In *Situ* Catalytic Activation and Regeneration Using Electrostatic Field Gradients as Demonstrated during Hydrogenolysis of Ethane and Ethylene on a Nickel Wire Catalyst

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A new method is described in which dramatic increases in catalytic activity are obtained *after* a Ni wire catalyst is subjected to relatively high applied electrostatic potentials. The potentials are applied under what is basically an open circuit arrangement in that the Ni wire is biased either positively or negatively with respect to an aluminum cylinder located *outside* the reactor. Activation is observed *only* when the Ni wire is biased negatively with respect to the Al cylinder. This activation and, in some cases, catalytic regeneration is believed to arise from the combined effect of high field gradients and small leakage currents generated during high potential application. The activation effect is demonstrated for hydrogenolysis of C_2H_6 and C_2H_4 on a Ni wire catalyst. The activation procedure described represents a direct, *in situ*, relatively inexpensive approach to improved catalytic efficiency. This method may well find utility in many other catalytic systems. © 1986 Academic Press, Inc.

INTRODUCTION

The nickel catalyzed hydrogenolysis of C_2H_6 to form CH_4 has been the subject of numerous kinetic studies. This reaction proceeds at a measurable rate starting at temperatures around 200°C with the observed rate increasing rapidly with temperatures up to around 250°C; and, thereafter, more slowly to 350°C (*1*). Above 350°C the reaction rate is relatively temperature independent. Finally, one notes that in the temperature range 500–700°C a *decreased* reaction rate is noted relative to those obtained at lower temperatures.

The temperature dependence of this reaction, including the high temperature inactivation of the Ni catalyst, has been the subject of much attention (*2–12, 19*). These studies show that the temperature effects are intimately entwined with the formation of Ni–C bonds in which this high tempera-

ture "coking" of the catalyst results in catalytic poisoning with respect to the hydrogenolysis reaction. Indeed, recent surface studies have produced not only molecular confirmation of coking but actual evidence of specific carbon molecular structures for surface-formed molecules. For example, cross-linking of initially formed unsaturated carbon chains with the eventual formation of two-dimensional graphite-like carbon deposits is believed to represent the high temperature inhibition of nickel in hydrogenolysis or dehydrogenolysis reactions (*13*). Other studies have implicated the formation of multiple metal–carbon atom bonds as playing an important role in this inactivation process (*14*).

Regardless of the exact nature of the carbon–nickel molecular formations, the important fact from the practical standpoint is that those molecular interactions (i.e., ultimate Ni deactivation) are significant at temperatures as low as 250°C and become progressively more important with increasing temperature. Regeneration of catalytic activity can be achieved with fair success at

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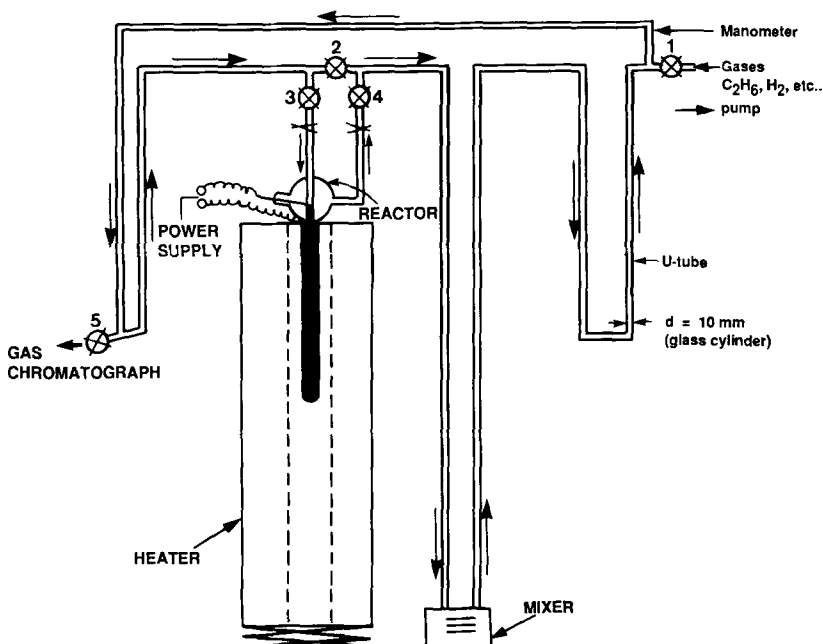
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FIG. 1. All glass reaction system used in obtaining rate measurements.

temperatures below 250°C through the use of H$_2$ or steam treatment (15–18). At higher temperatures the direct *in situ* regeneration of catalytic activity is much more difficult to achieve. It appears that the high temperature "coking" of the nickel catalyst results in virtual irreversible formation of metal–carbide bonds in terms of normal chemical regenerating activities. In this connection, one notes that treatment with oxygen removes carbon formations at lower temperatures but metal–oxide formation results at higher temperatures decreasing catalytic activity. Oxygen is apparently not successful in catalytic regeneration at temperatures above 360°C where graphite formation is observed (1).

The work reported in this paper describes a novel, inexpensive, and rapid method for the direct *in situ* regeneration of catalytic activity. The method developed centers on the application of a high electrostatic field gradient under what is essentially an open-circuit condition. Although catalytic regeneration is demonstrated specifically for Ni, it is important to note that

this method should be applicable to a wide variety of metal catalytic systems in which catalyst inactivation is observed. In this paper the *in situ* regeneration is demonstrated for Ni with extensive studies of the hydrogenolysis of ethane

$$C_2H_6(g) + H_2(g) \rightarrow 2CH_4(g) \quad (A)$$
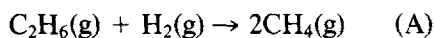
and, to a lesser extent, investigation of the reaction of hydrogenolysis of ethylene

$$C_2H_4(g) + 2H_2(g) \rightarrow 2CH_4(g). \quad (B)$$
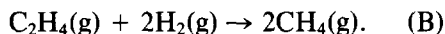
EXPERIMENTAL APPARATUS AND PROCEDURE

Reactions were carried out in a conventional glass reaction and gas handling system as shown in Fig. 1. The system included a metal bellows type circulation pump which was used to mix the reactant gases prior to use, as well as to circulate the reaction mixture during the kinetic runs. A 0.127-mm-diameter Ni wire of 50-m length was coiled around a heavier gauge length of Ni centered inside the reaction chamber. In the C$_2$H$_4$ hydrogenolysis, the length of Ni

wire was 120 m. The critical difference between this work and all previous studies of this type was the location of an aluminum cylinder (0.7-mm thickness, 21.5-mm diameter, and 261-mm length) around the exterior of the glass reactor. Both the Al cylinder and the nickel wire were connected by leads to a high voltage power supply (Fluke, Model 415B). The output from the power supply could be reversed and experiments were carried out with the Ni wire biased both positively and negatively with respect to the Al cylinder. A more detailed drawing of the reactor section is shown in Fig. 2. Although this arrangement represents what is basically an open circuit at sufficiently high applied potentials, small currents (μA range) were recorded on the microammeter located in the power supply circuit. For a given applied potential, the current observed was a sensitive function of both reactant gas pressure and reactor temperature, decreasing with increased pressure and increasing with increased temperature. The temperature dependence of the current observed would include contributions from both gas and glass reactor wall conductivity changes. For a given pressure and temperature, the current increased slowly with increased applied voltage up to the point at which electrical breakdown was observed at which time a sudden current surge was noted along with visible arcing between the Ni wire and Al cylinder. All kinetic data reported in this study were obtained under applied potentials well below the electrical breakdown values for any given pressure and temperature.

The progress of the reaction was monitored via aliquot sampling of the gas mixture for gas chromatographic analysis. Aliquots of the reactant mixture were expanded into the sample loop of a direct injection gas sampling valve (Varian Corp.). This loop was evacuated between successive runs. The gas chromatography utilized squalane columns and flame ionization detection.

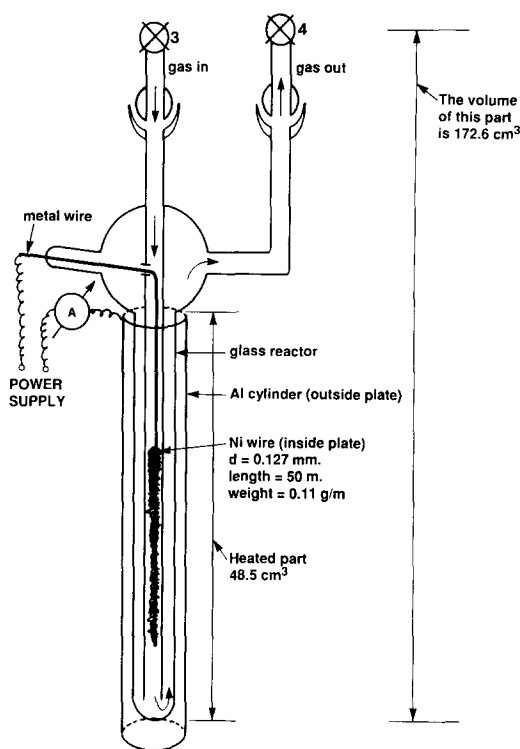Kinetic studies were carried out over the

FIG. 2. A detailed schematic of the reactor section showing essential dimensions, sizes, and physical arrangement of electrodes.

temperature range 210 to 350°C for both reactions (A) and (B). At each temperature, the Ni wire was first subjected to treatment with 33 Torr H_2 for 20 min to produce a standard catalytic surface. The "normal" catalytic reaction rate for either reaction (A) or (B) was then determined in a sequence of runs, each of which were of 20-min duration. It is important to note that treatment of the Ni wire with 33 Torr H_2 was carried out between all successive runs at the various temperatures, including runs immediately following the application of voltages to the electrodes. Both C_2H_6 and H_2 or C_2H_4 and H_2 were present in the reactor during the periods when potential was being applied. Prior to an experimental run, the reactant gases were first mixed in the reaction system for 5 min during which time the reactor was empty and stopcocks 3 and 4 were closed. The vast majority of the runs
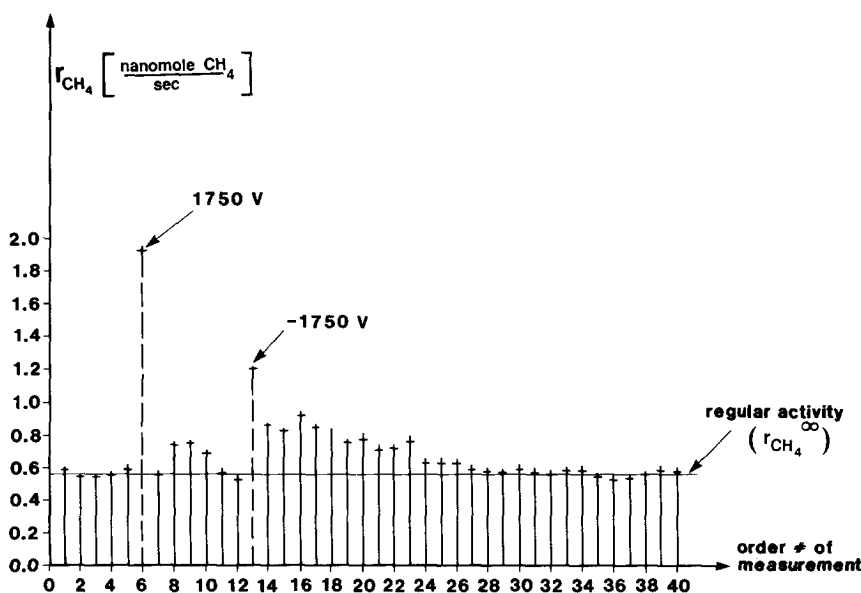
FIG. 3. The rate of methane production (r_{CH_4}) versus run number for experiments at 300°C. Positive and negative potentials of 1750 V were applied at run 6 and 13, respectively.

were carried out using reactant pressures of 33 Torr each unless otherwise noted. After mixing, the reaction was initiated with the simultaneous opening of stopcocks 3 and 4. Gas circulation was maintained during the kinetic runs. The rate of product formation was monitored via the aforementioned gas chromatographic analysis.

RESULTS

In general, reproducible rates of CH_4 formation were observed in a given series of runs at a specified temperature. For example, the rate of CH_4 formation would vary by approximately ±10% in a series of runs, in which each kinetic study involved the preparation of a new C_2H_6 + H_2 mixture and the pretreatment of the Ni wire with pure H_2 after every kinetic run. Dramatic increases in the CH_4 production rates were noted during the application of either a + or − potential to the nickel wire. Of significantly more interest is the fact that increased rates of CH_4 production persisted during certain runs carried out immediately *after* the application of potentials across the Ni and Al electrodes.

Typical results obtained in a series of kinetic runs at 300°C are shown in Fig. 3 for the hydrogenolysis reaction. In this figure, the rates of CH_4 production (r_{CH_4}), in nanomoles per second, are plotted during kinetic runs all involving identical pressures of C_2H_6 and H_2. The normal or regular activity of the Ni catalyst is evidenced in runs 1 through 5 in which good reproducibility of the r_{CH_4} is observed. A potential of +1750 V was then applied to the Ni wire (relative to the Al cylinder) and a dramatic increase in r_{CH_4} was obtained (run 6). Subsequent runs carried out in a manner identical to runs 1 through 5 produced what was essentially the regular catalytic rate, although fluctuations between successive runs were somewhat larger. In run 13, a negative potential was applied to the Ni wire (again relative to the Al cylinder) and an enhanced reaction rate observed. The subsequent runs (14 through 40) were carried out under normal conditions of zero applied potential and, as shown in Fig. 3, an initially enhanced rate of CH_4 formation is noted which decays slowly to the "regular activity."
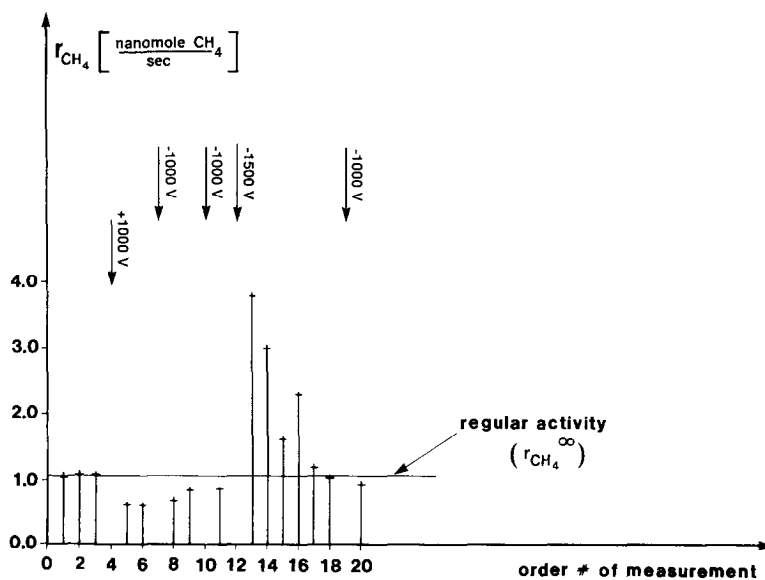
The aforementioned effects on r_{CH_4} for

FIG. 4. The rate of methane production (r_{CH_4}) versus run number for experiments at 350°C. Potentials were applied during runs 4, 7, 10, 12, and 19. The arrows indicate the magnitude and sign of the potentials employed. The value of r_{CH_4} is not shown for runs during actual potential application.

successive runs with and without applied potentials is even more dramatic at 350°C, as shown in Fig. 4. After initially establishing the normal catalytic rate (runs 1, 2, and 3) a series of experiments in which a +1000-V (run 4) and then a −1000-V (runs 7 and 10) potential on the Ni wire resulted in enhanced CH_4 production rates (actual rates during potential applications are not shown on this figure but are shown in Fig. 7). However, as shown in Fig. 4, the runs carried out immediately after the application of potentials (5, 8, and 11) did not exhibit increased CH_4 production. However, after the application of a −1500 V potential (run 12), subsequent runs without potential produced a greatly enhanced catalytic rate. The initial increases observed were substantially larger than those observed at 300°C. As can be seen by comparison of Figs. 3 and 4, the enhanced catalytic activity disappears much faster at 350°C than at 300°C.

Similar-type studies were carried out at both 250 and 210°C. At 250°C, as shown in Fig. 5, a series of potentials, including positive voltages as high as 3000 V, applied to the Ni wire had no perceptible effect on generating significantly enhanced catalytic activity in runs carried out immediately following the application of potentials. However after run 15, which involved the application of a −2500-V potential, increased rates were observed in the next eight runs (17 through 24). It is also of interest to note that this enhanced activity persists during all eight runs showing basically no trend toward decreased reactivity with time. Finally, runs carried out after the application of positive potentials appear to produce what is normal catalytic activity (e.g., runs 30 through 33). At 210°C, applications of potentials as high as + or −3000 V had no apparent effect on increasing catalytic activity in runs carried out immediately after the potentials were applied (Fig. 6).

As mentioned previously, but not shown explicitly in Figs. 4 through 6, an increased methane production rate is obtained during runs carried out with applied potentials. The acceleration in reactivity becomes more pronounced with increasing tempera-
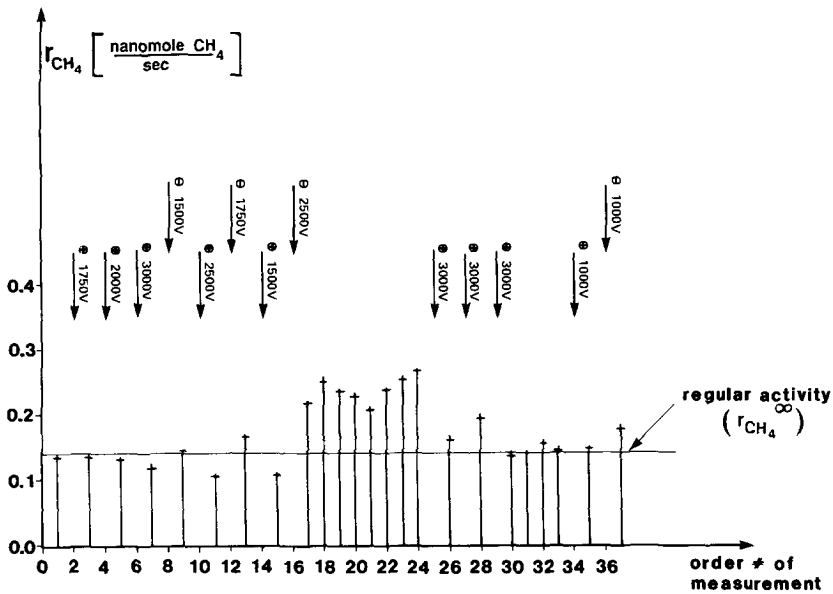
FIG. 5. The rate of methane production (r_{CH_4}) versus run number for experiments at 250°C. Arrows indicate the magnitude and sign of the potentials applied at runs 2, 4, 6, 8, 10, 12, 14, 16, 25, 27, 29, 34, and 36. The value of r_{CH_4} is not shown for runs during actual potential application.
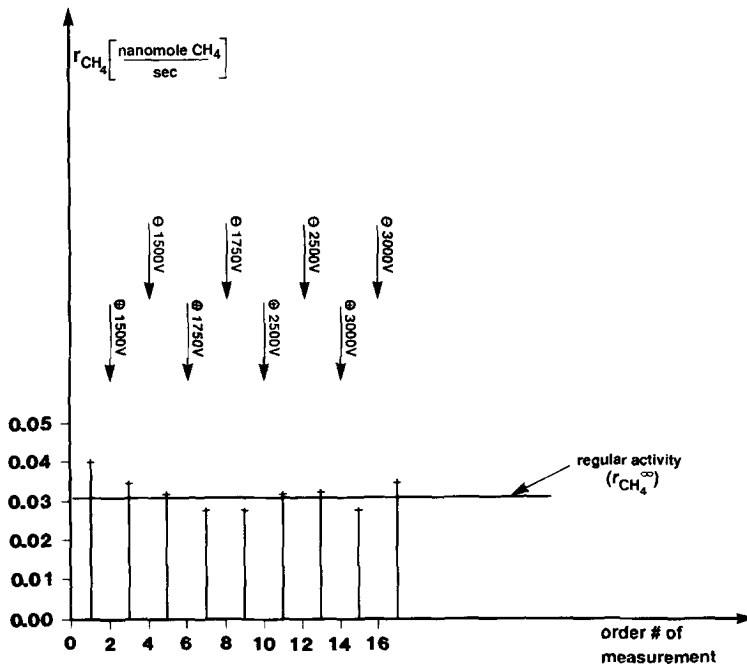

FIG. 6. The rate of methane production (r_{CH_4}) versus run number for experiments at 210°C. Arrows indicate the magnitude and sign of the potentials applied at runs 2, 4, 6, 8, 10, 12, 14, and 16. The value of r_{CH_4} is not shown for runs during actual potential application.
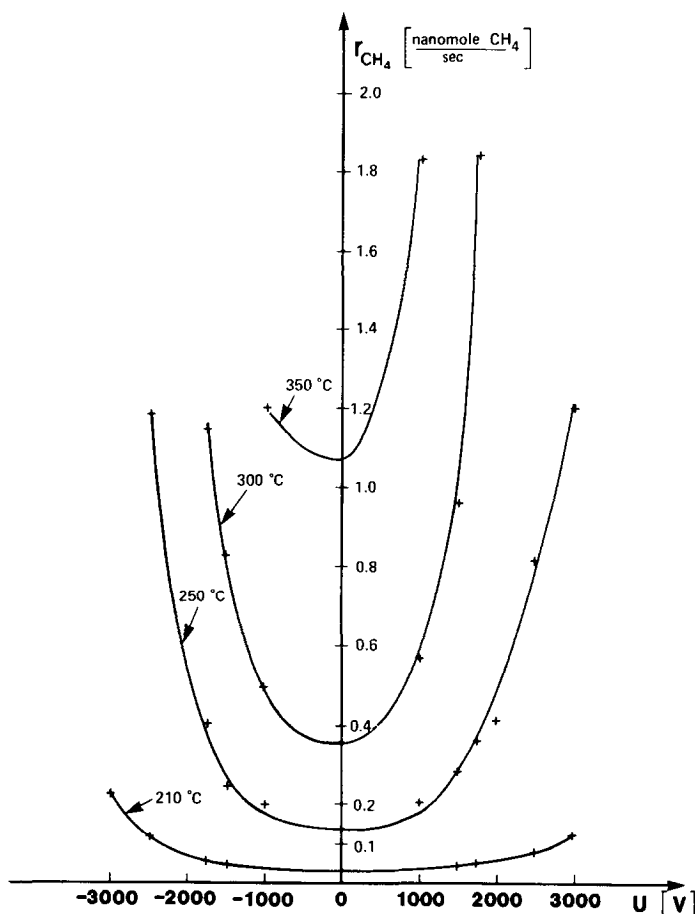
FIG. 7. The rate of methane production (r_{CH_4}) versus applied potential at temperatures from 210 to 350°C obtained during runs with applied potential.

ture and it is observed with both positive and negative potentials on the Ni wire. A summary of the reaction rates versus applied voltage at temperatures from 210 to 350°C is shown in Fig. 7. Experiments could not be extended to higher voltages at higher temperatures since the breakdown voltage decreased rapidly with increasing temperature.

A number of experiments were carried out on the Ni catalyzed hydrogenolysis of ethylene to form CH_4 [reaction (B)]. Previous work on this system shows that inactivation of the Ni catalyst occurs at high temperatures and this inactivation has been generally attributed to the formation of carbon deposits on the catalytic surface. In general, the results obtained during the application of potentials on CH_4 production in reaction (B) parallel those obtained during reaction (A). For example, Fig. 8 shows that immediately after the application of a -1750-V potential on the Ni wire a significantly enhanced catalytic activity is observed. Furthermore, this activity decreases rapidly on successive runs as was observed for the hydrogenolysis of ethane (cf. Fig. 4).

In view of the apparent improved catalytic activity obtained immediately following the application of certain minimum negative potentials, a series of experiments was carried out to determine if a time constant was involved in the regeneration of
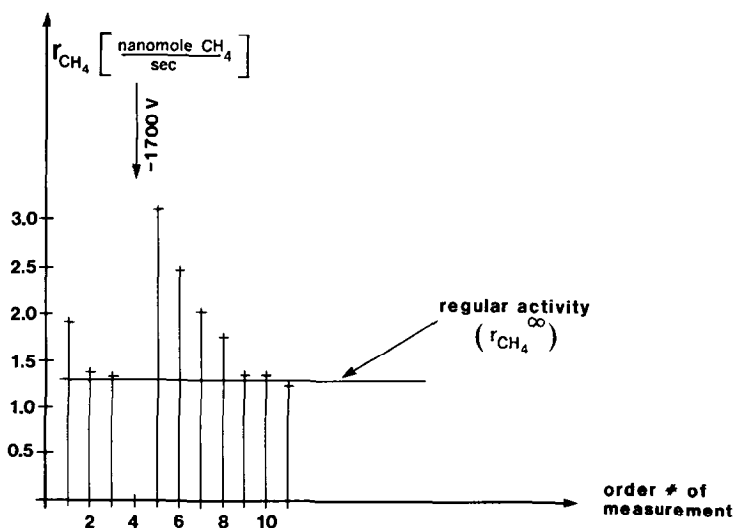
FIG. 8. The rate of methane production (r_{CH_4}) versus run number for experiments on the hydrogenolysis of ethylene at 350°C. A negative potential of 1750 V was applied at run 4. The value of r_{CH_4} during actual potential application is not shown.

catalytic activity during potential application. The results of these experiments carried out at 300°C and total pressure of 264 Torr are shown in Fig. 10. After establishing the baseline regular activity in the first three runs, a series of experiments involving the application of −2000-V potentials for varying times followed immediately with a run at zero potential were performed. As illustrated in this figure, there appears to be a minimum time (in this case around 10 min) for potential to be applied in order to restore maximum catalytic activity.

DISCUSSION

The increased rates of CH_4 formation during the runs involving an applied potential (Fig. 7) apparently arise from current induced ion–molecule reactions and do not represent enhanced reactivity from electrostatic field effects. Using the data shown in Fig. 7 and defining the quantity $r_{CH_4}-r_{CH_4}^{\infty}$ as the difference in CH_4 production in the presence and absence (regular activity) of potential, then as shown in Fig. 9, a plot of $r_{CH_4}-r_{CH_4}^{\infty}$ is roughly linear when plotted versus the measured current flows in runs

carried out at 300°C. This linearity is observed when the Ni wire is biased either positively or negatively. Similar plots, with approximately the same slopes, were observed at temperatures over the range from 210 to 350°C. These results are strong evidence that the enhanced CH_4 production during runs carried out with an applied potential simply represent gas phase ion–molecule reactions, some of which lead to CH_4 formation. Additionally, some of the extra CH_4 formation observed during potential application could have resulted from increased surface production via direct cleaning of the wire catalyst during current flow. Regardless of the reasons for increased CH_4 formation during current flow, the discussion which follows emphasizes CH_4 production in runs after the application of potential.

The acceleration in reaction rate during runs with applied potentials does not arise from a simple heating of the Ni wire. This explanation can be ruled out in view of the low power consumption involved in these experiments. For example, at 250°C and an applied potential of 2.5 kV the current leakage was less than 20 μA. The resistance of the Ni wire was less than 800 ohms. There-
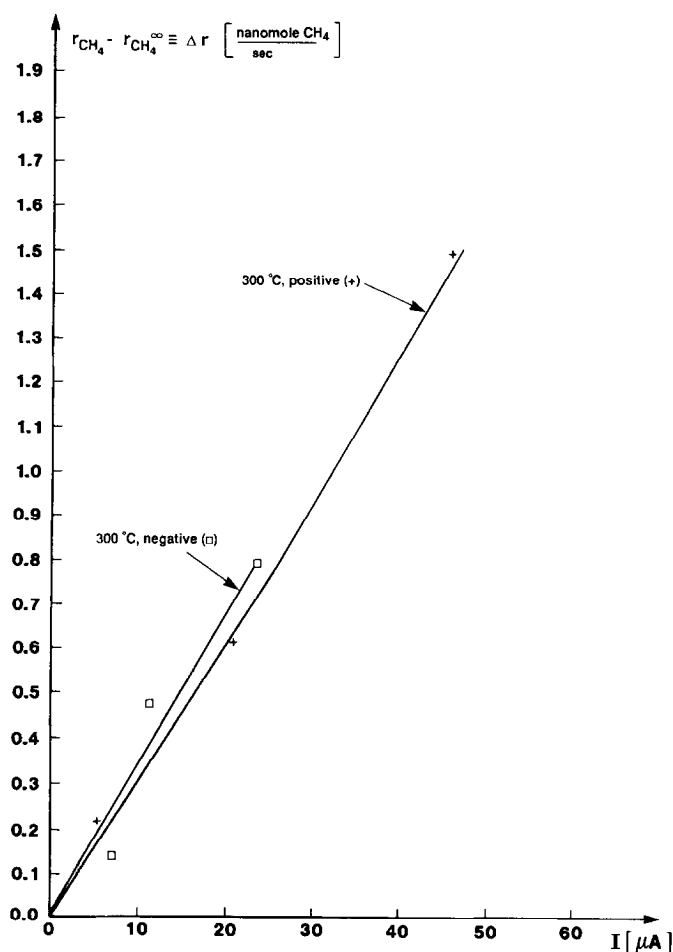
FIG. 9. The correlation between enhanced CH_4 production $(r_{CH_4}-r^\infty_{CH_4})$ during runs with applied potential and I (μA), the leakage current measured during these runs.

fore, power dissipation by the Ni wire is less than 3×10^{-7} W. On the basis of a 20-min run this represents 4×10^{-4} J of energy consumption by the wire. Since the heat capacity of the 5-g Ni sample was approximately 3 J/K, this translates to a maximum temperature rise of less than 0.0001 K.

Of much greater consequence than the increased methane yields during potential applications is the observation of the significantly increased reactivity immediately following certain runs in which negative potential has been applied. Under no circumstances were increases observed following the application of positive potentials to the Ni wire. The extent of this increase is

strongly dependent on the reaction temperature in terms of both the magnitude of the effect as well as the duration of the increase in subsequent runs carried out without applied potentials. It seems reasonable to conclude that during runs in which potential is applied (i.e., there is a measurable leakage current) surface processes occur in addition to the aforementioned ion–molecule reactions. Presumably these surface reactions represent a net increase in the number and/or nature of active sites present on the Ni surface. For example, an effective diminution of carbon deposits would presumably generate increased reactivity. In this connection it is important to
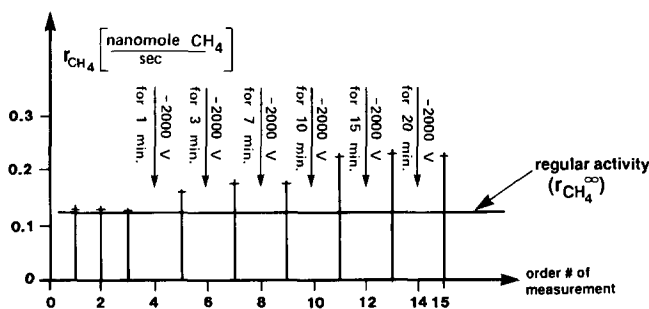
FIG. 10. An illustration of the time dependence involved in obtaining surface activation is C_2H_6 hydrogenolysis at 300°C and a total pressure of 132 Torr.

note two experimental facts associated with these observations. First, the effect is only observed when the Ni is negatively charged and at a relatively high potential (i.e., leakage current in excess of 20 μA). Second, as shown in Fig. 10, there is a time dependence associated with the creation of the enhanced reactivity. Thus the activation of the surface might be associated with direct electron emission or possibly reactions involving gas phase cations with surface carbon. The latter possibility could conceivably result from high energy collisions of the cations with the electron-rich carbon surface species leading, by charge transfer, to surface removal of the carbon atoms. In this connection, it was observed that the application of a negative potential to the Ni wire under conditions in which the cell was evacuated and which relatively small leakage currents were present ($P < 10^{-3}$ Torr) followed by catalytic runs at zero potential produced essentially no enhancement of reaction rate. This observation would argue in favor of the cation activation mechanism. Regardless of the detailed mechanism, it is clear that surface activation of the Ni wire is achieved under conditions in which one would normally have expected deactivation to occur [i.e., high temperature reactions in which carbide formation would be observed]. The rapid decrease in this activation with increasing temperature presumably represents the restoration of carbon surface deposits, a known high-temperature phenomena. In

connection with the apparent lack of activation observed at lower applied potentials (e.g., -1000 V at 350°C), it is important to note that during the period of potential application the normal catalyzed reaction is occurring and this involves continuous deposition of carbon on the Ni surface. At lower potentials (i.e., lower leakage currents), the magnitude of the cleansing effect may be insufficient to overcome completely the rate of carbon deposition. Apparently, as the leakage current increases, a condition is eventually attained at which a net decrease in carbon surface deposition is observed. Under our experimental conditions it appears that a current of around 20 μA is required before net activation is obtained.

The experimental observations at 210 and 250°C are interesting in light of the above discussion. Previous kinetic studies on these Ni catalyzed hydrogenolysis reactions have shown that catalytic poisoning below 250°C is a relatively slow process. For example, the generation of an activated catalyst at 250°C by application of a -3-kV potential to the Ni wire produced an increased activity which was essentially maintained without change during the next eight runs representing close to 3 h of catalysis. The fact that no enhanced activity was observed at 210°C presumably indicates that when experiments are commenced with a clean surface no significant carbon deposition occurs at these lower temperatures.

In conclusion, this research demon-

strates clearly that the applied potential method described in this paper represents a simple *in situ* method for catalytic regeneration in which significant rate increases are obtained. The method is inexpensive in that power consumption is minimal. Although this effect has been demonstrated for two reactions involving Ni catalysis, namely the hydrogenolysis of ethane and the hydrogenation of ethylene, it seems reasonable to anticipate that this procedure could be applied to a wide range of other catalytic processes. In particular, many other catalysts in which inactivation via surface deposition of sulfur or oxygen or carbon, etc. is a problem may well exhibit the same effect. Work on such processes is currently under way in our laboratories.

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