Relationship between Metal Ion Adsorption and Catalytic Properties of Carbon-Supported Nickel Catalysts

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During the preparation of supported metal catalysts, the adsorption of aqueous metal ions is influenced by the intrinsic properties of the support. Any attempt to model this adsorption phenomenon requires at least three elements: the pH-dependent surface charge speciation of the support, the pH-dependent aqueous phase speciation of the precursor ion, and a suitable model to describe the equilibrium exchange reaction. A series of activated carbons derived from a low ash content carbon source was prepared by controlled oxidation using nitric acid. The surface ionization constants for the protonation/deprotonation equilibria of the hydroxyl groups on each carbon were determined assuming a classical Gouy–Chapman diffuse layer. They were found to vary systematically with extent of oxidation. Nickel adsorption data were obtained over a wide range of pH and Ni concentration. Under the conditions of this study, Ni^{2+} was the dominant ion. A surface complexation model was employed to test the hypothesis that the model's parameters could be correlated to the results of characterization studies of these Ni/carbon catalysts. Specifically, it was found that the surface stability constant ($\approx \Delta G_{ads}$) of the precursor and the point of zero charge of the carbon varied in accordance with results from temperature-programmed reduction and temperature-programmed oxidation. It is proposed that the point of zero charge of the carbon support can serve as a convenient index for the design of carbon-supported metal catalysts with desired catalytic properties. © 1991 Academic Press, Inc.

INTRODUCTION

Carbon can be used as a catalyst support for gas–solid reactions if the temperature and pressure of the gas phase are such that the carbon support is stable under reaction conditions (*1, 2*). The use of carbon as a support has increased in the last two decades. However, carbon, as a support, has been studied less than others, and only a few studies have dealt with the method of preparation of carbon-supported metal catalysts (*3, 4*).

The presence of oxygen functional groups on carbon is well established. During the catalyst addition step, these groups can also serve as adsorption sites for metal ions. There are few systematic studies of the influence of surface functionalities of carbon on its aqueous ion adsorption properties. This is mainly due to the lack of proper tools for determining the surface acidity of the carbon. Recently, Corapcioglu and Huang (*5, 6*) investigated the surface acidity of carbon by measurements based on a surface ionization model. However, their work was limited to the use of activated carbon as an adsorbent for metal ions from solution, not as a catalyst support.

The present study seeks to establish a relationship between the nickel adsorption properties of carbon and this metal's properties as a catalytic precursor. To accomplish this objective, results from temperature-programmed reduction (TPRd) and temperature-programmed oxidation (TPO) of the catalytic precursors have been correlated with the parameters of a surface complexation model describing the adsorption process.

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Surface Complex-Formation Model

A surface complex formation model has been advanced in order to interpret metal adsorption phenomena (7). With Me^{m+} in solution and C representing a carbon atom, the surface can form complexes through two possible paths.

$$z\{-CO^-\} + Me^{m+}$$
$$= \{-(CO)_z Me\}^{(m-z)+} \quad (1)$$

$$z\{-COH\} + Me^{m+}$$
$$= \{-(CO)_z Me\}^{(m-z)+} + zH^+ \quad (2)$$
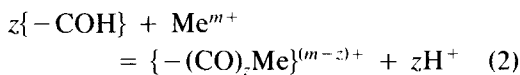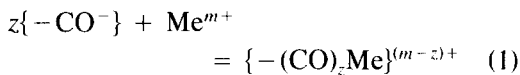
$$\beta_1 = \frac{\{-(CO)_z Me\}^{(m-z)+}}{\{-CO^-\}^z \{Me^{m+}\}} \quad (3)$$

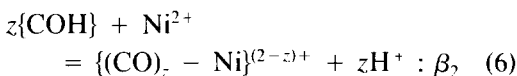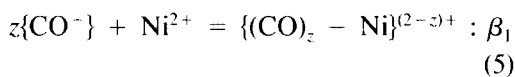$$\beta_2 = \frac{\{-(CO)_z Me\}^{(m-z)+}[H^+]^z}{\{-COH\}^z\{Me^{m+}\}}, \quad (4)$$

where { } represents surface sites or surface complexes with metal ions. The complex formation mechanism presented here reflects the fact that as metal adsorption occurs, the solution pH decreases. The equilibrium constants for these reactions, β_1 and β_2, are called stability constants. The formulation of this complexation is based on the following assumptions (8, 9):

1. Adsorption and/or coordination reactions occur between the surface sites and the metal species in solution according to a certain chemical equilibrium reaction.

2. Species adsorb according to their aqueous speciation distributions.

3. Interactions between neighboring species do not exist.

4. Metal adsorption is specific; the influence of electrostatic interaction energy is negligible.

Under these assumptions, there may be more than one type of surface complex since many aqueous metal hydroxy species are possible depending on the solution pH. For example, Ni species can exist in various forms such as Ni^{2+}, $NiOH^+$, $Ni(OH)_2$, $Ni(OH)_3^-$, and possibly $Ni(OH)_4^{2-}$. Most of these are available as free ions at low pH. At high pH values, metal precipitation may also occur.

In the present study pH values lower than 7 were considered. Under these conditions Ni^{2+} species are essentially the only species available, and the problem of possible precipitation can be eliminated. Experimentally, only total nickel uptake can be measured. Therefore, it is assumed here that there is only a single surface complex $\{(CO)_z - Ni\}$ and the activity of the surface complex is identical for both reactions. The stability constant β_2 can then be derived from β_1 because the relationship between $\{COH\}$ and $\{CO^-\}$ is known from the surface ionization model.

For activated carbons and nickel ions:

$$z\{CO^-\} + Ni^{2+} = \{(CO)_z - Ni\}^{(2-z)+} : \beta_1 \quad (5)$$

$$z\{COH\} + Ni^{2+}$$
$$= \{(CO)_z - Ni\}^{(2-z)+} + zH^+ : \beta_2 \quad (6)$$

If the stoichiometry (z) is known or fixed in the pH range studied, the surface complexation model needs the ionization constants to determine the parameter β_1. These former values have been determined using a diffuse layer model (10). The diffuse layer model possesses simplicity. All specific adsorption is assumed to occur in one surface layer, which eliminates multiple planes for adsorption at the surface and the associated fitting parameters (9).

Usually, the stoichiometry is determined from the measurement of the number of hydrogen ions released per adsorbed metal ion (7). Ideally, the z value is 2. However, a variation in stoichiometry with pH has been observed (11). This implies that a change in the form of the surface complex may occur as the pH varies. From a mathematical viewpoint, the choice of the surface complex is a convenient device to fit the experimental data. Therefore, it is reasonable to determine, as a model parameter, the stoichiometry from the best fit of experimental results. This may furnish a better prediction of nickel adsorption results. Either different z values may be found for different carbons to fit the adsorption data or different carbons

may have different stability constants according to the optimum stoichiometry. In some instances, it may be desirable to find a stoichiometry that can apply to all the carbons studied because the comparison of stability constants is more meaningful than that of the stoichiometry in interpreting the strength of the interaction between surface sites and nickel precursors. In this work, for comparison, the determination of the z and β values is carried out in the following hierarchy:

Case 1: $z = 2$ and the best stability constant ($pK_{Ni} = -\log \beta$) for each carbon

Case 2: best set of z and pK_{Ni} values for each carbon

Case 3: a constant z for all carbons and optimum pK_{Ni} values for each constant.

EXPERIMENTAL

Preparation of Carbon Supports

A common source carbon was treated in HNO_3 solution at different concentration levels, and the samples are designated by the HNO_3 concentration used: 0, 0.2, 0.4, 1, and 2 *M*. This treatment alters the surface chemical properties of the carbon support without affecting the surface area (*12*). The HNO_3 solution used was Fisher Reagent ACS Grade. North American carbon (G-21, lot #4033-4, less than 2% ash content) was the source carbon. Carbons were pre-washed for 18 h with deionized water using a soxhlet extractor. For each of these samples, 100 g of carbon was treated for 18 h in 500 cm^3 of HNO_3 solution, at its boiling temperature, using a soxhlet extractor. The carbons were then filtered and kept in an oven at 380 K.

Activated carbons contain a certain amount of ash minerals. Some mineral ingredients, especially Fe, may have a catalytic effect. To ensure that the presence of ash ingredient is marginal, each carbon sample was analyzed by X-ray photoelectron spectroscopy at Brookhaven National Laboratory, Upton, NY. Internal standards were used to estimate element concentra-

tions. The highest value of the potassium content, a leading species, was less than 0.05% by weight. Therefore, any effects of ash ingredients were assumed negligible. The total ash content was determined simply by burning the carbon. A crucible containing 1 g of carbon was placed in a furnace for 24 h at 1170 K. The ash was then weighed on a Mettler balance.

Characterization of Carbon Supports

Nitrogen BET surface areas were obtained on a Quantasorb System at liquid nitrogen temperature. The carbon samples (about 500 mg) were weighed in a Mettler balance and then heated to 470 K in a flow of He for 18 h. BET surface area measurements were carried out at gas phase compositions of 7 and 15% N_2 in He mixtures. All the gases, supplied by Linde Gas Company, were of primary standard or ultrahigh purity grade with a minimum purity of 99.999%. As recommended in the procedure manual, the surface area measurements were evaluated on the basis of desorption amounts. The area of a N_2 molecule was taken to be 0.162 nm^2 in the calculation of the surface area.

To determine if there is a relationship between the carbon surface properties and metal ion adsorption derived from the impregnation process and if this influences the properties of catalytic precursors, it is necessary to measure the surface ionization parameters. The requisite data base consists of determining the point of zero charge (PZC) and pH-dependent surface charge. Mass titration was used to determine the PZC and acid/base potentiometric titration was used to evaluate the surface charge. In addition, classical surface acidity was measured by gaseous base adsorption using NH_3 as the adsorbate. The details of these procedures have been described elsewhere (*10*).

Nickel Adsorption

A $Ni(NO_3)_2 \cdot 6H_2O$ solution was used as the impregnant. For each carbon sample, three different nickel concentrations

(10^{-3} M, 3.3×10^{-3} M, and 10^{-2} M) were used at eight different pH values in the range of 1 to 7.

For each nickel concentration, eight plastic vials were filled with 20 cm^3 of 0.1 M NaNO$_3$ solution. The pH values were adjusted using NaOH and HNO$_3$ solution, and 200 mg of carbon was weighed into each container. After 48 h, aliquots (250 μl) of Ni(NO$_3$)$_2$ solutions of 0.025, 0.08, and 0.25 M were added to the solution to make the desired concentrations of 10^{-3} M, 3.3×10^{-3} M, or 10^{-2} M, respectively. The samples were again put on the shaker for 48 h for equilibration and then filtered with Fisher Scientific P2 Filter Paper.

The equilibrium pH of each sample was measured by a Fisher Scientific pH meter (Model 740) calibrated at pH 4 and 10. The nickel concentration of the solution was analyzed with a Perkin Elmer Model 2380 atomic absorption spectrophotometer. The amount of metal adsorbed onto the carbon sample was determined from the difference between the initial concentration and the final concentration. The metal impregnated samples were dried and stored at 380 K for further experiments without additional heat treatment because heat can cause significant changes in the properties of the carbon surface.

Catalyst Characterization

Sample selection for catalysis experiments. Carbons having 0.6% weight loading were selected from the nickel-impregnated carbon samples obtained from the metal adsorption experiments. Detailed information on the preparation conditions of these samples is described in Table 1. It is known that different weight loadings of Ni on other supports lead to different catalytic activities.

Temperature-programmed oxidation. Gasification reactions of carbon samples with air were carried out using a Cahn Model RG 1000 microbalance. For each experiment, 20 mg of carbon sample was taken

TABLE 1

Preparation Conditions of Catalyst Samples

Sample	Ni (wt%)	Ni conc. (M/liter)	pH
0 M	0.64	0.01	3.08
0.2 M	0.65	0.01	7.01
0.4 M	0.58	0.0033	3.46
1 M	0.64	0.0033	4.22
2 M	0.59	0.0033	5.96

Note. In order to prepare samples having equal weight loading, the 0.01 M nickel solution is used for 0 M and 0.2 M carbons and the 0.0033 M solution is used for 0.4, 1, and 2 M carbons, respectively.

from the oven and weighed into the sample holder. The holder was made of stainless steel screen, 400 mesh size. The system was first evacuated at 380 K for 2 h to dehydrate the sample, and then the system was cooled to room temperature in argon. The system was evacuated again prior to experiment. After a pressure of less than 0.7 kP was reached, dry grade air was slowly taken from a compressed air cylinder. When the pressure became atmospheric, the flow rate was adjusted to 50 cm^3/min, and the valve to the vent was opened. When the sample weight became constant, the temperature programmer was turned on to heat the reaction system. To avoid weight correction due to imbalance in the temperature between the sample leg and the reference leg of the Cahn balance, both sides were heated. The heater was custom-made using Thermcraft Model RH242. The heating started at 300 K, and the heating rate was set at 20 K/min using an Omega temperature programmer Type K. The thermocouple (Chromium–Constantan, K type) was placed close to the sample holder. The weight changes as a function of temperature were measured, and the data were recorded by an IBM PC with a Hewlett–Packard data acquisition system 3421A. The experiment was stopped when the sample weight dropped to zero as a consequence of the complete burning of carbon with oxygen.

Temperature-programmed reduction. The hydrogen consumption rate during the reduction of the catalytic precursor was monitored by a Fisher Model 1200 gas partitioner in which a built-in thermal conductivity detector measured the changes in hydrogen concentration of the carrier stream. The temperature programmer and data acquisition were identical to that used in the gasification experiment. The sample was placed in a stainless-steel tubular reactor insert of dimensions: 20 mm long, 7.14 mm o.d., and 5.95 mm i.d.

For each experiment, 100 mg of carbon sample was placed in the reactor insert. Argon, with a flow of 40 cm^3/min, was established, and then the temperature was raised to 380 K for about 2 h to dehydrate the sample. The reactor was cooled to room temperature in argon. The argon stream was then switched to 8.5% H_2/Ar mixture at a flow rate of 40 cm^3/min. The temperature of the reactor was programmed to rise linearly from room temperature to 770 K with a heating rate of 20 K/min.

RESULTS

Carbon Surface Properties

The results of the BET measurements and ash analysis are summarized in Table 2. Although the surface areas appear to decrease with nitric acidic treatment (except with 2 M HNO_3), the changes are marginal. The esti-

mated error in the measurements was ±7%. It has been reported that the treatment of carbons with HNO_3 does not affect their physical morphology but alters their surface chemical properties (*12*), and that HNO_3 treatment is the most effective one to make carbons acidic. Also presented in Table 2 are ammonia uptake and the PZCs of each of the carbon samples. They demonstrate that increasing oxidation treatment increases acidity, which is reflected as a decrease in carbon PZC.

Nickel Adsorption

Effect of pH and surface acidity. Figure 1 demonstrates typical adsorption behavior for the carbons employed. The more oxidized carbons adsorb more nickel at a fixed condition of pH and nickel concentration. Oxidation lowers the PZC of the carbon (*13*) and increases the formation of surface acidic groups (such as carboxyl groups) on the carbon surface (*2, 13*). These changes result in the observed nickel adsorption behavior, and demonstrate that, if the carbon surface has more acidic groups (Brønsted acid sites), more sites will be available to attract cations in the solution. In the solution phase, cationic species compete with protons to occupy the deprotonated surface sites. As the oxidation treatment becomes stronger (the PZC value becomes lower), more nickel ions adsorb on the surface at a fixed pH. The strongest acidic carbon (treated in 2 M HNO_3 solution) shows the highest uptake, and the as-received carbon has the smallest uptake.

Catalyst Characterization

Temperature-programmed oxidation. The gasification profiles for each carbon support are shown in Fig. 2a. They demonstrate that HNO_3 treatment lowers the ignition temperature when the carbon surface reacts with air. This indicates that the acidic surface groups are more reactive with oxygen than are the basic groups. In the presence of Ni, the ignition temperatures for each carbon were further lowered in com-

TABLE 2

Characterization of Carbon Samples

HNO_3 treatment	0 M	0.2 M	0.4 M	1.0 M	2.0 M
BET area, m^2/g	1100	1055	1020	1015	1150
PZC	10	7.8	6	5.5	3.5
Ammonia uptake[a] mmol/g	2.35	3	4.24	5.18	6.14
Total ash, %	1.1	1	0.6	0.8	0.6
Ash analysis					
K, ppm	214.	86.1	638.	533.	302.
Ca	6.92	3.63	17.1	24.3	4.46
Mn	0.61	0.71	2.40	2.48	0.29
Fe	9.20	25.9	6.81	38.5	27.6
Ni	0.32	0.60	0.86	0.27	0.24
Cu	0.37	0.72	1.69	1.25	0.58
Rb	0.73	0.68	0.41	0.41	0.36

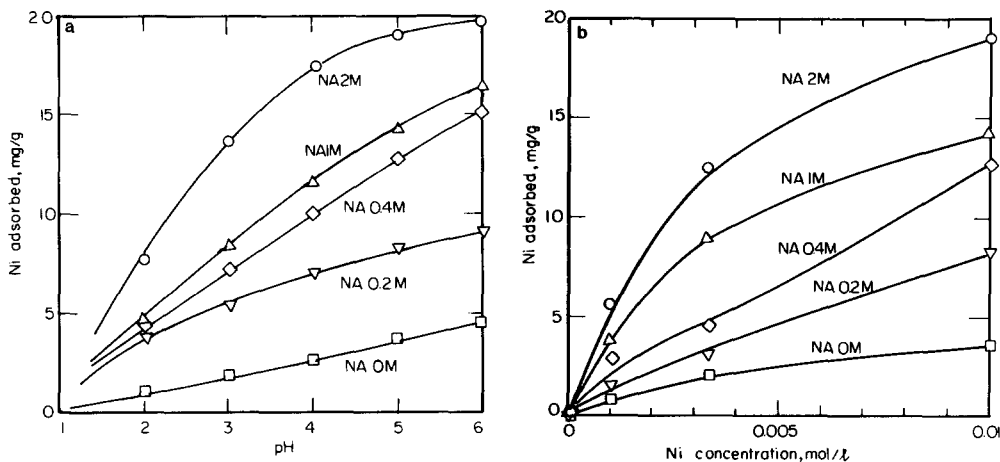[a] Measured at 40 kPa of ammonia at room temperature (*17*).

FIG. 1. Comparison of nickel adsorption results. The adsorbed amount increases with increasing pH and increasing electrolyte concentration. Smoothed curves are drawn through the experimental points. (a) pH effect (Ni conc. = 0.01 M); (b) concentration effect (pH 5).

parison to the support carbons alone. Figure 2b shows the gasification profiles for the nickel/carbon system. The results confirm that nickel is an effective catalyst for the gasification of carbonaceous materials. The most acidic carbon with nickel was gasified at a lower temperature than any other sample with or without nickel.

Temperature-programmed reduction. In the case of nickel-impregnated carbons, the carbon support can react with hydrogen to form a variety of hydrocarbons such as methane and ethane. The hydrogen consumption, therefore, depends on not only the catalytic species reduced but also the amount of surface reacted with hydrogen.
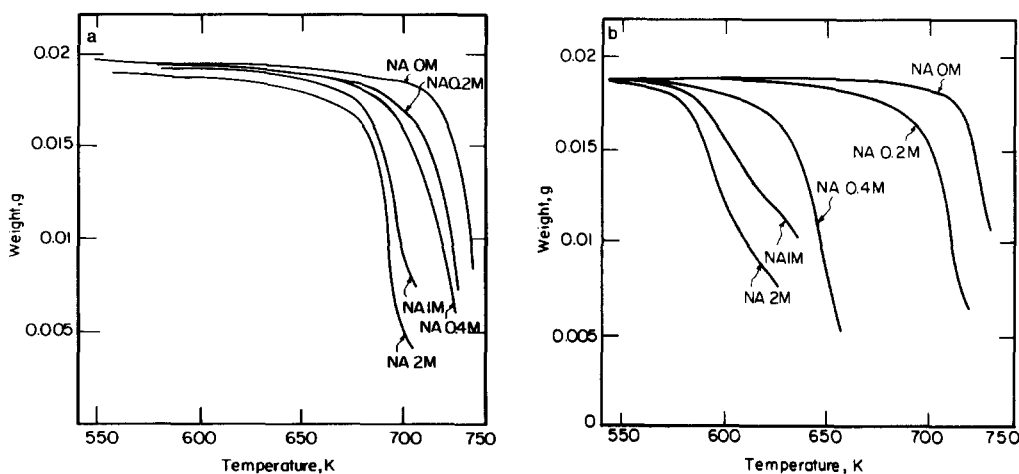

FIG. 2. Temperature-programmed oxidation results. Increasing oxidation lowers the ignition temperature. Smoothed curves here replace tracings of weight change recorded directly from microbalance: (a) carbon supports alone; (b) nickel impregnated carbons.
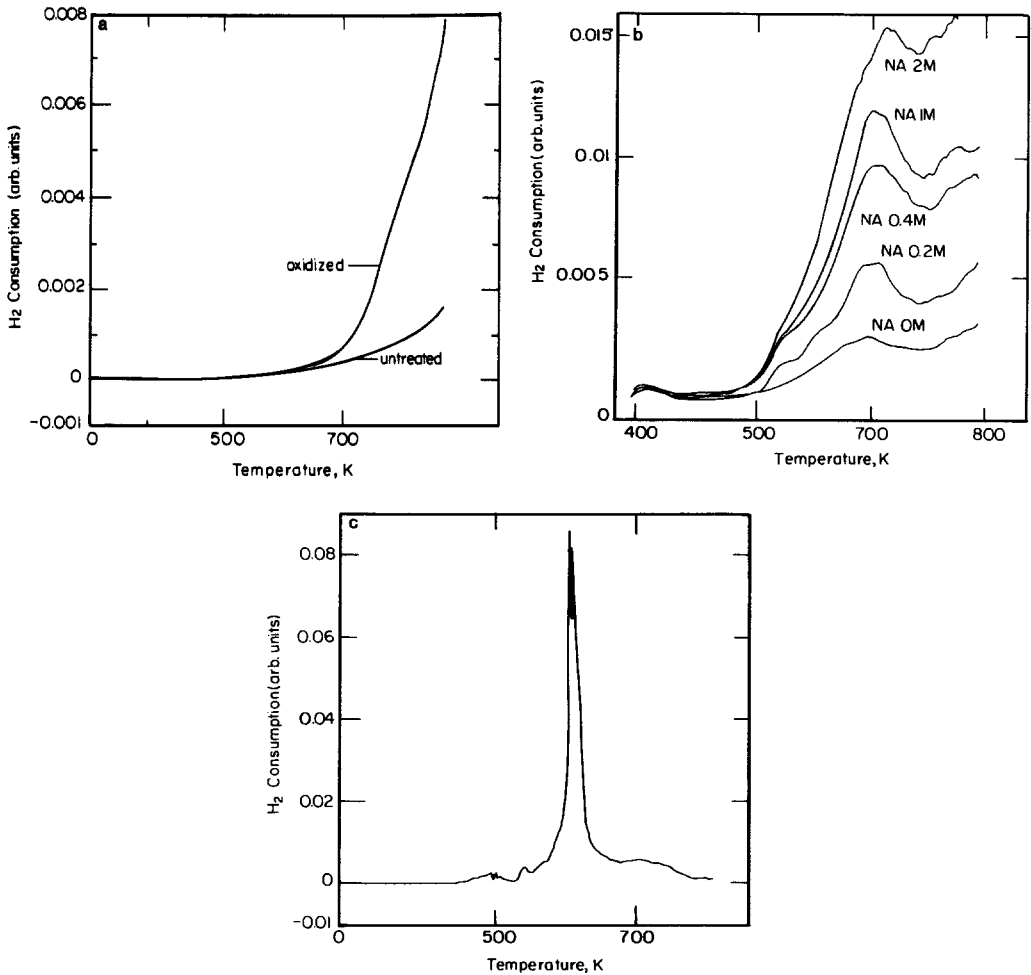
FIG. 3. TPRd profiles: (a) carbon supports alone; (b) Ni/C, 0.6%; (c) nickel nitrate.

The TPRd results are shown in Figs. 3a (carbon alone) and 3b (0.6% Ni/C). Figure 3c shows the TPRd results for unsupported Ni $(NO)_3 \cdot 6H_2O$. The results are summarized below:

1. All the carbon supports can react with hydrogen at or above 770 K, however, no peak is found.

2. The carbon that received the most extensive HNO_3 acid treatment appears to be more reactive with hydrogen than the as-received carbon since a larger amount is reduced or reacted above 770 K.

3. The nickel/carbon sample develops a peak temperature around 700 K due to the presence of nickel species. Note, however, that the peak temperature does not correspond to the peak temperature of unsupported nickel nitrate (610 K), Ni $(NO)_3 \cdot 6H_2O$.

4. There is no significant difference among the peak temperatures (T_{peak}) of the oxidized carbons. The peak temperature represents a distinct reduction characteristic of a particular chemical structure on the solid surface (20). This suggests that the types of surface complexes on each carbon are simi-

lar. In other words, it suggests that the choice of a constant value for the adsorption stoichiometry that applies to all carbons is reasonable.

5. The hydrogen consumption rate at the peak temperature (designated $H_{2,peak}$) increases as the carbon support becomes more acidic. Recall that the weight loadings of all catalysts used were the same. Since a single type of complex (structurally, but not necessarily electronically) is formed during adsorption, the increase reflects that either a more facile reducible species is present on the more oxidized carbon surface or the carbon is more reactive as a consequence of a better dispersed Ni species. The ease of reduction and the dispersion of a nickel precursor should be related to its degree of interaction with the carbon support. As the interaction with the support becomes weaker, the reduction process becomes easier, but the dispersion decreases. We show shortly that the adsorption free energy of the precursor decreases with increasing oxidation treatment of the carbon. Thus it appears that the hydrogen consumption rate, reflecting the reduction process, is greater due to the weaker interaction with the carbon rather than effects related to precursor dispersion.

DISCUSSION

Surface Complex Formation Model

The significance of the surface acidity constants is not only that they are convenient measures of the surface chemical properties but that they can provide a basis for modeling the adsorption phenomena from solution in a quantitative manner.

The regression results for finding the best values of model parameters for each case are listed in Table 3. The error value shown in Table 3 is the percentage ratio of the standard deviation of the estimated parameter to the absolute value of the estimate.

Case 1. The values of the stability constants for each carbon are the best single-valued stability constant obtained by simple regression analysis. It is interesting to note

TABLE 3

Determination of the Stability Constants

	Carbon	β	z	Error (%)
Case 1	0 M	−18.55	2	62.4
	0.2 M	−14.35	2	92.1
	0.4 M	−10.4	2	82.2
	1.0 M	−8.33	2	68.4
	2.0 M	−6.72	2	40
Case 2[a]	0 M	−1.03	0.174	9.58
	0.2 M	−0.57	0.141	13.3
	0.4 M	−1.09	0.235	9.1
	1.0 M	−1.3	0.297	6.29
	2.0 M	−2.37	0.586	9.43
Case 3	0 M	−4.45	0.5	21
	0.2 M	−3.65	0.5	24.1
	0.4 M	−2.67	0.5	17
	1.0 M	−2.21	0.5	9.24
	2.0 M	−1.82	0.5	7.31

[a] In Case 2, the errors shown in the table are in the z value estimate. (The errors in pK_{Ni} estimate were less than 0.03%.)

that the value of the stability constant increases with oxidation treatment. However, if the stability constant is calculated directly from the experimental results based on the assumed stoichiometry $z = 2$, a wide variation of the stability constants against pH is observed (pK_{Ni} increases with pH, Fig. 4). Similar trends have been reported by Corapcioglu (5) for nickel adsorption on various carbon products. However, the dependence of the stability constant on pH violates the assumptions involved in this surface complexation model because the mechanism, described earlier, already took into account the effect of pH. Note that the surface charge speciation is also pH dependent. The wide variation of the stability constant as a function of pH indicates the stoichiometric relation ($z = 2$) is not adequate for this carbon system. The large error (40 to 90%) in the parameter estimate results in predicted nickel adsorption results which are poor. Figure 5 shows the prediction for the 2 M HNO_3 treated carbon based on the single-valued stability constant.
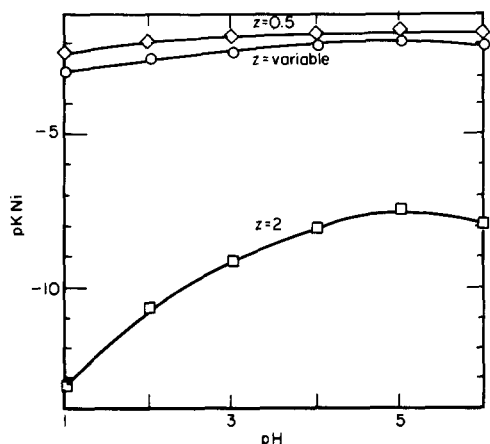
FIG. 4. Variation of the stability constants with pH for each case considered. See text for details. Smoothed curves are drawn through the calculated points. Note the wide variation with $z = 2$.

Case 2. The best set of optimum z and pK_{Ni} values for each carbon sample is shown in Table 3. The results show that most carbons have low values of z, less than 0.5. This may indicate that bidendate surface complexes, in which one nickel species interacts with two surface sites, are unlikely on the carbons used in this study. Interestingly, the value of the stability constant does not vary significantly, but the z values increase as oxidation increases. This suggests that nickel species can interact with more surface sites, in quantity, for the more oxidized carbons. If the optimum z value for each carbon is taken, the variation of the calculated values of the stability constants with pH becomes marginal (Fig. 4). The best prediction can apparently be obtained if allowance is made for differential values of both parameters for each carbon system. Note that the error in the parameter estimate is within 10%. The prediction of the model-Case 2 for the 2 M HNO$_3$ treated carbon is also shown in Fig. 5.

Case 3. If a constant z value for all five carbons is invoked ($z = 0.5$), the variation of calculated stability constants with pH becomes larger than in Case 2 (variable z for each carbon), but significantly smaller than

in Case 1 ($z = 2$). Figure 4 shows that the variation of the calculated stability constants with pH are relatively small in Case 2 as well as in Case 3. Note that the error in the parameter estimate ranges from 7 to 20%.

From the thermodynamic viewpoint, the stability constant indicates the strength of the metal ion–carbon interaction according to the corresponding stoichiometric relationship. It can be related to the free energy of adsorption by:

$$\Delta G = -RT \ln(K_{eq}) = -RT \ln(\beta). \quad (7)$$

As the stability constant (β) becomes higher, the surface complex becomes more stable. In other words, the interaction between the surface and the nickel ion becomes stronger if pK_{Ni} is smaller.

In light of this, the stability constant value may correlate with properties of these nickel species when the nickel adsorbed on carbon is characterized as a carbon-supported nickel catalyst. This topic is discussed further later. However, the comparison of stability constants for different samples is meaningless (Case 2) unless the stoichiometric relation is identical. Different z values mean that the definition of each stability constant is different. It is necessary to find
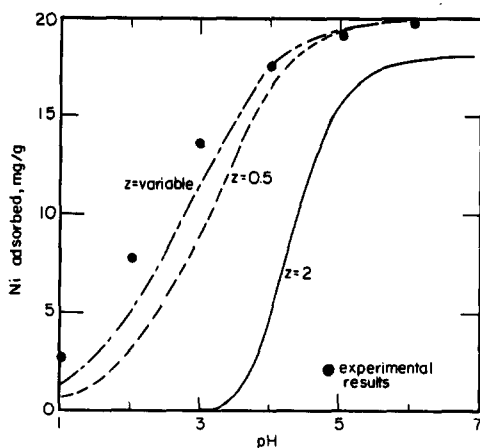

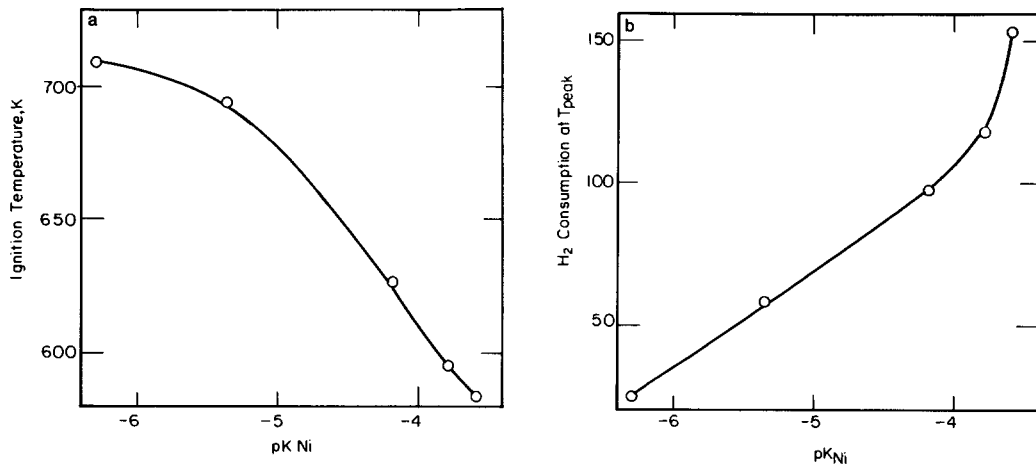FIG. 5. Prediction of nickel adsorption results for each value of the stoichiometric coefficient, z.

FIG. 6. Correlation of stability constant with (a) gasification temperature; (b) hydrogen consumption.

the best estimate of z that can apply to all the carbons employed (Case 3). Therefore, the regression results shown in Case 3 are preferred to those shown in Case 2 in order to have a meaningful comparison among carbons; TPRd data support this choice. Although Case 2 is a marginally better fit to the nickel adsorption results than Case 3, both can be considered reasonable in predicting the results within the experimental error. The probable error associated with the nickel adsorption experiments is 15%.

Correlations with the Stability Constant

If the ignition temperature T_{ig} is plotted against the stability constant, pK_{Ni}, an interesting correlation is found: pK_{Ni} increases in absolute value with increasing T_{ig} (Fig. 6a). If pK_{Ni} is an index of the strength of the metal-support interaction, the lower pK_{Ni} values (larger negative values) represent the stronger interaction. This suggests that when nickel species are more strongly bound to basic sites (for example, as-re-
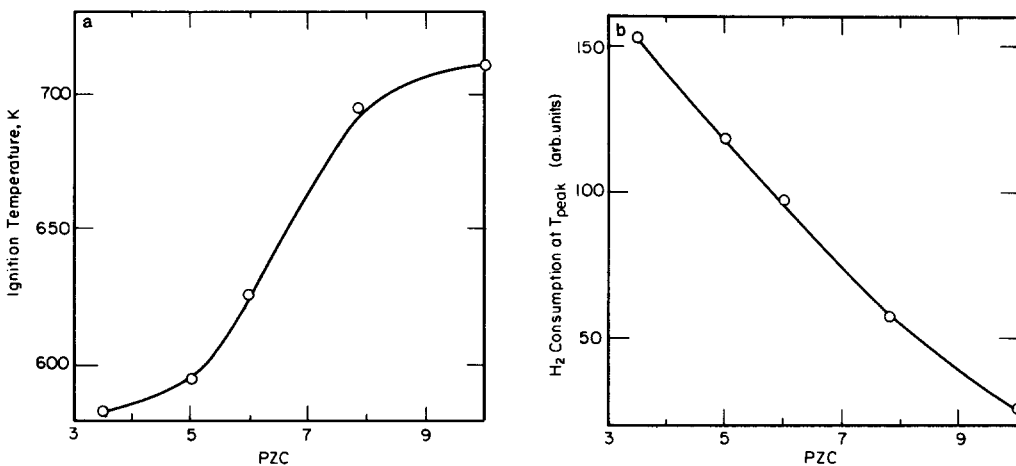

FIG. 7. Correlation of PZC with (a) gasification temperature; (b) hydrogen consumption.

TABLE 4

Free Energy of Adsorption

Sample	PZC	pK_{Ni}	ΔG, kJ/mol ($z = 0.5$)	$T_{ig,Ni}$ (K)	$H_{2,peak}$ (arb. unit)
0 M	10	-6.3	-47.9	710	25
0.2 M	7.8	-5.35	-40.9	698	58
0.4 M	6	-4.18	-31.9	628	97
1 M	5.5	-3.79	-28.9	595	118
2 M	3.5	-3.59	-27.4	586	153

ceived carbon) than to acidic sites, this bonding inhibits the role of nickel species as a catalyst.

Figure 6b demonstrates that the maximum in the hydrogen consumption rate can be correlated with the stability constant for the adsorbed precursor. The $H_{2,peak}$ increases as the absolute value of pK_{Ni} decreases. $H_{2,peak}$ reflects the amount reduced by or reacted with hydrogen at T_{peak}. T_{peak} can be considered to be a characteristic temperature related to the presence of a certain type of nickel precursor.

The smaller the $H_{2,peak}$ the smaller the pK_{Ni} is, or the more stable (in the thermodynamic sense) is the precursor ($pK_{Ni} = -\log \beta$). The portion of the hydrogen consumption during TPRd due to the nickel precursor is likely the results of the reduction of nickel oxide formed subsequent to preparation and after the material was exposed to the atmosphere. It is beyond the scope of this work to speculate on the nature of electronic effects that might be suppressing the reducibility of these nickel oxide type species on carbons with high PZCs.

In Table 4 the values of the free energy of adsorption, based on Case 3, for each carbon are listed. They range from -27.4 kJ/mol for the most oxidized carbon to -47.9 kJ/mol for the as-received carbon. Although these values are subject to the model, they are of the same order of magnitude as those of other systems (14). The negative sign indicates that the surface complexation is a favorable reaction.

The results of the gasification and TPRd studies in the present work clearly confirm the fact reported in the literature that the presence of surface groups (preferably acidic groups such as carboxyl groups) plays an important role during catalyst preparation. The role of the surface groups can be characterized by the surface ionization model and incorporated into the surface complex formation model. Collectively, these can serve as a foundation for establishing design criteria for the selection of optimum pH, nickel concentration, and the choice of support during catalyst preparation.

In conclusion, we find that the PZC is a significant factor that controls adsorption phenomena and catalytic behavior. The adsorption interaction strength of a carbon changes systematically with its PZC value, and experimental results from gasification and TPRd studies are correlated with the PZC (Fig. 7). Although the PZC alone cannot provide a full description of the surface properties of a carbon, it simplifies the characterization efforts, at least in a qualitative manner.

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