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Chang C D & Silvestri A J. The conversion of methanol and other O-compounds to hydrocarbons over zeolite catalysts. *J. Catalysis* 47:249-59, 1977.
[Central Research Division, Mobil Research and Development Corporation, Princeton, NJ]

The conversion of methanol and other O-compounds to C_2-C_{10} hydrocarbons using a new class of shape-selective zeolites is reported. Methanol, dimethyl ether, or an equilibrium mixture is converted in a first reaction sequence to olefins predominantly in the C_2-C_5 range. In the final steps of the reaction path, the C_2-C_5 olefins are converted to paraffins and aromatics. The final hydrocarbons are largely in the gasoline (C_4-C_{10}) boiling range. The thermochemistry of the methanol to hydrocarbon reaction is described, and possible reaction mechanisms are discussed. [The *SCI®* indicates that this paper has been cited in over 325 publications.]

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Serendipity is universally acknowledged as a critical ingredient in technological innovation. In the early 1970s, we were engaged in exploratory studies on novel approaches to octane enhancement in anticipation of the introduction of unleaded gasoline. The primary focus at the time was on new synthetic routes to high-octane blending components such as alkylbenzenes and highly branched alkanes. We had also been probing, along with many of our colleagues, the unique catalytic properties of the new Mobil synthetic zeolite ZSM-5. We tried, in an early experiment, to synthesize mesitylene (1,3,5-trimethylbenzene) selectively from acetone over ZSM-5. This reaction is well known to proceed in the presence of sulfuric acid, but with poor selectivity. We hoped that the new zeolite, which had superacid properties, would be more selective since it was nonoxidizing, in contrast to H_2SO_4. The experiment was a flop. A gasoline-like mixture rich in 1,2,4-trimethylbenzene resulted. Later mechanistic studies[1] showed that the reaction did not follow the classical Whitmore pathway in the presence of ZSM-5. Although the outcome foiled expectation, it nevertheless precipitated a study of O-compound transformations over zeolites.

Our next experiment was to see whether ZSM-5 would catalyze the methylation of isobutane by methanol to higher branched alkanes, a purely conjectural reaction. The mixture of methanol and isobutane yielded again a gasoline-like product containing aromatics. Material balance indicated that methanol was completely converted, while isobutane was largely untouched under the conditions. The experiment was repeated, omitting the isobutane. This confirmed that methanol itself was converted to a mixture of aromatics and isoalkanes over ZSM-5. Interestingly, the product carbon-number distribution ended around C_{10}, corresponding to the endpoint of conventional gasoline, and the C_5^+ fraction tested about 100 octane. It was clear to us that this reaction could be a final link in the conversion of coal and natural gas to gasoline, utilizing existing technology to produce methanol from these carbon sources. The Arab oil embargo of 1973 soon provided strong incentive for commercial development.

The process is now commercial. Known as the Mobil MTG (for methanol-to-gasoline) process,[2] the first plant was recently commissioned in New Zealand. This facility converts offshore natural gas from Mobil's Maui field to premium gasoline and supplies one-third of their current demand.[3]

The *Journal of Catalysis* paper broadly introduced the subject to the scientific community. We believe there are several reasons our work has been so frequently cited. In our opinion, it represented the first new development in synthetic fuels chemistry since Fischer-Tropsch. In addition, given the interest in synthetic fuels at the time, the work sparked not only development of the MTG process, per se, but also broader research on the use of zeolites and of zeolites in combination with metal/metal oxide co-catalysts for the conversion of single-carbon compounds to liquid hydrocarbons. Finally, the work raised an intriguing mechanistic question concerning methanol conversion to higher hydrocarbons, namely, how is the first C-C bond formed from a C_1 starting material? The question is unanswered at this writing and remains the subject of lively controversy.[4]

For our role in this development we received, along with our colleagues Warren Kaeding and Steve Butter, the Catalysis Society of Metropolitan New York Award for Excellence in Catalysis in 1984.

1. **Chang C D, Lang W H & Bell W K.** Molecular shape-selective catalysis in zeolites. (Moser W R, ed.) *Catalysis of organic reactions*. New York: Dekker, 1981. p. 73-94.
2. **Kam A Y, Schreiner M & Yurchak S.** Mobil methanol-to-gasoline (MTG) process. (Meyers R A, ed.) *Handbook of synfuels technology*. New York: McGraw-Hill, 1984. p. 2-75-2-111.
3. **Meisel S L.** A new route to liquid fuels from coal. *Phil. Trans. Roy. Soc. London A* 300:157-69, 1981. (Cited 15 times.)
4. **Chang C D.** Hydrocarbons from methanol. *Catal. Rev.—Sci. Eng.* 25:1-118, 1983.

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