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The Catalytic Activity of Nickel and Nickel Boride for Formic Acid Decomposition

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The sintering characteristics of nickel and nickel boride blacks have been studied *in vacuo* and in various gaseous atmospheres. The initial surface areas of the nickel borides have been found to be dependent on drying procedures used. Results show that the sintering resistance of vacuum-dried Ni_2B is superior to that of nickel and that the presence of strongly adsorbed gases (such as formic acid vapor) retards the sintering of both materials.

Studies of the decomposition of formic acid adsorbed on these materials reveal only small differences in activity between Ni and Ni_2B. The activation energies (24.0 kcal/mole for nickel, 24.9 kcal/mole for air dried nickel boride, and 23.4 kcal/mole for the vacuum-dried Ni_2B) are quite similar, while the frequency factor for nickel is found to be larger than for the nickel borides.

INTRODUCTION

Nickel boride has been shown to be an effective catalyst both for the anodic oxidation of hydrogen in alkaline fuel cells (*1*) and for several gas- and liquid-phase reactions (*2*, *3*). However, a lack of available data made it impossible to decide whether the cause of the enhanced activity of nickel boride, as compared with that of highly dispersed nickel, is due to its intrinsic properties or to a higher, stable surface area. This investigation has been undertaken to clarify this question.

Because sintering data on nickel and nickel boride blacks were nonexistent, a study was made initially of the sintering characteristics of both materials *in vacuo* and in various gaseous atmospheres. Besides providing a phenomenological description of the sintering characteristics, these measurements also permitted us to assess whether sintering would be a problem at temperatures chosen for the catalytic studies.

The decomposition of formic acid was chosen as the model reaction for comparing the catalytic behavior of these materials. A large amount of information exists on the kinetics of this reaction on nickel. Many authors (*4–6*) have studied the decomposition in both flow and static systems and observed decays in activity due to poisoning by impurities and products of the reaction itself. Spectroscopic data (*7–10*) indicate that the rate-determining step on nickel is the decomposition of an adsorbed formate group. After finding that this was also probably true for the nickel borides, it was decided that the most unambiguous way to investigate this reaction would be to study the decomposition of adsorbed layers of acid directly. Under these conditions the oxidation of the catalyst is much less pronounced than when studying the decomposition of the gaseous reactant in the temperature range selected for this work. The small fraction of surface oxide formed during the decomposition of the chemisorbed intermediate can be reduced by hydrogen without changing the surface area or the activity of the catalyst.

EXPERIMENTAL

Materials. The gases used—hydrogen, carbon monoxide, and nitrogen—were assayed grade obtained from the Air Reduction Corporation sealed in 1-liter Pyrex flasks. The formic acid was prepared by adding anhydrous calcium sulfate to analytical reagent formic acid. The acid was then distilled, collected, and stored over fresh anhydrous calcium sulfate to prevent readsorption of water.

The nickel catalysts were prepared by decomposition of nickel formate. Specifically, after the salt had been dehydrated by heating at 150°C for 1 hr, the material was decomposed in air at 190°C. The products were found to be mostly nickel with a small amount of nickel oxide, which was subsequently reduced with hydrogen.

The nickel boride "blacks" were prepared by the Schlesinger method (*11*) which consists of adding, drop by drop, a solution of sodium borohydride to one of nickel sulfate, washing the precipitate, and storing it under distilled water. The blacks were dried in air or under vacuum. All samples used for the sintering studies were taken from the same batch of prepared material. Initial surface areas, prior to hydrogen pretreatment, depended on the drying method; the air- and vacuum-dried samples from the same batch had areas of 69 ± 2 and 29 ± 1 m^2/g, respectively. These materials were observed to be nonferromagnetic even after hydrogen treatment. X-Ray, electron diffraction, and chemical analyses of samples prepared in the same manner revealed that they consisted of small crystals of Ni_2B even after exposure to air. This agrees with the findings of others (*12*).

Experimental technique. A static, volumetric apparatus with a two-stage mercury diffusion pump was used. The sample holder was directly sealed to the system to avoid greased joints and was protected from mercury vapor by means of gold foil and liquid nitrogen traps. The sample bulb could be heated by either an oil bath or an oven. Pressures were measured by a mercury manometer constructed of precision bore tubing and read to within ±0.02 mm by a cathetometer. The total volume of the system was about 140 cc.

In the initial sintering studies the samples were first treated with hydrogen at about 225°C in a closed system to reduce surface oxides. The water vapor formed was condensed into a liquid nitrogen trap which could be separately pumped, and the hydrogen was replaced several times during the reduction process. When (as judged from pressure measurements) no further formation of water vapor occurred, the gas phase was removed, the system pumped down overnight at 25°C to 1×10^{-6} torr, and an initial surface area determined by the conventional BET method (N_2 adsorption at −195°C).

The samples were then heated at fixed temperatures for selected time intervals *in vacuo* or in various gaseous atmospheres, which were introduced at 25°C, and their surface areas redetermined; this procedure was repeated until a complete sintering curve was obtained. Below 225°C, heating was conducted by means of the oil bath, controllable to within ±0.3°C. At higher temperatures, the oven was employed. In both cases, the heating device, already at the desired temperature, was raised around the sample holder. A fresh sample was used for each of the temperatures and gaseous atmospheres selected.

For kinetic studies, the areas of the catalysts employed were determined both by room-temperature chemisorption of H_2 and by N_2 adsorption at −195°C. For nickel, successive cycles of hydrogen reduction and degassing were continued at temperatures as high as 270°C until the two areas agreed to within 4% [using Klemperer and Stone's (*13*) value of 13 Å^2/H_2 molecule and the generally accepted value of 16.2 Å for nitrogen]. For the nickel borides the reduction and degassing cycles were carried out until no further increase in the H_2/N_2 area ratio could be seen, utilizing reduction temperatures of up to 300°C. At this point, area ratios of 0.65 and 0.5 were generally obtained for the vacuum- and air-dried materials, respectively. After each experiment, the samples were recleaned with H_2 at ~225°C and, when left overnight, were stored in 100 mm of H_2. The H_2 was removed at 200°C under vacuum and the sample holder rapidly pumped down to $\sim 3 \times 10^{-7}$ torr before each run. Prior to studying the decomposition of chemisorbed formate, the catalyst samples were sintered to near steady state at 250–300°C. In all cases the temperature selected for formic acid decomposition did not exceed 205°C.

Formic acid was chemisorbed at room temperature. The vapor phase was left in contact with the sample for 30 min. The gas was then removed by evacuation for about 20 min. The sample was rapidly brought to the desired temperature by raising a heated oil bath around the 20-cc sample holder. The release of material into the gas phase was then monitored with time. In a large number of cases, the percentage of released gas which was not condensable at —195°C was determined. These noncondensable gases are H_2 and CO. In all cases about 45% of the decomposition product was noncondensable, showing that decomposition of chemisorbed formic acid was occurring. Blank runs with pure formic acid indicated that all of it was condensable at —195°C. These results are shown in Table 1. The pressure changes caused by release of products were, in all experiments, in the 30–70 torr range. In preliminary experiments with nickel in the presence of formic acid vapor, it was demonstrated that vigorous stirring of the catalyst with an external magnet did not modify the rate of reaction, which shows that diffusion limitations are not important during either adsorption or dissociative desorption.

TABLE 1
NONCONDENSABLE GASES FROM FORMIC ACID DECOMPOSITION

Material	Run No.	% Not Condensable
Ni	1	45.2
	2	46.0
	3	46.8
	4	48.0
Ni_2B	1	43.0
(air-dried)	2	44.9
Ni_2B	1	46.0
(vacuum-dried)	2	44.9
	3	47.3

To determine, with confidence, that we were truly studying the decomposition of adsorbed formate groups, the following experiment was conducted using a nickel sample. Formic acid vapor was adsorbed on a sample at 20°C until 40 torr excess remained in the gas phase. At this point the gas phase was removed and the system evacuated for 20 min, the sample procedure later used in the kinetic experiments. Hydrogen was then adsorbed on the surface at 20°C and 350 torr pressure. Using 13.0 Å^2/molecule for the area of hydrogen, it was found that the area coverable by hydrogen at this point was 50% of the surface. This experiment was later repeated with the same result, which clearly indicates that hydrogen, initially formed by dissociative adsorption of formic acid, was removed from the surface and system during evacuation prior to conducting the kinetic experiments.

RESULTS

Sintering of nickel black. Curve (a) of Fig. 1 shows the sintering of a nickel

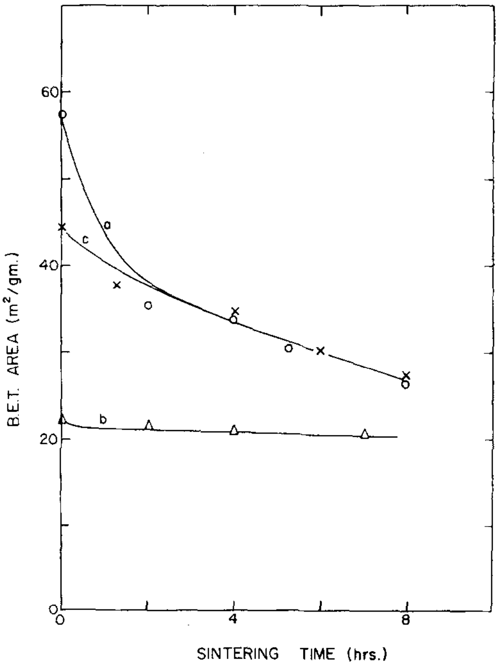

FIG. 1. Sintering of nickel and nickel boride blacks *in vacuo* at 220°C: ○, nickel; ×, Ni_2B, air-dried; △, Ni_2B, vacuum-dried.

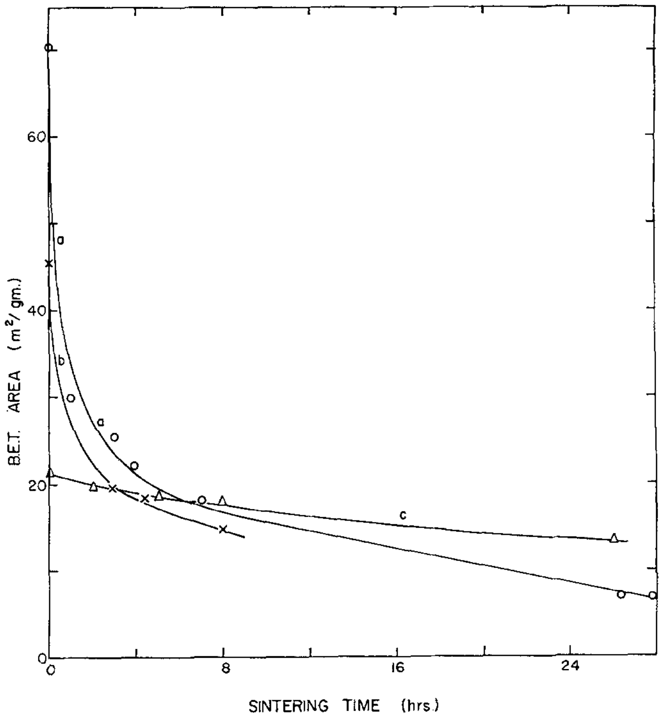

FIG. 2. Sintering of nickel and nickel boride catalysts *in vacuo* at 250°C: ○, nickel; ×, Ni_2B, air-dried; △, Ni_2B, vacuum-dried.

sample at 200°C *in vacuo*. There is a sharp loss in area over the first hour, followed by a slower decrease. This finding is similar to that noted by McKee (*14*) for platinum blacks.

Curve (a) of Fig. 2 shows the sintering of a nickel sample at 250°C *in vacuo*. A rapid decrease in area was observed during the first hour, about 50% of the initial area being lost in this interval; this was followed by a slower decline in area.

The effect of HCOOH vapor at 250°C on the sintering rate of nickel was determined. As can be noted from Fig. 3, the area loss is much less drastic than *in vacuo*.

The effect of hydrogen atmosphere on the sintering at 250°C of a nickel sample was also investigated [curve (c) of Fig. 3]. Results show that sintering, while not as pronounced as *in vacuo*, is still significantly greater than in formic acid.

Sintering of vacuum-dried nickel boride. Curve (b) of Fig. 1 and curve (b) of Fig. 2 show the sintering *in vacuo* of vacuum-dried nickel boride samples at 200° and 250°C, respectively. As can be noticed, the sintering resistance is superior to that of nickel.

Sintering of air-dried nickel boride. Curve (c) of Fig. 2 shows the sintering behavior of a sample of this material *in vacuo* at 200°C. While the early initial loss was less than that of nickel, the slower decline after the first hour was the same. Curve (c) of Fig. 2 shows the sintering of a sample at 250°C. Most of the loss was recorded in the first hour, with a slow decline after this interval.

The effect of formic acid vapor on the sintering at 250°C is shown in curve (e) of Fig. 3. In this case, also, the presence of strongly adsorbed species retards sintering.

Formic acid decomposition on nickel. Several decomposition experiments on one sample were carried out in the temperature range 140–170°C. The noncondensable portion of the desorbed material was determined at the close of each experiment to ensure that a decomposition and not a mere desorption was actually observed.

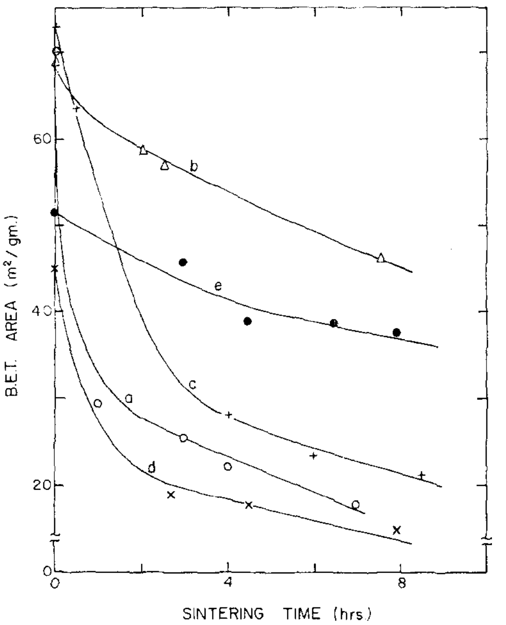

Fig. 3. Effect of adsorbed gases on the sintering rates of nickel and nickel boride: ○, nickel sintered under vacuum; △, nickel sintered under formic acid; +, nickel sintered under hydrogen; ×, air-dried boride sintered under vacuum; ●, air-dried nickel boride sintered under formic acid.

The sample was recleaned between runs, and at the end of the sequence the study at the first selected temperature was repeated and the original rate reproduced. The results (Fig. 4) show that first order kinetics are observed over two decades of reaction. From these data values of 24.0 kcal/mole for the apparent activation energy and 2.15×10^{10} molecules/site sec for the pre-exponential factor were computed. (See Fig. 5 and Table 2.)

TABLE 2
Kinetic Parameters for Formic Acid Decomposition

	BET (m^2/g)	H_2 ads. (m^2/g)	G (kcal/mole)	*A* factor (mole/site sec)[a]
Nickel	15.2	15.2	24.0	2.15×10^{10}
Ni_2B (air-dried)	8.5	4.25	24.9	3.60×10^9
Ni_2B (vacuum-dried)	10.4	6.76	23.4	3.45×10^9

[a] The number of sites is estimated from the hydrogen adsorption value, assuming each H atom occupies a site (i.e., 6.45 Å²).

Formic acid decomposition on air-dried nickel boride. This material was studied in the 155–185°C range using the same procedure as in the case of nickel. The kinetic plots were found to be similar to Fig. 4 (i.e., linear over two decades of reaction). The activation energy for dissociative desorption of formic acid in this material was very similar to that of nickel, while the frequency factor was smaller, even if only the hydrogen-adsorbing surface is taken into consideration. (See Fig. 5 and Table 2.)

Formic acid decomposition on vacuum-dried nickel boride. This material was studied in the 170–205°C range, the method of investigation being the same as in the preceding case. Plots similar to Fig. 4 revealed first order kinetics with an apparent activation energy of 23.4 kcal/mole and frequency factor 3.45×10^9. (See Fig. 5 and Table 2.)

Effect of HCOOH, CO, and H_2O on decomposition rate. Measurements of the rate of decomposition of HCOOH, with HCOOH vapor present (20 mm) in addition to the chemisorbed material and without treating the catalyst with H_2 between runs, show a decay of catalyst activity. When the catalyst had been presintered as described above, this rate decrease was relatively small but measurable (20% between two consecutive runs at 202°C).

To study the cause of the poisoning of the catalyst, the effect of preadsorbed CO or H_2O on the decomposition rate of chemisorbed HCOOH was studied.

Three experiments were conducted in succession at 170°C, on a well-sintered sample of vacuum-dried Ni_2B, with recleaning between runs. In the first run, pure formic acid was preadsorbed and the decomposition rate studied. In the second, CO was first adsorbed, the gas phase removed, and formic acid admitted. After allowing about 30 min for equilibration at 25°C, the gas phase was removed and the decomposition rate measured at 170°C. In the third, water was adsorbed, the system

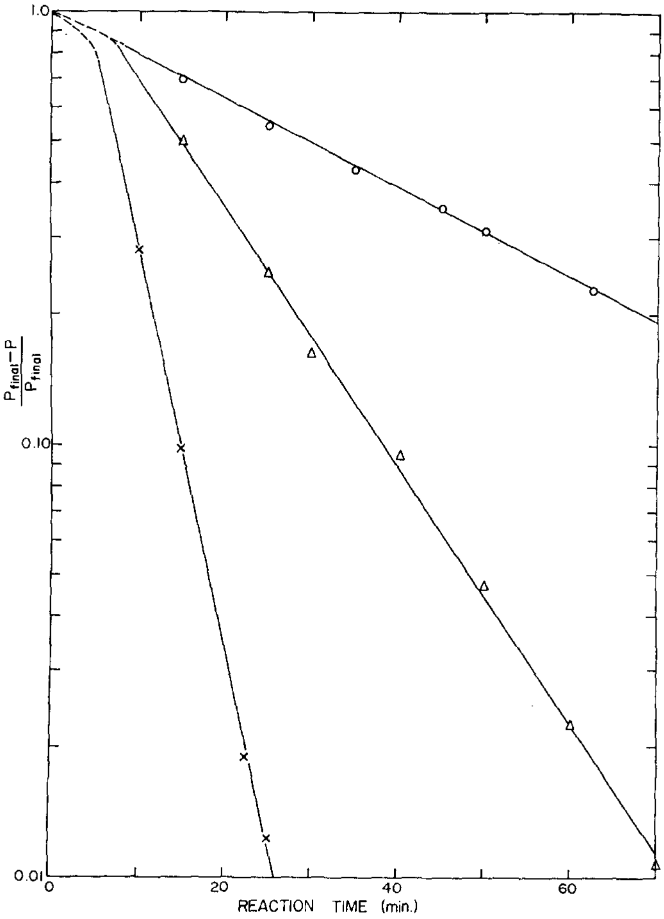

FIG. 4. Decomposition rates of adsorbed formic acid on nickel: ×, 170°C; △, 154.5°C; and ○, 139°C.

evacuated, formic acid vapor introduced, and the same time allowed for equilibration at 25°C as before. Next, the vapor was removed, and a desorption experiment conducted. The results indicate that preadsorption (at room temperature) of CO had little influence on the results, while water had a twofold effect: (1) The amount of desorbable material was only ~40% of that released in the previous experiment, and (2) the observed decomposition rate was about one-third of that observed on a clean sample.

Effects of specific surface area on reaction rates. An investigation of the effects of specific surface area on reaction rate was conducted at 170°C on the samples used in the kinetic studies. Between runs, the samples were sintered and cleaned at 260°C. For these experiments, formic acid was introduced at 25°C and was left in contact with the samples during the runs. The pressure of formic acid after the initial rapid chemisorption was 20 torr. The specific activities were gauged from the times required to decompose 50% of the adsorbed and gas-phase material. The results compiled in Fig. 6 can be fitted by hyperbolic curves in which the product of half-time and area is constant, indicating that in the range studied and within the experimental error, the intrinsic activity is independent of surface area.

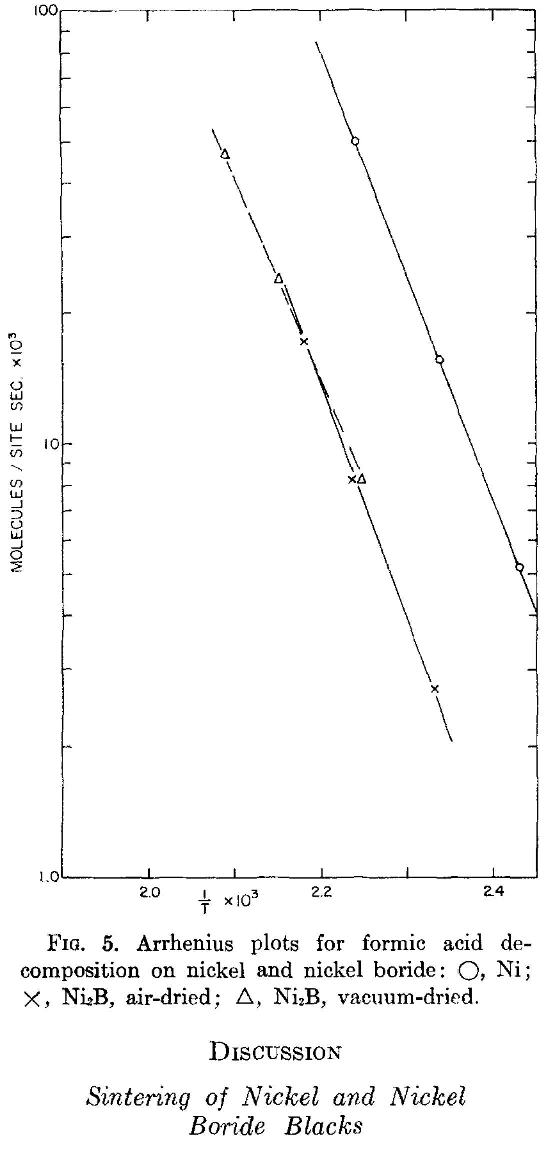

Fig. 5. Arrhenius plots for formic acid decomposition on nickel and nickel boride: ○, Ni; ×, Ni_2B, air-dried; △, Ni_2B, vacuum-dried.

Discussion

Sintering of Nickel and Nickel Boride Blacks

The kinetics of sintering of Ni and Ni_2B *in vacuo* are similar to those observed by McKee (*14*) for Pt black. The lower sintering rate observed with vacuum-dried Ni_2B, beyond that expected from the lower initial surface, is consistent with the slower surface migration which should be expected from a binary compound. The higher surface areas obtained with air-dried material and the more rapid sintering of these areas indicates an oxidation of the surface during drying which after reduction with H_2 produces a highly dispersed Ni phase.

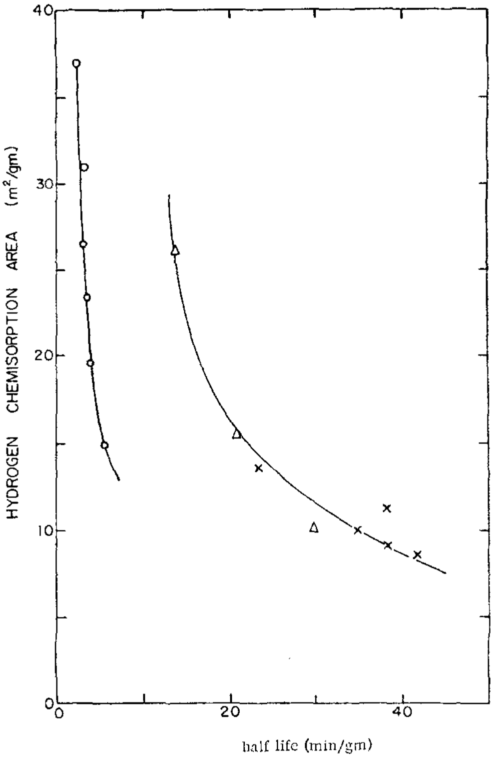

Fig. 6. Plots of specific surface area versus reaction half-life for formic acid decomposition on nickel and nickel boride catalysts at 170°C: ○, Ni; ×, Ni_2B, air-dried; △, Ni_2B, vacuum-dried.

On the other hand, the electron diffraction pattern, typical of Ni_2B, and the lack of substantial ferromagnetism suggest that this oxidation and consequent reduction involves only a few atomic layers of the Ni_2B particles.

The effect of HCOOH atmosphere can be explained by an inhibition of the surface migration caused by the strongly chemisorbed species. The practical implication of this inhibition is that during HCOOH decomposition studies, the sintering of the sample is low. Another practical implication refers to such cases as the fabrication of fuel cell electrodes where the electrodes containing Ni_2B or Ni catalysts are customarily prepared at temperatures of about 250°C. By appropriate selection of the atmosphere during sintering, it is possible to reduce drastically undesired decrease of the catalyst surface.

Formic Acid Decomposition

The experiments reported above show that after dissociative adsorption of formic acid according to the process

$$\mathrm{HCOOH \rightarrow HCOO_{(ads)} + H_{(ads)}} \qquad (1)$$

the hydrogen formed is only weakly held and, hence, is removed with the gas phase prior to the start of our kinetic experiments. The process

$$\mathrm{HCOO_{(ads)} \rightarrow CO_{2(g)} + \tfrac{1}{2}H_{(g)}} \qquad (2)$$

has been suggested by several authors as being the slow step in the reaction sequence. The observed first order kinetics in our studies give added weight to such ideas.

The observed product ratios (i.e., 45% noncondensable) warrant comment. For the processes

$$\mathrm{HCOO \rightarrow CO_{2(g)} + \tfrac{1}{2}H_{2(g)}} \qquad (3a)$$

$$\mathrm{2\ HCOO \rightarrow CO + CO_2 + H_2O} \qquad (3b)$$

33% of the released material should be noncondensable. The fact that a higher ratio is found suggests that processes which cause no net pressure changes, such as

$$\mathrm{Ni + CO_{2(g)} \rightleftharpoons Ni(O)ads + CO_{gas}} \qquad (4)$$

and

$$\mathrm{Ni + H_2O \rightleftharpoons Ni(O)ads + H_{2(gas)}} \qquad (5)$$

are occurring under our conditions. These processes can occur below about 210°C; thermodynamic calculations show that in our system they should decrease in magnitude in the forward direction with increasing temperature. At higher temperatures the same considerations show that the surface should remain in an essentially reduced state. Such behavior has been seen experimentally (*8*). The process stated immediately above could well account for the observed decays in activity between runs, if no recleaning was conducted. The 45% noncondensable result indicates that ~16% of the surface has been oxidized. This is about the same as the percent of rate decay observed under such conditions. The fact that reproducibility of rates has been observed between runs at the same temperature indicates that the small amount of surface oxidation, followed by hydrogen treatment and degassing via bakeout procedure, essentially returns samples to their initial well-sintered states. The sintering data presented earlier in this paper support such a view.

That H_2O, one of the products, can poison the surface has been shown experimentally. Such poisoning can easily occur via reaction (5). This is in accordance with the results of other workers who found retardation by water vapor and complete loss of activity due to exposure of samples to oxygen.

Although water can be produced from formic acid via reaction (3b), the process

$$\mathrm{Ni + HCOOH \rightarrow NiO + H_2 + CO} \qquad (6)$$

may still be possible to some degree.

The elimination of the gas phase and the reduction of the catalyst with H_2 between runs removes the complications due to oxidation of the surface, and still the studied reaction is relevant to the catalytic decomposition of HCOOH. Thus several authors (*6*, *7*, *15*, *16*, *17*) have postulated that the decomposition of adsorbed acid occurs in the following steps on nickel:

(a) $\mathrm{HCOOH \rightarrow HCOO\cdot_{(ads)} + H\cdot_{(ads)}}$ fast

(b) $\mathrm{HCOOH + H\cdot_{(ads)} \rightarrow H_2 + HCOO\cdot_{(ads)}}$ fast

(c) $\mathrm{HCOO\cdot_{(ads)} \rightarrow CO_2 + H\cdot_{(ads)} \rightleftharpoons \tfrac{1}{2}H_2 + CO_{2(ads)}}$ slow

Studies by infrared spectroscopy (*8*, *10*) have established that at higher coverages the species predominating on the surface is an adsorbed formate group. Fahrenfort *et al.* (*9*, *10*) have shown the desorption of this species to be a highly activated first order process, the rate of which could be best described by the relationship $K = 10^{10} \exp(-23.000/RT)$. From our data on dissociative desorption of the adsorbed layer on nickel, values of 24.0 kcal/mole for the apparent activation energy and 2.15×10^{10} for the pre-exponential factor, as well as first order kinetics, have been determined. Thus, the results of these authors are confirmed by another method. The fact that we observe the same first order reaction for Ni and Ni_2B, with the same activation energy, suggests that the mechanism is the same for nickel borides as for nickel. The difference in preexponential factors between Ni and Ni_2B (Table 2) is difficult to interpret unambiguously due to possible steric effects resulting from the presence of boron atoms or boron oxides on the surfaces studied. It is clear, however, that the nickel borides are not more active for the formic acid decomposition than pure nickel. Both for nickel and nickel boride the shape of the decline in activity with decreasing area (Fig. 6) indicates that the proportion of active areas in the catalysts is quite independent of the degree of sintering.

It is possible, of course, that Ni_2B is specifically more active than Ni for other reactions. However, a more probable explanation for observed higher activity of Ni_2B can be either the very high surfaces obtained with air-dried materials (this may be true in the cases in which a surface determination was not done) or the higher temperature stability of the borides. This result is not easily interpretable in terms of the band theory of catalysis, and judgement has to be reserved on questions relating to the source of activity. The nonmagnetic state of the material may indicate that if the surface composition after pretreatment is similar to that of the bulk, the source of activity may not be that of a nickel surface.

CONCLUSIONS

Comparison of the sintering rate on nickel and nickel boride shows that nickel boride is more resistant to sintering than nickel. Adsorbed formic acid retards the rate loss of area significantly.

Kinetic studies of the decomposition of chemisorbed formic acid on nickel and nickel boride show no differences either in mechanism or in apparent activation energy between the two materials, which is about 24 kcal/mole. The only dissimilarity between them was in their frequency factors which are smaller for Ni_2B, even when considering only the sites able to chemisorb hydrogen. This indicates that the effectiveness of the Ni sites of nickel boride is affected by geometric factors.

ACKNOWLEDGMENT

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Added Note: The recent work of W. Romanowski (*Roczniki Chemii,* March, 1967, p. 423) has been called to our attention. He found that the stoichiometry of nickel boride, prepared by a similar method to that used in this paper, corresponds to Ni_2B. Electron diffraction studies of freshly prepared material showed a highly distorted crystalline structure. After heating at 300–500°C, a large ratio of Ni_3B cementite phase is found. Activity losses after heating are explained by this author as due to the formation of this less active compound. In our work, under somewhat different conditions, the activity loss is interpreted as a mere surface area effect.

Differences in observed structure of prepared materials can also be caused by the variable degree of oxidation.

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