

6. Xing, Z., Hu, L., Ripatti, D.S., Hu, X., and Feng, X. (2021). Enhancing carbon dioxide gas-diffusion electrolysis by creating a hydrophobic catalyst microenvironment. *Nat. Commun.* 12, 136.
7. Heinzmann, M., Weber, A., and Ivers-Tiffée, E. (2018). Advanced impedance study of polymer electrolyte membrane single cells by means of

distribution of relaxation times. *J. Power Sources* 402, 24–33.

8. Nwabara, U.O., De Heer, M.P., Cofell, E.R., Verma, S., Negro, E., and Kenis, P.J.A. (2020). Towards accelerated durability testing protocols for CO₂ electrolysis. *Journal of Materials Chemistry A* 8, 22557–22571.

9. Chen, X., Chen, J., Alghoraibi, N.M., Henckel, D.A., Zhang, R., Nwabara, U.O., Madsen, K.E., Kenis, P.J.A., Zimmerman, S.C., and Gewirth, A.A. (2021). Electrochemical CO₂-to-ethylene conversion on polyamine-incorporated Cu electrodes. *Nature Catalysis* 4, 20–27.

Transforming inactive coke molecules into active intermediates in zeolites

Sophie H. van Vreeswijk¹ and Bert M. Weckhuysen^{1,*}

Generating active intermediates from deactivating coke molecules by a regeneration process that produces valuable syngas as a by-product almost sounds too good to be true. In a recent publication in *Nature Communications*, Zhou and co-workers demonstrated this innovative approach by converting coke molecules into active naphthalenic cations by steam cracking in the industrially used SAPO-34 material, after it was active in the methanol-to-olefins (MTO) reaction. In this way, the nature of the commonly found hydrocarbon pool species was altered resulting in an enhanced ethylene selectivity. Their finding has been confirmed by the use of advanced characterization methods and computational calculations.

Since its inception by Mobil Corporation in 1977, the methanol-to-olefins (MTO) process has been of great industrial and academic interest.¹ This is because of the ability to convert methanol, which can be made from almost any carbon source, including CO₂, to the more valuable ethylene and propylene molecules, which can serve as the building blocks for the synthesis of e.g., plastics. In the last decade, after its commercialization (in 2010), the process has become a key tool in the non-oil depleting production of these vital base chemicals.^{2,3} The reaction is catalyzed by zeolites and zeotype materials with a well-defined microporous structure, allowing shape selectivity. An important part of the reaction process is the formation of an autocatalytic hy-

drocarbon pool (HCP) in the pores and cages of the zeolite material. This HCP consists of different hydrocarbon molecules, such as methylated benzene carbocations and cyclopentadienyl species, acting as active intermediates and, when growing too large, ultimately deactivating compounds. Because the process is auto-catalytic, changing the hydrocarbon pool can change the end-products considerably. A conventional method to change the hydrocarbon pool is the introduction of specific hydrocarbons as co-feed, which can alter the selectivity to the desired ethylene or propylene products. However, such co-feed molecules are limited to the pore openings of the used zeolite. For instance, when small-pore silicoaluminophosphate (SAPO-

34) (with chabazite [CHA] topology) is used, the diffusion of larger HCP molecules is sterically hindered.^{2,4,5}

SAPO-34 consists of small-pore openings and large cages, allowing the formation of the active aromatic intermediates, but hindering the diffusion of these larger intermediate hydrocarbons out of the micropores, resulting in a very high selectivity toward the desired light olefins. However, this combination also leads to rapid deactivation due to coke formation.⁶ To solve this undesired rapid deactivation, in industry a fluidized bed reactor is used with a reaction-regeneration cycle to keep the activity of the catalyst high and decrease the importance of the catalyst lifetime.¹ This reaction-regeneration cycle has increased the attention on the regeneration process of the MTO catalyst. This process can be performed in different ways, e.g., air combustion (e.g., oxidation with air) and steam gasification (e.g., with H₂O).⁷

In their recently published paper, Zhou and co-workers⁸ show that regeneration processes can be used to enhance the catalytic selectivity toward ethylene by transforming coke molecules into active naphthalenic cations. With density functional theory (DFT) calculations, it was shown that these

¹Inorganic Chemistry and Catalysis group, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, the Netherlands

*Correspondence: b.m.weckhuysen@uu.nl
<https://doi.org/10.1016/j.joule.2021.03.008>



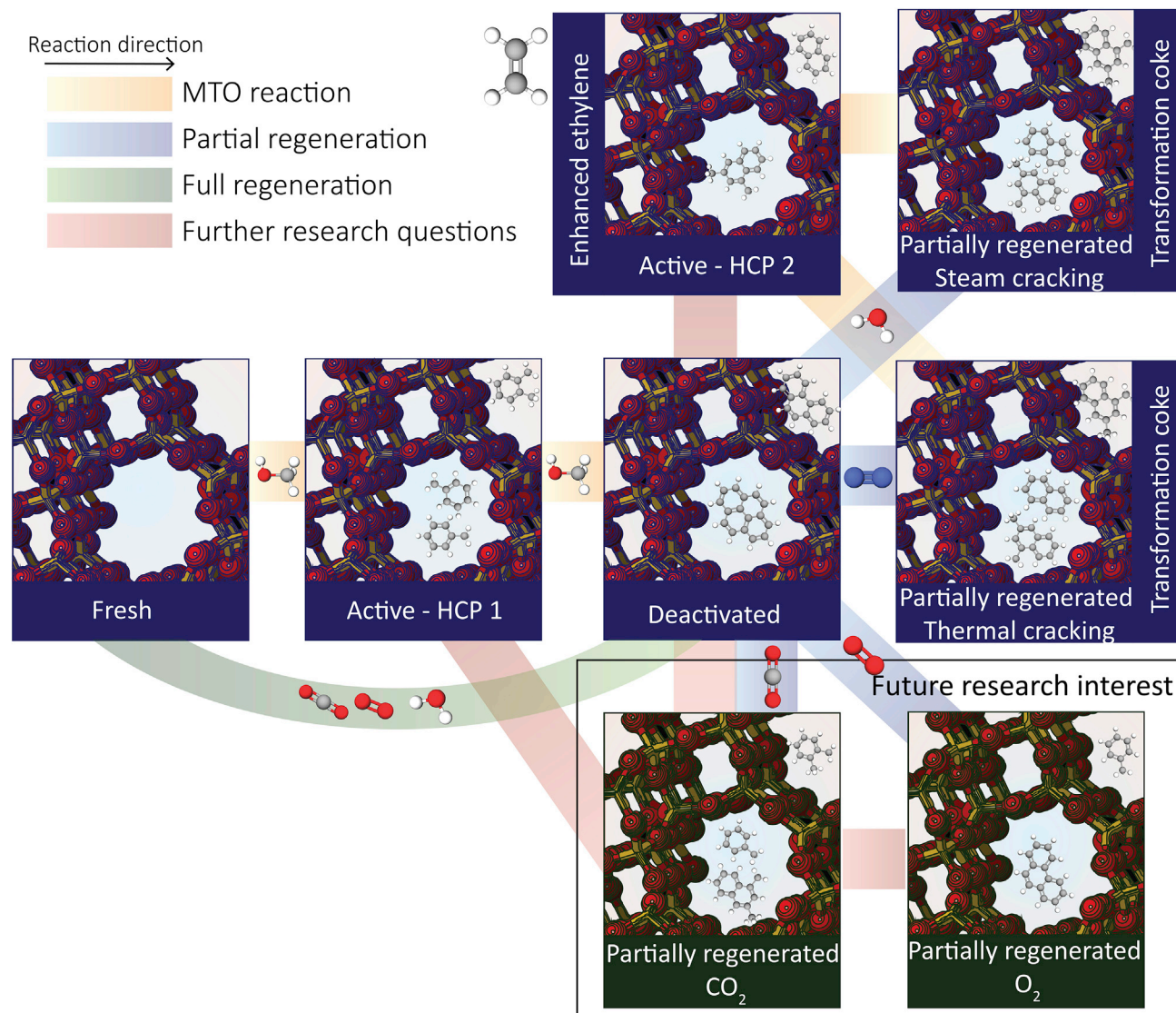


Figure 1. Schematic representation of the developed catalyst regeneration approach to transform coke-like molecules into active HCP intermediates in a SAPO-34 molecular sieve

This method, as described by Zhou et al.⁸ in *Nature Communications*, is visualized by the blue figures. Proposed catalyst regeneration approaches for further studies could aim for the transformation of coke deposits into aromatic intermediates by using gentler conditions (air combustion) or CO₂ to limit environmental contributions. These alternative routes are visualized by the green figures. Zeolite structures are modified from the IZA-structure database.

naphthalenic cations are stable in the CHA cages at high temperatures because of spatial confinement. Additionally, theoretical calculations indicate that starting with these naphthalenic cations at the beginning of the HCP or as coke precursors would enhance the selectivity to ethylene when higher reaction temperatures are used. The activity of the naphthalenic cations as active HCP intermediates

in the MTO reaction is also demonstrated. Transformation of coke molecules into naphthalenic cations was first attempted by thermal cracking under N₂ conditions as it was shown with DFT calculations that naphthalenic cations would be more stable than coke in the higher temperature regime. This resulted in a higher selectivity toward ethylene, but the catalytic activity was not restored. Steam gasifi-

cation, however, resulted in the formation of the naphthalenic HCP intermediates, leading to a higher ethylene selectivity and a complete restoration of the activity. In this way, the authors described a new HCP mechanism in SAPO-34 originating from coke molecules instead of the conventional HCP formation. Further research on the evident differences between the two regeneration methods could

contribute to the further understanding of this new mechanism. [Figure 1](#) illustrates the observed results of the catalytic strategy and performance of the research of Zhou and co-workers (blue figures).

In the same work,⁸ structured illumination microscopy (SIM) was used to spatially determine the location of hydrocarbon species in one of the large zeolite crystals under study, which showed that the naphthalenic species do not only act as active intermediates, but also hinder diffusion of larger hydrocarbon molecules. Recent work by the same research group has provided new insights in deep-data analysis for such experiments by combining simulations with SIM experiments.⁹

To be able to apply these new insights in chemical industry, the lab-scale reaction must be scaled up and industrially relevant conditions have to be applied. Therefore, the authors have explored their approach to transform deactivating coke molecules to active new HCP species at the level of a pilot plant by using a fluidized bed reactor with reaction-regeneration cycle capabilities. This showed that the increased ethylene selectivity is reproducible under industrially relevant conditions. Additionally, the authors found a very high selectivity to CO and H₂ (i.e., syn-gas) during regeneration, which can be used in the production of methanol thus helping to further close the carbon cycle of this MTO process (i.e., a higher carbon atom efficiency). Related to this, regeneration can also be performed with the use of CO₂, which would be interesting to investigate

further, especially when combined with steam gasification to further reduce CO₂ emissions, close the carbon cycle and contribute to the protection of our precious environment.¹⁰

Both steam cracking and thermal cracking use very high temperatures for the transformation or removal of coke molecules. It would therefore be interesting to study the regeneration by direct oxidation with O₂ given that lower temperatures are needed for full regeneration resulting in less energy usage. Additionally, not all zeolites and zeotype materials are as hydrothermally stable as the SAPO-34 material under study, which could make implementation of this technique to, for instance, zeolite socony mobil-5 (ZSM-5) more difficult.

This work has shown that the active HCP species can be modified through the application of a proper regeneration process, thereby paving the way for other analytical techniques to investigate the (partially) regenerated MTO catalysts. As illustrated in [Figure 1](#) in green, further research could focus on the influence of O₂ and CO₂ on the HCP formation and related catalytic performances. In this way, the research of Zhou and co-workers,⁸ has opened doors for further research, including the use of operando UV-Vis and infrared (IR) micro-spectroscopy, as well as combined operando X-ray diffraction-UV-Vis spectroscopy⁵ and atom probe tomography (APT).⁶

1. Tian, P., Wei, Y., Ye, M., and Liu, Z. (2015). Methanol to olefins (MTO): From fundamentals to commercialization. *ACS Catal.* 5, 1922–1938.

2. Yarulina, I., Chowdhury, A.D., Meirer, F., Weckhuysen, B.M., and Gascon, J. (2018). Recent trends and fundamental insights in the methanol-to-hydrocarbons process. *Nat. Catal.* 1, 398–411.
3. Olsbye, U., Svelle, S., Bjørger, M., Beato, P., Janssens, T.V., Joensen, F., Bordiga, S., and Lillerud, K.P. (2012). Conversion of methanol to hydrocarbons: how zeolite cavity and pore size controls product selectivity. *Angew. Chem. Int. Ed. Engl.* 51, 5810–5831.
4. Svelle, S., Joensen, F., Nerlov, J., Olsbye, U., Lillerud, K.P., Kolboe, S., and Bjørger, M. (2006). Conversion of methanol into hydrocarbons over zeolite H-ZSM-5: ethene formation is mechanistically separated from the formation of higher alkenes. *J. Am. Chem. Soc.* 128, 14770–14771.
5. Goetze, J., Yarulina, I., Gascon, J., Kapteijn, F., and Weckhuysen, B.M. (2018). Revealing lattice expansion of small-pore zeolite catalysts during the methanol-to-olefins process using combined operando X-ray diffraction and UV-Vis spectroscopy. *ACS Catal.* 8, 2060–2070.
6. Schmidt, J.E., Peng, L., Paioni, A.L., Ehren, H.L., Guo, W., Mazumder, B., Matthijs de Winter, D.A., Attila, Ö., Fu, D., Chowdhury, A.D., et al. (2018). Isolating clusters of light elements in molecular sieves with atom probe tomography. *J. Am. Chem. Soc.* 140, 9154–9158.
7. Zhou, J., et al. (2020). Regeneration of catalysts deactivated by coke deposition: A review. *Chin. J. Catal.* 41, 1048–1061.
8. Zhou, J., Gao, M., Zhang, J., Liu, W., Zhang, T., Li, H., Xu, Z., Ye, M., and Liu, Z. (2021). Directed transforming of coke to active intermediates in methanol-to-olefins catalyst to boost light olefins selectivity. *Nat. Commun.* 12, 17.
9. Gao, M., Li, H., Liu, W., Xu, Z., Peng, S., Yang, M., Ye, M., and Liu, Z. (2020). Imaging spatiotemporal evolution of molecules and active sites in zeolite catalyst during methanol-to-olefins reaction. *Nat. Commun.* 11, 3641.
10. Pereira, S.C., Ribeiro, M.F., Batalha, N., and Pereira, M.M. (2017). Catalyst regeneration using CO₂ as reactant through reverse-Boudouard reaction with coke. *Greenh. Gases Sci. Technol.* 7, 843–851.