

Operando Raman spectroscopy to pinpoint the onset of deactivation in zeolites

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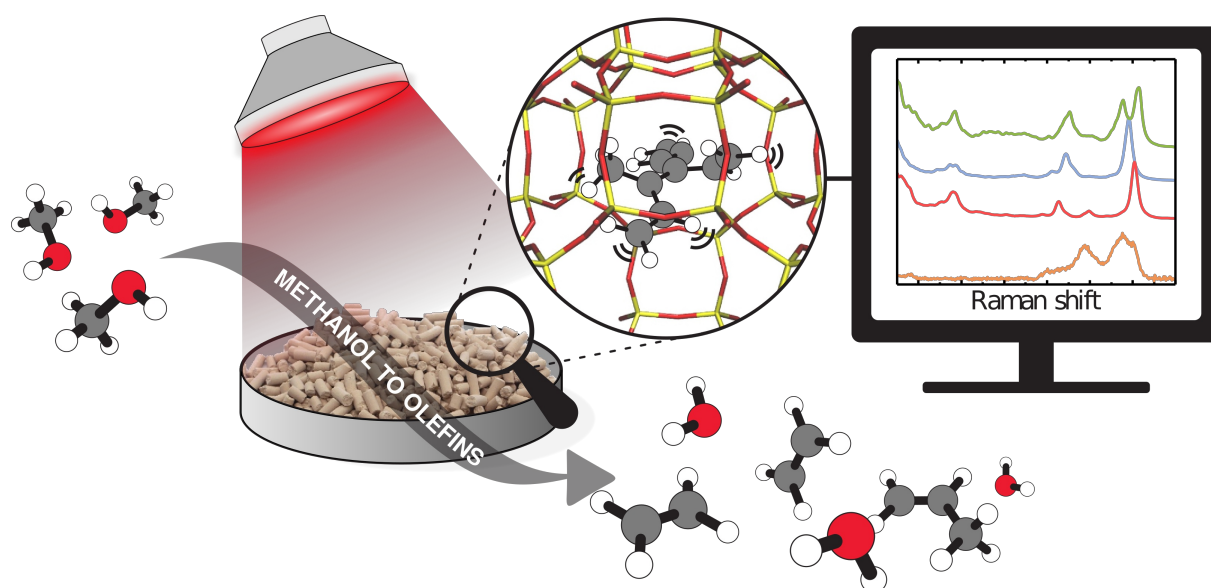
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The methanol-to-olefin (MTO) process over acidic zeolites is a sustainable alternative to crude oil for the generation of small hydrocarbons required for polymer production [1]. It proceeds through an indirect mechanism in which hydrocarbon pool species act as co-catalysts for the conversion [1,2]. Both reaction conditions and zeolite properties, such as topology and acidity, are important parameters that determine the eventual reaction products [2,3]. Consequently, the outcome of the MTO process can be tuned toward specific demands. An important limitation is catalyst stability, because spacious hydrocarbon species tend to pile up in the zeolite cavities decreasing the efficiency of methanol conversion [4]. Understanding the complex deactivation mechanism via comprehensive molecular insight is key to design new functional catalysts.

For that purpose, we tracked the evolution of hydrocarbon species during the MTO process via Kerr-gated Raman spectroscopy [5]. The Kerr-gate spectrometer circumvents the background fluorescence [6], usually present in the Raman signal, revealing the vibrational fingerprints under operando conditions with unprecedented detail. To identify the large amount of different reaction intermediates, theoretical simulations were indispensable as they could make a distinction between the vibrational fingerprints of different hydrocarbons. Via ab initio molecular dynamics simulations, it was possible to identify the reaction intermediates present at all stages of the MTO process in SSZ-13 zeolite. Our results showed that methanol conversion decreases from the moment linear polyenes are formed. These species proved to have limited mobility inside the chabazite cages blocking the pores and initiating deactivation. Branched polyenes have not been observed as we found them to undergo immediate cyclization, which eventually led to polyaromatic species. This refutes earlier assumptions that deactivation was caused by the latter.



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