

Vannice M A. The catalytic synthesis of hydrocarbons from H_2/CO mixtures over the Group VIII metals. I. The specific activities and product distributions of supported metals. *J. Catalysis* 37:449-61, 1975.

[Corporate Research Laboratories, Exxon Research and Engineering Company, Linden, NJ]

Specific activities (molecules CO per second per surface metal atom) for hydrocarbon synthesis from CO and H_2 were measured, and power rate laws were determined for methane formation. These relative activities for methanation are significantly different than similar comparisons in older studies that had not been corrected for variations in metal surface area. The results emphasize the use of chemisorption to count surface metal atoms and obtain specific rates. [The SCI® indicates that this paper has been cited in over 315 publications.]

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In 1971 I joined the Corporate Research Laboratories at Exxon after a year's postdoctoral experience. In retrospect, this period may have been the "good old days," when a new employee had a choice among a number of topics that had been selected by the company for "long-term" research. I was especially intrigued by both the lack of fundamental information about the kinetics of CO hydrogenation and the potential of this reaction, although neither I nor the company anticipated the enormous worldwide interest that would be generated following the first oil embargo in October 1973. As I was eager to move into a new research area, apply new concepts to control product selectivity, and study reaction kinetics, I quickly chose this project.

Over four decades had passed since this reaction had been intensively studied by Fischer and Tropsch,¹ and no major industrial interest had existed for two decades. Numerous advances had occurred in catalysis during this period, and I set about in a straightforward manner to employ selective chemisorption

techniques to measure metal surface areas and to utilize gas chromatography for product analysis under well-defined, low-conversion reaction conditions. All these results could be assembled to determine rates as turnover frequencies (molecules·s⁻¹·surface atom⁻¹), to estimate metal crystallite size, and to look for effects caused by different oxide supports. I had an excellent peer group at Exxon, and lunchtime conversations resulted in a number of new ideas that were applied to create new catalysts. Although some managers at one point expressed the opinion that my approach was too fundamental, the study was continued until a firm foundation was established regarding rates and selectivities of CO/ H_2 reactions over the Group VIII metals when dispersed on a wide variety of support materials.

This paper, and the series that followed it, has apparently had a significant influence in the field of hydrocarbon synthesis for several reasons. First, it was the first paper to compare specific activities, which must be done in modern catalysis, for all these metals. Second, the large number of investigations related to the catalysis of CO/ H_2 reactions that have been conducted during the past decade have frequently utilized this paper for comparison of rates. Strong interest continues in this reaction, as reflected by many review articles. (Two of the most recent are cited below.^{2,3}) Third, this approach resulted in the subsequent discovery that certain supports can markedly enhance rates and alter selectivity in this reaction.^{4,5} This catalytic metal-support effect has also received much attention during the past several years.⁶

I had the good fortune to conduct this study at an optimum time; the results have withstood the test of time and nine patents were produced from it. This work has been cited as the reason for a number of awards including that from the New York Catalysis Society in 1985 and the AIChE Professional Progress Award in 1986.

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2. Boudart M & McDonald M A. Structure sensitivity of hydrocarbon synthesis from CO and H_2 . *J. Phys. Chem.* 88:2185-95, 1984.
3. Ponce V, Fischer-Tropsch synthesis and some related heterogeneous reactions. *Coal Sci.* 3:1-62, 1984.
4. Vannice M A & Garten R L. Metal-support effects on the activity and selectivity of Ni catalysts in CO/ H_2 synthesis reactions. *J. Catalysis* 56:236-48, 1979. (Cited 165 times.)
5. Vannice M A. Catalytic activation of carbon monoxide on metal surfaces. (Anderson J R & Boudart M, eds.) *Catalysis: science and technology*. Heidelberg: Springer-Verlag KH, 1982. Vol. III, p. 140-98.
6. Imelik B et al., eds. *Metal-support and metal-additive effects in catalysis: proceedings of an international symposium*. Amsterdam: Elsevier, 1982. 384 p.

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