

Araki M & Ponc V. Methanation of carbon monoxide on nickel and nickel-copper alloys. *J. Catalysis* 44:439-48, 1976.
[Gorlaeus Laboratoria, Rijksuniversiteit Leiden, The Netherlands]

Two steps of the overall mechanism of methanation have been identified, namely, dissociation of carbon monoxide (CO) and hydrogenation of deposited carbon by adsorbed hydrogen. CO can be dissociated only on places where carbon atoms can be bound to several nickel atoms simultaneously. [The SCI® indicates that this paper has been cited in over 280 publications.]

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In the second half of 1974 I went to the State University of Leiden, The Netherlands, on a fellowship from the Japanese government. In Leiden I joined Vladimir Ponc, who headed a group studying the problems of the selectivity of metal catalysts. We studied the selectivity of alloys as well as pure metals. Our aim was to discover the factors (i.e., electronic structure of solids and geometric arrangements of surface atoms) that determined the observable selectivity and the extent to which these factors were of a determining influence.

Although researchers had been interested for a long time in selectivity studies involving the reactions of syngas (CO/H₂), it was the following events that actually allowed these studies to begin in 1974. In 1973 a crisis took place regarding the limited supply of crude oil, and everybody was confronted with some obvious points: an alternative for oil will be needed in the twenty-first century; there is more coal than oil in the world; and coal resources are more evenly spread over the world. Syngas reactions are one of the possible fuel alternatives for the petrochemical industry, and so on.

My arrival in Leiden, my interest in syngas reactions, and the general urgent need to solve the oil crisis made the decision concerning the subject of our study very easy.

As with many other studies, the main result of our work was not expected. Before 1974 the prevailing idea on methanation and Fischer-Tropsch synthesis of hydrocarbons was that carbon monoxide (CO) is first hydrogenated (to hydroxycarbene), and only then can the C-O bond be dissociated. Upon that dissociation, either a carbene or a C₂-hydrocarbon (by dehydrocondensation) is formed. This was the so-called Anderson-Storch-Emmett mechanism.¹⁻⁴ We also believed in this mechanism and wanted to study how alloying can influence the formation of higher hydrocarbons and olefins, and we wanted to learn how to achieve a possible restriction of the Flory-Schulz-Anderson distribution. However, the first experiments with pure nickel had already revealed that the Anderson-Storch-Emmett mechanism was not a correct starting point. Indications against the mechanism accumulated, and at that stage the experiment with isotopic labeling was performed, which excluded a "hydrogenation-dissociation" mechanism beyond any doubt and confirmed the "dissociation-hydrogenation" mechanism as the main mechanism of the formation on the metal surface of the CH₄ units. A few years later P. Biloen and coauthors⁵ performed analogous experiments at higher pressures and also analyzed the higher hydrocarbons. From these data the authors concluded that the main mechanism of (any) hydrocarbon formation is a stepwise polymerization of CH_x units.

Our "classic" paper and its conclusions were not accepted without hesitation. One of the referees found the conclusions unsupported and, in the first years after the paper had appeared, a substantial part of the citations were negative. However, other papers^{6,7} confirmed the results, and the conclusions are now accepted quite generally.^{8,9}

The paper has been frequently cited because, after 1973, many scientists began to study syngas reactions. Questions of mechanism are often touched on by papers dealing with other diversified subjects such as spectroscopy, catalyst design, catalyst deactivation, kinetics, and so on.

The paper also showed that the Fischer-Tropsch synthesis (methanation) is a reaction requiring a large ensemble of active metal sites, and just this aspect of the conclusions (a general feature of selectivity control) has in the last years been gaining increasing attention.

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2. Anderson R B. The thermodynamics of the hydrogenation of carbon monoxide and related reactions. (Emmett P H, ed.) *Catalysis. Volume IV. Hydrocarbon synthesis, hydrogenation and cyclization*. New York: Reinhold, 1956. p. 1-28.
3. ———. Catalysts for the Fischer-Tropsch synthesis. *Ibid.*, p. 29-256.
4. ———. Kinetics and reaction mechanism of the Fischer-Tropsch synthesis. *Ibid.*, p. 257-372.
5. Biloen P, Helle J N & Sachtler W M H. Incorporation of surface carbon into hydrocarbons during Fischer-Tropsch synthesis: mechanistic implications. *J. Catalysis* 58:95-107, 1979. (Cited 175 times.)
6. Wentrczek P R, Wood B J & Wise H. The role of surface carbon in catalytic methanation. *J. Catalysis* 43:363-6, 1976. (Cited 165 times.)
7. Rabo J A, Risch A P & Poutsma M L. Reactions of carbon monoxide and hydrogen on Co, Ni, Ru, and Pd metals. *J. Catalysis* 53:295-311, 1978. (Cited 185 times.)
8. Rofor-DePoorter C K. A comprehensive mechanism for the Fischer-Tropsch synthesis. *Chem. Rev.* 81:447-74, 1981. (Cited 110 times.)
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