

Carbon Deposit and Metal Surface Morphology During Hydrocarbon Synthesis

K.C. Khulbe, M.H. Back and J. Galuszka*

Ottawa-Carleton Institute for Research and Graduate Studies in
Chemistry, University of Ottawa Campus, Ottawa, Canada, K1N 9B4

*Energy Research Laboratories, CANMET, Ottawa, Canada, K1A 0G1

Iron and nickel both act as catalysts in the hydrogenation of carbon monoxide but produce a different distribution of hydrocarbon products. In both cases carbon is formed as an intermediate but its form and characteristics have not been well defined. The objective of the present studies was to compare the morphology of the carbon formed during the reaction on each catalyst using SEM. Differences were observed between iron and nickel in the product distribution, and in the effect of the reaction and oxidation/reduction treatment on the structure of the catalyst surface.

Introduction

Carbon has long been recognized as an important intermediate in the hydrogenation of carbon monoxide. It is generally believed to form by dissociative adsorption of carbon monoxide on the metal, but the subsequent steps whereby carbon either accumulates or reacts, are not well understood. Various experimental techniques for example TPR (1), XPS/AES (2,3), Mossbauer Spectroscopy (4), isotopic tracer (5) have been used to demonstrate the coexistence of different states of carbon formed on the surface of a catalyst during CO hydrogenation.

The present study was directed toward an examination of the characteristics of the carbon formed as an intermediate in the hydrogenation of carbon monoxide using Scanning Electron Microscopy in conjunction with kinetic studies.

Experimental

A close circulation system incorporated with a gas chromatograph was used for the present study. A thin layer of metal sputtered on a quartz plate acted as a catalyst. The quartz plates 1 mm thick were accommodated in a sample holder which could be positioned in the heated zone of a reaction vessel using a magnet. In each experiment two large quartz plates, 7.1 x 1.1 cm² and four small plates, 0.2 x 0.5 cm² (for SEM analysis), were used. Reactants were admitted to the desired pressure and mixed by the circulation pump. The reaction was started by moving the sample holder into the furnace zone. Carbon

monoxide hydrogenation was tested in the 200-300° temperature range and under total pressure not exceeding 500 Torr. Gaseous products were withdrawn through a 6-port valve and analyzed by gas chromatograph. The Edward Sputter Coater, Model S150A was used to prepare metal films on quartz plates. The total amount of metal on a quartz plate was quantitatively analyzed by the use of Direct Current Plasma Spectroscopy. Some sputtered metal films were oxidized with air and subsequently reduced with hydrogen at around 500°C prior to using them as a catalyst. Carbon monoxide (99.99%) was obtained from Air Products. Other hydrocarbons and hydrogen were obtained from Matheson Co.

Results and Discussion

The metal films as formed in the Sputter Coater showed no surface features by SEM. However, both iron and nickel surfaces were altered by oxidation-reduction treatment, although the final appearance of each film was quite different as can be seen in Figure 1. The oxidation-reduction treatment drastically reduced the activity of iron film for carbon monoxide disproportionation and hydrogenation reactions. Similar effect but to much lesser extent was observed in the case of nickel. From a comparison of the micrographs of the films before and after treatment it appears that the change in surface area is probably not sufficient to account for the change in reactivity, especially for iron. During the course of carbon monoxide hydrogenation reaction the background surface of the iron films did not change while the nickel films were affected

by the reaction showing structure similar to Figure 1B.

The most striking result from the present studies is the absence of any surface structure detectable by SEM which may be attributed to carbon deposition either during carbon monoxide disproportionation or carbon monoxide hydrogenation. In every reaction which was tested it was shown that carbon was indeed formed on the surface and could be recovered by reaction with hydrogen and subsequent oxidation at elevated temperature. It must be concluded that carbon formed rather uniform layer on the metal surface.

Hydrogenation of carbon monoxide over iron films at 300°C revealed an induction period which length increased with CO/H₂ ratio. An average selectivity for methane which was the main product of the reaction, showed opposite trend as can be seen in the table:

H ₂ /CO*	Induction Period (min)	Average Selectivity for CH ₄
2	105	0.69
5	68	0.73
55	60	0.78

*Total pressure = 480 Tr.

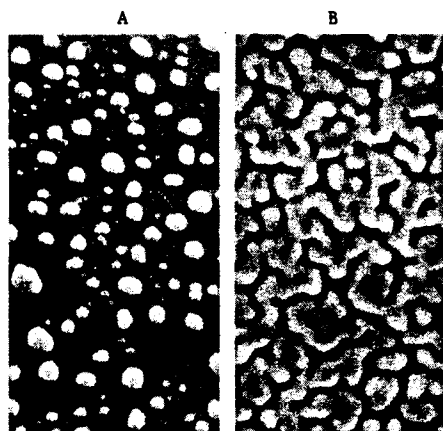


Fig. 1 SEM micrographs of; A-iron and; B-nickel films after oxidation-reduction treatment. Magnification 20 x 10

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A series of reactions with H₂/CO ratio = 55 were carried out under conditions described above. The first reaction, (I), was allowed to proceed for 40 minutes. The reactants and products were removed and reaction (II) was started by introducing fresh reactants. A similar procedure was repeated two more times. The obtained results are shown in Figures 2 and 3. As can be seen the induction period was shortened considerably in the consecutive runs. Carbon accumulated on the surface of iron was eventually hydrogenated and subsequently oxidized after the last run (IV) had been interrupted by evacuation. Only about 60% of that accumulated carbon could be recovered by hydrogenation. In spite of the existence of a reactive carbon on the iron film the induction period could not be brought to zero. The nickel film tested in the similar conditions did not show any induction period. Higher selectivity towards methane was observed, of course. A specific interaction between CO and metal surface seems to be important factor stimulating the selectivity in the hydrocarbons synthesis reaction. The above results emphasize limitation of a popular approach which treats carbon monoxide in the process of its hydrogenation as a source of carbon only.

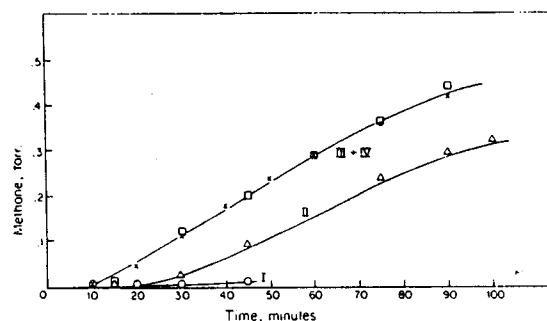


Fig. 2 Time course of methane in consecutive runs: o-run I; Δ-run II; □-run III; x-run IV.

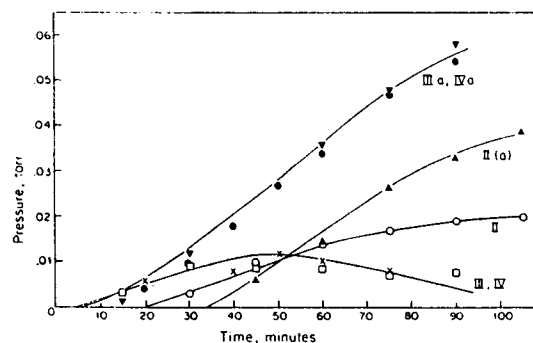


Fig. 3 Time course of ethane - Δ (IIa); ▽ (IIIa); ● (IVa) and ethylene - o (II); □ (III); x (IV) in consecutive runs.