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PYROLYSIS OF PROPYLENE OVER CARBON ACTIVE SITES—I. KINETICS

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Abstract—The influence of carbon active sites on the pyrolysis of propylene was studied in the temperature range 873–1073 K at a starting pressure of 1.6 Pa. Graphon, a graphitized carbon black, was used as a substrate for pyrolysis and subsequent carbon deposition. Pyrolysis was carried out in a static reactor at low pressures where secondary products were less likely to form and complicate the system. The pyrolysis of propylene over the Graphon substrate may be described by the expression $d(C_3H_6)/dt = (k)(C_3H_6)(ASA)$ moles/sec where ASA is the active surface area (cm^2) of the carbon measured by propylene chemisorption at 573 K, (C_3H_6) is the concentration of propylene in moles/cm^3, and k is the specific reaction rate constant having a value of $10^{9.62}$ exp $(-57$ kcal/mole/RT) cm/sec. The carbon active surface greatly enhanced the rate of cracking of hydrocarbons to elemental carbon which was deposited directly on the surface. The carbon was found to deposit on the active sites and become new active sites. Thus, the carbon deposit replicated the active surface area and was autocatalytic.

Key Words: Pyrolysis, Active sites, Propylene, Deposition, Carbon, Kinetics

1. INTRODUCTION

The pyrolysis of hydrocarbons has been studied since Dalton and Henry[1, 2], almost two centuries ago, subjected methane and ethylene to a continuous electric spark decomposing them to their elements. The first reported 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 Meinert[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 and initial concentration. Studies of the pyrolysis of propylene in the temperature range 773–973 K[5–8] have established with certainty 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. It appears that each investigator has his own pyrolysis mechanism to account for his own experimental results.

The thrust of this study was not to elucidate the mechanism of homogeneous propylene pyrolysis but to investigate the effect that a carbon substrate has on the pyrolysis and on the amount, type, location, and reactivity of elemental carbon formed.

During most of the propylene pyrolysis work cited, elemental carbon was found but was not studied. This carbon can either be formed in the gas phase (homogeneous formation) or on the surface of the reactor or substrate present (heterogeneous formation). The gas phase carbon is soft and sooty whereas the surface carbon is hard and dense. Both of these carbon types are usually formed in a pyrolysis reaction, but which one predominates depends on the experimental conditions which include temperature, pressure, contact time, and the geometry of the reactor. The structure and properties of a carbon deposit are related to the pyrolysis conditions because these conditions control the mechanism of carbon formation.

Although no theory exists that has a solid mathematical foundation, numerous models, theories, and mechanisms—all qualitative in nature—have been proposed to explain the phenomenology of carbon formation during the pyrolysis of gaseous hydrocarbons. Each of these is an attempt to show how carbon in a low molecular weight hydrocarbon can be aggregated during pyrolysis into huge planar "molecules" containing hundreds of carbon atoms in a hexagonal array. A process that begins with a small gaseous hydrocarbon and ends with large carbon particles must obviously involve growth or condensation as well as dehydrogenation. The various models differ because of the uncertainty in the identification of essential intermediate species and in the sequences involved in aggregation.

The various theories held today have been reviewed by Gill[19] and Gaydon and Wolfhard[20]. The principal theories are: The Atomic Carbon Theory, the Surface Decomposition Theory, the Condensation Theory, the Acetylene Theory, and the Hydrocarbon Polymerization Theories.

The data presented in this study and elsewhere[21, 22] support the surface decomposition theory proposed by Tesner[23]. According to this theory, carbon is formed through direct decomposition of hydrocarbons on the

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substrate. Deposition by direct condensation is energetically favored and is thus the dominant process during pyrolysis, provided that enough surface area is available to prevent supersaturation in the gas phase from reaching a level necessary to homogeneously nucleate a gas-born particle.

Although nucleation and the mechanisms of carbon deposition are still a mystery, the kinetics of growth of deposits are easy to measure with accuracy. The first attempt to measure the kinetics of deposition was by Grisdale *et al.*[24]. They pyrolyzed methane in a flow system at 1248–1573 K and measured the growth of the carbon film on a ceramic substrate by the change in electrical conductivity. Others[25, 26] have used a similar technique. Brown and Watt[27] measured deposition kinetics using a graphite rod as a substrate. Makarov and Pechik[28], using methane, compared the deposition rates on several carbon blacks.

The study of the kinetics of carbon deposition, on carbon in particular, is an important area that can yield valuable information leading to a better understanding of carbon composite infiltration and densification, coating of nuclear fuel pellets and orthopedic prosthetic devices, carbon black production, and fouling of cracking catalysts among others.

Although there is potential return, clearly little has been done in this area, especially in relating the deposition rate to the character of the original surface. Most of the effort in the pyrolysis area has been expended in theorizing mechanisms as well as in characterizing the deposited pyrolytic carbon and relating its structure to pyrolysis conditions. Although the knowledge obtained has been very practical, most of it has been empirical. Little work has been done to put the kinetics of deposition of pyrolytic carbon on a firm foundation. The purpose of the work described in this paper is three-fold:

(1) To obtain precise kinetic data for the deposition of pyrolytic carbon on a well characterized graphite surface.

(2) To determine whether the carbon surface is catalytic for deposition but more importantly whether the pyrolytic carbon deposit is auto-catalytic. It has been known for some time that carbon is a specific catalyst for some reactions[29, 30]. However, the literature contains only qualitative observations pertaining to the catalytic activity of carbon for the pyrolysis of hydrocarbons.

(3) To determine whether the extent of active surface area (ASA) as measured by oxygen or hydrocarbon chemisorption affects the rate of deposition. 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 exposed layer planes as well as at points of imperfections in the structure including vacancies, dislocations, and steps on the outer basal plane.

Much work has been done on characterizing these active sites on the grapitized carbon black (Graphon) that is being used in this study. Both hydrogen and oxygen have been extensively chemisorbed[31–37] employing a technique first used by Laine *et al.*[38].

If there is a relationship between ASA and the rate of carbon deposition, it would be possible to predict the rate of deposition by measuring the active surface area (ASA). It would also be possible to enhance the rate by increasing the ASA.

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 active surface area (ASA) without an appreciable increase in the total surface area of the sample[38]. Thus, the effect of the ASA on the pyrolysis reaction can be studied. Samples were burned-off up to 25% weight loss in air at 723 K in order to generate samples with varying amounts of active surface area.

After pre-oxidation the samples were treated in 10.0 kPa Cl_2 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 H_2 was introduced to remove any chlorine that remained. The sample was kept in this H_2 atmosphere for 1 hr. After this time gaseous H_2 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 which underwent this preparation were considered "clean," implying an insignificant amount of impurities and chemisorbed species.

The gases used in this study were obtained from Air Products and Chemicals Inc. The O_2 and H_2 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 reactions were studied in a volumetric apparatus with a total volume of 17,900 cm^3. The Pyrex high vacuum system was interfaced to a mass spectrometer and to a fused quartz reactor which held the sample. The reactor was of double wall design with the annular volume evacuated to prevent diffusion into the reactor tube from the atmosphere at high temperature. A Lindberg resistance furnace in conjunction with a West controller and chromel–alumel thermocouple controlled the temperature of the sample. A CEC model 21-614 residual gas analyzer was used to check the purity of each gas and to monitor the gas phase during adsorption, desorption, and pyrolysis.

Vacuum to 10^{-4} Pa was obtained using a liquid N_2-trapped silicone 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 an 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 O_2 Active Surface Area (ASA) was determined by the method of oxygen chemisorption first used by Laine *et al.*[38]. Using this technique, a pretreated Graphon sample that had been cleaned *in vacuo* (10^{-6} Pa) at 1223 K was exposed at 573 K for 24 hr to O_2 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 and held at that temperature for 15 min. The amount of CO and CO_2 that desorbed was measured with the mass spectrometer. The sample was then evacuated at 1223 K until the residual pressure was 10^{-6} Pa. Knowing the number of moles of each gas desorbed and taking the area of an edge carbon site that chemisorbed an oxygen atom as 0.083 nm^2, the surface area occupied by oxygen (active surface area) could be determined[38].

To start a pyrolysis run, which lasted up to 3500 min, 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 this 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 thermal 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.

Before each sampling, the pressure of the system was recorded as was the time. The gas was then introduced to the mass spectrometer and a scan of *m/e* from 2 to 50 Amu was performed. The metal valve to the mass spectrometer was then closed and the total system pressure drop was recorded. The material balance calculated from the mass spectrometric scan, corrected for pumping loss, gave the amount of carbon and hydrogen on the surface as a function of time.

After a pyrolysis run was completed, the sample was either removed, evacuated at pyrolysis temperature prior to subsequent pyrolysis, or heated to 1223 K *in vacuo* to clean the surface prior to another experiment.

3. RESULTS AND DISCUSSION

3.1 *Introduction*

Preliminary runs with and without the most active Graphon sample (25% burn-off) at 1073 K demonstrated that the observed pyrolysis rates were reproducible and that there was no diffusion control.

Another preliminary study involved determining whether cracking on the quartz reactor wall was significant. It was found that even at 1073 K the cracking on the quartz wall was not significant compared to that on the least activated Graphon sample for the weight used. Figure 1 shows the natural logarithm of propylene consumption during pyrolysis in arbitrary units plotted against time. The three curves represent results for propylene pyrolysis over the quartz reactor surface alone and over two impure Graphon surfaces of different burn-off. Starting pressure was 10 units of propylene in each case. Considering the 0% and 10% burn-off samples, it is obvious that an increase in Graphon ASA increases the rate of propylene consumption appreciably. Looking at the plot for the 10% burn-off sample, four distinct regions of the rate curve for propylene consumption can be clearly seen. All but the initial instantaneous rate curve (region I) are first order in propylene.

These results suggest that at least four different processes are taking place in the course of pyrolysis. These processes will each be briefly discussed in order to give the reader an overall picture of the pyrolysis system before each is discussed in detail later. The final rate curve (region IV) of propylene consumption is due to cracking on the Graphon ASA alone. The rate of pyrolysis was found to be very reproducible among "identical" samples. The rate curve in region III arises from the cracking of propylene on the Graphon ASA, as well as on surface impurity sites. The second region of propylene consumption in Fig. 1 involves simultaneous cracking on the Graphon ASA and impurity sites as well as the buildup of a surface hydrocarbon complex. The amount of propylene consumed by each of the three processes individually can be seen by extrapolating each of the slopes back to the ordinate. The initial rapid de-

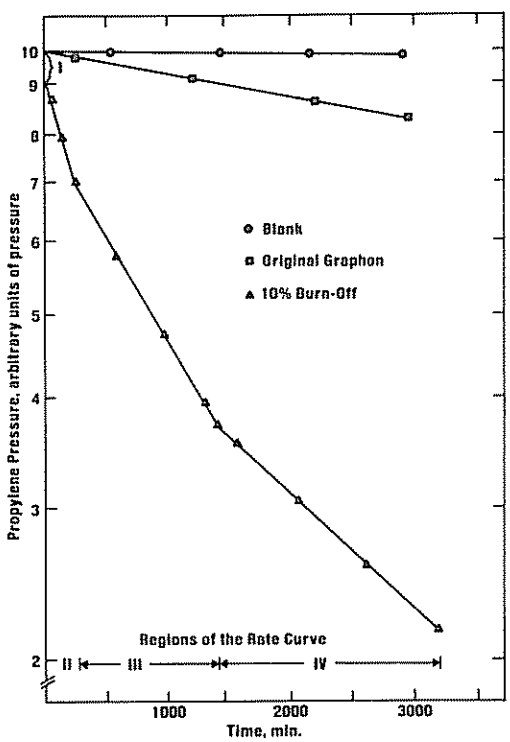

Fig. 1. Propylene pyrolysis on various surfaces at 923 K.

crease in propylene pressure (region I) is due to the chemisorption of propylene[39, 40].

Chemisorption took place on the Graphon ASA as well as on surface impurities. When the impurity level was decreased sharply by prechlorination of the Graphon, as previously described, the amount of propylene chemisorbed was decreased. Region I disappeared when the surface was not "clean." For instance, when a pyrolysis run was begun without first cleaning the surface from the previous pyrolysis, the initial region disappeared but reappeared when the sample was cleaned *in vacuo* at 1223 K before starting a pyrolysis run.

The buildup of a surface hydrocarbon complex takes place in region II of Fig. 1. The amount of complex formed was not found to be closely related to the Graphon ASA or surface impurity site concentration. Region II of the rate curve was not reproducible even with "identical" samples. No complex was formed on an unclean surface. The surface complex was seen as unaccounted-for carbon and hydrogen in the gas phase material balance. The ratio of H/C in the complex was equal to 1.4 at 923 K and was observed to decrease with an increase in temperature as will be shown in Table 3.

Figure 2 displays the products of a typical pyrolysis run at 923 K. Gas phase products include methane, ethylene and hydrogen. A material balance on the gas phase showed that a sizable amount of carbon and hydrogen was unaccounted for. The unaccounted-for hydrogen, surface hydrogen in Fig. 2, is thought to be associated with the Graphon surface as a complex. Carbon unaccounted for in the gas phase, surface carbon in Fig. 2, was on the surface both as a deposit as well as being associated with the surface hydrogen in a complex. The

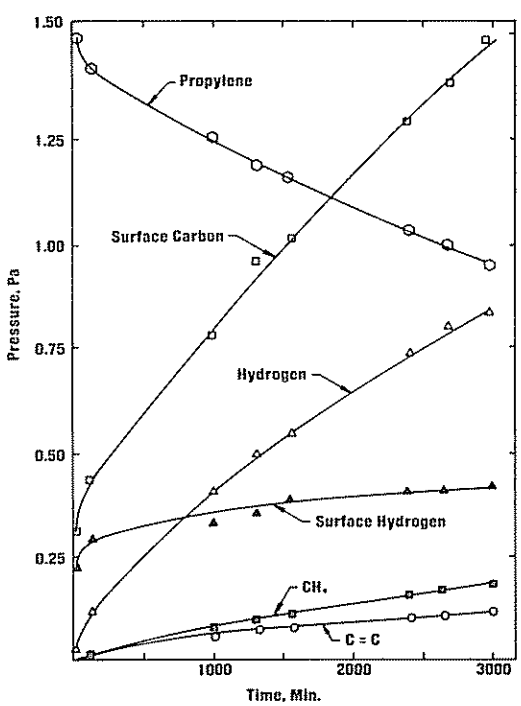

Fig. 2. Products formed during propylene pyrolysis at 923 K over a 5% burn-off sample.

pyrolysis products are discussed in detail in the second part of this study[22].

The rate of consumption of propylene in region III of Fig. 1 was observed to vary with the kind and amount of impurities on the surface and was not reproducible, even with "identical" samples. The surface impurities were mostly metallic and could be removed as volatile chlorides at 1223 K. A small concentration of surface impurities was observed to have a very large (dominant) effect on the rate of propylene pyrolysis. This has also been observed by Ehrburger *et al.*[21]. The impurities were rendered less active during carbon deposition.

3.2 *Relationship between active surface area and rate of propylene consumption*

As was stated, the pyrolysis of propylene in the temperature range 873–1073 K and at 1.6 Pa starting pressure is first order in propylene. It was shown in Fig. 1 that there was a substantial increase in the rate of propylene consumption with only 10% burn-off of the Graphon sample. This increase in rate paralleled the increase in active surface area. The calculated rate constant was observed to be invariant during the period of extensive carbon deposition as discussed later in this section.

In this section and those that follow, all propylene consumption rates refer to the rate of region IV of Fig. 1 (that is, pyrolysis over the Graphon ASA). Unless otherwise specified, the samples have been chlorinated to reduce the surface concentration of inorganic impurities to a negligible level, have been cleaned *in vacuo* at 1223 K, and have not been used in any previous runs.

Figure 3 shows Arrhenius plots for five Graphon samples varying in burn-off from 0 to 25%. The specific reaction rate constant, k_{BET}, is expressed per unit total surface area of the carbons as measured by the physical adsorption of N_2 at 77 K. As can be seen, at a given temperature the rate of propylene consumption increases significantly with burn-off. Samples 1–4 were "surface-impurity-free" samples of varying burn-off. Sample 5 was not treated with Cl_2, but the impurities were previously rendered much less active by carbon deposited on them. Figure 3 shows that all pyrolysis runs had the same activation energy (about 57 kcal/mole). It appears that the impurities had little effect on the rate of propylene consumption once they were rendered less active by the deposit. Since the activation energy is the same for all runs and is constant throughout the temperature range 873–1073 K, it appears that the pyrolysis mechanism remains unchanged throughout the entire temperature range.

One of the goals of this work was to attempt to correlate the rate of pyrolysis with the oxygen ASA. To determine if a correlation existed, the propylene consumption rates were normalized for samples 1–4 of Fig. 3 with the initial (before pyrolysis) oxygen ASA measured at 573 K. The active surface areas were determined on a "clean" (both of chemisorbed species and impurities) Graphon sample that was not subjected to previous adsorption or pyrolysis runs. Surface areas for the samples of Fig. 3 are given in Table 1. Figure 4 shows Arrhenius plots for samples 1–4 after being normalized

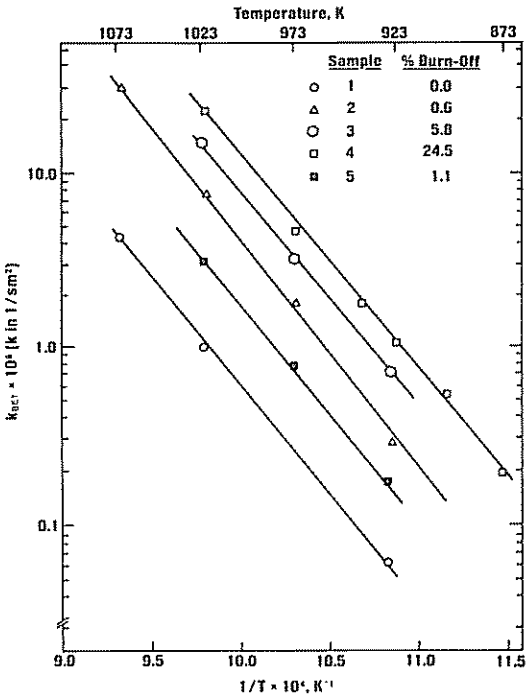

Fig. 3. Arrhenius plots of pyrolysis rates normalized to total surface area.

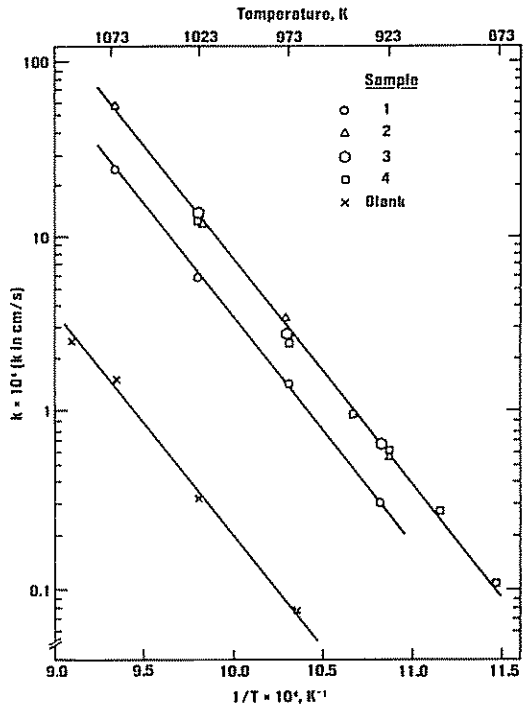

Fig. 4. Arrhenius plots of pyrolysis rates normalized to initial oxygen ASA.

to the oxygen ASA. Also included for comparison are data taken in the absence of a Graphon sample. These data labeled blank are normalized to the surface area of the quartz reactor (0.033 m^2). Note that the units of the rate constant are now cm/sec. These units are produced by multiplying the units (1/sec cm^2 of ASA) by the reactor volume used (cm^3). Thus, the rate constant is normalized for general use, if the ASA of the carbon is known. As can be seen, the initial 573 K oxygen ASA normalizes the burned-off samples to each other very well but does not normalize the 0% burn-off sample to the rest.

The initial oxygen 573 K ASA was used rather than that measured at the completion of the run because of surface changes during the run. As was shown in Fig. 2, a surface complex forms during pyrolysis. In order to measure an oxygen ASA this hydrocarbon complex had to be desorbed. This desorption leaves the carbon associated with the complex on the surface. This carbon from the complex alters the active surface area as does the deposit during pyrolysis[39]. Thus, the "cleaned" surface after pyrolysis has a lower ASA than that which propylene saw during the pyrolysis.

Since normalization with the 573 K oxygen ASA was only partially successful, normalization of the pyrolysis rates with the initial 573 K propylene ASA was attempted. It should be noted that the initial 573 K propylene ASA was determined on an aliquot of each sample not used for pyrolysis. Therefore, the carbon deposited upon desorption of the chemisorbed propylene would have no effect on the rate of pyrolysis. As Fig. 5 illustrates, normalizing the pyrolysis rates to the propylene ASA was successful. Linear regression analysis of the data gave a correlation coefficient of 0.989. The energy

Table 1. Surface areas occupied by the chemisorption of oxygen and propylene at 573 K on Graphon samples of varying burn-off

Sample	Burn-Off, %	Total Surface Area, m^2/g	Oxygen ASA, m^2/g	Propylene ASA, m^2/g
1	0	76	0.26	0.056
2	0.6 +	82	0.94	0.44
3	5.8+	92	2.25	1.06
4	24.5 +	124	5.00	1.89
5	1.1 *	80	0.75	0.35

+ Includes burn-off during pre-oxidation and prechlorination (39)

* Due only to pre-oxidation

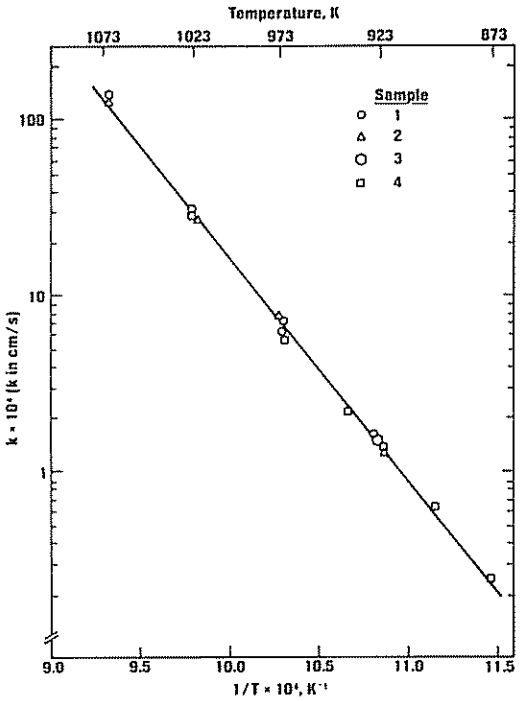

Fig. 5. Arrhenius plots of pyrolysis rates normalized to initial propylene ASA.

of activation was found to be 57 ± 0.5 kcal/mole. The 573 K propylene ASA is a very good index of propylene pyrolysis reactivity between 873–1073 K. The 573 K oxygen ASA was shown by Laine *et al.*[38] to be a good index of reactivity toward oxidation at higher temperatures, but this work shows that it should not be used for reactions of other gases with carbon. As has been shown[39], each molecular species that chemisorbs on carbon has its own ASA which is different for each gas. In determining the reactivity of a gas with carbon at elevated temperatures, the active area covered by that gas during chemisorption at 573 K should be used.

Figures 4 and 5 show that the oxygen and propylene active surface areas are related. From chemisorption studies at 573 K[39] it was shown that these two gases chemisorbed on some common sites. However, some sites were available to oxygen and not to propylene due to molecular size and site geometry limitations. The effect of this was most apparent on the original Graphon sample. The normalized rate constant for propylene pyrolysis over the original Graphon sample in Fig. 4 was lower than the rest because the ratio of the oxygen ASA to the propylene ASA at 573 K was twice that of the activated samples. This suggests that the geometric configuration of the active sites on the original Graphon and the activated samples was different. It suggests that for original Graphon samples, the ASA is primarily that located around vacancies in the carbon basal plane, whereas for the activated samples the ASA is primarily located along enlarged crystallite boundaries at the intersection of the polyhedral surfaces. Because of steric effects of size, propylene chemisorption at single vacancies would not be expected to occur.

The pyrolysis of propylene over Graphon was observed to be first order in propylene partial pressure. Since the rate of propylene consumption was also shown to be proportional to the propylene ASA, the rate of propylene disappearance R, in moles/s, can be expressed simply as:

$$R = [10^{9.62} \exp(-57 \text{ kcal/mole/RT}) \text{ cm/s}] \times [(C_3H_6)][(\text{ASA})]$$

where (C_3H_6) is the propylene concentration in moles/cm^3 and (ASA) is the 573 K propylene ASA in cm^2.

As shown above, the rate of pyrolysis was dependent on the initial propylene ASA for all Graphon samples. Even after the initial ASA was "covered" with deposit many times over, the rate constant remained invariant. Table 2 shows the change in both the oxygen and propylene ASA after a single pyrolysis run on each sample. The percent decrease in both active surface areas is also

Table 2. Effect of deposit on active surface area

Sample	O_2 ASA at start m^2/g	Propylene ASA at start m^2/g	% Weight Increase	O_2 ASA after Pyrolysis, m^2/g	Propylene ASA after Pyrolysis, m^2/g	O_2 ASA % Decrease	Propylene ASA % Decrease	Number of Carbon Atoms Deposited/Number of Carbon ASA Atoms	Temperature, K
1a	0.26	0.06	0.06	0.38	0.06	-44	0	45	973
1b	0.26	0.06	0.10	0.38	0.06	-44	0	77	1023
2a	0.94	0.44	0.08	0.78	0.31	15	30	7.8	923
2b	0.94	0.44	0.31	0.86	0.29	8	35	24	1023
2c	0.94	0.44	0.23	0.85	0.24	9	46	18	973
2d	0.94	0.44	0.33	0.84	0.35	11	21	26	1073
3a	2.25	1.06	0.17	2.11	0.50	17	53	6.6	923
3b	2.25	1.06	0.30	2.04	0.43	9	59	12	973
4a	5.00	1.89	0.27	3.99	1.26	22	33	6.1	923
4b	5.00	1.89	0.15	4.02	0.91	23	52	3.3	898

given. One can see that for the burned-off samples the per cent decrease in propylene ASA is always significantly greater than the per cent decrease in oxygen ASA. This is simply a result of the substrate used and occurs because the deposited carbon is consolidating the enlarged crystallite boundaries at the intersections of the polyhedral surfaces[18]. As a result of this consolidation, some of the ASA is still available to the oxygen but not propylene due to molecular size and site geometry effects.

Also shown in Table 2 is the ratio of the number of carbon atoms deposited to the number of ASA atoms as measured by propylene chemisorption. Thus, from Table 2 it can be seen that even if enough carbon is deposited to "cover" the propylene ASA 25 times the rate constant does not decrease during the pyrolysis.

Jachlewski *et al.*[41] observed a similar phenomenon. They noted that during carbon deposition the substrate continued to have an identical effect on deposition even after many monolayers had been deposited and the effect of the initial substrate should have disappeared. They postulated that the number of active sites on the surface remained constant.

Although the rate constant for propylene consumption in region IV does not decrease during pyrolysis, it does decrease for burned-off samples once the pyrolysis is terminated. This decrease in the measured rate constant was due to a decrease in the ASA and was observed after the pyrolysis system was evacuated. Of course, if the rate constant is normalized to ASA it will remain invariant.

When the pyrolysis system was evacuated and propylene was re-introduced the subsequent pyrolysis had a lower rate of propylene consumption. If the pyrolysis system was evacuated and the surface cleaned at 1223 K *in vacuo*, an even larger decrease in the rate of propylene consumption upon subsequent pyrolysis was observed. This decrease in rate after cleaning was due to a decrease in ASA caused by the pyrolysis of the hydrocarbon complex to a great extent. However, the decrease in ASA caused by carbon deposition during a pyrolysis run will be shown to be very small.

The above decrease in ASA with carbon deposition applied only to activated Graphon samples. On the original Graphon sample, the ASA was found to be increased with carbon deposition (Table 2). A subsequent pyrolysis run thus showed a slightly higher rate of propylene consumption. Makarov and Pechik[28] found a similar rate increase after carbon deposition on an unoxidized graphitized carbon black.

The observation that the rate of propylene consumption depends on the initial propylene ASA and remains unchanged throughout the pyrolysis, even after extensive deposition, suggests that the carbon is depositing on the active surface area and replicating the ASA. Thus, the deposit becomes an active site itself and is autocatalytic for deposition. Decreases in ASA after pyrolysis are due mostly to deposition of the hydrocarbon complex and, in part, to consolidation of the edge sites as the ASA replicates.

It has been shown that the 573 K propylene ASA is a very good index of pyrolysis activity in the temperature range 873–1073 K. The question arises as to whether the amounts of propylene chemisorbed initially during the pyrolysis (region I of Fig. 1) and the amount of complex formed (region II of Fig. 1) are also good measures of reactivity.

The amount of propylene chemisorbed in the initial 2 min of pyrolysis at 923 K was found to correlate well with the propylene consumption rate and the 573 K propylene ASA, as would be expected. In fact, the 923 K initial ASA calculated from the propylene pressure drop in region I was found to be almost identical to the 573 K ASA although it was not as reproducible. The 1023 K initial ASA was found to be approx. 1.35 times the 573 K ASA. This initial chemisorption was not used to normalize the pyrolysis rates because it could not be measured as easily or as accurately as the 573 K propylene ASA. The measurement of the amount initially chemisorbed during pyrolysis became less accurate with increasing temperature since pyrolysis was taking place simultaneously to a greater extent. The amount chemisorbed could be approximated fairly well by first measuring the oxygen ASA before pyrolysis and desorbing the oxygen. The pyrolysis was then started and quenched after 2 min by a rapid temperature drop and by pumping out the gas phase. Oxygen was then chemisorbed on this surface and the amount of surface area blocked by the chemisorbed propylene correlated well with the pyrolysis rate. Obviously, it was easier and more accurate to measure the 573 K propylene ASA.

It was difficult to measure the amount of complex formed in region II with much accuracy since it was necessary to extrapolate the slopes in regions II and III back to the ordinate. The amount of complex formed was taken as the amount of propylene consumed during region II, corrected for propylene consumption due to impurities and deposition on the carbon ASA.

Table 3 gives the ratio between the amount of propylene consumed during chemisorption in region I to the amount of propylene consumed during the formation of the hydrocarbon complex in region II. The ratio shows that even at the same temperature, the amount of propylene consumed in forming the complex is not closely related to the 923 K propylene ASA which is calculated from the amount of propylene consumed in region I. Thus, the amount of surface hydrocarbon complex was not found to be a good measure of pyrolysis activity among various samples. The reason for this lack of correlation is most probably due to the fact that at least two types of sites are involved. It is quite possible that the sites that rapidly chemisorb propylene at 923 K (region I) are the very active Type I sites described by Lussow[35]. The sites that gradually are occupied with hydrocarbon complex would then correspond to the less active Type II sites. These sites that are gradually occupied with hydrocarbon complex might be supplied by a process similar to that observed by Yang and Wong[42] during the oxidation of carbon. They observed that oxygen adsorbed on the basal plane was mobile and diffused to the ASA where it reacted. This premise that two types of sites are involved is supported by previous

Table 3. Data for hydrocarbon surface complex

Sample	Pyrolysis Temperature, K	Amount of Propylene Consumed in Region I, Pa/g	Amount of Propylene Consumed in Region II, Pa/g	Region I/ Region II	H/C Ratio in Complex
1a	973	0.065	0.11	0.61	1.44
1b	1023	0.055	0.335	0.16	0.62
1c	1073	0.201	1.81	0.11	0.74
2a	923	0.197	0.692	0.29	1.38
2b	1023	0.465	1.02	0.46	0.84
3a	923	0.933	0.551	1.70	1.42
3b	973	0.736	1.21	0.61	1.20
3c	1023	1.12	2.68	0.42	0.78
4a	923	1.29	2.32	0.56	1.36
4b	973	1.59	3.69	0.43	1.00
4c	898	1.46	1.67	0.88	1.60
4d	939	1.45	2.31	0.63	1.28
4e	873	1.40	2.11	0.67	1.62

chemisorption studies[39] where it was found that propylene chemisorbed at 1.6 Pa pressure occupied less than 30% of the active sites on the surface. It should be mentioned, however, that although there was not a correlation among samples, on a single sample subjected to several successive pyrolysis runs, the amount of complex formed did appear closely related to the rate of propylene consumption[18]. During the pyrolysis series the amount of complex was observed to decrease proportionally with the 573 K propylene ASA and the rate.

Table 3 shows the H/C ratio in the hydrocarbon complex. This was calculated after correcting for the carbon deposited on the surface during region II. From the samples pyrolyzed at 923 and 1023 K, it is apparent that the ratio is reproducible at constant temperature. The ratio decreases with increasing temperature. At 873 K the ratio is 1.62 while at 1023 K the ratio is 0.74. These ratios are only accurate to ±5% since they were calculated from the gas phase material balance and extrapolation of rate curves. These data suggest that at the lower temperatures the hydrocarbon complex consists of propyl radicals. As the temperature is increased, these species would crack resulting in species of greater unsaturation.

3.3 *Rate of carbon deposition*

In addition to being closely related to the propylene ASA, the rate of propylene consumption is also closely related to the rate of surface carbon deposition over a wide range of temperature and active surface areas[18]. The rate of carbon deposition, measured after the surface complex had reached an equilibrium value, was found to be first order with respect to the propylene partial pressure.

Figures 6 and 7 show the carbon deposition rate data over Graphon samples on Arrhenius plots. Clearly, there is much scatter. This is due to the fact that the amount of carbon deposited on the surface is calculated from the carbon mass balance in the pyrolysis system. The lines drawn through these experimental points are of the same slope as those in Fig. 3. Thus, the activation energy for deposition is equal to the activation energy for gas phase propylene consumption. This same result was obtained by several other workers[24, 25]. Therefore, the rates of propylene cracking and carbon buildup on the surface are both closely related to the fraction of the Graphon surface active for the chemisorption of propylene (i.e. the propylene ASA).

3.4 *Effect of gases present in the pyrolysis system on the rate of pyrolysis*

In an attempt to better understand the pyrolysis mechanism, the various gases present in the pyrolysis system at 923 K (H_2, methane, ethylene, and propylene) were preadsorbed on the substrate at 923 K prior to pyrolysis and were also introduced into the system during pyrolysis. The latter series of experiments consisted of dif-

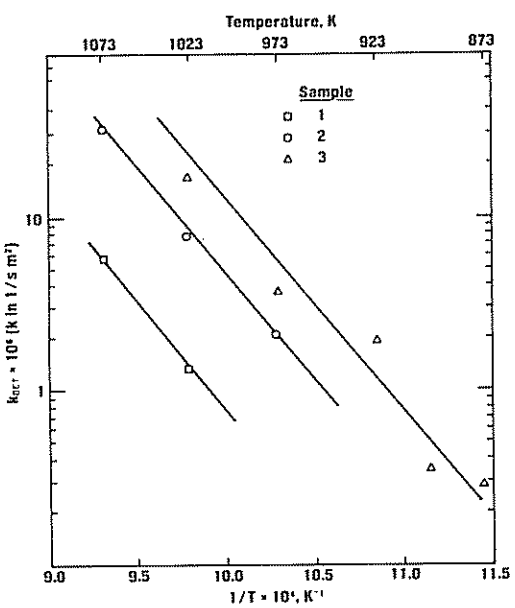

Fig. 6. Arrhenius plots for carbon deposition normalized to total surface area.

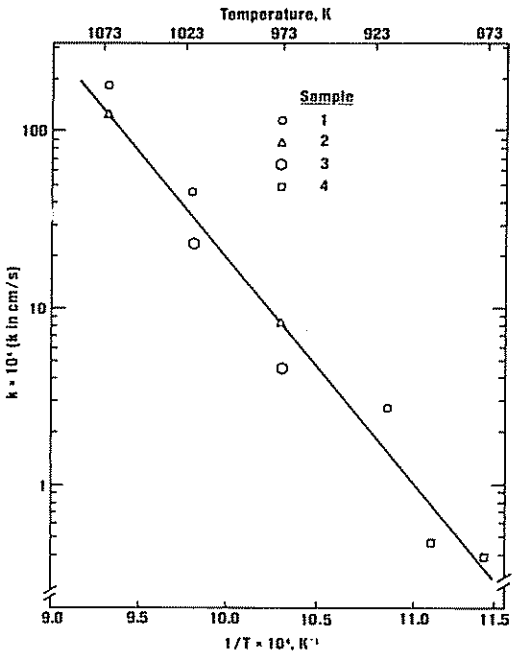

Fig. 7. Arrhenius plot for carbon deposition normalized to propylene ASA.

fusing the contents of a one liter bulb into the rest of the pyrolysis system. The gas in the bulb was at system pressure so that when its contents were diffused into the rest of the system the change in system pressure was negligible.

Neither preadsorption nor introducing the gas during pyrolysis had a profound effect on the rate of propylene pyrolysis. Preadsorption decreased the rate of propylene consumption to a greater extent. In preadsorption, the gases were already adsorbed on some or all of the propylene ASA and thus the gases blocked access to a portion of the propylene ASA. In the case of introducing the gases during the pyrolysis, the various gases had to compete with propylene for the ASA which to a great extent was already covered with propylene.

Preadsorbed propylene covered the most ASA and decreased the pyrolysis rate to the greatest degree. Methane chemisorbed to the least extent of the four gases studied and had the least effect on the rate.

During preadsorption, the hydrocarbons cracked to some extent. The rate of ethylene pyrolysis at 923 K on a clean surface was about 36% of the rate of propylene pyrolysis at equivalent pressures. The rate of methane consumption on a clean surface at 923 K was only 15% of that for propylene. It should be noted, however, in the case of methane that most of the methane stays on the surface and little cracks. Thus during propylene pyrolysis both methane and ethylene crack but to a much smaller degree than on a clean surface. Since methane does not chemisorb to a large extent methane cracking should be negligible during a propylene pyrolysis run where most of the propylene and methane ASA is already blocked. Ethylene, however, will crack since it chemisorbs on some sites not active for propylene chemisorption[39]. However, the rate of ethylene consumption will be much less than the 36% of the propylene rate measured on a clean surface, since the pressure of ethylene during a propylene pyrolysis run is small compared to that of propylene.

3.5 *Effect of impurities*

In Section 3.1 it was stated that the rate in the third region of Fig. 1 was due to the cracking of propylene on the carbon inorganic impurities as well as the carbon ASA. The 10% burn-off run of Fig. 1 is reproduced as the lower curve in Fig. 8. The upper curve of Fig. 8 shows a pyrolysis run on an aliquot of the same sample previously treated with Cl_2 at 1173 K. As can be seen, region III of this rate curve has disappeared. The amount of propylene chemisorbed initially during pyrolysis was reduced, as was both the rate of formation of complex and the amount of complex formed. However, the final rate curve due only to propylene cracking over the carbon ASA remained unchanged. Thus, the surface impurities, exposed along with the carbon ASA on burn-off, chemisorbed propylene and increased the amount and rate of complex formation. However, the impurities had no effect on the rate of pyrolysis over the carbon surface after they were rendered less active by the carbon deposit. From ASA measurements it was calculated that only one carbon atom deposited on an impurity atom was required to render the impurity atom less active.

As can be seen from the oxygen active surface areas measured at various times during the two runs shown in Fig. 8, the surface impurities accounted for more than half of the initial oxygen ASA on this sample. (Compare

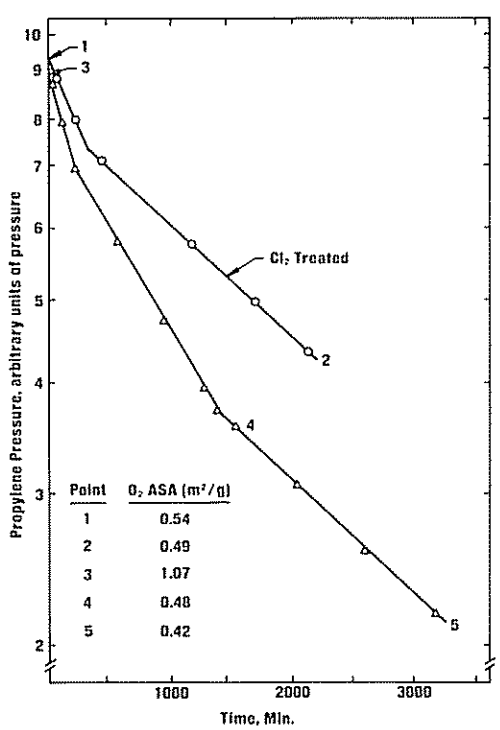

Fig. 8. Effect of chlorine treatment on the rate curve at 923 K on a 10% burn-off sample.

ASA at point 1 with that at point 3). When these impurities were rendered less active by the deposit, the ASA of the sample (point 4) dropped to that of the carbon surface pretreated with Cl_2 (point 2). Thus, a similar surface results in both cases. It can be seen by comparing points 4 and 5 that there is a slight decrease in ASA with deposition on the carbon surface in region IV.

Although the surface impurities accounted for a large portion of the ASA on some samples, it was impossible to detect them with conventional surface techniques (Auger, SEM Kevex, etc.) This is because the total bulk impurity concentration is <100 ppm and only a portion of the impurities are on the surface. Even though these surface impurities were undetectable by conventional means, it was desirable to determine the reactivity for pyrolysis of these impurity sites relative to the reactivity of the carbon ASA. In order to determine this, it was necessary to know the rate of propylene consumption by these sites and the number of impurity atoms available on the surface. The rate of propylene consumption was easily calculated by extrapolating the rate curves of Fig. 1 to the ordinate. The number of impurity atoms exposed at the surface was estimated by assuming, for the sake of simplicity, that all the impurity atoms on the surface are iron and that one oxygen atom chemisorbs on one impurity site. Each oxygen atom was assumed to occupy 0.0637 nm^2, i.e. the area occupied by an iron atom in its (100) plane[18]. The impurity specific rate constant for propylene cracking at 923 K over the 10% burn-off sample was estimated to be 7.89×10^{-5} cm/sec compared to 6.51×10^{-5} cm/sec over the active carbon sites.

4. CONCLUSIONS

The pyrolysis of propylene over a Graphon substrate is first order in propylene with an activation energy of 57 Kcal/mole. The activation energy is the same as that observed without a carbon substrate present. The rate curve for propylene consumption over a Graphon surface containing impurities showed that four processes were taking place during pyrolysis. These processes were: (1) rapid chemisorption of propylene on impurities and carbon active sites; (2) buildup of a surface hydrocarbon complex; (3) enhanced cracking and carbon deposition due to impurities; and (4) cracking on the carbon active surface area accompanied by carbon deposition.

The specific activity of the various surfaces as shown by the rate of propylene consumption is given in the following scheme: impurities > carbon active surface areas > quartz reactor surface > carbon basal plane.

The active surface area of the carbon was found to be catalytic for the pyrolysis of hydrocarbons. The active surface greatly enhanced the rate of cracking of hydrocarbons to elemental carbon which was deposited directly on the surface. The carbon was found to deposit on the active sites and become new active sites. Thus, the carbon deposit replicated the active surface area and was autocatalytic.

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