

## OSCILLATORY BEHAVIOR OF THE ETHYLENE HYDROGENATION REACTION AT HIGH TEMPERATURES OVER NICKEL CATALYST IN THE PRESENCE OF AN APPLIED MAGNETIC FIELD

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### ABSTRACT

The behavior of the ethylene hydrogenation reaction on powdered nickel and nickel-on-alumina catalysts was studied in the vicinity of the Curie temperature of nickel ( $T_c = 358^\circ\text{C}$ ) under the influence of an externally applied magnetic field by means of differential flow-reactor and gas chromatography.

A series of isothermal (from  $330^\circ\text{C}$  to  $430^\circ\text{C}$ ) experiments showed that depending on the degree of activity of the catalyst, application of the magnetic field (1 T) for each isotherm investigated brought about a set of decaying aperiodic oscillations in the conversion rate of the reacting system superimposed on the change in reaction rate. Below the Curie point of the catalyst, the applied magnetic field generally decreased the rate of the ethylene hydrogenation reaction but increased the reaction rate above the Curie point of the catalyst.

### INTRODUCTION

Lielmezs and Aleman [1] have observed that over commercial surfaces of nickel, cobalt and iron catalysts at  $86.3^\circ\text{C}$ , an externally applied magnetic field decreased the rate of the ethylene hydrogenation reaction. In the present work, we have studied the influence of an externally applied magnetic field on the ethylene hydrogenation reaction in the vicinity of the Curie temperature of nickel ( $358^\circ\text{C}$ ). The catalysts used were Ni powder and Ni on alumina without specially pretreated surfaces. The measurements were made as a function of time at the following isotherms: 330, 350, 360, 370, 380, 390, 400, 410, 420 and  $430^\circ\text{C}$ .

The application of the external magnetic field decreased the reaction rate at all temperatures below the Curie temperature, but increased it at  $370^\circ\text{C}$  and higher, while the isotherm at  $360^\circ\text{C}$  ( $2^\circ\text{C}$  above  $T_c$ ) showed little change in reaction rate in either direction. Both negative and positive

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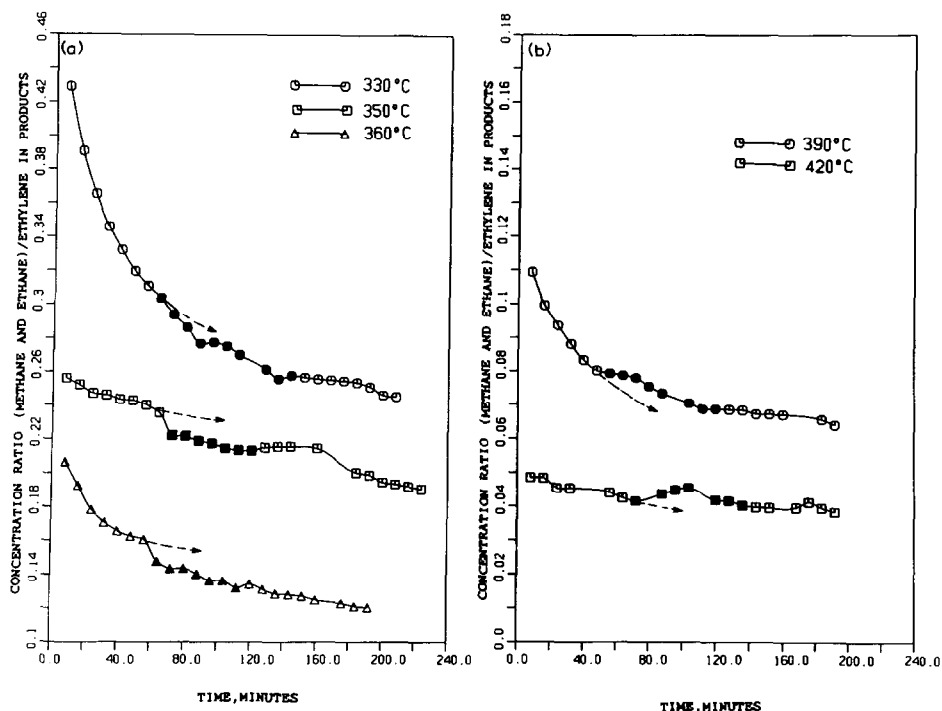


Fig. 1. Concentration ratio in products vs. time for nickel on an alumina catalyst: a, isotherms below and approximately at the Curie point of nickel; b, isotherms well above the Curie point of nickel. ▲, ■ and ●, External magnetic field is applied; △, □ and ○, external magnetic field is not applied.

changes in reaction rate were accompanied by superimposed oscillations, decaying with time (Figs. 1–4). The amplitude of the oscillation for each isotherm studied showed direct dependency on the degree of activity of the catalyst used (Fig. 4). The observations made in our work were confirmed by 47 independent experiments of which the graphs presented (Figs. 1–4) are representative.

#### THE ETHYLENE HYDROGENATION REACTION

The complexity of the heterogeneously catalyzed ethylene hydrogenation reaction, including its many probable mechanisms based on various modes of adsorption, formation of radicals, self-hydrogenation, polymerization and decomposition of ethylene from the vapor phase with hydrogen atoms, has been fully discussed by a number of authors, notably Selwood [2]. The kinetics of the reaction are further complicated by the frequently encountered poisoning effects. Generally, the activation energy increases to a maximum, usually between 100°C and 200°C, and then decreases [3,4],

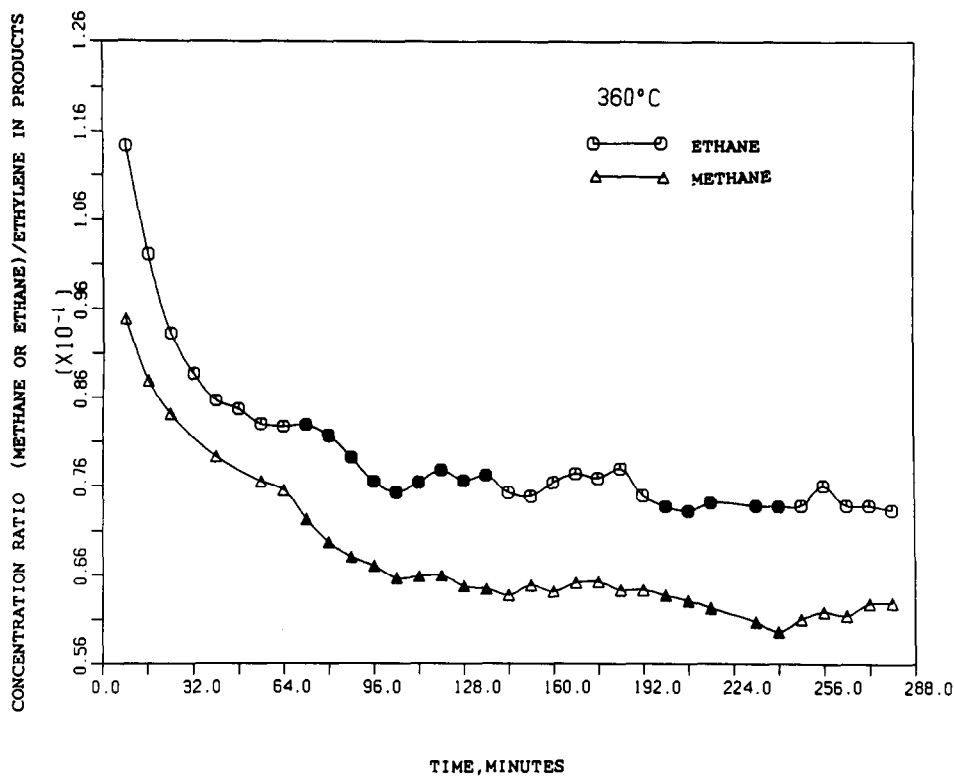


Fig. 2. Concentration ratio in products vs. time for methane and ethane on a nickel-powder catalyst in the vicinity of the Curie point: 360°C isotherm.  $\blacktriangle$  and  $\bullet$ , External magnetic field is applied;  $\triangle$  and  $\circ$ , external magnetic field is not applied.

chiefly due to the poisoning of the catalyst surface. Koh and Hughes [3] report that the poisoning in the ethylene hydrogenation reaction over a supported nickel catalyst occurs at both low and high temperatures and may be due to the traces of oxygen present in ethylene gas. Indeed, purification of the ethylene feed from oxygen impurities secured stable catalyst activity at least up to 140°C, but a gradual catalyst activity decrease continued at the higher reaction temperature [3].

Pareja et al. [5] have indicated that the activation energy maximum disappears and the catalyst activity is considerably lowered following drastic purification and removal of all traces of oxygen from the reacting mixture. They [5] concluded that a high activity of Ni catalyst as well as a maximum in the activity with respect to temperatures are caused by the autocatalytic synthesis of water from the oxygen traces carried by the reacting gas mixture.

Few data are available for high temperatures [6–14], particularly in the vicinity of the Curie point of nickel, but it has been demonstrated that the gradual decline in catalyst activity in this temperature region also results

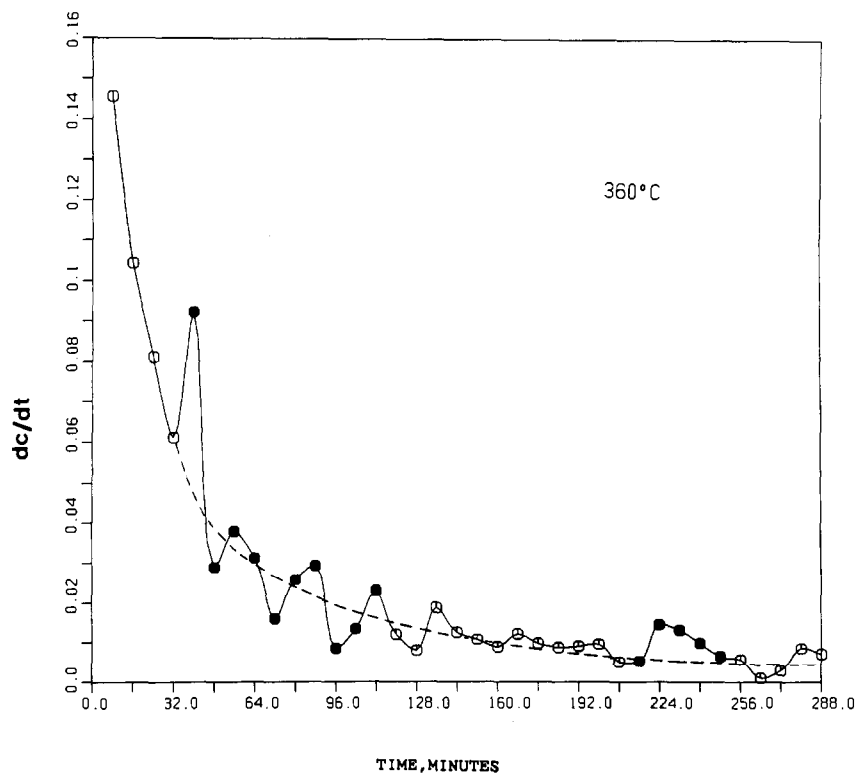


Fig. 3. Change in amount of ethylene reacted  $\Delta c$  during time interval  $\Delta t$  vs. time on a nickel-powder catalyst in the vicinity of the Curie temperature: 360°C isotherm. ●, External magnetic field is applied; ○, external magnetic field is not applied.

from a reduction in the number of active sites due to carbon formation [15–17].

In this work, we measured the amount of ethane and methane formed at the isotherms noted above. The amount of methane formed was small, practically negligible, on the nickel-on-alumina catalyst, its yield increasing at higher temperatures. Due to the small overall amount of methane formed, especially at low temperatures, it was not possible to detect the applied magnetic-field effect on the methane formation as clearly as that on the ethane formation (Fig. 2). However, high temperature experiments indicated that both methane and ethane production may be similarly affected by the applied magnetic field.

## EXPERIMENTAL

The apparatus, experimental methods used and measurement accuracy were generally the same as those reported by Lielmezs and Aleman [1] in

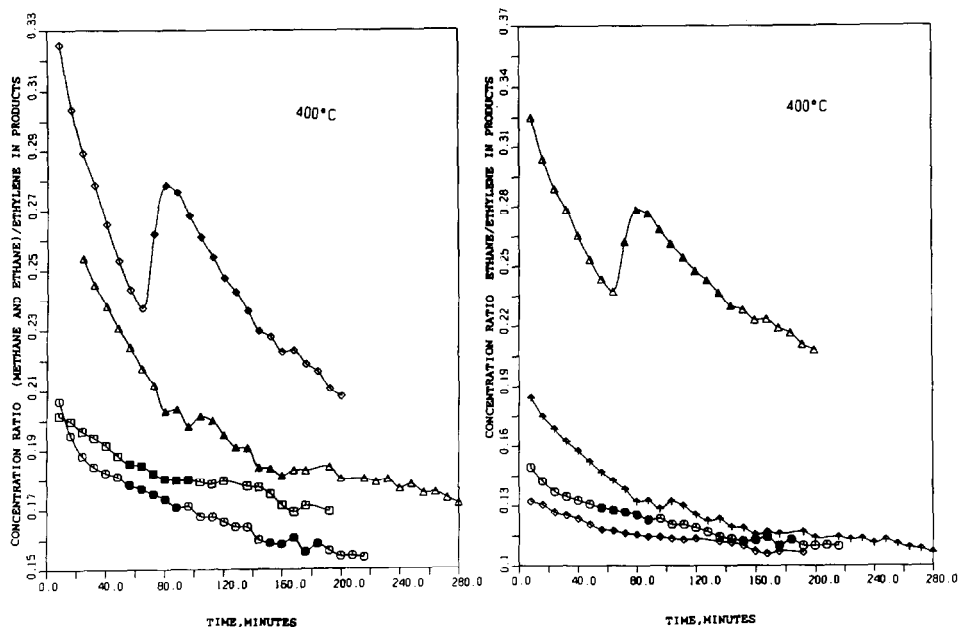


Fig. 4. The effect of an applied magnetic field on the conversion ratio in terms of the change in nickel-powder catalyst activity at 400°C: a, amount of ethylene reacted; b, amount of ethane formed. ▲, ■, ● and ◆, External magnetic field is applied; △, □, ○ and ◇, external magnetic field is not applied.

their study of the external magnetic-field effect on the ethylene hydrogenation reaction over ferromagnetic catalysts at 359.4 K. In this work, we used two types of nickel catalysts: nickel powder, m5N, -425 mesh size, supplied by Alfa Products, Morton Thiokol Inc., Danvers, MA, activated just before each experiment inside the reactor by passing hydrogen for 16 h at 360°C; and nickel supported on alumina. The nickel-on-alumina catalyst was prepared by adsorption of nickel nitrate (analytical reagent grade) from 10% aqueous solution to evacuated (to facilitate penetration of solution into the pores of the support) powdered alumina. To remove the excess solution, the impregnated alumina was spread over filter paper, dried in a vacuum oven at 100°C for 12 h and then heated at 400°C for an additional 4 h to convert nickel nitrate to nickel oxide. The obtained nickel oxide was reduced to nickel by passing hydrogen at 360°C for about 15 h inside the reactor immediately preceding each individual run. The temperature was controlled by a Leeds and Northrup precision set-point temperature control with magnetic amplifier. C.P. grade ethylene (99.5% minimum) and ultra-high purity hydrogen (99.999% minimum) were obtained from Matheson Company. A Deoxo unit installed in the experimental setup kept the oxygen concentration in the reacting gases below 10 ppm. Two mixing chambers connected by capillary tubing were installed in series to ensure proper

mixing of gases and, thus, to reduce undue fluctuations in the gas concentrations ( $\text{H}_2$  and  $\text{C}_2\text{H}_4$ ) entering the reactor.

As in our previous work [1], the catalysts were inserted into the inner narrow tube of the reactor in which they were supported by a layer of packed glass wool and also covered by glass wool to be held in place. Catalysts of very small particle size (nickel-on-alumina, particle size smaller than  $160\ \mu\text{m}$  diameter) were sandwiched with a layer of glass wool to prevent resistance to the flow of reacting gases. A chromel–alumel thermocouple was inserted into a special conduit placed in such a way that the tip of the thermocouple was next to the catalyst bed. The reactor tube and thermocouple were placed in the center of the wider glass tube surrounded by a heater coil. To check that the insulation around the heater was not damaged and that the nichrome tape would not act as a catalyst, the reactor was occasionally tested by running the experiment without a catalyst. For each run, following Selwood [18,19], after the catalyst was activated the system was allowed to cool rapidly to room temperature. The outlet hydrogen flow was measured using a soap-bubble meter, the ethylene flow was adjusted and the total flow measured again. Then the system was slowly heated to reacting temperature and after half an hour of stabilizing time, the reaction products were analyzed by a gas chromatograph (Hewlett–Packard, Model 5750, 6 ft silica gel (30–60 mesh) column). The outlet flow rate was periodically measured (once every hour) and the inlet flow rate was calculated with respect to the changing composition of reaction products. The inlet flow rate did not fluctuate more than 2%. The composition of the reacting gases ( $\text{C}_2\text{H}_4$  and  $\text{H}_2$ ) was kept at about 80%  $\text{H}_2$ . At the start of each run, 5 or more measurements were taken at the earth ( $H = 0$ ) magnetic field, then the external magnetic field was switched on. The electromagnet system consisted of a Varian Associates 9 in low-impedance electromagnet -VHF-3401 (maximum field strength about 1.5 T with a 1 in air space between the electromagnet poles), a field-regulated magnet power-supply (Fieldial-Mark I) and a heat exchanger.

## RESULTS AND DISCUSSION

Figures 1–5 present the experimental results for the ethylene hydrogenation reaction at several isotherms. The ratio  $R$  (Figs. 1, 2 and 4) of reaction products to reactants ( $R_1 = [\text{C}_2\text{H}_6]/[\text{C}_2\text{H}_4]$  and  $R_2 = [\text{CH}_4]/[\text{C}_2\text{H}_4]$ ) were plotted versus time,  $t$  (min), showing the intermittent application of the external magnetic field of fixed field strength of 1 T. Figures 1 and 4 show a positive extrinsic field effect at temperatures above the bulk Curie point ( $T_c = 358^\circ\text{C}$ ) of nickel and a negative effect below the Curie temperature of the catalyst. This observation concurs with the observation of Lielmezs and Aleman [1] that an externally applied magnetic field decreases the rate of the

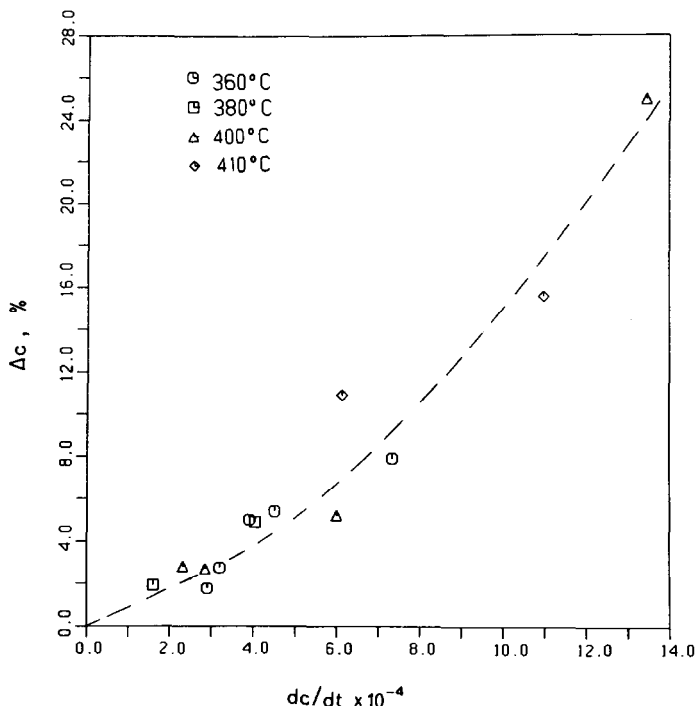


Fig. 5. Estimated %maximum change in the amount of ethylene reacted due to the externally applied magnetic field vs. the absolute value of the slope of the ethylene concentration-time relation (Figs. 1, 2 and 4), estimated at the time just before the application of the external magnetic field.

ethylene hydrogenation reaction over nickel, cobalt and iron catalysts at 81.3°C which is far below the Curie points of each of these respective catalysts, and indirectly relates to the work of Ng and Selwood [20] who measured *ortho-para* hydrogen conversion rates over antiferromagnetic  $\alpha\text{-Cr}_2\text{O}_3$  and CoO catalysts in an extrinsic magnetic field and found a positive field effect above the Neel point ( $T_N$ ) and negative effects both above and below the  $T_N$  of each catalyst. Figures 1–4 also show that for the ethylene hydrogenation reaction, in both the ethane and methane production-rate-time curves at each temperature studied, the application of the external magnetic field has induced an aperiodic oscillation around the quasi-steady state approaching equilibrium. As shown in Fig. 3 and also in Figs. 1, 2 and 4, these induced oscillations continue to exist for some time, even after removal of the applied magnetic field. Figure 5 presents a strong relation between the maximum change in ethylene conversion caused by application of the external magnetic field and the rate of decay of the catalyst at the time when the magnetic field was switched on. The data used to establish this correlation were taken from controlled experiments conducted at 400°C under the same conditions: weight of catalyst, flow rate,

hydrogen–ethylene ratio, amount of oxygen impurity in hydrogen and strength of applied external field. The initially different slope of the conversion–time curve observed at the exact time when the magnetic field was switched on, is caused by the difference in the time  $t_0$  measured when  $C_2H_4$  is introduced into the reactor and the time  $t_1$  when the magnetic field is switched on. However, despite the catalyst being pretreated in the same way in all the experiments performed, the initial activity of the catalysts did vary somewhat as did the methane/ethane ratio. This may be caused by a small variation in factors such as the rapid cooling of the reduced catalyst or the rate of heating to reach the given isotherm. Similar observations have also been made for all the other isotherms.

The general requirements of non-equilibrium thermodynamics [21] state that chemical oscillation is a possibility only if the reacting quasi-steady state system is sufficiently far from equilibrium. Consequently, at the high temperatures of this work, the activity of the catalyst essentially reflects a measure of the distance from equilibrium of the reacting system. The magnitude and behavioral patterns (Figs. 1–5) of the external magnetic field effect observed would, therefore, represent a degree of non-equilibrium cooperativity between the components of the reacting gas mixture–catalyst system; that is, it would indicate a measure of the response in sensitivity of the non-equilibrium reacting system to the interactions brought about on this system by the externally applied magnetic field [22–25].

The second requirement is the existence of a suitable feedback mechanism [26–31]. In our work, accepting the result of Pareja et al. [5] that the ethylene hydrogenation reaction and the water formation on the catalyst surface are coupled reactions, we note that the repetitive feedback mechanism can be expressed through the modification of the active sites on the nickel surface generated, first, by competitive adsorption and accumulation of reactants and, second, by desorption of a product of the coupled hydrogen oxidation reaction [5,32–41]. Thus, the reacting system consists of multiple stationary states leading to oscillations in the heterogeneous catalytic reaction. Niiyama and Suzuki [42] report the existence of such multiplicity in their work on the self-oscillations found in the catalytic hydrogenation of ethylene over Ni– $Al_2O_3$ . They connect the observed oscillations with periodic changes on the catalytic surface combined with mass and heat transfer limitations.

An explanation for the oscillations observed in this work (Figs. 1–5) can be found in connecting the inherent kinetic instability of the reacting system [42,43] with the perturbing influence of an externally applied magnetic field, thus providing a mechanism of communication between the inhomogeneous surface states.

During the catalytic hydrogenation of ethylene, the hydrogen oxidation over nickel proceeds in an excess of hydrogen and an exceedingly low concentration (less than 10 ppm) of oxygen in the gas phase; however, the



variations observed in the reaction rate are assumed to be solely due to the changes in the oxygen coverage of the nickel catalyst surface.

The complexity in attempting to connect the surface states of the nickel catalyst and the kinetic oscillations in the oxidation of hydrogen on nickel has already been discussed by Slinko and Slinko [30,31], Belyaev et al. [34–37], Schmitz et al. [39], Kurtanjek et al. [40] and, more recently, by Saranteas and Stoukides [41]. It has been observed that the presence of strong non-linear changes in the properties of the catalyst, caused by variations in the gas phase composition and in the amount of adsorbed and dissolved reactants in the catalyst, are necessary for the occurrence of the oscillations in the reaction rate behavior [37]. On the other hand, the transport phenomena (mass and heat transport), the propagation of electric charge changes induced by changes in the state of the surface, and the surface diffusion of species present affect the degree of synchronization among the various points on the catalyst surface and thus may alter the shape, amplitude and frequency of the oscillations [32,33,40,41]. For instance, Sault and Masel [44], in their investigation of the effect of surface protrusions on self-sustained thermal oscillations during hydrogen oxidation on nickel foil, found that the oscillations vanished when the surface protrusions were smaller than 5  $\mu\text{m}$ , and Kurtanjek et al. [33] observed that the kinetic oscillations in the  $\text{H}_2$  oxidation reaction on nickel at 270 °C occurred only in a specific oxygen concentration range.

It is interesting that, at the temperatures of our work, the antiferromagnetic NiO, or its structural rearrangements, is in the paramagnetic state (Neel temperature for NiO,  $T_N = 248^\circ\text{C}$ ) while the nickel surface is first ferromagnetic, then, passing through the Curie point of Ni ( $T_c = 348^\circ\text{C}$ ), also becomes paramagnetic. The cyclic sequence of the formation of paramagnetic epitaxial, small-domain NiO clusters on the catalyst surface and the reduction of these clusters to the initial ferromagnetic nickel surface may well prove to be significant in the overall oscillatory feedback mechanism of the hydrogen oxidation reaction, at least up to the Curie point of nickel.

## CONCLUSION

The observed external magnetic field effect on the ethylene hydrogenation reaction (Figs. 1–4) shows that the oscillatory ethane and methane formation rates superimpose on the primary magnetic field effect a decrease and an increase in the ethylene hydrogenation reaction rate below and above the Curie temperature of the nickel catalyst, respectively.

In this work, we have associated the appearance of oscillations in the concentrations of the gaseous products of the ethylene hydrogenation with the simultaneously occurring coupled hydrogen oxidation reaction over the nickel catalyst made possible by the promoting effect of traces of oxygen

found in the reacting gaseous mixture [5]. In accordance with previous observations [42], we accept that weak oscillations in the hydrogen reaction rate already existed in the surface state of the nickel catalyst involving, in fact, autocatalytic oxidation–reduction steps, but were not detected in the gas phase of the ethylene hydrogenation reaction products until the application of the external magnetic field. The applied magnetic field, apparently, has led to conditions under which the ethane and methane formation rate versus time curves begin to exhibit identifiable oscillatory behavior; that is, the amplitudes of the previously undetected surface oscillations is increased. While no separate study has been made concerning the nature of the observed oscillations seen in Figs. 1–4, nevertheless they do seem to resemble simple oscillations with a prolonged period (20–30 min), set up in somewhat irregular fashion. The observation that these oscillations are of low frequency suggests that some of the subsurface layers of the nickel catalyst may participate in the hydrogen oxidation reaction [37,40].

Further research is in progress with respect to variations in oxygen content and variations in magnetic field strength, as well as the increase of exposure time to the magnetic field.

#### ACKNOWLEDGMENT

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