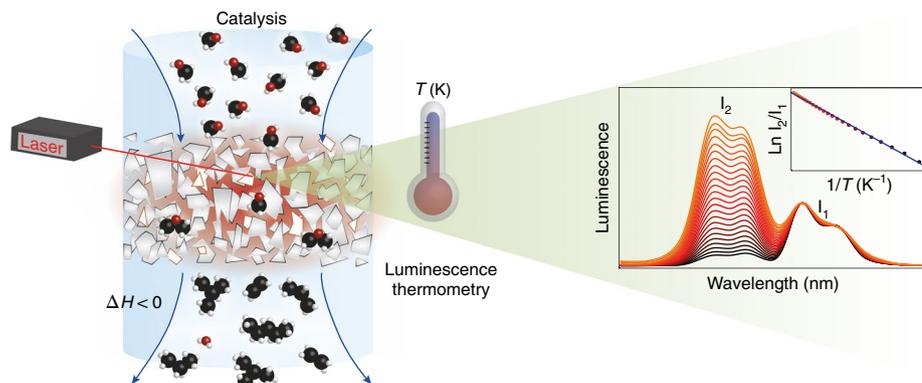


IN SITU SPECTROSCOPY

Temperature by light

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Credit: Robin G. Geitenbeek, Anne-Eva Nieuwelink and Bert M. Weckhuysen

The investigation of catalysts under working conditions is pivotal to optimizing and improving catalytic processes. Among the myriad of available in situ and operando techniques only a few can provide non-invasive local temperature measurements, and yet they fail at yielding high spatial and temporal resolution. Accurate determination of local fluctuations of the catalyst temperature allows for instance unveiling reaction and deactivation dynamics and heterogeneities in the catalyst. Now, Bert Weckhuysen, Andries Meijerink and colleagues at Utrecht University show that local temperature fluctuations can be measured in situ by making use of the luminescence properties of the catalyst.

The reported in situ luminescence thermometry technique is based on the temperature-dependent intensity ratio of two coupled emitting states of the catalyst upon absorption of multiple photons. Lanthanide-doped fluorides in particular display excellent upconversion luminescence properties. The authors show that the logarithm of the intensity ratio of the two emitting states of Eu(III), Yb(III)-doped NaYF₄ scales linearly with the inverse of the temperature — regardless of the morphology of the material. Therefore, the light emitted

from different regions of the catalyst can be collected in situ during the reaction and directly mapped onto temperature values.

The catalytic conversion of methanol into hydrocarbons is showcased as a proof-of-concept. The temperature is monitored by in situ luminescence thermometry at three different heights of the fixed-bed reactor containing microcrystalline Eu(III), Yb(III)-doped NaYF₄ mixed with a commercial zeolite, where methanol is introduced at the top and the products are collected at the bottom of the reactor. Full conversion is readily achieved yielding a variety of alkanes and alkenes. This exothermic process triggers sequential activation at the three measured heights of the bed — from top to bottom — until they successively reach a temperature maximum. At this point they subsequently decrease, shifting the heat front from top to bottom, as a result of the catalyst deactivation due to coke deposition. The results reveal how this technique can effectively uncover local activation–deactivation dynamics during reaction.

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