

## **Researchers regenerate deactivated catalyst** in methanol-to-olefins process

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a.First-principle-based simulations provide the criteria of stability and functionality of organic intermediates confined in nano-cavity. b Selective transformation of coke into specific naphthalenic species-rich catalyst, and improvement of MTO performance and atom economy implemented in the circulating fluidized bed reactor-regenerator configuration. Credit: GAO Mingbin

The MTO process, which was first commercialized in 2010, is a catalytic process converting methanol—which is typically made from coal, natural gas, biomass, and  $CO_2$ —over a SAPO-34 zeolite catalyst. It's becoming one of the main streams for producing light olefins, including ethylene and propylene, from non-oil resources.



One of the major challenges in MTO is the rapid deactivation of the zeolite <u>catalyst</u> due to the coke deposition.

In industrial practices, a fluidized bed reactor-regenerator configuration is normally used in order to maintain the continuous operation, in which air or oxygen is usually input to burn off the deposited coke to restore the catalyst activity in the regenerator. This involves the transformation of coke <u>species</u> to  $CO_2$ , with a substantial fraction of the carbon resource being converted to low-value greenhouse gas.

A research group led by Prof. Ye Mao and Prof. Liu Zhongmin from the Dalian Institute of Chemical Physics (DICP) of the Chinese Academy of Sciences regenerated deactivated catalyst in the industrially important methanol-to-olefins (MTO) process by directly transforming the coke deposited on the <u>zeolite</u> catalyst to active intermediates rather than burning it off to carbon oxide.

This work was published in Nature Communications on Jan. 4.

It was previously shown that MTO follows the hydrocarbon pool mechanism, i.e. the light olefins are favorably formed with the participation of active intermediate species, otherwise known as hydrocarbon pool species (HCPs), during the reaction. The HCPs will evolve into coke species that deactivate the catalyst.

By using density functional theory (DFT) calculations and multiple spectroscopy techniques, the team showed that naphthalenic cations, amongst HCPs were highly stable within SAPO-34 zeolites at high temperature, and steam cracking could directionally transform the <u>coke</u> species in SAPO-34 zeolites to naphthalenic species at high temperature.

This technology not only recovers the catalyst activity but also promotes the formation of light olefins owing to the synergic effect imposed by



naphthalenic species.

Furthermore, the researchers verified this technology in the fluidized bed reactor-regenerator pilot plant in DICP with industrial-alike continuous operations, achieving an unexpectedly high light olefins selectivity of 85% in the MTO reaction and 88% valuable CO and  $H_2$  with negligible CO<sub>2</sub> in regeneration.

This technology opens a new venue to control the selectivity of products via regeneration in industrial catalytic processes.

**More information:** Jibin Zhou et al, Directed transforming of coke to active intermediates in methanol-to-olefins catalyst to boost light olefins selectivity, *Nature Communications* (2021). DOI: 10.1038/s41467-020-20193-1

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