

Banks R L & Bailey G C. Olefin disproportionation: a new catalytic process.
Ind. Eng. Chem. Prod. Res. Develop. 3:170-3, 1964.
[Phillips Petroleum Company, Bartlesville, OK]

A new catalytic disproportionation reaction is described in which olefins are converted to homologues of shorter and longer carbon chains. Catalysts for the reaction are molybdenum hexacarbonyl and molybdenum oxide supported on alumina. The disproportionation of propylene to ethylene and *n*-butene is reported in detail. [The *SCI*[®] indicates that this paper has been cited in over 210 publications since 1964.]

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"My career and interest in heterogeneous catalysis research began when I joined the research department of Phillips Petroleum Company in 1946. Process research, at Phillips, was essentially research in catalysis, and I became involved in exploratory catalyst studies directed toward improved processes for upgrading light hydrocarbons. In 1959, working under G.C. Bailey's supervision, I was screening potential heterogeneous catalyst compositions for alkylation activity. That work utilized techniques evolving from our earlier development of supported chromium oxide polymerization catalyst (Phillips Marlex[®] Polyolefin Process),¹ especially the procedures for eliminating traces of catalyst poisons from the system.

"During the investigation, experimental quantities of molybdenum hexacarbonyl became available and we speculated that this zero-valent metal complex might exhibit unique catalyst properties if it could be supported on a substrate without destroying its integrity. I developed a nonaqueous impregnation technique, now commonly used in preparing homogeneous-heterogeneous compositions, to support molybdenum hexacarbonyl on preactivated alumina. In

the initial evaluation of this new composition of matter for alkylation activity, a small amount of liquid product equivalent to less than one percent of the butene-isobutane feed was recovered. This seemingly insignificant amount of material was found to be 2-pentene. The unexpected results were puzzling; i.e., butene/isobutane → 2-pentene? The experiment was repeated and detailed analyses (this was before GLC) of both gas and liquid products showed that part of the butenes had disappeared and that propylene, in addition to 2-pentene, was a reaction product. The two products were present in equal molar amounts, leading to the conclusion that a portion of the olefin content of the feed had been 'disproportionated' to shorter and longer chain homologues.

"Additional studies with numerous olefinic hydrocarbons verified that a new catalytic reaction had been discovered. We soon discovered that (cobalt) molybdena-alumina also catalyzed this new reaction. Results of these earlier studies were reported in 1964. A number of both heterogeneous and homogeneous catalysts are now known to catalyze this fascinating reaction,² which we named 'olefin disproportionation.' However, the scope of the reaction rapidly broadened and a more general term, 'olefin metathesis,' is more appropriate.³

"This paper has been highly cited for several reasons. Olefin metathesis, a new and exciting field of hydrocarbon chemistry, has given rise to more than 2,000 research publications,⁴ and has been the topic of five international symposia. Commercially, it is used for the interconversion of light olefinic hydrocarbons, the backbone of today's petrochemical industry, and in the synthesis of olefin hydrocarbons for the specialty chemical market.^{5,6}

"In recognition of the discovery disclosed in our 1964 publication, I have received the 1974 Oklahoma Chemist Award, the American Chemical Society 1979 Award in Petroleum Chemistry, and the American Institute of Chemists 1981 Chemical Pioneer Award, and have been honored by the University of Missouri-Rolla."

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2. Banks R L. Catalytic olefin disproportionation. *Top. Curr. Chem.* 25:39-69, 1972.
3. Discovery and development of olefin disproportionation (metathesis). *ACS Symp. Ser.* 222:401-14, 1982.
4. Olefin metathesis. (Kemball C, ed.) *Catalysis*. London: Chemical Society, 1981. Vol. 4. p. 100-29.
5. Industrial aspects of the disproportionation reaction. *J. Mol. Catal.* 8:269-76, 1980.
6. Banks R L, Banasiak D S, Hudson P S & Norell J R. Specialty chemicals via olefin metathesis. *J. Mol. Catal.* 15:21-33, 1982.