

## New Lewis Acid Catalyzed Pathway to Carbon–Carbon Bonds from Methanol

Johannes A. Lercher

Technische Universität München, Department Chemie, Lichtenbergstraße 4, Garching, D-85748, Germany  
Institute for Integrated Catalysis, Pacific Northwest National Laboratory, 902 Battelle Boulevard, Richland, Washington 99352, United States

The *methanol to hydrocarbon process*, discovered about 40 years ago, uses zeolites to catalyze the shape selective conversion of methanol to a mixture of hydrocarbons. It has recently gained very much interest, as it allows the conversion of fossil and renewable carbon sources, via synthesis gas and methanol, to a mixture of hydrocarbons. The composition of this hydrocarbon mixture may range from being rich in aromatic molecules, which can be blended in high-octane gasoline, to being very rich in propene and ethene. One of the attractive features of this process route lies in the fact that, by adjusting the operation conditions without changing the zeolite, very different product distributions can be obtained.<sup>1</sup> The product selectivity is determined by two interlinked catalytic cycles, which are based on aromatic as well as on olefinic intermediates. The zeolite acts as shape selective catalyst, which retains aromatic molecules larger than tri- or tetramethylbenzenes. Once a steady state of hydrocarbons in the zeolite pores is established, the overall catalysis has been well explored over the past decade.<sup>2</sup> A large number of theories, however, have been proposed as to how these hydrocarbon species in the zeolite pores are initially formed, i.e., how the first carbon–carbon bonds are formed, but have been discarded again when tested thoroughly. At present, the most likely start of this methanol to hydrocarbon chemistry has been attributed to impurities of larger olefins or alcohols in the methanol stream, which are alkylated and cracked in the course of establishing a steady state “carbon pool”.

This study shows elegantly that the carbon–carbon bonds can be formed under reaction conditions typical for the overall conversion of methanol to hydrocarbons.

The research groups of Copéret and Sautet have just shown a new possible route to form carbon–carbon bonds

Johannes Lercher discusses the implications for C–C bond forming alumina catalysis suggested by work by Comas-Vives et al.

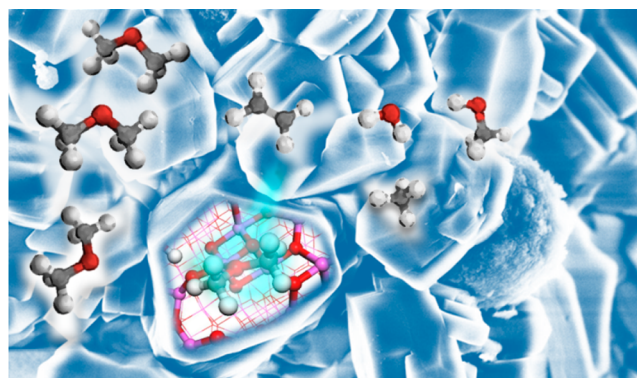


Figure 1. Alumina catalyzes carbon–carbon bond formation from methanol. Image credit: Christophe Copéret.

from methanol on alumina acting as catalyst (Figure 1).<sup>3</sup> The oxide has been known to catalyze dimethyl ether (DME) formation, but the authors showed that even the formation of higher olefins is possible, occurring in parallel to the observation of methane. Under the conditions employed, exposure of alumina to DME led to the formation of surface formate species and methane, which points to a stepwise redistribution of hydrogen between surface species and DME methyl groups, a redox transformation which requires a high density of reacting molecules and surface sites. Following adsorption and coordination of DME on exposed undercoordinated Al cations at the surface, the key elementary step has been identified to be the transfer of H between adjacent methoxy fragments, which leads to the formation of a highly reactive oxonium ion intermediate that readily reacts with C–H bonds. This could

Published: October 7, 2015

lead to carbon–carbon bond formation or alternatively to formate formation via the reaction with an adjacent methoxy group. This study shows elegantly that the carbon–carbon bonds can be formed under reaction conditions typical for the overall conversion of methanol to hydrocarbons. The new route opens, therefore, new design possibilities for more active catalysts for this family of processes. Density functional theory has identified that some water is crucial to facilitate the initial catalytic transformations of dimethyl ether; more experiments will be needed, however, to understand whether the high concentrations of water typical for industrial conditions of this process family will favor the observed catalysis.

#### Author Information

E-mail: [johannes.lercher@ch.tum.de](mailto:johannes.lercher@ch.tum.de).

#### REFERENCES

- (1) Stöcker, M. *Microporous Mesoporous Mater.* **1999**, *29*, 3.
- (2) Olsbye, U.; Svelle, S.; Bjørgen, M.; Beato, P.; Janssens, T. V. W.; Joensen, F.; Bordiga, S.; Lillerud, K. P. *Angew. Chem., Int. Ed.* **2012**, *51*, 5810.
- (3) Comas-Vives, A.; Valla, M.; Copéret, C.; Sautet, P. *ACS Cent. Sci.* **2015**, DOI: [10.1021/acscentsci.5b00226](https://doi.org/10.1021/acscentsci.5b00226).