

CARBON AS AN OXIDATION CATALYST

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KEYWORDS Oxidative dehydrogenation, Carbon catalyst, Mechanism, Surface chemistry

INTRODUCTION

There are numerous reports in the literature that carbonized metal oxides [1-7], carbons [8] and quinone containing polymers [9,10] can function as oxidative dehydrogenation catalysts. These reports, in combination with earlier work by Roth et al. [11], which showed that carbons can catalyze paraffin dehydrogenation, prompted our interest in assessing the utility of carbons or carbonized metal oxides as light paraffin upgrading catalysts.

It appeared as though there may be a common mechanism or surface chemistry operating in that reported work, so we conducted an extensive review of the literature to help our understanding of the fundamental processes before initiating our work. The purpose of that review was to gain some understanding of the stability and nature of surface functional groups formed on oxidation of carbon surfaces under conditions commonly used in the oxidative dehydrogenation of hydrocarbons in order to interpret mechanisms and potential improvements in oxidative dehydrogenations over carbonaceous catalysts. Several very good reviews on the surface chemistry of carbon do exist, but these do not attempt to interrelate surface chemistry to oxidation catalysis [12-15]. These reviews were utilized extensively in the formulation of our conclusions.

The information which we found relevant to oxidation catalysis from the diverse sources of information on carbon surface chemistry is illustrated in Figure 1. This may be summarized as follows. Carbons heated in inert atmospheres to above 1000-1200°C contain only carbon at their surfaces. All hydrogen and oxygen containing functional groups decompose (degas) below these temperatures to yield water and volatile carbon oxides respectively [12-18]. In degassed graphite, the edges of the basal planes must be composed of carbon in which all of the potential valance orbitals are not satisfied. This chemistry is believed to extend to high surface area carbons as well where the structures are much less developed and the size of the graphitic sheets is very small. One basic question is, just what is the nature of this pure carbon surface? It is known that degassed carbons contain high concentrations of unpaired electrons on their surfaces (as much as 0.2 meq/gm) [14]. In addition, Donnet has proposed that aroxylic radicals may account for many of the free radicals observed on carbons which contain some chemisorbed oxygen [14]. Certainly the surface is rich in free radicals, but what is their geometric configuration and what chemistry do they exhibit?

Two geometric orientations of the edges are possible and these have been referred to as zigzag and armchair. The preference for a given configuration has been shown to be influenced by the atmosphere used in preparation of the surface. Dry conditions favor the armchair configuration and wet conditions favor the zigzag configuration. It is also believed that only these edges interact with oxygen. Apparently, oxygen does not penetrate and react within the lamellar structure [19].

Three possible electronic structures have been proposed [20,21] for the edge carbons in which all of the valance orbitals are not satisfied. These structures contain either (1) one unpaired electron (e.g. free radical), (2) paired electrons (e.g. divalent carbon or carbene), (3) adjacent unpaired electrons or triple bond character (e.g. benzynes).

All of these structures would be expected to interact with oxygen to produce chemisorbed oxygen. The electrical properties of the carbon change drastically as oxygen is chemisorbed. The thermoelectric power of graphite has been shown to be increase algebraically with oxygen concentration on the surface [16a].

Depending on the nature of the carbon structure and the conditions of reaction, one would expect to favor the production of different types of carbon-oxygen functionalities. Freshly degassed carbons begin to chemisorb oxygen at -40°C. Clean carbon surfaces, on contact with oxygen at as low as 200°C evolve volatile carbon oxides simultaneously with the formation of chemisorbed oxygen [17]. At this temperature carbon dioxide is the only gas evolved and about 1 molecule of carbon dioxide is evolved for each three oxygens chemisorbed on the surface [16b]. As the temperature of oxidation is increased, both the rate of chemisorption and volatile carbon oxide evolution increase. The maximum rate of chemisorption occurs at about 400°C [16]. Above 500°C, decomposition of chemisorbed oxygen species becomes significant [16b] and at about 650°C one molecule of CO₂ is evolved for each oxygen chemisorbed. Above 950°C chemisorbed oxygen species are not stable and very little steady state chemisorbed oxygen exists on the surface [16b]. Chemisorbed hydrogen is somewhat more stable and is not completely removed until about 1100°C [16c].

Walker has proposed that there exist two different kinds of reactive surface carbon species [16c]. Both species produce carbon monoxide on reaction with carbon dioxide at gasification temperatures (900-1100°C). One type produces more stable chemisorbed oxygen species $C<O>1$. The other is much more reactive and produces a less stable chemisorbed oxygen species $C<O>2$ which decomposes rapidly to gaseous CO and regenerates the free carbon surface. In a parallel reaction $C<O>2$ also converts to $C<O>1$ which decomposes much more slowly. The overall rate of gasification thus goes through a maximum and declines to a steady state rate as $C<O>1$ builds up on the surface. Hydrogen sources, such as H₂ or water inhibit the rate of gasification due to build-up of $>CH_2$ species which are more stable than carbon oxide surface species. Walker also showed that 2 hydrogens are adsorbed for each site that adsorbs 1 oxygen and he proposed that these sites were carbonyl like [22].

The chemical nature of chemisorbed oxygen has been studied extensively and several excellent reviews are available. Almost every conceivable oxygenated organic functional group has been proposed and detected on

carbon surfaces. Characterization has been done using infra-red spectroscopy, polarography and a variety of diagnostic wet chemical reactions [12,13,14,23].

Methods are well established for the quantitative estimation of acidic groups using selective titrations with bases of varying strength. However, there are some arguments about subtleties in distinguishing between carboxylic acid groups on adjacent vs isolated carbons [12,14]. Quantitative estimation of the content of other functionalities are less reliable and in most types of carbons only about 75% of the oxygen has been accounted for [12,24].

The nature of the functional groups on the surface is very important to the adsorption properties of the carbon and much effort has been devoted to relating functionality to selectivity for gas adsorption [12,15]. It has also been shown that catalyst preparation by impregnation with metal salts is very sensitive to the nature of the functional groups on the carbon surface [23].

The distribution of oxygen containing functional groups on carbon surfaces is dependent on the reagents used to produce the functional groups and the conditions under which the carbon is treated [12,13,14,23]. As our work deals with functionality relevant to oxidative dehydrogenation little discussion will be given on chemical oxidants at low temperatures, other than to say that treatments with strong oxidants, such as HNO₃ lead to very high concentrations of carboxylic acid groups on the surfaces [23]. As will be discussed later, such carboxylic functional groups decompose at the temperatures commonly used in oxidative dehydrogenation.

For a large number of commercial carbons, Studebaker has shown that the relative concentrations of carboxyl, phenol and carbonyl groups are about 3/1/1 respectively. Carbonyl groups represented about 18% of the total chemisorbed oxygen. However only 75% of all of the chemisorbed oxygen was accounted for [24a].

Donnet has shown that gasification of carbons with steam at 900°C yields distributions of carbonyl, lactone and hydroxyl groups that is constant and independent of the degree of gasification of the carbon. This indicates a definite mechanism and stoichiometry for steam gasification [14].

In relating oxygen functionality to oxidative dehydrogenation chemistry, one must consider the conditions under which the reaction is conducted, the rate of oxygen chemisorption, the co-production of volatile carbon oxides, the thermal and oxidative stability of different functional groups and the reactivity of the functional groups with hydrocarbons. Complicating reactions include direct reaction of hydrocarbons with free carbon surfaces, the formation of stable C-H species on the surface and the subsequent oxidation of C-H species on the carbon surface.

Much is known of the thermal stability of different surface functional groups. Table 1 summarizes the temperature ranges of thermal decomposition for the different functional groups and the corresponding gases evolved on decomposition [12-18]. We have previously shown that aromatic ketones and quinones stoichiometrically abstract hydrogen from alkylaromatics, such as tetralin, at 400°C [25]. Thus, one might expect that carbons which form such groups easily and retain them on their surfaces under oxidative dehydrogenation conditions would be good catalysts or potential oxygen carriers. It is interesting to note that the groups which would not be expected to stoichiometrically dehydrogenate hydrocarbons are either quite unstable (decomposing below 500°C) or very stable (decomposing above 700°C).

Putting together the known chemistry of carbon surfaces, reactivity of different organic oxygen functionalities and the observations on oxidative dehydrogenation catalyzed by carbonaceous surfaces, it is possible to propose a catalytic sequence of surface reactions which can explain how carbons can catalyze the oxidative dehydrogenation of hydrocarbons. This proposed mechanism is illustrated in Figure 2.

The desired sequence of surface reactions would be as follows.

- (A) Formation of a reactive free carbon surface, <C>_s
- (B1) Oxidation of the surface to produce an active carbonyl species, <C=O>_s
- (C) Stoichiometric dehydrogenation of the reactive hydrocarbon, forming surface hydrides, <CH₂>_s
- (D1) Regeneration of the catalyst by oxidation of surface hydrides

This step can also proceed directly to a free carbon surface or surface carbonyl species (A or B).

Side reactions which lead to low selectivity are as follows.

- (E) Excessive Coke Deposition
- (F) Over Oxidation of Surface Carbonyl Species
- (G) Thermal Decomposition of Surface Carbonyl Species
- (H) Over Combustion of Carbon-Overlayers to Pure Metal Oxides
- (B2) Direct Oxidation of Free Carbon Surface to CO and CO₂

Thus there are a number of competitive surface reactions which dictate catalyst selectivity.

- o Formation of the desired carbon-overlayer is required (A), yet over condensation of hydrocarbons with free carbon surfaces (E) leads to excessive coke formation and eventual loss of catalyst surface area.
- o Formation of the desired surface carbonyl species (B1) is competitive with over condensation (E), carbon-overlayer combustion (B2) and over-oxidation of the carbonyl species (F).
- o Oxidative dehydrogenation to produce the desired product (C) is competitive with surface carbonyl species thermal decomposition (G) and over oxidation of the surface carbonyl species (F).
- o Catalyst regeneration to remove surface hydride species (D1) may be excessive and can remove the carbon-overlayer (D2 or B2).

In the sequence A $\xrightarrow{\text{R-CH}_2}$ B $\xrightarrow{\text{O}_2}$ C, a parallel reaction A $\xrightarrow{\text{R-CH}_2}$ E can occur which leads to product loss by excessive coke formation and perhaps coke which is too labile toward combustion. Thus, catalysts which promote non-selective condensation may exhibit poor selectivity by promoting coke formation. Literature reports on metal oxide catalysts do indicate that excessive acidity of catalysts lead to poor selectivities because of excessive coke build-up and product cracking [6c].

In the sequence $B \xrightarrow{\text{oxidation}} C$, a parallel reaction $B \xrightarrow{\text{oxidation}} G$ (reaction G) can occur which leads to non-productive loss of surface carbonyl species and poor selectivity due to the eventual formation of CO_2 . As was discussed earlier, surface species such as carboxyl, lactone and lactol are less thermally stable than carbonyls and would be expected to thermally decompose much more readily than the desired surface carbonyl species. Unfortunately, another parallel side reaction, $B \rightarrow C \rightarrow F$ (thermal decomposition of <O>s) also can occur which would lead to non-productive loss of surface carbonyl species. Thus, high hydrocarbon partial pressures should enhance reaction C over competitive reactions G and F. Alternatively, high hydrocarbon partial pressures would appear to inhibit reactions G and F.

If the above proposed mechanism is correct, one should be able to produce, isolate and identify oxidized carbon surfaces which will stoichiometrically react with hydrocarbons to produce olefinic products in the temperature range of 400-500°C. To test this postulate, we obtained a series of different carbons, oxidized them under a variety of conditions, determined their thermal stability and reacted them with selective reagents to determine the reactive oxygen content of their surfaces. The results of those studies is the subject of this paper.

EXPERIMENTAL

The carbons used in this study were obtained from the following sources.

- Amoco AX-21 - Dr. K.K. Robenson of Amoco Corporation.
- Anderson AX-21 - Anderson Development Company, Adrian, Michigan
- Barneby-Sutcliff 207-C & 209-C - Barneby-Sutcliff Corp., Columbus Ohio.
- Darco activated carbon - American Norit Co. Inc.
- Animal Bone Charcoal - EM Sciences - Macalaster-Bicknell Co.
- Wood Charcoal - Matheson Colman & Bell Manufacturing Chemists
- PVDC Carbon - Dr. D.F. Quinn of the Royal Military College, Kingston, Ontario.
- Si/C carbon, whisker by-product - Dr. D. J. Rhodes of Advanced Composite Materials Corp.
- C60 Soot - MER Corporation.
- Graphite flake - Aldrich Chemical Co. Inc.

Thermogravimetric analyses were obtained on a DuPont Series 99 Thermal Analyzer, using ultra pure purge gases. Each analysis consisted of a sequence of three programmed heatings and is referred to as STPD.

- 1) Argon Purge 20°C/min 25 to 750°C Cool to 25°C
- 2) Air Purge 20°C/min 25 to 450°C Cool to 25°C
- 3) Argon Purge 20°C/min 25 to 750°C Cool to 25°C

The % active oxygen (<O>s) was estimated from the weight loss between 550 and 750°C in step 3.

The procedure for estimating the % active oxygen (<O>s), by chemical reaction, consisted of preoxidizing the material to be studied in air in a muffle furnace at 450°C for 15-60 min to provide about 30% burnoff of the carbon. The sample (0.2 to 0.4g) was then weighed into a 10cc tubing bomb and 1.4g of a reagent consisting of 48wt% tetralin, 4wt% 1-methylnaphthalene and 48wt% diphenylether was added. The tube contents were purged with N_2 then sealed. The tube was placed in a muffle furnace, set at 450°C, for the desired reaction time then removed from the furnace and quenched in a water bath. A sample of the liquid product was taken and analyzed by gas chromatography.

Oxidative dehydrogenation reactions were conducted at atmospheric pressure in a quartz down flow reactor. Reactions were carried out by feeding EB to the preheated quartz reactor bed, which was then blended with a mixture of 5% $\text{N}_2/95\% \text{O}_2$. Liquid samples were collected in a chilled trap (2°C), while gas samples were collected in collection tubes. Good liquid mass balances could be obtained at times on stream of greater than 20 min. Liquid analyses were aided by dilution of the liquid products with acetone containing 10.0% 3-hexanone as an external standard, this solvent also provided a means to overcome niscibility problems associated with water.

RESULTS AND DISCUSSION

Thermal stability of oxidized carbon surfaces - In the carbon community, a standard procedure has evolved for the characterization of carbons by programmed thermal decomposition is and referred to as TPD [16] and references therein. This procedure consists of linear programmed thermal decomposition (3°C/min) of the carbon being studied in nitrogen atmosphere from 300 to 1300°C coupled with simultaneous detection of CO , CO_2 and often water and hydrogen. Typically, CO_2 is predominantly evolved below 550°C. For almost all carbons the maximum rate of evolution of CO_2 occurs at 500°C and CO at 600°C [12]. Coltharp has shown that for a wide variety of carbons, the pattern of CO_2 evolution varies considerably, perhaps due to different conditions in which the carbons were oxidized. However, the patterns of evolution of CO were quite similar for diverse carbons [18].

Unfortunately, this procedure only provides the total amount and distribution of gases from the carbon surface. In its present form, it cannot be used to estimate the concentration of reactive chemisorbed oxygen that is needed for oxidative dehydrogenation catalysis. As discussed above, carbonyl groups (ketones and quinones) are the most likely oxygen containing species which can promote oxidative dehydrogenation of hydrocarbons. Therefore if one could estimate the concentration of such carbonyl species on carbon surfaces, it may be possible to predict the dehydrogenation activity of carbons. The content of carbonyl groups on carbon surfaces have been estimated to be about 18% of the total chemisorbed oxygen [12a].

From the known thermal behavior of different chemical functionalities on carbons, it may be possible to estimate the concentration of carbonyls by determining the weight loss or amount of carbon monoxide evolved from a given carbon in a specific temperature range. As shown in Table 1, carbonyl groups have reasonable thermal stabilities below 550 °C but decompose in the range of 550-750°C. Functional groups which decompose at low temperatures (<550°C) or at very high temperatures (>750°C) are not expected to be important in oxidative dehydrogenation catalysis. On this assumption, we conducted a series of thermal analyses on a variety of carbons to see if major differences could be observed in a systematic way.

The carbons we used are described in the experimental section. Their physical properties varied widely in terms of surface area, degree of carbonization and ash content. To evaluate their thermal behavior each carbon was pretreated at 750°C in oxygen free argon to clean its surface. Each carbon was then oxidized in diluted air (14.7% O₂) by programming to 450°C and cooling to room temperature in that atmosphere. The thermal decomposition profile of the oxidized carbon was then determined by programmed decomposition up to 750-800°C in oxygen free argon. The sequential programmed thermal decomposition analysis will be referred to as SPTD.

Table 2 summarizes the observed rates of weight loss in each cycle at 400°C and the estimated amounts of chemisorbed oxygen found as either CO₂ or CO assuming that weight loss below 550°C was primarily CO₂ and between 550 and 750°C oxidatively active carbonyls decomposed to evolve primarily CO, as discussed above.

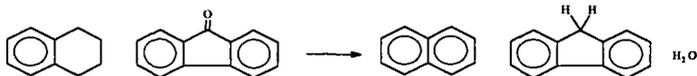
With the exceptions of animal bone charcoal and C60 soot the data appear to fall within the range of oxygen contents reported in the literature [12a]. The animal bone charcoal results may have been exaggerated due to the high correction factors necessary for this high ash content material. In the case of C60 soot it is believed that high contents of low molecular weight species vaporized from the sample simultaneously with the carbon oxide decompositions. The initial Argon cycle resulted in the loss of a great deal of weight in the temperature range in which a pure sample of C60 also rapidly volatilized. This result is interesting in that the C60 soot is believed to contain high concentrations of tubular fullerenes. This oxidation-thermal decomposition cycle may offer a route to the production of higher yields of lower molecular weight fullerenes from C60 soots.

In comparing the rates of weight loss in each cycle of the SPTD analyses 400°C, where the maximum rate of oxygen chemisorption has been reported [12a], it is interesting to note that only C60 soot showed a positive weight change at this temperature. There appeared to be two sets of sample behavior. Those with high ash (particularly alkaline ash) and those with low ash. For low ash samples, the surface area of the parent carbon offered the best correlation with the rate of weight loss. In the case of high ash samples, the rates of weight loss correlated well with ash content. However, two high ash samples had low rates of oxidation, silicon carbide by-product and coal derived charcoal (Darco). The majority of the ash constituents of the silicon carbide by-product was in fact SiC and would be expected to be inert. Coal charcoal ash is primarily silica-alumina and would not be expected to catalyze carbon oxidation. The other carbons ashes were found to be alkaline and would therefore be expected to catalyze such oxidations. Animal bone charcoal was not found to be highly alkaline but is composed primarily of calcium phosphate (hydroxyapatite) [26]. Calcium is known to be an active catalyst for carbon oxidation [16d].

On comparing the rates of thermal decomposition of oxidized carbons with the rates of oxidation in Table 2, it appears that carbons which oxidize rapidly also decompose rapidly. At this time it is not clear if ash components catalyze the thermal decomposition or they change the selectivity in the formation of different functional groups on the carbon surface during the oxidation cycle.

The results of these studies indicate that oxidized carbon surfaces can accommodate 1 to 10% by weight oxygen in the form of carbonyl functional groups. Such groups should have potential as stoichiometric oxidation reagents. In all cases the formation of these active groups occurs simultaneously with the oxidation of a portion of the carbon to volatile oxides. Thus, the selectivity for oxygen utilization in the formation of these groups will always be limited. This selectivity appears to be lower for carbons containing alkali or alkaline earth impurities. Thus supported carbons may require careful preparation. However, it may be possible to use carbons as oxygen carriers in which active oxygen species are formed in air then utilized as oxidation reagents in contact with hydrocarbons.

Measurement of the active oxygen capacity of carbons by stoichiometric reactions. Unfortunately, the STPD results does not give a quantitative measure of the reactive oxygen content of carbons. In past work involving hydrogen donor chemistry, we have described how it is possible to quantitatively measure either hydrogen abstraction capacity of a solid or hydrogen donor capacity of a liquid by a test chemical reaction. We showed that aromatic ketones and quinones stoichiometrically abstract hydrogen from alkylaromatics, such as tetralin, at 400°C [25]. Thus, one might expect that carbons which form such groups easily and retain them on their surfaces under dehydrogenation conditions would be good catalysts or potential oxygen carriers. We endeavored to use this same technique at 450°C to assess the potential of various carbons as dehydrogenation reagents and the results are presented in this section. The test reaction may be illustrated simply with model compounds as follows.



The results of model compound scoping experiments are presented in Table 3. It can be seen that the results are quite quantitative. However, the chemistry of quinones was not found to agree with proposals in the literature that quinones would convert to hydroquinones. Instead, we found that only one of the carbonyls of phenanthrene type quinones were active, as after hydrogen abstraction by the first carbonyl, the intermediate monocarbonyl rearranged to a stable monophenol which did not react further. Anthracene type quinones behaved like two independent carbonyls and did not form hydroquinones. Instead, they converted to dihydroanthracene. This compound was metastable under the reaction conditions and underwent some disproportionation.

In addition to stoichiometric hydrogen abstraction it was anticipated that some catalysis of hydrogen transfer or equilibrium dehydrogenation might occur. Roth reported that carbons supported on alumina were extraordinary catalysts which in some cases rivaled the performance of commercial supported noble metal catalysts [11]. Indeed, when oxidized carbons were tested with the test reagent, catalysis was observed. Thus, when attempting to relate the amount of naphthalene formed from tetralin in these tests, it was necessary to subtract out catalytic contributions of the carbons. This correction was possible by the inclusion of 1-methylnaphthalene in the reagent mixture which measured the kinetically parallel reactions of catalytic tetralin dehydrogenation and catalytic hydrogen transfer between tetralin and 1-methylnaphthalene. In addition corrections also had to be made for thermal isomerization of tetralin to 1-methylindan, the thermal dehydrogenation of tetralin and a small amount of hydrogenolysis of the diphenylether co-solvent.

Two methods of estimation were used. For low conversions of tetralin, direct stoichiometric calculations were employed. For high conversions of tetralin, the equilibrium distribution of tetralin/naphthalene/H₂ was calculated assuming that hydrogen lost in the formation of water was an indicator of the active oxygen content of the carbons.

Surprisingly, some carbons were almost as catalytically active as 5%Pd/charcoal for hydrogen transfer and dehydrogenation. A general observation was that highly graphitic carbons exhibited high catalytic activities and non-graphitic carbons exhibited high activities for stoichiometric reactions of active oxygen. Several carbons, when oxidized, were found to contain as much as 10wt% active oxygen. Petroleum cokes could also be oxidized to produce materials with as much as 5wt% active oxygen. Carbonized CaPO₃ catalysts produced during oxidative dehydrogenation studies were found to contain active oxygen contents (carbon only basis) that were comparable to some of the most active, highest capacity pure carbons examined. The results are summarized in Table 4.

CONCLUSIONS

The results of these studies indicate that oxidized carbon surfaces can accommodate 1 to 10% by weight oxygen in the form of carbonyl functional groups which are potential stoichiometric oxidation reagents. In all cases the formation of these active groups occurs simultaneously with the oxidation of a portion of the carbon to volatile oxides. Thus, the selectivity for oxygen utilization in the formation of these groups will always be limited. This selectivity appears to be lower for carbons containing alkali or alkaline earth impurities. Thus, supported carbons may require careful preparation. However, it may be possible to use carbons as oxygen carriers in which active oxygen species are produced in air and then utilized as oxidation reagents in contact with hydrocarbons. The mechanism of oxidative dehydrogenation over carbonaceous catalysts appears to be consistent with this chemistry.

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TABLE 1
THERMAL DECOMPOSITION OF ORGANIC OXYGEN COMPOUNDS

Functional Group	Decomposition Temp. Range (°C)	Gas Evolved
Carboxylic acid	200-600	CO ₂
Aldehyde	<400	CO
Lactone/Lactol	200-600	CO ₂ & CO
Ketone/Quinone	600-1000	CO
Phenol	600-1000	CO
Aromatic Ether	>700	CO
Anhydride	>700	CO ₂ & CO

TABLE 2
ESTIMATED REACTIVITIES AND OXYGEN CONTENTS OF CARBONS VIA STPD
(Ash free carbon basis)

Carbon	Rates of Weight Loss at 400°C (wt%/min)					Calculated % Chemisorbed O		
	Initial	After air	Argon-1			From CO ₂	From CO	Total
			Argon-1	Air	Argon-2			
C60 Soot	0	93	-4.78	0.72	-0.51	0.38	21.89	22.26
Animal Bone Charcoal	86	12	-5.24	-50.1	-15.7	22.47	15.38	37.85
Wood Charcoal	13	49	-4.82	-16.6	-2.37	3.31	8.40	11.71
PVDC Carbon	0	21	-0.72	-0.72	-0.37	1.61	4.61	6.22
Amoco AX-21	2	25	-1.51	-4.45	-0.24	2.57	2.55	5.12
Darco (20-40 mesh)	12	10	-0.84	-0.12	-0.56	1.15	1.70	2.84
Si/C By-product	34	8	-0.36	-1.36	-0.05	1.30	1.57	2.87
Barneby-Sutcliff 207C	3	15	-0.97	-6.29	-0.47	0.87	1.28	2.15
Graphite	0	2	-0.19	-0.07	-0.02	0.12	0.32	0.43

TABLE 3
Stoichiometry and Rate Constants for Reactions of Model Compounds With the Test Reagent

Compound	Mol. Wt.	Wt% O	Rx Time (min)	% Conv	Hydrogen Consumption		Reaction Rate Constants (1000xmmol prod/g.rgn/g.matrl/min)		
					Theory	Observed	k _{mind}	k _{usd}	k _{met}
Benzophenone	182	8.8	30	7.2	4	4.3	21	21	0
Benzophenone	182	8.8	60	27.8	4	4.1	33	21	0
Fluorenone	180	8.9	60	16.4	4	4.9	21	54	0
9-Anthrone	194	8.2	60	97	4.4	4.7	28	100	1
Anthraquinone	208	15.4	30	97	6.6	6	24	364	1
Phenanthrenequinone	208	15.4	30	100	4.2	4.2	10	255	1
Bi2O3 (42%)*	466	10.3	60	6	4.6	6	31	41	0
V2O5 (52%)*	182	17.6	60	4	3.9	3.9	20	94	2

* Metal oxides were supported on inert carriers, values shown are for pure metal oxides

TABLE 4

COMPARISONS OF THE ESTIMATED VALUES FOR ACTIVE OXYGEN CONTENTS OF CARBONS
(Weight % <O>s , ash corrected values)

Material	Rx Time		Estimated wt% <O>s		
	(min)	%	Stoich.	Equil.	SPTD
			Carbon		
PVDC	60	100	4.8	4.6	
AX-21 (41)	240	97	25.6	28.8	2.6
AX-21 (41)	60	97	7.1	7.0	2.6
AX-21 (41)	60	97	6.9		2.6
AX-21 (41)	30	97	2.0		2.6
Used AX-21 (41)	60	97	3.2		
AX-21 (93)	60	71	16.7		
Barney-Sutcliff 207c	240	95	8.2	6.0	1.3
Barney-Sutcliff 207c	60	95	3.9	1.7	1.3
Barney-Sutcliff 207c (dry)	30	95	2.8	1.3	
Barney-Sutcliff 207c (wet)	30	95	2.2	1.3	
Barney-Sutcliff 209c	60	95	1.0		
Darco (20-40 mesh)	60	82	6.1	5.2	1.7
Darco (20-40 mesh)	60	82	2.6	1.7	
Norit Activated Carbon	60	84	2.2		
Wood Charcoal	60	78	6.6	8.4	
Animal Bone Char	60	2	44.8	15.4	
Petroleum Shot Coke	60	100	5.3		
Petroleum Sponge Coke #1	60	100	4.1		
Petroleum Sponge Coke (as rec)	60	100	1.1		
			<u>No Cat. Max.</u>		
C60 Soot	60	100	0.3	9.4	21.9
Si/C By-product	60	52	-1.6	2.0	1.6
Graphite	60	100	-1.8	0.2	0.3
Graphite	60	100	-1.7	0.2	0.3
C/CaPOx (Run 228-4)	60	2.2	1.4	13.4	
C/CaPOx (Run 228-5)	60	1	-14.1	14.4	
CaPOx (Starting material)	60	0	-0.2	0.0	

FIGURE 1

CHEMISTRY OF CARBON SURFACES

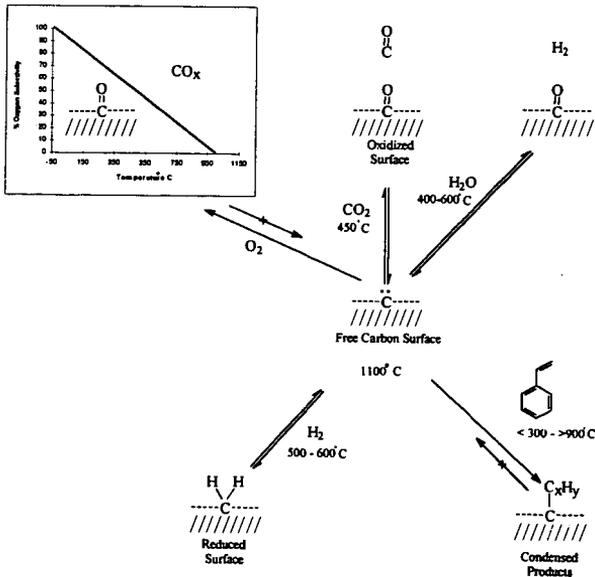


FIGURE 2
 CATALYTIC SEQUENCE IN OXIDATIVE DEHYDROGENATION

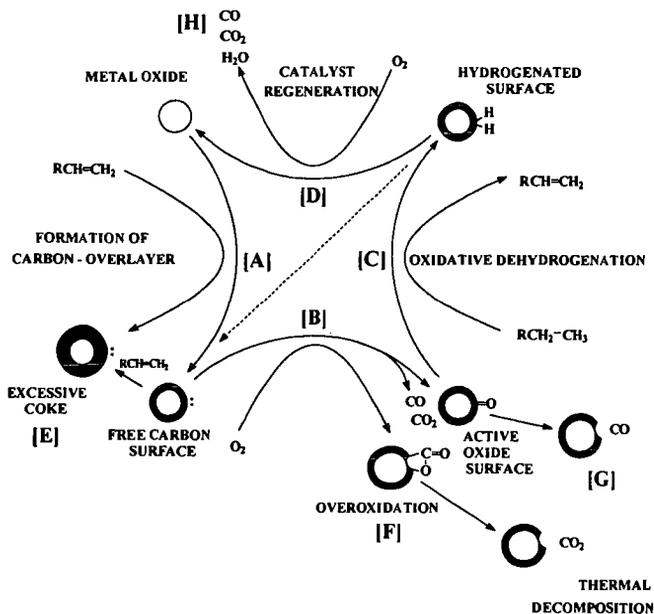


FIGURE 3
 REACTIONS OF THE TEST REAGENT

