

Effect of Methane Formation in Ethylene Hydrogenation over Nickel

LUCIO FORNI, CARLO GATTI, MASSIMO SIMONETTA, AND MARIO TESCARI

*Istituto di Chimica Fisica, Università di Milano, Centro CNR and Euteco SpA,
Via C. Golgi 19, 20133 Milan, Italy*

Received February 2, 1981; revised July 16, 1981

Ethylene hydrogenation has been investigated using as catalyst a nickel disk mounted in a stainless-steel chamber and capable of being pretreated under UHV conditions, including argon ion bombardment. Reaction conditions were $T = 398$ K, initial $p = 33$ Torr, and $H_2/C_2H_4 = 9:1$, using circulation. A close correlation was observed between ethylene conversion and selectivity to methane (S_M), the overall reaction rate being inversely proportional to S_M . This fact denotes a poisoning effect of C_1 radicals, adsorbed on the Ni surface, on both ethane and methane formation.

INTRODUCTION

Unexpected changes in reaction rate have recently been observed in catalytic hydrogenation of ethylene on Ni (1). The phenomena have been attributed to the promoting effect of oxygen traces present in the reacting gas mixture (1-3). It is also well known (4) that hydrogenolysis of ethane over Group VIII metals depends on the concentration of C_1 fragments present on the catalyst surface.

In the present paper we report some experimental results on ethylene hydrogenation to ethane over massive metallic Ni. A close connection has been observed between the overall catalyst activity (i.e., overall ethylene conversion) and the reaction selectivity to methane.

EXPERIMENTAL

Ethylene and hydrogen, SAPIO products, >99.98 and >99.99 mol% pure, respectively, were employed as reactants. Argon (>99.999), O_2 (>99.9), CH_4 (>99.995), and C_2H_6 (>99.5) were also used. A 1-cm-diameter, 1-mm-thick, massive metallic Ni disk was employed as catalyst. The purity of the metal was >99.5 wt%, the main contaminants being (ppm): Co <5000, Cu <900, Fe <1500, C <600, S

<50, oxides <1600. The disk was pretreated by the usual metallographic polishing techniques, including 7- to 0.25- μ m diamond paste treatment, followed by electrochemical polishing in diluted H_2SO_4 .

Ethylene hydrogenation runs were performed in a batch reactor (ca. 200 ml volume), with continuous recirculation (ca. 5 liters/min flow rate) of the reacting gas. The overall scheme of the apparatus is shown in Fig. 1. Facilities included a stainless-steel UHV system (Vacuum Generators Ltd.), completely bakeable up to 520 K, an argon ion gun, a metallic bellows pump (Metal Bellows Co.) for gas recirculation, and a small quadrupole mass spectrometer (Micromass, Q7). Details of the Pyrex-glass reactor, with a PTFE-sealed, removable glass cup, placed within the UHV chamber, are shown in Fig. 2. The catalyst sample was held in place by means of a thin molybdenum collar, connected with a tungsten wire, directly sealed through the glass wall, allowing the sample to be charged at a high negative potential during ion bombardment. An electric heater was placed within the hollow glass tube of the sample holder, immediately below the catalyst sample, together with a thin thermocouple for temperature monitoring/controlling.

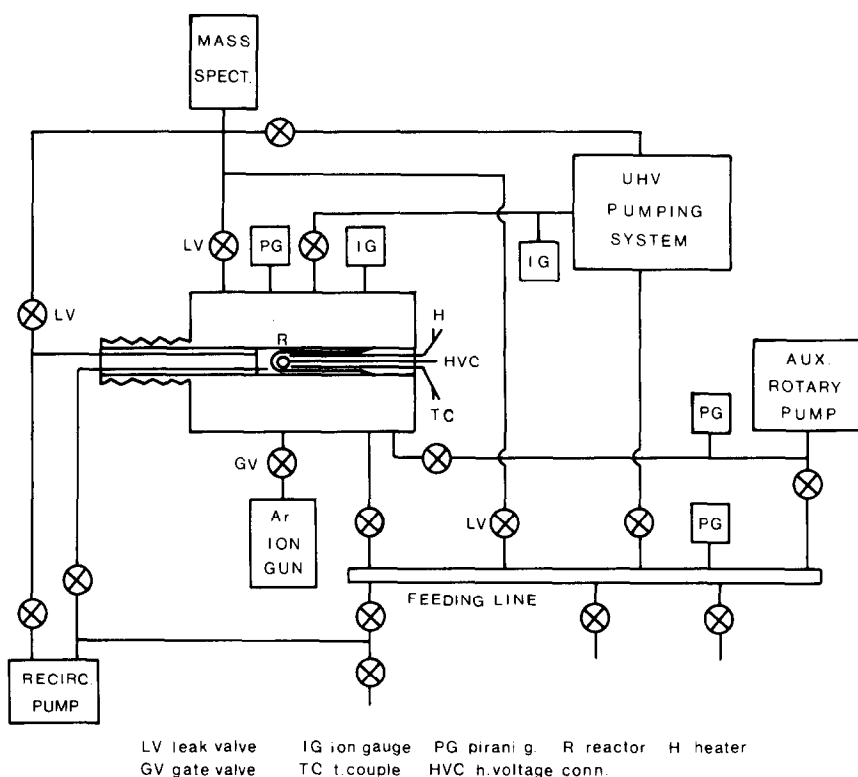


FIG. 1. Apparatus.

Before each run the following standard pretreatment procedure was applied. The whole apparatus was evacuated to 10^{-10} Torr by baking out for 16 h at 400 K and the catalyst treated twice as follows: (i) 30 min Ar ion bombardment at 700–1000 eV ($0.55 \mu\text{A}/\text{cm}^2$ current density), (ii) 20 min at 550 K in 2×10^{-8} Torr O_2 atmosphere, (iii) 30 min at 600 K in 10^{-5} Torr H_2 atmosphere.

The commercial-type purity of the metallic nickel employed and the low temperatures allowed by the Pyrex-glass sample holder did not permit a really "clean" surface to be obtained by any method. The pretreatment procedure previously described was then chosen due to its ability to give a reproducible final steady behaviour of the catalyst in each series of runs.

The whole set of runs was performed under standard conditions: 398 K, initial total pressure 33 Torr, and $\text{H}_2/\text{C}_2\text{H}_4 = 9:1$ (mol) feed mixture. After the catalyst had attained the reaction temperature *in vacuo*, the gaseous mixture was admitted into the UHV chamber, the reactor cup was closed, and the gas recirculation started up immediately. Whenever the chamber had to be opened for any reason, usually a "series" of three to five runs was necessary to attain steady final conditions. Gases were analysed by mass spectrometry. Samples could

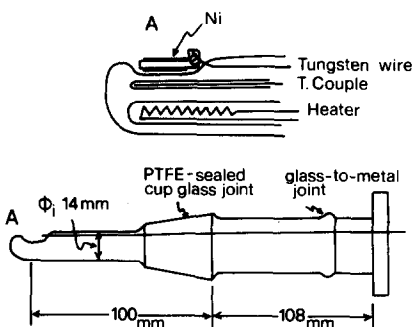


FIG. 2. Catalyst holder.

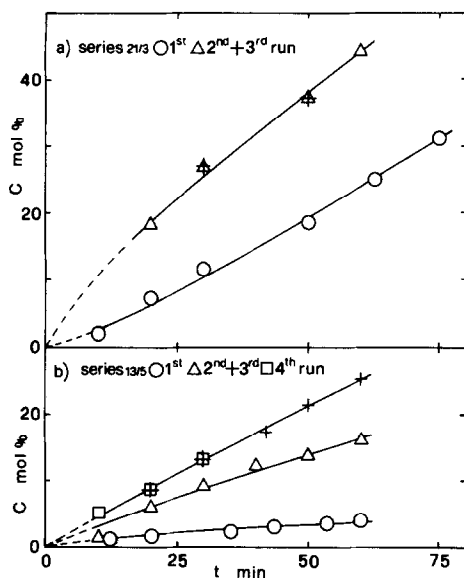


FIG. 3. Conversion vs reaction time.

be taken from either feeding line, UHV chamber or gas recirculation circuit (Fig. 1). The analytical apparatus was calibrated as usual by means of preformed mixtures of known composition and permitted quantitative determination, with reasonable reliability, of each substance present in the reacting gas mixture in concentrations as low as ca. 5×10^{-3} mol%.

RESULTS AND DISCUSSION

Many different series of runs have been conducted. Catalyst activity was expressed as overall mole percent ethylene conversion (C) and as mole percent selectivity (S_i) to products. Ethane and methane were the only reaction products, no other hydrocarbon species ever being detected in significant amounts. A small, variable, and usually hardly detectable trace of O_2 was always present in fresh feed gas, which was prepared by mixing the pure H_2 and C_2H_4 . Such a trace vanished within the first few minutes of reaction, with a corresponding formation of a trace of water.

After the collection of data, by plotting C vs reaction time t , it was often observed that apparently irreproducible results

seemed to be obtained from different series of runs, although within each series the catalyst seemed to behave in a reproducible manner. This is typically shown in Fig. 3. One can note that, run after run, within each series, the catalyst activity grows up to a steady and reproducible final level, but the level is about twice as high in Fig. 3a as in Fig. 3b. It is well known (5) that in many catalytic reactions and particularly on Ni, the catalytic activity depends on surface coverage, the true catalyst being not the metal alone, but the metal covered by all the species chemisorbed on it, even those that are not directly generated by the reaction. As a consequence, the number of runs required by each series in order to reach the steady state and the different levels of stationary activity attained, depend strongly on the quality and quantity of the species adsorbed on the metal, when the chamber is opened.

By keeping in mind the previous observations and the pretreatment procedure adopted, which does not ensure a "clean" surface, the results plotted in Fig. 3 should no longer be considered as merely "random" ones. However, notwithstanding the complexity of our system, the previously reported results could be rationalized when the very small (usually <0.1 mol% of over-

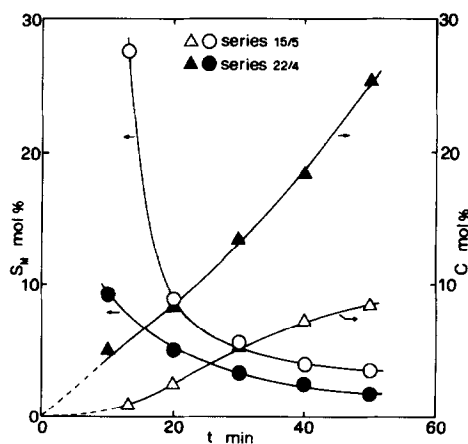


FIG. 4. Conversion and selectivity to CH_4 vs reaction time.

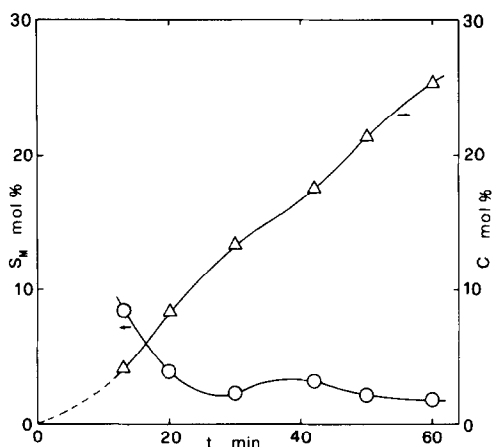


FIG. 5. As Fig. 4, but for series 22/5.

all gas mixture) quantity of methane, present in the gaseous phase, was carefully measured and taken into account. Three major observations could then be made, relative to the reaction selectivity to methane (S_M): (i) S_M usually decreases during each run, from initial values of 10–50 mol% to a 1–5 mol% steady value within 1 h; (ii) the reaction rate dC/dt appears to be inversely proportional to the prevailing value of S_M ; (iii) an initial induction period may be noted, which seems to be closely connected with the initial value of S_M . Examples are given in Fig. 4 and particularly in Fig. 5, showing not only that the shorter the induction period, the lower the initial value of S_M , but also that a temporary increase of S_M is accompanied by a corresponding decrease in reaction rate. This behaviour has been observed repeatedly and cannot be ascribed to inaccuracy of the analysis.

Two additional series of runs were then performed: (i) by adding 1 mol% of methane (i.e., an excess of more than one order of magnitude with respect to the concentration of methane produced by the reaction) to the fresh feeding mixture and (ii) pre-treating the catalyst with pure methane (total pressure ca. 3 Torr) at reaction temperature for 16–20 h, followed by evacuation to 10^{-6} Torr, before feeding the fresh mixture. In both such series the catalyst behaved

exactly as in the absence of added methane, thus excluding any effect of the preformed gaseous methane on the catalyst behaviour.

These observations suggested that a general correlation, relative to all runs performed, could be obtained between C and S_M , measured at the same reaction time t . Examples are given in Fig. 6, where it can be noticed that points corresponding to different times fall on the same curve. However, since the so-measured overall conversion should be connected not only with the corresponding instantaneous value of S_M , but also with the previous trend of such a parameter vs reaction time, a more correct treatment should correlate C to an "integral" value of S_M defined as

$$(S_M)_I = \int_{t_0}^t S_M(t) dt.$$

Indeed, Fig. 7 shows that a plot of C vs $(S_M)_I$ for the data of Fig. 6 at $t = 60$ min, allows a better correlation to be obtained.

As to the interpretation of the competition between hydrogenation and hydrogenolysis over our catalyst, the following experiment was performed. At the end of some reaction runs the overall apparatus was evacuated down to 10^{-6} Torr, without opening the reactor cup. Then the catalyst was heated in pure H_2 (16 Torr total pressure) and the CH_4/C_2H_6 ratio measured in

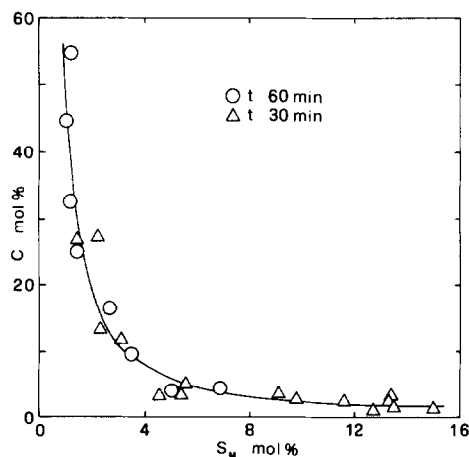


FIG. 6. Conversion vs selectivity to CH_4 .

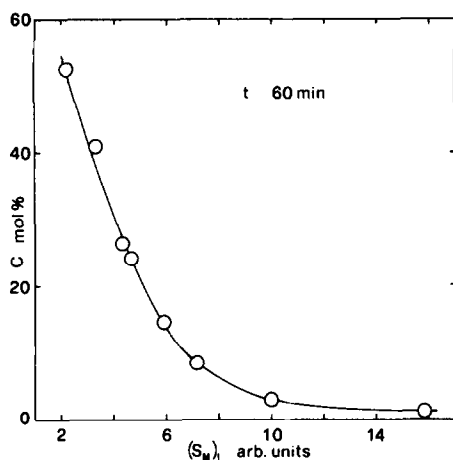


FIG. 7. Conversion vs "integral" selectivity to CH_4 .

the gaseous phase. The results, plotted in Fig. 8, are in line with a previously reported hypothesis (6), connecting the hydrocarbon hydro-dehydrogenation/hydrogenolysis relative rates with the competitive presence of CH_x and C_2H_y fragments on the metallic surface. The relative abundance of such fragments could very probably be connected with the promoting action of surface oxygen, as suggested for Ni and other Group VIII metals (1-3, 7-9). The correlation between the overall reaction rate and S_M seems to confirm that the rate-determining step of CH_4 formation should be the hydrogenative desorption of C_1 fragments from the catalyst surface (4). This fact, implying that the C_1 radicals are more strongly adsorbed than C_2 ones, would clearly explain the poisoning effect of the former on both ethane and methane formation.

Finally, as observed elsewhere (5), gaseous methane adsorbs slowly on Ni, even at 200°C , and forms only C_1 adsorbed radi-

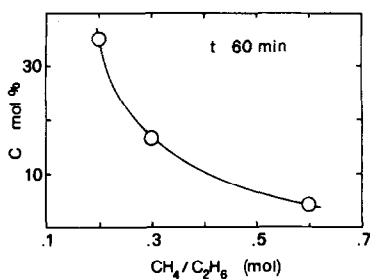


FIG. 8. Conversion vs $\text{CH}_4/\text{C}_2\text{H}_6$ ratio in the gas obtained after reaction, by heating the catalyst in H_2 .

cals, which are removed quite easily as CH_4 by gaseous hydrogen. Such C_1 radicals are then probably of a different nature and probably less dehydrogenated and less strongly adsorbed than those formed by dissociative chemisorption of ethylene. This could explain the inertness of preformed gaseous methane with our process.

ACKNOWLEDGMENT

We are indebted to Professor Gabor A. Somorjai for suggestions and stimulating discussions.

REFERENCES

1. Pareja, P., Amariglio, A., and Amariglio, H., *React. Kinet. Catal. Lett.* **4**, 459 (1976).
2. Pareja, P., Amariglio, A., and Amariglio, H., *J. Chim. Phys.* **71**, 50 (1974).
3. Pareja, P., Amariglio, A., and Amariglio, H., *J. Catal.* **36**, 379 (1975).
4. Frennet, A., Degols, L., Liénard, G., and Crucq, A., *J. Catal.* **35**, 18 (1974) and refs. therein.
5. Frennet, A., *Catal. Rev. Sci. Eng.* **10**, 37 (1974).
6. McCarty, J. G., and Madix, R. J., *J. Catal.* **48**, 422 (1977).
7. Pareja, P., Amariglio, A., Piquard, G., and Amariglio, H., *J. Catal.* **46**, 225 (1977).
8. Smith, C. E., Biberian, J. P., and Somorjai, G. A., *J. Catal.* **57**, 426 (1979).
9. Davis, S. M., and Somorjai, G. A., *Surf. Sci.* **91**, 73 (1980).