

CARBON AS A SUPPORT FOR CATALYSTS—III

GLASSY CARBON AS A SUPPORT FOR IRON

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Abstract—As described in the Hucke patent, glassy carbons containing not only open pores of molecular size but also pores in the transitional or macropore range can be produced from appropriate formulations. The formulation always consists of a carbon-yielding monomer, an organic to yield larger pores upon its removal once the monomer has been partially polymerized, and a polymerization catalyst. It may contain a dispersing agent, depending upon the size of the larger pores which is desired. In this study, furfuryl alcohol was the monomer. Great flexibility is shown to exist in the total surface areas of the carbons which can be produced, degree of carbon molecular sieving in the super micropores, and pore volume and pore size in the larger pores following polymerization and carbonization steps. Different ways of adding iron into the mix are explored which also can have pronounced effects on the nature of the porosity in the final carbons. Further modification is shown upon addition of potassium or boron into the mix. Carbons produced are expected to have potential as catalyst supports.

1. INTRODUCTION

Carbon is becoming increasingly important as a support for metal catalysts as the field of heterogeneous catalysis grows. Most often activated carbons are used because they are relatively inexpensive and provide a high surface area support. However, these carbons are invariably associated with inorganic impurities which, in some cases, may poison the catalyst and, in other cases, may catalyze unwanted side reactions. Moreover, activated carbons usually have a polymodal distribution of pores whose diameters vary from a molecular dimension to several hundred nanometers. Depending upon the sizes of the reactant and product molecules, a part of the area contained in smaller pores and, hence, the catalyst contained in such pores may be inaccessible for the reaction. There is thus interest in the production of relatively pure carbons with desired shape, porosity, pore size distribution, and surface area.

The use of carbon, in particular glassy carbon molecular sieves, as a support material for transition metals in the CO/H₂ synthesis reactions could offer improvements as a new catalyst for hydrocarbon production. First, they could affect product selectivity by altering diffusivities of hydrocarbons through these porous solids. The presence of wide variations in diffusivity can significantly affect the rates of different reactions, and such behavior could result in a large change in selectivity in the Fischer-

Tropsch reaction. The performance of shape selective reactions has already been demonstrated by carbon sieves[1]. Secondly, since carbon is an electrical conductor,[§] it can facilitate electron transfer to or from metal crystallites in contact with its surface. Thus, alkali metals added to carbon-supported transition metals may donate electrons to the transition metals through the carbons[3] and thereby alter activity and selectivity properties. Finally, glassy carbons have additional interest since they are very hard and resistant to erosion.

Iron is one of the most commonly used metal catalysts for CO/H₂ synthesis reactions. In this study we have used it supported on monolithic glassy carbon pellets with controlled porosity. To produce these carbonaceous materials, we have utilized the method outlined in the Hucke patent[4]. The iron was introduced into these systems either by the standard incipient wetness technique[5] or by adding it to the starting mix. The total surface area, pore size distribution, pellet density, chemisorption of CO and H₂ onto the iron, and iron crystallite sizes have been measured for these carbon-supported iron samples.

2. EXPERIMENTAL

2.1 Sample preparation

There are four basic ingredients for preparing monolithic glassy carbon pellets with controlled porosity, namely: a carbon-yielding binder, a liquid pore former, a dispersing agent and a consolidating agent or polymerization catalyst[4]. The carbon-yielding binder is an organic substance which when heated in a non-oxidizing

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[§]The electrical conductivity of glassy carbons varies with heat treatment temperature and amount of iron added[2].

2.4 X-Ray diffraction

CuK α radiation was used to determine the bulk chemical state of the metal in the samples and to calculate the average crystallite size of the iron. Large crystallite size α -Al $_2$ O $_3$ was used as an internal standard to correct for instrumental broadening in crystallite size determinations.

2.5 Chemisorption measurements

Uptakes of CO and H $_2$ were measured at 298 K on fresh reduced samples in a glass, mercury-free volumetric system, nearly identical to a system described previously[5]. The procedure used to measure the isotherms will be described elsewhere[6].

2.6 Materials

The chemicals used for preparing the glassy carbon pellets were obtained as follows: PEG and PTSA, Matheson, Coleman and Bell; Triton X-100, Ruger Chemical Company; FA, Quaker Oats Company; reagent grade oxalic acid and glycerol, Fisher Scientific; reagent grade Fe(NO $_3$) $_3$ ·9H $_2$ O, H $_3$ BO $_3$, KNO $_3$, HNO $_3$ and HCl, Baker; and 1-1' ferrocene dicarboxylic acid, Aldrich Chemical.

3. RESULTS AND DISCUSSION

Surface areas, pore volumes, pellet densities and D_m values of various carbons prepared in this study are given in Table 2. For each sample S_{CO_2} is larger than S_{N_2} . This means that the samples contain micropores in which N $_2$ adsorption at 77 K is restricted due to activated diffusion, indicating the presence of molecular sized pores of about 0.5 nm in thickness[7]. Superimposed on this presence of molecular sized pores is a pore system of much larger size whose distribution was measured by

mercury penetration under pressure. For samples studied in this work, pore volumes in the larger pores (V_p) vary from 0.05 to 0.57 cm 3 /g; pellet densities, from 0.80 to 1.43 g/cm 3 ; and D_m values, from 8 to 11,700 nm. Therefore, using the Hucke method, one can prepare glassy carbons with desired porosity, surface area, and pore volume by choosing the appropriate formulation and experimental conditions.

Comparison of properties for samples 5, 16 and 17 shows that major changes in certain properties can be effected by varying the starting formulation. In particular, addition of a dispersing agent to the formulation yields a marked decrease in D_m as seen by comparing samples 16 and 17 with sample 5. At the same time there is little change in the nature of the microporosity as given by S_{CO_2} and S_{N_2} . The magnitude of D_m can be important when glassy carbon is used as a catalyst support, since the size of the "feeder" pores affects the diffusion rate of reactant to the micropores and, hence, catalyst utilization. Addition of about 2% Fe to samples 5 and 16 produces some changes in properties. In particular, for sample 16 V_p is increased substantially, accompanied by a tripling of D_m . However, D_m still remains about two orders of magnitude smaller than that for the iron-containing sample 5. When Triton X-100 was used without PEG (sample 17), we could not prepare the iron-containing sample by adding Fe(NO $_3$) $_3$ ·9H $_2$ O to the mix. That is, during the thermal setting step there was separation of the sample inside the mold. This phenomenon was avoided when PEG was present in the mix as in sample 16.

The use of HCl as the consolidating agent for sample 5 instead of PTSA produced some changes in molecular sieving and in D_m as shown by sample H5. Both HCl and PTSA are strong acids and thus can polymerize FA at

Table 2. Properties of the glassy carbon samples

Sample	HTI, K	S_{CO_2} m 2 /g	S_{N_2} m 2 /g	$\frac{S_{CO_2}}{S_{N_2}}$	V_p cm 3 /g	D_m nm	Pellet density g/cm 3	Metal Loading, wt%
5	773	918	525	1.7	0.42	1,750	0.82	nil
5	973	938	528	1.8	0.38	2,035	0.89	nil
5	1273*	952	301	3.2	0.37	2,303	0.91	nil
H5	773	816	392	2.1	0.43	4,070	0.87	nil
5-Fe	773	650	494	1.3	0.43	1,522	0.85	2.0% Fe
5-Fe	973	949	499	1.9	0.38	1,750	0.94	2.0% Fe
05-Fe	773	605	106	5.7	0.39	3,500	0.89	2.5% Fe
16	773	816	466	1.8	0.23	8	0.94	nil
16	973	816	470	1.7	0.31	11	1.02	nil
016	973	748	23	33	0.05	13	1.43	nil
16-Fe	773	---	---	---	0.42	24	0.83	2.2% Fe
16-Fe	973	986	525	1.9	0.42	29	0.91	2.2% Fe
016-Fe	773	1013	159	6.4	0.09	10	1.14	2.5% Fe
N16-Fe	773	990	3	330	0.07	11	1.24	2.0% Fe
17	773	898	493	1.8	0.43	27	0.80	nil
17	973	917	489	1.9	0.38	28	0.90	nil
X-Fe	973	620	378	1.6	0.29	11,666	1.09	3.3% Fe
X-Fe-0.025K	973	666	350	1.9	0.39	7,960	0.97	3.4% Fe, 0.09% K
X-Fe-0.25K	973	490	328	1.5	0.46	7,960	0.97	3% Fe, 0.96% K
X-Fe-1K	973	272	195	1.4	0.45	9,722	0.99	2.7% Fe, 3.6% K
X-Fe-1.75K	973	357	169	2.1	0.49	9,722	0.99	2.2% Fe, 5.8% K
X-Fe-B	973	748	367	2.0	0.57	10,938	0.85	2.5% Fe, -2% B
SX	973	850	453	1.9	0.50	5,000	0.84	nil
SX	2073	2.8	1.3	2.2	0.46	5,469	0.90	nil
SX-B	973	782	414	1.9	0.55	2,823	0.84	-2% B

* Then treated in H $_2$ at 1223 K

room temperature. However, the use of oxalic acid (a weaker acid) as a consolidating agent requires an increase in polymerization and thermal setting temperature in order to achieve an acceptable product. The use of oxalic acid in the preparation of sample 16 instead of PTSA leads to a major increase in molecular sieving and pellet density and a major decrease in V_p .

When oxalic acid was used together with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, it was possible to polymerize the mix at room temperature and use the same thermal setting cycle as that used in the case of PTSA or HCl addition. This is because $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, being an acidic compound, increases the total acidity of the consolidating medium. The use of oxalic acid in samples 5-Fe and 16-Fe instead of PTSA resulted in samples exhibiting greater molecular sieving and variable changes in V_p and D_m , as shown by samples 05-Fe and 016-Fe.

For sample 16, when 1-1' ferrocene dicarboxylic acid was used to add iron, a stronger acid such as HNO_3 was needed as the consolidating agent. In addition, polymerization and setting were carried out at higher temperatures as described earlier. Major changes in properties result for sample N16-Fe when compared to sample 16-Fe. That is, molecular sieving is increased by over two orders of magnitude and V_p and D_m are reduced. By contrast, properties are changed less when compared to sample 016-Fe.

In the X-Fe series, both glycerol and PEG served as pore formers. As shown by a comparison of X-Fe to 05-Fe, this resulted in a further increase in D_m and a sharp decrease in the extent of molecular sieving. The addition of potassium or boron to the X-Fe samples primarily resulted in an increase in V_p and a decrease in D_m .

The formulation of sample 5 also has been modified in sample SX by the addition of glycerol as an added pore former. This addition produces an increase in D_m and V_p , with little change in the degree of molecular sieving. As discussed previously [8], if the low temperature glassy carbon samples are heated to higher temperatures there is a progressive decrease in surface area with little change in V_p and D_m . This is again shown when sample SX was heat treated to 2073 K. That is, heat treatment to elevated temperatures results in a progressive closing of the micropores in the glassy carbon. Such closing might be desired if one is concerned about catalyzing a reaction involving large molecules for which the micropores would be inaccessible. The addition of boron to sample SX produces a decrease in D_m but a negligible change in V_p or molecular sieving.

The possibility of superimposing a macropore volume having a narrow pore size distribution around a chosen pore size onto a micropore volume is well demonstrated in Fig. 1. As one proceeds from sample 17 to 5 to SX heated to 973 K, there is a major increase in D_m with little change in V_p or the extent of molecular sieving. Samples can also be produced with D_m values in the 100–1000 nm range, if desired, as previously shown [8].

Before using these iron-containing catalysts in CO/H_2 synthesis reactions or for chemisorption measurements, the iron must be reduced. Initial reduction studies were

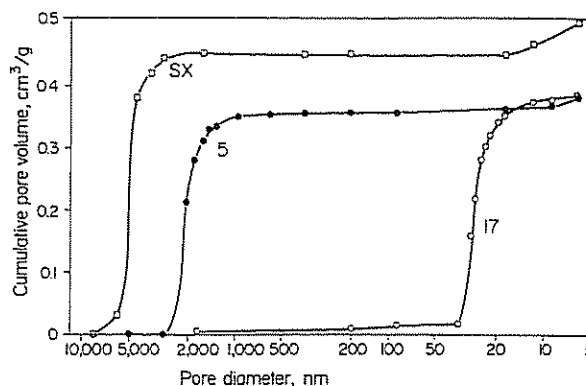


Fig. 1. Narrow pore size distributions exhibited by various glassy carbon supports heated to 973 K.

conducted in 0.1 MPa of flowing H_2 at 723 K for 16 hr. Reduction of the samples prepared using PTSA as the consolidating agent resulted in no changes in the pore volume or surface area of the glassy carbon. However, when the consolidating agent was either oxalic acid or HNO_3 , reduction brought about major changes in properties of the glassy carbon. That is, as seen in Table 3, molecular sieving decreased, V_p increased, and pellet density decreased. Obviously, in these samples iron has catalyzed the C- H_2 gasification reaction leading to the production of methane and an opening up of the micropore structure.

X-ray diffraction studies, summarized in Table 4, enabled the identification of the major iron compound in the original and reduced samples. For original (unreduced) samples 05, 016 and N16, Fe_3O_4 was identified as the major iron compound; and from the (311) diffraction peak an average crystallite size ranging from 13 to 27 nm was estimated. For the original X-Fe series, α -Fe was the major compound. Note that these samples were taken to 973 K where apparently Fe_3O_4 was reduced by carbon. Following reduction, α -Fe was identified as the major constituent in these samples, with an average crystallite size ranging from 25 to 33 nm. In the reduced X-Fe samples, the presence of potassium did not result in a significant change in crystallite size of α -Fe. Clearly, a portion of the iron is present as large crystallites.

For samples 5-Fe and 16-Fe, where PTSA was used as the consolidating agent, iron in the original samples was present as monoclinic pyrrhotite (Fe_7S_8), with an average crystallite size of 8–10 nm. In the samples treated in H_2 , α -Fe was identified by X-ray diffraction, with an average crystallite size ranging from 21 to 47 nm. However, the lack of catalytic activity of the iron phase for carbon gasification or for the CO/H_2 reaction [9], as well as inability to chemisorb either CO or H_2 (Table 5), suggests that pyrrhotite was not completely reduced to α -Fe in these samples. This is further substantiated by results summarized in Table 6. That is, samples 5 and 16 treated in H_2 at 723 K for 16 hr still contained considerable sulfur, as measured by the Leco combustion method followed by iodometric titration.

Sample 5, made with PTSA as a consolidating agent and seeing a HTT of 973 K, was subsequently impregnated with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ using an ethanol solution

Table 3. Properties of glassy carbon samples before and after reduction of supported iron in H₂

Sample	S _{CO₂} m ² /g	S _{N₂} m ² /g	$\frac{S_{CO_2}}{S_{N_2}}$	V _p cm ³ /g	D _m nm	Pellet density g/cm ³
05-Fe original	605	106	5.7	0.39	3,500	0.89
05-Fe reduced	750	540	1.4	0.55	3,500	0.75
016-Fe original	1013	159	6.4	0.09	9.7	1.14
016-Fe reduced	780	362	2.2	0.23	10.9	1.01
N16-Fe original	990	3	330	0.07	10.9	1.24
N16-Fe reduced	828	62	13.4	0.12	12.5	1.15
X-Fe original	620	378	1.6	0.29	11,666	1.09
X-Fe reduced	476	401	1.2	0.40	11,666	0.99

Table 4. X-ray diffraction results on selected iron-containing samples

Sample	Original	Reduced
5-Fe [*]	8, Fe ₇ S ₈ , (208) ^{***}	21, α-Fe, (110)
16-Fe [*]	10, Fe ₇ S ₈ , (208)	47, α-Fe, (110)
05-Fe	13, Fe ₃ O ₄ , (311)	26, α-Fe, (110)
016-Fe	15, Fe ₃ O ₄ , (311)	26, α-Fe, (110)
N16-Fe	27, Fe ₃ O ₄ , (311)	33, α-Fe, (110)
X-Fe	12, α-Fe, (110)	32, α-Fe, (110)
X-Fe-0.025K	9, α-Fe, (110)	25, α-Fe, (110)
X-Fe-0.25K	12, α-Fe, (110)	--
X-Fe-1K	14, α-Fe, (110)	--
X-Fe-1.75K	26, α-Fe, (110)	32, α-Fe, (110)

* HTT = 973 K

** Average crystallite size in nm

*** () indicates diffraction peak

Table 5. CO and H₂ chemisorption on selected iron-containing samples

Support	Fe Added	Fe Loading, wt %	Treatment Conditions	Uptake, μ moles/g catalyst		Fe Dispersion %
				CO	H ₂	
5	A	2.0	C	nil	nil	-
16	A	2.2	C	nil	nil	-
5	B	4.0	D	nil	nil	-
5	B	5.0	E	4.0	0.7	0.45
05	A	2.5	F	3.9	nil	0.87
016	A	2.5	F	7.7	nil	1.7

A - in original mix

B - by impregnation on carbon support

C - N₂, 973K, 2 hr; H₂, 723K, 16 hr.D - Support in N₂, 973K, 2 hr; catalyst in H₂, 723K, 16 hr.E - Support in N₂, 1273K, 2 hr; H₂, 1223K, 12 hr; catalyst in H₂, 723K, 16 hr.F - N₂, 773K, 2 hr; H₂, 723K, 16 hr.

Table 6. Sulfur contained in selected samples

Sample		S, wt%
5	N ₂ , 1273 K, 2 hr	0.46
5	N ₂ , 1273 K, 2 hr H ₂ , 1223 K, 12 hr	0.07
16	N ₂ , 773 K, 2 hr	0.27
16	N ₂ , 773 K, 2 hr H ₂ , 723 K, 16 hr	0.18
5-Fe	N ₂ , 773 K, 2 hr	1.35
5-Fe	N ₂ , 973 K, 2 hr	1.49
5-Fe	N ₂ , 973 K, 2 hr H ₂ , 723 K, 16 hr	0.96

(impregnation from an aqueous solution was not possible due to the hydrophobic character of the surface) to give a sample with 4% metal loading. Treatment of this sample in H₂ at 723 K for 16 hr was unsuccessful in yielding an active catalyst for the Fischer-Tropsch reaction[6] or for CO chemisorption (Table 5). Obviously during this treatment H₂S was produced by reaction with sulfur in the carbon matrix, leading then to sulfiding of the added iron.

If sample 5 was heated to 1273 K in N₂ and held for 2 hr followed by heating in H₂ at 1223 K for 12 hr, its sulfur content was sharply reduced (Table 6). This is in agreement with the findings of Puri[10]. Further, the sample exhibits greater molecular sieving than the sample taken to 973 K in N₂ as seen in Table 2. This suggests that insignificant gasification in H₂ occurred at 1223 K. Greater molecular sieving can probably be attributed to an increase in HTT from 973 to 1273 K, as discussed elsewhere[11].

Subsequent addition of iron to the above carbon by impregnation led to a sample (Table 5) which, following reduction in H₂ at 723 K, could chemisorb CO and H₂ and was active for CO hydrogenation[6]. It has been shown elsewhere[9] that when carbon black with a high sulfur content is used as a catalyst support for iron, it is also inactive for CO hydrogenation. Again treatment of the support in H₂ at 1223 K prior to its impregnation with iron leads to a sharp reduction in sulfur content[12] and the subsequent production of an active catalyst[9].

As seen in Table 5, samples 05-Fe and 016-Fe, which were prepared by heat treatment in N₂ at 773 K followed by reduction in H₂ at 723 K, chemisorbed CO but no H₂. Additional studies are underway to allow us to understand these chemisorption results. Assuming that one molecule of CO chemisorbed on one iron site (the linear form of adsorption), iron dispersions can be estimated. It is apparent that the percentage of the total iron atoms which are estimated to be in the surface is small. Such low dispersions are characteristic of iron supported on

various supports, but it was originally hoped that by introducing iron in the original mix, samples of glassy carbon-supported iron could be produced showing high iron dispersions. Large dispersions have, in fact, not yet been achieved.

The extent of carbon gasification during reduction in H₂ was measured quantitatively using a TGA apparatus. Following treatment in flowing H₂ at 723 K for 16 hr, weight losses of 10 and 4% were found for samples 05-Fe and 016-Fe. In order to reduce carbon gasification, treatment of 05-Fe in H₂ was also investigated at lower temperatures. At 648 K in H₂ for 16 hr, a weight loss of 8.4% was measured; and at 623 K for 24 hr, a weight loss of 3.7% was found. In both cases following this reduction treatment, only α -Fe was identified by X-ray diffraction. Samples reduced under these conditions were found to be active for CO hydrogenation[6].

Several TGA runs were also carried out under conditions at which the Fischer-Tropsch reaction is conducted to see if carbon gasification occurred. Between 523 and 573 K in 0.1 MPa of flowing CO and H₂ (ratio H₂/CO = 3), no gasification could be detected over a 20 min period. In fact, negligible gasification rates are expected at synthesis conditions both because the temperature is low and CO is competing with H₂ for iron sites. That is, CO will inhibit the C-H₂ gasification reaction.

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