

INFLUENCE OF OXYGEN FUNCTIONAL GROUPS ON THE PERFORMANCE OF CARBON-SUPPORTED CATALYSTS

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INTRODUCTION

Efficient catalyst supports are materials capable of increasing the dispersion (or *percentage exposed*) of a catalyst by virtue of their physical (e.g., high surface area) and chemical (e.g., ion exchange) properties [1,2]. Numerous reports dealing with how these properties affect the performance of a variety of supported catalysts have led in many cases to improvements in their preparation [2]. The development of carbon-supported catalysts has not paralleled that of, e.g., metal oxide supports, mainly because the much richer surface chemistry of carbons complicates their characterization. Paradoxically, their rich surface chemistry makes carbons very attractive, yet poorly exploited, support materials [3]. Indeed, the open literature is very scarce in reports dealing with systematic variations of carbon properties in relation to catalyst performance [3-6]. Such variations are difficult to attain because the treatments that change the chemistry of a carbon can also change its physics, and vice versa. However, by carefully following the physical and chemical changes that accompany selected oxidative and/or thermal treatments of highly pure carbons, it has become possible to produce materials with similar oxygen content and equivalent surface areas, which nonetheless differ substantially in their specific oxygen functional group content. These supports have been loaded with a number of metals and exposed to different reaction conditions (e.g., carbon gasification in 0.1 MPa air) in order to test their performance [7]. The aim of this paper is to illustrate how the surface chemistry of carbons can be tailored to enhance the performance of carbon-supported catalysts, using the copper-catalyzed gasification of carbon as an example.

EXPERIMENTAL

Carbon Supports. For clarity, only selected results for a highly pure polymer-derived microporous carbon (Saran 928, Dow) are presented in this report; further details and results on meso- and nonporous carbons will be given elsewhere [7]. Batches of the starting material were subjected to pyrolysis (in N_2) and/or oxidation (in air, H_2O_2 or HNO_3) treatments at different conditions (i.e., different temperatures, reactant concentrations and exposure times) in order to modify their surface properties [7-9]. Changes in physical properties were followed by N_2 and CO_2 adsorption [8,9], X-ray diffraction (XRD) [8,9], and others [7], while chemical modifications were monitored via acid/base neutralizations [8-10], temperature-programmed desorption (TPD) [8,9], electrophoresis [3,8], mass titration [8] and X-ray photoelectron spectroscopy (XPS) [7,9], among others [7,11]. The three samples chosen (henceforth referred to as CA, CN and CB) were found to resemble each other the most in terms of their physical properties, while differing substantially in their surface chemistry. Samples CA, CN and CB were prepared by oxidation in boiling concentrated H_2O_2 for 15 min, oxidation in dry flowing dry air at 673 K for 3 h, and oxidation in air at 673 K for 24 h followed by pyrolysis in N_2 at 923 K for 3 h, respectively [8,11]. The active surface area, ASA (at 373 K), and the uncatalyzed gasification reactivities of each support in 0.1 MPa flowing air were measured on a modified TGA-7 apparatus (Perkin-Elmer) under diffusion-free reaction conditions [9,12].

Carbon-Supported Copper Catalysts. Samples CA, CN and CB were impregnated with aqueous (pH ca. 5.3) copper acetate (Fisher) by incipient wetness to yield 5% Cu catalysts (dry carbon basis). In addition, the adsorption capacity for Cu amines at pH = 11.5 was determined using a Cu^{+2} ion selective electrode (Orion) coupled to a Fisher Accumet 925 pH meter [9]. The resulting catalysts were characterized by XPS, XRD and oxygen chemisorption at 373 K [12], and their gasification reactivity in 0.1 MPa air was evaluated as described above for the supports alone.

RESULTS AND DISCUSSION

Surface Chemistry and Physics of the Supports Used. Both TPD (Table 1) and ultimate analyses [7] indicated that carbons CA, CN and CB have similar oxygen contents. In all cases, the difference PZC-IEP fell within 1.6-2.3 pH units (Table 1), indicating (as discussed elsewhere [8,9]) that the external (geometric) surface of these materials is enriched in negative surface charges relative to their internal (porous) surface. However, the IEP and PZC values do not reflect the large differences in surface chemistry observed by contact angle measurements [11] or by oxygen functional group analysis (see Figure 1). Indeed, large differences in their oxygen functional group content are evidenced by their CO/CO₂ evolution ratios (mol/mol) upon TPD (Table 1). Since CO₂- and CO-evolving groups are thought to be produced primarily by the decomposition of strongly acidic (carboxyl, lactone) and weakly acidic (phenol, carbonyl) oxygen complexes [13-15], the CO/CO₂ evolution ratios can be taken as a measure of surface acidity, with lower ratios representing more strongly acidic surfaces [7,11]. Therefore, CO/CO₂ ratios have been used throughout this report as indicators of the differences in functional group quality among these samples.

Before examining Figure 1 in detail, let us consider the structural differences among samples CA, CN and CB. The corresponding changes in equivalent surface areas are shown in Figure 2. The three samples exhibited very similar N₂ isotherms at all partial pressures [7], with BET equivalent surface areas in the range 848-886 m²/g. In a recent report dealing with Pt dispersion over an unspecified microporous carbon black and its H₂- and H₂O₂-treated derivatives, it was assumed that the observed similarity in N₂ isotherm shapes and in BET surface areas (between 895 and 956 m²/g) indicated that differences in Pt dispersion were not related to the physical properties of the supports used, but to their oxygen functional group content [16]. Figure 2 shows that N₂ isotherms alone do not suffice to neglect any physical differences among microporous samples. Indeed, sample CA, pretreated with H₂O₂, has a significantly higher (and reproducible) Dubinin-Radushkevich (DR) surface area than that of samples CN and CB (Figure 2). Even though the actual physical meaning of equivalent surface areas of microporous materials is open to question [17,18], N₂ and CO₂ equivalent surface areas provide complementary information about the structure of a carbon [17]. Accordingly, sample CA appears to differ from samples CN and CB in that it contains a number of narrow micropores inaccessible (within reasonable time) to N₂ at 77 K [17]. These narrow micropores, either generated or opened by the H₂O₂ pretreatment, are also likely to offer little access to hydrated metal ions in solution. Hence, for catalyst preparation purposes the accessible surface areas of samples CA, CN and CB can be taken to be of comparable magnitude [16].

In light of the above observations, it is possible to estimate the distribution of specific functional group types from the data in Figure 1 and using the following assumptions [10,13-15]:

- NaOH titrates carboxyl, lactone and phenolic groups [10];
- NaHCO₃ titrates carboxyl groups only [10];
- CO desorption arises from phenolic and carbonyl groups only [15]; and
- CO₂ desorption arises from carboxyl and lactone groups only [15];

The individual content of each surface group type can then be calculated from [13,15]:

- Carboxyl groups = groups titrated with NaHCO₃;
- Lactone groups = groups desorbed as CO₂ minus those titrated with NaHCO₃;
- Phenol groups = groups titrated with NaOH minus those desorbed as CO₂; and
- Carbonyl groups = groups desorbed as CO plus CO₂ minus those titrated with NaOH.

The calculated functional group contents are listed in Table 2. Because of the numerous assumptions involved in their estimates, the numbers in Table 2 must be regarded as qualitative only [13,15]. Nonetheless, Table 2 shows that the increase in surface acidity with decreasing CO/CO₂ evolution ratio is likely to be due to increases in the concentrations of both carboxyl (pK_a ≈ 4.4) and lactone (pK_a ≈ 8.2) groups [19]. The apparent absence of phenolic groups in sample CA is probably related to the diffusion-limited accessibility of NaOH to some phenol group-containing narrow micropores (Figure 2). In all cases the total oxygen coverages [20] amounted to ca. 12-17% of the N₂-BET surface areas.

Surface Chemistry vs. Uncatalyzed Carbon Gasification. Carbon supports can undergo thermal degradation when exposed to high temperatures and/or reactive environments. Because most carbons have already experienced heat treatments during their preparation, thermal degradation below, e.g., 773 K, is relatively minor in inert or reducing conditions, but can be important in oxidizing environments. Figure 3 shows the influence of oxygen functional groups on the uncatalyzed rate of gasification of the supports. The gasification reactivity of the carbon supports was found to increase with increasing surface acidity. A similar increase (ca. 20%) in active surface area, ASA [21], was also determined. (Indeed, a remarkably similar turnover frequency, or reactivity per active site, of ca. 5 s^{-1} is yielded by all supports at these conditions.) Clearly, the total surface areas (Figure 2) fail to correlate with either reactivity or ASA variations, as expected because (a) the surfaces probed by adsorbates at low temperatures ($\leq 298 \text{ K}$) are not necessarily related to the surfaces remaining at reaction conditions (i.e., after high temperature treatments), particularly if the desorbable oxygen content of the carbons is high, and (b) only a portion of the surface (the most reactive [20-23]) participates directly in the gasification process. Figure 3 suggests that the thermal treatment of surfaces rich in acidic (carboxyl, lactone) groups produces more active sites than that of surfaces rich in CO-desorbing (carbonyl, phenol) oxygen complexes. Mechanistic interpretations of Figure 3 will be addressed at length elsewhere [7].

Surface Chemistry vs. Copper Adsorption and Distribution. Metal sorption onto a support is considered necessary in order to attain a high catalyst dispersion [2,3]. Carbon materials are more flexible than most conventional (e.g., metal oxide) supports in that their surfaces can be modified to contain different kinds and amounts of surface sites [7-9], as discussed above. In an accompanying report [9] preliminary evidence suggesting the participation of lactone-type groups (in addition to carboxyl groups) to the sorption of copper by modified Saran carbons was presented. Further evidence can be gathered from Tables 1 and 2. Table 1 lists the amounts of copper taken up (primarily as Cu^{+2} ammine complexes [9]) by each support at $\text{pH} = 11.5$. These amounts are proportional to, but clearly exceed, the estimated carboxyl group content of each support (Table 2). Since the maximum possible stoichiometry (at equilibrium) for site-specific adsorption of divalent cations on dissociated carboxyl anions is 1:1 (i.e., $[-\text{COO}^-]_n[\text{Cu}(\text{NH}_3)_n(\text{H}_2\text{O})_{6-n}]^{+2} \rightleftharpoons n(\text{OH}^-)$; $1 \leq n \leq 5$), carboxyl groups alone cannot accommodate all the dissolved copper. Oxygen functional groups with intermediate (lactone-type) or lower (phenolic-type, $\text{pK}_a = 10$ [19]) acid strength could also serve as adsorption sites. If both lactone and carboxyl groups participated in the copper adsorption process, at equilibrium a constant Cu/CO_2 ratio could be expected, with $\text{Cu}/\text{CO}_2 = 1$ resulting from a either 1:1 exchange or the decomposition of adjacent carboxyl sites [9,10,24], and $\text{Cu}/\text{CO}_2 = 0.5$ resulting from a 1:2 exchange on adjacent sites [10]. Similar arguments can be raised about the Cu/NaOH ratio, if carboxyl, lactone and phenol groups participated simultaneously in the adsorption process. As shown in Table 1 and elsewhere [9] the Cu/CO_2 ratios for modified Saran chars fluctuate between 0.32 and 0.87, with values > 0.5 corresponding to air- (vs. liquid phase-) oxidized carbons. Cu/NaOH ratios, on the other hand, are in some instances very low (see Table 1; the exception, i.e., that of sample CA, is again related to the limited accessibility of NaOH to some of its phenol group-containing narrow micropores, as mentioned earlier). These data can be understood by postulating that copper cations interact with oxygen complexes on carbons in order of decreasing acidity, i.e., carboxyl $>$ lactone $>$ phenol. Once most accessible dissociated carboxyl groups are populated, additional copper cations begin to adsorb onto dissociated lactones and, subsequently, onto dissociated phenol groups. (The transition between each group range is not sharp but rather smooth, judging from the corresponding copper adsorption isotherms [7,9].) Table 1 suggests that both carboxyl and lactone groups participate in Cu^{+2} ammine adsorption at $\text{pH} = 11.5$, giving Cu/CO_2 ratios close to 0.5, i.e., one divalent cation for every two negatively charged groups (or $\text{Cu}/\text{CO}_2 > 0.5$ for surfaces presumably containing some isolated sites). Phenol groups appear to contribute little towards copper adsorption at these conditions. For samples CA, CN and CB, copper saturation uptakes of ca. 2.0, 1.1 and 0.3 wt.% were determined, indicating that it is not the total oxygen content of a carbon (Table 1) but its quality (Table 2) that controls the cation adsorption process.

Drying the samples containing an excess (5 wt.%) Cu leaves in all cases well dispersed metal precursors; these yield no copper XRD patterns and block a portion of the micropores, since the BET and DR surface areas decrease upon loading by ca. 60 % and 30-50 %, respectively [7]. Figure 4 shows that the XPS ratios of the dried samples approach in all cases that of the salt (acetate) used for their preparation. The most significant difference among the dried samples was an upwards shift in

binding energy with increasing support acidity (Table 1). (In agreement with this, higher Cu loadings of nonacidic carbons were found to produce XRD patterns consistent with the formation of Cu^+ species [25].) Unsurprisingly, sintering the catalysts (in N_2 at 623 K) reduced the Cu/C XPS ratios to values ca. 5 times higher than bulk catalyst values (Figure 4), suggesting a significant external surface enrichment by Cu in all cases. In spite of this external surface enrichment by Cu, the dispersion (or fraction exposed) of Cu on each catalyst was estimated to be relatively high, and to go through an apparent maximum for carbons of intermediate surface acidity (Figure 5). Figure 5 suggests that maximizing Cu adsorption (Table 1) does not necessarily lead to the highest Cu dispersion; indeed, as discussed below the thermal stability of the adsorbed complex must also be taken into consideration.

Influence of Surface Functional Groups on the Copper-Catalyzed Gasification of Carbon. Besides promoting a high and stable initial catalyst dispersion, oxygen functional groups can affect the sintering behaviour, the degree of reduction, the volatility, etc., of a supported metal. In the case of the catalyzed gasification of carbon, the support itself is a reactant, and the oxygen complexes are deemed to participate as reaction intermediates. Since Cu-catalyzed gasification rates exceed uncatalyzed rates by 10^2 - 10^3 [9], the initial surface chemistry of the support (Figure 3) has little bearing on the former other than its influence on the state of the catalyst at reaction conditions. Figure 6 shows that for low sintering temperatures the most active catalyst is the one with the highest Cu dispersion (Figure 5). In contrast, after sintering the catalysts at ≥ 923 K the most acidic supports provided the highest reactivity. Hence, the most adequate surface chemistry for Cu/C catalysts is seen to depend strongly on the conditions of its utilization. Sintering up to 923 K, which causes primarily the decomposition of CO_2 -evolving groups [8], is accompanied by a drastic drop in reactivity, in particular for the least acidic carbons (Figure 7). Further sintering up to 1223 K, which parallels the desorption of CO -evolving groups [8], causes minor losses in reactivity, in particular for the most acidic carbons, whose small Cu particles are only then free to migrate and lose dispersion by their coalescence.

CONCLUSIONS

Oxygen functional groups influence virtually all stages of utilization of carbon-supported catalysts. The importance of the surface chemistry of carbon supports is strongly dependent on the end use of the catalyst. More than the quantity of oxygen it is the quality (type) of oxygen groups that controls the extent of metal precursor sorption, its distribution throughout the support, the resistance to active phase agglomeration upon drying/reduction, and ultimately the performance of carbon-supported catalysts.

REFERENCES

1. M. Boudart and G. Djega-Mariadassou, in "Kinetics of Heterogeneous Catalytic Reactions," Princeton University Press, Princeton (1984), Ch. 6.
2. J.R. Anderson, "Structure of Metallic Catalysts," Academic Press, New York (1975), Ch. 2.
3. J.M. Solar, C.A. Leon y Leon, K. Osseo-Asare and L.R. Radovic, *Carbon* **28**, 369 (1990).
4. A.J. Bird, in "Catalyst Supports and Supported Catalysts" (A.B. Siles, Ed.), Butterworths, London (1987), Ch. 5.
5. H. Jungten, *Fuel* **65**, 1436 (1986).
6. P. Ehrburger, *Adv. Colloid Interface Sci.* **21**, 275 (1984).
7. C.A. Leon y Leon and L.R. Radovic, in preparation.
8. C.A. Leon y Leon, J.M. Solar, V. Calemma, K. Osseo-Asare and L.R. Radovic, *Carbon*, Submitted (1991).
9. C.A. Leon y Leon and L.R. Radovic, "Effect of Thermal and Chemical Pretreatments on the Copper-Catalyzed Gasification of Carbon in Air," ACS Preprints, Div. Fuel Chem., New York (1991), in print.
10. (a) H.P. Boehm, E. Dehl, W. Heck and R. Sappok, *Angew. Chem. Internat. Edit.* **3**, 669 (1964); (b) H.P. Boehm, *Advan. Catal.* **16**, 179 (1966).
11. C.A. Leon y Leon, V. Calemma and L.R. Radovic, "Surface Chemical Heterogeneity of Oxidized Carbon Particles," 20th Biennial Conf. on Carbon, Santa Barbara, CA, June 23-28, 1991, p. 30.
12. C.A. Leon y Leon and L.R. Radovic, Proc. Int. Carbon Conf., Paris, France (1990), p. 44.
13. K. Kinoshita, in "Carbon: Electrochemical and Physicochemical Properties," Wiley, New York (1988), Ch. 3.
14. B.R. Puri, in "Chemistry and Physics of Carbon" (P.L. Walker, Jr., Ed.), Vol. 6, Dekker, New York (1970), p. 191.
15. D. Rivin, *Rubber Chem. Technol.* **44**, 307 (1973).
16. C. Prado-Burguete, A. Linares-Solano, F. Rodriguez-Reinoso and C. Salinas-Martínez-de Lecea, *J. Catal.* **115**, 98 (1989).
17. F. Rodriguez-Reinoso and A. Linares-Solano, in "Chemistry and Physics of Carbon" (Edited by P.A. Thrower), Vol. 21, Marcel Dekker, New York (1989), p. 1.
18. H. Marsh, *Carbon* **25**, 49 (1987).

19. J.S. Manson and H.B. Mark, Jr., "Activated Carbon," Marcel Dekker, New York (1971), p. 41.
20. N.R. Laine, F.J. Vastola and P.L. Walker, Jr., *J. Phys. Chem.* **67**, 2030 (1963).
21. L.M.K. Ismail and P.L. Walker, Jr., *Carbon* **27**, 549 (1989).
22. L.R. Radovic, A.A. Lizzio and H. Jang, in "Fundamental Issues in Control of Carbon Gasification Reactivity" (J. Lahaye and P. Ehrburger, Eds.), Kluwer, the Netherlands (1991), p. 235.
23. G.R. Hennig, in "Proceedings of the 5th Conference on Carbon," Vol. I, Pergamon Press, New York (1962), p. 143.
24. A. Linares-Solano, C. Salinas-Martinez de Lecea and D. Cazorla-Amoros, *Energy & Fuels* **4**, 469 (1990).
25. P. Ehrburger, J.M. Henlin and J. Lahaye, *J. Catal.* **100**, 429 (1986).

Table 1. Features of Modified Saran Carbons Used as Cu Catalyst Supports.

Sample	%O [wt.]	CO/CO ₂ ^a [mol/mol]	IEP ^b	PZC ^b	B.E. ^c [eV]	Cu ads. ^d [mmol/g]	Cu/CO ₂ ^e [mol/mol]	Cu/NaOH ^e [mol/mol]
CA	5.0	2.18	3.85	5.74	934.7	0.32	0.43	1.24
CN	4.5	7.29	3.65	5.23	933.7	0.17	0.58	0.14
CB	3.3	13.9	5.25	7.53	932.8	0.04	0.32	0.05

^a CO/CO₂ evolution ratio upon TPD.

^b IEP: isoelectric point (by electrophoresis); PZC: point of zero charge (by mass titration).

^c B.E.: XPS copper 2p_{3/2} peak binding energy (freshly dried catalysts).

^d Amount of copper withdrawn from solution at pH=11.5 (adjusted using NH₄OH).

^e Ratio of Cu adsorbed to CO₂ evolved (TPD) and acidic groups titrated with NaOH.

Table 2. Estimated Functional Group Content of Modified Saran Carbons.

Sample	Carboxyl		Lactone		Phenol		Carbonyl	
	[mmol/g]	%	[mmol/g]	%	[mmol/g]	%	[mmol/g]	%
CA	0.23	11	0.52	24	0	0	1.37	65
CN	0.05	2	0.25	11	0.96	44	0.93	43
CB	0.01	1	0.12	7	0.69	38	0.99	54

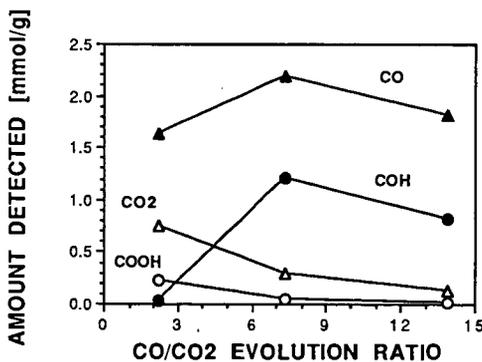


Figure 1. Variation in Oxygen Functional Group Content with CO/CO₂ Evolution Ratio (upon TPD) of Modified Saran Carbons. Triangles: amounts of CO₂ (CO₂, or carboxyl plus lactone [15]) and of CO (CO, or phenol plus carbonyl) evolved upon TPD; Circles: amounts of acidic groups titrated using NaHCO₃ (COOH, or carboxyl [10]) and NaOH minus NaHCO₃ (COH, or lactone plus phenol [10]).

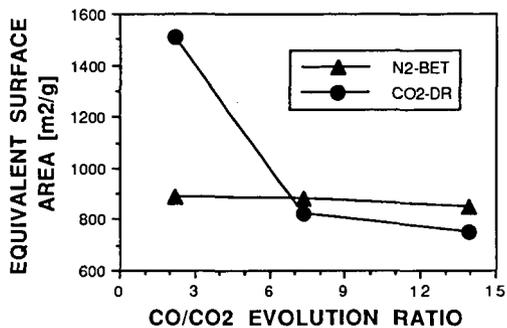


Figure 2. Equivalent Surface Areas of Modified Saran Carbons, Estimated From Volumetric N₂ (77 K) and CO₂ (298 K) Adsorption Isotherms Using the BET and Dubinin-Radushkevich (DR) Equations, respectively.

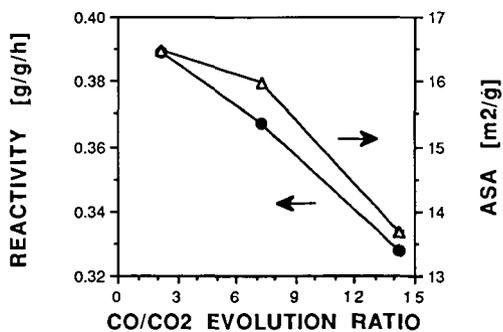


Figure 3. Influence of Oxygen Functional Groups on the Uncatalyzed Gasification Reactivity (773 K, 0.1 MPa air) and on the Active Surface Area, ASA (373 K), of Modified Saran Carbons.

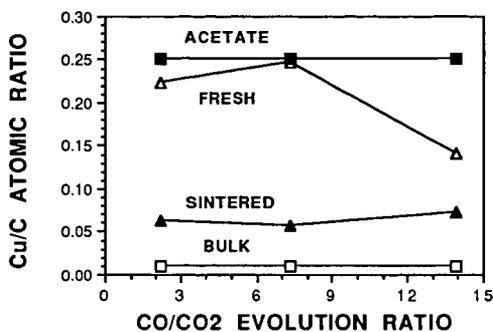


Figure 4. Comparison of Copper-to-Carbon XPS Ratios of Dried and of Sintered (in N_2 at 623 K) 5% Cu/Saran Catalysts With Those of the Precursor Salt (Acetate) and the Bulk Catalysts.

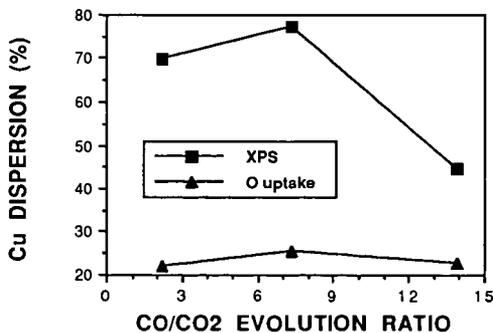


Figure 5. Copper Dispersion Over Modified Saran Carbons After Sintering 5% Cu/Support Catalysts in N_2 at 623 K, Estimated From XPS and Oxygen Chemisorption Data.

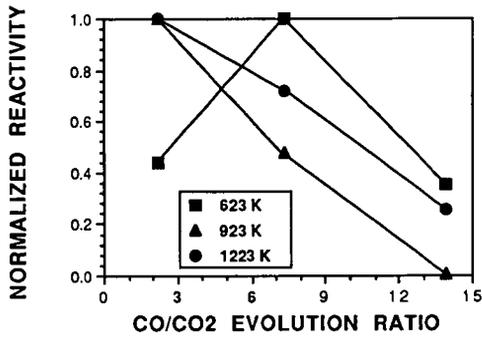


Figure 6. Influence of Carbon Surface Chemistry on the Normalized Gasification Reactivity (in 0.1 MPa air, Extrapolated to 623 K) of 5% Cu/Saran Catalysts Following Heat Pretreatments (in N₂) at Temperatures Shown.

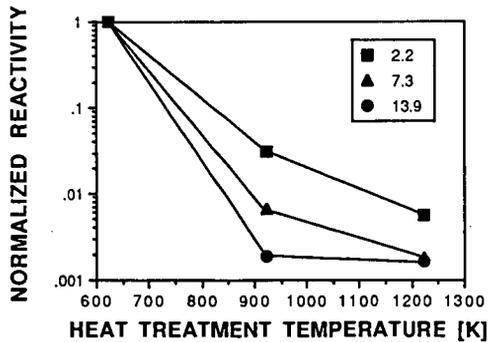


Figure 7. Effect of Heat Pretreatment on the Normalized Gasification Reactivity (in 0.1 MPa air, Extrapolated to 623 K) of 5% Cu/Saran Catalysts for Different Initial Surface Chemistry.