

Emerging techniques to monitor temperature and supply heat for multiscale solid-based catalysis processes[☆]

Mingbin Gao¹, Mao Ye¹ and Zhongmin Liu^{1,2}



To the achievement of carbon neutrality and sustainable chemical industries, optimization and reformation of energy (heat) management for catalyst design and catalysis process developments play a key role. This review examines the underlying mechanism of fundamental solid-based catalysis, for example, structure of active sites, chemical kinetics, and molecular transport, affected by temperature. *In situ/operando* multiscale thermometry aimed to the temperature-monitoring of local active sites, catalyst body, or reactor is overviewed. Toward precise heat supply for active sites, the examples of state-of-the-art heating techniques for solid catalysts are analyzed in detail. Through recent examples, we illustrate that innovative heating techniques combined with online spatiotemporal-resolved thermometry may initiate transformative industrial catalytic processes.

Addresses

¹National Engineering Research Center of Lower-Carbon Catalysis Technology, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, People's Republic of China

²University of Chinese Academy of Sciences, Beijing 10049, People's Republic of China

Corresponding author: Ye, Mao (maoye@dicp.ac.cn)

Current Opinion in Chemical Engineering 2023, 42:100969

This review comes from a themed issue on **Mesoscales in chemical engineering**

Edited by **Ning Yang, Mao Ye, and Liang-Yin Chu**

For complete overview of the section, please refer to the article collection, "[Mesoscales in chemical engineering \(2023\)](#)"

Available online 3 October 2023

<https://doi.org/10.1016/j.coche.2023.100969>

2211–3398/© 2023 Elsevier Ltd. All rights reserved.

Introduction

The fabrication of more than 85% of readily available energy, in the form of liquid fuel, and versatile multi-functional materials, in the form of plastics, in modern

society involves solid materials as heterogeneous catalysts [1,2]. The exploitation of solid catalysts is of crucial importance to the revolution of conventional petrochemical, coal, and biomass industries to carbon neutrality and sustainable society. Heat as a universal form of energy supply is of great importance to temperature-controlled catalytic efficiency (yield of products and kinetics), process economy (energy costs), and production safety (easy to control) during solid-based catalysis [3–5].

The thermodynamic equilibrium of chemical reaction can be represented by the laws of $K^{eq} = \exp(-\Delta G_r/RT)$, which involves the Gibbs free energy of chemical reaction and temperature, and can determine the primary product distributions. The essential role of the catalyst is to lowering the activation energy to enable chemical reaction rate. For most typical reactions, the reaction kinetic constant can be related to temperature exponentially by the Arrhenius equation $k = A \exp(E_a/RT)$ within a certain temperature range, where E_a is the activation energy. In addition, the geometric of active sites, for example, metal clusters/nanoparticles (NPs) [6] and proton acid [7], is found to be sensitive to temperature. In this sense, temperature plays a crucial role in the selectivity, reactivity, and stability of catalytic systems. However, prevailing techniques of temperature measurement for catalytic systems are mainly aimed at the scale of bulk catalysts and phases [3,8]. This calls urgent development on thermometry with high spatial- and temporal resolution that can read out local temperature at the active sites and desired spot of catalyst body under operating conditions. With local operating temperature in hand, the elusive interplay between reaction kinetics/catalyst deactivation and real temperature at different local active sites can be profoundly understood toward rational design of solid catalysts [3,5]. Based on the relationship between temperature and optimized catalytic behavior at the local active site, how to control heat supply and temperature precisely at the desired region is vitally important for the development of catalysis process and reactor engineering. Indeed, it aims at the development of protocols where the energy (heat) required for a given process to occur can be provided directly at the region of catalyst where it is needed [9–11].

[☆] Given the role as Guest Editor, Mao Ye had no involvement in the peer review of the article and has no access to information regarding its peer-review. Full responsibility for the editorial process of this article was delegated to Ning Yang.

To this end, this review briefly first summarizes the potential and prominent effect of temperature on the fundamental catalysis process. Then, we overview the development on thermometry toward spatial- and temporal-resolved at the multiscale from local active sites, desired catalyst region to the catalyst bed. The state-of-the-art heating modes that can provide heat to active sites pointedly and efficiently are introduced. The novelty of this review is the systematic summary of potential thermometry suitable for spatially and/or temporally monitoring temperature variations from active sites, individual catalysts to reactor. And the systematic introduction of novel heating techniques suitable for solid catalysis that can speed up achieving net-zero emission energy future. Besides, a brief outline of current problems and challenges was given to determine the direction for subsequent research.

The typical effect of temperature on solid-based catalysis process

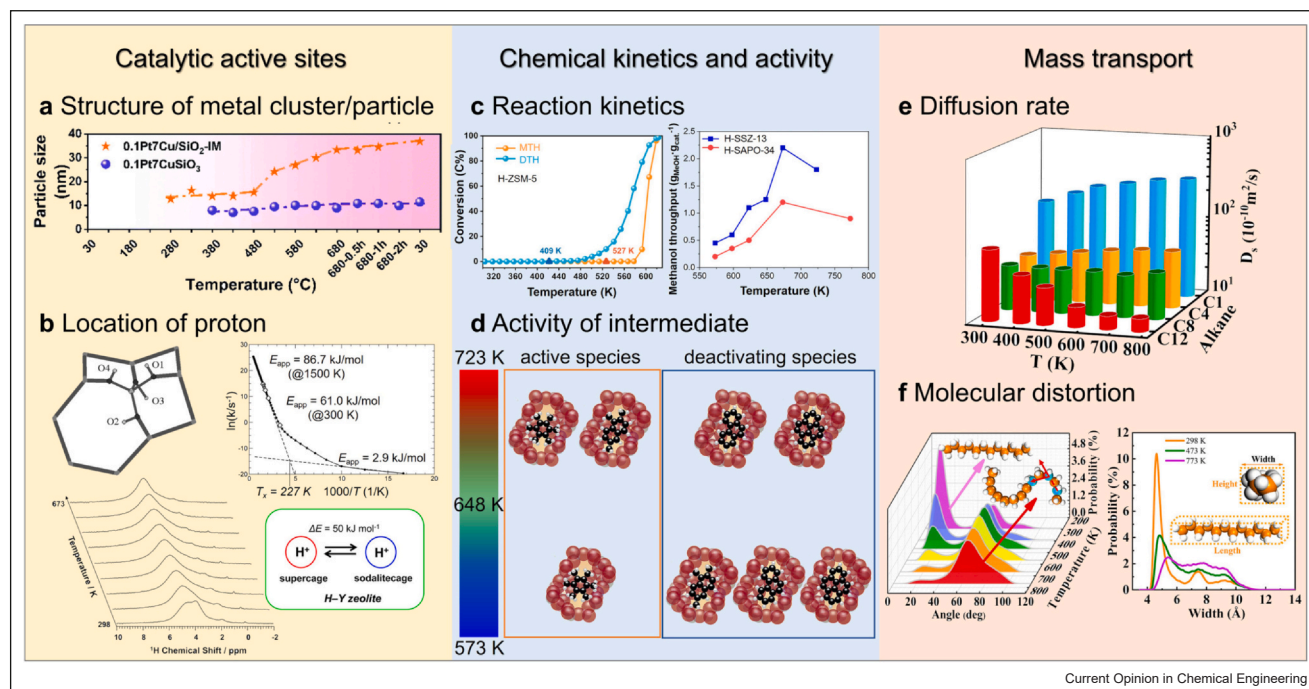
Figure 1 summarizes the most common fundamental aspect in catalysis determined by temperature, that is, structure of active sites, reaction kinetics, and molecular mass transport.

Supported-metal/metal alloy single-atom, clusters, and NP catalysts have been widely used in hydrogenation,

dehydrogenation, hydroisomerization, oxidation reactions, and so on [12,13]. However, metal particles suffer from severe sintering at elevated temperature, which makes the structure of metal-active sites and stability of such catalysts highly sensitive to temperature [6,14] (Figure 1a). Proton acid sites are other widely used catalysts in industry, for example, catalytic cracking of oil [15] and methanol-to-olefins [16,17]. In Figure 1b, Frisch [18] and Bada [7] et al. found that elevating temperature can facilitate the mobility of proton between adjacent sites, and such location of the proton has a crucial role in catalytic performance [19]. In brief, temperature has a crucial effect on the structure of metal particles and the location of proton in the catalyst framework, which can determine the intrinsic activity of active sites.

Temperature, a direct indicator of the kinetic energy and collisional frequency of reacting molecules [3], determines the kinetics of chemical reactions. However, due to the diverse response of reaction intermedia to temperature, the nonmonotonic relation between temperature and catalyst performance is shown [20–23]. For instance, for the methanol-to-hydrocarbon (MTH) reactions, low reaction temperature (below 573 K) cannot sufficiently accelerate the formation of hydrocarbon pool species (HCPs) to launch the autocatalysis characteristic

Figure 1



The effect of reaction temperature on (a) structure/(b) location of catalytic active sites, (c) chemical kinetics/(d) activity and (e and f) molecular mass transport.

Some elements or data in the figure are obtained from Ref. [6,7,18,20,28,29].

of MTH reactions [20], which shows low conversion of methanol and short lifetime. At the range of 573–673 K, increasing the reaction temperature can prolong the catalyst lifetime due to the sufficient activation of HCPs and growing species type of HCPs [21,22,24]. However, when temperature is above 673 K, the dominant role of deactivation kinetics at excessive temperature is revealed and leads to fast coke deactivation. For the hydrogenation of CO, the temperature can significantly affect the reaction intermedia on metal catalysts [5]. In this sense, the elusive relation between temperature and catalyst performance due to the complied reaction behavior of intermedia or variation in active sites needs to be further elucidated.

Molecular transportation is usually positively correlated with temperature due to thermal motion [25]. For most molecules, the diffusion rate can be empirically related to temperature by the Arrhenius equation [26]. Increased temperature is considered to provide kinetic energy for the molecule to cross diffusion energy barriers [27]. However, Zheng et al. [28] found that under higher temperature, molecules with long chain are inclined to distortion and such molecular deformation can significantly impede diffusion rate in the confinement of

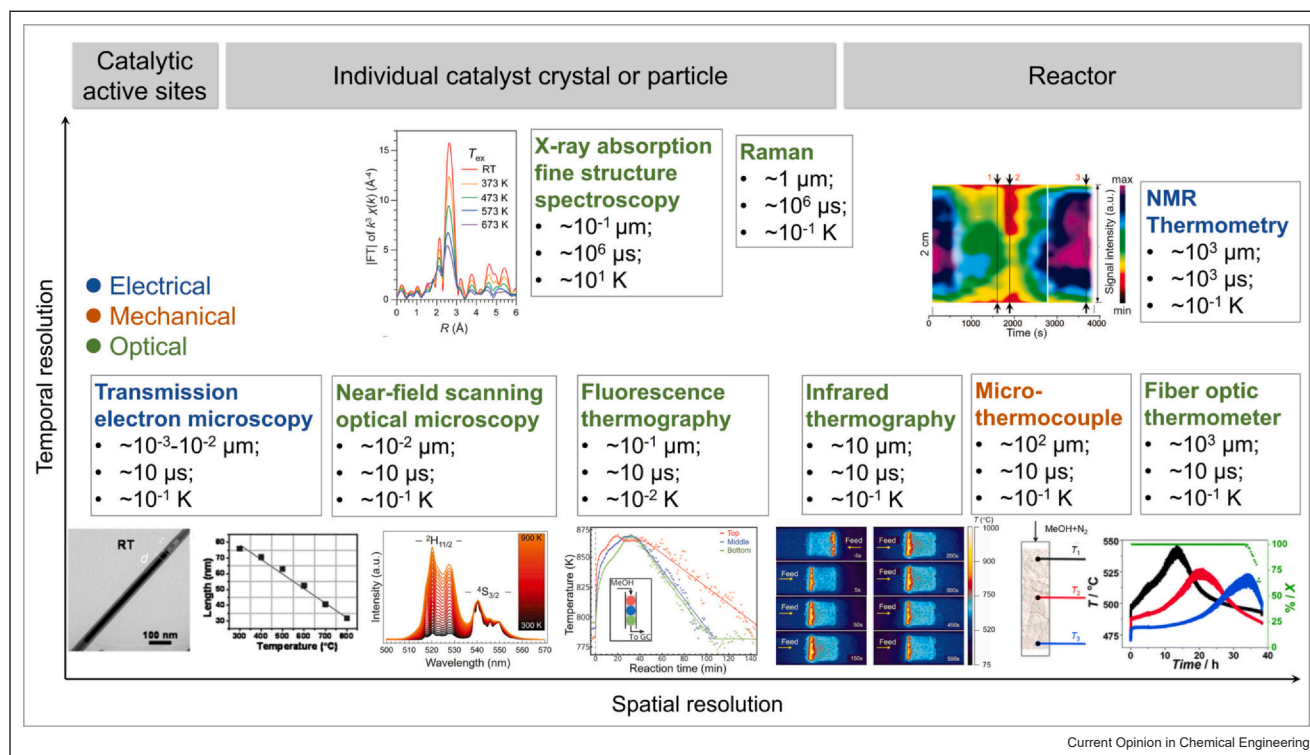
zeolite framework. Therefore, understanding an anomalous mechanism of molecular transport under high temperature or reaction temperature is highly desired.

To better understand the effect of temperature on catalysis, the reaction kinetics and molecular diffusion need to be considered simultaneously. However, under high temperature, differentiating the contribution of reaction and diffusion to catalyst performance remains a big challenge.

Advanced characterizations for temperature-monitoring

Figure 2 represents the representative thermometry for the multiscale catalysis process. At the scale of the catalyst bed, thermocouples with high accuracy are easy to fabricate and replace, which are the most commonly applied method of temperature-monitoring for bulk catalyst bed. Yarulina et al. [23] employed multiple thermocouples to monitor the temperatures at different axial positions inside the catalyst bed during MTH reactions. With the implementation of multiple thermocouples, the temporal evolutions of temperature at the specific position and the position of the hotspot in the catalyst bed can be detected. In addition, they found

Figure 2



Representative and potential thermometry suitable for *in situ/operando* monitoring temperature variations during multiscale catalysis process from active sites, individual catalyst to reactor.

Some elements in the figure are obtained from Ref. [5,23,31,32,35,39,41].

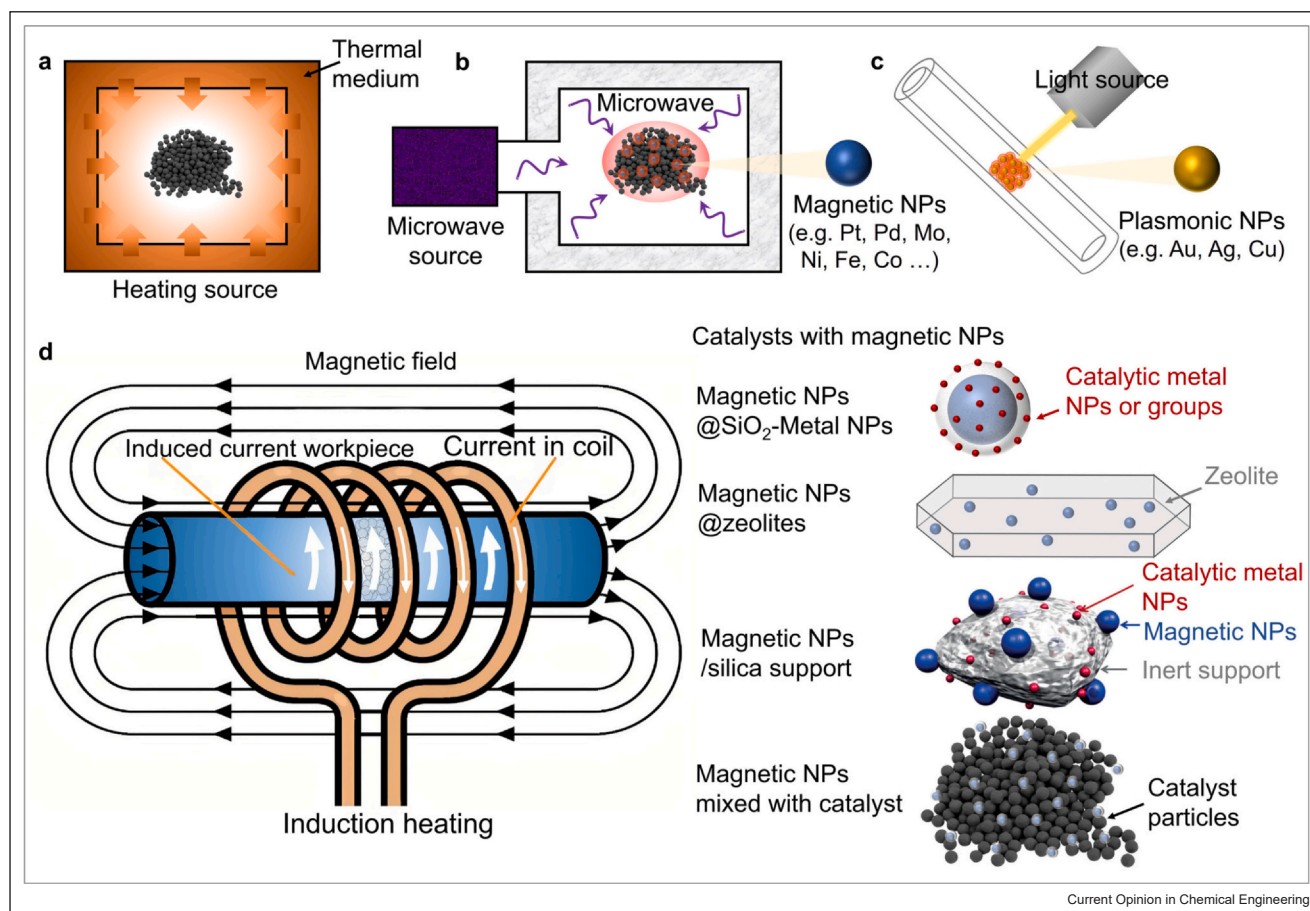
that when the reaction temperature is above 773 K, a lower temperature rise in the catalyst bed contributes to extended catalyst lifetime. Fiber-optic thermometer is an alternative noninvasive thermometry compared with the intrusive thermocouple [30]. However, the reactor is required to permit the transmission of light at the interested region to measure the internal temperature of the catalyst bed for fiber-optic thermometer. Nuclear magnetic resonance (NMR) thermometry can non-invasively detect one-dimensional signal of the axial direction of reactor, and changes in NMR signal can be related to temperature variations. Koptuyug et al. [31] correlated the ^{27}Al NMR signal intensity and temperature during the hydration of propylene over Pd/ $\gamma\text{-Al}_2\text{O}_3$ catalyst, and they obtained the temporal variations in temperature along the reactor axial direction. However, the changes in NMR signal can be related to various factors, for example, catalyst structure, humidity, and so on, thus, the feasibility of NMR thermometry to catalysis is still to be proven and developed. Limited to the low spatial resolution and layout mode of thermocouple and fiber-optic thermometer (\sim millimeter scale), infrared (IR) thermography can provide 2D thermal imaging within the catalyst bed during catalysis. Simeone et al. [32] used fast IR thermography to visualize the 2D temperature distribution of fixed bed reactor during catalytic partial oxidation of methane over Rh/ Al_2O_3 catalyst, and investigate the effect of internal heat recovery on reactor performance and catalyst thermal stress.

Obtaining spatiotemporal-resolved temperature distribution within individual catalyst body is of great concern to the understanding of the heterogeneities of kinetics and deactivation in catalyst [33]. At present, some available techniques can monitor temperature variations at the local region or external surface of individual catalyst particle during catalysis. Tsukahara et al. [30] used the intensity ratio of Stokes and anti-Stokes lines and by *in situ* Raman scattering measurements to detect the temperature around the external surface of Co NP catalyst (region: 10–20 μm). They found that compared with the measured results of bulk catalyst, the temperature at the local–external surface of Co NPs under the effect of microwave (MW) shows the occurrence of abnormally high temperatures than bulk temperature. Such observation verified the effect of ‘nonequilibrium local heating’ and demonstrated the enhancement in reaction rate over metal NPs under MW irradiation. Hu et al. [34] present a method capable of measuring the surface temperature of plasmonic nanostructures (e.g. Au NPs) decorated by phenyl isocyanide (PIC) molecule with surface-enhanced Raman spectroscopy. The stretching vibration of PIC is directly dependent on temperature, which can be reflected on the changes of the Raman shift. Wada et al. [35] implemented *in situ*-extended X-ray absorption fine

structure (EXAFS) to study the response of local temperature at Pt NPs to MW irradiation affected by the supported matrix. According to the finding that Debye–Waller factor of EXAFS spectra (Au NPs) is sensitive to temperature [36], they used Debye–Waller factor as an indicator to temperature of Pt NPs. In addition, the signals in Debye–Waller factor can only be related to variation of metal NPs by adjusting energy of X-ray, thus the measured temperature can be focused on metal NPs. They found the difference in the average temperatures between Pt NPs and the bulk under MWs reaches +26 K and +132 K for Pt/ Al_2O_3 and Pt/ SiO_2 , respectively. And they speculated lower thermal conductivity of the SiO_2 support may hinder the heat transfer from Pt NPs to the supported matrix. Luminescence thermometry exploits the relationship between temperature and luminescence properties to achieve thermal sensing from the spatial and spectral analysis of the light generated from the object to be thermally imaged [37]. There are six parameters that define the luminescence emission of a given material: intensity, band shape, spectral position, polarization, lifetime, and bandwidth [37], which can be applied as a temperature indicator depending on specific luminescence materials. The fruitful application cases of luminescence thermometry implemented by different subclass principles in the field of micro-/nanoelectronics, integrated photonics, and biomedicine is well-summarized in other reviews [37,38]. To measure temperature with sufficient spatial resolution and at elevated temperatures, luminescent NPs with excellent thermostability need to be developed for the application to catalysis. Weckhuysen et al. [8] developed thermostable $\text{NaY}_{0.8}\text{Yb}_{0.18}\text{Er}_{0.02}\text{F}_4/\text{SiO}_2$ core/shell ($\text{NaYF}_4@\text{SiO}_2$) up to 900 K and correlated the integrated intensity ratio of the $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ peak of $\text{NaYF}_4@\text{SiO}_2$ excited by 980-nm laser and temperature. And they implemented $\text{NaYF}_4@\text{SiO}_2$ NPs physically mixed with catalyst or attached to the external surface of catalyst particle as nanosensor to indicate the temperature variations during MTH [39] and syngas to hydrocarbons reactions [5], respectively. They found that the difference between temperature of the local–external catalyst surface and set temperature of the reactor can be up to +85 K for MTH or +40 K for syngas to hydrocarbons, respectively. Similarly, the ratio of integrated emission intensities of the $^5\text{D}_1$ and $^5\text{D}_0$ states of europium oxychloride (EuOCl) excited by 375-nm laser can be related to temperature [40]. They applied EuOCl as both solid catalyst for methane oxychlorination reaction and luminescence thermometer to *operando* determine the temperature of local EuOCl catalyst in fixed reactor.

At the nanoscale, for instance, when temperature is above 773 K, the linear expansion of liquid Au(Si) is related to the temperature observed by high-resolution transmission electron microscopy [41]. Thus, Au(Si)- β

Figure 3



(a) Conventional and the state-of-the-art (b) MW with metal NPs, (c) photo with plasmonic NPs, and (d) electromagnetic induction with magnetic NP heating techniques for solid-based catalysis process. Some elements in the figure are obtained from Ref. [54].

Ga₂O₃ nanocable can show the temperature changes at the nanoscale. However, thermometry with sufficient spatial resolution that can reach the scale of the catalytic active site (~subnanometer to nanometer) during catalysis needs to be further exploited.

In the future, the thermometry for individual catalyst is expected to present a complete temperature distribution within a catalyst with high spatial and temporal resolutions. The thermometry for the reactor is required to be suitable for various catalysis occasions, such as magnetic and electric fields.

The state-of-the-art heat supply techniques

In Figure 3a, for conventional heating (CH), the heat source (e.g. Joule heat generated by electricity) is transferred to the solid catalysts from the outside wall/thermal medium by heat conduction and convection. Rostrup-Nielsen et al. [42] estimated that only about 50% of the external heating provided to reformer

reactors is used for running the catalytic process. Such route often results in slow start-up times due to the high heat capacity of the system and high energy losses. In addition, the catalyst performance is often limited by heat transfer efficiency rather than to the intrinsic catalyst activity [11].

MW energy can directly and selectively supply heat to metal NPs (e.g. Pt [35], Mo [43], Ni [44], Fe [44,45], and Co [30]) as catalysts, which results in focused heating of the metal NPs. Some examples of MW-assisted heterogeneous catalysis include steam or dry reforming of methane, pyrolysis of biomass and petroleum oil, the regeneration of zeolites, and dehydrogenation reaction as summarized by Meloni et al. [10]. Compared with the efficiency of CH, MW heating affords shorter time to targeted temperature and significantly decreases the energy lost. Importantly, it has been widely verified that solid-based catalytic reactions can be accelerated by MW heating. Jie et al. [44,45] reported that the selective and

local heating of the Fe or Ni NPs by MW heating enhances the dehydrogenation reaction of fuel and hinders the unexpected side reactions of CO₂ formation due to the suppression of thermal cracking in gas atmosphere [46]. MW-promoted catalytic dehydrogenation of fossil hydrocarbon fuels greatly yields carbon-free hydrogen production. Because of the strong interaction between the electron of metal NPs and MW, some researchers demonstrated that, for instance, at the same conversion of ammonia decomposition, the required reaction temperature by MW heating (~673 K) is significantly lower than that by CH route (~873 K) [43]. However, the large-scale industrial applications of MW-assisted catalysis are still challenging. The four main key issues must be addressed: unclear interaction between MW and components, lacking thermometry in the MW field, heterogeneous heating by MW, and difficult control of energy distribution [9].

Plasmonic metal NPs (e.g. Au, Ag, and Cu) constitute a class of materials that interact strongly with light via localized surface plasmon resonance (LSPR) excitation [47]. It has been widely verified that substantial enhancements in the rates of chemical reactions on illuminated plasmonic NP catalysts compared with the corresponding systems in the absence of illumination. Two underlying mechanisms are proposed to explain such enhancement in reactivity, one assumes a local plasmon-induced hot charge-carrier-mediated activation of the reactants, while the other assumes an LSPR-induced local heating of the catalyst. The energy absorbed by NPs from light can be transferred to thermal energy to heat NPs, for instance, the difference between bulk temperature and local temperature of Ni@p-SiO₂ NPs under visible light illumination can reach up to +250 K [48]. Such high-temperature rise by light illumination is contributed by the thermal insulation of outer-nanoshell SiO₂. Linic et al. [47] demonstrated that for dense and high loading of Ag NPs in support, the dominant mechanism for the enhancement in reaction rate over plasmonic NPs is the local heating of catalyst, which resulted from the NPs that mutually heat each other due to the close proximity between NPs. This finding was supported by the well-designed annular reactor with thermocouples. With the implementation of plasmonic metal NPs, photothermal catalysis- absorbed energy from solar light and heat, as a promising technology, can dramatically enhance the catalytic activity and potentially revolute current thermal catalytic process [49]. However, the insufficient exposure of catalysts to light limits the large-scale applications of LSPR-induced heating.

The electromagnetic induction heating (EIH) of magnetic NPs exposed to a varying magnetic field produced

by an alternating current generator (Figure 3d) has been preliminarily exploited for solid-based catalysis. The heat can be originated by induction directly on the catalyst with magnetic NPs without the need to cross the whole reactor. To decorate magnetic NPs with catalytic active sites, Kirschning et al. [50–52] employed surface engineering via exohedral chemical functionalization and/or metal NP decoration to decorate catalytic active sites on silica layer of magnetic NP–silica core–shell. For instance, the Au⁰ and Pd⁰ NPs decorated on the outer SiO₂ layer, which encapsulates Fe₂O₃/Fe₃O₄ NPs, are implemented to the oxidation of allylic/benzylic alcohols [52] and Suzuki–Miyaura/Heck cross-coupling reactions [50,51], respectively. This can expand reactions that cannot be achieved by magnetic NPs through the grafting of catalytic sites on the SiO₂ layer. Deng et al. [53] used H-ZSM-5 as catalytic carrier to encapsulate magnetic NPs (NiFe₂O₄@TiO₂), which achieves the citronellal isomerization reaction heated by EIH through NiFe₂O₄@TiO₂ as a magnetically susceptible medium. Bordet et al. [54] developed iron carbide NPs with exceptional heating properties and coloaded them with catalytic metals (Ni and Ru) on silica alumina powder (SiRALox) support to improve the catalytic efficiency of CO₂ hydrogenation. For a simple situation, magnetic NPs can be physically mixed with catalyst particles in a reactor to achieve catalysis process by EIH [51]. The safe and simplified scale-up of EIH can be expected, however, the combination of magnetic susceptors featuring high hyperthermic efficiency with catalytic sites is a research area in its infancy [11].

Conclusions and perspectives

Temperature is of crucial significance to solid-based catalyst performance from the perspective of the structure of active sites, chemical kinetics and activity, and molecular transport. A profound understanding of the catalytic mechanism affected by temperature relies on sufficiently spatial/temporal-resolved and accurate thermometry. Obtaining spatiotemporal heterogeneity of temperature within individual catalyst body is the key to bridge the correlation of catalytic performance between active sites and macroscopic catalyst bed for temperature-controlled catalysis processes. However, such knowledge is hampered by the lacking of *in situ/operando* thermometry with microimaging function. Developing heating protocols with quick response, high efficiency, selectivity, and safe operation that can provide heat directly to catalytic active sites is of great importance to reform conventional industrial catalysis. The implementation of emerging MW, photo-, or/and EIH techniques not only facilitates the precise control of temperature at active sites but also provides new routes for solid-based catalysis, for example, photothermal catalysis. Toward carbon neutrality and

sustainable chemical industries, reformation of conventional industrial catalysis needs the consideration of heat transfer in catalyst design and the development of online monitoring-supplying heat to specific active sites.

Data Availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors thank the financial support from the National Natural Science Foundation of China, China (Grant No. 91834302, 21991093, and 22208337) and the Strategic Priority Research Program of the Chinese Academy of Sciences, China (Grant No. XDA21030200).

References and recommended reading

Papers of particular interest, published within the period of review, have been highlighted as:

- of special interest
- of outstanding interest.

1. Vogt C, Weckhuysen BM: **The concept of active site in heterogeneous catalysis.** *Nat Rev Chem* 2022, **6**:89-111, <https://doi.org/10.1038/s41570-021-00340-y>
2. Li Y, Yu J: **Emerging applications of zeolites in catalysis, separation and host-guest assembly.** *Nat Rev Mater* 2021, **6**:1156-1174, <https://doi.org/10.1038/s41578-021-00347-3>
3. Hartman T, Geitenbeek RG, Wondergem CS, van der Stam W, Weckhuysen BM: **Operando nanoscale sensors in catalysis: all eyes on catalyst particles.** *ACS Nano* 2020, **14**:3725-3735, <https://doi.org/10.1021/acsnano.9b09834>
- This review comprehensively overviews how to combine nano-sensors with the state-of-the-art spectroscopy technique to detect chemical species and temperature at the local active sites during catalysis.
4. Palma V, Ruocco C, Martino M, Barba D, Meloni E: **Chapter 14 - General catalyst-related issues.** In *Current Trends and Future Developments on (Bio-) Membranes*. Edited by Figoli A, Li Y, Basile A. Elsevier; 2020:303-324, <https://doi.org/10.1016/B978-0-12-816778-6.00014-X>
5. Hartman T, Geitenbeek RG, Whiting GT, Weckhuysen BM: **Operando monitoring of temperature and active species at the single catalyst particle level.** *Nat Catal* 2019, **2**:986-996, <https://doi.org/10.1038/s41929-019-0352-1>
- This work shows how to measure local external surface of solid catalyst during syngas to hydrocarbons reactions by the luminescence thermometry.
6. Liu X, Wang X, Zhen S, Sun G, Pei C, Zhao Z-J, Gong J: **Support stabilized PtCu single-atom alloys for propane dehydrogenation.** *Chem Sci* 2022, **13**:9537-9543, <https://doi.org/10.1039/D2SC03723H>
7. Asakawa N, Motokura K, Yashima T, Koyama T-r, O-nuki T, Miyajji A, Baba T: **Proton exchange reaction between hydroxyl groups in the supercage and those in the sodalitecage of Y zeolite as studied by variable temperature 1H MAS NMR.** *J Phys Chem C* 2012, **116**:17734-17738, <https://doi.org/10.1021/jp306004x>
8. Geitenbeek RG, Prins PT, Albrecht W, van Blaaderen A, Weckhuysen BM, Meijerink A: **NaYF4:Er3+,Yb3+/SiO2 core/shell upconverting nanocrystals for luminescence thermometry up to 900 K.** *J Phys Chem C* 2017, **121**:3503-3510, <https://doi.org/10.1021/acs.jpcc.6b10279>
9. Liu K, Zhao Z, Li H, Gao X: **Microwave-induced vapor-liquid mass transfer separation technology — full of breakthrough opportunities in electrified chemical processes.** *Curr Opin Chem Eng* 2023, **39**:100890, <https://doi.org/10.1016/j.coche.2022.100890>
10. Meloni E, Martino M, Palma V: **Microwave assisted steam reforming in a high efficiency catalytic reactor.** *Renew Energy* 2022, **197**:893-901, <https://doi.org/10.1016/j.renene.2022.07.157>
11. Wang W, Tuci G, Duong-Viet C, Liu Y, Rossin A, Luconi L, Nhut J-M, Nguyen-Dinh L, Pham-Huu C, et al.: **Induction heating: an enabling technology for the heat management in catalytic processes.** *ACS Catal* 2019, **9**:7921-7935, <https://doi.org/10.1021/acscatal.9b02471>
- This review discuss how to introduce EIH techniques to solid-based catalysis.
12. Liu L, Corma A: **Confining isolated atoms and clusters in crystalline porous materials for catalysis.** *Nat Rev Mater* 2021, **6**:244-263, <https://doi.org/10.1038/s41578-020-00250-3>
13. Sun Q, Wang N, Yu J: **Advances in catalytic applications of zeolite-supported metal catalysts.** *Adv Mater* 2021, **33**:2104442, <https://doi.org/10.1002/adma.202104442>
14. Aitbekova A, Zhou C, Stone ML, Lezama-Pacheco JS, Yang A-C, Hoffman AS, Goodman ED, Huber P, Stebbins JF, et al.: **Templated encapsulation of platinum-based catalysts promotes high-temperature stability to 1,100 °C.** *Nat Mater* 2022, **21**:1290-1297, <https://doi.org/10.1038/s41563-022-01376-1>
15. Vogt ETC, Weckhuysen BM: **Fluid catalytic cracking: recent developments on the grand old lady of zeolite catalysis.** *Chem Soc Rev* 2015, **44**:7342-7370, <https://doi.org/10.1039/C5CS00376H>
16. Ye M, Li H, Zhao Y, Zhang T, Liu Z: **MTO processes development: the key of mesoscale studies.** *Adv Chem Eng* 2015, **47**:279-335, <https://doi.org/10.1016/bs.ache.2015.10.008>
17. Yarulina I, Chowdhury AD, Meirer F, Weckhuysen BM, Gascon J: **Recent trends and fundamental insights in the methanol-to-hydrocarbons process.** *Nat Catal* 2018, **1**:398-411, <https://doi.org/10.1038/s41929-018-0078-5>
18. Viswanathan U, Fermann JT, Toy LK, Auerbach SM, Vreven T, Frisch MJ: **Modeling proton jumps in HY zeolite: effects of acid site heterogeneity.** *J Phys Chem C* 2007, **111**:18341-18347, <https://doi.org/10.1021/jp0759675>
19. Cnudde P, Redekop EA, Dai W, Porcaro NG, Waroquier M, Bordiga S, Hunger M, Li L, Olsbye U, et al.: **Experimental and theoretical evidence for promotional effect of acid sites on the diffusion of alkenes through small-pore zeolites.** *Angew Chem Int Ed* 2021, **60**:10016-10022, <https://doi.org/10.1002/anie.202017025>
20. Lin S, Zhi Y, Chen W, Li H, Zhang W, Lou C, Wu X, Zeng S, Xu S, et al.: **Molecular routes of dynamic autocatalysis for methanol-to-hydrocarbons reaction.** *J Am Chem Soc* 2021, **143**:12038-12052, <https://doi.org/10.1021/jacs.1c03475>
21. Borodina E, Meirer F, Lezcano-González I, Mokhtar M, Asiri AM, Al-Thabaiti SA, Basahel SN, Ruiz-Martinez J, Weckhuysen BM: **Influence of the reaction temperature on the nature of the active and deactivating species during methanol to olefins conversion over H-SSZ-13.** *ACS Catal* 2015, **5**:992-1003, <https://doi.org/10.1021/cs501345g>
22. Borodina E, Sharbini Harun Kamaluddin H, Meirer F, Mokhtar M, Asiri AM, Al-Thabaiti SA, Basahel SN, Ruiz-Martinez J, Weckhuysen BM: **Influence of the reaction temperature on the nature of the active and deactivating species during methanol-to-olefins conversion over H-SAPO-34.** *ACS Catal* 2017, **7**:5268-5281, <https://doi.org/10.1021/acscatal.7b01497>
23. 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, <https://doi.org/10.1039/C6CY00654J>
24. Zhou J, Gao M, Zhang J, Liu W, Zhang T, Li H, Xu Z, Ye M, Liu Z: **Directed transforming of coke to active intermediates in methanol-to-olefins catalyst to boost light olefins selectivity.**

- Nat Commun* 2021, **12**:17-27, <https://doi.org/10.1038/s41467-020-20193-1>
25. Kärger J, Binder T, Chmelik C, Hibbe F, Krautscheid H, Krishna R, Weitkamp J: **Microimaging of transient guest profiles to monitor mass transfer in nanoporous materials.** *Nat Mater* 2014, **13**:333-343, <https://doi.org/10.1038/nmat3917>
 26. Hibbe F, Chmelik C, Heinke L, Pramanik S, Li J, Ruthven DM, Tzoulaki D, Kärger J: **The nature of surface barriers on nanoporous solids explored by microimaging of transient guest distributions.** *J Am Chem Soc* 2011, **133**:2804-2807, <https://doi.org/10.1021/ja108625z>
 27. Gao M, Li H, Yu J, Ye M, Liu Z: **Quantitative principle of shape-selective catalysis for a rational screening of zeolites for methanol-to-hydrocarbons.** *AIChE J* 2023, **69**:e17881, <https://doi.org/10.1002/aic.17881>
 28. Yuan J, Liu Z, Wu Y, Han J, Tang X, Li C, Chen W, Yi X, Zhou J, et al.: **Thermal resistance effect on anomalous diffusion of molecules under confinement.** *Proc Natl Acad Sci USA* 2021, **118**:e2102097118, <https://doi.org/10.1073/pnas.2102097118>
 29. Haw JF, Song W, Marcus DM, Nicholas JB: **The mechanism of methanol to hydrocarbon catalysis.** *Acc Chem Res* 2003, **36**:317-326, <https://doi.org/10.1021/ar020006o>
 30. Tsukahara Y, Higashi A, Yamauchi T, Nakamura T, Yasuda M, Baba A, Wada Y: **In situ observation of nonequilibrium local heating as an origin of special effect of microwave on chemistry.** *J Phys Chem C* 2010, **114**:8965-8970, <https://doi.org/10.1021/jp100509h>
 31. Koptuyug IV, Khomichev AV, Lysova AA, Sagdeev RZ: **Spatially resolved NMR thermometry of an operating fixed-bed catalytic reactor.** *J Am Chem Soc* 2008, **130**:10452-10453, <https://doi.org/10.1021/ja802075m>
 32. Simeone M, Saleme 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, <https://doi.org/10.1002/aic.11565>
 33. Buurmans ILC, Weckhuysen BM: **Heterogeneities of individual catalyst particles in space and time as monitored by spectroscopy.** *Nat Chem* 2012, **4**:873-886, <https://doi.org/10.1038/nchem.1478>
 34. Hu S, Liu B-J, Feng J-M, Zong C, Lin K-Q, Wang X, Wu D-Y, Ren B: **Quantifying surface temperature of thermoplasmonic nanostructures.** *J Am Chem Soc* 2018, **140**:13680-13686, <https://doi.org/10.1021/jacs.8b06083>
 35. Ano T, Tsubaki S, Liu A, Matsuhisa M, Fujii S, Motokura K, Chun W-J, Wada Y: **Probing the temperature of supported platinum nanoparticles under microwave irradiation by in situ and operando XAFS.** *Commun Chem* 2020, **3**:86, <https://doi.org/10.1038/s42004-020-0333-y>
 36. Van de Broek B, Grandjean D, Trekker J, Ye J, Verstreken K, Maes G, Borghs G, Nikitenko S, Lagae L, et al.: **Temperature determination of resonantly excited plasmonic branched gold nanoparticles by X-ray absorption spectroscopy.** *Small* 2011, **7**:2498-2506, <https://doi.org/10.1002/sml.201100089>
 37. Jaque D, Vetrone F: **Luminescence nanothermometry.** *Nanoscale* 2012, **4**:4301-4326, <https://doi.org/10.1039/C2NR30764B>
 38. Brites CDS, Lima PP, Silva NJO, Millán A, Amaral VS, Palacio F, Carlos LD: **Thermometry at the nanoscale.** *Nanoscale* 2012, **4**:4799-4829, <https://doi.org/10.1039/C2NR30663H>
 39. Geitenbeek RG, Nieuwelink A-E, Jacobs TS, Salzmann BBV, Goetze J, Meijerink A, Weckhuysen BM: **In situ luminescence thermometry to locally measure temperature gradients during catalytic reactions.** *ACS Catal* 2018, **8**:2397-2401, <https://doi.org/10.1021/acscatal.7b04154>
 40. Terlingen B, Arens T, van Swieten TP, Rabouw FT, Prins T, de Beer MM, Meijerink A, Ahr M, Hutter EM, et al.: **Bifunctional europium for operando catalyst thermometry in an exothermic chemical reaction.** *Angew Chem Int Ed* 2022, **61**:e202211991, <https://doi.org/10.1002/anie.202211991>
 41. Wang C-Y, Chen L-J: **Nanothermometers for transmission electron microscopy – fabrication and characterization.** *Eur J Inorg Chem* 2010, **2010**:4298-4303, <https://doi.org/10.1002/ejic.201000591>
 42. Aasberg-Petersen K, Bak Hansen JH, Christensen TS, Dybkjaer I, Christensen PS, Stub Nielsen C, Winter Madsen SEL, Rostrup-Nielsen JR: **Technologies for large-scale gas conversion.** *Appl Catal A* 2001, **221**:379-387, [https://doi.org/10.1016/S0926-860X\(01\)00811-0](https://doi.org/10.1016/S0926-860X(01)00811-0)
 43. Guler M, Dogu T, Varisli D: **Hydrogen production over molybdenum loaded mesoporous carbon catalysts in microwave heated reactor system.** *Appl Catal B* 2017, **219**:173-182, <https://doi.org/10.1016/j.apcatb.2017.07.043>
 44. Jie X, Gonzalez-Cortes S, Xiao T, Wang J, Yao B, Slocombe DR, Al-Megren HA, Dilworth JR, Thomas JM, et al.: **Rapid production of high-purity hydrogen fuel through microwave-promoted deep catalytic dehydrogenation of liquid alkanes with abundant metals.** *Angew Chem Int Ed* 2017, **56**:10170-10173, <https://doi.org/10.1002/anie.201703489>
 45. Jie X, Gonzalez-Cortes S, Xiao T, Yao B, Wang J, Slocombe DR, Fang Y, Miller N, Al-Megren HA, et al.: **The decarbonisation of petroleum and other fossil hydrocarbon fuels for the facile production and safe storage of hydrogen.** *Energy Environ Sci* 2019, **12**:238-249, <https://doi.org/10.1039/C8EE02444H>
 46. Ramirez A, Hueso JL, Abian M, Alzueta MU, Mallada R, Santamaria J: **Escaping undesired gas-phase chemistry: microwave-driven selectivity enhancement in heterogeneous catalytic reactors.** *Sci Adv* 2019, **5**:eaau9000, <https://doi.org/10.1126/sciadv.aau9000>
 47. Elias RC, Linic S: **Elucidating the roles of local and nonlocal rate enhancement mechanisms in plasmonic catalysis.** *J Am Chem Soc* 2022, **144**:19990-19998, <https://doi.org/10.1021/jacs.2c08561>.
This work thoroughly analyzes the dominant mechanism for the enhancement in reaction rate by LSPR, that is a local plasmon-induced hot charge-carrier-mediated activation of the reactants or LSPR-induced equilibrium heating of the catalyst.
 48. Cai M, Wu Z, Li Z, Wang L, Sun W, Tountas AA, Li C, Wang S, Feng K, et al.: **Greenhouse-inspired supra-photothermal CO₂ catalysis.** *Nat Energy* 2021, **6**:807-814, <https://doi.org/10.1038/s41560-021-00867-w>.
This work shows the shell of silica can enable a supra-photothermal effect on metal NP catalysis by increasing local temperature.
 49. Song C, Wang Z, Yin Z, Xiao D, Ma D: **Principles and applications of photothermal catalysis.** *Chem Catal* 2022, **2**:52-83, <https://doi.org/10.1016/j.cheecat.2021.10.005>
 50. Ceylan S, Friese C, Lammel C, Mazac K, Kirschning A: **Inductive heating for organic synthesis by using functionalized magnetic nanoparticles inside microreactors.** *Angew Chem Int Ed* 2008, **47**:8950-8953, <https://doi.org/10.1002/anie.200801474>
 51. Ceylan S, Coutable L, Wegner J, Kirschning A: **Inductive heating with magnetic materials inside flow reactors.** *Chem Eur J* 2011, **17**:1884-1893, <https://doi.org/10.1002/chem.201002291>
 52. Chaudhuri SR, Hartwig J, Kupracz L, Kodanek T, Wegner J, Kirschning A: **Oxidations of allylic and benzylic alcohols under inductively-heated flow conditions with gold-doped superparamagnetic nanostructured particles as catalyst and oxygen as oxidant.** *Adv Synth Catal* 2014, **356**:3530-3538, <https://doi.org/10.1002/adsc.201400261>
 53. Deng L, Miura H, Shishido T, Hosokawa S, Teramura K, Tanaka T: **Strong metal-support interaction between Pt and SiO₂ following high-temperature reduction: a catalytic interface for propane dehydrogenation.** *Chem Commun* 2017, **53**:6937-6940, <https://doi.org/10.1039/C7CC03859C>
 54. Bordet A, Lacroix L-M, Fazzini P-F, Carrey J, Soullantica K, Chaudret B: **Magnetically induced continuous CO₂ hydrogenation using composite iron carbide nanoparticles of exceptionally high heating power.** *Angew Chem Int Ed* 2016, **55**:15894-15898, <https://doi.org/10.1002/anie.201609477>