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PERSPECTIVE

Operando Nanoscale Sensors in Catalysis: All Eyes on Catalyst Particles

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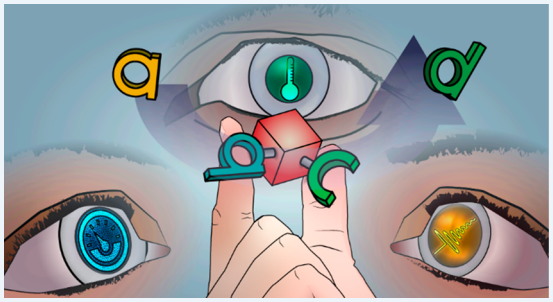
ABSTRACT: An era of circularity requires robust and flexible catalysts and reactors. We need profound knowledge of catalytic surface reactions on the local scale (*i.e.*, angstrom−nanometer), whereas the reaction conditions, such as reaction temperature and pressure, are set and controlled on the macroscale (*i.e.*, millimeter−meter). Nanosensors operating on all relevant length scales can supply this information in real time during *operando* working conditions. In this Perspective, we demonstrate the potential of nanoscale sensors, with special emphasis on local molecular sensing with shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) and local temperature sensing with luminescence thermometry, to acquire new insights of the reaction pathways. We also argue that further developments should be focused on local pressure measurements and on expanding the applications of these local sensors in other areas, such as liquid-phase catalysis, electrocatalysis, and photocatalysis. Ideally, a combination of sensors will be applied to monitor catalyst and reactor "health" and serve as feedback to the reactor conditions.



Catalysis is an essential component in the toolbox of chemists for making our chemical manufacturing processes more sustainable. By lowering the activation energy, catalysts enable chemical reactions to proceed more efficiently, requiring fewer resources, less energy, and less time to obtain the desired reaction products.[1] The transition from fossil fuels (*e.g.*, coal, crude oil, and natural gas) to renewable energy sources (biomass, municipal waste, and electricity from solar or wind power) requires versatile reactors and catalyst materials that can deal with changing feedstocks and energy supplies.[2]

The energetics of chemical reactions are determined by the laws of thermodynamics using the Gibbs free energy (eq 1):

$$G = U + PV - TS \tag{1}$$

It determines the final equilibrium of the reaction and is dependent on the internal energy of the reactants (U), the local pressure (P), concentration, temperature (T), and change in entropy (S). Furthermore, the Arrhenius equation (eq 2)

$$k = Ae^{-E_{act}/RT} \tag{2}$$

determines the kinetics of a chemical reaction, based on the activation energy (E_{act}) at a certain temperature. Pressure plays a smaller role in this equation but is typically included in the prefactor A.[3]

To tune the outcome of a chemical reaction while it is running, we thus have temperature and pressure in our toolbox at our disposal. Furthermore, we need to tailor our catalysts on the nanoscale, as the (molecular) structure of the catalyst and its interaction with analytes and intermediates plays a key role in lowering the activation energy and subsequently increasing the activity. Such active sites of solid catalysts involving metal nanoparticles are typically found on specific metal facets or edges.[4] In-depth understanding and control of chemical processes on the nanoscale will ultimately help to make the catalysts of the future during the transition from fossil fuels to a circular economy.

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Conventional spectroscopic techniques are used to measure a solid catalyst under ambient conditions before or after a reaction. To determine how catalysts actually operate under reaction conditions, researchers developed *in situ* tools that can assess the catalyst structure under controlled atmospheres. At the turn of this century, catalyst researchers realized that *in situ* characterization tools were not sufficient to explain the behavior of catalysts in a real reactor during reaction conditions because many characterizations were performed under different conditions than the actual (industrial) reaction.[5−8] The search for the perfect *in situ* experiment began, as described by James Haw: "A perfect *in situ* experiment would look inside an industrial reactor and reveal the most intimate details of a surface chemical reaction [. . .] on the scale of catalyst particles as well as spatial variations over the volume of the reactor [. . .]. Finally, the perfect method would correlate the composition of the catalyst bed with simultaneous measurements of product distributions in order to reveal structure−activity and structure−selectivity relationships."[9]

By employing spectroscopic tools in chemical reactors to observe a catalyst at work, we moved into the era of *operando* spectroscopy (derived from Latin, meaning operating or working). New reactors were developed with the intention of measuring the chemical structures of the catalyst while actively converting reactants into products, preferably by employing more than one online characterization tool. Ultimately, such tools could lead to reactor control: By monitoring the state of the catalyst in the reactor, adjustments can be made to the reaction conditions to keep the catalyst in its optimal state.[10]

In recent years, the field has moved more toward micro- and nanometer scales and active-site level understanding of the chemistry of catalytic reactions, resulting in advances in nanoscale-related techniques for catalysis.[11] Examples can be found in single-molecule fluorescence methods[12] and synchrotron-based characterization techniques (*e.g.*, scanning-transmission X-ray microscopy, STXM, and quick scan X-ray absorption fine structure, QXAFS).[13] These approaches can assess the dynamics of various aspects of both inter- and intraparticle heterogeneities within catalysts, such as the porous network and metal distribution. However, they have the disadvantage of requiring specialized equipment, such as synchrotron radiation or reaction-specific probes (*e.g.*, fluorescent molecules).

The perfect *operando* experiment would correlate nanoscale structure to bulk scale activity and selectivity due to spatiotemporal heterogeneities.[14] For this purpose, we need to understand important local chemical and physical conditions in real time—*e.g.*, molecular surface species, temperature, and pressure—and have the capability to measure these properties in a spatiotemporal manner under true reaction conditions (*i.e.*, *operando*).

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We see potential in "upgrading" the more conventional spectroscopic techniques by using (nanoparticle) sensors that can be tailored to monitor important parameters of the reaction remotely and in real time, namely, the local chemical species, temperature, and pressure (Figure 1a). Furthermore, these nanosensors can improve the spatial resolution using strong local enhancements, opening up possibilities such as measuring single nanoparticles or obtaining images that contain molecular information with nanoscale resolution by using local antennae. Recent examples of this approach can be found in single plasmon nanoparticle spectroscopy, which probes the localized surface plasmon resonance (LSPR) of the metal nanoparticles,[15] and plasmon-enhanced Raman spectroscopy (PERS).[16]

In future industrial reactors, nanosensors could eventually play a role in detecting local catalyst deactivation or thermal runaways. By monitoring reactor health in the macroscopic and microscopic ranges simultaneously in real time and providing local feedback of the reaction conditions (Figure 1b), we could prevent the death of a catalytic reaction by intervening in time. In previous work, our group used combined *operando* UV−vis/Raman spectroscopy to monitor and to control the coke deposition during propane dehydrogenation and regeneration of Cr/Al_2O_3 catalysts.[10] In addition, thermal runaways can be prevented by direct feedback of the catalyst temperature to the reactor temperature controller, as was demonstrated in the work by Cho *et al.*, in which temperature sensing was performed by magnetic crystallite thermometry on nickel catalysts during the ethane hydrogenolysis reaction.[17] Furthermore, the extension of heterogeneous catalysis to photocatalytic and electrocatalytic conversion processes—some of the pillars of future sustainable chemistry—will require flexible reactors with adaptable catalyst materials that can deal with varying feedstocks and reaction conditions. These changing feedstocks can have a big impact on reactor output and catalyst stability and, therefore, require fast performance feedback. Ideally, we would make use of nanosensors to study chemical processes on solid catalysts and to monitor and to control the catalyst and reactor "health" on a local and global scale, similar to a whole-body scan in life science. Is such a scenario far-fetched, or could it become reality?

In this Perspective article, we discuss the current and potential development of nanosensors within different catalysis disciplines based on two state-of-the-art techniques: PERS to measure chemicals and their surface adducts locally (Figure 1c) and band-shape luminescence thermometry (Figure 1d). It is not our intention to write a comprehensive review of these techniques but rather to provide insight into the state of the art and to offer our interpretation of the future prospects and requirements of local sensing in catalysis. The interested reader is directed to recent review articles in the literature.[16,18−22]

We start with a brief introduction to the state of the art of remote molecular and thermal sensing in heterogeneous catalysis, after which we discuss promising future applications of these techniques in various disciplines of catalysis, ranging from gas- and liquid-phase molecular detection in heterogeneous catalysis to (photo)electrocatalytic conversion processes. We furthermore argue the need to develop local sensors for reaction pressure monitoring. Ultimately, combining multiple nanoscale sensors will improve our insights not only in academic challenges, such as unraveling reaction pathways, but also in global industrial challenges, such as live reactor health monitoring and active control.

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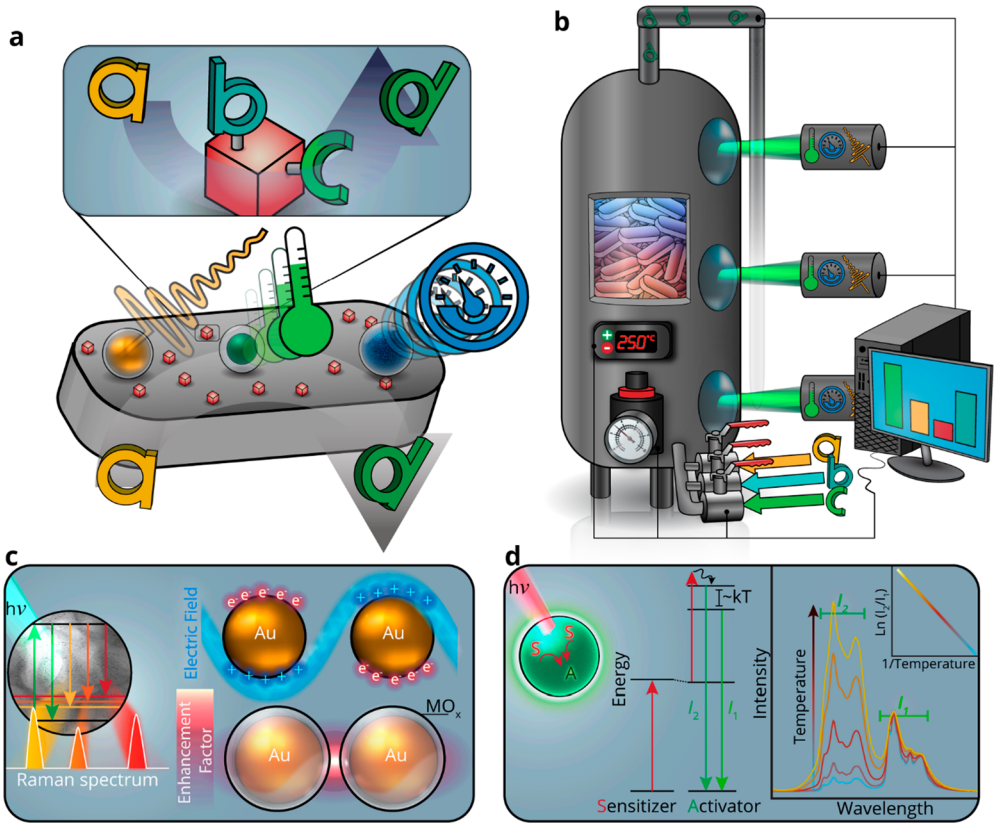

Figure 1. (a) Nanosensors providing local information on (bottom) the catalyst particle or (top) active-site level to improve the knowledge of spatiotemporal heterogeneities, such as chemical species using gold core−shell nanoparticles (that probe the catalyst structure and bonding to reactants a, b, c, and product d, for example), temperature using green core−shell nanoparticles, and pressure with blue core−shell nanoparticles. (b) In a future reactor, these combined sensors could monitor reactor and catalyst health in real time, giving insight into the spatiotemporal heterogeneities that can be used as feedback for the reactor input (temperature, pressure, and feedstocks a, b, and c). (c) Schematic illustration of the working principles of plasmon-enhanced Raman spectroscopy (PERS). Raman spectroscopy probes the inelastic scattering of light after excitation of matter using monochromatic light to obtain molecular structures. The Raman scattering intensity and the incident light can be enhanced by plasmonic nanoparticles by exciting the dipolar localized surface plasmon resonance. This Raman enhancement can be strongly improved in hot spots between two or more shell-isolated nanoparticles. (d) Schematic illustration of the working principles of luminescence thermometry. Absorption of near-infrared light results in the emission of upconverted green light using lanthanide sensitizers and activators. Temperature-dependent luminescence is governed by Boltzmann statistics; the logarithm of the luminescence intensity ratio plotted *versus* 1/*T* yields a linear correlation; the steepness of the fitted line corresponds to the energy difference between the excited states.

CHEMICAL SENSORS

During catalytic reactions over high-surface-area porous solids, the concentration of chemical species in the gas or liquid phase and on the catalytic surface can drastically change in time and space. As current techniques usually perform multiple (point) measurements to observe chemical gradients,[23] we need local sensors to account for changes in catalyst reactivity with great sensitivity to improve the temporal resolution. Such local chemical nanosensors are able to measure the concentrations of precursors and surface species on the solid catalyst with fast readouts.[15,16]

To the best of our knowledge, the most developed family of chemical sensor techniques for application in heterogeneous catalysis is PERS, including surface-enhanced Raman spectroscopy (SERS), shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS), and tip-enhanced Raman spectroscopy (TERS).[24] For PERS, noble metal nanostructures are applied to enhance the inelastically scattered Raman signal by factors of more than 10^6, which contains information on the molecular vibrations of the materials under study (Figure 1c). These noble metal nanostructures can effectively focus light within a few nanometers of their surfaces due to the collective resonant oscillation of free surface electrons upon excitation with visible light, which is referred to as localized surface plasmon resonance (LSPR, Figure 1c). The strongest enhancement factors (EFs) are found in hot spots, which are sites where multiple adjacent nanoparticles couple their resonances (Figure 1c), or at sharp antenna-like structures for TERS.[24] Although the Raman scattering cross section is typically very low, plasmonic nanostructures can upgrade the tool to become a strong surface-sensitive characterization technique with sensitivities up to, in principle, single-molecule detection.[25]

The advantage of SHINERS over other PERS techniques is that it is noninvasive when the plasmonic nanostructures are isolated by catalytically inactive dielectric shell materials with minimal damping of the LSPR.[26] The shells furthermore prevent chemical and thermal degradation of the nanosensors during the reactions.[27−30]

The Raman signal enhancement is extremely local as it dissipates by r^{-12} away from the plasmonic cores and, therefore, can be advantageously used to break the diffraction limit of visible light into the nanometer regime. Even without

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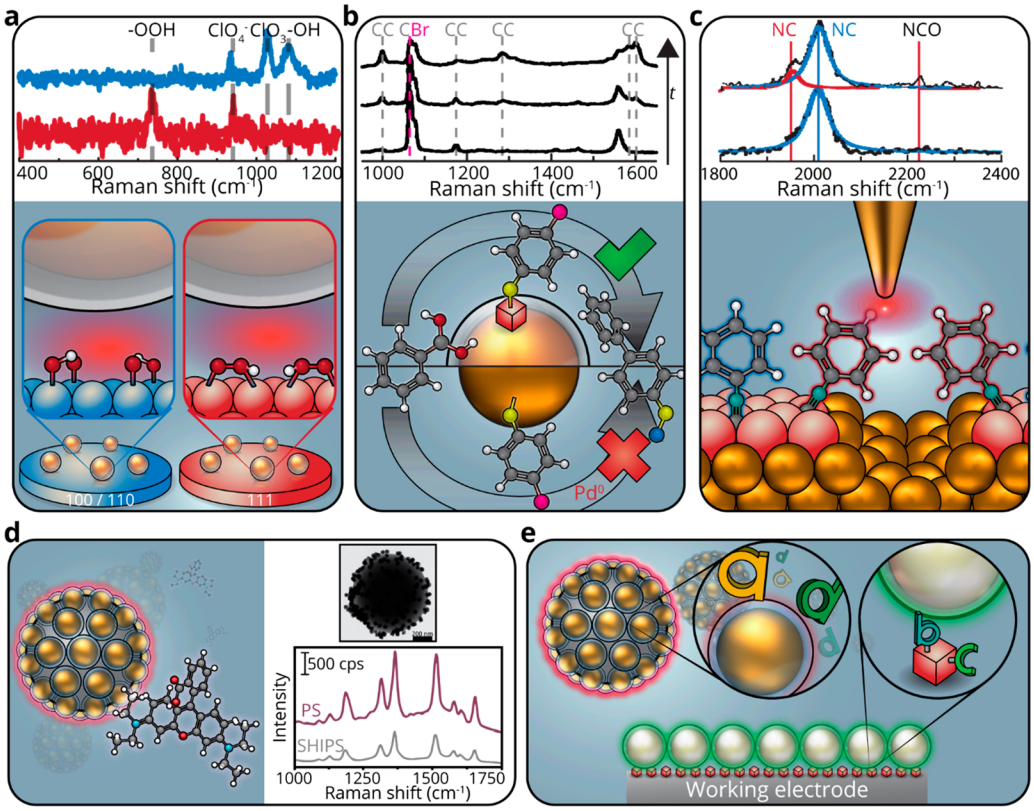

Figure 2. Plasmon-enhanced Raman spectroscopy for *in situ* studies of heterogeneous catalysts. (a) Using shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS), the structure−activity relationship was revealed on Pt single crystals during the oxygen reduction reaction in acidic conditions by the presence of −OH groups on (100) and (110) surfaces, and −OOH groups on (111) surfaces.[34] Adapted with permission from ref 34. Copyright 2018 Springer Nature. (b) SHINERS was applied to disentangle the heterogeneous and homogeneous reaction pathway for the Suzuki−Miyaura coupling between aryl bromides and phenylboronic acid over Pd nanoparticles.[30] Adapted from ref 30. Copyright 2019 American Chemical Society. (c) Tip-enhanced Raman spectroscopy was applied to resolve site-specific electronic and catalytic properties of a Pd/Au(111) bimetallic surface by observing a weakened N≡C bond of the adsorbed phenyl isocyanide on edge sites.[37] Adapted with permission from ref 37. Copyright 2016 Springer Nature. (d) Au and Au@SiO_2 can be assembled on larger SiO_2 spheres to form shell-isolated superstructures (SHIPS) for colloidally stable SHINERS experiments in liquids to observe Rhodamine 6G dye molecules up to picomolar quantities.[42] Adapted with permission from ref 42. Copyright 2019 John Wiley and Sons. (e) In electrocatalysis, combining SHINERS and SHIPS could be applied for *in situ* tracking of reactants (chemical a) and products (chemical d) in the liquid phase (by SHIPS) while following the chemisorbed species at the catalyst surface (chemicals b,c).

breaking the diffraction limit, SHINERS can deliver profound insights in chemical reactions over solid catalysts. For example, Tian and colleagues applied SHINERS to study CO oxidation over Pt, Pt−Fe, and Pd colloidal nanocatalysts supported on Au@SiO_2.[27] They studied electronic effects and catalyst−adsorbate interactions using SHINERS, enabling them to establish the mechanisms for CO oxidation over the different catalysts.[27] They further applied SHINERS to determine the strain effects of Au@Pd nanocatalysts by studying the N≡C stretching vibration of phenyl isocyanide.[31] Because the N≡C bond is sensitive to the metal structure, Tian and colleagues used it to explain the superior catalytic activity for benzyl oxidation of Au cores with five monolayers of Pd.[31] In addition, our group followed the hydrogenation of phenylacetylene over Pt nanoparticles using SHINERS.[32] We observed the sequential hydrogenation of phenylacetylene in H_2 into styrene and ultimately ethylbenzene. Furthermore, the reverse reaction took place in the absence of H_2, which enabled more detailed understanding of the reaction mechanism and the assignment of Raman peaks.[32] Later, our group studied acetylene hydrogenation over industrially relevant Ni catalysts.[33] We identified Ni−adsorbate interactions and followed the deactivation of the catalyst due to coke formation. In this work, spark ablation was implemented to obtain active metallic nanoparticles, thus circumventing high reduction temperatures (500 °C) which have high chances of destroying the SHINERS substrates.[33] These works are elegant demonstrations of how SHINERS can be applied as a spectroscopic tool in heterogeneous catalysis, where it can easily probe the low wavenumber regime for the detection of surface structures in addition to the full molecular fingerprint.

By smart assembly strategies, SHINERS can provide local information, as well. For example, Dong *et al.* assembled shell-isolated nanoparticles over single-crystal metal catalysts to study facet-dependent surface reactions in aqueous conditions selectively within electrochemical cells.[34] The authors applied the strong surface sensitivity of SHINERS for the real-time elucidation of previously unobservable reaction intermediates in the oxygen reduction reactions. Most notably, they observed the formation of superoxides on bridge sites of Pt(111) surfaces and hydroxyls on Pt(100) and Pt(110) surfaces under acidic conditions (Figure 2a). They could uniquely relate the difference in activity to the step sites on these Pt(*hkl*) surfaces.

More recently, Zhao and co-workers applied SHINERS to disentangle homogeneous from heterogeneous processes in the Suzuki−Miyaura cross-coupling reaction between aryl bro-

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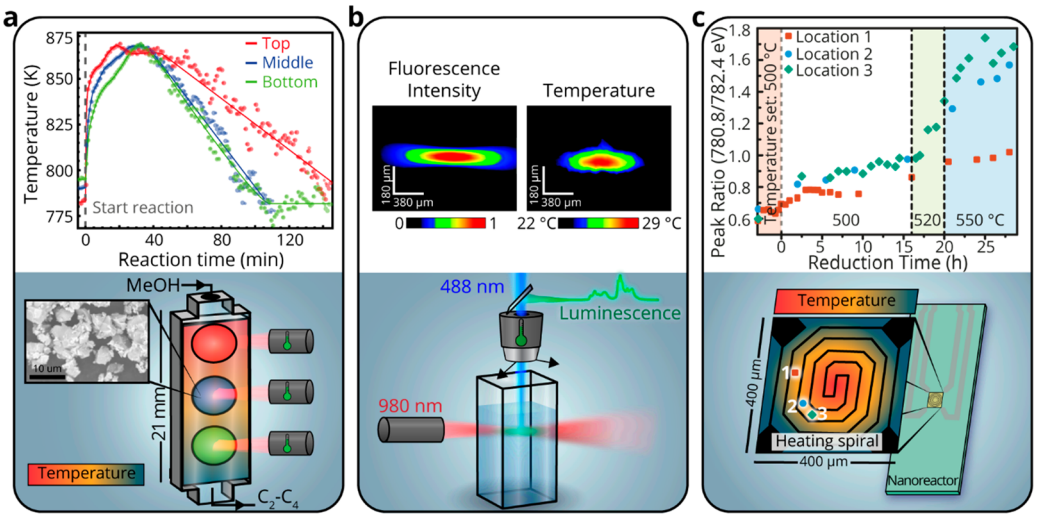

Figure 3. Luminescence thermometry applied at different length scales (a) Microcrystalline $NaYF_4$, doped with Er^{3+} and Yb^{3+}, was mixed with zeolite H-ZSM-5 to reveal a reaction front during the methanol-to-hydrocarbons (MTH) reaction due to the exothermic nature of the MTH reaction while measuring the products with online mass spectrometry (MS).[57] Adapted from ref 57. Copyright 2018 American Chemical Society. (b) Emission of $NaYF_4$:Er^{3+},Yb^{3+} nanoparticles after excitation with a 488 nm probe beam was used to measure the temperature profile of water heated by a 980 nm pump beam.[58] Adapted from ref 58. Copyright 2010 American Chemical Society. (c) Microcrystalline $NaYF_4$:Er^{3+},Yb^{3+} was used to explain deviating Co catalyst reduction behavior in a nanoreactor by showing large temperature variations within the reactor with up to 10 μm resolution.[60] Adapted with permission from ref 60. Copyright 2019 John Wiley and Sons.

mides and phenylboronic acid over Pd nanoparticles.[30] Using the design of supported Pd catalysts on shell-isolated nanoparticles, they demonstrated that the reaction is in fact heterogeneous in nature and no reaction takes place over leached Pd species (Figure 2b). Furthermore, they showed the importance of direct contact of the aryl bromides with the catalyst surface and that the catalyst activity can be tuned by modifying its surface groups and charge, and the Pd−Br distance.[30] Other work has demonstrated the use of SHINERS for investigating catalyst−support interactions, a key factor in heterogeneous catalysis for defining activity and selectivity.[35] So far, two support materials have been studied over Au@SiO_2 and Au@TiO_2 nanoparticles employed in the hydrogenation reaction of 4-nitrothiophenol to 4-aminothiophenol over Pt colloidal nanoparticles[28] and the CO hydrogenation over Ru nanoparticles prepared by the catalyst impregnation method.[29] The two studies revealed the effect of a reducible support material on catalysis with potentially faster kinetics due to effects such as hydrogen spillover.

These examples highlight the potential of SHINERS for molecular sensing of catalytic reactions at nanoscale events, but how can we go further? By combining the plasmonic properties of nanostructured noble metals with scanning probe microscopy (SPM), we obtain TERS.[36] Recent advances in this technique have increased the spatial resolution with scanning tunneling microscopy (STM), leading to the observation of site-specific electronic and catalytic properties of a Pd/Au(111) bimetallic surface with topographical and chemical information up to 3 nm resolution (Figure 2c).[37] It is evident that TERS can play a crucial role in elucidating chemical reaction pathways on nanometer length scales and differentiating between active and inactive sites. However, to reach spatial resolutions below 10 nm, conductive substrates are required under (ultra) high vacuum conditions, limiting such measurements in *operando* and time-resolved settings. Atomic force microscopy (AFM)-based TERS can be applied as a more universal method for studying chemical reactions in a variety of conditions, including aqueous solvents for use in electrochemical cells.[38] Similar to SHINERS, metallic TERS tips can be rendered chemically stable and noninvasive using thin isolating layers of metal oxide, such as SiO_2,[39] Al_2O_3,[40,41] and ZrO_2,[38] to make them suitable for applications in heterogeneous catalysis. As an added benefit, metal oxide coatings greatly enhance the plasmonic stability.

Both SHINERS and TERS are useful methods for measuring the adsorption of reactants, intermediates, and products on the catalyst; however, they could also play roles in analyses of reactions in the liquid phase. For example, in electrochemical studies, the product analysis is often performed by taking out microsamples for quasi-online high-performance liquid chromatography (HPLC) or online electrochemical mass spectrometry (OLEMS). Remote spectroscopy could make such measurements possible in real time. Real-time measurements would require colloidally stable, plasmonic nanostructures with intrinsic hot spots that arise from sharp edges or from clustering the metal nanoparticles into shell-isolated plasmonic superstructures (SHIPS, Figure 2d).[42] Such structures would be useful in electrochemical experiments for online monitoring of the reaction products in solution, which would give complementary information to the surface-bound intermediate species, measured with SHINERS, on electrocatalyst monolayers, for which small amounts of products and low signals are expected (Figure 2e). In order to use SHINERS as a quantitative analysis tool for product analysis, controlled substrates with internal standards for SHINERS are required.[18]

TEMPERATURE SENSORS

Similar to chemical concentration gradients, temperature plays a crucial role in the reactivity and stability of catalytic systems and can differ drastically over a catalyst bed and even within a catalyst body. Researchers have long been aware of the importance of measuring local temperatures on the catalyst

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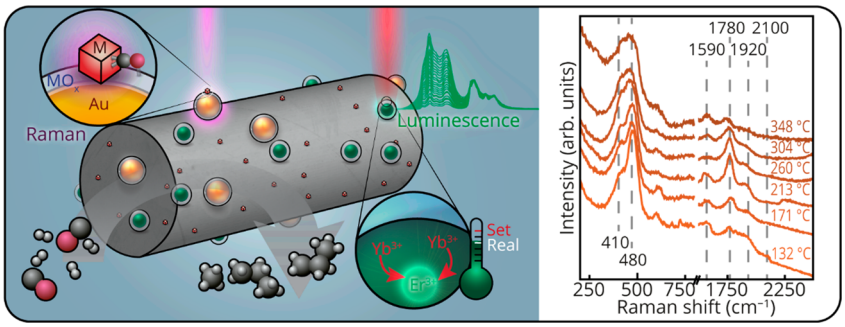

Figure 4. (Left) Two eyes on a single catalyst body for obtaining chemical and thermal information simultaneously during the CO hydrogenation reaction over Rh/SiO_2 by shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) and luminescence thermometry, respectively. Luminescence thermometry demonstrated a mismatch between the set temperature and the actual temperature. (Right) SHINERS revealed a tilted CO species adsorbed on the Rh surface at 1780 cm^{-1} at temperatures above 213 °C. The temperatures were measured on the same catalyst body by luminescence thermometry, whereas SHINERS provided chemical insights of the surface species on the Rh catalyst.[61] Adapted with permission from ref 61. Copyright 2019 Nature Springer.

level,[43] and early attempts involved the use of superparamagnetic nickel crystallites because the magnetic moment per unit volume of crystallite for nickel is temperature-dependent.[44] However, these examples were limited to one system and proved difficult to implement. A noninvasive and universally applicable tool that can read out the local temperature on any desired spot is needed.

Various other methods to monitor local temperatures exist, including the use of nuclear magnetic resonance (NMR),[45] blackbody radiation,[46,47] multiple thermocouples,[48] and luminescence thermometry using perovskites[49] and trivalent lanthanides.[50] Luminescence thermometry focuses on temperature-dependent luminescence phenomena such as luminescence intensity, wavelength, or lifetime.[51] For thermometry purposes, ratiometric band-shape luminescence thermometry (*i.e.*, monitoring the change in the luminescence intensity ratio between two different peaks) has the most potential because its ratiometric nature makes it independent of T-probe concentration.

Lanthanide-doped nanomaterials are preferred for temperature sensing because their luminescence involves sharp emission peaks whose spectral positions are independent of the surroundings,[52] enabling relatively straightforward interpretation of the luminescence signal up to the high temperatures (600 °C) that are relevant for catalysis.[53] Small energy differences (ΔE) between the excited states ensure that they are thermally coupled, leading to a Boltzmann distribution between the two excited states[53] and resulting in the typical temperature-dependent behavior, as shown in Figure 1d. By choosing different lanthanides, the emission wavelength, temperature range, and sensitivity are controlled; the host lattice ensures a thermally stable and low phonon energy material[54] for application at elevated temperatures up to 600 °C. Specific dopants and codopants can be exploited for upconversion,[55] meaning that multiple low-energy photons excite the system before anti-Stokes emission at higher energy occurs (Figure 1d), avoiding background fluorescence from other materials such as coke deposits.[56]

Luminescence thermometry can easily be applied to give insights in the millimeter range by using microcrystalline $NaYF_4$ doped with Yb^{3+} and Er^{3+} for exact local measurements during catalysis with a spot size of ∼5 mm. We used this method to follow the temperature distribution at three different heights in a 21 mm × 6 mm × 3 mm fixed bed reactor during the methanol-to-hydrocarbons (MTH) reaction, which revealed a temperature gradient along the catalyst bed without the need for multiple thermometers that could potentially interfere with the reaction of interest (Figure 3a).[57]

The real potential of temperature nanosensors lies in high-resolution temperature mapping at sub-millimeter or even sub-micron levels. By combining luminescence thermometry with (confocal) microscopy, temperatures can be monitored with a spatial resolution of <10 μm. Vetrone *et al.* demonstrated this finding by recording thermal gradients within an aqueous colloidal solution containing $NaYF_4$:Er^{3+},Yb^{3+} nanoparticles.[58] They heated the water using a 980 nm pump beam and performed the thermal imaging by recording the luminescence of the nanoparticles in a confocal plane orthogonal to the 980 nm laser using a 488 nm probe beam (Figure 3b). They followed the temperature within an individual cancer cell while heating it up to its death at 45 °C.[58] Our group applied luminescence thermometry to monitor chemical reactions in microfluidics using varying reactor materials and nanoprobes stabilized with either organic ligands (for apolar solvents) or charged SiO_2 (polar solvents).[59] In a subsequent study, our group used temperature mapping within a single nanoreactor to explain the varying reduction behavior of Co nanoparticles during X-ray microscopy experiments due to temperature heterogeneities (Figure 3c).[60] Current efforts conducted within our group have ensured spatial resolutions of ∼1 μm using confocal fluorescence microscopy, and future efforts will also focus on preparing three-dimensional reconstructions of the temperature distribution. In addition, by exploiting cathodoluminescence or X-ray-induced fluorescence, it might be possible to combine luminescence thermometry with electron microscopy measurements or synchrotron experiments to push the spatial resolution and versatility even further.

Other opportunities lie in the exploration of temperature-controlled experiments to tune the electrocatalytic CO_2 reduction reaction and to access new reaction pathways. Technical difficulties of electrocatalysis at elevated temperatures include catalyst stability, reactant/product adsorption/desorption, electrochemical cell design, and electrolyte choice, among others. We have a specific interest in obtaining local information at the reaction surface, such as local heat and reactant/intermediate adsorption, in order to design novel electrocatalysts rationally. The application of nanoscale molecular and temperature sensors will improve our understanding of the CO_2 reduction reaction and aid the

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development of advanced electrocatalysts with enhanced performance toward value-added chemicals by gaining information on the single electrocatalyst nanoparticle level. Although temperatures can be measured in the electrolyte *via* a thermocouple, local temperature variations are expected near the electrode surface due to variations in local current densities up to several hundred mA/cm^2 and local heating. When a combination of suspended and electrode-anchored temperature sensors can be used (similar to the applied SHINERS in Figure 2e), the temperature gradient toward the electrode surface can be measured with confocal microscopy. Direct measurement of such local temperature variations will aid the rational design of the ultimate electrocatalyst.

TWO EYES ON SINGLE CATALYST PARTICLES

Our aim is to develop multiple sensors to follow all essential conditions during a chemical reaction. Recently, we have combined two of these nanosensor eyes—chemical and temperature sensors—to obtain local thermal and chemical information simultaneously from a single catalyst body during the CO hydrogenation reaction over Rh/SiO_2 catalysts (Figure 4). $NaYF_4$@SiO_2 nanomaterials doped with Yb^{3+} and Er^{3+} were employed as temperature probes and were extruded together with SiO_2 as the catalyst body, and Au@SiO_2 shell-isolated plasmonic nanoparticles were assembled on the exterior surface of the catalyst body and served as chemical sensors (Figure 4, left side).[61] The results showed large effects of gas composition (50 °C) due to the thermal conductivity of H_2 *versus* CO, which can have a large influence on catalyst activity and selectivity. In addition, SHINERS enabled the identification of a new carbonyl surface species (1780 cm^{-1}) at exact local temperatures (Figure 4, right side), indicating that hydrogen-assisted CO dissociation is the preferred pathway for the CO hydrogenation reaction over Rh/SiO_2 catalyst.

TOWARD ALL EYES ON SOLID CATALYSTS

Over the past few years, great successes have been achieved in the application of nanosensors for chemical reactions. With the state-of-the-art examples discussed above, we see that we can obtain chemical and thermal information, even combined on the single catalyst body level. The future application of nanosensors for *operando* spectroscopy is dependent on its universal applicability. Spectroscopy-based nanosensing can readily be combined with complementary techniques to monitor both temperature and chemical species or other reaction parameters. The knowledge required to enable spectroscopic monitoring inside reactors (*i.e.*, *operando* studies) has already been obtained for vibrational spectroscopy (Fourier transform infrared and Raman) but also for UV−vis spectroscopy. The infrastructure required for these studies can readily be applied to luminescence thermometry, enabling easy, applicable *operando* temperature studies inside reactors and the combination of different spectroscopic techniques to enable the monitoring of chemical species and temperature simultaneously.

> Our aim is to develop multiple sensors to follow all essential conditions during a chemical reaction.

New developments are required to obtain universally applicable nanosensors for catalysis. First of all, the adaptation of nanostructures for more strenuous reaction conditions is required. Second, increasing the spatial and temporal resolution up to the nanometer range to monitor catalytic processes is desired for studying the active site. Third, by combining complementary characterization techniques (such as luminescence thermometry and SHINERS) and including new sensor materials for pressure sensing, we can obtain a more complete image of the chemical reactions inside a live reactor.

The application window of nanosensors should be increased to enable the monitoring of alternative environments, including solutions for liquid-phase heterogeneous catalysis and electrocatalysis, and to allow for high-temperature measurements up to 1000 °C that can be present during oxidative coupling of methane and methane to aromatics. Currently, the limitations for nanoparticle-based sensing during catalysis are the harsh chemical environments, high temperatures, and coke formation. The (nano)crystal probes should be chemically stable and inert to ensure probe stability as well as noninvasiveness. For temperature sensors, chemically stable Y_2O_3 host materials[62] as well as $NaYF_4$−SiO_2 core−shell nanomaterials[53] were applied for thermometry under typical catalytic conditions up to 600 °C with a variety of chemicals present. They demonstrated good thermal and chemical stability, without sintering, particle deformation, atomic diffusion, chemical etching, or crystal phase changes.[53,62] For applications above 600 °C, we expect Y_2O_3 to be the most viable host material because the melting point of 2425 °C is much higher than that of $NaYF_4$. The melting point is not the only limitation though, and therefore, further research is required on the mobility of the lanthanide ions in the host material at elevated temperatures.

Chemical sensing by SHINERS is even more prone to degradation at high temperatures and demanding chemical conditions because the isolating shell is required to be extremely thin to obtain strong EFs and nonporous to prevent sintering and side reactions. The stability is limited to 400−500 °C by implementing SiO_2 and TiO_2 coatings thinner than 3 nm because thicker shells will severely limit the EF.[29,63,64] Options to improve the thermal stability lie in the application of alloyed cores such as Ag/Au alloys[65] or other plasmonic materials such as metal nitrides, which have melting points above 2900 °C.[16] The effects of high pressure on the probe stability is a research question that remains to be answered. Furthermore, the sensor materials could influence the catalyst performance *via* chemical and electronic interactions[66] when the catalysts and probes are in close proximity; this influence could be exploited to study catalyst−support interactions. Additional challenges include the preparation of chemically stable sensors for application in liquids (typically aqueous electrolytes are used in electrocatalysis) and nanosensors that are able to withstand the large current densities of industrial conditions. These conditions might induce sintering and degradation of the sensors.

It has been established that carbon deposition (referred to as coke formation) during catalysis can severely limit the applicability for spectroscopic techniques due to competitive absorption of the incident or emitted light or by competitive emission of fluorescent species. The application of lanthanides for luminescence thermometry can partially overcome this problem as the lanthanide ions exhibit sharp anti-Stokes emission features that can help to distinguish the lanthanide emission from other emitting centers. However, synthesis

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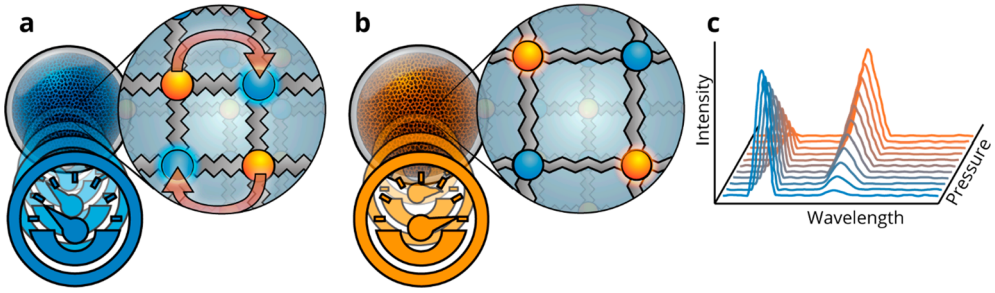

Figure 5. Future pressure sensors might involve a combination of two or more trivalent lanthanide ions in metal−organic frameworks (MOFs). Pressure-dependent band shapes can be observed in materials that experience changes in the efficiency of the energy transfer associated with the distance between the lanthanide ions related to the pressure. (a) MOFs emit blue light at low pressure because energy transfer is efficient when the metal ions are relatively close. (b) MOFs emit orange light at high pressure because the energy absorbed by the orange sensitizer cannot be transferred to the blue activator. (c) As a result, we observe a ratiometric pressure-dependent emission spectrum.

strategies should be optimized in order to increase the absorption cross section and quantum yield of these temperature probes, such as in the work by Haase *et al.*, where the quantum yield of lanthanide-doped $NaYF_4$ nanoparticles was increased by a factor of 100 by encapsulating the core particles in an inert $NaYF_4$ shell.[67] Raman spectroscopy is often used for detecting carbon deposition during catalysis,[68] and with SHINERS, it could be applied to study the early growth stages before self-absorption reduces signal intensities.[69] One of the challenges of spectroscopy-based nanosensors will be overcoming the competitive absorption and emission of coke species produced during reactions, so that we can rely on the signal from the nanosensors to regenerate catalysts.

The enhanced luminescence properties of the temperature probes will support the second goal, as well: to increase spatial and temporal resolution. Because the signal-to-noise ratio of the luminescence measurement is correlated to the temperature uncertainty, there is a trade-off between temperature accuracy, spatial accuracy (smaller spot size means fewer particles are probed), and temporal resolution (shorter acquisition times means less luminescence intensity). Current luminescence efficiencies enable steady-state investigations using microscopy techniques,[59,60] but acquiring time-resolved temperature maps is still a difficult challenge for which the nanosensors have to be optimized.

Using plasmon-enhanced Raman spectroscopy techniques, chemical species can be identified beyond the diffraction limit. In principle, using near-field optical thermometry[70] or a thermocouple in combination with atomic force microscopy,[71] it should be possible to break the diffraction limit in thermometry applications. However, these techniques require sophisticated equipment which limits their versatility, and they only probe the surface of materials and/or have a limited temperature range of 50 °C.

In addition, intelligent chemical preparation of samples can yield systems in which temperature values can be obtained on the single-catalyst particle level, breaking the diffraction limit while maintaining a high temperature range and the possibility of *operando* studies. Higher spatial and temporal resolution with sufficient luminescence signal can be reached by placing the temperature probes in a well-organized fashion. For instance, by preparing SiO_2-coated temperature probes and depositing catalyst nanoparticles on the surface, the local temperature of a single catalyst particle can be determined. If sufficient temperature probes are monitored, a good signal-to-noise ratio will be acquired, but the luminescence signal originates from only tens of nanometers from the catalyst particles. Although the temperature is monitored locally, the experiments do not provide any information regarding the temperature heterogeneity between different probe/catalyst particles. A second approach can be to prepare binary superstructures of the temperature probe and catalyst nanoparticles. Here, the temperature can be determined within the catalytically active self-assembled monolayer with the additional synergy that the temperature probes can prevent sintering of the catalyst nanoparticles and, thus, increase catalyst stability.

Pressure, like temperature, is a reactor-scale parameter that is not controlled on the nanoscale, but it can definitely change over the reactor bed due to pressure drops and reaction of adsorbates within the pores of catalyst bodies. At the moment, no spectroscopy-based nanosensors exist for pressure to the best of our knowledge, but we will speculate about a possible direction. One possible direction will be the implementation of distance-dependent energy transfer between different lanthanide ions in a flexible host material. Metal organic frameworks (MOFs) are interesting host materials for lanthanide ions, as they are flexible materials and respond strongly to differences in pressure by expanding or shrinking. For example, Eu^{3+} and Tb^{3+} in MOFs exhibit temperature-dependent luminescence due to the change in distance between the lanthanide ions and, with it, the change in the efficiency of the energy transfer (Figure 5).[72] Challenges in such pressure sensors will be the disentanglement of temperature- and pressure-related expansion/compression, but this question could be solved by applying the MOF pressure nanosensors simultaneously with nanoparticle-based luminescence thermometry. Furthermore, MOFs involving lanthanides are typically quite sensitive, but the search continues to find kinetically stable structures using intelligent ligand design to obtain structures resistant to the strenuous conditions found in a chemical reactor.[73]

ONLINE REACTOR AND CATALYST "HEALTH" MONITORING

With the implementation of nanosensors, we are entering a new era of catalyst characterization. We will have digital tools at our disposal that enable the construction of large databases to help answer the question of what (condition) makes a good or a bad catalyst. For example, what are the temperature windows at which a solid catalyst can operate efficiently with long lifetimes? Large temperature fluctuations, in particular, local hot spots, heavily impact catalyst activity/stability and are linked to sintering of supported metals and degradation of

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solid catalysts. Local temperature and chemical sensors could provide valuable insights in these events and help to increase the lifetime of catalysts.

> With online tools, catalyst regeneration can take place locally, based on actual chemical understanding.

Will we see the advent of multiple sensors in chemical reactors taking advantage of these or similar nanoparticle antennae to monitor the reactor health? Similar to total body scans, can we find and eliminate a potential illness before the catalyst dies, preferably with online tools on the local scale as well as the overall reactor? With local chemical sensors, we will be able to find possible catalyst poisons, such as sulfur-containing compounds or coke buildup on even smaller length scales, and to correlate them to the local conditions. With online tools, catalyst regeneration can take place locally, based on actual chemical understanding as opposed to empirical findings based on previous runs.

We have only seen the beginning of nanosensors in catalytic reactions. We should start filling this toolbox to visualize the local temperature, pressure, and chemical species, preferably all together. Ultimately, this combination will give us full insight into the thermodynamics and kinetics of chemical reactions. In catalyst and reactor diagnostics, seeing is believing, and without this toolbox we are working in the dark.

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ABBREVIATIONS

AFM, atomic force microscopy; EF, enhancement factor; FTIR, Fourier transform infrared spectroscopy; HPLC, high-performance liquid chromatography; LSPR, localized surface plasmon resonance; MOF, metal organic framework; MS, mass spectrometry; MTH, methanol-to-hydrocarbons; NMR, nuclear magnetic resonance; OLEMS, online electrochemical mass spectrometry; PERS, plasmon-enhanced Raman spectroscopy; QXAFS, quick scan X-ray absorption fine structure; SERS, surface-enhanced Raman spectroscopy; SHINERS, shell-isolated nanoparticle-enhanced Raman spectroscopy; SHIPS, shell-isolated plasmonic superstructures; SPM, scanning probe microscopy; STM, scanning tunneling microscopy; STXM, scanning transmission X-ray microscopy; TERS, tip-enhanced Raman spectroscopy; UV−vis, ultraviolet−visible

REFERENCES

(1) Dumesic, J. A.; Huber, G. W.; Boudart, M. Principles of Heterogeneous Catalysis. In *Handbook of Heterogeneous Catalysis*; Ertl, G., Knözinger, H., Weitkamp, J., Eds.; Wiley-VCH: Weinheim, Germany, 2008; pp 1−48.

(2) Marion, P.; Bernela, B.; Piccirilli, A.; Estrine, B.; Patouillard, N.; Guilbot, J.; Jérôme, F. Sustainable Chemistry: How to Produce Better and More from Less? *Green Chem.* **2017**, *19*, 4973−4989.

(3) Atkins, P.; de Paula, J.; Keeler, J. *Atkins' Physical Chemistry*, 1st ed.; Oxford University Press: Oxford, UK, 2018.

(4) Nørskov, J. K.; Bligaard, T.; Hvolbæk, B.; Abild-Pedersen, F.; Chorkendorff, I.; Christensen, C. H. The Nature of the Active Site in Heterogeneous Metal Catalysis. *Chem. Soc. Rev.* **2008**, *37*, 2163−2171.

(5) Bañares, M. A.; Guerrero-Pérez, M. O.; Fierro, J. L. G.; Cortez, G. G. Raman Spectroscopy during Catalytic Operations with On-Line Activity Measurement (Operando Spectroscopy): A Method for Understanding the Active Centres of Cations Supported on Porous Materials. *J. Mater. Chem.* **2002**, *12*, 3337−3342.

(6) Weckhuysen, B. M. Snapshots of a Working Catalyst: Possibilities and Limitations of in Situ Spectroscopy in the Field of Heterogeneous Catalysis. *Chem. Commun.* **2002**, 97−110.

(7) Bañares, M. A. Operando Methodology: Combination of in Situ Spectroscopy and Simultaneous Activity Measurements under Catalytic Reaction Conditions. *Catal. Today* **2005**, *100*, 71−77.

(8) Weckhuysen, B. M. Determining the Active Site in a Catalytic Process: Operando Spectroscopy Is More than a Buzzword. *Phys. Chem. Chem. Phys.* **2003**, *5*, 4351−4356.

(9) Haw, J. F. *In-Situ Spectroscopy in Heterogeneous Catalysis*; Wiley-VCH: Weinheim, Germany, 2002.

(10) Bennici, S. M.; Vogelaar, B. M.; Nijhuis, T. A.; Weckhuysen, B. M. Real-Time Control of a Catalytic Solid in a Fixed-Bed Reactor Based on in Situ Spectroscopy. *Angew. Chem., Int. Ed.* **2007**, *46*, 5412−5416.

(11) Buurmans, I. L. C.; Weckhuysen, B. M. Heterogeneities of Individual Catalyst Particles in Space and Time as Monitored by Spectroscopy. *Nat. Chem.* **2012**, *4*, 873−886.

(12) Cordes, T.; Blum, S. A. Opportunities and Challenges in Single-Molecule and Single-Particle Fluorescence Microscopy for Mechanistic Studies of Chemical Reactions. *Nat. Chem.* **2013**, *5*, 993−999.

(13) Meirer, F.; Weckhuysen, B. M. Spatial and Temporal Exploration of Heterogeneous Catalysts with Synchrotron Radiation. *Nat. Rev. Mater.* **2018**, *3*, 324−340.

(14) Grunwaldt, J. D.; Wagner, J. B.; Dunin-Borkowski, R. E. Imaging Catalysts at Work: A Hierarchical Approach from the Macro- to the Meso- and Nano-Scale. *ChemCatChem* **2013**, *5*, 62−80.

(15) Alekseeva, S.; Nedrygailov, I. I.; Langhammer, C. Single Particle Plasmonics for Materials Science and Single Particle Catalysis. *ACS Photonics* **2019**, *6*, 1319−1330.
(16) Ding, S.-Y.; Yi, J.; Li, J.-F.; Ren, B.; Wu, D.-Y.; Panneerselvam, R.; Tian, Z.-Q. Nanostructure-Based Plasmon-Enhanced Raman Spectroscopy for Surface Analysis of Materials. *Nat. Rev. Mater.* **2016**, *1*, 16021.
(17) Cho, C.; Chang, F. S.; Cale, T. S. Thermal Runaway Prevention in Catalytic Packed Bed Reactor by Solid Temperature Measurement and Control. *Korean J. Chem. Eng.* **1993**, *10*, 195−202.
(18) Langer, J.; Jimenez de Aberasturi, D.; Aizpurua, J.; Alvarez-Puebla, R. A.; Auguié, B.; Baumberg, J. J.; Bazan, G. C.; Bell, S. E. J.; Boisen, A.; Brolo, A. G.; et al. Present and Future of Surface-Enhanced Raman Scattering. *ACS Nano* **2020**, *14*, 28−117.
(19) Schlücker, S. Surface-Enhanced Raman Spectroscopy: Concepts and Chemical Applications. *Angew. Chem., Int. Ed.* **2014**, *53*, 4756−4795.
(20) Zhan, C.; Chen, X.-J.; Yi, J.; Li, J.-F.; Wu, D.-Y.; Tian, Z.-Q. From Plasmon-Enhanced Molecular Spectroscopy to Plasmon-Mediated Chemical Reactions. *Nat. Rev. Chem.* **2018**, *2*, 216−230.
(21) Wang, Y.-H.; Wei, J.; Radjenovic, P.; Tian, Z.-Q.; Li, J.-F. In Situ Analysis of Surface Catalytic Reactions Using Shell-Isolated Nanoparticle-Enhanced Raman Spectroscopy. *Anal. Chem.* **2019**, *91*, 1675−1685.
(22) Brites, C. D. S.; Lima, P. P.; Silva, N. J. O.; Millán, A.; Amaral, V. S.; Palacio, F.; Carlos, L. D. Thermometry at the Nanoscale. *Nanoscale* **2012**, *4*, 4799−4829.
(23) Sattler, J. J. H. B.; Mens, A. M.; Weckhuysen, B. M. Real-Time Quantitative Operando Raman Spectroscopy of a CrO_x/Al_2O_3 Propane Dehydrogenation Catalyst in a Pilot-Scale Reactor. *ChemCatChem* **2014**, *6*, 3139−3145.
(24) Ding, S.-Y.; You, E.-M.; Tian, Z.-Q.; Moskovits, M. Electromagnetic Theories of Surface-Enhanced Raman Spectroscopy. *Chem. Soc. Rev.* **2017**, *46*, 4042−4076.
(25) Etchegoin, P. G.; Le Ru, E. C. A Perspective on Single Molecule SERS: Current Status and Future Challenges. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6079−6089.
(26) Li, J. F.; Huang, Y. F.; Ding, Y.; Yang, Z. L.; Li, S. B.; Zhou, X. S.; Fan, F. R.; Zhang, W.; Zhou, Z. Y.; Wu, D. Y.; et al. Shell-Isolated Nanoparticle-Enhanced Raman Spectroscopy. *Nature* **2010**, *464*, 392−395.
(27) Zhang, H.; Wang, C.; Sun, H.-L.; Fu, G.; Chen, S.; Zhang, Y.-J.; Chen, B.-H.; Anema, J. R.; Yang, Z.-L.; Li, J.-F.; Tian, Z.-Q. In Situ Dynamic Tracking of Heterogeneous Nanocatalytic Processes by Shell-Isolated Nanoparticle-Enhanced Raman Spectroscopy. *Nat. Commun.* **2017**, *8*, 15447.
(28) Zhang, H.; Zhang, X.-G.; Wei, J.; Wang, C.; Chen, S.; Sun, H.-L.; Wang, Y.-H.; Chen, B.-H.; Yang, Z.-L.; Wu, D.-Y.; et al. Revealing the Role of Interfacial Properties on Catalytic Behaviors by In-Situ Surface-Enhanced Raman Spectroscopy. *J. Am. Chem. Soc.* **2017**, *139*, 10339−10346.
(29) Hartman, T.; Weckhuysen, B. M. Thermally Stable TiO_2- and SiO_2-Shell-Isolated Au Nanoparticles for In Situ Plasmon-Enhanced Raman Spectroscopy of Hydrogenation Catalysts. *Chem. - Eur. J.* **2018**, *24*, 3733−3741.
(30) Zhao, Y.; Du, L.; Li, H.; Xie, W.; Chen, J. Is the Suzuki-Miyaura Cross-Coupling Reaction in the Presence of Pd Nanoparticles Heterogeneously or Homogeneously Catalyzed? An Interfacial Surface-Enhanced Raman Spectroscopy Study. *J. Phys. Chem. Lett.* **2019**, *10*, 1286−1291.
(31) Wei, J.; Zhang, Y. J.; Qin, S. N.; Yang, W. M.; Zhang, H.; Yang, Z. L.; Tian, Z. Q.; Li, J. F. Understanding the Strain Effect of Au@Pd Nanocatalysts by: In Situ Surface-Enhanced Raman Spectroscopy. *Chem. Commun.* **2019**, *55*, 8824−8827.
(32) Wondergem, C. S.; Hartman, T.; Weckhuysen, B. M. In Situ Shell-Isolated Nanoparticle-Enhanced Raman Spectroscopy to Unravel Sequential Hydrogenation of Phenylacetylene over Platinum Nanoparticles. *ACS Catal.* **2019**, *9*, 10794−10802.
(33) Wondergem, C. S.; Kromwijk, J. J. G.; Slagter, M.; Vrijburg, W. L.; Hensen, E. J. M.; Monai, M.; Vogt, C.; Weckhuysen, B. M. In Situ Shell-Isolated Nanoparticle-Enhanced Raman Spectroscopy of Nickel-Catalyzed Hydrogenation Reactions. *ChemPhysChem* **2020**, *21*, 625−632.
(34) Dong, J. C.; Zhang, X. G.; Briega-Martos, V.; Jin, X.; Yang, J.; Chen, S.; Yang, Z. L.; Wu, D. Y.; Feliu, J. M.; Williams, C. T.; et al. In Situ Raman Spectroscopic Evidence for Oxygen Reduction Reaction Intermediates at Platinum Single-Crystal Surfaces. *Nat. Energy* **2019**, *4*, 60−67.
(35) Hernández Mejía, C.; van Deelen, T. W.; de Jong, K. P. Activity Enhancement of Cobalt Catalysts by Tuning Metal-Support Interactions. *Nat. Commun.* **2018**, *9*, 4459.
(36) van Schrojenstein Lantman, E. M.; Deckert-Gaudig, T.; Mank, A. J. G.; Deckert, V.; Weckhuysen, B. M. Catalytic Processes Monitored at the Nanoscale with Tip-Enhanced Raman Spectroscopy. *Nat. Nanotechnol.* **2012**, *7*, 583−586.
(37) Zhong, J. H.; Jin, X.; Meng, L.; Wang, X.; Su, H. S.; Yang, Z. L.; Williams, C. T.; Ren, B. Probing the Electronic and Catalytic Properties of a Bimetallic Surface with 3 nm Resolution. *Nat. Nanotechnol.* **2017**, *12*, 132−136.
(38) Kumar, N.; Wondergem, C. S.; Wain, A. J.; Weckhuysen, B. M. In Situ Nanoscale Investigation of Catalytic Reactions in the Liquid Phase Using Zirconia-Protected Tip-Enhanced Raman Spectroscopy Probes. *J. Phys. Chem. Lett.* **2019**, *10*, 1669−1675.
(39) Opilik, L.; Dogan, Ü.; Li, C. Y.; Stephanidis, B.; Li, J. F.; Zenobi, R. Chemical Production of Thin Protective Coatings on Optical Nanotips for Tip-Enhanced Raman Spectroscopy. *J. Phys. Chem. C* **2016**, *120*, 20828−20832.
(40) Kumar, N.; Stephanidis, B.; Zenobi, R.; Wain, A. J.; Roy, D. Nanoscale Mapping of Catalytic Activity Using Tip-Enhanced Raman Spectroscopy. *Nanoscale* **2015**, *7*, 7133−7137.
(41) Barrios, C. A.; Malkovskiy, A. V.; Kisliuk, A. M.; Sokolov, A. P.; Foster, M. D. Highly Stable, Protected Plasmonic Nanostructures for Tip Enhanced Raman Spectroscopy. *J. Phys. Chem. C* **2009**, *113*, 8158−8161.
(42) Wondergem, C. S.; van Swieten, T. P.; Geitenbeek, R. G.; Erné, B. H.; Weckhuysen, B. M. Extending Surface-Enhanced Raman Spectroscopy to Liquids Using Shell-Isolated Plasmonic Superstructures. *Chem. - Eur. J.* **2019**, *25*, 15772−15778.
(43) Luss, D. Temperature Rise of Catalytic Supported Crystallites. *Chem. Eng. J.* **1970**, *1*, 311−317.
(44) Cale, T. S. Nickel Crystallite Thermometry during Ethane Hydrogenolysis. *J. Catal.* **1984**, *90*, 40−48.
(45) Koptyug, I. V.; Khomichev, A. V.; Lysova, A. A.; Sagdeev, R. Z. Spatially Resolved NMR Thermometry of an Operating Fixed-Bed Catalytic Reactor. *J. Am. Chem. Soc.* **2008**, *130*, 10452−10453.
(46) Kimmerle, B.; Grunwaldt, J. D.; Baiker, A.; Glatzel, P.; Boye, P.; Stephan, S.; Schroer, C. G. Visualizing a Catalyst at Work during the Ignition of the Catalytic Partial Oxidation of Methane. *J. Phys. Chem. C* **2009**, *113*, 3037−3040.
(47) Simeone, M.; Salemme, L.; Allouis, C.; Volpicelli, G. Temperature Profile in a Reverse Flow Reactor for Catalytic Partial Oxidation of Methane by Fast IR Imaging. *AIChE J.* **2008**, *54*, 2689−2698.
(48) Yarulina, I.; Kapteijn, F.; Gascon, J. The Importance of Heat Effects in the Methanol to Hydrocarbons Reaction over ZSM-5: On the Role of Mesoporosity on Catalyst Performance. *Catal. Sci. Technol.* **2016**, *6*, 5320−5325.
(49) Yakunin, S.; Benin, B. M.; Shynkarenko, Y.; Nazarenko, O.; Bodnarchuk, M. I.; Dirin, D. N.; Hofer, C.; Cattaneo, S.; Kovalenko, M. V. High-Resolution Remote Thermometry and Thermography Using Luminescent Low-Dimensional Tin-Halide Perovskites. *Nat. Mater.* **2019**, *18*, 846−852.
(50) Brites, C. D. S.; Balabhadra, S.; Carlos, L. D. Lanthanide-Based Thermometers: At the Cutting-Edge of Luminescence Thermometry. *Adv. Opt. Mater.* **2019**, *7*, 1801239.
(51) Jaque, D.; Vetrone, F. Luminescence Nanothermometry. *Nanoscale* **2012**, *4*, 4301−4326.

https://dx.doi.org/10.1021/acsnano.9b09834
ACS Nano 2020, 14, 3725−3735

(52) Dieke, G. H. *Spectra and Energy Levels of Rare Earth Ions in Crystals*; Wiley: New York, 2008.
(53) Geitenbeek, R. G.; Prins, P. T.; Albrecht, W.; van Blaaderen, A.; Weckhuysen, B. M.; Meijerink, A. $NaYF_4$:Er^{3+}, Yb^{3+}/SiO_2 Core/Shell Upconverting Nanocrystals for Luminescence Thermometry up to 900 K. *J. Phys. Chem. C* **2017**, *121*, 3503−3510.
(54) Blasse, G.; Grabmaier, B. *Luminescent Materials*; Springer: Berlin, 1994.
(55) Auzel, F. Upconversion and Anti-Stokes Processes with f and d Ions in Solids. *Chem. Rev.* **2004**, *104*, 139−173.
(56) Li, X.; Zou, Q.; Li, W.; Chen, H. Investigation on Anti-Autofluorescence, Osteogenesis and Long-Term Tracking of HA-Based Upconversion Material. *Sci. Rep.* **2018**, *8*, 11267.
(57) Geitenbeek, R. G.; Nieuwelink, A.; Jacobs, T. S.; Salzmann, B. B. V; Goetze, J.; Meijerink, A.; Weckhuysen, B. M. In Situ Luminescence Thermometry To Locally Measure Temperature Gradients during Catalytic Reactions. *ACS Catal.* **2018**, *8*, 2397−2401.
(58) Vetrone, F.; Naccache, R.; Zamarrón, A.; Juarranz de la Fuente, A.; Sanz-Rodríguez, F.; Martinez Maestro, L.; Martín Rodriguez, E.; Jaque, D.; García Solé, J.; Capobianco, J. A. Temperature Sensing Using Fluorescent Nanothermometers. *ACS Nano* **2010**, *4*, 3254−3258.
(59) Geitenbeek, R. G.; Vollenbroek, J. C.; Weijgertze, H. M. H.; Tregouet, C. B. M.; Nieuwelink, A. E.; Kennedy, C. L.; Weckhuysen, B. M.; Lohse, D.; van Blaaderen, A.; van den Berg, A.; et al. Luminescence Thermometry for: In Situ Temperature Measurements in Microfluidic Devices. *Lab Chip* **2019**, *19*, 1236−1246.
(60) van Ravenhorst, I. K.; Geitenbeek, R. G.; van der Eerden, M. J.; van Omme, T. J.; Peréz Garza, H. H.; Meirer, F.; Meijerink, A.; Weckhuysen, B. M. In Situ Local Temperature Mapping in Microscopy Nano-Reactors with Luminescence Thermometry. *ChemCatChem* **2019**, *11*, 5505−5512.
(61) Hartman, T.; Geitenbeek, R. G.; Whiting, G. T.; Weckhuysen, B. M. Operando Monitoring of Temperature and Active Species at the Single Catalyst Particle Level. *Nat. Catal.* **2019**, *2*, 986−996.
(62) Geitenbeek, R. G.; Salzmann, B. B. V.; Nieuwelink, A. E.; Meijerink, A.; Weckhuysen, B. M. Chemically and Thermally Stable Lanthanide-Doped Y_2O_3 Nanoparticles for Remote Temperature Sensing in Catalytic Environments. *Chem. Eng. Sci.* **2019**, *198*, 235−240.
(63) Whitney, A. V.; Elam, J. W.; Stair, P. C.; Van Duyne, R. P. Toward a Thermally Robust Operando Surface-Enhanced Raman Spectroscopy Substrate. *J. Phys. Chem. C* **2007**, *111*, 16827−16832.
(64) Cunniff, C. Z.; Specht, S. E.; Love, A. M.; Uchupalanun, P.; Venegas, J. M.; Kruszynski, C. E.; Hermans, I. Investigation of Supported Metal Oxide Species with Shell-Isolated Nanoparticle-Enhanced Raman Spectroscopy. *J. Phys. Chem. C* **2019**, *123*, 25220−25227.
(65) Albrecht, W.; van der Hoeven, J. E. S.; Deng, T.-S.; de Jongh, P. E.; van Blaaderen, A. Fully Alloyed Metal Nanorods with Highly Tunable Properties. *Nanoscale* **2017**, *9*, 2845−2851.
(66) Campbell, C. T. Electronic Perturbations. *Nat. Chem.* **2012**, *4*, 597−598.
(67) Homann, C.; Krukewitt, L.; Frenzel, F.; Grauel, B.; Würth, C.; Resch-Genger, U.; Haase, M. $NaYF_4$:Yb, Er/$NaYF_4$ Core/Shell Nanocrystals with High Upconversion Luminescence Quantum Yield. *Angew. Chem., Int. Ed.* **2018**, *57*, 8765−8769.
(68) Espinat, D.; Dexpert, H.; Freund, E.; Martino, G.; Couzi, M.; Lespade, P.; Cruege, F. Characterization of the Coke Formed on Reforming Catalysts by Laser Raman Spectroscopy. *Appl. Catal.* **1985**, *16*, 343−354.
(69) Li, X.; Liu, M.; Lee, J.; Ding, D.; Bottomley, L. A.; Park, S.; Liu, M. An Operando Surface Enhanced Raman Spectroscopy (SERS) Study of Carbon Deposition on SOFC Anodes. *Phys. Chem. Chem. Phys.* **2015**, *17*, 21112−21119.
(70) Goodson, K. E.; Asheghi, M. Near-Field Optical Thermometry. *Microscale Thermophys. Eng.* **1997**, *1*, 225−235.
(71) Sadat, S.; Tan, A.; Chua, Y. J.; Reddy, P. Nanoscale Thermometry Using Point Contact Thermocouples. *Nano Lett.* **2010**, *10*, 2613−2617.
(72) Pan, Y.; Su, H.-Q.; Zhou, E.-L.; Yin, H.-Z.; Shao, K.-Z.; Su, Z.-M. A Stable Mixed Lanthanide Metal-Organic Framework for Highly Sensitive Thermometry. *Dalt. Trans.* **2019**, *48*, 3723−3729.
(73) Rieth, A. J.; Wright, A. M.; Dincă, M. Kinetic Stability of Metal-Organic Frameworks for Corrosive and Coordinating Gas Capture. *Nat. Rev. Mater.* **2019**, *4*, 708−725.

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