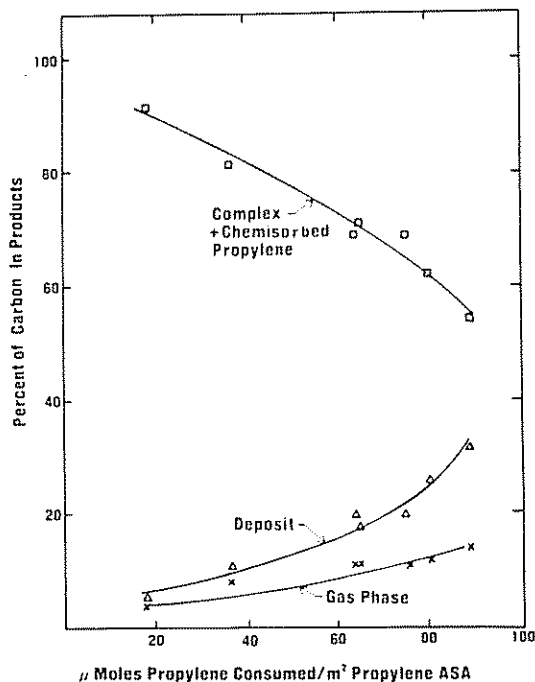


Fig. 12. Distribution of carbon in the products from propylene pyrolysis at 923 K over an unoxidized Graphon sample.

ple. The last difference between the unoxidized sample and the burned-off samples to be mentioned concerns the ethylene generated during the propylene pyrolysis. With all the burned-off samples the ethylene curve is always lower than the methane curve (Fig. 1) due to cracking and some chemisorption of ethylene. This is not the case with the unoxidized sample (Fig. 2).

The initial propylene ASA determines the global consumption of propylene[19]. However, the mechanism by which the propylene pyrolyzes on the surface to produce products depends on whether the sample is an as-received sample or a burned-off sample. All the burned-off samples behave similarly, but very differently from the 0% sample.

Vastola *et al.*[25] observed that the oxygen complex on Graphon above 773 K was not truly stable as was previously thought but, in fact, a small portion of the complex decomposed into gaseous products. If a parallel situation holds here, the discrepancy in Figs. 8 to 11 could be explained. Since the amount of ASA on the 0% sample is so small, the hydrocarbon complex that is thought to be on the basal plane covers an area significantly larger than the ASA at 573 K (Table 2). Decomposition of only a portion of the hydrocarbon complex would contribute significantly to the products from the ASA of the unoxidized sample. Complex decomposition would have a much smaller effect on the amount of products from the burned-off samples since the area covered by the complex is only ≈ 1 to 2 times the ASA at 573 K. In addition, the effect of complex decomposition would not be apparent among the

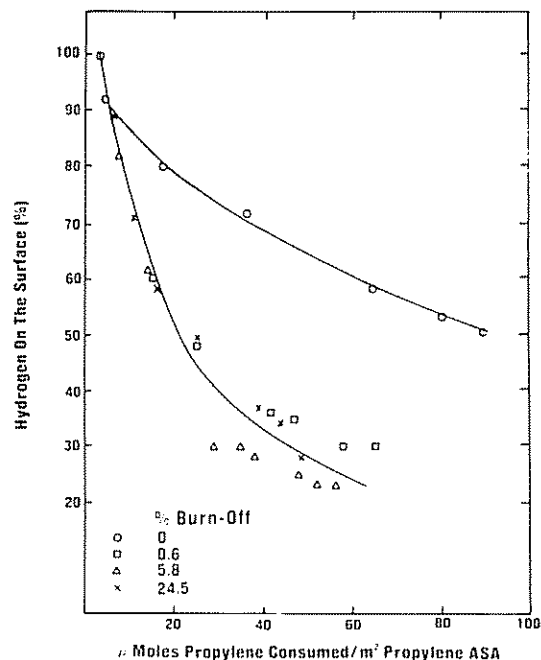


Fig. 13. Percentage of hydrogen in the products from pyrolyzed propylene on the surface of samples of different burnoff at 923 K.

burned-off samples since the ratio of the complex area to the ASA is approximately equal for all samples (Table 2). A final point is that the effect of complex decomposition would contribute much earlier in the run on the oxidized samples since the complex reaches saturation in a very short time compared to the unoxidized samples which usually only reach saturation after 3000 min. (Compare Figs. 1 and 2.) Since the complex was continuing to buildup on the 0% surface, this would explain the increased divergence between the curves in Figs. 8 to 11.

In conclusion to this section, the pyrolysis products arise from the propylene ASA. The principle reason why the curves for the production of the various products from the unoxidized surface can not be normalized to their counterparts from the oxidized surfaces is due mainly to the contribution from the hydrocarbon complex. The contributions from the hydrocarbon complex on the 0% surface are significant because the amount of ASA on the unoxidized sample is so small and because the surface is so different from the burned-off samples.

3.3 Effect of active surface area on the product distribution

Table 4 shows the effect that the presence of carbon ASA has on the nature of the gas phase products resulting from propylene cracking. The gas phase products from propylene pyrolysis at 1073 K over an original (0% B.O.) Graphon sample, as well as those from a blank run, are presented in this table. As can be seen, pyrolysis in the quartz reactor alone favors the production of hydrocarbon products over carbon deposition. This was observed by others[5-

Table 4. Effect of carbon ASA on product distribution at 1073 K

Burnoff, %	Time (min)	Gas phase species (mole %)						C=C and C—C—C
		C=C—C	C=C	CH ₄	H ₂	C=C=C	C≡C	
Blank	1350	90.6	3.5	1.4	2.2	1.8	—	0.4
	1825	86.4	4.9	2.2	3.4	2.5	0.2	0.4
	2725	78.5	7.5	3.8	5.4	3.6	0.4	0.8
	3400	73.2	8.4	4.8	7.4	4.4	0.6	1.2
0	100	91.7	1.0	0.7	6.9	0.4	0.3	—
	300	75.3	2.9	2.0	17.9	1.1	0.8	—
	475	65.9	3.9	3.2	24.1	1.8	0.8	0.3
	1300	41.0	7.9	6.2	40.8	2.4	0.9	0.8
	1575	35.5	7.9	6.8	45.9	2.0	1.1	0.7
	1905	29.6	8.3	7.6	50.0	2.1	1.2	0.8
	2600	20.3	8.3	8.7	59.1	1.7	1.2	0.7

7,10–14]. With Graphon as a substrate, the main gas phase product was H₂, indicating that carbon deposition and surface complex formation was favored over the production of gas phase hydrocarbons. It has been observed[19] that when propylene is pyrolyzed over Graphon the rate of propylene consumption is significantly increased. These data show that the increase in consumption is due mainly to an increase in surface carbon deposition.

3.4 Effect of temperature on the product distribution

The effect of temperature on the product distribution can be seen in Table 5. At all temperatures studied (923–1073 K) the gas phase H₂ (and thus u-carbon) were the major products. As the temperature was increased, the percentage of these products increased due to the cracking of the hydrocarbon species produced during the pyrolysis. Temperatures in excess of 973 K were needed to form allene and acetylene. Ethane and propane were produced above 1073 K after 500 min, but only in cases of low ASA (blank run and 0% B.O.).

All the hydrocarbons cracked in the temperature range 873 to 1073 K. However, the rate of methane cracking was negligible below 1048 K. At 923 K ethylene cracked mainly to H₂ and deposited carbon,

along with a small percentage of methane[18]. Above 973 K the percentage of ethylene in the gas phase products decreased further as acetylene and allene were produced in increasing amounts.

3.5 Effect of gases present in the pyrolysis system on the product distribution

In separate experiments H₂, methane, ethylene, and propylene were individually introduced into the pyrolysis system after 1000 min at 923 K to observe their effect on the product distribution. This series of experiments consisted of diffusing the contents of a 1.0-L bulb into the rest of the pyrolysis system. The gas in the bulb was at system pressure so that when its contents diffused into the rest of the system the change in system pressure was negligible. The introduction of any gas into the system will, of course, change the relative percentages of the gases present. However, apart from these expected changes there were no pronounced changes in the product gas distribution[18].

The gases mentioned above were also preadsorbed in another experiment at 923 K and 1.6 Pa starting pressure prior to pyrolysis of propylene in order to observe the effect on the product distribution. During preadsorption, the hydrocarbons cracked to some extent. The products resulting from the pyrolysis of

Table 5. Temperature dependence of the product distribution over a 5.8% burnoff sample

Temperature (K)	Time (min)	Gas phase species (mole %)					
		C=C—C	C=C	CH ₄	H ₂	C=C=C	C≡C
923	100	92.1	1.0	0.9	6.0	—	—
	375	84.4	2.0	2.0	11.6	—	—
	1375	71.1	3.4	4.1	21.4	—	—
	1825	66.8	3.9	4.8	24.5	—	—
	2700	58.3	4.9	6.2	30.6	—	—
	3000	55.6	5.1	6.8	32.5	—	—
1073	55	58.3	3.1	5.3	31.0	1.2	1.1
	100	40.3	4.3	7.5	45.5	1.2	1.2
	150	29.8	4.4	8.7	55.0	1.1	1.0
	200	22.3	4.4	9.5	61.7	1.1	1.0
	375	10.9	4.1	10.4	73.0	0.9	0.7

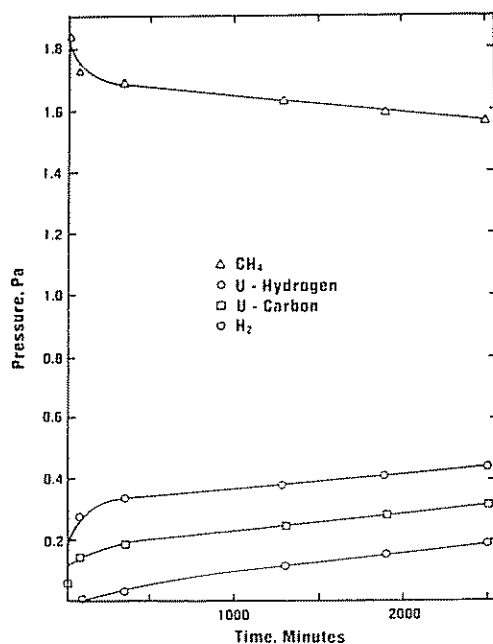


Fig. 14. Products resulting from methane preadsorption at 923 K on a 10% burnoff sample.

methane and ethylene are shown in Figs. 14 and 15. As can be seen from these figures, when a Graphon surface is exposed to methane or ethylene at 923 K, there is a rapid initial buildup of a chemisorbed species just as in the case of propylene. The surface complex originating from methane has an H/C atomic ratio of 3.72. With ethylene this figure decreases to 1.25. Comparing these values with the one given for propylene (1.39), it is apparent that the surface complex H/C ratio decreases with the degree of unsaturation of the precursor. During methane pyrolysis,

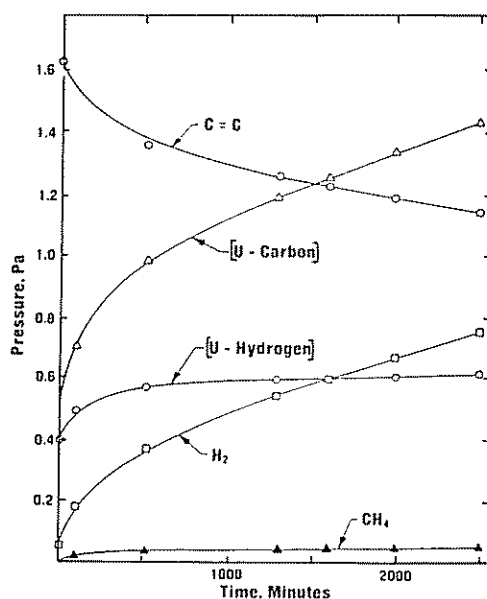


Fig. 15. Products resulting from ethylene preadsorption at 923 K on a 10% burnoff sample.

it takes more than 100 min, under the experimental conditions used, before a significant amount of carbon is deposited (as seen by gas phase H_2). However, once the process starts, it appears to proceed at a constant rate. In contrast, with ethylene the carbon deposition commences immediately, parallels the complex buildup, and continues at the same rate after complex buildup is complete.

Figures 14 and 15 show that under the conditions used for preadsorption and pyrolysis (1.6 Pa, 923 K), both methane and ethylene crack. However, the rate of cracking even on this clean surface was much less for each gas than for propylene. Table 6 shows that the rate of methane decomposition was only 8% of that for propylene, while the ethylene pyrolysis rate was 37% of that for propylene at an equivalent temperature and pressure.

Note, however, that the rate of methane and ethylene pyrolysis over a Graphon surface during propylene pyrolysis will be much less than the values over a clean surface given in Table 6. Methane decomposition, for example, should be practically negligible at this temperature during a propylene pyrolysis where most of the propylene and methane ASA is already blocked since even on a clean surface methane does not chemisorb well[23]. Ethylene, however, will crack to some extent since it chemisorbs on some sites not active for propylene chemisorption[23]. In any case, the rate of ethylene consumption will be much less than the 37% of the propylene rate measured on a clean surface. This results from the fact that the pressure of ethylene during a propylene pyrolysis run is small compared to that of propylene, and in addition to this most of the ethylene ASA is already blocked by propylene.

Although the rate of cracking of ethylene and methane is not as great as that of propylene at 923 K, their efficiency for carbon deposition is significantly greater. The ratio of the rate constants for parent gas consumption and carbon deposition for each gas in Table 6, show that methane is the most efficient gas studied for carbon deposition with 100% of the carbon atoms from the pyrolyzed methane depositing on the surface after the build-up of complex is complete. With ethylene this figure drops to 98% (1.96 out of the 2 carbon atoms). For propylene the efficiency for deposition drops still further to

Table 6. Data for pyrolysis of and carbon deposition from various gases at 923 K over a 10% burnoff sample

Gas	Rate constant for gas pyrolysis ^a (cm/sec)	Rate constant for carbon deposition ^a (cm/sec)	Efficiency of deposition
Propylene	6.25×10^{-5}	14.3×10^{-5}	0.76
Ethylene	2.32×10^{-5}	4.55×10^{-5}	0.96
Methane	0.51×10^{-5}	0.51×10^{-5}	1.00

^aThese pyrolysis and deposition rate constants were all normalized to the oxygen ASA because the methane and ethylene ASA were not available for these samples.

76% (2.3 out of the 3 carbon atoms). This figure for propylene increases to 83% at 1023 K as there is an increase in the rate of the cracking of the hydrocarbon pyrolysis products. Although the deposition efficiency is lowest for propylene, it is still useful as a feed gas for deposition since its rate of cracking and deposition is appreciable greater than either ethylene or methane at these temperatures.

Preadsorption of H₂ and methane had no effect on the propylene pyrolysis product gas distribution other than to slightly decrease the amount of u-hydrogen. This would be expected as H₂ and methane cover only a small fraction of the propylene ASA at 573 K (23-24). In addition, H₂ should have little effect on being introduced into the system since the surface is always exposed to H₂ associated with propylene and the hydrocarbon products. Although the hydrogen and methane had little effect on the product distribution, the preadsorption of ethylene and propylene did have a noticeable effect, since they covered the propylene ASA extensively.

During propylene pyrolysis after pre-adsorption of propylene (Fig. 16) and ethylene (Fig. 17), no rapid initial buildup of ethylene and methane was observed, since the sites responsible for this buildup had been covered during preadsorption. After preadsorption (pyrolysis) of propylene, the surface complex produced during the subsequent pyrolysis as seen by the u-hydrogen curve in Fig. 16 was greatly reduced. The amount of complex formed in this case

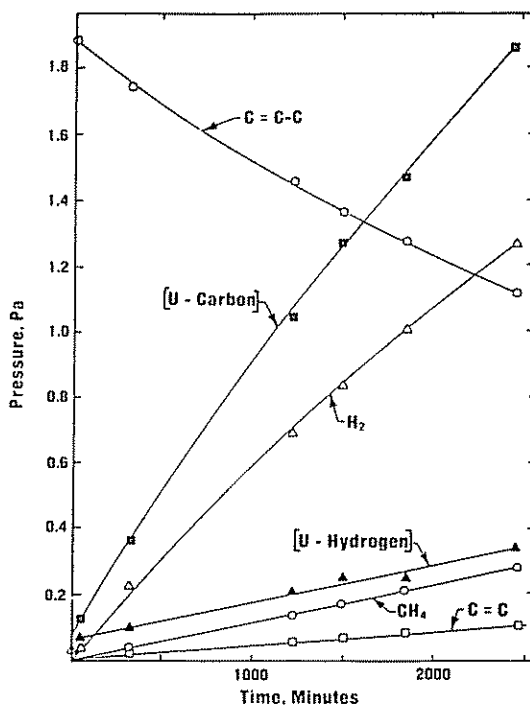


Fig. 17. Pyrolysis of propylene at 923 K following preadsorption of ethylene on a 10% burnoff sample.

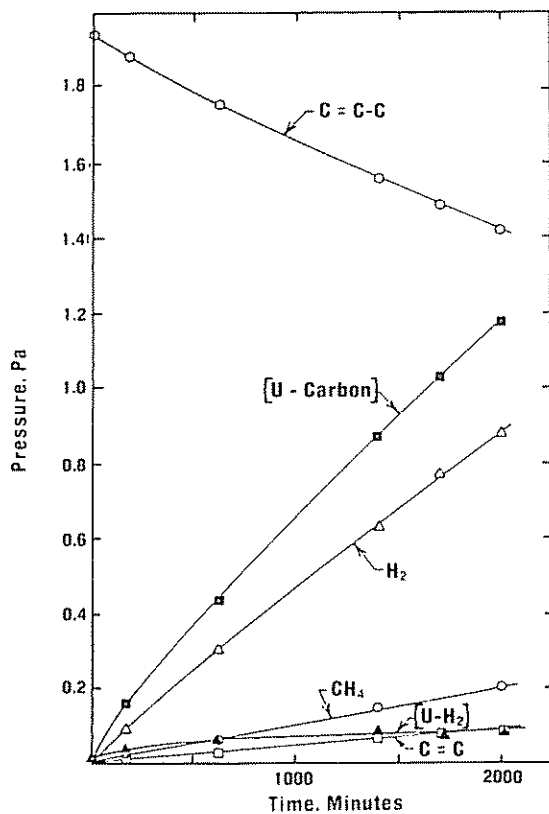


Fig. 16. Pyrolysis of propylene at 923 K following preadsorption of propylene on a 10% burnoff sample.

was limited by the near saturation complex coverage during the preadsorption (and pyrolysis) cycle. Thus, the surface has to be very clean for propylene to instantly chemisorb. In addition, the amount of complex buildup on the surface, although not as sensitive to cleanliness, still depends on the previous history of the sample and its state of cleanliness.

After preadsorption of ethylene, the surface complex produced during pyrolysis of propylene (Fig. 17) was greater than in the previous case (Fig. 16). This was probably due to propylene chemisorption and subsequent complex formation since propylene will chemisorb on sites that will not chemisorb ethylene[23]. Finally, it can be seen from Figs. 16 and 17 that ethylene preadsorption did not cause as great a reduction in the amount of pyrolysis products formed as did preadsorption of propylene. This is because the ethylene coverage of the ASA was not as extensive as that of the propylene coverage.

3.6 Proposed model

Given that the rate of propylene consumption in region IV of the rate curve[19], the initial chemisorption, the rate of carbon deposition, the production of gas phase products, and the rate of buildup of the hydrocarbon complex are all related to the propylene ASA measured at 573 K, one might inquire as to whether the same active sites at reaction temperature are responsible for all these processes. The answer to this question is not an easy one, but the data seem to point to at least two different types of sites at reaction temperature. This is similar to what others[22,29] observed with the oxygen reac-

tion. Laine *et al.*, for example, measured the oxygen ASA at 573 K starting with a pressure of 66.7 Pa O₂. They found that they could normalize the rate of oxidation at 948 K (5.2 Pa O₂ starting pressure) with the 573 K oxygen ASA if they subtracted out the amount of ASA that had a "stable" oxygen complex on it. Thus, they found two types of ASA at 948 K—ASA that formed a "stable" complex and ASA that gasified.

On the basis of the data presented in this study, it is thought that a portion of the propylene ASA at reaction temperature is responsible for the initial chemisorption and the subsequent methane and ethylene production as well as the buildup of the hydrocarbon complex. Another portion of the propylene ASA is responsible for the carbon deposition through short-lived surface intermediates. Comparing the methane and ethylene production with the carbon deposition, for example, should make it clear that these processes are not closely related.

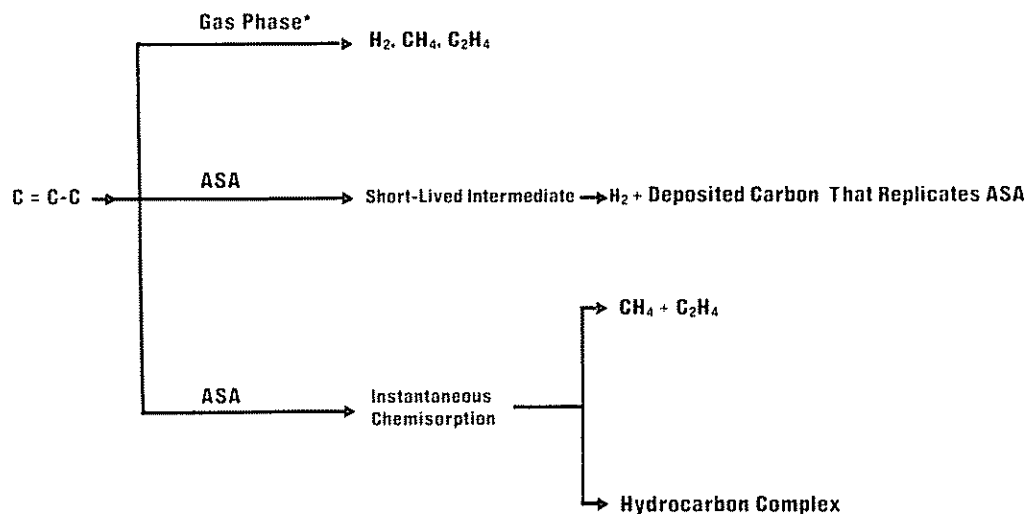
The rate of carbon deposition on the ASA is first order in propylene, is temperature dependent and can be normalized with the 573 K propylene ASA[19]. On the other hand, the production of methane and ethylene, although it can be normalized by the 573 K propylene ASA (Section 3.2), becomes zero order in propylene and over a small temperature range is essentially independent of temperature. For instance, with a drop of 75 K in the sample temperature, the rate of H₂ and deposited carbon produc-

tion dropped considerably while the rate of methane and ethylene production remained essentially constant. This additional information would appear to indicate that the rate of methane and ethylene production is dependent on the rate of desorption and not on the rate of cracking of propylene on the surface.

If one tries to fit the results given in this publication and the previous ones in this series[19,23] into a one-site model, there are problems. A one-site model would mean that there is an unsaturated complex that builds up on the entire active surface area and pyrolyzes with time ultimately resulting in deposited carbon. With this model it is difficult to explain, for example, why the amount of complex is not related to the ASA, how the H/C ratio can drop below 0.05, and why at a point in time the buildup of u-hydrogen ceases.

All the results given seem to fit best into the model shown schematically in Fig. 18. With the experimental conditions used in this study, the overall propylene consumption was found to be determined by the initial propylene ASA. With the samples studied, less than 5% of the propylene cracked in the gas phase. This percentage decreased with the amount of ASA and with a decrease in temperature. On some of the active surface area, propylene formed a short-lived surface intermediate which decomposed to deposited surface carbon and gas phase hydrogen. This carbon deposit replicated the original

Proposed Mechanism



* % of Products Depends on Amount of ASA and Temperature [5% below 1023K]

Fig. 18. Proposed mechanism of propylene pyrolysis over a Graphon substrate.

ASA[20]. On other sites the propylene first chemisorbed. Some of this chemisorbed propylene later decomposed to form methane and ethylene. Another portion of this chemisorbed propylene formed a less saturated hydrocarbon complex that is thought to spill-over to the basal plane where it becomes even more unsaturated.

4. CONCLUSIONS

All the pyrolysis products originate from reactions occurring on the 573-K propylene ASA or on ASA very closely related to it. There appears to be two main surface processes taking place. Propylene either cracks rapidly to elemental carbon and H₂ or it chemisorbs for a period of time. The chemisorbed propylene can either crack to methane and ethylene or form a hydrocarbon complex that then diffuses to the basal plane. It is thought that these two processes do not take place on the same active sites although the rates of elemental carbon deposition as well as methane and ethylene production can be normalized to the 573-K propylene ASA.

Acknowledgment—W.P.H. is grateful for support from the Gulf Oil Company Foundation.

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