Tableau 2. Comparaison des composés de premier stade graphite–potassium, graphite–mercure–potassium et graphite–thallium–potassium

Formule	KC_8	$KHgC_4$	$KTl_{1,5}C_4$
Prise de masse	41%	499%	720%
Dilatation selon l'axe c	59%	204%	261%
Distance interplanaire I_c	5,32 Å	10,16 Å	12,08 Å
Couleur	Jaune (bronze)	Rose (cuivre)	Blanc (vermeil)
Densité cristallographique	2,02	4,49	5,16
Rapport C/M	8	2	1,6

Dans le Tableau 2, nous comparons les trois composés de premier stade KC_8, $KHgC_4$ et $KTl_{1,5}C_4$.

Le composé ternaire de second stade graphite–thallium–potassium a pu être également observé et isolé. Il s'agit d'un composé rose de période d'identité I_c = 15,48 Å (= 12,08 + 3,35). La Fig. 2 et le Tableau 3 rassemblent les réflexions 00*l* de ce ternaire, dont la formule est voisine de $KTl_{1,5}C_8$.

D'une façon analogue, l'alliage de composition $RbTl_{1,5}$ s'insère dans le graphite, mais le phénomène semble cependant plus complexe, car il apparaît toujours un mélange de deux phases de premier stade de périodes d'identité respectives 12,65 et 13,40 Å. L'étude de ce phénomène doit être approfondie pour permettre de connaître la composition exacte du mélange et d'obtenir éventuellement la séparation de ces deux phases.

Tableau 3. Réflexions 00*l* du composé graphite–thallium–potassium de second stade

00*l*	d (Å)	I
001	15,50	m
002	7,75	m
003	5,17	m
004	3,88	f
005	3,09	F
006	—	0
007	2,21	m
008	1,93	F
009	1,72	F
0010	1,54	F
0011	1,41	m

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Oxygen chemisorption on as-received and acid-treated activated carbons

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The chemisorption of oxygen on activated carbons is important since it affects the behavior of the activated carbon when it is subsequently used in adsorption of gases and liquids. For example, the formation of oxygen functional groups on carbon sites converts these sites from a hydrophobic to a hydrophilic character[1]. The formation of acidic oxygen functional groups enhances the uptake of ammonia from water[2] but decreases the uptake of phenol from water[3]. Therefore, analytical techniques which can shed light on the phenomenon of oxygen chemisorption on carbon will be of interest. In this letter, we show the utility of the thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) techniques for following oxygen chemisorption on three as-received and acid-treated activated carbons. The carbons were in granular form and were supplied by three different manufacturers.

The TGA apparatus was constructed in this laboratory using a Cahn RG weighing mechanism. A sample weight between 50 and 100 mg was held in a quartz sample pan. Prior to studying oxygen chemisorption, the carbon sample was outgassed at 1173 K in the TGA apparatus under a vacuum of 1.3×10^{-3} Pa. The apparatus and operating procedure are described in detail elsewhere[4].

For the DSC apparatus, a cell was used in conjunction with a cell base module II and a 990 Thermal Analyzer—all from Dupont. About 10–12 mg were placed on an aluminum sample pan. Prior to studying oxygen chemisorption, the carbon was outgassed at 873 K in the DSC apparatus in a flowing stream of ultrahigh purity N_2. The apparatus and operating procedure are described in detail elsewhere[5].

Chemisorption of oxygen was studied on the outgassed as-received activated carbons and also on outgassed samples which had been acid treated to remove most of the inorganic impurities. Acid treatment consisted of washing with concentrated HF at 333 K, followed by thorough washing with hot distilled water and drying. Surface areas of the as-received and acid-washed carbons were measured (BET) using N_2 adsorption at 77 K. Table 1 summarizes data on the three activated carbons used. Acid

Table 1. Ash contents and surface areas in as-received and acid treated activated carbons

	Original	Acid-treated
Ash contents, %		
A	8.25	0.40
B	5.66	0.75
C	1.57	0.55
Nitrogen surface areas, m^2/g		
A	1193	1265
B	1002	1117
C	1120	1177

Table 2. Major inorganic elements in as-received activated carbons

Constituents in ash	Content, wt% A	B	C
Al_2O_3	3.10	32.0	12.8
SiO_2	71.2	41.0	32.2
MgO	0.75	0.85	1.00
CaO	2.15	2.25	2.20
Fe_2O_3	3.40	7.60	33.6
Na_2O	11.9	1.70	1.16

treatment is found to increase surface area by 10% or less. Table 2 presents analyses for major elements in the as-received carbons.

Figure 1 presents TGA results for weight gain when the activated carbons were exposed to 10^3 Pa of O_2 at 413 K. After 2 hr, weight gain is essentially complete for all samples. As-received sample A chemisorbs oxygen much more rapidly than samples B and C at short times and has about a 4-fold larger capacity for oxygen chemisorption at equilibrium, even though its surface area is only 6.5–20% higher than the other samples. Acid washing of the carbons produces variable effects, ranging from a marked decrease in rate of and capacity for oxygen chemisorption on sample A to no effect on sample B.

Figure 2 presents DSC results for heat released when the activated carbons were exposed to 10^5 Pa of air at 413 K. Note that the pressure of O_2 was about twenty times higher than that used in the TGA runs. Most effects are similar to those reported for the TGA runs. The exception is that there is now clearly a difference in the interaction with O_2 of as-received and acid-washed sample B. This difference may have been brought out by using a lower outgassing temperature prior to DSC measurements, working at the higher O_2 pressure, or it may mean that the enthalpy of oxygen chemisorption (cal/mole O_2 adsorbed) is different on the as-received and acid-washed samples.

Results in Figs. 1 and 2 can be compared with the level and

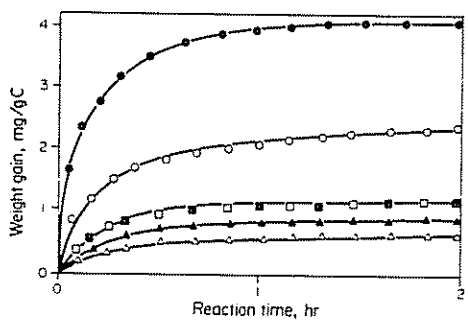

Fig. 1. Weight gain upon exposure of activated carbon A, ●; B, ■; and C, ▲: to 10^3 Pa of O_2 at 413 K. Open symbols are for the acid washed samples.

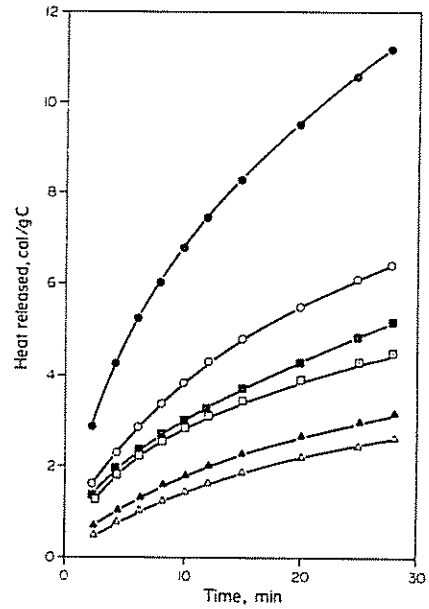

Fig. 2. Heat released upon exposure of activated carbon A, ●; B, ■; and C, ▲: to 10^5 Pa of air at 413 K. Open symbols are for the acid washed samples.

type of inorganic constituents present in the activated carbons. It appears that alumina and silica (probably derived primarily from clays and quartz) are not active catalysts for oxygen chemisorption. It further appears that iron oxide (probably derived primarily from pyrite) is not particularly active. This is consistent with the findings in this laboratory that kaolinite, quartz, pyrite and siderite are poor catalysts for the gasification of carbon by O_2[6]. On the other hand, carbon A appears to be particularly active for the chemisorption of oxygen because of the presence of a large concentration of sodium. Most of the sodium is expected to be removed by treatment in HF, resulting in a large decrease in the activity of the carbon to chemisorb oxygen, as is observed. Studies in this laboratory have shown that sodium is a particularly active catalyst for the gasification of carbon by O_2[7]. A substance active for catalyzing gasification of carbon in O_2 is also expected to be active for catalyzing oxygen chemisorption on carbon[8].

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Carbon as a support for catalysts—IV. Modification of molecular sieve character of glassy carbons by varying heat treatment temperature

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In a recent publication it was shown that glassy carbons having different molecular sieve characteristics can be produced by changing the proportions of carbon-yielding binder (furfuryl alcohol, FA), liquid pore former (diethylene glycol, DEG), dispersing agent (Triton X-100), and polymerization catalyst (*p*-toluene sulfonic acid, PTSA) in the original mix[1]. It will be shown in this letter that molecular sieve character can also be altered by varying the heat treatment temperature (HTT) of the glassy carbon.

Formulations for the production of the two samples used in this study are given in Table 1. The procedure used to prepare the 973°K glassy carbon samples is fully described in a recent publication[1]. Further heating of the samples to different temperatures up to 1773 K was conducted in an Ar flow using a heating rate of 10°K/min and a soak time at maximum temperature of 2 hr.

As discussed, when a liquid pore former is included in the formulation it is possible to not only produce a 973°K glassy carbon containing super micropores exhibiting molecular sieving but to also superimpose a pore system of larger size exhibiting a narrow distribution[1, 2]. For samples 1 and 2 the 973°K carbons had an average pore diameter (D_m) in the large pores of about 10 nm. These D_m values, as measured by mercury porosimetry, were essentially unchanged upon heating the glassy carbons to temperatures up to 1773°K. Also, as seen in Table 2, heat treatment has little effect on the pellet density and pore volume in the pores larger than 6 nm in diameter, as measured by mercury porosimetry. On the other hand, as seen in Table 2, heat treatment above 973°K results in major changes in surface areas measured by CO_2 adsorption at 298°K and N_2 adsorption at 77°K. The CO_2 surface area increases upon heat treatment from 973 to 1173°K and then decreases upon heat treatment to higher temperatures. The N_2 surface area monotonically decreases with increasing HTT above 973°K. The ratio of CO_2 area to N_2 area is indicative of the extent of molecular sieving in pores of about 0.5 nm in thickness in carbons, as previously discussed[3]. Thus, by varying HTT it is possible to alter the extent of molecular sieving in the glassy carbons over a wide range.

At HTT around 1673–1773°K the CO_2 and N_2 areas closely approach each other. This means that the thickness of the slits in the super micropores has been reduced to an extent that CO_2 at 298°K can no longer diffuse through them at a measurable rate. The N_2 surface areas for the 1773°K samples agree closely with the areas predicted for the large pore system from the equation

Table 1. Formulations for production of samples

Sample	FA, cm³	DEG, cm³	Triton X-100, cm³	PTSA, g
1	100	25	75	11.3
2	100	25	85	11.3

Table 2. Effect of heat treatment on properties of carbons

HTT, K	Surface area, m²/g		CO_2 Area / N_2 Area	Pellet density g/cm³	Volume in large pores cm³/g
	CO_2	N_2			
			Sample 1		
973	830	420	1.98	1.185	0.159
1173	994	282	3.52	1.192	0.162
1273	972	126	7.71	—	—
1373	513	92	5.57	1.217	0.161
1573	154	81	1.90	1.211	0.164
1673	72	72	1.00	—	—
1773	52	67	0.78	1.206	0.163
			Sample 2		
973	781	454	1.72	1.125	0.181
1173	846	384	2.20	1.178	0.181
1373	377	97	3.88	1.183	0.179
1573	156	87	1.79	1.171	0.180
1773	72	90	0.80	1.154	0.180

for cylindrical pores, that is area = (4) (volume in large pores)/(D_m). This is expected following the disappearance of the open super micropores.

This study thus shows that great flexibility exists in the preparation of glassy carbons as catalyst supports. If desired, samples can be prepared which have a system of large pores superimposed on an open super micropore system. On the other hand, samples can also be prepared which only have an open system of large pores. The choice of support will depend upon the size of the reactant and product molecules for the reaction to be catalyzed. If the reaction involves large molecules, such as in the hydrodesulfurization of heavy oils or liquefaction of coal, a glassy carbon having pores of only a large size will be chosen. If on the other hand, a selective catalysis reaction is of interest, such as selective hydrogenation of CO to low molecular weight organics, the presence of a super micropore system will be necessary.

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Cationic grafting of poly(tetrahydrofuran) onto the surface of carbon black

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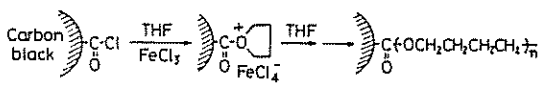
It has been well known that the organic compounds containing acid chloride group (COCl) or sulfonyl chloride group (SO_2Cl) act as cocatalyst in the polymerization of tetrahydrofuran (THF) catalyzed by metal halides[1]. Aoki *et al.*[2] have investigated the cationic grafting of poly-THF onto the polymers containing COCl groups or SO_2Cl groups with the use of anhydrous ferric chloride ($FeCl_3$) as catalyst. Furthermore, the cationic graft-polymerization of THF onto halogenated polymers has been studied in the presence of various catalysts[3,4].

On the other hand, the presence of carboxyl groups on the surface of carbon black has been supported in the literatures[5, 6]. It has been reported that the carboxyl groups easily react with thionyl chloride to give COCl groups on the surface[7,8].

In this communication, the cationic grafting of poly-THF onto the carbon black containing COCl groups (COCl-carbon black) was investigated with the use of $FeCl_3$ and COCl-carbon black as catalyst and cocatalyst, respectively.



Carbon blacks used were Philblack O, Carbolac 1 and FW 200. Philblack O was extracted with benzene by use of a Soxhlet extractor to remove the resinous substances present on the surface. These carbon blacks were dried *in vacuo* prior to use. Tetrahydrofuran was dried by refluxing over metallic sodium and distilled by a general method. Guaranteed reagent grade $FeCl_3$ from Wako Pure Chemical Ind., Ltd. was used without further purification. The carbon black containing COCl groups was prepared by the reaction of carbon black with thionyl chloride in benzene according to the method given in the literatures[7, 8].

In a 100 ml tear-drop type flask, the polymerization of THF (15.0 ml) was carried out using $FeCl_3$ (0.5–1.5 g) as catalyst in the presence of COCl-carbon black (1.0–2.0 g). The reaction mixture was stirred with a magnetic stirrer. After the polymerization at 30°C, the resulting polymer was precipitated by pouring a reaction mixture into a large amount of methanol containing a few percent of aqueous solution of hydrochloric acid [2].

The content of carboxyl groups on the surface of carbon black was determined according to the method of Rivin[9] and the results were shown in Table 1. Channel blacks such as Carbolac 1 and FW 200 contain more carboxyl groups than furnace black such as Philblack O. The carboxyl groups on the surface reacted almost quantitatively with thionyl chloride to give COCl groups.

The results of the polymerization of THF catalyzed by $FeCl_3$ in the presence of COCl-FW 200 are shown in Fig. 1. As is seen in Fig. 1, the polymer yield linearly increases with the increase of the initial content of COCl-FW 200. Therefore, it was found that COCl-FW 200 has a cocatalytic effect on the polymerization of THF.

The polymerization of THF was also carried out in the presence of various COCl-carbon blacks and the results are summarized in Table 2.

Although it has been reported that THF can polymerize in the presence of $FeCl_3$ of high concentration in the absence of cocatalyst[2], the polymer yield was slight. Untreated carbon black had no effect on the polymerization. On the other hand, in the presence of COCl-channel blacks the polymerization was accelerated. Accordingly, the cocatalytic effect of COCl-Carbolac 1 and COCl-FW 200 on the polymerization was apparent. On the contrary, no significant effect of COCl-Philblack O as cocatalyst

Table 1. The content of carboxyl groups on the surface of various carbon blacks

Carbon black	Specific surface area (m^2/g)	COOH groups (meq/g)
Philblack O (HAF)	79.6	0.04
Carbolac 1 (HCC)	839.2	0.54
FW 200 (HCC)	460	0.61